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Photoluminescence and stability properties of upconversion fluorescent nanomaterial SiNWs: Er^{3+},Yb^{3+}

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ABSTRACT

Rare earth upconversion fluorescent nanomaterials have drawn great attention as novel fluorescent probes because of their many unique merits, such as superior photostability, narrow emission spectra, long lifetime and larger Stokes shift. In this paper, the upconversion fluorescent nanomaterials SiNWs:Er^{3+},Yb^{3+} was prepared at the temperature of 1200 ℃, doping time is 60 min, gas flow rate of N_2 is 1000sccm by mixed Er_2O_3 (99.9%) and Yb_2O_3 (99.9%) (Yb:Er = 2:1) powders with Si nanowires (SiNWs). At room temperature, the photoluminescence characteristics of SiNWs: Er^{3+},Yb^{3+} were tested using near infrared laser with the wavelength is 980 nm, the power is 3 W as excitation light source. The results show that the SiNWs:Er^{3+},Yb^{3+} produced green and red emission band of Er^{3+} with 520–570 nm ($^2H_{11/2} \rightarrow {}^4S_{3/2}$) and 640–680 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) using laser excitation with a wavelength of 980 nm. The Yb^{3+} acting as a sensitizer absorbed the infrared light of near 980 nm and then transferred energy to the luminescence center of Er^{3+}. In addition, the SiNWs: Er^{3+},Yb^{3+} demonstrates good time stability, strong resistance to photobleaching capacity, better stability against acid and alkali, and good biocompatibility. Therefore, the fluorescent nanomaterials SiNWs: Er^{3+},Yb^{3+} has great potential application value in various areas such as solar cell, fluorescence labeling, and biological detection.

1. Introduction

Due to their unique anti Stokes luminescence mechanism, upconversion materials [1,2] have great potential to be applied in biomedicine [3,4], information storage, solar cells [5], and other applications. Particularly, in the biomedicine field, the rare earth upconversion fluorescent probes can effectively avoid the damage of biological cells or other biological tissue damage caused by high energy excitation and long continued irradiation of UV [6]. In addition, the infrared light has a high sensitivity for deep tissue detection [7].

The $Yb^{3+}/Ho^{3+}/Ce^{3+}$ codoped LaF_3 nanocrystals have been successfully prepared via a facile hydrothermal method. The red-to-green emission ratio of Ho^{3+} is enhanced 18.9-fold with Ce^{3+} concentration increasing to 12% [8]. The $BaBi_2Nb_2O_9$ (BBN) and BBN co-doped with Er^{3+}/Yb^{3+} were synthesized by the solid state method. The results show that the upconversion green emissions (centered at 525 nm and 550 nm) and red (around 660 nm) coming from ($^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) transitions, respectively, under excitation at 980 nm [9]. The $NaLuF_4$:Yb, Er/PEI–FA upconversion fluorescent nanoprobes with low cytotoxicity were prepared and used for the application in HeLa cells targeted fluorescent imaging [10]. A paper-based upconversion fluorescence

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resonance energy transfer assay device is proposed for sensitive detection of CEA. The device showed high anti-interfere, stability, reproducible and low detection limit (0.89090009 ng/mL) which is a promising prospect for a clinical point-of-care test [11]. $NaYF_4$:Yb, Er upconversion nanoparticles (UCNPs) was synthesised by employ polyacrylamide (PAAm) hydrogels as a template. It may pave the way for monitoring the in vivo behavior of biomimetic materials via deep tissue imaging [12].

Rare earth fluorescent probe has many advantages including strong light intensity, narrow emission spectrum, and large Stokes shift. However, due to its poor biocompatibility, sensitivity, and specificity for biomarkers, its application in nano biological technology is restrained to a certain extent. Recently, many core-shell nanoparticle materials have been developed, one of those is SiO_2 shell which exhibits many advantages such as non-toxic, pollution-free, good stability, and easy surface modification. Therefore, it has attracted the attention of researchers.

In this paper, the core-shell upconversion fluorescent nanomaterials SiO_2-SiNWs: Er^{3+},Yb^{3+} were prepared and studied, which combine the advantages of both rare earth and SiO_2 shell. Therefore, the fluorescent nanomaterials SiNWs: Er^{3+},Yb^{3+} has a certain application prospect.

2. Experiment

The SiNWs: Er^{3+},Yb^{3+} material was prepared by Yb_2O_3 (99.9%) and Er_2O_3 (99.9%) powders co-doped Si nanowires with the temperature ranging from 1000 ℃ to 1200 ℃. The doping time is 60 min, the N_2 flow rate is 1000sccm, and the mole ratio of Yb^{3+}:Er^{3+} is 2:1, 3:1 and 6:1 based on the traditional high temperate solid stated method. The morphology and microstructure of the Er,Yb-doped SiNWs were characterized and analyzed using a transmission electron microscope (TEM). At room temperature, the photoluminescence characteristics of SiNWs: Er^{3+},Yb^{3+} were tested used a HORIBA Fluorolog-3 fluorescence spectrophotometer and a near infrared laser with the wavelength of 980 nm and the power of 3 W as excitation light source. Finally, the time stability, stability against acid (pH = 1) and alkali (pH = 13), and resistance to photobleaching capacity of the sample were tested at room temperature.

3. Results and discussion

3.1. TEM

The TEM results are shown in Fig.1. The diameters of the SiNWs ranges from 50 nm to 300 nm and the lengths are several micrometers. It can be seen that the SiNWs surface is not smooth. A large number of nanoparticles with 10–60 nm appear on the surface of nanowires, as shown in Fig. 1. With the increase of magnification, we can see that the formed crystals are coated with SiO_2 with a thickness of 5–20 nm.

3.2. PL properties

The process conditions such as doping temperature and doping Er(Yb) proportion have a significant impact on the luminescence intensity of Er,Yb co-doped SiNWs. Fig.2(a) shows the influence of temperature (1000–1200 ℃) on Er, Yb co-doped SiNWs under the doping time 60 min and the gas flow rate of N_2 1000sccm. As observed, temperature is the main influencing factor for dopant gain energy which directly determines the diffusion rate of Er and Yb. On the other hand, the temperature also affects the migration ability and doping concentration of Er and Yb ions in SiNWs. The luminous intensity increases with temperature. When the temperature reaches 1200 ℃, the luminous intensity illustrates a significant increase. Specifically, the SiNWs:Er^{3+},Yb^{3+} produced strong green (520–570 nm) and red (640–680 nm)emission band of Er^{3+} using laser excitation with a wavelength of 980 nm. The emission band is associated with the energy level transition $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4H_{15/2}$ and $^4F_{9/2} \rightarrow {}^4H_{15/2}$ of Er^{3+}, respectively.

Fig. 2(b) shows the PL properties of different doping proportion of Yb: Er (2:1, 3:1, 6:1) at 1200 ℃. As shown, the luminous intensity reduces with the increase of Yb and decrease of Er while keeping the total amount of doping constant. Also, with the increase of Er^{3+} concentration, the green and red emission intensity shows a growing trend, but the 640–680 nm emission intensity

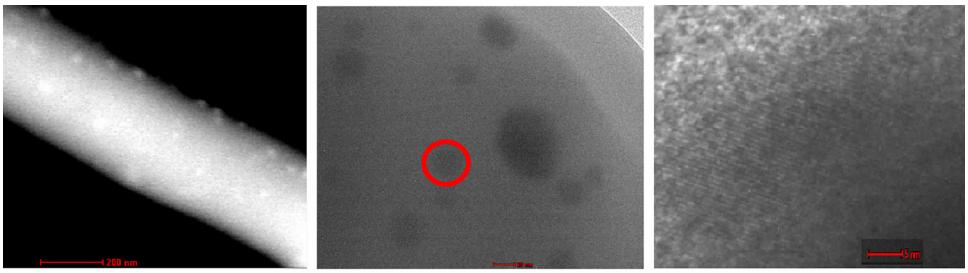

Fig. 1. The TEM images of SiNWs: Er^{3+},Yb^{3+} (a) 200 nm (b) 20 nm and (c) 5 nm.