



Letter

PEG-mediated solvothermal synthesis of NaYF₄:Yb/Er superstructures with efficient upconversion luminescence

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ARTICLE INFO

Article history:

Received 26 April 2010

Received in revised form 24 June 2010

Accepted 10 July 2010

Available online 16 July 2010

Keywords:

NaYF₄

Superstructures

Solvothermal synthesis

Upconversion luminescence

ABSTRACT

In this work, we report a facile solvothermal synthesis of NaYF₄:Yb/Er nano-structured materials with controlled shapes by tuning the solvents. Ethylene glycol as the solvent results in the preparation of NaYF₄:Yb/Er nanoparticles with diameter of about 10 nm, while polyethylene glycol (MW = 400, abbreviated as PEG-400) as the solvent facilitates the formation of NaYF₄ superstructures with the particle size of about 160 nm. These NaYF₄ superstructures are built from nanoparticles with diameter of about 10 nm. Their compositions have been confirmed by energy-dispersive X-ray analysis, and they have simultaneously cubic and hexagonal phase structures. Fourier transform infrared (FT-IR) spectrum reveals the presence of PEG-400 ligands on their surface, which confers high solubility of NaYF₄ superstructures in water. Under continuous-wave excitation of 980 nm laser, NaYF₄ superstructure aqueous solution exhibits efficient up-converting luminescence which is almost twice as strong as that of the building blocks (nanoparticles). This improvement may result from the fact that these NaYF₄:Yb,Er superstructures can serve as 980 nm laser-cavity mirrors. Therefore, these superstructures have great superiority as luminescent labeling materials for biological applications.

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1. Introduction

Rare earth-doped luminescent materials have played an outstanding role as phosphors in a wide variety of applications including display monitors, scintillators and amplifiers for fiber-optic communications [1,2]. In particular, rare earth-doped upconversion phosphors (REUPs), which emit higher-energy light (UV or visible) when excited by low-energy near-infrared (NIR, typically 980 nm) light, have attracted increasing attention because of their potential applications in solid-state lasers [3], flat-panel displays [4], solar cells [5], and optical-fiber-based telecommunications [6]. As for biological applications, REUP nanomaterials have exhibited many advantages over conventional downconversion fluorescent materials (dyes and quantum dots), such as high chemical stability, low toxicity, noninvasive and deep penetration of NIR radiation, and the absence of autofluorescence of biological tissues [7–9]. Very recently, based on up-converting luminescent properties of REUP nanomaterials and deep penetration of NIR radiation in biological tissues, our group has reported a 980-nm laser-driven photovoltaic cells as a kind of novel biological electrical source [10].

Generally, most of these applications require REUPs with high NIR-to-visible up-converting luminescence efficiency, and this efficiency is dependent on many factors, such as host materials, surface defects, particle sizes and shapes. Until now, NaYF₄ has been reported to be one of the most efficient host materials for Yb/Er (or Yb/Tm or Yb/Ho) co-doped NIR-to-visible upconversion phosphors [11]. Both cubic and hexagonal phase NaYF₄ nano/micro-particles have been successfully prepared by different methods [9,12–20]. It is well known that the luminescent efficiency can be enhanced if the nanoarrays are aligned with photonic-crystal microstructures, and/or the faceted end planes of well-shaped crystals serve as good laser-cavity mirrors [14,21]. Thus, up-converting luminescence efficiency of Yb/Er (or Yb/Tm or Yb/Ho) co-doped NaYF₄ may be further improved by tuning the array of NaYF₄ nanoparticles, for example, preparing NaYF₄ superstructures constructed by nano-substructures. However, there is little research on NaYF₄ superstructures until now.

Hydrothermal/solvothermal methods have been proved to be convenient and effective in preparing various inorganic materials with diverse controllable morphologies and architectures. Lanthanide-doped NaYF₄ monodisperse nanoparticles [9,12–14] and micro-particles [15] with different shapes have been prepared by using hydrothermal route assisted with oleic acid, linoleic acid or trisodium citrate. In the present work, for the first time we report a facile solvothermal synthesis of Yb/Er co-doped NaYF₄ super-

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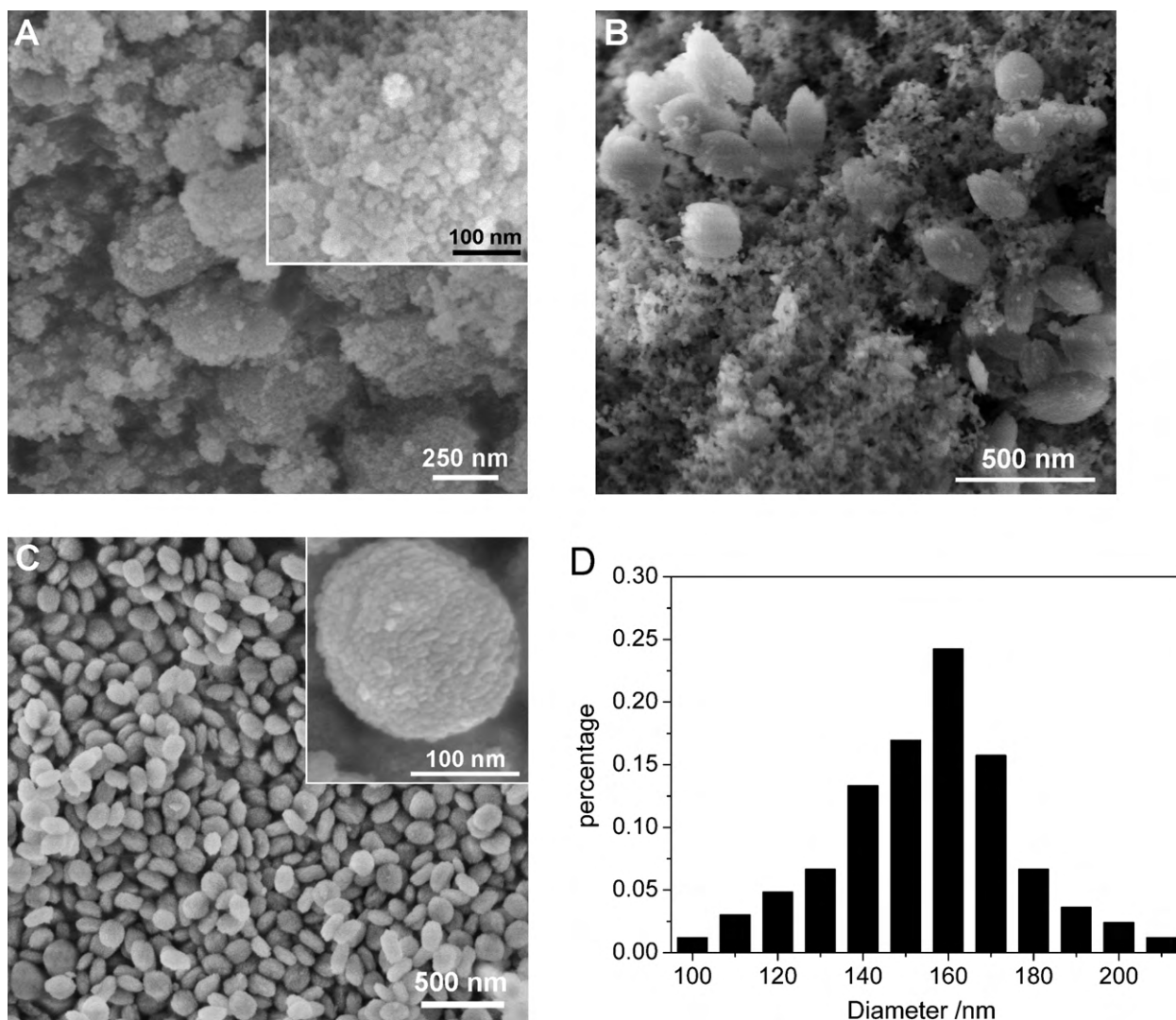


Fig. 1. SEM images of NaYF₄:Yb,Er samples prepared in different solvents: (A) ethylene glycol, (B) the mixture of PEG-400 and ethylene glycol (volume ratio: 1/6), (C) PEG-400, and particle size distribution (D) of NaYF₄:Yb,Er sample prepared in PEG-400.

structures by using polyethylene glycol (MW=400, abbreviated as PEG-400) as the solvent and ligand. These NaYF₄:Yb,Er superstructures with diameter of about 160 nm are constructed from plenty of nanoparticles with diameter of about 10 nm. The presence of PEG-400 ligands on their surface confers high solubility in water. Compared with nanoparticles, these superstructures exhibit efficient up-converting luminescence and therefore have potential application in bio-imaging, 980-nm laser-driven photovoltaic cells, etc.

2. Experimental details

All of the chemicals were of analytical grade and were purchased from Sinopharm Chemical Reagent Co. China. In a typical synthesis, 1 mmol (total amounts) of rare earth chlorides (0.78 mmol YCl₃·6H₂O, 0.20 mmol YbCl₃·6H₂O, 0.02 mmol ErCl₃·6H₂O) were added into 20 mL PEG-400 under magnetically stirring. Subsequently, 20 mL PEG-400 solution containing 4.5 mmol NaF and 0.3 mL water were injected rapidly into the above solution. The resulting solution was agitated for about 10 min, then transferred to a 50 mL autoclave, sealed, and solvothermally treated at 200 °C for 5 h. The system was cooled to room temperature naturally, and the solid sample was separated via centrifugation at a speed of 10000 rpm and washed three times by resuspending in ethanol and centrifugation, respectively. Finally, the 20 mol%Yb/2 mol%Er co-doped NaYF₄ (abbreviated as NaYF₄:Yb,Er) sample was dried in a vacuum. To investigate the effects of solvents on the shapes of NaYF₄:Yb,Er samples, two other NaYF₄:Yb,Er samples were also prepared by replacing pure PEG-400 with ethylene glycol or the mixture of PEG-400 and ethylene glycol (volume ratio: 1/6) as the solvent under other identical conditions.

Sizes and morphologies of samples were determined by using a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010F) and a field emission-scanning electron microscope (FE-SEM, Hitachi S-4800). Energy-dispersive X-ray analysis (EDXA) of the sample was also performed during SEM measurements. X-ray diffraction (XRD) measurement was performed on a Bruker D4 X-ray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm). Fourier transform infrared (FT-IR) spectrum was measured using an IRPRESTIGE-21 spectrometer (Shimadzu) from samples in KBr pellets. Up-converting luminescence spectra were measured by using a JASCO FP-6600 spectrometer, but the excitation source was an external 0–1 W adjustable 980 nm semiconductor laser device with an optic fiber accessory with a diameter of 800 μ m (Beijing Hi-Tech Optoelectronic Co., China) instead of the Xenon source in the spectrometer.

3. Results and discussion

It is well known that the selection of solvents and ligands is the key for obtaining nanomaterials with desirable shapes and surface properties. Polyethylene glycol (PEG) is a popular non-ionic and hydrophilic support for reagents because it is soluble in water as well as certain organic solvents. PEG with low molecular weight, such as PEG-400, is a liquid and has been found to be a superior solvent and ligand [22]. Herein, to prepare NaYF₄:Yb,Er superstructures with excellent water solubility, PEG-400 was used as the solvent, structure director and ligand. For comparison, pure ethylene glycol as well as the mixture of PEG-400 and ethylene glycol

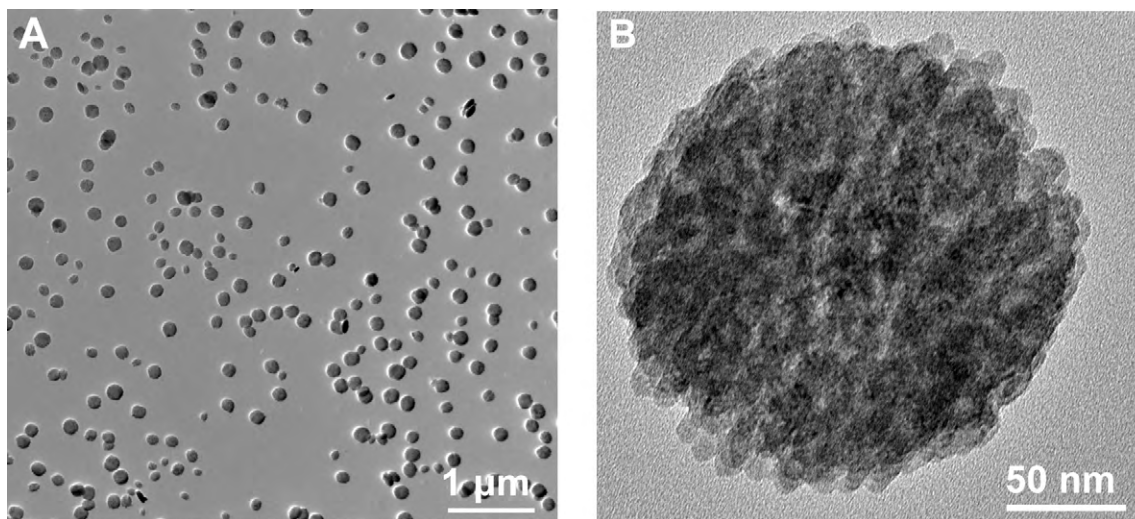


Fig. 2. TEM images of $\text{NaYF}_4:\text{Yb,Er}$ superstructure sample prepared in PEG-400.

was also used as the solvent. All $\text{NaYF}_4:\text{Yb,Er}$ samples were prepared by solvothermal synthesis at 200°C for 5 h.

The effects of solvents on the shapes and structures of $\text{NaYF}_4:\text{Yb,Er}$ samples have been investigated firstly. Fig. 1 presents representative SEM images of $\text{NaYF}_4:\text{Yb,Er}$ samples prepared in different solvents. When ethylene glycol was used as the solvent in the absence of PEG-400, only nanoparticles with the diameter of about 10 nm are found, and they exhibit agglomerated and polydisperse features (Fig. 1A). These nanoparticles cannot form nanoarray or nano-structured architecture. If the solvent was the mixture of PEG-400 and ethylene glycol (volume ratio: 1/6), sphere/oval-like particles with diameter of 100–210 nm appear, coexisting with the nanoparticles with the diameter of about 10 nm (Fig. 1B). Importantly, when only PEG-400 was used as the solvent, it can be found that the $\text{NaYF}_4:\text{Yb,Er}$ sample is composed of relatively big sphere/oval-like superstructures (Fig. 1C). From the data obtained by SEM micrograph (Fig. 1C), the particle size histograms of superstructures can be drawn as shown in Fig. 1D. It is clear that the particle size range is from 100 to 210 nm, and the median diameter is about 160 nm, which shows a relatively broad size distribution. Interestingly, these superstructures are in fact built from nanoparticles with diameter of about 10 nm, which can be vividly demonstrated by the SEM image with higher magnification (the inset in Fig. 1C). Further information is obtained from the TEM images (Fig. 2). They confirm that sphere/oval-like $\text{NaYF}_4:\text{Yb,Er}$ superstructures particles are uniform and have an average diameter of ~ 160 nm (Fig. 2A), which agrees well with that revealed by the SEM image (Fig. 1C). Simultaneously, these superstructure particles consist of many small nanoparticles and nano-pores, as shown in Fig. 2B.

Thus, it is clear that the solvent has strong effects on the shapes and structures of $\text{NaYF}_4:\text{Yb,Er}$ samples, and a proposed process

for the formation of $\text{NaYF}_4:\text{Yb,Er}$ superstructures in PEG-400 is presented in Fig. 3. The atom O in the PEG molecular chain has excellent coordination abilities with metal ions. When rare earth chlorides are dissolved in PEG-400, rare earth ions (Ln^{3+}) and the O atoms of PEG-400 molecular chain can form coordination bonds. One PEG-400 molecule may coordinate with several Ln^{3+} ions while one Ln^{3+} ion may also coordinate with several PEG-400 molecules (Fig. 3A). After PEG-400 solution containing NaF is added, Ln^{3+} ions react with NaF to produce $\text{NaYF}_4:\text{Yb,Er}$ nanoparticles. In the course of the reaction, PEG-400 molecules are coated onto the outer face of the in-situ generated $\text{NaYF}_4:\text{Yb,Er}$ nanoparticles through the interaction between Ln^{3+} ions and the O atoms of PEG-400 molecular chain. It is of course that one PEG-400 molecule may coordinate with several $\text{NaYF}_4:\text{Yb,Er}$ nanoparticles and one nanoparticle may also coordinate with several PEG-400 molecules (Fig. 3B). It has been reported that, although the formation of smaller crystallites is kinetically favored during the initial agglomeration, larger crystallites are thermodynamically favored [23]. Thus, during solvothermal treatment, the nanoparticles self-aggregate into $\text{NaYF}_4:\text{Yb,Er}$ superstructured architectures due to PEG-400 induced structure transition (Figs. 2 and 3C). It should be noted that only ethylene glycol as the solvent results in the formation of small nanoparticles with agglomerated and polydisperse features (Fig. 1A), which should be related to the fact that it is difficult for one ethylene glycol molecule to coordinate simultaneously with several Ln^{3+} ions and nanoparticles. With addition of a small quantity of PEG-400 in ethylene glycol as the solvent, some $\text{NaYF}_4:\text{Yb,Er}$ superstructured architectures are also produced due to PEG-400 induced structure transition, as shown in Fig. 1B.

Subsequently, $\text{NaYF}_4:\text{Yb,Er}$ superstructures prepared in PEG-400 were further characterized. The EDXA pattern (Fig. 4) confirms that $\text{NaYF}_4:\text{Yb,Er}$ superstructures are composed exclusively of Na,

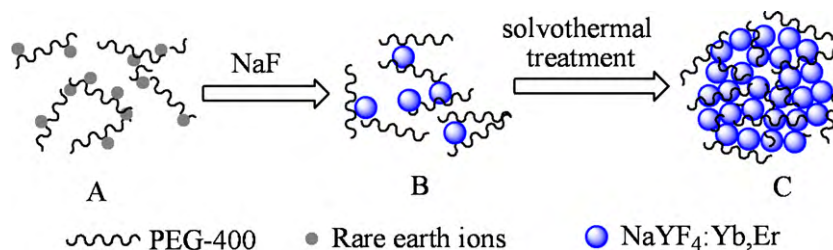


Fig. 3. A proposed formation process for $\text{NaYF}_4:\text{Yb,Er}$ superstructures prepared in PEG-400.

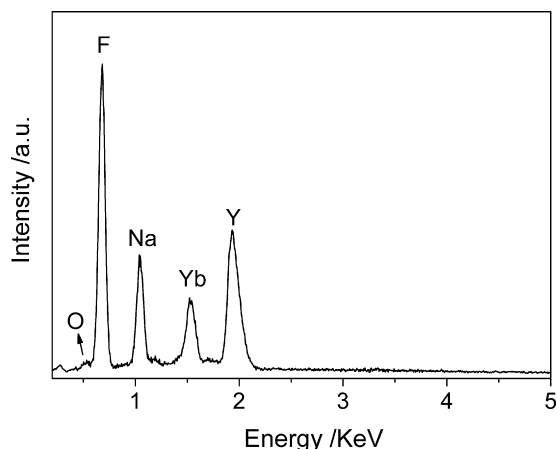


Fig. 4. EDAX pattern of NaYF₄:Yb,Er superstructure sample.

Y, Yb, and F, with the additional O peak being readily attributed to PEG-400 ligands. This indicates the formation of doped NaYF₄. A peak for the minor-doped Er ion cannot usually be discerned due to its low content (only 2 mol% Er in the rare earth elements). In addition, XRD pattern (Fig. 5C) of NaYF₄:Yb,Er superstructures show well-defined peaks, indicating the high crystallinity. Their peak positions and intensities confirm the existence of both cubic (JCPDs card 77-2042) and hexagonal (JCPDs card 16-0334) phase NaYF₄. For comparison, XRD patterns of NaYF₄:Yb,Er samples prepared in ethylene glycol and the mixture of PEG-400 and ethylene glycol (volume ratio: 1/6) are also supplied (Fig. 5A and B), and they are similar to that of NaYF₄:Yb,Er superstructures (Fig. 5C). Therefore, there is no obvious effect of solvents on the phases of NaYF₄:Yb,Er samples.

Surface functional chemical groups of NaYF₄:Yb,Er superstructures are important for their biological applications. The capping ligand on their surface was identified by FT-IR spectrum (Fig. 6). The sample exhibits a broad band at about 3450 cm⁻¹, due to the O–H stretching vibration of adsorbed water and/or PEG-400. The

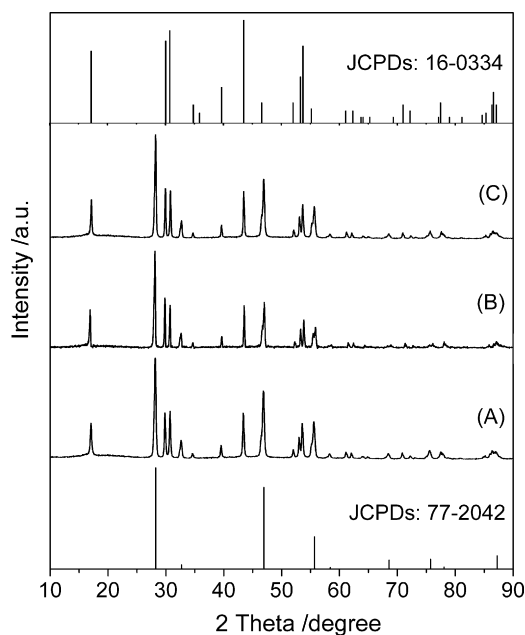


Fig. 5. XRD patterns of NaYF₄:Yb,Er samples prepared in different solvents: (A) ethylene glycol, (B) the mixture of PEG-400 and ethylene glycol (volume ratio: 1/6), (C) PEG-400. For comparison, standard patterns of cubic (JCPDs card 77-2042) and hexagonal (JCPDs card 16-0334) phase NaYF₄ are also supplied.

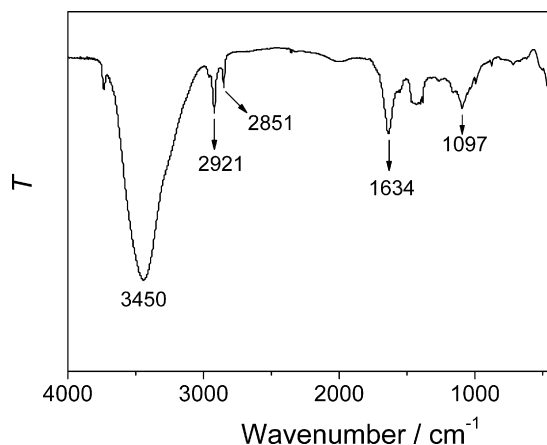


Fig. 6. FT-IR spectrum of NaYF₄:Yb,Er superstructure sample.

2921 and 2851 cm⁻¹ transmission bands are respectively assigned to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of methylene (CH₂) units in PEG-400 chain. The bands at 1634 cm⁻¹ should be related to the bending modes of the hydroxyls of adsorbed water [24,25]. The bands at about 1097 cm⁻¹ is corresponding to C–O stretching vibration coordinating to metal cations, which shifts about 10 cm⁻¹ to lower wavenumber comparing to the IR spectrum of pure PEG-400, suggesting the formation of chemical bonds between PEG-400 and inorganic components [25,26]. Based on the above results, it is concluded that there are PEG-400 ligands on the surface of NaYF₄:Yb,Er superstructure sample.

As a result of the presence of PEG-400 ligands on their surface, NaYF₄:Yb,Er superstructures could be readily dispersed in water and in some polar organic solvents such as DMF, or DMSO. The up-converting luminescence spectrum of colloidal aqueous solutions containing 1.0 mg/ml NaYF₄:Yb,Er superstructure under 980-nm laser excitation is shown in Fig. 7. For comparison, up-converting luminescence spectrum of aqueous solutions containing NaYF₄:Yb,Er nanoparticles prepared in ethylene glycol is also recorded. Both spectra are similar to what has been reported previously for these materials [8–20], and they exhibit three distinct Er³⁺ emission bands. The green emissions between 514 and 534 nm and between 534 and 560 nm are attributed to the ²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2} transitions, respectively. A dominant red emission is observed between 635 and 680 nm due to the transition from ⁴F_{9/2} to ⁴I_{15/2}. Importantly, both green and red emission bands of NaYF₄:Yb,Er superstructures are almost twice as strong as those of NaYF₄:Yb,Er nanoparticles (Fig. 7).

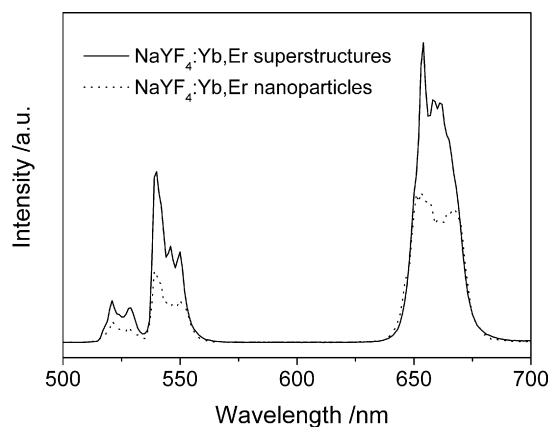


Fig. 7. Up-converting luminescence spectra of aqueous solutions respectively containing 1.0 mg/ml NaYF₄:Yb,Er superstructures and NaYF₄:Yb,Er nanoparticles, under continuous-wave excitation of 980 nm laser.

It is well known that the phase, crystallinity and surface properties of NaYF₄:Yb,Er samples alter their intensity ratios of green to red emission peaks [8–20]. However, in our case, both NaYF₄:Yb,Er superstructures and nanoparticles have similar intensity ratios of green to red emission peaks (such as $I_{540}/I_{654} \approx 0.5$). Since NaYF₄:Yb,Er superstructures are composed of nanoparticles as building blocks which are similar to NaYF₄:Yb,Er nanoparticles prepared in ethylene glycol (Figs. 1C, 2, and 5), this improvement of luminescence should be attributed to the difference in their structures instead of the phase, crystallinity and/or surface properties. NaYF₄:Yb,Er superstructures can serve as 980 nm laser-cavity mirrors, which efficiently improves reflection and absorption ability for 980 nm laser and is similar to previous luminescent results [14,21]. Further investigation of improvement reasons is still under research. The future work will be also done by using these NaYF₄:Yb,Er superstructures with efficient up-converting luminescence as photo-absorption layer to create 980-nm laser-driven photovoltaic cells with higher output power under irradiation of 980-nm laser with lower excitation power [10].

4. Conclusions

NaYF₄:Yb,Er superstructures have been prepared by a facile solvothermal synthesis method with PEG-400 as the solvent and ligand. These NaYF₄:Yb,Er superstructures with the particle size of about 160 nm are built from nanoparticles with diameter of ~10 nm. The presence of PEG-400 ligands on their surface confers high solubility in water. Compared with their building blocks (nanoparticles), these superstructures exhibit efficient up-converting luminescence and therefore have great superiority as luminescent labeling materials for biological applications.

Acknowledgements

This work was financially supported by the Program for New Century Excellent Talents of the University in China, the National Natural Science Foundation of China (Grant Nos. 50872020 and 50902021), the “Pujiang” Program of Shanghai Education Commission in China (Grant No. 09PJ1400500), the “Dawn” Program

of Shanghai Education Commission in China (Grant No. 08SG32), Specialized Research Fund for the Doctoral Program of Higher Education (Grant No. 20090075120014), “Chen Guang” project (Grant No. 09CG27) supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation, the Fundamental Research Funds for the Central Universities, and the Program of Introducing Talents of Discipline to Universities (Grant No. 111-2-04).

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