



# Host-sensitized multicolor tunable luminescence of lanthanide ion doped one-dimensional $\text{YVO}_4$ nano-crystals

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## ABSTRACT

We report the  $\text{Na}_2\text{EDTA}$ -assisted synthesis of the lanthanide ( $\text{Ln}^{3+}$ ) ion doped one-dimensional  $\text{YVO}_4$  nanobelts and nanorods by a facile hydrothermal route. XRD, TEM, EDS and FTIR techniques are used to characterize the microstructures of the synthesized nano-crystals. The morphology-dependent luminescent behaviors of  $\text{Eu}^{3+}:\text{YVO}_4$  are systematically investigated. Under a single wavelength UV light excitation, the  $\text{Ln}^{3+}:\text{YVO}_4$  ( $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{or Yb}$ ) nanorods exhibit visible to near-infrared (NIR) multicolor tunable luminescence via efficient host sensitization, while no emissions are detected for the  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ , or  $\text{Tb}^{3+}$  doped samples. Based on the results, possible mechanisms depicting the  $\text{YVO}_4$  host sensitizing or quenching of lanthanide emissions are proposed.

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## 1. Introduction

Recently, dramatic efforts have been dedicated to the elaboration of materials emitting multicolor tunable luminescence under a single wavelength excitation, for their important potential applications in the fields of light display, bio-labels and optoelectronic devices [1–3]. Among various luminescent materials, lanthanide ion ( $\text{Ln}^{3+}$ ) activated phosphors have attracted extensive attention because of their wide range of emission colors and excellent luminescent performance. To achieve highly efficient multicolor tunable luminescence of lanthanide ions, host sensitization via energy transfer from the excited host to the  $\text{Ln}^{3+}$  ions is an effective way to overcome the low absorptions of parity forbidden 4f–4f transitions of  $\text{Ln}^{3+}$  [4–7]. Semiconductor nano-crystals (such as  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SnO}_2$ ) have been considered as promising candidates for such hosts and sensitizers due to the ease to tailor their optical properties via size or morphology control [8–13]. However, owing to the necessary charge compensation or the unmatched radius between  $\text{Ln}^{3+}$  and cations of semiconductor, doping of high content of  $\text{Ln}^{3+}$  into the semiconductor nano-crystals is very tough [14].

Yttrium vanadate ( $\text{YVO}_4$ ) crystal has been demonstrated to be a useful host and sensitizer for lanthanide ions to produce a variety of colors [15]. A typical sample is the  $\text{Eu}^{3+}$  ion doped yttrium vanadate ( $\text{Eu}^{3+}:\text{YVO}_4$ ) powder, which has been widely used as red

phosphor in cathode ray tubes (CRT) and color television for its high luminescence efficiency upon electron-beam excitation. Recently, several works have been extended to the  $\text{Eu}^{3+}$  doped nano-sized  $\text{YVO}_4$  since inorganic nano-crystals have exhibited many fascinating novel size- and morphology-dependent properties [16–18]. Besides  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  or  $\text{Sm}^{3+}$  doped  $\text{YVO}_4$  nano-crystals have also been investigated since  $\text{Dy}^{3+}:\text{YVO}_4$  is a potential white phosphor due to the blue ( $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ ) and yellow ( $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ ) emissions of  $\text{Dy}^{3+}$ , and  $\text{Sm}^{3+}:\text{YVO}_4$  yields characteristic orange-red luminescence originated from the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$  ( $J = 5/2, 7/2$  and  $9/2$ ) transitions of  $\text{Sm}^{3+}$  [1]. In addition, by partial replacement of  $\text{VO}_4^{3-}$  by  $\text{PO}_4^{3-}$ , a new series of  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Eu}, \text{Dy}, \text{Sm}$ ) doped yttrium phosphate–vanadate ( $\text{YV}_{1-x}\text{P}_x\text{O}_4$ ) phosphors have been obtained with better optical properties [1,19,20]. Although the investigations on lanthanide ion doped  $\text{YVO}_4$  and  $\text{YV}_{1-x}\text{P}_x\text{O}_4$  nano-crystals are extensive, rare study has been focused on the synthesis and size- or morphology-dependent luminescence of the one-dimensional (1D) or quasi-one-dimensional (Q-1D)  $\text{YVO}_4$  and  $\text{YV}_{1-x}\text{P}_x\text{O}_4$  phosphors.

Herein, we report the  $\text{Na}_2\text{EDTA}$ -assisted synthesis of total group lanthanide ion doped  $\text{YVO}_4$  1D nanobelts and nanorods by a facile hydrothermal route. Using  $\text{Eu}^{3+}$  ions as structural probe, the morphology-dependent luminescent behaviors of  $\text{Eu}^{3+}:\text{YVO}_4$  are investigated. As a comparison, emissions of the irregular polyhedral nano-crystals and micro-crystals are also measured. In addition, the visible to near-infrared (NIR) multicolor tunable luminescence of the  $\text{Ln}^{3+}:\text{YVO}_4$  nanorods via host sensitization under a single wavelength excitation are demonstrated, and the possible luminescent mechanisms are discussed.

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**Table 1**

Summary of the synthesizing conditions as well as the corresponding morphologies and dimensions of the samples.

Sample	Synthesizing condition	Morphology	Diameter (nm)	Length (nm)
150EY	Hydrothermal treatment with the assistance of Na <sub>2</sub> EDTA at 150 °C for 12 h, pH = 9.5	Nanobelt	3–8	300–500
180EY	Hydrothermal treatment with the assistance of Na <sub>2</sub> EDTA at 180 °C for 12 h, pH = 9.5	Nanorod	15–20	200–300
PEY	Hydrothermal treatment with the assistance of Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> at 180 °C for 12 h, pH = 12.5	Polyhedral nano-crystal	20–30	20–30
BEY	Solid-state reaction	Polyhedral micro-crystal	1500–2000	1500–2000

## 2. Experimental

### 2.1. Reagents

All the chemical reagents, i.e., yttrium nitrate hexahydrate (Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), lanthanide nitrate hexahydrate (Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), disodium ethylenediamine tetraacetate (Na<sub>2</sub>EDTA), sodium orthovanadate dodecahydrate (Na<sub>3</sub>VO<sub>4</sub>·12H<sub>2</sub>O), cetyltrimethyl ammonium bromide (CTAB), sodium citrate dihydrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O) and sodium hydroxide (NaOH) were of analytical grade, purchased from Sinopharm Chemical Reagent Co. and used without further purification.

### 2.2. Synthesis of 1D nano-crystals

The 5 mol% Ln<sup>3+</sup>:YVO<sub>4</sub> 1D nano-crystals were synthesized through a facile hydrothermal method with the assistance of Na<sub>2</sub>EDTA. Firstly, Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (1.425 mmol) and Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.075 mmol) were dissolved in 30 ml deionized water, then metal-chelating agent Na<sub>2</sub>EDTA (1.5 mmol) was added to get a suspension. Secondly, Na<sub>3</sub>VO<sub>4</sub>·12H<sub>2</sub>O (1.5 mmol) was dissolved in 30 ml deionized water, forming a solution which was then added drop-wise to the suspension under vigorous stirring to get a transparent yellow-colored mixture. Subsequently, pH of the mixture was carefully adjusted to 9.5 by the NaOH solution, followed by the addition of the surfactant CTAB (0.06 g) under vigorous stirring. Finally, the obtained mixture was poured into a Teflon-lined stainless steel autoclave, and heated at 180 °C for 12 h. As the autoclave was cooled down to room temperature, the product was collected by centrifugation, washed with deionized water and absolute ethanol for several times, and dried in vacuum at 60 °C for 24 h.

The pure YVO<sub>4</sub> nano-crystals were synthesized in a similar way. To investigate the morphology-dependent luminescence, Eu<sup>3+</sup>:YVO<sub>4</sub> nano-crystals with different morphologies (denoted as 150EY and 180EY) were prepared by hydrothermal treatment at 150 °C and 180 °C for 12 h, respectively.

### 2.3. Synthesis of polyhedral Eu<sup>3+</sup>:YVO<sub>4</sub> nano-crystals

The polyhedral Eu<sup>3+</sup>:YVO<sub>4</sub> nano-crystals (denoted as PEY) were synthesized with the assistance of Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>. Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (1.84 mmol) and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.40 mmol) were dissolved in 30 ml deionized water, which was then added to the 20 ml solution of metal-chelating agent Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O (1.57 mmol) to form the Y–Ln citrate suspension. In another vessel, Na<sub>3</sub>VO<sub>4</sub>·12H<sub>2</sub>O (1.97 mmol) was dissolved in the 30 ml deionized water, and NaOH solution was added carefully to adjust pH to 12.5. The solution was then added drop-wise to the above suspension under vigorous stirring. After ageing at 90 °C for 30 min, the mixture was poured into a Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. As the autoclave was cooled down to room temperature, the product was collected by centrifugation, washed with deionized water and absolute ethanol for several times, and dried in vacuum at 60 °C for 24 h.

### 2.4. Synthesis of Eu<sup>3+</sup>:YVO<sub>4</sub> micro-crystals

Eu<sup>3+</sup>:YVO<sub>4</sub> micro-crystals (denoted as BEY) were prepared by solid-state reaction. The stoichiometric mixtures of Y<sub>2</sub>O<sub>3</sub>, NH<sub>4</sub>VO<sub>4</sub> and Eu<sub>2</sub>O<sub>3</sub> were ground together and heated in an alumina crucible at 650 °C for 24 h. The products were then removed from the furnace, cooled, finely ground and reheated at 850 °C for 48 h to complete the reaction.

A summary of the synthesizing conditions as well as the corresponding morphologies and dimensions of the samples is listed in Table 1.

### 2.5. Characterizations

X-ray diffraction (XRD) analyses on the products were carried out with a powder diffractometer (DMAX2500 RIGAKU) using CuK<sub>α</sub> radiation (λ = 0.154 nm). The microstructures of the samples were studied using a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive X-ray spectroscopy (EDS) system. The samples were ground into very fine powder that was placed onto a carbon-coated copper grid and introduced into the microscope. Fourier transform infrared (FTIR) spectra were measured on a Perkin-Elmer IR spectrometer using a KBr pellet technique. The emission, excitation spectra and decay curves of the as-prepared samples were recorded on an Edinburgh Instruments FLS920 spectrofluorometer equipped with both continuous (450 W) and pulsed xenon lamps. All the measurements were carried out at room temperature.

## 3. Results and discussion

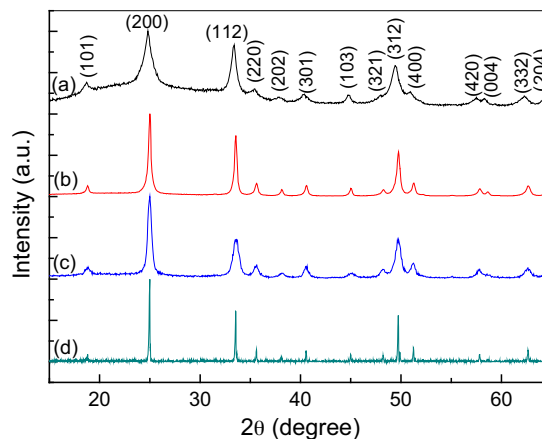
### 3.1. Microstructure

XRD patterns of the as-synthesized samples are presented in Fig. 1. All the samples exhibit diffraction peaks that can be easily indexed by the tetragonal YVO<sub>4</sub> phase (JCPDS 17-0341). Compared with those of the micro-crystalline sample (BEY), the broader diffraction peak widths indicate the smaller grain sizes of the three hydrothermally prepared samples. Based on Scherrer equation, the mean grain size of the synthesized 150EY, 180EY and PEY samples are evaluated to be 12 nm, 40 nm and 28 nm, respectively.

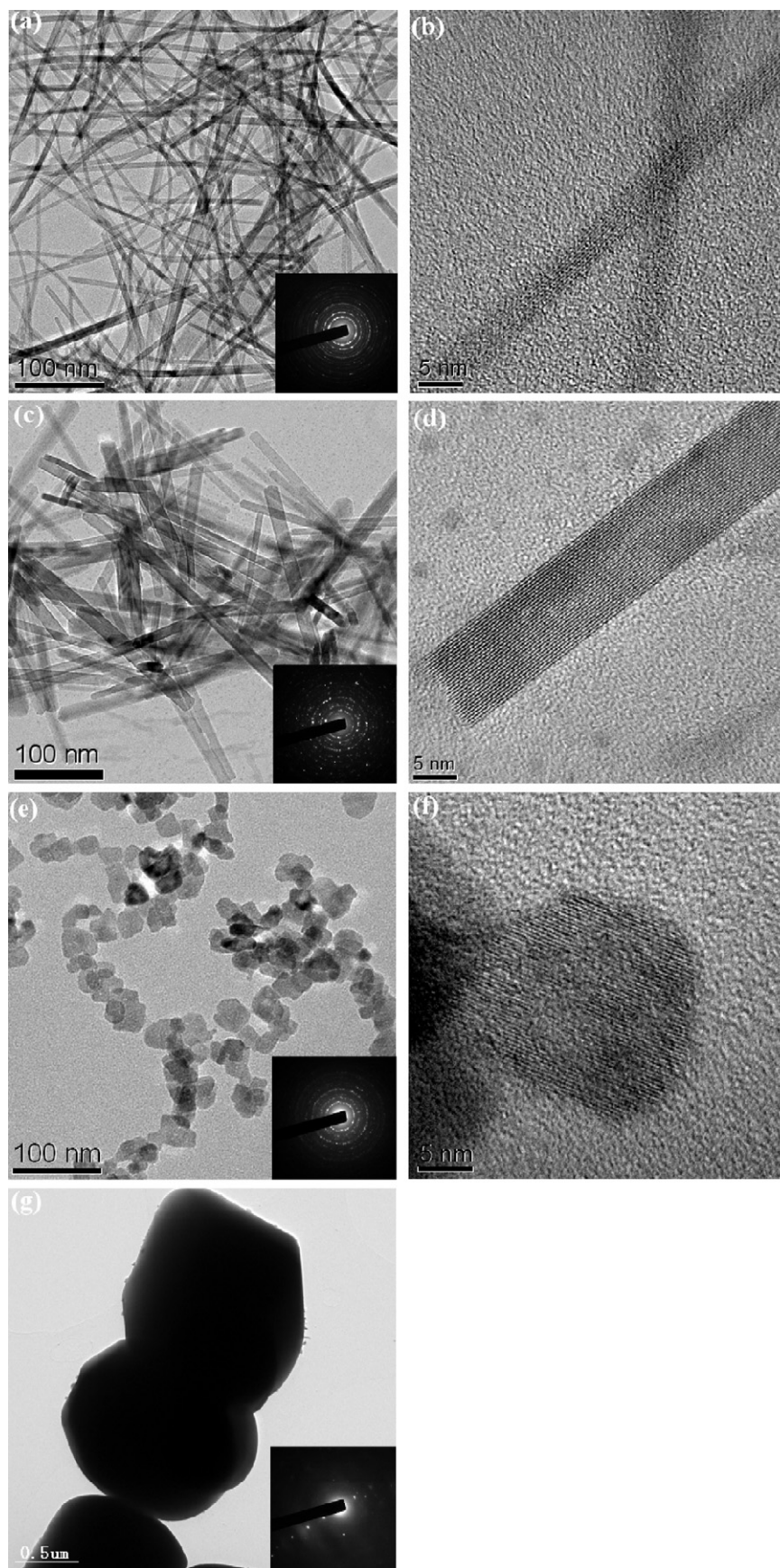
TEM images of the Eu<sup>3+</sup>:YVO<sub>4</sub> nano-crystals synthesized with the assistance of Na<sub>2</sub>EDTA are presented in Fig. 2(a) and (c). The 150EY sample exhibits nanobelts with width ranging from 3 to 8 nm and length from 300 to 500 nm; while the 180EY one shows nanorods with diameter ranging from 15 to 20 nm and length from 200 to 300 nm. The PEY sample prepared with the help of Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, as presented in Fig. 3(e), is irregular polyhedral nano-crystals sized 20–30 nm. Similarly, the micro-crystalline sample (BEY), shown in Fig. 3(g), are irregular polyhedral particles. However, the particle size is in the range of 1.5–2.0 μm. The corresponding selected area electron diffraction (SAED) patterns demonstrate that all the nanobelts, nanorods, polyhedral nano-crystals and microcrystals are tetragonal YVO<sub>4</sub>, agreeing well with the XRD results. HRTEM images presented in Fig. 2(b), (d) and (f) verify the mono-crystalline nature of the nanobelt, nanorod and polyhedral nanoparticles. The formation of various morphologies for the synthesized nanocrystals might be determined by the combined roles of the chelating agent and pH value of the solution, similar to the cases previously reported by Lin et al. [21–23].

Fig. 3 shows the typical EDS spectra taken from Ce<sup>3+</sup>:YVO<sub>4</sub>, Nd<sup>3+</sup>:YVO<sub>4</sub>, Eu<sup>3+</sup>:YVO<sub>4</sub> and Tb<sup>3+</sup>:YVO<sub>4</sub> nanorods. Obviously, these nanorods consist of Y, V, O and Ln (Ce, Nd, Eu, or Tb) elements, indicating that Ln<sup>3+</sup> ions are doped into the YVO<sub>4</sub> nano-crystals.

FTIR spectra of the nanobelts, nanorods, and micro-crystals are displayed in Fig. 4. The intense peak at about 800 cm<sup>−1</sup> is apparently associated with the characteristic vibrational mode of



**Fig. 1.** XRD patterns of as-synthesized samples: (a) 150EY, (b) 180EY, (c) PEY and (d) BEY.



**Fig. 2.** Typical TEM images and corresponding SAED patterns of (a)  $\text{Eu}^{3+}:\text{YVO}_4$  nanobelts (150EY), (c) nanorods (180EY), (e) polyhedral nano-crystalline (PEY) and (g) micro-crystalline samples (BEY); (b), (d), and (f) show HRTEM images of nanobelt, nanorod and polyhedral nano-crystals in (a), (c) and (e).

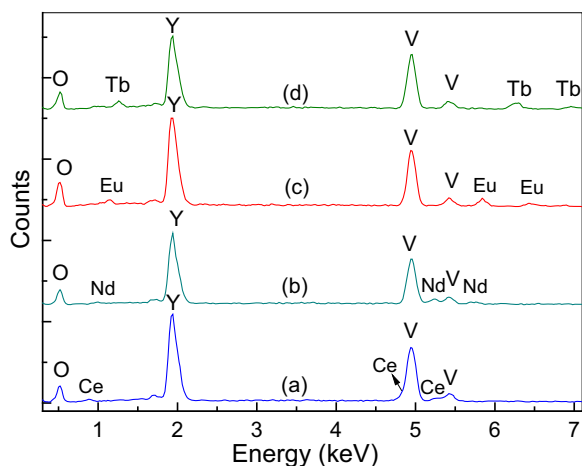


Fig. 3. EDS spectra of (a)  $\text{Ce}^{3+}:\text{YVO}_4$ , (b)  $\text{Nd}^{3+}:\text{YVO}_4$ , (c)  $\text{Eu}^{3+}:\text{YVO}_4$  and (d)  $\text{Tb}^{3+}:\text{YVO}_4$  nanorods.

V–O bond for all the samples [24,25]. However, compared with that of the micro-crystals, the vibrational peaks of V–O bonds of the nanobelts and nanorods are obviously broadened. The broad absorption band at  $3420\text{ cm}^{-1}$  and a weak one at  $1610\text{ cm}^{-1}$  are assigned to the symmetrical stretching vibration and the bending vibration of H–O–H ( $\text{H}_2\text{O}$  molecules), respectively. The peak at  $1396\text{ cm}^{-1}$  is assigned to the vibration of the carboxylate anion. In addition, two weak bands at  $2850\text{ cm}^{-1}$  and  $2931\text{ cm}^{-1}$  correspond to the symmetrical and asymmetrical stretching vibrational modes of the  $\text{CH}_2$  group, respectively. However, these vibrational organic groups are not detected in the micro-crystalline sample.

### 3.2. Morphology-dependent luminescence

The photoluminescence excitation (PLE) spectra for the 616 nm emission corresponding to  $\text{Eu}^{3+}:\text{VO}_4^{3-} \rightarrow {}^7\text{F}_2$  transition of the  $\text{Eu}^{3+}:\text{YVO}_4$  nanobelts, nanorods and micro-crystals are presented in Fig. 5. All the excitation spectra consist of an intense broadband ranging from 200 to 350 nm and several weak narrow bands in the range of 350–550 nm. The broadband is originated from the  $\text{O}^{2-} \rightarrow \text{V}^{5+}$  charge transfer (CT) within  $\text{VO}_4^{3-}$  group, which confirms that the emission of  $\text{Eu}^{3+}$  is ascribed to the efficient energy transfer from the excited  $\text{VO}_4^{3-}$  groups. Interestingly, the peak position of the  $\text{O}^{2-} \rightarrow \text{V}^{5+}$  CT band red-shifts gradually with the grain morphology changing from nanobelt to nanorod and

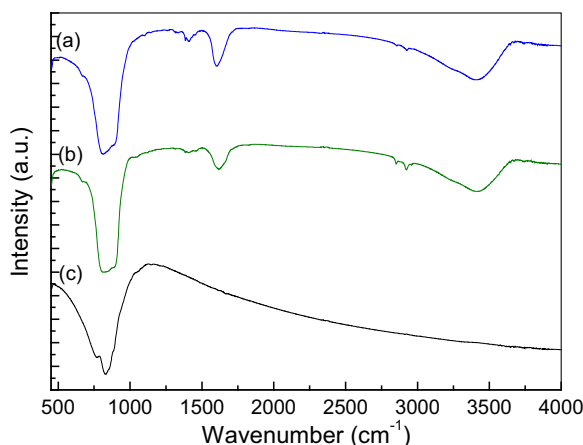


Fig. 4. FTIR spectra of (a) 150EY, (b) 180EY, and (c) BEY samples.

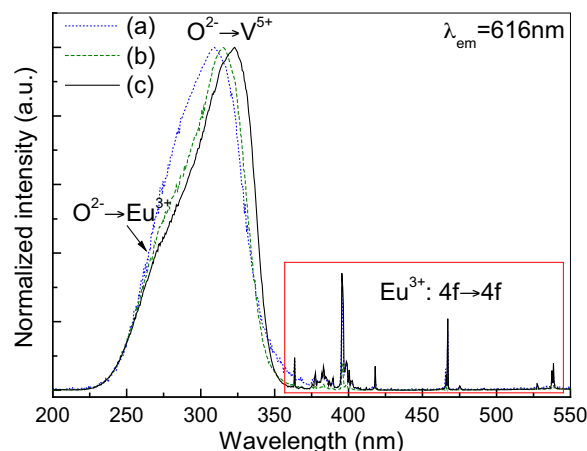


Fig. 5. Photoluminescence excitation (PLE) spectra of (a) 150EY, (b) 180EY and (c) BEY samples for the  $\text{Eu}^{3+}:\text{D}_0 \rightarrow {}^7\text{F}_2$  emission.

finally to micrometer-sized polyhedral particle, due to the effect of nano-size on the energy gap width of the CT band of the material.

The photoluminescence (PL) spectra of 150EY, 180EY, BEY and PEY samples under 310 nm excitation are shown in Fig. 6. When irradiated by 310 nm light, the electrons are excited from the ground state to the excited state of  $\text{VO}_4^{3-}$ , and then relax rapidly to the  $\text{Eu}^{3+}:\text{D}_{1,2,3}$  states. The emissions are generated by the subsequent radiative transitions from the  ${}^5\text{D}_0$  excited state to the  ${}^7\text{F}_j$  ( $j=1, 2, 3, 4$ ) ones. It is well known that  $\text{YVO}_4$  has the xenotime structure, which offers  $\text{Y}^{3+}$  ions the lattice site with a  $\text{D}_{2d}$  point symmetry. The main emission band around 616 nm originated from the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  electronic dipole transition is a consequence of the absence of the inversion symmetry of  $\text{Eu}^{3+}$  substituting  $\text{Y}^{3+}$  in  $\text{YVO}_4$  [26]. Notably, the dominant Stark-splitting peak of the one-dimensional nano-crystals is located at 616 nm, while that of the irregular polyhedral nano-crystals or micro-crystals at 619 nm. The change in the relative intensity of the two Stark-splitting peaks is attributed to the difference of the effect of the crystal field perturbation on the individual f–f transition.

The luminescence decay curves of the  $\text{Eu}^{3+}:\text{D}_0$  levels in different samples are exhibited in Fig. 7. The  $\text{Eu}^{3+}:\text{D}_0$  lifetimes in the nanobelts (150EY) and nanorods (180EY) are determined to be 0.21 and 0.92 ms, respectively. Compared with that of the

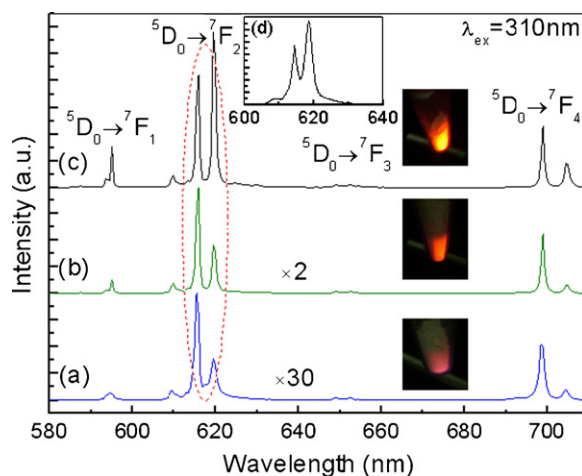
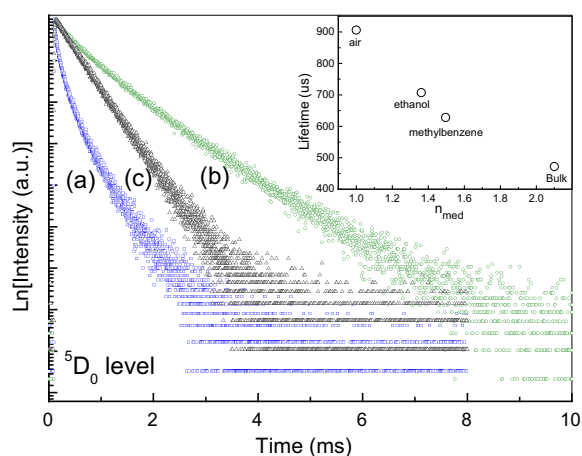


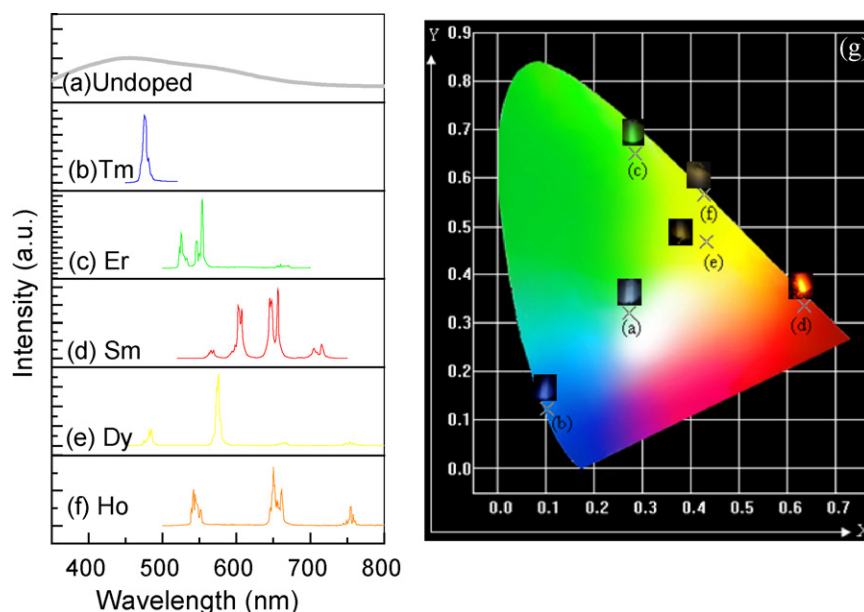
Fig. 6. Photoluminescence (PL) spectra of (a) 150EY, (b) 180EY, (c) BEY, and (d) PEY samples under 310 nm excitation; insets show the luminescence photographs of 150EY, 180EY and BEY samples respectively.



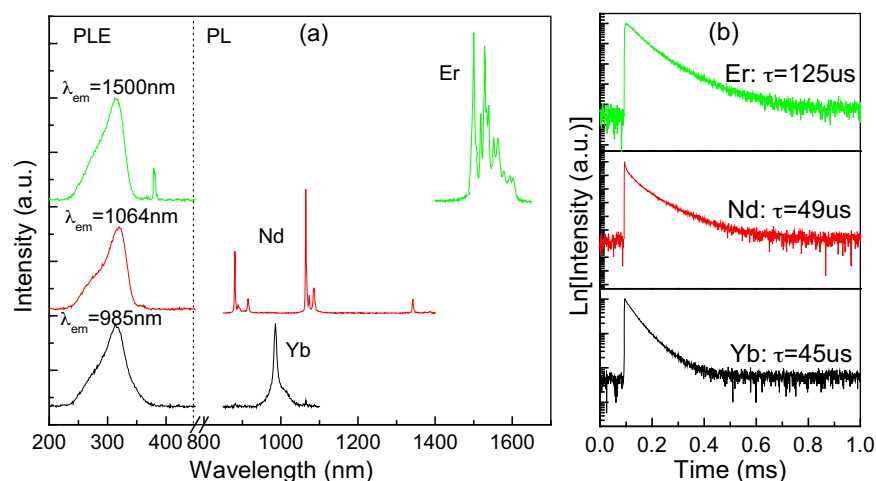


**Fig. 7.** The luminescence decay curves of  $\text{Eu}^{3+} : ^5\text{D}_0$  levels for (a) 150EY, (b) 180EY, and (c) BEY samples under 310 nm excitation; inset shows the dependence of the  $^5\text{D}_0$  lifetime of  $\text{Eu}^{3+}$  in  $\text{YVO}_4$  nanorods on the refractive index of the surrounding medium.

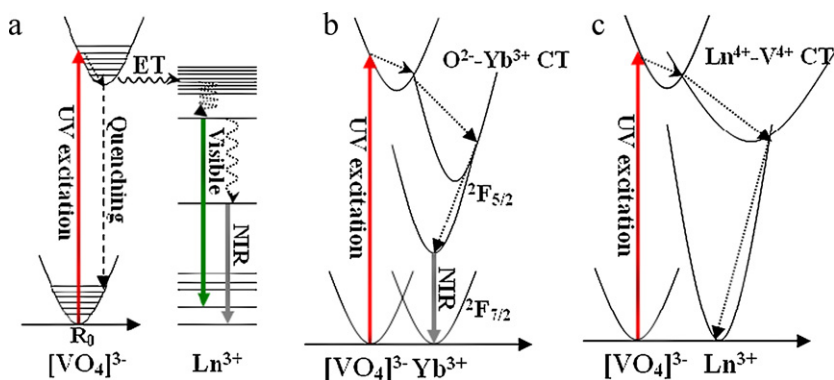
nanorods, the nanobelts have higher surface to volume ratio, and correspondingly, more surface defects which promote the non-radiative relaxation, resulting in shorter  $\text{Eu}^{3+}$  lifetime. Interestingly, the  $\text{Eu}^{3+} : ^5\text{D}_0$  lifetime in 180EY is significantly longer than that in the BEY sample (0.48 ms), attributing probably to the non-solid medium surrounding the nano-crystals which changes the effective refractive index and thus the radiative lifetime, similar to the cases previously reported in the  $\text{Ln}^{3+}$  doped  $\text{LaF}_3$  and  $\text{Gd}_2\text{O}_3$  nano-crystals [27,28]. It is well known that the radiative lifetime  $\tau_r$  is dependent on the refractive index  $n$ :  $\tau_r \propto (1/f)(\lambda_0^2/\chi)$ , where  $\chi = n[(n^2 + 2)/3]^2$  for electronic dipole transitions,  $f$  the oscillator strength,  $\lambda_0$  the wavelength in vacuum [28]. For nano-crystals,  $n$  should be replaced by the effective refractive index  $n_{\text{eff}}$ , where  $n_{\text{eff}} = xn_{\text{nc}} + (1-x)n_{\text{med}}$ ,  $x$  is the filling factor showing what fraction of space is filled by nano-crystals with a refractive index  $n_{\text{nc}}$ , and  $n_{\text{med}}$  the refractive index of the medium. In order to reveal the influence of the surrounding medium on the radiative lifetime of the nano-crystals, the fluorescence lifetime of  $\text{Eu}^{3+} : ^5\text{D}_0$  in the nanorods immersed in liquids with different refractive indices were measured, as shown in the inset of Fig. 7. Obviously, the lifetime



**Fig. 8.** Visible PL spectra of (a) pure, (b)  $\text{Tm}^{3+}$ , (c)  $\text{Er}^{3+}$ , (d)  $\text{Sm}^{3+}$ , (e)  $\text{Dy}^{3+}$ , and (f)  $\text{Ho}^{3+}$  doped  $\text{YVO}_4$  nanorods; (g) CIE (X, Y) coordinate diagram showing the corresponding luminescent chromaticity points of  $\text{Ln}^{3+}$  doped  $\text{YVO}_4$  nanorods.



**Fig. 9.** (a) Near-infrared PL and PLE spectra and (b) decay curves of  $\text{Er}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\text{YVO}_4$  nanorods.



**Fig. 10.** Energy transfer (ET) mechanisms describing the YVO<sub>4</sub> host sensitizing or quenching of Ln<sup>3+</sup> emissions. (a) Ln = Nd, Sm, Dy, Ho, Er, Tm; (b) Ln = Yb; and (c) Ln = Ce, Pr, Tb. The dotted arrows denote multi-phonon non-radiative transitions, the straight ones denote radiative transitions, and CT denotes charge transfer state.

is significantly affected by the surrounding medium. The larger refractive index of the surrounding medium leads to the shorter lifetime. Therefore, the measured longer lifetime of Eu<sup>3+</sup>:<sup>5</sup>D<sub>0</sub> in the YVO<sub>4</sub> nanorods is due to the low refractive index of air surrounding the sample.

### 3.3. Host-sensitized multi-color tunable luminescence

To demonstrate the emission versatility of the as-synthesized YVO<sub>4</sub> nanorods, PL and PLE spectra of the various Ln<sup>3+</sup> doped YVO<sub>4</sub> (Ln = Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm, Yb) nano-crystals were recorded, as shown in Figs. 8 and 9. For the pure YVO<sub>4</sub>, a broadband emission covering the whole visible region is observed, which might be originated from the defect centers since it is proved that the excited energy in the pure YVO<sub>4</sub> crystal will transfer easily to a quenching site through the VO<sub>4</sub><sup>3−</sup> groups and dissipate non-radiatively, therefore no visible emission can be detected at room temperature [29]. When Ln<sup>3+</sup> ions are doped into YVO<sub>4</sub>, Ln<sup>3+</sup> ions act as the activators to induce the characteristic emissions through efficient energy transfer from the excited state of VO<sub>4</sub><sup>3−</sup> to the activators. Interestingly, except Ce<sup>3+</sup>, Pr<sup>3+</sup> and Tb<sup>3+</sup>, all the other Ln<sup>3+</sup> ion doped YVO<sub>4</sub> nanorods exhibit visible or NIR emissions. As shown in Fig. 8, under 310 nm excitation corresponding to the VO<sub>4</sub><sup>3−</sup> group absorption, sharp emissions assigned respectively to the <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub> (blue), <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub>, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>5/2</sub> (green), <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>5/2,7/2,9/2,11/2</sub> (orange), <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2,13/2,11/2</sub> (yellow), and <sup>5</sup>F<sub>4</sub>, <sup>5</sup>F<sub>5</sub>, <sup>5</sup>I<sub>4</sub> → <sup>5</sup>I<sub>8</sub> (yellow) transitions are observed in the Tm<sup>3+</sup>, Er<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup> or Ho<sup>3+</sup> doped samples. The corresponding visible emission spectra of the nanorods doped with various Ln<sup>3+</sup> ions can be easily converted to the Commission International de l'Eclairage (CIE) 1931 chromaticity diagram, as plotted in Fig. 8(g).

In addition to the visible luminescence, the YVO<sub>4</sub> nanorods doped with appropriate Ln<sup>3+</sup> ions such as Er<sup>3+</sup>, Nd<sup>3+</sup> or Yb<sup>3+</sup> also exhibit near-infrared emissions with the help of host-sensitization of YVO<sub>4</sub>, as presented in Fig. 9(a). The emissions originated from Er<sup>3+</sup>:<sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub>, Nd<sup>3+</sup>:<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2,11/2,13/2</sub> and Yb<sup>3+</sup>:<sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub> transitions cover the whole NIR region between 850 and 1650 nm. The corresponding excitation spectra evidenced the efficient energy transfer from the excited state of VO<sub>4</sub><sup>3−</sup> to the NIR emission activators. All the lifetime curves of the Er<sup>3+</sup>:<sup>4</sup>I<sub>13/2</sub>, Nd<sup>3+</sup>:<sup>4</sup>F<sub>3/2</sub>, and Yb<sup>3+</sup>:<sup>2</sup>F<sub>5/2</sub> levels, shown in Fig. 9(b), exhibit the non-exponential decay behaviors, which is ascribed to the influence of surface defects of nanorods on the Ln<sup>3+</sup> radiative transitions. The effective lifetimes were estimated to be 125, 49 and 45 μs, respectively, by the formula  $\tau_{eff} = \int I(t)dt / \int I(t)dt$ , where  $I(t)$  represents the luminescent intensity at time  $t$ .

### 3.4. Host-to-Ln<sup>3+</sup> sensitization mechanisms

The possible mechanisms depicting the YVO<sub>4</sub> host sensitizing or quenching of Ln<sup>3+</sup> emissions are illustrated in Fig. 10. Under UV excitation, the VO<sub>4</sub><sup>3−</sup> groups are excited from the ground state to the excited one. When energy matching condition is met, the excited VO<sub>4</sub><sup>3−</sup> may serve as a universal sensitizer for a wide range of Ln<sup>3+</sup> activators such as Nd<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup> and Tm<sup>3+</sup>. After non-radiative relaxation to the metastable excited states, these Ln<sup>3+</sup> ions emit visible or NIR light, as shown in Fig. 10(a). As for the sensitizing emission of Yb<sup>3+</sup>, the energy transfer process can occur only with the help of the O<sup>2−</sup>–Yb<sup>3+</sup> charge transfer (CT) state, since the energy gap between the unique excited state Yb<sup>3+</sup>:<sup>2</sup>F<sub>5/2</sub> and the VO<sub>4</sub><sup>3−</sup> state is about 30,000 cm<sup>−1</sup>, being too large to be matched by phonons. As exhibited in Fig. 10(b), the electrons in VO<sub>4</sub><sup>3−</sup> group are firstly transferred to the O<sup>2−</sup>–Yb<sup>3+</sup> CT state, then non-radiatively relax to the Yb<sup>3+</sup>:<sup>2</sup>F<sub>5/2</sub> excited state from which the NIR emission is generated. For Ce<sup>3+</sup>, Pr<sup>3+</sup> and Tb<sup>3+</sup>, it is well known that they have a great tendency to be oxidized to quadrivalence, while V<sup>5+</sup> ions have a tendency to be reduced, forming the Ln<sup>4+</sup>–V<sup>4+</sup> CT state [15]. Therefore, the excited electrons are easily transferred to the Ln<sup>4+</sup>–V<sup>4+</sup> CT state followed by the non-radiative relaxation to the ground states of Ln<sup>3+</sup>, resulting in the quenching of Ln<sup>3+</sup> emissions, as shown in Fig. 10(c).

## 4. Conclusions

In summary, the lanthanide ion doped one dimensional YVO<sub>4</sub> nanobelts and nanorods were prepared, and their morphology-dependent luminescence was studied. Evidently, the excitation, emission and decay behaviors of Eu<sup>3+</sup>:YVO<sub>4</sub> nanorods are quite different from those of the micro-crystalline samples. Under UV excitation, visible to near-infrared multicolor tunable luminescence of Ln<sup>3+</sup>:YVO<sub>4</sub> (Ln = Nd, Sm, Eu, Dy, Ho, Er, Tm, or Yb) nanorods are achieved via efficient energy transfer from the excited VO<sub>4</sub><sup>3−</sup> groups to the lanthanide activators.

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