Synthesis and Characterizations of Mesoporous YVO₄: Eu³⁺@SiO₂

S W Li¹ and Y F Liu
College of Science, Changchun Institute of Technology, Changchun 130012, China

¹ E-mail: lx_lsw@ccit.edu.cn

Abstract. The mesoporous YVO₄: Eu³⁺@SiO₂ was synthetized by combination of in-situ synthesis with soft template method. At the same time, the mesoporous SiO₂ and YVO₄: Eu³⁺ nanocrystal were also synthesized. The structure, morphologies, UV–vis spectra, photoluminescence properties and fluorescence lifetimes were studied systemically. And the photoluminescence property of mesoporous YVO₄: Eu³⁺@SiO₂ was studied comparing with YVO₄: Eu³⁺ nanocrystal. The results showed that the mesoporous YVO₄: Eu³⁺@SiO₂ possessed highly ordered mesoporous structure. The intrinsic excitation bands of Eu³⁺ disappear. Under excited VO₄³⁻, the characteristic emission of Eu³⁺ ions was obtained in the mesoporous YVO₄: Eu³⁺@SiO₂. The lifetimes of Eu³⁺ become short in the mesoporous YVO₄: Eu³⁺@SiO₂. The photoluminescence efficiency of mesoporous YVO₄: Eu³⁺@SiO₂ was higher than that of the YVO₄: Eu³⁺ nanocrystal.

1. Introduction
Lanthanide ions doped materials have attracted significant attention due to their unique luminescent properties and their potential applications in laser materials, flat panel display, cathode ray tubes, up- or down- conversion materials, biomarkers and so on [1-4]. YVO₄ has been widely used as a host lattice for lanthanide ions to produce phosphors emitting a variety of colors [5-8]. YVO₄:Eu³⁺ material has higher thermal stability and is considered as the efficient red emission phosphor used in cathode ray tube and field emission display devices [5-8]. YVO₄:Eu³⁺ has the strong red emission lines (¹D₀→³F₂ emission transitions at 614 and 619 nm) by the energy transfer to Eu³⁺ ion following absorption of UV light in the VO₄³⁻ group. YVO₄: Eu³⁺ phosphors are attracting the attention for application to field emission display (FED) devices due to its sulfur-free composition and fabrication of thin film in relatively low temperature [9, 10]. Mesoporous material has nanosize pores whose size in the range 2 – 50 nm in structure has been expected for applications of adsorbent, catalyst carrier, separation membrane, fixing agent for biomolecule and semiconductor cluster, functional electronics and photonics materials [11-13]. Especially, mesoporous silica had been studied widely in the mesoporous materials [14-16]. Mesoporous silica are highly ordered mesoporous molecular sieves with a hexagonal array of uniform channels. They have a huge specific surface area more than 1000 m²/g and range of relatively uniform pore size from 1 to 2 nm. It has been numerous studied about mesoporous silica because of increasing need in expectations for new applications such as adsorbent and catalyst carrier. However, the photoluminescence mesoporous silica is studied rarely [17]. In this paper, we synthetized mesoporous YVO₄: Eu³⁺@SiO₂ materials through the combination of in-situ synthesis with soft template method. The structure, morphology and luminescent properties were studied in detail.
2. Experiments sections

The preparation of YVO₄: Eu³⁺ precursor solution: weighing suitable amount of Y₂O₃ and Eu₂O₃ (mole ratio of 95:5), adding suitable amount of glacial acetic acid, heating and stirring until it completely dissolved, continue heating until excess acetic acid solution boiled away. Taking 0.112 g of above rare earth acetate and dissolving in 30 ml deionized water, forming acetic acid rare earth salt aqueous solution. Adding 0.125 g of Na₃VO₄·12H₂O into the rare earth acetate solution, strong stirring for 2 h. Weighing proper amount of CTAB dissolved in 40 ml of deionized water, then adding 5 ml of TEOS into it under stirring for 2 h. The YVO₄: Eu³⁺ precursor solution is added dropwisely into the TEOS aqueous solution with CTAB. Then the mixing solution was transferred into a Teflon bottle held in a stainless steel autoclave, sealed, and maintained at 100 °C for 48 h. The autoclave was cooled to room temperature naturally. The precipitates were separated by centrifugation, washed three times with deionized water, and dried in air at 75 °C for 24 h. Then dried product was put into the temperature control furnace at 550 °C for 3 h. The resulting product is marked as YVO₄: Eu³⁺@SiO₂.

As a control, we synthetized YVO₄: Eu³⁺ nanocrystal according reference [18]. And the mesoporous SiO₂ synthesized in accordance with the above methods of mesoporous YVO₄: Eu³⁺@SiO₂.

X-ray powder diffraction (XRD) was tested on Bruker D8 Focus diffractometer (Cu-Kα as the radiation source (λ = 0.15405 nm). Transmission electron microscopic (TEM) image was taken with a FEI Tecnai G2 S-Twin. The photoluminescence spectra were obtained by a Hitachi F – 7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Ultraviolet-visible absorption spectra were taken with the U – 3310 scanning spectrophotometer. The decay curves were obtained via a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz).

3. Results and discussions

3.1. structure

Figure 1A showed the Wide-angle XRD image of mesoporous SiO₂, YVO₄: Eu³⁺@SiO₂ and YVO₄: Eu³⁺ nanocrystal. It is clearly that three peaks of diffraction were found in the mesoporous YVO₄: Eu³⁺@SiO₂, which matching with the four corners of the YVO₄ (2, 0, 0), (1, 1, 2), (1 2 3) (JCPDS No. 76-1649), besides the broad peak of mesoporous SiO₂ (JCPDS 29-0085). It indicated that YVO₄ crystal structure is formed in the mesoporous structure. The average size of YVO₄: Eu³⁺ nanocrystal was estimated from Schereer formula, D = Kλ/βcosθ, where D is the average size of particles, K is a constant (0.89), λ is X-ray wavelength (0.15405 nm), β is full width at half maximum, θ is the corresponding angle of diffraction peak, respectively. The results showed that the average size of YVO₄: Eu³⁺ nanocrystal about 0.8 nm, which is smaller than the thickness of the pore wall (~ 1.5 nm). It suggested that YVO₄ nanoparticles are formed in the mesoporous pore wall. Figure 1B showed Low angle XRD patterns of mesoporous SiO₂ and YVO₄: Eu³⁺@SiO₂. In the mesoporous YVO₄: Eu³⁺@SiO₂, three characteristic peaks (100), (110) and (200) could be clearly observed, which are similar to that of mesoporous SiO₂. It suggested mesoporous YVO₄: Eu³⁺@SiO₂ still had highly ordered two-dimensional hexagonal symmetric mesoporous structure.

Figure 1. A Wide-angle XRD patterns of mesoporous SiO₂ (a), YVO₄: Eu³⁺@SiO₂ (b) and YVO₄:Eu³⁺ nanocrystal (c); B Low-angle XRD patterns of mesoporous SiO₂ (a) and YVO₄: Eu³⁺@SiO₂ (b).
3.2. morphologies

Figure 2(a) and (b) showed the TEM of mesoporous SiO$_2$ and mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$, respectively. Figure 2(a) show that the mesoporous SiO$_2$ have regular hexagonal mesoporous structure. The YVO$_4$: Eu$^{3+}$@SiO$_2$ (Figure 2(b)) is similar to the mesoporous SiO$_2$. We did not find the single nanoparticle or other structure in the all TEM of YVO$_4$: Eu$^{3+}$@SiO$_2$. The selected area electron diffraction patterns (SAED) of YVO$_4$: Eu$^{3+}$@SiO$_2$ is shown in the illustration of Figure 2(b) and the crystal diffraction rings are clearly. The results and the results of XRD can prove that the YVO$_4$: Eu$^{3+}$@SiO$_2$ mesoporous structure is formed.

![Figure 2. TEM of the mesoporous SiO$_2$ and YVO$_4$: Eu$^{3+}$@SiO$_2$, inset: SAED.](image)

3.3. UV-vis absorption spectra

The UV-vis absorption spectra of YVO$_4$: Eu$^{3+}$ nanocrystal and mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ drawn in Figure 3. The shapes of UV-vis absorption spectra in both YVO$_4$: Eu$^{3+}$ nanocrystal and mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ are similar. In YVO$_4$: Eu$^{3+}$ nanocrystal, the absorption band located around 285 nm can be observed, corresponding to the absorption of VO$_4^{3-}$. The clearly blue-shifts are detected for the bands in the mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ samples, which can be attributed to the interaction of VO$_4^{3-}$ with the grids Si-O-Si.

![Figure 3. UV-vis absorption Spectra of the YVO$_4$:Eu$^{3+}$ and YVO$_4$: Eu$^{3+}$@SiO$_2$.](image)

3.4. Photoluminescence properties

The photoluminescence spectra of YVO$_4$: Eu$^{3+}$ nanocrystal and mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ were shown in Figure 4. In the excitation spectra (at left of Figure 4), the excitation band centered at 283 nm is attributed to the charge transfer from coordination oxygen to vanadium atom of VO$_4^{3-}$ in YVO$_4$: Eu$^{3+}$@SiO$_2$. The excitation band centered at 285 nm in YVO$_4$: Eu$^{3+}$ nanocrystal is attributed to the charge transfer from coordination oxygen to Eu$^{3+}$.
Eu$^{3+}$. Compared with YVO$_4$: Eu$^{3+}$ nanocrystal, the excitation band of YVO$_4$: Eu$^{3+}$@SiO$_2$ becomes narrowed and the intrinsic excitation bands of Eu$^{3+}$ at 394 nm and 456 nm disappeared, which implied that the local environment of Eu$^{3+}$ changed. In the emission spectrum (at right of Figure 4), the composition of emissions associated with the electronic transitions from excited $^5$D$_{0,1}$ levels to the ground $^7$F$_{1,4}$ levels of Eu$^{3+}$ ions. Among them, the emission at 592 nm ($^5$D$_0$ $\rightarrow$ $^7$F$_1$) originating from magnetic dipole transitions and the emission at 612 nm ($^5$D$_0$ $\rightarrow$ $^7$F$_2$) originating from electric dipole transitions are very remarkable. The shape and the emission peak position of the spectra in YVO$_4$: Eu$^{3+}$@SiO$_2$ and YVO$_4$: Eu$^{3+}$ nanocrystal are similar. However, the emission intensity of Eu$^{3+}$ ions in YVO$_4$: Eu$^{3+}$ nanocrystal is stronger. The reason can be attributed to the excellent crystallinity of YVO$_4$: Eu$^{3+}$ nanocrystal, and the local environments surrounding the Eu$^{3+}$ ions become relative order in YVO$_4$: Eu$^{3+}$ nanocrystal.

The fluorescence decay curves for the $^5$D$_0$-$^7$F$_2$ transition of Eu$^{3+}$ ions at 612 nm in YVO$_4$: Eu$^{3+}$ nanocrystal and mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ were measure at room temperature, and drown in Figure 5. It can be seen that the fluorescence decay curves were nonexponential. The fluorescence decay curves can be well fitted by the following equation,

$$I = I_1 \exp\left(-\tau_1 / t\right) + I_2 \exp\left(-\tau_2 / t\right)$$

where $\tau_1$ and $\tau_2$ are the faster and slower decay time constants, respectively. $I_1$ and $I_2$ present ratios of the faster and slower components, respectively. The fitted results were 746.1 $\mu$s ($\tau_1$), 186.9 $\mu$s ($\tau_2$) for YVO$_4$: Eu$^{3+}$, 535.2 $\mu$s ($\tau_1$) and 90.3 $\mu$s ($\tau_2$) for mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$. Compared the fitted result, both fast and slow decay time in mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ were smaller than that of mesoporous YVO$_4$: Eu$^{3+}$. It indicated that the around Eu$^{3+}$ had been changed. The the local environment of Eu$^{3+}$ is changed. When YVO$_4$: Eu$^{3+}$ is formed in the porous wall of mesoporous SiO$_2$, the -OH groups on the porous wall and the surface defects of mesoporous SiO$_2$ became nonradiation transition path, and the nonradiative relaxation increase and lifetime became short.

![Figure 4](image_url). Excitation spectra (left) and emission spectra (right) of the YVO$_4$:Eu$^{3+}$ nanocrystal and YVO$_4$:Eu$^{3+}$@SiO$_2$. 

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**Figure 4.** Excitation spectra (left) and emission spectra (right) of the YVO$_4$:Eu$^{3+}$ nanocrystal and YVO$_4$:Eu$^{3+}$@SiO$_2$. 

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**Figure 4.** Excitation spectra (left) and emission spectra (right) of the YVO$_4$:Eu$^{3+}$ nanocrystal and YVO$_4$:Eu$^{3+}$@SiO$_2$. 

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**Figure 4.** Excitation spectra (left) and emission spectra (right) of the YVO$_4$:Eu$^{3+}$ nanocrystal and YVO$_4$:Eu$^{3+}$@SiO$_2$. 

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Figure 5. Fluorescent decay curves of the $^5\text{D}_0-^7\text{F}_2$ transitions of Eu$^{3+}$ at 612 nm ions in YVO$_4$: Eu$^{3+}$ and YVO$_4$: Eu$^{3+}$@SiO$_2$. The solid lines are experimental data, and the black circles are fitting functions.

4. Conclusions
Using CTAB as template, mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ was prepared through in situ synthesis method. The YVO$_4$: Eu$^{3+}$ nanocrystals with size about 0.8 nm were formed in the porous wall. In the mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$, the excitation band of vanadate becomes narrow and the intrinsic excitation bands of Eu$^{3+}$ disappear. The characteristic luminescence of Eu$^{3+}$ ions was obtained in the mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ under excited VO$_4^{3-}$. The lifetimes of Eu$^{3+}$ become short for the mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$. The luminescent efficiency of mesoporous YVO$_4$: Eu$^{3+}$@SiO$_2$ is higher than that of the YVO$_4$: Eu$^{3+}$ nanocrystal.

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