Encapsulation of titanium(IV) oxide particles in hollow silica for size-selective photocatalytic reactions

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A core–shell composite of TiO_2 particles encapsulated in a hollow silica was fabricated, and the core–shell composite showed size-selective photocatalytic activity for decomposition of organics without reducing the intrinsic activity of the naked TiO_2 core.

Photocatalytic reactions occurring on the surface of photoirradiated TiO_2 have attracted much attention because of their possible environmental applications, such as photoinduced removal of contaminating harmful chemicals in indoor and outdoor atmospheres.[1] Such decomposition of organic compounds originates in the superior ability of the TiO_2 photocatalyst for non-selective cleavage of their chemical bonds under an atmospheric condition. On the other hand, selective decomposition of the targeted chemical(s) and/or conversion of organic compounds into valuable substances are other significant subjects to extend the practical utility of TiO_2 photocatalysis, *e.g.*, incorporation in various organic products, such as fibers and polymers, and application to benign catalysis in synthetic chemistry.[2–6] One of the attractive approaches for these purposes is the use of synthesized photocatalysts with defined nanostructures such as mesoporous TiO_2 and TiO_2 nanocrystals dispersed onto inorganic supports with large surface areas.[4,5] However, this approach often involves the problem of difficulty in fabricating a TiO_2 photocatalyst with sufficient activity comparable to that of commercially available TiO_2. In view of practical construction of selective photocatalytic systems, therefore, it is likely that the use of commercially available TiO_2 having a certain specific performance is much more promising than the use of such synthesized TiO_2 photocatalysts.

In order to utilize commercially available TiO_2, creation of a core–shell structure, *i.e.*, a TiO_2 photocatalyst covered with an organic or inorganic substance, has been studied extensively.[6] There have been many examples of successful use of such a structure for selective oxidative decomposition and organic conversion. However, the major drawback of the use of such a core–shell composite is reduction of intrinsic activity of the TiO_2 core because the surface-covered substances reduce the number of surface active sites.

As an another concept in the core–shell approach, we have recently reported a rattle-type nanostructure consisting of a cadmium sulfide (CdS) or platinum (Pt) nanoparticle core and hollow silica or carbon shell.[7] Owing to the presence of void spaces inside the hollow shells, the naked active surfaces of core nanoparticles could be utilized efficiently to induce various photocatalytic (CdS core) or catalytic (Pt core) reactions. These findings suggest that efficient photocatalytic systems for selective reactions can be constructed by using rattle-type photocatalysts based on commercially available TiO_2 as core materials. Hence, herein we describe the fabrication of a composite material composed of a commercial TiO_2 core and hollow silica shell (SiO_2/*void*/TiO_2), and we present results of evaluation of its photocatalytic activities for some reactions that seem to prove the validity of our concept.

Fabrication of SiO_2/*void*/TiO_2 was conducted by successive coating of TiO_2 with a carbon layer and a silica layer followed by heat treatment to remove the carbon layer, as shown schematically in Fig. 1. We previously proposed basically the same procedure for fabrication of hollow silica shells containing a strontium titanate core.[8] However, sufficient and complete control of the rattle-type morphology could not be achieved. Thus, we made many modifications in both the carbon grafting and silica coating steps. Commercial anatase TiO_2 supplied by Ishihara Sangyo with average particle diameter of *ca.* 140 nm (ST-41) was used as a model photocatalyst (Fig. 2(a)). First, the surface of the TiO_2

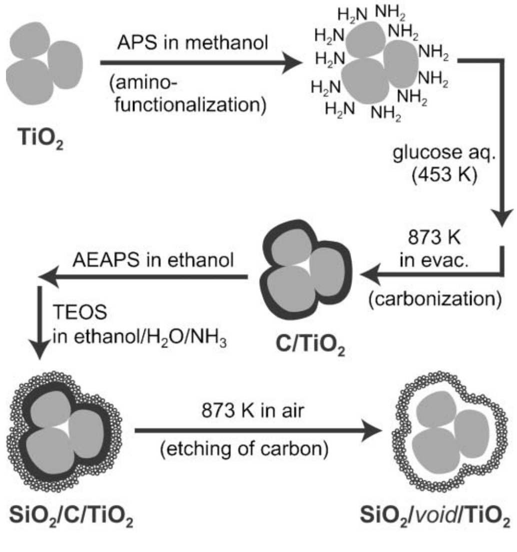

Fig. 1 Schematic representation of the procedure for fabrication of SiO_2/*void*/TiO_2.

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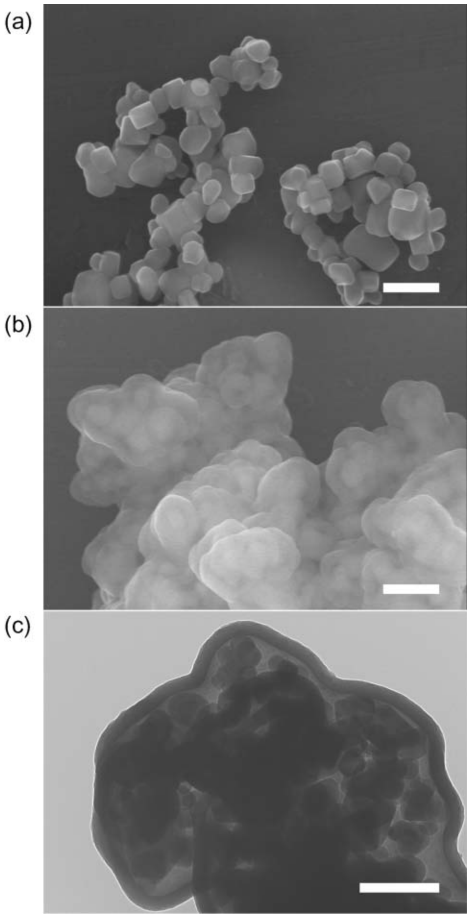

Fig. 2 SEM images of (a) TiO_2 and (b) SiO_2/*void*/TiO_2, and (c) a TEM image of SiO_2/*void*/TiO_2. Scale bars correspond to 300 nm.

powder was modified with amino groups by refluxing in a methanolic solution (10 cm^3) containing 560 μmol of 3-aminopropyltrimethoxysilane (APS). The amino-functionalized TiO_2 (200 mg) was added in an aqueous glucose solution (500 mmol dm^{-3}, 80 cm^3) and the suspension was maintained at 453 K for 6 h in a Teflon-sealed autoclave. The brown powder thus obtained was isolated by filtration, washed with water and ethanol, and heated at 873 K under evacuation for 2 h, followed by removal of surface-grafted amino groups with 5% aqueous hydrofluoric acid. Then the carbon-coated TiO_2 (C/TiO_2, 200 mg) was stirred in an ethanolic solution (10 cm^3) containing 420 μmol of *n*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) for 2 h at room temperature.[9] The resulting AEAPS-treated sample was put into a mixed solution containing 14 cm^3 ethanol, 2.2 mmol tetraethyl orthosilicate (TEOS), 0.5 cm^3 aqueous ammonia (28%) and 2 cm^3 water, and the suspension was shaken for 1.5 h. The solid part was collected by centrifugation, washed with water several times, and dried at 383 K under vacuum to yield TiO_2 particles covered successively with a carbon layer and a silica layer (SiO_2/C/TiO_2). Finally, carbon components in SiO_2/C/TiO_2 were removed by calcination at 873 K for 3 h in air. The SEM image of the thus-obtained white powder indicates complete coverage with a semi-transparent layer on TiO_2 particles (Fig. 2(b)).[10] The corresponding TEM image of the sample in Fig. 2(c) shows the presence of a void space of a few tens of nm in width and a lateral shell of *ca.* 60 nm in thickness, which encapsulated central TiO_2 particles. Moreover, analysis of silicon (Si) content by inductively coupled plasma atomic emission spectroscopy[11] showed the presence of 23% Si, corresponding to *ca.* 50% silica. These results, therefore, indicate the formation of the desired SiO_2/*void*/TiO_2 particle.

The BET surface area of the resulting SiO_2/*void*/TiO_2 measured by N_2 adsorption at 77 K is 18 m^2 g^{-1}. Using the BET surface area of the original TiO_2 (13 m^2 g^{-1}) and the silica content in SiO_2/*void*/TiO_2 reported above, the specific surface area of the silica shell could be estimated as 23 m^2 g^{-1}. This implies the presence of somewhat low level development of porosity in the silica shell. The successful etching of the medial carbon shell in SiO_2/C/TiO_2, as described above, is attributable to such a porous structure of the lateral silica shell. Previous studies on fabrication of hollow silica spheres based on base-catalyzed hydrolysis and polycondensation of TEOS to form silica shells indicated that the resulting shells were composed of aggregates of silica nanoparticles.[12] Thus, the porous nature of the silica shell probably results from the formation of interparticle micropores among the silica nanoparticles.

The porous silica shell will provide an exposure channel around the encapsulated TiO_2 for selective diffusion of organic substrates moving into and out of the shell depending on their molecular sizes. In order to study the function of the silica shell, photocatalytic activity was evaluated by gas-phase decomposition of acetaldehyde (ALD) and liquid-phase decomposition of acetic acid (AcOH) and poly(vinyl alcohol) (PVA) as model photocatalytic reactions. Fig. 3(a) shows results of the photocatalytic reaction of gas-phase decomposition of ALD on SiO_2/*void*/TiO_2.[13] For

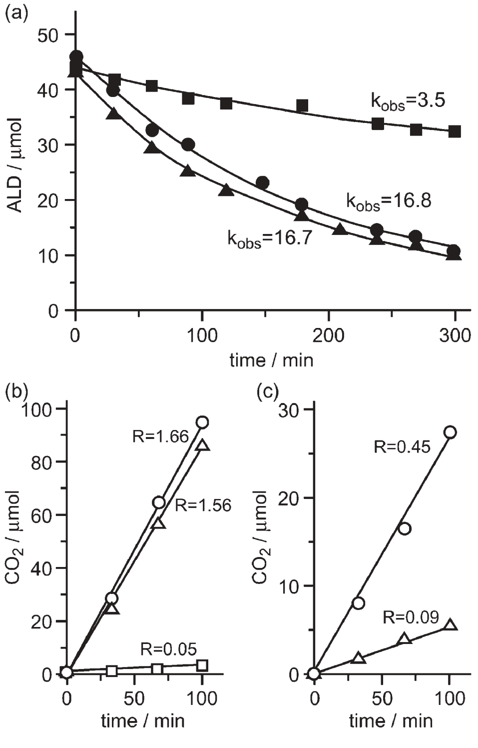

Fig. 3 (a) Photodegradation curves of ALD as a function of time; time course curves of CO_2 liberation from an aqueous (b) AcOH or (c) PVA solution over the original TiO_2 (circles), SiO_2/TiO_2 (squares) and SiO_2/*void*/TiO_2 (triangles) under UV-light irradiation; k_{obs} and R denote apparent rate constant of decrease in ALD (min^{-1}) and rate of CO_2 liberation (μmol min^{-1}), respectively.

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comparison, photocatalytic activities of the original TiO_2 and TiO_2 directly coated with a silica layer (SiO_2/TiO_2)[14] are also shown in this figure. Note that the silica shell in SiO_2/TiO_2 should have a porous structure because the shell was produced by base-catalyzed hydrolysis and polycondensatoion of TEOS in the same manner as production of the silica shell in SiO_2/*void*/TiO_2. Indeed, the BET surface area of SiO_2/TiO_2 (18 m^2 g^{-1}) was comparable to that of SiO_2/*void*/TiO_2. Thus, it is expected that the porous silica shell in SiO_2/TiO_2 will induce efficient diffusion of ALD on the surface of the TiO_2 core, leading to photocatalytic reaction. However, this sample showed a significant decrease in photocatalytic activity in comparison with that of the original TiO_2. As mentioned above, this deceleration is inevitable in a series of core–shell based photocatalysts, though this problem has not been emphasized. On the other hand, the present SiO_2/*void*/TiO_2 sample showed almost the same photocatalytic activity as that of the original TiO_2 for this reaction. Based on the idea for rattle-type nanoparticles reported previously,[7] this remarkable retention of photocatalytic ability originates in the presence of naked active surfaces of the TiO_2 core in the present SiO_2/*void*/TiO_2.

Fig. 3(b) and (c) show time course curves of CO_2 liberation on TiO_2, SiO_2/TiO_2 and SiO_2/*void*/TiO_2 photocatalysts during the decomposition of AcOH and PVA in water.[15] Results of the AcOH decomposition were similar to those obtained from the above gas-phase reaction, *i.e.*, only a slight decrease in activity was observed on SiO_2/*void*/TiO_2 compared to the original TiO_2 while SiO_2/TiO_2 had almost no photocatalytic function (Fig. 3(b)). Almost the same trend was also obtained on methanol dehydration in a similar aqueous suspension system (data not shown). These results imply the preservation of intrinsic photocatalytic function of TiO_2 core in SiO_2/*void*/TiO_2 even in such a liquid-phase reaction. On the other hand, despite the appreciable photocatalytic activity of the original TiO_2 for decomposition of PVA, the SiO_2/*void*/TiO_2 photocatalyst exhibited poor activity for this reaction, as far as the CO_2 liberation was concerned (Fig. 3(c)). These results, which contradict the above-described gas-phase and liquid-phase reactions for relatively small molecules, can be explained by the blocking effect of the hollow silica shell to prevent adsorption of such large molecules on the surface of the TiO_2 core. Thus, we have proved that fabrication of the SiO_2/*void*/TiO_2 structure is a promising strategy for designing novel photocatalysts with significant molecular selective properties toward the decomposition of organics without any reduction in intrinsic activity of TiO_2. Further study on control of the pore diameter and distribution of silica shells is now in progress.

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9 The preloaded AEAPS molecules on the surface of C/TiO_2 might facilitate the adsorption of silica layer. Details will be discussed elsewhere.

10 From the fact that no apparent weight loss accompanied by an exothermic event was observed on TG-DTA of the SiO_2/*void*/TiO_2 sample at the temperature up to 1073 K, complete removal of carbons should be achieved during the heat treatment of $SiO_2/C/TiO_2$.

11 For the measurements, Si components on the samples were dissolved by dispersing the samples in 0.1 mol dm^{-3} of NaOH solution for 6 h at 353 K, and the solution part was collected by centrifugal removal of remaining solid parts.

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13 To a Pyrex glass reactor (850 cm^3 in capacity) containing a photocatalyst (150 mg as TiO_2) fixed on a Petri dish (2.9 cm in diameter), *ca.* 50 μmol of ALD (*ca.* 1300 ppm) was injected. After standing in the dark for 2 h to achieve adsorption equilibrium, UV light was irradiated by using a 20 W black light. Photocatalytic activity was evaluated using apparent rate constant (k_{obs}) of decrease in acetaldehyde in gas-phase obtained by applying first-order kinetics.

14 The sample was prepared without coating with carbon in the first step of the procedure for preparing SiO_2/*void*/TiO_2. Analysis of Si content by ICP-AES showed that *ca.* 40% of silica, which was about equal to SiO_2/*void*/TiO_2, was involved in the sample.

15 An aqueous suspensions composed of 15–30 mg photocatalysts (15 mg as TiO_2) and a 20 cm^3 aqueous AcOH (17.5 mmol) or PVA (M_w = 22000, 2 mg) solution was put in a Pyrex cylindrical reaction vessel (6.8 cm in diameter, 240 cm^3 in capacity). Photoirradiation was performed using a 300 W Xe lamp from the upper part of the vessel in air with shaking of the suspension. Although various intermediates should be produced in these systems, especially for PVA decomposition, photocatalytic activity was evaluated by the rate of CO_2 liberation (R) for convenience.