Selective SnO₂ deposition on inner/outer shell surface of hollow SiO₂ nanoparticles by control of shell microstructure

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Abstract

A selective SnO₂ deposition on the inner or outer shell surface of hollow SiO₂ nanoparticles was proposed using the shell microstructure difference and electrostatic interaction between SiO₂ and tin precursor. Hollow SiO₂ nanoparticles were first prepared via the sol-gel route using a polystyrene template. The obtained hollow particles appeared to have similar morphologies based on microscopic observations, however, different micropore sizes were found; one was above 1 nm (type B) and the other was undetectable (type C) by the gas adsorption analysis. When they were mixed with the tin source, hollow particles were kept in a vacuum to induce the tin source solution to the inside of the hollow interior through the micropores in the shell. The mixed compounds were then filtered to remove any excess tin source. Our strategy is that the shell microstructure induces different tin source retention times in the hollow interior, which results in the selective SnO₂ deposition on the intended shell surface. The microscopic results clearly showed that SnO₂ depositions were observed on only the outer surface in type B and on the inner surface in type C. The SnO₂-deposited type B indicated an electro-conductivity, while the SnO₂-deposited type C showed a good optical property compared to commercial SnO₂.

Keywords: Hollow SiO₂ nanoparticle, SnO₂, Micropore, Chelate compound, Apparent shell density

1. Introduction

Hollow SiO₂ particles have a unique structure with a hollow interior and solid shell that provides solid/liquid loading, thermal and electrical insulations, corresponding optical abilities, etc [1,2]. The sacrificial templating methods are mostly utilized by employing soft and hard templates such as surfactant micelles, co-polymer micelles, organic/inorganic/metal particles, etc. [3].

Due to increased awareness of the importance of hollow microstructures, there have been reported mainly structure controlling techniques. Generally, in the templating methods, the hollow shapes can be a replica of the template shapes. The organic compounds mostly form spherical structures [4], while some of inorganic/metal templates form several shapes like rods, cubes, needle-like, cocoon, as well as spherical [5,6]. The hollow particle size is also related to the template size. In the shell forming process, they are mainly categorized into two techniques; an adsorption of pre-deposited particles at the template surface [7] and a precursor reacts at the template surface by a sol-gel reaction [8]. In the former, the shell thickness of the hollow particle can be controlled by the size and adsorbed amount of the pre-deposited particles. In the latter, the shell thickness depends on the ratio of the precursor/template. The controllable nanoscale shell thickness exhibits a unique optical performance [1].

When functional nanoparticles are dispersed and immobilized in the SiO₂ shell, additional functionalities can be expected as well as the mentioned abilities derived from the hollow structure. The applied interaction between the SiO₂ surface and nanoparticle or its precursor to immobilize is useful, e.g., to immobilize the Au nanoparticles, using the electrostatic interaction between the negative SiO₂ surface and positive precursor ([Ag(NO₃)₂]⁺) [9] and formation a covalent bond of Au (or its precursor) with amino groups which were introduced at the SiO₂ surface [10-12] were reported. However, these combinations still have a limitation in usable materials.

Mesoporous and microporous materials are known to be very useful hosts for the immobilization of various nanoparticles. So far, hollow SiO₂ nanoparticles with a mesoporous shell have been reported for surfactant micelles [13-15]. Yamada et al. reported mesoporous hollow silica with an inner surface decorated by TiO₂. The selective decoration can be achieved by a highly-ordered mesoporous structure. The precursor solution was easily introduced in the hollow interior through the mesopores and agglomerate to form TiO₂ nanoparticles. The TiO₂ decorated hollow SiO₂ showed a high photocatalytic activity compared to the TiO₂ decorated dense SiO₂ [16]. However, the effect of the micropore existence in the SiO₂ shell on the nanoparticle deposition behavior has never been discussed.

In our previous results, the sol-gel conditions, such as time and pH, are significantly important to adjust the shell microstructure of the hollow SiO₂ nanoparticles prepared using the polystyrene template. The results of a gas adsorption analysis showed that the micropores of less than 2 nm exist in the obtained SiO₂ shell. The shell density was calculated from the relationship between the specific surface area and shell thickness and it can be controlled between 1.4 and 2.2 g/cm³. The shorter

reaction time and lower volume of NH_4OH provided the low shell density and vice versa [17].

Tin oxide (SnO_2), which is an n-type oxide semiconductor with a wide band gap and transparent to visible light, can be applied as a chemical sensor, transparent conductive film, anode of lithium ion battery, etc. The performance of SnO_2 in these applications intimately depends on its structural features such as nanoparticles, other nanostructures, hollow spheres, etc. Particularly, hollow structures have attracted attention because of their improved performance, such as high surface area, efficient catalytic activity, and structural stability [18]. SnO_2 is synthesized via a sol-gel reaction starting from tin chlorides (II, IV) rather than tin alcoxides because of their low cost and good handling ability. To prevent the tin oxide aggregation/gelation during the reaction, the addition of ammonia [19] or the formation of a chelate with acetyl acetone [20] was reported as being useful. In our previous experiment, a homogeneous SnO_2 deposition at the dense SiO_2 nanoparticle surface was confirmed with the addition of SnCl_4 -acetyl acetonate chelation through interaction between the SiO_2 surface and the chelate compounds [21].

In this study, the selective SnO_2 deposition at the inner or outer shell surface of hollow SiO_2 nanoparticles was proposed using the shell microstructure difference and electrostatic interaction between the SiO_2 and tin chelate compound as the tin source. First, hollow SiO_2 nanoparticles were prepared. They appeared to have a similar morphology by microscopic observation, however, different micropore sizes existed; above 1 nm and undetectable by gas adsorption. When they were mixed with the tin source, the hollow particles were kept in a vacuum to induce the tin source solution to the inside of the hollow interior. The mixed compounds were then filtered to remove any excess tin source. Our strategy is that the shell microstructure induces a different tin source retention in the hollow interior, which results in a selective SnO_2 deposition on the intended shell surface.

2. Experimental section

2.1. Synthesis of hollow SiO_2 nanoparticles

Hollow SiO_2 nanoparticles with three different shell structures were prepared using the polystyrene (PS) beads template method according to our earlier method as follows [17]. The synthesis of the PS bead suspension is described. A 1.0 ml aliquot of a 5.4 mass % PS beads aqueous suspension was mixed with 100 ml of 2-propanol (2-PrOH) and a certain amount of 25 % ammonia solution (NH_4OH) to adjust the suspension pH. A 2.0 ml aliquot of tetraethoxysilane (TEOS) was then added and mixed at 20 °C for 2, 4, and 8 hours using a shaker to induce the SiO_2 coating on the PS template surface. The suspensions were pressure-filtered, washed twice by ethanol, and dried at 40 °C under vacuum for 24 hours. To remove the PS core, the core-shell particles were heated at 700 °C in air for 2 hours. Table 1 shows the synthetic conditions of three hollow SiO_2 nanoparticles as types A, B, C, respectively.

The hollow structures and surface morphologies of the obtained particles were observed by

scanning electron microscopy (SEM, JSM-7000F, JEOL Ltd., 10 kV) and transmission electron microscopy (TEM, 2000-EX, JEOL Ltd., 160 kV). The specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) equation to the 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 presence of pores in the SiO₂ shell was investigated by the *t*-plot.

To determine the apparent shell density (ρ_{shell} [g/cm³]) of the hollow particles, a model of spherical hollow nanoparticles was proposed with a shell thickness of *t* [nm] and inner radius (equal to PS radius) of *r* [nm]. According to our earlier report, the specific surface area S_A [m²/g] of the hollow particles can be defined as the sum of the inner and outer surface areas of the shell due to the micropores in which nitrogen gas can penetrate. Therefore, the relationship of ρ_{shell} and S_A , *r*, and *t*, can be represented by the following equation (1).

$$S_A = \frac{4\pi\{(r+t)^2 + r^2\}}{(4/3)\pi\rho_{shell}\{(r+t)^3 - r^3\}} \quad \text{Equation(1)}$$

2.2. Formation of SnO₂ deposited hollow SiO₂ nanoparticles with different precursors

2.2.1. Starting from SnCl₄ aqueous solution

A 100 mg of hollow particles were heated at 200 °C under vacuum for 2 hours using an oil sealed rotary pump and then cooled at room temperature. The 50 ml of SnCl₄ aqueous solutions (SnCl₄·5H₂O, >98 %, Kanto Chemical Co., Ltd., 5.0, 15.0, 70.0 mM) were added to the vessels in which the hollow particles had been placed after back to atmospheric pressure. The mixtures were stirred at 25 °C for 2 days, pressure filtered by supply 0.3 MPa nitrogen, washed by distilled water, and dried at 100 °C for 1 day. The obtained samples were then heated at 500 °C for 2 hours to oxidize the tin source.

2.2.2. Starting from chelate compound

An anhydride SnCl₄ and acetyl acetone were mixed under a nitrogen atmosphere to prepare the SnCl₄-acetyl acetate (Sn(acac)₂Cl₂) chelate solutions with a yellow color. The 100 mg of hollow particles were heated at 200 °C under vacuum for 2 hours using an oil sealed rotary pump and then cooled at room temperature. A 50 ml aliquot of Sn(acac)₂Cl₂ solution (0.50 M) was dropped onto the hollow SiO₂ particles after being back to atmospheric pressure. The mixtures were stirred at 25 °C for 5 days, pressure-filtered by supply 0.3 MPa nitrogen, dried at 50 °C for 12 hours under vacuum, then heated at 200 °C for 2 hours in air. The obtained samples were then heated at 600 °C for 1 hour under flowing oxygen(30 ml/minute) to oxidize the tin source.

2.3. Characterizations of the composite hollow particles

The SnO₂ depositions on the hollow SiO₂ particles were confirmed by SEM and TEM. The crystallinity and crystal structure of the deposited SnO₂ were analyzed by an x-ray diffractometer

(XRD, Ultima IV, Rigaku Corp.).

The amounts of the SnO₂ deposition on the hollow particles were determined by an inductively coupled plasma (ICP, SPS-7800, SII Nano Technology, Inc.) method. The measured hollow particles were dispersed in certain concentrations of a sodium hydroxide (NaOH) aqueous solution to dissolve the hollow particles and the deposited SnO₂. The solutions were filtered and the Sn ion concentrations the filtrates were analyzed.

To characterize the optical properties of the composite hollow particles, the absorbance spectra were measured by UV-vis spectrometry (UV-3150, Shimadzu Corp.) in the wavelength range of 300-600 nm. In addition, a fluorescence spectrophotometer (PL, FP-6500, JASCO Corp.) was used to measure the emission spectra of the composite hollow particles at the excitation wavelength of 350 nm in the wavelength range of 370-670 nm.

2.7. Measurement of electrical resistivity

It is difficult to measure the electrical property of one composite particle. Therefore, the electrical resistivity of a powder layer consisting of the composite hollow particles was measured as a function of the different compression stresses. Figure 1 shows a schematic drawing of the sample container whose inside and outside were made of conductive stainless steel and insulated Teflon, respectively. The composite hollow particles were introduced in the given space shown in Fig. 1 and the powder layer was compressed by a strength testing machine (Autograph AGS-G, Shimadzu Corp.) from the upper side of the container. The electrical resistivity was measured by a multimeter (2000 Multimeter, TFF Corporation Keithley Instruments) which was connected to the container.

As the background, the resistivity x [Ω] and height of the container a [cm] when the compression stress reached 50 MPa was first recorded (Fig. 1a)). After the composite particles were packed, each height of the container b [cm] and resistivity y [Ω] were then recorded for every 0.05 mm compression (Fig. 1b)). The resistivity of the powder layer R [Ω cm] was calculated by the following equation (2), where, S [cm²] represents the surface area of the powder layer.

$$R = \frac{S(y - x)}{(b - a)} \quad \text{Equation(2)}$$

3. Results and discussion

3.1. Synthesis of hollow SiO₂ nanoparticles

Figure 2 and S1 shows TEM observations of the hollow SiO₂ nanoparticles of the three types (A-C). Based on the SiO₂ shell structures by TEM, the three particles can be described as follows. For type A (Fig. 2a)), the thickness of the SiO₂ shell is relatively thin and a spherical shape of the stacked particulates is clearly identified in the shell. For type B (Fig. 2b)), the thickness of the SiO₂ shell is similarly thin like type A, however, the shape of the stacked particulates is identified as half-round.

For type C (Fig. 2c)), the SiO₂ shell is thick and no stacked particulates are recognized in the shell.

During the SiO₂ coating on the PS core by the sol-gel reaction, pH (volume of NH₄OH) and reaction time strongly affect SiO₂ shell microstructure. At relative low pH for short reaction time (Table 1a), hydrolysis and condensation of TEOS are not promoted. The formed SiO₂ layer composed of SiO₂ particulates is thin with weak interaction (type A). With increase in the reaction time (Table 1b), condensation is slightly promoted. The first SiO₂ layer is clearly shown while boundaries between neighboring SiO₂ particulates are becoming unclear because of condensation progress (type B). At relative high pH (Table 1c), hydrolysis and condensation are both promoted. Even for short reaction time, dense SiO₂ shell can be formed (type C).

The specific surface areas of these three were calculated as 178.0, 142.0, and 97.9 m²/g and the shell thicknesses were measured by TEM as 6.0, 7.1, and 10.8 nm, respectively. From these results, apparent shell density can be calculated as 1.87, 1.99, and 1.91 g/cm³ using eq. (1). The pore sizes calculated by *t*-plot were 1.56, 1.14 nm as type A, B, and undetected as type C.

The shell density increased in the order of type A, C, B. Type A and B have micropores which can be detected by gas adsorption, while type C seems to have another small pores which is undetectable by gas adsorption. The pores existed in type C shell are as like molecular defect of Si-O-Si bond. From these results, it can be thought that the calculated shell density of 1.91 g/cm³ is underestimated value.

3.2. Composite hollow particles prepared from SnCl₄ solution

Figures S2 and S3 show SEM observations of the composite particles prepared from SnCl₄ solutions of 5.0, 15.0, 70.0 mM using types A-C as the base hollow particles after drying at 100 °C for 1 day (Fig. S2) and after heating at 500 °C for 2 hours (Fig. S3). For the relative low SnCl₄ concentration of 5.0 and 15.0 mM (a-e) of Figs. S1 and S3), only hollow SiO₂ particles can be observed before and after the heat treatment. With an increase in the SnCl₄ concentration, a white-colored flocculation appeared after drying (Fig. S2f-i)) and the white compounds changed to dark aggregates after being heated (Fig. S3f-i)). From the XRD analysis of the composite particles after being heated (Figure S4), the dark aggregates are deposited SnO₂ particles.

The SiO₂ surface has a negative charge in the aqueous solution due to the rich Si-OH. When SiO₂ particles are mixed with the SnCl₄ solution, the Sn⁴⁺ ion tends to adsorb at the SiO₂ surface and react with the OH⁻ ion to form Sn(OH)₄. After filtration of the mixture to separate particles from the unreacted SnCl₄ solution, heat treatment at 500 °C produced SnO₂ crystals. Formation of the homogeneous SnO₂ deposition at the SiO₂ surface seems to be difficult by control of the SnCl₄ concentration or SiO₂ shell microstructure. Due to the high reaction rate of SnCl₄ and strong interaction among Sn(OH)₄ and Sn(OH)₄/SiO₂, Sn(OH)₄ tends to be trapped in the interspace among the hollow particles during the filtration. The excess amount of Sn(OH)₄ forms SnO₂ aggregates after the heat treatment not only on the SiO₂ surface, but also in the interspace among the hollow particles.

3.3. *SnO₂-deposited hollow SiO₂ particles prepared from Sn(acac)₂Cl₂ chelate solution*

To confirm the morphology changes of the composite particles at each heating step, Figure 3 shows SEM observations of the composite particles (type B as base hollow particle) after a) dried at 50 °C for 12 hours, b) heated at 200 °C for 2 hours, and c) heated at 600 °C for 1 hour. There were no significant differences in the dried (Fig. 3a) and heated 200 °C (Fig. 3b) samples, while bright colored fine particulates were observed after being heated at 600 °C (Fig. 3c). The XRD pattern indicates that the fine particulates are SnO₂ crystals.

The formation mechanism of SnO₂ starting from the Sn(acac)₂Cl₂ chelate compound can be described by the following scheme (1).

Thermal decomposition of the chelate organic ligands starts over 300 °C and the residues crystalize as SnO₂ near 550 °C. The tin-containing compounds remain in the SiO₂ shell after being dried and heated at 200 °C, which were undetectable by microscopic observations.

Figure 4 shows SEM observations of the composite particles after being heated at 600 °C using a) type A, b) type B, and c) type C as the base hollow particles. In the type A composite (Fig. 4a), deformed aggregations were observed along with spherical particles (these are hollow SiO₂ particles). Interestingly, the type B and C composites had quite contrasting results. In the type B (Fig. 4b), fine particulates deposited uniformly on the hollow SiO₂ surface, while in the type C (Fig. 4c), only spherical hollow particles were observed. To confirm the inside of the composite particles, Figure 5 shows TEM observations of a) type B and b) type C composite particles that correspond to Figs. 4b) and c). The type B composite (Fig. 5a)) have fine scattered dark colored particles on the SiO₂ shell surface, that is similar to the SEM result (Fig. 4b). For the type C composite (Fig. 5b), the dark-colored fine particles existed only in the inner shell surface. From the XRD patterns (Figure 6), the dark-colored fine particles were crystallized SnO₂.

When the hollow particles were mixed with the chelate solution by the force from vacuum to atmospheric pressure, the chelate solution penetrated into the hollow interior through the pores/defects in the SiO₂ shell. The pressure-filtration thus eliminates any excess chelate solution. According to ours and Feng's group, an electrostatic interaction exists between the SiO₂ surface and Sn(acac)₂Cl₂ chelate compound. The interaction generates from de-protonated SiO₂ surface and de-chlorinated chelate compound [20, 21]. Using the interaction, some amount of chelate solution could remain on the SiO₂ shell surface. When the SiO₂ shell has a relatively low density as type A, the permeated chelate solution easily tends to be eliminated to the outside of the hollow particle. The eliminated chelate solution seems to be trapped in the interspace among the hollow particles, because type A has a rough surface. The trapped excess chelate solution became SnO₂ aggregates among the hollow particles and shell surface. In comparison with types B and C, they have similar surface morphologies, but a

different shell density. In type B, the permeated chelate solution tends to be eliminated faster than in type C, but slower than type A. The eliminated chelate solution was trapped among the hollow particles and crystallized as SnO₂ on the outer SiO₂ surface. In type C, the elimination is the slowest and the chelate solution tends to be trapped in the hollow interior. During the retention, a significant amount of chelate compound could react with the inner SiO₂ shell surface. The pressure-filtration then completely removed any excess chelate solution. The smoothness of the SiO₂ shell surface of type C is the highest of the three, therefore, excess chelate compounds are easily removed by filtration. The quantities of the SnO₂ deposition were 9.40, 1.73, and 9.80 mass% for the types A, B, and C composite particles, respectively. These results agreed with the above microscopic observations.

3.4. Optical and electrical properties of SnO₂-deposited hollow SiO₂ particles

Through the use of the difference in the shell microstructure, selective SnO₂ deposition on the outer (type B) and inner (type C) SiO₂ shell surface has been achieved. It can be expected that the SnO₂ deposition at the outer shell surface provides an electro-conductive property to the insulated hollow SiO₂ particle.

Figure 7 shows the electrical resistivity of the powder layer consisting of the SnO₂-deposited hollow particles using type B (represented as black triangle) as a function of the compression stress. As a reference, the SnO₂-deposited dense SiO₂ particles prepared in the same way using dense SiO₂ nanoparticles (Quartron, PL-7, Fuso Chemical Co., Ltd.) were used and denoted by the white triangle. The electrical resistivity of the type B layer was undetected at a low compression stress, appeared at 35 MPa and decreased with the increase in the compression stress. The best value was 3.33×10^4 [Ωcm] at 52 MPa and it is much better than that of the SnO₂-deposited dense particles.

The optical property of the SnO₂-deposited hollow SiO₂ particle (type C) was characterized. Figure 8 shows the absorption spectra of type C, SnO₂-deposited type C, and commercial SnO₂ (Kanto Chemical Co., Inc.) as a reference. It is acceptable that the as-synthesized hollow particles showed no absorption property. The absorbed wavelength of the SnO₂-deposited type C shifted to a low wavelength compared to that of the commercial SnO₂. The band gap energies of the SnO₂-deposited type C and commercial product were calculated to be 4.0 and 3.7 eV, respectively. The 0.3 eV difference seems that the deposited SnO₂ have many defects and scattered as fine particles on the inner SiO₂ shell. Figure 9 shows the emission spectra of the SnO₂-deposited type C and commercial SnO₂ as a reference at the excitation wavelength of 350 nm. An emission intensity of the SnO₂-deposited type C was much higher than that of the commercial SnO₂ as the center wavelength of both emission spectra is similar at 460 nm. As mentioned above, the deposited SnO₂ has many defects, therefore, the energy transition mediated by the defect level increased. These improved optical properties of the SnO₂-deposited type C could be achieved by the SiO₂ shell microstructure.

4. Conclusion

Selective SnO₂ deposition on the inner and outer shell surfaces of the hollow particles separately occurred using the shell microstructure difference and interaction between SiO₂ and chelate compounds. The type A hollow particles have a rough surface and low shell density, therefore, retention of the chelate compounds in the hollow interior is not sufficient and trapped compounds in the interspace among the hollow particles formed a nonhomogeneous SnO₂ deposition. For the type B hollow particles with micropores, SnO₂ mainly deposited on the only the outer surface, while for the type C hollow particles with a high density, the SnO₂ mainly deposited on only the inner surface. These morphology-distinguished structures provided as-synthesized hollow particles with electrical and optical properties.

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Tables

Table 1. Synthetic conditions of hollow SiO₂ nanoparticles

	PS suspension (5.4 mass%) [ml]	2-PrOH [ml]	25 % NH ₄ OH [ml]	Suspension pH	TEOS [ml]	Reaction time [hours]
a) Type A			2.0	11.4		4
b) Type B	2.0	100.0	2.0	11.4	2.0	8
c) Type C			5.5	11.6		2

Figures and captions

Figure 1 Schematic drawing of sample container for characterization of electrical resistivity for measurement of a) background and b) powder layer.

Figure 2 TEM observations and schematic models of hollow silica nanoparticles of a) type A, b) type B, and c) type C.

Figure 3 SEM observations of composite samples prepared at each heating step; a) after drying at 50 °C for 12 hours, b) after heating at 200 °C for 2 hours, c) after heating at 600 °C for 1 hour.

Figure 4 SEM observations of composite samples after heating at 600 °C using a) type A, b) type B, c) type C as base hollow particles prepared from $\text{Sn}(\text{acac})_2\text{Cl}_2$ chelate solution.

Figure 5 TEM observations of composite samples after heating at 600 °C using a) type B and b) type C as base hollow particles prepared from $\text{Sn}(\text{acac})_2\text{Cl}_2$ chelate solution.

Figure 6 XRD patterns of composite samples after heating at 600 °C using a) type A, b) type B and c) type C as base hollow particles prepared from $\text{Sn}(\text{acac})_2\text{Cl}_2$ chelate solution.

Figure 7 Electrical resistivity of powder layer consisting of SnO₂-deposited type B and SnO₂-deposited dense particles as a reference as a function of compression stress.

Figure 8 Absorption spectra for type C hollow particle, SnO₂-deposited type C, and commercial SnO₂ as a reference.

Figure 9 Emission spectra of SnO₂-deposited type C and commercial SnO₂ as a reference at excitation wavelength of 350 nm.

Figure S1 TEM observations with low magnification of hollow silica nanoparticles of a) type A, b) type B, c) type C.

Figure S2 SEM observations of the composite particles prepared from different concentrated SnCl_4 solutions using type A-C as base hollow particles after dried at 100 °C for 1 day.

Figure S3 SEM observations of the composite particles prepared from different concentrated SnCl_4 solutions using type A-C as base hollow particles after heated at 500 °C for 2 hours.

Figure S4 XRD patterns of the composite particles prepared with different SnCl_4 concentrations using type A-C hollow particles after heated at 500 °C for 2 hours.

Graphical abstract

Selective SnO_2 deposition at inner/outer surface