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J. Phys. Chem. C, **2008**, 112 (44), 17397-17401 • DOI: 10.1021/jp8063068 • Publication Date (Web): 10 October 2008

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Significant Enhancements in the Fluorescence and Phosphorescence of ZnO Quantum Dots/SiO₂ Nanocomposites by Calcination

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Received: July 17, 2008; Revised Manuscript Received: September 1, 2008

As light-emitting fillers for functional transparent polymer nanocomposites as encapsulating materials for solid-state lighting, nanoparticles should have a high emission intensity and a matching refractive index with polymer resin. In this work, ZnO quantum dots (QDs)/SiO₂ (Z-S) nanocomposite particles with a prescribed Z-S ratio were facilely synthesized by hydrolyzing tetraethoxysilane in the ZnO QD containing ethanol solution. The fluorescence and phosphorescence of Z-S nanocomposite particles were investigated as a function of calcination temperature. The fluorescence emission intensity of the nanocomposite particles has been enhanced by 108% after calcination at 300 °C. The phosphorescence before calcination has a very low emission intensity of 0.34 au, while the phosphorescence has been significantly enhanced by 14.9 times after the calcination. Consequently, the calcined Z-S nanocomposite particles are promising as light-emitting fillers due to their intense fluorescence and phosphorescence and the matching refractive index with transparent epoxy matrix for functional transparent epoxy nanocomposites as encapsulating materials for solid-state lighting.

1. Introduction

Zinc oxide (ZnO) is a notable inorganic material closely related with ultraviolet light. In our previous works,^{1–3} ZnO nanoparticles with a size in a range of ~15 to ~70 nm have been investigated for effectively improving UV shielding efficiency of transparent epoxy resin as encapsulating materials for ultraviolet light-based white light-emitting diode (UVW-LED) lamps. ZnO is also a wide bandgap semiconductor with a bulk excitation peak at about 365 nm. ZnO quantum dots (ZnO QDs) with a size of a few nanometers (2–7 nm) showed a broad luminescence emission spectrum in the blue-yellow region.^{4–7} However, the QDs would continuously grow and agglomerate during storage,^{5,7} which is undesirable in practical applications. To avoid this problem, several techniques have been developed to make ZnO-QDs/SiO₂ (Z-S) nanocomposites; these techniques include a combination of the sol–gel process and a spray drying method,⁸ the target-attached radio frequency sputtering approach,⁹ and the ion implantation and thermal oxidation method.¹⁰ The Z-S nanocomposites, in which ZnO nanoparticles are dispersed in the amorphous silica matrix, can emit specific colors from blue to yellow-green, and the particle size of ZnO does not change with aging since the ZnO particles are trapped in and protected by the solid silica matrix due to the interfacial effect.¹¹

ZnO QDs have been successfully used as light-emitting fillers for transparent and light-emitting epoxy nanocomposites as functional encapsulating materials for the LED devices (lamps) in our recent preliminary work in which the ZnO QD content is up to 4 wt %.¹² A high transparency is the prerequisite for encapsulating materials for LED devices and a high filler content is also desired to get a high emission intensity for encapsulating

materials so that they can be successfully employed in practical applications. However, it is generally difficult to maintain the high transmittance of transparent polymer matrix especially at high filler contents due to light scattering caused by the inorganic fillers because of the mismatch of refractive index (RI) between the inorganic particles and the polymer matrix. Our very recent work¹³ has shown that the refractive index can be tuned for nanocomposite particles by changing the relative contents of the components. Moreover, the RI of the transparent epoxy resin is between those of ZnO and SiO₂.¹³ Therefore, the RI of the Z-S nanocomposite particles can be tuned by controlling the relative content of ZnO to SiO₂ so that the RI matching principle between inorganic fillers and transparent epoxy matrix can be met to achieve highly transparent polymer nanocomposites. Consequently, usage of Z-S nanocomposite particles as light-emitting fillers would be a good choice for functional transparent epoxy nanocomposites as encapsulating materials for LED devices.

In the previous works^{8–10} mentioned above, the fluorescent properties have been extensively studied for Z-S nanocomposites. Nonetheless, fluorescence emission intensity could be significantly reduced by insulation of silica matrix. As light-emitting fillers for functional polymer nanocomposites, enhancement in the fluorescent emission intensity is thus necessary for Z-S nanocomposite particles. In this work, the Z-S nanocomposite particles will be calcined at high temperatures to enhance the fluorescence emission intensity. On the other hand, the phosphorescence has not been reported so far for Z-S composite particles. In the present work, the Z-S composite particles are calcined at high temperatures and the interesting afterglow phenomenon will be reported for the first time.

Therefore, in this article, ZnO QD colloid was prepared using the modified Spanhel and Anderson method.¹⁴ Z-S nanocomposite particles with a prescribed ZnO to SiO₂ ratio for achieving the matching RI with transparent epoxy resin were then synthesized by simply hydrolyzing tetraethoxysilane (TEOS)

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in the ZnO QDs-containing ethanol solution. The as-prepared Z-S nanocomposite particles were calcined in air at high temperatures for 2 h. The significant enhancements in the fluorescence and phosphorescence of the Z-S nanocomposite particles are observed after calcination at proper temperatures. The calcined Z-S nanocomposite particles are promising as light-emitting fillers due to the intense fluorescence and phosphorescence and the matching refractive index for functional transparent epoxy nanocomposites as encapsulating materials for solid-state lighting.

2. Experimental Section

ZnO QD colloid was prepared using the modified Spanhel and Anderson method.¹⁴ First, 0.1 M $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was completely dissolved in 200 mL of boiling ethanol at atmospheric pressure for approximately 10 min and then directly cooled to 0 °C. 0.14 M $\text{LiOH} \cdot \text{H}_2\text{O}$ in 200 mL of ethanol solution was ultrasonically treated for more than 1 h, since the $\text{LiOH} \cdot \text{H}_2\text{O}$ powders were difficult to be dissolved in ethanol, and cooled to 0 °C. The above prepared two solutions were mixed at a temperature of around 0 °C followed by extensive stirring for several minutes, and the transparent colorless ZnO QDs solution was thus synthesized. ZnO QDs precipitation was formed by addition of water to the ZnO QDs containing ethanol solution. Then, the supernatant was removed by centrifugation, and ZnO QDs were obtained by drying the precipitation at room temperature for about 24 h.

Z-S nanocomposite particles were synthesized by hydrolyzing TEOS under the catalysis of ammonia in the ZnO QDs containing ethanol solution. First, calculated amounts of TEOS and ammonia were added to the freshly prepared ZnO QD containing ethanol solution under stirring at room temperature. After 24 h, the resulting Z-S particles were harvested by centrifugation. Finally, Z-S nanocomposite particles were obtained by calcination of the obtained solids in air at various temperatures for 2 h.

Thermal analysis was performed using a NETZSCH STA 409PC instrument under nitrogen atmosphere in the temperature range of 30–900 °C at a heating rate of 10 °C/min. XRD patterns were recorded on a RINT 2000 wide-angle goniometer with Cu K α radiation ($\lambda = 1.5406$ Å). TEM and SEM measurements were performed with a Hitachi JEOL JEM-2010 TEM and a Hitachi S-4300 SEM, respectively. The mean particle sizes from HRTEM were obtained from about 50 measurements with the software Photoshop 7.0. The element analysis of Z-S nanocomposite particles was preformed by the X-ray energy dispersive spectrometer (EDS) attached with the Hitachi JEOL JEM-2010 TEM. Fluorescence emission spectra, phosphorescence emission spectra, and phosphorescence lifetime were all performed on a Hitachi F-4500 Fluorescence Spectrophotometer at room temperature under the excitation light source of 370 nm. The samples for the spectra measurements were prepared by dispersing Z-S nanocomposite particles in alcohol solution and the resulting solutions contained 2 wt % Z-S nanocomposite particles. The solutions were then poured into a rectangular cell, which was employed for the spectra measurements.

3. Results and Discussion

Figure 1a shows the thermogravimetry differential scanning calorimetry (TG-DSC) curves of the prepared Z-S nanocomposite particles. The TG curve reveals that the weight loss proceeds in successive stages with increasing temperature and that the total weight loss is about 20 wt %. Most significant

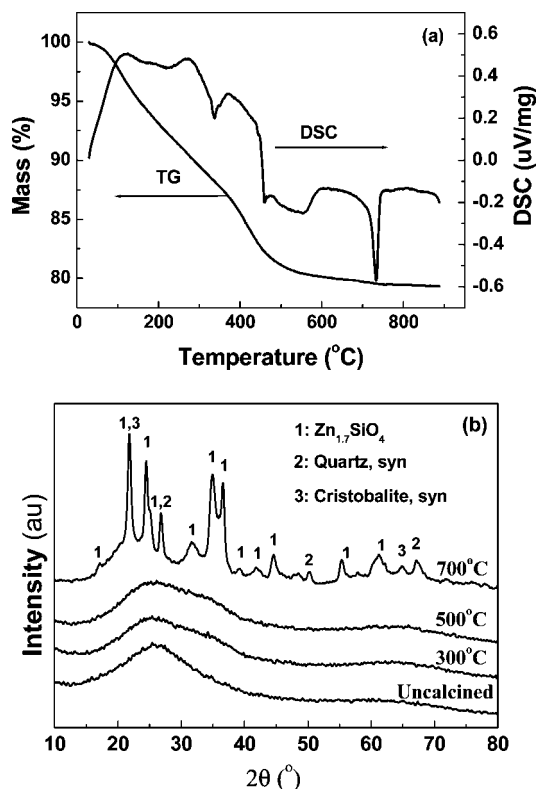


Figure 1. (a) TG-DSC curves and (b) XRD profiles of calcined Z-S nanocomposite at different temperatures.

weight loss occurs in the temperature range of 80–500 °C, which is associated with the removal of absorbed water and the decomposition of residual organic molecules such as TEOS and acetic acid. The two exothermic DSC peaks in the temperature range of 80–500 °C are induced by the thermal decomposition and oxidation of organic species. In addition, DSC curve displays a large endothermic peak at ~730 °C; the endothermic peak was induced by the reaction of ZnO QDs with the silica matrix to be shown by the XRD results below.

The XRD results are shown in Figure 1b, where the weight ratio of ZnO QDs to silica is 37/100 which is the optimal ratio in terms of the RI matching principle for transparent epoxy nanocomposites.¹³ The RI of Z-S nanocomposite particles, $n_{\text{Z-S}}$, can be calculated via the effective medium theory as follows¹⁵

$$n_{\text{Z-S}}^2 = n_{\text{ZnO}}^2 V_{\text{ZnO}} + n_{\text{silica}}^2 V_{\text{silica}} \quad (1)$$

where n_{ZnO} and n_{silica} are the RI of ZnO and silica, respectively. V_{ZnO} and V_{silica} are respectively the corresponding volume fractions of ZnO and silica. And the volume fractions can be obtained from the weight fractions since the densities of ZnO and SiO_2 are known as $\rho_{\text{ZnO}} = 5.7 \text{ g/cm}^3$ and $\rho_{\text{silica}} = 2.2 \text{ g/cm}^3$. The calculated RI (1.50–1.54) of the nanocomposite particles at the ZnO (RI = 2.0) to SiO_2 (RI = 1.42–1.46) ratio of 37 wt % in terms of our recent work¹³ is close to that (RI = 1.54) of the transparent epoxy resin, indicating that the RI was matched between inorganic particles and transparent polymer matrix. Thus, at this optimal ZnO QD to SiO_2 weight ratio, the light scattering due to the RI mismatch would be minimal, and the corresponding Z-S/epoxy supernanocomposite would show the optimal transmittance. The Z-S/epoxy supernanocomposites as encapsulating materials for LED lamps will be reported in detail elsewhere, and as an example, an LED lamp encapsulated with this optically transparent supernanocomposite is shown in Figure S1. Moreover, the broad peak at 20–30° corresponds to the

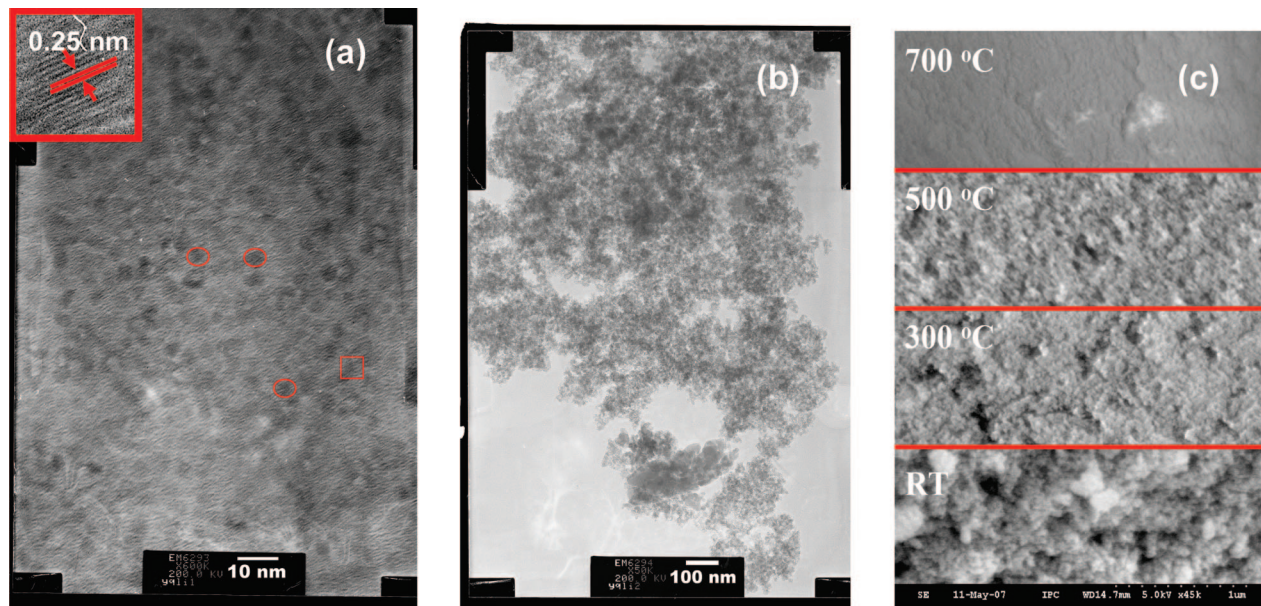


Figure 2. TEM micrographs of (a) ZnO QDs and (b) uncalcined Z-S and (c) SEM micrograph of calcined Z-S nanocomposite particles at different temperatures.

amorphous silica.¹⁶ The Z-S nanocomposite particles calcined at 300 and 500 °C have the similar XRD spectra to that of the uncalcined sample. However, when the calcination temperature is increased to 700 °C, the XRD spectrum becomes complicated, and the reaction of ZnO QDs with silica occurred at this temperature, which is in agreement with the DSC result. The resulting particles are composed of Zn_{1.7}SiO₄ (JCPDS No. 24-1466), quartz (JCPDS No. 46-1054), and cristobalite (JCPDS No. 39-1425). Because of the relatively low ZnO content, Zn_{1.7}SiO₄ instead of Zn₂SiO₄ was formed.^{17,18} In addition, the partial amorphous silica matrix has been transformed to quartz and cristobalite after calcination at 700 °C.

TEM image in Figure 2a displays that the ZnO QDs are spherical in shape with an average diameter of about 3 nm. Moreover, the inset of Figure 2a shows the lattice fringes of wurtzite ZnO nanocrystals with a ZnO (100) interplanar distance of 0.25 nm. After calcination, the structure of Z-S nanocomposite particles became compact (Figure 2b) and the packing degree increases with the calcination temperature. This is similar to the observation for the packing density of ZnO particles, which increases with the annealing temperature.¹⁹

To study the composition of Z-S particles in detail, element analysis was performed with TEM and EDS. The EDS results of Z-S particles before and after calcination at 500 °C are shown in Figure 3. Figure 3a shows that the uncalcined Z-S particles are composed of the elements of C, O, Si, Cu, and Zn. The Cu element is induced by the Cu grid used for the TEM sample. In addition, similar results have been obtained at various spots of the sample, revealing that the ZnO QDs have been homogeneously dispersed in the silica matrix. The weight ratio of ZnO QD/silica can be calculated to be 33.7 wt % from the result of Figure 3a, which is close to the stoichiometric ZnO content (37 wt %). On the other hand, Figure 3b shows that the Z-S particles calcined at 500 °C are still composed of C, O, Si, Cu, and Zn, but the content of C was greatly decreased due to the decomposition of organic residues. The remaining part of the element C is induced by the organic coating on the sample for TEM observation for supporting Cu grid.

The fluorescence emission spectra in Figure 4a gained under the excitation spectrum of 370 nm show a broad emission

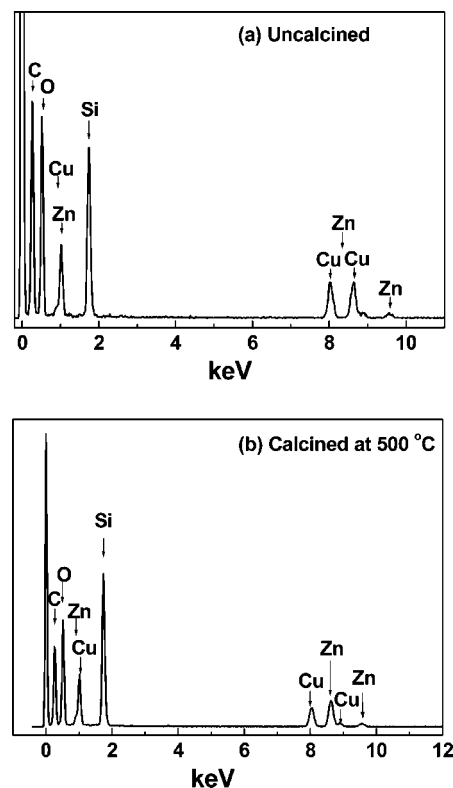


Figure 3. EDS spectra of Z-S particles (a) before and (b) after calcination at 500 °C.

spectrum of 400–500 nm for the uncalcined Z-S nanocomposite particles. There exist two strong emission peaks at 405 and 429 nm and a weak peak at 455 nm, respectively. For the Z-S nanocomposite particles calcined at 300 °C for 2 h, the emission band is broadened to 400–590 nm, and the strongest emission band is located at 415–455 nm. The fluorescence emission intensity at 439 nm is 269.63 au with a significant enhancement of 108% compared to that of the uncalcined Z-S particles at 429 nm where the emission intensity is 129.68 au. The photoluminescence (PL) bands of ZnO quantum dots have been attributed to the oxygen vacancies.^{20–22} When Z-S nanocom-

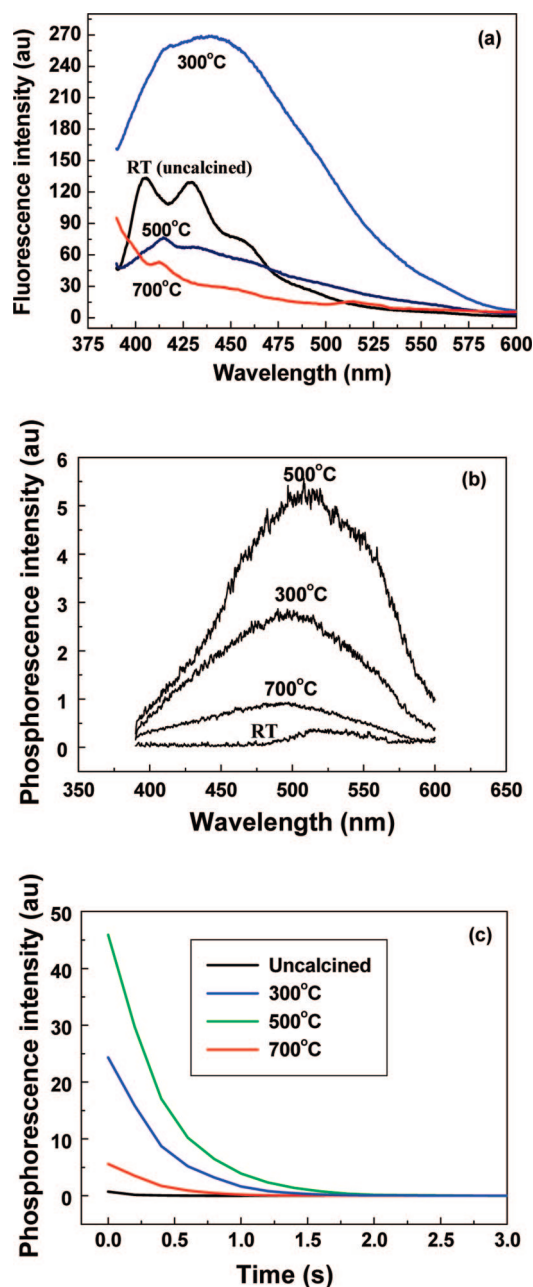


Figure 4. (a) Fluorescence emission spectra, (b) phosphorescence emission spectra, and (c) phosphorescence lifetime of Z-S nanocomposite particles using 370 nm as the excitation wavelength.

posite particles were calcined at 300 °C; the oxidation and decomposition of residual organic species such as TEOS and acetic acid would deplete the oxygen in the atmosphere, and the outer silica layer would slow down the oxygen diffusion, leading to the formation of a mass of oxygen vacancies and thus to the enhancement in the intensity of the visible fluorescence. Further increase in calcination temperature leads to a significant decrease in the emission intensity. As the calcination temperature was increased to 500 °C, the decomposition of organic species (see Figure 1 and Figure 3) would be almost completed to bring about the decrease of oxygen vacancies. Therefore, a higher calcination temperature would lead to lower fluorescence intensity. In addition, when the calcination temperature was further increased to 700 °C, the ZnO QDs have been transformed to $\text{Zn}_{1.7}\text{SiO}_4$ (Figure 1); thus it was natural to observe that the fluorescence peak has almost disappeared.

It is interesting to observe that the calcined Z-S nanocomposite particles show an afterglow phenomenon. Z-S nanocomposite particles were irradiated by a UV lamp for a few minutes. After removing the irradiation, the Z-S nanocomposite particles remained bright for a few seconds, which can be observed by naked eyes. Therefore, the phosphorescence emission spectra of Z-S nanocomposite particles were measured using 370 nm as the excitation wavelength, and the results are presented in Figure 4b. It shows that the uncalcined Z-S nanocomposite particles have a very weak phosphorescence peak with an emission intensity of 0.34 au located at 515 nm. The phosphorescence emission intensity was significantly enhanced by calcination of Z-S nanocomposite particles at 300 °C for 2 h. After calcination of Z-S nanocomposite particles at 500 °C for 2 h, the maximum phosphorescence emission peak of an intensity value of 5.42 au has been observed with a significant enhancement of 14.9 times compared to that of the uncalcined Z-S particles. Further increase in the calcination temperature to 700 °C leads to the rapid decrease in the phosphorescence emission intensity since ZnO QDs have been transformed to $\text{Zn}_{1.7}\text{SiO}_4$ (see Figure 1). Figure 4c displays that the phosphorescence lifetime at the half-intensity decay of Z-S nanocomposite particles using 370 nm is about 0.32, 0.31, and 0.28 s for Z-S nanocomposite particles calcined respectively at 300, 500, and 700 °C.

4. Conclusions

In summary, the facile synthesis of Z-S nanocomposite particles has been reported by hydrolyzing TEOS under the hydrolysis of ammonia in the ZnO QDs containing ethanol solution. The fluorescence and phosphorescence of Z-S nanocomposite particles have been investigated as a function of calcination temperature. The highest intensity of fluorescence and phosphorescence occurred after the calcination, respectively, at 300 and 500 °C and showed the significant enhancements of 108% and 1490% compared to those of the uncalcined Z-S nanocomposite particles. Consequently, the calcined Z-S nanocomposite particles are more promising than the uncalcined Z-S nanocomposite particles as light-emitting fillers for functional transparent polymer nanocomposites as encapsulating materials for solid state lighting due to the significantly enhanced fluorescence and phosphorescence and the matching refractive index with transparent epoxy matrix.

Acknowledgment. Financial support from Beijing Municipal Natural Science Foundation and National Natural Science Foundation of China is acknowledged.

Supporting Information Available: An LED lamp encapsulated using the highly transparent Z-S/epoxy supernanocomposite. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JP8063068