

Polyol synthesis of $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanophosphors and effect of silica coating on their photoluminescence properties

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$\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanophosphor is prepared from sodium orthovanadate and nitrates of yttrium, bismuth, and europium in a polyol solvent of diethylene glycol at 160 °C. The photoluminescence (PL) intensity of the nanophosphor is enhanced by a factor of 3.3 after silica coating via reverse micelle method. The gradual increase in the PL intensity is observed under the continuous excitation irrespective of silica coating. This increase in the PL intensity is attributed to the photooxidation of V^{4+} to V^{5+} , as confirmed by electron spin resonance spectroscopy. Finally, a highly luminescent and photostable nanophosphor can be prepared by combination of photooxidation pre-treatment and silica coating.

Key words: $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$, Nanophosphor, Polyol synthesis, Silica coating, Photostability.

Introduction

Nanosizing the inorganic crystalline phosphors has attracted much attention in many fields from the aspects of higher transparency in comparison with micron-sized inorganic phosphors, and higher photostability in comparison with organic fluorescent dyes. However, some kinds of nanosized phosphors show peculiar photobleaching behavior, i.e., the decrease in the photoluminescence (PL) intensity under the continuous excitation. We reported the wet chemical synthesis of red-emitting $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanophosphors via citrate precursor after the Boilot's method [1]. This $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanophosphor shows a photobleach under the irradiation of near UV light [2]. This photobleach is attributed to the photoreduction of V^{5+} to V^{4+} by citrate ions coordinating to the surface of nanoparticles and the simultaneous formation of oxygen vacancies, although the photobleach is remarkably suppressed by removing citrate ions using washing and hydrothermal post-treatments [3,4]. In this work, we synthesize $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanophosphor by wet chemical method without citrate ions, i.e., by polyol method. We also coat it with silica by reverse micelle method and discuss their PL and photostability properties.

Experimental Procedure

Synthesis of $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanoparticles by polyol

method

Sodium orthovanadate (V) heptahydrate (2.0 mmol, Mitsuwa, 99.0%) was dissolved in 30 mL of diethylene glycol (DEG, Kanto, 99.5%) at 60 °C. Yttrium nitrate (III) hexahydrate (0.70 mmol, Kanto, 99.99%), bismuth (III) nitrate pentahydrate (0.15 mmol, Kanto, 99.5%), and europium (III) nitrate hexahydrate (0.15 mmol, Kanto, 99.95%) were dissolved in 20 mL of DEG at 160 °C. Then both solutions were mixed, aged at 160 °C for 1 hr, and cooled rapidly to obtain the transparent colloidal solution of $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanoparticles (named S(YVO_4)). The DEG solvent was replaced with ultrapure water by dialysis to obtain the aqueous colloidal solution of S(YVO_4).

Coating of $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanoparticles with silica by reverse micelle method

Bis(2-ethylhexyl) sulfosuccinate sodium (AOT, 0.0168 mol, Wako, 75.0%) and 2.4 mL of ultrapure water were dissolved in 70 mL of n-heptane (Kanto, 99.0%) to obtain the reverse micellar (RM) solution. Next, 100 mL of aqueous colloidal solution of S(YVO_4) was dropped to 20 mL of the RM solution to obtain the RM colloidal solution of S(YVO_4). Then 50 mL of ammonia solution (Nacalai tesque, 28%) and 500 mL of the n-heptane solution of tetraethoxysilane (Kanto, 99%) were dropped in this order into 20 mL of this solution to obtain the silica-coated $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanoparticles (named S($\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ @ SiO_2)). We also prepared the silica-coated sample after the UV light irradiation: the RM colloidal solution of S(YVO_4) was irradiated by UV light for 2 hrs using a commercial 6 W UV lamp (UVP, 302 nm, 3.5 mW cm²) to obtain the UV-irradiated $\text{YVO}_4\text{:Bi}^{3+},\text{Eu}^{3+}$ nanoparticles (named S(YVO_4 -

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UV)). Then this sample was coated with silica by the same procedure to obtain the silica-coated sample with the UV light irradiation pre-treatment (named $\text{S}(\text{YVO}_4\text{-UV@SiO}_2)$).

The respective DEG and RM colloidal solutions were washed with ethanol using the centrifugation at 10,000 rpm for 15 min three times. The obtained precipitates were dried at 50 °C for 1 day to obtain the powdered samples $\text{S}(\text{YVO}_4)$ and $\text{S}(\text{YVO}_4\text{-UV})$.

Characterization

The powder X-ray diffraction (XRD) profile was measured using an X-ray diffractometer (Rigaku, Rint-2200) with a $\text{Cu K}\alpha$ radiation source. The metallic composition of the powdered sample was determined using an X-ray fluorescent analyzer (XRF, Rigaku, ZSXmini II) by means of the fundamental parameter method. The specific surface area was measured using an automatic surface area analyzer (Micromeritics, Tristar II 3020) by means of the BET-nitrogen adsorption method. The particle morphology was observed using a transmission electron microscope (TEM, Technai 12, accelerating voltage 120 kV) equipped with an energy dispersive X-ray spectrometer (EDX). The TEM sample was prepared by dropping a diluted RM colloidal solution of the sample on a copper microgrid and dried at 50 °C. PL and its excitation (PLE) spectra, and the change in the PL intensity under the continuous excitation were measured using a fluorescence spectrometer (JASCO, FP-6500) with a 150 W Xe lamp. The spectral response was calibrated using an ethylene glycol solution of Rhodamine B (5.5 g L^{-1}) and a standard light source (JASCO, ESC-333). Electron spin resonance (ESR) spectrum of the powdered sample was recorded at room temperature using a spectrometer (Bruker, ELEXSYS E500) operating in the X-band frequency with a modulation frequency of 100 kHz.

Results and Discussion

Particulate and photoluminescent properties

The as-prepared sample $\text{S}(\text{YVO}_4)$ is the phase-pure vanadate compound with tetragonal zircon-type structure, as confirmed from the XRD profile (Fig. 1). The XRF analysis reveals that the molar ratio of $\text{Y}:\text{Bi}:\text{Eu}$ for this sample is 60.8:22.8:16.4. The specific surface area of this sample is $142 \text{ m}^2 \text{ g}^{-1}$, and hence the primary particle size is estimated to be 8.4 nm assuming that particles are spherical in shape.

Aggregated nanoparticles are observed for the sample $\text{S}(\text{YVO}_4)$, as shown in the TEM image of Fig. 2(a). These nanoparticles are embedded in silica matrix for the silica-coated sample, $\text{S}(\text{YVO}_4\text{@SiO}_2)$, as shown in Fig. 2(b). The qualitative EDX spectroscopy (Fig. 2(c)) of this sample detects Si, S, and Na besides Y and V, indicating the existence of silica shell around nanoparticles and residual AOT molecules adsorbed on

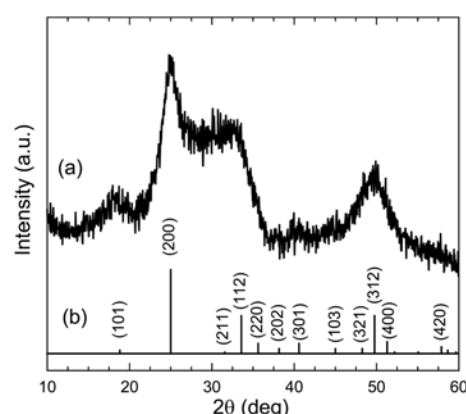


Fig. 1. XRD profiles of (a) the powdered sample of $\text{S}(\text{YVO}_4)$ and (b) ICDD card data of YVO_4 (No. 17-341).

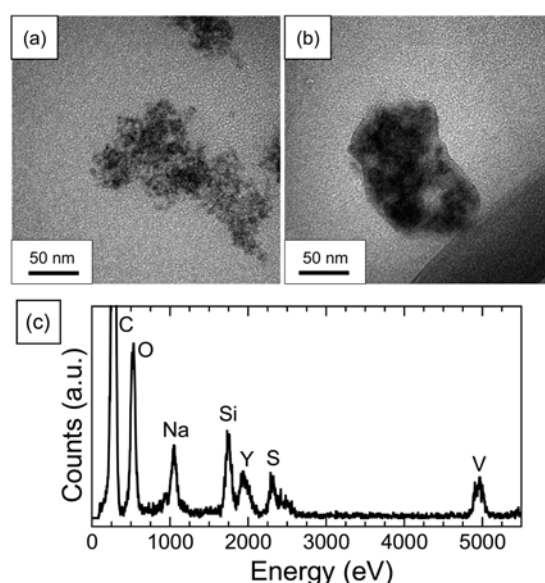


Fig. 2. TEM images of (a) $\text{S}(\text{YVO}_4)$ and (b) $\text{S}(\text{YVO}_4\text{@SiO}_2)$ and (c) EDX spectrum of image (b).

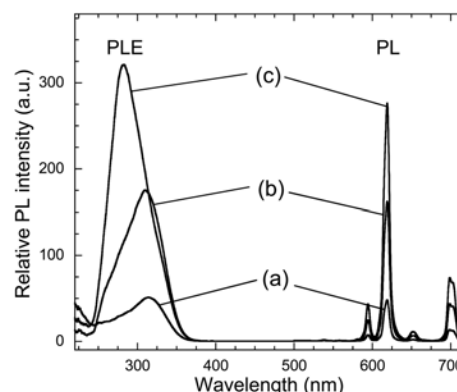


Fig. 3. PL and PLE spectra of RM colloidal solutions. (a) $\text{S}(\text{YVO}_4)$, (b) $\text{S}(\text{YVO}_4\text{@SiO}_2)$, and (c) $\text{S}(\text{YVO}_4\text{-UV@SiO}_2)$.

silica-coated nanoparticles.

Fig. 3(a) and (b) shows the PL and PLE spectra of the RM colloidal solutions of $\text{S}(\text{YVO}_4)$ and $\text{S}(\text{YVO}_4\text{@SiO}_2)$, respectively. The broad PLE band in

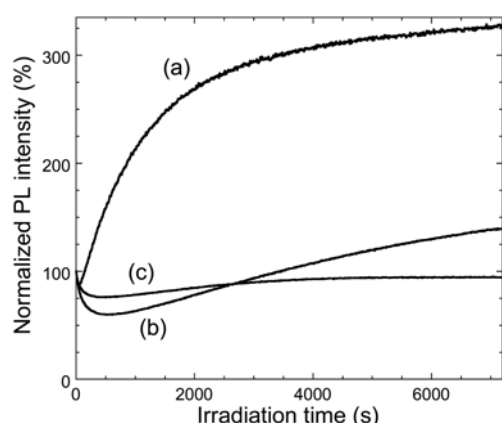


Fig. 4. Change in the PL intensities of RM colloidal solutions with the irradiation time of UV light. (a) S(YVO₄), (b) S(YVO₄@SiO₂), and (c) S(YVO₄-UV@SiO₂).

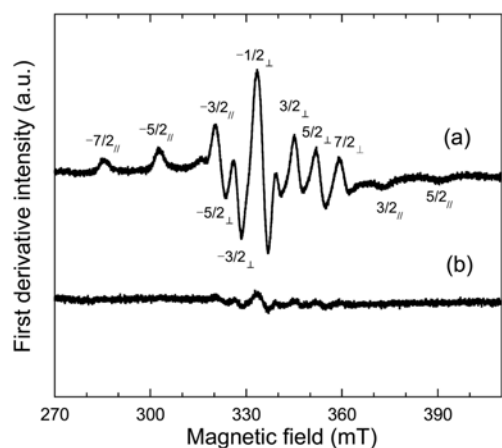


Fig. 5. ESR spectra of the powdered samples (a) S(YVO₄) and (b) S(YVO₄-UV).

the wavelength region of 250 - 370 nm is composed of two broad excitation peaks. Two peaks in the wavelength regions of 250 - 350 nm and 340 - 370 nm correspond to the charge transfer (CT) transitions from O²⁻ to V⁵⁺ and from Bi³⁺ to V⁵⁺, respectively, followed by energy transfer to Eu³⁺. The sharp PL peaks corresponding to the f-f transitions of Eu³⁺ are observed at 595 nm (⁵D₀ - ⁷F₁), 619 nm (⁵D₀ - ⁷F₂), 652 nm (⁵D₀ - ⁷F₃), and 699 nm (⁵D₀ - ⁷F₄). The PL intensity of the sample is enhanced by a factor of 3.3 by silica coating. This is attributed to the suppression of non-radiative relaxation by capping surface defects with silica.

Photostability property

Fig. 4 shows changes in the normalized PL intensity at 619 nm with the irradiation time of 302 nm UV light using the Xe lamp of the fluorescence spectrometer, for the RM colloidal solutions. The PL intensity of the sample S(YVO₄) (Fig. 4(a)) decreases to 88% of the initial value after the irradiation for 40 s, and then gradually increases and converges to ~330% after the irradiation for 7200 s. The silica-coated sample S(YVO₄@SiO₂) also shows similar behavior (Fig. 4(b)), but its change in the

PL intensity is smaller and slower than that of the sample S(YVO₄).

To investigate the reason for the change in the PL intensity, we measured the ESR spectra of the samples before and after the UV light irradiation using the commercial UV lamp. The octet signal due to the paramagnetic V⁴⁺ ions is observed for the as-prepared sample S(YVO₄), as shown in Fig. 5(a). The intensity of this signal for the UV-irradiated sample S(YVO₄-UV) is 1/8 times as high as that of the sample S(YVO₄), as shown in Fig. 5(b). At the same time, the color of the sample S(YVO₄) changes from brown to white after the irradiation of UV light. These results suggest that V⁵⁺ is reduced to V⁴⁺ by DEG molecules during polyol synthesis and that oxygen vacancies, i.e., color centers, are simultaneously formed to keep charge balance. At the beginning of UV light irradiation, the amounts of these V⁴⁺ and oxygen vacancies increase through photoreduction of V⁵⁺ to V⁴⁺ by DEG coordinating to the surface of the nanoparticles, resulting in the photobleaching. In contrast, after prolonged UV irradiation, i.e., after complete photodecomposition of DEG, the amount of these V⁴⁺ and oxygen vacancies decreases through photooxidation from V⁴⁺ to V⁵⁺, resulting in the increase in the PL intensity as shown in Fig. 4.

On the basis of the above-mentioned results, we tried to prepare the more photostable sample by silica coating after the UV light irradiation pre-treatment. As shown in Fig. 3(c), the PL intensity of the sample S(YVO₄-UV@SiO₂) is higher than those of the samples S(YVO₄) and S(YVO₄@SiO₂) because of surface passivation by silica coating in addition of the PL enhancement by UV light irradiation pre-treatment. The PLE peak for the sample S(YVO₄-UV@SiO₂) apparently shifts toward shorter wavelengths as compared to the samples S(YVO₄) and S(YVO₄@SiO₂), because the increase in the PL intensity under the excitation of O - V CT band (250 - 350 nm) is more prominent than that under the excitation of Bi - V CT band (340 - 370 nm). This might be explained by the difference in effects of surface passivation against two PL mechanisms, O - V and Bi - V CTs followed by energy transfer to Eu³⁺. Moreover, the change in the PL intensity of the sample S(YVO₄-UV@SiO₂) during the irradiation is smallest of all the three samples, as shown in Fig. 4(c).

Conclusions

YVO₄:Bi³⁺,Eu³⁺ nanophosphor of 8.4 nm in size with tetragonal zircon-type structure is synthesized by polyol method using DEG as a solvent. During polyol synthesis, a part of V⁵⁺ ions is reduced to V⁴⁺ ions which are accompanied with the formation of oxygen vacancies, leading to the low PL intensity. The amounts of these V⁴⁺ and oxygen vacancies decrease after the UV light irradiation, resulting in the gradual increase of PL intensity. On the other hand, silica coating increases the

PL intensity by a factor of 3.3 due to surface passivation. Based on these results, we demonstrate that the nanophosphor with high PL intensity and high photostability can be obtained by the UV light irradiation pre-treatment followed by silica coating.

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