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Role of organic molecules on upconversion luminescence of LaF_3 nanoparticles

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ABSTRACT

Yb and Er codoped LaF_3 nanocrystals were synthesized and studied. The upconversion luminescence properties of nanocrystals capped with different ligands are mainly dependent on the ligands, especially for the red emission which is sensitive to the nonradiative relaxation. The chelation between the ligands and rare earth ions can affect the morphology and fluorescent properties of samples. The chelating ligands will reduce the nonradiative quenching by isolating the RE ions from surrounding environment. So the upconversion luminescence properties of the samples vary correspondingly.

1. Introduction

In recent years, upconverting nanocrystals and nanostructure studies have attracted considerable attentions [1–3]. Rare earth (RE) ions doped upconversion nanocrystals have potential applications in display devices, lasers, biological imaging agents, diagnostics and therapeutics [4,5]. Recently, upconversion nanocrystals have been used for cancer treatment [6]. This makes the upconversion nanocrystals attractive for use in biological applications. It also evokes the studies of influence factors on the upconversion luminescence such as the concentration of dopant, particle size and the surface ligands. The studies about the surface ligands are significant for biological application of nanocrystals. The nanocrystals must be modified with functional groups such as –COOH and $-NH_2$ on their surfaces before being used to the biomolecules. However, a lot of details are still amphibolous, especially the surface ligand dynamics on the nanoparticles growth and their properties.

In this study, the effects of surface ligands on the upconversion properties of LaF_3: Yb^{3+}, Er^{3+} nanocrystals have been studied. Different surfactants are employed, e.g. oleic acid (OA), oleylamine (OM), and then the samples with OA and OM are compared with the nanoparticles without surfactant.

2. Experimental

All the chemicals were analytical grade reagents without further purification. $RECl_3 \cdot 6H_2O$ (RE=Yb and Er) were prepared by dissolving the corresponding RE_2O_3 in hydrochloric acid at elevated temperature followed by evaporating the solvent at vacuum. The LaF_3: Yb^{3+}, Er^{3+} nanocrystals were synthesized based on a reported procedure [7].

X-ray diffraction (XRD) patterns were recorded with X-ray diffractometer (Rigaku D/max-rA) using CuKα radiation ($\lambda = 1.5406$ Å). The sizes and morphologies of samples were characterized by field emission SEM (FESEM, Hitachi, S-4800). Upconversion emission spectra were measured with Jobin Yvon-LabRam Raman spectrometer and a Peltier air-cooled CCD detector. Samples were excited by a CW semiconductor diode laser at 980 nm. The FTIR spectra of samples were recorded on Nicolet Avatar 360 FTIR spectrometer with the KBr pellet technique. In making the KBr pellets, 1 mg of sample was diluted with approximately 100 mg of KBr power.

3. Results and discussion

In Fig. 1(a), the XRD patterns of the LaF_3: Yb^{3+}, Er^{3+} nanocrystals capped with OA and OM are identical with that of the sample without ligand. All peaks correspond to the characteristic peaks of hexagonal LaF_3 (JCPDS file No. 72-1435). The average sizes of nanocrystals which are calculated from the diffraction peak (111) by using the Scherrer's equation are 8.5 nm, 8.7 nm and 8.8 nm for samples capped with OA, OM and no ligand, respectively.

In the SEM images of samples (Fig. 1(b–d)), the nanocrystals have roughly spherical shape and average sizes are about 10 nm, 11 nm and 11 nm for samples capped with OA, OM and no ligand, respectively, which are in reasonable agreement with those calculated from XRD patterns. Compared with the other samples, the conglomeration is improved for the sample capped with OA because of the stronger chelation between OA and RE ions [8]. For the existence of water in the synthetic process, there will be much OH^- on the surface of

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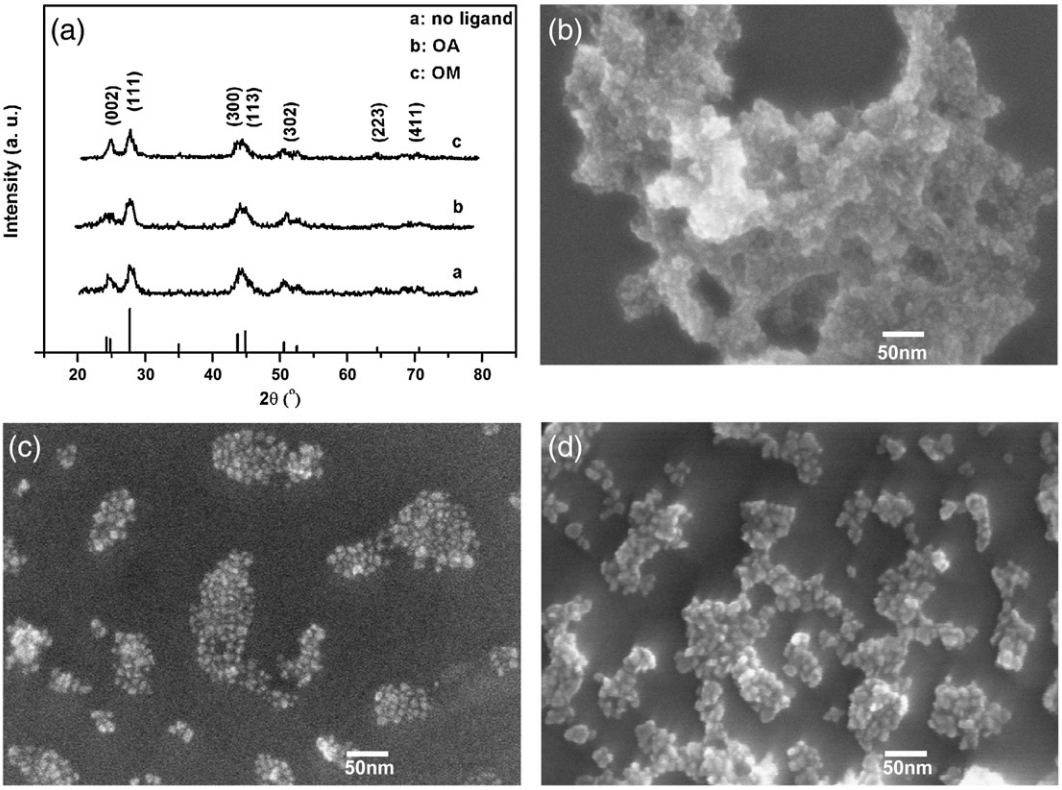

Fig. 1. XRD patterns of LaF_3: Yb^{3+}, Er^{3+} nanocrystals capped with different ligands (a); SEM images of LaF_3: Yb^{3+}, Er^{3+} nanocrystals capped with no ligand (b), OA (c) and OM (d).

nanocrystals which will result in the aggregation of nanocrystals. But the chelation effect between OA and RE^{3+} ions can reduce the quantity of OH^- through replacing the OH^- with OA. The long chain ligand bonding on the surface of nanoparticles can improve the dispersibility of the nanocrystals, and therefore will hinder the growth of nanoparticles. So the sample capped with OA has the smallest particle size and the best dispersibility.

Fig. 2(a) shows the typical FTIR spectra of LaF_3: Yb^{3+}, Er^{3+} nanocrystals with different ligands. The peaks at 2853 and 2925 cm^{-1} are assigned to the symmetric and asymmetric CH_2 stretching modes, respectively [9]. In the sample capped with OA, the peaks at 1709 cm^{-1} ($\nu(C{=}O)$), 1586 cm^{-1} ($\nu(COO^-)$) and 1410 cm^{-1} ($\nu(COO^-)$) corresponds to the carboxylate stretching [10,11] which confirm the observations that oleic acid molecules chelate with the RE ions. In the sample with no ligand, the bands around 3400 and 1635 cm^{-1} are due to stretching vibration of O–H bond of OH group and bending vibration of molecular H_2O, respectively[10]. But in the sample capped with OM, the broad band at 3422 cm^{-1} may include N–H stretching mode at 3300–3700 cm^{-1} [12,13], so it is difficult to assign it for the presence of OH^-. However, peaks at 1626 cm^{-1} ($\delta(NH_2)$) and 1389 cm^{-1} ($\nu(C{-}N)$) suggest that oleylamine are attached on the surface of nanocrystals [12,13]. For there is no RE–N stretch can be observed in the spectrum, the OM molecules are physisorbed on the surface of nanocrystals. From Fig. 2(a), the intensity of the band at 3400 cm^{-1} changes with the surface ligand. Based on the above analysis, we can assume that the chelation of RE ions and surface ligands are different, so the replacement of OH group will be accordingly different and consequently leads to the dissimilar upconversion emission in these samples.

Upconversion fluorescence spectra of LaF_3: 12% Yb^{3+}, 3% Er^{3+} nanocrystals capped with different ligands are shown in Fig. 2(b). As can be seen, there are three emission peaks at 520, 540 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions) and 654 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition) for these nanocrystals under 980 nm excitation [14]. The upconversion emission intensities of samples are different, and the sample capped with OA has the highest emission intensity. But the ratio of red emission

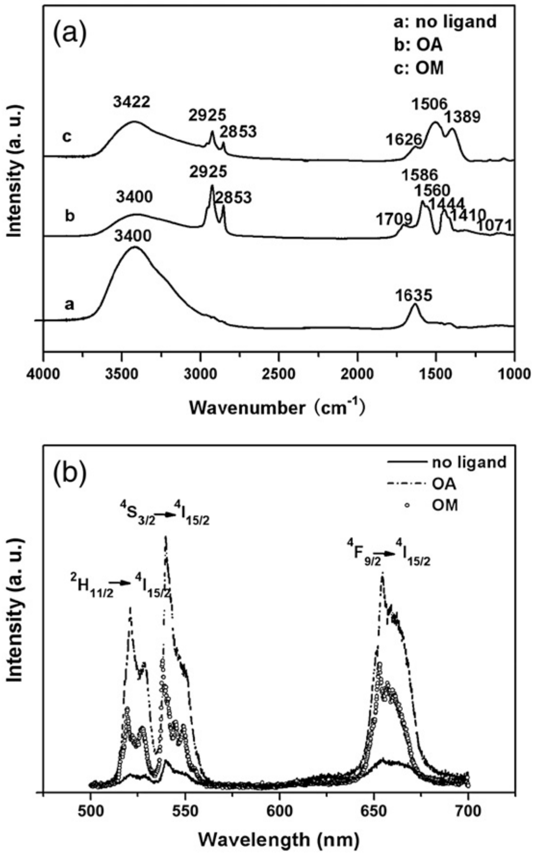

Fig. 2. FTIR spectra (a) and upconverted fluorescence spectra (b) of LaF_3: Yb^{3+}, Er^{3+} nanocrystals capped with different ligands ($\lambda_{exc}=980$ nm).

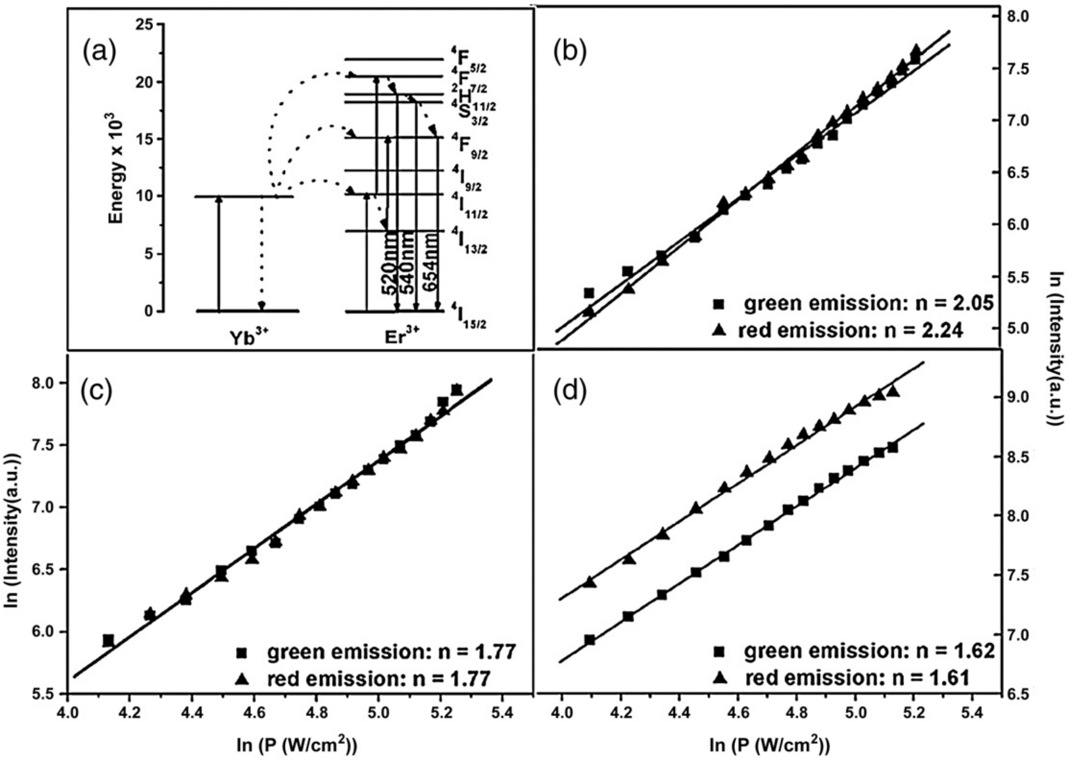

Fig. 3. The schematic energy level diagrams for Yb^{3+}, Er^{3+} system (a), power dependence of the upconverted emissions of LaF_3: Yb^{3+}, Er^{3+} nanocrystals capped with no ligand (b), OA (c) and OM (d).

($^4F_{9/2} \rightarrow {}^4I_{15/2}$) to green emission ($^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$) for the sample capped with OM is higher than that for the sample capped with OA. As shown in Fig. 3a, in the upconversion process, the green and red lights are emitted by electron transmission from corresponding energy levels to ground state. The nonradiative relaxation plays a key role in the population of these energy levels. So the fluorescence of RE ios will be influenced by chelating ligands greatly. There is indirect excitation by energy transfer from surface ligands to RE ions. The chelating ligands isolate the RE ions from the surrounding environment, thereby reducing the chance of environmentally induced nonradiative quenching of emissions [15,16]. As mentioned above, there are a great number of OH group which is the efficient quencher of upconversion emission on the surface of nanocrystals [17]. A portion of OH^- have been replaced by the corresponding ligand in the samples capped with OA and OM, and therefore the intensity of the upconversion emission increase, the extent of which is dependent on the degree of the replacement of OH^- on the surface. On the other hand, the vibration energy of amine at 3422 cm^{-1} is resonant with the transitions which are propitious to the population of energy levels involved red emission. So that makes the red emission fairly efficient in the sample capped with OM.

To better understand the procedure of upconversion, power dependence study of the emission intensity (I_{em}) versus pump power (I_p) is performed (Fig. 3). For upconversion process, the emission intensity (I_{em}) will be proportional to some power (n) of the excitation intensity (I_p) [18]:

$$I_{em} \propto I_p^n \quad \text{with}\, n = 2, 3\ldots \tag{1}$$

where n is the number of infrared photons absorbed per visible photon emitted. Fig. 3 shows the logarithmic plots of the emission intensity as a function of excitation power which is at relatively low excitation densities for the green and red emissions in these samples. By fitting the data points, the slope n of the curve can be determined. For the green emission, the values of n are determined to be 1.77, 1.62 and 2.05, respectively, in samples capped with OA, OM and no ligand. For red emission, the values are 1.77, 1.61 and 2.24, respectively, in samples capped with OA, OM and no ligand. This indicates that two photons are involved in the upconversion process. The two photon upconversion mechanism is described in Fig. 3a. It is also noted that the red emission of sample capped with OM is stronger than the green emission, which is consistent with the results in the upconversion spectra.

4. Conclusions

LaF_3: Yb^{3+}, Er^{3+} nanocrystals capped with different ligands have been synthesized and the upconversion luminescence properties have been investigated. The nature of the ligands on the surface of the nanocrystals plays a key role on the growth of nanocrystals and the upconversion luminescence of these samples. The chelation between RE ions and surface ligands influence the upconversion luminescence significantly.

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