

## Changes in the Moisture Stability of CaS:Eu<sup>2+</sup> Phosphors with Surface Coating Methods

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**Abstract:** To improve the moisture stability of the CaS:Eu<sup>2+</sup> red phosphor, surface coatings with silica nanoparticles were performed using five different methods, i.e., P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub>, and P<sub>5</sub>. The phosphors were coated with silica nanoparticles using a dip coating method (P<sub>1</sub>) and sol-gel method (P<sub>2</sub>). The phosphors were coated using a solution containing silica nanoparticles and poly(1-vinyl-2-pyrrolidone), PVP, (P<sub>3</sub>). The phosphors were also coated with silica nanoparticles by reacting with the 1-vinyl-2-pyrrolidone (VP) monomer (P<sub>4</sub>) or by reacting with mixtures containing VP and tetraethylorthosilicate (P<sub>5</sub>). A decrease in the photoluminescence (PL) intensity was observed regardless of the coating methods. However, the moisture stability of the phosphors was enhanced by the coating when aged in a temperature-controlled humidity chamber. Among these methods, the P<sub>4</sub> (or P<sub>5</sub>) method exhibited the greatest increase in moisture stability of the phosphors. The coated phosphors showed a relatively constant intensity with aging time, whereas the uncoated phosphor showed a decrease.

**Keywords:** CaS:Eu<sup>2+</sup> red phosphors, silica nanoparticles, phosphor coating, moisture stability.

### Introduction

Phosphors have been widely used in various applications such as plasma display panels (PDP) and light emitting diodes (LED).<sup>1-10</sup> In particular, white LEDs fabricated from phosphors are gaining significant attention because they have many advantages over the existing incandescent lamps.<sup>6-12</sup> Even though a blue light GaN (gallium nitride) LED chip loaded with a yellow phosphor is now widely used as a conventional white LED, this combination has serious drawbacks in the color rendering index. Because of this, the white LEDs based on red, green, and blue primary colors have been explored.<sup>3-11</sup> Since the photoluminescence (PL) intensity of the red phosphor is lower than that of the green and blue phosphors, the use of a phosphor mixture containing a large amount of red phosphors is required for sufficient color rendering.<sup>8-10</sup> The alkaline earth sulfides are widely used as the red emitting phosphors. Among the red phosphors, CaS:Eu<sup>2+</sup> is considered as the most promising red emitting phosphor because of its deep red emission with nice color purity.<sup>9-13</sup> However, the application of CaS:Eu<sup>2+</sup> has been limited by their instability when exposed to moisture. The problems with red phosphors should be solved for the advancement of white LEDs.

To overcome the drawbacks of the red phosphor, numerous studies have been performed.<sup>10-16</sup> Various alkaline earth

sulfides with rare earth ion activators exhibiting performance advantages over the CaS:Eu<sup>2+</sup> red phosphors have been introduced. However, the application of alkaline earth sulfides has been limited by their instability. The phosphor surface is often coated with oxides such as silica, ZnO, MgO, and organic polymers to yield excellent moisture stability of the phosphors and to improve the adhesion strength between phosphors and glass substrates. The coating has to be transparent, and a precise amount of coating must cover the surface of the individual phosphor particle homogeneously to minimize the decrease in PL intensity. From a stability point of view, a layer-like homogeneous coating would be also preferred over an island-like inhomogeneous coating.<sup>13-18</sup> In this study, coating of the phosphor with silica nanoparticles was performed using five different techniques to improve moisture stability of CaS:Eu<sup>2+</sup> red phosphor and to minimize the decrease in PL intensity. Changes in the morphology, PL intensity, and moisture stability of the phosphor with coating were explored.

### Experimental

High purity CaS:Eu<sup>2+</sup> red phosphor was supplied by Seoul Semiconductor Co. (Seoul, Korea). Tetraethylorthosilicate (TEOS), 1-vinyl-2-pyrrolidone (VP), poly(1-vinyl-2-pyrrolidone) (PVP, weight average molecular weight=10,000), and absolute methanol were purchased from Aldrich Chemical Co. Reagent grade ammonium hydroxide (30% NH<sub>3</sub>)

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and 2,2'-azobis(2-methylpropionitrile) (AIBN) were supplied by Junsei Chemical Co (Tokyo, Japan). Nearly monodispersed silica nanoparticles (average diameter: 5 nm) were synthesized by a sol-gel process, i.e., the Stöber method in our laboratory.<sup>19-21</sup> The detailed synthetic procedure for silica nanoparticles was described previously.<sup>10, 22</sup>

Phosphor coating with silica nanoparticles was performed via five different methods, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub>, and P<sub>5</sub>. The details of each are described below. P<sub>1</sub>: The proper amount of phosphor (10 g) was dispersed in a methanol (1 L) solution containing monodispersed silica nanoparticles (5 g, 5 nm) at 30 °C for 2 h. The resulting phosphor powders were separated by using ultracentrifuge (model:T-1180, Kontron, Italy) at a rotation speed of 3,000 rpm for 20 min. Then, the phosphor powders were dried at 80 °C for 1 day. P<sub>2</sub>: The proper amount of phosphor (10 g) was dispersed in methanol (1 L) solution containing TEOS (0.28 mol), water (20 mol), and NH<sub>4</sub>OH (2 mol), and then reacted at 80 °C for 1 h. Note that the aggregate with primary silica nanoparticles (5 nm) was formed at this reaction conditions when reaction mixture did not contain phosphors.<sup>10,22</sup> The resulting phosphor powders were also recovered with the same procedures as described for P<sub>1</sub>. P<sub>3</sub>: phosphor (10 g) was dispersed in a methanol (1 L) solution containing TEOS (0.28 mol), water (20 mol), and NH<sub>4</sub>OH (2 mol) and PVP (90 g) at 60 °C for 1 h. Note that monodispersed silica nanoparticles (5 nm) without aggregates formation was synthesized at this reaction conditions when reaction mixture did not contain phosphors.<sup>20</sup> The phosphor powders separated via ultracentrifugation were washed with methanol several times to remove PVP attached on the phosphor surface and dried at 80 °C for 1 day. P<sub>4</sub>: The proper amount of phosphor (10 g) was dispersed in methanol (1 L) solution containing silica nanoparticles (5 g), VP monomer (0.4 mol), and AIBN (0.5 wt% of VP), and then reacted at 80 °C for 1 h. The resulting phosphor powders were recovered with the same procedures as described for P<sub>3</sub>. P<sub>5</sub>: Methanol (1 L) solution containing TEOS (0.28 mol), water (20 mol), NH<sub>4</sub>OH (2 mol), VP (0.4 mol), AIBN (0.5 wt% of VP), and phosphor powders (10 g) was reacted at 80 °C for 1 h. Note that monodispersed silica nanoparticles (5 nm) without aggregates formation was synthesized at this reaction conditions when reaction mixture did not contain phosphors.<sup>10</sup> The resulting phosphor powders were also recovered with the same procedures as described for P<sub>3</sub>. Phosphors coated with various methods were cured at 300 °C for 5 h to convert Si-OH bonding to Si-O-Si bonding.

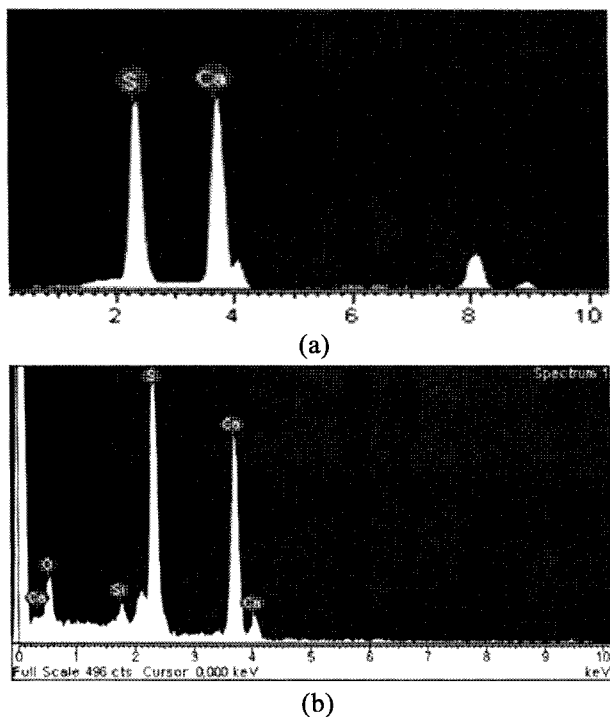
The morphologies of CaS:Eu<sup>2+</sup> before and after coating were investigated with a field emission scanning electron microscope (FE-SEM, model: JSM-6700F, Japan) and a high resolution transmission electron microscope (HR-TEM, model: JEM-3010, Japan). Phosphor coating with silica was also confirmed with FTIR (model: Magna 750, Nicolet, USA) and energy dispersive spectroscopy (EDS, model: ED2000, Oxford, England). The photoluminescence (PL) was mea-

sured with a photomultiplier detector (model: LH1751300, ORC, Korea) at 30 °C using a particular wave (465 nm) come from a xenon lamp (150 W) as an excitation source. All PL spectra exhibited here were recorded using band widths of 1 nm at emission slit. Five specimens of each phosphor were tested and their results were averaged. For the long-term stability examination of the phosphors before and after coating, samples were aged in a temperature-controlled humidity chamber (model: TH-G-180, Jeiotech, Korea) at 100 °C and 80% relative humidity and then changes in the PL intensity with aging time were examined.

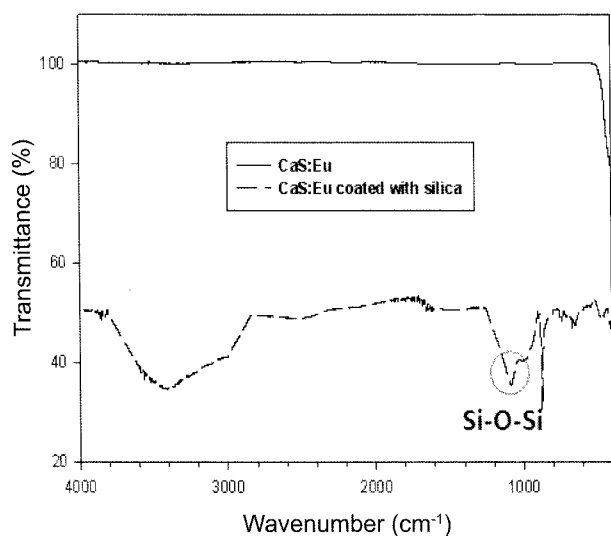
## Result and Discussion

**Characteristics of the Phosphors Coated with Silica Nanoparticles.** In a previous study, it was known that silica nanoparticles ranging from 10 to 450 nm could be synthesized via the Stöber method by changing the solvent (methanol or ethanol), amount of reactants (water and TEOS), and catalyst (ammonium hydroxide).<sup>18</sup> Nearly monodisperse and spherical nanoparticles were formed when particles larger than 25 nm were formed, while aggregates formed with primary silica nanoparticles (network structure) below about 25 nm. It was also known that the formation of aggregates could be prevented by adding PVP (or VP) to the reaction mixture and the size of the silica nanoparticles could be reduced below 3 nm by increasing reaction temperature.<sup>10,20</sup> Nearly monodisperse and spherical silica nanoparticles (5 nm) synthesized as described previously were used for phosphors coating.<sup>10,22</sup>

The formation of the silica coating layer using five different methods was confirmed with EDS and FTIR. Figure 1 shows the EDS pattern of the uncoated phosphor and that of the phosphor coated with silica nanoparticles using coating method P<sub>5</sub>. The peak resulted from the silica nanoparticles, which was not observed with uncoated phosphor, was observed in the phosphor coated with method P<sub>5</sub>. Note that the peak stemmed from the silica nanoparticles was also observed when phosphors were coated with methods P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, and P<sub>4</sub>. Figure 2 shows the FTIR spectrum of the uncoated phosphors and that of the silica nanoparticles-coated phosphors using coating method P<sub>5</sub>. The characteristic stretching peaks associated with the Si-O-Si linkages (around 1100 cm<sup>-1</sup>) and Si-OH linkage (3400 cm<sup>-1</sup>), which were not observed with uncoated phosphors, were observed in the FTIR spectrum of the coated phosphor. Note that stretching peaks associated with PVP were not observed in the FTIR spectrum of the coated phosphor. This result indicates that water soluble PVP (or methanol soluble PVP) was completely removed from phosphor during purification process. The typical peak resulting from silica nanoparticles were also observed in the FTIR spectra of the phosphors coated via other methods. Note that the characteristic peak of Si-OH bonds around 3400 cm<sup>-1</sup> in the FTIR spectrum was not



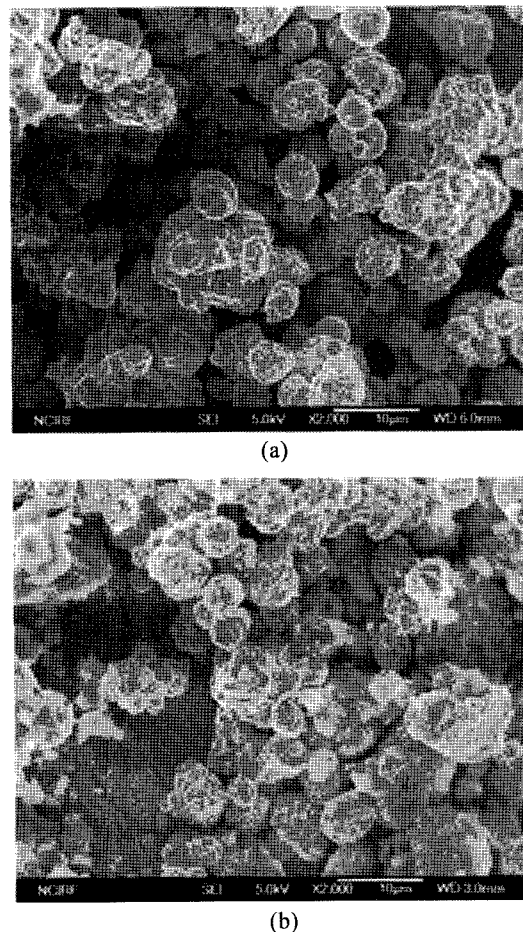
**Figure 1.** EDS patterns of the uncoated and coated phosphors with PMMA-silica nanocomposites; (a) uncoated CaS:Eu<sup>2+</sup> phosphor; (b) coated CaS:Eu<sup>2+</sup> phosphor with silica by coating method P<sub>3</sub>.



**Figure 2.** FTIR spectra of the uncoated and coated phosphors with silica nanoparticles by coating method P<sub>3</sub>.

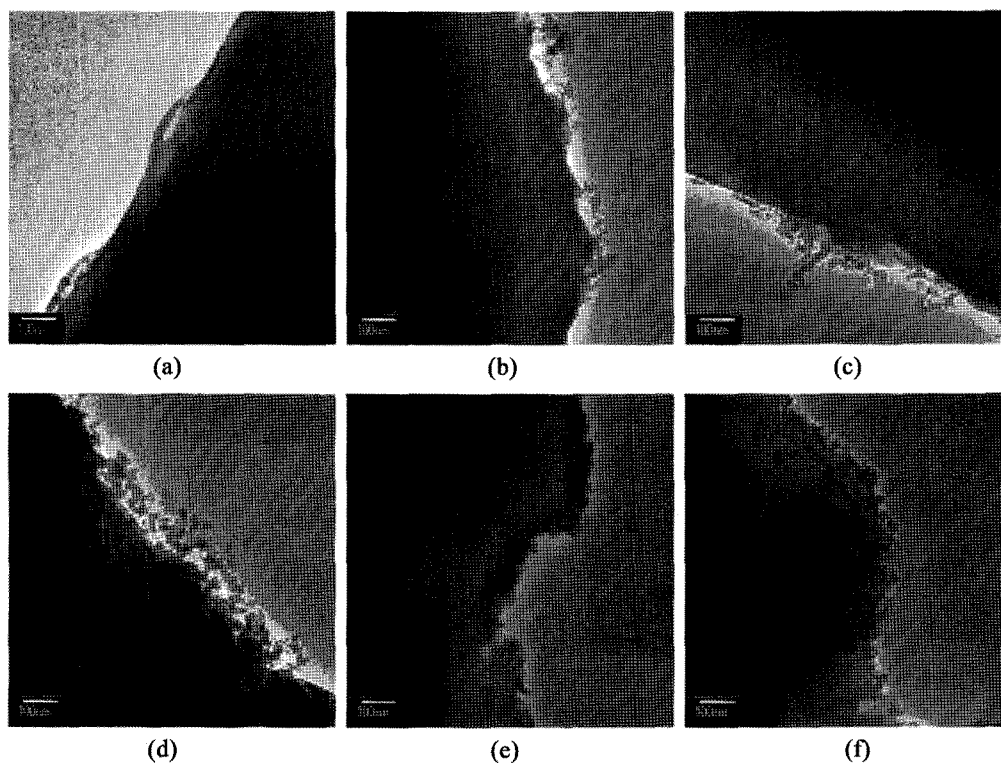
observed after curing at 300 °C for 5 h.

Regardless of the coating processes, the coated phosphor apparently had the same color (red) as the uncoated phosphor. However, changes in the detailed morphology were observed. As shown in Figure 3, the uncoated phosphor had a rough and wrinkled surface, and the surfaces of the coated phosphors were also rough regardless of coating methods.



**Figure 3.** FE-SEM microphotographs of the uncoated and coated phosphors with silica nanoparticles; (a) uncoated CaS:Eu<sup>2+</sup> phosphor; (b) coated CaS:Eu<sup>2+</sup> phosphor with silica by coating method P<sub>3</sub>.

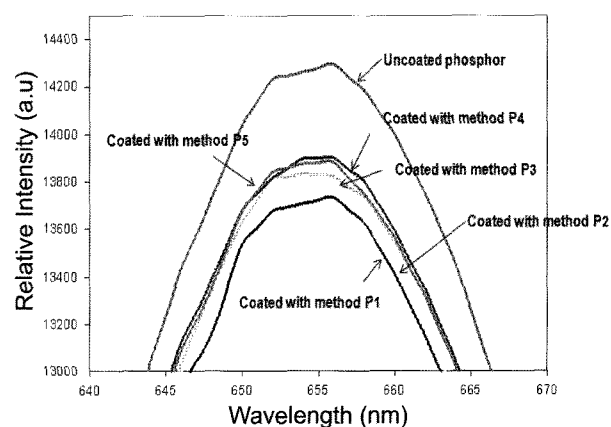
The rough and wrinkled surface of the uncoated phosphors may result in uneven coating. The detailed changes in the surface morphology with coating methods were observed with HR-TEM. As shown in Figure 4, when phosphors were coated with methods P<sub>1</sub> and P<sub>2</sub>, an uneven and discontinuous coating of the silica nanoparticles (Figure 4(b) and 4(c)) onto the rough surface of the uncoated phosphor (Figure 4(a)) was observed. Methods P<sub>3</sub> (Figure 4(d)) gave a better result in covering the phosphors surface with coating materials than P<sub>1</sub> and P<sub>2</sub>, even though silica nanoparticles were unevenly attached to the phosphor surface. A more even coating with silica nanoparticles was observed when phosphors were coated with methods P<sub>4</sub> (Figure 4(e)) and P<sub>5</sub> (Figure 4(f)). These results indicate that addition of PVP to the reaction mixture or radical polymerization of VP monomer during phosphor surface coating results in a better coverage on the phosphor surface and an even coating. It might come from that PVP in the reaction mixture (or on the phosphor surface) prevents aggregates formation with primary silica nanoparticles.



**Figure 4.** HR-TEM microphotographs of the uncoated and coated phosphors with silica nanoparticles; (a) uncoated CaS:Eu<sup>2+</sup> phosphor; (b) coated CaS:Eu<sup>2+</sup> phosphor by coating method P<sub>1</sub>; (c) coated CaS:Eu<sup>2+</sup> phosphor by coating method P<sub>2</sub>; (d) coated CaS:Eu<sup>2+</sup> phosphor by coating method P<sub>3</sub>; (e) coated CaS:Eu<sup>2+</sup> phosphor by coating method P<sub>4</sub>; (f) coated CaS:Eu<sup>2+</sup> phosphor by coating method P<sub>5</sub>.

#### Changes in the PL Intensity of Phosphors with Surface Coating.

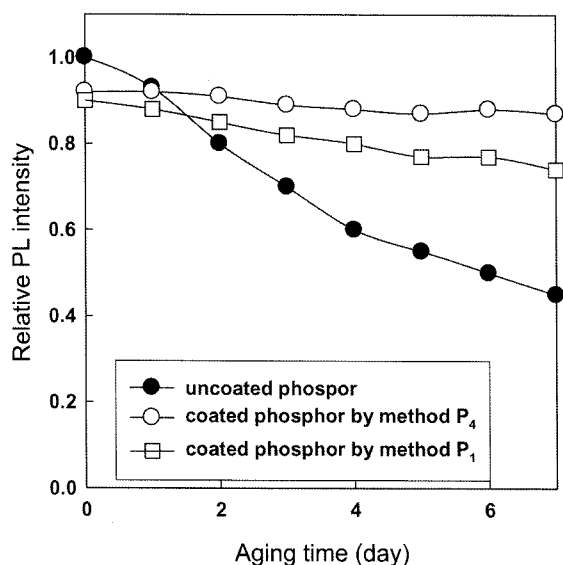
Changes in the PL intensities of the coated phosphors were investigated. As shown in Figure 5, the emission spectra of the phosphors before and after surface coating was always in the range from 570 to 720 nm, which demonstrates that the phosphors emit red visible light. Even though a slight change in the PL intensity was observed with sample, ranking in the PL intensity for a set of specimens (uncoated phosphor and coated phosphors with five different methods) was not changed. To standardize the measured PL intensity, PL intensities measured at each wavelength (measuring interval: 1 nm) for five samples were averaged, and then the average PL intensity at each wavelength was reported. A decrease in PL intensity was observed regardless of the coating methods used here. Uneven coating on the phosphor surface with silica nanoparticles might result in a decrease in PL intensity. PL intensity of the phosphors coated by methods P<sub>3</sub>, P<sub>4</sub> and P<sub>5</sub> was slightly higher than that of the phosphors coated by other methods (P<sub>1</sub> and P<sub>2</sub>). The coated phosphors with five different methods were cured at 300 °C for 5 h and then changes in the PL intensities were explored to examine curing effects on the PL intensity. Any significant changes in the PL intensity and the ranking in the PL intensity for a set of specimens (uncoated phosphor, coated phosphors with five different methods) were not observed. A more even coating



**Figure 5.** PL spectra of the uncoated and coated phosphors with silica nanoparticles by various coating methods.

with silica nanoparticles might result in a better PL intensity. Light scattering caused by uneven coating layer and refractive index mismatch between air and silica particle might result in further reduction in the PL intensity.

The most direct evidence of the protective nature of the phosphor coating could be found by PL aging analysis. When uncoated phosphor was aged in a temperature-controlled humidity chamber at 100 °C and 80% relative humidity, the



**Figure 6.** Normalized PL intensity as a function of the cumulated aging time for uncoated and coated phosphors. Note that phosphors were aged in a temperature-controlled humidity chamber at 100 °C and 80% relative humidity.

PL intensity was rapidly decreased with aging time as shown in Figure 6. Note that the PL intensity was reduced about 55% after 7 days. These results indicate that CaS:Eu<sup>2+</sup> phosphor is very unstable when it exposes to moisture. When phosphors coated by method P<sub>4</sub> was aged, a nearly constant value for coated phosphors with aging time, in contrast to a decreasing intensity for the uncoated phosphor, was observed. Similar results were observed when aging test was performed with phosphors coated with P<sub>5</sub>. However, the PL intensity was continuously and slightly decreased with aging time when aging test was performed with phosphors coated with method P<sub>1</sub> (or method P<sub>2</sub>). A slight decrease in the PL intensity with aging time might come from bare phosphor surface caused by uneven and island-like coating. The results related to the PL intensity indicate that the silica nanoparticle coated on the phosphors served as a protective layer by retarding the surface-related damage caused by moisture.

## Summary

The surface coating of the CaS:Eu<sup>2+</sup> phosphor was performed using five different methods for the enhancement of moisture stability. When phosphors were coated onto silica nanoparticles (5 nm) by dip coating or a sol-gel method, the phosphors surface was coated unevenly. A better surface coverage with silica nanoparticles was observed by simultaneously performing radical polymerization with VP monomer during coating process or by adding PVP to the reaction mixture. Reduction in PL intensity (8~10%) was observed when phosphors were coated with silica nanoparticles regardless of coating methods.

When uncoated phosphor was aged, the PL intensity was rapidly decreased with aging time (The PL intensity was reduced about 55% after 7 days). However, when phosphor coated by method P<sub>4</sub> (or P<sub>5</sub>) was aged, a nearly constant PL intensity with aging time was observed. As conclusion, moisture stability of the CaS:Eu<sup>2+</sup> red phosphor could be enhanced by surface coating of silica nanoparticles with proper methods.

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## References

- (1) W. Lehmann and F. M. Ryan, *J. Electrochem. Soc.*, **118**, 477 (1971).
- (2) K. Chakrabarti, V. K. Mathur, F. J. Rhodes, and R. J. Abbundi, *J. Appl. Phys.*, **64**, 1363 (1988).
- (3) R. Pandey and S. Sivaraman, *J. Phys. Chem. Solids*, **52**, 211 (1991).
- (4) K. Swiatek, M. Godlewski, L. Niinisto, and M. J. Leskela, *J. Appl. Phys.*, **74**, 3442 (1993).
- (5) D. Jia, W. Jia, D. R. Evans, W. M. Dennis, H. Liu, J. Zhu, and Y. M. Yen, *J. Appl. Phys.*, **88**, 3402 (2000).
- (6) H. Wu, X. Zhang, C. Guo, J. Xu, M. Wu, and Q. Su, *IEEE Photo. Tech. Lett.*, **17**, 1160 (2005).
- (7) C. Chung and J. Jean, *J. Am. Ceram. Soc.*, **89**, 2726 (2006).
- (8) H. Ozaki, S. Iwamoto, and M. Inoue, *Ind. Eng. Chem. Res.*, **47**, 2287 (2008).
- (9) C. Guo, L. Luan, C. Chen, D. Huang, and Q. Su, *Mater. Lett.*, **62**, 600 (2008).
- (10) Y. S. Chung, M. Y. Jeon, and C. K. Kim, *Ind. Eng. Chem. Res.*, **48**, 740 (2009).
- (11) W. Park, K. Yasuda, B. K. Wagner, C. J. Summers, Y. R. Do, and H. G. Yang, *Mater. Sci. Eng. B*, **76**, 122 (2000).
- (12) K. P. Velikov and A. Van Blaaderen, *Langmuir*, **17**, 4779 (2001).
- (13) C. Guo, D. Huang, and Q. Su, *Mater. Sci. Eng. B*, **130**, 189 (2006).
- (14) C. Feldmann and J. Merikhi, *J. Colloid Interf. Sci.*, **223**, 229 (2000).
- (15) H. Kominami, T. Nakamura, K. Sowa, Y. Nakanishi, Y. Hatanaka, and G. Shimaoka, *Appl. Surf. Sci.*, **113/114**, 519 (1997).
- (16) C. Guo, B. Chu, M. Wu, and Q. Su, *J. Lumin.*, **105**, 121 (2003).
- (17) T. W. Lee, O. O. Park, J. Kim, and Y. C. Kim, *Macromol. Res.*, **10**, 278 (2002).
- (18) S. E. Watkins, K. L. Chan, S. Y. Cho, N. R. Evans, A. C. Grimsdale, A. B. Holmes, C. S. K. Mak, A. J. Sandee, and C. K. Williams, *Macromol. Res.*, **15**, 129 (2006).
- (19) W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interf. Sci.*, **26**, 62 (1968).
- (20) J. W. Kim, L. U. Kim, and C. K. Kim, *Biomacromolecules*, **8**, 215 (2007).
- (21) D. L. Green, J. S. Lin, M. Z.-C. Hu, D. W. Schaefer, and M. T. Harris, *J. Colloid Interf. Sci.*, **266**, 346 (2003).
- (22) Y. S. Chung, M. Y. Jeon, and C. K. Kim, *Macromol. Res.*, **17**, 37 (2009).