Tip-Enhanced Upconversion Luminescence in Yb³⁺–Er³⁺ Codoped NaYF₄ Nanocrystals

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Supporting Information

ABSTRACT: Lanthanide doped upconversion nanoparticles reveal enormous potential for biomedical applications. However, they are limited by low upconversion efficiency. In this paper, we demonstrate tip-enhanced upconversion luminescence (UCL) from a single Yb^{3+} – Er^{3+} -codoped NaYF₄ nanoparticle with a maximum enhancement factor of 11 by the plasmonic effect, which is a solution for improving the conversion efficiency and will become a potential technique for the applications in sensitive imaging and detection via speeding up both the absorption and the emission processes of lanthanide doped upconversion nanoparticles. By investigating the optical properties of the tip-enhanced UCL at 550 and 660 nm separately in Yb^{3+} – Er^{3+} codoped NaYF₄ nanoparticles, we observe that the gold-coated tip influences the upconversion process in Yb^{3+} – Er^{3+} -codoped NaYF₄



particles by improving the reception and the transmission of incident electromagnetic fields.

INTRODUCTION

Trivalent lanthanide ion (Ln^{3+}) -doped materials, which can convert near-infrared or infrared radiation into visible luminescence via upconversion (UC) processes including excited state absorption or energy transfer to excited states,¹⁻⁴

have been widely investigated since their discovery in the 1960s.⁵ Compared with organic fluorophores and semiconducting nanocrystals, Ln^{3+} -doped upconversion nanoparticles (UCNPs) offer high photochemical stability, sharp emission bandwidths, and large anti-Stokes shifts (up to 500 nm) that reduce the near-infrared or infrared background noise and improve the signal-to-noise ratio.^{2,6} Ln^{3+} -doped materials have been found to have significant potential in a wide range of applications, such as in color displays,^{7,8} biological labeling,^{9,10} solar cells,^{11,12} solid state lasers,^{13,14} and so on. It is essential to obtain satisfactory UC emission efficiencies and desired color outputs. Many options have been investigated to improve the photoluminescence properties of Ln^{3+} -doped UCNPs,¹⁵ such as joining the appropriate sensitizers (Yb³⁺, Nd³⁺, etc.),^{16,17} changing the host or crystal structure and size,¹⁶ designing core—shell structures,¹⁸ and codoping with other ions (Mn²⁺).¹⁹

Recently, the enhancement of the photoluminescence (PL) in Ln³⁺-doped UCNPs by adding an additional electric field or magnetic field has attracted considerable interest.^{20,21} Increase of the upconversion efficiency can also be achieved by the

plasmonic effect to engineer the surrounding electromagnetic environment.

Plasmonic effect can trigger strong localized electromagnetic fields by coupling to incident light, bringing about higher effective nonlinearities of the metal itself or the surrounding dielectric material. Metallic nanomaterials and structures are usually designed and used for generating plasmonic effects.^{22–29} Among all of them, the metal tip is well-known for enhancing Raman signals or photoluminescence.^{30–33} A highly localized electromagnetic field can be produced at the metal tip because of the plasmonic oscillation. Therefore, the strengthened field at the tip will enlarge the absorption cross sections of the lanthanide ions and modify the local density of optical states, leading to higher radiative decay rate.³⁴ This induces enhancement of the upconversion luminescence (UCL).

In this paper, we demonstrate tip-enhanced UCL in a single $Yb^{3+}-Er^{3+}$ -doped $NaYF_4$ nanoparticle, which would be a potential technique for applications in sensitive imaging and detection by improving both absorption and emission processes of Ln^{3+} -doped UCNPs. The measurement of the optical properties of the tip-enhanced UCL at 550 and 660 nm in $Yb^{3+}-Er^{3+}$ -doped NaYF₄ nanoparticles indicated that both the excitation and emission of the $Yb^{3+}-Er^{3+}$ -doped NaYF₄

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nanoparticles were significantly enhanced by the gold-coated tip.

EXPERIMENTAL METHODS

The NaYF₄:Yb³⁺/Er³⁺ nanoparticles were synthesized by the coprecipitation method with a concentration of 20% for Yb³⁺ and 2% for Er^{3+} dispersed in cyclohexane. The details of the synthesis procedure are described in the Supporting Information.

The transmission electron microscopy (TEM, JEM-2100F) image of the synthesized NaYF₄:Yb³⁺/Er³⁺ nanoparticles is depicted in Figure 1a, indicating that the lateral size of the



Figure 1. (a) Transmission electron microscope (TEM) image of the NaYF₄:Yb³⁺/Er³⁺ nanoparticles. (b) X-ray diffraction (XRD) pattern of the NaYF₄:Yb³⁺/Er³⁺ nanoparticles, indicating a hexagonal phase structure.

nanoparticles is about 20–30 nm in diameter. X-ray diffraction (XRD) analysis of the synthesized nanoparticles was performed by using a diffractometer (Bruker D8 ADVANCE, LynxEye detector, operating at 40 kV and 40 mA) and applying Cu K α as the radiation light. As shown in Figure 1b, all the peaks of the XRD pattern are assigned as a hexagonal phase structure (JCPDS No. 16-0334).

In order to investigate the tip-enhanced upconversion properties of single nanoparticle, the sample was prepared by spin-coating the solution of NaYF₄:Yb³⁺/Er³⁺ nanoparticles in cyclohexane on a clean coverslip with an average distribution density of about 0.25 μ m⁻² for the experiment observation.

A combined system of a scanning confocal microscope and an atomic force microscope (AFM) was used for investigating the UCL properties of the NaYF₄:Yb³⁺/Er³⁺ nanoparticles with and without the gold-coated tip. As illustrated schematically in Figure 2, a continuous-wave diode laser emitting at 980 nm was used as the excitation source. The excitation laser was linearly polarized, and the polarization direction could be adjusted by a half-wave plate in front of the confocal microscope. Then the laser beam was focused on the coverslip by an oil-immersion



Figure 2. Experimental scheme combined with a scanning confocal microscope and an atomic force microscope. HWP, half wave plate; MO, microscope objective; UCNP, single NaYF₄:Yb³⁺/Er³⁺ upconversion nanoparticle; FM, flip mirror; L, lens; APD, single-photon detector based on Si-avalanche photodiode. See details in the text.

objective (×100, N.A. = 1.40, oil immersion, UPlanSApo, Olympus). The beam size at the focus was about 850 nm according to the diffraction limit. The resultant UCL from the single NaYF4:Yb3+/Er3+ nanoparticles was collected by the same microscope objective. The UCL signal was filtered spectrally by a dichroic mirror and a band-pass filter at 550 or 650 nm with bandwidth of 40 nm so that the main upconversion emission transition ${}^{4}S_{3/2} - {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} - {}^{4}I_{15/2}$ in Er³⁺ could be collected separately. And the beam was also spatially filtered by a pinhole with diameter of 75 μ m in a telescope system. The upconversion photons were finally detected by a single-photon detector based on a Si-avalanche photodiode (APD). The sample of the coverslip with NaYF₄:Yb³⁺/Er³⁺ nanoparticles was held on an x-y piezo stage. The confocal UCL images of the single $NaYF_4$: Yb³⁺/Er³⁺ nanoparticle were obtained by scanning the piezo stage.

On top of the scanning confocal microscope, an AFM (NanoWizard II, JPK) was installed to acquire the surface topograph of the nanoparticle. The tip used here for plasmonic enhancement was made of silicon with a gold coating layer of 70 nm thickness (SI-AF01-A, SEIKO). It was shaped into a pyramid structure of 12.5 μ m height with a curvature radius of 30 nm on the tip. The tip was aligned coaxially with the confocal microscope, which could be used for tip-enhanced UCL investigation. Since the size of the laser beam at the focus was much larger than the nanoparticle, the whole nanoparticle was within the illumination of the laser while the AFM tip was scanning the surface. Therefore, a mapping of the UCL intensity dependent on the position of the AFM tip could be obtained by scanning the gold-coated tip on top of the nanoparticle while the excitation beam was focusing on the single NaYF4:Yb3+/Er3+ nanoparticle. It indicated a tipenhanced UCL image of the nanoparticle. By switching on the flip mirror before the APD, the upconversion signals could be guided to the spectrometer for spectral measurement.

RESULTS AND DISCUSSION

Using the AFM part of the experimental setup in Figure 2, we first obtained the topographic image of the single $NaYF_4$:Yb³⁺/ Er^{3+} nanoparticle investigated in this paper, as shown in Figure



Figure 3. (a) Three-dimensional topographic image of a single NaYF₄:Yb³⁺/Er³⁺ nanoparticle obtained by the atomic force microscope (AFM). The AFM tip scan area is 100 × 100 nm². (b) UCL image of a single NaYF₄:Yb³⁺/Er³⁺ nanoparticle without the gold-coated tip. Excitation power density = 2.79×10^5 W/cm²; scanning size = $1.2 \times 1.2 \mu$ m². (c) Tip-enhanced UCL image of a single NaYF₄:Yb³⁺/Er³⁺ nanoparticle with the gold-coated tip approached. Excitation power density = 2.79×10^5 W/cm²; scanning size = $1.2 \times 1.2 \mu$ m². (c) Tip-enhanced UCL image of a single NaYF₄:Yb³⁺/Er³⁺ nanoparticle with the gold-coated tip approached. Excitation power density = 2.79×10^5 W/cm²; scanning size = $1.2 \times 1.2 \mu$ m². (d) Normalized UCL intensity profiles of the NaYF₄:Yb³⁺/Er³⁺ nanoparticle along line 1 in panel b (blue squares) and line 2 in panel c (red circles) with Gauss fits (black lines).

3a, which indicated that the height of the nanoparticle was about 15 nm.

Focusing on the single nanoparticle, the confocal UCL images without and with the gold-coated tip were obtained under excitation at 980 nm as presented in Figure 3b,c, respectively. It was obvious that the UCL of the NaYF₄:Yb³⁺/ Er^{3+} nanoparticle was highly enhanced when the tip approached it. Because the tip was close to the laser-focused area, the field enhancement was chiefly confined to the vicinity of the tip apex. As shown in Figure 3d, the full width at half-maximum (fwhm) of the UCL profile reduced from 880 to 490 nm by comparing the intensity profiles of lines 1 and 2 in Figure 3b,c, indicating a resolution improvement by a factor of 2.

A simplified energy level scheme for the Yb³⁺-Er³⁺-codoped system with a possible upconversion mechanism and the corresponding emission under excitation at 980 nm are indicated in Figure 4a. In the sensitizer-emitter pair Yb³⁺ and Er³⁺ system, there exists a two level system in an Yb³⁺ ion with an absorption band centered at 980 nm. Due to the larger absorption cross-section and much higher density than the Er³⁺ ions, Yb³⁺ ions absorb most of the excitation light.^{35,36} With the absorption of the excitation photons, Yb³⁺ ions are excited into the ${}^{2}F_{5/2}$ state and then decay back to the ground state ${}^{2}F_{7/2}$ via several different processes such as emission in infrared, nonradiative decay, or energy transfer. Since the excited state of Yb³⁺ ion $({}^{2}F_{5/2})$ is resonant with the ${}^{4}I_{11/2}$ level of Er³⁺, highly efficient energy transfer takes place, leading to the excitation of a nearby Er^{3+} ion into the ${}^{4}I_{11/2}$ level. This is the first step of the energy transfer upconversion process. Subsequently, a fraction of the excited Er³⁺ ions decay to $^4\mathrm{I}_{13/2}$ level and get excited to the $^4\mathrm{F}_{9/2}$ level via energy transfer from a nearby Yb³⁺ ion, from which red emission centered at 660 nm occurs. If the second-step energy transfer proceeds



Figure 4. (a) Energy diagram and simplified mechanism for energytransfer upconversion between Yb³⁺ and Er³⁺. Solid arrows denote absorption and emission, dashed arrows denote interspecies energy transfer, and dashed yellow arrows denote nonradiative relaxation. (b) UCL spectra of the NaYF₄:Yb³⁺/Er³⁺ nanoparticle with the goldcoated tip approached (red curve) or removed (blue curve), respectively. The green and red windows indicated the detection bands in the experiment.

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before the decay of the Er^{3+} ions in the ${}^{4}\mathrm{I}_{11/2}$ level, the Er^{3+} ions will be excited to the ${}^{4}\mathrm{F}_{7/2}$ level and rapidly decay to the ${}^{2}\mathrm{H}_{11/2}$ and ${}^{4}\mathrm{S}_{3/2}$ levels nonradiatively. Then upconversion green emission occurs with peaks at 525 and 550 nm. A portion of Er^{3+} ions in ${}^{4}\mathrm{S}_{3/2}$ level, which is an additional path for red luminescence. Furthermore, there exist three-photon upconversion processes, inducing blue emission and also contributing to the green and red emission.³⁷ However, it is expected that the three-photon processes make much smaller contributions than the two-photon processes except at very high pump powers.

As shown in Figure 4b, UCL spectra of the NaYF₄:Yb³⁺/Er³⁺ nanoparticle under excitation at 980 nm with and without the gold-coated tip approached were acquired. To avoid damage of the gold-coated tip by too much laser power, the excitation power density was kept at 1.257×10^6 W/cm². Without the tip, the upconversion emission occurred in the visible range with strong peaks at 550 and 660 nm. Two weak emission bands centered at 412 and 525 nm were also observed. When the tip was approached to the particle, the intensities of emission at 412, 525, 550, and 660 nm were highly enhanced. Moreover, other weak peaks at 470 and 506 nm also emerged, which indicate possible transitions of ${}^4F_{3/2}\!\!,\;\,{}^4F_{5/2}\!-\!{}^4I_{15/2}$ and ${}^{4}F_{7/2} - {}^{4}I_{15/2}$, respectively. These two emission bands were not detectable without the effect of the tip enhancement. Since the population of the ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ levels are mainly from the decay in the ${}^{4}F_{7/2}$ level, the simultaneous enhancement of the emission at 506, 525, and 550 nm implied an improved energy reception in the Er³⁺ ions with the influence of the tip. This can also be proved by the simultaneous enhancement of the emission at 412 and 470 nm for the same reason.

In order to study the tip-enhanced effect on the upconversion processes in NaYF₄:Yb³⁺/Er³⁺ nanoparticle, excitation power density dependence of UCL without or with the tip was investigated. The UCL of 550 and 660 nm was selected separately by inserting band-pass filters in front of the detectors. The UCL of both 550 and 660 nm was enhanced with the tip approached as a function of excitation power density and fitted in a double-logarithmic diagram as depicted in Figure 5, showing a maximum enhancement factor of 5.5 for the green emission and 11 for the red emission. As is wellknown, the emission intensity is normally proportional to norders of the excitation power density for any upconversion mechanism. The excitation power density dependence of UCL reveals the multiphoton nature of the upconversion emissions. By the slope of the power dependence curve acquired by fits of the data in a double-logarithmic diagram, the number of pump photons required to excite to the emitting state could be inferred.^{6,38} For the two-photon processes, n should be equal or close to 2. However, the experimentally observed decrease in the slope is determined by the competition between linear decay and upconversion processes for the depletion of the intermediate excited states. For Er³⁺ ions, there exist long-lived intermediate excited states,^{36,39} which can act like energy reservoirs when populating higher energy levels. On that condition, upconversion might occur by a more effective onephoton mechanism, resulting in efficient UCL generation even under lower power density excitation.^{6,38,40,41}

For UCL at 550 nm from the ${}^{4}S_{3/2} - {}^{4}I_{15/2}$ of the Er³⁺ ions in the nanoparticles without the tip enhancement, the UCL intensity increased with the excitation laser with a slope of 2.0 at low power density excitation, indicating that the emission at



Figure 5. Upconversion excitation power density dependence of the single NaYF₄:Yb³⁺/ Er³⁺ nanoparticle with (red curve) or without (blue curve) the gold-coated tip: (a) ${}^{4}S_{3/2} - {}^{4}I_{15/2}$ emission (550 nm); (b) ${}^{4}F_{9/2} - {}^{4}I_{15/2}$ emission (660 nm).

550 nm involved a two-photon process. The Er^{3+} decayed nonradiatively to the ${}^{4}S_{3/2}$ state from the ${}^{4}F_{7/2}$ state after absorbing two excitation photons sequentially from Yb³⁺ by energy transfer and emitted one photon at 550 nm. However, it was observed that the slope value dropped to 1.5 when the tip was approached to the particle. When the light was coupled to the surface plasmon induced by the gold-coated tip, the local electromagnetic field could be enhanced, equivalent to the enlarged absorption cross sections of both Yb³⁺ and Er^{3+} . That would augment the energy transfer upconversion (ETU) and excited state absorption (ESA) efficiency, which increased the UCL intensity and decreased the slope value.

Meanwhile, for the upconversion emission at 660 nm from the ${}^{4}F_{9/2} - {}^{4}I_{15/2}$ of the Er³⁺ ions in the nanoparticles without tip enhancement, the UCL intensity increased with the excitation laser with a slope of 1.5 at low power excitation, indicating that the emission at 660 nm also came from a two-photon process. The main transition for emission at 660 nm is as follows.⁴²⁻⁴⁴ The Er^{3+} decayed nonradiatively to the ${}^{4}\mathrm{I}_{13/2}$ state from the ${}^{4}I_{11/2}$ state after absorbing an excitation photon at 980 nm from Yb^{3+} by energy transfer and then was excited to the ${}^{4}F_{9/2}$ state by absorbing another photon at 980 nm by energy transfer and emitted a photon at 660 nm. Similar to the power dependence of the UCL intensity at 550 nm, the slope value decreased to 1.1 when the tip was approached to the particle at low excitation power. With the tip, the two-photon-induced emission revealed a more effective one-photon transition mechanism even under low power excitation, indicating that



Figure 6. Time-resolved spectroscopy for green (550 nm) and red (660 nm) emissions with the gold-coated tip approached (red circles) or removed (blue squares), respectively. Note that, the blue and red lines indicate the fits with a monoexponential decay.

the UCL efficiency was improved by the tip enhancement effect. 41

When the excitation power density was further increased, saturation of the UCL intensity occurred, and the slope of the power density dependence curve became smaller than 1 whether the tip approached or not, as shown in Figure 5. In nanoscale materials, the electron—phonon interaction is much stronger than that in the bulk. As excitation power density increases, the thermal effect caused by the exposure of the phonon-assisted energy transfer of ${}^{4}S_{3/2}(Er^{3+}) + {}^{2}F_{7/2}(Yb^{3+}) \rightarrow {}^{4}I_{13/2}(Er^{3+}) + {}^{2}F_{5/2}(Yb^{3+})$, leading to a quenching effect on the green emission and the enhancement of the red due to the improved nonradiative relaxation, 45,46 which explained the lower slope for emission at 550 nm than that at 660 nm without the tip.

When the excitation power density increased to the UCL intensity saturation and the tip approached to the particle, the slope value for the emission at 550 nm was a little higher as shown in Figure 5a, while the slope value for the emission at 660 nm became even smaller in Figure 5b. The plasmonic effect induced a faster upconversion transition and resulted in populating the excited states more for the green emission. It compensated the population loss caused by thermal effect, and led to an increased slope value for the emission at 550 nm. Meanwhile, the plasmonic effect also sped up the nonradiative relaxation to the long-lived intermediate state ${}^{4}I_{13/2}$, increasing the population of the "energy reservoirs" so that the slope value for the emission at 660 nm decreased.

In the upconversion process of the Yb^{3+}/Er^{3+} -codoped system, energy transfer plays a very important role. The enhancement of its rate should be taken into account for the tip-enhanced upconversion. In fact, it has recently been demonstrated that the energy transfer enhancement has no connection with the density of states enhancement, 47,48 and it is generally smaller than the spontaneous emission enhancement. In particular, the energy transfer enhancement depends strongly on the donor–acceptor distance.^{49,50} Accordingly, the energy transfer rates remain mostly unchanged for short donor–acceptor distances.^{51,52} For the NaYF₄:Yb³⁺/Er³⁺ nanoparticles here, the doping densities for Yb³⁺ and Er³⁺ are 20% and 2%, respectively. These densities lead to a mean donor– acceptor distance (i.e., the distance between Yb³⁺ and Er³⁺) of less than 1 nm. At such a short distance, the energy transfer rate is very high, and it is extremely difficult to increase it furthermore.^{52,53} It indicated that the variation of the energy transfer rate might contribute barely to the total enhancement in our case.

For analyzing the decay process, we measured the emission decay curve and simulated the emission lifetime of 550 and 660 nm by exponential decay fit as demonstrated in Figure 6a–d. The excitation beam was chopped with a repetition rate of 515 Hz, and the photons arriving after the falling edge of the laser pulse were collected as effective emission lifetime data for analysis. By setting an appropriate time bin and gathering the photon number in each time interval, the histograms of time-resolved luminescence were plotted to analyze the emission lifetime. The upconversion emission decay can be described by monoexponential decay function

$$I(t) = A e^{-t/\tau} + I_0$$

where τ is the lifetime of the emission. The excitation power density was tuned to 2.79 × 10⁵ and 1.257 × 10⁶ W/cm² for comparison.

As shown in Figure 6a–d, we observed a decrease of the decay lifetime for both green and red emission when the excitation power density is switched to 1.257×10^6 from $2.79 \times$

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 10^5 W/cm². It suggested that the higher power density would increase the spatial density of the excited Er³⁺ intermediate excited states, increasing the rate of upconversion emission and cross relaxation out of these states. That would result in a shorter lifetime for the emission states.⁵⁴

And the decay lifetime was clearly shortened with the goldcoated tip approached. The emission decay rate is the sum of the radiative decay rate, Γ_r , and nonradiative rate, Γ_{nr} , indicating that the shortening of the decay lifetime resulted from the enhancement of these two components.^{55,56} The enhanced nonradiative decay rate would lead to an emission quenching, while the strengthened radiative decay rate would attribute to the emission enhancement. The dominating effect of enhancement or quenching can be determined by the net increase in quantum yield, which is affected by the balance between the enhanced nonradiative decay rate and enhanced radiative decay rate.³⁴ For the low quantum yield transitions of visible upconversion emission from Er^{3+} , the intrinsic nonradiative decay rate is much faster than the radiative decay rate.³⁴ The change in nonradiative decay lifetime may therefore dominate the change in total decay lifetime.^{57,58} For this reason, the enhancement factor of Γ_{nr} is not significant, while that of Γ_{r} is remarkable even with the same increase value of Γ_{nr} and Γ_{r} by the tip-plasmonic effect. Hence, we observed 5-fold upconversion emission enhancement (in Figure 5) and less than 2-fold reduction in decay lifetime (in Figure 6).

CONCLUSIONS

We have investigated the influence of the gold-coated tip on the upconversion luminescence of single NaYF₄ nanoparticles codoped with Yb³⁺ and Er³⁺. By approaching a gold-coated tip to the nanoparticle, we observed the enhancement of upconversion fluorescence and the improvement of spatial resolution by the plasmonic effects. Excitation power density dependence and decay time measurements revealed that both the excitation and the emission processes were affected by the coupling to the plasmon resonance on the gold-coated tip. These findings show that the tip-enhanced technique can be applied to single nanocrystals and indicate the potential for sensitive imaging and detection by using tip-enhanced upconversion luminescence.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b04387.

The detailed synthesis procedure of the NaYF₄:Yb³⁺/Er³⁺ nanoparticles (PDF)

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Notes

The authors declare no competing financial interest.

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