

Synthesis of Phosphor Photonic Crystals by Self-Assembly of SiO_2/Y_2O_3 :Tb³⁺ Core/Shell Particles and Its Photoluminescence Properties

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The monodisperse spherical SiO_2/Y_2O_3 :Tb³⁺ core/shell particles were prepared by a heterogeneous precipitation coating of the phosphor shell on the surface of the core particles. The shell thickness and the calculated crystallite size were increased with the core size and, thus, the photoluminescence (PL) intensity was also increased. The phosphor photonic crystals (PCs) were fabricated by self-assembly of the core/shell particles. The PL intensity of the phosphor PCs was higher by around 2.0 times than that of the randomly stacked reference sample due to the high packing density and quality. The suppression of the PL emission peaks by the overlap with the stopband and the enhancement of the emission peak at the blue edge of the stopband were observed. The color purity of the phosphor PCs was definitely improved by the design of the stopband position. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3474219] All rights reserved.

Manuscript submitted May 17, 2010; revised manuscript received July 5, 2010. Published August 25, 2010.

High definition (HD) display has been one of the most interesting topics in the flat panel display industry. For the HD display with small pixels, inorganic phosphors with uniform size and spherical shape have many advantages. The uniform size helps to form a phosphor layer with uniform thickness and uniform luminescence distribution.¹ In addition, the spherical particles can be packed denser than the ones that are differently shaped so that a denser phosphor layer can be formed.² Moreover, a spherical phosphor is capable of minimizing light scattering on its surfaces so that the brightness of such a phosphor screen is expected to be improved. Therefore, many researchers have attempted to obtain monodisperse spherical phosphors by various methods, including homogeneous precipitation^{2,4} and spray pyrolysis.^{1,5,6} However, the size distribution of phosphor particles obtained using such methods was still large. Recently, Lin et al. have coated several kinds of phosphors on SiO₂ particles by the Pechini sol-gel method and obtained monodisperse spherical SiO₂ core/phosphor shell particles.⁷

The aforementioned features of the monodisperse spherical phosphor can provide one with a new application called phosphor photonic crystal (PC). Since Yablonovitch and John introduced a concept of the photonic bandgap in PCs, the effects of PCs on spontaneous emissions have been studied.^{14,15} The suppressions of the emission by overlaps between the stopband of a PC and the emission band of a light source were mainly observed.^{16,21} However, enhanced and highly directional emissions were observed at the edges of stopbands, where exist low group velocities.^{16,17,22-25} The lengthening lifetime due to the overlap,^{20,21,26} shortening of the lifetime at the edge of the stopbands,²¹ amplification of the emission by the multiple scattering,¹⁸ emission wavelength redistribution,²¹ consistency of the quantum yield,²¹ and luminescence enhancement by Bragg reflections²⁷ were reported. Moreover, either the trapping or the amplified emitting of lights by introduction of artificial defects in two-dimensional PC slabs was also reported.²⁸

In the previous studies, the emission sources such as quantum dots, organic dyes, as well as inorganic phosphors were mainly infiltrated into three-dimensional (3D) colloidal PCs.^{22,25,27} Occasionally, inverse opals of the PCs infiltrated with the emission sources were also synthesized and their properties were investigated. ^{16,17,19-21,26} However, the infiltration of the emission sources and the removal of the colloidal spheres could cause the collapse of the PC structure. However, there are few papers on the fabrication of a phosphor PC by self-assembly of the monodisperse

luminescent spheres and investigation of their optical and luminescence properties. It was because the synthesis of the monodisperse luminescent spheres, which could be used as building blocks of the PCs, was not easy. Although organic dye-doped polymer spheres were used for fabrication of PCs, ^{18,23} there are several drawbacks of organic dyes such as low chemical stability, their tendency to be agglomerated, a difficulty in uniform dispersion, and changeability of their luminescence properties.

In this study, we have prepared monodisperse spherical SiO_2/Y_2O_3 :Tb³⁺ phosphor core/shell particles not by Pechini solgel but by a precipitation method and fabricated the phosphor PCs by self-assembly of the core/shell particles. A uniform and smooth phosphor shell coated by the precipitation method was essential to promote self-assembly of the core/shell particles. Our core/shell particles have extraordinary merits such as high chemical stability and uniform distribution of the emission sources. The photoluminescence (PL) properties of both the core/shell particles and the phosphor PCs depending upon the particle sizes were investigated in detail. In addition, the advantages of the ordered structure on the luminescence intensity and the way of utilizing the stopband to improve the color purity were investigated.

Experimental

Synthesis of the monodisperse spherical SiO_2/Y_2O_3 : Tb^{3+} core/ *shell particles.*— The monodisperse spherical SiO_2 core particles were prepared by following the Stöber method.²⁹ Tetraethyl orthosilicate (99%, Aldrich), aqueous NH4OH (ammonia 28 wt %, Junsei Chemical Co.) solution, ethanol (99.9%, Merck), and deionized water were used as raw materials. The core particles with core sizes of 206, 236, 249, 343, and 468 nm in diameter were prepared under various synthesis conditions.³⁰ A precursor of the Y_2O_3 :Tb³⁺ phosphor, that is (Y,Tb)OHCO₃, was coated by a heterogeneous precipitation method, which is similar to the homogeneous precipitation method to prepare the monodisperse spherical Y_2O_3 :Eu³⁺ phosphor except that the nucleation of the phosphor precursor occurred on the surfaces of the core particles.^{4,31} Metal salts such as YCl₃·6H₂O (99.99%, Aldrich) and TbCl₃·6H₂O (99.99%, Aldrich) were used as sources of metal ions. The doping concentration of Tb³⁺ ion was fixed at 5 mol %. After dissolving the metal salts and urea (99%, Aldrich) in water, the core particles were added and dispersed by an ultrasonic treatment. The molar ratio of metal salts:core particle was 1:8.5. Subsequently, the solution was heated and aged at 80°C for 4 h under stirring, and the precursor coated particles were washed and separated by centrifugation. The precursor coated particles were dried at 60°C for 10 h and fired at 850°C for 4 h. Finally, the SiO₂/Y₂O₃:Eu³⁺ phosphor core/shell particles were obtained. The

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Figure 1. (Color online) The TEM images of the (a) CS C and (b) CS E particles. The insets show the SAED patterns of the core/shell particles. (c) The high resolution TEM image of the CS E particles. (d) The shell thickness and the BET surface area of the core particles depending upon the core size.

sample names of the core/shell particles synthesized by using core particles with core sizes of 206, 236, 249, 343, and 468 nm were CS A, CS B, CS C, CS D, and CS E, respectively.

Fabrication of the phosphor PC.— The colloidal solution was prepared by dispersing the core/shell particles in ethanol. The volume fraction of the core/shell particles was varied from 0.1 to 3.6 vol %. The colloidal solutions were just simply dropped on glass dishes cleaned by using chromic–sulfuric acid and purified water. The inner diameter of the dishes was 15 mm and the volume of the dropped solution was fixed at 0.3 mL. Then, the dishes were placed in a vibration-free oven at 25°C. During the evaporation of the solvent, the phosphor PCs were fabricated on the glass dishes. To investigate the effect of the ordered structure on luminescence intensity, a reference sample with a disordered structure was fabricated. The reference sample was fabricated by evaporation of the solvent at 80°C, but the other synthesis conditions were the same.

Characterization.— The morphologies and sizes of the prepared samples were observed by a Philips XL30SFEG scanning electron microscope (SEM). The mean diameter was determined by measuring the diameters of 100 core/shell particles in the SEM image and by taking an average of them. Furthermore, a particle size analyzer (ZetaPlus, Brookhaven Instruments) was used to investigate the mean diameter and size distribution of the core/shell particles more precisely. The Brunauer, Emmett, and Teller (BET) surface areas of the core particles were measured by a surface area and porosity analyzer (Micromeritics ASAP 2020) in Kr gas atmosphere. The morphologies and shell thicknesses were observed by using a transmission electron microscope (TEM, JEM 3010, JEOL). The crystallinity of the prepared particles was determined by a selected area electron diffraction (SAED) coupled with the TEM. The crystalline phases of the phosphor shell were analyzed by a Rigaku D/max–RC X-ray diffractometer (XRD) with Cu K α (λ = 1.542 Å) radiation operating at 40 kV and 45 mA. The scan rate was 1°/min and the measurement range was from 10 to 70°. PL excitation and emission spectra were recorded by a DARSA PRO 5100 PL spectrometer (Professional Scientific Instrument Co.) using a xenon lamp. The angle between the excitation light (230 nm) and the surface normal to the phosphor PC was 30° and the detector was aligned with the normal. The normal incidence transmittance spectra of the prepared samples were obtained by using a Shimadzu UV-3101 PC spectrophotometer.

Results and Discussion

Synthesis and characterization of SiO_2/Y_2O_3 : Tb^{3+} phosphor core/shell particles.— Figure 1a and b shows the TEM images of the CS C and CS E particles, respectively. The continuous and smooth phosphor shells were clearly observed. The shell thicknesses of the CS C and CS E particles were \sim 5.1 and 11.1 nm, respectively. The insets show the SAED patterns of the core/shell particles. Spotty annular rings in the SAED patterns show a polycrystalline nature of the Y_2O_3 :Tb³⁺ phosphor shell. The pattern of the CS E particles was clearer than that of the CS C particles, which indicates that the crystallinity of the phosphor shell on the CS E particles was higher than that on the CS C particles. In the pattern of the CS E particles, five diffraction rings corresponding to d-spacings of 4.32, 3.05, 2.64, 1.86, and 1.59 Å were definitely observed. They were attributed to the diffractions from the (211), (222), (400), (444), and (624) planes of the Y_2O_3 :Tb³⁺ phosphor shell, respectively. Figure 1c shows the high resolution TEM image of the CS E particles. The high resolution image showed the lattice fringe pattern with the d-spacing of 3.05 Å, which corresponds to the (222) plane of the Y_2O_3 : Tb³⁺ phosphor shell. Figure 1d shows the shell thickness and



Figure 2. (Color online) The XRD patterns of the (a) CS A, (b) CS B, (c) CS C, (d) CS D, and (e) CS E particles. (b) The shell thickness and the crystallite size calculated from Scherrer's equation.

the BET surface area of the core particles depending upon the core size. The BET surface area of the core particles decreased from 18.5 to 7.5 m^2/g , but the observed shell thickness was increased from 3.9 to 11.1 nm with the increase in core size. As the core size increased, the surface-to-volume ratio of the core particles was decreased and, thus, their total accumulated area was decreased. Because the same concentration of the metal salts was experimented on, the larger total accumulated area means the thinner shell thickness. Therefore, the shell thickness was increased with the increase in the mean diameter. Figure 2a shows the XRD patterns of the (a) CS A, (b) CS B, (c) CS C, (d) CS D, and (e) CS E particles. All of the peaks in the patterns correspond to the cubic structure of Y_2O_3 , as indexed in the figure. As the core size was increased, the peak intensity in the patterns increased and the full width at halfmaximum decreased. That means that the crystallite size was increased with the increase in the core size. Figure 2b shows the shell thickness and the crystallite size calculated from Scherrer's equation.³² The calculated crystallites size was increased from 4.3 to 10.6 nm with the increase in the core size and the calculated values were well matched with the observed shell thicknesses. The growth of the crystallite was restricted by the shell thickness and, thus, the crystallite size could be successfully controlled.

Figure 3a shows the PL excitation and emission spectra of the CS D particles. As indicated in the PL emission spectrum, characteristic emission peaks due to electronic transitions from the ⁵D₄ to ⁷F_j (j = 3, 4, 5, 6) levels of Tb³⁺ ion were observed at ~489, 543, 586, and 623 nm, respectively. The narrow emission peaks of Tb³⁺ ion, which are separated from one another, are suitable for the investigation of the effects of the stopband on the PL intensity of each emission peak. Among the four emission peaks, only the green emission peak at ~543 nm is practically useful, but the other undesired peaks are generally removed by color filters in display devices. In



Figure 3. (Color online) (a) The PL excitation and emission spectra of the CS D particles. (b) The relative PL intensity of the core/shell particles depending upon the core size.

the PL excitation spectrum, a broad band in the UV region corresponds to the $4f^8 - 4f^75d$ excitation of Tb^{3+} ion in the $Y_2O_3:Tb^{3+}$ phosphor.^{33,34} The shape and the position of the excitation and emission spectra were not significantly changed with the core size but only the intensities were varied. Figure 3b shows the relative PL intensity of the core/shell particles depending upon the core size. The relative PL intensity was increased with the increase in the core size, owing to the increased crystallite size.

Fabrication and luminescence properties of the phosphor PCs.— The phosphor PC samples, which are PPC A, PPC B, PPC C, PPC D, and PPC E, were fabricated by using CS A, CS B, CS C, CS D, and CS E, respectively. During the fabrication, the volume fraction of the core/shell particles was fixed at 2.0 vol %. Figure 4a and b shows the SEM images of the PPC A and PPC E samples. The triangular arrangement of the core/shell particles can correspond to the (111) surface of a face-centered cubic (fcc) lattice. Figure 4c shows the tilted SEM image of the PPC E sample. To check the packing quality of the inner side, the PPC E sample was partially destroyed. From the tilted images, the core/shell particles were well self-assembled. Figure 4d shows the relative PL intensity of the phosphor PC samples, fabricated by using the CS D particles, depending upon the volume fraction of the CS D particles. The PL intensity was linearly increased with the increase in the volume fraction; however, the PL intensity was saturated above 1.2 vol %. It is believed that the additional core/shell particles did not contribute to the luminescence above 1.2 vol %. Therefore, to remove the effect of the volume fraction on the PL intensity, the volume fraction of the core/shell particles was fixed at 2.0 vol % in the following experiments.



Figure 4. (Color online) The SEM images of the (a) PPC A and (b) PPC E samples. (c) The tilted SEM image of the PPC E sample. (d) The relative PL intensity of the phosphor PC samples depending upon the volume fraction of the CS D particles.

To investigate the effect of the ordered structure on the luminescence intensity, the reference sample with the volume fraction of 2.0 vol % was fabricated by using the CS D particles. The inset of Fig. 5a shows the SEM image of the reference sample. The evaporation rate of the solvent during the fabrication of the reference sample was so fast that the core/shell particles could not be self-assembled. Figure 5a shows the transmittance spectra of the PPC D and reference samples. In the spectrum of PPC D, a photonic stopband was clearly observed; however, the transmittance spectrum of the reference sample did not show the stopband. Figure 5b shows the PL excitation and emission spectra of the PPC \tilde{D} and reference samples. The PL intensity of PPC D was higher by around 2.0 times than that of the reference sample. Li et al. have compared their fluorescent latex films fabricated by using the dye-doped polystyrene microspheres with the non-PC reference sample.²³ In their study, the non-PC reference sample was prepared by immersion of the fluorescent latex film in the vapor of toluene to destruct the 3D-ordered structure. According to their results, the PL intensity of the ordered latex films was up to 7.9 times higher than that of the non-PC reference sample due to the longer optical path length and the multiple scattering. Although the same amount of the luminescence material was experimented on, the shape of the non-PC reference film was completely changed to the flat thin film, in which a total internal reflection of the emitted light could occur. There was a chance that the chemical and thus the optical properties of the dye could deteriorate during the toluene treatment. However, our comparative analysis was carried out between the ordered PPC D and the disordered reference sample composed of spherical core/shell particles. The stopband of PPC D was located far away from the PL emission peaks, and the excitation wavelength (230 nm) was not close to the periodicity of PPC D. Therefore, the edge effect and the multiple scattering could not be the main reasons for the two times enhancement. However, because only the packing density and quality of the core/shell particles were varied, the enhancement of the PL intensity observed in this study could originate from the packing density and quality. The filling factor of the monodisperse spheres in an fcc structure is 74%. However, according to the simulation results done by Shi and Zhang, the filling factor of randomly stacked monodisperse spheres is smaller than 58%.³⁵ Therefore, the packing density of the PPC D sample is higher than that of the reference sample. Liaparinos et al.

have reported that a granular phosphor screen with a higher packing density could present considerable better light emission based upon



Figure 5. (Color online) (a) The transmittance spectra of the PPC D and reference samples. The inset shows the SEM image of the reference sample. (b) The PL excitation and emission spectra of the PPC D and reference samples.



Figure 6. (Color online) The transmittance spectra of the (a) PPC A, (b) PPC B, (c) PPC C, (d) PPC D, and (e) PPC E. (f) The PL spectrum of PPC D.

their simulation results.³⁶ In addition, there is a large number of irregular-shaped pores between the randomly stacked core/shell particles and the reference sample has a rough surface. Therefore, the emitted lights could be more diffused in the reference sample and, thus, the directionality and the uniformity of the scattered lights were relatively low. Consequently, the light intensity detected could be decreased. Moreover, the lights emitted from the randomly stacked core/shell particles experienced a larger number of scattering while the lights moved toward the detector. Because there are many kinds of defects on the surfaces of inorganic phosphor particles, a larger number of scattering means larger losses of the emitted lights. Therefore, the PL intensity of the PPC D sample with the higher packing density and quality was higher than that of the reference sample.

Effects of the stopbands on the luminescence properties of the phosphor PCs.— Figure 6a-e shows the transmittance spectra of PPC A, PPC B, PPC C, PPC D, and PPC E, respectively. Well-

defined stopbands were observed in the spectra. The position of the stopband (λ) can be predicted from the Bragg equation^{37}

$$\lambda = \frac{2d_{(111)}}{m}\sqrt{n_{\text{eff}}^2 - \sin^2 \theta}$$
[1]

where d(111) is the interplanar spacing of the (111) planes in the fcc lattice, which is related to the mean diameter (*D*) of the core/shell particles by $(2/3)^{0.5}D$, θ is an angle between the incident beam and the normal to the film ($\theta = 0^\circ$, in this study), and *m* is an integer. n_{eff} is the effective refractive index, which is determined as

$$n_{\rm eff}^2 = \varepsilon_{\rm eff} = \varepsilon_{\rm CS} \times f_{\rm CS} + \varepsilon_{\rm air} \times (1 - f_{\rm CS})$$
[2]

where $f_{\rm CS}$ is the fractional volume of the core/shell particles (0.74 for the fcc lattice) and $\varepsilon_{\rm eff}$, $\varepsilon_{\rm CS}$, and $\varepsilon_{\rm air}$ are the effective dielectric constant, the dielectric constant of the core/shell particles, and the dielectric constant of air, respectively. According to Bruggman's effective medium theory, the $\varepsilon_{\rm CS}$ can be calculated from the following equation³⁸

$$f_{\rm C} \frac{\varepsilon_{\rm C} - \varepsilon_{\rm CS}}{\varepsilon_{\rm C} + 2\varepsilon_{\rm CS}} + f_{\rm S} \frac{\varepsilon_{\rm S} - \varepsilon_{\rm CS}}{\varepsilon_{\rm S} + 2\varepsilon_{\rm CS}} = 0$$
[3]

where $f_{\rm C}$ and $f_{\rm S}$ are the fractional volumes of the core and the shell, respectively, and $\varepsilon_{\rm C}$ and $\varepsilon_{\rm S}$ are the dielectric constants of the core and the shell, respectively. In this study, the $f_{\rm S}$ was around 0.11. The refractive indexes of the core and the shell are 1.45 and 2.00, respectively, thus the $\varepsilon_{\rm C}$ and $\varepsilon_{\rm S}$ are 2.10 and 4.00, respectively.³⁹ Therefore, Eq. 1 can be simply expressed by $\lambda = 2.29$ D. The observed positions were well matched with the calculated values. Figure 6f shows the PL spectrum of PPC D. Because the PL emission peaks were not overlapped with the stopband of PPC D, the PL spectrum of PPC D was regarded as a standard PL spectrum and the PL spectra of the other phosphor PC samples were compared with the PL spectrum of PPC D.

Figure 7a-d shows the PL emission spectra of PPC A, PPC B, PPC C, and PPC E, respectively. The spectra were compared with the standard PL spectrum of PPC D. In Fig. 7, the PL spectra were normalized based on the emission peak at 623 nm. Because the



Figure 7. (Color online) The PL emission spectra of (a) PPC A, (b) PPC B, (c) PPC C, and (d) PPC E.



Figure 8. (Color online) The CIE color coordinates of (a) PPC A, (b) PPC B, (c) PPC C, (d) PPC D, and (e) PPC E.

stopband was well overlapped with the emission peak at 489 nm, the emission intensity at 489 nm was significantly suppressed. In addition, the main emission intensity at 543 nm was also slightly decreased due to the overlap. In PPC B, the stopband was overlapped with the emission peaks at 543, 586, and 623 nm. When the PL spectra were normalized based on the emission peak at 489 nm, the three emission peaks were suppressed. As shown in Fig. 6, the stopband of PPC C was overlapped with the emission peaks at 586 and 623 nm, but the main emission peak at 543 nm was located at the blue edge of the stopband. When the PL spectra were normalized based on the emission peak at 489 nm, the emission peaks at 586 and 623 nm were suppressed but the PL intensity of the main emission peak was increased. Bechger et al. have also observed the enhancement of the PL intensity at the blue edge of the stopband, which is attributed to the escape of the diffuse light from the PC. Although the enhancements at the red edge of the stopband were also reported by other researchers,^{16,17} it was not distinguished in the present study. In PPC E, the second order stopband was overlapped with the emission peak at 586 nm. However, as shown in Fig. 7d, the suppression and the enhancement were not observed. Figure 8 shows the CIE color coordinates of the phosphor PC samples. Because the PL spectrum of PPC D was the standard PL spectrum, the CIE color coordinate of PPC D was regarded as the standard color coordinate. Because the main emission peak was suppressed, the color purity of PPC B was deteriorated. However, the color purity of PPC C was definitely improved due to the selective suppressions of the undesired emission peaks and the enhancement of the main emission peak without color filters.

Conclusion

In summary, the monodisperse spherical SiO₂/Y₂O₃:Tb³⁺ core/ shell particles were prepared. On the surface of the core particles prepared by the Stöber method, the phosphor shell was continuously coated by a heterogeneous precipitation. The shell thickness and the calculated crystallite size were increased with the core size and, thus, the PL intensity was also increased. The phosphor PCs were fabricated by self-assembly of the core/shell particles. To make the phosphor PCs, we simply dropped a small amount of the colloidal solution that contained the core/shell particles. It is believed that one could simply make a phosphor PC layer with the monodisperse

spherical phosphor particles in a small pixel by ink-jet printing. The ordered structure of the phosphor PCs has provided advantages such as high PL intensity and high color purity. The PL intensity of PPC D was higher by around 2.0 times than that of the randomly stacked reference sample due to the high packing density and quality. In addition, the color purity of the phosphor PCs could be definitely improved by an appropriate design of their stopband position. Therefore, it is believed that the beneficial phosphor PCs, which were fabricated by the simple method, could be a next type of inorganic phosphor layer in display devices.

Acknowledgment

This research was supported by World Class University (WCU) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R32-10051).

Korea Advanced Institute of Science and Technology assisted in meeting the publication costs of this article.

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