# 17TH INTERNATIONAL CONFERENCE ON PHOTOCHEMICAL CONVERSION AND STORAGE OF SOLAR ENERGY 2008

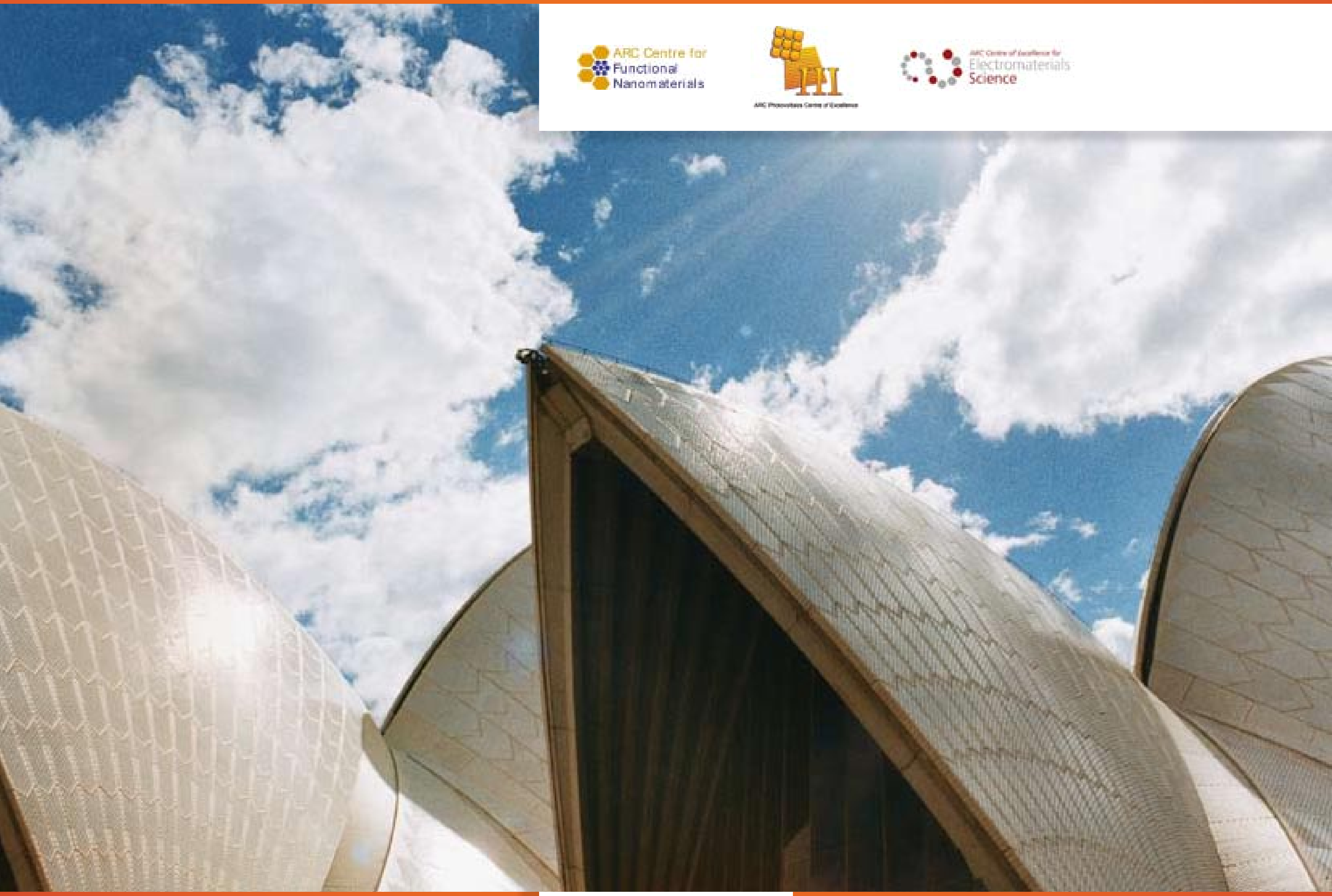
Sunday 27 July – Friday 1 August 2008
Sydney Convention and Exhibition Centre, Australia

## FINAL PROGRAM AND ABSTRACT BOOK

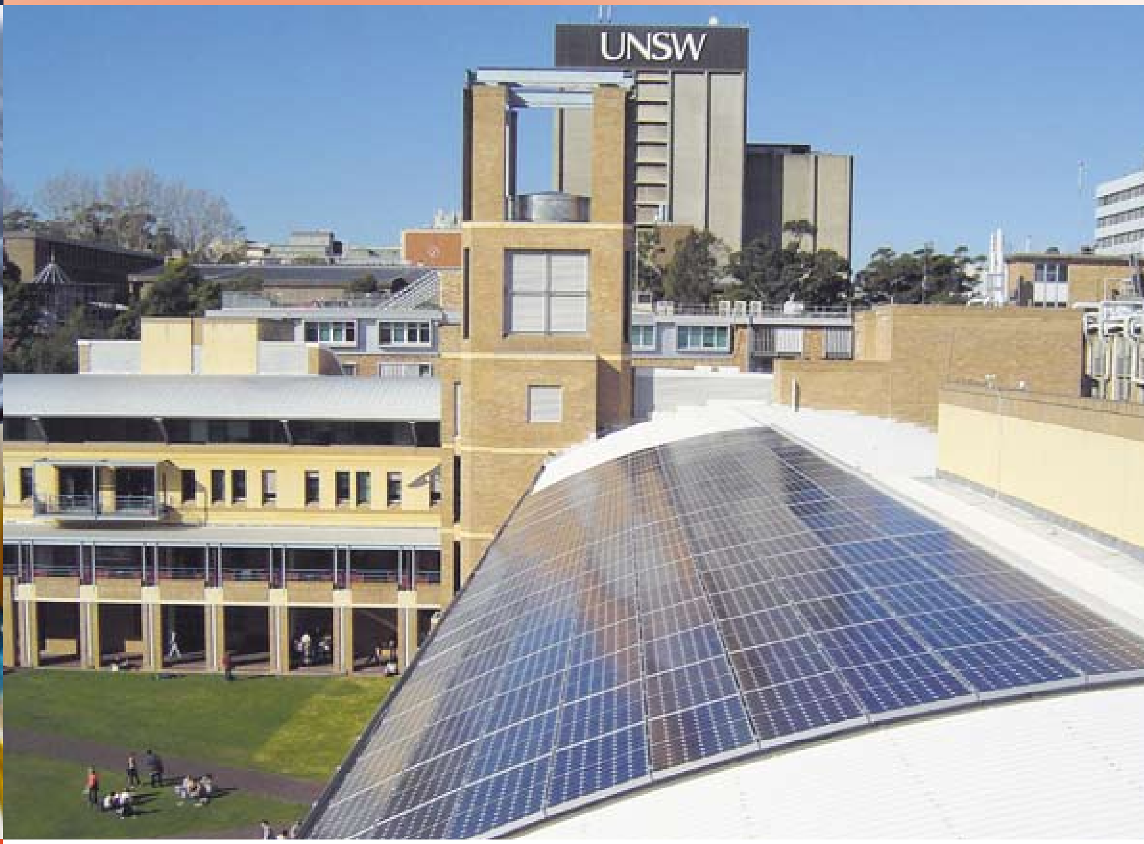
ARC Centre for Functional Nanomaterials

ARC Photovoltaics Centre of Excellence

ARC Centre of Excellence for Electromaterials Science



IPS-17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# General Information

## Welcome from Conference Chair and Co-Chairs

It is our pleasure to warmly welcome all participants to the *17th International Conference on Photochemical Conversion and Storage of Solar Energy* in Sydney, Australia 27 July – 1 August 2008. This biennial conference series represents a premier gathering of leading scientist from research institutions, universities, and industry, working on photochemical energy conversion, clean energy generation and storage and environmental applications, which continues to be a field of major international academic and commercial interest. Current international concerns with global warming and intense efforts dedicated to the search for renewable energy sources make IPS 17 a timely event which will contribute to addressing the issues and developing effective long-term action on climate change. Capturing both scientific progress and challenges as well as the visions for advancing solar technologies in the new millennium, IPS 17 is one of the most inclusive international events held in 2008.

The event places strong emphasis on the attendance of, and presentation by, leaders in solar-related fields and IPS17 aims to sustain this feature again through assembling a suite of renowned speakers. It will seek to stimulate interactions, promote discussion of strategically important technologies, and broaden and strengthen contacts and linkages between all participants. There are over 350 delegates at the conference, from different parts of the world, including America, Europe, Asia, and our own Australia.

The backdrop for IPS17 is Sydney's Darling Harbour, located within walking distance of famous landmarks such as the Sydney Harbour Bridge, The Rocks and the Sydney Opera House. Darling Harbour itself is a focal point for activity and entertainment and will provide you all with an excellent opportunity to mix business and pleasure during your time in Sydney.

IPS17 represents the first time an IPS event is being held in the southern hemisphere and is a fact we are very proud of and we will endeavor to provide an event which lives up to the high standards of its predecessors. We would like to thank you, the delegates, for your attendance and support of this conference.

Welcome!

Rose Amal, Chair
Gavin Conibeer, Co-chair
David Officer Co-Chair

## Conference Office

**ICMS Pty Ltd**
Level 3, 379 Kent Street
Sydney NSW 2000
Australia

Phone: +61 2 9290 3366
Fax: +61 2 9290 2444
Website: www.ips17.com
Email: ips17@icms.com.au

## Registration Desk

The Registration Desk will be open as follows:

| | |
|---|---|
| Sunday, 27 July 2008 | 15:00 – 19:30 |
| Monday, 28 July 2008 | 07.30 – 20.00 |
| Tuesday, 29 July 2008 | 08.00 – 18.30 |
| Wednesday, 30 July 2008 | 08.00 – 20.00 |
| Thursday, 31 July 2008 | 08.00 – 19.30 |
| Friday, 1 August 2008 | 08.00 – 14.00 |

Registration Desk Phone Number: 9282 5457
and Fax Number: 9282 5498

## Money

Access to ATM's and currency exchange services are available in the Harbourside Shopping Centre located next to the Sydney Convention and Exhibition Centre, Darling Harbour.

## Badges

Identification badges are mandatory and are required for admission to all sessions including Exhibition and social functions.

## Meeting Venue

Sydney Convention and Exhibition Centre Darling Drive, Darling Harbour, Sydney, Australia.

## Car Parking

The Exhibition Centre car park is conveniently located off Darling Drive, underneath the Centre's five exhibition halls. The car park has direct access to the venue and the many attractions and facilities available in Darling Harbour.

Car park opening hours:

Monday to Thursday – 6am to 1am the next day
Friday – open from 6am (24 hours)
Saturday – open 24 hours
Sunday – closes at 1am Monday morning

***Rates***

Day Rates for all vehicles are:

0-1 hours = $8.00
1-2 hours = $15.00
2-4 hours = $21.00
4-5 hours = $25.00
5+ hours = $27.00

Evening Rates for all vehicles are:

0-1 hours = $7.00
1-2 hours = $13.00
2+ hours = $18.00

Evening Rates apply for entry after 5pm and exit before 9am the following day.

# Keynote Speakers

**Professor Wonyong Choi**
School of Environmental Science and Engineering, Pohang University of Science and Technology, Korea

**Professor Mildred Dresselhaus**
Institute Professor of Electrical Engineering and Physics Massachusetts Institute of Technology, USA

**Professor James Durrant**
Professor of Photochemistry in the Dept. of Chemistry, Imperial College London. UK

**Professor Akira Fujishima**
Chairman at the Kanagawa Academy of Science and Technology, Japan

**Professor Michael Graetzel**
Director of the Laboratory of Photonics and Interfaces, Ecole Polytechnique Fédérale de Lausanne, Switzerland

**Professor Martin Green**
Director of CSG Solar and Research Director of the University's Photovoltaic Centre of Excellence, University of New South Wales, Sydney, Australia

**Professor Dirk M. Guldi**
Friedrich-Alexander University in Erlangen, Germany

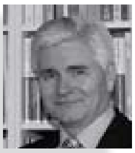
**Anders Hagfeldt**
Chair in physical chemistry at the University of Uppsala, Director of the Center of Molecular Devices, Royal Institute of Technology, Stockholm, Sweden

**Associate Professor Ben Hankamer**
Institute for Molecular Bioscience, University of Queensland, Australia, and a director of the Solar Biofuels Consortium.

**Professor Kauzhito Hashimoto**
Professor of Chemistry, University of Tokyo, Japan

**Professor Andrew Holmes**
ARC Federation and VESKI Fellow at the Bio21 Institute in the University of Melbourne, Australia

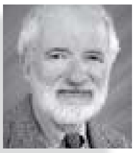
**Professor Akihiko Kudo**
Department of Applied Chemistry, Tokyo University of Science, Japan



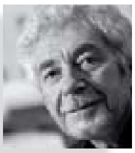
**Professor Wolfgang Lubitz**
Director at the Max Planck Institute for Bioinorganic Chemistry, Mülheim/Ruhr, Germany

**Professor Antonio Marti**
Instituto de Energia Solar – ETSIT, Universidad Politécnica de Madrid, Spain

**Professor Tsutomu Miyasaka**
Faculty of Engineering, Toin University of Yokohama, Japan. CEO of Peccell Technologies, Inc.



**Professor Arthur Nozik**
Senior Research Fellow at NREL and adjoint in Chemistry Dept, University of Colorado, USA



**Professor Stenbjörn Styring**
Department of Photochemistry and Molecular Science, Uppsala University, Sweden

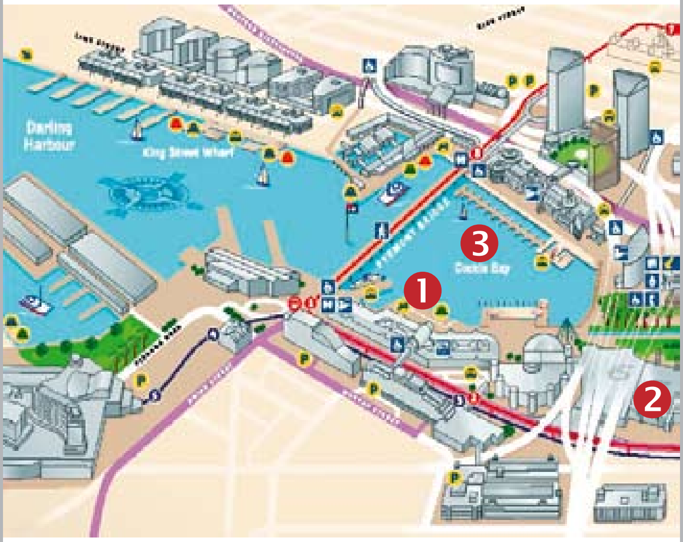
# Social Program

## Welcome Reception

**Date:** Sunday, 27 July 2008
**Time:** 18:00pm
**Venue:** Bayside Terrace, Sydney Convention and Exhibition Centre
**Dress:** Smart Casual

## Conference Dinner

**Date:** Thursday, July 31 2008
**Time:** 19:00pm for 19:15pm Departure
**Venue:** Captain Cook Cruises
**Dress:** Smart Casual



## Darling Harbour Location Map

❶ Harbourside South Steps Wharf – Board Captain Cook Cruise here for Conference Dinner Cruise

❷ Sydney Convention and Exhibition Centre

❸ Darling Harbour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Laser On
Inlet
Heat
Outlet
Injector

# IPS-17 Industry Forum

Materials and Protype Development for Solar Energy

Tuesday, 29 July 2008, Sydney Convention Centre, Sydney.

| | |
|---|---|
| | *Chairman: Professor Gordon Wallace* |
| 1.45 – 2.30 pm | **IPS-17 Conference Plenary [The Auditorium]** |
| | **Professor Mildred Dresselhaus, Massachusetts Institute of Technology, USA**<br>*New Thermoelectric Materials and Solar Energy* |
| 2.30 – 2.50 pm | **Professor Michael Grätzel, LPI Director, EPFL, Lausanne**<br>*Opportunities for Dye-sensitised Solar Cell Technology* |
| 2.50 – 3.10 pm | **Mr Gordon Stewart, Business Development Manager, Suntech Power Australia.** |
| 3.10 – 3.30 pm | **Mrs Sylvia Tulloch**<br>*Commercialisation and Scale-up of Dye Solar Cell Materials Manufacture* |
| 3.30 – 3.50 pm | **Tea & Coffee** |
| | *Chairman: Dr Attila Mozer* |
| 3.50 – 4.10 pm | **Dr Thomas Kolbusch, Solar Coating Machinery Gmbh, Germany**<br>*Coating and Printing Processes for flexible Solar Cell Technologies* |
| 4.10 – 4.30 pm | **Dr Frank Jozefick, Oriel Product Line, Newport Corporation, USA**<br>*QE Measurement of Solar Cells* |
| 4.30 – 4.50 pm | **Dr Chris Fell, Senior Research Scientist, CSIRO Energy Technology**<br>*Solar Energy Research at CSIRO* |
| 4.50 – 5.10 pm | **Dr Mark Bonnar, Investment Manager, Cleantech Ventures Pty Ltd**<br>*Early-stage investing in clean technologies. But how early?* |
| 5.10 – 5.20 pm | **10 minute break** |
| | *Chairman: Professor David Officer* |
| 5.20 – 5.40 pm | **Mr James White, Manager, Department of Environment and Climate Change NSW** |
| 5.40 – 6.00 pm | **Dr Ian Mackinnon, ARC Executive Director, Australian Research Council** |
| 6.00 – 8.30 pm | **Forum Cocktail Party** |

# 17TH INTERNATIONAL CONFERENCE ON PHOTOCHEMICAL CONVERSION AND STORAGE OF SOLAR ENERGY 2008

## Program

### SUNDAY, JULY 27

| | |
|---|---|
| 18:00–20:00 | WELCOME RECEPTION<br>Parkside Foyer |

### MONDAY, JULY 28

| | |
|---|---|
| 09:00–09:20 | OPENING CEREMONY – THE HON. IAN MACDONALD MLC<br>Parkside Auditorium<br>**Chair** *Rose Amal, ARC Centre for Functional Nanomaterials, School of Chemical Sciences and Engineering, The University of New South Wales* |
| 09:20–10:05 | MICHAEL GRAETZEL<br>Parkside Auditorium<br>**Chair** *David Officer, ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia* |
| | Power from the Sun: the Advent of Mesoscopic Solar Cells 101<br>*Prof Michael Graetzel, Laboratory of Photonics and Interfaces, Ecole Polytechnique Fédérale de Lausanne, Switzerland* |
| 10:05–10:50 | MARTIN GREEN<br>Parkside Auditorium<br>**Chair** *David Officer, ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia* |
| | Advanced Photovoltaic Concepts Based on Silicon Quantum Dots 102<br>*Prof Martin Green, ARC Photovoltaics Centre of Excellence, University of New South Wales, Australia* |
| 10:50–11:20 | MORNING TEA |
| 11:20–12:05 | AKIRA FUJISHIMA<br>Parkside Auditorium<br>**Chair** *Anders Hagfeldt, University of Uppsala, Sweden* |
| | New Direction in Photocatalysis 103<br>*Akira Fujishima, Kanagawa Academy of Science and Technology, Japan* |
| 12:05–12:50 | WOLFGANG LUBITZ<br>Parkside Auditorium<br>**Chair** *Anders Hagfeldt, University of Uppsala, Sweden* |
| | Light-Induced Water Splitting and Hydrogen Production in Nature 104<br>*Prof Wolfgang Lubitz, Max Planck Institute for Bioinorganic Chemistry, Germany* |
| 12:50–14:15 | LUNCH |

## MONDAY, JULY 28

| | | |
|---|---|---|
| **14:15–16:05** | **SOLAR CELLS 1: NANOSTRUCTURED SOLAR CELLS** | **PHOTOCATALYSIS 1** |
| | Parkside Auditorium<br>**Chair** *Udo Bach, Department of Materials Engineering, Monash University, Clayton, Victoria, 3800, Australia, Australia* | Room 110A<br>**Chair** *Jason Scott, ARC Centre for Functional Nanomaterials, School of Chemical Sciences and Engineering, University of New South Wales* |
| **14:15–14:35** | Advanced Photocurrent and Compositional Mapping of Nanostructured Solar Cells<br>*A/Prof Paul C Dastoor* | What is Degussa P25? Crystal Composition Analysis, Reconstruction from Isolated Pure Particles, and Photocatalytic Activity Test 110<br>*Prof Bunsho Ohtani, Catalysis Research Center, Hokkaido University, Japan* |
| **14:35–14:50** | Photoacoustic Spectra and Uultrafast Carrier Dynamics of Nanostructured TiO$_2$ Electrodes Adsorbed with CdS Quantum Dots 105<br>*Taro Toyoda, The University of Electro-Communications, Japan* | Synthesis of Titanate Nanotube Thin Film and Applications 111<br>*Dr Yupeng Guo, Sejong University,Korea, China* |
| **14:50–15:05** | ZnO-Nanorod Arrays for Solar Cells with Ultra Thin In$_2$S$_3$ and CuInS$_2$ Absorbers 106<br>*Abdelhak Belaidi, Hahn-Meitner-Institut-Berlin, Germany* | Efficient Photocatalysts from Titanate Nanofibres 112<br>*Huai Yong Zhu, Queensland University of Technology, Australia* |
| **15:05–15:20** | Copper Sulfide-Sensitized Nanoporous Metal Oxide Solar Cells 107<br>*Miles Page, Weizmann Institute of Science, Israel* | Polynuclear Metal Oxide Photocatalysts on Nanoporous Silica for Visible Light Water Oxidation and Carbon Dioxide Reduction 113<br>*Heinz Frei, Lawrence Berkeley National Laboratory, United States* |
| **15:20–15:35** | Supra-Hierarchical Nano-Structured Polymer Solar Cells as Efficient Organic Photovoltaics 108<br>*Prof Susumu Yoshikawa, Institute of Advanced Energy, Kyoto University, Japan* | Mechanism of Photoinduced Oxygen Evolution on Well-defined Single Crystal (rutile)TiO$_2$ Surfaces Studied by PL Emission 114<br>*Akihito Imanishi, Division of Chemistry, Graduate School of Engineering Science, Osaka University, Japan* |
| **15:35–15:50** | Long Range Charge Separation in Polymer: Polymer and Polymer: Fullerene Photovoltaic Devices 109<br>*Dr Justin Hodgkiss, University of Cambridge, United Kingdom* | Effect of Au Nanoparticles on the Photocatalytic Activities of Titanium Dioxide 115<br>*Elena Selli, Università degli Studi di Milano, Italy* |
| **15:50–16:05** | Gold Nanoparticle / Polythiophene Hybrid Solar Cell<br>*Kyungkon Kim* | Photocatalyst Preparation by Carbon Doping of Titanium Dioxide 116<br>*Prof Antoni Morawski, Szczecin University of Technology, Institute of Chemical and Environment Engineering, Poland* |
| **16:05–16:30** | **AFTERNOON TEA** | |
| **16:30–18:05** | **SOLAR CELLS 2: DSSC** | **PHOTOSYNTHESIS AND BIOMIMETICS** |
| | Parkside Auditorium<br>**Chair** *Paul M Sommeling, ECN, The Netherlands* | Room 110A<br>**Chair** *Stenbjörn Styring, Department of Photochemistry and Molecular Science; Uppsala University, Sweden* |
| **16:30–16:50** | Novel Indoline Dye for High-Conversion-Efficiency (9.5%) Organic Dye-Sensitized Solar Cells<br>*Seigo Ito* | Towards artificial photosynthesis: light harvesting using porphyrins 123<br>*Dr David Officer, ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia* |
| **16:50–17:05** | Highly Efficient Organic Sensitizers Comparable to Ruthenium Sensitizers 118<br>*Mr Jaejung Ko, Korea University, Korea* | Biosynthetic, Structural and Physiological Characterization of the Membrane Associated [NiFe] Hydrogenases in the Purple Sulfur Photosynthetic Bacterium, Thiocapsa Roseopersicina BBS 124<br>*Prof Kornél Kovács, Department of Biotechnology, University of Szeged, Inst. Biophysics, Biol. Res. Centre, Hungarian Academy of Sciences, Hungary* |
| **17:05–17:20** | P-Type Dye Sensitized Solar Cells: Early Time Dynamics Associated with a Series of Organic Sensitizers on Nanocrystalline NiO Films 119<br>*Amanda Smeigh, Uppsala University, Sweden* | Photosystem II and the Bio-mimetic Production of Hydrogen 125<br>*Dr Ron Pace, Department of Chemistry, The Australian National University, Canberra, Australia* |
| **17:20–17:35** | A Novel Design for Monolithic Solid-State Dye-Sensitized Solar Cells with Platinized Carbon Counter-Electrode 120<br>*Prof Yibing Cheng, Department of Materials Engineering, Monash University, Clayton, Victoria, 3800, Australia, Australia* | A Comparative Study of Manganese Based Catalysts for Water Oxidation<br>*Magnus F Anderlund* |
| **17:35–17:50** | Factors Influencing Electron Lifetime in Dye-Sensitized Solar Cells: Transport and Interfacial Transfer Limited Charge Recombination in the Case of Various Dyes and Semiconductors 121<br>*Dr Shogo Mori, Department of Fine Materials Engineering, Shinshu University, Japan* | Effect of Molecular Organization on Energy Transfer Dynamics in Biomimetic Light-Harvesting Systems 126<br>*Tom Savenije, Opto-Electronic Materials Section, DelftChemTech, Delft University of Technology, The Netherlands* |
| **17:50–18:05** | Nano-Dispersion of Commercial TiO$_2$ Powders for High Efficiency Dye-Sensitized Solar Cells 122<br>*Nam-Gyu Park, Korea Institute of Science and Technology, Korea* | Photo-oxidation of a Dimanganese Centre in an Engineered Bacterioferritin<br>*Brendon Conlan* |

# MONDAY, JULY 28

## 18:05–20:00 POSTER SESSION 1 – SOLAR CELLS AND PHOTOELECTROCHEMISTRY

### CATEGORY – MOLECULAR AND NANOSTRUCTURAL SOLAR CELLS

Parkside Foyer

UNSW School of Chemical Sciences and Engineering

Energy & Environmental Science

**600–609**

Hole Transport in $TiO_2$-Adsorbed Monolayers of Organic Dyes Containing Triarylamine Moieties 601
*Alexander Agrios, Uppsala University, Sweden*

Boradiazaindacenes as a New Class of Sensitizers for Dye-Sensitized Solar Cells 602
*Engin Akkaya, Bilkent University, Department of Chemistry & Mat.Sci. Nanotech Institute, Turkey*

Photoelectrochemical Characterisation of Nanostructured $NiTiO_3$ Thin Film Electrodes 603
*Mr Kenrick Anderson, CSIRO Energy Technology, Australia*

Ionic Materials for Photoelectrochemical Solar Cells 604
*Vanessa Armel, Monash University, Australia*

Porphyrins and N-confused Porphyrins as Dopants in Organic Solar Cells 605
*Warwick Belcher, University of Newcastle, Australia*

Exciton-Sensitized Nanostructured Solar Cells (XNSC) 606
*Mr Gerrit Boschloo, Royal Institute of Technology (KTH), Sweden*

Study of Electron Transfer Processes in Solid State Dye-Sensitized Solar Cells by Photoinduced Absorption Spectroscopy (PIA) 607
*Ms Ute Cappel, Dept. of Physical and Analytical Chemistry, Uppsala University, Sweden*

Effects of Anode Modification on the Improved Performance of Organic Solar Cells Based on Poly (3-hexylthiophene): Fullerene 608
*Dr Mei-Ying Chang, Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
*Dr Yu-Kai Han, Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Taiwan*
*Prof Wen-Yao Huang, Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
*Mr Shih-Chin Lin, Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
*Mr I-Fan Chen, Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
*Prof Ping-Tsung Huang, Department of Chemistry, Fu-Jen Catholic University, Taiwan*

Transient Absorption Spectrocopy of Polymer/Fullerene Films: Charge Generation and Recombination 609
*Tracey Clarke, Imperial College London, United Kingdom*

**610–619**

Fundamental Frequency Deep Level Transient Spectroscopy: Theory 610
*Dr Didier Debuf, School of Electrical and Information Engineering, The University of Sydney, Australia*

Study of Electro-Deposited Pt/Ni/ITO Cathode for the Efficient Dye-Sensitized Solar Cell 611
*Seok Joo Doh, Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea*

Conductance-Voltage Properties of Silicon Quantum Dot Metal-Insulator-Semiconductor Devices Fabricated by Sputtering 612
*Chris Flynn, ARC Photovoltaics Centre of Excellence, University of New South Wales, Sydney, NSW 2052, Australia., Australia*

Interfacial Structure of $TiO_2$ /Dye/Hole-Conductor Interface Assembled by a Combination of High Temperature and Low Pressure 613
*Kristofer Fredin, Department of Physics and Materials Science, Uppsala, Sweden*

A New Series of Ruthenium Complexes Containing an Anionic Bidentate Ligand for Dye Sensitized Solar Cells 614
*Takashi Funaki, National Institute of Advanced Industrial Science and Technology (AIST), Japan*

Self-Assembled Metalloporphyrin-Substituted Fullerene Photovoltaic Electrodes: Towards Nanostructured Organic Solar Cells 615
*Mr Matt Griffiths, Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*

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*Larissa Grinis, Bar-Ilan University, Israel*

Photocurrent Limiting Factors in Pressed $TiO_2$ Dye Solar Cells 617
*Janne Halme, Laboratory of Advanced Energy Systems, Department of Engineering Physics and Mathematics, Helsinki University of Technology, Finland*

Efficient P3HT:PCBM-Based Polymer Solar Cells Fabricated with One Dimensional Acid-Doped Polyaniline Nanotubes 619
*Dr Yu-Kai Han, Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Taiwan*

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*Dr Eiji Hosono, Nano-Energy Materials Group, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Techno, Japan*

C60 Clusters to Improve the Efficiency of a Dye-Sensitized Solar Cell 621
*Surat Hotchandani, Université du Québec à Trois-Rivières, Trois-Rivières, QC G9A 5H7, Canada*

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*Dr Dariusz Hreniak, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland, Poland*

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*Dr Linhua Hu, Institute of Plasma Physics, Chinese Academy of Sciences, China*
*Prof Kongjia Wang, Institute of Plasma Physics, Chinese Academy of Sciences, China*
*Songyuan Dai, Institute of Plasma Physics, Chinese Academy of Sciences, China*

Modification of ZnO Nanorods for Dye-Sensitized Solar Cell Application 624
*Fuzhi Huang, PFPC, School of Chemistry, The University of Melbourne, Melbourne Vic. 3010, Australia, Australia*

Tin Quantum Dot Materials for Third Generation Photovoltaics: Optical Properties 625
*Dr Shujuan Huang, ARC Photovoltaics Centre of Excellence, University of New South Wales, Australia*

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*Wen-Yao Huang, National Sun Yat-Sen University, Taiwan*

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*Prof Dr Siddik Icli, Solar Energy Institute, Ege University, Turkey*

## MONDAY, JULY 28

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*Dr Shinji Iwamoto, Department of Energy and Hydrocarbon Chemistry, Graduated School of Engineering, Kyoto University, Japan*

Characterisation of Dye-Sensitised TiO$_2$ Nanotube Based Solar Cells **631**
*James Jennings, University of Bath, United Kingdom*

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*Dr Seong Mu Jo, Korea Institute of Science and Technology, Korea*

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*Moon-Sung Kang, Samsung Advanced Institute of Technology (SAIT), Korea*

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*Ms Soon Hyung Kang, Seoul National University, Korea*

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*SoonHyung Kang, Seoul National University, Korea*

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*Cham Kim, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Korea*

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*Mr Harkjin Kim, Department of Chemistry, Inha University, Incheon, South Korea, Korea*

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*Dr Seok-Soon Kim, Gwangju Institute of Science and Technology, Korea*

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*Ms Su Jin Kim, Department of chemical engineering, Hanyang University, Korea*

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*YiBing Cheng, Monash University, Australia*

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*Dr Hideki Sugihara, National Institute of Advanced Industrial Science and Technology (AIST), Japan*

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*Dr Jing Zhang, Department of Physics, Wuhan University, China*
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# MONDAY, JULY 28

## CATEGORY – PHOTOELECTROCHEMISTRY AND NEW MATERIALS

Parkside Foyer

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*Masahiro Matsuda, Institute of Materials Science, University of Tsukuba, Japan*

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*Dr Ryuhei Nakamura, Department of Applied Chemistry, School of Engineering, The University of Tokyo, Japan*

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*Jun Young Lee*

## TUESDAY, JULY 29

09:00–09:45

### KAZUHITO HASHIMOTO

Parkside Auditorium

***Chair*** *Max Lu, ARC Centre of Excellence for Functional Nanomaterials, UQ, Australia*

Design of Highly Efficient Visible Light Sensitive Photocatalysts on the Basis of Interfacial Charge Transfer 201
*Dr Kazuhito Hashimoto, Department of Applied Chemistry, The University of Tokyo, Research Center for Advanced Science and Technology, The University, Japan*

09:45–10:30

### ANDREW HOLMES

Parkside Auditorium

***Chair*** *Max Lu, ARC Centre of Excellence for Functional Nanomaterials, UQ, Australia*

Synthesis and Properties of Electroactive Conjugated Polymers 202
*Andrew Holmes, University of Melbourne, Australia*

10:30–11:15

### AKIHIKO KUDO

Parkside Auditorium

***Chair*** *Max Lu, ARC Centre of Excellence for Functional Nanomaterials, UQ, Australia*

Solar Hydrogen Production Using Powdered Photocatalysts 203
*Akihiko Kudo, Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan*

11:15–11:40

### MORNING TEA

| | | |
|---|---|---|
| 11:40–13:20 | **SOLAR CELLS 3: DSSC AND ORGANIC CELLS** | **PHOTOSYNTHESIS 2/PHOTOINDUCED ELECTRON TRANSFER 1** |
| | Parkside Auditorium<br>***Chair*** *Attila Janos Mozer, Intelligent Polymer Research Institute and ARC Centre of Excellence in Electromaterials Science, The University of Wollongong, Australia* | Room 110A<br>***Chair*** *Nicolas Alonso-Vante, Lab. Electrocatalysis, UMR-CRNS 6503, University of Poitiers, France* |
| 11:40–12:00 | Cyclometallated Ruthenium Sensitizers as a New Paradigm Towards High-Efficiency Dye-Sensitized Solar Cells 209<br>*Dr Mohammad Khaja Nazeeruddin, Laboratory for Photonics and Interfaces, ISIC, EPFL, Switzerland* | Electrodeposited ZnO/CdSe Core-Shell Nanowire Arrays: Building Blocks for Nanostructured Solar Cells 210<br>*Prof Claude Levy-Clement, Institut de Chimie et Matériaux de Paris-Est, CNRS, 94320 Thiais, France*<br>*Jamil Elias, Institut de Chimie et Matériaux de Paris-Est, CNRS, 94320 Thiais, France*<br>*Dr Ramon Tena-Zaera, Institut de Chimie et Matériaux de Paris-Est, CNRS, 94320 Thiais, France*<br>*Dr Ivan Mora-Sero, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain*<br>*Dr Fran Fabregat-Santiago, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain*<br>*Prof Juan Bisquert, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain* |
| 12:00–12:15 | Supramolecular Electrolytes for Solid State Dye-Sensitized Solar Cells 205<br>*Prof Yong Soo Kang, Department of Chemical Engineering, Hanyang University, Korea* | Deep Donor States in InVO$_4$ and BiVO$_4$ Photo-Anodes 211<br>*Roel Van de Krol, Delft University of Technology, department DelftChemTech, The Netherlands* |
| 12:15–12:30 | Optimising P3HT/PCBM Organic Photovoltaic Cells: Identifying Key Parameters 206<br>*Prof Jeffrey Reimers, School of Chemistry, The University of Sydney, Australia* | Porphyrin Chromophore Contamination by Barbiturate Substituents: A Resonance Raman and DFT Study 212<br>*Prof Keith Gordon, MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago, Dunedin, New Zealand* |
| 12:30–12:45 | Back Contact Dye-sensitised Solar Cells<br>*Dr Liyuan Han* | Photogalvanic Cell as a Device for Solar Energy Conversion and Storage: EDTA-Toluidine System<br>*Chhagan Lal Gehlot* |
| 12:45–13:00 | Formation of Charge Carriers and Excitons in Polymer–Fullerene Solar Cells 208<br>*Hideo Ohkita, Kyoto University, Japan* | Unexpected Differences in the P700 Redox Potential Among Photosystem I of Oxygenic Photosynthetic Organisms 214<br>*Dr Akimasa Nakamura, Institute of Industrial Science, The University of Tokyo (Present Address: Technology R & D Department, Central Japan Railway ), Japan* |
| 13:00–13:20 | Limits to the Efficiency of Dye Sensitized and Organic Solar Cells: The Role of Interfacial Bimolecular Recombination 204<br>*Dr Piers Barnes, Imperial College London, United Kingdom* | Unexpected Properties of the Low-Energy Absorption in Photosystem II 215<br>*Prof Elmars Krausz, Research School of Chemistry, The Australian National University, Canberra, Australia* |

13:20–13:45

### LUNCH

## TUESDAY, JULY 29

13:45–18:00

### MATERIALS & PROTOTYPE DEVELOPMENT FOR SOLAR ENERGY

### INDUSTRY FORUM WITH MILDRED DRESSELHAUS

Parkside Auditorium

**Chair** *Gordon G Wallace, ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia*

DYESOL
CSIRO
NewSpec
SUNTECH
CLEANTECH VENTURES
SOLARCOATING MACHINERY GmbH

New Thermoelectric Materials and Solar Energy 216
*Prof Mildred Dresselhaus, Massachusetts Institute of Technology, USA*

18:00–20:00

### INDUSTRY FORUM COCKTAIL PARTY

Parkside Foyer

## WEDNESDAY, JULY 30

| | | |
|---|---|---|
| 09:00–09:45 | ARTHUR NOZIK<br>Parkside Auditorium<br>***Chair*** *Gavin Conibeer, University of New South Wales, Australia* | |
| | Multiple Exciton Generation: QDs, QD Arrays, QD Solar Cells, and Controversy 301<br>*Arthur Nozik, National Renewable Energy Laboratory Golden, United States* | |
| 09:45–10:30 | TSUTOMU MIYASAKA<br>Parkside Auditorium<br>***Chair*** *Gavin Conibeer, University of New South Wales, Australia* | |
| | Dye-sensitized conversion and storage of visible-light energy: Next challenge in photoelectrochemistry 302<br>*Prof Tsutomu Miyasaka, Toin University of Yokohama, Japan* | |
| 10:30–11:15 | ANTONIO MARTI<br>Parkside Auditorium<br>***Chair*** *Gavin Conibeer, University of New South Wales, Australia* | |
| | Intermediate Band Solar Cells 303<br>*Mr Antonio Marti, Universidad Politécnica de Madrid, Spain* | |
| 11:15–11:40 | MORNING TEA | |
| 11:40–13:15 | PHOTOCATALYSIS 2 | PHOTOELECTROCHEMISTRY 1 |
| | Parkside Auditorium<br>***Chair*** *Yaron Paz, Technion, Israel* | Room 110A<br>***Chair*** *Huijun Zhao, Griffith University, Australia* |
| 11:40–12:00 | New Nb-containing Oxide Photocatalysts for Efficient Decomposition of Organic Pollutants Under Weak Visible Light Irradiation 421<br>*Jinhua Ye, Photocatalytic Materials Center, National Institute for Materials Science, Japan* | Electrical Transport through a Single Molecule of $[Ru(tpy)_2](PF_6)_2$ 304<br>*Dr Mario Ruben, Institute of Nanotechnology, KIT Karlsruhe, Germany* |
| 12:00–12:15 | On the Intermediates and Mechanism of Photooxidation Reactions at C- and N-Doped Titanium Dioxide 311<br>*Alexander Kokorin, Institute of Chemical Physics, RAS, Russia* | Ultrafast Study of Plasmon Induced Charge Separation and Recombination Dynamics in Gold Supported on $TiO_2$ Nanoparticle Systems 305<br>*Luchao Du, National Institute of Advanced Industrial Science and Technology, Japan* |
| 12:15–12:30 | Photocatalytic Oxidation of Nitrogen Oxides Over (Iron, Nitrogen)-Codoped Titanium Dioxide Under Visible Light Irradiation 312<br>*Xin Tan, Tianjin University, China* | Theory of Electron Transfer in Nonpolar Solvents 306<br>*Masanori Tachiya, National Institute of Advanced Industrial Science and Technology (AIST), Japan* |
| 12:30–12:45 | Non-Metal (I, N and B, N Co-doping) Doped Mesoporous Nanocrystalline Titania as Visible Light Photocatalysts 313<br>*Gang Liu, ARC Centre of Excellence for Functional Nanomaterials, The University of Queenslands, Australia*<br>*Dr Lianzhou Wang, ARC Centre of Excellence for Functional Nanomaterials, The University of Queenslands, Australia* | Engineering Titanium Dioxide for the Role of Photo-Anode in the Photoelectrochemical Cell 307<br>*Irina Belova, The University of Newcastle, Australia* |
| 12:45–13:00 | Ti(IV)/Ce(III) Bimetallic Photocatalysts Sensitive to Visible Light 314<br>*Dr Ryuhei Nakamura, Department of Applied Chemistry, School of Engineering, The University of Tokyo, Japan* | Chalcogen Element (S, Se and Te) Doped Anatase TiO2 by DFT Calculations 308<br>*Dr Jianwei Zheng, Institute of High Performance Computing, Singapore* |
| 13:00–13:15 | Photocatalytic Oxidation of 4-Methoxybenzyl Alcohol to -Anisaaldehyde in a Fixed Bed Continuous Reactor<br>*Vittorio Loddo* | How Can ZnO-Based Dye-Sensitized Solar Cells be Improved ? An Investigation by Electrochemical Impedance Spectroscopy 309<br>*Torsten Oekermann, Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Germany* |
| 13:15–14:15 | LUNCH | |

## WEDNESDAY, JULY 30

| **14:15–16:05** | **SOLAR CELLS 4: NEW MATERIALS FOR DSSC AND ORGANIC CELLS** | **PHOTOCATALYSIS 3** |
|---|---|---|
| | Parkside Auditorium<br>**Chair** *Laurie Peter, University of Bath, United Kingdom* | Room 110A<br>**Chair** *Pierre Pichat, CNRS/Ecole Centrale de Lyon, France* |
| **14:15–14:35** | Self-Organization of Porphyrins and Carbon Nanostructures for Organic Solar Cells **321**<br>*Prof Hiroshi Imahori, Institute for Integrated Cell-Material Sciences, Kyoto University, Japan* | The Role of Surface Speciation on the TiO$_2$ Surface in Photocatalysis: Oxalate on Rutile Nanoparticles **322**<br>*Detlef Bahneman* |
| **14:35–14:50** | Iodine-Free Solid-State Dye-Sensitized Solar Cells: Effect of Ionic Liquid on Hole Conducting PEDOT **316**<br>*Prof Shozo Yanagida, Osaka University, Japan*<br>*Dr Naruhiko Masaki, Osaka University, Japan*<br>*Ms Yukyeong Kim, Seoul University, Korea*<br>*Dr Kejiang Jiang, Chinese Academy of Sciences, China* | Preferential Photodegradation of Contaminants by Molecular **323**<br>*Prof Yaron Paz, Technion- Israel Inst. of Technology, Israel* |
| **14:50–15:05** | Dye-Sensitized Solar-Cells with a Hydrothermally Grown ZnO-Nanoflower Photoanode **317**<br>*Prof X W Sun, Nanyang Technological University and Institute of Microelectronics, Singapore* | Fabrication and Characterization of TiO2 Nanowire Membrane for Water and Energy Production **325**<br>*Darren Delai Sun, School of Civil and Environmental Engineering, Nanyang Technological University, Singapore* |
| **15:05–15:20** | An Investigation of Nanostructured ZnO/ MEH:PPV Hybrid Solar Cells **318**<br>*Natalie Plank, The University of Cambridge, United Kingdom* | Controlled Synthesis of Hierarchical Metal Oxides Nanorods **326**<br>*Dr Sai Wei Lam, University of New South Wales, Australia* |
| **15:20–15:35** | Colloidal Array Templated TiO$_2$ Photoelectrode for Dye-Sensitized Solar Cells **319**<br>*Hyunjung Lee, Korea Institute of Science and Technology, Korea* | Highly Efficient WO$_3$ Photocatalysts Promoted with Various Co-Catalysts for Gradation of Various Organic Substances **327**<br>*Kazuhiro Sayama, National Institute of Advanced Industrial Science and Technology(AIST), Japan* |
| **15:35–15:50** | Development of Semiconductor Quantum Dots Sensitized Solar Cells by Controlling Interfacial Electron Transfer Reactions **320**<br>*Yasuhiro Tachibana, Osaka University, Japan* | Highly Efficient Decomposition of Organic Compounds Over Platinum-Loaded Tungsten Oxide Photocatalysts Under Visible Light Irradiation **328**<br>*Professor Ryu Abe, Catalysis Research Center, Hokkaido University, Japan* |
| **15:50–16:05** | Solid State Dye Sensitised Solar Cells: Addressing Pore-Filling by Means of Advanced Hole Conductor Deposition Techniques and Ordered TiO” Morphology<br>*Dr Frank O Lenzmann* | |
| **16:05–16:30** | **AFTERNOON TEA** | |
| **16:30–18:05** | **SOLAR CELLS 5: FUNDAMENTALS AND NEW MATERIALS** | **PHOTOCATALYSIS 4** |
| | Parkside Auditorium<br>**Chair** *Jinhua Ye, Photocatalytic Materials Center, National Institute for Materials Science, Japan* | Room 110A<br>**Chair** *James Durrant, Imperial College London, UK* |
| **16:30–16:50** | Solar-Powered Production of Molecular Hydrogen from Water **329**<br>*Michael Hoffmann, California Institute of Technology, United States* | Characterization and Modelling of Dye-sensitized Solar Cells **334**<br>*Laurie Peter, University of Bath, United Kingdom* |
| **16:50–17:05** | The Key Factor in Water Splitting: Long Lifetime Holes for O$_2$ Production **331**<br>*Dr Junwang Tang, Department of Chemistry, Imperial College London and UK Energy Research Center (UKERC), 58 Princeís Gate, Exhibition Road, Lond, United Kingdom* | A Generic Configuration for Improved Spectral Matching of Third-Generation Solar Cells **335**<br>*Prof Arie Zaban, Chemistry Department, Bar-Ilan University, Israel* |
| **17:05–17:20** | A Novel Synthesis Technique for α–Fe2O3 Photoanodes Based on Electrodeposition **332**<br>*Yongqi Liang, Delft University of Technology, department DelftChemTech, The Netherlands* | Solar Energy Conversion Calculations **336**<br>*Petter Persson, Lund University, Sweden* |
| **17:20–17:35** | Sustained Water Oxidation Photocatalysis by a Bioinspired Molecular Manganese Cluster **333**<br>*Prof Leone Spiccia, Monash University, Australia* | Studies of Electron Transport and Electron Transfer in Dye-sensitized Solar Cells **337**<br>*Halina Dunn, University of Bath, United Kingdom* |
| **17:35–17:55** | | Comparison of Band Gaps and Open Circuit Voltages in Si/SiO$_2$ Quantum Well Solar Cells **338**<br>*Derk Bätzner, Institute of Semiconductor Electronics, RWTH Aachen University, Germany* |
| **17:50–18:05** | | Hot Carrier Solar Cells **339**<br>*Gavin Conibeer, University of New South Wales, Australia* |

## WEDNESDAY, JULY 30

**18:05–20:00**

## POSTER SESSION 2 – PHOTOCATALYSIS, P/ INDUCED E ENERGY TRANSFER, SOLAR HYDROGEN, PHOTOSYNTHESIS/BIOMIMETICS

### CATEGORY - BIOMIMETIC SYSTEM

Parkside Foyer

UNSW School of Chemical Sciences and Engineering

Energy & Environmental Science

**707–709**

Well-defined Light-Harvesting Polymers for Organic Solar Cell Applications 705
*Matthias Haeussler, Ian Wark Laboratories, Australia*

Dependence of the efficiency of $TiO_2$ surface transformation to the syperhydrophilic state on light intensity and wavelengths of actinic light. 706
*A.V. Emeline, Kanagawa Academy of Science and Technology, Kawasaki-shi, Kanagawa, Japan*

Comparative experimental studies of photostimulated processes in pristine and F-doped nanosize dispersed ZrO2. 707
*A.V. Emelinea, V.A. Fock Institute of Physics, St-Petersburg State University, St.-Petersburg, Russia, Kanagawa Academy of Science and Technology, Kawasaki-shi, Kanagawa, Japan*

Hierarchically Structured Composite Materials for the Photocatalytic Splitting of Water with Visible Light 708
*Prof Thomas Maschmeyer, The University of Sydney, Australia*

Photo Synergistic Collaboration of Non-Linear Processes at Mesoscopic Level and Formation of Photoautotrophic Biomimetic Supramolecular Assemblies in an Irradiated Sterilized Aqueous Mixture of Some Inorganic and Organic Substances 709
*Dr Vinod Kumar Gupta, C.M.D. Post Graduate College, Bilaspur – 495001 (C.G.)India, India*
*C M Dubey, College,bilaspur(CG), India*

**710–719**

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*Surat Hotchandani, Université du Québec à Trois-Rivières, Trois-Rivières, QC G9A 5H7, Canada*

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*Dr Lianzhou Wang, ARC Centre of Excellence for Functional Nanomaterials, and Australian Institute of Bioengineering and Nanotechnology, UQ, Australia*
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## WEDNESDAY, JULY 30

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*Lorenzo Costanzo, University of Sydney, Australia*

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*Dr Kenji Saito, Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan*

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*Prof Luciana Silva, Universidade Federal da Bahia Campus de Ondina, Brazil*

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*Upul Wijayantha, Loughborough University, United Kingdom*

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*Mr Yunhua Xu, Department of Organic Chemistry, Royal Institute of Technology, 100 44 Stockholm, Sweden, Sweden*

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*Ahmad Zahedi, Monash University, Australia*

## THURSDAY, JULY 31

| | | |
|---|---|---|
| **09:00–09:45** | ANDERS HAGFELDT<br>Parkside Auditorium<br>**Chair** *Andrew B Holmes, University of Melbourne, Australia* | |
| | DSC Toolbox An Integrated Approach | |
| **09:45–10:30** | JAMES DURRANT<br>Parkside Auditorium<br>**Chair** *Andrew B Holmes, University of Melbourne, Australia* | |
| | Charge Photogeneration at Nanostructured Donor/Acceptor Interfaces **402**<br>*Professor James Durrant, Imperial College London, United Kingdom* | |
| **10:30–11:15** | DIRK GULDI<br>Parkside Auditorium<br>**Chair** *Andrew B Holmes, University of Melbourne, Australia* | |
| | Carbon Nano Hybrids for Solar Energy Conversion **403**<br>*Dirk Guldi, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany* | |
| **11:15–11:40** | MORNING TEA | |
| **11:40–13:00** | SOLAR CELLS 6: STABILITY OF DSSC | PHOTOELECTROCHEMISTRY 2 |
| | Parkside Auditorium<br>**Chair** *Tsutomu Miyasaka, Toin University of Yokohama, Japan* | Room 110A<br>**Chair** *Alex Kokorin, Institute of Chemical Physics, RAS, Russia* |
| **11:40–12:00** | Long Term Stability of Dye Solar Cells – from Cells to Modules **409**<br>*Johann Desilvestro, Dyesol Ltd, Australia* | Dye Sensitization of Metal Oxide Crystals **404**<br>*Bruce Parkinson, Colorado State, United States* |
| **12:00–12:15** | Long Term Stability of Dye Sensitized Solar Cells **410**<br>*Drs Paul Sommeling, Energy Research Centre of the Netherlands, ECN, The Netherlands* | Chromogenic Polymer Materials for Sun Protection **405**<br>*Dr Arno Seeboth, Fraunhofer Institute for Applied Polmer Research, Volmerstr. 7B, 12489 Berlin, Germany* |
| **12:15–12:30** | Quantitative Study of TBP Effect on Electron Injection Efficiency in Dye-Sensitized Nanocrystalline $TiO_2$ Films **411**<br>*Ryuzi Katoh, AIST, Japan* | Charge Separation in Layered Titanate Nanostructures: Effect of Ion Exchange Induced Morphology Transformation **406**<br>*Oliver Diwald, Institute of Materials Chemistry, Vienna University of Technology, Veterinaerplatz 1, A-1210 Vienna Austria, Austria* |
| **12:30–12:45** | Thermal Durability of Dye-sensitized Solar Cells and Submodules **412**<br>*Mr Hiroshi Matsui, Material Technology Laboratory, Fujikura Ltd., Japan* | Photoelectrochemical Manifestation of Photoelectron Transport Properties of Vertically Aligned Nanotubular $TiO_2$ Photoanodes **407**<br>*Prefessor Huijun Zhao, Griffith School of Environment, Gold Coast Campus, Griffith University, Australia* |
| **12:45–13:00** | Interfacial Electron Recombination Process on Extended Pi-conjugated Molecular Dyes in DSSC: An Approach Toward Understanding Dye Structure-Device Efficiency Relationship **413**<br>*Emilio Palomares, ICIQ, Spain* | Nanostructured Thin-Film Tungsten Trioxide Photoanodes for Photoelectrolytic Production of Hydrogen from Sea Water **408**<br>*Renata Solarska, Laboratory for High Performance Ceramics, Empa – Swiss Federal Laboratories for Materials Testing & Research, Switzerland* |
| **13:00–14:15** | LUNCH | |

## THURSDAY, JULY 31

| | | |
|---|---|---|
| **14:15–16:05** | SOLAR CELLS 7: NEW MATERIALS FOR DSSC | PHOTOCATALYSIS 4/SOLAR CELLS 8: DSSC |
| | Parkside Auditorium<br>**Chair** *Yi-Bing Cheng, Department of Materials Engineering, Monash University, Vic. 3800, Australia, Australia* | Room 110A<br>**Chair** *Detlef Bahnemann, Leibniz University Hannover Germany* |
| **14:15–14:35** | Full-Plastic Dye-Sensitized Solar Cells via Microwave Heating Process **415**<br>*Prof Satoshi Uchida, Research Center for Advanced Science and Technology, University of Tokyo, Japan* | Do $TiO_2$-Containing, Self-cleaning Materials Present a Potential Health Risk? **310**<br>*Pierre Pichat, CNRS/Ecole Centrale de Lyon, France* |
| **14:35–14:50** | Advancement of Plastic Solar Cells Employing Electrodeposited Porous Crystalline ZnO with Organic Photosensitizers **416**<br>*Tsukasa Yoshida, Gifu University, Japan* | Preparation and Characterisation of Fe-, Al- and Ca-doped Titanium Oxide ($TiO_2$) from Wastewater Sludge of Ti-salt flocculation **422**<br>*Dr H K Shon, University of Technology, Sydney (UTS), Australia* |
| **14:50–15:05** | A Novel Meso-Linked Porphyrin Sensitized Solar Cell **417**<br>*Dr Joanne Dy, Research Center for Advanced Science and Technology, The University of Tokyo, Japan* | Surface Free Energies of Rutile and Anatase Terminated by Nonmetals **423**<br>*Huagui Yang, Australian Institute of Bioengineering and Nanotechnology, Australia* |
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| | From Natural to Artificial Photosynthesis – Biomimetic Chemistry for the Production of Hydrogen from Solar Energy and Water **428**<br>*Professor Stenbjörn Styring, Department of Photochemistry and Molecular Science, Uppsala University, Sweden* | |
| **19:00–22:30** | SUNTECH CONFERENCE DINNER CRUISE<br>Please assemble at Darling Harbour side south steps for departure at 19:00 with Captain Cook Cruises | SUNTECH<br>Solar powering a green future™ |

## FRIDAY, AUGUST 1

| | |
|---|---|
| 09:00–09:45 | **BEN HANKAMER**<br>Parkside Auditorium<br>**Chair** *Leone Spiccia, Monash University* |
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| 09:45–11:15 | **EMERGING RESEARCHER'S SESSION**<br>Parkside Auditorium<br>**Chair** *Dirk Koening and Gavin Conibeer, University of New South Wales, Australia* |
| 09:45–10:00 | Synthesis of Conducting Polymers in Ionic Liquids for Photovoltaic Applications 502<br>*Dr Jennifer Pringle, ARC Centre of Excellence for Electromaterials Science, School of Chemistry, Monash University, Melbourne, Australia* |
| 10:00–10:15 | Charge Transfer Processes and Photovoltaic Performance in Blends of an Ambipolar Polyfluorene Co-Polymer in Combination with Different Electron Acceptors 503<br>*Agnese Abrusci, University of Cambridge, United Kingdom* |
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| 10:30–10:45 | Semiconducting Properties and Photoinduced Hydrophilicity on Nanostructured $TiO_2$ Deposits 505<br>*Miss Veronique Spagnol, Université Pierre et Marie Curie-Paris6, Laboratoire Interfaces et Systèmes Electrochimiques; CNRS, UPR15-LISE, France* |
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| 11:00–11:15 | Transparent Mesoporous Nanocomposite Films for Self-Cleaning Applications 507<br>*Morgan Gohin, Laboratoire de Physique de la Matière Condensée, École Polytechnique, France* |
| 11:15–11:45 | **MORNING TEA** |
| 11:45–12:30 | **WONYONG CHOI**<br>Parkside Auditorium<br>**Chair** *Kang-Jin Kim, Korea University, Korea* |
| | Controlling Photocatalytic Activities of Titania through Surface Property Modification: from Pollutant Degradation to Hydrogen Production 508<br>*Prof Wonyong Choi, Pohang University of Science and Technology, Korea* |
| 12:30–13:15 | **INTRODUCTION TO IPS-18 AND CLOSING SESSION**<br>Parkside Auditorium<br>**Chair** *Rose Amal, ARC Centre for Functional Nanomaterials, School of Chemical Sciences and Engineering, The University of New South Wales* |

# Exhibition

## Exhibition

| **Exhibitors** | **Booth** |
|---|---|
| Dyesol – Booths | 1–3 |
| NewSpec Pty Ltd | 4 |
| MEP Instruments | 6 |
| TJ Instruments Pty / Brookhaven Instruments | 5 |
| Suntech | 7–9 |
| RSC – Energy & Environmental Science Journal | display table |

### Exhibition Hours

The Exhibition will take place in the Bayside Gallery at the Sydney Convention and Exhibition Centre, Sydney, during the following times:

| | |
|---|---|
| Monday, 28 July 2008 | 08:30 – 20:00 |
| Tuesday, 29 July 2008 | 08.30 – 14:00 |
| Wednesday, 30 July 2008 | 08:30 – 20:00 |
| Thursday, 31 July 2008 | 08:30 – 17:30 |
| Friday, 1 August 2008 | 08:30 – 13:30 |


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# Author Index

# Abstracts

### Effect of Surface Functionalisation on the Performance of Dye Sensitised Solar Cells

**Alessandra Allegrucci,** *School of Chemistry, Monash University, Victoria 3800, Australia*
**Naomi Lewcenko,** *School of Chemistry, Monash University, Victoria 3800, Australia*
**Leone Spiccia,** *School of Chemistry, Monash University, Victoria 3800, Australia*

Due to their high photoelectric conversion potential, DSSCs are a promising source of renewable energy. One critical aspect limiting higher conversion efficiency is recombination of the photoinjected electrons with the oxidised redox species. One strategy currently under investigation to decrease recombination losses is the treatment of the titania film with various types of insulating layers. One approach that we are using involves the attachment of various organic groups on the titania surface following porphyrin dye adsorption/attachment. These organic molecules on 'free' titania sites have the potential to prevent contact between the triiodide and the surface, thereby reducing charge recombinations. In addition, they may also change the conduction band energy of the semiconductor and electron injection into the semiconductor.

In the project, the effect of treating the titania surface with various organic carboxylic, phosphonic or sulfonic acids on the performance of DSSCs is being examined. Treated titania films were analysed using IR spectroscopy to confirm chemical attachment and to develop correlations between treatment times and surface concentrations of the organic acid. The results of testing of DSSCs constructed using these treated films showed definitive trends with the agent used. For example, phosphonic acid treatment resulted in poorer performing cells than those that underwent sulfonic acid treatment.

## 101

### Power from the Sun: the Advent of Mesoscopic Solar Cells

**Michael Graetzel,** *Laboratory of Photonics and Interfaces, Ecole Polytechnique Fédérale de Lausanne, Switzerland*
**Mohammad Khaja Nazeeruddin,** *Laboratory of Photonics and Interfaces, Ecole Polytechnique Fédérale de Lausanne, Switzerland*

The field of photovoltaic cells has been dominated so far by solid state p-n junction devices made of silicon, CdTe and copper indium gallium diselenide profiting from the experience and material availability of the semiconductor industry. However there is an increasing awareness of the possible advantages of devices based on mesoscopic inorganic or organic semiconductors commonly referred to as 'bulk' junctions due to their interconnected three-dimensional structure. It is now possible to depart completely from the classical solid-state cells, replacing them by devices based on interpenetrating network junctions. These cells are formed, for example, from nanocrystalline inorganic oxides, ionic liquids and organic hole conductor devices, which offer the prospect of very low cost fabrication without expensive and energy intensive high temperature and high vacuum processes. They can feasibly be produced employing flexible substrates and are compatible with a variety of embodiments and appearances to facilitate market entry, both for use in domestic devices as well as in architectural applications. The prototype of this new PV family is the dye-sensitized solar cell (DSC), which accomplishes the separation of the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of nanocrystalline morphology. The DSC reaches today over 11 percent conversion efficiency and excellent stability rendering it a credible alternative to conventional p-n junction photovoltaic devices. Mesoscopic oxide semiconductors such as hematite show also great promise for use as photo-anodes in tandem cells for water splitting by visible light.

### Well-defined Light-Harvesting Polymers for Organic Solar Cell Applications

**Matthias Haeussler,** *CSIRO Molecular and Health Technologies, Ian Wark Laboratories, Bayview Avenue, Clayton Vic 3168, Australia*
**Ming Chen,** *CSIRO Molecular and Health Technologies, Ian Wark Laboratories, Bayview Avenue, Clayton Vic 3168, Australia*
**Ezio Rizzardo,** *CSIRO Molecular and Health Technologies, Ian Wark Laboratories, Bayview Avenue, Clayton Vic 3168, Australia*
**Scott E. Watkins,** *CSIRO Molecular and Health Technologies, Ian Wark Laboratories, Bayview Avenue, Clayton Vic 3168, Australia*
**Gerard J. Wilson,** *CSIRO Molecular and Health Technologies, Ian Wark Laboratories, Bayview Avenue, Clayton Vic 3168, Australia*

Electroactive polymers are finding increasing applications as light-harvesting systems that mimic the light collection processes of natural photosynthetic pigment arrays. In the photosynthetic unit an intricate array of pigments absorbs the incident radiation and then transfers the absorbed energy with almost 100% efficiency to the reaction centre where it is utilized to induce a charge separation as the primary step of photosynthesis. The synthesis of luminescent polymers with well-defined architectures is a requirement for the development of optimized structures for these and new applications. In particular the ability to place luminescent groups at specific locations along a polymer chain can potentially provide control of the process of excitation energy transfer. In this contribution, we will present the synthesis of a variety of functionalized linear and star polymers that are designed to optimize excitation energy transport of the absorbed radiation to a variety of luminescent energy trapping species (Figure 1.). The polymers have been synthesized using a living free radical polymerization technique, reversible addition-fragmentation chain transfer (RAFT) polymerisation, which can provide a high degree of control over molecular weight and polymer structure.

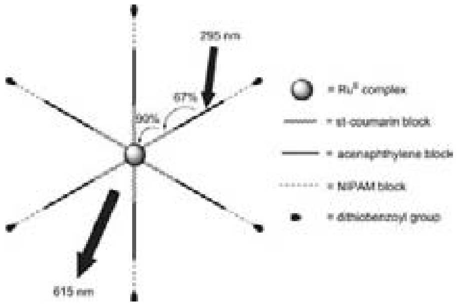


**Figure 1.** Schematic representation of the energy-transfer processes within a star-shaped block copolymer.

# 102

## Advanced Photovoltaic Concepts Based on Silicon Quantum Dots

**Martin Green,** *ARC Photovoltaics Centre of Excellence,*
*University of New South Wales, Australia*

To reach its full potential, photovoltaics has to evolve to a thin film implementation with energy conversion efficiency higher than that offered by the standard photovoltaic conversion process. Tandem or stacked cells offer the most widely demonstrated approach for such efficiency improvement but are usually associated with high costs.

A potentially lower cost option, based on silicon quantum dots embedded in a dielectric matrix, is being explored by the author's group. The nanostructure material's band gap is controlled by varying the diameter of the quantum dots. The same technology is also being investigated as a vehicle for implementing 'hot carrier' cells that have the same limiting efficiency as a large stack of cells but would be capable of being implemented in a simpler 2-terminal device. However, at present, the structure poses even more daunting physical challenges. Recent theoretical and experimental progress with both concepts will be described.

# 103

## New Direction in Photocatalysis

**Akira Fujishima,** *Kanagawa Academy of Science and Technology, Japan*

Almost 40 years ago, we succeeded for the first time, in the photoelectrochemical decomposition of water without any applied electric power, by using $TiO_2$ as the anode. This discovery attracted worldwide attention and triggered enormous research activity in numerous laboratories to photoelectrochemically decompose water with semiconductors. The principles and measurements obtained with photoelectrochemical studies at semiconductor electrodes have led to the research activity on heterogeneous photocatalysis. Again, in 1997 we reported the novel photo-induced superhydrophilicity of $TiO_2$, and proposed the concept of self-cleaning surface based on the photocatalytic and superhydrophilic properties of $TiO_2$.

Today, $TiO_2$photocatalysis has shown numerous applications in air and water purification, self-cleaning materials, and medical science. Essential point of the photocatalytic reactions is related to nanomaterials.

Just recently we have studied new application for printing by use of strong decomposition power and wettability conversion of $TiO_2$ photocatalysis.

Offset printing, which is a familiar process in the industry, can be an excellent candidate for the application of the superhydrophilic-superhydrophobic pattern on $TiO_2$surface. In the present work, we have fabricated superhydrophilic-superhydrophobic printing plate, which is made from anodized aluminum, with the use of a $TiO_2$ photocatalyst. The fabrication process consists of three steps; (1) coating of $TiO_2$ photocatalyst on the printing plate, (2) modification of TiO2-coated printing plate surface with a self-assembled monolayer(SAM) of ODS or ODP, and (3) site-selective decomposion of the SAM by $TiO_2$ photocatalysis under UV irradiation with an aqueous ink-jet printing system. In the prepared superhydrophilic-superhydrophobic pattern, water was selectively entrapped in the superhydrophilic area. After dampening the surface of the printing plate with water, an ink pattern is formed on the superhydrophobic area with a line width of 200 µm. Moreover, the possibility of these applications of pattern to the offset printing has been investigated.

# 104

## Light-Induced Water Splitting and Hydrogen Production in Nature

**Wolfgang Lubitz,** *Max Planck Institute for Bioinorganic Chemistry, Germany*

Hydrogen is considered the fuel of the future if produced from sun light-driven water splitting. A hydrogen economy based on genetically modified organisms, immobilized enzymes or biomimetic synthetic catalysts requires a profound knowledge of the structure and function of the respective enzymes in nature. Light-induced water splitting and oxygen release ($2H_2O$ &#8594 $4H^+ + 4e^- + O_2$ &#8593) is performed by a tetranuclear manganese cluster located in photosystem (PS) II which is highly conserved in all organisms performing oxygenic photosynthesis. A reliable model for the spatial arrangement of the cluster has recently been obtained from X-ray and XAS data of PS II single crystals (1). Details of the electronic structure of the cluster in its various states $S_n$ (n = 0, ...4) of the enzymatic cycle are available from spectroscopic experiments, e.g. from EPR and $^{55}$Mn ENDOR (electron-nuclear double resonance), which can be performed on the paramagnetic states of the cluster (2). Based on such data and additional experiments on water binding and oxygen release a catalytic mechanism is proposed.

The protons generated by PS II are used in various ways. One possibility is the conversion to molecular hydrogen by the enzyme hydrogenase ($2H^+ + 2e^-$ $H_2$), which is indeed found in green algae and cyanobacteria. [NiFe] and [FeFe] hydrogenases are the two main classes of this enzyme. They contain bridged binuclear transition metal cores in their active sites which are tuned by a special ligand environment to fulfil the task of efficient conversion of protons to hydrogen - or vice versa - via a heterolytic mechanism. The ligand sphere is characterized by thiolate ligands as well as an unusual coordination of the iron by small diatomic molecules ($CN^-$ and CO). The crystallization of representatives of both types of enzymes (4) has provides the spatial structure of the hydrogenases for the oxidized and reduced form. The various intermediate states in the catalytic cycle are studied by spectroscopic techniques; here results from FTIR and EPR (5) are presented. The activation of the enzyme, the inhibition by CO, the sensitivity to molecular oxygen as well as substrate binding and product formation have been investigated. This led to proposals for the catalytic cycles of the [NiFe] and the [FeFe] hydrogenases.

(1) J. Yano et al. Science 314, 821 (2006)
(2) L. Kulik, B. Epel, W. Lubitz, J. Messinger J. Am. Chem. Soc., 129, 13421 (2007)
(3) J.-H. Su, W. Lubitz, J. Messinger J. Am. Chem. Soc., 130, 786-787 (2008)
(4) J.C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet. Chem. Rev., 107 4273-4303 (2007)
(5) W. Lubitz, E. Reijerse, M. van Gastel Chem. Rev., 107, 4331-4365 (2007)

# 105

## Photoacoustic Spectra and Uultrafast Carrier Dynamics of Nanostructured $TiO_2$ Electrodes Adsorbed with CdS Quantum Dots

**Taro Toyoda,** *The University of Electro-Communications, Japan*
**Akira Sato,** *The University of Electro-Communications, Japan*
**Kenji Katayama,** *Chuo University, Japan*
**Tsuguo Sawada,** *Japan Science and Technology Agency, Japan*
**Qing Shen,** *The University of Electro-Communications, Japan*

To achieve light-harvesting efficiency more effectively, narrow-band-gap semiconductor quantum dots (QDs) have been the subject of considerable interest as a candidate for light harvesters alternative to organic dyes. The use of semiconductor QDs as photosensitizers has some advantages for sensitized solar cells. In this study, the optical absorption and ultrafasr carrier dynamics of nanostructured $TiO_2$ electrodes adsorbed with CdS QDs have been characterized by photoacoustic (PA) method and near-field heterodyne detection transient grating (NF-HD-TG) technique, respectively. PA method is effective for characterizing the optical absorption of opaque samples due to nonradiative processes. NF-HD-TG technique is a powerful time-resolved optical technique to characterize the photoexcited carrier dynamics including electron transfer from semiconductor QDs to $TiO_2$ electrodes for improving the photovoltaic conversion efficiency. Compared to conventional TG technique, NF-HD-TG technique is highly sensitive and is suitable for the measurements of rough solid samples. The shoulder part in PA spectrum, which is assumed to the first excitation energy of CdS QDs, are shifted to lower energy region with increasing numbers of the QD coatings, indicating the growth of CdS QDs. In the NF-HD-TG responses, two decay processes were observed. The fast decay one is the reflection of photoexcited hole relaxation, and the slow one corresponds to photoelectron relaxation processes, i.e., electron transfer and/or trapping. The decay time for fast decay process is almost constant for all the samples (3 ps). The decay time for slow decay process increases with the increase of growth for CdS QDs (40-80 ps).

## 106

### ZnO-Nanorod Arrays for Solar Cells with Ultra Thin $In_2S_3$ and $CuInS_2$ Absorbers

**Abdelhak Belaidi,** *Hahn-Meitner-Institut-Berlin, Germany*
**David Kieven,** *Hahn-Meitner-Institut-Berlin, Germany*
**Julian Tornow,** *Hahn-Meitner-Institut-Berlin, Germany*
**Thomas Dittrich,** *Hahn-Meitner-Institut-Berlin, Germany*
**Klaus Schwarzburg,** *Hahn-Meitner-Institut-Berlin, Germany*
**Martha Christina Lux-Steiner,** *Hahn-Meitner-Institut-Berlin, Germany*
**Atanas Katerski,** *Tallinn University of Technology, Estonia*
**Malle Krunks,** *Tallinn University of Technology, Estonia*

We report the photovoltaic properties of inorganic solid state solar cell based on ZnO-nanorod arrays with extremely thin absorbers. Two different absorbers are used; $In_2S_3$ prepared by spray ILGAR (ion layer gas reaction) and $CuInS_2$ by chemical spray pyrolysis. ZnO nanorod arrays are assuring the nano-structured of the substrate. CuSCN serves as hole conductor. Besides standard current-voltage and quantum efficiency measurements, the solar cells were investigated by scanning electron microscopy and surface photovoltage to characterize also the morphology of the structures, the bandgap and the defect-states within the bandgap.When using the $In_2S_3$ as absorber, a short-circuit current ($J_{sc}$)of 10 mA $cm^{-2}$ is recorded. The $J_{sc}$ decreases with increasing the thickness of the $In_2S_3$ absorber. The open-circuit potential increases with increasing thickness and values between 0.5 and 0.7 V are recorded. In the case of using $CuInS_2$ as absorber both the short-circuit current and the open-circuit potential increase with increasing thickness of the $CuInS_2$ film.

## 107

### Copper Sulfide-Sensitized Nanoporous Metal Oxide Solar Cells

**Miles G Page,** *Weizmann Institute of Science, Israel*
**Olivia Niitsoo,** *Weizmann Institute of Science, Israel*
**Yafit Itzhaik,** *Weizmann Institute of Science, Israel*
**Gary Hodes,** *Weizmann Institute of Science, Israel*
**David Cahen,** *Weizmann Institute of Science, Israel*

Copper sulfide ($Cu_{2-x}S$) is potentially a good candidate for an extremely thin absorber (ETA) nanoporous solar cell. While the material has a relatively high recombination rate compared to most photovoltaic semiconductors, the effectively thin layers of $Cu_{2-x}S$ (much thinner than those used in early $Cu_2S$/CdS thin film cells) in a three-component ETA cell should minimize this disadvantage. The availability and low toxicity of the material are other potential benefits. However, up to now, no experimental results have been published on such a cell; the closest being flat cell of $Cu_{1.8}S/TiO_2$ giving ca. 0.002% conversion efficiency.[1]

Here we demonstrate such porous cells wherein the $Cu_{2-x}S$ light-absorber, prepared by $Cu^+$ ion exchange from CdS or ZnS, is applied as an ultra-thin coating on a nanoporous n-type metal oxide substrate, coated with a buffer layer. The pores are filled with p-type copper (I) thiocyanate, CuSCN, as a hole conductor allowing charge separation from $Cu_{2-x}S$ into the electron- and hole-conducting phases.

Two main factors currently limiting such a cell have been identified: low efficacy of the buffer layer (at present, In-OH-S) and poor long-wavelength light absorption of the $Cu_{2-x}S$.

Combined current-voltage (I-V), transient photovoltage decay and contact potential difference (CPD) measurements are used to examine loss mechanisms and the efficiency of various buffer layers, informing the approach to realizing much improved ETA solar cells.

1. L. Reijnen et al., Mater. Sci. Eng C 2002, 19, p311.

## 108

### Supra-Hierarchical Nano-Structured Polymer Solar Cells as Efficient Organic Photovoltaics

**Susumu Yoshikawa,** *Institute of Advanced Energy, Kyoto University, Japan*

Combination of inorganic semiconductor and conjugated polymer as inorganic-organic hybrid solar cell with supra-hierarchical nanostructure such as interdigitated structure of perpendicularly oriented array of metal oxide and conductive polymer is promising to improve the solar cell efficiencies. We prepared high aspect ratio cylindrical metal oxides, such as ZnO or $TiO_2$ nanorod arrays and applied them for polymer solar cells in order to improve the absorption of the solar photons and effective collection of the photogenerated charge carriers. In order to improve the light absorption, we fabricated hybrid solar cells by using metal oxide nanorod arrays modified with some dye-molecules and P3HT/PCBM. For the first stage, ordered bulk heterojunction composed of ZnO nanorod arrays vertically on the substrate and filled with conductive polymer with surface modification of ZnO with N719 was constructed and evaluated the device performance in terms of electron transportation. Modification of the surface of ZnO nanorod arrays with N719 for inorganic-organic hybrid solar cell attained short-circuit current density of 8.89 mA/$cm^2$, which is 1.5 times higher than that in the case without the dye and such surface modification resulted 1.7 times enhancement of the power conversion efficiency up to 2.00%. Supra-hierarchical nanostructured cell is also fabricated from molecular assembly of new $C_{60}$ analogue and dye composite for the efficient exciton splitting and charge transport and by reducing the band gap of the polymer so that a larger fraction of the solar spectrum can be absorbed.

## 109

### Long Range Charge Separation in Polymer:Polymer and Polymer:Fullerene Photovoltaic Devices

**Justin M Hodgkiss,** *University of Cambridge, United Kingdom*
**Alex Marsh,** *United Kingdom*
**Agnese Abrusci,** *University of Cambridge, United Kingdom*
**Andrew R Campbell,** *United Kingdom*
**Ian A Howard,** *United Kingdom*
**Sebastian Westenhoff,** *Sweden*
**Chris R McNeill,** *University of Cambridge, United Kingdom*
**Richard H Friend,** *United Kingdom*

We have tailored transient absorption (TA) techniques to illuminate each step of polymer solar cell operation – from light absorption to charge collection. We present TA spectra with over nine decades of time resolution, allowing us to globally deconvolute a series of participating excitonic and polaronic states and the rates coupling them. Polarization resolution is used to extract nm-scale spatial dynamics, notably of long range charge separation, and electric-fields are applied to discriminate between trapped and mobile charges and extract in-situ mobilities.

We apply these techniques to a range of polymer:polymer and polymer:fullerene bulk heterojunction devices with well-defined morphologies, in conjunction with photovoltaic performance measurements. In F8BT/PFB blends (F8BT = poly(9,9´-dioctylfluorene-co-benzothiadiazole; PFB = poly(9,9´-dioctylfluorene-co-bis-N,N´-(4,butylphenyl)-bis-N,N´-phenyl-1,4-phenylene-diamine), diffusion-limited charge generation is resolved on a picosecond timescale and related to nm-scale phase separation, but device performance is thwarted by inefficient long range charge separation and subsequent collapse to a triplet exciton state. Devices comprised of combinations of P3HT, F8TBT and PCBM (P3HT = poly(3-hexylthiophene); F8TBT = poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl); PCBM = (6,6)-phenyl C61-butyric acid methyl ester) exhibit ultrafast charge generation, substantially improved charge separation yields and accordingly better external quantum efficiencies. We relate these measurements to local morphological/mobility effects near the heterojunction. Overall, we find that the efficiency of geminate charge pair dissociation is the key determinant of device efficiency, and our work draws from a range of materials and morphologies to generalize strategies for improvement.

## 110

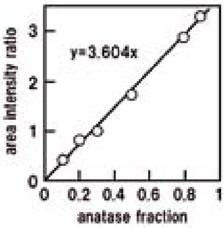
### What is Degussa P25? Crystal Composition Analysis, Reconstruction from Isolated Pure Particles, and Photocatalytic Activity Test

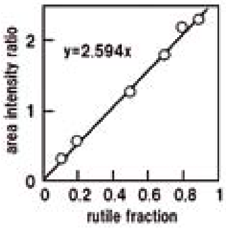
**Bunsho Ohtani,** *Catalysis Research Center, Hokkaido University, Japan*
**Ding Li,** *Graduate School of Environmental Science, Hokkaido University, Japan*
**Yasunobu Azuma,** *Graduate School of Environmental Science, Hokkaido University, Japan*
**Ryu Abe,** *Catalysis Research Center, Hokkaido University, Japan*

It is well known that Degussa P25, a very famous titania powder sample, is composed of anatase and rutile crystallites, but, as far as the authors know, there have been no reports on correct quantitative analyses for the crystal composition. Recently, the author's group succeeded in isolation of anatase crystalline phases from P25 [1]. Using this pure anatase as well as rutile [2], calibration curves (Figure) for the X-ray diffraction peaks were obtained to determine the ratio of anatase, rutile and amorphous phase to be 78 : 14 : 8.

Reconstitution of P25 was performed by mixing isolated pure anatase and rutile particles with a commercial amorphous titania in the above-mentioned ratio. An XRD pattern, BET surface area and a diffuse reflection spectrum of the reconstituted sample were almost the same as those of the original sample. The reconstituted sample showed the photocatalytic activities, in four reaction systems, which are almost the same as those by the original sample, even when the sample suspension was preparing only by putting two powders into an aqueous solution. This suggests that there is negligible synergetic effect by the co-presence of anatase and rutile in P25.

[1] Trans. Mater. Res. Soc. Jpn. 2007, 32, 401.
[2] J. Phys. Chem. B, 105, 2417-2420 (2001).



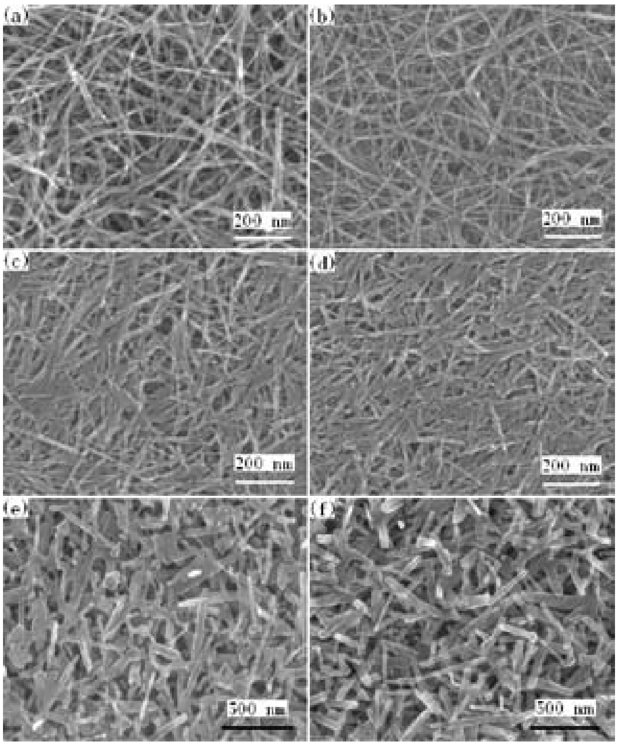


## 111

### Synthesis of Titanate Nanotube Thin Film and Applications

**Yupeng Guo,** *Sejong University,Korea, China*
**Nam-Hee Lee,** *Sejong University,Korea, Korea*
**Hyo-Jin Oh,** *Sejong University,Korea, Korea*
**Kyeong-Soon Park,** *Sejong University,Korea, Korea*
**Sang-Chul Jeong,** *Sunchon National University, Korea, Korea*
**Kyung-Sub Lee,** *Hanyang University,Korea, Korea*
**Sun-Jae Kim,** *Sejong University,Korea, Korea*

Layered titanate nanotubes thin films were prepared via the hydrothermal reaction of Ti metal flakes with concentrated NaOH solution and controlled post treatment conditions, such as washing with and without hydrochloric acid and calcination. The crystal structures, morphologies, and mechanism of formation of nanostructured titanate film are discussed through TEM, SEM, and XRD studies. Furthermore, potential applications of nanostructured titanates films in photocatalysis and hydrogen storage were investigated.



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### Efficient Photocatalysts from Titanate Nanofibres

**Huai Yong Zhu,** *Queensland University of Technology, Australia*
**Zhanfeng Zheng,** *Queensland University of Technology, Australia*
**Dongjiang Yang,** *Queensland University of Technology, Australia*
**Hongwei Liu,** *Guanxi University, China*
**Xueping Gao,** *Nankai University, China*
**Jincai Zhao,** *Institute of Chemistry, The Chinese Academy of Science, China*

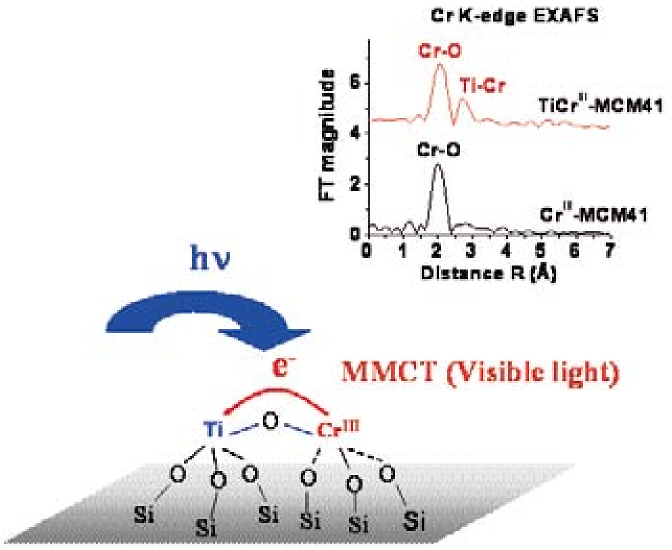
Titanate nanofibres can be produced by reacting concentrated NaOH solution with a titanium compound or titania (even a rutile mineral) under hydrothermal conditions (200°C or below). They have a large surface to volume ratio, and are able to react with dilute acids or transform to $TiO_2$ polymorphs at moderate temperatures. These properties are utilized to fabricate a series of efficient photocatalysts. They include nanofibres of mixed anatase and $TiO_2$(B) phases, $TiO_2$(B) nanofibres covered with anatase nanocrystals, metal ions doped nanofibres of the mixed titania phases, single-phase anatase nanofibres, $TiO_2$ nanofibres coated with other oxides. Such studies not only result in catalysts that possess high photocatalytic activity and can be readily dispersed into and separated from liquid phase, or exhibit considerable activity under visible light; but also provide us unique opportunity to acquire fundamental information. For instance, the detail structure of interfaces between two titania polymorphs because the nanofibre morphology is particularly suitable to the transmission electron microscopy study. The function of the interfaces in the photocatalysis processes is clarified. We also have better understanding of the pathways of the phase transitions from titanate to a titania polymorph or from one polymorph to another, and reactivity of the nanofibres to various chemicals. This knowledge can be use to design different nanostructures, particularly efficient photocatalysts.

## 113

### Polynuclear Metal Oxide Photocatalysts on Nanoporous Silica for Visible Light Water Oxidation and Carbon Dioxide Reduction

**Heinz M Frei,** *Lawrence Berkeley National Laboratory, United States*

Direct conversion of $CO_2$ to a low alcohol using $H_2O$ as electron source is an important long term goal for sunlight to fuel conversion. To take advantage of the flexibility by which energy flow, charge transport and catalytic transformations can be controlled by discreet molecular structures, we are exploring an inorganic 'molecular' approach for assembling artificial photosynthetic systems on nanoporous silica supports. Photocatalytic units consist of an oxo-bridged binuclear metal-to-metal charge-transfer group (MMCT), which is coupled to a multi-electron transfer catalyst. In some cases, the binuclear unit itself can act as redox site. We have developed mild synthetic methods for assembling and anchoring oxo-bridged binuclear MMCT units on silica nanopores with high selectivity, based on acidity differences between metal-OH groups and surface silanols (e.g. assembly of TiOCo(II), TiOMn(II)), or selective redox reactivity (TiOCr(III)). Structures of these all-inorganic units were determined by EXAFS, XANES, FT-Raman, FT-IR, EPR and optical spectroscopy. The MMCT groups serve as visible light electron pumps with adjustable potential that depends on the selected donor/acceptor metal and oxidation state. When coupling the TiOCr(III) unit to an Ir oxide nanocluster inside the silica nanopore of MCM-41 silica material, water oxidation was observed upon irradiation of an aqueous suspension with visible light. CO2 splitting to CO was achieved by exciting the MMCT transition of ZrOCu(I) units of ZrCu(I)-MCM-41 loaded with gaseous $CO_2$. The flexible assembly method of these photocatalytic units opens up opportunities for the efficient coupling of water oxidation with $CO_2$ reduction sites in robust nanoporous oxide scaffolds.



## 114

### Mechanism of Photoinduced Oxygen Evolution on Well-defined Single Crystal (rutile)$TiO_2$ Surfaces Studied by PL Emission

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**Ryuhei Nakamura,** *Department of Applied Chemistry, School of Engineering, The University of Tokyo, Japan*
**Yoshihiro Nakato,** *Department of Chemistry, School of Science and Technology Kwansei Gakuin University, Japan*

The oxygen photoevolution (or water-photooxidation) reaction at the surfaces of $TiO_2$ and related metal oxides has been attracting strong attention from the point of view of solar energy conversion (solar water splitting). We have recently reported that the oxygen photoevolution reaction is initiated by a nucleophilic attack of an $H_2O$ molecule to a surface-trapped hole (STH), accompanied by bond breaking. On this process, part of the trapped holes was extinguished by the recombination with electrons, which generates the PL at 840 nm. Thus, the PL observation gives the detail mechanisms of the oxygen photoevolution reaction.[1] In this work, we investigated about the properties of the photogenerated holes at the sub-surface layer of single crystal (rutile) $TiO_2$(110) and (100) surfaces by observing the PL with a focus being placed on how it changes with increasing of pH value of the solution. Figure 1 shows the PL intensity plotted against the pH of the electrolyte solution. We can see that the intensity of PL was drastically increased at the pH less than 5, which is close to the isoelectric point. This result was explained as follows; Under the alkaline condition, photogenerated holes are trapped not only STH but also -O- species on the surface, which reduced the intensity of PL. On the other hand, in the acidic solution, most holes were trapped at STH, resulting in the strong intensity of PL.

1) A. Imanishi et al., J. Am. Chem. Soc., 129(2007)11569.

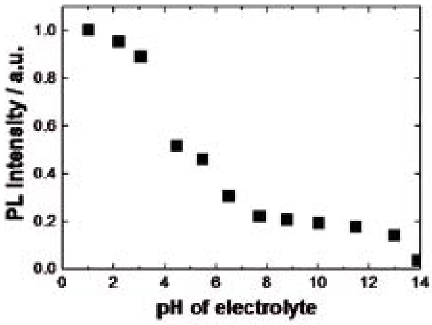

Fig.1 PL intensity plotted against pH of electrolyte

## 115

### Effect of Au Nanoparticles on the Photocatalytic Activities of Titanium Dioxide

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The photocatalytic activity of titanium dioxide-based photocatalysts obtained either by gold nanoparticles deposition or immobilisation of gold preformed sols on $TiO_2$, or synthesised by flame spray pyrolysis starting from gold containing Ti-isopropoxide precursor solutions, was tested both in the oxidative degradation of organic substrates of different nature and in the parallel hydrogen peroxide production in the presence of dioxygen. The photocatalytic hydrogen production from water photosplitting or from methanol photoreforming under an inert atmosphere were also employed as test reactions. The different activities of the various Au/$TiO_2$ samples could be related to their surface, cristallographic and textural properties, as well as to the size and oxidation state of gold nanoparticles. While the presence of gold was usually found to be beneficial in increasing the rate of all photoreductive paths, much minor and often controversial effects could be noticed in the oxidative photocatalytic degradation of organic compounds. This excludes a relevant role of gold nanoparticles in ensuring a better electron-hole separation after photocatalyst excitation. Thus, the higher hydroxyl radical production detected in preliminary electron spin trapping tests does not ensure higher oxidative degradation rates and most probably does not result from water oxidation by valence band holes, but from photoproduced hydrogen peroxide reduction by conduction band electrons.

# 116

### Photocatalyst Preparation by Carbon Doping of Titanium Dioxide

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The activity of new carbon modified titanium dioxide photocatalyst is presented. Initial materials were commercial titania (P25, Degussa, Germany) and titania nanotubes (TNT) prepared by method of Kasuga et al. [1]. The modification was conducted under elevated ethanol pressure at 180 and 220°C for 4 hours by method of Janus and Morawski [2]. New carbon modified photocatalyst were characterized by FTIR/DRS, UV-Vis/DR and TEM. The modification leads to build in carbon to titania structure without significant surface hydroxyl group's reduction. Moreover in the case of carbon modified nanotubes modification leads to changes in morphological structure of titania. The activity of new photocatalysts was tested during complied decolourisation of mono azo dye solution (Reactive Red, abs. max = 516 nm) under UV light irradiation. The photocatalytic activity of new carbon modified photocatalyst was higher than unmodified titania. Two times higher in the case of modified P25 and fifteen times higher in case of modified nanotubes.

1. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Langmuir, 14 (1998) 3160-3163.
2. M. Janus, A.W. Morawski, Applied Catalysis B: Environmental, 74 (2007) 118-123.

# 117

### DSC Toolbox - An Integrated Approach

**Anders Hagfeldt,** *Royal Institute of Technology (KTH), Sweden*

The talk will summarize our research and development activities of dye-sensitized solar cells (DSC), focusing on the development of characterisation techniques of complete DSC devices - what we call the 'tool-box'.

The scientific challenge of DSC is to handle the complex molecular interactions and the inherent multi-scaling properties, both in time and length. We have approached this scientific challenge by developing what we call 'tool'box' techniques. These techniques make it possible to extract information at the molecular level on complete DSC devices operating under normal working conditions. The methods provide information on for example energetics, charge transport and electron transfer processes. Some examples will be given at the meeting including Photoinduced Absorption Spectroscopy as a suitable method to study for example the quality of pore filling in case of solid hole conductors.

Some of our materials research will be presented. We have developed series of organic dye molecules with the general structure donor - conjugated linker - acceptor. Best efficiencies, above 7%, were obtained with polyene-diphenylaniline type dyes, using an iodide/triodide based redox electrolyte. The influences of substitutions of the donor group (a diphenylaniline moiety), the length of the conjugated linker chain and different acceptor/anchoring groups are presently being studied and will be discussed at the meeting.

The majority of studies in this field are based on the sensitization of a n-type semiconductor. However, DSCs in which the cathode is photoactive are also possible and the development of a photocathode can provide an entry to the preparation of a tandem solar cell, in which both electrodes are photoactive. Until now there have been few studies on the sensitization of p-type semiconductors. We will report on a new organic dye, designed for a p-type DSC, and its performance in a photovoltaic device based on NiO as the photocathode and a passive anode. The external quantum yield of this system has a maximum of about 18%, which is among the highest values recorded so far for p-type DSCs.

# 118

### Highly Efficient Organic Sensitizers Comparable to Ruthenium Sensitizers

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**Chul Baik,** *Korea University, Korea*
**Duckhyun Kim,** *Korea University, Korea*
**Hyunbong Choi,** *Korea University, Korea*
**Chulwoo Kim,** *Korea University, Korea*
**Sanghyun Paek,** *Korea University, Korea*
**Nara Cho,** *Korea University, Korea*
**Jaejung Ko,** *Korea University, Korea*

Dye-sensitized nanocrystallin $TiO_2$ solar cells (DSSCs)have attracted considerable interest because of their high conversion of sunlight to electricity and easy fabrication. To overcome the prohibitive cost of ruthenium metal complexes, several groups have developed metal free sensitizers and obtained efficiencies in the range of 5-8%. However, a major factor for the low photoconversion efficiency of many organic dyes in dye-sensitized solar cell is due to the formation of dye aggregates on the semiconductor surface. Therefore, for obtaining efficient photoconversion based on organic dyes, aggregation needs to be avoided through the structural modification of the dye. Another important issue for organic dyes is the stability, which are generally less stable than metal complexes for redox reactions due to formation of unstable radicals. In order to incorporate these required properties, we have designed and developed novel unsymmetrical organic sensitizers. Novel organic sensitizers composed of donor, electron-conducting, and anchoring groups were engineered at molecular level and synthesized. Here, we show synthesis, characterization and photovoltaic properties of the several sensitizers. One of them, upon anchoring onto $TiO_2$ film exhibit incident photon to current conversion efficiency 91%. The photovoltaic data revealed a short circuit photocurrent density of 19.55 mA/cm$^2$, an open circuit voltage of 718 mV and a fill factor of 0.72, corresponding to an overall conversion efficiency of 10.15% under standard AM 1.5 sunlight. In this seminar, we would like to introduce the synthesis of a variety of dyes and their photovoltaic properties.

# 119

### P-Type Dye Sensitized Solar Cells: Early Time Dynamics Associated with a Series of Organic Sensitizers on Nanocrystalline NiO Films

**Amanda L Smeigh,** *Uppsala University, Sweden*
**Hongjun Zhu,** *Uppsala University, Sweden*
**Libby Gibson,** *Uppsala University, Sweden*
**Jérôme Fortage,** *Université de Nantes, France*
**Gerrit Boschloo,** *Uppsala University, Sweden*
**Fabrice Odobel,** *Université de Nantes, France*
**Anders Hagfeldt,** *Uppsala University, Sweden*
**Leif Hammarström,** *Uppsala University, Sweden*

In 1999, prompted by the expanding research on n-type semiconductor based dye sensitized solar cells (DSSCs), the first observation of photocurrent from a sensitized p-type nanocrystalline material was reported by He et al.[1] Research on n-type semiconductors as photoelectrodes has seen a steady increase for the past 16 years, while the field of p-type semiconductors has been comparatively unexplored. The feasibility of NiO-based photocathodes has been demonstrated by only a few groups and remains a promising area of DSSC research. Ultrafast spectroscopic studies of sensitized NiO suggest that the strong electronic coupling between the NiO and the sensitizer is detrimental to the efficiency of NiO-based cells, due to the rapid back electron transfer observed for both sensitizers.[2,3]

The results we present focus on the hole-injection (< 1 ps) and subsequent recombination processes (~100 ps) associated with sensitized NiO nanocrystalline thin films. By employing femtosecond time-resolved visible transient absorption spectroscopy we are able to examine how the intrinsic early time dynamics of NiO-based dye sensitized solar cells vary between different organic sensitizers. Ultrafast measurements on complete cells are also reported in an effort to illustrate the influence of electrolyte on the observed dynamics of these novel p type devices.

[1] He, J. et.al. J. Phys. Chem. B. 1999, 103, 8940-8943.
[2] Borgström, M. et.al. J. Phys. Chem. B 2005, 109, 22928.
[3] Moranderia, A. et.al. J. Phys. Chem. B 2005, 109,19403.

## 120

### A Novel Design for Monolithic Solid-State Dye-Sensitized Solar Cells with Platinized Carbon Counter-Electrode

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**Rachel A Caruso,** *School of Chemistry, The University of Melbourne, Melbourne, Victoria, 3010, Australia, Australia*

Conversion efficiencies of dye-sensitized solar cells (DSSCs) have been reported to reach 10~12%. However, these values have only been obtained using a liquid electrolyte. Recently much effort has been directed towards development of solid-state DSSCs, avoiding the associated issues of liquid electrolytes such as leakage, dye desorption, and electrode corrosion. Compared to conventional DSSCs, monolithic solid-state DSSCs offer the prospect of being lower cost and require a simpler manufactories process. Unfortunately, solid-state DSSCs show low conversion efficiencies compared with their liquid analogues, which is in part due to incomplete filling of the dye-sensitized nanoporous semiconductor and intrinsically high internal resistance. Recently we have reported a vacuum filling method, which allows effective filling of the nanoporous structure of a dye-sensitized $TiO_2$ electrode [1]. Reducing the internal resistance of these devices becomes the main challenge for further efficiency improvement in solid-state DSSCs. Here we present a novel design of monolithic solid-state DSSCs with platinized carbon counter-electrode. We could show that the internal ohmic resistance decreases dramatically when high-surface-area platinized carbon layers are used as counter-electrode, resulting in significant improvement of energy conversion efficiency and fill factor.

[1] HW Han, U Bach, YB Cheng, RA Caruso, Appl. Phys. Let. 90, 213510, 2007

## 121

### Factors Influencing Electron Lifetime in Dye-Sensitized Solar Cells: Transport and Interfacial Transfer Limited Charge Recombination in the Case of Various Dyes and Semiconductors

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**Masanori Miyashita,** *Department of Fine Materials Engineering, Shinshu University, Japan*
**Kenji Sunahara,** *Department of Fine Materials Engineering, Shinshu University, Japan*
**Yosuke Fukai,** *Japan*
**Yukiko Uzawa,** *Japan*
**Akihiro Asano,** *Japan*
**Yu Uemura,** *Japan*
**Eiji Suzuki,** *Department of Fine Materials Engineering, Shinshu University, Japan*

The highest efficiency of dye-sensitized solar cells (RuDSC) has been achieved with a Ru complex dye and nano-porous $TiO_2$. In order to increase the efficiency, novel dyes and matched semiconductors are desired. To date, some dyes have shown comparable short-circuit current with RuDSC, but none of them showed comparable open-circuit voltage (Voc). The lower Voc was attributed to shorter electron lifetime in these DSCs. Besides $TiO_2$, various semiconductors such as $SnO_2$, ZnO, and $In_2O_3$, have been examined, but $TiO_2$ have been the best. The lower efficiency of some semiconductors has been interpreted with higher electron mobility in the semiconductors, resulting in the faster interfacial recombination. In order to design DSC, it is important to understand the mechanism of the electron transfer processes, especially the transfer from the semiconductor to dye cation and/or $I_3^-$. The transfer rate is governed by transfer rate in the semiconductors, that is, transport limited, and interfacial transfer rate. To understand the mechanism, the effect of these should be ruled out, and then factors influencing each should be studied. For the purpose, we examined the electron diffusion and lifetime in DSCs prepared with semiconductors having different conduction band edge potentials and electron mobility, and with various dyes including both metal and metal-free dyes. It was found that the effective diffusion coefficients in $SnO_2$ and $In_2O_3$ were comparable and higher with that of $TiO_2$, respectively, and free energy difference has influences on the interfacial charge transfer rate. The degree of the influence of transport rate is discussed.

## 122

### Nano-Dispersion of Commercial $TiO_2$ Powders for High Efficiency Dye-Sensitized Solar Cells

**Nam-Gyu Park,** *Korea Institute of Science and Technology, Korea*

Nanodispersion of agglomerated TiO2 powders has been performed by microbead milling and its effect on photovoltaic performance has been investigated with dye-sensitized solar cell. Plasma-treated 30 μm-diameter zirconia beads are used to disperse commercially available Degussa P25 TiO2 in ethanolic medium. Particle size distribution, surface area, film morphology, porosity, transmittance and haze are investigated with different milling speed of 30 Hz and 45 Hz and milling time of 30 min and 90 min. After microbead milling, average particle size is reduced with narrow size distribution, as a result surface area is increased. A slight phase transformation from anatase to rutile is observed during microbead milling. Film porosity is significantly changed from 76% to about 51% after microbead milling due to highly dispersed nature. Microbead milling has also influence on optical property, where transmittance increases and haze decreases with increasing milling speed and/or milling time. Compared with photovoltaic performance of dye-sensitized solar cell based on the as-received P25, overall conversion efficiency with the aperture-masked cell is substantially improved from 4.46% to 6.42% after microbead milling at 30 Hz for 90 min, corresponding to 44% increment, which is mainly due to a noticeable increase in photocurrent density, associated with highly dispersed characteristics by microbead milling.

## 123

### Emulating Photosynthesis: A New Paradigm for Photovoltaic Light Harvesting

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**George Tsekouras,** *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia*
**Ying Dong,** *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*
**Pawel Wagner,** *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia*
**Gordon Wallace,** *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia*
**Ana Morandeira,** *Centre for Electronic Materials and Devices, Department of Chemistry, Imperial College London, United Kingdom*
**James R Durrant,** *Imperial College London, United Kingdom*

Replicating photosynthetic processes in devices could provide a new generation of economical photovoltaic devices and lay the foundation for sustainable hydrogen production through water splitting. In the dye-sensitised solar cell (DSSC) or Grätzel photoelectrochemical cell, light is harvested using a large surface area of dye (that may be a chlorophyll-like molecule) bound to a mesoporous thin film of nanostructured titanium dioxide and, following charge separation and injection of an electron into the semiconductor, the oxidised dye is reduced by a redox mediator. This has often been likened to the light harvesting component of photosynthesis. However, in the exquisitely structured photosynthetic light harvesting process, light is absorbed by a 3-dimensional non-covalent array of up to three hundred chlorophyll 'dyes' that make up the light harvesting antenna, and the energy transferred to the 'special pair' of bacteriochlorins in the Reaction Centre, within which charge separation occurs. In other words, in photosynthesis, the energy absorption and transfer, and charge separation processes are somewhat isolated from each other. Emulating this in the titanium dioxide solar cell would offer the potential to improve cell efficiency both through enhanced light harvesting as well as control of the energy and electron transfer processes. In this lecture we will discuss our progress in understanding the action of porphyrins in the DSSC towards developing structures on titanium dioxide that emulate photosynthesis.

## 124

### Biosynthetic, Structural and Physiological Characterization of the Membrane Associated [NiFe] Hydrogenases in the Purple Sulfur Photosynthetic Bacterium, Thiocapsa Roseopersicina BBS

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Tímea Balogh, *Department of Biotechnology, University of Szeged, Inst. Biophysics, Biol. Res. Centre, Hungarian Academy of Sciences, Hungary*
Gergely Maróti, *Department of Biotechnology, University of Szeged, Inst. Biophysics, Biol. Res. Centre, Hungarian Academy of Sciences, Hungary*
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Lívia S Palágyi-Mészáros, *Department of Biotechnology, University of Szeged, Inst. Biophysics, Biol. Res. Centre, Hungarian Academy of Sciences, Hungary*
Roalnd Tengölics, *Department of Biotechnology, University of Szeged, Inst. Biophysics, Biol. Res. Centre, Hungarian Academy of Sciences, Hungary*
Gábor Rákhely, *Department of Biotechnology, University of Szeged, Inst. Biophysics, Biol. Res. Centre, Hungarian Academy of Sciences, Hungary*

Thiocapsa roseopersicina BBS, a purple sulfur photosynthetic proteobacterium, contains five [NiFe] hydrogenases: two membrane-bound (HupSL and HynSL) enzymes, two NAD+ reducing soluble (Hox1 and Hox2) hydrogenases and one soluble regulatory hydrogenase (HupUV).

The structural genes (hynS, hynL) in the hyn operon are separated by a 2 kbp region containing two orfs: isp1 and isp2. In silico analysis revealed, that Isp1 is a cytochrome b like transmembrane protein, while Isp2 is a cytoplasmic protein belonging to the heterodisulfide reductase family. The in silico analysis of the recently sequenced T. roseopersicina genome and the functional analysis of the hynS-isp1-isp2-hynL genes suggested that the Hyn enzyme had connection to the sulfur metabolism and NAD+ house-keeping via the Isp1,2 proteins.

Downstream of the hupSL genes several protein coding genes, localized on a single transcript were identified. Their protein products are involved in the posttranslational maturation, membrane anchoring of the enzyme, electron transport processes or transcriptional regulation. The physiological role of the HupSL enzyme is to reoxidize hydrogen. In this process, the cytochome b type HupC transfers the electron to the quinone pool.

The maturation of the NiFe hydrogenases is a complex process requiring the concerted action of numerous accessory proteins affecting the biosynthesis of the various hydrogenases. The genes coding for these maturation enzymes were identified and a maturation model will be presented.

This work has been partly supported by EU 6th Framework Programme projects (HyVolution SES6 019825 and NEST STRP SOLAR-H 5166510), and by domestic funds (NKTH, GVOP, Asbóth, Baross, DEAK-KKK, KN-RET)

## 125

### Photosystem II and the Bio-mimetic Production of Hydrogen

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Many reactions in Photosynthesis occur with efficiencies unmatched by man-made catalytic systems. A key such step is the electro-chemical splitting of water into $H^+$ and molecular Oxygen in Photosystem II (PSII). This 'solves' the most chemically demanding reaction in the electrolytic decomposition of water into $H_2$- and $O_2$, vis the anodic oxidation of water (or $OH^-$) to molecular oxygen and protons. The Mn containing water splitting catalytic site in PSII performs this reaction at close to thermodynamically limiting efficiency (< 0.2V over-voltage), at a high turnover rate (~103 $s^{-1}$), under mild external pH and in the presence of significant concentrations of environmentally common anions, such as $Cl^-$. A bio-mimetic electrolysis system based on the natural PSII catalytic site would have substantial thermodynamic and kinetic advantage.

The PS II oxygen evolving complex (OEC) contains 4 Mn and 1 Ca in a compact, exchange coupled cluster. While full structural detail of the site is yet to be resolved, most of the protein ligands, which define the cluster geometry, are located in a very small region near the C terminus of the D1 polypeptide of the PSII reaction centre. This suggests that functioning catalytic site analogs may be assembled from small model peptides or other synthetic constructs. Proposals for such a structures have been made and some existing Mn complex OEC models show promise of useful catalytic function. (for details, see [1])

Recently computational chemistry has been employed to explore possible intermediate structures and catalytic pathways to water oxidation which the Mn cluster might utilize [2]. This approach shows great promise and reveals aspects of the system essentially inaccessible by other techniques. Here the latest results of this and other work will be discussed and the possibilities for a practical, fully bio-mimetic cathodic water oxidiser will be assessed.

[1] R. Pace in 'Artificial Photosynthesis: From Basic Biology to Industrial Application' A.F. Collings and C. Critchley eds. ,WILEY-VCH , Weinheim, 2005, Chapt. 2
[2] S. Petrie, R. Stranger, P. Gatt and R. Pace, European J. Chem. (2007) 13, 5082-5089

# 126

## Effect of Molecular Organization on Energy Transfer Dynamics in Biomimetic Light-Harvesting Systems

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**Bart MJM Suijkerbuijk,** *Organic Chemistry and Catalysis, Utrecht University, The Netherlands*
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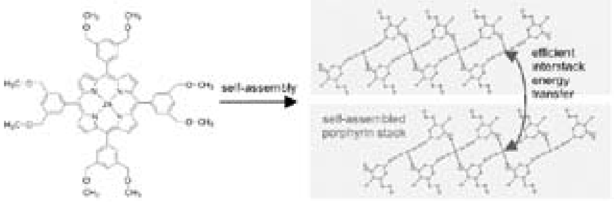
Energy transfer over considerable long distances plays an important role in photosynthetic energy conversion processes. The occurrence of energy transfer over distances of typically 10-20 nm is in general attributed to the specific organization of the dye molecules in the light-harvesting complexes in photosynthetic organisms. In contrast to natural systems, energy transfer in artificial dye layers only occurs over distances of typically a few nanometers, which is often related to the amorphous nature of the dye layer. The aim of this research is to provide a fundamental understanding of the influence of the molecular organization of biomimetic dye molecules on the energy transfer dynamics. To this end, we have determined the exciton diffusion length in various structured porphyrin layers on top of a smooth electron-accepting semiconductor surface using the time-resolved microwave conductivity technique. In addition, layer structures have been characterized using optical spectroscopy including polarized optical microscopy and X-ray diffraction.

For ZnOP layers (see Figure) it is found that excitons diffusive between the self-assembled stacks, with the exciton diffusion length being as long as 15 nm. For more amorphous layers considerably shorter exciton diffusion lengths of less than 3 nm are found. Combining the exciton diffusion length with the exciton lifetime of 160 ps yields an exciton diffusion coefficients equal to 1.4×10-6 m2/s for the ZnOP layer. The large exciton diffusion coefficient originates from a strong excitonic coupling for interstack energy transfer. For this reason application of such self-assembled porphyrins in thin dye sensitized solar cells is promising.



# 201

## Design of Highly Efficient Visible Light Sensitive Photocatalysts on the Basis of Interfacial Charge Transfer

**Kazuhito Hashimoto,** *Department of Applied Chemistry, The University of Tokyo, Research Center for Advanced Science and Technology, The University, Japan*

We recently reported a novel visible-light-sensitive photocatalyst by grafting Ti(IV)-O-Ce(III) hetero-bimetallic assemblies onto the inner walls of mesoporous silica and successfully demonstrated that photocatalytic oxidative decomposition can be initiated by a metal-to-metal charge transfer (MMCT) induced by visible light, i.e., electron transfer proceeds from Ti(IV) to Ce(III)(1). Moreover, on the basis of this observed MMCT and the fact that the conduction band (CB) of $TiO_2$ mainly consists of Ti3d orbitals, we expected that photoirradiation can directly induce a charge transfer from atomic metal ions to the CB of $TiO_2$ when they are atomically grafted onto a $TiO_2$ surface. In reality, $TiO_2$ powder with either Ce(III) or Cr(III) ion grafts was successfully demonstrated to show photocatalytic activity under visible light irradiation(1,2). This process corresponds to a type of interfacial charge transfer (IFCT) between discrete energy levels of molecular species and continuous one of solids, which was predicted by Hush(3) and theoretically formulated by Creutz et al.(4). Therefore, we further hypothesized that photoirradiation also induces charge transfer directly from an oxide VB composed of O2p orbitals to atomic metal ions atomically grafted on the oxide surface. In addition, it is reported that a Cu(I) ion occasionally catalyzes multi-electron oxygen reduction. Based on those considerations, we designed novel photocatalysts sensitive to visible light, namely, Cu(II)-grafted $TiO_2$ and $WO_3$ (5). The fabricated Cu(II)/$TiO_2$ and Cu(II)/$WO_3$ photocatalysts decomposed gaseous 2-propanol(IPA) to $CO_2$ via acetone very efficiently under visible light. Compared to N-doped $TiO_2$, which had previously been believed to be the most efficient visible light photocatalyst, the decomposition of IPA under visible light (> 400 nm) by Cu(II)/$TiO_2$ had 5.5 and 2.1 times higher quantum efficiency (QE) and $CO_2$ generation rate, respectively. As for Cu(II)/$WO_3$, it had 11 and 16 times higher QE and $CO_2$ generation rate, respectively.

Reference

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(5) H.Irie, S. Miura, K. Kamiya, K. Hashimoto, Chem. Phys. Lett., in press.

# 202

## Synthesis and Properties of Electroactive Conjugated Polymers

**Andrew B Holmes,** *University of Melbourne, Australia*

This presentation will summarize research on the synthesis and properties of semiconductive conjugated polymers for applications as organic electronic materials.

For display applications copolymers based on polyfluorenes are the polymer of choice. The presentation will describe the preparation of polyfluorenes and contributions of our research group in minimizing the long wavelength (green) emission which evolves as a result of formation of fluorenone emissive units through an oxidation process. Advances in harnessing the triplet state in electroluminescence will be reported, in which solution processible electrophorescent organometallic derivatives are incorporated in suitable copolymers. Double charge injection to produce emission of light in conjugated polymers should in principle be capable of being reversed to generate light harvesting devices. At the University of Melbourne we are interested in both dye sensitized solar cells and bulk polymer heterojunction cells. The work has been underpinned by both an International Science Linkage Project funded by the Australian Government and a consortium funded by the Energy Technology Innovation Strategy (ETIS) of the Victorian State Government.

## 203

### Solar Hydrogen Production Using Powdered Photocatalysts

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Various photocatalyst materials aiming at water splitting are introduced [1]. Alkali and alkaline earth tantalates have arisen as a new group of photocatalyst materials for water splitting into $H_2$ and $O_2$ under ultraviolet light irradiation. Among the tantalates, a NiO (0.2 wt %)/$NaTaO_3$:La (2%) photocatalyst with a 4.1-eV band gap showed high activity for water splitting into $H_2$ and $O_2$ with an apparent quantum yield of 56% at 270 nm. The NiO/$NaTaO_3$:La photocatalyst have demonstrated highly efficient water splitting using a powdered photocatalyst system. Many visible-light-driven photocatalysts have also been developed through band engineering by doping of metal cations, new valence formation, and by making solid solution. $BiVO_4$, $AgNbO_3$, and $TiO_2$ co-doped with Rh and Sb photocatalysts showed high activities for $O_2$ evolution in the presence of sacrificial reagent ($Ag^+$) under visible light irradiation. Pt/$SrTiO_3$ doped with Rh showed high activity for $H_2$evolution from aqueous solutions containing a reducing reagent. Solar water splitting under visible light irradiation has been achieved by construction of a Z-scheme photocatalysis system employing the visible-light-driven photocatalysts, Ru/$SrTiO_3$:Rh for $H_2$evolution and $BiVO_4$ for $O_2$ evolution, and an $Fe^{3+}$/ $Fe^{2+}$ redox couple as an electron relay. On the other hand, $AgInS_2$-$CuInS_2$-ZnS solid solution photocatalysts showed activity for solar $H_2$ productoin from aqueous solutions including sulfur compounds as electron donor.

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## 204

### Limits to the Efficiency of Dye Sensitized and Organic Solar Cells: The Role of Interfacial Bimolecular Recombination

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**Piers Barnes,** *Imperial College London, United Kingdom*
**Sara Koops,** *Imperial College London, United Kingdom*
**Tracy DosSantos,** *Imperial College London, United Kingdom*
**Chris Shuttle,** *Imperial College London, United Kingdom*
**Ana Morandiera,** *Imperial College London, United Kingdom*
**Assaf Anderson,** *Imperial College London, United Kingdom*
**James R Durrant,** *Imperial College London, United Kingdom*

In photovoltaic cells, bimolecular recombination 'competes' with other loss mechanisms, such as shunts and sub-optimum charge separation (geminate recombination). It is important to understand which of these loss mechanisms dominates a given cell parameter (Voc, Jsc, FF) in order to have a reasonable strategy for improvement. Perhaps even more important, it is critical to examine the loss routes when new materials fail to preform as desired, in order to develop design rules for future efforts. Concurrent charge density and charge lifetime measurements, along with transient absorption, can convincingly determining the major contribution to losses for both existing and new cell materials.

The 'holy grail' of dye sensitized cells is a dye that has strong absorption at >700 nm and yet functions as well as the present best dye, 'N3'. Many hundresds of new dyes have been synthesized and tested. Despite this effort, design rules for optimized dyes remain poorly developed. By comparing charge density and recombination rates, and by examination of the literature, we have come to the conclusion that many, if not most, dyes are catalysts for the recombination of the electron with the electrolyte. This catalysis of recombination can strongly decrease the Voc and fill factor relative to N3, which does not catalyze recombination. We will present recombination measurements covering a range of dyes and dye classes, with the hope that motifs that encourage and discourage recombination will be identifiable.

Given time, new charge density, TAS, and recombination measurements in polymer/PCBM cells will also be discussed.

## 205

### Supramolecular Electrolytes for Solid State Dye-Sensitized Solar Cells

**Yong Soo Kang,** *Department of Chemical Engineering, Hanyang University, Korea*
**Yong-Gun Lee,** *Seoul National University, Korea*
**Sun Young Kim,** *Department of chemical engineering, Hanyang University, Korea*
**Su Jin Kim,** *Department of chemical engineering, Hanyang University, Korea*

The development of solid state dye sensitized solar cells (DSSCs) is desirable because of their advantages such as low production cost by roll-to-roll process and prolonged durability. However, their energy conversion efficiency is still very low 2~4% compared to that corresponding to liquid type DSSCs (~11%). Thus, oligomeric supramolecules containing double and triple hydrogen bonding sites at both chain ends of the poly(ethylene glycol) oligomers have been utilized to improve the overall energy conversion efficiency by enlarging interfacial contact area between the solid state electrolyte and dyes, and also by improving ionic conductivity. Double hydrogen bonding sites were introduced at both chain ends of the poly(ethylene glycol) (PEG, MW=2,000) by reacting PEG-dimesylate with pyrimethamine, which were in situ polymerized with glutaric acid by double hydrogen bonds (2H-Polymer). The oligomers with triple hydrogen bonding sites were also synthesized by reacting PEG-dimesylate with guanine and cytosine (3H-Polymer). DSSCs employing the 2H- and 3H-polymer electrolytes resulted in the overall energy conversion efficiency of 4.63 % and 4.53 %, respectively, at one sun conditions with active area = 0.16 cm2, TiO2 layer thickness = 10 µm. Short circuit current densities of (JSC) 10.41 and 10.09 mAcm-2, open circuit voltages (VOC) of 0.71 and 0.69 V, fill factors (FF) of 0.62 and 0.65, were obtained from 2H- and 3H-polymers, respectively.

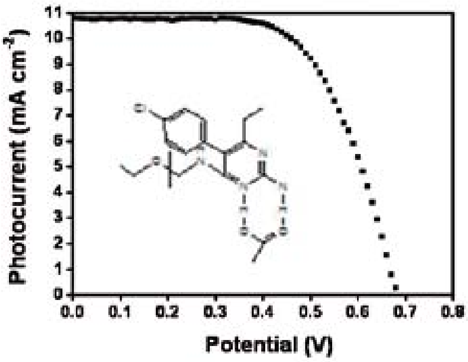

Figure 1. I-V curve of DSSC employing 2H-polymer electrolyte.

## 206

### Optimising P3HT/PCBM Organic Photovoltaic Cells: Identifying Key Parameters

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**Maxwell J Crossley,** *School of Molecular and Microbial Biosciences, The University of Sydney, Australia*
**Noel S Hush,** *The University of Wollongong, Australia*
**David L Officer,** *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia*
**Paul C Dastoor,** *School of Mathematical and Physical Sciences, University of Newcastle, Australia*

Porphyrins are added in ternary blends of organic fullerene-polymer solar cells, allowing the concentration of polymer in functioning polymer/fullerene blends to be reduced to under 10% with little impact on device functionality. By varying the concentrations in this low-doping region, the solar cell absorption is partitioned into contributions from each component. This allows the observed internal quantum efficiency (IQE) to be partitioned into contributions based on the nature of the absorbing material (polymer, fullerene, or porphyrin). Addition of the porphyrin increases the IQE following light absorption by the polymer or fullerene, adds broadband character to the photocurrent, but slightly decreases the open-circuit voltage so that the overall efficiency changes only slightly. Most significantly, the IQE partitioning process reveals that the majority of the photocurrent produces in 'standard' (20%) polymer/fullerene solar cells is produced following light absorption by the fullerene. This result connects with known results for fullerene-oligomer dyads that demonstrate significant primary charge separation following fullerene irradiation.

# 207

## Gold Nanoparticle / Polythiophene Hybrid Solar Cell

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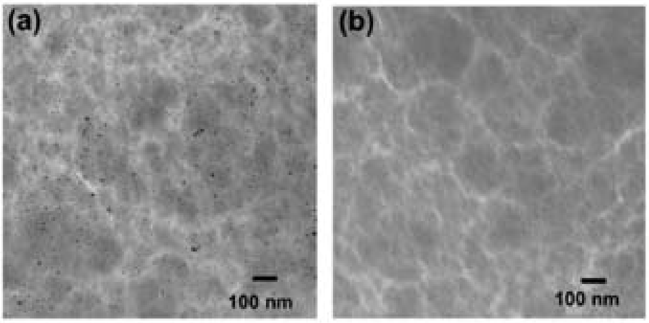
**Nam-Gyu Park,** *Korea Institute of Science and Technology, Korea*

We obtained improved polythiophene / PCBM bulk heterojunction photovoltaic devices by doping with stable and highly electrically conductive Au nanoparticles (NPs). Figure 1 shows TEM images of thermally annealed polythiophene / PCBM films with Au nanoparticles (fig 1(a)) and without (fig.1(b)) Au nanoparticles. We can clearly observe the formation of nanodomains of polythiophene and PCBM. In addition, Au nanoparticles are dispersed homogeneously in the film even after thermal annealing at 140oC.

The Au nanoparticle doped hybrid devices showed improved efficiency. The improvement is mainly ascribed to the increased photocurrent density.

We suggest that a dominate mechanism for the efficiency enhancement of hybrid photovoltaic device is the improved electrical conductivity and enhanced optical strength due to the surface plasmon of the Au NPs. The detailed voltage-current density characteristics and wavelength dependence of external quantum efficiency of the hybrid solar cell will be discussed in detail.



# 208

## Formation of Charge Carriers and Excitons in Polymer–Fullerene Solar Cells

**Hideo Ohkita,** *Kyoto University, Japan*
**Jiamo Guo,** *Kyoto University, Japan*
**Hiroaki Benten,** *Kyoto University, Japan*
**Shinzaburo Ito,** *Kyoto University, Japan*

Formation dynamics of excitons and charge carriers in polythiophene–fullerene blend films were studied by near-IR femtosecond transient absorption spectroscopy and highly sensitive microsecond transient absorption spectroscopy at room temperature. Singlet excitons generated in a regiorandom poly(3-hexylthiophene) (RRa-P3HT) pristine film were converted into triplet excitons with a time constant of > 100 ps through intersystem crossing under low excitation condition. At a high excitation, the singlet decay was much faster because of singlet–singlet annihilation but the triplet formation yield remained relatively high. This finding suggests that triplet excitons are formed via charge recombination of polaron pairs generated from hot excitons. On the other hand, singlet excitons generated in RRa-P3HT/[6,6]-phenyl $C_{61}$ butyric acid methyl ester (PCBM) blend films rapidly decayed with a fast time constants (< 100 fs) and a slow one (~ ps). The fast component is ascribed to the prompt charge formation at the interface between P3HT and PCBM. The slow component is ascribed to singlet exciton migration in large domains to the charge separation interface. The efficient triplet formation was still observed for the blend films even though singlet excitons were strongly quenched. The formation of triplet excitons was slower than the charge formation but much faster than that through intersystem crossing from singlet excitons observed for the RRa-P3HT pristine film, suggesting the triplet formation via charge recombination of ion pairs.

# 209

## Cyclometallated Ruthenium Sensitizers as a New Paradigm Towards High-Efficiency Dye-Sensitized Solar Cells

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**Takeru Bessho,** *Laboratory for Photonics and Interfaces, ISIC, EPFL, Switzerland*
**Eiji Yoneda,** *Laboratory for Photonics and Interfaces, ISIC, EPFL, Switzerland*
**Jun-Ho Yum,** *Laboratory for Photonics and Interfaces, ISIC, EPFL, Switzerland*
**Matteo Guglielmi,** *Laboratory of Computational Chemistry and Biochemistry, Switzerland*
**Ivano Tavernelli,** *Laboratory of Computational Chemistry and Biochemistry, ISIC, EPFL, Switzerland*
**Ursula Rothlisberger,** *Laboratory of Computational Chemistry and Biochemistry, ISIC, EPFL, Switzerland*
**Michael Graetzel,** *Laboratory for Photonics and Interfaces, ISIC, EPFL, Switzerland*

Dye-sensitized solar cell (DSC) that mimics natural photosynthesis in the conversion of solar energy is expected to contribute significantly in next generation of photovoltaics. The high efficiency of the DSC associated with low cost, and ease of production attracted the attention of many research groups focussing on fundamental aspects of dye sensitized solar cell components. In these cells on of the key component is the sensitizer containing acceptor/donor ligands that controls light harvesting, charge injection and charge separation assisted with donor thiocyanate ligands. Attempts to replace thiocyanate donor ligand however, met with limited success in obtaining high efficiency. In this presentation we report thiocyanate free novel cyclometalleted ruthenium sensitizer (YE05) and its application in DSC. Solar cell using the YE05 sensitizer exhibit remarkable incident monochromatic photon-to-current conversion efficiency 83%, and a short circuit photocurrent density of 17 mA/cm$^2$, the open circuit voltage was 809 mV and a fill factor of 0.73, corresponding to an overall conversion efficiency of 10.04% at standard AM 1.5 sunlight. The structural, electronic and optical properties of the cyclometalleted ruthenium sensitizer were investigated using both spectroscopic, and density functional and time dependent density functional theory.

## 210

### Electrodeposited ZnO/CdSe Core-Shell Nanowire Arrays: Building Blocks for Nanostructured Solar Cells

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**Ramon Tena-Zaera,** *Institut de Chimie et Matériaux de Paris-Est, CNRS, 94320 Thiais, France*
**Ivan Mora-Sero,** *Departament de Física, Universitat Jaume I, 12071 Castelló, Spain*
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Electrodeposited ZnO/CdSe core-shell nanowire arrays present highly interesting properties to be used as building blocks for nanostructured solar cells. ZnO/CdSe/CuSCN ETA (Extremely Thin Absorber)-solar cells based on this nanostructure exhibited promising photovoltaic efficiencies ~2.5% [1]. A strong influence of the annealing temperature on the electronic performance of ZnO/CdSe nanowires has been found, the best results being obtained after annealing in air at 400°C. External quantum efficiency > 70% has been reached for ZnO/CdSe nanowire arrays in ferro/ferricyanide solutions [2]. The annealing effects on the structural properties of ZnO/CdSe nanowires have been analyzed by X-ray diffraction. Electrochemical impedance spectroscopy measurements [3] have been performed in polysulfide solutions to study the influence of the annealing temperature on the charge transfer at ZnO/CdSe interface. The variation of (micro) structural properties and charge transfer will be discussed in the frame of solar cell applications. On the other hand, the effects of dimensions, density and verticality of the ZnO nanowire arrays on the light scattering have been investigated by optical spectroscopy. An overview of the influence on the absorption of solar light by ZnO/CdSe core-shell nanowires will be presented. Some strategies to reduce the thickness of CdSe shell without decreasing the solar light absorption will be discussed, opening new approaches to get nanostructured solar cells less sensitive to the properties of the light absorber layer.

[1] C. Lévy-Clément et al. Adv. Mater. 17, 1512 (2005)
[2] R. Tena-Zaera et al. Chem. Mater. 19, 1626 (2007)
[3] I. Mora-Sero et al. Appl. Physics. Letters 89, 203117 (2006)

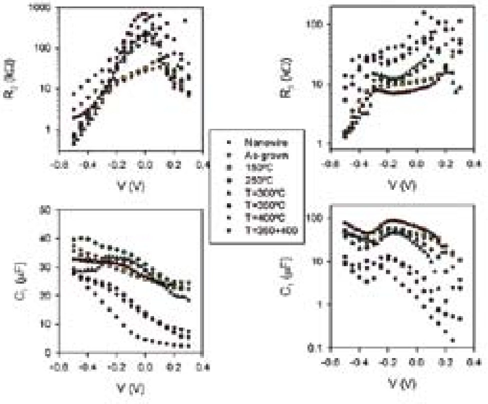

Figure 1. Electrochemical Impedances of ZnO/CdSeNanowires in Polysulfide Electrolyte, as a function of the annealing temperature

## 211

### Deep Donor States in $InVO_4$ and $BiVO_4$ Photo-Anodes

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**Steven Kleijn,** *Delft University of Technology, Department DelftChemTech, The Netherlands*
**David Lloyd,** *Delft University of Technology, Department DelftChemTech, The Netherlands*
**Cristina S Enache,** *Delft University of Technology, department DelftChemTech, The Netherlands*

In the search for efficient photo-catalysts for solar water splitting, the past few years have shown an increasing interest in complex metal oxides. When dispersed as a powder in an aqueous solution, several of these materials (e.g. $In_{1-x}Ni_xTaO_4$, $InVO_4$, $BiVO_4$, $NaTaO_3$, etc.) can evolve oxygen and/or hydrogen. However, with typical evolution rates of 1 to 100 μmole.g$^{-1}$.h$^{-1}$, efficiencies are still too low for practical applications.

To investigate the relevant materials properties, thin dense films of $InVO_4$ were made by spray pyrolysis. The optical absorption spectra reveal a bandgap of 3.2 eV, which seems to contradict earlier reports on visible light absorption by $InVO_4$. Detailed impedance analysis shows a high donor density (6x10$^{19}$ cm$^{-3}$) and a very low conductivity (3x10$^{-8}$ Scm$^{-1}$). This can be explained by the presence of deep donors in the material (cf. Figure 1A). The presence of ionized deep donors in the depletion layer gives rise to an optical transition from the valence band to the donor level, and we believe that this transition is responsible for the visible light photo-activity observed for $InVO_4$ powders. A similar effect is observed for $BiVO_4$ powders, which change color from yellow to reddish when annealed in air at 700°C (Figure 1B). No changes in the crystal structure occur, and the change in color is attributed to oxygen vacancies that form deep donor states in $BiVO_4$. Experimental evidence for the deep donor model will be presented, and the consequences for the design of efficient photocatalysts based on complex oxides will be discussed.

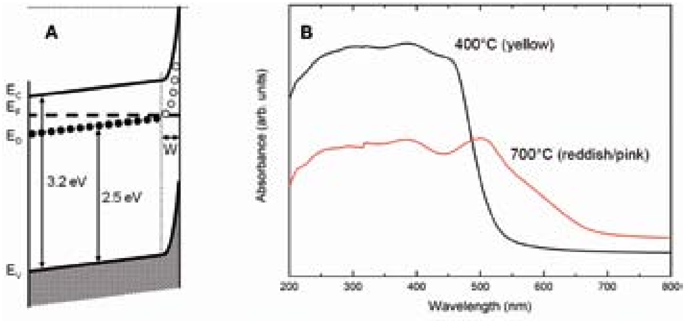

*Figure 1. A: Proposed energy diagram for $InVO_4$ indicating the presence of deep donors. B: Absorption spectrum of $BiVO_4$ pellets annealed in air at 400°C and 700°C.*

## 212

### Porphyrin Chromophore Contamination by Barbiturate Substituents: A Resonance Raman and DFT Study

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**Penny J. Walsh**
**David L Officer,** *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia*
**Pawel Wagner,** *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Australia*

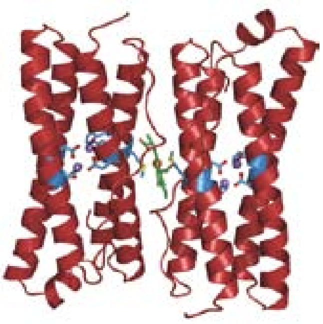
Porphyrins may be used as dyes in solar cells. They are characterized by intense B band absorptions at about 420 nm and very weak Q-band absorptions due to the electronic structure of the porphyrin core. This distinctive optical behaviour may be satisfactorily modeled by time-dependent DFT (density functional theory) calculations. Computational chemistry may also be used to conduct accurate normal coordinate analyses. We have studied porphyrin linked to barbiturate chromophores. These compounds have a B band split into two strong bands and intense Q-bands. Resonance Raman spectroscopy of the porphyrins showed enhancement of vibrations associated with the linking moiety as well as the barbiturate group. Time-dependent DFT calculations showed that the substituents perturb the frontier MOs of the porphyrin to the extent that the HOMO-2 and the LUMO+2 are strongly involved in the low energy transitions. This deviation from the ‘normal’ porphyrin behaviour, or the four-orbital model, causes the red-shifts and enhancement of the Q bands, and the red-shifts of the B bands. The use of such substitutents may offer a way to produce porphyrin dyes which are spectrally efficient absorbers throughout the visible region.

## 213

### Photo-oxidation of a Dimanganese Centre in an Engineered Bacterioferritin

**Brendon Conlan,** *Australian National University, Australia*
**Warwick Hillier,** *Australian National University, Australia*
**Tom Wydrzynski,** *Australian National University, Australia*

Natural photosynthesis involves the conversion of light into chemical energy through a series of electron transfer reactions within membrane-bound pigment/protein complexes. In the unique Photosystem II complex these electron transfer events result in the oxidation of water to molecular oxygen and hydrogen ions. Production of an in-vitro model of photosystem II will help in the elucidation of the water splitting mechanism. We have developed an artificial light-activated, metal-binding protein, using the naturally occurring bacterioferritin protein (cytochrome b1 or BFR) from E. coli. This protein is not light-active but has many design features which can be utilized to engineer light-driven electron transport. In particular each BFR subunit is a four helix bundle containing a di-iron metal binding site while two identical subunits dimerise to form a hydrophobic heme-binding pocket. The heme group can be easily removed and replaced with a photoactive zinc-chlorin molecule and the iron at the di-metal binding site can be replaced with two divalent manganese ions. Using this modified BFR protein and EPR measurements we have been able to show that the manganese is bound in a redox active form and that upon illumination of the engineered pigment protein complex, the metal centre is oxidised.



## 214

### Unexpected Differences in the P700 Redox Potential Among Photosystem I of Oxygenic Photosynthetic Organisms

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**Yuki Kato,** *Institute of Industrial Science, The University of Tokyo, Japan*
**Tomoyuki Suzawa,** *Institute of Industrial Science, The University of Tokyo, Japan*
**Tadashi Watanabe,** *Institute of Industrial Science, The University of Tokyo, Japan*

The primary electron donor of photosystem(PS) I (P700), consisted of a dimer of chlorophyll a-type pigments, generates strong reduction power upon illumination which is utilized for $CO_2$ fixation in the dark. Though numerous data have been accumulated for the P700 redox potential, which is one of the keys for understanding the molecular basis of highly efficient photosynthetic light reaction, over decades, the reported values are heavily scattered. A part of these scattering might be arisen from inaccuracy in the measurements. It is also possible that the P700 redox potential itself varies significantly among oxygenic photosynthetic organisms, though little attention is generally paid for such possibility due to highly conserved amino acid sequences of core polypeptides surrounding P700 throughout species.

Here, the P700 redox potentials were determined systematically for oxygenic photosynthetic organisms belong to different phyla by highly accurate spectroelectrochemical means recently developed by us. We revealed that the P700 redox potential is varied by about 70 mV among the organisms depending roughly on its phylum. The P700 redox potential was lowest for primitive cyanobacteria and the potential shifted gradually to positive direction in an order of red algae, cyanobacteria, green algae and higher plants. We will discuss possible causes for the shifts of the P700 redox potential in the light of kinds of in vivo electron donor proteins for $P700^+$ reduction they employed and its redox potential.

## 215

### Unexpected Properties of the Low-Energy Absorption in Photosystem II

**Elmars Krausz,** *Research School of Chemistry, The Australian National University, Canberra, Australia*

Nature's ability to split water into oxygen and protons lies at the heart of oxygenic photosynthesis. Solar energy is absorbed, leading to the excitation of the lowest energy states of the reaction centre of Photosystem II (PSII). Rapid charge separation of the enigmatic entity P680, leads to the formation of $P680^+$. This highly oxidative photogenerated state enables, in an intricate, four-photon, four-electron, ratchet-like process to drive the oxidation of two molecules of water to molecular oxygen and four protons at the manganese cluster of PSII. $P680^+$ has the highest oxidative potential in all biology and derives its name from the transient bleach at 680 nm seen upon short pulse excitation of PSII. This state has long been held to be the lowest energy state of the reaction centre. We have made the remarkable discovery that the lowest energy optically accessible state of PSII is a weaker, broader transition of an unexpected electronic state at 730 nm. This state has distinctly different properties to the state at 680 nm and is assigned as having charge transfer, rather than dominantly chlorophyll Q band character. The properties of this state are discussed in relation to the overall process of water splitting.

## 216

### New Thermoelectric Materials and Solar Energy

**Mildred Dresselhaus,** *Massachusetts Institute of Technology, USA*

Significant progress has been made in the last decade in increasing the efficiency and performance of thermoelectric materials. Therefore interest has developed in the utilization of advanced thermoelectric materials for solar energy applications. A review of thermoelectric materials from this viewpoint is presented. The concept of using self-assembled nano-composites to enhance the thermoelectric figure of merit relative to bulk materials is discussed in general terms. The scientific advantages of the nano-composite approach for the simultaneous increase in the power factor and decrease of the thermal conductivity are emphasized along with the practical advantages of scale-up of nanostructured building blocks into bulk quantities of material suitable for solar device fabrication.

## 301

### Multiple Exciton Generation: QDs, QD Arrays, QD Solar Cells, and Controversy

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**M C Beard,** *National Renewable Energy Laboratory Golden, United States*
**R J Ellingson,** *National Renewable Energy Laboratory Golden, United States*
**M Law,** *National Renewable Energy Laboratory Golden, United States*
**J M Luther,** *National Renewable Energy Laboratory Golden, United States*
**Q Song,** *National Renewable Energy Laboratory Golden, United States*
**M C Hanna,** *National Renewable Energy Laboratory Golden, United States*
**J E Murphy,** *National Renewable Energy Laboratory Golden, United States*

We have observed very efficient multiple exciton generation (MEG) in PbSe, PbS, PbTe, and Si colloidal nanocrystals (quantum dots (QDs)) at threshold photon energies of 2-3 times the HOMO-LUMO transition. For Si, the first indirect semiconductor QD exhibiting MEG and the most important semiconductor for solar cell applications, QDs with a radius about equal to the exciton Bohr radius (5 nm) show only a small blue shift (weak quantum confinement) but still exhibit efficient MEG.. This has very important implications for QD solar cell applications. Very recently, some controversy has arisen regarding the reproducibility of reported MEG efficiencies in InAs and CdSe QDs. This controversy will be addressed and possible reasons for non-reproducibility of certain QD syntheses and measurement techniques will be discussed. We have studied MEG in close-packed PbSe QD arrays where the QDs are electronically coupled in the films and thus exhibit good carrier mobility. We have demonstrated that the MEG efficiency in such conductive PbSe QD films is comparable to isolated QDs in colloids. This is important since a promising device geometry for MEG solar cells is a 3D QD array forming a film that is the intrinsic region of a p-i-n or metal-i-metal structure; the extended states formed from the electronically coupled QDs allow the delocalized photogenerated carriers to separate, traverse the film, and be collected at the electrical contacts.. Exchanging the bulky capping ligands used in the QD synthesis with shorter molecules after film formation dramatically increases the carrier mobility of QD films by reducing the interdot spacing while retaining well-passivated surfaces. Distinct excitonic features, similar to that in isolated QDs in solution, are preserved in these electronically- coupled arrays. We have developed a simple, all-inorganic metal/QD/metal sandwich solar cell that produces a large short-circuit photocurrent (~20-30 mA/cm2) via a Schottky junction at the negative electrode without the need for sintering, superlattice order or separate phases for electron and hole transport. The PbSe NC film, deposited via layer-by-layer (LbL) dip coating, yields a solar power conversion efficiency of 2 to 2.5% at AM1.5. Experiments to determine MEG photocurrent quantum yields are in progress.

## 302

### Dye-sensitized conversion and storage of visible-light energy: Next challenge in photoelectrochemistry

**Tsutomu Miyasaka,** *Toin University of Yokohama, Japan*

Photoelectrochemistry of the dye-sensitization of oxide semiconductors, based on technology of silver halide photographic materials, has started late 1960's and evolved to realise utility-type photovoltaic (PV) modules that compete with thin-layer silicon PVs. Organic PVs, now being aggressively studied, are coming to combine dye-sensitised mesoporous layer to develop hybrid PVs. Flexible plastic dye-sensitized solar cell (P-DSC) proved itself to be a cost effective device for industries of consumer electronics with environmental recyclability. In order for an energy device to capture consumer's market, it should have high credibility in minimising process cost. We are focused on developing extremely low-cost power source and storage device of fairly high durability by eliminating high-temperature & vacuum preparation processes. This challenge leads to partial replacement of heavily consumed batteries of high environmental load with solar energy. We recently showed several routes to realizing easy-to-make P-DSCs, which reached a highest power efficiency of 7%. Large lightweight P-DSC modules proved to be sensitive to weak diffused light, indicating advantage for indoor and ubiquitous application. Electrochemistry and use of ionic electrolytes show various possibilities toward solidification of the cell and endowing charge (storage)-discharge ability for solar cell (design of photo-capacitor). Current experiments in our laboratory are to be introduced.

## 303

### Intermediate Band Solar Cells

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**A Luque**

Intermediate band solar cells (IBSCs) are conceptually devised to increase the efficiency of solar cells by absorbing below bandgap energy photons at the time they preserve the cell output voltage. The absorption of below bandgap energy photons is carried out thanks to the existence of an electronic band -the so called intermediate band- within the semiconductor bandgap. This work reviews our present understanding of the concept covering essential topics such as the inhibition of the non-radiative recombination rate, the existence of intermediate band materials and the review of the experimental results obtained so far when the concept is implemented in practice by means of quantum dots.

The inhibition of the non-radiative recombination that deep centres typically introduce in semiconductors is proposed to be achieved when the density of impurities is sufficiently high as the wavefunction of the electrons in these states transits from being localised to delocalised. On the other hand, the existence of these deep centres, introduced by certain impurities, also give the clue to propose intermediate band material candidates. Quantum dots have been used to take the intermediate band concept to practice and actual solar cells have already been manufactured. These cells, although have not exceeded the efficiency of their single gap counterparts, have proven useful to demonstrate the basic principles of operation of the IBSC.

## 304

### Electrical Transport through a Single Molecule of $[Ru(tpy)_2](PF_6)_2$

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**Emanuel Lörtscher,** *IBM Zürich Research Laboratory, Rüschlikon, Switzerland*
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**Helmar Görls,** *Institut für Anorganische und Allgemeine Chemie, Universität Jena, Germany*
**Heiko Weber,** *Institute für Angewandte Physik, Universität Erlangen, Germany*
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**Ferdinand Evers,** *Institute of Nanotechnology, KIT Karlsruhe, Germany*

The electronic transport through a single Ruthenium(II) atom hold by two terpyridine ligands in the $[Ru^{II}(L)_2](PF_6)_2$molecule (1) was investigated experimentally as well as by ab intitio methods. In order to achieve electronic contact, the Ruthenium(II)-bis-(terpyridyl) core was equipped synthetically with rigid, conjugated linkers of para-acetyl-mercapto phenylacetylene. The structure of the molecular wire (1) was determined by single crystal X-ray crystallography (Figure 1A) and found to be in high agreement with structure calculations based on the density functional theory (DFT). The current-voltage curve (I-V) of (1) was studied experimentally in a metal-molecule-metal junction using the mechanically controlled break-junction technique (Figure 1B). The results demonstrates that reproducible IV's can be obtained for molecules of the $[M^{II}(L)_2]$-type in breakjunction measurements. Quantum transport calculations for these big systems confirm the single-molecule character of the I/V experiment. Studies concerning influence of light irradiation on the electrical transport properties are under investigation.

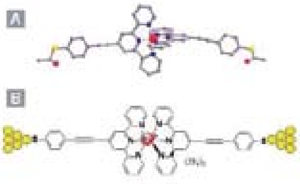

Figure 1

## 305

### Ultrafast Study of Plasmon Induced Charge Separation and Recombination Dynamics in Gold Supported on $TiO_2$ Nanoparticle Systems

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**Akihiro Furube,** *Japan*
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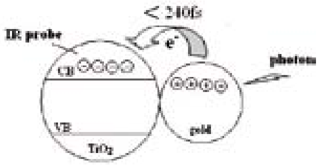
Study of plasmon-induced charge transfer mechanisms in gold-$TiO_2$ system is very significant in the solar cell application. Gold nanodots exhibit a broad interband in the UV region and a pronounced narrow surface plasmon band in the visible region originating from the collective oscillation of free conduction electrons. Under the plasmon band excitation (at 550 nm), photo-induced electron injection from gold to $TiO_2$ has been observed by our group using IR-probe femtosecond transient absorption spectroscopy. Transient absorption kinetics probed at 3440 nm were studied to observe intraband free electron adsorption in $TiO_2$. To further clarify plasmon induced charge transfer mechanism, $TiO_2$ particle size effect has been studied. In our experimental study, $TiO_2$ with different diameter (9, 20, 30, 50 nm) were loaded with 10 nm gold nanodots. We found that the electron injection times were within 240 fs and that the measured back electron transfer kinetics up to 1.5 ns were strongly dependent on the diameter of $TiO_2$. We explained different charge recombination kinetics by different diffusion distance of free electrons within $TiO_2$ particle and different contact area at the gold/$TiO_2$ interface. To compare the electron injection efficiency between plasmon band excitation and interband excitation, we changed the excitation wavelength from 400 nm to 600 nm that covered both interband and plasmon bands, and the electron injection efficiencies in gold/$TiO_2$ systems were investigated. The plasmon-induced mechanisms will be discussed in detail.



## 306

### Theory of Electron Transfer in Nonpolar Solvents

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**Masanori Tachiya,** *National Institute of Advanced Industrial Science and Technology (AIST), Japan*

In polar solvents the energies of the initial and final states change with time due to the fluctuation of the polarization of the solvent, and electron transfer takes place when they coincide. In nonpolar solvents the fluctuation of the polarization is essentially absent. In this case, how is the energy coincidence of the initial and final states brought about? In nonpolar solvents the energy $E_{IP}(r)$ of the ion pair changes significantly with donor-acceptor distance r because the Coulomb interaction is not screened by the solvent, while the energy $E_{NP}(r)$ of the neutral pair changes little with r. In nonpolar solvents the energy coincidence of the initial and final states is brought about by the change of donor-acceptor distance.

From the condition of energy coincidence the distance R at which electron transfer takes place is calculated as a function of the energy change $\Delta E_\infty$ of reaction, which represents the energy difference between the ion pair and the neutral pair at infinity. The electron transfer rate is expressed in terms of the distribution of acceptors around a donor, Landau-Zener transition probability at R, and the distribution of the relative velocity of donor and acceptor. We have calculated the electron transfer rate as a function of $\Delta E_\infty$ in the kinetic control case in which the diffusion of donor and acceptor is much faster compared with electron transfer at R. The effects of intramolecular vibration and diffusion of donors and acceptors are investigated. Comparison with experiment is also made.

## 307

### Engineering Titanium Dioxide for the Role of Photo-Anode in the Photoelectrochemical Cell

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**Graeme E Murch,** *The University of Newcastle, Australia*

It has been known for over thirty years that hydrogen can be produced directly from sunlight and water by making use of a photo-electrochemical cell. The most promising material for the key component of the cell, the photo-anode, is titanium dioxide, largely on account of its exceptionally high corrosion resistance and reasonable electronic conductivity. However, because bulk titanium dioxide has a band gap of 3eV (the optimal band gap is approximately 2eV) the cell's efficiency (roughly 2%) is much too low for commercialization (estimated to require an efficiency of about 10%). Much research has been directed to finding ways to reduce the band gap of titanium dioxide whilst retaining its corrosion resistance and basic stability. In this paper, the various strategies for reducing the band gap of titanium dioxide are reviewed including cation and anion doping, departure from the stoichiometric composition, particle size and shape, near surface segregation and defect disorder are reviewed and evaluated. The special role of multi-scale computations to direct the experimentation and the need for a multi-variate approach to optimize the required properties are specifically commented on.

## 308

### Chalcogen Element (S, Se and Te) Doped Anatase TiO2 by DFT Calculations

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**Ping Wu,** *Institute of High Performance Computing, Singapore*
**Zhong Chen,** *School of Materials Science and Engineering, Nanyang Technological University, Singapore*
**Rong Xu,** *School of Chemical & Biomedical Enginnering, Nanyang Technological University, Singapore*
**James Highfield,** *Institute of Chemical and EngineeringSciences, Singapore*
**Zhili Dong,** *School of Materials Science and Engineering, Nanyang Technological University, Singapore*

Modification of the electronic structure, defect formation and optical properties of anatase $TiO_2$ through chalcogen element (S, Se and Te) doping was studied by DFT calculation.

All chalcogen element doping prefer to substitute Ti atom at O-rich condition and O atom at Ti-rich condition. Both anionic and cationic doping can extend the absorption edge of anatase $TiO_2$ to visible region but anionic Se and Te doping is more effective. Anionic S and Se doping generate states just above the top of the valence band but anionic Te doping generates broad localized gap states. All cationic chalcogen element doping generates sharp localized gap states. The position of these gap states shifts towards the conduction band with increasing the atomic number.

Anionic doping slightly decreases the oxygen vacancy formation energy but drastically decreases the titanium vacancy formation energy, indicating that these chalcogen element doped anatase $TiO_2$s are probably good photocatalysts for water splitting under the visible light.

Mulliken charge analysis and molecular bonding analysis show that Ti - chalcogen element bonds display more covalent nature when the atomic number of chalcogen elements increases.

## 309

### How Can ZnO-Based Dye-Sensitized Solar Cells be Improved ? An Investigation by Electrochemical Impedance Spectroscopy

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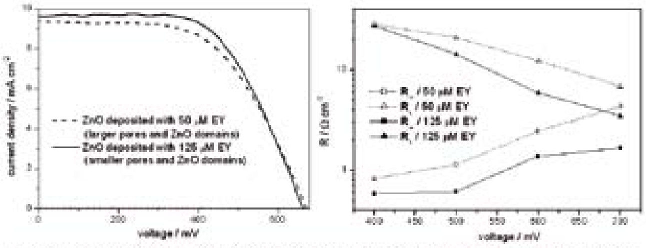
Highly porous and fully crystalline ZnO films suitable for (flexible) plastic solar cells can be electrodeposited using structure-directing additives at low temperature (< 100°C). This kind of low-temperature film recently achieved efficiencies of up to 7.2 % at 1 sun, higher than low-temperature $TiO_2$ films. However, efficiencies are still lower compared to high-temperature $TiO_2$ films, even if sensitizers with good adsorption properties on ZnO such as the indoline dye D149 are employed, due to lower open-circuit voltages and fill factors.

In order to determine the reasons for these findings and further increase the efficiency, we investigated different ZnO-based cells by electrochemical impedance spectroscopy. Measurements were made at different potentials along the whole I-V-curves in order to explain differences in the fill factor. The morphology and pore sizes of the electrodeposited ZnO films as well as the their dye loading and the kind of sensitizer dye were varied. Sintered films as well as films made from ZnO nanoparticles were investigated for comparison. It has been found that a finer porous structure with smaller ZnO domains leads to a lower electron transport resistance and therefore a higher fill factor, while on the other hand a lower back reaction resistance in these structures leads to a lower open-circuit voltage (see example in the figure). Measures therefore have to be taken to suppress back reaction, e.g. by co-adsorbants on the ZnO surface. Electron transport and back reaction resistances were also found to depend strongly on the adsorption and aggregation behaviour of the dye.



Left:I-V-curves of D149-sensitized ZnO films electrodeposited with different concentrations of eosin Y (EY) in the electrodeposition bath. Right: Electron transport resistances ($R_w$) and electron back reaction resistances ($R_k$) of the same ZnO films.

## 310

### Do $TiO_2$-Containing, Self-cleaning Materials Present a Potential Health Risk?

**Pierre Pichat,** *France*

Until now, $TiO_2$ was regarded as an innocuous compound whose use has been approved in drugs, toothpastes, food and cosmetics.

Concern about atmospheric particles and the growing development of nanoparticles has generated new research on the effects of fine particles upon health. The main questions addressed were whether these particles can go through the biological barriers, be transported by blood, be excreted or accumulated in the body, and what damage they can cause. The results have clearly pointed out a danger. Furthermore, on the basis of new in vitro experiments, $TiO_2$ is now classified as potentially carcinogenic.

To assess the ensuing risk, there is a lack of measurements about the release of particles from photocatalytic materials under appropriate conditions. It does not seem that commercialized self-cleaning glass can release significant daily amounts of $TiO_2$ particles because the coating is only ca. 100 nm thick and the adhesion is high. However, in cement-based materials, 0.3-3 wt% of $TiO_2$ is simply mixed. According to a manufacturer, no loss of $TiO_2$ was found for concrete after several years. However, to more satisfactorily respond to the new concern about fine particles, laboratory experiments and on-site evaluations must be performed.

Because the concentration of particles in air regarded as harmless is gradually lowered considering new information about health effects (cf. asbestos), these data are essential even if, given the durability of most photocatalytic materials, the daily release of $TiO_2$ particles is probably very low compared to the emissions of other particles, e.g. from combustions.

## 311

### On the Intermediates and Mechanism of Photooxidation Reactions at C- and N-Doped Titanium Dioxide

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Titanium dioxide nanoparticles, surface and volume doped with such elements as carbon or nitrogen, are active in mineralization of various pollutants under visible light illumination [1, 2]. During the last years, published experimental and theoretical results indicated that these dopants generate localized energy levels (surface states) just above the valence band from which visible light excitation becomes feasible [1, 2], and the C- or N-doped titania exhibits a weak light absorption starting at about 550-700 nm. Presence of elemental carbon and also carbonate in C-doped materials was indicated by X-ray photoelectron spectra (XPS) [3]. C-doped materials were investigated in more detail by the EPR technique, allowed us to detect and characterize the paramagnetic defects and their changes [4]. However, the question about intermediates and certain mechanisms of photooxidation in the presence of such systems is still not solved.

This paper reports recent results on visible light photocatalysis on C- and N-doped TiO2 in comparison with published data. XPS and X-band EPR studies of the surface- and bulk-doped samples at temperatures 5-300K were carried out both in dark and under illumination at different wavelengths; kinetic curves were recorded. The nature of defects, their dynamics under illumination and probable mechanisms of photooxidation will be discussed.

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## 312

### Photocatalytic Oxidation of Nitrogen Oxides Over (Iron, Nitrogen)-Codoped Titanium Dioxide Under Visible Light Irradiation

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**Xin Tan,** *Tianjin University, China*

In order to remove nitrogen oxides by visible light photocatalytic oxidation (PCO) and promote the removal rate, (iron, nitrogen)-codoped titanium dioxide was prepared by hydrolytic precipitation and impregnation methods. As-synthesized photocatalysts were characterized by XRD, XPS, TEM and UV-vis spectra, to derive crystal structure, elemental composition and oxidation states, surface morphology, and visible light response, respectively. PCO processes of nitrogen oxides were investigated under the irradiation of LEDs (blue, green, or red). The (iron, nitrogen)-codoped titanium dioxide exhibited marked photocatalytic activity, producing higher removal rates than un-doped and nitrogen-doped $TiO_2$. Optimum removal effects were achieved with 0.2 at% iron doping ratio, and deactivated photocatalysts after long-term usage could be regenerated by rinsing with deionized water.

## 313

### Non-Metal (I, N and B, N Co-doping) Doped Mesoporous Nanocrystalline Titania as Visible Light Photocatalysts

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**Lianzhou Wang,** *ARC Centre of Excellence for Functional Nanomaterials, The University of Queensland, Australia*
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In the past decade, the search for visible-light photocatalysts that are highly active under visible light irradiation has been a hot race worldwide. This is mainly due to the great significance of such photocatalysts in clean energy and environmental applications such as alternative solar cells, water splitting for hydrogen production and photochemical degradation of pollutants in water and air. Nanocrystalline titania has been widely investigated due to its low cost, non-toxicity and potential in numerous applications. To overcome the limitation of UV-only photocatalytic activity of titania, nearly all possible and known strategies including dye-sensitization, non-stoichiometric modification of TiOx, coupling with other narrow band-gap semiconductors, transition metal and nonmetal doping have been attempted. Among these strategies, non-metal doping has shown a great potential in increasing visible-light photocatalytic activity. Recently, we have developed modified mesoporous nanocrystalline titania by iodine, nitrogen and also the combination of boron and nitrogen, respectively, as highly efficient visible light photocatalysts. These photocatalysts exhibited excellent visible light photocatalytic activity in degradation of organic pollutants. Detailed photoelectrochemical study and the first principle calculations on these photocatalysts led to better understanding of the relationships among material synthesis, structural modification and photocatalytic performance, which can shed light on the rational design of efficient visible light photocatalysts.

## 314

### Ti(IV)/Ce(III) Bimetallic Photocatalysts Sensitive to Visible Light

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Photocatalytic systems working under visible light have been studied extensively from the viewpoints of energy conversion and environmental accountability. Recently, it was discovered that substitutional doping with anion elements to semiconductor photocatalysts leads to extension of the photoactive region to visible light. However, the present achievements are not enough compared to the performance demanded by the practical application. The main obstacle toward this is the fact that design and control of properties of semiconductor photocatalysts is strictly limited in flexibility, since the doping needs to be made under highly reactive conditions. In the present work, we have shown the use of metal-to-metal charge transfer (MMCT) of Ti(IV)-O-Ce(III) bimetallic moieties as a new class of visible-light sensitive photocatalysts. 1

The advantage of hetero-bimetallic photocatalysts is their high flexibility to design and control the electronic properties of photoreaction centers. 2 The oxidation/reduction potential as well as absorption wavelength of photocatalysts can be readily controlled by selecting the proper combination of two metal ions according to their redox potential. Furthermore, such control can be realized without using organic ligands. The choice of metal combination of Ti(IV) and Ce(III), in this work, enabled to drive the photocatalytic reactions under the visible-light induced MMCT. Their activities for catalytic oxidation of organic compounds were found to be remarkably higher than those for one of the most active visible-light photocatalysts, nitrogen-doped $TiO_2$.

Reference

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## 315

### Novel Indoline Dye for High-Conversion-Efficiency (9.5%) Organic-Dye-Sensitized Solar Cells

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**Masakazu Takata,** *Mitsubishi Paper Mills Limited, Japan*

Dye-sensitized solar cells (DSCs) have been investigated extensively as potential alternatives to conventional silicon solar cells, by using wide-bandgap nanocrystalline TiO2 sensitized with sensitizing dyes. By using ruthenium complexes through novel molecular design, SHARP [Jpn. J. Appl. Phys., 45, (2006) L638.] and our group [J. Am. Chem. Soc., 127 (2005) 16835.] reported over-11%-efficiency DSCs against AM1.5 (AM: air mass) simulated solar light of 100 mWcm–2 (1 sun). However, Ru dyes are not suitable to cost-effective environmental-friendly photovoltaic systems, because the Ru atom is an expensive heavy metal. Therefore, investigation of an organic-dye-sensitized solar cell is very important. In 2006, we reported that a metal-free organic dye (indoline dye: D149) [Adv. Mater., 18 (2006) 1202.] reached 9.03% power-conversion efficiency, which has been the best result as an organic-dye-sensitized solar cell. In order to enhance the photoenergy-conversion efficiency, it is necessary to control the aggregation between the dyes. For example, D149 shows J-aggregation on nanocrystalline-TiO2 electrodes. And each Ru dye (black dye and N719) shows the best record with using chenodeoxycaulic acid (CDCA), which worked as an anti-aggregation reagent. For controlling the aggregation, in this paper, the D149 is remodeled by introduction of bulk substitutes of octhyl chain: D205. By using CDCA, specially, the DSC with D205 exhibited high values of open-circuit photovoltage over 700 mV, resulting in 9.52% power-conversion efficiency under 1-sun irradiation(Fig.). This is the best record published as an organic-dye-sensitized solar cell so far.

## 316

### Iodine-Free Solid-State Dye-Sensitized Solar Cells: Effect of Ionic Liquid on Hole Conducting PEDOT

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**Naruhiko Masaki,** *Osaka University, Japan*
**Monica Lira-Cantu,** *Institut de Ciencia de Materials de Barcelona, Spain*
**Yukyeong Kim,** *Seoul University, Korea*
**Kejiang Jiang,** *Chinese Academy of Sciences, China*

Fabrication of iodine-free and heat tolerant solid-state dye-sensitized solar cells (DSC) will be presented. DSC faces low (>-40°C) to high (<85°C) temperature stability issue to pass standardized packaging durability tests of solar cells. One of the solutions is the fabrication of DSC without using iodine-containing volatile electrolytes. PEDOT, poly (3,4-ethylenedioxythiophene) works as an excellent hole conducting polymers, being successfully used as an substitute of the liquid I-/I3- redox electrolytes in DSC. In this work we cleared the in-situ photoelectropolymerization technique to synthesize PEDOT in mesoscopic $TiO_2$ anodes, and carried out a careful analysis of the effect of ionic liquid-derived anions on overall solar cell performance. The ionic liquid anions analyzed in this work were bistrifluoromethanesulfonylimide anion (TFSI-), ClO4-, CF3SO3-, BF4-, and the best solar cell performance was obtained when the TFSI- anion was used. Photo-electrochemical and impedance studies revealed that the doped anions in the PEDOT hole conductor system have great influences on I-V curves, conductivity, and impedance. The optimization of these parameters allowed us to obtain an iodine-free solid state DSC with a maximum Jsc of 5.3 mA/cm2, Voc of 750 mV and a conversion efficiency of 2.85%, which is the highest efficiency obtained so far for an iodine-free PEDOT-based DSC.

## 317

### Dye-Sensitized Solar-Cells with a Hydrothermally Grown ZnO-Nanoflower Photoanode

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**H Y Yu,** *Nanyang Technological University, Singapore*

We report a dye-sensitized solar cell (DSSC) using a ZnO-nanoflower film photoanode, which was grown by a hydrothermal method at 95°C. The dye used was cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N-719). At AM 1.5G irradiation with 100 mW/cm2 light intensity, the DSSC based on ZnO-nanoflower film showed an energy conversion efficiency of 1.9%, which is much higher compared to that (1.0%) of the control device constructed using a photoanode of up-standing ZnO-nanorod array fabricated by hydrothermal method as well. The better performance of ZnO-nanoflower DSSC was due to a better dye-loading and light harvesting of the ZnO nanoflower film. The results demonstrate potential application of ZnO nanoflower array for efficient dye-sensitized solar-cells.

## 318

### An Investigation of Nanostructured ZnO/MEH:PPV Hybrid Solar Cells

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**Swee C Tan,** *The University of Cambridge, United Kingdom*
**Mark E Welland,** *The University of Cambridge, United Kingdom*

Inorganic nanostructures/organic polymer-based hybrid photovoltaic devices are an attractive future alternative to conventional solar cell technology due to the potential of low cost fabrication processes. However, optimising the efficiency of hybrid solar cells remains a key issue [1-4]. With exciton diffusion lengths in conducting organic materials, of approximately 10 nm, a device geometry whereby the hole and electrons can be separated and efficiently transported is required. Hence optimising the area of the active interface should optimise the device performance.

Here, ZnO NW hybrid cells have been fabricated using nanowires with a high level of control using low temperature solution based synthesis [2]. Arrays of nanoscale metal-oxide nanowires shown in figure 1 (a) are an example of highly ordered ZnO nanowires fabricated by hydrothermal growth methods at low temperature. Changes to the nanostructure morphology are achieved by maintaining the same growth solution and temperature, either by adding small volumes of ammonia, figure 1 (b) to produce randomly ordered NW structures or by extending the NW growth times to 2 days, figure 1 (c), to achieve perpendicular microtubular ZnO arrays.

The characteristics of nanostructured ZnO hybrid solar cells will be discussed with emphasis on the morphology and junction area dependence of the photovoltaic properties.

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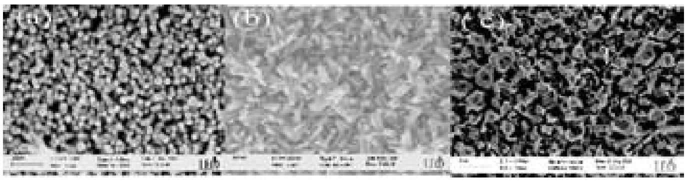

## 319

### Colloidal Array Templated $TiO_2$ Photoelectrode for Dye-Sensitized Solar Cells

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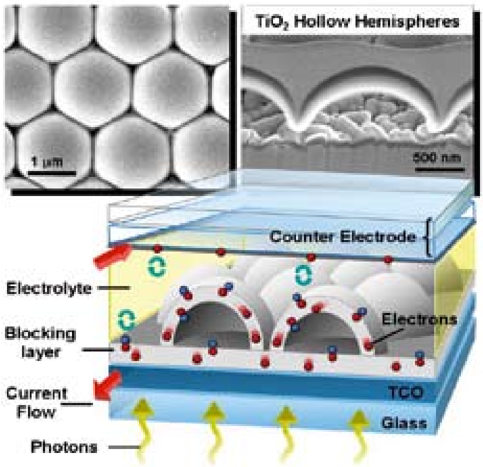
**Eun-sik Kwak,** *Korea Institute of Science and Technology, Korea*
**Il-doo Kim,** *Korea Institute of Science and Technology, Korea*
**Junkyung Kim,** *Korea Institute of Science and Technology, Korea*
**Hyunjung Lee,** *Korea Institute of Science and Technology, Korea*

Nanocrystalline titanium dioxide ($TiO_2$) materials have been widely used as an electron collector in DSSC. In $TiO_2$ electrode structures, their geometrical structures and crystalline phase have been extensively investigated as important issues. In this study, we present a new strategy to fabricate a photoelectrode having a periodic structured $TiO_2$ film templated from 2D or 3D polystyrene(PS) colloid array(CA). One is the igloo-shaped electrode prepared by $TiO_2$ deposition by RF-sputtering onto 2D CA. The existence of voids at the interface between the film and substrate might be expected to play the predominant roles as scattering spherical voids to promote a light harvesting effect, a spacious structure for electrolytes with higher viscosity and effective paths for electron transfer. Additionally $TiO_2$ phase prepared by RF-sputtering method was previously reported to improve the electron drift mobility. This yields solar cells with a cell efficiency of 2.45 % or more at AM 1.5 illumination and at the thickness of 2 µm. The other is the inverse opal photonic crystal electrode prepared by titania particles infusion within 3D CA. To obtain the enlargement of ordered area and high quality of crystallinity, the synthesis of titania particles coated with a organic thin layer were applied and well dispersed. This ordered mesoporous structure provides the large surface area and have an light harvesting effect due to the photonic band gap properties. These materials may have promising potentials for future applications of membrane, sensor and so on as well as solar cells.



## 320

### Development of Semiconductor Quantum Dots Sensitized Solar Cells by Controlling Interfacial Electron Transfer Reactions

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Semiconductor quantum dots (QD) have recently been recognized as an alternative sensitizer for dye sensitized solar cells. Intensive studies have focused on combining a different type of metal oxide nanoporous substrate; in this scenario the QDs absorb a wide range of visible and near IR wavelengths. We have reported that QDs/$TiO_2$ systems can generate efficient sandwich type photovoltaic devices by employing an appropriate electrolyte,[1,2] although the efficiency remains low in comparison to ruthenium dye sensitized solar cells.

Solar cell performance improvement can be achieved by controlling the interfacial kinetics, (i) accelerating charge separation rates which lead to a high quantum yield and (ii) retarding charge recombination processes. However, elucidation of the kinetic factors, i.e. electron transfer mechanisms, has rarely been studied despite the obvious impact and significance these investigations would generate. Material composition modification at the interface is an important additional factor in controlling the electron transfer reactions. For example, by introducing barrier layers at the interfaces, one can readily modulate the electron transfer kinetics,[3] as shown in Fig. 1.

We will present the kinetic mechanism participating in QDs sensitized solar cells by employing various techniques including transient absorption spectroscopy and dynamic electrochemistry. Additionally introducing a barrier layer at the conducting glass/electrolyte interface and the corresponding influence on the device performance will be considered.

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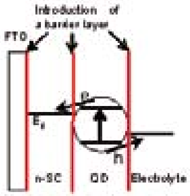

Fig. 1. Introduction of a barrier layer at FTO/n-SC/QD/Electrolyte interface.

## 321

### Self-Organization of Porphyrins and Carbon Nanostructures for Organic Solar Cells

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Extensive efforts have been made in recent years to explore the photovoltaic and photoelectrochemical properties of electrodes modified with various donor and acceptor components toward the realization of highly efficient organic solar cells. It is of vital importance to select suitable donor and acceptor and organize the donor and acceptor on the electrode surface in nanometer scale for achieving high cell performance. In this talk, we will present versatile approaches to organize donor and acceptor molecules on electrodes. In particular, various donors and acceptors and their composites have been successfully deposited electrophoretically onto nanostructured tin dioxide and titanium dioxide electrodes which exhibit efficient photocurrent generation. For instance, bottom-up self-organization of porphyrin and fullerene molecules onto the nanostructured tin dioxide electrodes has led to highly efficient photocurrent generation with an incident photon-to-current efficiency (IPCE) of up to ~60%. Cell performance with power conversion efficiency of ~5% has also been obtained for the tin dioxide cell modified with pi-extended tetraphenylporphyrin. Such examples will give a deep insight into the design of molecule-based solar cells.

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## 322

### The Role of Surface Speciation on the $TiO_2$ Surface in Photocatalysis: Oxalate on Rutile Nanoparticles

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**Cecilia B Mendive,** *Institut für Technische Chemie, Leibniz Universität Hannover, Germany*
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**Miguel Blesa,** *Unit of Chemical Activity, National Commission of Atomic Energy, Argentina*

The photocatalytic activity of $TiO_2$ is the result of an interplay between a considerable number of parameters, e.g., phase composition, electronic structure, particle size, exposed surface area, degree of aggregation, mobility of charge carriers, presence of impurities, amount and kind of defects, adsorption molecules from gas or aqueous phase, lateral interactions between adsorbed species, nature of solvent, etc. The specific function and influence of a given feature for the photocatalytic performance of a $TiO_2$ sample is difficult to characterize since many of the parameters are strongly coupled. Consequently, due to this plurality of variables driving the nature of the photocatalytic activity, it is of primary importance to develop a method to understand and control these properties (or at least some of them).

As a first approach to this complex problem we have carried out a combined experimental and theoretical study in order to explore these phenomena. The adsorption of oxalic acid from the aqueous phase at the surface of rutile nanoparticles has been investigated by ATR-FTIR measurements. The aqueous system was also studied quantum-chemically using the semiempirical method MSINDO. Geometry optimizations have been performed, and the vibration spectra of the most stable surface complexes have been calculated. A sequence of model types has been applied in the quantum-chemical calculation in order to take into account the effect of interaction of water and oxalic acid on the adsorption mechanism and the vibration spectra. It was found that the presence of the aqueous phase significantly changes the stability of the oxalic acid surface complexes compared with the bare $TiO_2$ surface. The combination of experimental and theoretical information allowed identification of three species as the main contributors to the surface speciation. Two bidentate species were found with the C-C bond parallel to the $TiO_2$ surface, one monoprotonated and one deprotonated, and a third species being monodentate and monoprotonated. These results have been used to interpret the experimental data obtained upon photocatalytic studies performed with this system.

# 323

## Preferential Photodegradation of Contaminants by Molecular

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The photocatalytic degradation of organic contaminants on titanium dioxide is basically non-selective. While this seems at first glance to be an advantage, this is not the case when a stream containing low concentrations of highly toxic substances together with high concentrations of low-toxic organics has to be treated.

A method for obtaining preferential degradation by means of preparation of molecularly imprinted photocatalyst is presented hereby. The method is demonstrated with two model compounds simulating the nerve gas Sarin: Diisopropyl methyl phosphonate (DIMP) and Diethyl hydroxymethyl phosphonate (DEHMP).

An improvement by a factor of 3 for these compounds was obtained upon imprinting. This enhancement in the degradation rates was not observed when using the molecularly imprinted photocatalyst for the degradation other molecules, thus negating the possibility that the increase in the degradation rates originated from enhanced surface area.

Effects on the appearance of by-products, ways to further increase the efficiency, and the prospects and limitations of this method will be discussed.

# 324

## Photocatalytic Oxidation of 4-Methoxybenzyl Alcohol to P-Anisaldehyde in a Fixed Bed Continuous Reactor

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**Sedat Yurdakal,** *Anadolu Üniversitesi, Turkey*
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**Gustavo E Imoberdorf,** *Universidad Nacional del Litoral, Argentina*
**Horacio A Irazoqui,** *Universidad Nacional del Litoral, Argentina*
**Orlando M Alfano,** *Universidad Nacional del Litoral, Argentina*
**Vincenzo Augugliaro,** *Università di Palermo, Italy*
**Leonardo Palmisano,** *Università di Palermo, Italy*

Photocatalytic oxidation of 4-methoxybenzyl alcohol to p-anisaldehyde was performed in water organic-free solutions by using a fixed bed continuous photoreactor containing Pyrex beads on which $TiO_2$ home prepared photocatalyst (ex $TiCl_4$) was supported. The influence of liquid flow rate, inlet alcohol concentration, catalyst amount and incident photonic flow on the photoprocess was studied. The highest selectivity to p-anisaldehyde was about 47% being $CO_2$ the other main oxidation product; traces of 4-methoxybenzoic acid were also detected. The radiation field inside the photoreactor has been modelled by applying the Monte Carlo method thus allowing the determination of the local volumetric rate of photon absorption (LVRPA). It was found the optimum amount of $TiO_2$ supported on the beads. The radiation modelling allowed the determination of the dependence of reaction kinetics on light intensity. The Langmuir-Hinshelwood approach has been satisfactorily applied for modelling the photoreactivity results and the values of all the model parameters have been determined.

# 325

## Fabrication and Characterization of TiO2 Nanowire Membrane for Water and Energy Production

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**Alan Jianhong Du,** *School of Civil and Environmental Engineering, Nanyang Technological University, Singapore*
**James O'Leckie,** *Department of Civil and Environmental Engineering, School of Engineering, Stanford University, Stanford, United States*

Nanotechnology has great potential in water and energy applications by offering more precise structural controlled materials for such needs. Titanium oxide ($TiO_2$) nanosized particle is a popular photocatalyst which attract much attention from both fundamental research and practical application. Dramatic effects have been added in this area by many researchers. Using nano-structured $TiO_2$ microsphere(1-4), $TiO_2$ compositing membrane(5,6). Recently, immense efforts (6-11) are devoted to the study of organizing of nanowire/fiber/tube into free standing membrane or sheet.

Given the potential of nanofabricated membrane to advance molecular separation, photocatalytic oxidation and photovoltaic, we have developed a robust and inexpensive $TiO_2$ nanowire membrane by filtration of $TiO_2$ nanowires suspension. We herein first time report the use of $TiO_2$ nanowire membrane for the removal of HA in water and solar cell application. The membrane perspectives in practical application were investigated by evaluating its ability of photodegradation. The advantages of the $TiO_2$ nanowire membrane are: (1) full surface exposure to UV or solar light for self-regeneration, which effectively eliminates the membrane fouling problem; (2) concurrent membrane filtration for separation purpose; (3) high surface area, which allows higher adsorption rate of NOMs for improving water quality, dye for DSSC and hydrogen production; (4) higher acid/basic and temperature resistance; (5) environmentally friendly and longer membrane life span; (6) flexible property which enables the membrane to be formed into various membrane modules for larger commercial application. These unique properties give rise to the water and energy industry particularly in producing cost effective commercial filtration membrane that could dramatically reduce the cost of water and energy production.

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## 326

### Controlled Synthesis of Hierarchical Metal Oxides Nanorods

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**Ken Chiang,** *University of New South Wales, Australia*
**Rose Amal,** *University of New South Wales, Australia*

There is a growing interest in developing new advanced materials such as 1-D nanomaterials owing to their distinctive geometries that offer high surface area-to-volume ratio and quantum confinement effect. In particular, titanium dioxide and tungsten oxide nanorods have been paid considerable attention for their unique applications including photocatalysts, catalysts, sensors, solar cells, hydrogen storage devices, batteries and etc.

While titanium dioxide and tungsten oxide nanorods have been synthesised by a plethora methods, wet chemical techniques provide versatile routes with the advantages of mild synthetic conditions and precise control of size, shape and dimension. To our best knowledge, the application of wet chemical techniques to assemble nanorods into well-organised sructures without the use of surfactants or templates has not been reported. Here, we report a simple one step method to fabricate highly-ordered titanium dioxide and tungsten oxide nanorods.

Preliminary results showed that well-aligned titanium dioxide nanorods with different aspect ratios and shapes can be obtained by altering the pH and aging conditions. Similarly, by simple manipulation of pH, concentration of inorganic ions and type of organic species, an urchin-like tungsten oxide nanorods with controlled aspect ratios can be attained. In this work, we also demonstrated that the as-synthesised metal oxides nanorods were highly active when used as photocatalysts for environment remediation. It is expected that the novel method will offer the opportunity for large scale production of well-aligned metal oxides nanorods.

## 327

### Highly Efficient $WO_3$ Photocatalysts Promoted with Various Co-Catalysts for Gradation of Various Organic Substances

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**Takeo Arai,** *National Institute of Advanced Industrial Science and Technology(AIST), Japan*
**Yoshinari Konishi,** *National Institute of Advanced Industrial Science and Technology(AIST), Japan*
**Masatoshi Yanagida,** *National Institute of Advanced Industrial Science and Technology(AIST), Japan*
**Hideki Sugihara,** *National Institute of Advanced Industrial Science and Technology(AIST), Japan*

Many semiconductor photocatalysts with a narrow band gap, especially those based on $TiO_2$ species such as $TiO_{2-x}M_x$ (M = N, C, S, metals), have been extensively investigated with the goal of developing catalysts for the decomposition of harmful organic substances such as volatile organic compounds (VOCs) under visible or fluorescent light for indoor and inside-vehicle applications. However, the ability of these catalysts to completely oxidize organic compounds into $CO_2$ under visible light has so far been unsatisfactory. $WO_3$ is a visible-light–responsive photocatalyst and an n-type semiconductor photocatalyst for $O_2$ generation using sacrificial reagents, but reports on the degradation of organic substances over $WO_3$ are limited. In addition, there are some practical problems with its use; a precious Pt was used as co-catalyst to increase the activity, and the ability of $WO_3$ to catalyze complete oxidation into $CO_2$ was not clearly demonstrated. We previously reported that because of the formation of stable byproducts, acetaldehyde ($CH_3CHO$) cannot be completely oxidized in the presence of a $WO_3$ photocatalyst without a co-catalyst under visible light. In the present study, we investigated how loading various metals and metal oxides as co-catalysts on $WO_3$ photocatalyst affected the oxidation of VOCs such as $CH_3CHO$ under visible and UV light. We found that various Cu-compounds such as CuO and $CuBi_2O_4$ were very effective co-catalysts over $WO_3$ for the complete oxidation of various VOCs into $CO_2$. The reaction mechanism on the loading effect of Cu-compounds was discussed in detail.

## 328

### Highly Efficient Decomposition of Organic Compounds Over Platinum-Loaded Tungsten Oxide Photocatalysts Under Visible Light Irradiation

**Ryu Abe,** *Catalysis Research Center, Hokkaido University, Japan*
**Hitoshi Takami,** *Catalysis Research Center, Hokkaido University, Japan*
**Bunsho Ohtani,** *Catalysis Research Center, Hokkaido University, Japan*

Tungsten oxides ($WO_3$) loaded with platinum (Pt) nanoparticles exhibited high activity for the decomposition of organic compounds in the presence of molecular oxygen under visible light irradiation. An action spectrum analysis for decomposition of acetic acid in an aqueous solution has shown that the reaction over the Pt-$WO_3$ can be ascribed to the band-gap photoexcitation of $WO_3$ utilizing visible light up to 470 nm, and the apparent quantum efficiency in visible light region was much higher than that of the titania ($TiO_2$)-based visible light-driven photocatalysts such as sulfur-doped $TiO_2$. Transient photoabsorption analysis using photoacoustic (PA) spectroscopy indicated that the photoexcited electrons in $WO_3$ reacted with molecular oxygen in spite of more positive conduction band level of $WO_3$ compared to the potential of oxygen reduction, and the rate of reaction was significantly increased by Pt loading.

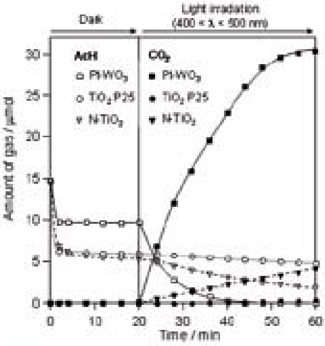


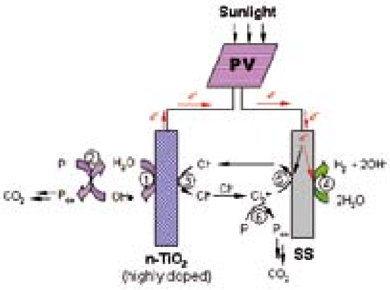
**Figure** Time course of acetaldehyde decomposition over Pt(0.1 wt%)-$WO_3$, $TiO_2$, and nitrogen-doped $TiO_2$ (N-$TiO_2$) under visible irradiation (400 < λ < 500 nm)

## 329

### Solar-Powered Production of Molecular Hydrogen from Water

**Hyunwoong Park,** *California Institute of Technology, United States*
**Michael R Hoffmann,** *California Institute of Technology, United States*

We report on a novel high-efficiency electrochemical approach for the production of molecular hydrogen that is indirectly powered by sunlight with through the use of photovoltaic (PV) arrays. Water splitting coupled with organic chemical contaminant oxidation under very mild conditions is achieved with the PV-powered electrolysis cell that is based on the coupling of bismuth-doped titanium dioxide semiconductor anodes (BiOx-TiO2) with simple stainless steel cathodes (SS). In this hybrid system, the production of molecular oxygen at the anode is suppressed by the simultaneous oxidation and mineralization of organic chemicals present in water. Anodic oxidation of organic contaminants has a synergistic effect on cathodic hydrogen gas production that results in a maximum 53 % increase in H2 production energy efficiency at the pH of natural waters with low background electrolyte concentrations. Overall energy efficiencies are found to be comparable to industrial-scale electrolysis that, in contrast, is carried out under high electrolyte concentrations and very basic conditions, pH 14.



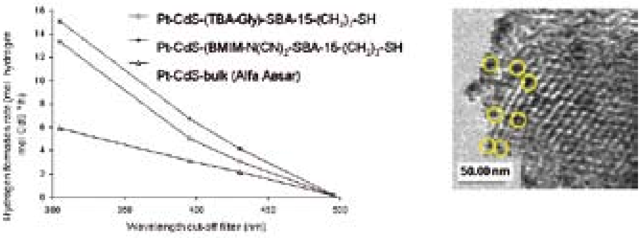
## 330

### Hierarchically Structured Composite Materials for the Photocatalytic Splitting of Water with Visible Light

**Leon van de Water,** *The University of Sydney, Australia*
**Vincent Lau,** *The University of Sydney, Australia*
**Anthony F Masters,** *The University of Sydney, Australia*
**Thomas Maschmeyer,** *The University of Sydney, Australia*

In this contribution we report the synthesis, characterization and photocatalytic performance of a range of composite materials that have been designed to utilize the visible part of the solar spectrum for the photocatalytic water splitting reaction. Nanoscopic cadmium sulfide (CdS) has been synthesized by controlled precipitation of Cd2+ and S2- precursors in the presence of ionic liquids (ILs). The resulting well-defined nanoparticles were subsequently immobilised inside the pores of SBA 15-(CH2)3SH, a mesoporous silica material modified with propyl thiol groups. The photocatalytic activity of the composite materials, thus prepared, was found to be substantially higher than that of highly crystalline (Wurtzite structure) commercial bulk CdS reference materials.

Figure Hydrogen formation rates of Pt-CdS-(IL)-SBA-15-(CH2)3-SH catalysts, compared to a commercial CdS-bulk sample. Inset: TEM image of Pt-CdS-(TBA-Gly)-SBA-15-(CH2)3-SH, showing the presence of CdS nanoparticles inside the channels of the SBA-15 host.



## 331

### The Key Factor in Water Splitting: Long Lifetime Holes for $O_2$ Production

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Improving the quantum efficiency (QE) for photocatalytic water splitting for solar $H_2$ production is a key research challenge. Reported quantum efficiencies are to date relatively modest. Besides developing new materials absorbing more visible light, increasing the photogeneration and utilization of the charge carriers is of particular interest. It has been reported that under some conditions 90 % of photoelectrons and photoholes recombine within 10 ns in $TiO_2$ colloids,which would make it very difficult to achieve high efficiency for water splitting as the reactive steps would have to occur on a timescale faster than this. Measuring charge recombination processes and in particular reactions between water and charge carriers in candidate photocatalysts are therefore important steps in evaluating the materials and understanding mechanisms that underlie water splitting by inorganic materials. In the work, we confirm the spectral fingerprint of photoholes and photoelectrons in nanocrystlline $TiO_2$ (nc-$TiO_2$) films, and then systematically study the dynamics of photoholes under weak laser excitation down to levels below one photon absorbed per nanoparticle using transient absorption spectra. Furthermore, for the first time we present evidence that four holes are required to produce one molecule of oxygen. The kinetics of water oxidation for $O_2$ production is also studied in order to explore the timescale of $O_2$ evolution and to elucidate the rate-determining step in water splitting. Finally we use this new information to suggest some factors that must be addressed to maximise the efficiency of photocatalytic water splitting in both $TiO_2$ and other materials.

## 332

### A Novel Synthesis Technique for α–Fe2O3 Photoanodes Based on Electrodeposition

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**Arjen Didden,** *Delft University of Technology, department DelftChemTech, The Netherlands*
**Cristina S Enache,** *Delft University of Technology, department DelftChemTech, The Netherlands*
**Roel Van de Krol,** *Delft University of Technology, department DelftChemTech, The Netherlands*

With a band gap of 2.2 eV and good chemical stability in water, α-$Fe_2O_3$is almost an ideal material for photoelectrochemical water splitting. Recently, it was shown that $Fe_2O_3$ dendrite nanostructures can split water with an efficiency (solar-to-hydrogen) of 3.2% [1]. Despite this encouraging breakthrough, two major challenges remain. First, more insights into the materials properties are required to improve the efficiency to the theoretical value of 12.9%. Second, alternative synthesis methods are needed for practical application, and these methods should have good reproducibility and should be easy to scale up.

In this work, a novel process called EDOX (ElectroDeposition and thermal OXidation) was developed for the fabrication of $Fe_2O_3$ photoelectrodes. During the process, Fe films are first synthesized by electrodeposition on a conductive substrate, after which the metal films are oxidized under controlled atmosphere to form α-Fe2O3 films. While the $Fe_2O_3$ nanowire arrays are reported to grow during oxidation of iron [2], we will show that this is not trivial and depends strongly on the nature of the metallic iron substrate and the oxidation conditions.

The viability of the technique will be demonstrated by some first results on Ti-doped α-$Fe_2O_3$ films (~200nm thick) deposited on the TCO substrate. These films show a photocurrent of 0.33 mA/cm2 at a bias of 1.23 V vs. RHE under illumination with AM1.5 simulated sunlight.

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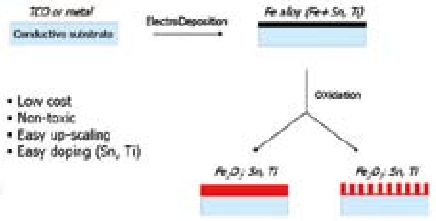

## 333

### Sustained Water Oxidation Photocatalysis by a Bioinspired Molecular Manganese Cluster

**Leone Spiccia,** *Monash University, Australia*

Devices capable of the solar-driven splitting of water into molecular oxygen and hydrogen offer the potential of an unlimited renewable fuel. Such devices would need to combine a photoanode, where light driven water oxidation occurs, with a cathode, where protons are reduced to hydrogen. There is general consensus that one of the most challenging barriers to the generation of renewable energy from water is the oxygen-evolving half reaction. We have developed a bioinspired molecular catalyst comprised of a cubical [Mn4O4]7+ core which when suspended within the aqueous nanosized pores of a proton-conducting Nafion-membrane sustains the light driven oxidation of water for several days, with little loss in activity. Further, we have coupled the Mn water oxidation catalyst to a dye sensitizer and have shown that this assembly achieves light driven water oxidation without the application of a bias.

## 334

### Characterization and Modelling of Dye-sensitized Solar Cells

**Laurie Peter,** *University of Bath, United Kingdom*

The development of strategies for optimizing dye-sensitized solar cells (DSC) has been hampered by lack of understanding of some of the fundamental processes involved in cell operation. Whereas the injection and collection of electrons at short circuit is evidently not a problem, the factors that determine the achievable open circuit voltages and fill factors are less clear. The description of electron transfer from the $TiO_2$ to the redox electrolyte of hole conducting medium is not well understood, and the possible role of surface states remains to be established. Attempts to optimize cells have often been based on a misinterpretation of the transient photocurrent and photovoltage response of DSCs. For example, changes in electrolyte composition or in the adsorbed dye are reported as 'increasing the electron lifetime' or 'enhancing electron transport'. In fact, the effects may arise simply from changes in the conduction band energy of the $TiO_2$. The transient photocurrent and photovoltage response are strongly influenced by electron trapping, so that the actual values of the diffusion coefficient and lifetime of free electrons can only be found by assuming a model. Unfortunately, current models are clearly too simple to describe the behaviour of real cells. Questions arise concerning the role of surface sates in electron transfer and of possible voltage dependent barriers to electron extraction at the substrate in determining fill factors. This lecture explores some of these issues and shows how a self-consistent experimental approach combined with new modelling results can help give a clearer understanding of DSC function.

## 335

### A Generic Configuration for Improved Spectral Matching of Third-Generation Solar Cells

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**Shlomit Greenwald,** *Chemistry Department, Bar-Ilan University, Israel*
**Igor Lubomirsky,** *Dept. of Materials & Interfaces,*
*Weizmann Institute of Science, Israel*
**David Cahen,** *Dept. of Materials & Interfaces,*
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Direct solar energy conversion to electricity by the photovoltaic effect is limited by the energy spectrum of the solar irradiation. It is therefore essential to minimize the energy losses associated with the mismatch between the photon energies and the active materials in the cell.

Third generation solar cells (dye-sensitized, organic, and polymer cell types) suffer from an additional fundamental difficulty. They are limited to thin layers of the photoactive materials. These limitations arise from the charge separation mechanism and from the charge transport resistance of the layers. Consequently, the optical density of these cells is lower than the optimum for efficient solar spectrum utilization.

We research a generic configuration of photovoltaic systems for efficient energy conver-sion over the whole solar spectrum. Our design involves elements that collect the incom-ing solar radiation and enforce spectral selective absorption of the radiation by a series of individual cells, each optimized for a different part of the solar spectrum. While splitting the solar radiation into different solar cells, illumination within our system does not suffer from either the need for current matching or the multiple reflection losses associated with presently known tandem and spectral splitting photovoltaic systems.

In third generation solar cells, the new design increases the optical path thus resulting in high effective optical density even with ultra-thin layers of the photoactive material. Consequently, a significantly larger fraction of the solar radiation can be used than is possible now.

Results of dye-sensitized and organic solar cells of the new design will be presented.

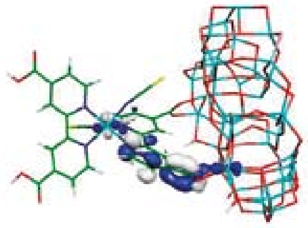
## 336

### Solar Energy Conversion Calculations

**Petter Persson,** *Lund University, Sweden*

Computational modelling is used to predict photoelectrochemical properties of new dye molecules with the aim to find better dye molecules for use in solar energy conversion systems, including dye-sensitized solar cells and artificial photosynthesis. Electrochemical and photophysical properties are calculated from first principles for both organic dyes and metal complexes. Of particular relevance for the photoelectrochemical applications are predictions of new dyes that combine favourable light-harvesting capabilities, redox energies, and excited-state properties. The dye-sensitized solar cell calculations also include the use of model $TiO_2$ nanocrystals to investigate surface binding and interfacial electronic properties. Recent results for new dye molecules for both dye-sensitized solar cells and artificial photosynthesis will be presented, together with a general discussion of the emerging capabilities for atomistic calculations to guide the search for better solar energy conversion components.

The Figure shows a model interface of a dye-sensitized solar cell showing strong mixing of a ligand $\pi^*$ molecular orbital of a ruthenium dye with $TiO_2$ nanocrystal conduction band levels.



## 337

### Studies of Electron Transport and Electron Transfer in Dye-sensitized Solar Cells

**Halina K Dunn,** *University of Bath, United Kingdom*
**Laurence M Peter,** *University of Bath, United Kingdom*
**Alison B Walker,** *United Kingdom*
**Jonathan H T Williams,** *United Kingdom*

The performance of dye-sensitized solar cells operating at the maximum power point depends on competition between electron transport and back transfer to the redox electrolyte or hole conducting medium. Most methods to study electron transport involve measuring transient photocurrents under short circuit conditions. However, the distribution of electrons in the cell at the maximum power point differs substantially from the distribution at short circuit, so the question arises whether the transport properties measured at short circuit are relevant to the operating cell. We have used a method introduced by O'Regan eta al (1) in which transient charging of the capacitance of the substrate electrode in response to pulsed illumination under open circuit conditions is used to derive the apparent diffusion coefficient of electrons (the illumination pulse is superimposed on steady state illumination in order to obtain a small increment of photovoltage that allows linearization of the system response). The subsequent decay of the photovoltage allows determination of the apparent electron lifetime. As a consequence, it is possible to measure the electron diffusion length under conditions relevant to the cell operation. Measurements were carried out over a wide range of cells with and without a blocking layer of $TiO_2$. The charging process was also modeled numerically within the framework of the multiple trapping model. The results give new insights into the behavior of dye-sensitized solar cells under working conditions.

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## 338

### Comparison of Band Gaps and Open Circuit Voltages in Si/SiO$_2$ Quantum Well Solar Cells

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**Birger Berghoff,** *Institute of Semiconductor Electronics, RWTH Aachen University, Germany*
**Derk L Bätzner,** *Institute of Semiconductor Electronics, RWTH Aachen University, Germany*
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**Heinrich Kurz,** *Institute of Semiconductor Electronics, RWTH Aachen University, Germany*

On the way to highly efficient new generations of Silicon based photovoltaics, new approaches in the solar cell material area are indispensable to overcome the limiting factors, i. e. hot carrier relaxation and IR photon transmission in todays bulk Si solar cells. One way to minimize hot carrier losses is the use of multiple absorbers with different band gap energies consisting of Si-quantum wells embedded between potential barriers .

The approach shown here is the fabrication of Si/SiO2 multiple quantum wells (MQWs) by remote plasma enhanced chemical vapor deposition (RPECVD) and subsequent rapid thermal annealing (RTA) for recrystallization of Si layers. With this method it is possible to fabricate quantum wells with down to 1 nm thickness, where effective band gap energies are shifted to 1.6 eV as confirmed by photoluminescence (PL) and absorption measurements (Fig. 1, left).

To overcome the inherent problem of poor conductivity in a MQW absorber containing insulating barriers an innovative solar cell design is explored. There, lateral transport parallel to the Si/SiO$_2$ interfaces of 2 dimensional quantum wells is investigated.

In a first attempt we fabricated lateral Si-QW solar cells with adjacent Al and Pt contacts resulting in an Schottky barrier induced internal field. Details of the increase in absorption energies shown in fig. 1 as afunction of QW thickness and of the corresponding open circuit voltages will be presented.

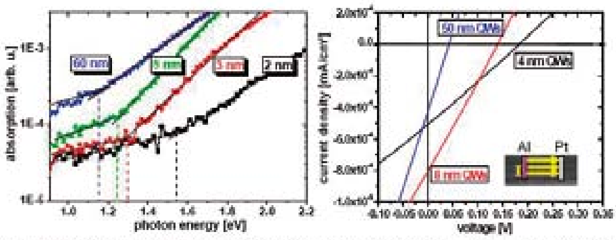


Fig. 1: Left: PDS absorption spectra on Si/SiO$_2$ QW's constant SiO2 thickness of 3 nm and varying Si layer thicknesses of 1 x 60 nm (triangles down), 12 x 5 nm (triangles), 20 x 3 nm (circles) and 30 x 2 nm (squares). The effective band gaps are shown (dashed lines) are extracted from the intersection of the exponential fits of defect induced and band to band absorption, respectively (solid lines).
Right: Illuminated IV characteristics of lateral Pt/QW/Al Schottky cell structures with varying Si QW thicknesses of 1 x 50 nm (dotted), 12 x 8 nm (dashed) and 12 x 4 nm (solid line). The inset shows the lateral contact scheme.

## 339

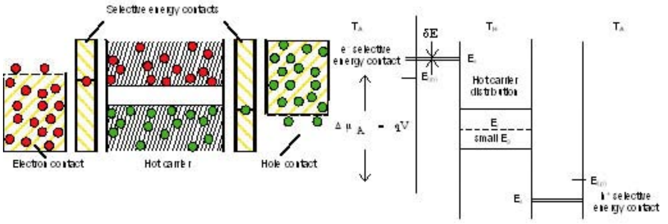
### Hot Carrier Solar Cells

**Gavin Conibeer,** *University of New South Wales, Australia*
**Nicholas Ekins-Daikes,** *Imperial College, United Kingdom*
**Jean-Francois Guillemoles,** *IRDEP: joint CNRS-EDF-ENSCP, France, France*
**Dirk Koenig,** *University of New South Wales, Australia*
**Santosh Shrestha,** *University of New South Wales, Australia*
**Eun-Chel Cho,** *University of New South Wales, Australia*
**Martin Green,** *ARC Photovoltaics Centre of Excellence, University of New South Wales, Australia*

Hot Carrier cells aim to tackle the carrier thermalisation loss in solar cells. The concept is to slow the rate of photoexcited carrier cooling to allow time for the carriers to be collected whilst they are still at elevated energies ('hot'), and thus allowing higher voltages to be achieved from the cell [1,2]. Significant reduction in cooling has been observed at very high illumination intensities via a 'phonon bottleneck' mechanism which has been demonstrated to be enhanced in QW nanostructures. In order to reduce the illumination intensities at which this mechanism gives significantly slower cooling towards one sun intensities, it is necessary to block the decay of optical phonons into acoustic phonons.

The current work seeks to emulate the behaviour of some bulk materials which have a large gap between acoustic and optical phonon modes by the use of Bragg reflection of phonon modes in quantum confined nanostructures. Developments in this modeling which indicate the critical importance of the interface are also presented.

In addition to an absorber material that slows the rate of carrier relaxation, a hot carrier cell must allow extraction of carriers from the device through contacts which accept only a very narrow range of energies (energy selective contacts or ESC). Previous work has proved the concept of these selective energy contacts using resonant tunneling in Si QD double barrier structures. This can be characterisaed by demonstration of negative differential resistance. Experimental work on electrical and optical excitation of these structures will be presented.



**Schematic and band diagram of an ideal hot carrier solar cell. The absorber has a hot carrier distribution at temp $T_H$ . Carriers cool isoentropically in the mono-energetic contacts to $T_A$ . The difference of the Fermi levels of these two contacts is manifested as a difference in chemical potential of the carriers at each contact and hence an external voltage, V.**

## 401

### Nanocrystal Based Solar Cells

**Paul Alivisatos,** *Univ of Calif, Berkeley, United States*

This talk will describe the potential advantages as well as the many difficulties which must be overcome if we are to make future generation solar cells using nanoscale materials. Nanoscale PVs have the possibility of being manufactured on an enormous scale. They also offer the possibility of harnessing new physics which arises in dimensionally controlled systems to control energy dissipation. Yet, nanoscale systems have high surface areas with many potential trap sites and present difficulties for how to spatially organize electrical transport pathways. These issues will be illustrated with recent experiments utilizing colloidal inorganic semiconductor nanocrystals. This talk will include discussion of hybrid nanorod/polymer solar cells, dual nanocrystal derived thin film solar cells, and single Nanorod solar cells.

## 402

### Charge Photogeneration at Nanostructured Donor/Acceptor Interfaces

**James R Durrant,** *Imperial College London, United Kingdom*

The reaction centres of photosynthetic organisms are undoubtedly the most sophisticated examples of photochemical energy conversion systems. They have inspired chemists to synthesise artificial photosynthetic systems, such as molecular donor / acceptor systems and light harvesting arrays capable of emulating at least key elements of their function. In parallel with these advances in artificial photosynthesis, attention has increasingly turned to the possibility of fabricating photovoltaic solar cells based upon molecular or polymer light absorbers. Molecular based solar cells offer the potential for efficient solar energy conversion using low cost materials and fabrication techniques1. Significant progress is now being made towards the commercial production of such devices for specific market applications. However at present the efficiencies and durabilities of molecular and polymer based devices remain modest in comparison to silicon based solar cells, and much research and development work remains to be undertaken before such devices can effectively compete with silicon devices for large scale solar energy conversion.

In this paper, I will focus upon the light driven charge separation which underlies the function of molecular based photovoltaics. Issues I will try to cover will include:

- A comparison of the parameters determining charge separation in dye sensitised, bilayer and bulk heterojunction solar cells
- Thermodynamic versus kinetic control of charge separation
- Limits to energy storage efficiency
- Overcoming the coulomb attraction of photogenerated charges.

1. Durrant, JR, Haque, SA, Palomares, E, Photochemical energy conversion: from molecular dyads to solar cells, Chem. Comm., 2006, 3279 – 3289.

## 403

### Carbon Nano Hybrids for Solar Energy Conversion

**Dirk M Guldi,** *Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*

Multifunctional carbon nanostructures are currently under active investigation for producing innovative materials, composites, and optoelectronic devices, whose unique properties originate at the molecular level. Among the wide variety of carbon allotropes recently discovered, $C_{60}$, single wall carbon nanotubes (SWNT) and single wall carbon nanohorns (SWNH) are of particular interest. $C_{60}$ is entirely made of pentagons and hexagons resulting in 0.78 nm sized truncated icosahedral carbon spheres. In contrast, the structure of SWNT has a cylindrical shape, which can be conceptually generated by wrapping a one-atom-thick layer of a graphene sheet into a seamless cylinder. The diameter of most SWNT is around 1 nm - similar to that of $C_{60}$ - with a tubular length that can reach many thousands of times their diameter. Importantly, based on different arrangements, SWNT possess different electrical properties, which are the result of the electrons moving differently in the tube depending on the SWNT arrangement. SWNH, on the other hand, are typically constituted by tubes of about 2-5 nm of diameter and 30 to 50 nm long, which associate with each other to give rise to round-shaped aggregates of 100 nm of diameter. Their large surface areas and inner nanospaces are of great importance, since they ensure a great affinity, for example, with organic electron donors. The accomplishment of multiple-performance objectives in a single system necessitates combining these carbon allotropes with other classes of materials. Our past work has mapped out compounds that proved particularly useful: active organic materials such as porphyrins / phthalocyanines and oligomers / polymers. We have demonstrated that linking these molecular building blocks creates enormous synergisms in going much beyond just harnessing the features of the individual subunits or constituents. Eventually it enables the control over molecular arrangement - well-defined ensembles and superstructures with widely differing property values - and results in the development of the necessary tools for fine-tuning properties on the molecular, nanoscale level. I will highlight the opportunities that rest on carbon nanostructures within the context of charge transfer reactions in novel chemical as well as light driven systems with high tensile strength. A fundamental aspect of our research is to integrate such functions without sacrificing the structural and electronic integrity of the material. In this context, I will survey our concepts to generate functional entities using the bottom up approach, that is, to design, manipulate, characterize, examine, and understand the potential of carbon materials as a novel platform for stable electron donor-acceptor hybrids and conjugates. Important aspects will include the impact, the benefits and some of the promises that evolve from charge transfer reactions involving carbon nanostructures with high tensile strength on i) the stabilization of radical ion pair states, ii) multi electron catalytic reactions, and iii) photoelectrochemical / photovoltaic solar energy conversion.

## 404

### Dye Sensitization of Metal Oxide Crystals

**Bruce A Parkinson,** *Colorado State, United States*
**Yunfeng Lu,** *United States*
**Mark T Spitler,** *United States*

We will report systematic studies of the dye sensitization of metal oxide single crystal surfaces. Techniques for preparing atomically flat surfaces that reproducibly adsorb the carboxylated dye molecules were developed. Low index surfaces of both anatase and rutile were studied with adsorbed dicarboxylated cyanine dyes and the popular ruthenium based sensitizers. Photochronocoulometry was used to measure the surface coverage of the dye molecules in tandem with photocurrent spectroscopy. Photocurrent spectroscopy revealed the aggregation state of the dyes on the crystal surface. Adsorption isotherms for a series of structurally similar dyes were measured in order to speculate about the arrangement of the dye molecules on the various surfaces. Adsorption rates and desorption rates of the various dye molecules were studied and modeled with both analytical models and Monte Carlo simulations. It was found that the identity of the regenerator can have large influence on the desorption of carboxylate-bound dyes. Implications of these fundamental studies on the behavior of dye sensitized solar cells will be discussed.

## 405

### Chromogenic Polymer Materials for Sun Protection

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**Olaf Mühling,** *Fraunhofer Institute for Applied Polmer Research, Volmerstr. 7B, 12489 Berlin, Germany*
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In the last decade chromogenic polymers have found lively interest, especially regarding sun protecting glazing systems. The background for sun protection is based on absorption and reflection phenomena of solar ray.

According to the external stimulus which affects their optical properties chromogenic materials are separated into subclasses, e.g. thermochromic, electrochromic and photochromic polymers. Presented work focuses on thermochromic

- hydrogels by endowing indicator dyes
- polyolefines by embedding leuco dye systems

The origin of thermochromism in hydrogels endowed with indicator dyes is a temperature dependent molecular interaction between dye and gel matrix which affects the dye structure. Neither the dyes nor the hydrogels exhibit thermochromic properties themselves. In the present study highly transparent hydrogel networks – based on crosslinked polymer / indicator dye systems – are obtained. Novel microenvironment properties are resulting. The outstanding property of this material class is the possibility to switch from colourless to colour on heating – suitable for absorption effects.

Thermochromic thermoplastics can be obtained by doping the polymer matrix with a thermochromic complex. Thermochromic polyolefin foils based on leuco dye-developer-solvent systems which withstand the flat foil extrusion process will be presented. Colour and switching temperature of the thermochromic foils can be tailored. A linear dependence of the colour intensity on the additive concentration was found. Furthermore, the surface tension of thermochromic foils, as an indicator for potential migration processes, will be discussed.

## 406

### Charge Separation in Layered Titanate Nanostructures: Effect of Ion Exchange Induced Morphology Transformation

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**Thomas Berger,** *Institute of Materials Chemistry, Vienna University of Technology, Veterinaerplatz 1, A-1210 Vienna Austria, Austria*
**Hinrich Grothe,** *Institute of Materials Chemistry, Vienna University of Technology, Veterinaerplatz 1, A-1210 Vienna Austria, Austria*
**Johannes Bernardi,** *USTEM, Vienna University of Technology, Wiedner Hauptstrasse 8-10/137, A-1040, Vienna Austria, Austria*
**Erich Knözinger,** *Institute of Materials Chemistry, Vienna University of Technology, Veterinaerplatz 1, A-1210 Vienna Austria, Austria*
**Oliver Diwald,** *Institute of Materials Chemistry, Vienna University of Technology, Veterinaerplatz 1, A-1210 Vienna Austria, Austria*

Morphology changes induced by surface chemistry can provide important insights into photoexcitation processes on solids which are critical to photovoltaic and photocatalytic applications. This opportunity region is of particular relevance for $TiO_2$ based nanomaterials which have become available as sheets, wires, and tubes since only recent.[1]We investigated charge separation processes on $Na_2Ti_3O_7$ nanowires and scrolled up $H_2Ti_3O_7$ nanotubes, two types of morphologies which by means of acid/base treatment can reversibly be transformed into each other [2]. Their photochemical activity depends on the branching ratio between the three pathways photoexcited states can undergo: they can deactivate under photoluminescence emission or generation of heat, become persistently trapped or undergo interfacial charge transfer at the particle surface. Some of these competitive processes can be tracked by means of EPR and photoluminescence spectroscopy. A complementarity between efficient charge separation [2], on one and, and radiative recombination of photoexcited states [3], on the other, was observed and clearly demonstrates the critical influence morphology and interlayer composition on the photoelectronic properties of layered oxide nanostructures.

Financial support from the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (FWF P17514N11) is gratefully acknowledged.

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## 407

### Photoelectrochemical Manifestation of Photoelectron Transport Properties of Vertically Aligned Nanotubular $TiO_2$ Photoanodes

**Huijun Zhao,** *Griffith School of Environment, Gold Coast Campus, Griffith University, Australia*
**Haimin Zhang,** *Colombia*

A simple photoelectrochemical method was proposed to quantitatively evaluate the electron transport process of photoelectrocatalytic oxidation of water at vertically aligned nanotubular $TiO_2$ photoanodes. The photoelectrocatalysis reaction resistance (R = k/Jsph+R0 = RI+R0) was measured and used to express the electron transport characteristics of the nanotubular $TiO_2$ electrode. The overall resistance was found to consist of a variant (RI) and an invariant component (R0). The RI was found to be inversely proportional to the saturation photocurrent and depends on the experimental conditions. The proportional constant, k, represents the minimum applied potential bias required to remove 100% of the photogenerated electrons from the photocatalyst layer and was found to be independent of the anodization time. The invariant component of the resistance (R0) is an inherent property of the semiconductor photocatalyst that represents the sum of ohmic contact impedance at the conducting substrate/$TiO_2$ interface and crystalline boundaries impedance. The magnitude of R0 linearly increased with anodization time. The real saturated photocurrent density (Jreal-sphd) was found to be independent of R0 indicating the electron collection efficiency is independent of nanotube length.

## 408

### Nanostructured Thin-Film Tungsten Trioxide Photoanodes for Photoelectrolytic Production of Hydrogen from Sea Water

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**Artur Braun,** *Laboratory for High Performance Ceramics, Empa – Swiss Federal Laboratories for Materials Testing & Research, Switzerland*
**Jan Augustynski,** *Department of Chemistry, University of Warsaw, Poland*

Template-assisted sol-gel route offers attractive possibilities of the controlled production of microporous and mesoporous oxide films. We recently prepared mesoporous tungsten oxide films through the sol-gel method involving ultrasonic stirring step as the main modification of the previously described procedure[1]. Investigation of solar-light-driven photo-electrolysis cell employing such a WO3 photoanode showed that the amount of the delivered steady-state photocurrent was improved by ca. 20%. This improvement is related to changes in the morphology of the nanostructured films shown in Fig. 1, consisting in a marked decrease in the particle size and, apparently, also in the film porosity.

Inspection of photocurrent-voltage curves, recorded under simulated AM 1.5 solar illumination, showed that stable photocurrents of the order of 3 mA/cm2 are attained in a 0.5 M NaCl(Fig.1). This solution, which resembles the sea water, does not require any preliminary acidification as the formation of chlorine sets locally the solution pH to ca. 2. It should be noted that, although in 0.5 M NaCl ca. 20% of chlorine is formed at the WO3 photoanode, oxygen remains the main photo-electrolysis product. Prolonged electrolysis experiments, demonstrated perfect stability of the WO3 photoanodes under conditions of mixed chlorine/oxygen evolution which allows anticipate its suitability for the sea-water photo-electrolysis [2]. The sea water is an abundant, non-toxic electrolyte suitable for massive hydrogen/production via photo-electrolysis.

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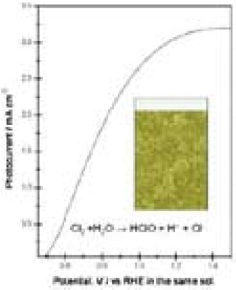

## 409

### Long Term Stability of Dye Solar Cells – from Cells to Modules

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**Ravi Harikisun,** *Dyesol Ltd, Australia*
**Tai Tran,** *Dyesol Ltd, Australia*
**Daniel Ball,** *Dyesol Ltd, Australia*
**Matt Holding,** *Dyesol Ltd, Australia*
**Graeme Evans,** *Dyesol Ltd, Australia*

Dye Solar Cell (DSC) technology has attracted continually growing interest over the last few years. One of the main incentives is to offer an alternative to silicon photovoltaics where prices have not decreased any further since mid 2004 and have plateaued just below US5 $/W$_p$ at the retail level.

Since DSC panels are not available in commercial quantities yet, only limited information is available on product durability. The purpose of this work is to provide data on long term durability at the cell and module level through a range of accelerated tests, such as continuous exposure to artificial sun light at elevated temperature, high temperature storage, thermal cycles and humidity tests. Promising stability over 14,000 artificial sun shine hours, corresponding to more than 20 years cell life time in areas experiencing 1,000 kWh/m$^2$ annual solar irradiation (e.g. Middle Europe), has recently been demonstrated by Dyesol. Since then Dyesol has significantly progressed in electrolyte formulation and data from such systems will be presented and discussed in relationship to the observed long term changes in IV characteristsics at various light levels and based on EIS.

Prototype DSC modules were characterised by the same procedures and durability data will be presented and discussed in terms of some of the practical challenges encountered with cell-to-cell series connections, sealing of larger area panels and managing the mechanical stress issues. Finally product conformance in relationship to existing standards will be examined with particular emphasis on some of the specific characteristics of Dye Solar Cells.

## 410

### Long Term Stability of Dye Sensitized Solar Cells

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**Matthias Junghänel,** *Q-cells, Germany*

Long term stability of dye-sensitized solar cells (DSC) is required for successful implementation of this technology. In earlier studies, DSC performance decreased substantially at elevated temperature. This situation improved significantly with the introduction of a new generation of dyes and electrolytes[1]. Efficiency levels could be maintained at 90-98 % of initial values after ageing[1].

Here, we report on the long term stability of DSC under various testing conditions and with variations in composition. The influence of the $TiO_2$ surface and humidity levels has been studied. Unexpectedly it was observed that addition of a small amount of water to specific electrolytes is beneficial to the initial cell performance. This is mainly resulting from an increased $V_{OC}$. The underlying mechanisms for this improvement will be discussed.

Ageing of these cells at elevated temperature in the dark results in a stronger degradation. This effect however totally changes upon a $TiCl_4$ after treatment of the nanocrystalline $TiO_2$ (prior to staining): The beneficial effect of moisture on initial performance remains but the adverse effect on stability disappears, i.e. water containing cells are rendered more stable by a $TiCl_4$ after treatment of the $TiO_2$ film.

This is studied in more detail under various conditions, i.e. at elevated temperature in the dark and under illumination. Impedance spectroscopy has been applied to gain more insight in specific changes in various parts of the DSC during long term stability testing.

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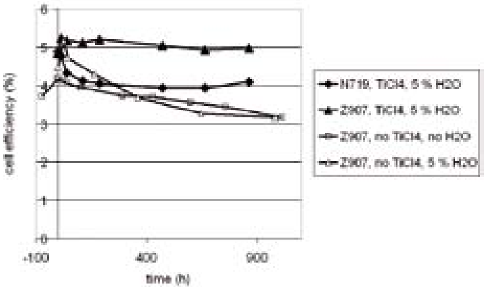

## 411

### Quantitative Study of TBP Effect on Electron Injection Efficiency in Dye-Sensitized Nanocrystalline $TiO_2$ Films

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**Motohiro Kasuya,** *Japan*
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**Nobuhiro Fuke,** *Japan*
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Electron injection process is a key process for realizing high performance solar cells (Fig.1). Thus, we have studied electron injection process in dye-sensitized nanocrystalline semiconductor films so far by using transient absorption (TA) [1] and time-resolved microwave conductivity (TRMC) methods. We estimated the absolute value $\Phi$ of injection efficiency [2] and studied the effect of sensitizer dyes [3], semiconductors [4] and excitation wavelength [5]. We examined here the effect of the additives, 4-tert-butylpyridine (TBP) and lithium ion, which are known to markedly improve the performance of solar cell devices.

For black-dye/TiO2 film in air, electron injection occurred in the picosecond time range with relatively low efficiency (F=0.4). Efficiency was improved by immersion of the film in acetonitrile (F=0.65). By adding 4-tert-butylpyridine (TBP), decrease of efficiency was observed, owing to an increase in the energy level of the conduction band. Similar tendency was observed in N3/TiO2 films. The decrease of injection efficiency can be explained using the model considering heterogeneity of free energy change for electron injection [3].

We gratefully acknowledge financial support from the New Energy and Industrial Technology Development Organization (NEDO).

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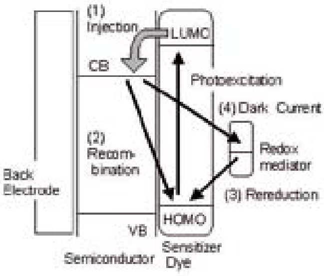

## 412

### Thermal Durability of Dye-sensitized Solar Cells and Submodules

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**Hiroshi Matsui,** *Material Technology Laboratory, Fujikura Ltd., Japan*
**Kenichi Okada,** *Material Technology Laboratory, Fujikura Ltd., Japan*
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Large-area and highly durable dye-sensitized solar cells with current collecting silver grid and their submodules were fabricated. Ionic liquids were used as the nonvolatile solvent for electrolytes instead of conventional organic solvents. In the case of applying ionic liquid-based electrolyte, no obvious leakage of solvent and/or solute, such as ionic liquid itself, iodine and iodide salt, was detected on keeping the cell at 85°C for several thousand hours. Optimization of protection materials for the grid, improvement of sealant, and modifying the sealing methods lead significant enhancement of stability of the cell. On the other hand, it was clarified that moisture intrusion into the cell during the manufacturing process deteriorated thermal stability. Several accelerated endurance tests were carried out to investigate the reliability of dye-sensitized solar cells and modules under the conditions by referring JIS-C8938 standard, which were designated for amorphous silicon solar cells and modules. Our cells and modules showed almost no degradation of the performance under the heat and humidity environment (85°C, 85% RH) for more than 1,000 hours and under the heat and cool cycle stress (–40°C and 90°C) for more than 200 cycles.

## 413

### Interfacial Electron Recombination Process on Extended Pi-conjugated Molecular Dyes in DSSC:An Approach Toward Understanding Dye Structure-Device Efficiency Relationship

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**Amparo Forneli**, *ICIQ, Spain*
**Eugenia Martinez-Ferrero**, *ICIQ, Spain*
**Antonio Sanchez-Diaz**, *ICIQ, Spain*
**Maria Angeles Sarmentero**, *ICIQ, Spain*
**Anton Vidal-Ferran**, *ICIQ, Spain*
**Pablo Ballester**, *ICIQ, Spain*
**Emilio Palomares**, *ICIQ, Spain*

A series of results, based on charge transfer studies on complete functional devices, using as sensitizers organic and heteroleptic Ruthenium(II) polypiridyl dyes has led us to establish a direct relationship between the dye structure-the $TiO_2$/electrolyte$^+$/ and device efficiency. The results are in good agreement with previous work on $\pi$-extended Ruthenium (II) complexes and the use of hydrophobic alkyl chains as inhibitors of back electron transfer reactions from the semiconductor to either the oxidized dye or the oxidized electrolyte. In an effort to understand the details of such differences we have also utilized high level DFT computational calculations to explore the role of the HOMO-LUMO energetics on the interfacial charge transfer kinetics.

## 414

### Dye-sensitized Solar Cells Based on Nanocrystalline Tin Oxide: The Nature of Recombination Losses and Methods of their Suppression

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**YPYP Ariyasinghe**, *Institute of Fundamental Studies, Sri Lanka*
**TRCK Wijayarathna**, *Institute of Fundamental Studies, Sri Lanka*
**EVA Premalal**, *Institute of Fundamental Studies, Sri Lanka*
**MKI Senevirtane**, *Institute of Fundamental Studies, Sri Lanka*
**AGU Perera**, *Georgia State University, United States*
**PVV Jayaweera**, *Georgia State University, United States*

The detailed kinetics of charge injection and recombination in dye-sensitized solar cells are not fully understood. The optimum efficiency achievable seems to be a compromise of many factors which depend on the nature of the oxide material and the dye as well as the morphology of the nanocrystalline film. Although tin oxide in pure form is generally inferior to titanium dioxide, the cells with surface modified films deliver comparable efficiencies. Again there are instances of dyes yielding higher energy and quantum efficiencies for tin oxide instead of titanium dioxide. Experiments with different surface modifications and dyes indicate that the apparent inferiority of tin oxide largely depends on faster rate of non-geminate recombination at surface of this oxide. The surface states on tin oxide acting as trapping sites mediate recombination of the injected electrons with the acceptors in the electrolyte and these states can be passivated by surface treatment with inorganic materials and chelation by suiable ligands on the dye itself. With this strategy an optimum efficiency of ~ 7% has been obtained for tin oxide cells sensitized with indoline dyes. The advantages of tin oxide as an alternative material for dye-sensitized solar cells will be discussed.

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### Full-Plastic Dye-Sensitized Solar Cells via Microwave Heating Process

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A new type of solar cell based on dye-sensitized nanocrystalline titanium dioxide (DSSC) has been developed by M. Grätzel et al. Remarkably high quantum efficiency in combination with the expected ease and low cost of manufacturing makes this new technology interesting as an alternative to existent solar cell technologies. Various elemental technologies of dye-sensitized solar cells have therefore been researched, including the sensitized dye, semiconductor particles, electrolyte, electron transfer process and photovoltaic mechanism.

In spite of these vigorous studies, the assembling of flexible $TiO_2$/dye solar cell is still under investigation. Flexible electrodes, like polyethylene terephthalate sheet coated with tin-doped indium oxide (PET-ITO), present lower costs and technological advantages relative to conductive glass electrodes, e.g. lower weight, impact resistance and less form and shape limitations. However, deposition of nano particulate $TiO_2$ on PET-ITO is difficult, because the thermal treatment must be limited to 150°C or so. It decreases adhesion strength, electrical contact of $TiO_2$ particles and adsorption of the dye.

To achieve the selective heating of organic-inorganic composite film, microwave processing is an attractive field in modern material science. Various inorganic phases have been synthesized using microwave ovens operating at a frequency of 2.45 GHz. Here in this work, a 2.45 GHz microwave irradiation process is newly proposed for selective heating the nanocrystalline titanium oxide films of DSSC. The cell performance improved by microwave heating from 3.9 % to 5.5%.

## 416

### Advancement of Plastic Solar Cells Employing Electrodeposited Porous Crystalline ZnO with Organic Photosensitizers

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We are challenging to develop high efficiency plastic solar cells by combination of originally developed materials and methods, i.e., nanostructured porous crystalline ZnO photoelectrodes prepared by electrodeposition and metal-free organic photosensitizer dyes. Modification of the ZnO nanostructure combined with indoline dyes specially developed for ZnO continue to improve the cell efficiency as well as the stability. The highest efficiency was pushed up to 5.84%. Full plastic submodule of 10×10 cm size also achieved a promising efficiency of 3.2% (Both under AM 1.5, 100 mW $cm^{-2}$).

Scaling down the geometry of the ZnO nanowire structure was found to improve the electron transport to improve the fill factor. Electrodeposition of compact ZnO bottom layer improved adhesion of porous layer thus achieving maximum IPCE reaching 90% and good fill factor. On the other hand, D149 dye was found to form multilayer under excessive soaking in dye solution, leading to decrease of the fill factor. At the same time, however, the same dye is desorbed in contact with the electrolyte solution causing problems with cell stability. Such problems were significantly reduced by chemical modification of the dyes. Various new dyes such as asymmetric squarilium dyes were also synthesized to harvest photons in the near-IR region.

Stability tests of the plastic solar cells with ZnO and organic dye have indicated encouraging results to confirm ‘usable’ stability already at the present level, although not yet to guarantee over 10 years life for outdoor use.

This work was supported by NEDO.

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### A Novel Meso-Linked Porphyrin Sensitized Solar Cell

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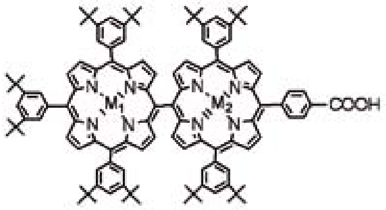
The dye-sensitized solar cell (DSSC) is a promising candidate for the next-generation low-cost renewable energy device. For the typical DSSC, ruthenium-based dyes on $TiO_2$ have been used and produced up to 10% photoelectric conversion efficiency ($\eta$), thus fueling the search for new high efficiency dyes.

Porphyrin, which is similar in structure to chlorophyll, is well-known for its strong light absorption that allows it to participate in energy and electron transfer processes. This macrocyclic ring possesses a large $\pi$-conjugation that reduces the HOMO-LUMO energy gap attractive for photosynthetic mimics, and electronic and photonic applications. Another feature of porphyrin is the facile functionalization of its meso and $\beta$ positions, which can be exploited to fine-tune its electronic properties. Several porphyrin monomers have been previously used in DSSC and were reported to give reasonable performance. However, the DSSC properties of porphyrin arrays are yet to be explored. Herein, we report three meso-linked porphyrin dimers as potential sensitizers for nanocrystalline $TiO_2$ DSSC.

Bis-freebase (J1), mono-zinc inserted (J2) and bis-zinc inserted dimers (J3) were prepared by Suzuki coupling of their respective monomeric components. The conversion efficiency increased according to the number of zinc-inserted atoms: J1&ltJ2&ltJ3 (1.5%, 1.7%, 2.3% under AM 1.5 solar irradiation). In addition, the zinc-inserted compounds gave IPCE peaks of ~60% while the freebase dimer only reached a maximum IPCE of 30%. Considering these values, meso-linked porphyrin dimers are attractive candidates for DSSC applications. Optimization of the DSSC fabrication conditions may further increase the conversion efficiencies and are currently underway.



J1: $M_1$, $M_2$ = 2H
J2: $M_1$ = Zn, $M_2$ = 2H
J3: $M_1$, $M_2$ = Zn

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### Dye-sensitsed Tandem Solar Cells

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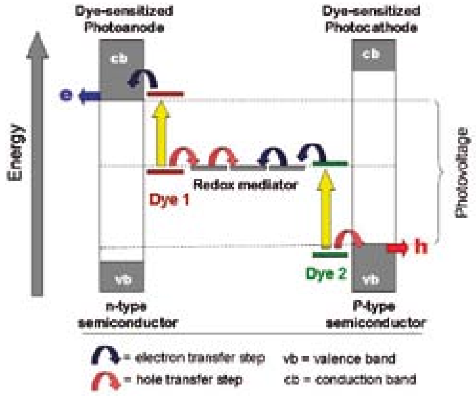
Tandem solar cell concepts are currently successfully applied in conventional pn-junction solar cells with up to 40 % conversion efficiencies. Several tandem concepts have so far been introduced in the area of dye-sensitised solar cells, such as stacking of preassembled dye-sensitised solar cells, the combination of complete dye-sensitised solar cells with CdTe inorganic solar cells as well as the combination of dye-sensitised photocathodes with dye-sensitised photoanodes (pnDSSCs). The latter is of particular interest as it requires only marginally higher fabrication costs, compared to other concepts that involve stacking of complete preassembled cells, which de facto results in a doubling of manufacturing costs.

In this work we will present a more detailed analysis of dye-sensitised p-type nano-structured nickel(II)oxide electrodes as a model system for dye-sensitised photocathodes. We introduce a novel preparation method to fabricate nanostructured NiO electrodes based on a preformed NiO nanopowder.. Film preparation conditions strongly influence the nanostructure and photovoltaic performance of dye-sensitised nanostructured NiO photocathodes. Under optimised conditions NiO based cells show photon-to-electron conversion efficiencies beyond 50%, suggesting that there are no fundamental limitations to achieving photocathodes that can match the photocurrent outputs of conventional dye-sensitised photoanodes.

Several aspects of this model system will impede its future use in tandem dye-sensitised solar cells. Nevertheless this work shows that there should be no fundamental limitations for the development of novel efficient dye-sensitised tandem solar cells. Further advancements will require the identification of nanostructured p-type semiconductor materials with optimised band positions for their use in conjunction with dye-sensitised $TiO_2$ photoanodes.



## 419

### Enhanced Stability of Dye-Sensitized Solar Cells by Employing Polymeric Additives in the Electrolyte Solutions

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Advancing the technology of dye-sensitized solar cells (DSSCs) with liquid electrolytes from laboratory level to industrial level was impeded owing to the problems related to sealing and evaporation of liquids at high temperatures. Replacement of liquid electrolytes with ionic liquids or molten salts has been one of the strategies.

Here, we report the effects of (1) a silane substituted ruthenium complex (Fig. 1) linked with tetraethyl orthosilicate (TEOS), (2) polymers of alkyl imidazolium salts (Fig. 2), and (3) electro-spun poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP) membranes on photocurrent-voltage characteristics of DSSCs. The ruthenium complex was prepared by hydrosilation between a vinyl-containing complex and trimethoxysilane, followed by linking with TEOS through formation of siloxane links. The polymeric alkyl imidazolium salts were synthesized by photo-polymerization of alkyl imidazolium salts directly in the $TiO_2$ film. Electrospun PVdF-HFP membrane was prepared from 16 wt% of PVdF-HFP solution in a mixture of acetone/N,N-dimethyl acetamide (7:3 wt%) at an applied voltage of 12 kV. It was then activated by immersing in 0.6 M 1-hexyl-2,3-dimethyl imidazolium iodide, 0.1 M LiI, 0.05 M I2, 0.5 M tert-butylpyridine in EC/PC(1:1 wt%) to obtain its corresponding membrane electrolyte with ionic conductivity of 10-3 S cm-1 at 25°C.

We have found that DSSCs with polymeric additives have enhanced stabilities, compared with those obtained in the absence of the polymeric additives. The results will be discussed in terms of charge transfer resistance at the $TiO_2$/electrolyte interface, increased viscosity of the electrolyte solutions, and facilitated ion transfer in the electrolyte media.

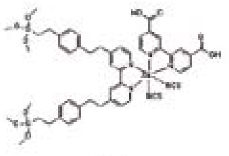

Fig. 1

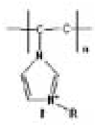

Fig. 2

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### Highly efficient Quasi-Solid-State Dye-Sensitized Solar Cells Based on Electrospun $TiO_2$ Nanorod

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**Dong Young Kim,** *Korea Institute of Science and Technology, Korea*
**Sung-Yeon Jang,** *Korea Institute of Science and Technology, Korea*

Enhancement in device efficiency of dye sensitized solar cells (DSSC) has been continuously reported by many researchers. Most of high performance devices were fabricated using $TiO_2$ nanoparticles with a diameter of a few tenths of nanometer and liquid electrolytes systems. However, the conventional $TiO_2$ nanoparticle based DSSCs with polymer gel electrolytes showed much lowers device efficiency. Besides slower charge transfer in high viscosity polymer gel, small pore size of $TiO_2$ nanoparticles film hinders complete penetration of gel electrolyte resulting in the lower device efficiency. Network of $TiO_2$ nanorods is certainly an attracting structure for DSSCs in terms of high surface area and porosity. In this work, quasi-solid-state dye sensitized solar cells (DSSC) were demonstrated using $TiO_2$ nanorods and a polymer gel electrolyte. Networks of $TiO_2$ nanorods were obtained using electrospinning technique. Electrospinning is a remarkably simple method to generate one-dimensional (1D) nanostructures of polymers and metal oxides. The $TiO_2$ nanorods were 60 - 100 nm long with a diameter of ~ 15 nm, and the network has approximately two times larger surface area compared to the same weight of conventional nanoparticles (diameter ~ 25 nm). Furthermore, the highly porous nature of the networks helps the viscous polymer gel electrolyte to penetrate efficiently. As a result, the electrospun nanorod based DSSC showed improved efficiency of approximately 20% compared to the conventional $TiO_2$ nanoparticle based quasi-solid state DSSCs.

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### New Nb-containing Oxide Photocatalysts for Efficient Decomposition of Organic Pollutants Under Weak Visible Light Irradiation

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**Tetsuya Kako,** *Photocatalytic Materials Center, National Institute for Materials Science, Japan*
**Guoqiang Li,** *Photocatalytic Materials Center, National Institute for Materials Science, Japan*
**Defa Wang,** *Photocatalytic Materials Center, National Institute for Materials Science, Japan*
**Zhigang Zou,** *Nanjing University, China*

Development of new photocatalytic materials sensitive to visible light irradiation has attracted increasing interests because of the importance of effective utilization of the solar energy and indoor illumination. Although many efforts have been directed to the development of visible-light-sensitive photocatalysts, by modifying TiO2, or by developing new materials, the practical applications are still restricted, mainly owing to the limited option of catalysts and to the still low photocatalytic activities.

Up to now, we have focused our concerns on the development of new photocatalysts, by controlling crystal and electronic structures of oxide semiconductors. We have reported various new materials, such as: (In1-xNix)TaO4, CaBi2O4, CaMoO4-BiVO4, AgNbO3-NaNbO3 solid solutions, NaBiO3, [1-3], etc., for photocatalytic water splitting, or photocatalytic degradation of organics contaminats.

In this talk, we will report the preparation and characterization of new Nb-containing oxide photocatalysts. The new photocatalysts can effectively decompose various volatile organic compounds, such as acetaldehyde, 2-propanol, etc, under irradiation of weak visible light (0.01 mW/cm2) emitting from blue-light-emitting diodes (400< wavelength <550 nm). Designing guidelines and future prospects for development of new photocatalytic materials will also be discussed, basing on systematic studies on the materials syntheses, photophysical properties, and photocatalytic activities of these new photocatalysts, obtained by various experimental measurements and theoretical calculations.

[1] Z. Zou, J. Ye, K. Sayama and H. Arakawa, Nature, 414, 625(2001).
[2] J. Tang, Z. Zou, J. Ye, Angew. Chem. Int. Ed., 43, 4463 (2004).
[3] T. Kako, Z. Zou, M. Katakiri, J. Ye, Chem. Mater., 19(2), 198, 2007.

## 422

### Preparation and Characterisation of Fe-, Al- and Ca-doped Titanium Oxide ($TiO_2$) from Wastewater Sludge of Ti-salt flocculation

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**J H Kim,** *Chonnam National University, Korea*

We have recently developed a novel process to overcome the sludge disposal problem through flocculation using Ti-salt which could also economically recover valuable $TiO_2$ from wastewater. A large amount of $TiO_2$ doped with carbon (C) and phosphorus (P) ($TiO_{1.42}C_{0.44}P_{0.14}$) was produced from the wastewater sludge generated by the Ti-salt flocculation. A simple and novel method to synthesise iron-, aluminium- and calcium-doped titanium dioxide ($TiO_2$) was investigated. Titanium tetrachloride ($TiCl_4$) was used as a coagulant to remove pollutants (organic matter and phosphorus) from wastewater. The settled Ti-floc (sludge) was incinerated at 600 °C. The resultant by-product from the waste sludge was valuable $TiO_2$. The Ti-salt coagulant was added with $FeCl_3$, $Al_2(SO_4)_3$ and $Ca(OH)_2$ coagulants to dope iron, aluminium and calcium on $TiO_2$. The effect of iron, aluminium and calcium on $TiO_2$ was investigated in terms of the physical, chemical and electronic properties of doped $TiO_2$ nanoparticles. The $TiO_2$-WO (without any doping materials), Fe/$TiO_2$, Al/$TiO_2$ and Ca/$TiO_2$ exhibited the majority of the anatase phase after 600°C calcination. The XRD pattern on the Fe/$TiO_2$ showed some peaks of hematite ($\alpha$-$Fe_2O_3$). The majority of acetaldehyde with $TiO_2$-WO and Ca/$TiO_2$ was completely removed under UV irradiation within 40 minutes. Al/$TiO_2$ led to high photoactivity with removal of 90%. However, at high iron concentration (6.5 at.%), acetaldehyde removal by photoactivity under UV irradiation was marginal. Under visible light, the photo-decomposition of acetaldehyde using $TiO_2$-WO, Fe/$TiO_2$, Al/$TiO_2$, Ca/$TiO_2$ and P-25 was marginal.

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### Surface Free Energies of Rutile and Anatase Terminated by Nonmetals

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**Huagui Yang,** *ARC Centre of Excellence for Functional Nanomaterials, AIBN, University of Queensland, Australia*
**Shizhang Qiao,** *ARC Centre of Excellence for Functional Nanomaterials, AIBN, University of Queensland, Australia*
**Sean C Smith,** *ARC Centre of Excellence for Functional Nanomaterials, CCMS, AIBN, University of Queensland, Australia*
**Max Lu,** *ARC Centre of Excellence for Functional Nanomaterials, AIBN, University of Queensland, Australia*

The surface free energies of rutile and anatase terminated by 12 nonmetals (H, B, C, N, O, F, Si, P, Cl, Br, I) have been investigated with the framwork of density funtional theory. It is found that, surfaces terminated by different nonmetals show totally different relative stabilities, suggesting that the morphologies of rutile and anatase can be adjusted with use of surface morphology controlling agent. For anatase, for instance, F-terminated surfaces of anatase $TiO_2$ can be dominated by {001} facets, rather than {101} as predicted in the case of clean surfaces. Following this prediction, anatase $TiO_2$ single crystals with a large percentage of {001} facets have been successfully synthesized.

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### Effect of Annealing Temperature on the Photocatalytic Activity of Iitrified Si-Doped Titanias with and Without Fe Loading

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**Hirotaka Ozaki,** *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Japan*
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**Masashi Inoue,** *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Japan*

We previously reported that nitrified Si-doped titanias exhibited relatively high photocatalytic activities under visible-light irradiation [1] and that the Fe addition to the N- and Si-co-doped titanias markedly improved the activities [2]. In this study, the effect of annealing on the photocatalytic activity of the N- and Si-co-doped titanias with and without Fe loading was studied.

Nanocrystalline Si-doped titanias were synthesized by a glycothermal method. The products were calcined in air at 500°C for 30 min, and treated in an $NH_3$ flow at 600°C for 1 h. Fe loading was conducted by an impregnation method, and the samples were annealed in air at various temperatures. Photocatalytic activity was evaluated by decomposition of acetaldehyde and Rhodamine B under visible-light irradiation with a xenon lamp and a UV cut-off filter.

Without annealing, the catalysts without Fe loading showed quite low activities. As the annealing temperature increased up to 500°C, the photocatalytic activity increased. The anneal treatment brought about a decrease in the population of the oxygen vacancies in the samples, which dominantly affected the activity. For the catalysts with Fe loading, on the other hand, increased annealing temperature decreased the activity as shown in Fig. 1. By the addition of Fe, the recombination of holes and electrons were efficiently suppressed. Therefore, the higher activities obtained with the catalysts annealed at lower temperatures are due to the higher amounts of nitrogen doped in the catalysts.

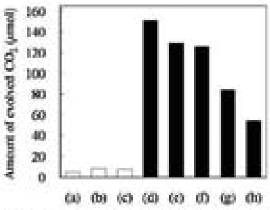

Fig. 1. Amounts of $CO_2$ generated after 1 h of visible-light irradiation: (a)–(c) nitrified Si-doped titania without Fe loading annealed at: (a) 400 °C, (b) 500 °C, and (c) 600 °C; (d)–(h) Fe-loaded nitrified Si-doped titania (Fe/Ti = 0.03) annealed at: (d) 200 °C, (e) 300 °C, (f) 400 °C, (g) 500 °C, and (h) 600 °C.

[1] H. Ozaki, et al., *J. Mater. Sci.*, 42 (2007) 4007.
[2] H. Ozaki, et al., *J. Phys. Chem. C*, 111 (2007) 17061.

## 425

### Three Dimensional $TiO_2$ Electrodes for High Efficiency Dye-Sensitized Solar Cell

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**Yuhei Ogomi,** *Kyushu Institute of Technology, Japan*
**Yohie Kashiwa,** *Kyushu Institute of Technology, Japan*
**Yusuke Noma,** *Kyushu Institute of Technology, Japan*
**Tatsuya Fijita,** *Kyushu Institute of Technology, Japan*
**Yoshiiro Yamaguchi,** *Nin-Nippon Steel Chemical, Japan*
**Mitsuru Kono,** *Nin-Nippon Steel Chemical, Japan*

We propose $TiO_2$ electrodes consisting of two-dye-stained-$TiO_2$ layer and three dimensional porous Ti electrodes as shown in Figure 1 to absorb light with wider wavelength.

The cell consists of two-dye stained-$TiO_2$ layers (Two-layer-cell)), where upper and bottom layers are stained with dyes having longer and shorter wavelength respectively. It was difficult to stain the $TiO_2$ layer selectively with two dyes respectively by using a mere dipping process. We found that Two-layer-cell can be prepared by staining the substrate under pressurized $CO_2$ atmosphere. It was proved that the two-layer-cell has advantage over cells consisting of randomly-stained-$TiO_2$ layer (Cocktail type cell) in terms of high efficiency. In addition, we report advantages of the dye-staining-process under pressurized $CO_2$ process which enables extremely quick dye-uptake and inhibits inconvenient dye aggregation and makes it possible to passivate surface states of $TiO_2$ effectively which was observed by thermally stimulated current. 10.4% efficiency is reported.

In order to collect the electrons in $TiO_2$ layers effectively, the $TiO_2$ layer was covered with porous Ti electrodes. When the Ti electrode thickness became thick (150nn), the electrolyte diffusion was disturbed at the sacrifice of the increase in the conductivity of the Ti layer. Thick and porous Ti electron collecting layer fabricated by our new process solved the problem. In addition, it is reported that high efficiency FTO-free dye sensitized solar cells were fabricated by using the porous Ti electrode and the efficiency reach 7.4%.

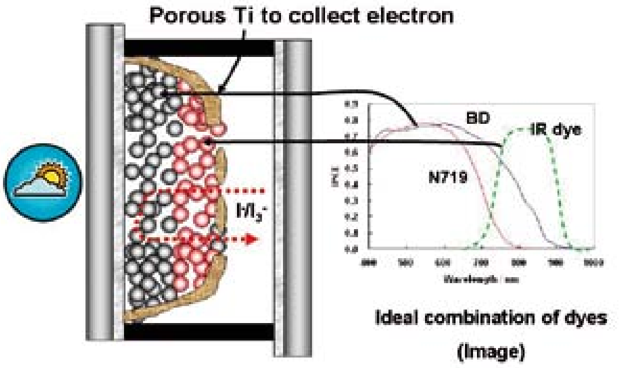

Figure 1. DSC consisting of Two-dye-stained-$TiO_2$ layer and porous Ti electron collecting layer

# 426

## Main Parameters Influencing the Response of Solid State Dye Solar Cell

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**Juan Bisquert,** *Universitat Jaume I, Spain*
**Michael Grätzel,** *Ecole Polytechnique Federale de Lausanne, Switzerland*

The strong interest shown by the companies in the development of the dye solar cell as a commercial device has generated a big interest in the development of solid state devices. One of the approaches to substitute the liquid phase used in the original solar cells is to use spiro-OMeTAD as hole conductor. Although efficiencies between 4 and 5%[1,2] have been reached in several labs on this device, the improvement of these values is currently limited by the lack of a deep knowledge of the main parameters influencing their electrical behavior.

In this presentation, the more relevant elements contributing to the electrical response of the spiro-OMeTAD based solid state dye solar cells will be identified. Then the influence of each of these elements in the efficiency and fill factor will be analyzed and the evolution of these parameters and effects and mechanism of degradation described.

1 L. Schmidt-Mende et al. Adv. Mater. 2005, 17, 813
2 S.Handa et al. Chem. Com. 2007, 1725–1727.

# 427

## Improvement of the Crystallinity and Pore Structure of Electrodeposited Titania Films by Low Temperature Treatment Methods

**Katrin Wessels,** *Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry, Germany*
**Michael Wark,** *Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry, Germany*
**Torsten Oekermann,** *Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry, Germany*

The preparation of porous metal oxide semiconductor films at low temperature (< ca. 150°C) is of high interest in view of the production of (flexible) plastic-based dye-sensitized solar cells (DSSC), which would allow reductions in weight and costs. In case of ZnO, porous films electrodeposited at temperatures as low as 70°C have shown superior performance in DSSC even if compared to nanoparticular films sintered at high temperature [1]. Recently we were also able to directly electrodeposit crystalline $TiO_2$ films consisting of rutile with a small amount of anatase. The films are anodically electrodeposited from TiCl3-solution at 80°C using surfactants, e.g. sodium dodecyl sulfate (SDS), as structure-directing additives to generate a porous structure [2].

Before the use in DSSC the additives have to be removed in order to obtain pores with sufficient accessibility. Various solvents for the desorption of SDS, e.g. ethanol and aqueous solutions of HCl and KOH, were tested, of which the latter was the most successful. Furthermore, water vapor treatment in an autoklav at temperatures of up to 150°C led to an improved crystallinity of the anatase phase, while the rutile phase stays unaltered. This texture change lead to a significantly higher dye loading in comparison to untreated films (see Figure) and a corresponding increase in efficiency.

[1] T. Oekermann, T. Yoshida et al., J. Phys. Chem. B 109 (2005) 12560.
[2] K. Wessels, A. Feldhoff, M. Wark, J. Rathousky, T. Oekermann, Electrochem. Solid-State Lett. 9 (2006), C93.

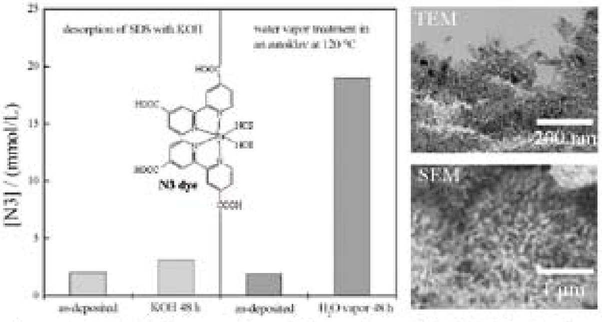

Figure 1: dye loading capacity of electrodeposited $TiO_2$ films before and after KOH (left) or water-vapor (right) treatment. TEM and SEM mirographs of as-deposited $TiO_2$ films.

# 428

## From Natural to Artificial Photosynthesis - Biomimetic Chemistry for the Production of Hydrogen from Solar Energy and Water

**Stenbjörn Styring,** *Department of Photochemistry and Molecular Science, Uppsala University, Sweden*

The lecture will cover our recent research in the Swedish Consortium for Artificial Photosynthesis and the European network SOLAR-H. Our research aims for the production of a valuable fuel, hydrogen, from the endless resources solar energy and water. The idea is that water shall be oxidized in a molecular, catalytic process using solar energy. The electrons extracted from water shall be used in a second catalytic process to reduce protons to molecular hydrogen. To manage our chemistry we use a biomimetic approach where we copy key principles from natural enzymes that accomplish partial reactions. Water oxidation using solar energy is carried out by the Photosystem II reaction center using a catalytic Mn4 complex. In our chemistry we use a photoactive ruthenium center to absorb light energy and trigger the electron transfer reactions. This photoactive Ru-center is coupled synthetically to synthetic multinuclear manganese-complexes. The lecture will describe our research on light driven, multi-electron transfer in these Ru-Mn systems. Recent chemical oxidation experiments that lead to the oxidation of water in synthetic Mn-systems, will also be described and analyzed with a combination of EPR spectroscopy and isotope-labeling techniques. To accomplish reduction of protons to hydrogen we mimic the di-iron center in hydrogenase enzymes. Some of our recent results on these biomimetic Fe-Fe complexes will be described.

# 501

## The Solar Biofuels Consortium: Developing 2nd Generation Microalgal Biofuel Systems

**Ben Hankamer,** *Institute for Molecular Bioscience, Australia*
**Olaf Kruse,** *University of Bielefeld, Germany*
**Clemens Posten,** *University of Karlsruhe (TH), Germany*
**Peer Schenk,** *University of Queensland, Australia*
**Ute Marx,** *Institute for Molecular Bioscience, Australia*
**Anthony Larkum,** *University of Sydney, Australia*
**Michael Hippler,** *Germany*

The Stern Review 'The Economics of Climate Change' and the Nov 2007 IPCC Synthesis report on Climate Change both conclude that urgent action is needed to develop $CO_2$ free energy technologies. Importantly the IPCC also reports that atmospheric $CO_2$ levels above 450 ppm $CO_2$-e (i.e. e=equivalent contribution of all greenhouse gases) are in the dangerously high range and that we have already exceeded this threshold (currently 455 ppm $CO_2$-e) 10 years earlier than had previously been predicted. It is therefore highly advisable that that globally ~11TW-yr $CO_2$ free energy capacity should be installed by 2025 (compared with a total global energy demand of ~15 TW-yr).

Currently fuels make up ~67% of the global energy market. 2nd generation biofuel systems based on microalgal bioreactors are increasingly recognized as offering an important route to producing clean fuels in the form of bio-hydrogen, bio-diesel, bio-ethanol and bio-methane. Furthermore their production can be coupled to $CO_2$ sequestration. Here the advances made by the Solar Biofuels Consortium (www.solarbiofuels.org) at the level of light harvesting antenna engineering, metabonomics, the development of salt tolerant microalgal strains as well as large scale bioreactor systems will be presented.

## 502

### Synthesis of Conducting Polymers in Ionic Liquids for Photovoltaic Applications

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Conducting polymers can have a number of different applications in photovoltaics, i.e. as the light harvester and charge transporter in bulk heterojunction cells, or as the hole transporter in dye sensitized solar cells. In these applications, properties such as the conductivity and morphology are paramount.

Ionic liquids - liquids composed entirely of ions – are of increasing interest to the photovoltaic community as they are excellent electrolytes, with negligible vapor pressures and stabilities that can significantly increase the lifetimes of photoelectrochemical cells.

However, ionic liquids are also ideal media for both chemical and electrochemical synthesis. We have utilized ionic liquids for the chemical and electrochemical synthesis of conducting polymers poly(pyrrole), poly(terthiophene) and PEDOT.[1] Electrochemical synthesis of these polymers in ionic liquids can yield smoother surface morphologies and improved electrochemical activities, which is predicted to be greatly beneficial for the performance of these materials as hole transporters.

The use of ionic liquids for the chemical synthesis of conducting polymers can also be extremely advantageous, used either in one phase or as part of a biphasic system. Conducting polymer-noble metal nanocomposites can be synthesised using a one-phase ionic liquid system, while using a biphasic ionic liquid/water system can yield conducting polymers with unusual fibrillar morphologies (Figure 1).[2] The testing of such fibrillar conducting polymers in bulk heterojunction systems will be reported.

[1] Pringle et al. Polymer, 2005, 46, 2047-2058.
[2] Pringle et al. Macromolecules, 2007, 40, 2702-2711.

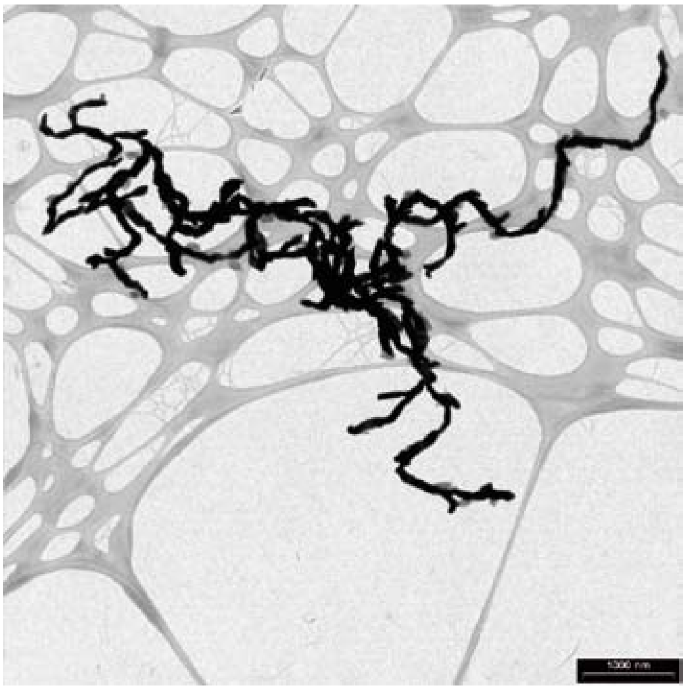

**Figure 1;** TEM of PEDOT fibrils synthesized in a biphasic ionic liquid/water system.

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## 503

### Charge Transfer Processes and Photovoltaic Performance in Blends of an Ambipolar Polyfluorene Co-Polymer in Combination with Different Electron Acceptors

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**Robert A Marsh,** *University of Cambridge, United Kingdom*
**Chris R McNeill,** *University of Cambridge, United Kingdom*
**Jonathan JM Halls,** *Cambridge Display Technology Ltd., United Kingdom*
**Neil C Greenham,** *University of Cambridge, United Kingdom*

We present a comparative study of the photovoltaic properties of an alternating polyfluorene co-polymer (F8TBT: poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole]-2',2"-diyl) blended with two different electron acceptors, namely CdSe nanoparticles and PCBM (PCBM = (6,6)-phenyl C61-butyric acid methyl ester). Such photovoltaic devices take advantage of both the high electron mobilities of inorganic semiconductors/fullerenes and the solution processing possibilities of polymer semiconductors.

We employed transient absorption laser spectroscopy to resolve the cascade of excitonic and polaronic intermediate states participating in the photovoltaic processes. This study was complemented by steady-state photoluminescence quenching and quantum efficiency measurements to probe excited-state charge transfer, and photoinduced absorption measurements to identify long-lived charged species. We were able to correlate the phototophysical measurements with well-defined and controllable morphological parameters and ultimately with the photovoltaic performance..

This work demonstrates that polyfluorenes are versatile polymers for photovoltaic applications and points to how further improvements might be made. Initial photovoltaic devices based on these two blend systems, show a spectral response extending to 600 nm and solar power conversion efficiency of 1.7% under Air Mass 1.5 Global (AM1.5G) conditions.

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## 504

### Efficient CdSe QD-Sensitized $TiO_2$ Inverse Opal Solar Cells

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**Taro Toyoda,** *The University of Electro-Communications, Japan*

$TiO_2$ inverse opal could offer a promising solution in search to enhance the light harvesting efficiency of dye-sensitized solar cell (DSSC) due to its large interconnected pores for better penetration of dye and photon localization in the red edge of photonic band gap for significant enhancement of dye absorption. In view of sensitizers, semiconductor quantum dots (QDs) have attracted much attention as dye substitute due to its tunable optical properties to maximize the solar absorption and capability of carrier multiplication through impact ionization. Furthermore, its instability generally irritating the efficiency could be covered by coating with more stable materials. In this study, we propose the use of $TiO_2$ inverse opal solar cells sensitized with CdSe QDs by chemical deposition and introduce a suggestion for better solar cells, namely surface modification with ZnS and insertion of fluoride ($F^-$) ions on the TiO2/CdSe and CdSe/ZnS interfaces. The photovoltaic properties increased by surface modification and larger latex template size. The former indicates the passivation of surface states on TiO2 (by $F^-$ ions) and CdSe QDs (by $F^-$ ions and ZnS). The latter shows that the resulted larger pores in the $TiO_2$ inverse opal favoring the easy penetration of Cd and Se precursors during deposition, as well as the electrolyte. Further investigations are still continuing to determine the exact effect of each modification and the potential of other latex size. The energy conversion efficiency to 3.4% could be achieved; where best to our knowledge this value is the highest for QD sensitized solar cells.

| Electrode | Jsc (mA/cm2) | Voc | FF | Efficiency (%) |
|---|---|---|---|---|
| TiO2(394 nm)/F/CdSe/F/ZnS | 14.34 | 0.71 | 0.34 | 3.4 |
| TiO2(204 nm)/F/CdSe/F/ZnS | 9.70 | 0.62 | 0.30 | 1.8 |
| TiO2(204 nm)/CdSe | 4.40 | 0.57 | 0.24 | 0.6 |

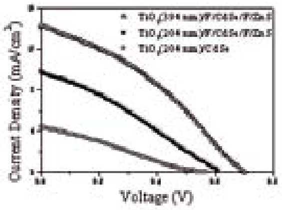

**Fig. 1** J-V characteristic of two different $TiO_2$ inverse opal electrodes made from latex template with diameters of 204 and 394 nm ($TiO_2$/CdSe and $TiO_2$/F/CdSe/F/ZnS).

## 505

### Semiconducting Properties and Photoinduced Hydrophilicity on Nanostructured $TiO_2$ Deposits

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**Hubert Cachet,** *Université Pierre et Marie Curie-Paris6, Laboratoire Interfaces et Systèmes Electrochimiques; CNRS, UPR15-LISE, France*
**Debiemme-Chouvy,** *Université Pierre et Marie Curie-Paris6, Laboratoire Interfaces et Systèmes Electrochimiques; CNRS, UPR15-LISE, France*
**Bernard Baroux,** *Laboratoire de Thermodynamique et de Physico-chimie Métallurgique, ENSEEG, France*
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Photo-induced super-hydrophilicity of $TiO_2$ surfaces [1], providing self-cleaning and anti-fogging properties, is generally attributed to some chemical surface modifications such as an increased concentration of Ti OH groups under illumination. $TiO_2$ is also known to undergo light induced hydrogen insertion [2], especially in nanostructured material, but up to now no clear correlation has been evidenced between super-hydrophilicity and hydrogen evolution or intercalation.

In the present work, light-induced superhydrophilicity on nanostructured $TiO_2$ layers deposited by PVD on stainless steel was characterized by contact angle measurement and impedance spectroscopy, as a function of the thickness of the layer (50 to 300 nm), light intensity and duration of exposure. The dielectric constant of $TiO_2$ is determined by Mott-Schottky analysis from the change in the M-S slope when the depletion layer reaches the $TiO_2$/substrate interface, showing a significant increase under illumination, while the water contact angle decreases. Further storage in the dark, shows the reversibility of light –induced modifications. Such behaviour could be the consequence of hydrogen insertion during illumination [3] followed by extraction in the dark and which will be discussed as a function of the structure and the thickness of the titanium oxide layer.

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## 506

### Diffusion Coefficient and Electron Lifetime Measurements in Dye Sensitized Solar Cells Using Flame Spray Pyrolyzis-Made $TiO_2$ Nanoparticles

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**Gordon G Wallace,** *Intelligent Polymer Research Institute and ARC Centre of Excellence in Electromaterials Science, The University of Wollongong,, Australia*
**Wey Yang Teoh,** *ARC Centre for Functional Nanomaterials, School of Chemical Engineering and Industrial Chemistry, The University of New South W, Australia*
**Rose Amal,** *ARC Centre for Functional Nanomaterials, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales*
**Masanori Miyashita,** *Department of Fine Materials Engineering, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567 (Japan), Japan*
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Dye sensitized solar cells (DSSCs) have been fabricated using Flame Spray Pyrolysis (FSP) made $TiO_2$ nanoparticles. The particle size, surface area and anatase content was varied by controlling precisely the rate of combustion enthalpy of the flame, and characterized by HRTEM, XRD and BET measurements. Dye sensisitzed solar cells using three different powders with increasing particle size have been fabricated. Electron diffusion coefficient and electron lifetime have been determined using the Step Light Induced Measurements of Photocurrent and Photovoltage (SLIM-PCV) technique. It was found that by increasing the particle size from (12 nm to 22 nm), the electron diffusion coefficient increased and the electron lifetime decreased. This result is explained by the decreasing surface area with increasing particle size, and consequently, lower surface trap concentration and less grain boundaries. Finally, the performance of DSSCs based on FSP $TiO_2$ particles is compared to commercial P25 based devices.

## 507

### Transparent Mesoporous Nanocomposite Films for Self-Cleaning Applications

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**Isabelle Maurin,** *Laboratoire de Physique de la Matière Condensée, École Polytechnique, France*
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A versatile approach is studied for the elaboration of $TiO_2$ based photocatalytic coatings for self-cleaning applications on transparent substrates. The basic principle of the synthesis relies on the use of preformed $TiO_2$ colloidal particles that are further dispersed within a transparent silica binder with a mesoporous structure. Film porosity in the nanometer range is controlled by achieving the sol–gel silica condensation around self-organized micellar assemblies of a templating copolymer surfactant. The latter also acts as a stabilizer for the $TiO_2$ particles, thus preserving their high dispersion within the film so that excellent optical properties are maintained even for high $TiO_2$ loading (up to 50%).

The photocatalytic activity of the films was measured by monitoring the degradation of stearic acid deposited on the film under UV-A irradiation. Although the kinetics are found to follow a first order law over all the degradation curve, they exhibit a more complex behaviour, since the calculated rate constant $k_1$ values calculated for different experiments were found to decrease drastically when increasing the initial stearic acid concentration.

Studies show that such mesoporous films are at least 15 times more active than films synthesized with a microporous silica binder. Moreover, the measured quantum-yield efficiency (1.1%) is found to be among the highest reported up to now. Improved photoactivity of the films is discussed as resulting from the closer proximity between the organic molecules and the surface of the $TiO_2$ crystallites as well as the improved diffusion rate of water and oxygen through the interconnected pore network.

## 508

### Controlling Photocatalytic Activities of Titania through Surface Property Modification : from Pollutant Degradation to Hydrogen Production

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Solar energy utilization through semiconductor photocatalysis has been intensitively investigated for both environmental and energy applications. Heterogeneous photocatalytic reactions are mostly surface chemical reactions and the surface properties of the semiconductor play a critical role in determining the reaction efficiencies and mechanisms. The surface properties of $TiO_2$, the most popular semiconductor photocatalyst, are related with various parameters that include pH, surface charge, surface hydroxyl group density, particle size, crystalline phase, surface defects, surface metal (e.g., Pt, Au) deposits, and adsorbates or surface complexes. $TiO_2$ surface can be actively modified by manipulating the above parameters in order to optimize or control the photocatalytic reactions. This talk will introduce and discuss various examples that show how surface modification influences the photocatalytic activities in relation with pollutant degradation and hydrogen production. The methods of surface modification of $TiO_2$ include dye sensitization, surface platinization, surface fluorination, surfactant adsorption, and nafion coating. The effects of surface modification are widely varying depending on the method and the kind of substrates. In particular, the simultaneously platinized and fluorinated $TiO_2$ exhibited unique behaviors in anoxic degardation of organic substrates and the simultaneous degradation of organic substrates and production of hydrogen. Understanding the relation between the surface property and the photocatalytic activity is essentially required to control the activity but not much is understood awaiting more elaborate studies at the molecular level.

## 601

### Hole Transport in $TiO_2$-Adsorbed Monolayers of Organic Dyes Containing Triarylamine Moieties

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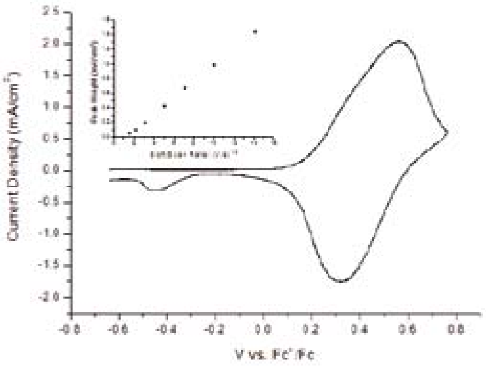
**Gerrit Boschloo,** *Uppsala University, Sweden*
**Anders Hagfeldt,** *Uppsala University, Sweden*

Certain dyes, especially those containing the triarylamine moiety, can perform hole transport via intermolecular hole hopping [see, for example, Bonhôte et al., JACS 121:1324 (1999)]. We shall report on our observations of hole transport in the triarylamine-containing organic dye D5 and a related family of dyes under development.

Calculations have shown that the positive charge in oxidized D5 resides primarily on the triarylamine moiety [Hagberg et al., Chem. Commun. 2006:2245 (2006)], and hole transport is presumed to occur between these groups. Cyclic voltammetry of D5 adsorbed to a nanostructured $TiO_2$ film shows a reversible oxidation peak near +0.45 V vs. $Fc^+/Fc$, which, since this level lies within the bandgap of the $TiO_2$, must be due to hole transport through the dye (see figure; inset shows peak current vs. square root of scan rate, indicating diffusion-like oxidation and hopping).

Hole transport in a dye is not necessarily beneficial: it can provide an additional route for recombination as holes are conducted to the collector. However, this effect appears minor in D5, which gives high efficiencies in a DSC. In any case, a $TiO_2$ blocking layer between the substrate and semiconductor film should minimize any recombination problem.

On the other hand, a hole-transporting dye opens the possibility of constructing a solid-state DSC with no additional hole transport material (HTM). Alternatively, when used in cells containing an HTM such as spiro-OMeTAD, a hole-transporting dye can alleviate problems due to incomplete HTM pore filling by shuttling holes from unfilled pores to the HTM.



## 602

### Boradiazaindacenes as a New Class of Sensitizers for Dye-Sensitized Solar Cells

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Boradiazaindacenes (a.k.a., BODIPY dyes, borondipyrrins, BDP) are well-known fluorophores with remarkable photophysical properties, i.e., high quantum yields and large extinction coefficients. In recent years, a number of research groups including ours, revealed another attractive property of these dyes, their versatile chemistry.[1-3] Thus, boradiazaindacene dyes can be modified in many ways to push the absorption wavelength beyond 600 nm, and inherent polarization in the excited state allows straight-forward functionalization for DSSC applications.

In a previous study,[4] we have also demonstrated that, with dendritic systems having peripheral boradiazaindacene units, very efficient light harvesting seems to be possible. Following a promising pilot experiment using a boradiazaindacene dye as a DSSC sensitizer, we initiated a systematic study of these dyes, trying to incorporate differentially functionalized boradiazaindacene dyes to ensure a panchromatic character. In addition, structural modifications aiming minimization of aggregation will be discussed.

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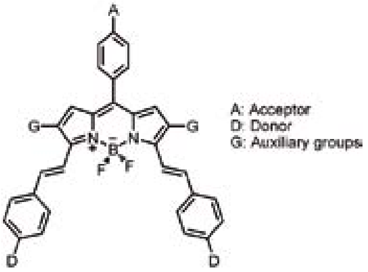

## 603

### Photoelectrochemical Characterisation of Nanostructured $NiTiO_3$ Thin Film Electrodes

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**Christopher J Fell,** *CSIRO Energy Technology, Australia*
**Sten-Eric Lindquist,** *CSIRO Energy Technology, Australia*

The yellow substance nickel titanate ($NiTiO_3$) has a bandgap around 2.2eV, making it a suitable material for photoelectrochemical (PEC) harvesting of sunlight as a future energy source. Although the PEC properties of this material were robustly investigated in the early 1980s [1, 2], such studies used flat solid films with often undefined crystallinity and porosity. The recent development of simple techniques to produce well-defined nanoporous thin film electrodes has created the opportunity to reinvestigate the nickel titanate system. Re-examining the theoretical treatment is also interesting, because the early work was based on the classical Schottky barrier junction model, which we now know is inappropriate for nanoporous materials. In this work we will examine the structure and morphology of nanostructured $NiTiO_3$ thin films using X-ray diffraction and electron spectroscopy, and use the photocurrent action spectrum as a tool to verify the zone of efficient charge separation. The results will be explained in light of more recent findings on charge transport mechanisms in porous electrodes [3-5].

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## 604

### Ionic Materials for Photoelectrochemical Solar Cells

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**Douglas R MacFarlane,** *Monash University, Australia*

There are several factors that limit the performance of the DSSC such as corrosion of the counter electrode by the iodide/triiodide redox couple, leakage of the electrolyte, and insufficient light absorption by sensitizers. The liquid electrolyte causes several technological issues such as desorption of the dye and degradation of the cell. The aim of this work is to investigate new electrolytes for dye sensitized solar cells (DSSCs). This research work concerns the preparation and characterization of organic salts which form ionic liquids and organic ionic plastic crystals.

The aim is to have better understanding of the properties of these materials in solar cell applications. Electrochemical methods such as cyclic voltammetry, microelectrode diffusion measurements and impedance spectroscopy are used to determine the electroactive window of the electrolytes and their transport properties respectively. The work also involves the construction of dye sensitized solar cells for the evaluation of these electrolytes. Transport properties of some ionic liquids and organic ionic plastic crystals have been studied. The diffusion coefficient of these ionic liquids and organic ionic plastic crystal are 2 order magnitudes lower than the liquid based electrolytes, but a high concentration of iodine can be used to overcome mass transport problems. In some cases, there have been formations of crystal at room temperature.

## 605

### Porphyrins and N-confused Porphyrins as Dopants in Organic Solar Cells

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**Paul C Dastoor,** *University of Newcastle, Australia*
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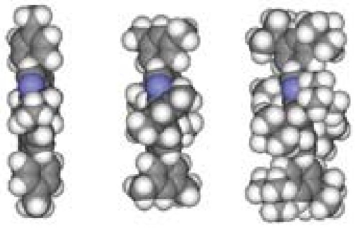
Organic photovoltaic cells show promise as a new technology for renewable energy. However one major problem with these devices is that the polymers typically employed absorb light in only a limited part of the solar spectrum (approximately 600nm and less). One way to further extend the spectral response of these devices is the addition of complimentary dye molecules. It has been shown that the absorption of light by the Q-bands of porphyrins incorporated into MEH-PPV/PCBM blends contributes to the total photocurrent generated by the device. Furthermore, N-confused porphyrins could be used to extend the absorption spectra of these devices even further, because they have Q-bands extending well beyond the region of a typical porphyrin. Despite this promise porphyrin aggregation within these ternary devices leads to disruption of the crucial morphology of the active layer and lowered device efficiency.

Porphyrin aggregation can be controlled by controlling the steric bulk of peripheral substituients. A series of tetraphenylporphyrins and N-confused tetraphenylporphyrins have been prepared in which the steric bulk of the peripheral substituents, and thus degree to which aggregation occurs, was varied. These have been used to manufacture a series of MEH-PPV/Porphyrin/PCBM ternary organic photovoltaic devices. The effect that these structural changes have on device performance will be presented.



## 606

### Exciton-Sensitized Nanostructured Solar Cells (XNSC)

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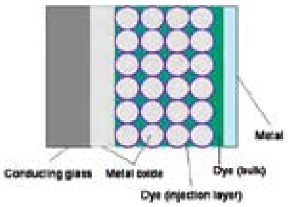
A new type of solar cell is presented that combines features of dye sensitized nanostructured solar cells and organic bulk heterojunction cells. A dye-sensitized inorganic metal oxide like TiO or ZnO serves as n-type contact while the liquid electrolyte is replaced with a p-type organic hole conducting dye. A metal film evaporated directly onto the organic dye serves as counter electrode.

Excitons created in this 'bulk' dye diffuse to the dye attached at the surface of the metal oxide where the excitation energy is trapped. After injection of an electron into the conduction band of the metal oxide the remaining hole on the injection dye is transferred to the hole conducting bulk dye layer.

Currently, suitable materials for bulk and injection dyes are investigated. Organic dyes with a triaryl moiety are expected to have good hole conducting properties. The injection dye has to be energetically matched to the bulk dye in order to collect excitons and it has to be equipped with a suitable anchoring group to the inorganic semiconductor to promote fast electron injection. The presence of an injection dye layer should improve the interpenetration between the organic and inorganic materials.

We will present preliminary results on the transport of charge carriers in the dye and metal oxide phases and the recombination of charge carriers at the interface in these new devices. The regeneration of the oxidized dye by the hole-conductor and the interpenetration of the materials will be investigated by photoinduced absorption spectroscopy (PIA).



## 607

### Study of Electron Transfer Processes in Solid State Dye-Sensitized Solar Cells by Photoinduced Absorption Spectroscopy (PIA)

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**Martin H Karlsson,** *BASF AG, Ludwigshafen, Germany*
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**Felix Eickemeyer,** *BASF AG, Ludwigshafen, Germany*
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There are many attempts to replace the liquid electrolyte in dye-sensitized solar cells (DSCs) by organic hole conductors. However, these solid state DSCs do not perform as well as their liquid equivalents due to high recombination rates and inactivity of some dye molecules because of inefficient pore filling by the hole conductor.

Photoinduced Absorption Spectroscopy (PIA) is a good tool for studying electron transfer processes in DSCs. It measures the difference in absorption of a white probe light for the on/off cases of a monochromatic pump light. This way the oxidized dye can be observed if the excited dye injects electrons into $TiO_2$ and the regeneration of dye molecules can be measured in the presence of electrolyte [1]. In addition, the kinetics of the recombination processes can be studied by time- or frequency-resolved PIA.

Here, we will present the use of PIA to study the interaction of dye-sensitized $TiO_2$ surfaces with organic hole conductors. This gives an insight on whether a given hole conductor is able to regenerate the dye and on the quality of pore filling. The PIA spectra were measured in the range from 400 to 2000 nm using two different detectors. When spiro-MeOTAD was used as hole conductor, two characteristic absorption peaks of its oxidized form could be observed when it was regenerating the dye: at 530 nm and a broad absorption centered on 1500 nm.

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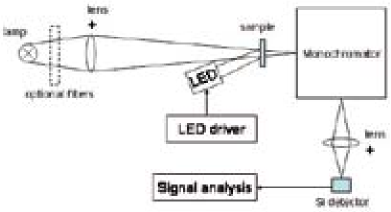

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## 608

### Effects of Anode Modification on the Improved Performance of Organic Solar Cells Based on Poly (3-hexylthiophene): Fullerene

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**Yu-Kai Han,** *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Taiwan*
**Wen-Yao Huang,** *Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
**Yun-Leong Huang,** *Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
**Shih-Chin Lin,** *Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
**I-Fan Chen,** *Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
**Ping-Tsung Huang,** *Department of Chemistry, Fu-Jen Catholic University, Taiwan*

Films fabricated from commercially available poly(3,4-ethylene dioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) aqueous dispersions have been widely used in many electronic and optoelectronic applications. We investigated that glycerol doped PEDOT:PSS (G-PEDOT) are used for polymer solar cells based on poly(3-hexylthiophene) : [6,6]-phenyl C61 butyric acid methyl ester) (P3HT:PCBM). The structure was composed of ITO/PEDOT (adding glycerol or not)/P3HT:PCBM/Al. The power conversion efficiency was 3.5% by using G-PEDOT more than 2.3% by using PEDOT:PSS. We found Jsc was increased and Voc was not changed. The absorption spectrum and energy level of HOMO were the same by UV-Vis and AC-2. In addition, the conductivity of PEDOT:PSS layer was increasing by adding glycerol. This resulted in better charge balance and better performance of polymer solar cells.

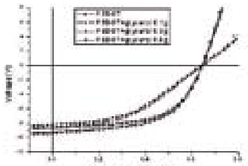

Figure 1. Measured current density-voltage (J-V) characteristics for different concentrations of glycerol added to PEDOT:PSS as an anode buffer layer for ITO/PEDOT:PSS/P3HT:PCBM/Al cells.

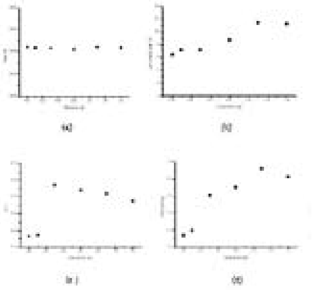

Figure 2. (a) Open-circuit voltage ($V_{oc}$), (b) short-circuit current ($J_{sc}$), (c) fill factor (FF), and (d) power conversion efficiency ($\eta_{AM}$) for different concentrations of glycerol added to PEDOT:PSS as an anode buffer layer for ITO/PEDOT:PSS/P3HT:PCBM/Al cells.

## 609

### Transient Absorption Spectrocopy of Polymer/Fullerene Films: Charge Generation and Recombination

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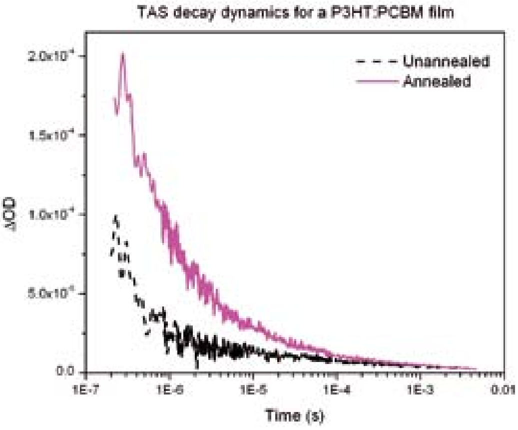
**Amy M Ballantyne,** *Imperial College London, United Kingdom*
**Jenny Nelson,** *Imperial College London, United Kingdom*

Organic solar cells formed from blends of semi-conducting polymers and substituted fullerenes are gaining considerable interest for low cost solar energy conversion. The function of these solar cells is based on a photo-induced charge separation reaction between the polymer electron donor and fullerene electron acceptor. As such, elucidating the processes of charge generation, recombination and transport in blend films is of great importance in order to improve the efficiencies of the resultant devices. Transient absorption spectroscopy (TAS) has proven useful in this regard and can monitor the formation and decay dynamics of the charged species present in films. In this work, TAS has been applied to P3HT and polythiophenes with one or more selenium heteroatoms, in blends with C60, C70 and C84 derivatives. The results show that localised ('trap') polaron states strongly influence the recombination dynamics.

Thermal annealing significantly improves P3HT:PCBM photovoltaic device efficiency, primarily through a large increase in the short circuit current (JSC). Despite the correlations observed between the enhanced JSC and the effects of annealing (such as increases in the charge carrier mobility), no consensus has been reached regarding the origin of the improved JSC. The effect of annealing is investigated using TAS on P3HT:PCBM films. It has been found that annealing produces a significant increase in the charge generation yield: this is the probable cause of the increased JSC rather than an increase in mobility.



## 610

### Fundamental Frequency Deep Level Transient Spectroscopy: Theory

**Didier Debuf,** *School of Electrical and Information Engineering, The University of Sydney, Australia*

A focus of this work is to present a defect-level measurement technique based on the multiple-level-defect analytic solution to differential rate equations [Debuf04a] representing multiple defect levels. These rate equations describe the full set of carrier transitions via the defect levels. It is shown that the new theory yields a more accurate spectroscopic method of multiple-level measurement namely Fundamental Frequency Deep Level Transient Spectroscopy (FFDLTS).

Fourier transform DLTS (FTDLTS) [Weiss88] uses Fourier transforms to decompose the multiexponential decay into a form from which the Fourier coefficients may be evaluated. The component time constants are determined from the coefficients. Laplace Deep Level Transient Spectroscopy (LDLTS) [Dobaczewski94] is a mathematical refinement over the usual Deep Level Transient Spectroscopy, giving better resolution of the spectral peaks. This method requires a calculation of the inverse Laplace transform of the capacitance transient. Both methods produce a linear Arhenius plot the slope of which represents the level depth. This plot may be represented by the linear equation y = mx + b. In the event that the intercept b should have a temperature dependence the slope m traces out a curve instead of a straight line. This temperature dependence can arise from the temperature dependence of the band gap, the effective masses, density of states and the capture cross sections. This curve may amount to a twelve percent error in the evaluation of the slope m with a further three percent from the temperature measurement. The present work addresses this issue by calculating the level depth at constant temperature using both the intercept and the slope. At constant temperature the intercept and the slope are constants.

In order to demonstrate the FFDLTS method of defect analysis the theory presented applies to the single-level-defect and may be extended to multiple levels. The form of the pulsed excitation may be a pulse of light or a voltage pulse applied to a pn junction generating excess carriers of concentration ?n(0) at t=0^+ in the conduction band.

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J. Appl. Phys.,76:194, (1994).

The Special Research Centre of Excellence for Advanced Silicon Photovoltaics and Photonics is supported by the Australian Research Council's Special Research Centres scheme.

## 611

### Study of Electro-Deposited Pt/Ni/ITO Cathode for the Efficient Dye-Sensitized Solar Cell

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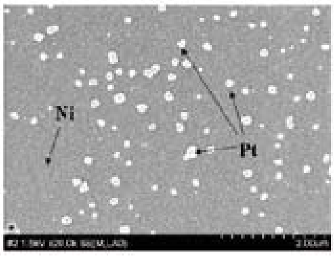
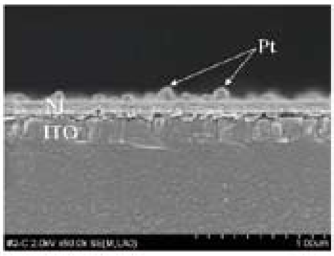
**Cham Kim,** *Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea*
**Kiseob Hwang,** *Keimyung University, Korea*
**Se Geun Lee,** *Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea*
**Sung Jun Lee,** *Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea*
**Hoyoung Kim,** *Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea*

We studied electro-deposited Pt/Ni/ITO cathode for efficient dye-sensitized solar cell (DSSC). First, we deposited metal Ni as an adhesion layer by applying electric potential to ITO substrate in the electroplating solution. Then, we deposited metal Pt on the metal Ni layer by electroplating. We found that the island type metal Pt (10 nm to 220 nm) and layer type metal Ni were deposited on the ITO substrate. The adhesion characteristics were dependent on the preparation condition of the Ni layer and the optimization were proceeded to enhance the adhesion ability between layers. As a result, we found that the short circuit current, fill factor and efficiency of DSSCs with the electro-deposited Pt/Ni/ITO cathode were much larger than those of DSSCs with thermally formed Pt cathode. The larger cell efficiency with the Pt/Ni/ITO cathode was attributed to lower charge transfer resistance and sheet resistance. We suggest that the electro-deposited Pt/Ni/ITO cathode should be suitable for the efficient DSSCs which are prepared at low temperature.





## 612

### Conductance-Voltage Properties of Silicon Quantum Dot Metal-Insulator-Semiconductor Devices Fabricated by Sputtering

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**Dirk König,** *ARC Photovoltaics Centre of Excellence, University of New South Wales, Sydney, NSW 2052, Australia., Australia*
**Ivan Perez-Wurfl,** *ARC Photovoltaics Centre of Excellence, University of New South Wales, Sydney, NSW 2052, Australia., Australia*
**Gavin Conibeer,** *ARC Photovoltaics Centre of Excellence, University of New South Wales, Australia*
**Martin A Green,** *ARC Photovoltaics Centre of Excellence, University of New South Wales, Sydney, NSW 2052, Australia., Australia*

Double-barrier structures consisting of a layer of Silicon (Si) quantum dots (QDs) embedded within a Silicon Dioxide ($SiO_2$) matrix are candidates for energy-selective contacts, which are necessary for realisation of the Hot Carrier solar cell concept. $SiO_2$/Si:QD/$SiO_2$ double barrier structures have been grown on crystalline Si (c-Si) substrates by reactive radio frequency (RF) magnetron sputtering. Subsequent deposition of top Aluminium (Al) electrodes resulted in formation of metal-insulator-semiconductor (MIS) devices, with the insulating layer of an individual device consisting of a $SiO_2$/Si:QD/$SiO_2$double-barrier structure (Si:QD-MIS devices). In order to characterise the role played by QDs in carrier transport conductance-voltage (G-V) measurements were performed on the Si:QD-MIS devices, as well as reference MIS devices devoid of QDs. Frequency-dependent conductance peaks were observed in both the Si:QD-MIS devices and the reference MIS devices. The conductance peaks are attributable to (i) the conductance of interface states at the interface of the $SiO_2$ layer and the Si substrate, and (ii) a small signal inversion layer response in the transition region between tunnel-limited and semiconductor-limited device current. Observed conductance peak dependence on the bias voltage sweep direction indicates coupling to an inversion layer external to the top Al electrodes.

## 613

### Interfacial Structure of $TiO_2$ /Dye/Hole-Conductor Interface Assembled by a Combination of High Temperature and Low Pressure

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**Erik M J Johansson,** *Department of Physics and Materials Science, Uppsala, Sweden*
**Stefan Plogmaker,** *Department of Physics and Materials Science, Uppsala, Sweden*
**Maria Hedlund,** *Department of Physics and Materials Science, Uppsala, Sweden*
**Tobias Blom,** *Department of Engineering Sciences, Uppsala, Sweden*
**Klaus Leifer,** *Department of Engineering Sciences, Uppsala, Sweden*
**Anders Sandell,** *Department of Physics and Materials Science, Upssala, Sweden*
**Hans Siegbahn,** *Department of Physics and Materials Science, Upssala, Sweden*
**Håkan Rensmo,** *Department of Engineering Sciences, Uppsala, Sweden*

Dye sensitized solar cells generally contain a dye adsorbed at a nanostructured oxide surface, a liquid electrolyte and a counter electrode. Recently also a combination with solid molecular hole-conductors, replacing the liquid phase, has shown great promise. Here we present a method for assembling such solid state devices utilizing a combination of high temperature for deposition of the hole-conductor and low pressure for improved purity. The contact between the hole-conductor and the nanostructured oxide is investigated with respect to the microscopic structure, and basic photovoltaic measurements are performed. However, the conversion efficiency also depends on energy matching and fast electron transfer between the dye and the semiconductors. This in turn depends on the detailed interfacial molecular and electronic structure of the dye at the interface. We show how X-ray based spectroscopies can be used to obtain element specific information of the interfacial structure.

## 614

### A New Series of Ruthenium Complexes Containing an Anionic Bidentate Ligand for Dye Sensitized Solar Cells

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**Masatoshi Yanagida,** *National Institute of Advanced Industrial Science and Technology (AIST), Japan*
**Nobuko Onozawa-Komatsuzaki,** *National Institute of Advanced Industrial Science and Technology (AIST), Japan*
**Yuji Kawanishi,** *National Institute of Advanced Industrial Science and Technology (AIST), Japan*
**Kazuyuki Kasuga,** *National Institute of Advanced Industrial Science and Technology (AIST), Japan*
**Hideki Sugihara,** *National Institute of Advanced Industrial Science and Technology (AIST), Japan*

Dye-sensitized solar cells (DSSCs) have been intensively investigated over the past decade. In order to improve the photovoltaic performance of DSSCs, extensive efforts have been focused on the synthesis of new highly efficient sensitizers. Among the numerous sensitizers, ruthenium polypyridine complexes have received much attention due to their superior performance in DSSCs. In this study, we have designed and synthesized a new series of ruthenium complexes, Ru(tctpy)(L1)(L2) (tctpy = 4,4',4'-tricarboxy-2,2':6',2'-terpyridine, L1 = an anionic bidentate ligand, L2 = an anionic monodentate ligand) . The Ru(tctpy)(L3)(NCS) (dye 1) shows broad metal-to-ligand charge transfer (MLCT) absorption bands in visible region, and its maximum is 515 nm (The structure of L3 will be shown in the presentation). Although, MLCT absorption maximum of dye 1 is blue shifted compared with that of black dye, the molecular extinction coefficient is increased ($\varepsilon$ = 8900 $M^{-1}$ $cm^{-1}$). The photovoltaic performances of the solar cells based on dye 1 were investigated under AM 1.5 irradiation (100 mW $cm^{-2}$). The short-circuit current density, open-circuit voltage, fill factor, and overall solar light-to-electrical conversion efficiency were 18.2 mA $cm^{-2}$, 626 mV, 0.72, and 8.2%, respectively.

*This work was supported by the Incorporated Administrative Agency New Energy and Industrial Technology Development Organization (NEDO) under Ministry of Economy, Trade and Industry (METI).

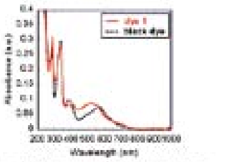

Figure 1 Absorption spectra of dye 1 and black dye in NaOH aq. [ruthenium complex] = 5 x 10⁻⁵ M.

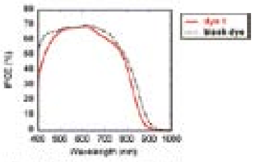

Figure 2 Photocurrent action spectra of photovoltaic devices with dye 1 and black dye.

## 615

### Self-Assembled Metalloporphyrin-Substituted Fullerene Photovoltaic Electrodes: Towards Nanostructured Organic Solar Cells

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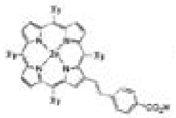
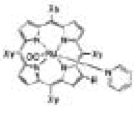
**Susan J McGinty,** *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*
**Matt Griffiths,** *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*
**David L Officer,** *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*
**Peter Innis,** *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*
**Gordon G Wallace,** *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*

The efficient light-harvesting potential of porphyrins, exemplified by their primary role in photosynthesis, makes them attractive candidates for use as photosensitizers in organic solar cells. In order to enhance the efficiency of light to electricity conversion, substituted fullerenes, which have proven efficacy as electron acceptors in organic solar cells, have been introduced into porphyrin conjugates. Previous investigations into the effect of porphyrin substitutent, functional group position, linker conjugation and binding group on porphyrin light harvesting efficiency has indicated that the β-substituted monoporphyrin carboxylic acid derivative (1) with a conjugated linker shows significant advantage over any multiporphyrin arrays[1].

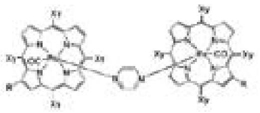
As part of our efforts to design self-assembled metalloporphyrins for use in solar cells, we have now prepared novel ruthenium(II) porphyrin-pyridyl derivatives (2), (3) and (4) as well as fullerene conjugate (5). Spectroscopic analysis and electrochemical characterisation of the conjugates indicate that they possess the desired characteristics to perform as light-harvesting materials in solar cells. The assembly of the ruthenium-porphyrin conjugates onto ITO electrodes has also been investigated.

1. Campbell, W.M.; Burrell, A.K.; Officer, D.L.; Jolley, K.W. Coordination Chemistry Reviews 2004, 248, 1363-1379.


1


2a R=H
2b R = CH=CHPhCO$_2$H


3a R=H
3b R = CH=CHPhCO$_2$H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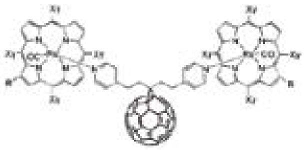
5a R=H
5b R = CH=CHPhCO$_2$H

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## 616

### A New Blocking Layer at the Transparent Conductive Oxide/ TiO$_2$ Interface for Solid Dye Sensitized Solar Cell (DSSC)

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**Shay Yahav,** *Israel*
**Zvi Pomerantz,** *Israel*
**Arie Zaban,** *Chemistry Department, Bar-Ilan University, Israel*

Direct contact between the hole transport phase and conductive substrate in DSSC causes a short circuit that significantly reduces the cell performance. It is well accepted that in order to avoid this recombination process a compact blocking layer should be deposited on the conducting substrate especially in the case of solid and quasi-solid cells. Spray pyrolysis, sputtering and chemical vapor deposition have been reported as the fabrication methods for compact layer of materials like TiO$_2$, TiO$_x$ and Nb$_2$O$_5$. However, sputtering and chemical vapor deposition require relatively expensive equipment, while spray pyrolysis requires multistage processing.

We present here a new blocking material fabricated by a different method. The new blocking layer consists of the compositional oxide TiO$_2$-Al$_2$O$_3$. The compact layer is deposited by sol-gel electrophoretic deposition (sol-gel EPD) on the conductive substrate prior to the deposition of the nanoporous film. Consequently, by a simple one step process we were able to replace resistor like J-V curves of a solid state DSSC by ones having good fill factor and open circuit voltage. We found that blocking properties can be achieved also by sol-gel EPD onto preformed TiO$_2$-mesoporous layer. Using HRSEM, X-ray photoelectron spectroscopy, cyclic voltammetry and photovoltaic characteristics of both liquid electrolyte and solid hole conductors cells we optimized the composition, thickness and sol-gel EPD conditions of the new TiO$_2$-Al$_2$O$_2$ blocking layer. In this report we will show the simplicity, flexibility and reproducibility of the new method as well as basic studies of the blocking phenomena in these materials.

## 617

### Photocurrent Limiting Factors in Pressed $TiO_2$ Dye Solar Cells

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**Gerrit Boschloo,** *Center of Molecular Devices, Department of Chemistry, Physical Chemistry, Royal Institute of Technology (KTH), Sweden*
**Anders Hagfeldt,** *Center of Molecular Devices, Department of Chemistry, Physical Chemistry, Royal Institute of Technology (KTH), Sweden*
**Peter Lund,** *Laboratory of Advanced Energy Systems, Department of Engineering Physics and Mathematics, Helsinki University of Technology, Finland*

Dye-sensitized nanostructured solar cells (DSC) is a promising new class of photovoltaic devices for the harvesting of solar energy. Besides improving cell efficiencies there is interest towards roll-to-roll production of DSCs on flexible plastic substrates. In this case, the cell preparation is restricted to relatively low temperatures, which usually leads to reduced photocurrent output. We have studied the photocurrent limiting factors of DSCs with nanostructured $TiO_2$ photoelectrodes prepared by compression technique on glass using both steady state and dynamic techniques.

A new methodology for quantitative spectral decoupling of the IPCE into the partial quantum efficiencies of light harvesting, electron injection, and electron collection is presented and demonstrated with experimental results, analyzing the data as a function of photoelectrode film thickness (d). The injection efficiency was relatively low and strongly wavelength dependent (Figure a), attributed to a poor energetic matching between the dye excited states and the $TiO_2$ acceptor states. Self-consistent estimation of the effective electron diffusion length (L) at the short circuit condition was achieved in the spectral region of constant electron generation rate. Strikingly, L was an increasing function of d (Figure b), attributed tentatively to the electron concentration dependence of L, resulting in increase of the electron collection efficiency with d.

The steady state analysis will be complemented and contrasted with results from dynamic characterization of these cells with frequency domain (EIS, IMPS, IMVS), time domain and charge extraction techniques, making remarks on the interpretation, relevance and usability of the steady state vs. transient methods.

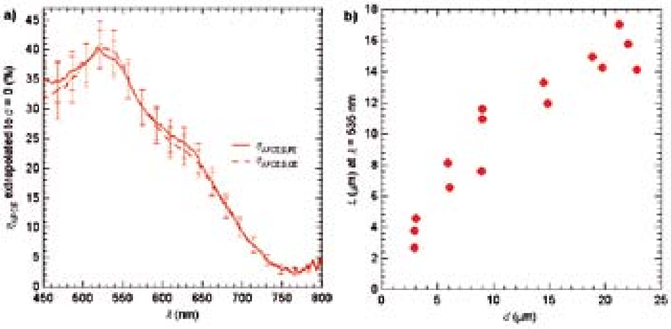

Figure: a) Wavelentgh dependence of the electron injection efficiency, b) Effective electron diffusion lenght vs. photoelectrode film thickness

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## 618

### Back Contact Dye-sensitized Solar Cells

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**Nobuhiro Fuke,** *Japan*
**Atsushi Fukui,** *Advanced Energy Technologies Laboratories, Sharp Corporation, Japan*
**Yasuo Chiba,** *Advanced Energy Technologies Laboratories, Sharp Corporation, Japan*
**Ryoichi Komiya,** *Advanced Energy Technologies Laboratories, Sharp Corporation, Japan*
**Ryosuke Yamanaka,** *Advanced Energy Technologies Laboratories, Sharp Corporation, Japan*

Since dye-sensitized solar cells was proposed by Prof. Grätzel, a lot of studies have been focused on developing new dyes, the way to prepare titanium dioxide ($TiO_2$) films and composition of electrolyte for the purpose of improving efficiency, while there is little study on modifying the structure of DSCs in contrast to Si solar cells.

In this presentation, a new structure for DSCs was investigated, as shown in figure 1, in which the transparent conducting oxide (TCO) is omitted and the back contact electrode (BCE) is located on the opposite side of the $TiO_2$ film surface to reduce the incident light loss at the front electrode. We named this structure as back contact dye-sensitized solar cells (BCDSCs), since it is similar to that of back contact silicon solar cell (BSC) 1,2). After the methods for preparing the BCE was investigated, a BCDSC with conversion efficiency of 8.07% were achieved (Figure 2), although the photovoltaic layer was composed of polycrystalline TiO2 nano particles. The mechanism was also studied in comparison with BSC.

1) W. P. Mulligan, D. H. Rose, M. J. Cudzinovic, D. M. De Ceuster, K. R. McIntosh, D. D. Smith, and R. M. Swanson: Sunpower Corporation Tech. Rep. June (2004) P1.
2) K. Nakamura, T. Isaka, Y. Funakoshi, Y. Tonomura, T. Machida, and K. Okamoto: SHARP Tech. Rep. ED93 (1993) 11.

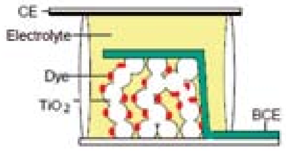

Figure 1: Sketch of dye-sensitized solar cell.

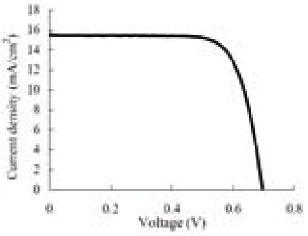

Figure 2: Current-voltage characteristics of the BCDSC. Results were measured at 25 °C with an aperture area of 0.221 cm$^2$ using a black metal mask and irradiance of 100.0 mW/cm$^2$. Short circuit current density $J_{sc}$ = 15.5 mA/cm$^2$, open circuit voltage $V_{oc}$ = 0.697V, fill factor FF = 0.747 and overall conversion efficiency = 8.07%.

## 619

## Efficient P3HT:PCBM-Based Polymer Solar Cells Fabricated with One Dimensional Acid-Doped Polyaniline Nanotubes

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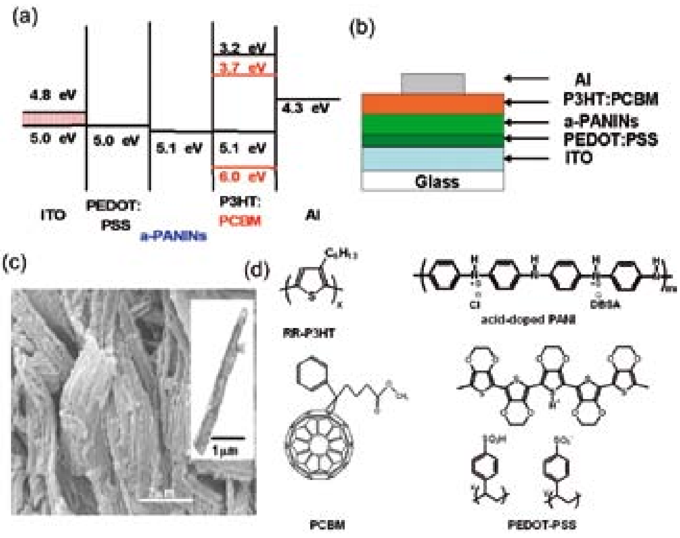
**Wen-Yao Huang,** *Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
**I-Feng Chen,** *Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
**Ko-Shan Ho,** *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Taiwan*
**Tar-Hwa Hsieh,** *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Taiwan*
**Yu-Kai Han,** *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Taiwan*
**Ping-Tsung Huang,** *Department of Chemistry, Fu-Jen Catholic University, Taiwan*
**Bi-Zen Hsieh,** *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Taiwan*

In this report, acid-doped polyaniline nanotubes (a-PANINs) were synthesized, and acted as an interfacial layer in P3HT:PCBM-based polymer bulk heterojunction solar cells to collect holes efficiently from the active layer and transport them to the buffer layer under the internal electric field of the fabricated ITO/buffer/ a-PANINs/ P3HT:PCBM/Al device. The sub-micron scale of the a-PANIN surface fits into the P3HT/PCBM domain and provides a well-defined contact for the transport of free charge carriers. Generally, a-PANINs provide a high-contact surface area between the interfaces and efficient pathways for the transportation of free charge carriers toward electrodes, thus reducing charge-carrier recombination within the photoactive cell. Polymer solar-cell devices based on poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) were fabricated with a one-dimensional (1-D) nanostructure of acid-doped polyaniline nanotubes (a-PANINs) as an interfacial layer. The power conversion efficiency (PCE) of the annealed device fabricated with an a-PANINs layer shows about 35% increase, up to 2.7% under AM 1.5 G (100 mW/cm$^2$) illumination, when compared with the annealed device without an a-PANIN interfacial layer. Here the a-PANINs were incorporated in solution-processed (spum from o-xylene solution) polymer solar cells, yielding reproducible and controlled a-PANIN nanoscale morphology, which gave better hole-transporting pathways to the anode while maximizing the surface area for the collection of holes and the suppression of exciton recombination, thereby improving the photovoltaic performance.

| Device Type | Voc(V) | Jsc(mA/cm2) | FF(a.u.) | PCE (%) |
|---|---|---|---|---|
| A | 0.48 | 5.53 | 0.47 | 1.2 |
| B | 0.52 | 6.67 | 0.41 | 1.4 |
| C | 0.58 | 7.7 | 0.48 | 2.0 |
| D | 0.62 | 8.37 | 0.51 | 2.7 |



## 620

## High Efficiency Dye-Sensitized Solar Cells by Metal-Free Organic Dye and Perpendicular ZnO Nanosheet Thick Film

**Eiji Hosono,** *Nano-Energy Materials Group, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Techno, Japan*
**Yosuke Mitsui,** *Tokyo University of Science, Japan*
**Haoshen Zhou,** *Nano-Energy Materials Group, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Techno, Japan*

ZnO has attracted attention as a fascinating alternative to TiO2 in DSC because ZnO and TiO2 exhibit the similar level of the lowest conduction band and electron injection process from excited dyes in DSC. Moreover, the carrier lifetime in ZnO is significantly longer. However, the studies of high efficiency DSC using ZnO with exception of basic study have been very few because the conversion efficiency of around 2 % is much lower than that using TiO2.

Recently we reported the high efficiency DSC of around 4%[1] using ZnO and N-719 dyes. The nanostructure control of the ZnO electrode was very critical in order to obtain the high efficiency solar cells.

Moreover, in the development of DSC, the works of metal-free dyes are important in addition to the study of high efficiency solar cells. The general dyes for high efficiency cells are Ru complex dyes such as N3 and N-719. The ruthenium metal, which is rare metal, is high cost and a few in the earth.

In this work, we repot the high efficient DSC using metal-free organic dyes (D149) and nanostructured ZnO electrodes. The efficiency of 4.27% is larger than that of around 4% by the DSC using ZnO and N-719. The result, which indicates that the efficiency of DSC using organic dyes is larger than that using ruthenium dyes, is very important for the study of DSC.

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[1] E. Hosono, et al., Adv. Mater., 17, 209 (2005). J. Photochem. Photobiol. A: Chem., 179, 81 (2006).

## 621

## C60 Clusters to Improve the Efficiency of a Dye-Sensitized Solar Cell

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The redox couple that has been found to be most effective for the regeneration of the sensitizer (dye) in dye-sensitized solar cells is the iodide/iodine couple. The iodide ions donate electrons to the oxidized sensitizer, thereby minimizing the loss of electrons in charge recombination. However, the presence of high concentrations of iodide and iodine increases the probability of their interaction with the excited state of the sensitizer. Thus, ways to minimize the excite-state interaction with the redox couple is important in order to maximize the photoconversion efficiency of a dye-sensitized solar cell.

To this end, we have employed C60 clusters to separate the sensitizer, a Ru(II) complex, and the redox couple to minimize the excited sensitizer-redox couple interactions. It has been observed that the cells with C60 clusters delivered a much higher photocurrent than those without them. C60 clusters, incorporated between the dye and redox couple, shield the dye and, at the same time, act as electron relay to regenerate the dye. The advantage of C60 clusters in diminishing the interaction between excited dye and redox couple is also observed in the suppression of luminescence quenching of the excited dye by iodine following the deposition of a layer of C60 clusters. Various other photochemical and photoelectorochemical properties will also be discussed.

## 622

### Photovoltaic Properties of Nanostructured $TiO_2$ Subjected to Isostatic High Pressure

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The photovoltaic (PV) solar cells consisting of titania thin films sandwiched between a transparent indium-tin-oxide (ITO) conductor and reflecting silver metallic film were studied. The synthesis of nanocrystalline $TiO_2$ and ITO powders are presented. The thin films of $TiO_2$ and ITO were deposited by spin-coating method and densified by applied isostatic pressure. The PV properties of such fabricated heterojunctions were investigated.

## 623

### The Electron Transport Characteristics in Dye-Sensitized Solar Cells with Different Nanoporous Films

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The high light-to-energy conversion efficiencies achieved with dye-sensitized solar cells (DSC) may be attributed to the nanoporous $TiO_2$ electrodes. Until now, the electron transport characteristic in DSC is still not clear, and it is very important to understand how electrons transport in DSC, which will help us to understand the mechanism and optimization of DSC. Intensity modulated photocurrent spectroscopy (IMPS) has been used to obtain values of the electron diffusion coefficient (Dn). Intensity-modulated photovoltage spectroscopy (IMVS) is shown to be valuable in elucidating the contributions of band edge shift and recombination kinetics.

In the present work, the electron transport characteristic was discussed by investigating the change of the absorption coefficient, electron diffusion coefficient and electron lifetime in DSC. Nanoporous films are prepared from two different sized $TiO_2$ nanoparticles, and DSC is prepared from these films with different thickness. The results show that the Dn increases at first, with the increase of films thickness, but Dn decrease in the range of 12 to 22 µm. Results also indicate that the electron lifetime (τn) increase with the increase of films thickness in the range of 5 to 22 µm. The increase of the Dn is interpreted with the density increase of photogenerated electrons, and then the decrease of Dn is considered as the combination in thicker films, where the more charge trap sites and grain boundary are likely to exist. The decrease of τn is discussed with the change of absorbance coefficient (α) and Dn with the films thickness.

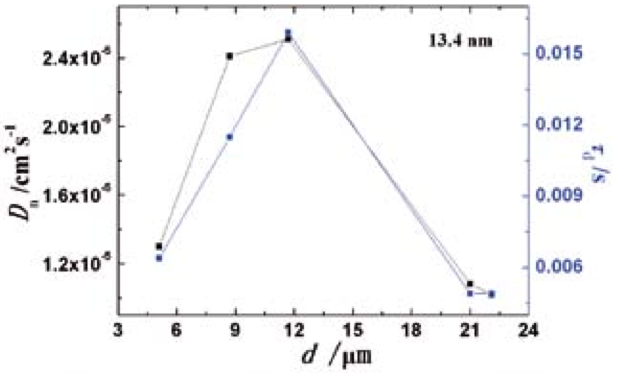

**Figure 1 Influence of films thickness on the electron diffusion coefficient and electron transit time of DSC.**

## 624

### Modification of ZnO Nanorods for Dye-Sensitized Solar Cell Application

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In the last decade, a large research effort has been devoted to the development and optimization of Dye-Sensitized Solar Cell (DSSC) as a potential alternative for the traditional Si solar cell due to its low cost and easy fabrication. For commercial purpose, the flexible DSSC with plastic substrate has attracted great interest. As the main part of the DSSC, the working electrode, on which most of the research is based on $TiO_2$, has been well studied to improve the overall efficiency. However, the sintering of $TiO_2$, requires high temperature (around 450°C), such temperatures would damage plastic substrates. Alternatively, well crystallized ZnO nanorods can be synthesized via a low temperature hydrothermal process. In addition, the ordered 1D crystallite is favourable for collection of electrons. However, the low surface area limits the performance of the DSSC due to the low adsorption of dye.

Here we employed different processes to modify the surface properties and morphology of the ZnO nanorods, with an aim to increase the surface area of the electrode and hence the overall efficiency of the ZnO based DSSC. For example, coated ZnO nanorods and branched ZnO nanorods were synthesized. The materials were characterized via X-ray diffraction to check the crystals structure. Electron microscopy was applied to investigate the surface morphology. Gas sorption was used to measure the surface area along with the dye sorption test. Finally, the materials were assembled in DSSC to compare their performance, which was correlated with the surface properties of the ZnO nanorods.

## 625

### Tin Quantum Dot Materials for Third Generation Photovoltaics: Optical Properties

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**Gavin Conibeer,** *University of New South Wales, Australia*
**Y Huang,** *ARC Photovoltaics Centre of Excellence, University of New South Wales, Australia*
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Objective

The tandem cell is one of the most promising approaches to breakthrough the conventional efficiency limit of photovoltaic cells [1]. In a tandem device, each cell has a different bandgap, and absorbs and converts a different part of the solar spectrum, more efficiently. Our group concentrates on all-silicon tandem cell based on engineering wider band gap materials using quantum confinement in Si nanocrystals. Recently we have extended this work to tin (Sn) because of the possibilities of low process temperatures and greater bandgap flexibility. This work aims to make Sn-based QD materials with controlled energy bandgap and to study the optical properties.

Experimental methods

The Sn-rich precursor layers were prepared by magnetron co-sputtering of Sn and dielectric materials such as $SiO_2$ and were subsequently annealed in a vacuum chamber to precipitate Sn nanocrystals embedded in a matrix [2]. Sn QDs with very uniform size were fabricated by depositing multilayer structures of alternating Sn-rich $SiO_2$ layer and $SiO_2$ layer and then annealing at relatively low temperatures. We studied the optical absorption and photoluminescence (PL) of the Sn QD materials.

Results and conclusion

The formation of Sn nanocrystals with low temperature annealing at 400~600°C was confirmed by TEM and XRD [2]. Sn oxide nanoclusters 2.5-5.0 nm in diameter were also observed by TEM. Sn-based films showed wide optical bandgap of about 4.2 eV, believed to be dominated by Sn oxide nanoclusters and oxygen-related defects formed in $SiO_2$ matrix. In addition, the Sn QD samples showed strong violet PL at ~3.2 eV at room temperature. The detailed optical studies on the Sn-based QD samples will be presented and discussed.

[1] M.A. Green, Third Generation Photovoltaics, Springer, 2003.
[2] S. Hunag, et al. *J.* Appl. Phys. 102, 114304 (2007).

## 626

### Electro-Optical Property of Novel Discotic Liquid Crystals and Poly (acrylamide) Cross-Linking Compounds within Organic Solar Cells

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Two discoltic-like and self-assembly organic materials are synthesized successfully. One is discotic liquid crystal (DLC; Acid-6) monomer and the other is novel discotic liquid crystal polymer (DLC-PAM). The molecular structures of DLC monomer Acid-6 and DLC-PAM are identified by FT-MS, 1H-NMR and FT-IR DLC-PAM is a side-chain liquid crystal polymer with polyacrylamide (PAM) as main chain and grafting the DLC monomer Acid-6 onto PAM as side chain; therefore, the physical properties of DLC-PAM are not only plastic like but also have DLC function. UV-Vis absorption spectra show that absorption bands are located between 200 ~ 450 nm for both compounds, suitable to be a photo-sensitized dye. X-ray diffraction study demonstrates that DLC-PAM and Acid-6 possess hexagonal columnar structure because their reciprocal spacings follow the ratio $1:\sqrt{3}:\sqrt{4}$. Self-assemble to hexagonal columnar makes better carrier mobility. Two kinds of dye-sensitized solar cell (DSSC) devices are fabricated with both materials as photosensitive dyes. Through qualitative and optical analysis, it shows that the device performance of the DLC-PAM and Acid-6 used as photo-sensitized dyes within DSSCs are relatively good and power conversion efficiency of 0.28 % and 2.2 % are achieved, respectively. This proved that both DLC and DLC polymeric compounds have potential to be used as photo-sensitized dyes.

## 627

### Nanocrystalline $TiO_2$ Films Deposited via Rapid Expansion Supercritical Solution for Dye-Sensitized Solar Cells

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Sol-gel method is a way to obtains broad scale processing of nanostructure materials. This study utilized five different sol-gels with adjust various pH values and post-sintering conditions to derive the formation of nano-titania particles. It is successfully to control particle size and phase under mulit parameters. Amorphous titania was obtained at low post-sintering temperatures about 300°C, Mixtures of anatase and rutile phase titania were observed at intermediate temperatures of 350 ~ 600°C, Escalate temperature until 800°C, There are 100% rutile titania was obtained. The phase formations of transfigurations have been proved via multi parameters by XRD. Particle morphology, size and agglomeration are observed by TEM. Within different pH values, the sizes of titania particles varied from 20 to 100 nm. Depending process conditions can be effect nano-titania size directly. Achieve to increase contact area or porous structure. The rapid expansion supercritical solution (RESS) method has been applied to deposit dense (30 nm thick) and porous nano-crystalline $TiO_2$ (5–20 μm thick) layers incorporated in dye-sensitized solar cells (DSSCs). The DSSCs fabricated with the $TiO_2$ layers deposited by RESS method on ITO glass showed a power conversion efficiency of 4.3% under an illumination of 10 $mW/cm^2$.

## 628

### Structure Design and Measurement of Dye-Sensitized Solar Cell Modules

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**Jian Weng,** *Division of Solar Energy Materials and Engineering, Institute of Plasma Physics, Chinese Academy of Sciences, China*
**Yifeng Sui,** *Division of Solar Energy Materials and Engineering, Institute of Plasma Physics, Chinese Academy of Sciences, China*
**Shangfeng Xiao,** *Division of Solar Energy Materials and Engineering, Institute of Plasma Physics, Chinese Academy of Sciences, China*
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New photoelectric conversion efficiency record up to 11.18% was achieved, which showed a very exciting result for future large-scale dye-sensitized solar cells (DSC). In the present work, DSC was fabricated with the purpose of decreasing the electron loss resulted by square resistance and increasing electron collection. Two single cells (active area 11cm2) parallel connection was designed with the width and length of 0.5 cm, 11 cm respectively. The photoelectric conversion efficiency of the solar cells were greatly improved after the structural optimization. And then, DSC (15 cm × 20 cm) was investigated under parallel connection. At the same time, the total output power and the shape of single cell under various widths and Jsc were simulated and calculated based on theoretic model. The optimizing width is 6-7mm for world-class DSC (22 mA/cm2), 8 mm for standard DSC (16 mA/cm2), and 10 mm for mediocre DSC (10 mA/cm2).

The characteristic of large-scale DSC under different testing condition was also investigated. The results indicated that testing conditions, such as spectrum conditions of light source, testing interval, temperature and light intensity have obvious effects on DSC photovoltaic performance. The most suitable measurement conditions for DSC were discussed ultimately.

## 629

### A Novel Boron-Dipyrrin Dye for Dye Sensitized Solar Cell Applications

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Boron-dipyrrin, BDP, derivatives have been synthesized and studied as chemosensors in fluorescence emissions for their resonance energy transfer properties by Akkaya group1,2. We now report a novel boron-dipyrrin derivatives of BDP-phenyl-ethenyl(triphenylamine), BDP-PETA, and BDP-cyanocarboxylethenylphenyl-ethenyl(triphenylamine), BDP-CCPETA, as sensitizers in Graetzel type dye sensitized solar cells-DSSC.3,4 HOMO and LUMO energy levels of BDP-PETA, EHOMO= 5.43 eV, ELUMO= 3.59 eV, indicates that these molecular structures are suitable for efficient photo-electron transfer in DSSC via nanostructured titania thin films. BDP-PETA presented Isc [mA/cm2] = 2.0, Voc [mV] = 500, Efficiency [%] = 0,78, and BDP-CCPETA Isc [mA/cm2] = 4.0, Voc [mV] = 562, Efficiency [%] = 1.66. Cyano carboxyl group appear to improve the efficiency of photo-electron transfer from dye to porous TiO2, by improved surface interactions.

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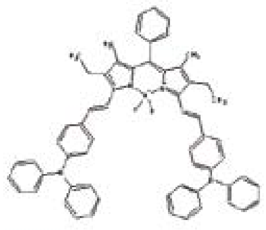
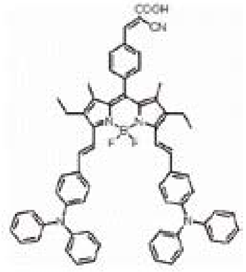
2 – A. Coskun, M. D. Yilmaz, E. U. Akkaya, Organic Letters 9 (2007) 607.
3 – B. O'Regan, M. Graetzel, Nature, 353 (1991) 737.
4 – C. Zafer, M. Kus, G. Turkmen, H. Dincalp, S. Demic, B. Kuban, Y. Teoman, S. Icli, Solar Energy Materials and Solar Cells, 91(2007) 427.



BDP-PETA



BDP-CCPETA

## 630

### Enhancement of Open-Circuit-Voltage of Dye-Sensitized Solar Cells by Using Organic Dye Sensitizers and TiO$_2$ and ZnO Electrodes Doped with Mg

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Dye-sensitized solar cells (DSSCs) are potential photovoltaic devices with high efficiency, which can be fabricated with low costs. As the electrodes of DSSCs, TiO$_2$ and ZnO are usually used. In this study, addition of Mg to TiO$_2$ and ZnO electrodes were examined to improve the open-circuit-voltage (V$_{oc}$).

Mg-doped titanias with the anatase structure (Mg(x)-TiO$_2$, where x is Mg/Ti charged ratio) were prepared by the thermal reaction of mixtures of titanium tetraisopropoxide and magnesium acetate tetrahydrate in 1,4-butanediol. XRD, XPS, and XANES analyses indicated that Mg$^{2+}$ ions were incorporated in the anatase structure for the products of $x \le 0.2$.

As the amount of Mg added increased, the absorption edges of the products were gradually shifted to the lower wavelength side, indicating the increase in the band gap energy. The flat band potentials of Mg(x)-TiO$_2$ electrodes estimated from the Mott-Schottky analysis were shifted to the negative potential side by Mg-modification; for instance, -0.73, -0.91, and -1.00 V (vs. Ag/AgCl), for the non-modified TiO$_2$, Mg(0.1)-TiO$_2$, and Mg(0.2)-TiO$_2$, respectively.

In Figure 1, photovoltaic properties of DSSCs using Mg(x)-TiO$_2$ electrodes are shown. Using Mg(x)-TiO$_2$ electrodes, higher Voc values were obtained. Especially, quite a high V$_{oc}$, 0.99 V, was obtained with an acrylic acid organic dye (NKY-003) having a higher LUMO level than N719.

Mg-doped zinc oxides were synthesized by thermal reaction of zinc acetate dehydrate and magnesium acetate tetrahydrate in 1,4-butanediol, and the products were characterized by several methods. An increase in V$_{oc}$ using the Mg-doped ZnO electrodes was also observed.

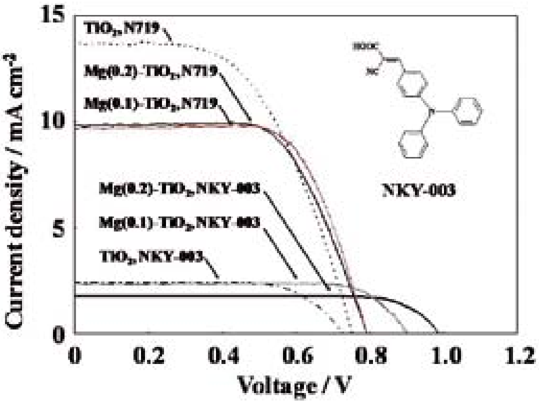

Figure 1. *I-V* curves of DSSCs using Mg(x)-TiO$_2$ electrodes.

## 631

### Characterisation of Dye-Sensitised $TiO_2$ Nanotube Based Solar Cells

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**Laurence M Peter,** *University of Bath, United Kingdom*
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**Patrick Schmuki,** *University of Erlangen-Nuremberg, Germany*

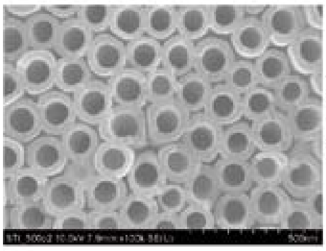
Dye-sensitised solar cells based on $TiO_2$ nanotubes have been extensively characterised using a range of steady-state, time- and frequency-resolved techniques. In most cases the results can be explained fully in terms of models previously developed for dye-sensitised solar cells based on nano-particulate $TiO_2$ layers.[1]

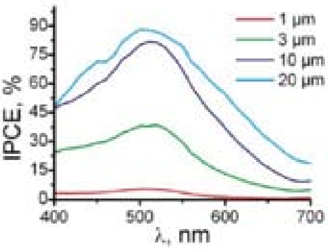
$TiO_2$ nanotubes were grown by anodisation of Ti foil in fluoride containing electrolytes. The use of a Ti substrate naturally leads to a crack-free layer of compact $TiO_2$ at the base of the nanotubes which completely eliminates shunting via the substrate, this leads to improved efficiency under low-light conditions and simplifies analysis of kinetic data.

The effect of changing parameters such as tube length, wall thickness and crystallinity have been investigated and correlated with the kinetic characteristics of the cells as well as with overall power conversion efficiencies. Perhaps surprisingly it is found that neither transport nor recombination properties are markedly affected on changing from a nano-particulate to a nano-tubular morphology.

The most striking difference between nanotube and nanoparticle based cells is the highly non-ideal variation of steady-state photovoltage with incident light intensity in the case of nanotube based cells. Attempts at controlled surface modification are being made in order to establish the origin of the non-ideal steady-state photovoltage response to variation in incident light intensity.

[1] L. M. Peter, J. Phys. Chem. C, 111, 6601-6612, 2007





## 632

### Electrospun $TiO_2$ Nanorod Based Dye-Sensitized Solar Cells with High Efficiency

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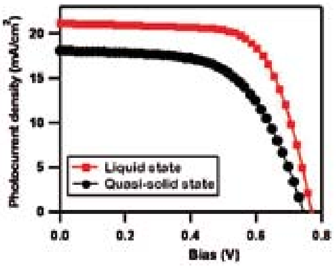
**Sung-Yeon Jang,** *Korea Institute of Science and Technology, Korea*

Dye-sensitized solar cells are one of the promising candidates for the next generation of solar cells because of their simple structure with relatively high conversion efficiencies. For a high performance DSSC requires highly nanocrystalline $TiO_2$ electrode with large surface areas and the electrolyte penetrates the porous film all the way to the back-contact. Therefore, we have introduced the electrospinng technique. $TiO_2$ fibers were electrospun directly onto FTO glass substrate from the mixed solution containing poly(vinyl acetate) and titanium(IV) n- propoxide with acetic acid as a catalyst for sol-gel reaction in DMF. To fabricate the electrode used in the DSSC, the electrospun $TiO_2$ web is pressed directly between preheated plates at a temperature, 120°C. It have made one dimentional highly nanocrystalline $TiO_2$ nanorod electrode with lengths of 60-100nm and diameter of 15nm. The detailed morphology was observed by the field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microcopy (HR-TEM). The calcined nanorods were fully crystalline with the anatase (101) crystal plane comprising most of the surface. The electrospun nanorod film contains about 23% more absorbed dye molecule and 40% more porosity than nanoparticle film. As a result, DSSCs based on liquid electrolytes, the energy conversion efficiency of 11.1% has been achieved. Also the porous structure of the electrospun $TiO_2$ nanorod-based DSSCs was found to be efficiently penetrated by a viscous PVDF based quasi-solid state electrolyte, the energy efficiency obtained 8.03%.

| | Liquid Electrolyte | Quas-isolid electrolyte |
|---|---|---|
| Voc | 0.770 | 0.744 |
| Jsc(mA/cm2) | 21.07 | 18.11 |
| FF(%) | 68.4 | 59.58 |
| EFF(%) | 11.09 | 8.03 |



## 633

### Dye-sensitized Solar Cells Employing Polymer-Gel Electrolytes and Novel Pt-Counter Electrodes

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Dye-sensitized solar cell (DSC) has attracted great attention over the past decade owing to its high energy conversion efficiency and low production cost. However, the leakage of liquid solvent from such cells has been suggested as the one of the critical factors limiting the long-term stability of DSC. Therefore, one of the most significant issues in developing DSCs is the use of non-volatile electrolytes, which have high ion conductivity at ambient temperature and excellent long-term stability. In this work, quasi-solid state DSCs employing ternary component polymer-gel electrolytes have been prepared. We have focused on the development of polymer-based gel electrolytes with high ion mobility. The polymer-gel electrolytes were designed to facilitate ion transport in the highly viscous medium and to utilize incident light more effectively in the cell. We have employed non-volatile solvents of multiple molecular size distributions and nanofillers to prepare the polymer-gel electrolytes. In addition, novel Pt-counter electrodes prepared by self-assembly technique have been employed in this study. The counter electrodes were prepared by spin-coating the mixture solution consisting of hexachloroplatinic acid ($H_2PtCl_6$), non-ionic surfactant, and inorganic oxide precursor on transparent conductive oxide (TCO) substrates and successive sintering. The result shows that the photovoltaic performances of the DSCs are enhanced by employing the new Pt-counter electrodes mostly due to the increase in the photocurrent. The enhanced photon-to-electricity conversion efficiency of the DSCs would be associated with the increase in the surface area of Pt layer on TCO substrate. More detailed results will be discussed in the meeting.

## 634

### Nanorod and Nanotube-Based Dye-Sensitized Solar Cells

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**Yu-Kyung Kim,** *Seoul National University, Korea*
**Jae-Yup Kim,** *Seoul National University, Korea*

Nanoparticles and nanostructures could be applicable to photoelectrochemical devices, such as, solar cells and photoelectrochromic devices, and so on. Dye sensitized solar cells (DSSCs) have attracted considerable attention after a breakthrough, the introduction of anode electrode composed of nanoporous and interconnected $TiO_2$ nanoparticles as an electron conductor. In this presentation, we will report design and synthesis of nanotubes and nanorods for the application in DSSC by various techniques including co-sputtering.

In addition, for the high conversion efficiency of DSSCs based on the glass-based cells, followed by high temperature sintering process, the insufficient electron diffusion coefficient in traditional electrodes composed of nano-sized $TiO_2$ particles (e.g. several orders of magnitude smaller than those in bulk single crystal $TiO_2$) should be recovered due to the limitation of the photon-to-electricity conversion efficiency. This point has promoted research toward photoanode comprised of various shaped nanoporous materials, in particular, nanotubes and nanorods. Nanorod based $TiO_2$ films were prepared using chemical-based synthesis based on oriented attachment. Synthesis and characteristics of anatase $TiO_2$ nanoparticle and nanorod will be presented. Furthermore, properties of electron transport and charge recombination of the electrons in the nanorod based $TiO_2$ film will be also discussed and compared with other nanostrucutres in the conference.

## 635

### The Growth of Porous $TiO_2$ Film Using RF Magnetron Sputtering Technique and the Application for Photoelectrochemical Device

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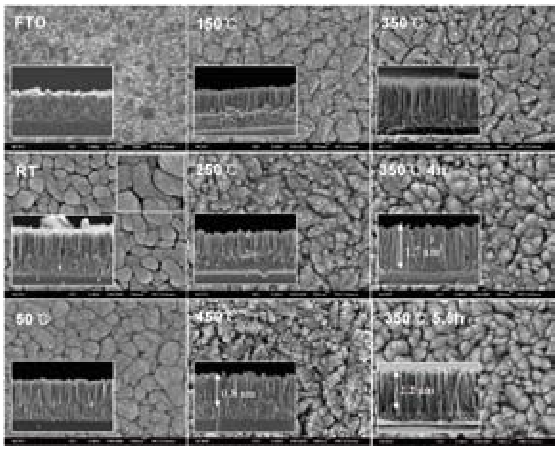
**Jae-Yup Kim,** *Seoul National University, Korea*
**Hyun-Sik Kim,** *Seoul National University, Korea*
**Yung-Eun Sung,** *Seoul National University, Korea*

Titanium dioxide, $TiO_2$, have been widely studied because of attractive advantages, such as nontoxic, cheap, and various applications which are photoelectrochemical solar cells, photocatalyst, and photoelectrochemical splitting of water.1 Especially, the nanoporous $TiO_2$ film was pursued to improve the solar to electricity power conversion efficiency because of its high surface area. For the increase of the specific surface area and film porosity, we try to grow the columnar structured $TiO_2$ film by changing the substrate temperature (Tsub) during 2h. As the Tsub is increased, the specific surface area and porosity of $TiO_2$ thin film are also increased, confirmed by the measurement of refractive index. Meanwhile, the high Tsub (> 350°C) provides the driving force to predominantly form the $TiO_2$ rutile phase, following the abruptly degraded conversion efficiency. Furthermore, as the Tsub is increased, the light absorption of $TiO_2$ film is extended to visible light wavelength, resulted from the formation of rutile phase and various defect states grown in the pure Ar ambient. Above results were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) etc. Furthermore, grown $TiO_2$ film at T350°C showed the high efficiency (1.68%), even though the slightly thin film (~ 800 nm). Then, at this condition, as the thickness of $TiO_2$ film is increased by the increase of sputtering time, the maximum efficiency was achieved at approximately 2.74% with the 2.2µm thickness. Figure 1 shows grown $TiO_2$ morphology by sputtering method, depending on the Tsub and growth time. Added results and discussion will be presented.



## 636

### Study on the System of Mass-Produce for Flexible Dye-sensitized Solar Cell

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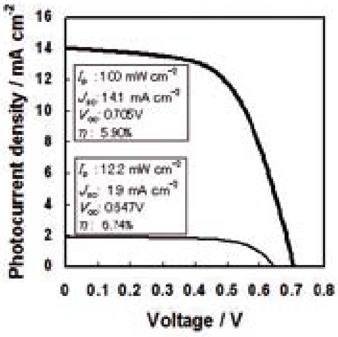
Dye-sensitized Solar Cell (DSC) is one of the next new energy resources, as is well known. The list of those advantages goes on and on; low cost productivity (short pay-back time), colorful design, free module types, possibility of gigantic cells and so on. The great-granddaddy of them all is ease of 'Flexible Cell' which many researchers have been researching since it was clarified by some revolutionary works that the strong flexible $TiO_2$ electrode on the plastic conductive substrate could be available to be made at room temperature without other additive components such as polymer or oligomer.

Peccell Technologies has been devoting our energy to produce the practical flexible DSC for several years. PECC series is one of the best pastes to generate the good $TiO_2$ mesoporous electrode at low temperature, having well adherence property to the substrate, high efficiency (η≈6%). The transparent conductive film (with Fujimori Kogyo Co., Ltd.) has low electric resistivity (< 1Ω/□) and high transparency (> 70%). Also the electrolyte, the sealant and the counter electrode have been developed for the good flexible DSC. However those ingredients especially the $TiO_2$ paste and the conductive films were made by small lot size, and then there were limited numbers of the cell made continuously or in large quantities. We have succeeded in gain how to make the reliable materials, the $TiO_2$ paste, the substrate and the others, so eventually the mass-production is available with some general machines at lower-cost energy.



**Flexible Cell (small size) I-V curve**

**6 (4 series) Flexible Cells**

## 637

### Photoanode Modification in a Dye-Sensitized Solar Cell Using Cr-Doped $TiO_2$

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**Se Geun Lee,** *Daegu Gyeongbuk Institute of Science and Technology (DGIST), Korea*
**Sung Jun Lee,** *Daegu Gyeongbuk Institute of Science and Technology (DGIST), Korea*
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A dye-sensitized solar cell (DSSC) is mainly composed of a dye-adsorbed semiconductor (photoanode), an electrolyte, and a counter electrode. When incident light is illuminated, excited electrons from the dye are injected into the semiconductor. The electrons migrate through the semiconductor and attain to an external circuit. However, charge recombination can occur in the semiconductor layer, and it leads to efficiency diminution of a DSSC. Therefore, various investigations have been reported on modification of the semiconductor to minimize charge recombination.

Meanwhile, we tried to modify a $TiO_2$ electrode with a metal-doped $TiO_2$. Pure $TiO_2$ generally known as an n-type semiconductor was gained via hydrothermal process. In addition, we prepared 0.25 mol% Cr-doped $TiO_2$ via similar procedure to the $TiO_2$ synthesis above. The resulting $TiO_2$s were sequentially deposited on a FTO (F-doped tin oxide) substrate by using a polymer binder and calcined at 500°C for 30 min.

According to I-V measurement (Fig. 1), the double-layered electrode worked as a species of diode, thus we confirmed that Cr-doped $TiO_2$ became a p-type semiconductor and a p-n homojunction was successfully formed at the interface of the $TiO_2$ layers. This p-n homojunction was expected not only to enhance charge transport but to also repress charge recombination since electrons would be forced to transfer to the direction in accordance with electric field appearing in the junction. Consequently, the DSSC adopting this p-n homojunction as a photoanode exhibited improved overall conversion efficiency by ca. 18 % with respect to that employing pure $TiO_2$.

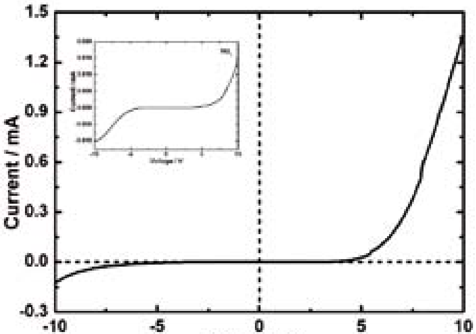

**Fig. 1.** ***I-V* characteristic of the double-layered and pure TiO2 electrode (inlet).**

## 638

### Interfacial Layer by Self-Assembly for High Efficiency Dye-Sensitized Solar Cells

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$SnO_2$, $TiO_2$ and $ZrO_2$ nanoparticles were synthesized by a solvothermal reaction, and applied to the fabrication of interfacial layers between transparent conducting electrode and nanocrystalline $TiO_2$ layer in Dye-Sensitized Solar Cells. The size of the synthesized nanoparticles was determined to 2.5 - 4.5 nm by TEM and XRD. The thickness of each interfacial layer was controlled layer-by-layer by the self-assembly of those nanoparticles. Then, the main $TiO_2$ layer with a thickness of 10 µm was formed by doctor-blade method. These coupled systems demonstrated higher photovoltaic conversion dfficiency of the dye-sensitized solar cells than the conventional system without thin interfacial layer. Especially, $SnO_2/TiO_2$ coupled system had a higher short-circuit current ($J_{sc}$) than the conventional system without $SnO_2$ buffer layer. It is suggested that the $SnO_2$ layer expedites the electron transfer from main $TiO_2$ layer to FTO glass, and blocks the back-transport of electrons to the electrolyte.

## 639

### Low-Cost Solution Processes for the Fabrication of Efficient Plastic Solar Cells

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**Seok-In Na,** *Gwangju Institute of Science and Technology, Korea*
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**Dong-Yu Kim,** *Gwangju Institute of Science and Technology, Korea*

Among Solution processes, spin coating has been the most widely used. However, the spin coating process can not be used in large area devices or on flexible substrates with a high throughput roll-to-roll process, which is one of the most cost-efficient processes for the production of plastic products.

Spray coating and brush painting are widely used for painting in commercial production and is one of the cheapest processes for coating of polymer solutions. Combining the roll-to-roll process and these low-cost processes for the fabrication of active materials of OSCs could be ideal solutions for low-cost power generation.

We report on a spray coating method and a brush painting as a cost-efficient methods for the fabrication of efficient and flexible solar cells. Although the spray deposited film showed a relatively rougher surface than spin coated ones, an sprayed OSC showed 2.83 % of power conversion efficiency and 52 % of incident photon to current conversion efficiency even though the device was fabricated in air. The brushed polymer films showed comparable rms roughness with spin coated ones and the optimized brushed OSC showed even higher efficiency than spin coated devices. The brushed OSC fabricated in a glove box showed 5.4 % of power conversion efficiency, 0.66 V of open circuit voltage, 11.65 mA/cm2 of short circuit current, 70.1 % of fill factor under 100 mW/cm2 illuminations with air mass (AM) 1.5 G condition.

# 640

## Electrochemical Characterization of Solid State Polymer Electrolyte for Dye-Sensitized Solar Cells

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Using solid state polymer electrolyte, the overall energy conversion efficiency of solid state DSSCs was improved up to 5-6 % recently. In particular, PEO/PEGDME/XI/I2 electrolyte system showed a good solar cell performance, where X is either K or 1-methyl-3-propylimidazolium (MPI). The overall energy conversion efficiency was not different very much (6.20 % for KI and 5.79 % for MPII with the cell size of 0.09 cm2 at 1.5 AM and one sun conditions) although the large difference was expected in the electrochemical properties including the electron diffusion coefficient in the $TiO_2$ layer, the diffusion coefficient of triiodide, and charge transfer resistance at the counter electrode side. The electron diffusion coefficients through the $TiO_2$ semiconductor layer were 1~2*E-4 and 7~8*E-5 cm2/s, respectively, for KI and MPII. The electron diffusion length values measured were thus obtained 19.29um for KI and 7.70um for MPII. While the electron diffusion length value of polymer electrolyte employing KI was detected 3 times higher, the diffusion coefficients of iodide/triiodide redox couple measured by symmetric cells were 2.19x10-6 cm2/s for KI and 5.00x10-6 for MPII. It was thus concluded that the effects of the diffusion coefficient of electrons and ions on the overall energy conversion efficiency in the solid state DSSCs were compensated each other, resulting in not very different overall energy conversion efficiency.

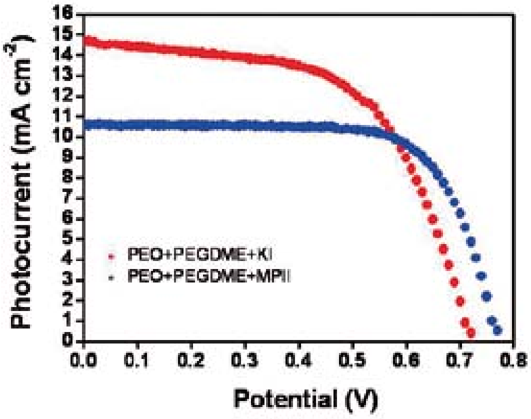

**Figure 1.** J-V curves of dye-sensitized solar cells employing PEO/PEGDME/KI or MPII/$I_2$ electrolytes, measured at 100mW/cm².

# 641

## Surface Modification of Platinum Counter Electrode with PEG-thiols and Application

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In solid state dye-sensitized solar cells (DSSCs), interfaces of solid electrolyte with both working and counter electrodes play particularly important roles in determining the overall energy conversion efficiency because processes such as photogeneration, separation and recombination of charges take place at the interfaces. For solid state DSSCs, in particular, it is expected that the charge transfer resistance at the solid polymer electrolyte/Pt counter electrode interface could also play an important role in determining the energy conversion efficiency in addition to the ionic conductivity of triiodide. The large charge transfer resistance is primarily due to the fact that the polymer electrolyte is less compatible with solid Pt counter electrode than liquid electrolyte. Therefore, the charge transfer resistance was attempted to be reduced by improving the compatibility between the solid polymer electrolyte and solid Pt counter electrode. For example, poly(ethylene glycol) (PEG) containing a thiol group at one side of the polymer chain (PEG-thiol) was used to modify the Pt counter electrode as a surface compatibilizer. DSSC using the modified Pt counter electrode with PEG-thiol yielded high cell performance of 4.1% at one sun conditions (cell size of 0.13 cm2) with the Voc= 0.60 V, Jsc=11.8 mA/cm2, and FF=0.58. Therefore, it is concluded that the reduction of the charge transfer resistance of solid-state DSSCs is also important in improving the efficiency in addition to the most widely blamed ionic conductivity for low efficiency.

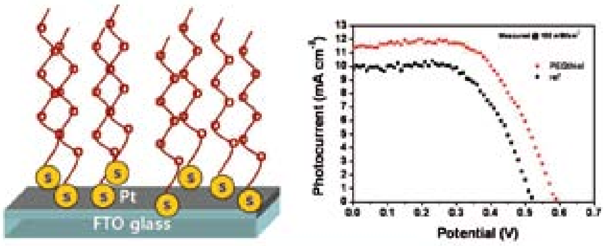

**Figure 1.** Schematic illustration of SAM(self-assembly monolayer) formation on the Pt counter electrode and current-voltage characterization of solid state dye-sensitized solar cell employing PEG-thiols coated Pt counter electrode.

| Polymer electrolyte | Voc(V) | Jsc(mA/cm^2) | FF | Eff.(%) | Diffusion Length(um) | Dtriiodide(cm^2/s) | Rct |
|---|---|---|---|---|---|---|---|
| PEO+PEGDME+KI+I2 | 0.72 | 14.8 | 0.58 | 6.20 | 19.21 | 2.19E-6 | 328 |
| PEO+PEGDME+MPII+I2 | 0.78 | 10.7 | 0.69 | 5.79 | 7.66 | 5.00E-6 | 20 |

## 642

### Photovoltaic Properties of Colloidal ZnTe/ZnSe (core/shell) Type II Quantum Dots

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**Jiwon Bang,** *Department of Chemistry, Department of Chemical Engineering, Pohang University of Science and Technology, Korea*
**Ji-Hwang Lee,** *Department of Chemistry, Department of Chemical Engineering, Pohang University of Science and Technology, Korea*
**Juwon Park,** *Department of Chemistry, Department of Chemical Engineering, Pohang University of Science and Technology, Korea*
**Jutack,** *Department of Chemistry, Department of Chemical Engineering, Pohang University of Science and Technology, Korea*
**Kilwon Cho,** *Department of Chemistry, Department of Chemical Engineering, Pohang University of Science and Technology, Korea*

Colloidal II- ? semiconductor quantum dots (QDs) are prepared and exploited for photovoltaic devices. To further optimize the efficiency of solar cells by using different type of QDs, we investigate type-II core/shell QDs. Type-II QDs can have small effective band gaps than those of the constituent materials and can have potentials to effectively transfer the photoinduced carriers by the unique band offset characteristics. Therefore, type-II QDs can be advantageous for photovoltaic devices because of their broad absorptions and capable photoinduced charge separation. We synthesize colloidal ZnTe/ZnSe (core/shell) type-II QDs and their absorption spectra covered from UV to 600 nm. These type-II QDs are made of relatively less toxic elements when compared to conventional QDs such as CdSe QDs, and can be potentially more viable for commercialization. We made ZnTe/ZnSe (core/shell) QDs - P3HT hybrid solar cell device, and characterize their photovoltaic properties. ZnTe/ZnSe (core/shell) QDs - P3HT hybrid solar cell has more efficient light harvesting and increase power conversion efficiency compared with P3HT solar cell.

## 643

### Investigation of Static Hot Carrier Populations and Energy Selective Contacts by Optically Assisted IV

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**Gavin Conibeer,** *ARC Photovoltaics Centre of Excellence, the University of New South Wales, NSW 2052, Sydney, Australia, Australia*
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Optically assisted current-voltage (oa-IV) is a characterization technique for measuring both, a hot carrier (HC) population and the selectivity of an energy selective contact (ESC) in a static regime as in a HC solar cell. A HC population is generated by a concentrated photon flux from a Xenon (Xe) lamp. Its properties can be controlled further by selective wave length filtering from 1000 to 500 nm in 50 nm steps, thereby providing a narrow energy range of optical excitation up to 0.7 eV below the conduction band offset from Si to $SiO_2$. Measurements can be carried out down to liquid nitrogen temperature, thereby diminishing trap-assisted tunneling currents and inelastic electron scattering.

We report on the working principle, experimental setup and results of MESA samples containing a single Si-QD array as an energy selective contact below a nc-Si absorbing layer. Dark IV measurements revealed a weak resonant tunneling feature, while the massive optical excitation showed an enhancement of the resonant tunneling feature by one order of magnitude along with the bias range of the resonant tunneling feature being reduced significantly. With these experimental results, a static distribution of hot carriers being extracted by an energy selective contact was observed at room temperature.

## 644

### Influence of Coadsorbent on the Adsorption of N719 on the Surface of $TiO_2$ Films and its Application in Dye Sensitized Solar Cells

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Dye-sensitized solar cells (DSC) have attracted wide-spread academic and commercial interests for their potential low cost, simple assemble technology and high efficiency. Up to now, the efficiency in the laboratory for DSC was more than 11%. 200 m2 DSC showcase founded by STI Company in Australia, showed us the future of industrialization for DSC. In the industrialization process of DSC, how to decrease the cost of production is a problem to be solved. In this article, we introduced several organic carboxylic acids as the coadsorbent for N719 dye on the surface of $TiO_2$ films. The influence of coadsorbent on the adsorption of N719 on the surface of $TiO_2$ films and its application in dye-sensitized solar cells were studied by X-ray photoelectron spectroscopy and I-V characterization. It was found that steric acid is a good coadsorbent for N719 on the surface of $TiO_2$ films, which can save the amount of expensive N719 dye in DSC and increase the efficiency of dye-sensitized solar cells. The proper concentration of coadsorbent is 0.5 mmol/L for N719 dye on $TiO_2$ surface. Proper concentration of steric acid can remove the weakly adsorbed NCS group on the surface of $TiO_2$ surface, which is benefit for the electron transfer from excited dye into conduction band of the semiconductor.

## 645

### Improvement of Organic Dye-Sensitized Solid-State Solar Cell by Controlling Dye Adsorption

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As devices free of encapsulated liquids, dye-sensitized solid-state solar cells (DSSSCs) where the electrolyte is replaced by a solid hole collector are extensively studied. In this paper we present our observation on DSSSCs using copper iodide as a hole collector. The improvement of this DSSSCs have been achieved by employing organic dyes which have higher extinction coefficients than those of ordinary Ru complex dyes. The organic dyes having indoline or coumarine moiety sensitized DSSSC produce overall energy conversion efficiency of 3.6 % or 2.0 % respectively under standard AM 1.5 irradiation (100 $\text{mW cm}^{-2}$). The indoline dye sensitized DSSSC efficiency is higher than that of the cells of similar configuration sensitized with N3 dye. It has been reported that indoline dyes forms J aggregates that are not susceptible to concentration quenching. In this aspect indoline dyes have several major advantages in use as sensitizers for DSSSCs. The second issue of this paper is the effect of surface treatment of nanocrystalline $TiO_2$ electrode with some metal oxides or acetates on the performance of DSSSCs. When the nanocrystalline $TiO_2$ electrode was dipped into magnesium acetate solution before or after the dyeing process, the open-circuit voltage (Voc) of the $TiO_2$/Dye/CuI DSSSC was improved. The suppression of the charge recombination at the surface of nanocrystalline $TiO_2$ electrode by thin layer coating of magnesium acetate was suggested. The effect was depending on the kind of dyes. Finally, we could fabricate the most efficient DSSSC using D-149 dye with the efficiency of 4.2%.

# 646

## Preparation of Porous $TiO_2$ Microspheres and Application to DSSC

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First, the hollow $TiO_2$ microspheres with size of 1.5–4 micron were synthesized by the solvothermal reaction of titanium isopropoxide in tetrabutylammonium hydroxide (TBAH) solution. The shell of hollow $TiO_2$ microspheres, with a thickness of ~250 nm, was constructed by the assembly of highly crystallized $TiO_2$ nanoparticles with the size of 18 nm. The synthesized thermally-stable hollow $TiO_2$ microspheres were applied as the scattering layer of DSSC, and it was found that they are more efficient than other scattering materials such as rutile or zirconia. We achieved conversion efficiency as high as 10.34% under AM-1.5G one sun light intensity. Second, several dense $TiO_2$ microspheres with the size of 0.4–1 micron were synthesized. They were applied either to main electrode layer or scattering layer in the DSSC. The transport property of the injected electrons and electrolytes through this structure was analyzed and compared with the nanocrystalline electrodes derived from $TiO_2$ nanoparticles.

# 647

## Dye-sensitized Solar Cells Based on Several Nitrogen-doped Titania Electrodes

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**Tingli Ma,** *State Key Laboratory of Fine Chemicals,Dalian University of Technology, China*
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Dye-sensitized solar cell(DSC) is a new type of photoelectric material. It is considered a technically and economically credible alternative to silicon photovoltaic devices. In order to commercialize DSCs,it is necessary to further improve the energy conversion efficiency. Recently, we successfully introduced the nitrogen-doped titania electrode prepared by dry method into the DSC system. In this paper, we mainly describes several DSCs based on nitrogen-doped titania prepared by wet methods. The physical and photoelectrochemical properties of nitrogen-doped titania powder, paste, electrodes and DSCs were investigated. We also discussed the influence of the preparing methods to the performance of the DSC. The UV-Vis spectra of the nitrogen-doped powder and film showed visible light absorption in the wavelength range from 400 nm to 535 nm. An enhancement of the overall conversion efficiency of the DSCs was achieved. We found that the influence of the different preparation methods for nitrogen-doped titania to the peformance characteristics of DSCs is unremarkable.

# 648

## Hunting for the Limiting HOMO LUMO Bandgap by Structure Modifications of D-L-A of Organic Dyes for DSCs; Broadening the Spectra with Minimum Drawbacks

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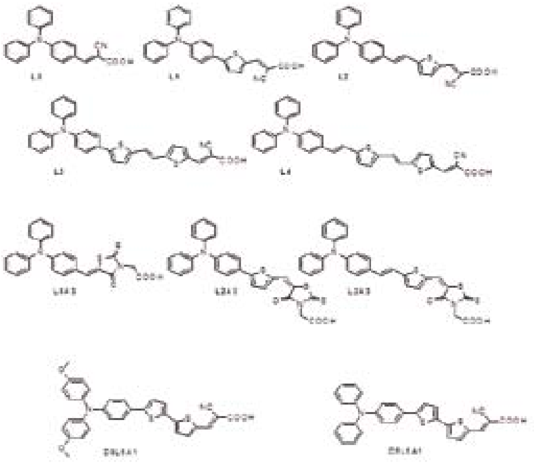
**Daniel Hagberg,** *KTH Organic Chemsitry, Sweden*
**Licheng Sun,** *KTH Organic Chemsitry, Sweden*
**Anders Hagfeldt,** *KTH Physical Chemistry, Sweden*

At present, there is a strong interest in developing metal free sensitizers for substitution of conventional ruthenium complexes in dye sensitized solar cells, DSC. The main limitation at present is the deficiency in collection of low energy photons while the standard ruthenium based dyes are able to absorb photons in the 800 nm region even if only at comparatively low absorption coefficients. For the organic dyes to be viable broader spectral responses are needed and to find such dyes is the main objective of this study. Systematic structure modifications were done on the donor, linker and acceptor groups (D-L-A) for a series of dyes. Even though all modifications successfully resulted in broader spectra, in agreement with theory, the dyes showed very different behavior in the dye sensitized solar cell. A rhodanine acetic acid was compared with the cyanoaceticacid as anchor group and this revealed that the compatibility of the anchor group and linker chain plays a role in kinetic related properties. The linker was varied by increasing the conjugation with different numbers of methine and thiophene units. The longer flexible linker length showed higher sensitivity to aggregation problems and needed coadsorbers or additional modifications to be feasible as sensitizers in DSCs. The donor group was also modified starting from a triphenylamine group adding different electron donating moieties. This study revealed that there are other energetical limitations for organic dyes in comparison to ruthenium dyes when applied in DSC and those will be further discussed.



## 649

### Understanding the Relationship Between Dye Structure and Device Efficiency: Use of New Heteroleptic Ruthenium (II) Polypyridyl Complexes as Dyes in DSSC

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**Amparo Forneli,** *ICIQ, Spain*
**Eugenia Martinez-Ferrero,** *ICIQ, Spain*
**Antonio Sanchez-Diaz,** *ICIQ, Spain*
**Anton Vidal-Ferran,** *ICIQ, Spain*
**Emilio Palomares,** *ICIQ, Spain*

The study of the charge transfer reactions that take place at the different interfaces of Dye Sensitised Solar Cells (DSSC) shows that electron transfer reactions are very much optimised. However, there are recombination reactions between the oxidised dye and the photo-injected electrons, and between these electrons and the oxidised electrolyte, which result critical for the overall efficiency of the devices. Recently, it has been demonstrated that several dyes, which show poor light-to-energy conversion performance, increase the rate of electron recombination between the photo-injected electrons and the oxidised electrolyte when used as sensitizers. These dyes have in common the presence of extended π-conjugated systems that lie close to the semiconductor surface. Taking into account these observations, we have designed a series of heteroleptic Ruthenium (II) complexes where one of the 4,4'-dicarboxy, 2,2'-bipyridine ligands has been substituted by a phenanthroline moiety. Furthermore, the phenanthroline ligand has been modified with the introduction of electron donating or electron withdrawing groups to achieve the desired control over the molecular orbitals. Whilst electron-donating groups will increase the energy gap (HOMO-LUMO gap) the introduction of electron withdrawing groups will have the opposite effect. Our aim is to study and rationalise the possible effects over the interfacial charge transfer reactions, under working device conditions that the introduction in the dye of a more conjugated ligand, such as a phenanthroline, and its functionalization will have on the overall device efficiency.

## 650

### Performance and Stability of Dye Solar Cells on Stainless Steel

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**Janne Halme,** *Laboratory of Advances Energy Systems, Finland*
**Minna Toivola,** *Laboratory of Advances Energy Systems, Finland*
**Peter Lund,** *Laboratory of Advances Energy Systems, Finland*

The conductive glass substrates constitute one of the most costly components of a dye solar cell. Hence, investigation of alternative materials is highly motivated. In this contribution we focus on using stainless steel which has been shown to be stable in electrolyte soaking tests.

The suitability of stainless steel both as a photoelectrode and counter electrode substrate was examined in respect to performance and stability. Complete solar cells were built and analysed using photovoltaic characterization methods, electrochemical impedance spectroscopy (EIS), and open circuit voltage decay. Recombination from the substrate to the electrolyte was investigated with substrate - counter electrode cells.

The results show 4.7 % and 3.5 % efficiencies for dye solar cells with stainless steel as a photoelectrode and counter electrode substrate, respectively. A significant part of this work was to make quantitative analysis of a single electrode performance. Here the voltage over a single electrode was determined in two electrode mode based on EIS measurements made as function of cell current. The conventional data analysis based on external cell voltage was found to be inadequate and even misleading. As a result of these detailed studies, we were able to find that the stainless steel photoelectrode substrate had affected negatively the electrochemical response of the dye TiO$_2$ layer whereas in the case of counter electrode substrate it remained unaffected. This observation is important for practical design of a reliable flexible dye solar cell.

## 651

### Synthesis of CIGS Thin Film via Non-Vacuum Processes

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**Jun Haeng Lee,** *Korea Institute of Science and Technology, Korea*
**Oh Shim Joo,** *Korea Institute of Science and Technology, Korea*

CIGS thin film solar cell has been considered to one of the most promising way to convert sunlight into electrical energy due to its high efficiency as well as high durability. The obstacles of the CIGS solar cell fabrication for commercial application may be relatively difficult manufacturing synthetic method and high processing costs because it is conventionally fabricated by vacuum co-evaporation techniques. Here, we suggest the simpler and lower cost synthetic method of CIGS thin film which can be applicable in continuous role-to-role process by applying the paste coating process. Specifically, CIG oxide powder was firstly synthesized by a co-deposition method from Cu, In, and Ga nitrate by controlling the composition of each compound. CIG oxide was then mixed and dispersed with SeO$_2$ followed by addition of surfactant and adhesive. After deposition and annealing of the CIGS oxide paste on the conducting glass or metal plate, the thin film shows typical XRD patterns of the CIGS thin film. The film was further characterized by XPS, SEM, and TEM to confirm high quality of the film.

## 652

### Influence of the Structure of Metal Free Organic Dyes on Electron Transfer Kinetics in Dye Sensitized Solar Cells

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Dye sensitized solar cells (DSC) prepared with Ru complex dye have shown over 11% energy conversion efficiency. While the efficiency of RuDSC has not improved largely for last decade, the efficiency of DSC prepared with metal-free organic dyes has been improved. Recent organic dyes have shown comparable short-circuit current with that of RuDSC. However, all of them have shown lower values of open-circuit voltage. We have measured the electron lifetime in DSCs with five different organic dyes, two coumarin dyes, and three carbazole dyes, and found that all of them had shorter electron lifetime than in the case of Ru dye. Among the organic dyes, the values of lifetime varied depending on the structure of the dyes. Two tendencies were found: dyes having larger molecular size and alkyl chains showed longer electron lifetime. In order to study the molecular structure dependent electron lifetime, electron diffusion coefficients, electron density, and transient absorption of the DSCs with these dyes were measured under various electrolyte compositions and amount of dye adsorptions. It was found that electron lifetime was increased with the increase of LiI concentrations and leveled off at certain concentrations, and the concentrations depend on the dyes. This suggests that some organic dyes needed more I$^-$ concentrations to be reduced effectively. In view of amount of dye adsorption, dyes having alky chain showed longer lifetime when the amount of adsorbed dye is large, showing that these dyes block the approach of I$_3^-$ to the surface of TiO$_2$.

# 653

## Effects of Character of $TiO_2$ Pastes on the Properties of $TiO_2$ Film for DSC

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The purpose of this research was to study the effects of printable $TiO_2$ pastes which have different solvent, composition and preparation conditions on the properties of $TiO_2$ electrodes and conversion efficiency. In order to form films, various printable $TiO_2$ pastes were prepared by changing preparation conditions and types of solvents (high/low boiling point solvents, water-based solvents). Screen-printing paste PST-18NR supplied by CCIC consists of 20nm $TiO_2$ particles, organic solvent and polymer. The paste could form a $TiO_2$ film that has an average pore diameter of 18-20 nm and a pore volume of 0.38-0.42 ml/g. The result of measuring the I-V curve of fabricated DSC which used PST-18NR (20 nm $TiO_2$ particles) and PST-400C (400 nm $TiO_2$ particles) is shown in Fig. 1. The conversion efficiency is 8.78 %.

Changing the preparation method and composition of $TiO_2$ paste could control the average pore diameter and pore volume of $TiO_2$ film. The results of measuring pore distribution of some $TiO_2$ films are shown in Fig. 2. Although the pore distributions were different, conversion efficiencies of these films were 6.0-6.4% using organic solvent electrolyte. In this report we will give the conversion efficiency results using other electrolytes such as ionic liquid.

Moreover, we are preparing $TiO_2$ pastes that consist of water or light organic solvent. We would like to discuss the properties of $TiO_2$ films which are made of these pastes and the effects of the solvent of $TiO_2$ pastes on the conversion efficiency.

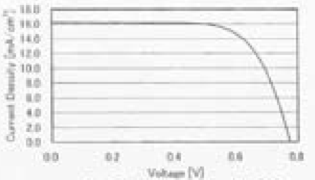

Fig. 1 Photocurrent-voltage of the DSC

The film thickness consists of a 12μm (PST-18NR) plus a 4 μm (PST-400C). The sensitizer used was the ruthenium complex N719. The electrolyte contained 0.6M 1-ethyl-3-methylimidazolium dicyanamide, 0.05M iodine, 0.1M lithium iodide and 0.5M 4-tert-butylpyridine in acetonitrile.

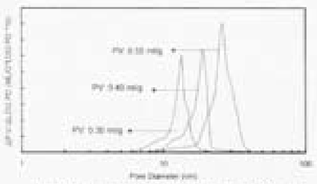

Fig. 2 The pore distribution spectra of $TiO_2$ films from different $TiO_2$ pastes

# 654

## Tandem Dye Sensitised Solar Cells Incorporating Photoanodes and Photocathodes

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Organic solar technology offers many advantages when compared to more traditional types of photovoltaics, with dye sensitised solar cells (DSSCs) offering the highest conversion efficiencies of this class to date. In spite of this, the efficiencies still lag behind crystalline silicon, limiting the potential for application of this low cost technology.

The highest reported efficiencies of DSSCs have not risen dramatically in recent times. One way to overcome the stagnation is to look at tandem structures. In this system each electrode more efficiently harvests different sections of the solar spectrum.

By incorporating a photocathode and a photoanode in one device the expected increase in cost is minimal when compared to a single photoelectrode DSSC. In this case the two electrodes are in series, meaning that a high voltage can be produced when compared to a single electrode cell. Unfortunately the current density is limited by the weakest of the two electrodes.

Nickel (II) oxide has been shown to be useful as a model photocathodic system, however current densities are low, and the maximum voltage achievable is modest. A number of methods are being used to improve the performance of these devices, as well as a more in depth investigation into the photocathodic process, which is much less understood than the photoanodic one.

# 655

## Modelling of DSCs at Different Film Thicknesses with Experimental Validation

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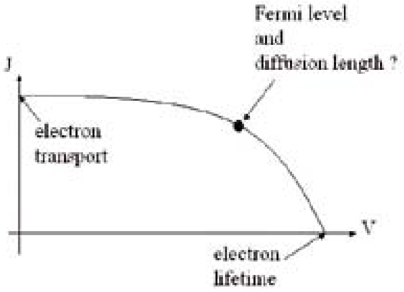
**Gerrit Boschloo,** *Royal Institute of Technology (KTH), Department of Chemistry, Sweden*

We present a model and experiments where the local fermi-level determines the properties of electron transport and recombination in mesoporous $TiO_2$ at different applied voltages and light intensites. A series of experiments have been performed for DSCs at different film thicknesses. This series of experiments includes IV measurements, transport time, life time and average fermi level. This study connects the electron lifetime and transport measurements with efficiency limitations of the solar cells and is therefore of high importance.



# 656

## Characterization of New Ru Complex Dyes for Dye-Sensitized Solar Cells which Have High Extinction Coefficient

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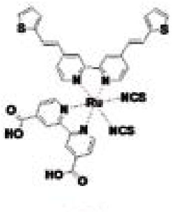
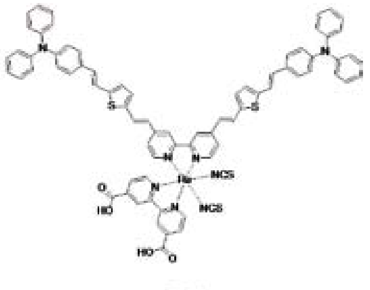
New Ru-complex dyes were synthesized for dye-sensitized solar cells (DSSCs) to increase the extinction coefficients and to improve the intramolecular charge separation. Structure of new dyes is shown in figure and dyes are named E311 and E322. Both dyes showed a wide absorption spectrum in the visible region. E322 has a high extinction coefficient of 42000 $M^{-1}$ $cm^{-1}$ at 469 nm, and 13000 $M^{-1}$ $cm^{-1}$ at 535 nm for E311. Both dyes worked as sensitizers for DSSCs. The obtained efficiency was 3.24, 1.83 % for E311 and E322, respectively. 4.06 % was obtained from N719 as reference. The difference in the photovoltage (624, 538 and 770 mV for E311, E322 and N719, respectively) was one of the key issues to explain the difference of the efficiency. Moreover, dye aggregation especially for E322 diminishes the efficiency significantly. It was observed by photoinduced absorption spectroscopy that the regeneration of the oxidized dye molecules was poor since the dyes were lacking contact with the redox electrolyte due to aggregation. For the cell with E322, an enhancement of the photocurrent was observed during illumination under short-circuit condition with light containing UV. After this treatment, the amount of the adsorbed dye on $TiO_2$ decreased and the regeneration of the oxidized dye started to work well. The total efficiency was improved 2-10 times by this treatment. The details will be discussed in the poster.



E311



E322

## 657

### A Solar Cell Concept Based on Transparent Conducting Metal Oxide Film Electrodes with Organized Mesoporous Architecture

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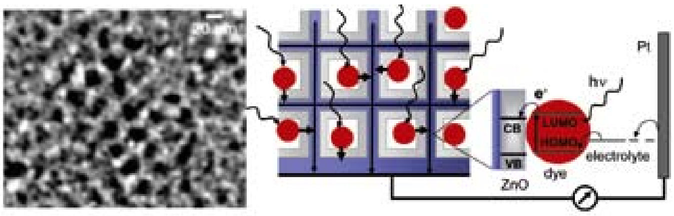
A number of solar cell concepts based on nanostructured semiconducting materials has been developed in recent years, e.g. dye-sensitized solar cells (DSSC), extremely thin absorber layer (ETA) solar cells and other interpenetrating networks of polymers or semiconductors. However, slow electron transport by diffusion in the nanoporous films often leads to a loss of efficiency as a part of the photogenerated charge carriers recombine before they can reach the back contact. Fully accessible 3D mesoporous architectures with a high conductivity are an approach to overcome these shortcomings. We succeeded in the synthesis of such pore architectures based on highly transparent and highly conductive mesoporous indium tin oxide (ITO) with pore sizes suitable for the deposition of a thin semiconductor layer on the pore. The concept was probed by electrodeposition of thin layers of ZnO on the pore walls and their subsequent dye-sensitization. Transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDXS) shows that all the pore walls can be covered with ZnO in the electrodeposition process. Compared to dye-sensitized ZnO layers of the same thickness on flat ITO, the photocurrent is increased by a factor of up to 50. This matches well with the 40-50 times higher specific surface area of the mesoporous ITO films (typically 45 +/- 3 $cm^2/cm^2$), showing the good electron transport properties of the porous ITO network. The concept should be of interest not only for use in DSSC, but also for other types of solar cells based on interpenetrating inorganic networks.



Left: HAADF micrograph showing the cross-section of a mesoporous ITO film in bright contrast.
Right: Scheme of the concept of a DSSC based on a mesoporous conducting layer.

## 658

### High Performance Dye-sensitized Solar Cell with Novel Dye System

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**Masahiro Morooka,** *Sony Corporation, Japan*
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**Kazuhiro Noda,** *Sony Corporation, Japan*

Dye-sensitized Solar Cell (DSC) reported by M. Graetzel in 1991 promised easy, low-cost fabrication compared with the conventional photovoltaic solar cell. DSC achieved high photon-electron conversion efficiency because the dye adsorbed semiconductor electrode (mostly $TiO_2$) with the dye adsorbed absorbs light and generates electricity by that external quantum efficiency. The single ideal dye in a DSC should absorb all visible light and smoothly transfer electrons to the $TiO_2$ electrode, but this ideal dye has not yet been developed. The problem is that using a single dye with a long wavelength, it is difficult to inject electrons from the dye to $TiO_2$ electrode because the LUMO of the dye approximates the conduction band of $TiO_2$. But if a mixture of dyes with different wavelengths is used, it is still difficult to inject electrons from the dyes because the electron transfer would occur between the dyes. Here we show a DSC using novel dye system to achieve high external quantum efficiency as sensitizers.

## 659

### Solid State Dye Sensitized Solar Cells: Addressing Pore-Filling by Means of Advanced Hole Conductor Deposition Techniques and Ordered $TiO_2$ Morphology

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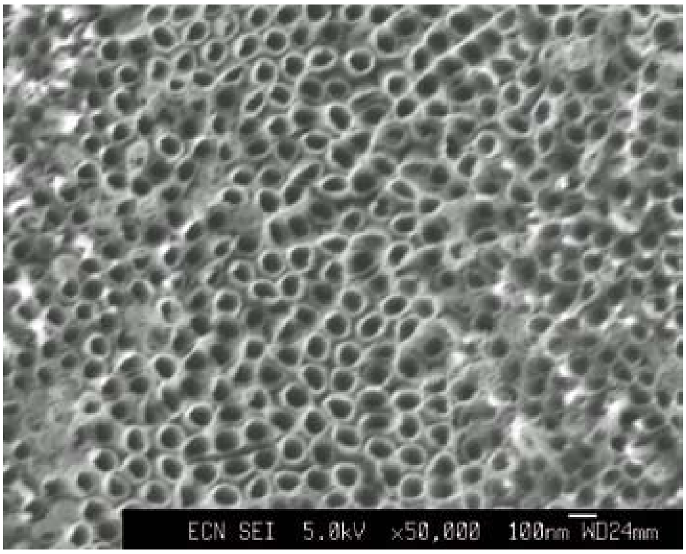
**Gerrit Boschloo,** *Center of Molecular Devices, Dept. of Chemistry, Royal Institute of Technology, Sweden*

One of the main limitations of current solid state dye sensitized solar cells (ss-DSC) is incomplete pore-filling of solid state hole conductors (e.g., spiro-OMeTAD) into the mesoporous $TiO_2$ films. Good pore-filling is essential, since it provides the required intimate interfacial contact between the dye molecules, attached to the $TiO_2$ surface, and the hole conductor phase. Pore-filling becomes increasingly more problematic with thicker films, which is why the best conversion efficiencies (4-5%) are currently still reached when $TiO_2$ films of sub-optimized thickness (2 um) are employed.

We address the issue of pore-filling by both advanced hole conductor deposition techniques and the application of ordered $TiO_2$ morphologies (nanotubes). The hole conductor of choice in our current work is spiro-OMeTAD but the concepts presented here can also be applicable to other hole conductors, including metallic ones.

For the deposition of the spiro-OMeTAD, we applied post-annealing at temperatures up to 150°C as well as variations in spin-coating conditions and vacuum application. Transparent $TiO_2$ nanotube layers on SnO2:F coated glass substrates (including a dense $TiO_2$ underlayer of ~ 50-100 nm thickness) were developed and investigated with respect to their potential to improve the pore-filling and/or slow down the interfacial recombination kinetics.

We will present a comparative study of a series of solid state DSC devices, prepared with the concepts outlined above. The photovoltaic performance of the devices will be rationalized in terms of pore-filling and interfacial recombination by using characterization methods, such as photoinduced absorption spectroscopy (PIA), photovoltage transient measurements and impedance spectroscopy.



## 660

### Quasi-Solid State Electrolyte for Dye-Sensitized Solar Cells

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In this article, for the fist time we reported the preparation of a mostly solid-state high efficient electro-conductive material comprising 1-methyl-3-propylimidazolium iodide (MPII), benzimidazole (BI), iodine and lithium iodide. In this electrolyte, BI act not only additives but also gelators.Although materials mentioned above have already been widely used in many researches, the solid state electrolytes comprising these components have never been reported yet. Since MPII has been known as ionic liquid and used in DSCs for its favorable properties such as thermal stability, nonflammability, high ionic conductivity, negligible vapor pressure, and a possible wide electrochemical window, electrolytes containing these components are environment-friendly and easy to manufacture with their low liquid-to-solid phase transition temperature. Because the solidification does not need any additional gelator, it is very convenient for the preparation of cells, which is very important for industrial manufacture. And with their significant electrochemical properties, overall efficiency of 3.07% was achieved under AM 1.5 (100mW/ cm2).

## 661

### Inorganic/Organic Hybrid Solar Cells Using Photo-Electrochemically Deposited Electroactive Polymers as Hole Transporting Materials

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Inorganic/organic hybrid solar cells fabricated by a photo-electrochemical deposition method of PEDOT (poly-3,4-ethylenedioxythiophene) as hole transporting material (HTM), a commercially available ruthenium complex Z907 as photo-sensitiser and a nanostructured $TiO_2$ as photo anode material will be presented. The dye-sensitized films containing various deposits of PEDOT were characterised using UV-Vis spectroscopy, and the current voltage curves of the corresponding solar cells were measured under 100 mW cm-2 air mass (AM 1.5) calibrated white light illumination. The polymer growth is controlled by varying the light intensity, wavelength and applied potential. Finally, a range of imaging and spectro-electrochemical mapping techniques are employed including AFM, SEM, confocal Raman spectroscopy and scanning electrochemical microscopy to investigate the correlation between solar cell performance and HTM morphology, pore filling and doping level.

## 662

### Dye-Sensitized Solar Cells Employing Solid-State Oligomer Electrolyte with Secondary Interaction

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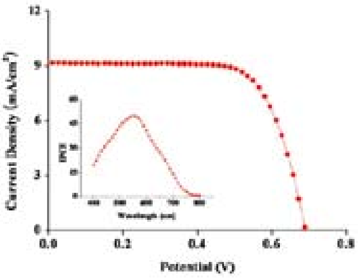
**Sang-Soo Lee,** *Korea Institute of Science and Technology, Korea*

On purpose to prepare solid-state dye-sensitized solar cells (DSSCs) with high energy-conversion efficiency, poly(ethylene glycol) (PEG) oligomer having specially designed terminal groups was used as the electrolyte for DSSCs. PEG oligomers exhibit good ionic diffusivity, negligible vapor pressure at room temperature and great thermal and long-term stability. Accordingly, they can be employed as alternatives to common volatile electrolytes for DSSCs. In spite of these advantages, however there have been few applications of oligomers to DSSCs since PEG oligomers are still liquid-state not solid-state. To solve this problem, we introduced novel oligomers which could be easily solidified via secondary interaction. Compared with the oligomers having secondary interaction sites and other oligmers with similar molecular weight to the totally interacted oligomers but not containing interaction groups, the ionic diffusion coefficients of $I^-$ and $I_3^-$ in the former were much higher than those for the latter. As a result of the J-V measurement, the DSSCs using the oligomer showed high energy-conversion efficiency over 4.5% and finally, a further test involving storage at room temperature demonstrated that the DSSCs employing the oligomer electrolytes showed superior stability to those of employing volatile electrolytes.



## 663

### The Study of Organic Dyes for Sensitization of P-Type Semiconductors

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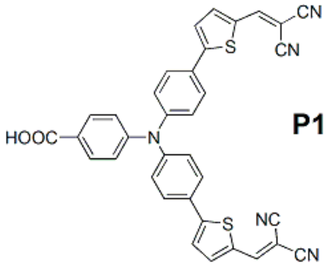
**Hongjun Zhu,** *Royal Institute of Technology (KTH), Sweden*
**Gerrit Boschloo,** *Royal Institute of Technology (KTH), Sweden*
**Anders Hagfeldt,** *Royal Institute of Technology (KTH), Sweden*
**Licheng Sun,** *Royal Institute of Technology (KTH), Sweden*

The main focus of present studies on dye-sensitized solar cells (DSSCs) is based on the sensitization of n-type semiconductors, which consist of photoactive anodes and passive cathodes (n-type DSSCs). However, DSSCs in which the cathode is photoactive are also possible and the development of photocathode can provide an entry to the preparation of a tandem solar cell.

In this presentation we will show a new organic dye (P1) which can be used in sensitization of p-type DSSCs. In P1, we use triphenylamine moiety as the electron donor, malononitrile moiety as the electron acceptor and thiophene unit as the conjugated linker. By introducing two electron acceptor groups and having the anchoring group on the donor moiety, light excitation is associated with electron flow from the donor part of the dye to the acceptor part, providing efficient electron transfer pathway from the dye to the electrolyte.

P1 has very high extinction coefficient and under AM 1.5 irradiation, the highest incident photo-to-current conversion efficiency (IPCE) of 18% in visible region has been obtained in the preliminary tests based on the $NiO_2$ film. This is the highest value so far in p-type DSSCs. Now we are optimizing the p-type systems and we hope that we can get a better efficiency in p-type DSSCs in the future.



P1

## 664

### Solid State Nanoporous $TiO_2$ Solar Cells Sensitised with Natural Dyes

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**Sivapathasundaram Sivaraya,** *Department of Physics, University of Jaffna, Sri Lanka*
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Dye-sensitized nanoporous $TiO_2$ solar cell is a promising system for cost-efficient solar energy conversion application. In these solar cells, Ru-based dye molecules, adsorbed on the surface of a nanoporous sintered $TiO_2$ film, are used to absorb visible light and to inject electrons into the $TiO_2$ conduction band. I-/I3- redox couple in a liquid electrolyte is used to regenerate the photo-oxidized dye molecule. Efficient dye-sensitised solar cells utilising several natural dyes have been reported.

Here we report the relative photoluminescence(SPEX 750M) and UV-VIS absorbance of nanocrystalline $TiO_2$ films coated with either commercial Z907 [cis-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(2,2'-bipyridyl-4,4'-dinonyl) ruthenium (II)] dye or natural dye, containing anthocyanin, extracted from grape (Vitis vinifera) fruit coat, Jambolan (Eugenia jambolana) fruit, beetroot (Beta vulgaris) and white yam (Dioscorea alata) tuber. Adsorption of these natural dyes on the nanoporous $TiO_2$ film is similar to commercial Z907 dye. The grape fruit coat extract displays an excellent sensitising behaviour among other natural dyes. This may be attributed to the strong interaction between the surface of $TiO_2$ nanoporous film and the carbonyl and hydroxyl groups of anthocyanin molecule on grape fruit coat extract. Current-voltage and external quantum efficiency spectra measurements of these dyes-sensitized samples were obtained under solar simulator(Sciencetech) with AM 1.5 spectral filter. We compare the photoluminescence spectra and the photovoltaic performances of dyes coated $TiO_2$ samples. The studies show that the performance of the natural dyes is similar to the commercial dye.

Acknowledgement: Author thanks National Research Council, Sri Lanka and International Foundation for Science, Sweden for their financial assistance.

## 665

### Modified Photoelectrode with Carbon Nanotubes for Dye Sensitized Solar Cell

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**Kwang-Hoon Jeong,** *Department of Applied Chemistry, Konkuk University, Chungju,380-701,Korea, Korea*
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A very thin film of $TiO_2$ was used to make dye sensitized solar cell (DSSC). To study the interfacial electron transfer between substrate and $TiO_2$ layer, the photoelectrode was modified with carbon nanotubes (CNT) and carbon nanofibers (CNF), which have excellent electrical conductivities and good chemical stability. The correlation between the properties of the modified interface and the morphology of the electrode were studied by Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), X-ray Diffraction (XRD) and UV/VIS spectroscopy were used for the characterization of modified photoelectrode. The performance of the DSSC was measured by photocurrent-voltage curve.

## 666

### Aligned 1-Dim $TiO_2$ Nanofibers Array for Hybrid Photovoltaic Cell

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**Yeon-Su Kim,** *Gwangju Institute of Science & Technology (GIST), Korea*
**Sang Hoon Nam,** *Gwangju Institute of Science & Technology (GIST), Korea*
**Yong Seok Kim,** *Gwangju Institute of Science & Technology (GIST), Korea*
**Jeong-Won Kim,** *Gwangju Institute of Science & Technology (GIST), Korea*
**Dong-Yu Kim,** *Gwangju Institute of Science & Technology (GIST), Korea*
**Won Bae Kim,** *Gwangju Institute of Science & Technology (GIST), Korea*

Hybrid photovoltaic cells are defined as a combination of nanostructures of inorganic semiconductor as an electron acceptor and organic polymer semiconductor as an electron donor. This solar cell is getting interesting and attractive in recent years due to its potential advantages such as low cost synthesis, easy processability and variable manufacturing of thin film devices. The current key issues in this field are how to enhance the exciton dissociation yield and separated-carrier transporting rate.[1,2]

Herein, we introduce highly aligned TiO2 nanofibers with good crystalline property as an electron acceptor material to improve the electron dissociation and transporting in hybrid solar cells. Aligned TiO2 nanofibers array was prepared by electrospinning synthesis equipped with rotating disk collector. To investigate the photovoltaic properties with respect to the degree of aligning and number of layer, hybrid solar cells were fabricated by a combination of the poly[2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylenevynylene] (MEH-PPV) and the ordered 1D architectures, which was compared with the cases of flat TiO2 thin film and randomly collected TiO2 nanofibers. These solar cells are analyzed through various analyses such as photoluminescence (PL), UV-vis spectroscopy and solar performance test along with the structural analyses of synthesized TiO2 nanofibers by using X-ray diffraction (XRD), X-ray absorption near edge structure (XANES), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The detail characteristics will be described and discussed.

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2. J. Bouclé, P. Ravirajan and J. Nelson, J. Mater. Chem., 2007, 17, 3141.

## 667

### Progress on Energy Selective Contacts for Hot Carrier Solar Cells at UNSW

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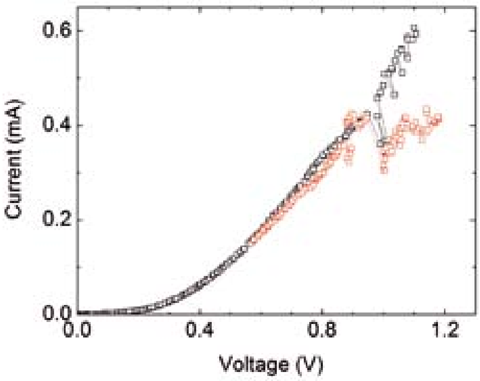
Hot Carrier solar cells are promising third generation photovoltaic devices. One of the important requirements of HC solar cells is the extraction of 'hot' carriers within a narrow range of energies with Energy Selective Contacts (ESCs) so that only a small fraction of their excess energy above the band edge is lost when the hot carriers comes in contact with the cold carriers in the metal electrodes.

In this paper we present progress on the fabrication and characterisation of ESCs at UNSW. Double barrier resonant tunnelling devices consisting $SiO_2$/Si QD/$SiO_2$ layers have been fabricated for ESCs by RF magnetron sputtering using quartz and silicon targets followed by high temperature annealing.

Electrical characterisation has shown the evidence of negative differential resistance (NDR) for these types of structures. Results of an I-V measurement on a typical resonant tunnelling device are shown in Fig. 1. Here, the black and the red data points are results of two subsequent measurements on a device with an interval of few minutes. In both I-V profiles, NDR resonance can be observed. This demonstrates that NDR characteristic is repeatable. Similar results have been observed for other similar devices. However, further work is required to improve the quality factor of the resonance (ratio of peak height to peak width).



## 668

### Efficient Photoelectrochemical Solar Cell with Noble Metal Nanoemitters

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A novel efficient Si-based photoelectrochemical solar cell is described that operates in the photovoltaic and photoelectrocatalytic mode. Silicon surface nanostructuring by electrochemical conditioning was used for the realization of the concept of a nanoemitter solar cell. The cell consists of a nanoporous passivating silicon dioxide mask on the silicon surface, made using a specific anodic conditioning protocol, and metallic nanoemitter islands that were deposited into the oxide nanopores. For efficient devices, a pore deepening procedure was applied. The metal nanorods act as nanoemitters for minority charge carrier collection. The photoelectrochemical solar cell n-Si / SiO2 /Pt / I-/I3- / Pt CE is stable and has efficiencies above 10%. Present limitations in solar-to-electrical conversion efficiency, due to interfacial recombination, will be addressed. The fact, that the observed open circuit voltage is large is explained by the formation of an electrolyte-metal-oxide-semiconductor junction. Due to simultaneous Si oxidation upon Pt deposition we assume an ultrathin oxide layer between the Pt nanoislands and the Si substrate. Model experiments on the electrodeposition process were performed using synchrotron radiation photoelectron spectroscopy (SRPES) to investigate surface chemistry and -electronics. The competition between valence band- and conduction band processes in the metal deposition reactions will be discussed.

## 669

### Photovoltaic Properties of Nanostructured $TiO_2$-$CeO_x$ / ITO and $TiO_2$-$TbO_x$ / ITO Layers

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The photovoltaic junctions consisting of titania thin films doped with cerium and terbium ions on indium-tin-oxide (ITO) layer were studied. The synthesis of nanocrystalline doped $TiO_2$ and ITO layers deposited by the spin-coating method is presented. The photoelectrochemical properties of the obtained junctions were studied under dark and illuminated conditions.

## 670

### Discotic Liquid Crystals Photovoltaic Applications

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Discotic liquid crystals, arranged into columnar stacks, have shown high mobility along the aromatic core of the liquid crystalline phase.[1] This property has already been exploited in other photovoltaic devices[2], however maintaining the quality of the liquid crystal mesophases can be quite challenging. The concept is to control the morphology and alignment of well characterised liquid crystals, and then to polymerise the side-chains of the liquid crystals along the column in order to solidify the structure of the liquid crystal (Figure 1). The resulting polymerised liquid crystals theoretically provides a structure more suitable to charge conduction by hindering rotational and translational fluctuations.[3] The project will involve much structural analysis based on wide angle 2D x-ray[4], small angle x-ray and neutron scattering[5], allowing us to investigate both the intracolumnar, and intercolumnar, distances of these new materials, whilst the dynamics of the fluctuations within the columns will be investigated using quasielastic neutron scattering[6]. These materials should have greater stability and conductivity, which will be important for potential applications in photovoltaic and other organic electronics. The hope of this project is to develop a new approach organic semiconductor technology; integrating organic conducting polymers and liquid crystal conductors, which could pave a new way of producing solution deposed organic solar cells or LED lighting.

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## 671

### Cyclometallated Ru Complexes as Sensitizers for Dye-sensitized Solar Cells

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Dye-sesitized solar cells have been extesively investigated during the past decade. Many efforts have been carried out on the development of photosensitizers in order to improve the efficiency, the most well-known sensitizers are N719 and black dye. Solar energy of over ca. 850nm is not effectively converted even by using black dye. Development of sensitizers with extended absorption and spectral sensitivitiy into the infrared region is expected. Replacing a nitrogen donor atom by a carbon atom in a multidentate ligand containing pyridin rings dramatically changes its electronic properties and cyclometallation itself has a strong effect on the photophysical properties of the resulting complexes. We have synthesized new type of cyclomatallated ruthenium compounds , Ru(tctpy)(L1)(L2) (tctpy = 4,4',4'-tricarboxy-2,2':6',2'-terpyridine, L1 = a bidentate ligand, L2 = an anionic monodentate ligand) and applied them as photosensitizers for dye-sensitized solar cells. The MLCT absorption maxima of these complexes are ca. 740-900 nm and these complexes functioned as effective photosensitizers for dye-sensitized solar cells. Details of experiments will be presented.

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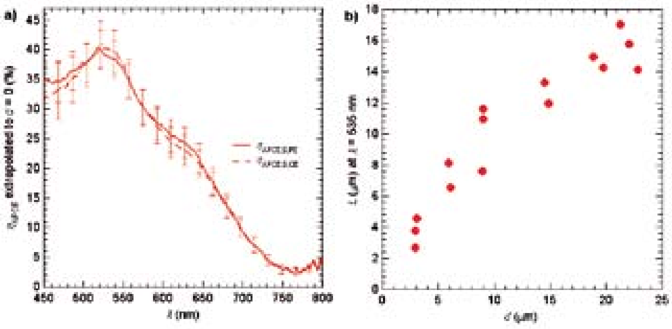

Figure: a) Wavelentgh dependence of the electron injection efficiency, b) Effective electron diffusion lenght vs. photoelectrode film thickness

## 672

### Electron Lifetime in Dye-Sensitized Solar Cells Fabricated with Various Dyes: Comparison Between Porphyrin Dyes and Metal Free Organic Dyes

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Highly efficient dye-sensitized solar cells have been fabricated with Ru complex dyes adsorbed on nano-porous $TiO_2$ electrodes (RuDSC). While the efficiency of the RuDSC has not been improved much for last decade, various dyes including metal complex and metal free organic dyes for DSC have been synthesized. In view of short-circuit current, some dyes have shown comparable values with that of RuDSC. On the other hands, open-circuit voltage (Voc) is always lower than that of RuDSC. It has been reported that lower value of Voc in the case of metal free organic dyes was attributed to the shorter electron lifetime, which corresponds to the transfer rates to dye cations and $I_3^-$. DSC prepared with porphyrin dyes have shown relatively high efficiency among metal complex dyes, but have the same problem with organic dyes, that is lower values of Voc. In order to study the causes of the low Voc, we measured the electron lifetime and diffusion coefficient (D) in DSCs prepared from porphyrin dyes, and found that shorter lifetime and faster D. We then compared the results with those in DSCs with organic dyes and Ru complex dyes under different electrolyte compositions. We also measured transient absorption of cationic state of these dyes. The electron transfer rates to dye cation and $I_3^-$ are discussed in view of the structure of these dyes.

## 673

### Syntheses of Directly-Linked Heterometallic Porphyrin Dimers and Applications to the Dye-sensitized Solar Cells

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In the natural photosynthesis of all plants and bacteria, porphyrin-based chromophores play important roles not only as strongly light-harvesting pigments but also as sequential intermolecular photoinduced energy and electron transfer components.
Many researchers have been attracted to the porphyrin-based chromophores in the wide field of science, such as biology, chemistry, photophysics, and so on. In this study, novel directly-linked heterometallic porphyrin dimers were synthesized and used for the artificial electrochemical solar cells based on titanium oxide nanocrystals as sensitizers adsorbed on the surface bearing high photon-to-electron conversion efficiency.

Though some porphyrin-based chromophores have been applied to the dye-sensitized solar cells (DSSCs) previously, it was reported that the efficiency of many of the DSSCs was not so high. In order to improve the efficiency of the DSSC, directly-linked heterometallic porphyrin dimers which work as intramolecular charge separators have been prepared by cross-coupling reaction. Generally, it is well known that the redox potential of metalloporphyrin shifts depending on the metal ion inserted into the porphyrin core. It is expected that photoinduced intramolecular charge separation occurs between the two metalloporphyrin cores and then the electron is injected from the negatively-charged metalloporphyrin core into the titanium oxide conduction band effectively. In the DSSC adsorbed the heterometallic porphyrin dimers, relatively high photon-to-electron conversion efficiency (2.8% under AM 1.5 solar condition) was observed. The IPCE of the DSSC in 400-600 nm visible light range was over 50%. Improvement of performance of the DSSC using the synthesized porphyrin dimer is now in progress.

## 674

### The Role of the Scattering Layer in Monolithic Dye Sensitised Solar Cells

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Monolithic DSSCs have been investigated with regard to the role of the scattering layer. Monolithic DSSCs have the same operating procedure as a standard DSSC, but with an alternative architecture. This structure involves replacing the platinum coated FTO-glass counter-electrode with a graphite/carbon-black layer on top of the $TiO_2$ layer and the scattering layer, thus removing the need for the FTO-glass in the counter-electrode. This is advantageous as conducting glass is known to contribute to a considerable portion of the cost DSSCs. The monolithic design may also have advantages in that it allows for simplified manufacture and better sealing of cells, especially with solid state devices.

A scattering layer is employed because of its ability to improve light harvesting and to separate the working and counter-electrodes. However the role and structure of this layer has not yet been fully understood in the monolithic DSSC.

Scattering layers considered here are made from 400nm $TiO_2$ and/or 300nm $ZrO_2$, with comparison to cells without scattering layers to investigate the function of this layer and its optimal composition. In previous work this layer has been made of $ZrO_2$, which is photovoltaicly inactive and an insulating layer between the $TiO_2$ and graphite layers, to prevent transfer of $TiO_2$ conduction band electrons to the graphite. This assumption is investigated and challenged as $TiO_2$ and graphite make a blocking contact. This means the scattering layer can be made of large particles of photovoltaicly active anatase $TiO_2$ allowing for an increased light harvesting ability of the cell.

## 675

### Characterization of Electron Transfer from CdSe Quantum Dots to Nanostructured $TiO_2$ Electrode Using a Near-Field Heterodyne Transient Grating Technique

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Narrow-band-gap semiconductor quantum dots (QDs) have been the subject of considerable interest as the promising candidates for replacing in dye-sensitized solar cells (DSSCs). The use of semiconductor QDs as the sensitizers has some advantages over the use of dye molecules in sensitized solar cell applications. The photoexcited carrier dynamics in QDs, including the electron transfer form QDs to $TiO_2$, are very important for improving the conversion efficiency of QD-sensitized solar cells (QDSSCs). Some studies have been reported on investigating the dynamics using transient absorption and time-resolved photoluminescence techniques. However, such carrier relaxation processses are still poorly understood and more investigations are necessary. In this study, we applied a recently developed near-field heterodyne detection transient grating (NF-HD-TG) technique to investigate the ultrafast carrier dynamics of the chemical bath deposited (CBD) CdSe QDs on nanostructured $TiO_2$ electrodes and on glass substrate. TG technique is a powerful time-resolved optical technique for measurements of various kinds of dynamics. In the NF-HD-TG respoeses, two decay processes were observed. The fast decay one is the reflection of photoexcited hole relaxation due to surface trapping and/or relaxation into intrinsic nanocrystal states. The slow decay one is attributed to photoexcited electron relaxation process, i.e., electron transfer and/or trapping. The slow decay time constants are different for the two kinds of substrates ($TiO_2$ and glass). Since no electron transfer from CdSe QDs to glass substrate could occur, the electron transfer rate from CdSe QDs into nanostructured $TiO_2$ electrodes was estimated to be approximately 5.6 x $10^9$ $s^{-1}$.

## 676

### Crystal growth of CdSe quantum dots Adsorbed on Nanoparticle, Inverse Opal, and Nanotube $TiO_2$ Photoelectrodes Characterized by Photoacoustic Spectroscopy

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There is great interest in the numerous technological applications of $TiO_2$ to photocatalyst, gas sensors, and dye-sensitized solar cells (DSSCs) made from nanostructured $TiO_2$ electrodes. In organic dyes, Ru-based dyes adsorbed on the electrodes with larger surface areas absorb solar light energy more efficiently. To achieve light-havesting efficiency more effectively, semiconductor quantum dots (QDs) have been the subject of considerable interest as a candidate for light harvesters, which are alternative to organic dyes. The use of semiconductor QDs as photosensitizers has some adbvantages for sensitized solar cells. The crystal growth of semiconductor QDs adsorbed on nanostructured $TiO_2$ photoelectrodes is important not only for crystallographic studies but also for improving the photovoltaic efficiency for the solar cells. Only a few general aspects of the growth kinetics of semiconductor QDs were described. In this study, nanoparticle, inverse opal, and nanotube $TiO_2$ electrodes were prepared, becuase the morphologies of the electrodes are important factors for improving DSSC photovoltaic efficiency. These electrodes are then adsorbed with CdSe QDs as photosensitizers to investigate crystal growth. The average diameters of the CdSe QDs can be estimated from the photoacoustic (PA) spectra. PA spectroscopy is a powerful tool for evaluating the optical absorption of opaque and scattered samples. When the adsorption time increases, the CdSe QD diameter increases and then shows saturation. Normal solution growth plus suppression (negative growth) can be obtained by PA analysis. Both of them depend on the morphology of $TiO_2$ electrodes and the final solution concentration for the CdSe QD preparation.

## 677

### Effect of ZnS Coating on the Photovoltaic Properties of CdSe Quantum Dot-Sensitized Solar Cells

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Narrow-band-gap semiconductor quantum dots (QDs) have been the subject of considerable interest as the promising candidates for replacing the sensitizers in dye-sensitized solar cells (DSSCs). The use of semiconductor QDs as the sensitizers has some advantages over the use of dye molecules in sensitized solar cell applications. In this study, we characterize the photovoltaic properties of CdSe QD-sensitized solar cells (QDSSCs) made from $TiO_2$ nanoparticles electrodes. In addition, ZnS was coated on the CdSe QDs and the effect of ZnS coating on the photovoltaic properties were investigated. CdSe QDs were adsorbed onto nanostructured $TiO_2$ electrodes for different times using a chemical bath deposition (CBD) method for QDSSCs applications. The optical absorption and current-voltage characteristics of these devices were investigated. The optical absorption was characterized using a photoacoustic (PA) technique which is a powerful tool for characterizing the optical absorption of opaque and scattered samples, because the PA signal is directly proportional to the thermal energy resulting by nonradiative processes. The size of CdSe QDs increases with the increase of adsorption time and there is an optimum CdSe adsorption time for achieving the best photovoltaic conversion efficiency. The photovoltaic properties of short circuit current intensity, open voltage, and photovoltaic conversion efficiency are significantly improved by surface modification with ZnS. An efficiency as high as 2.02% for the CdSe QDSSC is achived under the solar illumication of 100 $mW/cn^2$.

## 678

### Monolayer Formation of Silicon Quantum Dots from Colloidal Dispersions Using Langmuir Blodgett Technique

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Highly ordered quantum dot (QD) arrays are of interest for use as absorber materials in Hot Carrier solar cells. In such a cell carrier thermalization must be slowed and restriction of specific phonon modes – which can occur in these ordered QD arrays – has been shown to potentially exhibit such slowing of carrier cooling [1]. This project strives to create an ordered monolayer from colloidal dispersions of Si NPs. By means of Langmuir-Blodgett (LB) technique to construct the monolayer and wet chemistry methods to encapsulate the Si NPs with organosilanes, we seek to fabricate a highly ordered Si molecular film.

The LB technique leads to the development of ordered monolayers at an air-water interface using sophisticated apparatus while exploiting the self-organization mechanism of the colloidal dispersion. This unique technique allows transfer of a monolayer onto a wide range of solid substrates such as glass or Si wafers. The spacing between adjacent NPs can be manipulated by varying the alkyl chain lengths of organosilanes that can be bound to the Si NPs, essentially 'capping' or surface passivating the particles.

Work is underway to characterise Si QDs suspended in toluene. Characterisation includes UV-visible spectroscopy to investigate the absorption of the NPs, scanning and transmission electron microscopy to analyse size distribution, alongside photoluminescence to study emission spectra of the NPs. Structural and optical properties will be discussed. Future work includes the formation and characterisation of the constructed Si NP monolayer.

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## 679

### Interactions between Nanocrystal Quantum Dots in the Weak and Strong Coupling Regime

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It has been advocated that nanocrystalline quantum-dot (QD) systems will form the basis of a new generation of solar cells with an efficiency that would exceed the limit of 31 % of a conventional mono-gap solar cell. We believe that QD systems hold promise for the spectral up- and down-conversion of solar light, and perhaps in a full quantum-dot solar cell. For each of these applications, the electronic properties of the individual QD building blocks, and the electronic interactions between them have to be understood and under control.

We have studied the electrostatic and electronic interactions between quantum dots with cryo-TEM, advanced optical spectroscopy and electrical scanning tunneling spectroscopy. Here, we present experimental results which include (1) dipole-dipole interactions between nanocrystals in the ground-state, (2) exciton energy transfer between weakly coupled quantum dots in a QD-molecule, (3) strongly coupled hetero-nanocrystals with charge-separated excitons and (4) variable quantum mechanical coupling between PbSe QDS assembled in a QD solid. The relevance of these results for applications in third-generation cells will be highlighted.

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## 680

### Dye-Sensitized Solar Cells Based on ZnO Prepared by Sol-Gel Processing

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Zinc oxide is a promising material for dye-sensitized solar cells (DSSCs) due to its electronic structure and transport properties, and cells with efficiencies up to 5% have been reported. In order to achieve high efficiency cells, the ZnO nanomaterials properties need to be optimized, which requires a thorough understanding of the synthesis process. We have used sol-gel processing under a variety of experimental conditions to obtain ZnO nanomaterials for application in DSSCs.

In this work, we present two methods for the controlled synthesis of ZnO nanomaterials from ethanol solutions and zinc acetate: forced hydrolysis (with addition of water and NaOH) and auto-hydrolysis (with addition of only water). Special care was taken in preparing ZnO nanopowder due to the tendency of particle growth upon washing and drying. The nanomaterials were characterized using X-ray diffraction and transmission electron microscopy. In both methods, the ZnO nanoparticles size can be controlled in the range of 10 - 30 nm, by changing concentration, time, and temperature.

ZnO nanoparticles of different size, prepared by the two methods, were applied in DSSCs, using both commercial dye (N-719) and organic dyes, such as mercurochrome and eosin-Y. The cell efficiency is strongly dependent on the ZnO synthesis method, dye chemistry, dye sensitization time, and solution chemistry. With N-719 an efficiency of 2% was obtained, while with organic dyes the efficiency was close to 1%. The efficiency is expected to increase by optimizing the cell components.

# 681

## Photovoltaic Performance of Colloidal Zinc Oxide Sensitised with Xanthene Dyes

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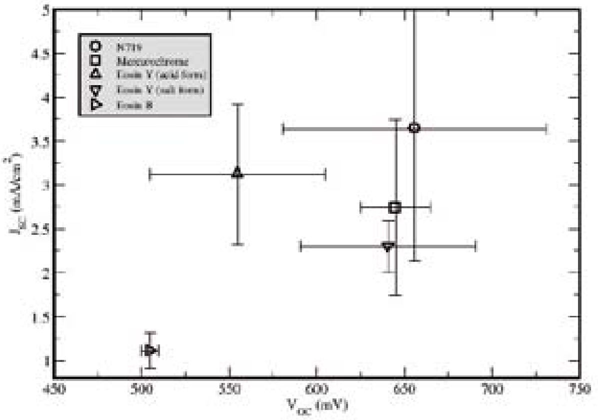
Titanium dioxide is by far the most utilized semiconductor for dye-sensitized solar cells (DSSCs). However, in the last years zinc oxide has been also studied as an interesting alternative to $TiO_2$. ZnO presents similar photoelectrochemical and transport properties to $TiO_2$. Nevertheless, the efficiency of ZnO-based solar cells still remains far from their $TiO_2$ counterparts.

The low performance of ZnO cells has been attributed to poor sensitisation with the most common Ruthenium-based dyes. In addition to that, it has been reported that ZnO performs particularly well when sensitised with organic dyes. These dyes have the advantages of being much cheaper than those based in a precious metal such as ruthenium.

In this work, the photovoltaic properties of nanostructured ZnO electrodes sensitised with xanthene dyes are explored. We have used Eosin-Y, Eosin-B and Mercurochrome and compared their performance with respect the N719 Ruthenium dye. We observe that these dyes sensitise efficiently commercial ZnO nanopowder and yield efficiencies that are, in general, more than a half of those provided by N719. We have prepared polymer-sealed cells and measured the stability of the devices under 2-sun illumination at short circuit. They show very good stability properties.

In summary, the combination of a versatile metal oxide as ZnO and cheap organic dyes similar to those utilized in this work should be considered as a promising alternative in the field of dye-sensitised solar cells.



# 682

## Numerical Model for Charge-Transport and Recombination in Dye-Sensitized Solar Cells: Short-Circuit Current Versus Cell Thickness and Open-Circuit Voltage Versus Time

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Dye-sensitized solar cells (DSC) are based on a porous, nanostructured metal oxide film sensitized by a dye with a large absorption coefficient in the visible. The transport properties of the solar cell are complicated as both the electron diffusion coefficient in the metal oxide film and the lifetimes are generally found to be dependent on electron density. Electron transport is usually assumed to be limited by trapping and de-trapping of electrons in states in the band gap. Recombination corresponds to the process of transfer of photogenerated electrons to acceptors in the solution or to oxidized dye molecules, leading to a decrease in the efficiency of the cell. The continuity equation describing these processes consists of a second order, non-linear differential equation which cannot be solved analytically.

In this work, we have extended a previous numerical model [J. Phys. Chem. B, 2006, 110, 5372], suitable to obtain current-voltage characteristics under these premises. We pay especial attention to the recombination mechanism and study two alternative models: electron transport limited and electron transfer limited recombination. We obtain mathematical expressions to reproduce experimental open-circuit voltage decays and discuss their relationship to the 'quasi-static' approximation of Walker et al. [J. Phys. Chem. B 2006, 110, 25504]. The model is also used to make theoretical predictions on the thickness dependence of the short-circuit current [Ito et al. Adv. Mater. 2006, 18, 1202].

# 683

## Photoelectrochemical Properties of Highly Porous Titania Films Electrodeposited from Ti-Alkoxide Solutions

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Electrodeposition is a convenient method for the preparation of $TiO_2$ films on conductive substrates, e.g. for dye-sensitized solar cells (DSSC). A recently proposed method [1] employs basic Ti(IV)-alkoxide solutions containing hydroquinone, which is oxidized to benzoquinone, generating protons that induce the precipitation of Ti(IV)-oxo-hydroxide. Benzoquinone is incorporated into the films, providing conducting pathways and thereby promoting film growth. Calcination of the films results in formation of crystalline $TiO_2$ and removal of the benzoquinone, leading to pore formation. Utilization of other proton suppliers (e.g. 2-methyl-hydroquinone) allows for pore size variation [2].

We have now studied the influence of the calcination temperature on the DSSC performance of the films. Higher temperatures lower the porosity of the films by grain coarsening, decreasing the dye loading capacity, whereas the electron collection efficiency increases as confirmed by intensity modulated photocurrent / photovoltage spectroscopy. Due to these contrary effects the efficiency reaches its optimum at a calcination temperature of 500°C (Figure 1a). The main limiting factor in DSSC performance for these films was found to be the low film thickness of less than 1 µm. Since thicker films deposited in a single step tend to be unstable, we developed a layer-by-layer deposition method with intermediate calcination steps, by which the efficiency could be increased (Figure 1b).

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[2] K. Wessels, M. Maekawa, J. Rathousky, T. Yoshida, M. Wark, T. Oekermann, Micropor. Mesopor. Mater., in press.

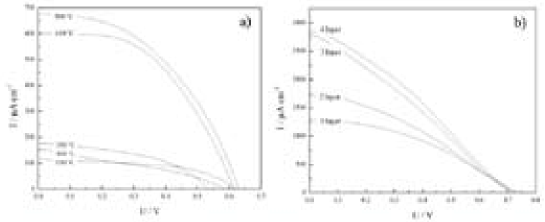

Figure 1: UI-Curves of DSSCs prepared from $TiO_2$ films deposited from tetraisopropylorthotitanate and HQ. Films were calcined at different temperatures (a) or deposited in several layers (b).

## 684

### Effect of Self-Organization:P3HT as a Hole Conductor in Dye-Sensitized Solar Cells

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**Sten-Eric Lindquist,** *CSIRO Energy Technology, Australia*

Objective: Dye-sensitized solar cells (DSSC) have attracted much attention due to their low cost, easy fabrication and high energy conversion efficiency. However, the traditionally used liquid electrolytes make the sealing and long-term stability of DSSC problematic. Poly-3-hexyl-thiophene (P3HT), a hole conductor, was used in this study to substitute liquid electrolytes. The effect of self-organization of P3HT was studied by varying the experimental conditions.

Methods: Porous $TiO_2$ films were deposited on FTO glass and sintered. N3 dye was adsorbed onto $TiO_2$ films from ethanol solution. P3HT was dissolved in different solvents and deposited onto $TiO_2$/dye anodes by spin-coating. The drying process of P3HT layers was varied by controlling temperature, time, atmosphere, etc. Al counter-electrodes were deposited by evaporation. All cells were tested by a solar simulator with AM 1.5G illumination.

Results: It is found that different drying processes have dramatic influence on the performance of DSSC. The reason for the performance variations are related to the self-organization of P3HT film, which can be demonstrated by UV-vis spectra. The optimized drying process renders highest efficiency in DSSC.

Conclusions: The relationship between DSSC performance and self-organization of P3HT films can be explained by hole transport effectiveness. P3HT is a polymer with long chains. For the randomly arranged P3HT chains, holes can easily be recombined before reaching the counter-electrode, while they are more likely to transport freely and contribute to external current in an ordered P3HT film. High performance DSSC can be achieved by the effective hole transport.

## 685

### Research and Development for Cost-effective and Durable-reliable Dye-sensitized Solar Cells

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Taking into account the importance of fill factors and cost effectiveness for fabrication of large DSC modules, a research and development for utilization of aluminum metal sheets as grid-free conductive anode substrates was undertaken. Passivation of aluminum metal sheet with nano-order chromate-phosphate surface treatment and formation of highly porous nano-$TiO_2$ layer lead to conversion efficiencies of more than 5% (5x5cm) under illumination from cathodes. One of the fabricated DSC showed more than 7 months stability. These facts were rationalized by successful prevention of electron leakage from substrates, and corrosion resistance to iodine. In establishing production process, development of a new adhesive sealant having durability in the wide temperature range (up to 85 degrees C from -45 degrees C) and construction of a prototype machine for the dye adsorption process after gluing was achieved.

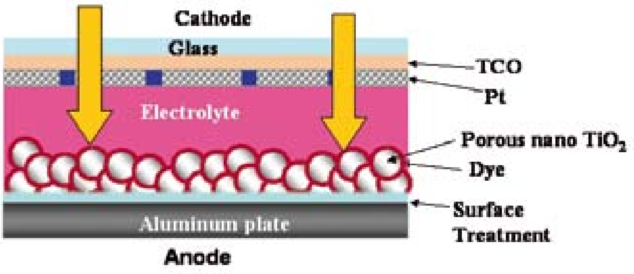

Figure Structure of Aluminum DSC

## 686

### Self-Assembly of End-Functional Silicone Coupling Agent in PEO/P(VDF-HFP)/$SiO_2$ Nanocomposite Polymer Electrolyte DSSC

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**Sheng Xu,** *Department of Physics, Wuhan University, China*
**Ying Yang,** *Department of Physics, Wuhan University, China*
**Conghua Zhou,** *Department of Physics, Wuhan University, China*
**Hao Hu,** *Department of Physics, Wuhan University, China*
**Bolei Chen,** *Department of Physics, Wuhan University, China*
**Xingzhong Zhao,** *Department of Physics, Wuhan University, China*

End-functional silicone coupling agent (dodecyl-trimethoxysilane, DTMS in short) was used to modify the PEO/P(VDF-HFP)/$SiO_2$ nanocomposite polymer electrolyte (CPE in short) and the effects of different amount DTMS modification were studied. The experiments showed the silicone coupling agent with hydrophobic alkyl chains ($-C_{12}H_{25}$) self-assembled on the $SiO_2$ nanoparticles, and the formation of the Si-O-Si cross-linked network in the new nanocomposite polymer electrolyte. Proper content of DTMS modified CPE exhibited improved ionic conductivity and the connection with the photoanode and counter electrode. However, too much content of the DTMS modification changed the conformation of the polymer network and deteriorated the ionic movement. Compared with the performance (3.84%) of original DSSC, the DSSC with functional silicone coupling agent self-assembled CPE (DTMS:$SiO_2$=2:1, mol ratio) exhibited improved Jsc (7.94mAcm$^{-2}$), Voc (0.624V) and the optimal efficiency (5.2%) (measured at AM1.5, light intensity of 58.4mWcm$^{-2}$). The Voc of the silicone coupling agent modified polymer electrolyte DSSC is improved obviously, which is mainly due to the hydrophobic alkyl chain end groups formed an insulate layer that retarded the electron recombination at the $TiO_2$ nanoporous photoanode/polymer electrolyte interface. The DTMS:$SiO_2$=2:1 modified CPE type DSSC exhibited performance of 6.42% at light intensity of 32.1 mWcm$^{-2}$ and 4.94% at 99.2 mWcm$^{-2}$.

## 687

### Highly Sensitive Optical Oxygen Sensing Material Based on the Platinum(II) Dinuclear Complex Immobilized onto Anodic Oxidized Aluminum Film

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**Naoko Araki,** *Nara Women's University, Japan*
**Isamu Kinoshita,** *Osaka City University, Japan*
**Makoto Obata,** *Nara Women's University, Japan*
**Shigenobu Yano,** *Nara Women's University, Japan*

The series of platimun(II) dinuclear complexes were synthesized for new optical oxygen sensing material instead of conventional platinum porphyrins. An optical oxygen-sensing activity of anchored platimun(II) dinuclear complexes on ordered anodic oxidized aluminum film was studied in relevance to development of new oxygen-sensing systems. The luminescence intensity of platinum(II) dinuclear complexes onto anodic oxidized aluminum film decreased with increasing oxygen concentrations. The response time for the change of the atmospheric gas from oxygen to argon in platimun(II) dinuclear complex on ordered anodic oxidized aluminum film was faster than that of the sensor device based on the conventional platinum porphyrins.

## 688

### Preparation of $SrTiO_3$-Coated $TiO_2$ Electrodes and their Application in Dye-Sensitized Solar Cells

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A $TiO_2$ electrode coated with a thin film of $SrTiO_3$ was synthesized for photoelectrochemical application.

The $TiO_2$ colloidal solution was prepared by grinding in a mortar with a pestle 6 g of $TiO_2$ powder in 2 ml of distilled $H_2O$ and 0.2 ml of acetylacetone; the substances were ground for 40 min. Finally, 8.0 ml of distilled water and 0.1 ml of Triton X-100 were slowly added with continuous mixing for 10 min. Several drops of this solution were spread onto the electrode surface using a glass rod. The electrode was dried in air and fired at 450 oC for 30 min, cooled to 70 oC and then immersed in a 0.5 X 10-3 mol L-1 ethanolic solution of the sensitizer dye cis-bis (isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxilic acid) – ruthenium (II), Ruthenium-535 from Solaronix for 16 h at room temperature. The gel polymer electrolyte based on poly (ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidylether) / P(EO-EM)78:22, g-butyrolactone as plasticizer, 12-crown-4 ether, LiI and I2 was prepared.

The results indicate that the $TiO_2$-$SrTiO_3$ core-shell electrodes provide a significant increase in photovoltage resulting in a 10% improvement of the conversion efficiency of the solar cell.

## 689

### Synthesis of Nanostructured Photocatalysts and their Enhanced Photoactivities

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Nanosized photocatalysts have attracted much attention because of their unique physical properties, such as large surface area, small particle size and good crystallinity, which are closely related to better photocatalytic activity. To date, soft chemical process has become a promising method for the direct preparation of functional nanostructures since it generates highly crystalline products with high purity, narrow size distribution, high surface area and low aggregation. Meanwhile, the morphology and crystal form of the products can also be controlled by adjusting the reaction conditions.

In this study, we reported the selectively synthesis of nanostructured photocatalyst from hydrothermal process, taking $SrSnO_3$ as an example. With a simple adjustment, $SrSnO_3$ nanostructures with dumbbell-like and rod-like morphologies were successfully synthesized. Besides simple experimental procedures, their chemical and physical properties, such as surface and photocatalytic properties etc., have also been studied in detail and systematically. Moreover, the formation mechanism and the relationships between nanostructures and photocatalytic properties of catalysts were investigated detailed. The as-prepared $SrSnO_3$ nanostructures were found to show much higher activity for water splitting than the bulk sample from the solid state route under UV-vis light irradiation. We have also adopted the similar approach to fabricate other oxide photocatalysts, such as $PbSnO_3$, $WO_3$ etc., and have achieved enhanced activity for organic degradation. These results highlight that the shape-controlled synthesis of catalyst with favorable photocatalytic properties is a promising strategy to develop highly efficient catalysts. It is expected to design and synthesize some photocatalysts with enhanced photocatalytic activity from the soft chemical process.

## 690

### Photoelectron Transport Properties of Mesoporous Titanium Dioxide Films

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**Huijun Zhao,** *Australian Rivers Institute, Griffith University, Australia*
**Ken Chiang,** *ARC Centre of Excellence for Functional Nanomaterials, The University of New South Wales, Australia*
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Mesoporous titanium dioxide films have attracted attention in recent years due to their potential application in electrochromic devices, sensors, photocatalysis and solar cells. Such material possesses large effective surface area and pore volumes which facilitate educt/product transportation into/out of the structure. This, in turn, leads to enhanced reactivity. On the other hand, the porous nature of the material constitutes an unexpected high resistance for electron transport across the semiconductor network and impedes the electron collection efficiency of the films. In this work, mesoporous titanium dioxide films were synthesized via a sol-gel method. The surface area and porosity of the films were adjusted by varying the humidity during dip-coating process. The photoelectrocatalytic activity of the films towards water and organic contaminants were quantitatively evaluated in a photoelectrochemical cell. The photoelectrocatalysis reactions resistance was measured and used to express the electron transport characteristics of the films.

## 691

### Synthesis of Nano-Crystalline $TiO_2$ by Sol-Gel Combustion Hybrid Method and its Application to Dye Solar Cell

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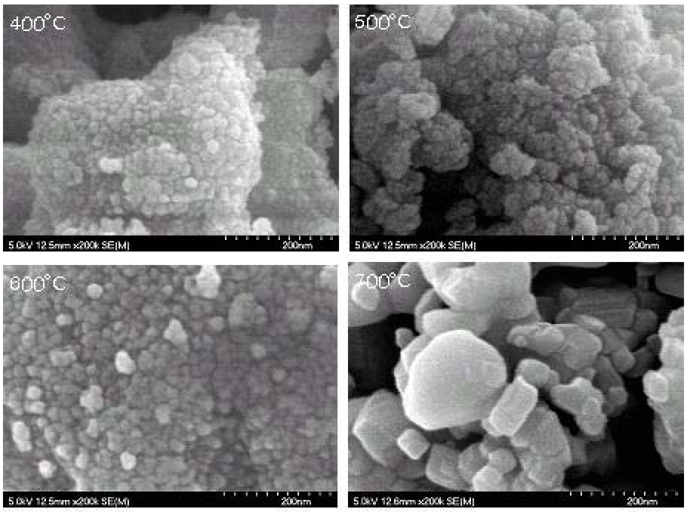
**Jihye Gwak,** *Korea Institute of Energy Research, Korea*

Sol–gel combustion is a novel method, with a unique combination of the chemical sol–gel process and the combustion process. Sol–gel combustion method is based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and inorganic fuel like acetylene black, giving a voluminous and fluffy product with a large surface area. This process has the advantages of inexpensive precursors, a simple preparation method, and a resulting nano-sized powder.

$TiO_2$ has been widely used in various devices such as dye solar cells, photocatalysts, photochromic glasses, self-cleaning of windows, and gas sensors. $TiO_2$ nano-powders were synthesized employing a new route sol-gel combustion hybrid method using acetylene black as a fuel. The dried gels exhibited auto-catalytic combustion behavior. Anatase structure $TiO_2$ nano-powders with narrow size distribution were obtained at 400 ~ 600°C. Crystal structures were examined by powder X-ray diffraction and particle morphology as well as crystal size was investigated by scanning electron microscopy. The size of nano-powder was found to be in the range of 10 nm to 20 nm. $TiO_2$ powders synthesized at 500°C and 600°C were applied to dye solar cell. A solar energy to electricity conversion efficiency of 5.2% was attained under AM 1.5 irradiation (100mW/cm$^2$) using a novel $TiO_2$ nano-powder synthesized by sol-gel combustion hybrid method at 500°C.



## 692

### Energy Migration and Excimer Formation in Discotic Liquid Crystalline Derivatives: Dibenzo[a,c]phenazines

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**Chun-Che Lee,** *Taiwan*
**Yu-hung Chuen,** *Taiwan*
**Chin-Feng Su,** *Taiwan*
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**Wen-Yao Huang,** *National Sun Yat-Sen University, Taiwan*

Synthesis and characterization of three novel discotic liquid crystalline derivatives of dibenzo[a,c]phenazine (DBP), substituted at the periphery by four n-hexyloxy chains and a chain of N-alkylene carbazol carboxy group (nC-CAB) containing 3, 6, 11 different carbon chain length are described in this study. All new compounds were characterized by 1H, 13C-NMR, MASS, UV-Vis and PL spectroscopy. Preliminary mesophase characterization is carried out by differential scanning calorimeter (DSC) and polarized optical microscopy (POM). The concentration study of the discotic liquid crystals in dilute solutions shows that all three compounds possess two absorption bands at 335 and 420 nm, which are almost independent of concentration. However, PL spectra operate in different ways. At lower concentrations (less than 1.25 ppm), time resulted PL spectra show that there are three main bands at 375, 480 and 520 nm, which could be ascribed to emissions from carbazole, dibenzo[a,c]phenazine and their complex, respectively. In addition, each band in every compound presents a different decay mode, i.e. emissions from various excitons. In contrast, at higher concentrations (higher than 5 ppm), only a red-shifted broad band at 575 nm is observed, and lifetime study shows it is a single exponential decay. The result of concentration study indicates that the influence of molecular association was shifted from intra-molecular interaction to inter-molecular interaction when concentration was increased from 1.25 ppm to 5 ppm.

## 693

### Novel Arylene Ether Polymers for Flexible Substrates

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**Tzu-I Tsao,** *Taiwan*
**Kuan-Lung Huang,** *Taiwan*
**Mei-Ying Chang,** *Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Taiwan*
**Wen-Yao Huang,** *National Sun Yat-Sen University, Taiwan*

Three novel 2-trifluoromethyl-activated bisfluoro monomers have been synthesized successfully using a Suzuki-coupling reaction of 4-fluoro-3-trifluoromethyl phenyl boronic acid with 4,4’-dibromo-p-terphenyls with varied phenyl substitution on the middle phenylene ring. Three monomers were converted to a series of phenyl substituted poly(arylene ether)s by nucleophilic displacement of the fluorine atoms on the benzene ring with 1,1 dihydroxydiphenyl cyclododecane. Thermal analysis studies indicated that these polymers did not show melting endotherms but showed ultrahigh Tg values up to 320°C in DSC and good thermal stability up to 460°C for 5% weight loss in TGA under nitrogen atmosphere. These polymers are soluble in a wide range of organic solvents. Transparent and flexible films were easily prepared by solution casting from chloroform solution of each of the polymers. The UV absorption spectra of thin films showed no absorption and transparencies greater than 90% in the visible light region of the spectrum. The refractive indexes of these polymer thin films were identified by an elipsometer, proving non-birefringence; the measured surface contact angles and estimated surface energies implied that there are weak polarities and hydrophobic properties. According to the above-mentioned results, polymers constructed from poly arylene ethers with high transparencies within the range of visible light, good thermal stabilities (high Tg), low polarities, and hydrophobicities were successfully prepared. This reveals the great potential of such materials in industrial applications, such as plastic substrate for devices.

## 694

### Plastic Film-type Dye-sensitized Solar Cell of High Durability with Using Ionic Liquid Based Electrolyte

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**Tsutomu Miyasaka,** *Toin University of Yokohama, Japan*

Improvement in durability of dye-sensitized solar cell (DSC) is very important subject for the practical usage. We have developed plastic film type DSC based on flexible polyethylenenaphthalate (PEN) film for heading for practical applications such as ubiquitous power sources.

Usually, DSC has an organic liquid electrolyte containing iode/iodine redox couple. Volatile organic electrolytes often decrease the durability, and therefore, many researchers have tried to replace them with solvent having higher boiling point, and also with ionic liquid.

We have been investigating organic solvent-based electrolyte as well as ionic liquid based electrolyte from the view point of durability for plastic film type DSCs. As a result, a plastic film DSC consisting of propylenecarbonate-based electrolyte maintained its energy conversion efficiency of 2% over 220 hours under a condition of 55°C and 95% relative humidity. One of key materials damaging plastic DSC under durability test is lithium iodide, which damages ITO layer on plastic substrate. And therefore, we have succeeded to improve durability a plastic film type DSC by using ionic liquid based electrolyte without containing lithium iodide.

## 695

### Photoelectrochemistry of Au(core)-CdS(shell) Composite Nanoparticles-Loaded TiO$_2$ Films

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**Tomokazu Kiyonaga,** *Kinki University, Japan*

Au nanoparticle (NP) with strong surface plasmon absorption is an attractive alternative to organic photosensitizers in dye-sensitized solar cells with a view to long-term stability. However, Au NPs absorb only a part of visible light, while the energy of the infrared region occupies over 50% of the total solar energy. We have found that the absorption in the infrared region of Au NPs loaded on TiO$_2$ films drastically increases by forming CdS nanolayers on the Au NPs (Au@CdS/TiO$_2$). In this study, the photoelectrochemical properties of Au@CdS/TiO$_2$ were examined to use as a photoelectrode for solar cells. Au NPs were loaded on sol-gel TiO$_2$ films by a deposition-precipitation method (Au/TiO$_2$). Further, CdS nanolayers were formed selectively on the Au NPs of Au/TiO$_2$ by the photodeposition from an ethanol mixed solution of cadmium perchlorate and elemental sulfur. Figure 1 compares the visible light-induced photocurrent response of Au/TiO$_2$ and Au@CdS/TiO$_2$. Anodic photocurrents are observed for Au/TiO$_2$ and Au@CdS/TiO$_2$, whereas no current flew in the TiO$_2$ system. Also, the photocurrent of Au@CdS/TiO$_2$ is much greater than that of Au/TiO$_2$. This finding may be explained partly in terms of the increase in the absorption strength in the infrared region with the formation of CdS shell layer. The application of Au@CdS/TiO$_2$ to solar cell is currently under investigation.

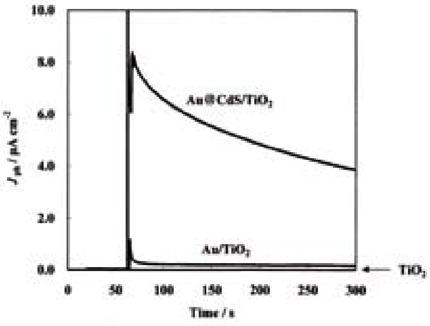

Figure 1. Visible light-induced photocurrent response.

## 696

### Photostability of Rhodamine 6G

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**Shunsuke Ohashi,** *Institute of Materials Science, University of Tsukuba, Japan*
**Masami Kobayashi,** *Institute of Materials Science, University of Tsukuba, Japan*

Rhodamine 6G is a xanthene dye with high fluoresce quantum yield, and hence it has been used for organic-dye laser and organic light-emitting diode. Rhodamine 6G is, however, very unstable for continuous light irradiation in acetone and water. We demonstrated that rhodamine 6G in acetone was stabilized by addition of *t*-butyl-4-hydroxyanisole (BHA) without decrease of fluoresce intensity. Rhodamine 6G in acetone was not stabilized by β-carotene. These results suggest that instability of rhodamine 6G in acetone was caused by not active oxygen but some radical species produced by light irradiation. Rhodamine 6G was found to be remarkably stable in acetone/water (1/1, v/v), where *gem*-diol was generated. The formation maximum of *gem*-diol was estimated to be performed when the ratio of acetone/water = 1/1 (v/v) from the viewpoint of equilibrium reaction. Therefore rhodamine 6G in acetone/water = 1/1 was stabilized by *gem*-diol. High stability of rhodamine 6G in ethanol and methanol also support the hypothesis.

## 697

### Direct Electron Transfer From Living Bacteria to Semiconductor Materials

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Current generation from living microorganisms was first discovered by Potter over 90 years ago 1. This phenomenon is now attracting significant attention from the viewpoint of their potential application to the bacteria based fuel cell. In this fuel cell electricity are generated in the course of bacterial metabolisms using organic pollutants as well as varieties of renewable biomass as a energy resources. Besides the effective utilization of renewable energy, bacterial abilities of self-reproducing and self-renewing offers the long-term fuel cell operation, making this system distinct from the well-developed hydrogen- and methanol- driven fuel cell. Despite above mentioned the great potencies, MFC has not attracted much attention mostly due to its low current density. Furthermore, there are few reports on the mechanisms of interfacial-electron transfer between bacteria and electrodes. Here we report the electron transfer from metal reducing bacteria to the metal and also semiconductor electrodes (graphite, ITO, $\alpha$-$Fe_2O_3$, and $WO_3$). It was confirmed that the metal reducing bacteria can inject the electrons into the conduction band of $Fe_2O_3$ and $WO_3$ in the course of metabolisms, but not for $TiO_2$. This is first observation of direct electron transfer from living bacteria to semiconductor electrodes.

Reference:

[1] M.C.Potter, Proc. Univ. Durham Phil. Soc., 1910,3, 245-249

## 698

### Tuning the Pore Size of Electrodeposited ZnO Films for Dye-Sensitized Solar Cells

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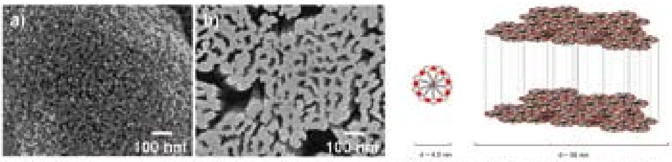
**Keigo Ichinose,** *Environmental and Renewable Energy Systems (ERES) Division, Graduate School of Engineering, Gifu University, Japan*
**Tsukasa Yoshida,** *Environmental and Renewable Energy Systems (ERES) Division, Graduate School of Engineering, Gifu University, Japan*

ZnO films can be electrodeposited cathodically from aqueous zinc salt solutions in the presence of oxidants like $O_2$. The electrodeposition of nanoporous ZnO was first demonstrated using water-soluble organic dye molecules with anionic groups, which adsorb on the growing ZnO surface, as additives. Especially the dye eosin Y as additive was found to cause a high porosity. In this study we have varied the pore size of the eosin-templated films by addition of anionic surfactants and variation of the supporting salt and its concentration.

The cations of the supporting salt interact with the dye molecules in the electrodeposition bath in competition to dye interaction with the ZnO surface. Consequently, more dye molecules are incorporated in the films at lower supporting salt concentrations. The incorporation of more dye molecules in turn leads to a finer porous structure of the ZnO, i.e. the formation of smaller pores and ZnO domains. The same effect is achieved by use of larger cations.

A significant increase in the pore size could be achieved by the use of cationic surfactants in combination with anionic eosin Y. Surfactant-dye interaction causes the formation of large aggregates, leading to pore sizes of up to ca. 50 nm (see figure), which would for example enable an easier pore filling for the preparation of solid-state solar cells. Interestingly, the surfactant without the dye does not lead to the formation of porous ZnO at all, showing the importance of the anionic group in eosin Y for interaction with the ZnO.



Left:SEM micrographs of ZnO films deposited with a) eosin Y (EY), b) EY + n-dodecyl pyridinium chloride (NDPC). Right: Model of possible formation of EY / NDPC aggregates.

## 699

### Characterization of Electrodeposited P-Type CuSCN Films Towards their Application in Solid-State Dye-Sensitized Solar Cells

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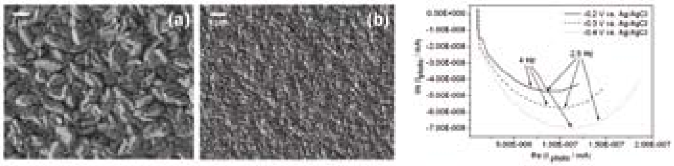
One approach to improve the stability of dye-sensitized solar cells (DSSC) is the substitution of the liquid electrolyte by a p-type semiconductor. Our goal is the fabrication of such dye-sensitized p-n solar cells at low temperature by electrodeposition. ZnO is a promising n-type material, since highly porous ZnO films with excellent electron collection characteristics can be electrodeposited at low temperature using structure-directing additives. In this study, electrochemically deposited CuSCN films were investigated towards their applicability as p-type component in our concept.

CuSCN films were deposited from solutions of $Cu(ClO_4)$ and LiSCN in ethanol/water mixtures at 0°C and at potentials between 0.4 V and -0.4 V vs. Ag/AgCl. The film morphology was studied by scanning electron microscopy, since the formation of small CuSCN particles is necessary to achieve efficient pore filling of dye-sensitized ZnO films. It was seen that lower deposition potentials (left figure), a higher fraction of ethanol in the solvent and the addition of surfactants added to the deposition solution decreased the particle size.

Electron transport and back reaction in the dye-sensitized CuSCN films have been studied by intensity modulated photocurrent and photovoltage spectroscopy. Low $f_{min}$ values with almost no dependence on the applied potential prove that porous CuSCN films have been formed (right figure). Hole lifetimes more than one order of magnitude higher than transit times indicate efficient hole collection. A flatband potential of -0.05 V and donor density of $4.3*10^{-17}$ $cm^{-3}$ of the CuSCN films were determined by Mott-Schottky plots derived from electrochemical impedance spectroscopy.



Left: SEM micrographs of CuSCN films deposited from ethanol / water (3:1) solution at (a) +0.2 V vs. Ag/AgCl, (b) -0.4 V vs. Ag/AgCl. Right: Complex plane IMPS plots measured at different electrode potentials.

## 700

### Study of Luminescent Rare-Earth Doped and Co-Doped Y2O3 Nanocrystals for Potential Bio-Imaging Applications

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The endeavor to develop novel fluorescent nanomaterials in the fields of nanobiotechnology, photonics and optoelectronics has been burgeoning in the past decade. The synthesis of rare earth compound nanocrystals has attracted considerable attention due to their potential applications in biological chemical probes and medical diagnostics. Rare earth (RE) compound nanocrystals have many advantages as biolabels due to their large Stokes shift, sharp emission spectra, long lifetime, multiphoton and up-conversion excitation, reduced photobleaching and low toxicity over semiconductor nanocrystals like quantum dots and organic phosphors molecule.

The current work reports the synthesis, characterization and bio-functionalization of rare-earth (RE) doped and co-doped Y2O3 nanocrystals for potential bio-imaging application. We have used other RE dopants such as europium (Eu), erbium (Er) and ytterbium (Yb). These RE ions are successful doped, and Er-Yb co-doped into Y2O3 nanocrystals. Room temperature photoluminescence (PL) spectra showed characteristic emission peaks of Tb, Eu, Er, Yb ions doped and Er-Yb co-doped Y2O3 samples at 255 and 365nm excitations. Co-doped samples showed enhanced PL intensity which is attributed to the presence of a sensitizer. By varying RE concentrations in the range of 0.2 - 20mol%, it was observed that 5mol% dopant PL intensity was the highest in both cases (see Figure). The nanocrystals were surface functionalized with amine (NH2) group via reverse microemulsion method to render the nanocrystals highly water soluble and also afford them further functionalization by other molecules for potential bio-imaging applications. Cytotoxicty of the modified nanocrystals was also investigated. The current nanomaterials have demonstrated potential in Bioimaging.

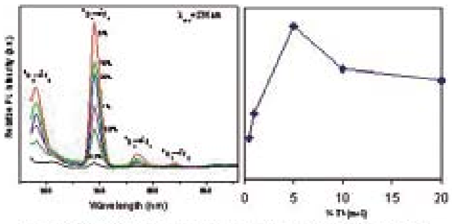

**Figure** Effect of dopant concentration variation on PL for $Y_2O_3$: Yb, Er

## 701

### Photocapacitor; Improvement of Discharging Property to Support Ruthenium Oxide into Activecarbon for Electric Storage Material

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We have first constructed a photo-rechargeable solar cell named photocapacitor. The three-electrode type photocapacitor comprises a dye-sensitized mesoporous $TiO_2$ electrode, two carbon-coated electrodes, and two liquid electrolytes. The three-electrode type photocapacitor is very easy to improve electro-generation and storage layers independently. One of the methods to improve the storage layer is modification of capacitance of the electric storage materials. Both active carbon and ruthenium oxide are well known to use as the material of electrochemical capacitors, which have different electric storage mechanisms. To combine use with both materials by introducing ruthenium oxide into active carbon, it is expected to improve the capacitance of electric storage material of photocapacitor. In this study, we try to use composite material as the electric storage material. The result showed that the capacitance was greatly improved, and these made output energy about 1.5 times larger.

## 702

### Preparation and Photochemical Properties of Highly Luminescent ZnS-AgInS2 Solid Solution Nanoparticles

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Semiconductor nanoparticles, such as CdSe and CdTe, have attracted much attention, because they exhibit the intense band gap emission and the peak wavelength can be adjusted by controlling particle size. In this paper, we report the preparation of novel ZnS-$AgInS_2$ solid solution (ZAIS) nanoparticles and their photochemical properties.

ZAIS nanoparticles were synthesized by the thermal decomposition of $(AgIn)_xZn_{2(1-x)}(S_2CN(C_2H_5)_2)_4$ precursors in a hot oleylamine solution (180 °C). The resulting suspension was subjected to centrifugation to remove large particles. ZAIS nanoparticles were separated from the supernatant by addition of methanol.

TEM observation revealed that spherical nanoparticles having clear lattice fringes were formed regardless of the chemical composition of precursors. The average sizes were determined to be 4.4, 4.4 and 4.1 nm at x=1.0, 0.6 and 0.4, respectively. X-ray powder diffraction analyses revealed that the fraction of ZnS in ZAIS nanoparticles was enlarged with an increase in the content of Zn in the precursors used. The particle surface was covered by oleylamine to prevent the coalescence between nanoparticles. The absorption onset of particles were blue-shifted from ca. 700 to ca. 500 nm with a decrease in x, indicating that the energy gap was enlarged with an increase in the fraction of ZnS in solid solution. The ZAIS nanoparticles exhibited intense photoluminescence at room temperature. The peak wavelength of PL was adjustable between 720 and 540 nm, depending on the composition of precursors used. The highest quantum yield of ca. 24% was obtained for ZAIS nanoparticles prepared with x= 0.86.

## 703

### Electrical and Optical Properties of $BiVO_4$ Photo-Catalysts

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With a bandgap of 2.4 eV, $BiVO_4$ is an interesting material for photocatalytic applications in the visible part of the spectrum.[1] We report on the photo-electrochemical performance of doctor-bladed films of 0.5 μm $BiVO_4$ particles. Addition of methanol to the solution results in a significant increase of the anodic photocurrent (Figure 1), and values of up to 20 μA/cm² were observed under AM1.5 illumination. When annealing $BiVO_4$ pellets in air at 700°C, sintering of the particles occurs and the color of the material changes from bright yellow to reddish/pink. This can be explained by evaporation of Bi or $V_2O_5$ from the $BiVO_4$ lattice, since both these species have fairly high vapor pressures ($>10^{-4}$ torr at 500°C). This results in the formation of oxygen vacancies which form energy levels deep in the bandgap. The reddish/pink color is attributed to optical excitations involving these energy levels. When crushing the fired pellet in a mortar, the material reverts back to its original yellow color. This is consistent with oxygen vacancies being re-filled by atmospheric oxygen, since $BiVO_4$ is also known for its high oxygen ion conductivity. Electrical conductivity measurements show an activation energy of 0.23 eV, indicating that electron transport occurs via a hopping mechanism. The conductivity remains constant as a function of $p(O_2)$, indicating that oxygen vacancies are not the main defect in this material.

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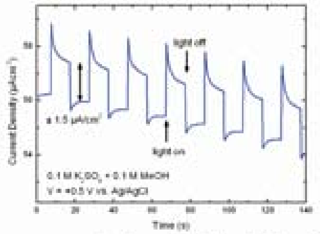

*Figure 1. Photo-current response of a doctor-bladed film of 0.5 μm $BiVO_4$ particles on transparent conducting glass.*

## 704

### Band-Gap Engineering of Layered Transition Metal Oxides and their Photocatalytic Properties

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The global concern over the declining fossil fuels and global warming has seen great efforts being directed toward the development of new energy generation /conversion systems. Innovative materials for energy conversion hold the key for renewable energy production. The ability to design these nanomaterials with tailored structures and functionalised properties is an important challenge that researchers strive to meet. Aimed at developing new nanostructures for visible light driven photcatalytic air/water pollutant decomposition and photo-current generation, we have recently developed the synthesis, band-gap modification, exfoliation and re-assembly of several types of layered transition metal oxides including titanate and niobate-based pervoskites. The successful exfoliation of these layered structures led to the formation of colloidal suspensions containing paper-like individual metal oxide nanosheets. These unique nanosheets can be surface and/or structural modified into ideal two-dimensional building blocks for new nano-architecture fabrication. The layer-by-layer self-assembly and flocculation of nanosheets via electrostatic interaction led to multilayer ultrathin films and restacked nanoporous structures. These newly-developed nanostructures showed excellent visible light photocatalytic performance and promising electrochemical conversion activities.

## 705

### Anatase $TiO_2$ Single Crystals with a Large Percentage of {001} Facets

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Due to their extraordinary scientific significance and technological importance, inorganic single crystals with highly reactive surfaces have long been targeted. Unfortunately, surfaces with high reactivity usually diminish rapidly during the crystal growth process as a result of the minimization of surface energy. A typical example is titanium dioxide ($TiO_2$), which has promising energy and environmental applications. Most available anatase $TiO_2$ crystals are mainly dominated by the thermodynamically stable {101} facets (more than 94% according to Wulff construction), as opposed to the much more reactive {001} facets. Here, we demonstrate that for fluoride-terminated surfaces this stability is reversed - {001} surfaces are energetically preferable to {101}. We explored this effect systematically for a range of non-metallic atoms (H, B, C, N, O, F, Si, P, S, Cl, Br, I) by first-principle quantum chemical calculations. Based on this theoretical prediction, we have synthesized uniform anatase $TiO_2$ single crystals with a high percentage (47%) of {001} facets by using hydrofluoric acid (HF) as morphology controlling agent. Moreover, high quality anatase $TiO_2$ single crystal nanosheets mainly enclosed by {001} facets (61%) have also been prepared, which is based on the synergistic functions of chemisorbed F to lower the surface energy and 2-propanol to act as protective capping agent. With the well-defined anatase single crystals reported in this communication, it may be practical to study the functions (i.e., photocatalysis) of high-reactive {001} facets of anatase more accurately after surface activation.

## 706

### Electronic Structure and Photocatalytic Characterization of Some New Oxide Semiconductor Photocatalysts

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Recently, we found some new series of oxide semiconductor photocatalysts: AgAlO2, Bi2O3/SrTiO3 and Ti1-xZrxO2 Solid Solutions. These photocatalysts have different crystal structure, leading to different electronic structures. The new photocatalysts were synthesized by the solid state reaction and sol-gel method. Their photocatalytic degradation of organic contaminants was investigated systematically, by selecting acetaldehyde as a model gaseous contaminant, chloroform as a model solvent contaminant and methylene blue(MB) as a model dye contaminant, respectively. The photocatalytic decompositon of these contaminants was investigated under visible light irradiation using Xe lamp or fluorescent lamp with cut-offf filters of different wavelength at room temperature. It was found that the new photocatalysts showed a high activity for acetaldehyde decomposition and MB degradation in a wide wavelength range of visible light up to 640nm. Understandings on the relations among the materials syntheses, photophysical properties, and photocatalytic activities of these new photocatalysts obtained by various experimental measurements and theoretical calculations will be discussed. Improvement of photocatalytic activity by surface modification will also be reported. And we found also some new photocatalysts: LiNbO3, Ca2NiWO6, CoTa2O6 and Bi2GaTaO7. These photocatalysts were found to split water into H2 and/or O2. We have demonstrated the surface characteristics of these photocatalysts. One of the most important key factors for increasing activity might be to suppress the recombination of separated electron and hole by excitation of photon.

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## 708

### A Comparative Study of Manganese Based Catalysts for Water Oxidation

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Today it is clear that mankind's use of fossil fuel can not continue. It is an ending resource that should be used in more useful ways than to be burned as fuel. Instead, we should turn to renewable energy sources, and why not use the sun? Why not mimic nature and use sun and water, as Photosystem II in green plants, to produce tomorrow's fuels?

In green plants, reducing equivalents is taken from water to produce biomass. This water oxidation is the key reaction to understand and master the necessary processes to build an artificial system that instead of biomass, produce a chemical fuel. Here we present a systematic study were we for the first time compares different synthetic manganese complexes towards water oxidation under the same condition. With the help of Membrane Inlet Mass Spectrometry (MIMS) we have been able to track the oxygen atoms in the released oxygen and identified different mechanistical behavior depending on the nature of the manganese catalyst or the oxidant used.

## 709

### Photo Synergistic Collaboration of Non-Linear Processes at Mesoscopic Level and Formation of Photoautotrophic Biomimetic Supramolecular Assemblies in an Irradiated Sterilized Aqueous Mixture of Some Inorganic and Organic Substances

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Sunlight exposed sterilized aqueous mixture of ammonium molybdate, di-ammonium hydrogen phosphate, biological minerals and formaldehyde show photosynergistic collaboration of non-linear processes and formation of self-sustaing biomimetic supramolecular assemblies, 'Jeewanu'. They are capable of showing multiplication, growth and metabolic activities. They have a definite doubled walled boundary for charge separation and intricate internal structure. They have been found contain a number of chemical of biological interest Viz: aminoacids in free as well as in peptide combination, sugars as ribose as well as de-oxyribose, nucleic acid bases as purines and pyrimidinesand phospholipids –like material in them. The presence of various enzyme –like activities have been detected in the Jeewanu mixture, The EPR spectra of Jeewanu have shown the presence of ferredoxin-like material in them. Under certain specific conditions Jeewanu can catalyse photolytic decomposition of water and hydrogen thus released is utilized in photochemical fixation of N2 and Co2. Such structurally organised and functionally integrated photoautotrophic system is built on supramolecular architecture.

## 710

### Absorption Spectroscopic Properties of Carotenoid Canthaxanthin Monolayers

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In order to better understand the optical properties of carotenoids in photoreceptor membrane, the absorption spectroscopic studies of a carotenoid canthaxanthin (Cantha) in solution and in artificial membrane model system, i.e., the monolayers, have been carried out. The monolayers deposited on hydrophilic and hydrophobic quartz lamelles at surface pressure of 20 mN/m display a large hypsochromic shift relative to solution spectra in various organic solvents, for example, acetone, benzene, chloroform, etc. This blue shift in monolayers has been attributed to the formation of card-pack or H-aggregates brought about by water.

The presence of water is necessary to induce the formation of aggregates. This is suggested by the blue-shifted spectra of acetonic solution of Cantha in which small amount (10%, v/v) of water has been added. The spectra of Cantha monolayers placed in vacuum (10-6 Torr) for 24 hours or heated at 50 degree celsius for one hour also confirm the requirement of water. These spectra show absorption maxima similar to those observed in organic solvents. The vacuum or the heating seems to remove the water and disrupt the aggregates. The importance of intermolecular separation in the formation of card-pack aggregates in Cantha is demonstrated by the spectra of mixed monolayers of Cantha with a phospholipid phosphatidylcholine in varying molar ratios.

## 711

### Carotenoids Quench Tetrapyrrole Singlet Excited States: Mimicking Nonphotochemical Quenching in Oxygenic Photosynthesis

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Under excess illumination, photosystem II of oxygenic photosynthesis dissipates excess energy through the quenching of chlorophyll fluorescence, a process known as non-photochemical quenching (NPQ). This rapidly reversible photoprotective mechanism is vital for oxygenic photosynthetic organisms to cope with varying light conditions. Activation of NPQ has been linked to the conversion of a carotenoid with a conjugation length of 9 double bonds (violaxanthin) into an 11 double-bond carotenoid (zeaxanthin). Recently, we have mimicked NPQ in an artificial dyad model systems comprising a phthalocyanine covalently linked to a carotenoid of various conjugation lengths (Berera et al., PNAS 103, 2006, 5343-5348). Remarkably, the addition of only one double bond can turn the carotenoid from a non-quencher into a very strong quencher of the phthalocyanine singlet excited state. By applying femtosecond transient absorption spectroscopy it was shown that the quenching proceeds through energy transfer from the excited phthalocyanine to the optically forbidden S1 state of the carotenoid, coupled to an intramolecular charge-transfer state. Here, we further investigate the quenching capabilities and quenching mechanisms of caroteno-tetrapyrrole dyads by varying physical-chemical parameters such as the nature of the covalent linkage, the linker length, substitutions on the carotenoid backbone and redox potential of the tetrapyrrole. These studies may aid in the development of photoprotective feedback mechanisms in artificial photosynthetic devices.

## 712

### Synthesis of Mesostructured Inorganic-Organic Hybrids from Porphyrin Derivatives possessing amphiphilic side chains

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In the primary process of photosynthesis, chlorophyllous pigments have been immobilized into the protein matrices, and their arrangements are regulated precisely. This indicates that the immobilization of photofunctional organic molecules into inorganic matrices instead of the proteins and the regulation of the arrangements of the pigments is the first step for the construction of artificial photoredox systems because the energy conversion was performed by pigments themselves.

Mesoporous silica and mesostructured materials have attracted many interests toward various applications such as adsorbents for relatively large molecules and nanosized reaction vessels because of its high surface area and ordered mesopores. Ordered mesopores are quite useful to control of arrangements of photofunctional organic molecules because the pore diameters are comparable to the size of these molecules. However, it is difficult to control the arrangements of these molecules precisely in the mesopores by the simple liquid-phase adsorption or solubilization.

In order to synthesize a mesostructured porphyrin-silica hybrid with ordered arrangements of porphyrin, a Cu-porphyrin derivative possessing polyethylene glycol chains (PEG-Cu-Por) was used as a template. The XRD pattern of PEG-Cu-Por-$SiO_2$ film had three peaks (3.9, 2.2 and 1.9 nm) attributed to a 2D-hexagonal structure. The TEM images exhibited well-defined striped and honeycomb patterns. The UV-vis absorption spectrum of the film gave split Soret bands at 411 and 431 nm. All these results indicate that porphyrin rings assembled with a slip structure to form a mesostructure, which promises a new way to construct mesostructured inorganic-organic hybrids consisting of porphyrin derivatives.

## 713

### Visible Light-driven Hydrogen Generation Catalyzed by Bio-inspired $Fe_2S_2$ Complexes

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The design and synthesis of homogeneous catalysts for visible light-driven hydrogen production inspired by the active sites of [FeFe] Hydrogenases have been conducted in our groups during the past years. In this presentation, biomimetic active site models of [FeFe] Hydrogenases with different CO/P ligands as catalysts for electrochemical proton reduction will be discussed. Photo-induced electron transfer between photosensitizers and $Fe_2S_2$ catalysts in both intramolecular and intermolecular systems will be shown. Successful hydrogen production driven by visible light catalysed by related dinuclear $Fe_2S_2$ complexes in the presence of electron donor provides further progress for solar energy conversion into a fuel.

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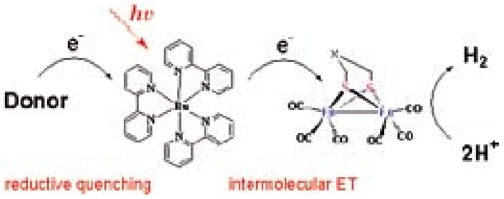

## 714

### Novel Nanostructures for Hydrogen Storage

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Materials and nanostructures underpin the advance and sustainability of technologies. Much of the clean energy technologies rely on development of new materials and finely tuned nanostructures to meet practical targets of increased efficiency and reduced cost. Hence, fundamental understanding of electronic structure, atomic bonding and nonstructural assembly is essential, e.g. for the design of hydrogen storage solids including C, B-N, MgH2 and LiH systems. Electronic simulations can reveal the nature of hydrogen interactions with host atoms/structures, indispensable for the design of new materials, whereas higher scale modeling approaches are important for storage system design.

## 715

### Dye sensitised solar cells based on ruthenium porphyrins

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**Peter Innis,** *Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Australia*
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For over ten years, we have been synthesising porphyrins and investigating their potential as light harvesting dyes in the dye sensitised solar cell (DSSC). The syntheses of porphyrins that we have developed have allowed us to systematically vary the porphyrin chromophore by substitution (R), metallation (M) or array formation, as well as the linker and binding group. This approach has led recently to the design of the highest efficiency zinc porphyrin dye (7%) used in a DSSC. Other metallated porphyrins such as ruthenium porphyrins are of interest given their ability to act as triplet sensitizers. Therefore, we have synthesized a number of ruthenium porphyrins with conjugated binding groups and investigated their potential as light harvesting materials for DSSCs.

## 716

### Photoelectrochemical Behaviour of Electrophoretically Deposited $TiO_2$ Thin Film onto Tin Oxide and Steel Substrates Towards Decontamination

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We report on the electrochemical/photoelectrochemical behaviour of commercial P25 titanium dioxide deposited onto fluor-doped tin oxide and stainless steel substrates via electrophoresis. An experimental design [1] was applied to find optimum conditions for the photoelectrochemical responses of such thin film layers. Adhesion strength of film coatings, and the fill factor (FF) were used as key parameters to compare the photoactivity of the semiconducting layers. Organic molecules such as carmine indigo in aqueous solution were used as representative water pollutants in a reactor containing six electrode plates. The UV lamp (black light blue, 6W, lambda = 365 nm) was used as an irradiation source for 8 h under continuous stirring conditions. The decolouration of the solution reached 87.5 % after 8 h. The total organic carbon (TOC) was measured. The results indicate that the mineralization of the carmine indigo was around 36 % after 8 hours. A comparative study was done using titanium dioxide deposited on paper (Ahlstrom) and stainless steel.

Acknowledgements:
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## 717

### Visible-Light-Induced Photocatalytic Oxidative Decomposition of Organic Compounds Over Bismuth Tungstate Polycrystalline Flake-ball Particles Prepared by Hydrothermal Reaction

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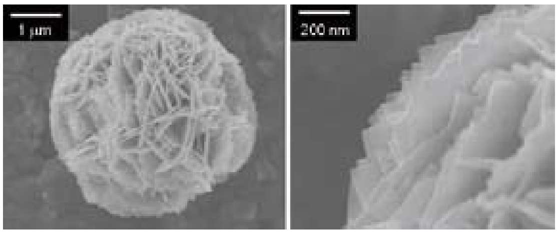
We investigated visible-light-induced photocatalytic activities of bismuth tungstate ($Bi_2WO_6$) polycrystalline particles with hierarchical 'flake-ball' architecture. The flake-ball particles, which are assemblies of polycrystalline flakes composed of rectangular plate-like crystallites, were prepared by a facile hydrothermal reaction of bismuth nitrate and sodium tungstate solution at 433 K for 20 h. Figure shows FE-SEM images of the flake-ball particles. The diameter of the spherical particles was 3-4 micrometers. The lateral size and the thickness of the rectangular plate-like crystallites in flakes were a few hundreds of nanometers and 20-35 nm, respectively. The flake-ball particles exhibited the highest photocatalytic activity among a series of $Bi_2WO_6$ prepared by hydrothermal reactions. It is suggested that the high photocatalytic activity is due to not only the large surface area but also the high crystallinity. The flake-ball particles promote photocatalytic oxidative decomposition of acetic acid and gaseous acetaldehyde into carbon dioxide under visible light irradiation. The photocatalytic activities were higher than those of nitrogen-doped titanium dioxide as a visible-light-sensitive photocatalyst. Calcination at 873 K in air enhanced the visible-light-induced activity for oxidative decomposition of acetic acid. The ball-like morphology was remained after calcination, although the BET specific surface area was decreased. The flake-ball particles would be beneficial for practical use in photocatalytic water-purification systems because of the visible-light-induced photocatalytic activity for oxidative decomposition and the feasible separation of photocatalyst powders from aqueous solution by sedimentation and filtration.



## 718

### Utilization of Ferric and Cupric Ions to Promote the $WO_3$-Catalyzed Photodegradation of Organic Substances

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$WO_3$ is a visible-light–responsive n-type semiconductor photocatalyst, but reports on the degradation of organic substances over $WO_3$ are limited because of its low photocatalytic activity towards organic substances. However, the activity can be enhanced by loading co-catalyst or utilizing redox mediator. In this study, we tried to utilize several transition metal ions to promote the photodegradation activity over $WO_3$, and found that ferric and cupric ions were suitable to promote the reaction. We estimated the activity of $WO_3$ in the photodegradation of organic substances by the amount of $CO_2$ generated in the reaction, and it was determined using a gas chromatograph equipped with a methanizer. For ferric ion, the photoexcited electron of $WO_3$ reduced it to ferrous ion instead of oxygen reduction reaction. This reaction promoted the charge separation and enhanced the photodegradation activity. However, ferric ion worked sacrificially because the oxidation rate of ferrous ion by air was pretty low compared with the generation of ferrous ion by the photocatalytic reduction in the acidic aqueous solution medium. On the other hand, cupric ion could work cyclically as redox mediator. Cupric ion was reduced to cuprous ion by photoexcited electron from $WO_3$ and cuprous ion easily oxidized to cupric ion again by oxygen in air. This redox cycle could assist the reduction reaction of oxygen in photodegradation of organic substances. In our presentation, we will discuss the details of the reaction and show the suitable systems to utilize ferric and cupric ion, respectively.

## 719

### Exposed Crystal Surface Controlled of Rutile $TiO_2$ Nanorods in the Presence of Polymer from $TiCl_3$ under Hydrothermal Conditions

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$TiO_2$ has three crystal phases and each phase exhibits different properties. The applications for $TiO_2$ strongly depend on the crystal structure, morphology, and size of the particles. For instance, anatase $TiO_2$ powders consisting of particles with large surface areas are used as photocatalysts, which are advantageous for absorption of compounds included in the reaction system at low concentrations. In contrast to the case of anatase $TiO_2$ photocatalysts, oxidation of water, which is difficult to oxidize, proceeds efficiently on large rutile $TiO_2$ particles. Anatase $TiO_2$ photocatalysts don't have photocatalytic activity for oxidation of water. Size, shape, and phase structure controlled synthesis of $TiO_2$ nanocrystallites has long been one of the main themes in $TiO_2$ research. Main synthetic techniques have been utilized in the preparation of $TiO_2$ nanocrystals, among which hydrothermal treatment has been drawing much attention considering that it directly produces well-crystallized nanocrystallities of a wide range of compositions within a short period of reaction time. In this study, we carried out hydrothermal growth of rutile $TiO_2$ rods by using aqueous titanium trichloride ($TiCl_3$) solutions containing NaCl and PVP. Under the condition, a rutile uniform ultrafine $TiO_2$ particle was obtained, on which developed crystal faces were observed by a transmission electron microscopy (TEM) and scanning electron microscope (SEM). The obtained rutile fine particles showed high activity for degradation of 2-propanol and acetaldehyde under UV irradiation. These results suggested that the crystal faces help the separation of electrons and holes. The high activity and controlled crystallization of rutile $TiO_2$ will be discussed.

## 720

### Development of Sensitive Hybrid Rutile Titanium Oxide by Loading Metal Ions

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Titanium(IV) oxide ($TiO_2$) has been one of the most attractive materials as a photocatalyst due to low cost, nontoxicity, photostability, and availability. Photocatalytic reactions on such semiconductor are induced by photoexcited electrons and holes, which are generated by above-bandgap irradiation. However, electrons and holes recombine each other without influencing chemical reactions. Therefore, it is important to prevent recombination in order to improve photocatalytic efficiency. In this study, various transition metal ions, such as $Fe^{3+}$,$Cu^{2+}$,$Ni^{2+}$,$Cr^{2+}$, and $Rh^{3+}$ were prepared by a wet impregnation method. These metal ions are expected to accelerate reduction reaction by acting as electron acceptor and prevent electrons and holes from recombination. Photocatalytic activity of the sample adsorbed metal ions ($M^{n+}/TiO_2$) were estimated with decomposition of acetaldehyde. As a result of experiment, the photocatalytic activity was improved by transition metal ions adsorbed. This result suggests that transition metal ions accelerate photocatalytic activity by acting as electron acceptor. Moreover, the $M^{n+}/TiO_2$ sample showed photocatalytic activity even under visible light irradiation. Then, We measured the photoacoustic spectroscopy (PAS) intensities of $Ti^{3+}$ of the $M^{n+}/TiO_2$ samples in order to inquire the behavior of photoexcited electrons under UV irradiation and visible irradiation. We presumed the following thing from the measurement results. Under visible light irradiation, photoexcited metal-ion adsorbed on $TiO_2$ surface inject electrons into $TiO_2$, and subsequent reduction. These behaviors were discussed on the correlation with photcatalytic activity on various kinds of $Mn+/TiO_2$ samples.

## 721

### Synthesis of Titania Impregnated Kaolinite Nano-photocatalysts for Enhanced Photocatalytic and Recovery Ability in Water Treatment

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**Shaomin Lei,** *Wuhan University of Technology, China*
**Vipasiri Vimonses,** *The University of Adelaide, Australia*
**Bo Jin,** *The University of Adelaide, Australia*
**Chris Chow,** *Australian Water Quality Centre, Australia*
**Chris Saint,** *Australian Water Quality Centre, Australia*

Semiconductor photocatalysis employing titanium dioxide ($TiO_2$) has been widely reported for its efficacy in removing bio-recalcitrant contaminants in water remediation. However, the low adsorption ability and poor recovery characteristics of the commercial available nano-sized photocatalysts have limit the application of $TiO_2$ for a commercial process. In this work, a modified two steps sol-gel method has been developed to synthesize a titania impregnated kaolinite nano-photocatalysts. The resultant photocatalysts have a constant coating layer of 7 nm while maintaining a relatively shell core with average particle diameter length up to 3.5 microns. The newly synthesized titania/kaolinite nano-photocatalysts was found to not only enhance the adsorption and photo-oxidation ability but provides a photoactive anatase $TiO_2$ for reuse. Results from the photo-degradation trials in a reactor system indicated that the nano-photocatalysts demonstrate a relatively superior photo-activity by completely degrade 40 ppm of aqueous Congo Red in 6 hours. A recycling test for the subsequent photocatalysis application showed that the recovered nano-photocatalysts remain not only a comparable photo-activity, but exhibits an enhance separation ability as compared to the Degussa P-25 $TiO_2$. Current results reveal that the titania/kaolinite nano-photocatalysts have shown promising outcomes of its photocatalytic ability and potential application for an industrial process.

## 722

### Improved Light Distribution in Gas-Phase Photoreactors for Air Purification Purposes

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**Jason A Scott,** *The University of New South Wales, Australia*
**Gang-Ding Peng,** *The University of New South Wales, Australia*
**Rose Amal,** *The University of New South Wales, Australia*
**Vishnu Pareek,** *Curtin University of Technology, Australia*

$TiO_2$ photocatalysis for gas-phase applications is a promising technology but can be limited by the uniform delivery of photons to the photocatalyst surface. Optical fibres, as a possible solution to this issue, have been under investigation for over a decade. Cylindrical optical fibres act both as a photocatalyst support and as a light guide for directing photons to the photocatalyst surface. Improved light utilisation has been reported to occur in some instances [1,2].

Light propagation in cylindrical optical fibres suffers from exponential decay along the fibre axis. This decay limits the application of optical fibres in air purification systems. Strong light guidance in holey optical fibres may provide a solution to the exponential decay problem. Holey optical fibres comprise a core through which a number of air channels run along the axis and hold potential for gas phase applications. The small channels increase the available irradiated surface area and reduce mass transfer limitations.

In this work, a 6mm holey optical fibre with twenty 0.4mm-hexagonal channels was employed as a reactor for the gas-phase photocatalytic oxidation of ethylene. $TiO_2$ particles were coated on the channel wall. The $TiO_2$-coatings were characterised by secondary electron microscopy (SEM) and Focused-Ion Beam (FIB) spectroscopy. The effects of ethylene concentration, incident photons and gas flow rate have been studied.

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## 723

### Photocatalytic Oxidation of Molinate in Aqueous Solutions

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**Eri A Bizani,** *Environmental Pollution Control Laboratory, Chemistry Department, Aristotle University of Thessaloniki, Greece*
**Ioannis Poulios,** ** *Laboratory of Physical Chemistry, Chemistry Department, Aristotle University of Thessaloniki,, Greece*

In this study, the degradation of molinate using heterogeneous and homogeneous photocatalytic methods has been investigated. The main objectives of the study were: I) to evaluate the kinetics of the pesticide disappearance in aqueous media of different composition such as river, lake and deionized water, II) to compare the photocatalytic efficiency of the two different types of photocatalysis, III) to examine the influence of various parameters such as initial concentration of pesticide or catalyst, pH value and presence of oxidants such as $H_2O_2$ and $K_2S_2O_8$ or different inorganic anions in the case of homogeneous process IV) to evaluate the degree of mineralization, V) to assess the detoxification efficiency of the studied processes.

Parameters such as iron's and oxidant's concentration and inorganic ions strongly affect the oxidation rate. In comparison to $TiO_2$ assisted photocatalysis, this system achieved slightly higher degradation rates.

The detoxification efficiency was found to be dependent on the system studied and, although it did not follow the rate of pesticide disappearance, it took place in considerable extent. From the point of view of practical application, it should be also noted that these methods give the opportunity of using the solar irradiation as well and they can be selected among the most popular solar technologies. Combining this fact with the effectiveness of the methods and the ability to be teamed up with other conventional technologies, photocatalysis could be considered as an alternative, promising method for the treatment of pesticide contaminated waters and wastewaters.

## 724

### The Development of 2nd Generation Microalgal Biofuel Production Processes

**Ben Hankamer,** *Institute for Molecular Bioscience, Australia*

2$^{nd}$ generation microalgal biofuel production systems have the potential to play an important role in global strategies aimed at reducing $CO_2$ emissions, producing fuels for the future and eliminating the competition between food and fuel production associated with 1st generation biofuel production (e.g. bio-ethanol produced from corn). This is because microalgal bioreactors can be located on non arable land to capture sunlight and $CO_2$ to produce feedstocks for a wide range of biofuels (e.g. oil for biodiesel). The use of salt tolerant algae has the further advantage of fresh water conservation. Furthermore as $CO_2$ is captured in the biomass, it is possible to convert a proportion of the biomass to charcoal for long term C-sequestration. Detailed industrial and biochemical feasibility studies have been completed. These indicate that it is possible to develop economically viable 2$^{nd}$ generation microalgal biofuels systems. Here key developments being conducted by the Solar Biofuels Consortium (www.solarbiofuels.org) will be presented.

## 725

### Co-Doping of Platinum (Pt), Chromium (Cr), and Vanadium (V) in $TiO_2$ for Enhanced Visible-Light Photocatalytic Activity

**Jina Choi,** *California Institute of Technology, United States*
**Michael R Hoffmann,** *California Institute of Technology, United States*

$TiO_2$ is the most widely used photocatalyst for the decomposition of various organic pollutants because of its high activity, chemical stability, low price, and nontoxicity. Doping $TiO_2$ with transition metal ions has been frequently attempted to extend the spectral response of $TiO_2$ into visible region since pure $TiO_2$ requires near UV light absorption because of its wide band gap of 3.2 eV. In this research, the effect of co-doping metal ions such as Platinum (Pt), Chromium (Cr), and Vanadium (V) in $TiO_2$ which separately shows visible-light photoactivity have been investigated in an attempt to enhance the photocatalytic activity under visible light irradiation. Pt-Cr-, Pt-V-, and Cr-V- co-doped $TiO_2$ samples were successfully synthesized by sol-gel methods and studied by means of X-ray diffraction, UV-Vis diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy. Photocatalytic activities were demonstrated for the degradation of Methylene Blue (MB), phenol and the oxidation of iodide in aqueous solution under visible light irradiation at wavelengths > 400 nm. Co-doped $TiO_2$ with 0.3 % Pt and 0.3% Cr showed better photocatalytic activity in both MB degradation and oxidation of iodide than separately doped, whereas reaction rates of MB degradation and I- oxidation decreased in co-doped $TiO_2$ with 0.3% Pt and 0.3% V. Co-doped $TiO_2$ with V and Cr also showed good activity for the oxidation of iodide to tri-iodide. However, for the degradation of phenol, all co-doped $TiO_2$ samples didn't show significantly enhanced photocatalytic under visible light irradiation compared to their single doped counterparts.

## 726

### Photocatalytic Degradation of N-Nitrosodimethylamine (NDMA) by Using Metal-Doped $TiO_2$ Under Visible-Light (> 420 nm)

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**Michael R Hoffmann,** *California Institute of Technology, United States*

N-Nitrosodimethylamine (NDMA) contamination has become an issue since trace levels of NDMA have been observed in drinking water in California and Canada. NDMA, which is generated during water treatment as a disinfection byproduct (DBP), is known to be highly carcinogenic and resistant to biodegradation in the aquatic environment. Several advanced technologies such as ozonation, Fenton's Reagent oxidation, and reduction by zerovalent iron have been employed to remove NDMA. In this research, we synthesized metal-doped $TiO_2$ such as platinum (Pt), chromium (Cr) by sol-gel methods and investigated the photocatalytic degradation of NDMA in aqueous solution under visible light irradiation > 420 nm. In aqueous suspensions, NDMA was degraded with 0.3% Platinum (IV)-doped $TiO_2$ under illumination at wavelengths > 420 nm whereas commercial $TiO_2$ (Degussa P-25) did not show significant degradation of NDMA under visible light irradiation. Under UV light irradiation > 300 nm, Pt(IV)-doped $TiO_2$ showed higher photocatalytic activity for NDMA degradation than un-doped $TiO_2$ over a wider pH range. In addition, the degradation rates were enhanced with Pt metal deposition on the $TiO_2$ particle surfaces. The effects of doping concentration, calcination temperature, oxidation states, and pH on the photocatalytic degradation of NDMA were determined. The clearly identified degradation products give insight into the mechanism of oxidation under visible light irradiation.

## 727

### Development of Photocatalysts, Sensitive to Visible Light

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**Kazuhito Hashimoto,** *Department of Applied Chemistry, The University of Tokyo, Japan*

Development of novel visible light sensitive photocatalysts has attracted much attention to use solar energy and indoor light effectively. Numerous studies have reported the sensitization to visible light with respect to $TiO_2$-based photocatalysts [1]. However, up to now, it seems that they have insufficient activities, especially under visible light. We are investigating now to enhance the activities by focusing on the overlap of the introduced anion p-orbital with O 2p-orbiral, constituting the valence band of $TiO_2$.

With the exception of $TiO_2$-based materials, several researchers have examined oxide or oxynitride materials that are sensitive to visible light for the oxidative decomposition of organic compounds. We have investigated various such novel photocatalysts, controlling electronic band structures and crystalline structures. For example, we have already reported $Ag^+$-inserted $NbO_2F$ with a $ReO_3$ structure and a-$AgGaO_2$ with a delafossite structure utilizing $Ag^+$ [2]. $Ag^+$ cation in a $4d^{10}$ configuration mixes the O2p orbitals, forming the highly dispersed upper valence band. This can be favorable for visible light sensitivity and high photocatalytic activity, because mixing Ag4d with O2p decreases in the band-gap energy and the dispersed valence band leads to high mobility of photo-generated holes. The key factors in realizing high-efficiency visible light sensitive photocatalysts are modulation of the closed shell with ligand O2p orbitals and finding crystal structure favorable for holes' mobility. The details will be introduced at the conference.

[1] e.g., R. Asahi et al., Science, 293, 269 (2001). [2] e.g., H.Irie et al., J. Phys. Chem. B., 110, 23274 (2006).

## 728

### Photocatalytic Properties of $BiVO_4$ Photocatalyst Prepared in an Aqueous Acetic Acid Solution

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**Akihiko Kudo,** *Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan*

Recently, the development of visible-light-driven photocatalysts has extensively been studied in terms of using sunlight. The $BiVO_4$ is a highly active photocatalyst for water oxidation reaction (apparent quantum yield: 9% at 450 nm). The $BiVO_4$ is usually obtained by a reaction of layered vanadate powder ($KV_3O_8$ and $K_3V_5O_{14}$) with $Bi(NO_3)_3{\bullet}5H_2O$ in aqueous media at room temperature and a urea method. In the present study, we investigated the photocatalytic and photoelectrochemical properties of the $BiVO_4$ photocatalyst prepared in acetic acid solution. The $BiVO_4$ photocatalyst was prepared by mixing $Bi_2O_3$ and $V_2O_5$ in an aqueous acetic acid solution. The obtained $BiVO_4$ was calcined at 673 K for 5 ~10 hours in the air. SEM observation revealed that the particle size of obtained $BiVO_4$ (50 ~300 nm) was smaller than those obtained by reported methods. This $BiVO_4$ photocatalyst showed photocatalytic activities for oxygen evolution from an aqueous $AgNO_3$ solution and methylene blue degradation under visible light irradiation. The photoelectrochemical properties of $BiVO_4$ were also examined. $BiVO_4$ electrodes were prepared by pasting the $BiVO_4$ powder on an ITO plate and subsequently calcination. This electrode gave an excellent anodic photocurrent under visible light irradiation. Thus, we have successfully developed a visible-light-responsive the photo-electrode.

## 729

### Application of a Cooling System Using Photo-induced Hydrophilicity and Watering

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To reduce the heat island phenomenon, we have designed an original system to secure water surfaces by continuously sprinkling stored rainwater onto the surfaces of a building coating with photoactive $TiO_2$ film. The solar light converts the building surface coated with $TiO_2$ film to a highly hydrophilic one, minimizing the amount of water needed to form thin water film on the surface. Then, the evaporation from the water film generates the effective latent heat flux and cools down the building surfaces and its surrounding atmosphere. The cooling effect also decreases the amount of air conditioning usage, which reduces energy consumption and artificial heat emission. Thus, our system achieves both increasing water surface and saving energy to reduce the heat island phenomenon without losing comfortable life.

The cooling system applied to glass curtain walls (130 $m^2$) coated with $TiO_2$ films in a room of an actual building. The minimal amount of water was sprinkled by a special hose on the top of the glasses in this summer, and the room and the glass surface temperatures were measured. And also, thermal loading was evaluated when the air conditioner was set for 25°C. Figure shows that this system cuts the thermal loading by 14 % on average. The results suggest that the system is effective on reducing energy consumption and also the cooling down the building surface and the room within it in the actual building.

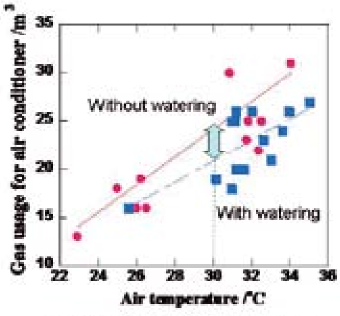

Fig. Thermal loading for air conditioner

## 730

### Fabrication of Spherical Shaped $BiVO_4$ Photocatalysts Through the Solution Combustion Synthesis Method

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**Hirotaka Natori,** *Japan*
**Masayuki Nagai,** *Japan*
**Koichi Kobayashi,** *Japan*

Spherical shaped BiVO4 photocatalysts were prepared by the solution combustion synthesis method. The as-prepared photocatalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and ultraviolet-visible diffraction reflection spectroscopy (UV-vis). The BiVO4 crystallites showed a monoclinic structure with a spherical shape particle with diameter of about 400-600 nm. Ultraviolet-visible diffusion absorption spectra indicated that the band gap absorption edge of pure BiVO4 was 523 nm, corresponding to a band gap energy of 2.45 eV. It was also found that the photocatalytic activity of degradation of methylene blue improved when the molar ratio of fuels to oxidizer was 5.

## 731

### Synthesis of BiOCl/$Bi_2O_3$ Composite and its Photocatalytic Activity Under Visible Light

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A junction structure between BiOCl and $Bi_2O_3$ were prepared by one-step procedure. The synthetic procedure is simple, low cost and the BiOCl/$Bi_2O_3$ system is safe for the environment. The mole ratio of BiOCl in $Bi_2O_3$ particles was controlled to 0-100 % by the added HCl molarity. It was found that the photocatalytic efficiency of BiOCl/$Bi_2O_3$ was considerably higher than that of $TiO_2$ (Degussa P25) under a visible light. The structures and the optical properties as well as their photocatalytic activities were characterized for the several BiOCl/$Bi_2O_3$ composite in different composition and annealed at different temperature. The junction structure with 65 mol % BiOCl, heat-treated at 60°C, provided the highest efficiency in decomposing terephtalic acid in aqueous solution. On the other hand, the junction structure with 75 mol % BiOCl, annealed at 250°C, provided the optimum photocatalytic efficiency under visible range in decomposing gaseous 2-propanol. A photocatalytic mechanism for the BiOCl/$Bi_2O_3$ working under visible light has been proposed in the present work.

## 732

### Pt-deposited Cerium-Doped $TiO_2$ Photocatalyst, Sensitive to Visible Light

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Visible light sensitive photocatalysts are required to use solar energy effectively and for indoor applications. Since Asahi et al. reported that nitrogen-doped $TiO_2$ showed photocatalytic activity under visible light irradiation, various types of $TiO_2$ doped wth anions, such as sulfur, carbon, iodine etc. have been widely studied. All of them are sensitive to visible light due to an isolated narrow composed of anion p orbital above valence band.[1] In contrast, there are few reports on the sensitization of $TiO_2$ to visible light by controlling electronic structure of the conduction band because its bottom is very close to the potential of one electron oxygen reduction.

However, Ohtani et al. reported that platinum-deposited $WO_3$ showed efficient activity under visible light irradiation although the potential of the conduction band bottom of $WO_3$ is more positive than that of one electron oxygen reduction.[2] Platinum is an efficient oxygen reduction catalyst in that it proceeds through two or four electron transfer process. So, we can expect the generation of visible light sensitivity by utilising multi-electron oxygen reduction process, even if the bottom of $TiO_2$ conduction band shifts to more positive position in order to absorb visible light.

In the present study, we confirmed that platinum-deposited Ce-doped $TiO_2$ under visible light irradiation could effectively decompose gaseous 2-propanol into acetone and $CO_2$. The details will be introduced at the conference.

[1] For example, R. Asahi et al., Science 2001, 293, 269 [2] Ohtani et al., photocatalysis 2007, 23, 58

## 733

### Visible Light Active $BiVO_4$ Photocatalyst by Flame Spray Pyrolysis

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**Rose Amal,** *ARC Centre for Functional Nanomaterials, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales*

The utilisation of visible light (&lambda>400 nm), the most abundant component of solar spectrum, in conventional photocatalysis has long been met with difficult challenges. Bismuth containing oxides have lately emerged as the candidates of visible light sensitive oxides.[1-4] In particular, $BiVO_4$, is an attractive materials stemming from its exclusivity in participating in photocatalytic water splitting [5] and organics degradation.[6]

The presentation describes the rapid synthesis of $BiVO_4$ nanoparticles via one-step Flame Spray Pyrolysis (FSP). Particles ranging from 10 to 90 nm were prepared and assessed for photocatalytic oxygen evolution and photo-oxidation of organic contaminants. $BiVO_4$ photocatalysts prepared by FSP has bandgap energy of 2.50 - 2.60eV.

Crystal structure and defects in the powder are expected to play a significant role in determining the photocatalytic activity. A scheelite-monoclinic $BiVO_4$ with minimum defects is desirable for photocatalytic oxygen evolution. When prepared at lower rate of combustion enthalpy $BiVO_4$ has showed low or negligible activity. This is attributed by the inappropriate structure, together with defects such as oxygen vacancy in the powder. The characteristics of $BiVO_4$ photocatalyst have been improved by allowing the particle to reside longer in the flame. This, not only increased the particle size, but also allows formation of fully ordered crystal. Photocatalysts contained mainly monoclinic structure and have reduced oxygen vacancy were obtained. Enhancement in the photocatalytic activity has been observed on these particles.

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## 734

### Anoxic Degradation of Organic Compounds on Simultaneously Fluorinated and Platinized Surface of $TiO_2$ Photocatalyst

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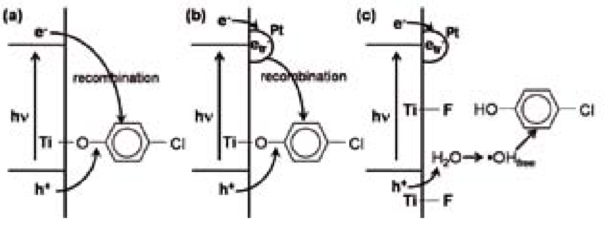
Most $TiO_2$ photocatalytic reactions for environmental cleanup are the hole-driven oxidation of organics coupled with the dioxygen reduction. Therefore, dioxygen is an essential reagent of $TiO_2$ photocatalysis and the overall photocatalysis does not proceed in the anoxic condition. Here we demonstrate that the anoxic photocatalytic reactions can be enabled by using a modified $TiO_2$ with simultaneous surface fluorination and platinization (F-$TiO_2$/Pt). This anoxic degradation in F-$TiO_2$/Pt can be related to the substrate-surface interaction and the charge transfer/recombination characteristics that should depend on the surface property of $TiO_2$. On F-$TiO_2$/Pt, Pt deposits can serve as a temporary electron reservoir whereas the surface adsorption of organic compounds is hindered by the surface fluorination. Under this condition, while the substrate is oxidized by the mobile OH radical off the surface, the electrons remain trapped in the Pt phase. With this scenario, the overall photocatalytic conversion taking place on F-$TiO_2$/Pt can be highly enhanced even in the absence of $O_2$ that serves as a dominant electron acceptor in most photocatalytic reactions.



## 735

### Preparation of $TiO_2$-Embedded Carbon Nanofibers and their Photocatalytic Activities for the Oxidation of Gaseous Acetaldehyde

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$TiO_2$-embedded carbon nanofibers were prepared by electrospinning method. Polyacrylonitrile (PAN) solution containing $TiO_2$ was electrospunned ($TiO_2$/PAN) and subsequently calcined under $N_2$ atmosphere, which resulted in the carbonization of PAN polymer ($TiO_2$/CNF). And then carbonized composite fibers further oxidized by thermal treatment under oxidative condition (Oxi.-$TiO_2$/CNF). Gaseous $CH_3CHO$ was efficiently degraded and $CO_2$ was simultaneously produced on Oxi.-$TiO_2$/CNF compoistes under UV illumination. Although UV-illuminated $TiO_2$/PAN composites could also oxidize gaseous $CH_3CHO$, they slowly degraded themselves. On the other hand, $TiO_2$/CNF had no effect on the photocatalytic oxidation of $CH_3CHO$, which was due to the reduction and phase transformation of $TiO_2$ during carbonization. XPS results show that $TiO_2$ was partly reduced by carbonization and then oxidized by post-oxidation process. There was no anatase phase of $TiO_2$ in $TiO_2$/CNF composites whereas anatase phase of $TiO_2$ was obviously observed in Oxi.-$TiO_2$/CNF composites. Moreover, BET surface area was hightly enhanced by post-oxidation process, which was responsible for the adsorption of gaseous $CH_3CHO$ on Oxi.-$TiO_2$/CNF. Therefore, post-oxidation process affects not only oxidation but also surface modification of carbon nanofibers.

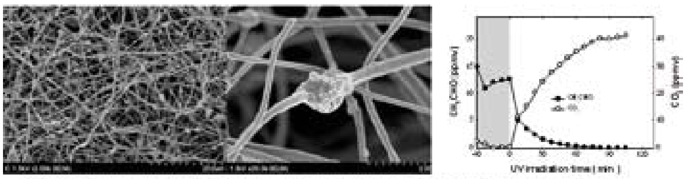

**Figure.** SEM images of Oxi.-$TiO_2$/CNF composites and photocatalytic oxidation of $CH_3CHO$ and production of $CO_2$ on Oxi.-$TiO_2$/CNF composites under UV illumination.

## 736

### On the Solid-State Speciation of Fe-$TiO_2$ for Visible-Light Photocatalysis

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Substitutional doping of TiO2 with Fe(III) via Flame Spray Pyrolysis (FSP) was recently shown to effectively extend the photocatalytic response to visible light [1]. Nevertheless, little information regarding the solid-state speciation of Fe and its role in photocatalysis is currently understood. Hence the work investigates by EPR the multi-speciation of Fe(III) in $TiO_2$ matrix.

At low concentrations (0.5 at.%<[Fe]<5 at.%), two groups of spectral lines were seen: g~2.0 and at g ~ 4.2. Both groups are complex, e.g., several different isolated paramagnetic centers, attributed to the high-spin Fe(III) ions (S=5/2) in rhombic ligand fields state [2,3]. Increasing Fe content resulted in noticeable line broadening of both groups up to [Fe]=5 at.%. At [Fe]=10 at.% the spectrum became very broad and weak, and at [Fe]>10 at.% it transformed to a broad (line width ΔB~200 mT) single line at g~2.07, typical for Fe(III) ferromagnetic clusters.

Interesting correlations were obtained when comparing the EPR results with the activity of Fe(III)-$TiO_2$. From 0.5 to 5 at.% Fe content, the photocatalytic mineralisation of oxalic acid increased approximately 3.5 times [1]. This is in strong agreement with the monotonous increase of isolated Fe(III) ions concentration. At [Fe]>5 at.%, ferromagnetic Fe clusters started forming at the expense of isolated ions, and resulting in the loss of visible light photocatalytic activity.

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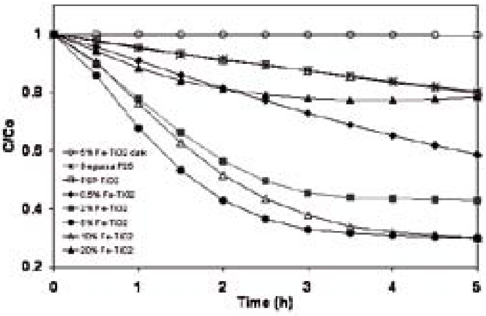

## 737

### Selective Photocatalytic Oxidation of Methanol to Methyl Formate Over Titanium(IV) Oxide

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Photocatalytic oxidation of methanol in air over titanium(IV) oxide with large surface area of 300 m2g-1 was examined using a flow-type reactor at room temperature and elevated temperatures (298 to 623 K). In the reactor, titanium(IV) oxide coated on the outer surface of a glass tube was photoirradiated by an external black light lamp and was heated by a heater inserted in the glass tube. At room temperature, methyl formate was formed as the main product with a high level of selectivity (91 mole%) without catalyst deactivation for 5 h. The activity increased with an increase in the reaction temperature and the high selectivity was maintained at temperatures up to 523 K, whereas combustion of methanol to carbon monoxide and dioxide occurred above 573 K. On the basis of FTIR data for adsorbed species on titanium(IV) oxide, a mechanism involving formation of methoxide on the surface of titanium(IV) oxide, photocatalytic oxidation of methoxide to formaldehyde and photocatalytic formation of methyl formate via dimerization of formaldehyde is proposed.

# 738

## Photo-Oxidation of Industrial Important Thioglycolic Acid by Fenton Reagent

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In the environment sulphur containing compounds are present in the effluents of industries like dyeing & printing, pharmaceuticals etc. photo-Fenton process was used for treatment of these industrial effluents. Fenton sensitized photo-oxidation of Thioglycolic acid has been studied. The rate of photo-oxidation on different reaction parameters like substrate, $H_2O_2$, $FeSO_4$, $H_2SO_4$ and polarity of solvent were studied. Involvement of free radical has been confirmed. A probable mechanism has been proposed with overall reaction.

# 739

## Photocatalytic and Photoelectrocatalytic Reactivities of Titanium Oxide Nanotubes

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**Jihoon Jung,** *Kyonggi University, Korea*

In order to maximize the reactivity of photocatalyst, the transmission rate of electrons, that were produced by absorbing light energy, need to be increased in order to suppress their recombination with holes. Titanium oxide nanotubes are called electron highway, because electrons can move freely through the nanotubes. For that, titanium oxide nanotubes were anodized by various conditions, and its reaction rate was compared to photocatalytic reaction and potential applied photoelectrocatalytic reaction, and they were characterized by XRD, FE-SEM and UV-DRS.

The electrolytes used in anodization for preparing titanium oxide nanotubes were HF+acetic acid, KF+NaHSO4 and NH4F+glycerol, and for the anatase crystal growth of the prepared titanium oxide nanotubes, calcination was carried out. The diameter of the titanium oxide nanotubes prepared by anodizing was 50nm to 150nm, and their length was 300nm to several micrometers. In the XRD analysis of titanium oxide nanotubes after calcination, anatase crystals, which have photocatalytic activity, appeared. In the photocatalytic degradation of dye using titanium oxide nanotubes, the degradation rate was the twice in comparison to that using conventional titanium oxide thin films that was prepared by sol-gel and anodizing. It is interpreted that titanium oxide nanotubes quickly transmit the electrons to inside, and suppress their recombination with the holes, thus increase the production of OH radicals that are used in photocatalytic reactions. When electric potential was applied to titanium oxide nanotubes, the degradation rate was increased by about 50%, but the effect of the length of titanium oxide nanotubes on reactivity was not big.

# 740

## Preparation and Characterization of Nitrogen-Doped Lamellar Niobic Acid with Visible Light-Responsive Photocatalytic Activity

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**Naoki Kikugawa,** *Japan*
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Semiconductor photocatalysis is currently attracting increasing interest in both scientific and engineering areas [1]. In view of the better utilization of the solar light and the indoor illumination, it is appealing to develop visible light-sensitive photocatalysts. Thus, some new photocatalysts with visible light-responsive characteristics have been developed in the recent years [2]. Solid acids are among the most important compounds in materials science, and have a large number of applications like catalysts, ion conductors, and electrode materials. Ti- and Nb-based lamellar solid acids are more attractive because of some particular properties like the layered structure, favorable electron-transfer character, and the protonic acidity. In the present study, a lamellar solid acid, viz. HNb3O8, had been successfully doped with nitrogen for visible light photocatalysis. It was found that the nitrogen-doped HNb3O8 photocatalyst shows superior activity for Rhodamine B photodegradation than the nitrogen-doped KNb3O8, Nb2O5, and TiO2 samples under visible light irradiation. The sample preparation methodology was studied with detail. The physico-chemical properties of the photocatalysts were investigated by using a variety technique such as XRD, BET, SEM, TG-DTA, and UV-visible diffuse reflectance spectroscopy. It turned out that the unique properties like the layered structure and the protonic acidity of HNb3O8 could have profound impacts on both nitrogen doping and the resultant visible light photocatalysis.

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# 741

## Nanocrystalline $TiO_2$ Photocatalysts Obtained by Thermohydrolysis of $TiCl_4$ in Aqueous Solutions

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**Marianna Bellardita,** *Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Italy*
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Nanosized $TiO_2$ has received increased attention as photocatalyst for environmental purification and for self-cleaning effects. TiO2 exists in three different crystalline habits: rutile, anatase and brookite. Thermohydrolysis of $TiCl_4$ in suitable aqueous solutions allows to obtain nanocrystalline pure anatase, brookite and rutile or various mixtures of the three phases.

In this study different routes were followed to obtain the various samples: $TiCl_4$ was hydrolyzed in pure water, in HCl solutions or in NaCl solutions. $TiCl_4$ was added at room temperature under stirring and the resulting solutions were heated at 100°C in an oven. The composition of the $TiO_2$ powders strongly depended on the acidity of the medium. Only rutile was formed at low pHs whereas binary or ternary mixtures of the three phases were obtained in H2O or in chloride solutions. Pure brookite nanoparticles were easily separated by peptization from the binary mixtures of brookite and rutile.

The various $TiO_2$ powders were characterized by X-ray diffraction, thermal analysis, diffuse reflectance spectroscopy and BET surface area determinations. The reactivity of all samples, both pure phases and mixtures, was tested for the photocatalytic degradation of 4-nitrophenol.

All the powders obtained by thermolysis of $TiCl_4$ were active under UV irradiation. Brookite revealed a good photocatalytic activity whereas that of rutile was scarce. The highest activities were generally obtained with powders consisting of more than one crystalline phase. Some samples exhibited similar or higher activities than commercial active Degussa P25.

## 742

### Photoassisted Mineralization of N-Heterocycles in $TiO_2$ Aqueous Suspensions: Fate of the N-Heteroatoms

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Heterogeneous photocatalysis in the presence of semiconductor oxides is a fast advancing field of research especially for the oxidation for organic pollutants in water or air. The photoassisted degradation of aromatic heterocycles (pyrrole, imidazole, pyrazole, isoxazole, oxazole and thiazole) and N-containing alicycles (pyrrolidine, 4-butanelactam and 5-pentanelactam) was examined in liquid-solid dispersions of $TiO_2$ Degussa P25 (100 mg) with the aim of ascertain the fate of the N atom. The initial solution (0.1 mM, 50 mL) was irradiated with a medium pressure Hg lamp (2 $mW{\cdot}cm^{-2}$, 310-400 nm. Complete mineralization of the aromatic heterocycles was attained within ca. 1 h of UV irradiation in acidic (pH 3), near-neutral (pH 6.0–7.6), and alkaline (pH 11) media. Mineralization kinetics were not appreciably influenced by the presence of acid but were slower in alkaline media. N-alicycles were photomineralized more slowly than the aromatics. The former could be mineralized in acidic and near-neutral media in less than 2 h, but not in alkaline media in which they were not mineralized even after 3 h of irradiation. The final products obtained were in all cases $CO_2$, ammonium and nitrate ions, along with sulfate anion in the case of thiazole. $N_2$ gas was also obtained for the photo-oxidation of pyrazole. The molar amount of $NH_4^+$ /$NO_3^-$ formed after long irradiation time was closely related to the chemical structure, however, the ammonium amount was in nearly all cases significantly greater than nitrate. Mineralization of isoxazole produced mostly nitrate; probably because of the presence of the N-O function.

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## 743

### $TiO_2$ Supported Over Hβ and HZSM-5 Photocatalysts for Salmonelle and Escherichia Coli Disinfection

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**Leonardo Palmisano,** *University of Palermo, Italy*
**Giulia Sciandrello,** *University of Palermo, Italy*
**Irene Catanzaro,** *University of Palermo, Italy*
**M Subrahmanyam,** *Indian Institute of Chemical Technology, India*
**V Durgakumari,** *Indian Institute of Chemical Technology, India*
**B Srinivas,** *Indian Institute of Chemical Technology, India*

Solar photocatalysis is a promising technology for the disinfection of water and wastewater; indeed it is an economic and clean methodology working at low temperature. Photocatalytic removal of bacteria has been investigated for the purification of wastewater. $TiO_2$ is the most used photocatalyst for this purpose and it has been found to be able to decompose a large variety of organic compounds and also bacteria. The photocatalytic efficiency of $TiO_2$ is greatly influenced by the surface area exposed to the light irradiation and also by its ability to adsorb the organic molecule to be degraded. The use of $TiO_2$ in suspension is efficient but the catalyst must be removed from the solutions after the treatment. The fixation of $TiO_2$ powder on porous materials of larger particle size and high surface areas, such as zeolites, seems to be the most suitable method in view of the sense and shoot approach to increase the efficiency. In the present study, we have prepared, characterised and tested over zeolites supported $TiO_2$ samples for the disinfection of two kinds of bacteria (Salmonelle and E. coli). Photocatalysts were prepared by supporting $TiO_2$ (5 wt %) on Hβ or HZSM-5 supports. The tests were performed irradiating 75 ml of Salmonelle or E. coli aqueous solution with solar light in the presence and also in the absence of the photocatalysts. The typical results obtained are shown in Figure-1 and it is evident that the presence of photocatalyst greatly increases the rate of E. coli deactivation.

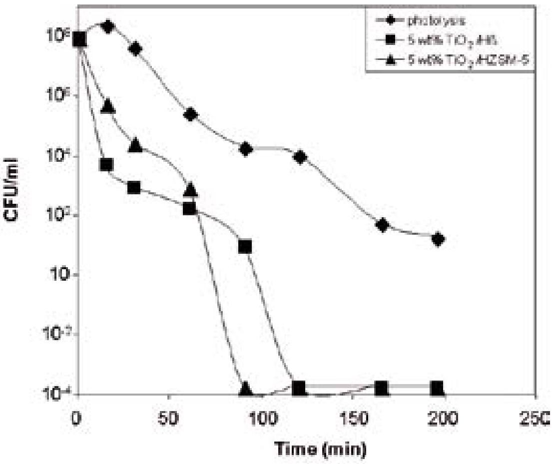

Figure-1. E. *coli* deactivation *vs.* solar irradiation time

## 744

### Water Splitting into $H_2$ and $O_2$ over $ALa_4Ti_4O_{15}$ (A=Ca, Sr, and Ba) Photocatalysts with Layered Perovskite Structure

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**Akihiko Kudo,** *Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan*

Development of active photocatalysts for water splitting into $H_2$ and $O_2$ is an important topic. In the present study, photophysical and photocatalytic properties of $ALa_4Ti_4O_{15}$ (A=Ca, Sr, and Ba) with layered perovskite structure were investigated. $ALa_4Ti_4O_{15}$ (A=Ca, Sr, and Ba) powder was prepared by a polymerizable complex method. Water splitting reactions were carried out in a gas-closed circulation system equipped. In an inner irradiation reaction cell made of quartz equipped with a 400-W high-pressure mercury lamp. The amounts of evolved $H_2$ and $O_2$ were determined using on-line gas chromatography. Diffuse reflection spectra indicated that the band gaps of $ALa_4Ti_4O_{15}$ (A=Ca, Sr, and Ba) were 3.8~3.9eV. Native $BaLa_4Ti_4O_{15}$ showed no activity for water splitting. In contrast, $NiO/BaLa_4Ti_4O_{15}$ showed high activity for water splitting when the pretreatment of $H_2$ reduction at subsequent $O_2$ oxidation was carried out. The activity of $NiO/BaLa_4Ti_4O_{15}$ was higher than that of $NiO/CaLa_4Ti_4O_{15}$. This is due to difference in distribution alkaline earth cations and La between $CaLa_4Ti_4O_{15}$ and $BaLa_4Ti_4O_{15}$ at perovskite slab and interlayer space. The optimized NiO (0.5 wt %)/$BaLa_4Ti_4O_{15}$ photocatalyst steadily produced $H_2$ and $O_2$ at the rates of 2.4 and 1.2 mmol/h, respectively. The apparent quantum yield was 15% at 270 nm. In conclusion, $ALa_4Ti_4O_{15}$ (A=Ca, Sr, and Ba) with layered perovskite structure was found to be new photocatalyst materials for water splitting.

## 745

### Hydroponic Cultue System with New $TiO_2$ Photocatalyst

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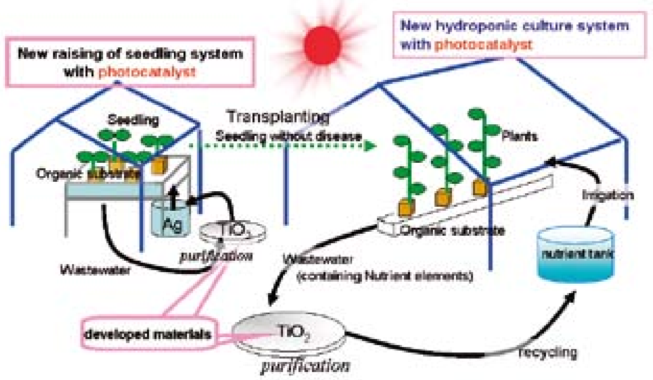
In Japan, main of hydroponic culture is run-to-waste system and rockwool as a substrate. To reduce environmental problems, recycling of nutrient solution and using organic substrate such as rice chaff and coir as a substitute for rockwool are anticipated. However, they cause the accumulation of organic pollutants from plant and organic substrate in the nutrient solution, which results in the inhibition of the plant growth.

We tried to decompose the organic pollutants utilizing $TiO_2$ photocatalyst under the solar illumination, and to establish a new raising seedling system and hydroponic culture system.

New systems are shown in Figure 1. Tomatos were planted on the system. New photocatalyst was developed with low-cost material and $TiO_2$ . The raising seedling system with this photocatalyst and Ag.

The amount of Total Organic Carbon in the wastewater after the $TiO_2$ treatment was lower than before in both systems. Using Ag together with photocatalyst for the raising seedling system, there was less number of the attack stocks than time only using Ag.

These results show that new $TiO_2$ materials under the solar illumination can be actually used in new raising seedling system and hydroponic culture system, leading an environmentally friendly agriculture.



## 746

### Visible Light Induced Super-Hydrophilicity on Nanostructured $TiO_2$ Thin Films

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Single crystalline nitrogen and sulfur doped anatase $TiO_2$ bipyramidal nanoparticles were synthesized by a hydrothermal reaction on titanate nanotubes. The surface of these nanoparticles was oriented to the (101) face. The (101) face of anatase consists of bridged-site oxygen ions, which is very reactive for photoinduced hydrophilic conversion. These nanoparticles were highly dispersed in water, and thin films were coated by a facile spin-coating method using colloidal solution of nanoparticles. The crystal face of thin films was oriented to the (101) direction perpendicular to substrates. Thin films of these nanoparticles on the $WO_3$ layer exhibited super-hydrophilic conversion under visible light illumination. The observed highly hydrophilic conversion was due to the visible light absorption and the crystal orientation of the bipyramidal $TiO_2$ nanoparticles. Spin-coating method is an economical coating for large areas, and thin films in the present study have potential in applications on indoor products that possess antifogging and self-cleaning properties.

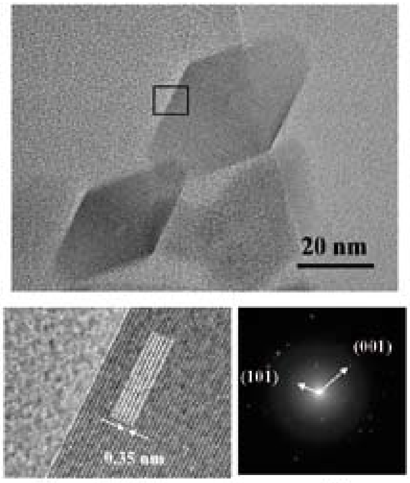

Figure. 1 TEM images for nanoparticles

## 747

### New Method for Receiving Vis Active N-Doped Titanium Dioxide Photocatalyst by Modification Under Elevated Pressure

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The new method for improving photocatalytic activity of commercial titanium dioxide (anatase, Police, Poland) is presented. The modification was conducted under elevated pressure in ammonia water atmosphere in pressure reactor. It leads to built in nitrogen in titanium dioxide structure without surface hydroxyl group's reduction. The photocatalyst was characterised by XRD, FTIR/DRS, UV-Vis/DRS. New N-doped titanium dioxide photocatalyst had also better adsorption of dyes than unmodified material. The analysis of OH radicals formation on the photocatalyst surface under UV and Vis irradiation were performed by fluorescence technique with using coumarin, which reacts with OH radicals to produce highly fluorescent product, 7-hydroxycoumarin. Under Vis light irradiation N-doped titanium dioxide photocatalyst produced about seven times higher amount of hydroxyl radicals than unmodified titanium dioxide. The photocatalytic activity of modified titanium dioxide was tested during three azo dyes decomposition (monoazo dye – Reactive Red, diazo dye – Reactive Black and poliazo dye – Direct Green) under UV and Visible light irradiation. The photocatalytic activity of N-doped titanium dioxide was always higher than unmodified one as well as P25 of Degussa.

## 748

### Synthesis, Characterization, and Photocatalytic Properties

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A series of catalysts containing tris(2,2'-bipyridine)iron(II) ($Fe(bpy)_3^{2+}$) complexes inside zeolite Y cages with various ion-exchanged alkali metal cations ($Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$) have been synthesized. In this study, the influences of the alkali metal cations on the physicochemical properties of the catalysts as well as their catalytic performances were investigated. Formation of the $Fe(bpy)_3^{2+}$ complexes was ascertained by XRD, diffuse-reflectance UV-vis spectroscopy, and Fe K-edge XAFS measurement. The steric constraint induced by increasing the size of the alkali metal cations resulted in a decrease in both Fe content and BET surface area. The intensity of the MLCT absorption band of Fe complexes associated with zeolites increased in the presence of heavier alkali metal cations, while the electron density of the Fe atoms decreased as the ionic radius of the alkali metal cations increased. The encapsulation of Fe complexes within zeolite Y cages resulted in the creation of a new photocatalytic system enabling efficient oxidation of styrene to benzaldehyde and styrene oxide under visible-light irradiation in the presence of molecular oxygen. The TON was found to correlate with the increased intensity of the MLCT band and the decreased electron density of the Fe atoms. It is suggested that the electron density of the Fe atom predominantly determines the oxidation rate; this may be rationalized in terms of mechanistic considerations.

## 749

### Shape-Controlled Anatase $TiO_2$ Particle Prepared by Hydrothermal Treatment in the Presence of Hydrophilic Polymer

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Semiconductor particle is attractive material as a photocatalyst in advantage of a large number of reaction sites. Photocatalytic reactions are induced by photoexcited electrons and positive holes, which induce reduction and oxidation reaction on the surface of same particle. Therefore, inverse reaction and recombination are easily occurred compared to electrode reaction system, resulting in largely reducing an efficiency of photocatalytic reaction. In recent years, it is reported that titanium(IV) oxide ($TiO_2$) consisted of specific exposed crystal-surfaces has higher photocatalytic activity. Electrode experiment of semiconductor single crystal has indicated that photoelectrochemical properties strongly depend on crystal surface. Therefore, different energy levels of conduction and valence band are thought to drive the electrons and holes to different crystal face, leading separation of reaction sites and enhancement of photocatalytic reactions on the $TiO_2$ particle. In this study, we synthesized anatase $TiO_2$ particles consisted with specific exposed crystal-surfaces. Titanium(III) chloride and peroxy titanium acid were used as precursor, and they were hydrothermal-treated in the presence of inorganic anion and hydrophilic polymer as controller reagent of exposed crystal-surface. Synthesized particles appeared octahedral or decahedral shape of anatase structure from SEM and TEM observation, and its structure strongly depended on the hydrothermal condition (temperature, hydrothermal reaction time, kind of polymer, pH). Moreover, the $TiO_2$ particles showed relatively higher photocatalytic activity of acetaldehyde decomposition due to separation of reaction site. Therefore, we carried out further study on relationship between exposed crystal-surface and photocatalytic activity.

## 750

### Hydrogen and Oxygen Evolution from Aqueous Solutions Under Visible Light Irradiation Using Rhodium and Antimony-Codoped $SrTiO_3$ Photocatalyst

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Photocatalytic activities of rhodium and antimony-codoped $SrTiO_3$ ($SrTiO_3$:Sb/Rh) under visible light irradiation were investigated in order to develop new visible-light response oxide photocatalysts.

$SrTiO_3$:Sb/Rh was prepared by a hydrothermal synthesis. Photocatalytic reactions for $H_2$ evolution from an aqueous methanol solution (10 vol%) and for $O_2$ evolution from an aqueous silver nitrate solution (0.02 mol $L^{-1}$) were carried out in a gas-closed circulation system. A 300-W Xe lamp with attached cutoff filter was employed for visible light irradiation.

$SrTiO_3$:Sb/Rh showed new absorption bands in the visible light region in addition to the intrinsic absorption band due to band gap transition (Energy gap = 2.4 eV). Pt-loaded and $IrO_2$-loaded $SrTiO_3$:Sb/Rh showed photocatalytic activities for the $H_2$ evolution and the $O_2$ evolution under visible light irradiation, respectively. The visible-light response was due to charge transfer transition from electron donor levels formed by doped $Rh^{3+}$ ions to the conduction band of the host. The photocatalytic activity of $SrTiO_3$:Sb/Rh strongly depended on the synthetic condition and the ratio of the Sb/Rh dopant. The synthetic condition and codoping of antimony affected the oxidation state and the environment around the doped rhodium species, and the surface active site of the $SrTiO_3$:Sb/Rh photocatalyst, resulting in that photocatalytic properties of $SrTiO_3$:Sb/Rh were improved.

It was found that $SrTiO_3$:Sb/Rh is a new oxide photocatalyst for $H_2$ and $O_2$ evolution from aqueous solutions containing sacrificial reagents under visible light irradiation.

## 751

### Solar Photocatalytic Degradation of Phenol Wastewater : Potential,Challenges and Opportunities - An Indian Perspective

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**M Premalatha,** *NIT,Trichy, India*
**N Anantharaman,** *India*

Quantity of water use in Indian industries is very high compared to other countries water usage. Inefficient water use by industry in India creates lot of problems. This quantity could be reduced to a minimal by recycling the water after sufficient treatment. The available treatment processes do not aim at sufficient treatment required for recycling of water but it concentrates more on achieving the standards, hence complicating the process. Complicated Effluent Treatment Process neither help in recycling of water nor getting standards achieved but results in higher energy consumption for Effluent Treatment Plant. This work aims at sufficient in-situ treatment of wastewater and recycling of water for low-grade applications in the industry. Complete destruction of the contaminant is possible using inexhaustible, free source of energy from sunlight thus consuming very less primary energy for its operation. Photocatalytic experiments were carried out using laboratory photo reactor for degradation of phenol wastewater. The experiments were carried out with 8W UV lamp with 0.2 g/L of $TiO_2$ catalyst for different concentration of phenol wastewater ranging from 20,40,60,80,100,200,300,400,500 and 600 ppm. It is found that complete degradation of phenol is possible in a reasonable time (i.e. less than 5 hrs) when concentration of phenol is ≤100 ppm. This observation is used for design of solar collector and to calculate its economics.

## 752

### Overall Water Splitting Under Visible Light Irradiation by Z-Scheme Photocatalysis System Using Co-Based Electron Mediators

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**Akihiko Kudo,** *Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan*

Photocatalytic overall water splitting has been studied as a potential technique for $H_2$ production by photon energy conversion. It is important to develop visible-light-driven photocatalysts in terms of utilization of the solar energy. Recently, it was reported that overall water splitting under visible light irradiation proceeded for using two-step photoexcitation systems (Z-scheme). The Z-scheme photocatalysis system is composed of two kinds of photocatalysts and a reversible redox couple. Thus, the development of redox couples in the Z-scheme photocatalysis systems is important. In the present study, we studied to construct a visible-light-driven Z-scheme photocatalysis system using Co-complexes, $[Co(phen)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$, as redox couples. Rh-doped $SrTiO_3$ (denoted as $SrTiO_3$:Rh) powder for the $H_2$ evolution photocatalyst was prepared by a solid state reaction. A Ru cocatalyst was loaded on $SrTiO_3$:Rh by photodeposition. $BiVO_4$ powder for the $O_2$ evolution photocatalyst was prepared by a liquid-solid-reaction. $[Co(phen)_3]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$ redox couples worked as electron mediators for overall water splitting by the Z-scheme photocatalysis system, (Ru/$SrTiO_3$:Rh)-($BiVO_4$). The photocatalytic activity depended on pH. The pH dependence is due to the change in potential differences between band positions of $SrTiO_3$:Rh and $BiVO_4$ photocatalysts, and redox potential of the Co-complexes. In conclusion, we succeeded in the construction of the new Z-scheme systems for overall water splitting under visible light irradiation.

## 753

### Study of Au-$TiO_2$ Photocatalysts Toward Visible Photodegradation of Acid Red 88 in the Presence of Electron Acceptors

**P Sathish Kumar,** *India*

Nanoparticulate Au catalysts are active under mild conditions, even at ambient temperature or less, and this makes them unique. Further, use of mixed precious metal-semiconductor catalysts can produce even higher activities than the use of Au alone. Hence, with an attempt to extend light absorption of semiconductor based photocatalyst ($TiO_2$) towards visible light range and eliminate the rapid recombination of excited electrons/holes during photoreaction, here Au-$TiO_2$ photocatalyst were prepared by deposition-precipitation using NaOH for photocatalytic degradation of azo dye (Acid Red 88; AR 88). The materials were characterized and the superiority of Au-$TiO_2$ photocatalyst over bare $TiO_2$ particles for the photocatalytic degradation of AR 88 is explained. Mineralization of target pollutant was also performed by Total Organic Carbon (TOC) analysis and a suitable mechanism is proposed for photodegradation of AR88 in the presence and absence of electron acceptors [Peroxomonosulfate (PMS), Peroxodisulfate (PDS) & Hydrogen peroxide ($H_2O_2$)] to prove Au-$TiO_2$ is a better photocatalyst for advanced oxidation technologies (AOTs).

## 754

### The Role of Chloride in Trichloroethylene on its Photodegradation by Metallised (Ag, Pt) Titanium Dioxide

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**Tuti M Lim,** *Institute of Environmental Science and Engineering, Nanyang Technological University, Singapore*
**Ken Chiang,** *ARC Centre for Functional Nanomaterials, University of New South Wales, Australia*
**Jason Scott,** *ARC Centre for Functional Nanomaterials, University of New South Wales, Australia*
**Rose Amal,** *ARC Centre for Functional Nanomaterials, University of New South Wales, Australia*

The presence of nanosized metal deposits on the surface of titanium dioxide is generally beneficial for photocatalytic oxidation. Platinum deposits regularly improve photocatalytic performance moreso than silver deposits, although this was not the case for the gas-phase photodegradation of trichloroethylene (TCE) in this study. Here, Pt deposits were detrimental for photoactivity, irrespective of the loading, while Ag loadings up to 1 at% were beneficial. XPS spectra of fresh and used metallised titanium dioxide indicated both an increase in the percentage of oxidised metal on the surface as well as the presence of both organic and inorganic chloride species following TCE photodegradation. The contribution of chloride to the respective positive and negative effects of Ag and Pt on the photodegradation of TCE is discussed in light of these findings as is the influence of deposit characteristics on the extent of the effect.

## 755

### Photocatalytic Sheet for Cleanup of Soil Polluted by VCOCs

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**Hisae Kiriya,** *RCAST, The Univ. of Tokyo, Japan*
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Volatile chlorinated organic compounds (VCOCs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) have been indiscriminately disposed by the middle of the 1980's, causing soil and groundwater pollution. We have designed a cleanup system for polluted soil utilizing '$TiO_2$ photocatalytic sheets' and solar light. In this paper, we report the constituents of the photocatalytic sheet to trap and decompose VCOCs from the soil, and a cleanup test utilizing the sheets in an actual polluted field.

The constituents of photocatalytic sheet were examined by evaluating photodecomposition activity of TCE and observing undesirable intermediates such as phosgene and chloroform released by the photodecomposition. First, the ratio of adsorbent (activated carbon) to $TiO_2$ powder was determined to decompose TCE completely as fast as possible without releasing the intermediates. Next, one activated carbon ('Small' in Fig) having main pore size of 1 nm was selected from the adsorption ability of TCE and the intermediates. Finally, photocatalytic sheet has been made of corrugated nonworen material containing both $TiO_2$ powder and the activated carbon, and the adsorption and photodecomposition activities of the sheets have been confirmed.

The VCOCs gases from actual polluted soil were extracted by the fan through the drilling well, and led to the photocatalytic sheets within the adsorption device. The sheets saturated with the gases were irradiated with solar light to renew and reuse. It was confirmed that the system using the photocatalytic sheets was effective in an actual polluted field of a cleaning shop.

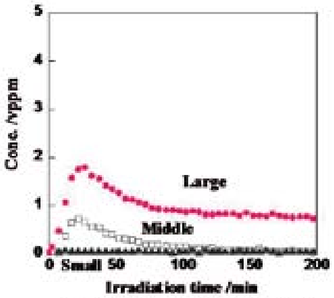

Fig. Intermediates generation using photocatalysts mixed with three kinds of activated carbon

## 756

### Photodeposition of CdS Nanocrystals on the Surface of $TiO_2$

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**Junya Tanikawa,** *Kinki University, Japan*
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Ultraviolet light-irradiation (excitaion wavelength > 300 nm) of a mixed ethanol solution of cadmium perchlorate and elemental sulfur ($S_8$) under deaerated conditions has led to deposition of CdS nanoparticles on the surface of $TiO_2$ ($CdS/TiO_2$). With increasing irradiation time, the number density of CdS particles increased, whereas their mean size hardly changed. Also, the deposition of which rate decreased with increasing irradiation time ceased on the whole coverage of the $TiO_2$ surface with CdS. The deposition of CdS was found to be caused by $TiO_2$ photocatalysis via the oxidation of ethanol to acetaldehyde and the reduction of $S_8$ to $S^{2-}$ ions. Electron energy loss spectra and high-resolution transmission electron micrograph images of $CdS/TiO_2$ confirmed the deposits to be hexagonal CdS crystals in a good contact with $TiO_2$. The electronic absorption spectra of $CdS/TiO_2$ had absorption below ca. 550 nm due to the interband transition of CdS in addition to the absorption of $TiO_2$ below 390 nm. As a result of further photodeposition of Pt on $CdS/TiO_2$, Pt particles were deposited almost selectively on the $TiO_2$ surface ($Pt/CdS/TiO_2$). The time evolution for the CdS photodeposition was well-fitted by a rate equation drawn by assuming efficient photoinduced electron transfer from CdS to $TiO_2$ (Fig. 1): $CdS(t) = CdS_{sat}[1 - \exp(-kt)]$, where $CdS_{sat}$ and k are the saturated deposition amount of CdS and the apparent rate constant, respectively. Visible light-irradiation (excitation wavelength > 440 nm) of an ethanol suspension containing $Pt/CdS/TiO_2$ gave rise to $H_2$.

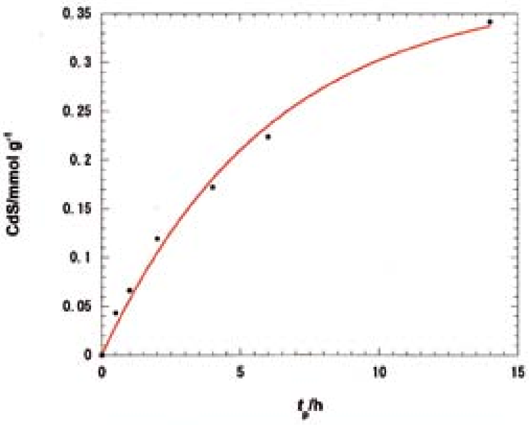

Fig. 1 Plots of the amount of CdS photodeposited vs. irradiation time.

## 757

### Investigation of Nanosized Titania Synthesized via a Modified Sol-Gel Route as Self-Cleaning Surface Materials

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Titanium dioxide ($TiO_2$) or titania is a photocatalyst and has been regarded as a promising material in waste abatement since it was discovered that water could be decomposed on titania under ultraviolet (UV) irradiation. In this study, anatase sols are prepared at low temperature by hydrolysis and condensations of titanium tetraisopropoxide. Titania thin films are produced on glass substrates from colloidal sols by spin coating process. The superhydrophilic and photocatalytic properties of the titania thin films are evaluated.

XRD patterns shows sharp anatase peak of titania, confirming presence of crystalline anatase phase. The absorption of UV light mainly results from the promotion 3d electrons in the crystal field. Typical TEM micrographs of titania calcined at 450°C for 3 hours shows the anatase crystallites of about 17-20 nm in diameter, which is in agreement with the size of the crystallites determined by XRD analysis. In HRTEM image, lattice fringes corresponding to (101) planes of anatase phase was observed. Figure 1 shows the comparison between uncoated and coated glass when dry and with water droplet. The titania coated glass is superhydrophilic with contact angle less than 3° (water spreads out on the glass surface). Photocatalytic activity of anatase titania thin films was confirmed by measuring the salicylic acid degradation under UV illumination. The study shows encouraging preliminary results which warrant further investigation of nanotitania as coating material for self-cleaning surface.

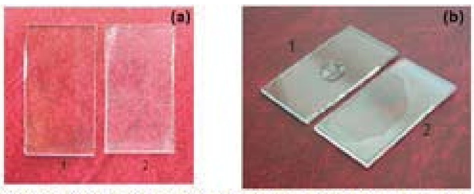

Fig.1(a) Uncoated (1) and coated glass (2); (b) water droplet on uncoated (1) and coated glass. Contact angle of uncoated glass ca.90° (1) and coated glass ca. <3°(2)

## 758

### Photocatalytic Conversion of TCDD and PCDD in a Novel Photoreactor

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TCDD and PCDD are persistent organic pollutants and they have induced a series of severe influences on pro-environment and human health. So how to reduce their harmful effects is the most urgent and tough works we were facing now. In this paper, a novel photoreactor possessing high photocatalytic conversion efficiency of TCDD and PCDD was fabricated with modified photocatalysts which were loaded on the activated carbon fibers. During the photo-conversion process, TCDD and PCDD were enriched on activated carbon fibers first, and then they were photoconversed by modified photocatalysts effectively. The modified photocatalyst was prepared by doping nitrogen into commercial available titania. Analysis by X-ray photoelectron spectroscopy (XPS) indicated that the peak at 396eV is attributed to N bound to Ti atoms, which is the main reason of photocatalytic activity enhancement. For the results of XRD didn't indicate the formation of Ti-N crystallite, we could deduce the substitution of N for lattice O. A significant shift of the absorption edge to a longer wavelength and a higher absorption in the visible light region were observed. These N-doped $TiO_2$ powders exhibited excellent photocatalytic activity for the conversion of TCDD and PCDD under irradiation.

## 759

### Flame-Made F-$TiO_2$: An Efficient Second Generation Photocatalyst

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**Rose Amal,** *ARC Centre of Excellence for Functional Nanomaterials, The University of New South Wales, Sydney, Australia*

Recent breakthroughs in the modification of $TiO_2$ photocatalysts by nonmetal-dopant has centred primarily around C, N and S elements. These dopants extend the absorption of the host materials to visible-light range, rendering them photocatalytically-active under UV and visible-light. In a less studied dopant, we have synthesised F-doped $TiO_2$ in a rapid one-step Flame Spray Pyrolysis (FSP). FSP has been shown to yield highly-active photocatalysts of different types [1-4].

Unlike other visible-light photocatalysts, F-doping did not shift the band-edge position of $TiO_2$ to visible-light regime. The F-dopant has characterictic binding energy at 685eV, attributed to the ≡Ti-F species [5]. It is expected that the fluoride-doping induces F-type oxygen or Ti3+ vacancies. This is consistent with the increasing tail absorption in the visible-light range with increasing fluorine concentrations (F:Ti = 0.1-2.0).

The F-TiO2 photocatalysts were highly active in mineralizing acetaldehyde under both UV ($\lambda$>350 nm) and visible-light ($\lambda$>420 nm). In fact the F-$TiO_2$ was much more active than standard Degussa P25 and Ishihara ST-01 $TiO_2$ even under UV-illumination. Similarly, F-TiO2 continues to show visible-light activity, while both P25 and ST-01 were relatively dormant. The visible light activity of F-$TiO_2$ could be traced to the defect-induced extrinsic bandgap excitations [6].

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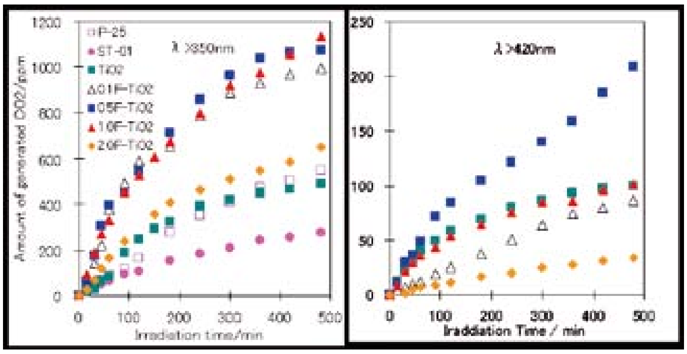

## 760

### Decomposition of Humic Acids Over Titania Dioxide Doped with Iron and Carbon

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**Antoni W Morawski,** *Szczecin University of Technology, Institute of Chemical and Environment Engineering, Poland*

Titania dioxide of anatase structure was doped with iron and a residue carbon through the mixing of $TiO_2$ with $FeC_2O_4$ in the ratio of 10:1 and heating at different temperatures, 500-800°C under Ar flow. The pure titania dioxide and prepared samples were used for humic acids decomposition under UV irradiation. It was proved that humic acids were decomposed through the preliminary adsorption on the photocatalyst surface, which was confirmed by FTIR measurements. Modification of $TiO_2$ by iron doping, especially at low temperature of heat treatment, caused increased adsorption of humic acids on its surface and enhanced photocatalytic activity. At lower temperatures of heat treatment iron was present in the form of magnetite and hematite whereas at higher temperatures was inbuilt in $TiO_2$ lattice and formed $FeTiO_3$ phase, which showed lower photoactivity. Degradation of humic acids was controlled by the particle size measurements in the solution, and also by UV absorbance at 254 nm, Fluorescence Spectroscopy and Total Organic Carbon.

## 761

### Device Tailored Specificity of Titania Nanoparticle

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Recent interest in titanium dioxide ($TiO_2$) nanomaterials has been largely driven by the photocatalytic properties exhibited by the anatase and rutile phases. We have concentrated on the relationship between the synthetic pathways to $TiO_2$ and the properties of the resulting products, demonstrating that the control of the relative reactant diffusion rates during solvothermal reaction leads to the prediction and control of the phase, size and nanostructures type. This degree of control has made it possible for the systematic synthesis of $TiO_2$ nanostructures by varying parameters such as solvent chain length, reaction temperature and time, and the addition of surfactants into the reaction mixture. Each of these parameters has been found to play a distinct role in the synthetic mechanism and judicious variation allows for the tailoring of nanostructures, vital for the optimisation of nanostructure for specific photocatalytic applications.

The photocatalytic activity of the $TiO_2$ samples were evaluated by the photo-degradation of the organic dye methylene blue (MB) in aqueous solution with $TiO_2$ nanoparticles. We found no significant relationship between the particle size and the rate of MB degradation, despite the large difference in surface area of the photocatalyst. These studies also showed that whilst pure anatase samples degrade MB reasonably well, rutile samples were found to be inactive. In contrast, mixed-phase $TiO_2$ particles resulted in an increased rate of photo-degradation.

The custom synthesis of $TiO_2$ nanostructures can lead to significant differences in photocatalytic activities, making it of particular interest in tuning the properties of $TiO_2$ for potential applications.

## 762

### Visible Light Photocatalytic Degradation Using Ion-Doped Titania Impregnated Kaolinite Nano-photocatalysts

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**Shaomin Lei,** *Wuhan University of Technology, China*
**Meng Nan Chong,** *The University of Adelaide, Australia*
**Bo Jin,** *The University of Adelaide, Australia*
**Chris Chow,** *Australian Water Quality Centre, Australia*
**Chris Saint,** *Australian Water Quality Centre, Australia*

Water remediation utilising semiconductor titanium dioxide has received enormous attention owing to its proven capability in mineralising a wide range of recalcitrant compounds into innocuous final by-products. However the practical implementation of such novel technology still faces some limitations, such as the difficulty in downstream separation and limited photo-activation by ultraviolet (UV) light spectrum. Recently the titania impregnated kaolinite ($TiO_2$/K) nano-photocatalysts has been successfully synthesized to enhance its ability of photo-degradation and recovery in downstream separation. In this work, the main objective is to expand the photo-activation of titania/kaolinite photocatalysts into visible solar region ($\lambda \geq$ 400nm) by the introduction of foreign dopants (i.e. Fe and N). The synthesis of the ion-doped nano-photocatalysts was accomplished through a modified two steps sol-gel method and also the direct amination of titanium precursors with triethylamine. The synthesis conditions in terms of the concentration and loading of the dopants are investigated for optimum photo-activity under the irradiation of visible light. The doped nano-photocatalysts are subjected to characterisations using specific surface area measurements (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).The photocatalytic ability of the newly doped nano-photocatalysts is evaluated using 40 ppm of Congo Red as the model reaction.

# 763

## Photocatalytic Application of Porous Au/$TiO_2$ Nano-hybrids Prepared by a Templating Technique

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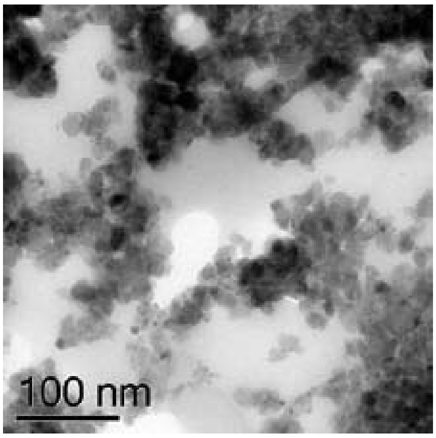
Gold doping or deposition in $TiO_2$ can effectively improve the photocatalytic performance of the titania by either modifying the bandgap and thereby inducing photoactivity under visible light or decreasing the recombination of excited electron and hole. Templating techniques can produce materials with designed morphology and porosity. The objective of this project was to couple controlled porosity allowing faster molecule diffusion through the porous channels with gold deposition to further increase the photocatalytic activity of $TiO_2$.

Templating and sol-gel techniques were combined to synthesise Au/$TiO_2$ nano-hybrids with improved photocatalytic activity. The porous structures directed by the agarose gel template were examined by SEM. X-ray diffraction analysis ascertained the materials to be anatase phase, and the gold peaks were observed when the gold content was over 0.25 wt%. TEM further confirmed the highly porous structure of the composites (Figure 1). The gold particle sizes, influenced by both the synthesis methods and initial gold content, ranged from ~ 2 to 40 nm. The gold distribution and content were identified by means of secondary ion mass spectrometer and inductively coupled plasma mass spectrometry, respectively. Finally, the catalytic performance of the Au/$TiO_2$ was assessed by photodecomposition of methylene blue under UV light. The influence of parameters such as synthesis methods, material properties and photocatalytic test conditions (e.g., pH, catalyst and dye concentration) on the photocatalytic efficiency was also investigated. The photocatalytic efficiency improved by a maximum 40% for the Au/$TiO_2$ sample with a gold particle size of 2 nm and 2 wt % gold content.



# 764

## Enhancement of Photocatalytical Activity by Gold Nanostructures in

**Inga Bannat,** *Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry, Germany*
**Katrin Wessels,** *Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry, Germany*
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**Michael Wark,** *Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry, Germany*

Besides their adjustable optical, electronic and photoelectrochemical properties, which are of interest in view of applications in biosensors and other nanodevices, gold nanoparticles have been attracting much attention because they can enhance the photocatalytical properties of $TiO_2$ due to a more efficient charge separation of the generated electron-hole pairs and an increase of their lifetime.

Transparent mesoporous $TiO_2$ films (MT) prepared by the EISA (evaporation-induced self-assembly) process offer very high porosities and thus potentially a higher number of catalytic centers [1]. Pure mesoporous $TiO_2$ films, however, show a low photocatalytic conversion of NO of only 3 % caused by a poor crystallinity of the $TiO_2$ framework and a film thickness of only about 200 nm currently reachable with the preparation method, which is significant lower than that for powder catalysts.

In this study we have prepared gold nanowires inside the mesoporous $TiO_2$ films by pulsed cathodic electrodeposition from HAuCl4 solution (Figure 1 A). The length and density of the nanowires could be controlled by the number and potential of the applied pulses. Individual gold nanoparticles were prepared by self-assembled anchoring on thiol groups and reduction with NaBH4 (Figure 1 B).

The gold nanoparticles (AuNP-MT) and nanowires (AuNW-MT) within the film increase considerably the NO oxidation to 16 % and 30 %, respectively (Figure 1 C). Because the growth of the nanowires appears from the conductive ITO layer this avoids blocking effects and ensures good accessibility of the pore system.

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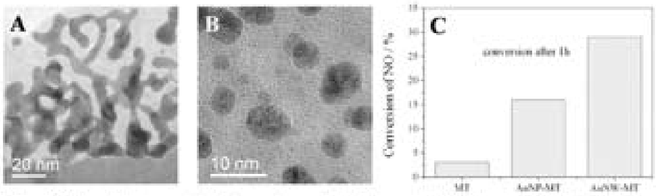

**Figure 1:** High-resolution transmission electron micrographs of gold nanowires (A) and nanoparticles (B) in mesoporous $TiO_2$ and the corresponding photocatalytic conversion of NO

# 765

## Modified Layered Tantalate Semicoductors as Efficient Visible Light Photocatalysts

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**Gang Liu,** *ARC Centre of Excellence for Functional Nanomaterials, and Australian Institute of Bioengineering and Nanotechnology, UQ, Australia*
**Lianzhou Wang,** *ARC Centre of Excellence for Functional Nanomaterials, and Australian Institute of Bioengineering and Nanotechnology, UQ, Australia*
**Gaoqing Max Lu,** *ARC Centre of Excellence for Functional Nanomaterials, and Australian Institute of Bioengineering and Nanotechnology, UQ, Australia*

Semiconducting photocatalyst is an important class of functional materials that underpins the development of new technologies for solar energy utilization such as photocatalytic water/air purification, hydrogen production from water splitting and photovoltaic cells. A main drawback for most existing oxide semiconductors lies in their large band gap and hence only photo-activity in the UV range. To utilize visible light dominant solar energy, it is highly desirable to develop efficient visible light photocatalysts. Herein, we demonstrate that simple nitrogen doping in a layered tantalate compound could lead to significant red shift in its absorption edge up to 460 nm. Moreover, this enhanced visible light absorption is originated from an intriguing band-to-band activation instead of a commonly observed shoulder for other photocatalysts. Detailed characterisations including XRD, XPS, nitrogen adsorption, UV-visible spectra, SEM and FIIR were employed to gain better understanding of this new layered compound. The photocatalyst exhibited superior visible light photocatalytic performance in photodegradation of organic pollutants than that of benchmarking P-25 powder.

## 766

### An Efficient Photocatalyst Structure: $TiO_2$(B) Nanofibers Covered with Anatase Nanocrystals

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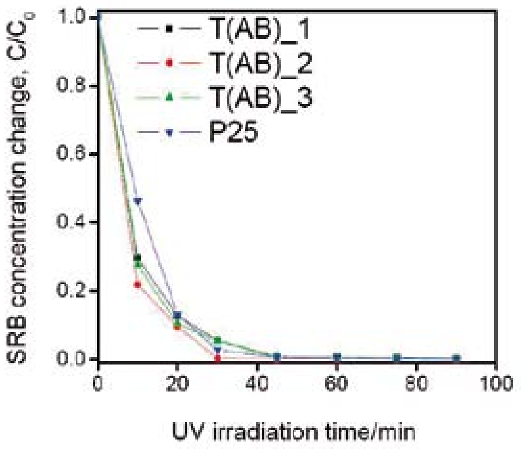
Titania photocatalysts have been widely studied for use in industries ranging from chemical synthesis, energy production and storage, environmental remediation, and sensors and odor control. $TiO_2$ catalysts are commercially advantageous due to a band gap that can be activated by sunlight and spans the redox properties of water. The performance of the catalysts depends on, such as $TiO_2$ polymorph, impurities, specific surface area, morphology and surface chemistry. Catalysts with a delicate composite structure, in which $TiO_2$(B) fiber is covered with anatase nanocrystals are developed. Such a structure possesses several advantages. First, The band gap of $TiO_2$(B) phase is narrower than that of anatase, thus there will be difference between conduction band edges of the two phases. This difference will facilitate irreversible charge transfer from one phase to the other, and thus reduces the recombination of photo-generated electrons and holes. The efficient separation of the photo-generated charges facilitates the redox reaction involving these charges. Second, the fibril structure has good mechanic strength because of the core $TiO_2$(B) fiber and large specific surface area because of the fibril morphology and anatase nanocrystals on the fibre surface. Third, they can be easily dispersed into and separated from a solution, and this property is important to the commercial applications of the photocatalysis process. They exhibit superior photocatalytic activity to the well known P25 powder for degradation of SRB dye (Figure 1). Finally the catalysts of such structure were prepared via a facile hydrothermal process from industrial grade titanias, even rutile minerals.



## 767

### Doping Trace Metal Ions ($Ce^{3+}$, $Co^{3+}$, and $Cu^{2+}$) on Nanofibers of Mixed $TiO_2$(B) and Anatase Phases

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**Moses Adebajo,** *School of Physical and Chemical Sciences, Queensland University of Technology, Brisbane QLD, Australia*
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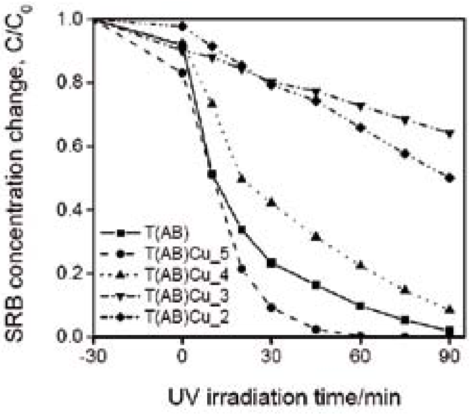
One approach to improve the photocatalytic activity of TiO2 catalyst is doping metal/metal ion on $TiO_2$ catalyst. Usually metal elements are doped on single phase $TiO_2$ catalysts and the content of dopant is usually larger than 1%. In this study, we dope trace ions of transitional metals, Co and Cu, and lanthanide metal Ce on the nanofibers of mixed anatase and $TiO_2$(B). There have been limited studies on photocatalytic activity of $TiO_2$(B) phase and no study on the doping on nanostructure of the mixed anatase and $TiO_2$(B). The doping on the mixed phase systems could be very different from that on a single phase. The dopants may distribute preferably on one of two phases or in the interface region. This can effect the mechanism and activity photocatalytic reactions. Sulforhodamine-B (SRB) was used as a model chemical to carry out the photocatalytic activity tests under UV light irradiation. It was observed that the trace metal ions doped $TiO_2$ fibers with pure crystalline phase, anatase or $TiO_2$(B), all displayed less photocatalytic activity than the non-doped fibers, and only the doped mixed phase fibers showed improved photocatalytic degradation activity (Figure 1). Obviously, the phase interface between anatase and $TiO_2$(B) play an important role in enhancing the activity of the photocatalysts. We believe that the trace metal ions promote the separation of photogenerated charge carriers, and thus to improve its photoactivity, only when they exist in the phase interface. This study highlights new opportunities for the design and preparation of highly efficient photocatalysts.



## 768

### Photodegradation of Dye by Polyoxometalate/$TiO_2$ Composite Catalysts Under Visible Light Illumination

**Jiman Yeo,** *School of Environmental Science and Engineering, Pohang University of Science and Technology, Korea*
**Wonyong Choi,** *Pohang University of Science and Technology, Korea*

Recently, polyoxometalates (POMs) have been widely investigated as a homogeneous photocatalyst and their photocatalytic activity has been successfully demonstrated. The photocatalytic oxidation capability of POMs is comparable to that of the heterogeneous $TiO_2$ photocatalyst. Like $TiO_2$, POMs are inactive under visible light irradiation. However, the dye-sensitization process was recently demonstrated for the dye/POM system as the dye degradation in visible light-illuminated $TiO_2$ is enabled through the sensitization mechanism. In this respect, we may expect that the photosensitized degradation of dye is enhanced with POM/$TiO_2$ composite compared with $TiO_2$ alone. In this study, POM/$TiO_2$ composite catalysts were synthesized using titanium-butoxide via sol-gel method. The physicochemical properties of these catalysts were investigated. The original Keggin structure of POM was retained in the POM/$TiO_2$ catalysts. SiW12/$TiO_2$ calcined at 350oC has higher photocatalytic activity than PW12/$TiO_2$ and PMo12/$TiO_2$ for the degradation of Rhodamine B (RhB) under visible irradiation. Acid Orange 7 (AO7), an anionic dye, was not degraded by POM/TiO2 under visible irradiation since the surface charge of POM/$TiO_2$ catalysts is predominantly negative and the electrostatic repulsion hinders the sensitization process. The effects of various experimental parameters were investigated and discussed.

## 769

### Photocatalytic Performance of Silica-Immobilized Polyoxometalates for the Oxidation of Gaseous Acetaldehyde

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**Wonyong Choi,** *Pohang University of Science and Technology, Korea*

Acetaldehyde in air is known to be one of the primary indoor air pollutants and the most abundant carbonyl compounds in the atmosphere. Therefore, the photocatalytic oxidation (PCO) of gaseous acetaldehyde has been frequently studied as a test reaction in the studies of photocatalytic air purification. Polyoxometalates (POMs) as a homogeneous photocatalyst successfully demonstrated their activity to degrade aquatic pollutants and so did the silica-immobilized POM (POM/SiO2) as a heterogenized photocatalyst in water. In this study, the performance of POM/SiO2 on the PCO of acetaldehyde under the ambient air condition was investigated. The catalysts were prepared using tetraethoxysilane as a silica precursor and commercial POM powder without further purification by the sol-gel hydrothermal method. After the acetaldehyde adsorption equilibrium was attained on the catalyst surface in the dark, the irradiation of UV light was immediately followed and then the concurrent generation of carbon dioxide and removal of acetaldehyde was monitored by GC analysis as a function of reaction time. Pure POM powder, bare silica, and POM/SiO2 were compared for the adsorption and the photodegradation of acetaldehyde. The silica-immobilized POMs (Na3O40PW12, H3Mo12O40P, and H4O40SiW12) exhibited marked activities for the decomposition of pre-adsorbed acetaldehyde under UV irradiation whereas pure POM powders were little active. The effects of various experimental parameters were investigated in detail.

## 770

### Photocatalytic Activity and Interface Structure of Nanofibers with Mixed Anatase and $TiO_2$(B) Phases

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**Huaiyong Zhu,** *School of Physical and Chemical Sciences, Queenland University of Technolgy, Australia*
**Hongwei Liu,** *School of Physical and Chemical Sciences, Queenland University of Technolgy, Australia*
**Xueping Gao,** *Institute of New Energy Material Chemistry, Nankai University, China*
**Lingxuan Wang,** *Institute of Chemistry, The Chinese Academy of Science, China*
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$TiO_2$ is the most extensively studied materials for photocatalysts because of its strong oxidizing power, low toxicity, and long-term photostability. $TiO_2$ exists mainly in four polymorphic forms in nature, anatase, rutile, brookite and $TiO_2$(B). Generally, anatase phase is considered to have higher photoactivity than other phase. However, it was also found that the $TiO_2$ powders consisted of mixed anatase and rutile nanocrystals (P25), exhibit a better photoactivity than pure anatase in many reaction systems. This phenomenon has been extensively investigated because it could be important for design of efficient $TiO_2$ photocatalysts. It is believed that the difference between conduction band edges of the two phases may facilitate irreversible electron transfer from anatase to rutile, and thus reduce the recombination of photo-generated electrons and holes.

In principle, the mechanism of efficient charge separation via irreversible charge transfer should be applicable to other systems of mixed $TiO_2$ phases as long as there is a difference between the conduction band edges to causing irreversible charge transfer from one phase to another. In the present study, we investigated the photoactivity of a series of nanofibers with mixed $TiO_2$(B) and anatase phases and verified that the irreversible charge transfer enhanced the photocatalytic activity of the mixed phase nanofibers. The structure of the interfaces between the two phases in nanofibers was investigated in detail, and we found that interfaces formed by well-matched two phases are important for photoactivity of the nanofibers.

## 771

### Exploring the Photo-physical Properties of Nanostructure $TiO_2$ Films in Dye Sensitized Solar Cell

**Michal Adler,** *Bar Ilan University, Israel*
**Arie Zaban,** *Chemistry Department, Bar-Ilan University, Israel*

Since their discovery, Dye Sensitized Solar Cells (DSSC) are at the foremost research which deals with the conversation of solar to electrical energy. Nevertheless, many question marks are still open despite the intensive study in the field. In particular, one of the parameters that influence the activity of the cell is the electron transport in the nanoporous $TiO_2$ films.These processes are not well understood especially under operation conditions of the cell.

We are developing a unique method that will open a new window to the most internal events taking place during the operation of the dye cell. This method will enable us to simultaneously determine the exact position of both the Fermi level ($E_F$) and the conduction band ($E_{CB}$)of the semiconductor, by parallel measurements of the photovoltaic parameters and the semiconductor conductivity in an operating cell. Our technique is based on depositing the $TiO_2$ film on a transparent conductive substrate with a narrow non-conducting gap. This gap is covered by $TiO_2$ particles thus allowing measurements of the electrons flow between the two parts of the electrode.

Finding $E_{CB}$ as a function of the photovoltage will be applied for the understanding of the effect of various manipulations of the electrodes, including particles size, sintering procedure and coating. Finally, impedance spectroscopy will add more detailed view of the electron transport processes.

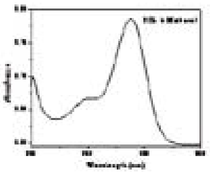
All these findings will dramatically improve our understanding of the basic events in operating cells. The method and new results will be presented.

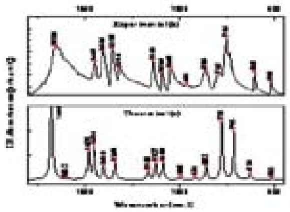
## 772

### Intramolecular and Intermolecular Charge Transfer Spectroscopy in UV-VIS and IR Region in Different Environment

**Papia Chowdhury,** *JAYPEE INSTITUTE OF INFPRMATION TECHNOLOGY UNIVERSITY, India*

Among different hydrogen bonds, the O-H…O and N-H…O bonds most often occur in liquid phase. It plays a crucial role in biological systems such as proteins and DNA base pairs and is essential for life processes. In all hydrogen bonded molecules there is a strong possibility of solute and solvent interaction. An effort to explain the ground and excited state intra/intermolecular charge transfer photophysics of Pyrrole-2-Carboxyldehyde (PCL), Pyrrole-2-carboxylic acid (PCA) and its related compounds in UV-VIS and IR region has been reported here.Quantum chemical calculations indicate that PCA, PCL are good candidate for intramolecular proton transfer in excited state. The absorption spectra of PCA in different solvent point the presence of intramolecularly hydrogen bonded closed conformer in the form of 280 nm band. Stokes shifted fluorescence of PCA at 310 nm in hydrocarbon solvent and hydroxylic solvents have been identified to be due to normal molecule. Variation of pH results enhancement or decrease of emission from ionic conformer with parallel dwindling of emission of neutral species. Possibility of intramolecular and intermolecular hydrogen bonding of PCL in ground state was established theoretically by the distance N5-H6………O11 of acidic and basic moieties of PCL and experimentally it is verified by the IR stretching and bending mode vibrations of different parts of the molecule. The possibility of transfer of hydrogen from pyrrole ring towards formyl ring in excited state indicates in the light of difference in bond length and bond angle, dipole moment, enthalpy, Gibbs free energy etc.





## 773

### Electronic Properties of Adjoined $TiO_2$ Nanocrystals

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**Nicolas Siedl,** *Institute of Materials Chemistry, Vienna University of Technology, Veterinaerplatz 1/GA, A-1210 Vienna, Austria, Austria*
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To include particle attachment and porosity in the discussion of the electronic properties of nanostructured oxide materials is indispensable for deeper insights into electronic conduction across grain boundaries and thus essential to electronics, sensor technology and photovoltaics. We investigated the condensation of isolated $TiO_2$-nanocrystals which results from the application of a simple hydration-dehydration cycle. After contact with water and subsequent dehydration and adsorbate removal under high vacuum conditions the powder of originally isolated nanocrystals [1] is transformed into a monolithic solid which consists of a particle network with a mesoporous structure. These monoliths show significant changes in the optical absorption properties as investigated by UV-diffuse reflectance spectroscopy. In addition, polarizable conduction band electrons [2] are only observed in the network which consists of adjoined $TiO_2$-nanocrystals [3]. Since photo-assisted tunneling between localized states in the oxide particle network represents an important conduction mechanism in dye-sensitized solar cells, UV induced charge separation processes were studied on nanocrystal aggregates using EPR and IR spectroscopy. Corresponding results will be discussed in the light of associated structural data.

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[3] M. J. Elser, T. Berger, D. Brandhuber, J. Bernardi, O. Diwald, E. Knözinger, J. Phys. Chem. B 2006, 110, 7605.

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## 774

### A Spectroscopic and Computational Study of Zinc Porphyrin Antennae

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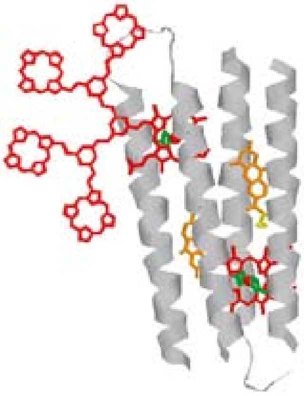
**Keith C Gordon,** *MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago, Dunedin, New Zealand*
**David L Officer,** *Intelligent Polymer Research Institute and Department of Chemistry, ARC Centre of Excellence for Electromaterials Science, Univ, Australia*

Photosynthesis is carried out by one of the most elaborate nanoscale biological machines in nature. An integral part of the so called photosystem is the 'antennae' which consist of many hundreds of chlorophyll molecules which capture energy from sun-light and filter it through to a single 'reaction centre'. In this manner the reaction centre enjoys a constant stream of excitation energy, which drives the energy conversion and storage processes even under low light.

We are attempting to create structurally simpler analogues of the photosystem which, in principle, replicate the 'antennae effect'. These are based on multi Zinc-Porphyrin (ZnP) arrays which have been designed such that energy is collected in peripheral ZnP sites and directed to a bound core site via a covalent linkage. The ZnP arrays may be incorporated into a synthetic peptide known as a maquette (Figure 1). This will be achieved using a ferrous porphyrin (FeP) to bind to the peptide interior and act as a redox centre for energy storage.

Ultimately it is hoped that such artificial constructs will lead to the creation of an efficient light harvesting bio-mimetic material that could be used as a photo-catalyst, or in photonic devices and solar cells. To this end, a detailed understanding of the electrochemical and photo-physical properties of the component units is required. This presentation will outline progress towards the computational and spectroscopic characterization of some ZnP-FeP dimers with a view toward their intended use as part of the supra-molecular construct.



## 775

### Zr(IV) and Hf(IV) Porphyrinate complexes as Suitable dyes for Photovoltaic Devices

**Alexander Falber,** *The University of Sydney, Department of Chemistry*
**Allan Larsen,** *The University of Sydney, Department of Chemistry*
**Max Crossley,** *The University of Sydney, Department of Chemistry*
**Charles Drain,** *The University of Sydney, Department of Chemistry*
**Udo Bach,** *The University of Sydney, Department of Chemistry*

As porphyrins play a critical role in photosynthesis, we continually strive to synthesise porphyrin complexes that can harvest incident light energy and effect charge transfer from photo-induced porphyrin excited states. Major goals in this field of work include 1. creation of large arrays of porphyrins over which charge separation can be stabilised and 2. harvest the charge within a photovoltaic device. Recently published work as well as our current work in Hf(IV) and Zr(IV) porphyrinate complexes offer a versatile template on the out-of-plane metal ion that easily binds to both organic and inorganic substrates bearing oxygen binding sites. We have observed dimer formation that may hold the key to more complex self-assembled porphyrin arrays. In particular we present Zr(IV) porphyrinates derivatives with extended β-pyrrolic systems. Analogous free base and Zn(II) metallated systems have shown potential applications for photovoltaics. Crystal structures, cyclic voltammetry, and UV-Vis spectra of these various derivatives display new and interesting architectures of porphyrin systems.

## 776

### Preparation of Novel Oligopyridines and Dyes for Application in Solar Cells

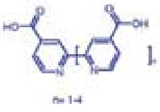
**Reza Ali Fallahpour,** *Switzerland*

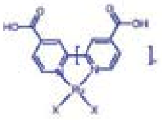
Dye sensitized solar cells (DSC) are currently attracting widespread academic and commercial interest for the conversion of sunlight into electricity because of their low cost and high efficiency. Over the past few years, considerable progress has been made in understanding the function of various components of DSC. An important component of the cell is preparation of a suitable dye which is our speciality.

HetCat, located at the University of Zurich, Switzerland, is a dynamic and reliable supplier of heterocyclic compounds (oligopyridines) and dyes for DSC-system.

HetCat Switzerland specialises in research and preparation of novel as well as known oligopyridines and their metal complexes. Functionalised oligopyridines are mostly used in DSC due to their properties. Our offer covers the whole range of pyridine, bipyridine, terpyridine, quaterpyridine and also higher oligopyridine derivatives.

Scientists working in Supramolecular chemistry, metal complexes, DSC, photosynthesis, photocatalysis, photoconversion and nanomaterials may benefit. We offer known products or research work, and our knowledge helps you saving time and money. We guaranty for high quality using all analytic instruments (IR, UV, MS, GC, NMR, X-ray). All products are available in from mg range to bulk.





## 777

### Electro-Optical and Electrochemical Studies of Dye Sensitized Solar Cells

**Alberto Fattori,** *University of Bath, United Kingdom*
**Laurie M Peter,** *University of Bath, United Kingdom*
**Mike Ward,** *University of Sheffield, United Kingdom*
**Juan M Herrera,** *University of Sheffield, United Kingdom*
**Amitava Das,** *University of Sheffield, United Kingdom*

The choice for dyes for dye-sensitized solar cells (DSC) depends on different parameters such stability, suitable attachment groups able to bind the dye on the surface of $TiO_2$, broad absorbance in the visible range. Photo-induced absorption spectroscopy (PIA)(1) is a powerful tool to obtain information on the efficiency of dye regeneration reactions in the cell. Studies have been made on the $TiO_2$ electrode and on the complete device on air using N719 and a wide range of other dyes, including polynuclear cyanoruthenate compounds(2) as well as several metal free organic dyes. The influence of the solvent on dye regeneration and stability has been investigated by PIA as well as by electrochemical and spectroelectrochemical measurements.

1. Gerrit Boschloo, Andres Hagfeldt, Chemical Physical Letters; 2003; (370), 381-386.
2. Juan-Manuel Herrera, Michael D. Ward, Harry Adams, Simon J.A.Pope and Stephen Faukner, Chem Comm; 2006; 1851-1853

## 778

### Water-Dispersed Conjugated Polymers as Viable Options for Water-Based Polymeric Solar Cells

**Alessandro Fraleoni Morgera,** *Univ. of Bologna, Dept. of Industrial and Materials Chemistry, Italy*
**Leonardo Setti,** *Univ. of Bologna, Dept. of Industrial and Materials Chemistry, Italy*
**Ivan Mencarelli,** *Univ. of Bologna, Dept. of Industrial and Materials Chemistry, Italy*

Polymeric solar cells are receiving considerable attention as promising candidates for cheap and diffused energy generation. However, devices realized on the basis of this technology relies on heavy use of high-boiling point and often chlorinated solvents: Although these solvents may be in principle safely manipulated in a properly designed industrial plant, it could be of interest to explore the possibility of fabricating prototypical devices based on water-soluble materials, hence avoiding the use of organic solvents.

In this view, we developed a technique able to deliver well dispersed mixtures of conjugated polymers (polythiophenes) and hydroxylated fullerenes C60. We report the results of this techniques in terms of photophysical behaviour of the mixture, including the evidences of energy transfer from the water-dispersed polymer to the hydroxylated fullerene C60. Work aimed to characterize practical devices fabricated on these principles is in progress.

## 779

### Photogalvanic Cell as a Device for Solar Energy Conversion and Storage: EDTA-Toluidine Blue-Thionine System

**Chhagan Lal Gehlot,** *Harcourt Butler Technological Institute, Kanpur - 208002 (INDIA), India*

The photogalvanic effect was studied in a photogalvanic cell containing ethylene diamine tetra-acetic acid [EDTA] as reductant, Toluidine blue and Thionine as photosensitizers. The photopotential and photocurrent generated were 695.0 mV and 105.0 mA, respectively. The observed conversion efficiency was 0.16 percent, the fill-factor was 0.16 and the maximum output of the cell was 72.9mW. The photogalvanic cell can be used at this power level for 42.0 minutes in the dark due to the storage capacity of the cell. The effects of different parameters on electrical output of the cell were observed and a mechanism for the generation of photocurrent in photogalvanic cells has also been proposed.

With the help of current-potential curve, the fill factor and conversion efficiency were determined using the formula:

Vpp x ipp
Fill-factor (n) = ----------- (1)
Voc x isc
Vpp x ipp
Conversion efficiency = ---------- x 100% (2)
10.4 (mW/cm2)

Where Vpp, ipp, Voc and isc are the potential at power point, current at power point, open circuit voltage and short circuit current, respectively.

The observed convesion effinciency (0.16 percent) was determind with a tungsten lamp of 200 W (as light source), which has light intensity around 15 times less than direct sunlight. Therefore, convesion efficiency has experimentally been observed as 2.4 percent.

The investigated electrochemical device is advantageous with respect to charging time (2 hrs), storage capacity (42.0 min) and better electrical output than devices reported so far.

## 780

### Solar Energy Conversion and Storage by Photogalvanic Solar Cells

**K R Genwa,** *Department of Chemistry,Jai Narain Vyas University, Jodhpur, India*

The consumption of non renewable sources of energy had caused more environmental damage than any other human activity. Electricity generated from fossil fuels such as coal, crude oil has led to high concentration of harmful gases in atmosphere. This has in turn led to problems such as ozone depletion and global warming. Due to the problems associated with the use of fossil fuels, alternative source of energy have become important and relevant in today's world. These sources such as sun and wind can never be exhausted and therefore called renewable or non conventional source of energy, they cause less emission are available locally. Solar energy is currently thought to cost about twice as much as traditional sources (coal, oil etc.) obviously, as fossil fuel reserve become depleted, their cost with rise until a point is reached where solar cells become economically viable source of energy. Efforts are continuously going to increase the efficiency of these cells. The photogalvanic cell can become the low cost renewable source. The objectives of the studies are to study the fundamental processes operative in solution phase photogalvanic solar cell, mechanism of photochemical reactions in photogalvanic cell containing two electrodes, development of and effective photogalvanic solar system with enhanced storage capacity and fabrication of low cost, pollution free, hazardless, device for solar energy conversion and storage.

## 781

### Photogalvanic Effect: Triton X – 100 – Rhodamine 6G – Oxalic Acid System

**Mahaveer Genwa,** *DDU College, Delhi University, India*

The effects of various parameters like pH, Diffusion length, electrode area and temperature on electrical output of the cell were observed and photogalvanic effect was studied in a photogalvanic cell containing TritonX-100 as surfactant, Rhodamine 6G as photosensitizer and Oxalic acid as reductant. The observed photopotential and photocurrent were 672.0 mV and 165.0 µA, respectively. The observed conversion efficiency was 0.55 % and the maximum output of cell was 57.06 µW. The photogalvanic cell can be used for 96 minutes in the dark and a mechanism has also been proposed for the generation of photocurrent in photogalvanic cell.

Keywords

Triton X-100, Rhodamine 6G, Fill Factor, Power Point, Conversion Efficiency.

## 782

### Waveguide Combined Solar Cells

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**Sven Rühle,** *Department of chemistry, Bar-Ilan University, Israel*
**Arie Zaban,** *Chemistry Department, Bar-Ilan University, Israel*

A new configuration of photovoltaic systems utilizes solar cells via wave-guides that collect the incoming solar radiation. The waveguide set-up opens new ways to exploit the sun light, among which are light concentration, increased efficiency of longer wave-lengths and enforced spectral selective absorption of the radiation. This spectral splitting into various solar cells along the illumination path aims at a tandem-like solar cell, while avoiding the current matching entanglement.

When light enters a waveguide it propagates along it due to total internal reflection. While grazing surroundings, the evanescent wave penetrates the waveguide surface to a distance of a wavelength magnitude. If the surrounding is a solar cell, the grazing light will be converted into electricity. This leads to decoupling of the charge carriers path from the optical photon path. The longer optical path preserves the effective high optical density, while the work within thin layers reduces the distance that the separated charges need to travel to the current collectors, and thus decreases the recombination of the formed charges.

The system may utilize any solar cell types. The concepts of the above innovation are tested using dye-sensitized solar cells. A single cell is fabricated on a flat waveguide, and characterized by a current-voltage sweep under a one-sun intensity solar simulator. IPCE (Incident Photon to Current Efficiency) spectra of the cell demonstrate the wavelength dependence of the efficiency.

## 783

### Sequential FRET Processes in Calix[4]arene-Linked Orange-Red-Green Perylene Bisimide Dye Arrays

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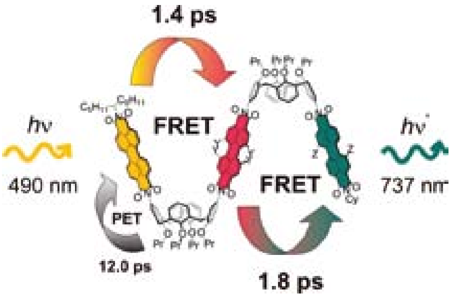
Ivo HM van Stokkum, *Vrije Universiteit van Amsterdam, The Netherlands*
Marcel Gsaenger, *University of Wuerzburg, Germany*
Michiel M Groeneveld, *Universiteit van Amsterdam, The Netherlands*
R M Williams, *Universiteit van Amsterdam, The Netherlands*
F Wuerthner, *University of Wuerzburg, Germany*

A comprehensive series of perylene bisimide (PBI) – calix[4]arene arrays composed of up to three different types of PBI chromophores (orange, red and green) has been synthesized. Within these arrays calix[4]arene scaffolds are applied to organize the PBI chromophores in a zigzag-type arrangement providing defined distances and angles between the individual dye units (see Figure). The characteristic feature of the as such constructed arrays is that the individual chromophoric building blocks can be easily replaced by each other as well as their optical properties can be fine-tuned without influencing the overall geometric arrangement of the supramolecular system. Owing to the excellent spectral overlap of the individual dye units, these arrays display very efficient sequential energy transfer processes. A quantitative analysis of the photophysical processes after photoexcitation as well as their rates have been obtained by using UV/vis absorption, steady state and time-resolved emission, femtosecond transient absorption spectroscopy and spectrotemporal analysis of the femtosecond transient absorption data. According to these studies, rate constants for the energy transfer from the orange perylene bisimide chromophoric unit to the red chromophoric unit (k = 6.4 x E11s-1 for compound or), from the red PBI moiety to the green dye unit (k = 4.0 x E11s-1 for compound rg), and slightly less efficient from the orange to the green PBI chromophore (k = 1.5 x E11s-1 for compound og) have been determined within these systems. The experimentally obtained rate constants are in very good agreement with those calculated according to the Förster theory.



## 784

### The Improvement of Dye Sensitized Solar Cells with Metal Substrates

Yongseok Jun, *Electronics and telecommunications research institute, Korea*
Hunkyun Pak, *Electronics and telecommunications research institute, Korea*
Ho Gyoung Yun, *Electronics and telecommunications research institute, Korea*
Man Gu Kang, *Electronics and telecommunications research institute, Korea*

The efforts to improve the efficiency of dye sensitized solar cells (DSSCs) have been made over a couple of decades. One of the essential components in DSSCs is underlayer formation. There have been a few well known studies for the underlayer formation and interconnection of $TiO_2$ nano-particles. The best known method is $_4$ treatment, which is an acidic condition. Due to the acidity of the solution, this method is not appropriate for treating metal substrates. Since metals can be etched by acidic solution, other methods must be considered.

We have applied a few different methods to have the same effect as $TiCl_4$ treatment, and have optimized to obtain maximum efficiency for metal substrates. For the optimum condition and feasibility, FTO coated glass substrates are used and analysed. The methods include treatment of titanium isopropoxide solution in isopropanol, neutralized $TiCl_4$ treatment, and other metal oxide formation such as $Nb_2O_5$.

For the analysis, electrochemical impedance spectroscopy, transient electron spectroscopy, and incident photon-to-current efficiency have been employed in addition to the common analysis methods.

## 785

### Mathematical Computer Modelling and Optimization of the Operation of Photovoltaic Cells and Solar Hydrogen Panels Using New Mathematical Models Based on Dynamic Equations on Time Scales

Tomasia Kulik, *University of New South Wales, Australia*

A new mathematical computer model for the operation of photovoltaic cells and solar hydrogen panels will be presented. It is possible to calculate the average output and efficiency as a function of certain key parameters and furthermore, calculate the optimal parameter values that achieve maximum output and maximum efficiency. Certain new external conditions can be used to significantly increase the output and efficiency to significantly larger values. This can make solar energy and hydrogen significantly cheaper, requiring smaller areas of photovoltaic cells and solar hydrogen panels and smaller initial capital investment, to achieve the required output.

The new mathematical model allows us to take into account very accurately a different rate of change in different stages of operation with the aid of dynamic equations on time scales and the Hilger derivative. An iterative computational method of successive approximations is then used to calculate numerically, to any desired accuracy, the operation of the photovoltaic cell or solar hydrogen panel, depending on the values of the key parameters and certain external conditions. Moreover, the optimal parameter values and optimal external conditions can be calculated in this model.

## 786

### Multicomponent Photoactive Arrays Based on Novel Bistridentate Ruthenium Complexes

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The recent development in our laboratories of novel bistridentate ruthenium comlexes with excellent photophysical properties[1] based on 2,6-di(quinolin-8-yl)pyridine (dqp),[2] prompted the exploration of routes to donor-photosensitizer-acceptor arrays based on this motif. The rod-like character and lack of geometrical isomers, combined with the photophysical properties, gives an ideal system in which to investigate electron transfer phenomena, with the view to move to multiple electron, metal containing or photocatalytic systems.

The synthetic strategies employed in the ligand synthesis for the donor and acceptor components of the system and an investigation of the co-ordination chemistry are discussed here (Figure 1). A variety of $Ru^{II}$ and $Ru^{III}$ intermediates were investigated in order to allow co-ordination of reactive and redox active functional groups to the metal center. This has allowed the incorporation of a quinone unit, observed to act as an electron acceptor in the corresponding dyad. The preliminary photophysical investigation of this compound in organic and aqueous solutions as well as efforts toward the corresponding phenothiazine containing triad will be presented.

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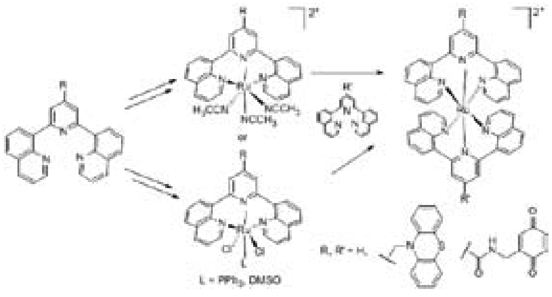
2. Jäger, M.; Eriksson, L.; Bergquist, J.; Johansson, O. Synthesis and Characterization of 2,6-Di(quinolin-8-yl)pyridines. New Ligands for Bistridentate $Ru^{II}$ Complexes with Microsecond Luminescent Lifetimes. The Journal of Organic Chemistry 2007.



# 787

## Geometry Dependence of Photoinduced Electron Transfer in β,β'-Pyrrolic Fused Ferrocene-Porphyrin-Fullerene Systems

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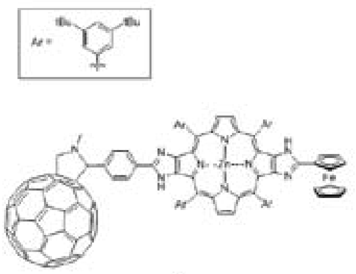
Mimicry of the natural photosynthetic reaction centre has been a very active research area in recent years due to the possibility of achieving improved efficiencies in solar energy conversion devices. The high efficiency of the natural system is due to the multi-step electron sequence. Donor-bridge-acceptor triads are the most common approach in the mimicking of the multi-step electron transfer sequence.1

Porphyrins are often used in artificial photosynthetic system as they are similar to the natural chromophores; in particular, they contain an extensive conjugated π-system that is suitable for efficient electron transfer.2 The incorporation of fullerene as an electron-acceptor is widespread because of its symmetrical shape, large size and π-electron system,3 while ferrocene is a stable electron donor that is often used as a reference in electrochemical experiments owing to its simplicity and regularity.4

The ferrocene-porphyrin-fullerene systems using short conjugated imidazole linkages, such as 1 and 2 and other extended systems, were synthesised. Their photochemistry observed using picosecond and microsecond transient absorption spectroscopy supported by electrochemical measurements and density-functional theory calculations. This study is made to test the hypothesis that the observed long charge separated state arises as a consequence of anionic charge delocalization between the ferrocene and its conjugated porphyrin in the final charge-separated state. The prediction made based on theses model that small changes in the system such as those associated with regioisomerisation can significantly effect the charge delocalization and consequently the charge-recombination rate.



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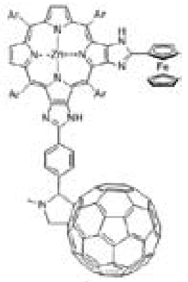

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# 788

## Enhanced Photocurrent in RuL2(NCS)2/Di-(3-aminopropyl)-Viologen/ SnO2/ITO System; Electrode Surface Modification Using SnO2

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This paper reported the use of SnO2 with high surface area improve photocurrent of viologen/Ru-complex in photoelectrochemical cells. The nanocrystalline SnO2 was prepared using the chemical-bath-deposition method. The preparation of Ru(2,2'-bipyridine-4,4'-dicarboxylic acid)2(NCS)2 [(RuL2(NCS)2)]/di-(3-aminopropyl)-viologen (DAPV) in SnO2/tin-doped indium oxide (ITO) is easily prepared using self-assembled monolayers (SAMs). The energy levels of RuL2(NCS)2, DAPV, SnO2, and ITO were well arranged, and the system forms an efficient acceptor-sensitizer. The photocurrent measurement of the systems showed excellent photocurrent of 30 nA/cm2 under the air mass (AM) 1.5 conditions (100 mW/cm2), which was increased by a factor of four compared to ones without tin-oxide layers.

# 789

## Silane Based Ionic Liquids as Electrolytes for Dye Sensitised Solar Cells

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Alkoxysilane alkyl ammonium iodides have shown promise as electrolytes for DSSC's, reaching open circuit voltages in excess of 800mV at 1 Sun. This concept has been extended to include a family of alkoxysilyl iodides containing piperidinium, pyrrolidinium and imidazolium cations and various length spacers to develop correlations between cation structure and the resultant effects on cell performance.

The synthesised ionic liquids were fully characterised using a wide range of physical techniques, including $^{1}$H, $^{13}$C and $^{29}$Si NMR, ESIMS, DSC, TGA as well as electrochemical ones including impedance and redox diffusion coefficients. The developed compounds were used as the sole iodide source for the construction of DSSCs and their performance therein was evaluated. Interestingly, the compounds containing an 11 carbon spacer between the siloxy functionality and the cation exhibited much higher open circuit voltages than the analogous 3 carbon compounds (Table I). In addition to the increased potentials obtained using the 11 carbon compounds, an increase was also witnessed to the current of the cells, although fill factors were significantly less than those found using the analogous 3 carbon compounds.

In addition to an increase in potential, the longer spacers also increased the electron lifetime within the cell, as demonstrated by electron lifetime measurements.

In conclusion, the developed compounds show good potential as iodide sources for DSSCs, with the longer carbon chains furnishing relatively high potentials and currents when compared to the analogous three carbon spacers.

| | Voc (mV)† | Jsc (mA/ cm2)† | FF† | % n† | Voc (mV)‡ | Jsc (mA/ cm2)‡ | FF‡ | % n‡ |
|---|---|---|---|---|---|---|---|---|
| 2 | 802 | 13.84 | 0.646 | 7.17 | 740 | 1.45 | 0.757 | 8.55 |
| 3 | 768 | 13.14 | 0.687 | 6.94 | 703 | 1.38 | 0.786 | 8.00 |
| 4 | 761 | 13.57 | 0.671 | 6.93 | 701 | 1.39 | 0.795 | 8.12 |
| 5 | 806 | 13.93 | 0.620 | 6.96 | 745 | 1.45 | 0.754 | 8.54 |
| 6 | 763 | 13.22 | 0.707 | 7.13 | 704 | 1.36 | 0.795 | 8.00 |

# 790

## Novel Metathetic Approach for the Synthesis of Oxide Photo Catalysis

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**Purnendu Parhi,** *Colorado State University, United States*

Photo catalysis using solar energy and semiconductors is emerging as a viable alternative energy source to solve global energy demands. Since visible light accounts for about 45% of the entire solar spectrum intense research is in progress to discover visible-light-driven photo catalytic materials. Inorganic ceramic oxide materials are potential candidate materials since the work of Fujishima [1]. Recently Wang et al [2] reported the photo physical and catalytic properties of M3V2O8 [M = Mg, Ni, Zn]. Such materials are synthesized by high temperature method for extended period of time (ex 1000 deg C for 40 hrs).
We propose a novel solid-state metathetic (SSM) approach for the synthesis of such materials [3]. In a typical SSM reaction, a salt with high lattice energy was formed as a by product which provides the driving force for the process. The reactions can be initiated by using external sources like heated filament, microwave energy etc., A variety of inorganic materials such as nitrates, complex oxides have been synthesized by this approach [4]. SSM method of synthesis are simple, relatively inexpensive and most importantly not time consuming at al. In this presentation, we apply such procedure for the synthesis of novel inorganic materials for photo catalytic applications.

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4. P. Parhi and V. Manivannan, MRB in press.

## 791

### Calculated Influence of Anchor and Spacer Groups on Photoinduced Surface Electron Transfer Processes

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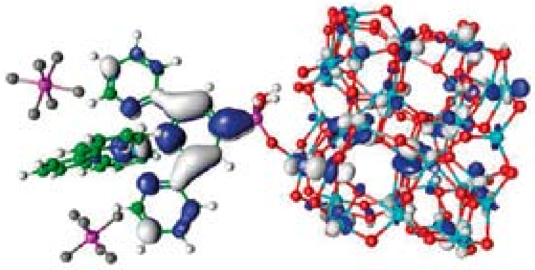
Quantum chemical calculations are presented for several dye-sensitized $TiO_2$ nanocrystalline systems with the aim to elucidate fundamental electron transfer properties in photoelectrochemical devices such as dye-sensitized solar cells. The calculations have been performed using model $TiO_2$ nanocrystals, and both organic and ruthenium dyes have been investigated. Effective electronic coupling strengths have been extracted from the calculated densities of states, and are used to predict femtosecond photo-induced electron injection rates across the molecule-metal oxide interface. Direct comparisons with femtosecond spectroscopy experiments show that the calculations predict injection rates of the right order of magnitude, and correctly reproduce experimental trends with regards to the variations in injection rates for different anchor-cum-spacer groups. This shows the central role played by the interfacial electronic coupling for ultrafast surface electron transfer processes in molecular photovoltaics.



## 792

### Solid-State Dye-Sensitized Solar Cells Constructed with an Electrochrome Impregnated Elastomeric Electrolyte

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A new type of hybrid polymer electrolyte matrix based on benzidine impregnated polyepichlorohydrine (PEC) with $TiO_2$ nanofiller was developed for dye-sensitized solar cells (DSSCs). The polymer electrolytes were characterized by SEM, TGA, XRD and FT-IR, and the assembled DSSCs by photocurrent density–voltage and energy conversion efficiency measurements. The ionic conductivity and the interfacial contact with dye attached $TiO_2$ particles were enhanced markedly by the addition of electrochrome impregnated polymer electrolyte, resulting in very high overall energy conversion efficiency.

| Electrolyte | Sigma(x10-5, Scm-1) at 300 K | Voltage (V) | Current (mA) | FF | efficiency (%) |
|---|---|---|---|---|---|
| PEC:Bz:KI/I2 (E1) | 1.78 | 0.207 | 2.24 | 0.26 | 0.80 |
| PEC:Bz:TiO2:KI/I2 (E2) | 29.13 | 0.372 | 5.53 | 0.25 | 3.43 |

## 793

### Design of Visible-light Absorbing Polyoxometalates; Photoinduced Ce(III) to $W_6O_{19}^{2-}$ Charge Transfer

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**Kazuhito Hashimoto,** *Department of Applied Chemistry, School of Engineering, The University of Tokyo; JST, ERATO, Japan*

It is known that two metal ions placed closely enough for their electronic coupling show the metal-to-metal charge transfer (MMCT) in visible-light to near-infrared region. Recently, hetero-bimetallic assemblies located on the pore of mesoporous silica, MCM-41, has been developed as a new class of visible light absorbing chromophore[1], and we have reported that Ti(IV)/Ce(III)/$SiO_2$ have photocatalytic activity for oxidative decomposition of organic compounds and their quantum efficiency was 5-fold higher than that of N-doped $TiO_2$ under 460 nm irradiation.[2] In this study, we have extended the synthesis of Ti(IV)/Ce(III) bimetallic photocatalysts[2] to polynuclear metal-oxide assemblies by replacing the Ti(IV) ions to polyoxometalates ($Mo_6O_{19}^{2-}$, $W_6O_{19}^{2-}$, $PW_{12}O_{40}^{3-}$). Polyoxometalates, which are atomically well defined metal-oxide clusters, have been reported to have the varieties of molecular structures (shape, size, and charge), thus showing the interesting catalytic and electronic properties. Moreover, polyoxometalates have abilities to store and release the multi number of electrons. Therefore, constructing the Ce(III) to polyoxometalate charge-transfer chromophore allows us to fabricate the all-inorganic molecular photosystems which can induce the multi-electron transfer (MET) reactions under visible-light irradiation. In this presentation, we report the synthesis and photochemical properties of Ce(III)/polyoxometalate assemblies. It was confirmed that Ce(III) ions were replaced by organic ligand of $(NBu_4)_2W_6O_{19}$, which lead to the formation of an intense CT band in visible-light region.

1. W. Lin, H. Frei. J. Phys. Chem. B, 2005, 109, 4929
2. R. Nakamura, K. Hashimoto et al. JACS, 2007, 129, 9596

## 794

### Effects of Structure on Charge Generation in Confined Chromophores Derived from PPV

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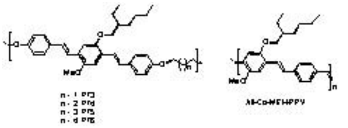
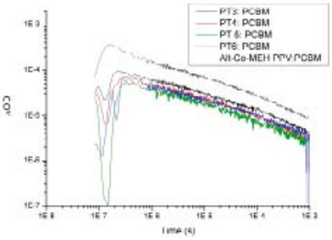
**Jonathan M White,** *Bio21 Institute, School of Chemistry, The University of Melbourne, Australia*
**Kenneth P Ghiggino,** *Bio21 Institute, School of Chemistry, The University of Melbourne, Australia*
**James R Durrant,** *Department of Chemistry, Imperial College London, United Kingdom*
**Tracey Clarke,** *Department of Chemistry, Imperial College London, United Kingdom*
**David James,** *Department of Chemistry, Imperial College London, United Kingdom*

A series of PPV derivatives with confined conjugation length were prepared by conventional Horner-Emmons chemistry. These materials were fabricated into thin films in a 1:1 ratio of polymer: PCBM and investigated using transient absorption spectroscopy. Initial steady-state quenching experiments indicated the fluorescence of the polymer was quantitatively quenched by PCBM, with the absence of the emission peak at ~750nm, corresponding to the excited state of PCBM, indicating efficient electron transfer from the polymers to PCBM.

Transient absorption spectroscopy revealed no significant difference in the decay dynamics between the various confined length conjugated polymers, with the decay dynamics being similar to that of Alt-Co-MEH PPV and MDMO-PPV. This suggests that the intermolecular forces are more important in defining the trap distribution rather then the intramolecular forces. However, the charge generation yield is significantly reduced as the chromophore is confined, implying that geminate recombination occurs more readily in the PT's.





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## 795

### A Study on the Intramolecular Energy and Charge Transfer of Triphenylamine dyes for Dye-Sensitized Solar Cells

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**Xichuan Yang,** *State Key Laboratory of Fine Chemicals, Dalian University of Technology, China*
**Ruikui Chen,** *State Key Laboratory of Fine Chemicals, Dalian University of Technology, China*
**Licheng Sun,** *KTH School of Chemical Science and Engineering, Center of Molecular Devices, Physical Chemistry, Royal Institute of Technology, Sweden*

Photosensitization of semiconductors by molecular dyes has attracted much attention to researchers since Graetzel and co-workers reported the new type dye-sensitized solar cells in 1991. In this study, we focus our interests on the intramolecular energy and charge transfer of the new synthesized Donor-(π-Bridge)-Acceptor dye, 2TPA-R, which contains two triphenylamine (TPA) units connected by vinyl group as the electron donor with rhodanine-3-aceticacid as the electron acceptor. Other two dyes, 2TPA and TPA-R, which consist of two TPA units connected by vinyl and a TPA unit linked with rhodanine-3-aceticacid, respectively, were synthesized as references. The molecular structures are shown in Figure 1. Intramolecular energy transfer of 2TPA-R was observed in CH2Cl2 solution by absorption and emission spectra (see Figure 2). Cyclic voltammetry and density functional theory (DFT) computations were employed to support the argument. When 2TPA-R was attached on TiO2 surface, both intramolecular energy and charge transfer were observed by laser flash and theory computations. To further study the effect of intramolecular energy and charge transfer on DSSC, the performance of DSSC based on 2TPA-R was measured and then compared with that of DSSC based on TPA-R (see Figure 3). The intramolecular energy transfer could improve the light harvest ability of the dye in DSSCs, and the intramolecular charge transfer process could effectively suppress the dark current in DSSCs. The result suggests that the intramolecular energy and charge transfer exhibited positive effect on DSSC performance.

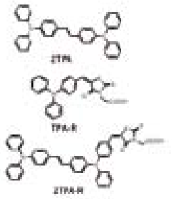

Figure 1. The molecular structures of the dyes

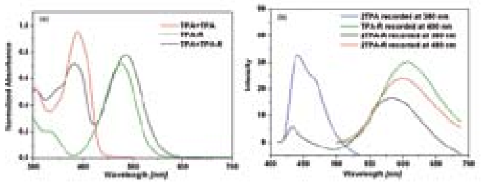

Figure 2. The absorption (a) and emission spectra (b) of the dyes in $CH_2Cl_2$

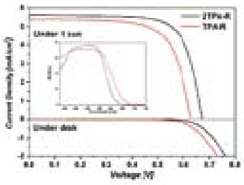

Figure 3. The I-V curves and IPCE spectra of the DSSCs based on **2TPA-R** and **TPA-R**

## 796

### Mechanisms of the Delayed Luminescence of N-Methylindole and Indole in the Gas Phase

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Indole molecules are chromophores of biologically important organic compounds. Nowadays, problems on determining the lifetime of triplet states of indole and its derivatives in different media and on studying the influence of the microenvironment on the relaxation processes of triplet states are important. The objectives of the present work were to reveal the mechanisms for the delayed luminescence and to measure the lifetime of the triplet states of these molecules in the gas phase.

Spectral and kinetic characteristics of delayed luminescence of N-methylindole and indole in the gas phase have been studied. The mechanisms of the delayed luminescence of indole and N-methylindole in the gas phase are essentially different. N-methylindole delayed luminescence represents P-type delayed fluorescence in the spectral region at $\lambda$max= 310 nm. Its spectrum approximately coincides with a fluorescence spectrum. Indole P-type delayed fluorescence has not been recorded, however, its delayed luminescence in the spectral region with a maximum at $\lambda$max = 535 nm has been observed and interpreted as luminescence of free radicals to be formed due to the N-H bond dissociation. It is supposed that the excited states of free radicals are populated due to nonradiative energy transfer from the triplet states of indole to the doublet states of free radicals. Calculated from the kinetics of the delayed luminescence lifetimes of the triplet states of N-methylindole and indole at $\kappa$ = 373 K are 2.5 and 1 ms, respectively.

## 797

### Generation and Control of Photomagnetic Behaviour in Heterobimetallic Prussian Blue Analogs

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A new challenge in the field of molecular magnetism is the design of optically and thermally switchable solid state magnetic materials for which various kinds of application may be feasible. Our research activities involve preparative methods, the study of the physical properties and associated mechanisms, as well as the exploration of further possibilities.

Particular focus is on heterobimetallic Prussian Blue analogs, such as on RbMn[Fe(CN)6] [1], in which the interplay between the two different adjacent metal ions is crucial for the observation of photo-induced phenomena. Our studies revealed that modification of the preparative conditions lead to differences in structural features that allowed tuning of the magnetic and electron transfer properties of RbxMn[Fe(CN)6]y.zH2O [2].

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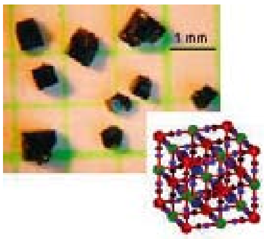
[2] E. J. M. Vertelman, E. Maccallini, D. Gournis, P. Rudolf, T. Bakas, J. Luzon, R. Broer, A. Pugzlys, T. T. A. Lummen, P. H. M. van Loosdrecht, P. J. van Koningsbruggen, Chem. Mater. 18, 1951 (2006).



## 798

### Coadsorption Modified Energy Level Alignment at the Interface of Dye-Sensitized Solar Cell

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Since the invention of the dye-sensitized solar cell, great endeavors have continuously been applied to improve the performance. New dyes with different fascinating properties have been synthesized and tested. However, adsorption of dyes on the inorganic semiconductor substrates can always tune their properties due to either strong or weak interactions. The energy level alignment in the dye molecule/ inorganic substrate heterojunction is a significant factor affecting the transfer of photoexcited electrons. Phthalocyanines are well-known dyes which have been widely used in photo-electronic devices and are good candidates in the solar cell application.

In this work, two different phthalocyanines (Pc); FePc and TiOPc adsorbed on single crystal rutile $TiO_2$(110) have been used as the test systems in ultra high vacuum conditions, using synchrotron based photoelectron spectroscopy (PES), near edge X-ray absorption fine structure (NEXAFS) and scanning tunneling microscopy (STM).

When adsorbed directly on the pristine unreconstructed (1x1) $TiO_2$(110) surface, both molecules display a strongly modified electronic structure in the first monolayer, whereas the ones in the second layer displays the ‘unperturbed’ molecular electronic structure. Pre-adsorption of different pyridines on the $TiO_2$ surface reduces the strong interface interaction and the first layer Pc exhibits molecular electronic structure.

The different Pc morphologies and their different bond states lead to different energy level alignments at the interface on the bare substrate and on the modified surface. Hence, through this work, we show a possible route to improve the performance of solar cells by simply changing the surface properties through coadsorption of other organic molecules.

## 799

### Photoinduced Hydrogen Production with the Light Harvesting Protein Chlorophyll-a/b Complex PSII (LHCII) and Platinum Colloid System

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**Takashi Joke,** *Nagoya Institute of Technology, Japan*
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Photosynthesis in green plant is consists of two photochemical reactions; one is the photosystem I (PSI) is photoreduction of NADP+ and the other is the photosystem II (PSII) is photoinduced water oxidation. The light harvesting protein chlorophyll complexes (LHCs) which act as the light harvesting and light energy transfer to above photosystems also exists in photosynthesis. In this work, photoinduced hydrogen production system with light harvesting protein chlorophyll-a/b complex PSII (LHCII), an electron donor, NADH, an electron carrier, methylviologen, and catalyst, platinum colloid are developed.

# 800

## Photoinduced Hydrogen Production with the Carotenoid-Chlorophyll Immobilized Micelle as an Artificial Photosynthesis Protein

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**Yoshiko Fuchino,** *Department of Applied Chemistry, Oita University, Japan*

Light-harvesting site in photosynthesis protein consists of Mg chlorophyll-a, b (MgChl-a, b) and carotenoid dye such as β-carotene. MgChl-a and b play an important role in photosynthesis such as light harvesting, the photoinducued electron transfer and so on. On the other hand, carotenoid dyes also have important functions such as the absorption of UV light, photo-protection of MgChl-a and b, and photosynthesis protein. In photosyhthesis protein, MgChl-a, b and carotenoid dyes are assembled via the hydrogen bond, hydrophobic interaction and coordination bond, not covalently. Thus, MgChl-a, b and carotenoid dyes can be assembled using hydrophobic interaction of surfactant micellar as photosynthesis protein mimetics. In this work, artificial photosynthesis system, anionic water-soluble carotenoid dye crocetin electrostatically immobilised onto the surface of cationic surfactant cetyltrimethylammonium bromide (CTAB) micellar including MgChl-a and b, is prepared and applied to the photoinduced hydrogen production system with platinum colloid catalyst.

# 801

## The Changes in Photochemistry of Photosystem II, Photosynthetic Pigment Contents and Enzymes During Senescence of Marrow Leaves

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The changes in photosystem II photochemistry and photosynthetic pigment contents were investigated in marrow leaves during senescence. Through the development of senescence, the efficiency of PSII photochemistry declined slightly under low light condition at early morning and substantially under high light condition at midday. The photochemical quenching expressed significant decrease both in the early morning and at midday. The decrease was more pronounced at midday rather than early morning. The actual efficiency of PSII and photochemical quenching followed the same pattern of the photochemical quenching. Non-photochemical quenching and the content of both antheraxanthin and zeaxanthin increased in the early morning and at midday on the expense of violaxanthin, with remarkable increase at midday. During leaf senescence the content of chlorophyll, b-carotene and neoxanthin decreased, however xanthophy and lutein cycle pigments were slightly affected. This resulted in increases in lutein/chlorophyll and xanthophylls cycle pigments/chlorophyll ratios. Appreciable increase in the ratio of chlorophyll a/b was also observed. Thus, the present results implicate that there was a change in photosynthetic pigment stoichiometry during leaf senescence and that a down-regulation of PSII occurred in senescent leaves when exposed to high light. In addition, the results demonstrate that the xanthophylls cycle-related thermal dissipation in the PSII antenna was enhanced in senescent leaves, which may protect the photosynthetic apparatus from damage by photoinhibition in senescent leaves when exposed to high light. The activities of ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco), glutamate dehydrogenase (GDH; EC 1.4.1.4) and glucose-6-phosphate dehydrogenase (G-6-P DH; EC. 1.1.1.49) were decreased after induction of senescence.

# 802

## Effect of Nitrogen Deficiency in Lupine (Lupinus Termis) on Photosynthetic CO2 Assimilation, Chlorophyll Fluorescence and Photoinhibition

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**Essam Mohamed Abukassem,** *Egypt*

This study aimed to investigate how nitrogen deficiency affects PSII primary photochemistry and PSII electron transport in lupine plants grown under natural illumination. Plants with low nitrogen expressed considerably lower values in chlorophyll content, maximal $CO_2$ assimilation capacity and the apparent quantum yield of photosynthesis than plants with high nitrogen. Plants with low nitrogen expressed a small decrease in maximal photochemical efficiency of PSII, which was due to a decrease in the maximal fluorescence. Compared to the plants with high nitrogen, the plants with low nitrogen exhibited lower average in both quantum yield of PSII electron transport and the efficiency of excitation energy capture by open PSII reaction centers at all photosynthetic flux density (PFD) and the differences were more apparent at moderate and high PFD than at low PFD. The maximum photochemical efficiency of PSII was declined when plants with low nitrogen and those with high nitrogen were photoinactiavted. A greater decrease of photochemical quenching coefficient was observed in both types of plants during photoinhibition. In contrast, nonphotochemical quenching coefficient increased with increasing the time of photoinhibition but a greater increase occurred in plants with high nitrogen. Plants with low nitrogen expressed 25 % increase in the percentage inactive PSII centers. Thus, the results in the present investigation implicate that increase susceptibility could be associated with the greater accumulation of inactivated PSII reaction centers, less capability for dissipation of excess excitation energy, as well as the higher fraction of reduction state of primary electron acceptor of PSII.

# 803

## Self-Assembly of Light-Harvesting Complexes on Various Electrodes for Construction of an Artificial Photosynthetic System

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Light-harvesting complexes absorb solar energy and transfer it to the reaction center at the beginning of the photosynthetic process. The RC converts the absorbed energy into electrochemical energy. These reactions take place within a ‘core complex’ consisting of a RC located inside the LH complex. We are interested in understanding the rapid and efficient energy transfer between LH and RC, and have been aiming to construct an artificial solar energy device based on a natural solar energy conversion system such as the core complex. The core complex, isolated from the photosynthetic bacterium or plant was successfully assembled onto various electrodes modified with various terminated. Efficient energy transfer and photocurrent responses of the complexes were observed upon illumination. Further, the photocurrent generated from the core complexes on the electrode depended on the wavelength of the exciting light. An action spectrum of this photocurrent showed a maximum at the wavelength corresponding to the absorption band of the LH core complexes.

# 804

## Molecular Assembly of Chlorophyll Complexes on Electrodes for Construction of an Artifical Photoenergy Conversion System

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Chlorophyll complexes in light-harvesting complexes absorb solar energy and transfer it to the reaction center (RC) at the beginning of the photosynthetic process. The RC converts the absorbed energy into electrochemical energy. We are interested in understanding the rapid and efficient energy transfer between chlorophyll complexes, and have been aiming to construct an artificial photoenergy conversion material based on a natural solar energy conversion system. The chlorophyll complexes, isolated from native bacterium or plant and their synthetic model complexes were successfully assembled onto various electrodes modified with various terminated. Efficient energy transfer and photocurrent responses of the complexes were observed upon illumination.

An enhanced photocurrent was also observed in the case of LH model polypeptides assembled with chlorophyll derivatives onto an electrode. In this case the photocurrent response depended on the structure of the model complex. Various combinations of these complexes are being tested for their usefulness in constructing artificial solar energy conversion materials.

# 805

## Electrochemistry of Chlorophylls - New Scheme for $O_2$ Evolution in PS II

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In 1996, a Chl *d*-dominated cyanobacterium *Acaryochloris marina* was discovered. In the PS I reaction center of *A. marina*, Chl *d'* functions as the primary electron donor P740: a heterodimer of Chl *d/d'*, like Chl *a/a'* for P700, and Chl *a* as the primary electron acceptor. The primary electron acceptor of PS II in *A. marina* has been defined as Phe *a*, however, whether Chl *d* acts as the special pair in PS II is a matter of controversy. The oxidation potential of Chl *d* was found to be +0.88 V vs. SHE in acetonitrile, which was higher than that of Chl *a* (+0.81 V), and lower than that of Chl *b* (+0.94 V). Corresponding pheophytins showed significantly high values around +1.2 V. For water oxidation, very high oxidation power is believed to be needed, but oxidation power of Chl *a* is the lowest of all Chls. To explain the enigma, we will present a unique model for $O_2$ evolution. In our model, oxidation potential of Chl *a* (or *d*) is not high enough to oxidize water, but the stepwise positive shifts of oxidation potentials of the Mn-complex take place during the S-cycle to create the great high oxidation power to oxidize water. Lower oxidation states of the Mn-complex may accept holes from $P680^+$, but higher oxidation state(s) cannot do this and should utilize photon energy to attain the final state to oxidize water.

# 806

## Novel Photosystems in *Acaryochloris Marina*

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In 1996, a Chl *d*-dominated cyanobacteria *Acaryochloris marina* was discovered from colonial ascidians, and much research on the pigment composition of this unique organism has been performed. In *A. marina* cells, Chl *a*, Phe *a* and Chl *d'* are present as minor components as well as dominant Chl *d*. P740 was initially proposed to be a Chl *d* homodimer, later a Chl *d'* homodimer, and finally a Chl *d/d'* heterodimer, just like a Chl *a/a'* heterodimer for P700. The primary electron acceptor, $A_0$, in PS I of *A. marina* is Chl *a*, supporting our hypothesis that Chl *a* derivative is a general feature of $A_0$ in the PS I-type reaction centers (RCs). The secondary electron acceptors of PS I in *A. marina* have been identified as phylloquinone (PhQ). In the case of PS II of *A. marina*, whether Chl *d* acts as the special pair in PS II is a matter of controversy; it has been suggested that the special pair is a Chl *d* dimer, a Chl *a* dimer, or a Chl *a/d* heterodimer, while the identity of the primary electron acceptor of PS II in *A. marina* has been well defined as not Phe *d* but Phe *a*, like other cyanobacteria. Our heterodimer model of Chl *a/d* was recently supported in part by the difference spectra of the PS II RC of *A. marina* in the blue light region.

# 807

## Connecion of the NAD+-Reducing Hydrogenases to Various Bioenergetic Pathways in the Purple Sulfur Photosynthetic Microbe, Thiocapsa Roseopersicina BBS

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**Gergely Maroti,** *Department of Biotechnology, University of Szeged, Szeged, Hungary, Hungary*
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**Julia Novak,** *Department of Biotechnology, University of Szeged, Szeged, Hungary, Hungary*
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Thiocapsa rosoepersicina BBS, a purple sulfur anaerobic photosynthetic bacterium utilizes reduced sulfur compound for its growth. The strain accumulates elementary sulfur globules and can synthesize various storage materials like glycogen or polyhydroxyalkanoates.

T. roseopersicina BBS, as world recorder, contains five NiFe hydrogenases (HynS-Isp1-Isp2-HynL, HupSLC, HupUV, Hox1EFUYH and Hox2FUYH) having various physiological roles [1]. The cells, grown in the presence elevated thiosulfate in the medium, can evolve hydrogen under illumination only, while in dark, low thiosulfate concentration stimulates the hydrogen production. In both cases, the NAD+-reducing Hox1 hydrogenase is responsible for the hydrogen evolution [2]. The HoxYH subunit of this hydrogenase is responsible for the proton reduction/hydrogen oxidation, while the hoxFU genes encode for the diaphorase subunits. The fifth subunit, the HoxE, likely has an electron transferring role. The in vivo hydrogen evolving capacity could be significantly reduced by using Nuo and photosynthesis inhibitors, hence, it seems that the Hox1 hydrogenase has direct connection to the respiratory chain, photosynthesis and sulfur metabolism [3].

In the genome, recently sequenced, a second NAD+-reducing hydrogenase – composed of four subunits - could be identified. This second soluble enzyme, named as Hox2 could evolve or oxidize hydrogen in cells grown in the presence of glucose, therefore it seemed to be related to the (photo)fermentative processes.

Taking into account for genomic and experimental data, an integrated network could be established, which connected the hydrogen, sulfur and nitrogen metabolism to photosynthesis, respiration, fermentation and metabolism of various storage materials.

## 808

### Regulation of the Hox Genes in the Cyanobacterium Synechocystis PCC 6803

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The cyanobacterium Synechocystis 6803 contains a bi-directional hydrogenase, encoded by the hox (E, F, G, Y, H) genes, which form an operon. Regulation of the hox genes is poorly understood, therefore, we applied quantitative RT PCR to follow changes in the mRNA level of hoxE in light and dark, as well as in the absence and presence of oxygen. We show that the expression level of hoxE is induced by anaerobiosis, in darkness, and also after inhibition of photosynthetic electron transport in the light at the level of the secondary quinone electron acceptor by DCMU. Addition of H2O2 prevents the increase of the hoxE transcript under the above conditions, and leads to the decrease of the transcript level induced by darkness or anaerobic conditions. Similiar effects were observed with the other members of the hox operon.Our data demonstrate that the regulation of the hoxE gene (and of the whole hox operon) is under light- and redox control, which leads to enhanced expression in the absence of photosynthetic electron transport through Photosystem II, and in anaerobiosis. This appears to be a crucial step in the regulation pathways which ensure that the oxygen sensitive hydrogenase enzyme is produced in the absence of oxygen.

## 809

### Zinc Oxide as Photocatalyst in Water Splitting Reaction

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Fossil fuels play a vital role in supplying energy to the world population. However, utilizing fossil fuels causes the emission of greenhouse gases, which are implicated in global warming and climate change. Therefore, alternative energy sources should be implemented. Hydrogen appears to be an environmentally friendly form of energy. In principle, it can be produced simply via the photocatalytic splitting of water, where excited electrons generated from the photocatalyst are responsible for the reduction of protons to produce hydrogen. In the past few decades, an enormous amount of work has been done in this area. We report that under ultraviolet (UV) illumination, zinc oxide facilitates the photocatalytic splitting of water to produce hydrogen. The efficiency of zinc oxide as a photocatalyst can be improved through bandgap engineering. The bandgap of zinc oxide can be tuned so that it will absorb not only the ultraviolet but also the visible light. Consequently, a great fraction of the solar spectrum can be absorbed to produce more excited electrons, and eventually hydrogen. In order to provide more reaction sites, mesoporous zinc oxide has been synthesized. The fabrication step involves using mesoporous carbon as a template, which can be easily removed by calcination. The structure of the resultant material and the process of photocatalytic splitting of water are also discussed.

## 810

### $TiO_2$ Aerogels for the Photocatalytic Production of $H_2$ from Water

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A sustainable method of hydrogen production for use as a fuel for energy generation is one area of research aimed at reducing carbon emissions from fossil fuels. This $H_2$ can, in principle, be supplied by the photocatalytic splitting of water, using sunlight. Titanium dioxide is a well known photocatalyst sensitive to UV wavelengths, and can be activated for visible light absorption with the use of photosensitive materials and dyes. A mesoporous $TiO_2$ aerogel was prepared by means of a sol-gel process followed by solvent extraction with a supercritical (SC) solvent, such as ethyl acetate or ethanol. In this way it was possible to synthesize a material with a large surface area, and use this porous structure as a support for CdS nanoparticles, a catalyst sensitive to visible light, having a lower bandgap than that of $TiO_2$. Studies on the effect of different SC solvents and the performances of the material in the photogeneration of $H_2$ are reported.

## 811

### In-Situ Pump-Probe DRIFTS Studies of Photocatalytic Reforming of Simple Alcohols

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Oxygenates are good candidates for fuel processing to a hydrogen-rich fuel gas via endothermic catalytic steam-reforming (SR):-
CHO + (2n-k) HO = n CO + [2n + m/2 – k] H

Band-gap (UV) photons are sufficiently energetic to drive full reforming, but photo-dehydrogenation of alcohols, although a highly efficient process over Pt/TiO, yields only one H molecule per alcohol. Hence, photo-reforming of alcohols is an attractive objective.

Here, pump-probe DRIFTS spectroscopy is used to elucidate mechanistic aspects of alcohols SR over TiO (Degussa P25) containing 1 wt.% Pt as HPtCl. During photo-metallization under band-gap irradiation (15 mW cm) in the presence of a few % ethanol/water in N2, the most striking observation is the rapid development of a strong IR band at 2030 cm, characteristic of CO adsorbed on Pt nanoparticles. The implication is that photocatalysis not only drives complete dehydrogenation, but even C-C bond cleavage. However, build-up of adsorbed CO and the observed slow evolution of CO indicates a kinetic botleneck in which the water-gas-shift(WGS)process is rate-determining. This also explains why photo-dehydrogenation is effectively arrested at the aldehyde product. Weak bands of adsorbed formate, a probable WGS intermediate, also appear at 1580 and 1360 cm.

Future work will attempt to identify which stage in the WGS reaction is slower, viz., formate creation or decomposition. Water-activating additives such as Cu and Ru will be tested, while modest heating may be explored to promote rate-determining dark reaction(s). A mass spectrometer will be incorporated to measure H levels.

## 812

### Potential Application of Photovoltaics for Hydrogen Production Using the Hybrid Sulfur Process

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Thermochemical cycles based upon sulfur species are among the most promising options being considered for the large scale production of hydrogen from water splitting. These cycles include sequential redox reactions in which sulfur species move between the S(IV) and S(VI) valence states. This separates the overall water splitting process into an oxygen liberation step and a hydrogen production step.

The Hybrid Sulfur Process is one of the best known of the sulfur cycles and uses both thermal and electrical energy. The thermal energy is used to decompose sulfur trioxide at high temperatures to liberate oxygen and form sulfur dioxide. The sulfur dioxide is converted to sulfuric acid by electrolysis, in the process splitting water to produce hydrogen. This process is attractive compared to conventional alkaline electrolysis because the presence of sulfur dioxide substantially reduces the required voltage from around 2 V to 0.6 V.

This paper explores the potential for the use of photovoltaic cells to drive the electrolysis step of the hybrid sulfur process. A well designed system will have good matching of the current/voltage characteristics of the photon capture step (i.e. photovoltaic cell) and the electrochemical step (i.e. electrolyser). This decoupling of photon capture and electrochemistry enables much more efficient use of solar energy than in situ photo-electrochemical methods. Carbon free hydrogen production is possible using such a system if coupled to a concentrating solar facility for the high temperature decomposition step.

## 813

### Solar-Powered Production of Molecular Hydrogen from Water

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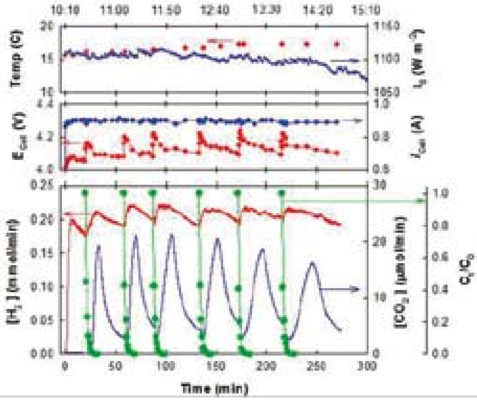
Electrochemical water splitting powered by conventional electricity or photovoltaic arrays produces molecular hydrogen at the cathode while organic compound oxidation under mild conditions takes place at the anode in competition with the production of oxygen. An electrolytic cell, which is based on the coupling of bismuth-doped titanium dioxide anodes ($BiO_x$-$TiO_2$) with stainless steel cathodes (SS), is characterized in terms of hydrogen production efficiency and organic compound degradation. In the solar-powered PV-electrochemical system, the production of molecular oxygen at the anode is suppressed by the simultaneous oxidation and mineralization of organic compounds dissolved in water. In addition, the anodic oxidation of organic substrates has a synergistic effect on hydrogen production at the cathode that results in a 53% increase in the energy efficiency for $H_2$ generation at circum-neutral pH in the presence of dilute electrolyte solutions.

We envision that hybrid PV electrochemical systems could be used for solar powered water purification coupled with the generation of a potentially useful and energy rich byproduct

Hydrogen generation in realtime can be seen at http://www.youtube.com/watch?v=UDpbxEvXb_o



## 814

### Hydrogen Production from Water Using a Photoelectrochemical Cell

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Hydrogen produced from water using solar light is a clean, renewable, and sustainable energy, which can solve the shortage of fossil fuel and the environmental problems what we will be confronted in the future. Solar energy is a form of electromagnetic radiation which is available over a wide spectral range (300-2100nm). The radiation needs to be converted into an energy form suitable for our needs. The solar radiation can be converted into a chemical energy like H2 by a photoelectrochemical cell(PEC cell). It is very important because of its potential to produce H2 from water using solar light. The energy more than of 1.23eV is needed for water splitting reaction. But pure water does not adsorb solar radiation except in the infrared, where photon energies are too low to split water. Semiconducting materials used as electrodes can absorb solar radiation and make charges, which have energies depending on size of the band gap. Water splitting can take place on the electrodes, where the charges have energy enough to produce hydrogen.

A PEC cell is fabricated using a electrode absorbing the solar light, two catalytic films, membrane separating of H2 and O2.We have obtained solar to hydrogen efficiency of about 9 percent in the PEC cell, which is fabricated using silicon electrode, nickel ferrite, and Pt mesh in the 1M NaOH solution. The efficiency is evaluated from the energy illuminated on the electrode surface and hydrogen energy produced. The cell size is 12x12cm2 and the light intensity is 100mW/cm2.

## 815

### Efficient Overall Water Splitting Under Visible Light Irradiation Using Z-Scheme System with $SrTiO_3$:Rh Photocatalyst Prepared by Polymerizable Complex Method

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The photocatalytic overall water splitting under visible light irradiation is an attractive reaction from the viewpoint of a solar energy conversion. The authors have recently succeeded in the construction of two-step photocatalysis systems (called as Z-scheme systems) constituted of two visible-light-driven photocatalysts, Pt/$SrTiO_3$:Rh and $BiVO_4$, and an iron ion redox couple of an electron mediator. However, low activity of $SrTiO_3$:Rh, which functions as a hydrogen evolution photocatalyst in the Z-scheme systems, limits the overall quantum yields of the Z-scheme systems to 0.4%. In the present research, the authors investigated in preparation of the $SrTiO_3$:Rh photocatalyst via a soft chemical root using a polymerizable complex method to improve the activity.

Powder of the $SrTiO_3$:Rh photocatalyst was prepared using a polymerizable complex method or a conventional solid state reaction. The photocatalytic reactions were conducted in a gas-closed circulation system connected to an on-line gas chromatograph. A Xe-arc lamp (300-W) was used as a visible light source.

$SrTiO_3$:Rh photocatalyst prepared by the polymerizable complex method showed higher activity for hydrogen evolution with $Fe^{2+}$ as an electron donor in one order of magnitude than that prepared by the solid state reaction. The overall quantum yield of the Z-scheme system with an $Fe^{3+}/Fe^{2+}$ electron mediator was improved to 4% when $SrTiO_3$:Rh prepared by the polymerizable complex method was used. Thus, the improvement of overall efficiency of the present Z-scheme system has been achieved by the efficient $SrTiO_3$:Rh photocatalyst prepared by the polymerizable complex method.

## 816

### Photocatalytic Hydrogen Production Using Tin-Porphyrin/$TiO_2$ System

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Photochemical hydrogen production under visible light irradiation represents one of the most challenging issues in solar energy conversion. Intensive efforts have been made to achieve this goal for the last 30 years. Among them, dye-sensitized semiconductor oxides (e.g., $TiO_2$) have been frequently studied and shown promising results. In such systems, an efficient visible light sensitization requires a strong binding between $TiO_2$ surface and sensitizers. Many sensitizers such as Ru-complexes, metaloporphyrins and Pt-complexes can be attached to $TiO_2$ surface through chemical anchoring groups (e.g., carboxylate linkage). In this study, we used water-soluble tin-porphyrin [SnIV (OH2)2TPyHP]6+(SnP) to achieve a non-attached SnP/$TiO_2$ system for photocatalytic hydrogen production. Although SnP hardly adsorbs on $TiO_2$, hydrogen was successfully produced under visible light. The electron transfer from the sensitizer to $TiO_2$ conduction band is believed to occur through a collisional mechanism. The high charge on Sn(IV) makes the SnP ring the most electrophilic one among all metaloporphyrins. Therefore, the excited state of SnP (SnP*) has a high electron affinity, favoring the formation of reduced SnP (SnP-) which is relatively stable and long-lived. The subsequent electron transfer from SnP- to $TiO_2$ results in the production of hydrogen. This porphyrin-sensitized production of hydrogen was compared with the conventional anchored sensitized systems employing ruthenium bipyridyl complexes. Ru-complexes with hexacarboxylate (C6) and diphosphonate (P2) as the anchoring group were selected. The amount of $H_2$ produced in SnP/$TiO_2$ was significantly higher than that in C6/$TiO_2$ and similar to P2/$TiO_2$.

## 817

### Manganese-Oxo Water Oxidation Catalysts Towards Solar Hydrogen

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Bioinspired catalysts of the water oxidizing complex of photosystem II are one of the promising routes to efficient water splitting. We have conducted an investigation on a series of manganese-oxo complexes containing a cubical $[Mn_4O_4]^{7+}$ core in solution and suspended in nafion. This study has yielded important insights into the redox properties of the strongly oxidizing cubane core. More relevant, we have discovered conditions that enable it to catalyze the sustained photo-assisted electrolysis and photo-driven oxidation of water.

## 818

### Ionic Liquid Synthesis of CdS Nanoparticles for the Photocatalytic Generation of Hydrogen from Water

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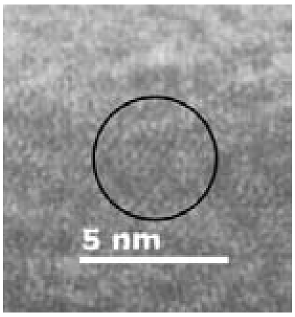
**Thomas Maschmeyer,** *The University of Sydney, Australia*

In recent years, ionic liquids have been recognized as effective nanoparticle stabilizers. Their low interface tension leads to high nucleation rates and thus very small particles can be synthesised. Our research group has synthesised cadmium sulfide nanoparticles (CdS) using methylimidazolium- and tetrabutylammonium-based ionic liquids in a simple, low temperature synthesis procedure, and the nanoparticles were immobilised in propylthiol-functionalised SBA 15. The samples were characterized with HRTEM, electron diffraction and UV-Vis analyses. The test reaction was the photocatalytic generation of hydrogen from an aqueous sulfide-sulfite sacrificial solution, using a mercury lamp as the source of irradiation, with the spectrum controlled by a set of cut-off filters (305 nm, 395 nm, 430 nm). We have found that the CdS samples have substantially higher hydrogen generation rates than the commercial bulk CdS reference, with the performance dependant on the functional groups of the ionic liquid.

Figures: HR-TEM of CdS synthesised with tetrabutylammonium glycinate immobilised in propylthiol-functionalised SBA 15



## 819

### Visible-Light-Induced Hydrogen Production over Novel Maya blue-like Organic-inorganic Hybrid Material Composed of Eosin Y and Palygorskite

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A new system for the production of hydrogen, with a novel Maya blue-like organic-inorganic hybrid material as a photocatalyst, in which palygorskite acts as a matrix and Eosin Y as a photosensitizer, and Pt as a cocatalyst, has been reported. The pH value of the solution and the concentration of Eosin Y have remarkable effects on the rate of hydrogen evolution. It was also found that palygorskite has a significant effect on the rate of photosensitized hydrogen evolution. Electron transfer in photosensitized processes could be carried out via the dimers of Eosin Y. Based on the activities of hydrogen generation and the experimental measurements of UV-Vis absorbance and fluorescence, the probable mechanism for photosensitized hydrogen evolution has been postulated.

## 820

### Progress in the Combinatorial Search for Metal Oxides to Photoelectrolyze Water

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Direct photoelectrolysis of water has the advantage of converting solar energy directly to hydrogen, an ideal non-carbon energy carrier, by replacing both a photovoltaic array and an electrolysis unit with one potentially inexpensive device. Semiconducting metal oxides could potentially be stable under illumination in an aqueous electrolyte for many years making them the most promising materials for solar water photoelectrolysis. The problem is that no known oxide semiconductor can efficiently carry out this process. We have developed a simple, high-throughput approach to prepare and screen many complex oxides for water photoelectrolysis activity. The approach uses ink jet printing of overlapping patterns of metal oxide precursors, metal nitrate salts, onto conductive glass substrates. Subsequent firing produces metal oxide phases that are screened for photoelectrolysis activity by measuring photocurrents produced by scanning a laser over the printed patterns in aqueous electrolytes. Several promising and unexpected compositions have been identified. We are in the process of optimizing and understanding the physical structure, electronic structure and catalytic ability these new photocatalysts. In addition we have developed distributed screening approach that uses simple and inexpensive printing and screening devices and protocols designed to enlist many undergraduate student researchers into the search for the 'Holy Grail' of materials.

## 821

### Z-Scheme Type Water Splitting Reactions Utilizing Copper Complexes as Biomimetic Electron Mediators

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**Akihiko Kudo,** *Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan*

Water splitting using a large portion of solar spectrum will be a major advance in solar energy conversion and the critical breakthrough with respect to the rising concern of environmental pollution caused by the use of fossil fuels. Recent efforts have been devoted to achieve the water splitting using photocatalysts under visible light irradiation, in addition to the combination of the active photocatalysts for $H_2$ and $O_2$ production in the presence of redox couples. However, there are only a few reports so far on the use of metal salts as electron mediators. We report our recent development of copper complexes as biomimetic electron mediators for water splitting by a Z-scheme photocatalysis system.The Ru-loaded $SrTiO_3$ doped with Rh ($Ru/SrTiO_3:Rh$) and $BiVO_4$ were prepared by previously reported procedures. The complex ($[CuCl_2(bpy)]$) was obtained by mixing the copper(II) chloride with the stoichiometric amount of 2,2'-bipyridine in methanol. Electron transfer occurs from $BiVO_4$ to $[CuCl_2(bpy)]$, and then to $Ru/SrTiO_3:Rh$ under visible light irradiation (? > 420 nm) to afford the $H_2$ and $O_2$ evolution with high efficiency from pure water, although the photocatalytic activity decreases as a reaction time. This may arise from the intrinsic photoresistance of the complex. To overcome this problem, we have examined the photocatalytic activities using coordination polymers given by the copper (I) halide and bidentate ligands, and the results will also be presented. In summary, we have constructed the Z-scheme type water splitting systems which are combined by using the copper complexes affording efficient $H_2$ and $O_2$ evolution.

## 822

### Photocatalytic Hydrogen Production over Hybrid CdS Nano-composites with Visible Light

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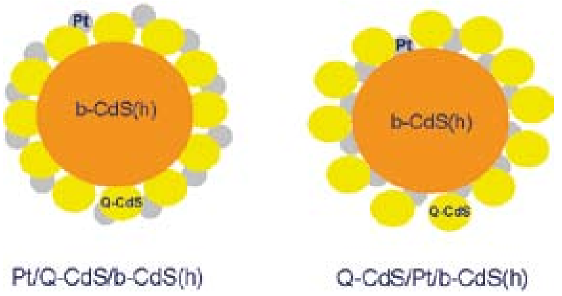
**Su Young Ryu,** *California Institute of Technology, United States*
**Michael R Hoffmann,** *California Institute of Technology, United States*

A new hybrid photocatalytic system based on a mixed-phase cadmium sulfide matrix composed of Q-sized and hexagonal CdS interlinked with elemental platinum deposits has been developed. This unusual hybrid composite catalyst is effective for the photochemical reduction of gaseous hydrogen from water with visible light irradiation.

Orange crystallites of hex-CdS were synthesized by the thermal treatment of commercial grade cubic-phase CdS at 800°C under a flowing-nitrogen atmosphere for one hour. Platinum was photodeposited on the hex-CdS surfaces before sol-gel synthesized Q-CdS deposition to form a hybrid Q-CdS/Pto/hex-CdS composite. TEM images show Q-CdS islands on Pt/hex-CdS surfaces with an average radius of 6.5 nm.

The average rates of hydrogen production for Pt/Q-CdS/hex-CdS and Q-CdS/Pt/hex-CdS composites were 537 micromol/g/hr and 668 micromole/g/hr, respectively, under visible light irradiation at wavelengths > 420 nm in the presence of reduced sulfur electron donors at pH 14.



## 823

### Photoelectrochemical Hydrogen Generation using Iron Oxide Semiconductor Nanoparticle Electrodes

**Upul Wijayantha,** *Loughborough University, United Kingdom*

In a typical water splitting photoelectrochemical (PEC) cell, once the light is being absorbed by the semiconductor electrode and generated charges upon excitation, the majority carriers (electrons in a n-type semiconductor) travel to the substrate and collected at the substrate before transferred to the counter electrode where the hydrogen evolution takes place. The remaining holes need to travel to the semiconductor/electrolyte interface to under go water oxidation [1].

Maximising the light absorption while overcoming the electron-hole recombination is a key challenges in the PEC water splitting. A range of transition metal oxide semiconductor electrodes is being currently investigated with the aim of meeting those challenges in our group [2]. We have recently prepared nanostructured alpha-$Fe_2O_3$ electrodes by aerosol assisted chemical vapour deposition of a hexanuclear Iron(III) complex [2]. These electrodes have shown 0.3 mAcm-2 without any dopants. Photoelectrochemical properties of those electrodes show that they are suitable for the PEC water splitting process. This presentation describes the synthesis of hexanuclear complex, preparation of thin film $Fe_2O_3$ electrodes and photoelectrochemical characterisation. Our recent work on other nanostructured metal oxide semiconductors such as $NiTiO_3$ will also be included in the presentation.

References:

(1). K.G.U.Wijayantha and D.H. Auty, Twin Cell Technology for Hydrogen Generation. (In: Encyclopaedia of Materials: Science and Technology Updates, Elsevier, Oxford, pages 1-5, 2005.

(2). Asif A. Tahir, K.G.U. Wijayantha, Vickie McKee, Muhammd Mazhar, and Sina Saremi, Nanostructured Haematite thin films derived from hexanuclear Fe(III) complexes for PEC water splitting, in preparation.

## 824

### A New Dinuclear Ruthenium Complex as Efficient Catalyst for Electrochemical and Chemical Water-oxidation

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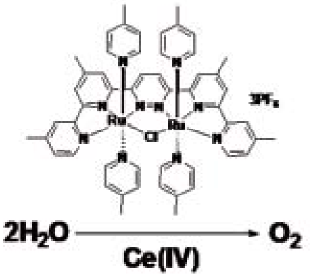
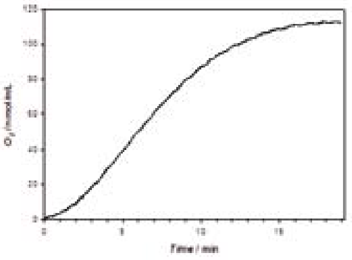
A new dinuclear ruthenium complex as a bioinspired molecular catalyst for water oxidation has been synthesized and characterized. The complex was prepared by the reaction of $Ru(DMSO)_4Cl_2$ and the bis-tridentate ligand 3,6-bis(4,4´-dimethyl-2,2´-bipyridine-6-yl) pyridazine, and characterized by $^1H$ and $^{13}C$ NMR and high-resolution mass spectrometry (HRMS). Its electronic and electrochemical properties were studied by UV-Vis spectroscopy and cyclic voltammetry. The catalytic activity of this complex toward water oxidation was investigated by chemical and electrochemical methods, and the turnover number of this catalyst for water oxidation with Ce(IV) as chemical oxidant was found to be of the order of $10^3$. In comparison with the one reported by Thummel et al.,[1] this new complex is structurally simpler but exhibits similar catalytic features. Moreover, the methyl groups in the bipyridine ligands offer possibilities to introduce other functional groups to the dinuclear ruthenium catalyst, for immobilization of the catalyst on electrode surface or coupling to a photosensitizer. Synthesis of new type ligands for dinuclear ruthenium complexes that can catalytically oxidize water at lower oxidation potential is in progress.

[1] R. Zong and R. P. Thummel, J. Am. Chem. Soc. 2005, 127, 12802-12803.





## 825

### Modelling and Computer Simulation of a Solar Photovoltaic and Hydrogen System for Sustainable & Zero Emission Electricity Production

**Ahmad Zahedi,** *Monash University, Australia*

Global environmental concerns are leading to the development of advanced processes and technologies for sustainable energy production.

Most of the conventional energy production processes convert carbon to carbon dioxide, which is discharged into the atmosphere. The growing awareness of the impact of greenhouse gas emissions on global climate change has necessitated a reassessment of the conventional approach to achieve a sustainable and environmentally-friendly energy.

Author of this paper believes that, because of environmental advantages that hydrogen has, it can play an important role as one of the important components of clean and sustainable power supply in the future.

The objective of this paper is to discuss the technical and economical aspects of an electricity production system in which electricity is generated by an intermittent and renewable energy source i.e. solar photovoltaic array in location, where this resource is plentifully available, but grid network is not necessarily available to absorb the electricity produced by PV array. This paper proposes the option of converting the electricity into hydrogen, being used for transportation or in Fuel Cell for reproduction of electricity.

A further objective of this paper is to present the results of a computer simulation program developed for investigation of the optimal sizing and performance prediction of the entire solar PV and hydrogen system for a certain electricity demand.

## Dependence of the efficiency of $TiO_2$ surface transformation to the syperhydrophilic state on light intensity and wavelengths of actinic light.

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**S. Nishimoto,** *Kanagawa Academy of Science and Technology, Kawasaki-shi, Kanagawa, Japan*
**T. Murakami,** *Kanagawa Academy of Science and Technology, Kawasaki-shi, Kanagawa, Japan*
**A. Fujishima,** *Kanagawa Academy of Science and Technology, Kawasaki-shi, Kanagawa, Japan*

This presentation reports the results of experimental studies of the efficiency of photoinduced transformation to superhydrophilic state of $TiO_2$ surface as functions of intensity and wavelengths of actinic light. The $TiO_2$ coating samples were prepared by dip-coating of glass plate covered with $SiO_2$ nano-film in solution of titatium tetra-isopropoxide followed by its calcinations at 500 C for 30 min. XRD analysis confirms anatase structure of the $TiO_2$ coating. The efficiency of surface transformation to the superhydrophilic state was estimated using the initial rates of alteration of water contact angle and total surface energy calculated by Owens-Wendt method (water contact angle versus methylene iodide contact angle). Also the ultimate water contact angle at $t \rightarrow \infty$ was monitored.

The dependence of transformation efficiency on light intensity was measured using monochromatic light (365 nm) within range of 0 – 21,5 mW $cm^{-2}$. The dependence of the initial rate of contact angle decay on the light intensity ($\rho$) can be approximated with

$$d\Theta/_{dt} = \frac{a\rho}{b\rho+1}$$

Similar dependence was obtained also for alteration of surface total energy. Obviously, at lower light intensity, $b\rho << 1$, the dependences becomes quasi-linear that makes possible to measure the spectral dependence of the efficiency of photoinduced surface transformation to superhydrophilic state presented in the Figure.

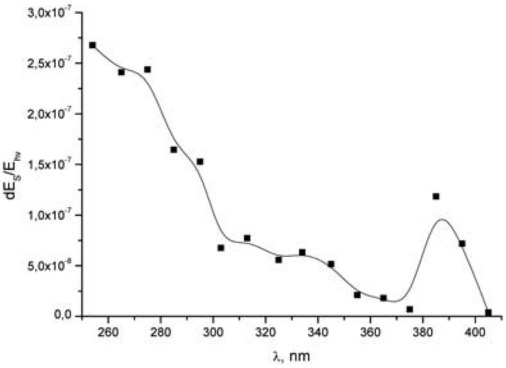

**Figure.** Spectral dependence of the energy yield $dE_S$ /$dE_{hv}$ (ratio between the alteration of surface energy and the energy of actinic photons).

Remarkably, that obtained dependences on both intensity and wavelengths of actinic light correspond to the dependences of the reaction rate on light intensity and spectral dependences of the quantum yields or photonic efficiencies of surface photostimulated reactions at $TiO_2$ (for example, phenol degradation) that infers that there are similar primary photoexcitation processes responsible for both photochemical activity and photoinduced transformation into superhydrophilic state of titania surface. Detailed discussion of the experimental results is given during presentation.

## Comparative experimental studies of photostimulated processes in pristine and F-doped nanosize dispersed ZrO2.

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**N.V. Sheremetyeva,** *V.A. Fock Institute of Physics, St-Petersburg State University, St.-Petersburg, Russia*
**N.V. Khomchenko,** *V.A. Fock Institute of Physics, St-Petersburg State University, St.-Petersburg, Russia*
**G.N. Kuzmin,** *V.A. Fock Institute of Physics, St-Petersburg State University, St.-Petersburg, Russia*
**V.K. Ryabchuk,** *V.A. Fock Institute of Physics, St-Petersburg State University, St.-Petersburg, Russia*
**W.Y. Teoh,** *School of Chemical Engineering and Industrial Chemistry, and ARC Centre for Functional Nanomaterials, University of South Wales, Sydney, Australia*
**R. Amal,** *School of Chemical Engineering and Industrial Chemistry, and ARC Centre for Functional Nanomaterials, University of South Wales, Sydney, Australia*

This presentation reports the results of comparative studies of the activity of pristine and F-doped nanosize dispersed $ZrO_2$ synthesized by Flame Spray Pyrolysis in photostimulated heterogeneous processes. Both samples possess similar specific surface areas, crystallites sizes and crystal structure (mainly tetragonal with small content of monoclinic structure as demonstrated by XRD method). XPS spectra of F-doped $ZrO_2$ demonstrate incorporation of F-anions into the crystal lattice of zirconia.

Photostimulated adsorption of oxygen and hydrogen was chosen as probe reactions representing the reduction and oxidation parts of photocatalytic cycle. The lifetimes of active states of corresponding surface active centers were estimated form the dependences of the rate on gas pressure to be $8,0*10^{-2}$ s and $8,7*10^{-3}$ s at pristine $ZrO_2$ and $2,3*10^{-2}$ s and $2,5*10^{-3}$ s at F-doped $ZrO_2$ for hydrogen and oxygen photoadsorption, respectively.

The effect of surface photoreactions on photoinduced defect formation was studied by DRS and interpreted on the basis of charge conservation law:

$$\Delta[F] + [O_{2\ ads}] = \Delta[V]$$
$$\Delta[F] = \Delta[V] + [H_{2\ ads}]$$

where $\Delta[F]$ and $\Delta[V]$ are the changes in the numbers of electrons and holes trapped by corresponding pre-existing intrinsic defects, respectively. Accordingly, the photostimulated adsorption of oxygen causes to increase of the number of hole color centers (V), while hydrogen photoadsorption leads to increase of the number of electron color centers (F). DR spectra of photoinduced defects demonstrate that F-doping does not cause the formation of new type of defects and alters only their quantity.

In addition, the spectral dependences of the quantum yield of corresponding surface photoreactions were measured. Comparison of these dependences infers that the spectral regions of photochemical activity of both pristine and F-doped $ZrO_2$ extend to the extrinsic absorption region well beyond the band gap energy. The similarity between two spectral dependences suggests that F-doping of zirconia causes no formation of new type of light absorbing centers. Also the lower values of the quantum yield obtained for F-doped $ZrO_2$ indicates the higher efficiency of recombination in the sample.

A comparative analysis of the experimental data let us infer that F-doping of nano-dispersed zirconia does not create new types of electronic localized states within band gap and alters the quantity of the pre-existing and photoinduced intrinsic defects in zirconia thus, changing the efficiency of charge carriers recombination. The discussion of the experimental results is given during presentation.

Frontier Photoelectrochemistry

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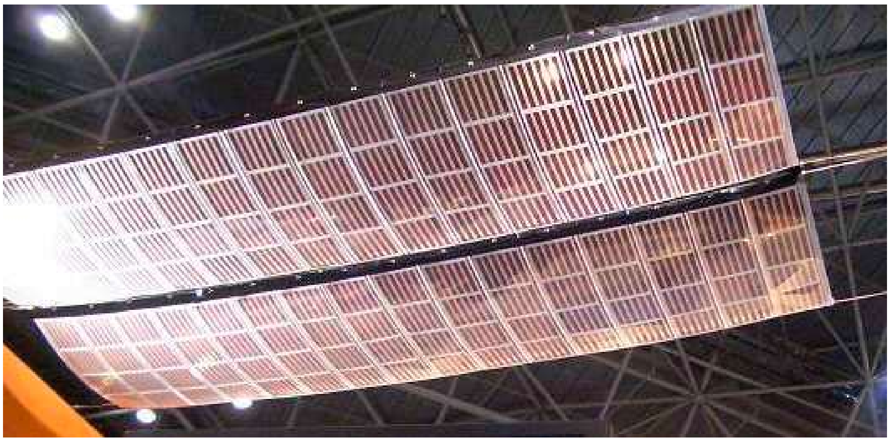
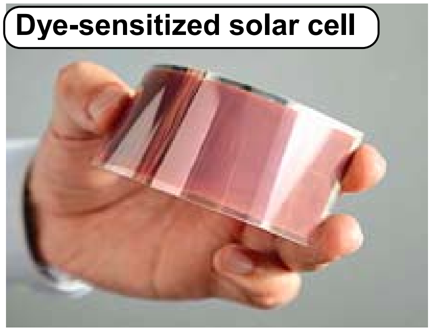


*Peccell*'s Plastic dye-sensitized solar cell integrated module exhibited at PV EXPO 2008



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