Controlled Photocatalytic Ability of Titanium Dioxide Particle by Coating with Nanoporous Silica

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We have successfully deposited nanoporous silica layers on titania nanoparticles, commercial P25 (Degussa), by the reaction of P25 with aqueous mixture of TEOS (silica source) and CTA (porogen) and the subsequent calcination. The thickness of nanoporous silica layer was controlled by changing the added amount of TEOS.

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 are extensive works on the nanoporous silica layers on flat substrates, studies on the deposition of nanoporous silica layer on particles are limited.[7–11] Nanoporous silica coating is a way to modify the surface properties of particles as well as to impart new functions such as molecular sieving one on catalysts and adsorbents. In addition, it seems to be possible to impart additional functions on particle surface by utilizing the host–guest chemistry of nanoporous silica shell with desired function of guest species.[12–15] Thus, the coating of particles with nanoporous silica is a versatile method for the preparation of functional composite core–shell particles. Accordingly, systematic study on the deposition of naostructured and nanoporous silica layer on particle surface is worth conducting. In the present study, the coating of titanium dioxide particle with nanoporous silica layer was investigated.

The experimental procedure for the preparation of nanoporous silica/titania composite particle (hereafter termed as NPS@TiO$_2$) was based on the method described in our preliminary communication on the deposition of nanoporous silica layer on solid substrates.[11,16,17] Dodecyltrimethylammonium (abbreviated as CTA) chloride, deionized water (17.7 g), methanol (200 mL), 28% aqueous ammonia solution (7.2 g), and TiO$_2$ (2.0 g) were mixed, and the mixture was ultrasonicated for 3 h. A commercially available TiO$_2$, P25 (Degussa), was used. Tetraethoxysilane (abbreviated as TEOS) was added to the solution, and then the suspension was aged at room temperature for another 24 h under static condition. The solid particles were collected by centrifugation (3500 rpm, 3 min) and washed with methanol. The products were calcined in air at 550 °C for 10 h to form porous silica shell. In order to vary the thickness and the morphology of the shell, the reaction was conducted by changing the added amount of TEOS. The molar ratio of TEOS/TiO$_2$ was changed as shown in Table 1. The added amount of CTA was also changed with higher concentration of TEOS in the starting solution. The molar ratio of CTA/TEOS was fixed to 0.4. The calcined samples were named as NPS@TiO$_2$-L, NPS@TiO$_2$-M, and NPS@TiO$_2$-H.

Table 1. Experimental condition and the BET surface area of the products

Sample	Composition of the starting mixture		S_{BET}[a] /m^2·g^{-1}	d_{p}[a] /nm	l_{s}[a] /nm	X_{MB}[a] /mg·g^{-1}
	TEOS /mL	Si/Ti molar ratio				
NPS@TiO$_2$-L	1.84	0.33	182	0.8	8	61.1
NPS@TiO$_2$-M	3.68	0.66	346	0.8	10	—
NPS@TiO$_2$-H	7.36	1.31	415	0.8	20	45.3

[a] S_{BET} = BET surface area, d_{p} = pore diameter, l_{s} = the thickness of the silica shell, X_{MB} = the adsorbed MB amount.

In the infrared spectra of the as-coated products, the absorption bands due to CTA (ν(CH$_3$/CH$_2$): 2940, 2870 cm^{-1}, ν(C–N): 1480 cm^{-1}, δ(–CH$_2$–CH$_2$–): 1450 cm^{-1}) and silica (ν(Si–O): 1200, 1080 cm^{-1}, δ(Si–O): 460 cm^{-1}) were observed in addition to those of TiO$_2$ (ν(Ti–O): 500–700 cm^{-1}). The infrared spectra showed that the relative absorbance of the bands due to CTA and SiO$_2$ to those of TiO$_2$ increased when higher concentration starting solution was employed, suggesting the greater content of coating. The bands due to CTA disappeared by the calcination. The absorption bands due to ν(Si–O–Ti) was observed at around 950 cm^{-1}, which suggests the formation of Si–O–Ti bond on the TiO$_2$ surface.[18]

Figure 1 shows TEM images of the calcined products. TiO$_2$ particle was coated with thin layer of NPS. The thickness of the shell was 8, 10, and 20 nm for NPS@TiO$_2$-L, NPS@TiO$_2$-M, and NPS@TiO$_2$-H, respectively. To our knowledge, there is no report on the successful control of the shell thickness.

It should be noted that spherical particle of silica–surfactant forms[19] when the present starting solution is allowed to react in the absence of TiO$_2$ particle. Such spherical particle did not form in the present study, where TiO$_2$ particle was present. This result

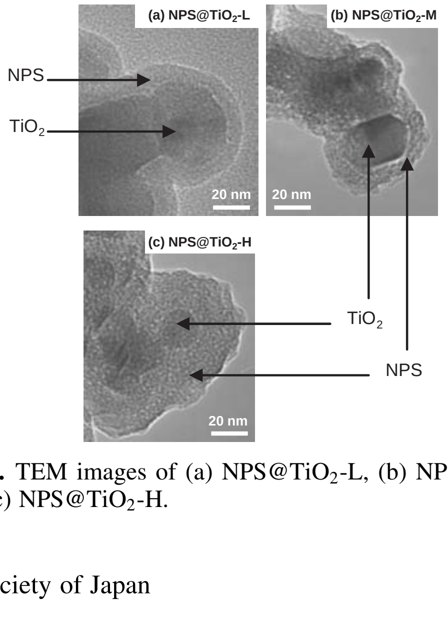

Figure 1. TEM images of (a) NPS@TiO$_2$-L, (b) NPS@TiO$_2$-M, and (c) NPS@TiO$_2$-H.

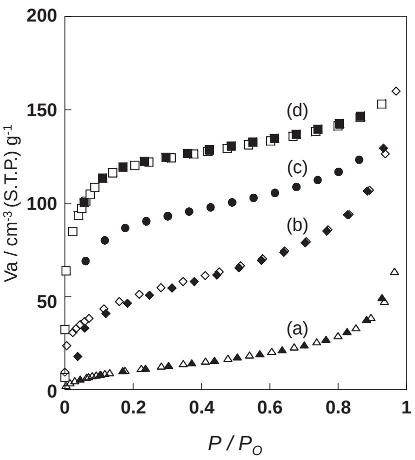

Figure 2. Nitrogen adsorption/desorption isotherms of (a) parent TiO_2 particle, (b) NPS@TiO_2-L, (c) NPS@TiO_2-M, and (d) NPS@TiO_2-H.

suggests that CTA was adsorbed on TiO_2 surface and cooperatively assemble with silica preferentially at the particle surface to form the shells composed of silica and CTA.

The nitrogen adsorption/desorption isotherms of the parent TiO_2 and the nanoporous-silica-coated TiO_2 are shown in Figure 2.[20] The nitrogen adsorption isotherm of the calcined particle showed BET surface area[21] of 182, 346, and 415 $m^2 g^{-1}$ for NPS@TiO_2-L, NPS@TiO_2-M, and NPS@TiO_2-H, respectively. The BET surface area corresponded to the value of ca. 1000 m^2 (g of silica)$^{-1}$. The pore size was determined by MP method to be 0.8 nm. Thus, it was shown that TiO_2 particle was successfully coated with nanoporous silica shell. The BET surface area are increased (182 to 415 $m^2 g^{-1}$) without any alteration of the pore size reflecting the homogeneity of the NPS layer.

The photocatalytic decomposition of Methylene Blue (MB) in aqueous solution (the initial MB concentration was 40 mg/L; P25 amount was 60 mg) was investigated under the illumination by a low-pressure Hg lamp (20 W). For all the products including the parent TiO_2, the adsorption of MB occurred without irradiation and the adsorption reached equilibrium within 15 min. The adsorbed MB amounts increased with the increase in the thickness of NPS layer. (The adsorbed MB amounts for P25, NPS@TiO_2-L, and NPS@TiO_2-H were 23.3, 61.1, and 45.3 mg/g sample, respectively). This difference was ascribed to the adsorption of MB on the pore of the NPS layer.

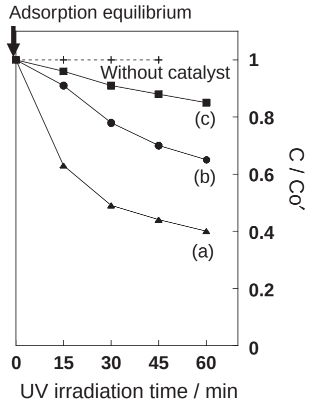

Figure 3. Photocatalytic decomposition of methylene blue in the aqueous suspensions of (a) parent TiO_2 particle, (b) NPS@TiO_2-L, and (c) NPS@TiO_2-H. C_0': The MB concentration after the adsorption equilibrium (15 min), C: The MB concentration after the irradiation.

Figure 3 shows the change in the concentration of the residual MB in the solution by the irradiation after the adsorption equilibrium. It is clearly shown that the photocatalytic decomposition of MB was suppressed for the NPS-coated products if compared with that on naked P25. It is also shown that the thicker layer of NPS showed enhanced effects on suppressing the photocatalytic decomposition of MB.

In summary, we have successfully deposited nanoporous silica layers on titania nanoparticles by the reaction of P25 with aqueous mixture of TEOS and CTA and the subsequent calcination. The thickness of nanoporous silica layer was controlled by changing the added amount of TEOS. The coating of titania nanoparticles effectively suppressed the photocatalytic activity (decomposition of Methylene Blue). The thickness of the shell was controlled by simply changing the synthetic condition, and the thickness affected the degree of modification of the catalytic ability.

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