

Preparation of Transparent Red-Emitting $\text{YVO}_4\text{:Eu}$ Nanophosphor Suspensions

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Received October 9, 2010, Accepted October 30, 2010

Key Words: Transparent suspension, $\text{YVO}_4\text{:Eu}$ nanophosphor, Photoluminescence

Inorganic nanophosphors are in high demand for advanced flexible and transparent display devices.¹⁻⁴ Because inorganic nanophosphors do not show any scattering effect in the visible region, transparent luminescent matrices can be fabricated by embedding inorganic nanophosphors on transparent matrices, such as glass and plastics.⁵⁻⁸ However, nanophosphors agglomerate easily. Accordingly, the preparation of monodispersed inorganic nanophosphors is essential for the formation of transparent suspensions.

$\text{YVO}_4\text{:Eu}$ is a well-known bright red-emitting phosphor that is used in cathode ray tubes (CRTs) and fluorescent lamps.^{9,10} Normally, micron-sized $\text{YVO}_4\text{:Eu}$ phosphors are prepared by solid state reactions.¹¹⁻¹³ Nano-sized $\text{YVO}_4\text{:Eu}$ phosphors have been prepared by sonochemical methods, hydrothermal reactions and polymer complex processing methods.¹⁴⁻¹⁹ $\text{YVO}_4\text{:Eu}$ thin films have been prepared through various techniques such as pulsed laser deposition (PLD), chemical vapor deposition (CVD), and electrochemical method.²⁰⁻²² In general, these techniques need expensive and complicated equipment set-ups, and complicated processing. Colloidal $\text{YVO}_4\text{:Eu}$ phosphors can be synthesized and stabilized by sodium hexametaphosphate.^{23,24} The preparation of colloids makes possible an alternative approach to fabrication of $\text{YVO}_4\text{:Eu}$ thin films by dispersion of colloidal $\text{YVO}_4\text{:Eu}$ phosphors in polymer matrix.²⁵ However, there are few reports on the preparation of $\text{YVO}_4\text{:Eu}$ nanophosphors for transparent suspensions. This paper reports a simple synthetic method for $\text{YVO}_4\text{:Eu}$ nanophosphors and its transparent suspensions. A simple and room temperature processing method for fabrication of the transparent and flexible

$\text{YVO}_4\text{:Eu}$ thin film is also reported.

Figure 1 shows the powder X-ray diffraction (XRD) patterns of the as-prepared $\text{YVO}_4\text{:Eu}$ nanophosphors. A series of Bragg reflections in the XRD pattern can be indexed perfectly as tetragonal YVO_4 (JCPDS 17-0341, $a = 0.7119$ nm, $c = 0.6289$ nm). Since the mole fraction of europium to yttrium is only 0.05, the europium ion is expected to occupy the yttrium sites in YVO_4 . Moreover, the ionic radius of Eu^{3+} (0.095 nm) is slightly larger than that of Y^{3+} (0.089 nm), allowing easy insertion into the yttrium site in YVO_4 .²⁶ No other peaks were observed in the XRD pattern, indicating that $\text{YVO}_4\text{:Eu}$ had been successfully synthesized.

Figure 2(a) presents transmission electron microscopy (TEM) images of the $\text{YVO}_4\text{:Eu}$ nanophosphor. Well organized superlattices were observed. Individual $\text{YVO}_4\text{:Eu}$ nanowires with lengths and widths of 15 nm and 3 nm, respectively, were obtained, as shown in Figure 2(b) and 2(c). A series of self-assembled superlattices were formed due to the presence of surfactant molecules on the external surfaces of the nanowires. The high-resolution TEM (HRTEM) image of an individual $\text{YVO}_4\text{:Eu}$ crystal revealed a lattice spacing between the different layers of 0.26 nm, which corresponds to the (112) plane of a tetragonal

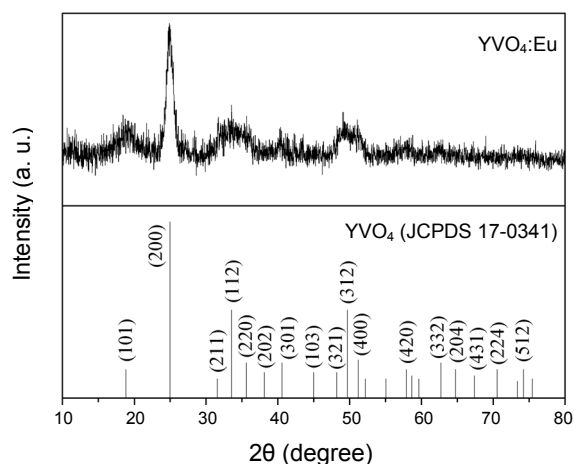


Figure 1. XRD patterns of the $\text{YVO}_4\text{:Eu}$ nanophosphor.

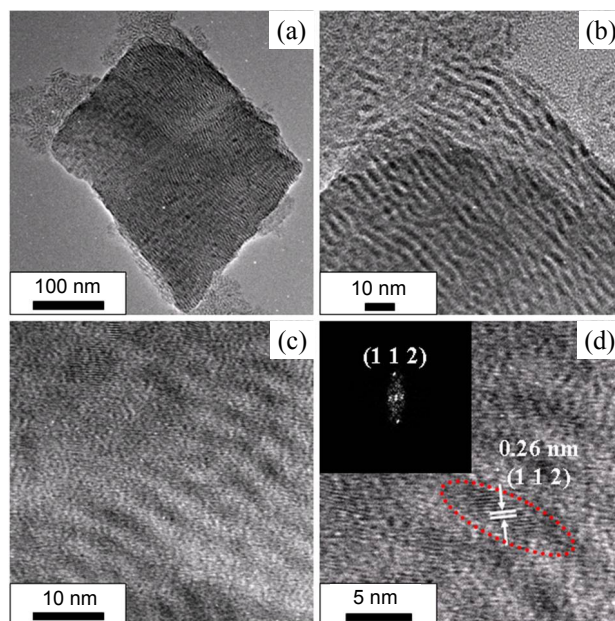


Figure 2. (a-c) TEM and (d) HRTEM images of the $\text{YVO}_4\text{:Eu}$ nanophosphor with different magnifications. The inset in (d) shows the FFT patterns of individual $\text{YVO}_4\text{:Eu}$ nanowires.

YVO₄ crystal, as shown in Figure 2(d). The inset in Figure 2(d) shows the fast Fourier transform (FFT) patterns of the YVO₄:Eu crystal corresponding to the lattice fringes. The HRTEM image of an individual YVO₄:Eu crystal revealed its highly crystalline nature.

Figure 3(a) and 3(b) shows the photoluminescence excitation and emission spectra of the YVO₄:Eu nanophosphor, respectively. The broad excitation band at approximately 310 nm arose from a charge transfer transition between Eu³⁺ and VO₄³⁻ anions.^{13,24} The emission spectrum, which consisted of a series of emission lines between 550 and 750 nm, were assigned to transitions from the ⁵D₀ → ⁷F_J of Eu³⁺. The strongest red emission line at 618 nm was assigned to the ⁵D₀ → ⁷F₂ transition. The chromaticity coordinates of the YVO₄:Eu nanophosphor were x = 0.64 and y = 0.34, which is close to the National Television Standard Committee (NTSC) red coordinate of x = 0.67 and y = 0.33.²⁷ Therefore, YVO₄:Eu can be used as a red-emitting phosphor excited by UV irradiation.

YVO₄:Eu suspension was obtained by dispersing the YVO₄:Eu nanophosphors in toluene. The YVO₄:Eu nanophosphor suspension was highly transparent, as shown in Figure 4(a), and quite stable without sedimentation after being left to stand for weeks. The dispersion of YVO₄:Eu nanophosphors in non-polar toluene was attributed to oleic acid and oleylamine capping

agents. The surfactants made the surface of the YVO₄:Eu nanophosphors hydrophobic, which protected them from agglomeration in nonpolar organic solvents. Therefore, oleic acid and oleylamine play an important role in preparing transparent YVO₄:Eu suspensions. Intense red light emission was observed under a 254 nm hand-held UV light, as shown in Figure 4(b).

The YVO₄:Eu suspension was mixed with PAS ink and applied as a 30 μm thick film to commercial overhead transparency film using an applicator. Figure 4(c) shows the YVO₄:Eu nanophosphor coated layer on the overhead transparency film. Both the uncoated film and YVO₄:Eu nanophosphor coated film showed high transparency according to naked eye observations in daylight. Figure 4(d) presents a flexible YVO₄:Eu nanophosphor coated layer on an overhead film under UV lamp irradiation. The emitted color of the film was slightly different from that of the YVO₄:Eu nanophosphor suspension in toluene due to the commercial overhead transparency containing optical bleaching agents. The observed color was generated by additive color mixing of the deep-red light emitted by the YVO₄:Eu nanophosphor and the violet light emitted by the optical bleaching agents in the overhead transparency itself pumped by the UV lamp.

The UV-vis spectra were recorded to compare the optical transparency of the uncoated overhead film and YVO₄:Eu nanophosphor coated overhead film, as shown in Figure 5. The reflection of the transparency was affected slightly due to the PAS ink. This indicates that the YVO₄:Eu nanophosphor coated layer on an overhead film has excellent visible transparency and can be used for flexible and transparent display devices.

In conclusion, YVO₄:Eu nanophosphor were prepared using a surfactant-assisted hydrothermal reaction of Y(NO₃)₃, Eu(NO₃)₃ and NH₄VO₃. Well superlatticed YVO₄:Eu nanowires, 15 nm in length, were obtained. Oleic acid and oleylamine were used

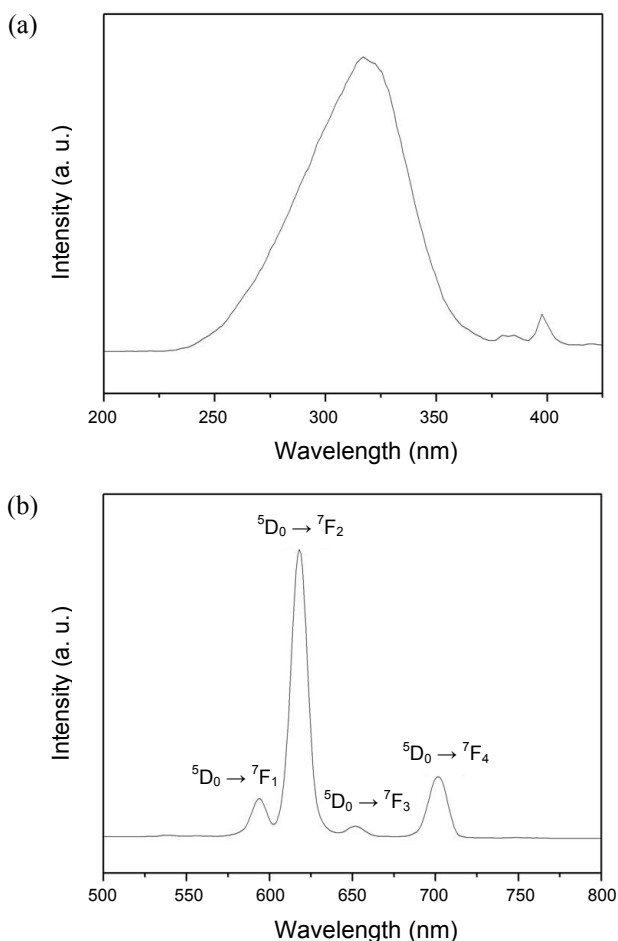


Figure 3. Photoluminescence (a) excitation ($\lambda_{em} = 618$ nm) and (b) emission ($\lambda_{ex} = 310$ nm) spectra of YVO₄:Eu nanophosphor.

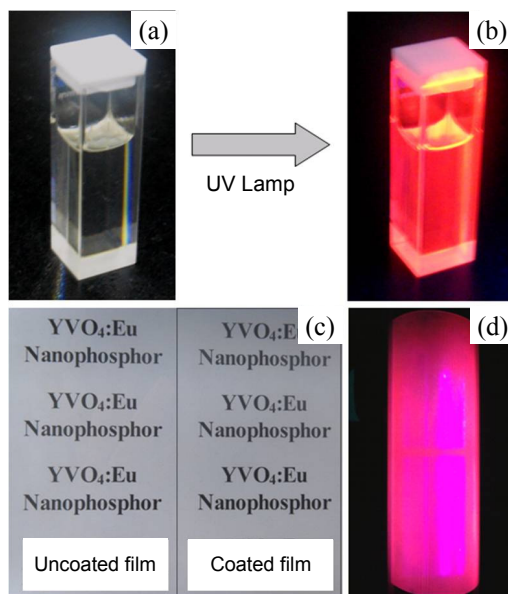


Figure 4. Transparent suspensions of YVO₄:Eu nanophosphors in toluene (a) in daylight and (b) under UV excitation. (c) Photograph of the transparent YVO₄:Eu nanophosphor coated layer on overhead transparency film. (d) Photograph of the flexible YVO₄:Eu nanophosphor coated layer on overhead film under UV excitation.

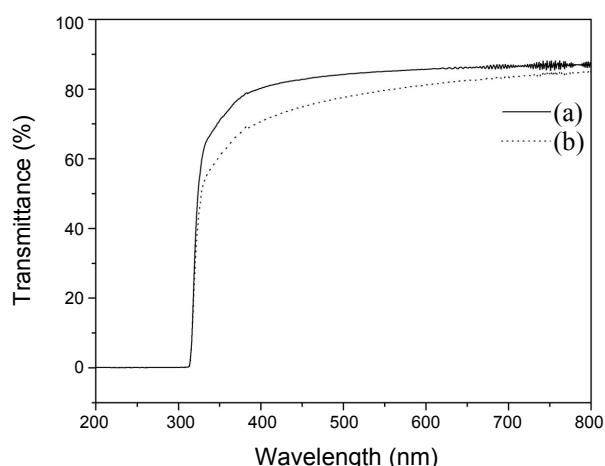


Figure 5. UV-vis transmittance of (a) the original overhead transparency film and (b) YVO₄:Eu nanophosphor coated layer on overhead transparency film.

as the capping agents of the YVO₄:Eu nanophosphors. A highly transparent suspension was obtained by dispersing the YVO₄:Eu nanophosphor in toluene, which was stable after being left to stand for several weeks. This suspension was found to be suitable for transparent red-emitting phosphors by excited UV light. A simple and efficient method for fabrication of the flexible and transparent display devices was also confirmed by preparing a YVO₄:Eu nanophosphor coated layer on overhead film.

Experimental Section

Y(NO₃)₃·6H₂O (Aldrich), Eu(NO₃)₃·6H₂O (Aldrich), NH₄VO₃ (Aldrich), sodium oleate (TCI), oleic acid (Aldrich) and oleylamine (TCI) were used as received. In a typical synthesis, 0.3325 M of Y(NO₃)₃·6H₂O and 0.0175 M of Eu(NO₃)₃·6H₂O were dissolved in 10 mL of water. The mole fraction of Eu to Y was 0.05. Subsequently, 1.06 g of sodium oleate, 5 mL of oleic acid, 5 mL of oleylamine and 40 mL of hexane were added to the above solution with vigorous stirring at room temperature for 1 h. 0.350 M of NH₄VO₃ was dissolved in 10 mL of water. The pH of the NH₄VO₃ aqueous solution was adjusted to 9.0 by the dropwise addition of an ammonium hydroxide solution with vigorous stirring. The two optically transparent solutions were mixed. The mixed solution was transferred to a 100 mL Teflon-lined autoclave, and heated to 180 °C for 12 h. The autoclave was cooled naturally to room temperature. The solution in a hexane layer was separated from the bottom solution of an aqueous layer by a separating funnel. The hexane solution was centrifuged at 4000 rpm for 15 min. A clear top solution was obtained by separating the bottom nontransparent solution. The YVO₄:Eu nanoparticle precipitate was obtained by adding 40 mL of ethanol to the clear solution. The precipitate was centrifuged, washed several times with water and ethanol, and dried at 60 °C for 12 h.

0.05 g of the YVO₄:Eu nanophosphor was dispersed in 3 mL of toluene in a 10 mL vial for 10 min. 2.0 g of PAS (series 800, Jujo) ink was dispersed into the above mixture and stirred for 15 min. The YVO₄:Eu suspension was coated onto commercial

overhead transparency film to a thickness of 30 μm using an applicator.

The structures of the as-prepared YVO₄:Eu phosphor were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) using Cu Kα radiation. The morphology of the products was observed by transmission electron microscopy (TEM, JEOL JEM-3010). The photoluminescence excitation and emission spectra of the YVO₄:Eu phosphor was measured using a spectrum analyzer (DARSA, PSI) with a 27.5 cm monochromator, a photomultiplier tube and a 500 W Xe lamp as the excitation source. The incident beam was perpendicular to the sample surface and the observation angle was 45° relative to the excitation source. A hand-held 12 W UV lamp (Uvitec, λ_{max} = 254 nm) was used for UV excitation of the YVO₄:Eu suspension.

Acknowledgments. This study was supported by the research fund of Dankook University in 2010.

References

1. Meyssamy, H.; Riwozki, K.; Kornowski, A.; Naused, S.; Hasse, M. *Adv. Mater.* **1999**, *11*, 10.
2. Boilot, J. P.; Gacoin, T.; Perruchas, S. *C. R. Chimie* **2010**, *13*, 186.
3. Wang, H.; Uehara, M.; Nakamura, H.; Miyazaki, M.; Maeda, H. *Adv. Mater.* **2005**, *17*, 2506.
4. Gupta, B. K.; Haranath, D.; Saini, S.; Singh, V. N.; Shanker, V. *Nanotech.* **2010**, *21*, 055607.
5. Chai, R.; Lian, H.; Yang, P.; Fan, Y.; Hou, Z.; Kang, X.; Lin, J. J. *Colloid Interface Sci.* **2009**, *336*, 46.
6. Song, W. S.; Choi, H. N.; Kim, Y. S.; Yang, H. *J. Mater. Chem.* **2010**, *20*, 6929.
7. Bühler, G.; Feldmann, C. *Appl. Phys. A* **2007**, *87*, 631.
8. Seo, K. I.; Park, J. H.; Kim, J. S.; Kim, G. C.; Yo, J. H. *J. Lumin.* **2009**, *129*, 715.
9. Ozawa, L.; Itoh, M. *Chem. Rev.* **2003**, *103*, 3835.
10. Jüstel, T.; Nikol, H.; Ronda, C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3084.
11. Ropp, R. C. *J. Electrochem. Soc.* **1968**, *115*, 940.
12. Rambabu, U.; Amalnerkar, D. P.; Kale, B. B.; Buddhudu, S. *Mater. Res. Bull.* **2000**, *35*, 929.
13. Tian, L.; Mho, S. I. *J. Lumin.* **2007**, *122-123*, 99.
14. Zhu, L.; Li, J.; Li, Q.; Liu, X.; Meng, J.; Cao, X. *Nanotech.* **2007**, *18*, 055604.
15. Sun, L.; Zhang, Y.; Zhang, J.; Yan, C.; Liao, C.; Lu, Y. *Solid St. Commun.* **2002**, *124*, 35.
16. He, F.; Yang, P.; Niu, N.; Wang, W.; Gai, S.; Wang, D.; Lin, J. J. *Colloid Interface Sci.* **2010**, *343*, 71.
17. Wang, J.; Xu, Y.; Hojamberdiev, M.; Wang, M.; Zhu, G. *Mater. Chem. Phys.* **2010**, *119*, 169.
18. Cho, Y. S.; Huh, Y. D. *Bull. Korean Chem. Soc.* **2010**, *31*, 2368.
19. Althues, H.; Simon, P.; Kaskel, S. *J. Mater. Chem.* **2007**, *17*, 758.
20. Yi, S. S.; Bae, J. S.; Choi, B. C.; Shim, K. S.; Yang, H. K.; Moon, B. K.; Jeong, J. H.; Kim, J. H. *Opt. Mater.* **2006**, *28*, 703.
21. Bai, G. R.; Zhang, H.; Foster, C. M. *Thin Solid Films* **1998**, *321*, 115.
22. Watanabe, T.; Cho, W. S.; Suchanek, W. L.; Endo, M.; Ikuma, Y.; Yoshimura, M. *Solid State Sci.* **2001**, *3*, 183.
23. Huignard, A.; Gacoin, T.; Boilot, J. P. *Chem. Mater.* **2000**, *12*, 1090.
24. Riwozki, K.; Hasse, M. *J. Phys. Chem. B* **2001**, *105*, 12709.
25. Althues, H.; Simon, P.; Kaskel, S. *J. Mater. Chem.* **2007**, *17*, 758.
26. Weast, R. C. *Handbook of Chemistry and Physics*, 70th ed.; 1989; F-187.
27. Kojima, T. *Phosphor Handbook*; Shionoya, S., Yen, W. M., Eds.; CRC Press: New York, 1998; Ch. 10.