Preparation of ZnO-core/Nanoporous Silica-shell Particle and the Conversion to Hollow Nanoporous Silica Particle

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ZnO particle was coated with thin nanoporous silica layers, and hollow nanoporous silica particles were obtained by removing ZnO (core).

After the successful preparation of nanostructured and nanoporous silica films by the solvent evaporation method,[1,2] the preparation of nanoporous silica films has been extensively investigated.[3–6] Although there have been extensive works on the nanoporous silica layers on flat substrates, studies on nanoporous silica layer on particles are limited.[7–11] Nanoporous silica coating is a way to modify the surface properties of powders as well as to impart new functions such as molecular sieving one on catalysts and adsorbents, so that systematic study on the deposition of nanostructured and nanoporous silica layer on particle surface is worth investigating. In addition to the functions of the core–shell particles formed by the deposition of nanoporous silica layer (shell) on particle (core), hollow particles can be obtained by removing the core from the core–shell particles.[10] In the present study, zinc oxide particle was used as the core to be coated with nanoporous silica layer. Zinc oxide is well known and very useful semiconductor for a wide range of applications including pigments, cosmetics, catalysts, and optical materials such as phosphor and solar cell. Coating of ZnO particles has been performed previously to prevent particle aggregation as well as to suppress the catalytic activity.[12–15] The surface modification of ZnO with nanoporous silica may result in the controlled optical properties as well as improved chemical stabilities.

The deposition of nanoporous silica layer was conducted by the following procedure; hexadecyltrimethylammonium chloride (abbreviated as CTAC) (0.211 g), deionized water (17.7 g), methanol (200 mL), 28% aqueous ammonia solution (7.2 g), and zinc oxide (1.0 g) were mixed, and the mixture was shaken for 15 s at room temperature. The mixture was aged at 3 °C for a day. Tetraethoxysilane (abbreviated as TEOS) (0.368 mL) was added to the solution and then the mixture was shaken for another 3 s. The molar ratio of TEOS:CTAC: deionized water:methanol:ammonia was 1:0.4:774:3000:72. The suspension was allowed to react at 3 °C for 3 h. In order to avoid the sedimentation of ZnO during the reaction, the mixture was shaken for 3 s every 30 min. The solid particles were collected by centrifugation (3500 rpm, 3 min) and washed with methanol.

In the TG-DTA curves of the as-coated product, two steps of weight loss were observed at around 100 and 300 °C. The weight loss (5 mass %) at around 100 °C, which accompanied endothermic reaction in the corresponding DTA curve, was due to the dehydration. Since exothermic reaction was observed at around 300 °C in the corresponding DTA curve, the weight loss at around 300 °C was ascribed to the oxidative decomposition of CTA. From the weight loss, the CTA content was determined to be 1.5%. The IR spectrum of the coated product showed absorption bands due to CTA (δ(–CH$_2$–CH$_2$–): 1400 cm^{-1}) and silica (ν(Si–O): 1065 cm^{-1}) in addition to those of ZnO (at around 460 cm^{-1}) (Figures 1a–1c).

In order to vary the thickness of the shell, the reaction was conducted with smaller amounts (200 and 600 mg) of ZnO particle to increase the TEOS/ZnO ratio in the starting solution. The sample weight increased (0.20 to 0.25 and 0.60 to 0.68 g) showing the formation of silica-based coating on ZnO particle. The infrared spectra showed that the relative absorbance of the bands due to CTA and SiO$_2$ increased for the products obtained with lower loading ZnO amounts. Judging from the sample weight, the relative contribution of the coating to the hybrid particle was roughly estimated to be 25, 13, and 8% for the products obtained when TEOS/ZnO ratios were 0.67, 0.22, and 0.13, respectively. The FT-IR spectra also indicated that silica/ZnO ratios of the products were increased as TEOS/ZnO ratios were increased. (Figures 1a–1c) Thus, it was shown that the composition of the hybrid particle was controlled by simply changing the TEOS/ZnO ratio in the reaction mixture. When 1.0 g of ZnO was employed, the prolonged reaction period resulted in the

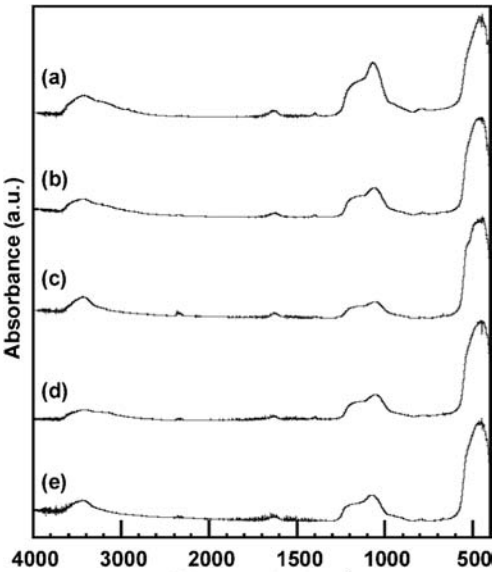

Figure 1. FT-IR spectra of the products (a–d) before and (e) after the calcination. The products were prepared at the TEOS/ZnO ratios of (a) 0.67, (b) 0.22 and (c–e) 0.13; the starting mixture was allowed to react for (a–c) 3 and (d and e) 5 h.

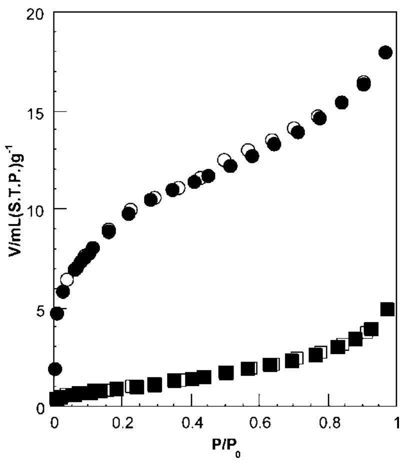

Figure 2. Nitrogen adsorption (closed symbol)/desorption (open symbol) isotherms of nanoporous silica-coated ZnO particles (circle) and parent ZnO particles (square).

greater sample amounts. (1.08 (3 h) to 1.10 g (5 h)) The sample was used for the following experiments.

It should be noted that spherical particles of silica–surfactant nanocomposite form when the present starting solution is allowed to react in the absence of ZnO particle.[16] Such spherical particle was not observed in the present study showing that the CTA was adsorbed on ZnO surface and that the cooperative assembly with silica occurred preferentially at the particle surface to form shells composed of silica and CTA.

The product obtained by the reaction where 1 g of ZnO was employed in the reaction for 5 h was calcined in air at 550 °C for 10 h to form porous shell. The infared absorption bands due to CTA disappeared by the calcination, indicating the surfactant removal. (Figures 1d and 1e) The XRD patterns of all the products (data not shown) showed that the structure of ZnO was retained during the coating and calcination procedures. TEM image showed that the thickness of silica shell was ca. 20 nm. The nitrogen adsorption/desorption isotherms of the parent ZnO and the nanoporous silica-coated ZnO, which were measured at −196 °C, are shown in Figure 2. The nitrogen adsorption isotherm of the calcined particle showed BET surface area[17] of $35\,\mathrm{m^2\,g^{-1}}$. From the ICP analysis, the SiO_2/ZnO mass ratio was determined to be 9.6%. Taking the composition into account, the BET surface[17] was converted to the value of $365\,\mathrm{m^2}$ (g of silica)$^{-1}$. Thus, it was shown that ZnO particle was successfully coated with nanoporous silica shell.

The calcined hybrid ZnO core–nanoporous silica shell particle was allowed to react with an aqueous HCl (pH 2) to dissolve the core. The dissolution of ZnO was confirmed by the ICP analysis. The TEM image of the washed product is shown in Figure 3. Hollow particle replicating the shape of the parent ZnO was seen to show the ZnO dissolution and the formation of hollow nanoporous silica particles with the thickness of ca. 20 nm. Since the shell is porous silica, the aqueous HCl could react with the core to dissolve ZnO, and the formed Zn ion permeated through the pore to the aqueous phase. It is well known that a variety of shapes are available for ZnO,[18,19] ZnO particles are promising morphology template to shape hollow nanoporous silica particles. Tuning the shape and size of hollow nanoporous silica particle is an important subject for the practical applications of nanoporous silica in such fields as drug delivery and separation. The present process using morphology template is promising, and further variation of the shapes will be reported subsequently.

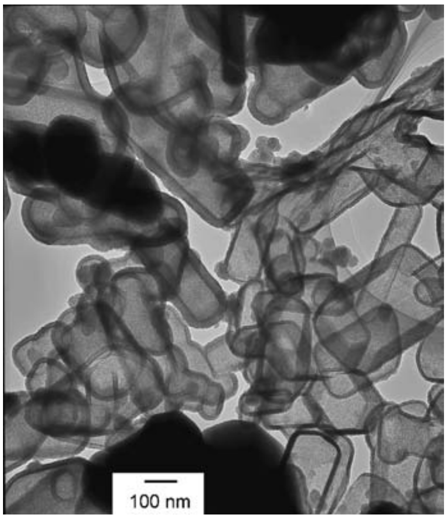

Figure 3. TEM image of the hollow nanoporous silica particles.

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