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染料敏化增强 Ho^{3+} 单带上转换红光

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Enhancing Single-band Red Upconversion Luminescence of Ho^{3+} Through Dye-sensitization

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Abstract: Single-band red upconversion emission has important applications for high-resolution biomarkers and 3-dimensional color display. However, the cross-relaxation of $\text{Ho}^{3+}/\text{Ce}^{3+}$ co-doping system normally yield the weak single-band red emission. In this paper, the dye-sensitized $\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%) @ $\text{NaYF}_4:\text{Nd}$ (20%) nanoparticles were prepared to address such an issue. Highly uniform upconversion nanoparticles were prepared by solvothermal method, and the single-band red emission was obtained by increasing the Ce^{3+} doping concentration (from 0% to 10%) inside the core. When the near-infrared dyes of IR-806 were further conjugated, the up-conversion luminescence intensity exhibited a 22-fold enhancement, and the red-to-green emission ratio also increased from 4.8 to 8.4. This paper provides a new way to improve the intensity and the purity of single-band red upconversion luminescence through dye sensitization, which is beneficial to high-resolution bioimaging.

Key words: upconversion luminescence; single-band red emission; dye-sensitization; nanoparticles

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染料敏化增强 Ho^{3+} 单带上转换红光

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摘要: 单带上转换红光发射在高分辨生物标记及三维彩色显示方面具有重要应用。本文针对 $\text{Ho}^{3+}/\text{Ce}^{3+}$ 共掺杂纳米体系单带上转换红光较弱的问题, 设计制备了染料 (IR-806) 敏化的 $\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%) @ $\text{NaYF}_4:\text{Nd}$ (20%) 纳米晶, 显著增强了上转换红光发射。采用溶剂热法制备了均匀的上转换纳米粒子, 通过调控核内部 Ce^{3+} 离子掺杂浓度比例 (0 ~ 10%) 逐步获得单带上转换红光发射。在此基础上, 通过上

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转换纳米粒子表面连接近红外 IR-806 染料分子, 808 nm 激发下其上转换发光强度提高了约 22 倍, 特别地, 红绿荧光强度比从 4.8 增至 8.4。结果表明, 染料敏化可用于增强上转换单带红光发射, 并提高红光色纯度, 这有利于高清晰的生物成像应用。

关键词: 上转换发光; 单带红光发射; 染料敏化; 纳米粒子

1 Introduction

Lanthanide ions (Ln^{3+}), characterized by unique $4f^n$ electronic configuration, can generate the radiative emission ranging from the ultraviolet to the infrared region^[1-2]. Especially, Ln^{3+} -doped upconversion nanoparticles (UCNPs) can convert two or more low-energy near-infrared photons into high-energy ultraviolet/visible photons. Their features of the large anti-Stokes shift, narrow emission band, long luminescence lifetime^[3-4], could find promising applications in bioimaging, photodynamic therapy and display devices^[5-8]. Moreover, due to that biological tissues have weak light scattering and absorption for near-infrared (NIR) light, NIR-excited upconversion luminescence is of particular interest in biomedicine^[9-10].

As well known, single-band red emission has excellent applications in 3D full-color display and high-resolution bioimaging^[11]. At present, to achieve the bright single-band red emission, Yb/Er codoping systems were most widely studied by further doping with Mn^{2+} or Tm^{3+} ions. In such systems, doping ions could induce the cross-relaxation process with Er^{3+} , leading to the quenching of the green emission and consequent increase of the red to green (R/G) emission ratio^[12-14]. Similarly, introducing Ce^{3+} ions into the Yb/Ho upconversion luminescence system could also cause the cross-relaxation process and increase the R/G luminescence intensity ratio^[15]. However, the obtained single-band red upconversion emission is normally weak, which is unfavorable for the following applications such as high resolution of biological imaging. Although the cross-relaxation strategy could produce the single band red emission, the total upconversion luminescence (UCL) was greatly reduced. Therefore, how to produce single-band red emission while simultane-

ously maintaining the UCL intensity becomes a critical issue need to be addressed.

In this paper, we reported the preparation of the dye-sensitized $\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%)@ $\text{NaYF}_4:\text{Nd}$ (20%) nanoparticles towards enhanced single-band red upconversion luminescence of Ho^{3+} . The UCNPs were first prepared through a facile solvothermal method, and then conjugated with the dye molecules of IR-806. The UCL was studied by varying the doping concentration of Ce^{3+} .

2 Experiments

2.1 Synthesis of UCNPs

$\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/ $x\%$, $x = 0, 3, 5, 7, 10$)@ $\text{NaYF}_4:\text{Nd}$ (20%) core/shell nanoparticles were synthesized according to previous reports^[16-17]. For synthesizing 0.5 mmol samples, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, 0.395, 0.38, 0.37, 0.36, 0.345 mmol), $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, 0, 0.015, 0.025, 0.035, 0.05 mmol), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, 0.1 mmol) and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, 0.005 mmol) were dispersed in a solution containing 3 mL of OA and 7.5 mL of ODE. The suspension was first heated at 155 °C for 0.5 h to get a clear Ln -OA complex solution. Then NH_4F (2 mmol) and NaOH (1.25 mmol) dissolved in 6 mL of methanol were added to the reaction solution. Afterwards, the solution was heated to 70 °C to remove the methanol and subsequently heated at 300 °C for 1 h. After that, 1 mmol of $\text{NaYF}_4:\text{Nd}$ (20%) active shell solution was injected into the above reaction mixture and maintained 15 min for ripening. Finally, the solution was cooled down to room temperature and precipitated using ethanol for three times.

2.2 Synthesis of IR-806 Modified UCNPs

According to the reported methods^[18-19], the IR-780 dye molecule was first carboxylated to obtain the IR-806 dye. Dimethylformamide (10 mL), IR-

780 molecule (250 mg), 4-mercaptobenzoic acid (115.5 mg) were mixed and dissolved. After reaction for 17 h under argon, the solution was filtered and distilled under reduced pressure to remove dimethylformamide. The obtained product was re-dissolved in 5 mL of dichloromethane, followed by further filtration, precipitation with glacial ether and vacuum drying. The resulting product was IR-806 and was kept in the dark for use. For surface conjugation of UCNPs with dyes, the obtained 1 mL IR-806 (2 mg/mL) and 10 mg $\text{NaYF}_4 : \text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%)@ $\text{NaYF}_4 : \text{Nd}$ (20%) nanoparticles (dissolve in chloroform), were mixed and stirred at room temperature under dark conditions for 24 h, then centrifuged and re-dispersed in 1 mL of chloroform. Finally, the surface-modified UCNPs of IR-806 were diluted 200-fold for further spectroscopic analysis.

2.3 Characterizations

The power X-ray diffraction (XRD) patterns of the UCNPs were recorded on a Rigaku Miniflex 600 bench top powder X-ray diffraction instrument with $\text{Cu-K}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation, operating at 40 kV and 15 mA. The morphology and particle size distributions of the samples were also checked using a FEI Tecnai G220 transmission electron microscope (TEM). Fourier transform infrared (FTIR) spectra were recorded with 2 cm^{-1} resolution (Paragon 1000, Perkin-Elmer, USA). The room-temperature photoluminescence emission spectra were measured on a Horiba Fluoromax-3 fluorometer upon excitation with a continuous 808 nm fiber coupled diode lasers. The absorption spectra were acquired on a Maya 2000 spectrometer (Ocean Optics).

3 Results and Discussion

3.1 Characterizations of Nanoparticles

As shown in Fig. 1, transmission electron microscopy showed that UCNPs were uniform in size and the particle size was approximately 31 nm. XRD data showed (Fig. 2(a)) that the diffraction peaks of the prepared nanoparticles were in agreement with the standard NaYF_4 hexagonal phase pattern (JCPDS: 16-0334), confirmed that the prepared nanoparticles were hexagonal phase structure. Next, the

IR-806 dye was prepared by carboxylation of a commercially available IR-780 dye (Fig. 2(b)). As shown in Fig. 2(c), the absorption peak of the dye molecule was centered at 806 nm, confirming that the IR-806 dye was successfully prepared. On the other hand, the infrared absorption spectra analysis of the structure of dye-sensitized UCNPs (UCNPs@ dye) also confirmed the success of conjugating dyes on the surface of UCNPs. Fig. 2(d) shows the FTIR spectra of the obtained UCNPs and UCNPs@ dye. Due to the presence of oleic acid ligands on the surface of UCNPs, infrared vibration peaks of 2929 and 2850 cm^{-1} were observed, which correspond to the symmetry and antisymmetric vibrations of the methylene group of the oleic acid ligands, respectively. After further conjugation with the IR-806 molecules, in addition to the vibration modes of oleic acid molecules, a new vibration peak appeared at 1251 cm^{-1} for UCNPs@ dye, which corresponded to the C-O stretching mode of IR-806. The appearance of this new vibration peak suggested that IR-806 molecules were coordinated on the surface of UCNPs

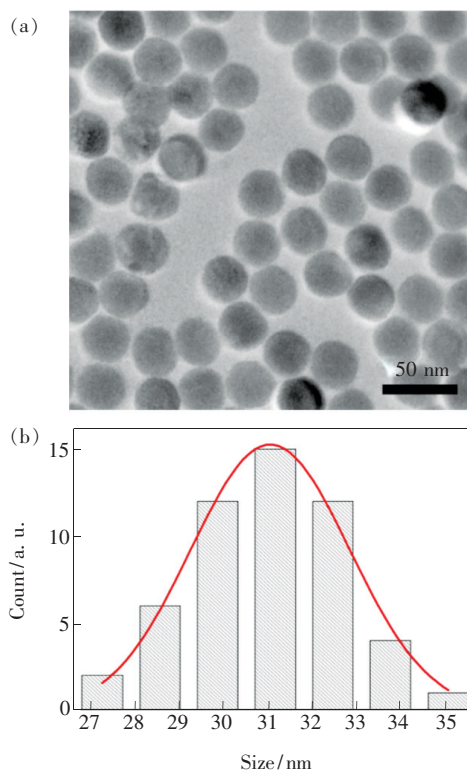


Fig. 1 (a) TEM image of $\text{NaYF}_4 : \text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%)@ $\text{NaYF}_4 : \text{Nd}$ (20%) upconversion nanoparticles. (b) Size distribution of UCNPs.

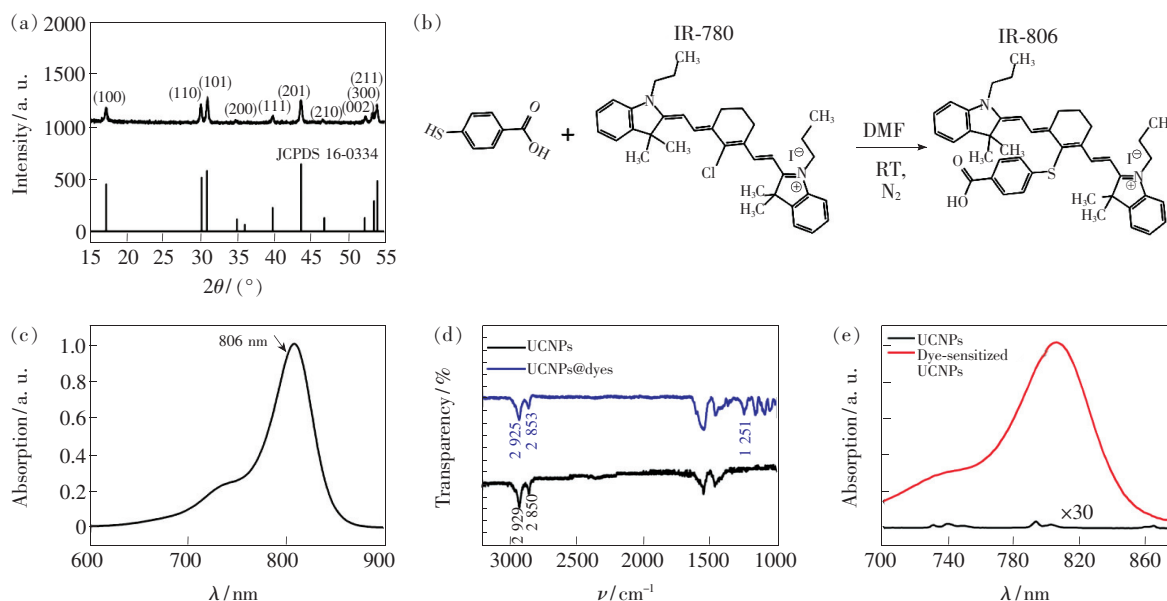


Fig. 2 (a) XRD patterns of UCNPs and the standard card of $\beta\text{-NaYF}_4$ (JCPDS-16-0334). (b) Synthesis process of IR-806. (c) Absorption spectrum of IR-806. (d) FTIR spectra of UCNPs and UCNPs@ dye. (e) Absorption spectra of UCNPs and dye-sensitized UCNPs.

via carboxyl group. Moreover, a broad absorption peak (~ 806 nm) appeared well following that of dye conjugation, which further indicated the successful synthesis of UCNPs@ dye.

3.2 Upconversion Luminescence of Ho^{3+} in $\text{NaYF}_4\text{:Yb/Ho/Ce@NaYF}_4\text{:Nd}$ Nanoparticles

The designed $\text{NaYF}_4\text{:Yb/Ho/Ce@NaYF}_4\text{:Nd}$ (20%) nanostructure could produce the single-band upconversion red emission upon 808 nm excitation due to the cross-relaxation (CR) strategy between Ho^{3+} and Ce^{3+} . According to previous reports^[20-21], the Nd^{3+} ions sensitized core-shell nanostructure was adopted to avoid the quenching effects between the activators and Nd^{3+} ions. The Nd^{3+} -shell could suppress the surface-related quenching and further transfer excitation energy to the activators located in the inner core for UCL. Fig. 3(a) shows the luminescence spectra of $\text{NaYF}_4\text{:Yb/Ho/Ce}$ (20%/2%/x%, $x=0, 3, 5, 7, 10$)@ $\text{NaYF}_4\text{:Nd}$ (20%) UCNPs. The green emission (540 nm) and the red emission (645 nm) originating from the $^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_8$ and $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transitions of Ho^{3+} respectively, were observed. As shown in Fig. 3(e), the luminescence mechanism follows the first energy migration from Nd^{3+} to Ho^{3+} via Yb^{3+} , and subsequent energy transfer upconversion (ETU) with $^5\text{I}_6$ as the metastable

level. Fig. 3(b) shows that as the Ce^{3+} doping concentration increased, the R/G emission ratio gradually increased. In addition, as shown in Fig. 3(c), the overall upconversion luminescence intensity gradually decreased with increasing Ce^{3+} doping concentration. Moreover, as shown in Fig. 3(d), the Commission Internationale de L'Eclairage (CIE) chromaticity coordinate (calculated using the colorimetry system as suggested in the CIE 1931) of the upconversion luminescence of different samples also indicated that the luminescence gradually moved from the green to the red region. According to previous report^[15], the observed luminescence evolution with Ce^{3+} doping could be reasonably explained as being due to the three CR processes (Fig. 3(e)): CR1: $^5\text{I}_6(\text{Ho}^{3+}) + ^2\text{F}_{5/2}(\text{Ce}^{3+}) \rightarrow ^5\text{I}_7(\text{Ho}^{3+}) + ^2\text{F}_{7/2}(\text{Ce}^{3+})$, CR2: $^5\text{S}_2/^5\text{F}_4(\text{Ho}^{3+}) + ^2\text{F}_{5/2}(\text{Ce}^{3+}) \rightarrow ^5\text{F}_5(\text{Ho}^{3+}) + ^2\text{F}_{7/2}(\text{Ce}^{3+})$, CR3: $^5\text{F}_5(\text{Ho}^{3+}) + ^2\text{F}_{5/2}(\text{Ce}^{3+}) \rightarrow ^5\text{I}_4(\text{Ho}^{3+}) + ^2\text{F}_{7/2}(\text{Ce}^{3+})$. The CR process induced by Ce^{3+} was more effective to quench the green emission of Ho^{3+} than red emission, resulting in a significant increase in the R/G emission ratio (Fig. 3(b)). However, the effective CR process also greatly decreased the overall UCL intensity, as shown in Fig. 3(c), more than 90% of

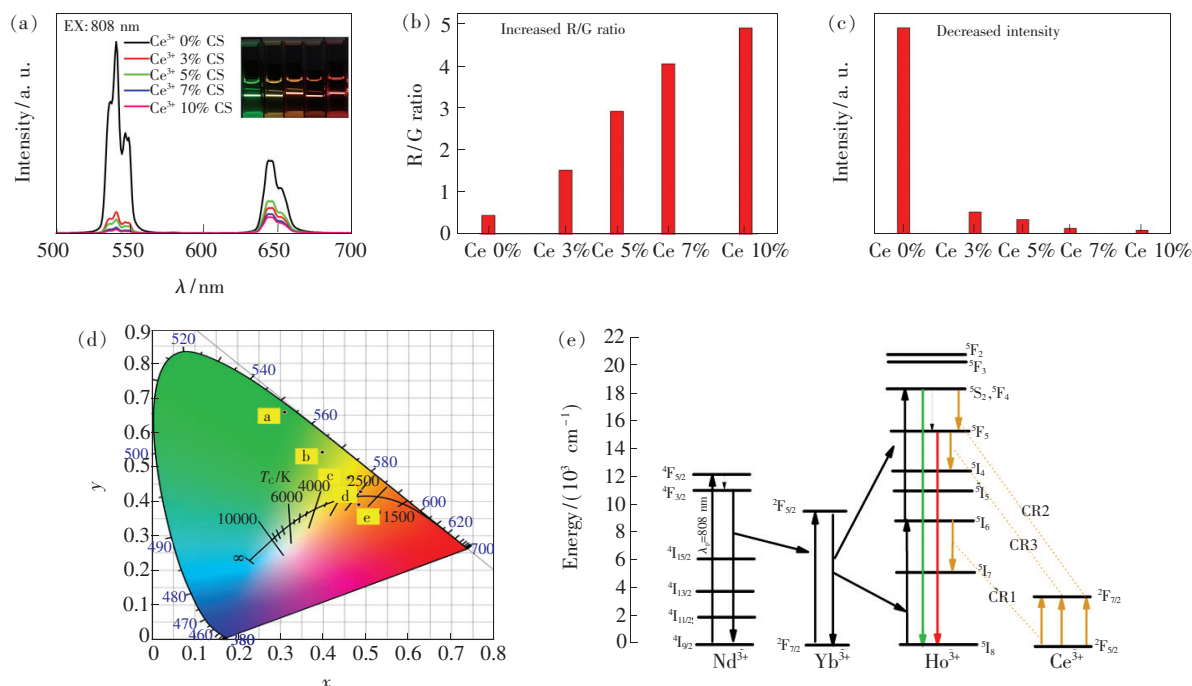


Fig. 3 (a) UC luminescence spectra of the samples of $\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}$ (20%/1%/ $x\%$, $x = 0, 3, 5, 7, 10$) @ $\text{NaYF}_4:\text{Nd}$ (20%) UCNP samples under 808 nm excitation. The increased R/G (b) and the decreased luminescence intensity (c) with the doping concentration of Ce^{3+} . (d) CIE chromaticity diagram of the samples with different Ce^{3+} concentrations (a – e corresponding to $x = 0, 3, 5, 7, 10$). (e) Schematic diagram of the energy levels and the proposed UC mechanism.

UC emission was quenched when doping 10% Ce^{3+} . Therefore, how to maintain the intensity of single-band red upconversion luminescence becomes an issue needed to be addressed.

3.3 Upconversion Luminescence of $\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}@\text{NaYF}_4:\text{Nd}@\text{dye}$

To achieve the enhancement of single-band red upconversion luminescence, we designed and prepared the dye-sensitized $\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%) @ $\text{NaYF}_4:\text{Nd}$ (20%) UCNP samples, where the Nd^{3+} ions located in outer layer served as energetic acceptors from IR-806 before further transferring the excitation energy to the internal luminescence centers, due to the fact that Nd^{3+} ions have multiple absorption bands overlapping with the emission of the near-infrared dyes of IR-806^[19–20]. As shown in Fig. 4(a), the single-band red upconversion luminescence of UCNP samples was enhanced by a factor of 22. Similar to our previous report^[19], this significant upconversion luminescence enhancement was mainly attributed to the strong near-infrared light absorption

ability of the conjugated dye molecules. The dyes could transfer a large amount of absorbed excitation energy to Nd^{3+} , and then further to the internal luminescent centers, as a consequence, the upconversion luminescence was enhanced greatly. It should be noted that, as shown in Fig. 4(b), the dye-sensitization also increased the R/G emission ratio of Ho^{3+} from 4.9 to 8.4. According to our previous publication^[22], such results could be explained as bellow. When the slope of the power-dependent multi-photon processes of the red emission was larger than that of green emission, the R/G emission ratio increased with excitation power density. Herein, dye sensitization played a role of increasing excitation power due to their larger absorption cross-section at the excitation wavelength, then it could increase the R/G emission ratio under the equivalent excitation power density. We tested the power-dependent multi-photon processes of the $\text{NaYF}_4:\text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%) @ $\text{NaYF}_4:\text{Nd}$ (20%) UCNP samples. Fig. 4(c) shows the double logarithm plot resulting

from the luminescence intensity *versus* pump power density, where the slope values of n for the $^5\text{S}_2$, $^5\text{F}_4 \rightarrow ^5\text{I}_8$ (540 nm) and $^5\text{F}_5 \rightarrow ^5\text{I}_8$ (645 nm) transitions of the Ho^{3+} ions were 2.0, 1.9, respectively. The slope of the red emission was larger than that of green emission. The same case holds for the dye-sensitized $\text{NaYF}_4 : \text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%) @ $\text{NaYF}_4 : \text{Nd}$ (20%) UCNPs (Fig. 4(d)). It is obvious that the intensity of the red emission increases

faster than the green emission with the excitation power density. Therefore, the R/G will gradually increase with the excitation power density. The effect of dye-sensitization is similar to increase the excitation power^[22], and could therefore increase the R/G ratio. Therefore, dye-sensitization not only increased the intensity of single-band red upconversion luminescence of Ho^{3+} , but also improved the red purity of the UC emission.

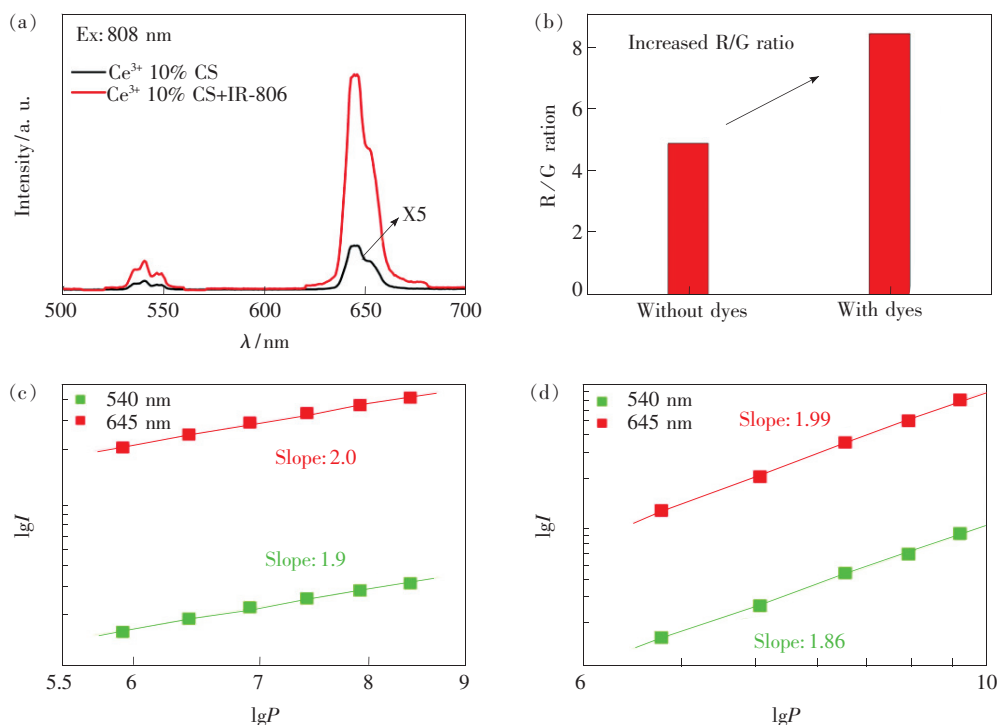


Fig. 4 (a) UC luminescence spectra of $\text{NaYF}_4 : \text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%) @ $\text{NaYF}_4 : \text{Nd}$ (20%) UCNPs (black line) and dye-sensitized UCNPs (red line). (b) Increased R/G ratio after conjugating UCNPs with dyes. Lg-ly plots of the UCL intensity *versus* laser power density for the green and red emissions of the UCNPs (c) and dye-sensitized UCNPs (d) under excitation of 808 nm.

4 Conclusion

In this work, highly uniform hexagonal phase $\text{NaYF}_4 : \text{Yb}/\text{Ho}/\text{Ce}$ (20%/2%/10%) @ $\text{NaYF}_4 : \text{Nd}$ (20%) UCNPs were prepared by solvothermal method, and thus IR-806 molecules were successfully conjugated on the surface of UCNPs. By varying the Ce^{3+} doping concentration (0% ~ 10%), the R/G of Ho^{3+} gradually increased with the Ce^{3+} doping concentration. Especially for 10% Ce^{3+} doping concentration, a single-band red UC luminescence was

achieved, though more than 90% of the total UCL intensity was quenched by Ce^{3+} ions. After further surface conjugation with near-infrared IR-806 molecules, the luminescence intensity of the UCNPs was significantly increased by a factor of 22. More importantly, the R/G emission ratio of Ho^{3+} increased from ~4.9 to 8.4. Therefore, the dye-sensitization method not only enhanced Ho^{3+} single-band upconversion luminescence intensity, but also improved the red emission purity, which is beneficial to single-band red emission for high-resolution bioimaging.

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