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Plasmonic enhanced upconversion luminescence of β -NaYF₄: Yb³⁺/Er³⁺ with Ag@SiO₂ core-shell nanoparticles

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ABSTRACT

Ag@SiO₂ nanoparticles (NPs) are proposed and synthesized to enhance β -NaYF₄:Yb³⁺/Er³⁺ luminescence by mixing with β -NaYF₄:Yb³⁺/Er³⁺ in the solution. Luminescence enhancements are found to be dependent on the amount of addition and the silica shell thickness of the Ag@SiO₂ NPs. For the same silica shell thickness of Ag@SiO₂ NPs, the optimum mass ratio of Ag@SiO₂/microcrystals for the enhancement is 1:21500. For different silica shell thickness of Ag@SiO₂ NPs, the maximum luminescence enhancement occurs at the silica shell thickness of 8 nm under the condition of optimal mass, an overall enhancement factor of 3.5 fold is obtained.

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1. Introduction

The up-conversion (UC) luminescent materials have attracted enormous interest, especially for solar cell applications because of their ability to convert two or more lower energy photons to one higher energy photon [1]. Integrated behind a solar cell, they can reduce the transmission losses and result in significant improvement of the conversion efficiency of solar cell. Theory analysis shows that the upper limit of the photovoltaic conversion efficiency of a single junction silicon solar cell is raised from near 30% up to 47.6% by coupling an ideal UC device [2].

However, the existing UC phosphors generally suffer from inherently low efficiency due to the parity forbidden intra-4f electronic transitions and the low doping concentrations, which limits the application of UC materials for photovoltaic (PV) industry. Until now, no significant performance enhancement due to UC has been reported for natural solar irradiation. So, it is necessary to improve the UC intensities for their practical application. Prior studies suggest that metallic NPs (such as gold or silver) offer a unique advantage of enhancing luminescence due to the localized surface plasmon resonance [3,4]. The mechanism of luminescent enhancement can stem from the local field enhancement effect and the plasmon coupling effect. The absorption and emission properties of rare earth doped materials can be affected significantly by them. The absorption strength of the upconverter is enhanced by local field enhancement effect; the emission strength is enhanced

by nearby plasmon coupling effect. Importantly, the degree of interactions strongly depends on the distance between the emitters and the metal surface [5]. In order to control the distance between emitters and the metal surface, Yuan [6] et al. prepared the NaYF₄:Yb,Er@SiO₂@Ag nanostructures to modulate the UC luminescence. Saboktakin [7] fabricated a metal-oxide (Al₂O₃)-UC nanocrystals trilayered structure to investigate the relationship between the precisely controlled oxide spacer thickness and the enhanced UC luminescence.

In general, UC intensity tends to decrease with reducing the particle size by an order of magnitude [8]. Up to now, small particles are not very efficient spectral converters because of the surface quenching. For PV applications, microcrystals should be favored due to the strong UC luminescence. In this text, we have prepared Ag@SiO₂ NPs to enhance the luminescence of NaYF₄:Yb³⁺/Er³⁺ microcrystals for PV application. The main purpose of overcoating with silica is to (i) offer the chemical inertness (ii) control the distance between silver core and emitters. So far, SiO₂-coated Ag colloids showing desirable physical and chemical properties have been successfully used in metal-enhanced quantum dots fluorescence [9] and SERS-based protein detection [10,11]. But, to the best of our knowledge, there is no report on NaYF₄:Yb³⁺/Er³⁺ luminescence improvement with monodisperse Ag@SiO₂ NPs.

2. Experimental

All the chemical reagents used in this experiment are analytical grade without further purification. Silver nitrate, sodium citrate,

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tetraethyl orthosilicate (TEOS), ethanol, and ammonia solution (25%), $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), Yb_2O_3 (99.99%), Er_2O_3 (99.99%) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Water used in the experiment was purified to resistivity of 18.2 M Ω .

The crystal structures of the products were determined using X-ray diffraction (XRD, Rikaku, ATX-XRD) with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) in a θ - 2θ mode. Scanning electron microscopy (SEM) images and high resolution transmission electron microscopy (HRTEM) were performed to investigate the morphology of the material. Scanning electron microscopy (SEM) images were recorded on a Jeol JSM-6700F. HRTEM was carried out by using Philips Tecnai G²F20. Combined with an integrating sphere diffuse reflection in a single beam system, ultraviolet–visible–near-infrared (UV–Vis–NIR) absorption spectra were recorded using a Shimadzu UV–Vis–NIR spectrophotometer model NO. UV-3600PV. The UC emission spectra of the powder samples were measured on a Fluorolog-3 luminescence spectrometer under a 980 nm laser excitation with a power of 30 mW, the power density is 0.03 W/mm². The decay curves of Er^{3+} ions were recorded using a 980 nm Raman shifter pulsed laser with a pulse width of 10 ns and a repetition rate of 10 Hz, a monochromator, and a digital oscilloscope. All the measurements were performed at room temperature.

2.1. Preparation of the core-shell Ag@SiO₂ nanoballs

To enhance the emission of the UC luminescence, we have prepared Ag@SiO₂ NPs with different silica shell thickness through a modified Stober method [12,13], as shown in TEM micrographs Fig. 1.

First, Silver NPs were prepared by reducing silver nitrate with trisodium citrate. Briefly, 18 mg AgNO₃ was dissolved in 100 ml deionized water and brought to boiling, then, 2 ml 1% sodium citrate solution was added dropwise under vigorous stirring. After boiling for 30 min the solution was cooled to room temperature.

To deposit a silica shell, 25 ml synthesized silver NPs were dispersed in 100 ml absolute ethanol under vigorous stirring. After adding 3.75 ml 25% ammonia solution, the pH value of the mixture solution was adjusted to approximate 9–10. Immediately, different amounts of TEOS were added to obtain different thickness of silica shell. The volume of TEOS was set to 5, 8 and 20 μl to obtain silica thicknesses $t = 6.5, 8$ and 22 nm, respectively. The reaction was stirred at room temperature for 24 h. After centrifuging and washing three times with deionized water and ethanol, the precipitate was dried in air for further measurements. Finally, 2.8 mg Ag@SiO₂ NPs were re-dispersed into absolute ethanol and the concentration of the solution was adjusted to 0.08 mg/ml.

2.2. Preparation the mixture of $\beta\text{-NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystals and Ag@SiO₂ NPs

$\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystals were synthesized according to the procedures described in Ref. [12,13]. Briefly, 15 ml RECl₃ (0.2 M) (RE = Y³⁺, Yb³⁺, Er³⁺ and Y³⁺:Yb³⁺:Er³⁺ = 49:9:1) aqueous solution and 15 ml NaCl solution along with 24 ml EDTA solution, were dissolved in ethanol. Then 0.56 g NH₄F was added into the mixture, which was vigorously stirred for 30 min. The resulting mixture was transferred into a 100 ml stainless Teflon-lined autoclave, which was sealed and heated at 200 °C for 24 h in an electric drying oven. A reaction mixture solution containing 1.032 g $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ was thoroughly mixed with Ag@SiO₂ NPs solution under vigorous stirring and collected via centrifugation. These mixtures were washed with deionized water and ethanol several times and then vacuum dried at 80 °C for 8 h.

3. Results and discussion

The number of Ag@SiO₂ NPs and the silica shell thickness are two key parameters to affect the luminescence properties of the mixtures made with $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystals and Ag@SiO₂ NPs. The former may affect on the crystallization quality of the mixtures, the latter determines the coupling strength of Ag NPs and the emitters. We first determined the optimal amount of Ag@SiO₂ solution so as to achieve the most efficient UC enhancement. Fig. 2(a) depicts XRD patterns of the mixtures of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystals and different volumes of Ag@SiO₂ NPs. We can see that, when adding 0.2–0.6 ml, the Ag@SiO₂ NPs have a negligible effect on the crystallization due to the adding of a small amount. However, when the volume of Ag@SiO₂ increases to 0.8 ml, too much Ag@SiO₂ will decrease the crystallization degree. The details can be seen in Fig. 2(b).

Room temperature UC luminescence spectrum of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ microcrystals were measured under 980 nm laser excitation with a power density of 0.03 W/mm², as shown in Fig. 3(a). These emission spectra displays two strong emission bands of approximately equal intensity in the green (~ 540 nm) and red (~ 652 nm), a weak emission bands in the green (525 nm), corresponding to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ and $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ electronic transition, respectively. A much weaker violet emission at 407 nm is observed and attributed to the $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ electronic transition. The detailed UC mechanism and population processes in Er^{3+} and Yb^{3+} co-doped systems are presented in Fig. 3(b), which has also been described in Ref. [14]. It can be seen that the emission intensity of the $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ is sensitive to the volume of Ag@SiO₂ NPs. As the amounts of Ag@SiO₂ increase, the emission intensity first decreases and then increases. The observed luminescence quenching can be ascribed to the competed absorption among the Ag@SiO₂ NPs [15]. Plasmonic excited by Ag@SiO₂ NPs can increase the UC radiative transitions, however the excited plasmonic has small “hotspot” and low energy due to the addition of a small amount of Ag@SiO₂ NPs. As a result, the role of the negative effect may restrain the positive one and then UC intensity tends to decrease. As the amounts of Ag@SiO₂ increase, the emission intensity is increased due to plasmonic enhancement emission effect. When the volume of Ag@SiO₂ is 0.6 ml, the largest enhancement is obtained. However, beyond a certain amount, the further increase in the Ag@SiO₂/microcrystals ratio results in a decreasing UC emission intensity. In this mixture sample quenching is the dominant process. This may be caused by the decreased crystallization degree. The optimum Ag@SiO₂/microcrystals mass ratio is determined as 1:21,500; this optimal ratio is used in all subsequent experiments.

This demonstrates that an appropriate amount of Ag@SiO₂ contributes to enhancing emission intensity.

To further investigate the influence of the distance between $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ and Ag NPs on the luminescence properties of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$, UC microcrystals was mixed with 0.6 ml different silica shell thickness of Ag@SiO₂ in solution and then vacuum dried at 80 °C for 8 h. Fig. 4 depicts VIS–NIR absorption spectra of pure $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ without and with Ag@SiO₂ for different silica shell thickness. The pure UC microcrystals show very low optical absorption. In contrast, except an absorption peak at 980 nm, which can be assigned to the absorption of Yb³⁺ ions, the other absorption peak was detected in the spectral range from 400 to 600 nm due to the presence of Ag@SiO₂ NPs. The intensities of absorption in those samples with Ag@SiO₂ for different silica shell thickness enhanced a lot and reached a maximum at the shell thickness of 8 nm, which were contributed from surface plasmonic resonances of isolated.

Fig. 5(a) shows UC emission spectra of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ with 0.6 ml Ag@SiO₂ for different silica shell thickness (0–22 nm) under 980 nm laser excitation. To give a further insight into the relationship

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