Reducing Photon Avalanche Excitation Threshold of Tm^{3+}-doped $NaYF_4$ Up-Conversion Nanoparticles by Resonant Waveguide Grating Structure

Thanh-Thu Le-Vu, Jia-Rong Chang, Jiunn-Yuan Lin*, Hung-Chih Kan, and Chia-Chen Hsu*[1].

[1] *Department of Physics, National Chung Cheng University, Ming-Hsiung, Chia-Yi 621, Taiwan.*
**Email of Corresponding author: phycch@ccu.edu.tw*

Abstract: Photon avalanche (PA) upconversion luminescence (UCL) of rare earth ion-doped upconversion nanoparticles (UCNPs) have attracted great interest due to their extreme nonlinear response to the excitation light intensity via a looping energy transfer mechanism. In this work, we demonstrated the generation of PA UCL of Tm^{3+}-doped $NaYF_4$ UCNPs with an excitation intensity threshold of 6 $kWcm^{-2}$. Furthermore, we showed that the excitation intensity threshold of the PA UCL of these core UCNPs can be reduced by the guided mode resonance effect generated by a resonant waveguide grating structure.

Keywords: photon avalanche, upconversion nanoparticle, resonant waveguide grating..

1. Introduction

Photon avalanche (PA) upconversion nanoparticles (UCNPs) are useful for super-resolution fluorescence microscopy, because they exhibit an abrupt increase in upconversion luminescence (UCL) when they are excited beyond a certain excitation intensity [1, 2]. When PA occurs, the intensity of UCL (I_{UCL}) emitted from PA UCNPs increases with increasing excitation intensity (I_{EXC}), following a highly nonlinear response, i.e., $I_{UCL} = c(I_{EXC})^n, n \gg 1$ [1]. Here, we demonstrated PA UCL of Tm^{3+}-doped $NaYF_4$ ($NaYF_4$:Tm^{3+}) UCNPs synthesized by our group via the thermal decomposition method and reduced the PA excitation intensity threshold of these UCNPs through a resonant waveguide grating (RWG) structure. RWG is an all-dielectric nanostructure consisting of a subwavelength grating on top of a waveguide layer [3]. When the incident light matches with the guided mode resonance (GMR) condition of the RWG, the incident light will be coupled into and subsequently coupled out of the waveguide layer through the grating, generating a strong local field distribution on the surface of the RWG [4]. In this work, we deposited $NaYF_4$:Tm^{3+} UCNPs on the surface of a RWG structure and exploited the GMR effect to increase excitation light intensity on the surface. Therefore, the PA excitation intensity threshold of these UCNPs was reduced.

2. Technical Work

Figure 1 (a)-(c) show TEM images of $NaYF_4$:Tm^{3+} (core, C), $NaYF_4$:Tm^{3+}@ $NaYF_4$ (core@shell-1, CS1) and $NaYF_4$:Tm^{3+}@ $NaYF_4$ (core@shell-2, CS2), respectively. Their average diameters are 16.9±1.88 nm (C), 20.6±1.95 nm (CS1), and 23.9±1.78 nm (CS2). The three types of UCNPs were drop-casted on a glass substrate respectively and then excited by a 1064-nm CW laser to generate 800-nm UCL. Figure 1 (d) shows UCL intensity versus excitation intensity in a log-log plot for the three samples. It is clear that all three types of UCNPs exhibited PA UCL; that is a sudden increase of UCL intensity when excitation exceeds a threshold intensity.

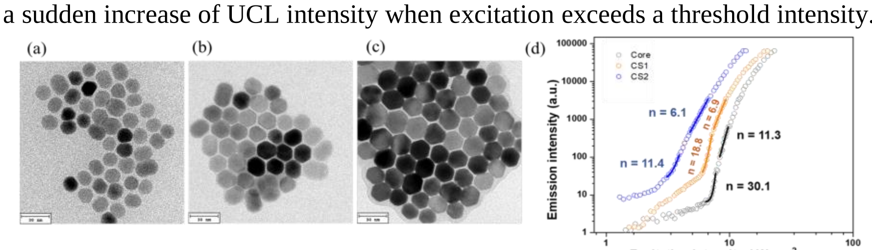

Fig. 1. TEM images of (a) NaYF4:Tm3+ core UCNPs (b) NaYF4:Tm3+@NaYF4 CS1 UCNPs (c) NaYF4:Tm3+@NaYF4 CS2 UCNPs (d) 800 nm emission intensity versus 1064 nm excitation intensity for the three samples.

For the core UCNPs, a large nonlinear order (n～30.1) was observed, when UCNPs were excited above a threshold intensity (6 $kWcm^{-2}$). For the CS1 and CS2 UCNPs, the excitation intensity thresholds decreased to 3 kWcm^{-2} and 1.5 kWcm^{-2}, respectively. The inclusion of a $NaYF_4$ inert shell onto the core UCNP surface can lower the excitation intensity threshold because the inert shell can reduce the non-radiative decay of Tm^{3+} ions caused by surface quenching effect [1]. However, the core@shell structure also leads to reduction of the nonlinear order, namely n∼18.6 for CS1 and n∼11.4 for CS2, which is adverse for applications. Therefore, we propose to utilize the GMR effect of RWGs to improve PA performance of $NaYF_4:Tm^{3+}$ UCNPs, which cannot not only lower the excitation intensity threshold but also increase the nonlinear order.

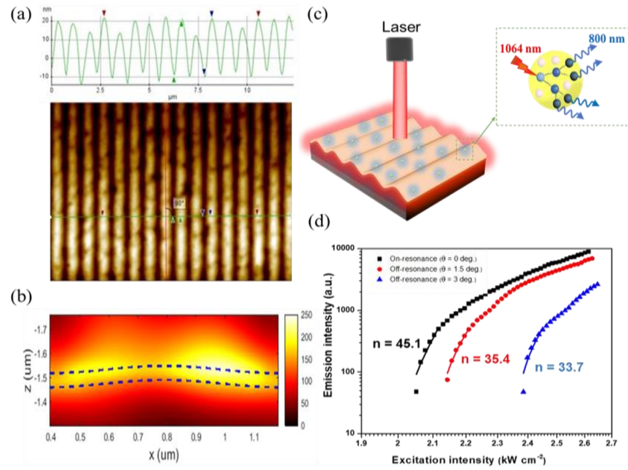

Fig. 2. (a) The AFM image of the RWG. (b) Simulated TE mode electric field intensity distribution of the incident light inside and outside of the RWG under GMR condition with aqueous environment. (c) Experimental scheme for the generation of UCL from NaYF4:Tm^{3+} UCNPs deposited on the surface of the RWG. (d) 800 nm UCL emission intensity versus 1064 nm excitation intensity obtained under resonant excitation and non-resonant excitation configurations.

The RWG structure used in this work was fabricated via the nanoimprinting method [4]. Figure 2(a) shows the AFM image of the RWG surface with a period of 789 nm and a modulation depth of 31 nm. Figure 2 (b) shows the TE-polarization local electric field intensity distribution of 1064 nm normal incident light obtained by RCWA simulation. It is obvious that a strong local field is formed on the top surface of the RWG. Figure 2 (c) shows the experimental scheme for the generation of UCL from $NaYF_4:Tm^{3+}$ UCNPs deposited on the surface of the RWG. When the excitation light is normal incident, strong excitation light is formed on the RWG surface, resulting in strong UCL emission. Figure 2(d) shows the dependence between the UCL intensity and the excitation light intensity obtained under resonant excitation (θ = 0º) and non-resonant excitation (θ = 1.5º and θ = 3º). As revealed, UCNPs indeed produced PA UCL for both resonant and off-resonant excitation configurations. Compared with $NaYF_4:Tm^{3+}$ UCNPs on glass samples, the threshold of excitation intensity of $NaYF_4:Tm^{3+}$ UCNPs on RWG samples was reduced to 2.05 kWcm^{-2} at θ = 0º (resonance), and to 2.15 kWcm^{-2} at θ = 1.5º, and 2.40 kWcm^{-2} at θ = 3º (off-resonance). Furthermore, higher nonlinear orders were achieved in resonance (n∼45.1) and off-resonance (n∼35.4, at θ = 1.5º and n∼ 33.7 at θ = 3º) configurations. The RWG approach proposed in this work not only reduces the PA UCL excitation intensity threshold but also increases the nonlinear order, which will be helpful for biosensing application.

3. Conclusions

In conclusion, we achieved PA UCL of $NaYF_4:Tm^{3+}$ UCNPs on glass substrates with an excitation intensity threshold of 6 kWcm^{-2} and a high nonlinear order (n∼30.1). By using a core@shell structure, the excitation intensity threshold of UCNPs can be decreased to 3 kWcm^{-2} and 1.5 kWcm^{-2}. However, it also reduced the nonlinear order of PA UCL. We showed that the PA UCL performance of $NaYF_4:Tm^{3+}$ UCNPs can be improved by exploiting the GMR effect of RWG. The method not only reduced the excitation intensity threshold (2.05 kWcm^{-2}) but also increased the nonlinear order (n∼45.1).

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