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Photocatalytic-ready Supraparticle Lasers

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***Abstract*— A photocatalytic-ready supraparticle laser consisting of a micron-scale CdS_xSe_{1-x}/ZnS quantum dot assembly and a titania shell is demonstrated. Such multifunctional supraparticles could find use in future defence, environment, energy and medical technologies.**

Keywords—colloidal quantum dots, lasers, photocatalysis

I. Introduction

We propose and demonstrate microscopic photonic supraparticles (SP) having the dual functionality of laser emission and photocatalysis. The laser capability can be used for sensing/imaging, to detect pollutants/toxicants or pathogens in a given environment, while photocatalysis enables the destruction of toxicants in-situ [1]. This novel material platform could find applications in defence (for example for the detection and destruction of Biological/Chemical Warfare Agents), in medicine, and in environment technologies. To our knowledge, this is the first demonstration of such SP lasers.

The SPs are composed of a micron-scale (here green-emitting) CdS_xSe_{1-x}/ZnS colloidal quantum dot (CQD) assembly, which acts as both the gain material and cavity of the laser [2]. Due to the presence of whispering gallery modes, these lasers are in principle able to detect minute changes in their local environment. The SPs are coated in a thin titania shell – titania can destroy nearby organic molecules through photocatalysis when excited directly by UVA or indirectly by a sensitiser [1]. These titania coated SPs are synthesised by first growing a silica shell on the CQD assembly. This provides a platform for the controlled epitaxial growth of titania which can be further functionalised with a range of organic molecules.

II. Materials and Methodology

A. Synthesis of photocatalyic-ready lasers

The CQD SPs were synthesised by an oil-in-water emulsion technique [2]. The titania shell was grown in two steps. Firstly, the growth of a silica shell, using a technique previously described [3]. The titania shell was then grown on top of the silica using a sol-gel process, through the hydrolysis of titanium butoxide in the presence of the non-ionic surfactant polysorbate 20.

B. Optical characterisation

The silica and silica-titania coating shells were confirmed through Energy Dispersive X-ray Spectroscopy (EDX). Three samples were made by dropcasting, respectively, titania coated ($SP@SiO_2 – TiO_2$), silica coated ($SP@SiO_2$) and uncoated SPs (SP) onto an aluminium pin stub. The latter was used instead of a silicon substrate so we could ascertain whether the presence of silicon was from the SP and not the substrate. The EDX spectra were obtained by focusing the beam at the centre of the three respective SPs using a JSM-IT100 Scanning Electron Microscope (SEM).

The SPs were also optically pumped, one at a time, using a 355 nm, 5 ns pulsed, Nd:YAG laser with a repetition rate of 10 Hz and spot size of $2.8 \times 10^{-5} \pm 0.2 \times 10^{-5}$ cm^2, focused on the sample using an objective lens (Nikon 10x/0.25NA). The pump intensity was controlled with a neutral density filter, and the emission spectra acquired with a CCD spectrometer (Avantes Ava-Spec-2048-4-DT) with a resolution of 0.4 nm.

III. Results and Discussion

SEM images of the three type of SPs are shown in Fig. 1. The SPs are spherical but have pores due to the nature of the

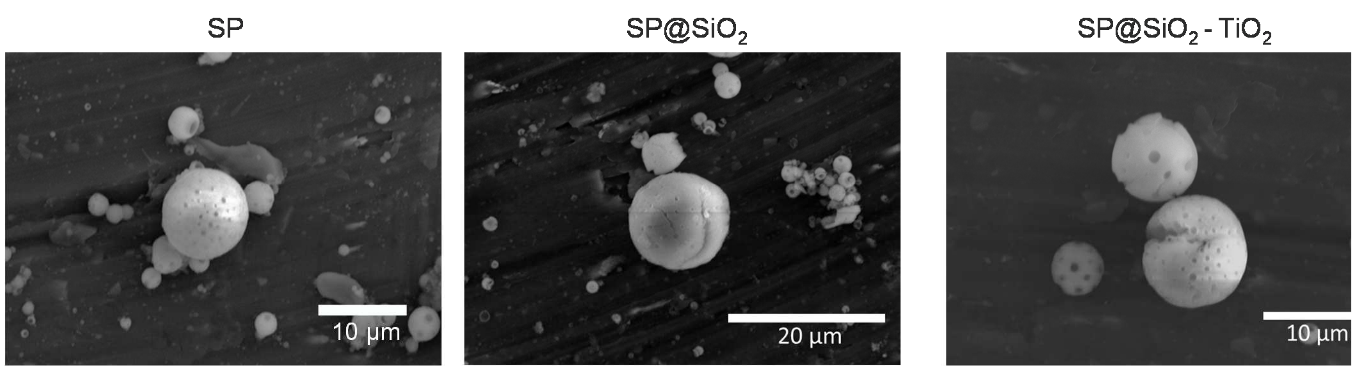

Fig. 1. SEM images of uncoated (SP), silica coated ($SP@SiO_2$) and silica-titania coated ($SP@SiO_2 – TiO_2$) SPs.

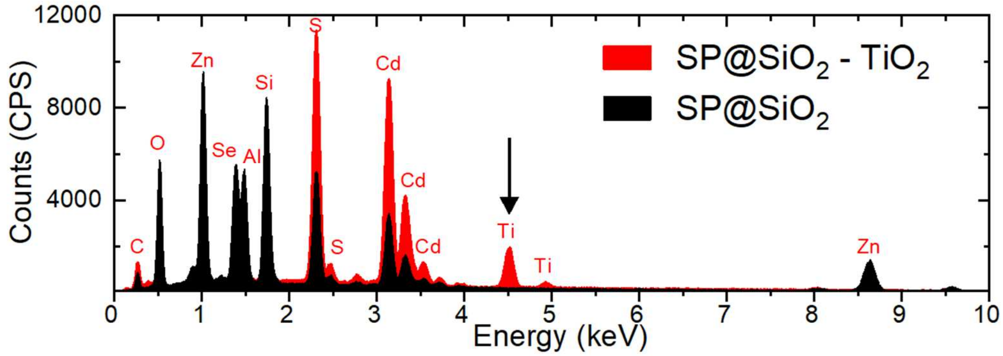

Fig. 2. Energy Dispersive X-ray (EDX) spectra of silica and titania coated supraparticles obtained from a point spectrum measured at the centre of the respective supraparticles on an aluminium pin stub. The peak at 4.51 keV is evidence of titanium and 1.74 keV of silicon. The Cd, Se, S and Zn are from the quantum dots and are present in both samples.

emulsion during the synthesis. The EDX spectra (Fig. 2) shows a clear peak at 4.5 keV from titanium which is only present for the titania coated SP. The peak at 1.7 keV, representative of silicon is present for both silica and titania SPs.

All three types of SPs showed evidence of laser oscillation. The lasing threshold for all three SPs were measured and found to be 25.4 ± 2.3 mJ/cm^2, 8.5 ± 0.7 mJ/cm^2 and 107.6 ± 8.9 mJ/cm^2 for the uncoated SP, silica coated SP, and titania coated SP, with diameters of 5.4, 5.1 and 3.9 µm, respectively. These values correspond to an incident pump energy between 230 nJ and 3 µJ while the actual pump energy absorbed by the SPs is at best a few percent. The emission intensity versus pump power for titania coated SP can be seen in Fig.3(a); the change in the slope of the plot is indicative of onset lasing. The emission spectra above (215 ± 18.0 mJ/cm^2) and below threshold (72.9 ± 6.7 mJ/cm^2) is shown in Fig. 3(b). The linewidth of the lasing mode at 547 nm is resolution limited.

The threshold for the silica coated SP decreases almost 3-fold compared to the uncoated SP. This is most likely due to the silica coating passivating surface defects in the assembly,

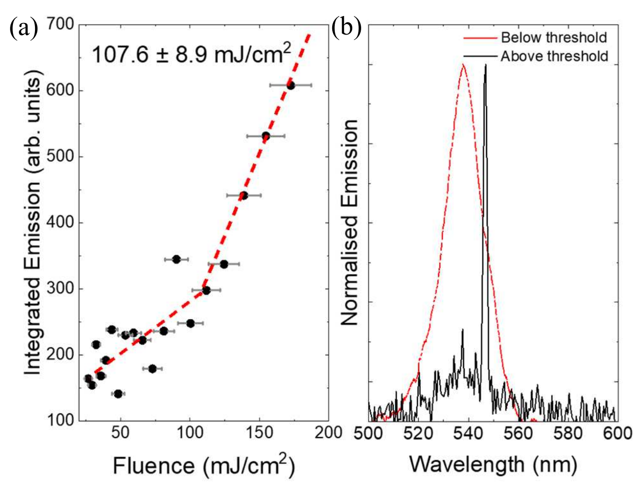

Fig. 3. (a) Laser transfer function of silica-titania coated SP. The lasing thresholds was 107.6 ± 8.9 mJ/cm^2. The diameter of the SP was 3.9 µm. (b) Normalized emission spectra of silica-titania supraparticles. The incident pump fluence were 72.9 ± 6.7 mJ/cm^2 and 215 ± 18.0 mJ/cm^2 for below and above lasing threshold respectively.

creating a smoother interface from the SP to air. The threshold for the titania coated SP increased by over 12-fold compared to the silica coated SP. The increase may due to several factors which include; lower coupled pump energy due to the higher refractive index of titania leading to higher scattering losses, pulling of resonating modes into the titania layer, and defects in the titania.

The surface of the titania shell allows for functionalisation with a variety of ligands in order to interact and capture analytes. For example APTES 3-(aminopropyl)triethoxysilane can be added to have amine functional groups on the surface which could subsequently be reacted with a wide range of molecules or structures, including cyclodextrins [4] shown to bind Chemical Warfare Agents and other toxic compounds.

IV. Conclusion

A novel system composed of photocatalytic-ready SP lasers that has the potential to detect and destroy toxicants has been demonstrated. The material platform could find use in applications requiring the combined functionalities of sensing and photocatalysis.

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