

Quantum dot and silica nanoparticle doped polymer optical fibers

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Abstract: A novel and highly versatile doping method has been developed to allow active dopants, including materials incompatible with the polymer matrix, to be incorporated into microstructured polymer optical fibers through the use of nanoparticles. The incorporation of quantum dots and silica nanoparticles containing Rhodamine isothiocyanate is demonstrated.

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1. Introduction

Photonic crystal fibres (PCF), also known as microstructured optical fibers (MOF) [1], can guide light by means of refractive index modulations created by the hole pattern surrounding the core. The development of such fibers has led to unprecedented control over a range of optical fiber properties including dispersion, numerical aperture and various nonlinear effects [1]. Originally fabricated in silica, microstructured fibers were rapidly demonstrated based on other materials, the most relevant here being the development of microstructured polymer optical fiber (mPOF) using polymethylmethacrylate (PMMA) [2,3]. In addition to the versatility of fabrication methods available to polymers, and the corresponding variety of microstructures, the relatively low processing temperatures employed (~ 200 °C) allow for in principle the incorporation of both organic and inorganic materials, either through adding material to the monomer prior to polymerization [4] or by solution doping at the preform stage [5]. Such doping can further tailor mPOF properties beyond what is possible through the microstructure alone, for example, through the addition of specific 'gain material' [6] or by an enhanced electro-optic response [7].

Silica nanoparticles synthesized using microemulsion and sol-gel technologies have generated considerable recent interest in applications as diverse as drug-delivery [8], bioanalysis and diagnostics [9]. Such nanoparticles are a versatile 'delivery system' as they have the ability to encapsulate a variety of dopants including magnetic material [10], rare-earths [11] and dyes [9]. In the latter case, for example, dye encapsulation can enhance photostability by preventing photobleaching [9]. This approach also offers the flexibility to simultaneously tailor the particle size, so as to control scattering, and modifying the silica surface to make it compatible with the polymeric matrix. A second class of nanoparticles considered here are quantum dots (QDs). These are made from semiconductor crystals with diameters smaller than the exciton Bohr radius [12]. QDs have a number of interesting features including easy tunability (through their particle size), broad excitation spectra, narrow emission spectra and nonlinear properties [9]. Unlike dyes, they are not susceptible to photobleaching. Diamond nanocrystals containing a single nitrogen vacancy which can be used as a single photon source [13] are yet another nanoparticle dopant.

By creating a generic dopant delivery system for mPOF suitable for a wide range of nanoparticles, it is possible to simultaneously tailor both the dopant embedded within the particles themselves and the microstructure in the fiber to achieve novel fiber properties

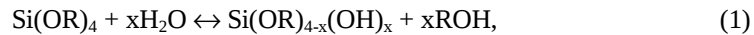
beyond the reach of each modification option on its own. Previous attempts at doping fibers with nanoparticles involved introducing QDs suspended in solvent into the cladding holes of a silica PCF [14-16]. Being in the cladding (while remaining suspended in solvent), however, there was minimal interaction between the QDs and the guided light, as this occurred only through the evanescent field. In previous work, we achieved a fixed spatial distribution by embedding QDs and organo-silica nanoparticles (containing an encapsulated dye) in the cladding holes of mPOF by doping an intermediate sized preform (diameter ~ 10 mm) prior to it being drawn to fiber [17]. Silver nanoparticles have also been added to polymers to change the refractive index, although this has only been reported for bulk optics applications [18].

In this paper, we present a doping technique that allows nanoparticles to be embedded in an mPOF core. The potential is thus to incorporate a wide variety of dopants and achieve a homogeneous, controlled and fixed spatial distribution while maximizing the interaction of the nanoparticles with the guided light.

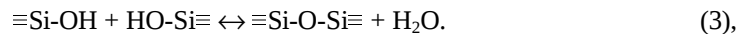
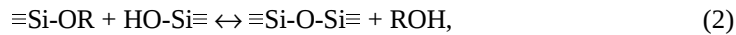
2. Nanoparticles

Silica nanoparticles were fabricated by combining sol-gel science and emulsion technology. The water-in-oil microemulsion consists of nonionic surfactant, co-surfactants, water as suspended phase and oil as continuous phase. The bulk oil phase surrounds the water droplets which retain their spherical shape by interfacial tension created by both the surfactant and co-surfactants. The water droplet size can be 'tuned' by altering the surfactant, co-surfactant and solvent used, along with the water to surfactant mole ratio. Each stable water droplet then acts as a nano-reactor where the silica nanoparticles are formed.

The silicon alkoxide precursor [Tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS)], used to form the silica matrix, is hydrolyzed on addition of water, according to the following reaction,



where R denotes CH_3CH_2 and CH_3 for TEOS and TMOS respectively [8]. The hydrolysis is followed by condensation where partially hydrolyzed molecules polymerize to form oligomers, generating alcohols [eq. (2)] or water [eq. (3)] in the process:



Polymerization continues building ever larger silica chains that form the essentially spherical nanoparticles.

Prior to encapsulation in silica of Rhodamine isothiocyanate (RITC), the dye molecule was attached to 3-amino-propyltriethoxysilane (APTES) by reacting the isothiocyanate and amine groups. The conjugated dye-APTES solution was then added to a mixture of Tergitol NP-9, cyclohexane, 1.33M NH_4OH , and TMOS. The solution was stirred at room temperature for 48 hours, during which both alkoxides were hydrolyzed and condensed as described above to form the nanoparticles inside the water droplet nano-reactors. This approach resulted in the dye being covalently bound to the silica nanoparticles, minimising potential leaching [19].

After the formation of these dye-doped 'core' nanoparticles, additional NH_4OH , NP-9, cyclohexane, pentanol and TMOS were added for post coating of the core with undoped silica shells. By adjusting the amount of additional materials used, the thickness of the coating can be tailored from a few nanometres to tens of nanometres. In this work, two post-coatings were applied which grew the nanoparticles from an initial core diameter of ~ 20 nm to a final size of some 50 nm. TEOS was also used as the silica precursor (instead of TMOS). This produced much larger nanoparticles with an initial core of ~ 60 nm which can then be grown to 2-3 times this diameter, as shown in Fig. 1.

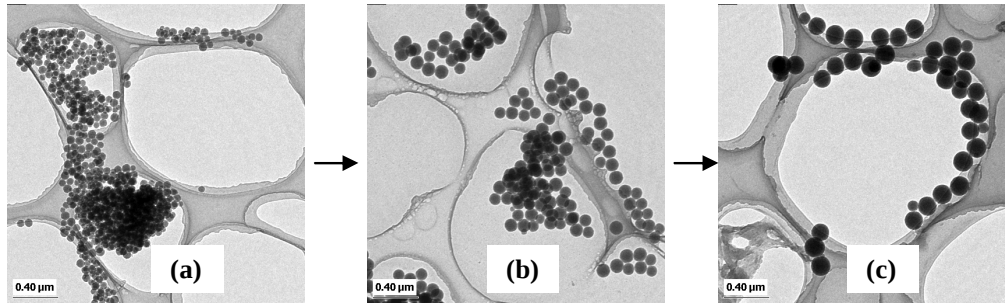


Fig. 1. Transmission Electron Microscope images of silica nanoparticles containing encapsulated RITC dye molecules. (a) The ‘core’ particles after 48 hrs growth (~ 60 nm in diameter), (b) particles after one shell has been added (~ 125 nm in diameter), and (c) particles after two shells have been added to the core (~ 185 nm in diameter).

The QDs were purchased from Evident Technologies, they were supplied suspended in toluene. These ‘Hops Yellow’ QDs are comprised of a CdSe core and a ZnS shell. They have an absorption peak at 552 nm and an emission peak at 561 nm. Their emission spectrum in toluene is shown in Fig. 3(a)(ii). The fluorescence of the dots was enhanced by using long chain amines as ligands, which also serves to prevent aggregation of the dots thus allowing them to disperse uniformly in the toluene [20].

3. Embedding of nanoparticles

PMMA was dissolved in acetone (to give a 10-20 wt % solution) and the desired nanoparticles (here TMOS particles with two shells and a final diameter ~ 50 nm) were suspended in the solution and sonicated to ensure a homogeneous distribution. The concentration of RITC in the PMMA was approximately 0.12 wt %. This solution was evaporated with the solid residue dried at room temperature (up to 48 hrs) before being ground to powder and placed in a dehydrating oven at 90°C for 12 hours to remove any residual solvent. The complete removal of any solvent is critical as any remaining solvent will bubble during the fabrication process. Grinding the PMMA into powder provides a larger surface to volume ratio which allows the solvents to evaporate much more efficiently.

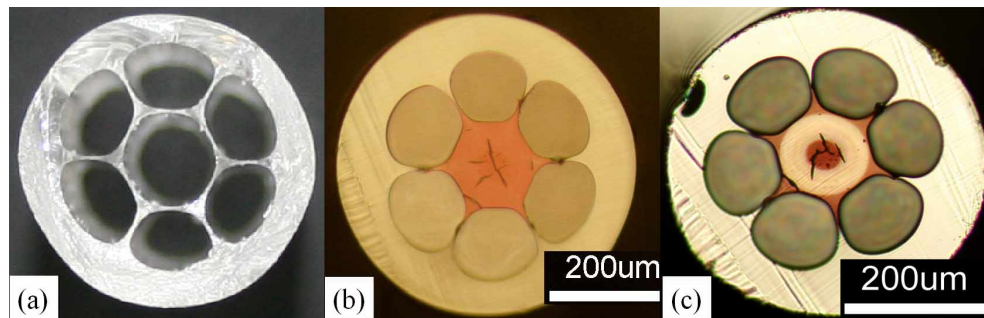


Fig. 2. (a) Intermediate size preform with an external diameter of 11mm, (b) dye-doped mPOF, endface viewed in reflection, and (c) central region where the nanoparticles are present can be clearly seen when viewed in transmission – note that the white ring surrounding the core is the undoped PMMA sleeve used. The (pink) fluorescence is guided between the sleeve and the thin bridges at the edge of the core.

The dry powder was fused under vacuum into a rod (~ 5 mm in diameter) which was sleeved by placing it inside a PMMA tube and stretching to a diameter of 2.5 mm. This doped rod was inserted into the central hole of an intermediate size fiber preform (~ 11 mm in

diameter), as shown in Fig. 2(a), which was then drawn to fiber [21]. This suspended-core fiber had outer and core diameters of 400 μm and 130 μm , respectively.

Images of this doped fiber under white light excitation are shown in Figs. 2(b) and 2(c). Nanoparticle fluorescence was efficiently guided in the core, as indicated by the intense pink coloration. Suspended-core fibers doped with QDs were also fabricated using a similar technique, but with toluene as the solvent and the concentration of QDs in PMMA was approximately 0.017 wt %.

4. Fiber characterization

The doped (with either QDs or silica nanoparticles) fibers were characterized using a 532 nm single-line semiconductor laser operating at 15 mW using 35 cm lengths of fiber. Fiber output was filtered by a notch filter and coupled into a spectrum analyzer. The spectrum for the QD-doped fiber is shown in Fig. 3(a) and that of the dye-doped fiber in Fig. 3(b). In each case, spectrum (i) corresponds to the doped fiber and spectrum (ii) to 'free' particles suspended in toluene as a reference.

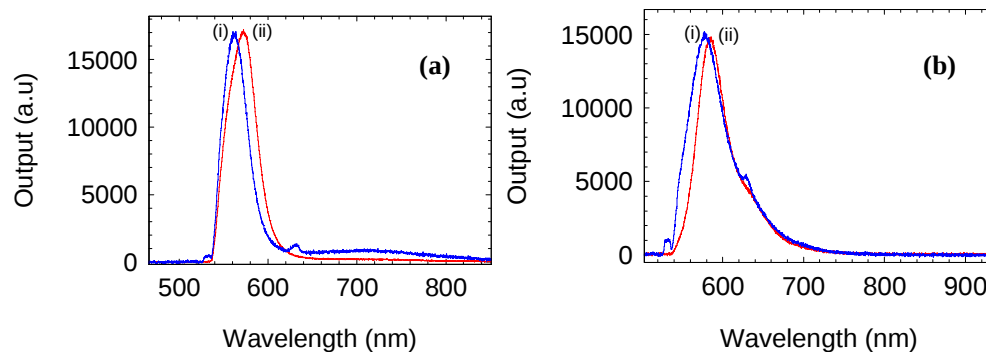


Fig. 3. (a) 'Hops Yellow' quantum dots - (i) embedded in a suspended-core mPOF and (ii) in a toluene suspension - excited by a (15 mW) 532 nm semiconductor laser; (b) dye-doped silica nanoparticles - (i) embedded in suspended core mPOF and (ii) suspended in toluene - excited by the same 532 nm laser.

For both doped fibers, a shift to shorter wavelengths of ~ 10 nm was observed when compared to the free particle suspension. The emission peak for nanoparticles doped rods and their fiber counter parts however are the same. The full-width half-maximum (FWHM) for the QDs was reduced from 40 nm prior to embedding in the fiber to 34 nm after embedding. The dye-doped nanoparticles had an initial FWHM around 49 nm which increased to 56 nm after embedding within the fiber. The observed changes in peak emission and FWHM are due to two main reasons, firstly, the local environment influences the electronic transitions associated with the particles' emission bands. For QDs the structure of its energy levels are highly dependent on their size and the surrounding dielectric as it changes the shape of the absorption lines and hence the emission characteristics [22], for RITC encapsulated silica nanoparticles, a change in the surrounding environment also produces a change in the emission spectrum [23]. Secondly, the change in nanoparticles concentration would vary the intensity of interaction between particles thus causing a shift in emission spectrum, this is evident in both QDs [22] and dye molecules [24].

In Fig. 3(a), a broad secondary emission peak at longer wavelengths (~ 640 nm to 800 nm) was also observed, a feature that is characteristic of QDs without a ZnS shell. This suggests that the QD shell was affected either during the doping process or else is being influenced by the local polymer environment. Both fiber spectra exhibit a small peak at 631 nm which is the result of Raman scattering in the PMMA [25].

5. Conclusion

In this paper, we have reported on a generic method that readily allows the introduction of dopant nanoparticles into the core of a polymer optical fiber. This fabrication technique, together with the versatility afforded by sol-gel encapsulation technology, potentially allows the embedding of a wide range of dopant materials, including those that are inherently incompatible with the polymer or monomer. This approach not only results in a fixed spatial distribution of the embedded nanoparticles but also allows the nanoparticles to be embedded in a highly homogeneous manner in a chosen position within the fiber, for a wide range of possible microstructures. Although unnecessary for the examples demonstrated here, the surface of the nanoparticles can also be modified to make it compatible with the monomer, allowing the dopant particles to be suspended within the monomer prior to polymerization [18].

Potential applications of nanoparticle-doped mPOF include the insertion of rare-earth materials for amplification in optical fibers [11], the creation of efficient in-fiber single-photon sources for quantum communication [13] and magneto-optically active fibers for use in optical switching and isolator devices [10]. We are currently progressing a number of these applications in parallel with extending the basic technique outlined here to encompass a wider range of dopant materials.

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