

Core–shell structured $\text{SiO}_2@YVO_4:\text{Dy}^{3+}/\text{Sm}^{3+}$ phosphor particles: Sol–gel preparation and characterization

H. Wang^{a,b}, M. Yu^{a,b,*}, C.K. Lin^a, J. Lin^{a,*}

^a Key laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b Department of Chemistry, Northeast Normal University, Changchun 130024, PR China

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Abstract

Spherical SiO_2 particles have been coated with $YVO_4:\text{Dy}^{3+}/\text{Sm}^{3+}$ phosphor layers by a Pechini sol–gel process, leading to the formation of core–shell structured $\text{SiO}_2@YVO_4:\text{Dy}^{3+}/\text{Sm}^{3+}$ particles. X-ray diffraction (XRD), Fourier-transform IR spectroscopy, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), photoluminescence (PL) spectra as well as lifetimes were used to characterize the resulting $\text{SiO}_2@YVO_4:\text{Dy}^{3+}/\text{Sm}^{3+}$ core–shell phosphors. The obtained core–shell phosphors have perfect spherical shape with narrow size distribution (average size ca. 300 nm), smooth surface and non-agglomeration. The thickness of shells could be easily controlled by changing the number of deposition cycles (20 nm for one deposition cycle). The core–shell particles show strong characteristic emission from Dy^{3+} for $\text{SiO}_2@YVO_4:\text{Dy}^{3+}$ and from Sm^{3+} for $\text{SiO}_2@YVO_4:\text{Sm}^{3+}$ due to an efficient energy transfer from YVO_4 host to them. The PL intensity of Dy^{3+} and Sm^{3+} increases with raising the annealing temperature and the number of coating cycles.

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1. Introduction

Over the past few years, spherical core–shell structured particles have been interestingly studied due to their potential applications in photonic crystals, catalyst, photonics and biological labeling [1–5]. For the core–shell structured particles, the structure, size and composition can be easily altered in a controllable way to tailor their functions [6].

The ideal morphology for phosphor particles includes a perfect spherical shape, narrow size distribution ($<2\ \mu\text{m}$), and non-agglomeration. Spherical morphology of the phosphors is good for high brightness and high resolution. Additionally, high packing densities and low scattering of light can also be obtained by using spherical phosphors [7]. So far, many synthetic routes have been developed to control the size and distribution of phosphor particles, such as spray pyrolysis [8] and urea homogeneous precipitation [9].

As host materials used for laser oscillation, YVO_4 is easy to handle and has a strong birefringence that ensures the polarization state of emitted light [10]. Eu^{3+} -activated YVO_4 is an important commercial red phosphor used in color television, the cathode ray tube and the high-pressure mercury lamp, which was first reported by Levine and Palilla [11]. If YVO_4 hosts are doped with other rare-earth ions such as Dy^{3+} and Sm^{3+} , highly efficient lasers and luminescent materials in the yellow ($YVO_4:\text{Dy}^{3+}$) or orange ($YVO_4:\text{Sm}^{3+}$) spectral regions will be produced [12]. In this paper, we developed a large-scale and facile method to obtain monodisperse and spherical core–shell structured $\text{SiO}_2@YVO_4:\text{Dy}^{3+}/\text{Sm}^{3+}$ phosphors by functionalization of silica spheres with $YVO_4:\text{Dy}^{3+}/\text{Sm}^{3+}$ layers via sol–gel process. The advantages of this method include the easy control of the morphology of the final phosphor particles by silica cores (which can be easily made controllably in spherical morphology from nano to micron size [13]) and lowering the cost of the final phosphors due to the partial substitution of cheaper SiO_2 for the expensive rare earth materials.

* Corresponding authors.

E-mail address: jlin@ns.ciac.jl.cn (J. Lin).

2. Experimental

2.1. Synthesis of silica cores

The highly monodisperse spheres of silica in the size range of 300–330 nm were synthesized by the well-known Stb er process [13]. This process produces the silica particles with a narrow size distribution in the sub-micrometer range, and the particle size depends on relative concentration of the reagent. In the current work, 0.17 mol/L of TEOS (99 wt%, analytical reagent, A.R.), 7.5 mol/L of deionized H₂O, and 1 mol/L of NH₄OH (25 wt%, A.R.) were added into absolute ethanol and stirred at room temperature for 5 h, resulting in the formation of white silica colloidal suspension. The silica particles were centrifugally separated from the suspension and washed with ethanol three times.

2.2. Coating on SiO₂ cores with YVO₄:Dy³⁺/Sm³⁺ shells

The SiO₂@YVO₄:Dy³⁺/Sm³⁺ core-shell particles were prepared by a Pechini sol-gel process [12,14]. The doping concentration of Dy³⁺ and Sm³⁺ is 2 mol% that of Y³⁺ in YVO₄ host. Stoichiometric amount of Ln₂O₃ (Ln = Y, Dy, Sm) (99.99%, Shanghai Yuelong Nonferrous Metals Ltd.) and NH₄VO₃ (99.9%, analytical reagent, A.R.) were dissolved in nitric acid HNO₃ (A.R.), and then were mixed with a water-ethanol (V/V = 1:7) solution containing citric acid (A.R.) as chelating agent for the metal ions. The molar ratio of metal ions to citric acid was 1:2. Then polyethylene glycol (PEG, molecular weight = 10 000, A.R.) was added with a final concentration of 0.10 g/mL. The solution was stirred for 3 h to form sols, and then silica particles were added and stirring. After being stirred for another 5 h, the suspension was separated by centrifugation. The particles were dried at 100 °C immediately and then annealed to the desired temperature with a heating rate of 120 °C/h and held for 2 h. The above process was repeated several times to increase the thickness of the YVO₄:Dy³⁺/Sm³⁺ shells. In this way the core-shell structured SiO₂@YVO₄:Dy³⁺ and SiO₂@YVO₄:Sm³⁺ materials were obtained. For the objective of comparison, the coating sols were evaporated to form gels, and then the gels were annealed in a similar process to produce the pure YVO₄:Dy³⁺/Sm³⁺ phosphors.

2.3. Characterization

The X-ray diffraction (XRD) of the powder samples was examined on a Rigaku-Dmax 2500 diffractometer using CuK α radiation ($\lambda = 0.15405$ nm). FT-IR spectra were measured with Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. The morphology of the samples was inspected using a field emission scanning electron microscope (FESEM, XL30, Philips) and a transmission electron microscope (JEOL-2010, 200 kV). The excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. Luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using 280 nm laser (pulse width =

4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO). All the measurements were performed at room temperature (RT).

3. Results and discussion

3.1. Formation and morphology of core-shell particles

The formation and morphology of studied core-shell particles were performed representatively on SiO₂@YVO₄:Dy³⁺ sample by XRD, FT-IR, FESEM and TEM, respectively. The results for SiO₂@YVO₄:Sm³⁺ are similar to those of SiO₂@YVO₄:Dy³⁺ and will not further be performed and shown here.

3.1.1. XRD

Fig. 1 shows the XRD patterns for the 700 °C annealed SiO₂ (a), core-shell SiO₂@YVO₄:Dy³⁺ (b), pure YVO₄:Dy³⁺ powder samples (c) as well as the JCPDS card (No. 17-0341) for YVO₄ (d) as a reference, respectively. For SiO₂ particles annealed at 700 °C (Fig. 1a), no diffraction peak is observed except for a broad band centered at $2\theta = 22.00^\circ$, which is the characteristic peak for amorphous SiO₂ (JCPDS 29-0085). For the SiO₂@YVO₄:Dy³⁺ core-shell particles annealed at 700 °C (Fig. 1b), apart from the broad band from amorphous SiO₂ ($2\theta = 22.00^\circ$), diffraction peaks at $2\theta = 18.76^\circ$ (101), 25.0° (200), 33.6° (112), 35.58° (220), 38.20° (202), 40.68° (301), 45.06° (103), 48.42° (321), 49.82° (312), 51.28° (400), 57.96° (420), 62.78° (332) and 64.82° (204) are present, all of which can be indexed to pure YVO₄ phase (JCPDS Card 17-0341). This indicates that the layer of YVO₄:Dy³⁺ has crystallized on the surface of amorphous silica spheres. No other phase is detected for SiO₂@YVO₄:Dy³⁺ core-shell sample annealed at 700 °C. In general, the nanocrystallite size can be estimated from the Scherrer formula: $D_{hkl} = K\lambda/(\beta \cos \theta)$, where λ is the X-ray wavelength (0.15405 nm), β is the full-width at half-maximum, θ is the diffraction angle, K is a constant (0.89) and D_{hkl} means the size along (hkl) direction [15]. Here the diffraction data along the (200), (112) and (312) direction were

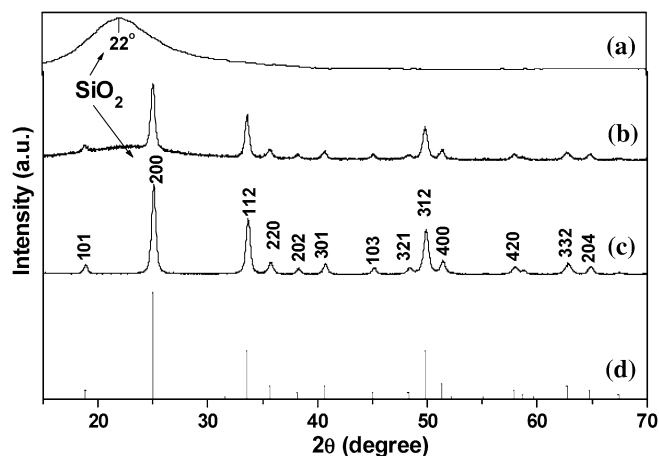


Fig. 1. X-ray diffraction patterns for SiO₂ (a), SiO₂@YVO₄:Dy³⁺ core-shell particles (b), pure YVO₄:Dy³⁺ powders (c) and the JCPDS card 17-0341 for YVO₄ (d). All the samples were obtained after annealing at 700 °C for 2 h.

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