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Synthesis and characterization of zinc oxide fine particles coated with titania/PDMS hybrid

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Abstract Zinc oxide nanoparticles were coated with titania/polydimethylsiloxane hybrid by co-hydrolysis and co-condensation of the sols prepared from titanium tetraisopropoxide and methoxy-functionalized polydimethylsiloxane to synthesize a new class of hierarchically designed composite materials. The successful formation of the shell, which is composed of titania/polydimethylsiloxane hybrid, was evidenced by SEM, TEM, IR, EDS and zeta potential data. The hydrophobicity and the dispersibility in decamethylcyclopentasiloxane changed dramatically by the shell formation.

Introduction

There has been a great deal of interest in coating particles of nanometer to micrometer sizes with materials of different composition for the purposes of tailoring the properties of the particles [1–4]. Both organic and inorganic particles have been coated with either organic or inorganic materials by various synthetic methods including sol–gel processes, layer-by-layer method and so on [5–8]. In the present study, we chose nanometer sized zinc oxide (ZnO) particles as the core to be coated with titania/polydimethylsiloxane (PDMS) hybrid. ZnO possesses various functions for such uses as pigments, piezoelectric devices, luminescent devices, gas sensors, catalyst, and cosmetic materials. In particular, ZnO nanoparticles have been commonly used in sunscreen products as an excellent UV-filter due to its transparency in visible light wavelength region and the broad absorption in UV light wavelength region [9–11]. In such applications, coating of ZnO nanoparticles has been performed mainly to prevent particle aggregation as well as to suppress the catalytic activity [11–13].

Inorganic/organic hybrid materials of which inorganic and organic moieties are hybridized in nanometer scale have also attracted considerable attention since such materials may have a combination of properties of both phases and have functions depending on the compositions [14–18]. We have synthesized the titania/PDMS hybrid spherical particles from titanium tetraisopropoxide and methoxy-functionalized PDMS by using sol–gel method and co-precipitation method and have reported their optical and mechanical properties [19]. Coating the colloidal particles with inorganic/organic hybrids may provide a mean to tailor the properties of the particles as well as to construct novel functional hierarchically designed hybrids.

Here we report the coating of ZnO nanoparticles with the titania/PDMS hybrid in a suspension by using the sols prepared from titanium tetraisopropoxide and methoxy-functionalized PDMS as a new hybrid materials composed of hybrid shell (Scheme 1). The core–shell particle achieved in the present study is a new class of hierarchically designed composite material.

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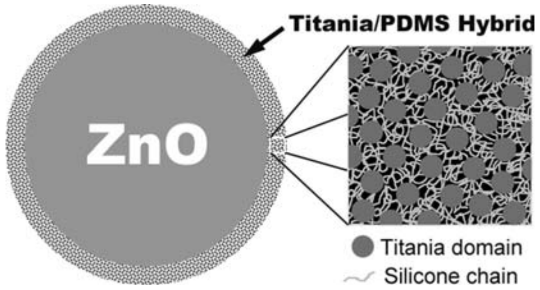


Scheme 1 Schematic illustration of ZnO particle coated with titania/PDMS hybrid

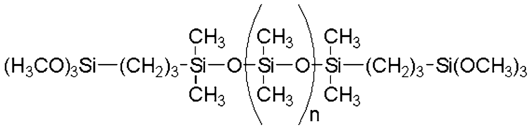
Experimental

Materials

Ultra fine grade ZnO with average particle size of 10–30 nm was purchased from Sumitomo Osaka Cement Co., Ltd. Titanium tetraisopropoxide (TTP) (Wako 1st grade 95 wt%+) was purchased from Wako Pure Chemical Ind., Ltd. 2-Propanol (analytical grade), aqueous ammonia solution (28.0% NH_3) and hydrochloric acid aqueous solution (35 wt%) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Methoxy-functionalized PDMS with a number-average molecular weight of 1,080 (Scheme 2) was supplied by Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). These chemicals were used without further purification.

Synthesis

The synthesis of transparent titania sol was based on the method reported by Wang et al. [20]. Deionized water and hydrochloric acid aqueous solution diluted with 2-propanol were slowly added to TTP at room temperature. The molar ratio of TTP, water, and hydrochloric acid was 1:1:0.02, and the amount of 2-propanol was 400 mL for 1 mol of TTP. The sols containing titanium dioxide and oligomeric PDMS were prepared by mixing the titania sols with 21.0 g of methoxy-functionalized PDMS diluted with 20 mL of 2-propanol. The molar ratios of TTP and methoxy-functionalized PDMS were 10:1 and 5:1 and the products were designated as TS (10) sol and TS (5) sol, respectively. The coating process is as follows. 9.5 g of ZnO particles was dispersed in 2.5 g of TS (10) sol diluted with 47.5 g of 2-propanol by a homogenizer (T. K. Auto Homo Mixer, Tokushu Kika Kogyo Co., Ltd.). Then, 2.0 g of aqueous ammonia solution diluted with 98 g of 2-propanol was added to the dispersion under vigorous stirring at room temperature. After the mixture was allowed to react for several minutes at room temperature, ZnO particles were collected by centrifugation (3,500 rpm, 20 min) and subsequently washed with 2-propanol and dried at 80 °C. For the coating by TS (5) sol, 9.77 g of ZnO particles and 2.0 g of TS (5) sol diluted with 48 g of 2-propanol were used.



$$(H_3CO)_3Si-(CH_2)_3-\underset{CH_3}{\overset{CH_3}{Si}}-O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3-Si(OCH_3)_3$$

Scheme 2 Chemical structure of the methoxy-functionalized PDMS

Characterization

X-ray diffraction (XRD) patterns were obtained with Rigaku Multiflex (Cu Kα) operated at 40 kV and 30 mA in the $2\theta = 5–60°$ range. Fourier transform infrared (FT-IR) spectra of the particles were measured with a JASCO FT/IR 660 Plus in the range of 4,000–400 cm^{-1} using KBr disks. Scanning electron microscopy (SEM) images were obtained with JEOL JSM-6700F operated at 10 kV of acceleration voltage. Before the observation, samples were coated with platinum by using an ion sputter. The energy-dispersive X-ray spectra (EDS) of these samples were measured by the EDS microanalysis system (EX-23000BU, JEOL) connected to the SEM apparatus. Transmission electron microscopy (TEM) images were obtained with JEOL JEM2400EXII operated at 80 kV of acceleration voltage. Sample for the TEM observation was put on a copper micro-grid. The zeta potential of the particles before and after the reaction was measured to evaluate the surface charge by using an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics Co., Ltd.) at 25 °C, which was calculated from electrokinetic mobility using Smoluchowski equation. For the measurements, the coated and uncoated ZnO particles were dispersed in distilled water (pH 6.0) by sonication for 10 min. The single point N_2 BET surface areas of the particles before and after the coating reaction were obtained at 77 K using Macsorb Model-1201 (Mountech Co., Ltd.). Before the measurements, samples were dried in a mixed gas (nitrogen 30% + helium 70%) at 120 °C for 30 min.

The hydrophilicity/hydrophobicity of the coated particles was evaluated by the method described by Kobayashi et al. [21]. They evaluated the hydrophilicity of hydrophobic pigment (Copper Phthalocyanine Blue) by the wettability of the pigment particles with acetone and water mixed solution. The solubility parameter (Hansen parameter) of the mixed solution was used as a measure of the hydrophilicity of the pigment. The coated ZnO particles (0.05 g) were added to 25 mL of deionized water to float on the water surface. Then 2-propanol, instead of acetone, was dropped under continuous stirring by magnetic stirrer until the floated particles sedimented and/or dispersed completely.

The hydrophilicity/hydrophobicity was also evaluated by the contact angle of the droplet of distilled water on the surface of the pressed powders. The coated ZnO particles were pressed into an aluminum dish (1.7 cm × 0.5 cm) by a hydraulic press at 100 kg/cm^2 and a water droplet was put on the flat surface of the compressed particles, followed by measuring the contact angle by the goniometer type contact angle meter (ERMA Inc., Model G-I).

Dispersibility of the coated particles was evaluated by UV–Vis spectra of the dispersions. 5.0 g of the uncoated and coated particles were mixed with 10 g of decamethylcyclopentasiloxane, and were then dispersed with 2.0 mm φ zirconia beads as media in a paint shaker (Asada Iron Works Co., Ltd.) for 2 h. For the measurement of UV–Vis transmittance spectra, the dispersions were cast on the quartz plates by a doctor blade with a gap of 6 µm. The UV–Vis transmittance spectra were measured just after the casting (to prevent an aggregation due to the evaporation of decamethylcyclopentasiloxane) by a spectrophotometer (Shimadzu UV-2500PC) with an integrating sphere assembly (Shimadzu ISR-240A). The quartz plates were set in the sample holder at the entrance of the integrating sphere to detect the scattered light in addition to the transmitted one.

Results and discussion

Preparation of ZnO particles coated with titania/PDMS hybrid

The products prepared from TS (5) and TS (10) sols were white powders. There was no recognizable change in the XRD patterns of ZnO by the coating process (data not shown; all the diffraction peaks were ascribed to ZnO.). In the IR spectra, the absorption bands due to silicone appear at 1,261, 1,089, and 1,022 cm^{-1} (Fig. 1). These three bands are assigned to Si–CH$_3$ bending vibrations (1,261 cm^{-1}) and to Si–O stretching vibrations (1,089 and 1,022 cm^{-1}) typical of PDMS units [22]. Additively, an absorption band due to alkyl chain was observed around 2,960 cm^{-1} for the particle treated by TS (5) sol. This band as well as the Si–CH$_3$ and Si–O related bands for the particle treated by TS (10) sol were very weak and broad. This difference was attributed to the lower silicone content in the coating layer. Peaks due to Ti, Si and Zn were detected in the EDS spectrum of the coated particles (data not shown). These results demonstrated the presence of organopolysiloxane and Ti on the surface of the coated particles.

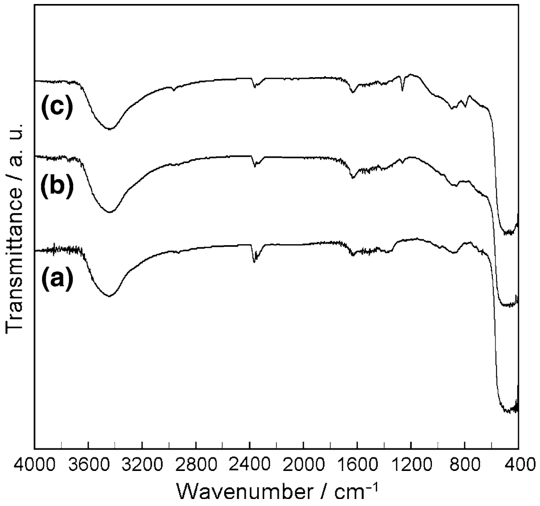
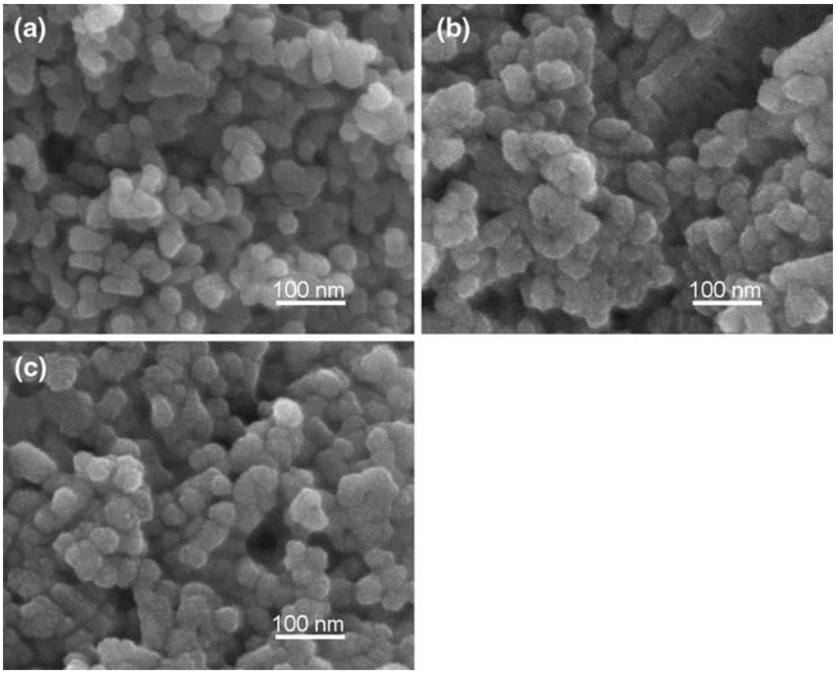


Fig. 1 IR spectra of the particles: (**a**) uncoated, (**b**) treated by TS (10) sol, (**c**) treated by TS (5) sol

Figure 2 shows the SEM images of the particles before and after the coating procedure. The coated particles were large aggregates of several micrometers. Similar aggregates were also seen in the SEM image of the uncoated particles. For the isolated particles, the surface texture changed after the coating procedure as shown in Fig. 1b, c. The coating layer was depicted as a weak contrast surrounding the aggregate of particles in the TEM image (Fig. 3), which was consistent with the SEM image. There was no recognizable phase separation between titania and PDMS within the coating layer as shows in the previously reported spherical particles and films of titania/PDMS hybrids [19, 23]. From these results, it was confirmed that the ZnO particles were coated by the titania/PDMS hybrid. The uniformity of the coating would be affected by dispersibility of the ZnO particles in the sols. Further experiments are required to find the parameter to coat the individual particles in a controlled manner.

The mean zeta potential of the uncoated ZnO particles was +27.5 mV at pH 6.0. This positive value is a typical one for ZnO since the zero point of charge of ZnO ranges from pH 9 to 10 [24, 25]. At pH 6.0, hydroxyl groups on the surface should be protonated to produce positively charged surface. On the other hand, those of the particles after the reaction were –12.0 mV and –10.4 mV for TS (10) and TS (5) sol, respectively.

Fig. 2 SEM images of the ZnO particles: (**a**) uncoated, (**b**) treated by TS (10) sol, (**c**) treated by TS (5) sol



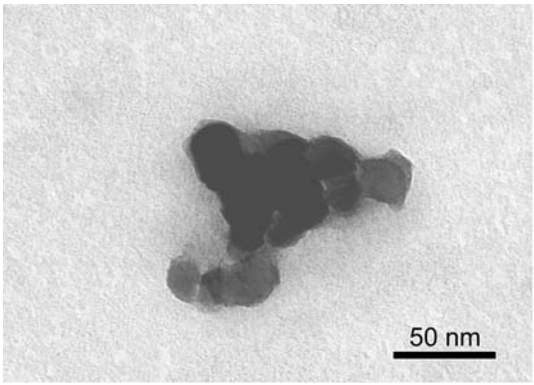


Fig. 3 TEM image of the ZnO particles treated by TS (10) sol

These negative values were attributed to the amorphous titania and PDMS, which have negative charge in an aqueous solution at pH 6.0 [26, 27], though it is still unclear which constituent plays a major role for this effect. Measuring the pH dependency of zeta potential of the coated particles will be necessary to evaluate the relative contribution of titania and PDMS part on the surface. This inversion of the surface charge of the particle supported the SEM and TEM results that the surface of the ZnO particles was covered by the products derived from TS (10) and TS (5) sols.

As to the nanostructure of the present titania/PDMS hybrid layer, we have already reported that of the titania/PDMS hybrid spherical particles prepared by similar procedure in the absence of core particle[19]. STEM/HAADF measurement demonstrated that the hybrid particles have an islet-like nanostructure, which is composed of the nanometer-sized domains of titania and PDMS. The self-standing films prepared from the same sols by the solvent evaporation were transparent in visible light wavelength region, and no recognizable phase separation between titania and PDMS was observed by the SEM observation (~100,000×) [23]. Based on these previous data, we speculate that the coating layer of the present core–shell particles was made of titania/PDMS hybrid, which formed by the hydrolysis and the polycondensation of the sols on the surface of the particles, though there is no direct evidence of the domain structure at this stage.

Assuming that (1) the coating layer on the ZnO particles is uniform in the thickness, (2) there is no residual methoxy or isopropoxy groups in the coating layer, (3) the specific gravities of the coating layers are 1.9 and 1.6 for TS (10) and TS (5) sol, respectively, which are the weighted average values of the amorphous titania (3.0) and PDMS (0.98), (4) the ZnO particles are spherical with a diameter of 20 nm, the thickness of the coating layer is estimated to be 0.5–0.6 nm. On the other hand, the thickness of the coating layer was shown to be several nanometers by the TEM observations. This discrepancy might be due to the fact that the coating layer is not dense and/or the surface area to be coated decreased by the aggregation of the ZnO particles. In fact, the specific surface area of the particles increased slightly by the coating reaction (from 26.5 to 33.0 m^2/g for TS (5) sol and 42.7 m^2/g for TS (10) sol), suggesting the possibility of porous structure of the coating layers.

Hydrophobicity

The hydrophilicity/hydrophobicity of the coated particles was estimated by the wettability with water/2-propanol mixed solution to characterize the surface of the coated particles. The ZnO particles treated by TS (5) sol were floated at the air–water interface due to the hydrophobic character of silicone. The floated particles sediment and partially dispersed in the solution gradually by the addition of 2-propanol drop by drop under continuous stirring. On the other hand, for the particles treated by TS (10) sol, only a part of them floated at the air–water interface and the rest of them sedimented immediately. It is assumed from the result of SEM and zeta potential measurements that the uniformity of the coating is at the same level for each sample, so that the particles treated by TS (10) sol have more hydrophilic character relative to those treated by TS (5) sol. The average amount of 2-propanol ($N = 3$) at which none of the particles was seen on the water surface was 6.1 and 2.9 mL for TS (5) sol and TS (10) sol, respectively. The solubility parameter of 2-propanol aqueous solution δ_m was calculated from following equation by using those of water ($\delta_{\text{WATER}} = 47.8\ \text{MPa}^{1/2}$) and 2-propanol ($\delta_{\text{2-PROPANOL}} = 23.5\ \text{MPa}^{1/2}$) [28] and the amount of 2-propanol (A mL):

$$\delta_m = (25 \cdot \delta_{\text{WATER}} + A \cdot \delta_{\text{2-PROPANOL}})/(25 + A)$$

According to this equation, the solubility parameters of water and 2-propanol mixed solution at the point were 43.0 and 45.2 $\text{MPa}^{1/2}$, respectively, which correspond to the degree of hydrophobicity of the particle surface.

The hydrophilicity/hydrophobicity of the coated particles was also estimated by the contact angle between the pressed surface of the particles and a droplet of water. The contact angle of the ZnO particles treated by TS (5) was about 148°, while that of the ones treated by TS (10) was 132°. These results revealed that the latter one is more hydrophilic, which corresponded to the result of the wettability, even though the contact angle of the water droplet was affected by the surface texture of the pressed particles. It is possible that the difference in the hydrophobicity of these particles is attributed to the amount of the silicone part exposed to the outer surface of the particles.

Dispersibility

The dispersibility of the coated particles in decamethylcyclopentasiloxane was also investigated. The dispersion of the particles treated by TS (5) sol had good fluidity, while that of those treated by TS (10) sol was creamy. The same treatment for the uncoated ZnO particle gave a hard paste with no fluidity. Generally, the fluidity of the dispersion may reflect the dispersibility of the particle in a vehicle though the fluidity is affected by various factors such as the content of the particles in the dispersion. Figure 4 shows the UV–Vis transmittance spectra of the casting film of the dispersions. In the visible light wavelength region (400–800 nm), the dispersions of the coated particles were more transparent than that of the uncoated ones. On the other hand, in the UV wavelength region (200–400 nm), the dispersions of the coated particles absorbed UV light more efficiently than that of the uncoated ones. Among the coated particles, the dispersion of TS (5) sol treated particles absorbed UV light slightly greater than that of TS (10) sol treated ones. All these results demonstrated that the coating by the sols improved the dispersibility of ZnO in decamethylcyclopentasiloxane, which was caused by the affinity of the silicone part on the particle surface with the dispersion medium. Assuming that the coating is uniform for both the particles treated by TS (10) sol and TS (5) sol, the silicone content of the coating, which correlate with the thickness of the shell, is thought to affect the dispersibility of the particles.

Thus, it was shown that the ZnO nanoparticles were successfully coated with titania/PDMS hybrid of which

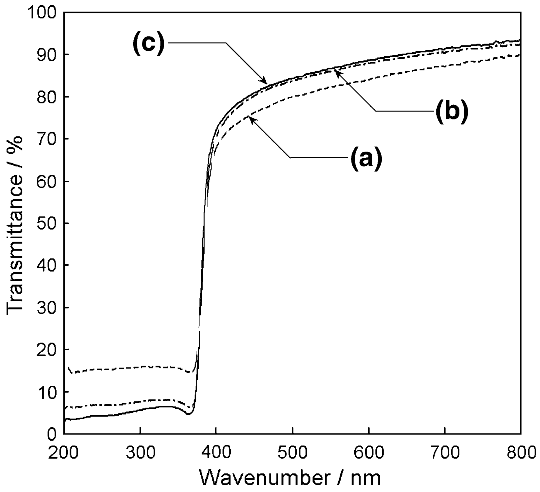


Fig. 4 UV–Vis transmittance spectra of the casting film of the dispersion: (**a**) uncoated, (**b**) treated by TS (10) sol, (**c**) treated by TS (5) sol

titania and PDMS were hybridized in nanometer scale. It seems possible to coat oxide particles of other composition and size with titania/PDMS hybrid shell due to the simple synthetic procedure. Further study on the composition and nanostructure of the hybrid shell is worth conducting to control the properties of the hybrid particles more precisely.

Conclusions

ZnO nanoparticles with average size of 10–30 nm in diameter were successfully coated with titania/polydimethylsiloxane hybrid by hydrolysis and condensation of the precursor sols containing prehydrolyzed titanium tetraisopropoxide and methoxy-functionalized PDMS on the surface of the ZnO particles in suspension. The hydrophobicity and the dispersibility in a silicone medium of the ZnO particles changed dramatically by the hybrid shell formation. The present ZnO–titania/polydimethylsiloxane hybrid core–shell particle is a new class of hierarchically designed composite material.

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