Pure red visible emission via three-photon excitation of colloidal Na_3ZrF_7 :Er nanoparticles using a telecom-band laser

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We provide the first demonstration of pure red emission in the visible light region via three-photon excitation in monodisperse Na₃ZrF₇:Er nanoparticles (NPs) by using a laser operating in the telecommunication band. NPs of ~22 nm in diameter are synthesized at 260°C by the thermal decomposition method. The experimental results reveal that the Na₃ZrF₇:Er NPs exhibit pure red emission in the visible region under 1480 nm laser excitation, and the emission intensity is significantly influenced by the Er³⁺ ion concentration. The decay times of the ${}^{4}S_{3/2} \rightarrow {}^{4}F_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}F_{15/2}$ transitions of the Er³⁺ ions at 540 and 655 nm, respectively, are reduced by increasing the Er³⁺ ion concentration in the Na₃ZrF₇:Er NPs. The suppressed emission intensity result from the defect-related quenching effect: when trivalent Er³⁺ ions replac tetravalent Zr⁴⁺ ions, extra Na⁺ ions and F⁻ vacancies are formed to re-balance the charge in the Na₃ZrF₇ matrix. The emission color of the Na₃ZrF₇:Er NPs is related to the cross relaxation between Er³⁺ ions. These results provide an important step toward more effective biological imaging and photodynamic therapy by minimizing the scattering of the excitation light and increasing the penetration depth.

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The multiphoton effect based on two-photon or threephoton technology is receiving increasing attention due to its comprehensive applications in biomedicine, photovoltaics, optical telecommunications, etc. [1-10]. Similar to other nonlinear optical technologies, the common multiphoton effect has very low efficiency to upconvert the energy of excited photons, as the intermediate levels are virtual^[11]. In comparison, lanthanide-doped upconversion nanoparticles (UCNPs) can effectively convert low-energy photons (always infrared light) into ultraviolet, visible, or near-infrared (NIR) photons, owing to their ladderlike system of energy levels^[12]. Until now, owing to their high efficiency, the most frequently used UCNPs have been hexagonal β -NaYF₄ nanoparticles (NPs) doped with Yb^{3+}/RE^{3+} (RE = Er, Tm, Ho)^[13,14]. Upon laser excitation at 980 nm, these UCNPs emit visible light by a two-photon process.

For biomedical applications, it is often important for the excitation light to penetrate far into the sample; however, the penetration depth is limited by Rayleigh scattering, owing to the effect on the beam quality. Since Rayleigh scattering scales as λ^{-4} , long-wavelength multiphoton excitation seems promising for biomedical applications, e.g., in vivo biological imaging and photo dynamics therapy (PDT) of deep tumors. It has been shown that an optimum wavelength window, owing to scattering and absorption in tissue, lies close to the telecom band^[15].

Recently, Er^{3+} ions have been considered to be a promising choice, owing to their strong absorption at ~ 1500 nm, which corresponds to the energy transfer from the ${}^{4}I_{13/2}$ energy level to the ${}^{4}I_{15/2}$ energy level^[16]. LiYF₄:Er³⁺ NPs were first reported by Chen *et al.*^[17] to exhibit multicolor emission under 1490 nm laser excitation by three-photon upconversion (UC) process. Subsequently, $NaYF_4:Er^{3+}$ UCNPs excited at 1550 or 1523 nm were reported^[18,19], and it was found that the emission intensity could be largely enhanced by the inert $NaYF_4$ shell^[20]. These UCNPs irradiated almost multicolor light containing $\sim 540 \,\mathrm{nm}$ (green), $\sim 660 \text{ nm} (\text{red})$, and $\sim 800/980 \text{ nm} \text{NIR}$ wavelengths. However, red emission is widely considered to be the most promising candidate for deep tissues, owing to its penetration capabilities^[21,22]. Additionally, the most frequently used photosensitizer in PDT applications strongly absorbs in the red light region^[23].

Many studies have investigated UCNPs with pure red emission under a 980 nm laser excitation by a two-photon UC process^[24–29], but no studies were published on NPs upconverting from the telecom band to red light by a three-photon process. In this work, Er^{3+} -doped Na₃ZrF₇ NPs were synthesized by following a procedure that had been previously used^[30]. Upon 1480 nm laser excitation, these UCNPs irradiated pure red light centered at 660 nm in the visible light region. The effect of the Er^{3+} ion concentration on the emission intensity of Er^{3+} -doped



Fig. 1. (a) XRD patterns of $\rm Er^{3+}-doped~Na_3ZrF_7$ NPs with different $\rm Er^{3+}$ concentrations, and (b) typical TEM image of Na_3ZrF_7: Er^{3+}5\% NPs.

 $\rm Na_3ZrF_7$ NPs was investigated. The mechanism behind the pure red emission was explained by considering the cross-relaxation effect.

Figure <u>1(a)</u> shows the X-ray diffraction (XRD) patterns of Er^{3+} -doped Na₃ZrF₇ NPs with different Er^{3+} ion concentrations. The patterns revealed that all the as-synthesized NPs had a pure tetragonal phase structure (according to the standard Na₃ZrF₇ host lattice of JCPDS No. 12-0562). No other phase was detected. This result indicated that the dopant Er^{3+} ions completely replaced Zr⁴⁺ ions in the Na₃ZrF₇ lattice. The typical transmission electron microscope (TEM) morphology of Na₃ZrF₇: $\mathrm{Er}^{3+}5\%$ NPs is shown in Fig. <u>1(b)</u>. The as-synthesized Na₃ZrF₇: $\mathrm{Er}^{3+}5\%$ NPs were monodispersed and tetragonal and exhibited a size of ~22 nm. Notably, the concentration of Er^{3+} -doped Na₃ZrF₇ NPs.

Figure <u>2</u> shows the UC emission spectra of the synthesized Er^{3+} -doped Na₃ZrF₇ NPs under 980 and 1480 nm laser excitations. In our previous report, we confirmed that Er/Yb co-doped Na₃ZrF₇ NPs displayed a single red emission under 980 nm laser excitation. However, the Er^{3+} -doped Na₃ZrF₇ NPs displayed multiband emission under 980 nm laser excitation even at the Er^{3+} ion concentration of 20%, as shown in Fig. <u>2(b)</u>. Upon 1480 nm laser excitation, the Er^{3+} -doped Na₃ZrF₇ NPs displayed pure red emission (~660 nm, corresponding to ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$) in the visible light region, whereas the green emission corresponding to the energy transfer from the ${}^{4}S_{3/2}$ level to the ${}^{4}I_{15/2}$ level almost disappeared, as shown in Fig. <u>2(a)</u>. A weak emission at ~820 nm (corresponding to ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$) and a strong emission at ~980 nm



Fig. 2. Spectra of $\rm Er^{3+}$ -doped $\rm Na_3ZrF_7$ NPs with different $\rm Er^{3+}$ concentrations excited by (a) 1480 and (b) 980 nm lasers. The insets are the photographs of the $\rm Na_3ZrF_7:5\%Er^{3+}$ NPs dispersed in hexane.

(corresponding to ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$) were observed in the NIR region. The emission intensity of Er^{3+} -doped Na₃ZrF₇ NPs was significantly affected by the concentration of Er^{3+} ions. The emission intensity of the Na₃ZrF₇: $\mathrm{Er}^{3+}2\%$ NPs was very weak, whereas the Na₃ZrF₇: $\mathrm{Er}^{3+}5\%$ NPs displayed the strongest emission.

To investigate the influence of the Er³⁺ concentration on the emission intensity of Na₃ZrF₇:Er NPs, the decay profiles of the ${}^{4}S_{3/2} \rightarrow {}^{4}F_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}F_{15/2}$ transitions of Er³⁺ ions at 540 and 655 nm, respectively, were also measured under 1480 nm laser excitation, as shown in Fig. <u>3</u>. The effective lifetime τ_m is given by the following formula:

$$\tau = \frac{\int_0^{+\infty} tI(t) \mathrm{d}t}{\int_0^{+\infty} I(t) \mathrm{d}t},\tag{1}$$

where I(t) is the intensity of the emission at time t. The effective decay times were 73.7, 54.3, and 31.6 µs for the ⁴S_{3/2} states and 580.9, 534.3, and 415.6 µs for the ⁴F_{9/2} states of Er³⁺ ions in Na₃ZrF₇ NPs with Er³⁺ concentrations of 5%, 10%, and 20%, respectively. The decay curves of the Na₃ZrF₇:Er³⁺2% NPs were ignored, as the signal was very low and could be hardly detected. Clearly, the emission intensity of the Na₃ZrF₇ NPs was closely related to the decay times: as the decay time decreased, the emission intensity of the Na₃ZrF₇ NPs significantly declined. The short lifetime was mainly attributed to the appearance



Fig. 3. Decay profiles of transitions of Er^{3+} ions under 1480 nm laser excitation: (a) ${}^{4}\mathrm{S}_{3/2} \rightarrow {}^{4}\mathrm{I}_{15/2}$ at 540 nm and (b) ${}^{4}\mathrm{F}_{9/2} \rightarrow {}^{4}\mathrm{I}_{15/2}$ at 655 nm.

of defect-related quenching effects. When trivalent Er^{3+} ions replaced tetravalent Zr^{4+} ions, extra Na⁺ ions and F⁻ vacancies were formed in the Na₃ZrF₇ matrix to re-balance the charge. These defects resulted in quenching effects that reduced the emission intensity of the Na₃ZrF₇:Er NPs. By increasing the Er^{3+} concentration in the Na₃ZrF₇:Er NPs, the defect-related quenching effects were enhanced, and the emission intensity was reduced. The very weak emission of Na₃ZrF₇:Er³⁺2% NPs was mainly related to two aspects: weak absorption to the excited photons, and weak energy transfer between neighboring Er^{3+} ions, due to the low Er^{3+} concentration.

Figure 4 shows the Er^{3+} ion energy levels and the proposed energy transfer UC mechanisms under the 1480 and 980 nm laser excitations. As shown in Fig. 4(a), under 1480 nm laser irradiation, the excitation of Er^{3+} ions from the ground ${}^{4}I_{15/2}$ state to the ${}^{4}I_{13/2}$ state occurs through a ground state absorption (GSA) process, followed by energy transfer to the neighboring Er^{3+} ions, which are then promoted to the higher ${}^{4}I_{9/2}$ and ${}^{4}H_{11/2}$ states. The emission centered at 820 nm [shown in Fig. 2(a)] was generated from the radiative decay from the ${}^{4}I_{9/2}$ state to the ${}^{4}I_{15/2}$ state by two-photon emission. Simultaneously, nonradiative relaxations occur from the ${}^{4}I_{9/2}$ state to the ${}^{4}I_{11/2}$ state, which produce the emission centered at 980 nm [Fig. 2(a)]. The radiative decay from the ${}^{4}H_{11/2}$ and ${}^{4}S_{3/2}$ state to the ${}^{4}I_{15/2}$ state by two-photon emission could produce the emissions at 525 and 540 nm (green emission). The disappearance of the green emission in the spectrum of Na₃ZrF₇:Er NPs [Fig. 2(a)] was attributed to the cross relaxation



Fig. 4. Diagram of UC via energy transfer UC processes between two $\rm Er^{3+}$ ions under (a) 1480 and (b) 980 nm laser excitation.

between Er^{3+} ions. Notably, Er^{3+} clusters can easily form in the Na₃ZrF₇ matrix because of the large mismatch between Zr^{4+} ions and Er^{3+} ions, which reduced the distance between Er^{3+} ions and enhanced the cross relaxation between Er^{3+} ions $[{}^{4}S_{3/2} \rightarrow {}^{4}F_{9/2} (3121 \text{ cm}^{-1}): {}^{4}I_{9/2} \rightarrow {}^{4}F_{9/2}$ (2928 cm^{-1}) ; Fig. 4(a)]. Owing to the cross-relaxation effect, the red emission (660 nm) was enhanced, whereas the green and 800 nm emissions were reduced, resulting in pure red emission in the visible light regions of the Na_3ZrF_7 : Er NP spectra [Fig. <u>2(a)</u>]. When the Na₃ZrF₇:Er NPs are excited by the 980 nm laser, excitation of the Er^{3+} ions from the ground ${}^{4}I_{15/2}$ state to the ${}^{4}H_{11/2}$ state through a GSA process occurs, followed by a transfer of energy to the ${}^{4}F_{7/2}$ state of neighboring Er^{3+} ions. The energy of the ${}^{4}F_{7/2}$ state is partly transferred to the ${}^{4}\mathrm{F}_{9/2}$ state by the cross relaxation between Er^{3+} ions $[{}^{4}F_{7/2} \rightarrow {}^{4}F_{9/2} (5190 \text{ cm}^{-1}): {}^{4}I_{11/2} \rightarrow {}^{4}F_{9/2} (5030 \text{ cm}^{-1})]$ to enhance the red emission. Meanwhile, nonradiative relaxation occurs from the ${}^{4}F_{7/2}$ state to the ${}^{4}H_{11/2}$ and ${}^{4}S_{3/2}$ states, producing green emissions centered at 525 and 540 nm. This mechanism explains exactly why the Na₃ZrF₇:Er NPs exhibit pure red emission under 1480 nm laser excitation, whereas they show strong red emission and weak green emission under 980 nm laser excitation.

Monodisperse Na_3ZrF_7 :Er NPs with different Er^{3+} ion concentrations are synthesized at 260°C. A negligible effect of the Er^{3+} concentration on the Na_3ZrF_7 :Er NP microstructure and sizes is observed. These Na_3ZrF_7 :Er NPs irradiate pure red emission in the visible light region under 1480 nm laser excitation. The emission intensity is influenced significantly by the Er^{3+} ion concentration. The suppression of the emission intensity with the increase in the Er^{3+} ion concentration in the Na₃ZrF₇:Er NPs results from the defect-related quenching effect, which emerges when tetravalent Zr⁴⁺ ions are replaced by trivalent Er^{3+} ions. The pure red emission of the Na₃ZrF₇:Er NPs under 1480 nm excitation is related to the cross relaxation [${}^{4}\mathrm{S}_{3/2} \rightarrow {}^{4}\mathrm{F}_{9/2}$ (3121 cm⁻¹): ${}^{4}\mathrm{I}_{9/2} \rightarrow {}^{4}\mathrm{F}_{9/2}$ (2928 cm⁻¹)] between Er^{3+} ions, which becomes closer to each other owing to the formation of Er^{3+} clusters.

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