Silica Spheres Coated with YVO\textsubscript{4}:Eu\textsuperscript{3+} Layers via Sol–Gel Process: A Simple Method To Obtain Spherical Core–Shell Phosphors

M. Yu, J. Lin, and J. Fang

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China, and Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148

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Spherical SiO\textsubscript{2} particles have been successfully coated with YVO\textsubscript{4}:Eu\textsuperscript{3+} phosphor layers through a Pechini sol–gel process. The resulted YVO\textsubscript{4}:Eu\textsuperscript{3+}@SiO\textsubscript{2} core–shell phosphors were characterized by X-ray diffraction (XRD), Fourier-transform IR spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, UV/vis absorption spectra, general and time-resolved photoluminescence spectra, as well as kinetic decays. The XRD results demonstrate that the YVO\textsubscript{4}:Eu\textsuperscript{3+} layers begin to crystallize on the SiO\textsubscript{2} particles after annealing at 400 °C, and the crystallinity increases with raising the annealing temperature. The obtained core–shell phosphors have perfect spherical shape with narrow size distribution (average size ca. 500 nm), nonagglomeration, and smooth surface. The thickness of the YVO\textsubscript{4}:Eu\textsuperscript{3+} shells on SiO\textsubscript{2} cores could be easily tailored by varying the number of deposition cycles (60 nm for two deposition cycles). The Eu\textsuperscript{3+} shows a strong photoluminescence (PL) (dominated by \( \text{Eu}^{3+} \rightarrow \text{F}_{2} \) red emission at 617 nm) due to an efficient energy transfer from vanadate groups to Eu\textsuperscript{3+}. The energy transfer process was further studied by the time-resolved emission spectra as well as kinetic decay curves of Eu\textsuperscript{3+} upon excitation into the VO\textsuperscript{4}\textsuperscript{3−} ion. The PL intensity of Eu\textsuperscript{3+} increases with raising the annealing temperature and the number of coating cycles, and optimum polyethylene glycol concentration in the precursor solution was determined to be 0.08 g/mL for obtaining the strongest emission of Eu\textsuperscript{3+}.

I. Introduction

In recent years, advanced materials derived from core–shell composite particles are of extensive scientific and technological interests due to the ability to fine tune their properties.\(^1\text{–}^5\) Core–shell materials consist of a core structural domain covered by a shell domain. The core and shell domains may be composed of a variety of materials including polymers, inorganic solids, and metals. The structure, size, and composition of these particles can be easily altered in a controllable way to tailor their magnetic, optical, mechanical, thermal, electrical, electrooptical, and catalytic properties.\(^1\text{–}^8\) The core–shell morphology can be used as a precursor form to produce hollow spheres\(^9\) or to lower the cost of precious materials by coating them on inexpensive cores.\(^10,11\) Core–shell materials can also be used to protect medicines or other materials from dissolution or hydrolysis\(^12\) and to strengthen polymeric materials.\(^13\) Up to now, many routes have been developed to fabricate such core–shell materials such as sol–gel process,\(^1\) layer-by-layer technique,\(^14\) template-directed self-assembly,\(^15\) and encapsulation of silica nanoparticles by in situ polymerization.\(^16\)

On the other hand, the current demand for high-resolution and increased efficiency in phosphors for cathode ray tubes (CRT) and field emission displays (FEDs) has promoted the development of phosphors that perform at low voltages.\(^17\) In particular, phosphors made up of small, ideally spherical particles are of interest because they offer the possibility of brighter cathodoluminescent performance, high definition, and much improved screen packing.\(^18\) The ideal morphology of phosphor particles includes a perfect spherical (\(< 3 \mu m\)) shape, narrow size distribution, and nonagglomeration. Spherical morphology of the phosphors is good for high

\(^{a}\) To whom correspondence should be addressed. E-mail: jlin@mi.ciac.jl.cn.
\(^{b}\) Chinese Academy of Sciences.
\(^{c}\) University of New Orleans.

brightness and high resolution. Additionally, high packing densities and low scattering of light can also be obtained by using spherical phosphors. Nowadays, many synthetic routes have been developed to control the size and distribution of phosphor particles, such as spray pyrolysis\(^\text{19}\) and fluxes precipitation.\(^\text{20}\)

Silica can be easily made controllably in spherical morphology from nanosize to micrometer size.\(^\text{21}\) If the silica spheres are coated with layers of phosphors, a kind of core–shell phosphor materials with spherical morphology will be obtained, and the size for the phosphor particles can be controlled by the silica cores. Furthermore, because silica is cheaper than most of the phosphor materials (which often employ the expensive rare-earth elements as the activators and/or host components), the core–shell phosphor materials will be cheaper than the pure phosphor materials in unit mass. However, so far this kind of core–shell phosphor materials has not been reported in the literature. Our group has been preparing various kinds of phosphor coatings on bulk silica glass and silicon wafer substrates via the sol–gel process.\(^\text{22}\)

It would be of great interest and importance to check if the core–shell phosphor materials can be prepared in a similar process. Eu\(^{3+}\)-activated YVO\(_4\) is an important commercial red phosphor used in color television and the high-pressure mercury lamp, which was first reported by Levine and Palilla.\(^\text{23}\) Recently, the preparation and optical properties of nanocrystalline YVO\(_4\):Eu\(^{3+}\)\(^\text{24,25}\) and related LaPO\(_4\):Eu\(^{3+}\)\(^\text{24}\) (Ce\(^{3+}\), Tb\(^{3+}\)/LaPO\(_4\) core–shell nanocrystals\(^\text{26}\) as well as LaPO\(_4\):Ce\(^{3+}\), Tb\(^{3+}\) nanocrystals conjugated to protein\(^\text{27}\) or assembled on polystyrene spheres\(^\text{14}\) have attracted great interests for potentially biological labeling applications.

II. Experimental Section

Synthesis of Silica Cores. Amorphous sub-micrometer spheres in silica in the size range of 500–600 nm were synthesized by base-catalyzed hydrolysis of tetraethoxysilane (TEOS) via the well-known Stöber process, i.e., the hydrolysis of TEOS in an ethanol solution containing water and ammonia.\(^\text{21}\) This method yielded the colloidal solution of silica particles with a narrow size distribution in the sub-micrometer range, and the particle size of silica depended on relative concentration of the reactants. In a typical experiment, 21 mL of TEOS (99 wt. %, analytical reagent, (AR)), 9 mL of deionized H\(_2\)O, and 245 mL of NH\(_4\)OH (25 wt. %, AR) were added into 225 mL of absolute ethanol and stirred at room temperature for 4 h, resulting in the formation of white silica colloidal suspension. The silica particles were centrifuged separately from the suspension and washed with ethanol for four times.

Coating of SiO\(_2\) Cores with YVO\(_4\):Eu\(^{3+}\) Shells. SiO\(_2\) core–YVO\(_4\):Eu\(^{3+}\) shell particles (YVO\(_4\):Eu\(^{3+}\)@SiO\(_2\)) were prepared by a Pechini sol–gel process.\(^\text{22}\) The doping concentration of Eu\(^{3+}\) was 5 mol % of that of Y\(^{3+}\) in YVO\(_4\) host (Y\(_{0.95}\)Eu\(_{0.05}\)VO\(_4\)), which had been optimized previously.\(^\text{24,25}\) Stoichiometric weights of Y\(_2\O\) (99.99%), Eu\(_2\O\) (99.99%), and NH\(_4\)VO\(_3\) (99%, AR) were dissolved in dilute HNO\(_3\) (AR) and then were mixed with a water–ethanol (v/v = 1:7) solution containing citric acid (AR) as a chelating agent for the metal ions. The molar ratio of metal ions to citric acid was 1:2. As a cross-linking agent, polyethylene glycol (PEG, molecular weight = 10 000, AR) was added with a final concentration ranging from 0.04 to 0.20 g/mL. The solution was stirred for 1 h to form a sol, and then the silica particles were added under stirring. The suspension was further stirred for another 3 h, then the silica particles were separated by centrifugation. The samples were dried at 100 °C for 1 h immediately. Then the dried samples were annealed to the desired temperature (300–700 °C) with a heating rate of 1 °C/min and held there for 2 h in air. The above process was repeated for several times to increase the thickness of the YVO\(_4\):Eu\(^{3+}\) shells. In this way, the core–shell structured YVO\(_4\):Eu\(^{3+}\)@SiO\(_2\) materials have been obtained, and the whole process is shown in Scheme 1. For the purpose of comparison, the coating sol was evaporated to form powders, which were annealed in a similar process to produce the pure YVO\(_4\): Eu\(^{3+}\) powder phosphors.

Characterization. The X-ray diffraction (XRD) of the powder samples was examined on a Rigaku-Dmax 2500 diffractometer using Cu Kα radiation (λ = 0.154 05 nm). Fourier-transform IR spectra were measured with a Perkin-Elmer 580B IR spectrophotometer with the KBr pellet technique. The morphology of the samples was inspected using a scanning electron microscope (JEOL JXA-840) and a transmission electron microscope (JEOL-2010, 200 kV). The X-ray photoelectron spectra (XPS) were taken on a VG ESCALAB MK II electron energy spectrometer using Mg Kα (1253.6 eV) as the X-ray excitation source. The UV/vis absorption spectra were measured on a TU-1901 spectrophotometer. The excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150-W xenon lamp as the excitation source. Time-resolved photoluminescence spectra and luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1GHz) using a 278-nm laser (pulse width = 4 ns, gate = 50 ns) as the excitation source.
III. Results and Discussion

Formation and Morphology of YVO₄:Eu³⁺@SiO₂ Core–Shell Particles.

XRD study revealed that both the as-formed silica particles and the 300 °C annealed core–shell particles are amorphous, and the core–shell particles begin to crystallize after annealing at 400 °C. Figure 1 shows the XRD patterns for the 500 °C annealed SiO₂ (a), YVO₄:Eu³⁺@SiO₂ (b), pure YVO₄:Eu³⁺ (c) powder samples as well as the JCPDS card (No. 17-341) for YVO₄ (d) as a reference. For SiO₂ particles annealed at 500 °C (Figure 1a), no diffraction peak is observed except for a broad band centered at 2θ = 22.00°, which is the characteristic peak for amorphous SiO₂ (JCPDS 29-0085). For the YVO₄:Eu³⁺@SiO₂ core–shell sample fired at 500 °C (Figure 1b), besides the broad band at 2θ = 22.00° from amorphous SiO₂, all the diffraction peaks belonging to crystalline YVO₄ are present, suggesting that the coatings of YVO₄:Eu³⁺ have crystallized well on the surfaces of amorphous silica particles. This is in good agreement with the situation for the pure YVO₄:Eu³⁺ powder sample annealed at 500 °C (Figure 1c), in which well crystalline YVO₄ is observed. No other phase is detected for YVO₄:Eu³⁺@SiO₂ core–shell samples even after annealing at 700 °C (which only increases the intensity of the diffraction peaks of YVO₄ to some extent due to the improvement of crystallinity).

It is interesting to note that the diffraction peaks of YVO₄ in YVO₄:Eu³⁺@SiO₂ core–shell samples (Figure 1b) are broader than those of the pure YVO₄:Eu³⁺ powder (Figure 1c), indicating that the crystallite size of YVO₄:Eu³⁺ grains on the surfaces of the silica particles is smaller than that in the pure powders of YVO₄:Eu³⁺. In general, the nanocrystallite size can be estimated from the Scherrer equation, D = 0.94λ/β cos θ, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half-maximum (in radian) of an observed peak, respectively. The strongest peak (200) at 2θ = 25.0° was used to calculate the average crystallite size (D) of YVO₄:Eu³⁺ on the surfaces of silica particles and in the pure YVO₄:Eu³⁺ powders. The estimated average crystallite sizes are 20 nm for the former and 50 nm for the latter, respectively. Furthermore, the calculated crystal cell parameters (a = 0.710 nm, c = 0.628 nm, V = 0.316 nm³) for the crystalline YVO₄:Eu³⁺ in the YVO₄:Eu³⁺@SiO₂ core–shell sample are a little smaller than those (a = 0.725 nm, c = 0.629 nm, V = 0.330 nm³) in the pure YVO₄:Eu³⁺ powder. This may be caused by slightly different crystallization behaviors of YVO₄:Eu³⁺ on the silica surfaces and in pure YVO₄:Eu³⁺ powders. The above results and the

bonds, respectively. This suggests that crystalline phase one at 453 cm$^{-1}$ OH($\text{from the coating sol and forming the YVO}_4$ :Eu$^{3+}$) has formed after annealing at 500 °C.

Figure 2a for the as-formed SiO$_2$ particles, the absorption bands due to OH (3435 cm$^{-1}$) with the results of XRD. For the YVO$_4$:Eu$^{3+}$ (1634 cm$^{-1}$) the Si-O bond may be covered by the bending vibration of Si-O (832 cm$^{-1}$) and Si-O on their surfaces. The surface Si-OH groups play an important role for bonding the metal ions (Y$^{3+}$, Eu$^{3+}$) from the coating sol and forming the YVO$_4$:Eu$^{3+}$ layers on the SiO$_2$ surfaces in the following annealing process, as shown in Scheme 1. In Figure 2b for pure YVO$_4$:Eu$^{3+}$ powders, a strong absorption peak at 832 cm$^{-1}$ has appeared, which are attributed to the absorption of V-O (from VO$_4^{3-}$ group) and Y(Eu)-O bonds, respectively. This suggests that crystalline phase (YVO$_4$) has formed after annealing at 500 °C, agreeing well with the results of XRD. For the YVO$_4$:Eu$^{3+}$@SiO$_2$ core–shell sample (Figure 2c), the characteristic absorption peaks of the V–O bond (832 cm$^{-1}$) for YVO$_4$:Eu$^{3+}$ (Figure 2b) and the Si–O–Si bond (1114 cm$^{-1}$) for amorphous SiO$_2$ (Figure 2a) have been observed clearly, and the weak signal from the Y–O bond may be covered by the bending vibration of Si–O at 471 cm$^{-1}$. The signal of OH groups from the as-formed silica particles have disappeared completely in the 500 °C annealed YVO$_4$:Eu$^{3+}$@SiO$_2$ core–shell particles. These results are consistent with those of XRD and further demonstrate the formation of crystalline YVO$_4$:Eu$^{3+}$ coatings on the silica surfaces via the sol–gel deposition and annealing process.

**SEM, XPS, and TEM.** Figure 3 shows the SEM micrographs of the as-formed SiO$_2$ particles (a), the pure YVO$_4$:Eu$^{3+}$ powders (b), and SiO$_2$ particles coated by 1–4 layers of YVO$_4$:Eu$^{3+}$ (c–f), respectively. From the SEM micrograph of Figure 3a, we can observe that the as-formed SiO$_2$ consists of spherical particles with an average size of 500 nm, and these particles are nonaggregated with narrow size distribution. On the contrary, the pure YVO$_4$:Eu$^{3+}$ powders contain irregular particles with wide size distribution (150–500 nm), as shown in Figure 3b. After the silica particles were functionalized by YVO$_4$:Eu$^{3+}$ coatings, the resulting YVO$_4$:Eu$^{3+}$@SiO$_2$ particles still keep the morphological properties of the silica particles, i.e., these particles are still spherical and nonaggregated but slightly larger than the pure silica particles due to the additional layers of YVO$_4$:Eu$^{3+}$ on them, as shown in parts c–f of Figure 3. Moreover, the irregular fine particles such as the pure YVO$_4$: Eu$^{3+}$ powers in Figure 3b cannot be observed in parts c–f of Figure 3. This indicates that all of the YVO$_4$:Eu$^{3+}$ materials have been coated on the surfaces of silica particles by our experimental process. However, it should be mentioned that the SEM micrographs can only provide the basic information on the morphology of YVO$_4$:Eu$^{3+}$@SiO$_2$ particles in the large scale (namely, all of the SiO$_2$ particles remain spherical and nonaggregated after being subjected to the sol–gel coating of YVO$_4$:Eu$^{3+}$ layers on them), and

![Figure 2](image2.png)

**Table 1.** Crystallite Sizes, Cell Parameters, and Structural Characteristics for YVO$_4$:Eu$^{3+}$ in YVO$_4$:Eu$^{3+}$@SiO$_2$ Spheres and YVO$_4$:Eu$^{3+}$ Powders

<table>
<thead>
<tr>
<th>YVO$_4$:Eu$^{3+}$</th>
<th>core–shell spheres</th>
<th>pure powders</th>
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<td>crystallite size</td>
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<td></td>
<td>$c = 0.628$ nm</td>
<td>$c = 0.629$ nm</td>
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<tr>
<td></td>
<td>$V = 0.316$ nm$^3$</td>
<td>$V = 0.330$ nm$^3$</td>
</tr>
<tr>
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<tr>
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<td>$I$</td>
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<tr>
<td>coordination environment of Y$^{3+}$ (Eu$^{3+}$)</td>
<td>all the O atoms belong to VO$_4$ tetrahedra</td>
<td></td>
</tr>
<tr>
<td>site symmetry of Y$^{3+}$ (Eu$^{3+}$)</td>
<td>$D_{2d}$</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 3](image3.png)
the core–shell structure of YVO₄:Eu³⁺@SiO₂ particles cannot be resolved from the SEM micrographs due to the low magnification.

To further confirm the existence of YVO₄:Eu³⁺ layers on the surfaces of silica particles, the sample in Figure 3c was subjected to XPS analysis, which is a powerful tool for determining the surface composition of a material qualitatively. Figure 4 shows the XPS analysis result of the sample. Signals of bonding energy from the Eu (3d5/2, 1134.7 eV), V (2p, 517.7 eV), O (1s, 532.9 eV), and Si (2p, 102.6 eV) can be seen clearly in parts a–e of Figure 4, respectively. By combination of the previous results of XRD and FT IR, we can deduce that these signals arise from the YVO₄:Eu³⁺ shells (a–d) and SiO₂ cores (d–e) of the sample, respectively. This provides additional evidence for the formation of coatings of crystalline YVO₄:Eu³⁺ on the SiO₂ particles.

To see the core–shell structure of YVO₄:Eu³⁺@SiO₂ particles, TEM was performed. Representative TEM micrographs for the SiO₂ particles coated by two times (layers) of YVO₄:Eu³⁺ shells as well as for the pure SiO₂ particles (as reference) are shown in parts a–d of Figure 5, respectively. In Figure 5a, the core–shell structure for the YVO₄:Eu³⁺@SiO₂ particles can be seen clearly due to the different electron penetrability for the cores and shells. The cores are black spheres with an average size of 500 nm (similar to the pure SiO₂ particles in Figure 5d), and the shells have gray color with an average thickness of 60 nm. The high-resolution TEM and electron diffraction measurements were performed in the interface region of the core and shell of a particle as labeled in Figure 5a, and the micrographs are shown in parts b and c of Figure 5, respectively. The lattice fringes of crystalline phase (YVO₄:Eu³⁺) can be seen clearly in Figure 5b, and the electron diffraction rings with some disorder in Figure 5c just demonstrate the coexistence of crystalline phase (YVO₄:Eu³⁺) and amorphous phase (SiO₂) in the interface region of the core–shell particle.

**Photoluminescence Properties. Spectral and Kinetic Properties of YVO₄:Eu³⁺@SiO₂ Core–Shell Phosphors.** The obtained YVO₄:Eu³⁺@SiO₂ core–shell phosphor particles can be dispersed in ethylene glycol to form a relatively stable colloid, whose UV/vis absorption spectrum was measured, as shown in Figure 6a. A strong absorption band peaking at 278 nm is observed, agreeing well with the reported absorption spectra of nanocrystalline YVO₄:Eu.²⁴,²⁵ Obviously, this band is ascribed to a charge transfer from the oxygen ligands to the central vanadium atom within the VO₄³⁻ group ions. From the viewpoint of molecular orbital theory, it corresponds to transitions from the ³A₂(1T₁) ground state to ¹A₁(1E) and ¹E(2T₁) excited states of VO₄³⁻ ion.³¹

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Figure 6. Absorption (a), excitation (b), and emission (c) spectra of YVO₄:Eu³⁺@SiO₂ core–shell particles. The absorption spectrum was taken in the colloidal solution of YVO₄:Eu³⁺@SiO₂ particles dispersed in ethylene glycol.

Upon UV excitation, the YVO₄:Eu³⁺@SiO₂ core–shell phosphors exhibit strong red luminescence. Parts b and c of Figure 6 show the excitation and emission spectra of the core–shell phosphors annealed at 500 °C, respectively. In agreement with the absorption spectrum in Figure 6a, the excitation spectrum (Figure 6b) monitored with 617-nm emission of Eu³⁺⁺ (5D₀→7F₂) consists of a strong absorption band with a maximum at 279 nm due to the VO₄³⁻ ion. The general f–f transition lines of Eu³⁺ in the longer wavelength region have not been observed due to their weak intensity relative to that of the VO₄³⁻ ion. This indicates that the excitation of Eu³⁺ is mainly through the VO₄³⁻ ions, i.e., by energy transfer from VO₄³⁻ to Eu³⁺. Excitation into the VO₄³⁻ group at 279 nm yields the emission spectrum (Figure 6c), which not only contains the characteristic transition lines from the lowest excited 5D₀ level of Eu³⁺ but also those from higher energy levels (5D₁, 5D₂, 5D₃) of Eu³⁺ with a very weak intensity (which can be seen more clearly by enlarging the emission spectrum in the short wavelength region). No emission from the VO₄³⁻ group is observed, suggesting that the energy transfer from VO₄³⁻ to Eu³⁺ is very efficient. The locations for the main emission lines of Eu³⁺ and their assignments are labeled in the figure. Obviously, the emission spectrum is dominated by the red 5D₀→7F₂ hypersensitive transition of Eu³⁺ due to the low local symmetry (D₂h, without inversion center, Table 1) for the sites of Eu³⁺ in the YVO₄ host lattices. Note that the 4D₀→5F₂ transition of Eu³⁺ (which is only allowed for C₃, C₅, Cᵥ site symmetry) is absent in the emission spectrum. In addition, the crystal field splitting of Eu³⁺ 5D₀→F₁, 2, 4 transitions can be seen clearly, indicating that the sample is well crystallized. In general silicate host lattices with high phonon energy (1100 cm⁻¹, the vibration frequency of Si–O–Si bond), the emission from the higher energy levels (5D₁, 5D₂, 5D₃) of Eu³⁺ is quenched completely by the multiphonon relaxation process. However, in YVO₄:Eu³⁺@SiO₂ core–shell phosphors the emission from higher excited states of Eu³⁺ is present despite the high-energy phonons of Si–O–Si from the SiO₂ cores (1114 cm⁻¹, Figure 2c). This indicates that the SiO₂ cores have little influence on the luminescence properties of the phosphors due to the long distance of between Si–O–Si networks and the Eu³⁺ ions. The emission properties of Eu³⁺ are mainly determined by the nearest coordinated VO₄³⁻ ions, whose lower vibration energy (832 cm⁻¹) is not able to bridge the gaps between the higher energy levels and 5D₀ level of Eu³⁺ completely, resulting in the weak emission from these levels. All the above spectral properties for the YVO₄:Eu³⁺@SiO₂ core–shell phosphors are basically consistent with the reported bulk, nano-crystalline powder, and thin film of YVO₄:Eu³⁺, further confirming the formation of nanocrystalline layers of YVO₄:Eu³⁺ on SiO₂ spheres.

The strong luminescence of Eu³⁺ results from an efficient energy transfer from the VO₄³⁻ group to Eu³⁺ in YVO₄:Eu³⁺ layers of the core–shell phosphors as reported previously. The energy-transfer process from VO₄³⁻ to Eu³⁺ as well as the emission process of Eu³⁺ is schematically shown in Figure 7. To obtain more information about the energy transfer process from VO₄³⁻ to Eu³⁺, time-resolved emission spectra of Eu³⁺ in the YVO₄:Eu³⁺@SiO₂ core–shell phosphors were recorded at room temperature by exciting into the absorption of VO₄³⁻ using a 278-nm laser with delay time ranging from 1 to 1000 μs, as shown in Figure 8. Clearly, the emission of Eu³⁺ increases from t = 1 to 20 μs, then begins to decay from t = 20 to 40 μs until t = 1000 μs. The initial increase for the luminescence of Eu³⁺ within 20 μs is in good agreement with the result for nanocrystalline YVO₄:Eu³⁺ powder and can be attributed to the finite transfer time involved in the VO₄³⁻ → Eu³⁺ energy-transfer process and the population of the 5D₀ level via the higher level (5D₁) after energy transfer, as schematically shown in Figure 7. It has been reported that the VO₄³⁻ → Eu³⁺ energy transfer is dominated by exchange interaction at room temperature, and VO₄³⁻ → Eu³⁺ energy transfer rate is of the order of 10⁷ s⁻¹ (10 μs⁻¹), which is much faster than the radiative rate of Eu³⁺ (5D₀, 10⁻⁵–10⁻⁴ s⁻¹). As a result, the excited state of Eu³⁺ (5D₀) can be populated many times (10 μs⁻¹ × 20 μs = 200) by the energy transfer from VO₄³⁻ before the depopulation occurs, resulting in the increase of emission intensity during...
allowed feature of 5D0 of YVO4:Eu3+. However, the decay curve for main emission 5D0→5F2 (617 nm) of Eu3+ (Figure 9b) cannot fit into the single-exponential function like the 5D1→5F1 emission but can be well fit into a double-exponential function as $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, and the fitting results are shown inside Figure 9b. Two lifetimes, a fast one, $\tau_1 = 134 \mu s$, and a slow one, $\tau_2 = 729 \mu s$, have been obtained for 5D0→5F2 emission of Eu3+. The double-exponential decay behavior of the activator is frequently observed when the excitation energy is transferred from the donor. A very similar situation was observed in the nanocrystalline β-Ga2O3: Dy3+ system, where an efficient energy transfer occurred from the β-Ga2O3 host to Dy3+ like YVO4:Eu3+, and a double-exponential decay of Dy3+ emission was observed upon exciting into β-Ga2O3 host at 254 nm. Hsu and Powell proposed a model for the luminescence and energy transfer in YVO4:Eu3+ and predicted that the activator (Eu3+) luminescence can exhibit either a double decay or an initial rise in the emission followed by a decay upon excitation into the VO4− absorption band of the host. Our results are consistent with this model, i.e., both the double decay (5D0→5F2, Figure 9b) and the initial rise in the emission followed by a decay (time-resolved emission spectra in Figure 8) have been observed in the YVO4:Eu3+@SiO2 core–shell phosphors. The average lifetime of Eu3+, 5D0→5F2 emission, defined as $\langle \tau \rangle = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$, can be determined to be 648 μs, which is basically in accord with the literature values given for the bulk (525 μs23 and 475 μs24) and nanocrystalline (740 μs25) YVO4: Eu3+ materials.

Tuning of the PL Intensity in the YVO4:Eu3+@SiO2 Core–Shell Phosphors. The photoluminescence intensity of YVO4: Eu3+@SiO2 core–shell phosphors can be tuned by several experimental factors, such as annealing temperature, PEG concentration in the precursor solution, and the number of coatings. Figure 10 shows photoluminescence intensity of the core–shell phosphor as a function of annealing temperature. Clearly, the PL intensity increases with raising the annealing temperature from 300 to 700 °C. This is a common phenomenon due to the improvement of crystallinity of YVO4: Eu3+ shells with raising the annealing temperature.22

The YVO4:Eu3+@SiO2 core–shell phosphors also show different PL intensity when the PEG concentration was changed in the precursor solutions. Figure 11 exhibits the photoluminescence intensity of the sample as function of the PEG concentration in the precursor solutions. The photoluminescence intensity of Eu3+ first increases with the increase of PEG concentration from 0.04 to 0.08 g/mL, reaching a maximum at PEG concentration = 0.08 g/mL, then decreases gradually until the PEG concentration increases to 0.20 g/mL. In the precursor solution, the citric acid can form chelates with the metal ions (Y3+, Eu3+). These chelates can be bonded together to form a polymer when


PEG is added (the two −OH groups in PEG can connect with the −COOH groups in citric acid via hydrogen bonding, making them more homogeneously distributed in the solution). The PEG concentration will affect the viscosity of the polymer sol solution. Low viscosity of the sol will result in easy deposition of a thin layer of YVO₄:Eu³⁺ on the SiO₂ particles, and proper increase of sol viscosity can increase the thickness of YVO₄:Eu³⁺ layer followed by the increase of PL intensity. However, when the sol viscosity exceeds a critical value, it will be difficult for the sol to be coated on the SiO₂ particles homogeneously and more organic impurities (such as −OH, −OR, −CH₂, etc.) will be introduced on the SiO₂ particles. These impurities might not be removed completely in the following annealing process and impair the photoluminescence intensity.

Another important factor affecting the photoluminescence intensity of the sample is the number of the coatings (N). The photoluminescence intensity increases with the increase of the coating number, as shown in Figure 12. Obviously this can be attributed to the increase of the thickness of YVO₄:Eu³⁺ shells on the SiO₂ spheres. The photoluminescence intensity of four-layer YVO₄:Eu³⁺ coated SiO₂ core—shell phosphor can reach about 70% that of the pure YVO₄:Eu³⁺ powder phosphor as indicated in Figure 12.

IV. Conclusions

An effective and simple sol—gel process has been developed to deposit YVO₄:Eu³⁺ layers on SiO₂ spheres. The obtained YVO₄:Eu³⁺@SiO₂ core—shell phosphors have spherical morphology, sub-micrometer size, and narrow size distribution. The spectral and kinetic properties of the core—shell phosphors are similar to those of the reported bulk and nanocrystalline YVO₄:Eu³⁺ phosphors. The photoluminescence intensity of the core—shell phosphors can be tuned.
by the annealing temperature, PEG concentration in the precursor solutions, and the number of coatings. With the increase of annealing temperature and the number of coatings, the photoluminescence intensity increases. The optimum concentration for PEG in the precursor solution is determined to be 0.08 g/mL. The current method can be extended to prepare various other core–shell phosphors with homogeneous morphology and decrease the cost of phosphors to some degree.

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