Preparation of Hollow Titania Nanoparticles of Single-nanometer Size Using a PAMAM Dendrimer Template

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Abstract: Hollow titania nanoparticles of single-nanometer size have been prepared from titanium oxysulfate (TiOSO₄) using poly(amidoamine) (PAMAM) dendrimer molecules (Generations 5 with amino terminal groups) as a template. At low pH (pH 1), hydrolysis of the titania precursor was attenuated and the sol-gel reaction preferentially proceeded at the dendrimer surface. Calcination at 450°C yielded crystalline titania nanoparticles of 5.5 nm diameter with a ~2 nm cavity. These hollow titania nanoparticles showed a larger band-gap energy than solid particles of corresponding size.

Key words: titania, hollow nanoparticles, PAMAM, dendrimer, template

1 INTRODUCTION

Titanium dioxide or titania is one of the most extensively explored semiconductor materials for various applications such as pigments¹⁾, optical coatings^{2,3)}, wettability control^{4,5)}, photocatalysis⁶⁻⁸⁾ and photovoltaics^{9,10)}. In particular, hollow titania nanoparticles have attracted increasing attention due to their lower density and higher reflectivity compared with the solid ones. Several different approaches have been developed for their synthesis, which can be classified into template-assisted¹¹⁻¹³⁾ and template-free methods¹⁴⁻¹⁹⁾. In the former method, hard (e.g., polymer latex) or soft templates (microemulsions, vesicles) are utilized. Template-assisted methods can provide hollow nanoparticles with uniform sizes, but the removal of templates by dissolution or calcination process often causes disruption of particles. In the latter method, hollow titania nanoparticles are produced by Ostwald ripening¹⁴⁾ or chemically or thermally induced self-transformation of solid particles¹⁵⁻¹⁷⁾. These template-free methods are free from the removal problems, but size uniformity is attainable for limited systems and the crystallization of titania while maintaining hollow structure is not straightforward. Furthermore, in both methods, the hollow titania nanoparticles have diameters of more than several tens of nanometers and the fabrication of smaller hollow particles is still challenging.

It is well known that the band gap energy of titania depends on the particle size²⁰⁻²²⁾. Moreover, a recent theoretical study²³⁾ indicated that various properties of titania, e.g., sun protection factor (SPF), transparency in the visible regime, and production of reactive oxygen species (ROS), are also dependent on the nanoparticle size. Interestingly, SPF and the visible transparency are maximal for the diameter of 25 nm or less, while the production of ROS shows the maximum at about 35 nm and steeply decreases with further decrease in the particle size²³⁾. Accordingly, the synthesis of titania nanoparticles with single-nanometer size is significant not only in basic research but also in practical applications.

We report herein the synthesis of monodisperse hollow titania nanoparticles of about 5 nm in diameter using a dendrimer as a template. Dendrimers have several unique characteristics, i.e. uniform molecular size and chemically modifiable terminal groups²⁴⁾. Regarding the dendrimer-assisted synthesis of titania nanoparticles, Imae and co-workers^{25, 26)} reported poly(amidoamine) (PAMAM) dendrimers-protected titania nanoparticles using TiCl₄ as a precursor, as well as their photocatalytic properties for the photodegradation of an organic pollutant. Each titania nanoparticle was protected with several dendrimer molecules, and thus, the role of dendrimers was not being a template but a stabilizer for titania nanoparticles. On the other hand, Kunita-

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Accepted March 13, 2013 (received for review February 18, 2013)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjocs>

ke and co-workers²⁷⁾ prepared mesoporous titania film using glass-supported PAMAM dendrimers as a template for mesopores. More recently Yamamoto and co-workers²⁸⁾ reported the quantum size effect of small titania clusters prepared by the coordination of $\text{Ti}(\text{acac})\text{Cl}_3$ with poly(azomethyne) dendrimers.

We report herein that individual PAMAM dendrimer molecules can act as a template for titania nanoparticles and that the removal of dendrimer templates by calcinations leads to monodispersed hollow nanoparticles.

2 EXPERIMENTAL

Fifth generation poly(amidoamine) dendrimers (denoted as PAMAM G5) with 128 terminal amino groups per molecule was purchased as 5 wt% solution in methanol from Aldrich and used as received. After removing the solvent with a rotary evaporator, 5.56×10^{-5} mol (terminal group concentration) of dendrimer was dissolved in 5 cm³ of de-ionized water (Barnstead Nanopure). After stirring for 30 min at ambient temperature, pH was adjusted with sulfuric acid (initial pH was 10). Separately, 0.69 g of titanium(IV) oxysulfate (TiOSO_4 , Aldrich) was dissolved in 100 cm³ of water to make 0.5 mol dm⁻³ aqueous solution of the titania precursor. Subsequently a 100 mm³ aliquot of the precursor solution was quickly injected into the dendrimer solution under vigorous stirring. The mixture was left stirring for 1 d at ambient temperature. Then, the whole amount of aqueous titania dispersion was transferred to an alumina crucible and calcined at 450°C for 2 h with heating rate at 1°C min⁻¹. Ten milligrams of the powder product was redispersed in 5 cm³ of water. For TEM analysis, 2 mm³ of the supernatant was mounted on carbon-coated Cu grids and imaged with Hitachi H-7650 (120 kV) or H-9500 (200 kV) transmission electron microscope. Energy-dispersive X-ray analysis was performed with a Horiba EDX system attached with H-7650. UV-vis absorption spectra were re-

corded on an Agilent 8453 diode array spectrophotometer at 1 cm of light path.

3 RESULTS AND DISCUSSION

Figure 1 presents the TEM images of titania particles prepared at different pH conditions. Well-dispersed spherical nanoparticles of 15 nm in diameter are found at pH 1. Closer observation reveals that each particle contains a 6-nm pore, which is close to the molecular size of PAMAM G5 (6.6 nm)²⁴⁾. With increasing pH, large and irregular-shaped particles become abundant. This is because at pH 1, the hydrolysis of TiOSO_4 is slow and proceeds mainly on the amino groups at the dendrimer surface, whereas at higher pH, rapid hydrolysis proceeds at bulk solution phase. Accordingly, all experiments described hereafter were performed at pH 1.

Figure S1 presents the EDX profile of as-prepared titania nanoparticles at pH 1. Three discernible peaks are detected for Ti corresponding to L_α (0.452 and 0.458 keV), K_α (4.508 keV) and $K_{\beta 1}$ (4.931 keV) lines, and one peak for O corresponding to K_α (0.525 keV) line²⁹⁾. Apart from these two elements, an S K_α line (2.307 keV) was detected, originating from sulfate ions adsorbed on the titania surface. Meanwhile, the electron diffraction presents a hallow pattern (not shown), indicating the amorphous nature of these nascent titania nanoparticles.

Successively, this sample was calcined at 450°C for 2 h. When the powder was redispersed in water, most particles aggregated and precipitated. However, a small fraction (ca. 5 wt%) could be dispersed in the supernatant, where monodisperse titania nanoparticles were observed. When PAMAM G5 was used as a template, the mean particle size was 5.5 nm ($\sigma = 0.76$ nm), as shown in Fig. 2a. Compared with the as-prepared sample, an obvious size decrease was detected. In addition, the magnified images (Fig. 2b and Fig. S2) indicate a ~2 nm cavity for each particle. Appar-

Fig. 1 TEM images of titania nanoparticles prepared from the hydrolysis of TiOSO_4 in the presence of PAMAM G5 at various pH conditions.

Fig. 2 (a) TEM image of titania nanoparticles formed with PAMAM G5 and (inset) their electron diffraction pattern, (b) high-magnification image of (a).

ently burning off of the dendrimer template and crystallization of titania nanoparticles are taking place during the calcination process. When we change the template from PAMAM G5 to G7, there was a slight increase in the particle size ($d = 6.2$ nm ; $\sigma = 0.67$ nm). This is because the size decrease due to burning off of the template and crystallization of titania counterbalances the increased size of template molecules with higher generations.

The crystalline nature of calcined titania nanoparticles can be verified from Debye-Scherrer rings of the electron diffraction pattern (Fig. 2a inset). However, it is difficult to determine unambiguously whether these particles are anatase, rutile, or their mixture, because of the significant broadening of diffraction rings associated with small particle size. Note that these nanometer-sized titania nanoparticles were obtained only when ionic titanium complex (titanium oxysulfate) was employed as a precursor, although we tried nonionic titanium complexes, e.g., titanium tetraisopropoxide and titanium tetrabutoxide. This suggests that electrostatic interaction between the titania precursor and dendrimer surface plays a crucial role in the formation of hollow titania particles.

As we previously reported for the preparation of mesoporous titania in the presence of cetyltrimethylammonium bromide (CTAB)³⁰⁾, quaternary ammonium group promotes the hydrolysis and condensation of TiOSO_4 . We found that micellization of C_nTAB (n = alkyl chain length) is crucially important for a template, since non-micelle-forming C_nTAB bearing shorter alkyl chains ($n \leq 8$) do not function as a template. Similarly, when we tried PAMAM dendrimers of different generations from G3 to G7, only generations higher than G5 proved to work as templates. This suggests that the congestion of surface amino groups is a prerequisite for the formation of hollow titania nanoparticles.

Figure 3 displays a UV-vis extinction spectrum of hollow titania nanoparticles derived from PAMAM G5 template. The threshold wavelength (energy) is 340 nm (3.65 eV), which is significantly blue-shifted from that of bulk titania in anatase form, 380 nm (3.26 eV). Moreover, the band-gap

Fig. 3 UV-vis extinction spectrum of hollow titania nanoparticles in aqueous dispersion.

wavelength of these hollow particles is significantly blue-shifted from that of solid nanoparticles of corresponding size (375 nm)²⁰⁾. This can be attributed to thin walls of hollow titania nanoparticles.

4 CONCLUSION

Hollow titania nanoparticles of single-nanometer size ($d \sim 5.5$ nm, pore size ~ 2 nm) can be prepared from TiOSO_4 using PAMAM G5 molecules as a template. Attenuated hydrolysis of titania precursor at strongly acidic condition (pH 1) is essential. Crystalline nature of calcined titania nanoparticles was confirmed by electron diffraction. Electrostatic interaction between the titania precursor and the amino groups at the dendrimer surface is responsible for the success of dendrimer molecules as a template. The threshold wavelength (340 nm) of hollow nanoparticles was significantly blue-shifted from those of bulk titania (anatase) and solid anatase particles of corresponding size.

Supporting Information

This material is available free of charge via the Internet at <http://dx.doi.org/10.5650/jos.62.637>

ACKNOWLEDGMENT

We are grateful for Prof. Iwao Hashimoto (TUS) and Prof.

Makoto Tadokoro (TUS) for providing us their TEM facilities (H-9500).

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