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To cite this article: Suzanne V Smith 2011 *J. Phys.: Conf. Ser.* **262** 012055

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The role of nuclear sensors and positrons for engineering nano and microtechnologies

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Abstract. A sustainable nano-manufacturing future relies on optimisation of the design and synthetic approach, detailed understanding of structure/properties relationships and the ability to measure a products impact in the environment. This article outlines how bench-top PALS and nuclear techniques can be used in the routine analysis of a wide range of nanomaterials. Traditionally used in the semiconductor industry, PALS has proven to be useful not only in measuring porosity in polymeric materials but also in the monitoring of milling processes used to produce natural fibre powders. Nuclear sensors (radiotracers), designed to probe charge, size and hydrophilicity of nanomaterials, are used to evaluate the connectivity (availability) of these pores for interaction with media. Together they provide valuable information on structure/properties relationship of nanomaterials and insight into how the design of a material can be optimised. Furthermore, the highly sensitive nuclear sensors can be adapted for monitoring the impact of nanomaterials *in vivo* and the environment.

1. Background

Today, a successful product requires the analysis of its life-cycle and the potential side-effects of a design solution before it enters the market. Our communities expect our manufacturers to display philosophies that encourage the creation of new technologies to enhance our quality of life at a reduced cost, but also reduce the negative impacts on our environment.

Advances in micro and nanotechnologies have the potential to be wide reaching, influencing industry sectors such as healthcare, agrifood, transport, energy, materials and information and communications technologies. However, there are issues that continue to challenge the field such as the ability to;

1. predict and accurately measure performance of these materials
2. develop cost-effective scale up of their synthesis and
3. assess or forecast potential risk of these materials.

The community and regulatory bodies continue to demand a better understanding of the impact of these materials in their direct, manufacturing and ecological environments. Furthermore, there is high expectation that the next generation of products will have “zero” waste.

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Many manufacturers are actively pursuing chemical processing strategies that align with the philosophy of Green Chemistry. Here the creator of a product chooses chemicals or chemical processes to actively reduce or eliminate negative impacts on the environment and waste. Such strategies have been common practice in the field of nuclear chemistry for many years and are summarised in Figure 1. The article will illustrate how we are adapting the practices in the nuclear chemistry and radiopharmaceutical field to aid the design, optimise the production, and evaluate the impact of nano and microtechnologies in their environment.

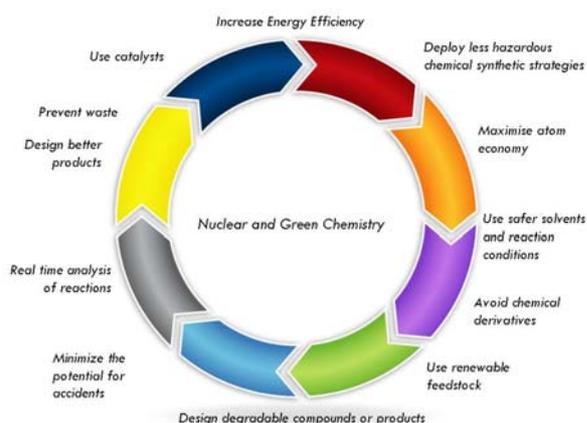


Figure 1. Philosophies of green and nuclear chemistry align.

2. Nuclear techniques

Nuclear techniques are the application of radioisotopes and detection systems for probing questions at the atomic and molecular level. They are widely deployed in the medical field, where radiotracers or radiopharmaceuticals are designed to specifically locate a disease site for imaging or treat it with radiation. Most of the radioisotopes used in radiopharmaceuticals are short-lived (i.e. hours to days). Their synthesis must be simple in design, 100% reliable, and chemically and energy efficient. Imaging is possible at extremely low concentration (10^{-10} to 10^{-12} M) with the intent of keeping toxicity to a minimum.

3. Engineering nanomaterials

As the nanoparticles decrease in size, the ratio of surface area to volume increases, often resulting in changes in their electronic properties (e.g. quantum dots) or reactivity (e.g. catalysts). Properties change drastically from the bulk material to small clusters of atoms [see Figure 2a and 2b).¹ Particles of the same chemical composition but different size and shape can have dramatically varied performance and interaction with biological systems.² The change in the available atoms on the surface of a particle is the rationale for such changes in behaviour.

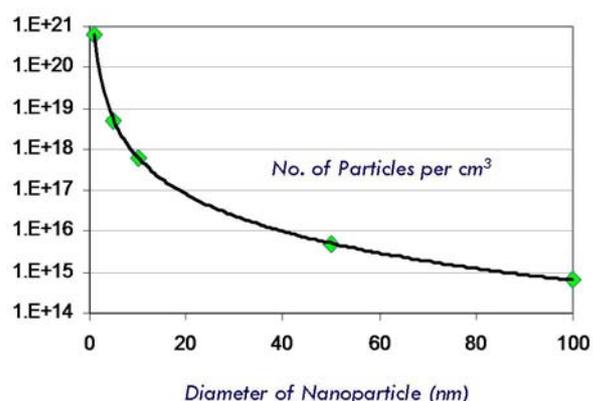


Figure 2a Number of particles in the bulk increase per volume as the diameter decreases.

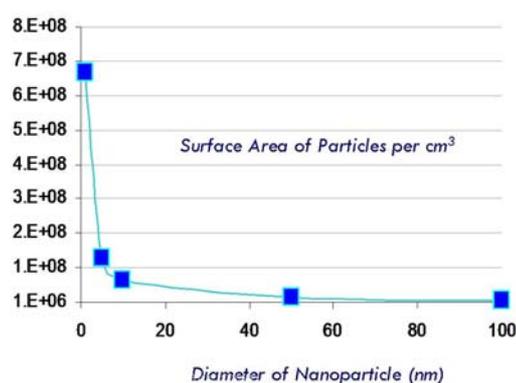


Figure 2b The surface area of the materials increases dramatically as the particles decrease in size.

The strategies to synthesize nanomaterials (see Figure 3) are generally described as *Top Down* and *Bottom Up* approaches. *Top-down* involves the grinding or milling of materials into small particles and the *Bottom up* requires the building of layers on a surface, atom by atom. *Top-down* approach, often termed as atomization, uses less chemicals but involves physical processes, such as milling to break

down materials into smaller particles. The challenge here is to maintain the overall distinct molecular structure but generate micro and nanoparticles of the bulk material which will improve the overall properties of the bulk material such as diffusion and/or surface reactivity. The bottom-up approach can involve the generation of defects or vacancies in materials such as those found in wasteforms or semi-conductors. These defects and voids act to compensate for charge deficiencies and therefore provide greater stability. Induced microporosity (free volume) can improve the strength of a material such as synthetic bone, or it can also weaken a film whose role is to protect the underlying surface from the environment.

4. Porosity and PALS

The sizes of the holes in materials can be readily determined using a number of conventional techniques, such as transmission electron microscopy (TEM), BET surface analysis, and small angle neutron and X-ray scattering (SANS and SAXS). However, extensive sample manipulation, vacuum conditions, high skill level and limited availability prevents their routine use. Recent advances in detectors, digital oscilloscopes and software analysis for positron annihilation techniques is providing new opportunities for the bench-top Positron Annihilation Lifetime Spectroscopy systems (PALS).

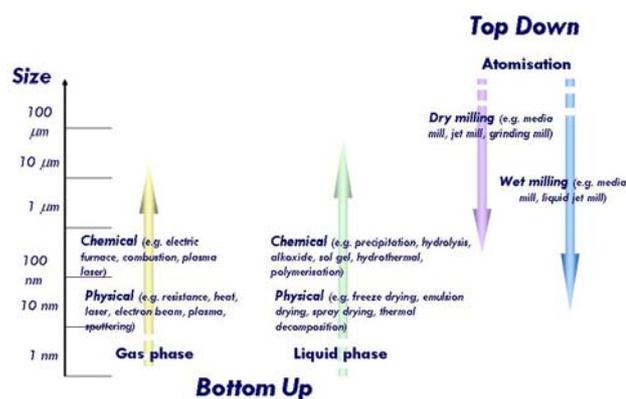


Figure 3. Summary of *Bottom Up* and *Top Down* approaches to the synthesis of nanomaterials

Classically used in the measurement of vacancies in semi-conductors and wasteforms, PALS is becoming a powerful tool for the analysis of soft matter. Requiring minimal sample preparation it can be used to analyse vacancies from defects (0.1 nm) to voids (up to 10 nm) in a wide array of materials. More recently it has been used to measure the porosity of polymeric materials and we are now interested to evaluate its potential role for assessing biological materials such as wool and silk powders.

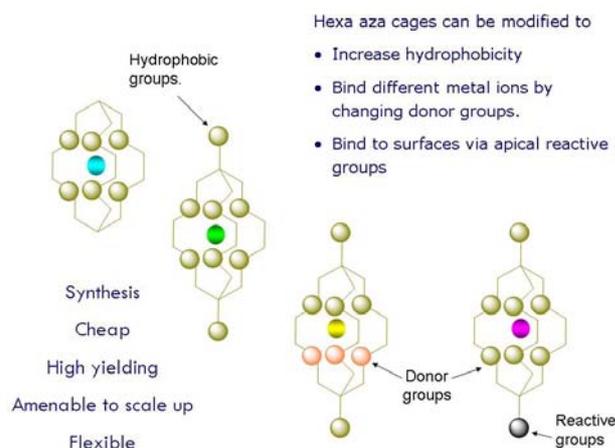
Wool and silk fibres are traditionally used in the textile industry, but fibres too short for weaving go to waste. Increasing demand for renewable products has encouraged scientists to explore new applications for these fibres in areas such as wound dressing, constituents, cosmetics and pharmaceuticals. Re-crystallisation and milling processes have been investigated for the production of smaller fibrous particles, with the former more attractive for translation to large scale production.

Generating a fibrous powder from silk and wool fibres can dramatically enhance features such as rate and selectivity of metal binding properties.^{3,4} PALS was used to evaluate the change in microporosity of fibres compared to jet-milled particles. PALS showed no change in size or incidence of micropores in natural fibres compared to milled samples. Solution studies investigating the binding of heavy metal ions confirmed total amount metal ion absorbed per mg of material had not changed. However a dramatic increase in the rate of metal ion absorbed was demonstrated.

5. Nuclear Sensors

A library of nuclear sensors (radiotracers) is under development to probe the charge, size and hydrophobicity of meso and micropores in materials. They are designed around the hexa aza cage compound, *sarar*, originally designed for use in ⁶⁴Cu labelling of antibodies and peptides for Positron Emission Tomography (PET).^{5,6} The hexa aza cage can be synthesized via a metal template synthesis and readily modified to change the size and charge of the ligands (Figure 4).⁷ The hexa aza cages can stably bind quantitatively to both long and short lived radioisotopes (⁵⁷Co and ⁶⁴Cu, respectively) and therefore can be used to monitor a range of processes in materials. Attaching a linker group to the hexa

aza cages allows one to monitor the reactive groups on the surfaces of films and particles.⁸ While PALS can provide information on the porosity within a material, it cannot indicate if the pores are connected or non-connected. Hence the nuclear sensors provide information on not only if the pores



are available but also the charge within those pores. As the nuclear sensors can be detected at extremely low concentrations (up to 10^{-5} ppb), only small quantities (milligrams) of the nanomaterials are required for analysis. Furthermore the materials under investigation can be evaluated under conditions relevant to intended application providing more accurate information on the materials' properties. Highly adaptable for high-through-put applications, the nuclear sensors are currently being evaluated for on-line monitoring of the synthesis and stability of materials.

Figure 4 Schematic of the design of hexa aza cages

6. Application of PALS and Nuclear Sensors

We have used both PALS and nuclear sensors to provide insight into the relationship between structure and function of a wide range of materials and also for the optimisation of their synthesis and quality control of batch to batch production of nanomaterials. A selection of studies conducted in our laboratory will be described here.

Recent advances in the synthesis of mesoporous silica materials with controlled particle size, morphology and porosity has enabled their application in medicine, environment and industry. Amorphous silica is difficult to analyse by conventional techniques and understanding how to optimise the number of available pores and determining the physical properties within these pores continues to challenge the field.

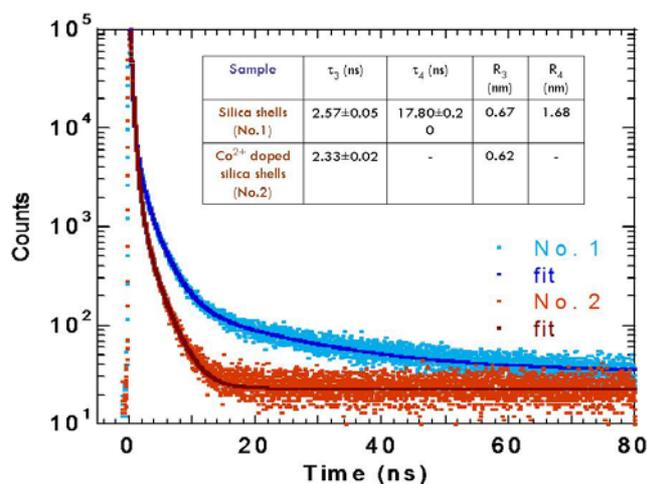


Figure 5. A comparison of PALS spectra for free and Co(II) doped hollow silica shells.

Hollow silica shells synthesized via a polymer template and high temperatures were studied using PALS and nuclear sensors.⁹ Studies with nuclear sensors, outlined in detail elsewhere by Mume *et al* in these proceedings, show the porous silica preferentially bound positively charged molecules under basic conditions. In addition the micropores of the hollow silica shells preferred hydrophobic molecules over hydrophilic molecules. A PALS investigation into the microporosity of hollow silica shells, revealed that there were two types of micropores present (see Figure 5). When the hollow silica shells were doped with Co(II) ions, PALS showed there was an absence of large pores indicating that the metal ions were housed within the largest pores of the hollow silica shells.

Clay particles are another interesting class of materials, readily deployed in a range of applications from cosmetics and pharmaceuticals, to clean up agents for harmful oxyanions and for the efficient dispersion of pesticides. They are found in nature or can be easily synthesized. They have a high aspect ratio and their interlayer spacing can be readily manipulated by metal ion substitution. The interlayer spacings and morphology of the clay particles are usually determined using XRD and TEM, however small platelet size, lack of long-range order and sample preparation can interfere with full analysis. As these characteristics do not interfere with PALS it was investigated as an alternative tool for the analysis of a series of natural and synthetic clay particles.¹⁰ A difference in the PALS spectra was clearly evident and the o-Ps lifetimes, their intensities and the pore shape (spherical and square channel geometries) were analysed. The data clearly showed that PALS was able to detect differences in interlayer spacing of the clays and was sensitive to changes as a result of metal ion doping. Further work will explore the sensitivity of PALS to changes in metal ion doping of clays and its value as a routine analysis tool for clay materials.

The alloys developed for the aerospace industry are selected for their superior weight to mechanical performance ratio. However, because of their poor corrosion resistance they must be coated with films to protect them. These self-healing films are generally paint based, incorporating chemical inhibitors that have the ability to prevent or slow corrosive processes. The free volumes or voids are important properties to incorporate into the films for the inhibitor to work efficiently. We are developing methods to analyze the relationship between the voids and the stability of these films and using this information to model diffusion properties of these materials.

Nuclear sensors or radioactive analogues of the inhibitors are synthesized and incorporated into the films. The films are exposed to corrosive environments and the release of the radioactivity or inhibitor can be monitored by gamma detection. Production of the films to a consistent level of porosity is an important element of this work. Slow positron beamline techniques are ideal for depth profiling porosity in films. However it is important to establish the effect of density of the films and the doping of the inhibitor on the annihilation of positrons. Initial studies have shown the potential PALS has for not only characterizing a range of anti-corrosion films but also for the selection of films suitable for slow positron beam analysis.¹¹

7. Conclusion

PALS and nuclear sensors are ideal tools for understanding the relationship between porosity and performance of a wide range of materials from hard to soft matter, and including biological and composite materials. They are ideal for optimising materials synthesis and proving to be useful for the quality control or assessment of batch to batch reliability of production processes. Both techniques require minimal sample preparation and therefore are more likely to provide information relevant to sample applications. Extremely sensitive and independent of media, the nuclear sensors have the potential for high-throughput screening and on-line monitoring of materials.

Acknowledgments

The author wishes to acknowledge financial support from Australian Research Council Centre of Excellence in Antimatter Matter Studies and contribution from students, post-doctorates and collaborators from Deakin University, University of Western Australia and Australian National University in Australia and University of Tsukuba in Japan and Exilica Ltd. UK.

Abbreviations

Because the IUPAC names for the ligands are long and complicated, those ligands described in this paper have been abbreviated as follows:

sarar = 1-*N*-(4-aminobenzyl)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane-1,8-diamine

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