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Highly Spectral Dependent Enhancement of Upconversion Emission with Sputtered Gold Island Films[†]

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Abstract

We report an five-fold overall enhancement of upconversion emission in NaYF₄:Yb/Er nanocrystals when coupled with gold island films. Spectroscopic studies show that the enhancement factors are highly dependent on the exact spectral positions and excitation power density, with a largest enhancement factor more than 12 observed at selected spectral position, which may be attributed to different upconversion processes involved.

The ability to tune the spectroscopic properties of fluorophores, especially the enhancement of the emission intensity, by coupling fluorophores with surface plasmonic noble metal nanostructures can lead to exciting opportunities in applications such as sensing technologies and single molecule studies.^{1–2} The origin of plasmonic enhancement can be fundamentally attributed to two major effects: (1) an increased excitation rate due to local field enhancement (LFE); (2) an increased emission rate by surface plasmon coupled emission (SPCE), which can change both the fluorescence lifetime and quantum yield.^{3–4} In many systems, both factors play important roles in enhancing the emission intensity and are extremely sensitive to the relative spectral position of excitation and emission spectra of the fluorophores versus the plasmonic resonance frequency of the metallic nanostructures. However, it is often difficult to differentiate these two factors, especially in traditional organic dyes with broad overlap in the excitation and emission spectra.⁴ In upconversion nanocrystals (NCs) that are able to convert lower energy photons (typically near-infrared (NIR)) into higher energy photons (usually visible), the excitation and emission wavelengths can be substantially different and usually do not have significant overlap.⁵ Therefore, it allows for the investigation of the interplay between the excitation-plasmonic resonance or emission-plasmonic resonance coupling, and the possibility to distinguish their effects on the plasmonic enhancement.

Here we report the plasmonic enhancement of the upconversion emission in NaYF₄:Yb/Er NCs using gold island films (GIFs). In contrast to isolated gold nanoparticles,⁶ continuous gold films feature plasmonic resonance wavelengths in the NIR region⁷ where the excitation wavelength (980 nm) for upconversion NCs is located. Confocal fluorescence images show

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a more than five-fold overall increase in upconversion emission when coupled with GIFs. Spectroscopic studies indicate that the enhancement is highly spectral dependent with the largest enhancement factor over 12 at selected spectral positions. Excitation power density dependent studies suggest the spectral dependent enhancement is closely related to the difference in the excitation process for different emission peaks, in particular the number of excitation photons involved. It is found that high enhancement factors are observed for emission peaks with an excitation process that involves more photons, which is consistent with the increase of effective excitation flux due to LFE. This result indicates that the emission intensity can be significantly modified with noble metal nanostructures and may open exciting opportunities in biomedical imaging, sensing and therapeutics.⁸

NaYF₄:20%Yb,2%Er NCs was synthesized by thermal decomposition of rare-earth/sodium trifluoroacetate precursors in oleic acid (OA) and octadecene (ODE) as reported previously.⁹ All chemicals were purchased from Sigma-Aldrich and used without further purification. In a typical procedure, 0.975 mmol of yttrium(III) oxide (Y₂O₃, 99.99%), 0.25 mmol of ytterbium(III) oxide (Yb₂O₃, 99.9%) and 0.025 mmol of erbium(III) oxide (Er₂O₃, 99.9%) were dissolved in 5 ml trifluoroacetic acid (TFA, 99%) in a 100 ml three-necked flask. The slurry was then heated to 80 °C with vigorous magnetic stirring under vacuum for 30 minutes to remove water and excessive TFA. Next, 2.5 mmol sodium trifluoroacetate (NaCOOCF₃, 98%) was added, along with 7.5 mL of oleic acid (OA, 90%) and 7.5 ml of 1-octadecene (ODE, 90%) at 100 °C. Afterwards, the solution was heated to 330 °C at a rate of 30 °C min⁻¹ and maintained at 330 °C for 60 minutes to obtain the NCs. The NCs were thoroughly washed and can be readily dispersed in non-polar organic solvents such as chloroform and toluene. The microstructure and composition of the NaYF₄:Yb/Er NCs were characterized by a JEOL 6700 FEG scanning electron microscope (SEM), transmission electron microscope (TEM) and energy dispersive X-ray (EDX).

The gold island films were prepared by an Anatech LTD Hummer[®] 6.2 sputtering system. Confocal fluorescence images were taken on a Leica TCS-SP2 AOBS inverted Confocal and Multiphoton Microscope (Mannheim, Germany) equipped with a Spectra-Physics MaiTai picosecond pulsed infrared laser (Mountain View, CA) set at 980 nm for infrared excitation. Room temperature emission spectra were collected on a Spec-10[®] system from Princeton Instruments including a liquid-nitrogen cooled CCD camera with variable excitation power density using a 980 nm diode laser. The UV-vis spectra were taken with a Beckman-Coulter spectrophotometer (DU[®] 800).

Typically, the as synthesized NaYF₄:Yb/Er NCs have a hexagonal plate morphology with uniform size distribution (Fig. S1a). As determined by EDX (Fig. S1b), the composition of the upconversion NCs is NaY_{0.723}Yb_{0.25}Er_{0.027}F₄, slightly different from the nominal targeted composition. The upconversion emission intensity was measured both before and after sputtering GIFs. To make sure we compare the upconversion emission from the exact same location, photolithography was used to create alignment markers on the glass slide. The upconversion NCs were first spin-coated onto the substrate. The optical image of the NCs on glass slide showed well separated NCs or NC clusters (Fig. 1a). Figure 1b shows the confocal fluorescence image of the same area in Figure 1a, in which each bright spot corresponds to the emission from a single NC or a few-NC cluster. GIFs were then sputtered on the surface of the upconversion NCs. The average size of the gold island was around 20 nm based on AFM image and SEM image studies (Fig. S2). The confocal image of the same area after sputtering GIFs (Fig. 1c) clearly shows that the upconversion emission intensity is significantly stronger than that before sputtering GIFs (Fig. 1b). Quantitative analysis of the confocal images shows that an average intensity enhancement factor of c.a. 5.1 is achieved, corresponding to a more than 400% increase in the overall emission intensity (Fig. 1d).

To compare the enhancement factors at different spectral positions and further explore the underlying photophysics responsible for the emission modulation, upconversion emission spectra at variable excitation power density were monitored before and after sputtering GIFs. Recognizing the significant variations in emission intensity of individual NCs, we have taken spectra from a high density film of NCs obtained using Langmuir–Blodgett (LB) assembly approach² (Fig. S3). In this case, spectra were taken from an ensemble average of a large number of NCs with the overall intensity variation about 20%. To further reduce the impact of location variation and achieve reliable determination of overall spectral enhancement, we have taken and averaged 10 spectra at different locations of the NC film, both before and after sputtering GIFs (Fig. S4). The averaged spectra show three major emission peaks at 522 nm, 550 nm and 652 nm for the upconversion NCs, which are consistent with previous studies on similar NCs.⁹ Importantly, a significant increase of upconversion emission intensity is observed at all spectra positions for the NCs with GIFs compared to those without GIFs (Fig. 2a).

The plot of emission intensity at three different spectral positions as a function of excitation power density (Fig. 2b) reveals several interesting observations: (1) The upconversion NCs with GIFs need significant lower excitation density (~20–30%) than NCs without GIFs to achieve a comparable emission intensity; (2) For NCs without GIFs, a super linear dependence is observed without apparent saturation, while for the NCs with GIFs, a super linear dependence observed at low excitation power density and tends to saturate at high excitation power density; (3) For NC without GIFs, the emission peak at 522 nm is the weakest among three main emission positions throughout the excitation power density range, while for the NCs with GIFs, the 522 nm emission peak was the weakest at low excitation power, but increases much faster with increasing excitation power density and become the strongest emission peak in the end.

It is also interesting to note that the enhancement factors vary significantly with the excitation power (Fig. 2c). In general, the enhancement factors first increase and then decrease with increasing excitation power for all three major emission peaks, which can be attributed to the saturation of emission at high excitation power for NCs with GIFs. The enhancement factors are also highly dependent on the exact spectral positions. Specifically, a maximum increase in emission intensity of more than 12 fold is observed at 522 nm, while only a 5 fold enhancement is achieved at 550 nm and 652 nm.

To further understand the relationship between spectral dependent enhancement factors and excitation power density, we have plotted the upconversion emissions intensities *vs.* the excitation power density in the log-log scale, in which the slope indicates the number of photons responsible for the upconversion process.^{5,9} Although in principle, both a 2-photon process and a 3-photon process can result in any of the three emission peaks (Fig S5), the slope of the log-log plot is 2.1 for the 522 nm emission peak, which is larger than those (1.6 and 1.7) of the other two emission peaks (Fig. 3a), indicating the 522 emission is more likely to involve 3 photons in the upconversion process. After introducing GIFs onto the upconversion NCs, all the slopes are increased with slope of the 522 nm peak remaining the largest (slope of 2.7, 2.0 and 2.2 for 522, 550 and 653 nm emission peaks). This suggests that the existence of GIFs can also modify the excitation process, which may enhance the upconversion processes involving more photons. Based on these studies, we suggest that LFE is playing an important role here because an increased excitation flux by LFE will impact a more-photon involved upconversion process more significantly. Therefore, the emission intensity at 522 nm can be increased significantly more than the other two emission wavelengths. Meanwhile, the SPEC effect is less likely to be responsible for the large difference in the enhancement factor at different spectral positions because no

substantial intensity difference was observed in GIF plasmon resonant spectra among these three different spectral positions (Fig. S6).

In conclusion, we have observed a plasmonic enhanced upconversion emission with an average enhancement factor of 5.1 and a largest enhancement factor more than 10 at selected spectral positions. Spectroscopic and excitation power density studies showed that a more-photon-involved upconversion process resulted in a larger enhancement factor, suggesting that the increased excitation flux originated from LFE may be largely responsible for the enhancement disparity at different spectral positions. We believe these studies in upconversion NCs will offer further insight into the plasmonic-excitation-emission interaction between noble metal nanostructures and nanoscale fluorophores, as well as provide a new route to rationally modulate the emission of the fluorophores.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. (a) Reflection image of upconversion NCs on glass slide. (b, c) Confocal upconversion fluorescence images of the upconversion NCs on glass slide before (b) and after (c) gold sputtering obtained with 980 nm excitation. (d) Histogram of the enhancement factors of 50 bright spots (intensity ratio between (b) and (c)). (Scale Bar: 2 μm for a, b, c and 100 nm for inset)

Figure 2.

(a) Emission spectra of upconversion NCs on glass slide before and after gold sputtering excited with a 980 nm diode laser at the power density of 11 mW/cm², 40 mW/cm² and 67 mW/cm² for (1), (2) and (3) respectively. (b) Power dependent upconversion emission before (open) and after (solid) gold sputtering. (c) Power dependent enhancement factor of upconversion emission on glass slide at different wavelengths.

Figure 3. Power dependence of upconversion emission on glass slide excited with a 980 nm diode laser before (a) and after (b) gold sputtering. Only data before saturation is plotted here.