Formation of Titania Nanotubes with High Photo-Catalytic Activity

Motonari Adachi,* Yusuke Murata, Makoto Harada, and Susumu Yoshikawa
Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011

(Received May 22, 2000; CL-000495)

Titania nanotubes with high photo-catalytic activity were synthesized in laurylamine hydrochloride / tetraisopropyl orthotitanate modified with acetylacetone system. Formation of nanotubes was confirmed by transmission electron microscope images. These titania nanotubes had crystal structure of anatase and showed high photo-catalytic activity, i.e., the activity is about three times higher than Degussa-P-25 and higher than ST-01.

Titania nanotubes with large surface area offer a prospect to provide a highly active photo-catalytic materials and are expected to be utilized as materials for high efficient solar cells.[1,2] They are also expected to provide a functional catalyst for chemical reactions,[3,4] adsorbents for chemicals[5] and nanotechnological applications like carbon nanotubes.[6,7]

We have reported formation of silica nanotubes by templating mechanism in laurylamine hydrochloride (LAHC) / tetraethoxysilane (TEOS) system.[8,9] Recently, Kasuga et al.[10] reported formation of titania nanotubes with diameter of 8 nm by chemical treatment of fine TiO_2–SiO_2 particles with 10 M NaOH aqueous solution at 383 K. Unfortunately, their formation mechanism is unknown, and photo-catalytic activity of their nanotubes was not high. In comparison with their synthetic method, our method for nanotube formation by templating mechanism is applicable to various synthetic conditions, anticipating that our method has possibility to make highly active photo-catalytic titania nanotubes.

Here, we present synthesis of titania nanotubes with high photo-catalytic activity in LAHC / metal alkoxide system using tetraisopropyl orthotitanate (TIPT) modified with acetylacetone (ACA) as titanium source. Since hydrolysis and condensation reaction rates of TIPT are much faster than those of TEOS,[11] TIPT was modified with ACA, which caused the change in the coordination number of titanium from 4 to 5, resulting in the change in color of the solution to yellow.

The experimental procedure is as follows. Same moles of ACA and TIPT were mixed. This yellow TIPT solution was added to 0.1 M LAHC aqueous solution (pH 4–4.5). The mole ratio of TIPT to LAHC was 4. The solution was kept stirring for several hours at 313 K until the solution became uniform yellow solution. Then, the solution was put into the oven kept at 353 K and the reaction was started. After 72 h, the sample was dried at 353 K. Then the dried sample was washed by 2-propanol to remove LAHC from the produced materials. Then the materials were calcined for desired period at desired temperature.

Characterization of the produced materials was made by small angle X-ray scattering (SAXS), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and isotherm of nitrogen adsorption. Photo-catalytic activity of titania nanotubes was measured through the formation rate of I_3^- due to the oxidation of I^- to I_2. The produced titania materials were ground in mortar made of agate, and 50 mg of them were suspended by magnetic stirring in 10 mL of 0.2 M KI aqueous solution, and the solution was irradiated with 365 nm ray (UV-lamp 15W).

The aqueous solution of LAHC / TIPT modified with ACA changed as follows. The solution became gel after about 2 h from the start of the reaction. After about 3 to 4 h, the gel turned to sol again. After about 26 h, the solution became gelatinous gel with supernatant transparent thin layer. Thereafter, the state was kept until 72 h.

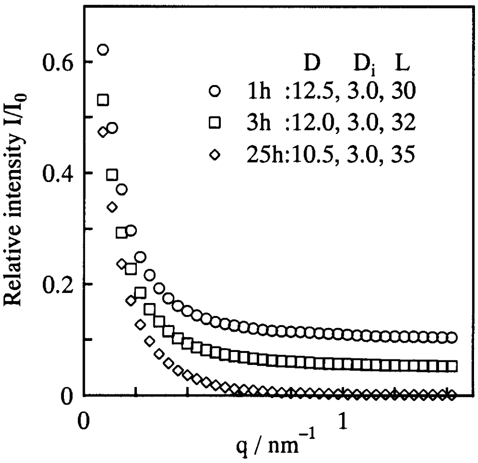

Figure 1. SAXS results of liquid samples during the formation processes. Cylindrical aggregates formed. I: scattering intensity, q: scattering vector, D: outer diameter of cylinder, D_i: inner diameter, L: length of cylinder.

SAXS results for the liquid samples taken at 1 h, 3 h and about 25 h from the start of the reaction showed formation of cylindrical aggregates as shown in Figure 1. Nitrogen adsorption isotherm for the dried samples after washing by 2-propanol showed hysteresis, indicating existence of meso-pore. This means that LAHC could be removed by the washing from titania nanotubes in dried samples. TEM image shown in Figure 2 clearly shows the formation of titania nanotubes. The central part is white and the both edges are black, indicating nanotube formation.

The results of XRD showed that all dried and calcined samples had crystalline structure of anatase. The volume fraction of TiO_2 of anatase crystalline in the aqueous reaction solution (0.4 M TiO_2) was calculated as 0.83% from the density of anatase crystalline. Gelation, which was observed at the reaction time of 2 h and after 26 h, strongly indicates that most of TiO_2 must exist as long cylinders, otherwise gelation could not occur. Therefore, titania nanotubes are inferred to have crystalline structure of anatase. This is quite different from silica

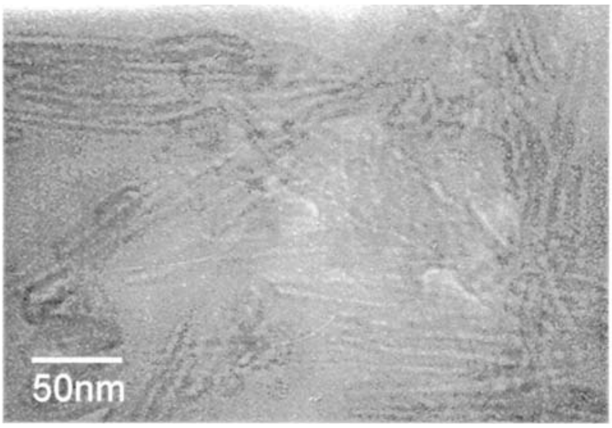

Figure 2. TEM image of the produced materials calcined for 4 hours at 773 K. Many single titania nanotubes are observed. Central part is white, and both edges are black, indicating nanotube formation.

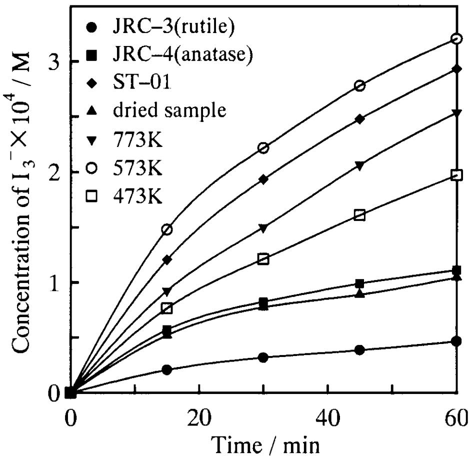

Figure 3. Dependence of photo-catalytic activity of titania nanotubes upon calcination temperature, together with activities of the standard titania particles of JRC-3 (rutile) and JRC-4 (anatase), and ST-01. JRC-4 has similar activity to Degussa-P-25, and ST-01 is known as high active photo-catalytic titania particles.

nanotubes, which have thin amorphous wall. The direct confirmation and formation mechanism of the crystalline structure of titania nanotubes are interesting subjects for future study.

Figure 3 shows the results of photo-catalytic activity of the produced materials in the present work, together with the standard titania-particles of The Catalysis Society of Japan (JRC-3 (rutile) and JRC-4 (anatase), which has the similar performance to Degussa P-25) and ST-01, which is known as pretty high photo-catalytic activity among the commercially available titania particles. The dried samples after washing by 2-propanol showed the almost same performance with Degussa P-25. The activity depended significantly on both calcination period and calcination temperature. The calcination period at various temperatures was adjusted to the earliest time, at which the brown color of the samples due to carbonization of LAHC left in the materials turned white by calcination. The best activity at present was obtained under the condition of calcination for 24 h at 573 K. The best activity was 7 times higher than JRC-3, 3 times higher than JRC-4, and even higher than ST-01.

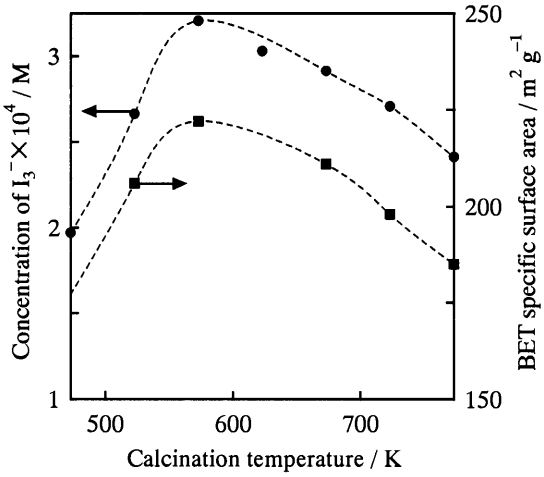

Figure 4. Relationship between photo-catalytic activity (I_3^- formed at reaction time 60min) and BET specific surface area. Proportionality between BET surface area and activity indicates that adsorption of I^- on the titania surface is the rate determining step.

Figure 4 shows BET surface area of the samples calcined at various temperatures in the way described above, together with the photo-catalytic activity shown as the absorbance of I_3^- at the reaction time 60 min. The photo-catalytic activity was almost proportional to the BET surface area, indicating that adsorption of I^- on titania surface was rate determining step in the initial stage of the reaction (before 15 min).

The present study was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

References

1 B. O'Regan, J. Moser, M. Anderson, and M. Gratzel, *J. Phys. Chem.*, **94**, 8720 (1990).
2 W. C. Sinke, and M. M. Wienk, *Nature*, **395**, 544 (1998).
3 D. R. C. Huybrechte, L. DeBruycker, and P. A. Lacob, *Nature*, **345**, 240 (1990).
4 V. T. Zaspalis, W. van Praag, K. Keizer, J. G. van Ommen, A. J. Burggraaf, and J. R. H. Ross, *Appl. Catal.*, **74**, 205 (1991).
5 H. P. Boehm, *Faraday Discuss. Chem. Soc.*, **52**, 264 (1971).
6 S. J. Tans, A. R. M. Verschveren, and C. Dekker, *Nature*, **393**, 49 (1998).
7 G. Che, B. B. Lakshmi, E. R. Fisher, and C. R. Martin, *Nature*, **393**, 346 (1998).
8 M. Adachi, T. Harada, and M. Harada, *Langmuir*, **15**, 7097 (1999).
9 M. Adachi, T. Harada, and M. Harada, *Langmuir*, **16**, 2376 (2000).
10 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, *Langmuir*, **14**, 3160 (1998).
11 C.J. Brinker and G.W. Scherer, "Sol–Gel Science," Academic Press, San Diego 1990, Chap. 2.