Preparation and formation mechanism of ZnO supported hollow SiO₂ nanoparticle by an interfacial reaction through micropores

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Abstract

A ZnO supported hollow SiO₂ (ZnO/h-SiO₂) composite nanoparticle with a strong yellow emission has been prepared using the Zn(OAc)₂ precursor with a catalytic amount of NaOH. A single nano-sized ZnO having defective oxygen homogeneously dispersed on the SiO₂ shell. How this desired structure was achieved is discussed by comparison of three carrier nanoparticles of h-SiO₂, calcite core-SiO₂ shell (CS), and dense SiO₂ (d-SiO₂) which have several spaces where the precursor solution was trapped. That is, h-SiO₂ has a micropore/hollow interior/interspace among the particles, CS has a micropore/interspace, and d-SiO₂ only has an interspace. On the CS carrier, similar ZnO single nanoparticles were dispersed and the ZnO/CS composite showed a strong yellow emission. On the d-SiO₂ carrier, aggregated ZnO nanoparticles were localized on part of the SiO₂ surface. Consequently, the existence of micropores is the key structure to obtain the ZnO nanoparticle dispersion. During penetration of the ZnO precursor into the hollow interior through the micropores, dissociated Zn²⁺ ions adsorb on the SiO₂ surface. Hydroxide ions (OH⁻) of NaOH then make contact with the adsorbed Zn²⁺ on the SiO₂ shell to form ZnO. The micropore could work as a mold to prevent excess growth of the ZnO. The strong emission was also contributed by defects among the siloxane bonds in the SiO₂ shell due to its light scattering ability. The obtained ZnO/h-SiO₂ can be useful as a yellow phosphor of a white light emitting diode (LED).

Keywords: hollow SiO₂ nanoparticle, ZnO, Zn(OAc)₂, micropore, fluorescent

1. Introduction

Hollow SiO_2 (h- SiO_2) nanoparticles have attracted much attention due to their unique characteristics such as thermal insulation, drug carrier, optical performance, etc [1-10]. These characteristics are derived from a combination of a solid shell with a nano-sized hollow interior. Many preparation techniques for h- SiO_2 nanoparticles have been developed, which are mainly categorized as a soft template and hard template. SiO_2 is typically coated on the template and then the template is removed by a suitable chemical process like burning, dissolution, etc. In the hard template method, polystyrene (PS) beads as the organic template [11], and calcium carbonate (CaCO_3) [1] and hydroxyapatite (HAp) [12] as inorganic templates are utilized. Especially, CaCO_3 is removed by a diluted acid solution and is so-called an environmental friendly process. Their size control from nano-size to micro-size and shape control have already been established. The size and shape of the h- SiO_2 particle can be a replica of the used template [13]. Control of the microstructures of the SiO_2 shell, e.g., shell thickness, apparent density, and pore size, is done by adjustment of the ratio of SiO_2 precursor/template, reaction time, and solution pH, during the sol-gel processing [14]. Previously, a h- SiO_2 /polyurethane composite film with both superior thermal insulation and visible transparency was developed. The SiO_2 shell with a designed low apparent density has many defects among the siloxane bonds, which reduces the thermal conduction in the composite film by phonon-phonon scattering [6]. As just described, such a high performance can be achieved by not only a nano-sized hollow interior, but also by the microstructure of the SiO_2 shell.

Zinc oxide (ZnO) is known as an oxide semiconductor with a 3.3 eV bandgap and exhibits a green-centered fluorescent with ultraviolet excitation [15]. Many researchers have synthesized nano-sized ZnO and discussed the relation between the particle size and emission wavelength [16-18]. Recently, it was clarified that the fluorescent emission including yellow could be controlled by adjustment of the drying conditions of the layered zinc hydroxide without any rare-earth compound [19]. For the strong emission, nano-sized ZnO with a high specific surface area is strongly required, however, nanoparticles easily aggregate which results in a performance degradation. As one of the solutions, a technique to use carrier particles in which the functional nanoparticles (i.e., ZnO) were immobilized was developed. Selective SnO_2 nanoparticle depositions inside or outside the h- SiO_2 shell were reported. The SnO_2 precursor interacts with either the inside or outside of the SiO_2 shell depending on the microstructure [20]. Yamada et al. reported a mesoporous h- SiO_2 whose inner surface was coated by TiO_2 . The selective coating was achieved due to a highly-ordered mesoporous structure. The TiO_2 coated h- SiO_2 showed a high photocatalytic activity compared to the TiO_2 coated dense SiO_2 [21].

Previously, ZnO/h- SiO_2 with a strong yellow emission was successfully synthesized by optimization of the reaction time and amount of the catalytic NaOH [22]. Single nano-sized ZnO homogeneously dispersed on the SiO_2 shell and the ZnO containing defective oxygen was

determined by an XPS analysis. An investigation of how such a desired structure is achieved is the objective of this study. During the sol-gel route for ZnO, the $\text{Zn}(\text{OAc})_2$ precursor is hydrolyzed by NaOH into $\text{Zn}(\text{OH})_2$ then it is dehydrated into ZnO. The reaction system in which the ZnO formation preferentially occurs near the SiO_2 shell surface should be considered. To immobilize the ZnO nanoparticle on the SiO_2 surface, dissociated Zn^{2+} ions first adsorb on the SiO_2 surface, then it is hydrolyzed and dehydrated to form ZnO. Many Zn^{2+} adsorption sites are required in the SiO_2 shell. The carrier h- SiO_2 nanoparticle was prepared using the CaCO_3 template via sol-gel processing. According to our earlier results, the obtained h- SiO_2 shell has micropores of less than 2 nm [1] through which precursor solution penetrates into the hollow interior [20]. Additionally, there are many defects among the siloxane bonds, which can be effective adsorption sites for the Zn^{2+} ions. Using the h- SiO_2 carrier with such a microstructure, ZnO formation is thought to be preferentially promoted near the SiO_2 surface. That is, the $\text{Zn}(\text{OAc})_2$ precursor solution penetrates into the hollow interior through the micropores and is trapped in the hollow interior and maybe in the micropores and interspaces among the h- SiO_2 nanoparticles. During this time, Zn^{2+} adsorption is induced on the SiO_2 surface due to the electrostatic force between them. The adsorbed ions then contact the OH ion of NaOH to become ZnO. In order to clarify this postulated ZnO formation mechanism, two different carrier nanoparticles were chosen in addition to the h- SiO_2 carrier nanoparticles. One is the calcite core- SiO_2 shell, which is the particle before core removal of the h- SiO_2 , therefore, the shape, size, and physical property of the shell are the same as that of h- SiO_2 . The other is dense SiO_2 , which has a smooth surface without pores. That is, h- SiO_2 has micropores, a hollow interior, and interspace among them, the core-shell has micropores, and a interspace, and the dense SiO_2 has only an interspace.

2. Experimental section

2.1. Preparation of carrier nanoparticles

Hollow SiO_2 (h- SiO_2) nanoparticles were prepared using an inorganic template method based on our earlier report [1]. As the template, calcium carbonate nanoparticles were prepared by incorporation of CO_2 gas into a calcium hydroxide solution [23]. Figure 1 shows an SEM image of the template calcite crystal with a cubic shape and the size of approximately 60 nm. The calcite nanoparticles (3.26 g) were dispersed in 24.0 ml of ethanol (99.5 %, Wako Pure Chemical Industries, Ltd.) with 4.48 ml of distilled water by an ultrasonic treatment (SONIFIER250, BRANSON, duty cycle: 50 %, Output: 3) for 10 minutes. A 2.0 ml aliquot of a 25 % ammonia aqueous solution (Wako Pure Chemical Industries, Ltd.) and 2.0 ml of tetraethoxysilane (TEOS, Wako Pure Chemical Industries, Ltd.) were added to the suspension and mixed in a shaking bath (SB-20, As One, 196 rpm) for 2 hours at 20 °C. The suspensions were washed with ethanol and distilled water to remove any unreacted TEOS and ammonia. After drying under vacuum for 24 hours at room temperature, the

calcite core-SiO₂ shell (CS) nanoparticles were obtained. To remove the core, a 3M HCl solution was added to the suspension. The suspensions were washed with ethanol/distilled water to remove the HCl and calcium ions. After drying under vacuum for 24 hours at room temperature, the h-SiO₂ nanoparticles were obtained.

2.2. Preparations of composite nanoparticles

Three kinds of carrier nanoparticles were utilized; i.e., h-SiO₂ nanoparticles, CS nanoparticles, and dense silica (d-SiO₂) nanoparticles. The former two nanoparticles were prepared as already described and their SiO₂ shells have micropores similar to our earlier experiment [1]. The d-SiO₂ nanoparticle (75 nm, 484 mg, Quatron PL-7, Fuso Chemical) was commercially obtained and its surface obtained no micropores.

For comparison, the ratio of Zn/Si was equalized by volume among the three carrier nanoparticles, that is, 200 mg of h-SiO₂ nanoparticles, 520 mg of CS nanoparticles, and 484 mg of d-SiO₂ nanoparticles were added. Before preparation, the three carrier particles were heated at 200 °C for 2 hours under vacuum to remove any adsorbed water on the SiO₂ surface. Zinc acetate (anhydride) (abbreviated as Zn(OAc)₂, 2.29 g, Wako Pure Chemical Industries, Ltd.)-ethanol (150 ml) solutions were added to the dried carrier nanoparticles under vacuum for penetration of the Zn(OAc)₂ solution into the hollow interior through the micropores in the SiO₂ shell. The suspensions were mixed using a magnetic stirrer for 15 minutes under air at room temperature. The particles were collected by filtration using an aspirator. Sodium hydroxide (abbreviated as NaOH, 1.0 g, Wako Pure Chemical Industries, Ltd.)-ethanol (50 ml) solutions were added to the particles and mixed for 5 minutes using a magnetic stirrer. The suspensions were vacuum-filtered and vacuum-dried for 24 hours at room temperature.

2.3. Characterizations

To confirm the ZnO formation on the particles, the obtained composites were observed by a scanning electron microscope (SEM, 15 kV JEOL Ltd.) with scanning electron and transmission electron images, and analyzed by an x-ray diffractometric (XRD, UltraVI, Rigaku Corporation). The fluorescence property of the obtained composite particles were characterized by photoluminescence spectrometry (FP-6500, JASCO Corporation) in the range between 370 and 670 nm. The sample powder was filled in a quartz container (PSH-001) and analyzed using an integrating sphere (ISF-513). To determine the band-gap energy of the particles, the absorption spectra of the composite particles were analyzed by UV-vis spectrometry (UV-3150, SHIMADZU CORPORATION) in the diffusion refraction mode using an integrating sphere (LISR-3100) in the range between 800 and 300 nm. Based on the obtained absorption spectrum, a Tauc plot was made using $h\nu$ vs $Ah\nu/d\log_{10} e$, in which h , ν , A , d , and e , are Planck's constant, frequency of electromagnetic, absorbance, sample

thickness, and base of natural logarithm, respectively. In the Tauc plot, the band-gap energy was calculated by the intersection between the abscissa axis and the approximate line on the rising near absorption end. The ZnO nanoparticle size on the carrier particles was calculated by the Brus equation (1) with the band-gap energy [24], where E^* and E_g^{bulk} are the band-gap energies of particles and bulk, and $\hbar$, e , r , m_e , m_h , m_0 , ε , and ε_0 are the reduced Planck's constant, elementary charge, particle size, effective mass of the electron, effective mass of the hole, static mass of the electron, relative permittivity, and electric permittivity of vacuum.

$$E^* = E_g^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2er^2} \left(\frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r} \quad \text{equation(1)}$$

In this equation, the second and third term on the right side represent the quantum confinement effect and Coulomb interaction of electron and hole, respectively. The third term is typically ignored. For calculation of the particle size from the bandgap energy, equation (1) can be simplified into the following equation (2) using $\hbar = h/2\pi$.

$$r = \sqrt{\frac{h^2(m_h + m_e)}{8em_0m_em_h(E^* - E_g^{\text{bulk}})}} \quad \text{equation (2)}$$

To determine the quantity of ZnO on the carrier particles, the quantity of Zn atoms was determined by an inductively coupling plasma (ICP, SPS7800, Seiko Instruments Inc.) method. Before the measurement, the sample particles (22 mg) were added to 50 ml of HCl and shock for 5 hours at 40 °C. The suspensions were vacuum filtered by washing with an HCl solution. The standard curve was made using a diluted 1000 ppm Zn standard solution (Wako Pure Chemical Industries, Ltd.) as 10, 50, 100, and 200 ppm.

The specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) equation to nitrogen adsorption isotherms, which were measured by a surface area analyzer based on the volumetric method (BEL-Sorp max, BEL Japan, Inc.). The cross-sectional area of the nitrogen molecule was taken as 0.162 nm². The existence of pores in the SiO₂ shell was investigated by the t-plot which is the experimental volume adsorbed as a function of the thickness of the adsorbed layer for each experimental relative pressure.

The surface chemical analysis of the ZnO/h-SiO₂ nanoparticles was investigated by X-ray photoelectron spectroscopy (XPS) (Physical Electronics, Inc.). MgK α (1253.6 eV) was the excitation source for identification of the elements and their oxidation states. The obtained O1s spectrum was calibrated to a C1s electron peak at 284.8eV.

For the cathode luminescence measurement, an SEM (JSM-6510, JEOL Ltd.) was used at 15 kV.

3. Results and discussion

Figure 2 shows SEM and STEM observations of (a)(b) as-synthesized hollow SiO₂ (h-SiO₂) and

(c)(d) ZnO/h-SiO₂ composite nanoparticles which were prepared with 1.0 g of NaOH and a 5-minute reaction time. The reaction conditions were fixed based on our earlier results [22]. The surface of the as-synthesized h-SiO₂ was slightly round-off cubic (Fig. 2(a)) compared to the calcite template (Fig. 1) and a hollow interior with a SiO₂ shell was clearly shown in Fig. 2(b). For the ZnO/h-SiO₂, fine particulates covered the h-SiO₂ and neither aggregation nor localization was observed (Fig. 2(c)(d)). Figure 3 shows XRD spectra of (a) the ZnO/h-SiO₂ with (b) commercial ZnO. The three vertical dashed lines represent the main ZnO peaks as (110), (002), and (101) with a wurtzite crystal. The spectrum of ZnO/h-SiO₂ shows the three peaks to be rather broad, which suggests a smaller ZnO formation on the h-SiO₂. Another broad peak observed around 22 ° was derived from the amorphous SiO₂. According to the XRD, the particulates seen in Fig. 2(c)(d) were wurtzite ZnO nanoparticles. Figure 4 shows the PL spectra of the ZnO/h-SiO₂ with commercial ZnO, which were excited by a 350 nm wavelength. The inserted digital photographs were the corresponding particles in the quartz cell under UV light irradiation (365 nm). The ZnO/h-SiO₂ exhibited a fluorescent emission with a top peak of 543 nm and the bright yellow emission can be also confirmed by visual contact. Figure 5 shows (a) UV-vis spectra and (b) Tauc plots of ZnO/h-SiO₂ with commercial ZnO. The UV absorption of the ZnO/h-SiO₂ started at less than 400 nm and the rise in the absorption slightly shifted to a shorter wavelength compared to that of the commercial ZnO, which suggested a large bandgap energy of the formed ZnO. From the Tauc plots, the bandgap energy and ZnO particle size in the composite were 3.236 eV and 7.66 nm, respectively. That of the commercial ZnO were 3.205 eV and 21.1 nm, respectively. Figure 6 shows the XPS spectrum of O 1s of the ZnO/h-SiO₂. It exhibited a broad asymmetric feature indicating the presence of multi-component oxygen species. The first peak on the low binding energy side (530.25 eV) of the O 1s spectrum can be attributed to the O²⁻ ions on the wurtzite structure of the Zn²⁺ ion array, which are surrounded by zinc atoms with their full complement of nearest-neighbor O²⁻ ions. The intermediate binding energy (531.55 eV) peak is associated with O²⁻ ions that are in oxygen deficient regions within the ZnO matrix. The higher binding energy peak at 532.65 eV usually corresponds to adsorbed H₂O or O₂ molecules on the surface [25].

A strong yellow emission of ZnO/h-SiO₂ seems to be achieved by the single nano-sized ZnO with deficient oxygen homogeneously dispersed on the h-SiO₂ shell. How these desired structures are formed is discussed. When the precursor solution was added to the dried h-SiO₂, the solution penetrates into the hollow interior through micropores in the shell with the help of the vacuum. After filtration of the suspension, the solution still remains in the micropores and possibly in the hollow interior and interspace among the h-SiO₂ nanoparticles. Over time, the dissociated Zn²⁺ ions adsorb on the negative site of the SiO₂. When the catalytic NaOH solution was added, the OH⁻ ions diffuse into the SiO₂ shell and react with the Zn²⁺ ions to form ZnO. According to our earlier results, there are many defects among the siloxane bonds in the shell, where the Zn²⁺ ions adsorb. In support of

this hypothesis, the Zn/Si ratio was 19.64/80.36 by molar based on the ICP measurement. In addition to ZnO observed by STEM, an invisible ZnO that is hidden by the SiO₂ shell seems to exist.

As already mentioned, to obtain the desired structure, the existence of nano-spaces, such as micropores, hollow interior, and interspace among the carrier nanoparticles seem to play an important role. In order to clarify the above assumption of the ZnO formation mechanism, two carrier nanoparticles were chosen, that is, the calcite core-SiO₂ shell (CS) and dense SiO₂ (d-SiO₂) nanoparticles as a comparison with the h-SiO₂ carrier. The former nanoparticles are obtained before core-removal of the h-SiO₂ nanoparticles, therefore, particle size and physical property of the SiO₂ shell are similar between the two. In support of this, Figure 7 (a)-(d) shows the nitrogen adsorption/desorption isotherms and *t*-plots of the h-SiO₂ and CS nanoparticles. The specific surface area of h-SiO₂ was 228.0 m²/g which is the sum of the inner and outer SiO₂ shell surfaces, and the micropore size was calculated to be 1.44 nm. The CS nanoparticles, the specific surface area was 17.3 m²/g and the micropore size was 1.49 nm. The latter nanoparticles are commercial d-SiO₂ nanoparticles whose surface is nonporous as shown in Figure 7(e)(f). The specific surface area is 36.5 m²/g. Summarizing the features of the three carrier nanoparticles, the h-SiO₂ has hollow micropores, and interspace among them, CS has micropores and interspaces, and d-SiO₂ only has an interspace.

Figure 8 shows microscopic observations of the as-synthesized core-shell (CS) nanoparticles ((a) SEM, (b) STEM) and ZnO/CS nanoparticles ((c) SEM, (d) STEM). The as-synthesized CS nanoparticles were round-off cubic and the SiO₂ coating was slightly observed in Fig. 8(b). In the ZnO/CS nanoparticles, particulates had formed on the surface (Fig. 8(a)) and its particulate layer was around 10 nm thick (Fig. 8(d)). Figure 9 shows an XRD spectra of the (a) ZnO/CS composite with the (b) commercial ZnO and (c) calcite core as a reference. The strong peak of the composite (Fig. 9(a)) was derived from the calcite core. For confirmation of the ZnO formation, the spectrum in the range between 30 and 38 ° was enlarged as shown in Fig. 9(d). Although the peaks were small, two peaks appeared near 31.8 and 34.5 ° (represented by dashed arrows) due to ZnO. The third peak near 36.3 ° was barely visible because of overlapping with the calcite peak of (110).

Figure 10 shows the PL spectra of (a) ZnO/CS composite nanoparticles with (b) ZnO/h-SiO₂ (same as Fig. 4(c)), (c) commercial ZnO, and (d) CS carrier nanoparticles, as references. The ZnO/CS composite nanoparticles showed the highest fluorescent performance. The top peak of the emission was at a 550-560 nm wavelength, which is similar to that of ZnO/h-SiO₂ (Fig. 10(b)). The inserted figures (a)-(d) were corresponding samples in quartz cells under ultraviolet irradiation at 350 nm. Although the PL intensity of ZnO/CS was higher than that of ZnO/h-SiO₂, the ZnO/h-SiO₂ under UV light emitted stronger than that of ZnO/CS by visual observation. The PL detector could not detect whole emission of the ZnO/h-SiO₂. The commercial ZnO did not show a fluorescent property due to the lack of defects. However, in both the ZnO/h-SiO₂ and ZnO/CS nanoparticles, the

formed ZnO had defects which contributed to generating the fluorescent ability. Naturally, the CS carrier did not have any fluorescent emission.

Figure 11 shows (a) UV-vis spectra and (b) Tauc plots of ZnO/CS nanoparticles with ZnO/h-SiO₂ and commercial ZnO as references. The adsorption rise started at less than 400 nm, which is similar to that of ZnO/h-SiO₂. From the Tauc plots, the band gap energy of ZnO/CS was 3.263 eV, which is higher than that of ZnO/h-SiO₂ (3.236 eV). Based on the Brus equation, the formed ZnO size was 5.76 nm, which is smaller than that of ZnO/h-SiO₂ (7.66 nm).

Even when CS nanoparticles were used as the carrier for ZnO, a strong yellow emission was obtained. Regardless of the presence or absence of the hollow interior, single nano-sized ZnO was formed. The formed ZnO of ZnO/CS has a higher bandgap energy and smaller nanoparticles compared to that of ZnO/h-SiO₂. However, the emission usually observed of ZnO/h-SiO₂ was higher than that of ZnO/CS. The difference in the results is caused by the ZnO formation state in the shell and SiO₂ shell's light scattering ability due to its defects among the siloxane bonds. Although the Zn/Si ratio of ZnO/CS was 20.93/79.07 by molar which is similar to that of ZnO/h-SiO₂ (19.64/80.36), the ZnO formation on the CS carrier occurs rather outside the SiO₂ shell compared to on the h-SiO₂ carrier based on microscopic observations. That is, the ZnO formation in ZnO/h-SiO₂ occurs rather in/inside the SiO₂ shell. The higher PL intensity of the ZnO/CS was contributed by a high amount of ZnO outside of the SiO₂ shell. According to earlier results, the SiO₂ shell via the sol-gel route has many defects among the siloxane bonds which induces phonon-phonon scattering [6]. As mentioned in the introduction, heat conduction can be reduced by the scattering ability. Similar phenomena occur in this experiment, that is, the bare SiO₂ frame outside the ZnO/h-SiO₂ scatters light from the ZnO's yellow emission. That is why the PL intensity of ZnO/h-SiO₂ is not very high, but usual emission is the highest of the two.

Figure 12 shows microscopic observations of commercially dense SiO₂ (d-SiO₂) nanoparticles ((a) SEM, (b) STEM) and ZnO/d-SiO₂ nanoparticles ((c) SEM, (d) STEM). The as-received d-SiO₂ nanoparticles have a spherical shape with a smooth surface based on a gas adsorption analysis (Fig. 7(e)(f)). Unlike the case of the other two carrier nanoparticles, aggregated particulates were nonhomogeneously observed on part of the d-SiO₂ surface. From the XRD analysis (Figure 13), the aggregated particulates were wurtzite ZnO. The three main peaks were rather sharp, which suggests a larger ZnO formation. The peaks other than ZnO are still under investigation, but it could be due to layered zinc hydroxide according to our earlier experiment [19]. The d-SiO₂ carrier nanoparticles are nonporous dense particles. The precursor solution remains only in the interspace among the d-SiO₂ nanoparticles. The d-SiO₂ surface was smooth and there were not many sites for Zn ion adsorption in the trapped area. Lots of free Zn ions gather and transfer to the large ZnO nanoparticles on the d-SiO₂ surface. In support of this, the bandgap energy and particle size of the ZnO/d-SiO₂ were calculated as 3.228 eV and 8.63 nm (data not shown), respectively.

Summarizing the results, to obtain a single nano-sized ZnO dispersion on SiO₂, the existence of micropores was the most important factor. The ZnO precursor solution is trapped in the hollow interior, then many Zn²⁺ ions adsorb on the inside of the SiO₂ shell surface as well as the outside surface. The many defects among the siloxane bonds in the SiO₂ shell also contribute to supplying many reaction sites for the Zn²⁺ adsorption. In addition, the defects increase the light emission from the ZnO. The micropores could work as a mold to prevent excess ZnO formation inside the SiO₂ shell.

As merits for the ZnO support on the h-SiO₂, attenuation of the emitted light can be reduced due to the hollow's transparency. When the ZnO/h-SiO₂ is dispersed in a polymer matrix, transparency of the composite film or coating is also expected. Figure 14 shows the cathode luminescence of the ZnO/h-SiO₂ composite nanoparticles. A broad peak was observed at around 600 nm. The intensity was not high, due to the hollow structure's insulating property.

4. Conclusion

A strong yellow emission of ZnO/h-SiO₂ has been achieved using a Zn(OAc)₂ precursor with a catalytic amount of NaOH. The desired fluorescent performance was due to the dispersion of single nanosized ZnO on the SiO₂ shell. By comparison of three carriers, i.e., h-SiO₂, CS, and d-SiO₂, the ZnO formation mechanism was discussed. On the CS carrier, similar ZnO nanoparticles were formed on the SiO₂ shell. On the d-SiO₂, aggregated ZnO was localized on part of the SiO₂ surface. Consequently, the existence of micropores in the SiO₂ shell is required for a uniform ZnO formation. The precursor solution penetrates into the hollow interior through the micropores and dissociated Zn²⁺ ions adsorb on the SiO₂ inside/in/outside the shell. There are many defects in the SiO₂ shell, therefore, enough sites for Zn²⁺ adsorption. When the catalytic NaOH was added, the OH⁻ ions reacted with the Zn²⁺ ions in the SiO₂ to form ZnO. The micropores can be a mold to prevent excess growth of the ZnO. The strong emission of ZnO/h-SiO₂ could also be attributed to the SiO₂'s light scattering ability. The obtained ZnO/h-SiO₂ can be used as an effective yellow phosphor of a white light emitting diode (LED), etc..

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Acknowledgements

This study was supported by the Advanced Low Carbon Technology Research and Development Program (ALCA) of the Japan Science and Technology Agency (JST).

Figure 1 SEM image of calcium carbonate as a template

Figure 2 Microscopic observations of as-synthesized hollow SiO_2 nanoparticles ((a) SEM, (b) STEM) and ZnO/h-SiO_2 nanoparticles ((c) SEM, (d) STEM).

Figure 3 XRD spectra of (a) ZnO/h-SiO₂ with (b) commercial ZnO

Figure 4 PL spectra of (a) ZnO/h-SiO₂ composite nanoparticle with (b) commercial ZnO. Inserted digital photographs are corresponding particles under UV light irradiation.

Figure 5 (a) UV-vis spectra and (b) Tauc plot of ZnO/h-SiO₂ composite nanoparticle

Figure 6 XPS spectrum of O 1s of the ZnO/h-SiO₂

Figure 7 Nitrogen gas adsorption/desorption isotherms and t-plots of three carrier nanoparticles (a)(b) h-SiO₂, (c)(d) CS, and (e)(f) d-SiO₂ nanoparticles.

Figure 8 Microscopic observations of as-synthesized core-shell (CS) nanoparticle ((a) SEM, (b) STEM) and ZnO/CS nanoparticle ((c) SEM, (d) STEM).

Figure 9 XRD spectra of (a) ZnO/CS composite nanoparticles with (b) commercial ZnO and (c) calcite core as reference. (d) shows an enlarged spectrum of ZnO/CS composite between 30 and 38 ° range.

Figure 10 PL spectra of (a) ZnO/CS composite nanoparticle with (b) ZnO/h-SiO₂ (same as Fig. 4(c)), (c) commercial ZnO, and (d) CS carrier nanoparticles, as references.

Figure 11 (a) UV-vis spectra and (b) Tauc plots of ZnO/CS nanoparticles with ZnO/h-SiO₂ and commercial ZnO as references.

Figure 12 Microscopic observations of commercial dense SiO_2 (d-SiO₂) nanoparticles ((a) SEM, (b) STEM) and ZnO/d-SiO₂ nanoparticles ((c) SEM, (d) STEM).

Figure 13 XRD spectra of (a) ZnO/d-SiO₂ nanoparticles with (b) commercial ZnO

Figure 14 Cathode luminescence of the ZnO/h-SiO₂ composite nanoparticles