

Surface modification of oxide phosphors using nano powders

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A red phosphor ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), a green phosphor ($\text{LaPO}_4:(\text{Ce}^{3+}):\text{Tb}^{3+}$) and a blue phosphor ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$) have been modified using colloidal suspensions containing La_2O_3 and Al_2O_3 , Y_2O_3 nano particles, respectively. The zeta potential of the matrix phosphors and the nano particles were measured in determining the surface modification conditions. The optimum adsorption (pH) conditions, based upon the zeta potential-pH relations, were applied for the maximum electrostatic interaction between the oxide phosphors and nano particles. The microstructural morphologies of the oxide phosphors coated with the nano-sized oxide particles were observed by SEM images. The photoluminescence behavior and the color coordinates (chromaticity diagrams) of the oxide phosphors modified with nano particles were examined to compare with those of the raw phosphors.

Key words: Phosphors, Surface modification, Nano particles, Isoelectric point (IEP).

Introduction

Several phosphor materials have been applied to the backlight unit (BLU) of liquid crystal displays (LCD) such as flat panel displays and fluorescent lighting fixtures. The luminescent behavior and the brightness as well as the stability of phosphor particles are very important factors in determining the qualities of a BLU lamp in a LCD [1, 2].

Numerous attempts have been made to enhance the luminescent properties and the chemical stability of such phosphor particles [3-7]. Generally, the phosphor materials used in BLU lamps of LCDs are damaged by the heat treatment of lamp manufacturing process and the mercury radiation of the lamp operation as well as the adsorption of mercury in long term operation. The color and the luminescent behavior of phosphor particles would undergo degradation after lamp manufacturing and long term operation. Thus the surface region of phosphor particles are coated with a protective layer composed of fine particles [8-10]. A surface coating or surface modification using nano-particles is frequently applied to enhance the chemical stability and improve the luminescence characteristics of several phosphors [11-13]. Several oxides are used to coat and modify the outer surface of the individual phosphor particles.

In this study, the zeta potential-pH relations of La_2O_3 and Al_2O_3 , Y_2O_3 nano particles and matrix phosphors; a red phosphor ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), a green phosphor ($\text{LaPO}_4:$

$(\text{Ce}^{3+}):\text{Tb}^{3+}$) and a blue phosphor ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$) were examined for the surface coating. The absorption behavior of the oxide phosphors and the nano particles was controlled according to the zeta potential-pH relations. Surface morphologies of the oxide phosphors modified with the nano particles were observed by SEM (scanning electron microscopy) images. The photoluminescence (PL) behavior of the coated phosphors was investigated with PL spectra and chromaticity diagram.

Experimental Details

Water base slurries (Sukgyung, Korea) containing the nano-sized Al_2O_3 , La_2O_3 and Y_2O_3 particles were used as the sources of the coating materials. The oxide phosphors, red phosphor ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), green phosphor ($\text{LaPO}_4:(\text{Ce}^{3+}):\text{Tb}^{3+}$) and blue phosphor ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$) synthesized by solid-state reaction from oxide powders were adopted for the surface modification. A zeta Sizer 2000 (Malvern, England) was used to analyze the zeta potential of phosphors and nano particles using an electrophoresis technique. To determine the zeta potential of samples, all of the powders were rinsed 3 times with distilled water using a centrifuge to remove the surface impurities of each powder and dried at 100°C for 12 hours. Then, the oxide phosphors were rinsed and made into the zeta potential samples with 1% slurries. NH_4OH and p-toluene sulfonic acid were used to control the pH value of these samples. The particle size of the nano particles was measured by a particle size analyzer (Zeta Sizer 1000, Malvern, England). The phosphor powders were dispersed into the suspensions at 10% concentration in

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distilled water. The nano particles were added to the phosphor suspension (0.5 and 0.1% to the amount of phosphor powder) and then NH_4OH and p-toluene sulfonic acid were added to the suspension to control the pH during strong stirring for 30 minutes. These phosphors, modified with nano particles, were filtered and rinsed, dried at 100°C for 10 hours. Surface morphologies of the nano particle coated-oxide phosphors were observed by SEM (Shimadzu, Japan). The PL spectra of the phosphors modified were measured by a spectrometer (PSI, Korea).

Results and Discussion

The zeta potential-pH relations and isoelectric point (IEP)s were examined to estimate the adsorption conditions of the oxide phosphors and nano particles. The

red phosphor ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), green phosphor ($\text{LaPO}_4:(\text{Ce}^{3+}):\text{Tb}^{3+}$) and blue phosphor ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$) showed isoelectric points (IEP) at pH 8.3, pH 5.1 and pH 7.8 by changing pH level from alkali region to acid region, respectively (Fig. 1). The pH control from the acid region to alkali region indicated the isoelectric points at pH 10, pH 4.6 and pH 7.4 for ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), ($\text{LaPO}_4:(\text{Ce}^{3+}):\text{Tb}^{3+}$) and ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$) phosphors, respectively (Fig. 2). The nano particles, Y_2O_3 , La_2O_3 and Al_2O_3 indicated IEPs at pH 9.7, pH 10.75 and pH 10 for the change of pH level from alkali region to acid region, respectively (Fig. 3). Also, the nano particles, Y_2O_3 and La_2O_3 indicated the IEP at pH 9.4 and pH 10.4 for the change of pH level from the acid region to the alkali region, respectively (Fig. 4). The mean particle size of Y_2O_3 , La_2O_3 and Al_2O_3 nano particles were approximately 247 nm, 108.6 nm and 240.5 nm, respectively.

In this study, the surface coating using an adsorption behavior between the oxide phosphors and the nano

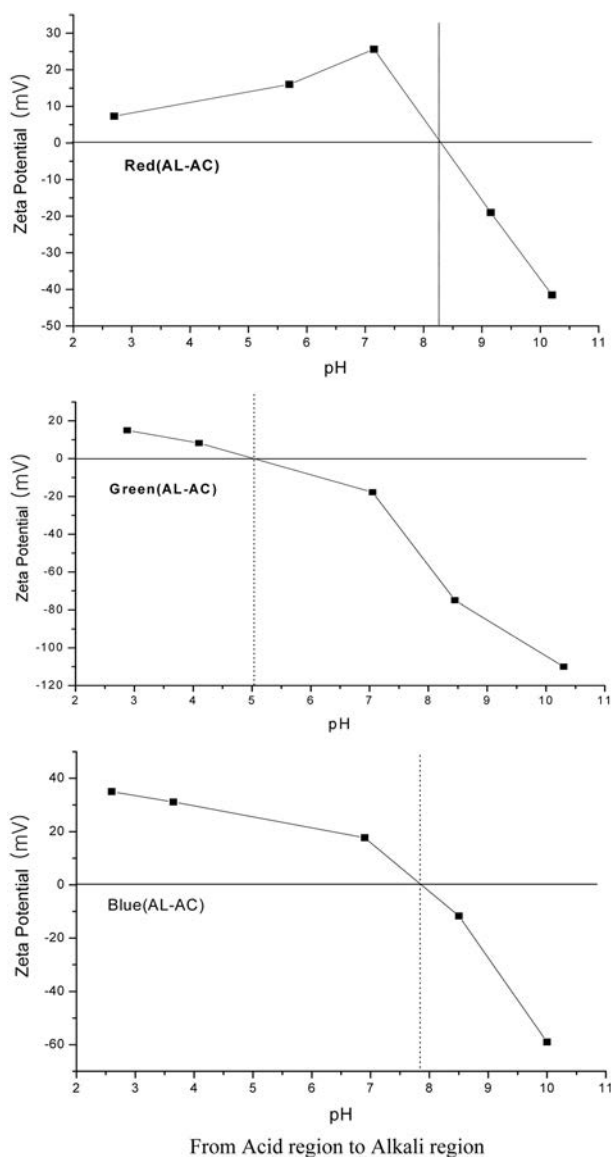


Fig. 1. Zeta potential of the matrix phosphors according to the pH change.

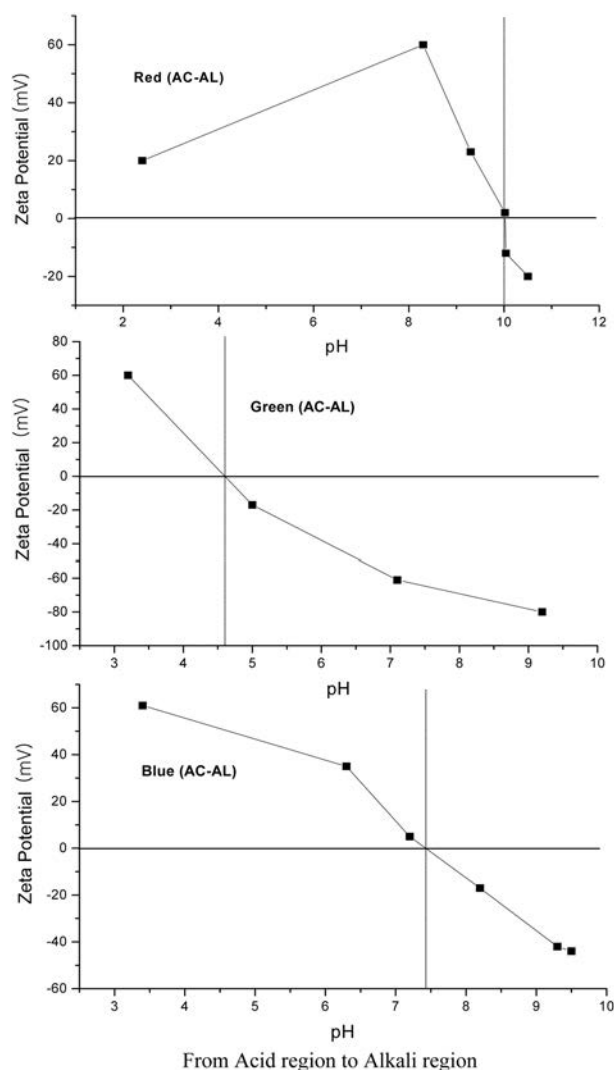


Fig. 2. Zeta potential of the matrix phosphors according to the pH change.

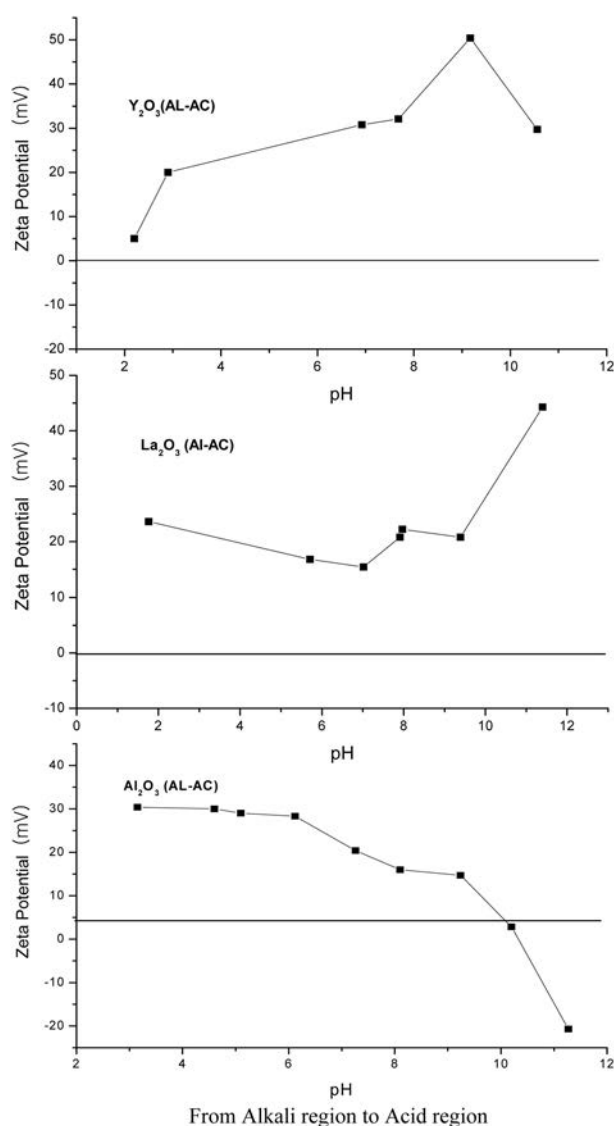


Fig. 3. Zeta potential of the nano particles according to the pH change.

particles was carried out at the optimum pH levels of the suspensions obtained from the starting materials. The adsorption behavior between the oxide phosphors and the nano particles could be explained as the results of the electrostatic interaction with the function of the pH range. The electrostatic force might be changed according to the zeta potential-pH relations between the constituent components. The optimum adsorption (pH) conditions for the maximum electrostatic interaction were selected from the zeta potential-pH relations of the phosphors and nano particles. The pH conditions, which might show the maximum electrostatic interaction between the phosphor powders and nano particles, were determined as follows; the red phosphor ($Y_2O_3:Eu^{3+}$)- Al_2O_3 (9.1), the red phosphor- Y_2O_3 (9.1), the red phosphor- La_2O_3 (10.5), the green phosphor ($LaPO_4:(Ce^{3+}):Tb^{3+}$)- Al_2O_3 (8.5), the green phosphor- Y_2O_3 (9.0), the green phosphor- La_2O_3 (10), the blue

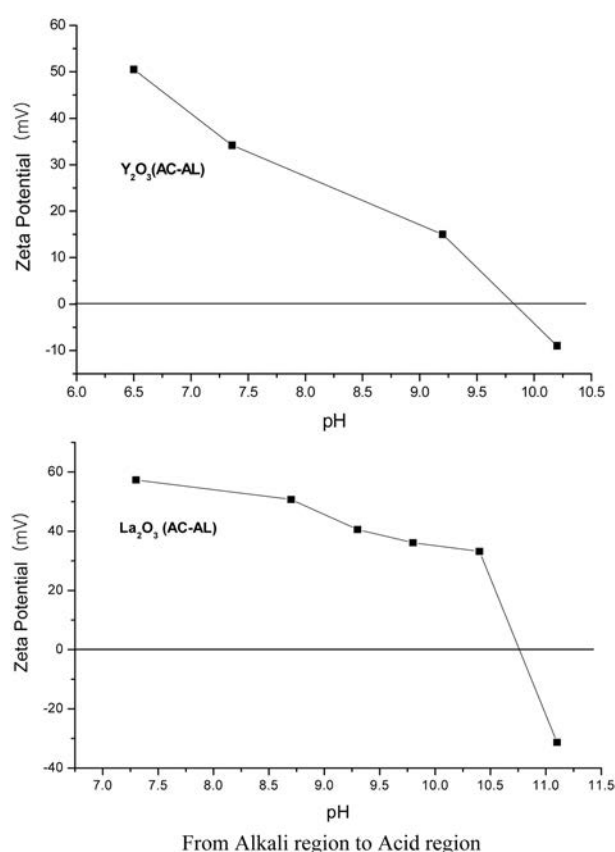


Fig. 4. Zeta potential of the nano particles according to the pH change.

phosphor ($BaMgAl_{10}O_{17}:Eu^{2+}$)- Al_2O_3 (9.2), the blue phosphor- Y_2O_3 (9.2), the blue phosphor- La_2O_3 (10), respectively. The nine systems of the red, green and blue modified phosphors were obtained using the pH conditions for optimum adsorption behavior.

SEM morphologies of the phosphors modified with nano particles were observed (Fig. 5). The red, green and blue phosphors modified with Al_2O_3 and La_2O_3 nano particles showed a good adsorption behavior. Although the optimum conditions from the zeta potential-pH relations were applied for the adsorption process, the phosphors modified with Y_2O_3 nano particles rarely showed adsorption behavior in SEM images. It was inferred that this result was related to the isoelectric point-pH relation of the Y_2O_3 nano particle, showing very different behavior, a remarkable hysteresis for the pH change from acid to alkali or from alkali to acid region (Fig. 3 and Fig. 4).

The photoluminescence behavior of the red phosphor ($Y_2O_3:Eu^{3+}$), green phosphor ($LaPO_4:(Ce^{3+}):Tb^{3+}$) and blue phosphor ($BaMgAl_{10}O_{17}:Eu^{2+}$) modified by nano particles were examined in the range of the red, green and blue emission, respectively. The phosphors coated with nano powders showed very small differences of the emission intensity without a wavelength shift in the core-level region (Fig. 6) and the color coordinates (x, y) in the chromaticity diagrams (Table 1). The presence

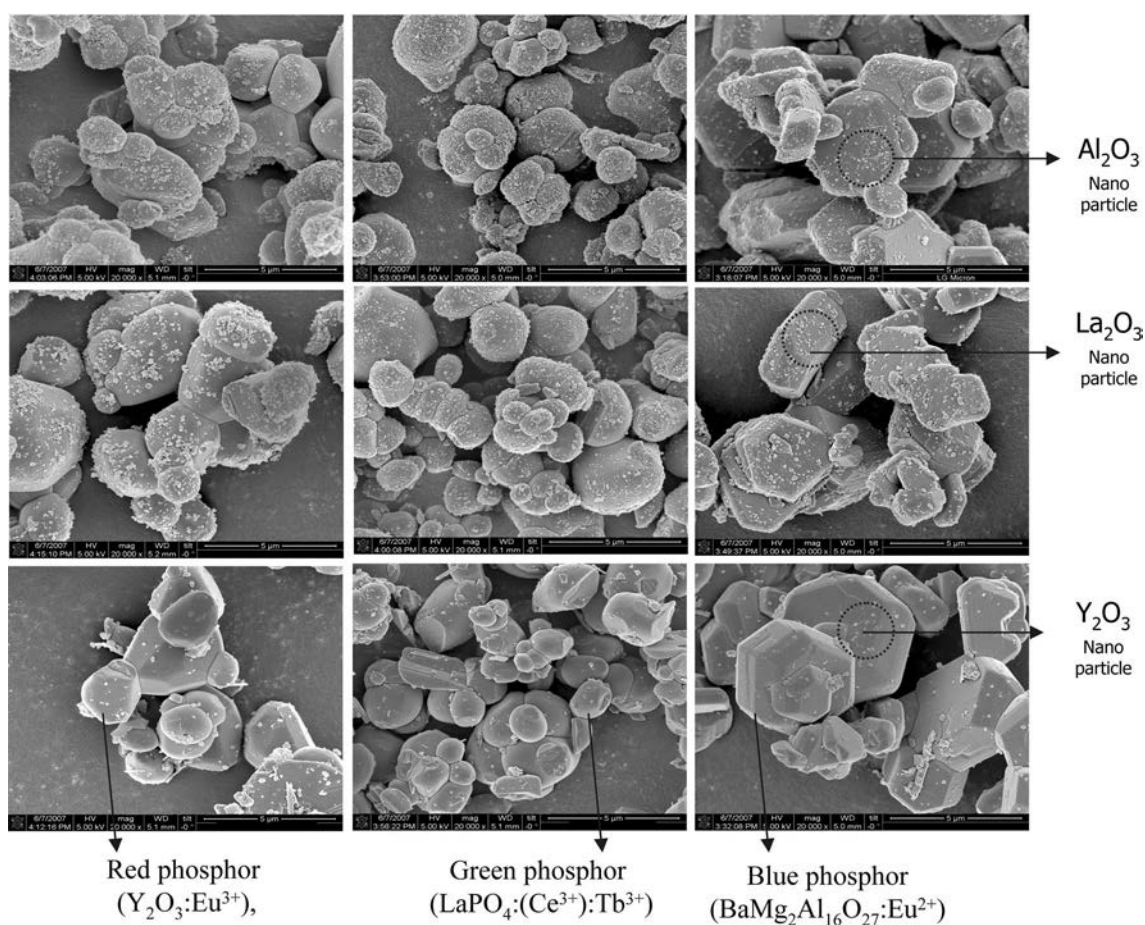


Fig. 5. Surface morphologies of the phosphors modified with nano particles.

Table 1. Color coordinates of the phosphors modified with nano particles

RED phosphor		GREEN phosphor		BLUE phosphor	
Material	Color	Material	Color	Material	Color
Raw-Red	X 0.6498 Y 0.3425	Raw-Green	X 0.3495 Y 0.5877	Raw-Blue	X 0.1459 Y 0.0714
Red-Al ₂ O ₃ (p)	X 0.6508 Y 0.3432	Green-Al ₂ O ₃ (p)	X 0.3497 Y 0.5877	Blue-Al ₂ O ₃ (p)	X 0.1458 Y 0.0715
Red-Y ₂ O ₃ (p)	X 0.6508 Y 0.3432	Green-Y ₂ O ₃ (p)	X 0.3496 Y 0.5877	Blue-Y ₂ O ₃ (p)	X 0.1457 Y 0.0710
Red-La ₂ O ₃ (p)	X 0.6504 Y 0.3431	Green-La ₂ O ₃ (p)	X 0.3498 Y 0.5876	Blue-La ₂ O ₃ (p)	X 0.1455 Y 0.0710

Color coordinates: (x, y) position in chromaticity diagram

of the nano particles had an effect on the emission intensity of the phosphors. In particular, the red phosphor (Y₂O₃:Eu³⁺) modified with nano particles showed rather a high intensity compared to that of the raw red phosphor. The variation of the emission behavior of the red phosphors is represented in the color coordinates (x, y) of Table 1. It is inferred that the intensity variation of the modified phosphors is related to the drift of the color coordinates (x, y) in the chromaticity diagram.

Conclusions

Oxide phosphors, a red phosphor (Y₂O₃:Eu³⁺), a green phosphor (LaPO₄:(Ce³⁺):Tb³⁺) and a blue phosphor (BaMgAl₁₀O₁₇:Eu²⁺), coated intermittently with Y₂O₃, La₂O₃ and Al₂O₃ nano particles, were obtained by strong stirring. The adsorption conditions (pH) for the maximum electrostatic interaction of the oxide phosphors, estimated from the zeta potential-pH relations and isoelectric point (IEP), were applied to the nine

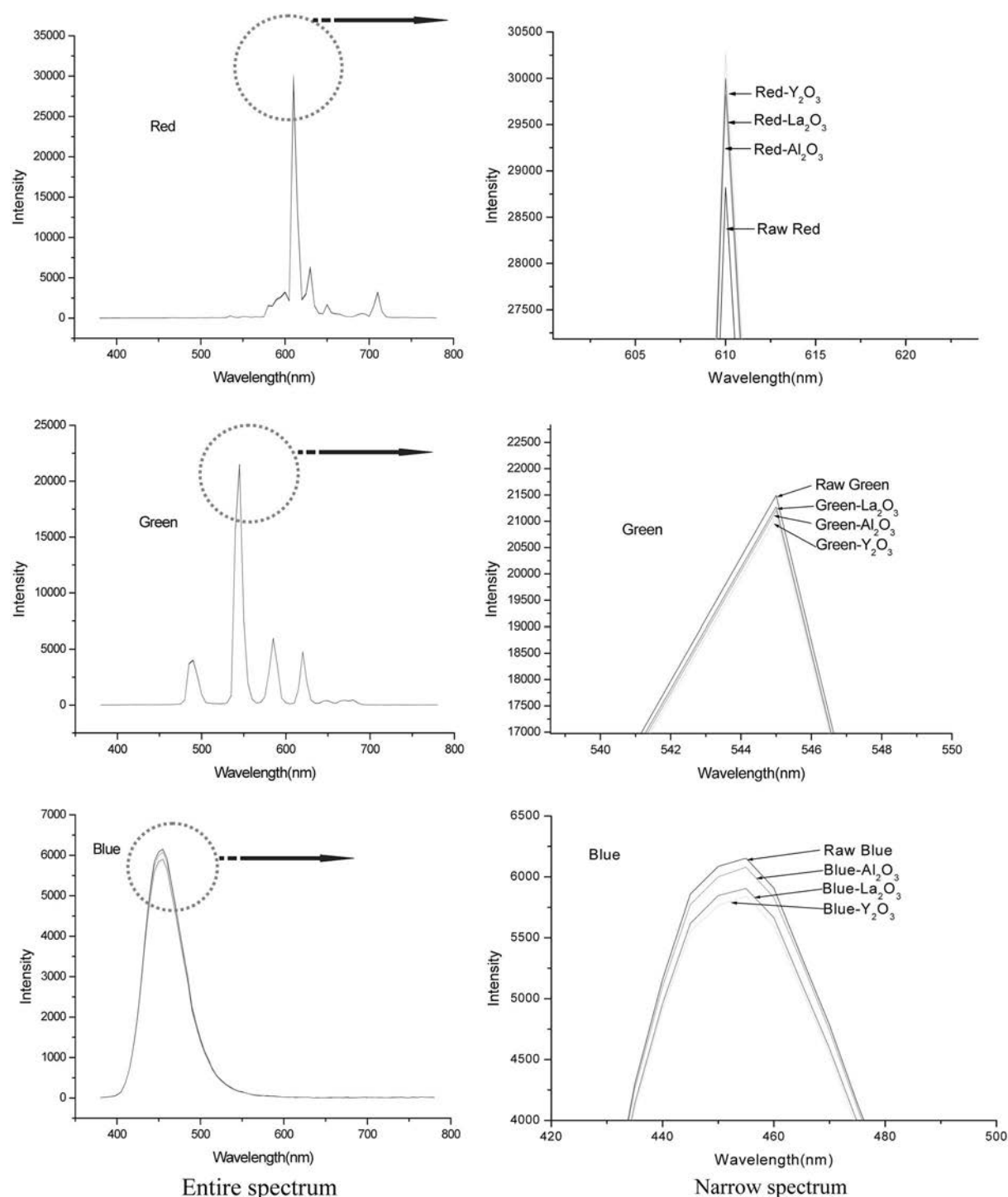


Fig. 6. Photoluminescence spectra of the phosphors modified with nano particles.

phosphor systems. The red, green and blue phosphors modified with nano particles showed a good adsorption behavior in SEM images. However the phosphors modified using Y_2O_3 nano particle, which represented a conspicuous hysteresis of the zeta potential-pH relation for the pH changes (acid \rightarrow alkali or alkali \rightarrow acid region), showed scarce adsorption phenomena in SEM images. The PL spectra of the red, green and blue modified phosphors showed very small intensity differ-

ences with the raw phosphors in the red, green and blue emission regions, respectively.

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