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CW Stimulated Emission in a Self-Assembled $NaYF_4$:$Yb^{3+,}$ Tm^{3+} Upconverting Microresonator

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Abstract*— A novel design and synthesis method for $NaYF_4$:$Yb^{3+,}$ Tm^{3+} upconverting nanoparticle microlasers is demonstrated by using a temperature-controlled self-assembly oil-in-water emulsion technique. The supraparticle acts as both the gain medium and the optical cavity, and has great potential for diverse biomedical application*s

Keywords—Upconverting nanoparticles, microresonators, supraparticles

I. INTRODUCTION

Upconverting nanoparticles (UCNPs) have gained significant interest due to their low toxicity and ability to emit UV or visible light when excited in the near infrared (NIR). This is particularly useful for bioimaging applications, due to infrared light's large penetration depth in biological media. These features also make UCNPs an attractive option as a gain material for new types of microscopic lasers. This has previously been achieved by coating dielectric microspheres with UCNPs, with reported laser thresholds on the order of 10 kW/cm^2 [1,2]. Herein, we demonstrate a novel design and synthesis method for UCNP microlasers utilizing a temperature-controlled, self-assembly oil-in-water emulsion technique. This method results in supraparticles (SPs); i.e., tightly packed UCNPs, here $NaYF_4$:Yb^{3+}, Tm^{3+}, that can then act as both the gain material and microresonator. In contrast to other solution-based gain materials such as organic fluorophores and cadmium-based colloidal quantum dots, UCNPs exhibit additional, distinct advantages, including: extended fluorescent lifetimes, chemical stability, photostability, and reduced toxicity.

II. MATERIALS AND METHODOLOGY

A. *Synthesis of $NaYF_4$:Yb^{3+}, Tm^{3+} supraparticles*

The SPs were synthesised using a temperature-controlled, self-assembly oil-in-water emulsion technique [3], whereby the oil-phase was a 20 mg/ml solution of $NaYF_4$:$Yb^{3+,}$ Tm^3 suspended in chloroform and the water phase contained 1.25% of polyvinyl alcohol (PVA).

B. *Optical Characterisation*

Exploration of the surface, size, and shape of SPs was confirmed through Scanning Electron Microscopy (SEM). The sample was drop cast to a silica coated aluminium pin stub.

A NIR µ-photoluminescent (µ-PL) setup with a 976 nm continuous-wave laser was used to optically pump individual SP with a spot size of 2.24x10^{-6} cm^2. The pump was current controlled and focused with an objective lens (Mitutoyo 10x/0.26NA). Spectral analysis was carried out using a spectrometer (Avantes AvaSpec-2048-4-DT) with a resolution of 0.13 nm. Two types of samples were compared under optical pumping in order to assess the cavity effect of the SP on the optical characteristics of the UCNPs: (i) a SP and (ii) drop cast UCNPs; both samples were on a glass substrate.

III. RESULTS AND DISCUSSION

The presence of dropcast $NaYF_4$:$Yb^{3+,}$ Tm^{3+} UCNP, Fig.1A, and SPs, Fig.1B. from the respective samples was confirmed through imaging with the µ-PL setup. Further investigation of the shape, size and surface of SPs was also carried out on an SEM as shown in Fig.1C. The SPs were shown to be spherical in shape, on the micron scale and have a relatively smooth outer surface.

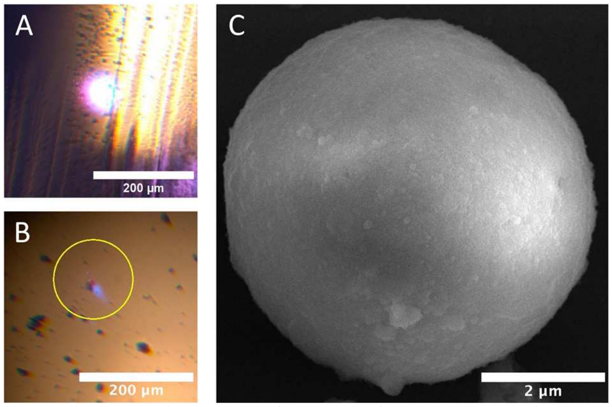

Fig. 1: Microscope images, x10/0.26NA, of UCNPs (A) and SPs (B) mounted on NIR µ-PL setup. (C) SEM images of SP.

Emission characteristics were determined by optically pumping a single SP, ~10 µm in diameter, at varying pump powers, Fig. 2. For comparison, the sample of dropcast UPNCs was measured in the same conditions (Fig. 3). The SP spectra between 400 nm and 500 nm for a 34mW and 340mW pump power are shown in Fig.2A. There are 2 main PL pedestals corresponding to the $^1D_2 \rightarrow {}^3F_4$ (450 nm) and $^1G_4 \rightarrow {}^3H_6$ (475nm) transitions of Tm^{3+}. At a 340mW pump power, two prominent, resolution-limited peaks at 473.56 nm and 477.14 nm, attributed to two successive polar modes of the cavity formed by the SP, dominate the photoluminescence pedestal of the $^1G_4 \rightarrow {}^3H_6$ transition. The dropcast UPNC sample does not show such features but a smoother spectrum (Fig. 3A), indicating that the modes originate from resonances of the SP. The peak intensity of these two SP modes versus pump power is plotted in Fig 2.B. The intensity increases until 150 mW where it plateaus. Other

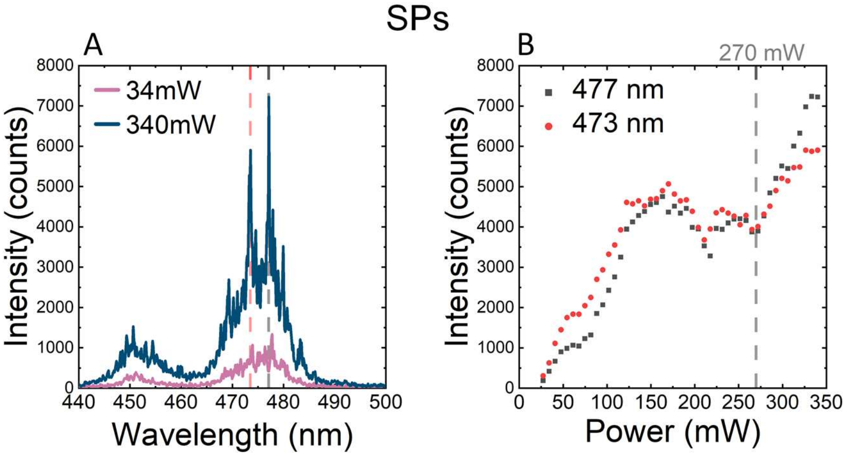

Fig. 2 (A) $\text{NaYF}_4\text{:Yb}^{3+,}$ Tm^{3+} SP emission spectra above (blue) and below threshold (pink). (B) Intensity versus pump power of the cavity modes at wavelength 477.14 nm (black) and 473.56 nm (red). The threshold is at 270 mW (dashed line).

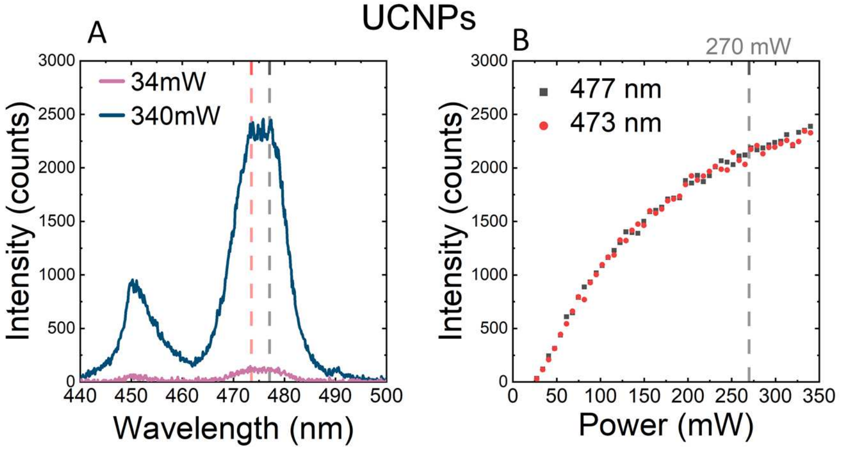

Fig. 3: (A) $\text{NaYF}_4\text{:Yb}^{3+,}$ Tm^{3+} UCNPs emission spectra at 34 mW and 340 mW (B) Laser transfer function of UCNPs at wavelengths 477.14 nm and 473.56 nm.

modes in fact exist with wavelengths close to each of these dominating modes and there are signs of competition, which explains at least partly the plateau. A threshold behavior is observed though at 270 mW (120 kW/cm^2) where the intensity of both modes increases again with a sudden change of the slope, which is attributed to the onset of stimulated emission/lasing, while the competing modes and the PL pedestal saturate. The intensity versus pump power function for the dropcast UCNP sample plotted at the same wavelengths is smooth (does not display any threshold behavior) and sublinear, saturating at the higher powers.

IV. CONCLUSION

A novel design and synthesis method for upconverting nanoparticle $\text{NaYF}_4\text{:Yb}^{3+,}$ Tm^{3+} microlasers is demonstrated by using a temperature-controlled self-assembly oil-in-water emulsion technique. Stimulated emission into resonant modes of the SP was achieved with their output intensity currently limited by the pump power. Further investigation is on-going to verify at what pump level the regime of laser oscillation is fully established. This holds significant implications for advancing upconverting microresonators in diverse biomedical application. Future research will focus on post-functionalization strategies aimed at facilitating biological interfacing. Coating the microresonators with dielectric shells such as silica represents a promising approach to mitigate challenges associated with quenching effects, optimize upconversion efficiency, and ensure compatibility with complex aqueous environments.

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