

Research Note

Preparation of titania foams having an open cellular structure and their application to photocatalysis

Akinori Yamamoto, Hiroaki Imai *

Department of Applied Chemistry, Faculty of Science and Technology, Keio University Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

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Abstract

Titania foams were prepared by calcination of polyacrylamide gels containing titanyl sulfate and urea. Decomposition of the inclusions resulted in foaming of the polymer body with the formation of anatase crystals. An open cellular structure consisting of anatase nanoparticles was then obtained after combustion of residual organic components. The photocatalytic activity of this new type of titania morphology was obviously higher than that of powdery titania for the decomposition of organic molecules in water and air.

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1. Introduction

Since the discovery of photochemical dissociation of water by Fujishima and Honda [1], titania photocatalysts have attracted much attention for applications over a diverse area. Powdery anatase-type titania and its coating on a substrate are commonly used as a practical photocatalyst. Porous and thick films consisting of fine particles exhibited a high efficiency for photocatalytic decomposition. Controlling the macroscopic morphology of titania is required for further promotion of the photochemical reaction because the activity is influenced by the adsorption and diffusion behavior of target molecules. Therefore, a variety of morphologies, such as tubes [2–4], fibers [5,6], honeycombs [7], three-dimensional networks [8], and other complex shapes [9–11], have been prepared with the crystalline titania. Since a macrocellular structure is effective for adsorption and diffusion of the target molecules, a foamy style would be useful for photochemical purification of air and water. However, a titania foam composed of closed spherical shells [12] was not applicable to photocatalysis. Here, we propose a novel route for the preparation of porous ceramic materials and present a new type of titania foam having an open cellular

structure. The titania foam having a low density and a high specific surface area showed excellent photocatalytic activity for air and water purification.

2. Experimental

Fig. 1 illustrates a schematic procedure for the preparation of titania foams. Precursor solutions were prepared by dissolution of 5 g acrylamide (AAm; $\text{CH}_2=\text{CHCONH}_2$), 0.05 g *N,N'*-methylenebisacrylamide ($(\text{CH}_2=\text{CHCONH}_2)_2\text{CH}_2$), and 0.15 g ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) into 45 g purified water. After the addition of a certain amount of urea ($(\text{NH}_2)_2\text{CO}$) and titanyl sulfate hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$, $x = 4.6$, Nacalai Tesque), the solutions were kept for polymerization at 60 °C for 90 min in an electric oven (steps 1 and 2). Resultant hydrogels of polyacrylamide (PAAm) containing urea and titanyl sulfate were dried at 60 °C for 24 h in air and then calcined at 500 °C for 3 h in air (steps 3 and 4). Finally, we obtained titania foams after combustion of organic compounds.

Characterization of the products was performed by thermal gravimetry (TG) and differential thermal analysis (DTA) using a Seiko TG-DTA 6200 and X-ray diffractometry with a Rigaku RAD-C system. Scanning electron micrographs (SEM) and transmission electron micrographs (TEM) were obtained using a Hitachi S-4700 and Philips TECNAI

* Corresponding author.

E-mail address: hiroaki@aplc.keio.ac.jp (H. Imai).

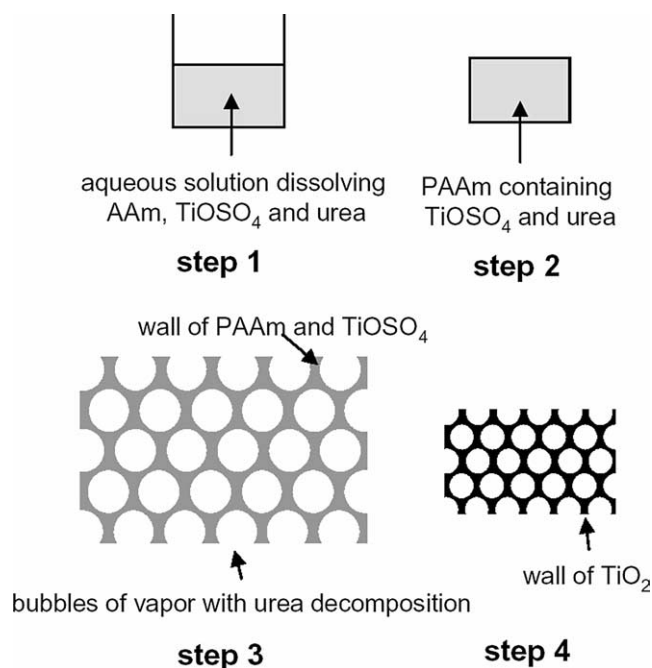


Fig. 1. A schematic procedure for the preparation of titania foams: step 1, dissolution of reagents into a precursor solution; step 2, gel formation with polymerization; step 3, foaming of gel body with decomposition of urea; step 4, formation of a titania skeleton with removal of organics by calcination.

F20, respectively. Nitrogen adsorption–desorption isotherms were recorded using a Micromeritics TriStar 3000. The photocatalytic activity was evaluated by decomposition of acetaldehyde in air under illumination of a conventional black light ($6 \text{ W} \times 2, 0.1 \text{ mW/cm}^2$) with 0.2-g samples placed in a closed vessel of 6 dm^3 in volume. The thickness of the foam samples was about 1 cm. The concentrations of acetaldehyde and carbon dioxide were monitored with a Shimadzu GC-8A gas chromatograph. The decomposition of methylene blue (MB) in water under illumination was also measured with 0.1-g powders deposited in an open container of 30 cm^3 in volume. The variation of the MB concentration was monitored by a Shimadzu UV2500 UV–vis spectrometer. The bulk densities of the titania foams were estimated by weighing the sample filled in a vessel having a certain volume.

3. Results and discussion

The formation process of titania foams from PAAm gels was monitored by thermal analysis and XRD patterns. Fig. 2 shows the results of the thermal analysis on the formation process. In the early stage below 250°C , an endothermal reaction with a weight loss was associated with the expansion of PAAm gels due to foaming (step 3). The foaming of the gel body is ascribed to generation of gaseous NCOH and NH_3 with decomposition of urea. An exothermal reaction with a weight loss was observed between 250 and 500°C . In the latter stage, the porous gel body was transformed

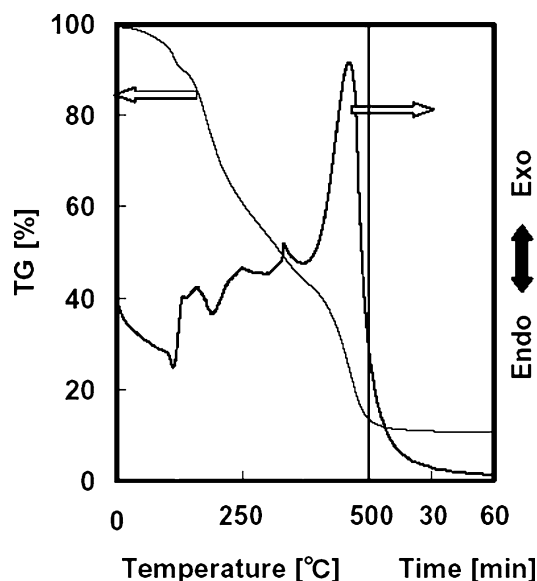


Fig. 2. TG-DTA analysis on the formation process of titania foams. Temperature was raised to 500°C with a rate of $5^\circ\text{C}/\text{min}$ and then kept at 500°C for 60 min.

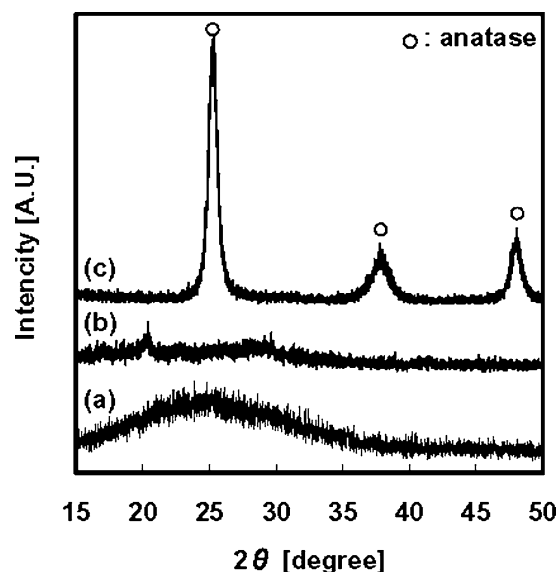


Fig. 3. XRD patterns of the samples dried at 60°C (a), heated at 250°C (b) and 500°C (c) on the formation process of titania foams.

into an inorganic skeleton through the combustion of PAAm. The XRD patterns shown in Fig. 3 indicate that anatase-type titania crystals were formed by decomposition of titanyl sulfate (TiOSO_4) at this stage. Finally, we obtained a highly porous body consisting of pure titania. Figs. 4a and b indicate that titania foams had an open cellular structure having macrovoids of $100\text{--}1000 \mu\text{m}$ in diameter. This structure originated from the bubbles of gases generated with decomposition of urea. SEM and TEM images (Figs. 4c and d) clarify that thin walls of ca. $1 \mu\text{m}$ in thickness in the macrocellular structures were composed of anatase particles of ca. 10 nm in diameter.

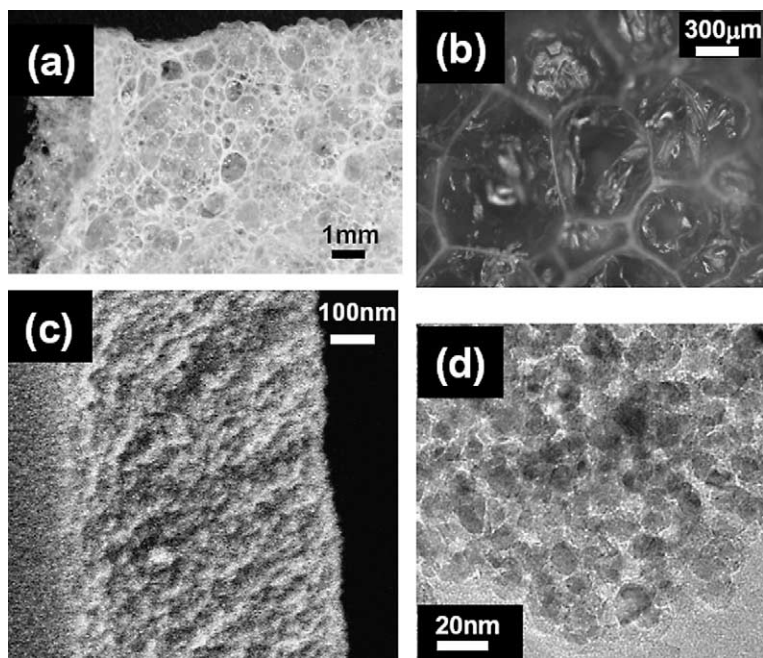


Fig. 4. Images of titania foams obtained with an optical microscope (a and b), SEM (c), and TEM (d).

Table 1

Apparent bulk density, specific surface area, and photocatalytic performance for acetaldehyde of titania foams prepared with various contents of TiOSO_4 and urea

	TiOSO_4 (M)	Urea (M)	Bulk density (g/cm^3)	Surface area (m^2/g)	Decomposition time (min)
Foam					
	0.4	1.50	0.0134	78	160
	0.6	2.25	0.0091	117	130
	0.8	3.00	0.0088	89	130
	1.0	3.75	0.0079	107	90
	1.2	4.50	0.0074	122	90
	1.4	5.25	0.0063	125	80
	1.6	6.00	0.0057	125	70
	1.8	6.75	0.0050	133	60
Powder					
P25				46	240
ST-01				350	190

The cellular structure of titania foams depended on the contents of TiOSO_4 and urea and their ratio in the precursor solutions. When the molar ratio of TiOSO_4 /urea was 0.27, relatively stable and homogeneous porous bodies were obtained. At a ratio smaller than 0.27, titania foams were easily collapsed during the combustion process of PAAm because the amount of titania in the walls was insufficient for supporting the porous structure. On the other hand, the expansion with foaming through the decomposition of urea was inhomogeneous in the PAAm body at a ratio higher than 0.27. Finally, we successfully obtained various structures of homogeneous titania foams by varying the contents of TiOSO_4 and urea with a proper molar ratio of 0.27. The apparent bulk density and specific surface area of titania foams prepared with various amounts of TiOSO_4 and urea are listed in

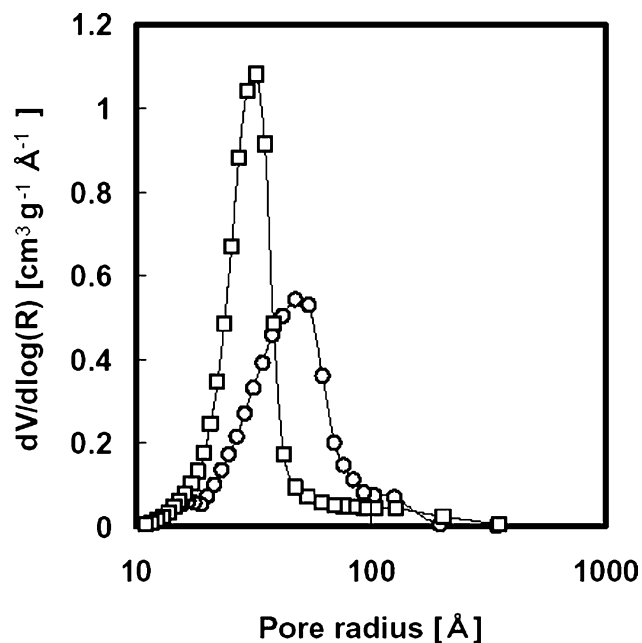


Fig. 5. The pore-size distribution obtained from nitrogen desorption isotherms with the BJH method. Open squares and circles indicate results for the foams prepared with $[\text{TiOSO}_4] = 1.8$ and 0.4 M, respectively.

Table 1. The bulk density decreased and the specific surface area increased with an increase in the contents of TiOSO_4 and urea. An extremely low bulk density was achieved by generation of a large amount of gaseous species though decomposition of urea. Fig. 5 shows the pore-size distribution obtained from nitrogen desorption isotherms with the BJH method. The presence of mesopores is ascribed to the interparticle spacing among the anatase grains. Since the size distribution was sharpened with an increase in the contents,

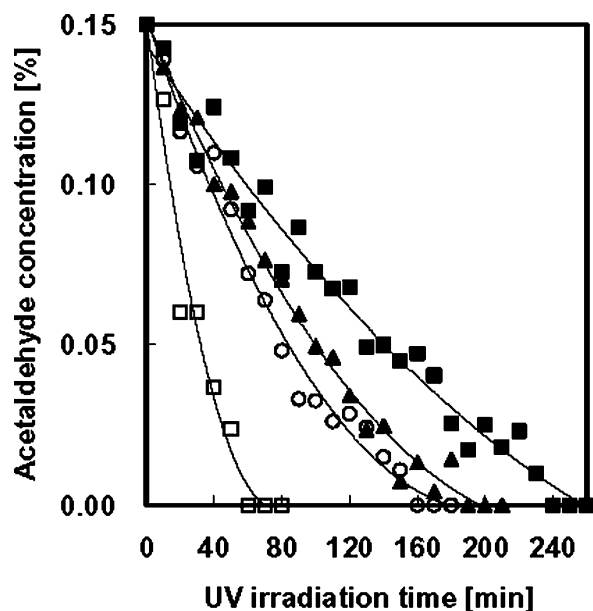


Fig. 6. Changes in the concentration of acetaldehyde with the titania foams and commercially available standard titania powders (Ishihara ST-01 and Degussa P25) under a black light illumination. Open squares and circles indicate results for the foams prepared with $[\text{TiOSO}_4] = 1.8$ and 0.4 M, respectively. Filled triangles and squares indicate results for ST-01 and P25, respectively.

it is suggested that monodispersed small particles of anatase crystals were formed under that condition. This fact is supported by an increase in the specific surface area. An increase in the urea content in the gel body promoted a larger expansion of a PAAm body with decreasing the thickness of the walls in the early stage. Monodispersed fine particles of anatase were produced with homogeneous combustion of the organic compound in the thin walls. Although the highly porous titania was obtained by increasing the contents, the mechanical strength of the products decreased.

Fig. 6 exhibits a decrease in the concentration of acetaldehyde with the prepared titania foams and commercially available standard titania powders (Ishihara ST-01 and Degussa P25) under illumination from a black light. The photocatalytic activity of the titania foams was clearly higher than that of the powdery samples, although the specific surface area of the foams was smaller than that of ST-01. Especially, the decomposition rate with titania foams having the lowest bulk density was higher than three times that of ST-01. As listed in Table 1, time for the complete decomposition of 0.15% acetaldehyde under UV illumination

decreased with an increase in the bulk density of the titania foams. Thus, the excellent photocatalytic performance of titania foams is attributed to high accessibility for the target molecules and high transparency of UV light due to an open cellular structure having wide channels and thin walls.

We evaluated the photocatalytic activity of the titania foam for decomposition of 20 ppm MB in water under UV illumination. The decomposition rate of the dye molecules with the typical foams was ca. 2.5 times greater than that with powdery samples such as P25 and ST-01. Thus, the highly porous morphology would be effective for various photocatalytic reactions regardless of the medium.

4. Conclusions

We successfully prepared titania foams from polyacrylamide gels containing titanyl sulfate and urea. The apparent bulk density and specific surface area of titania foams composed of anatase nanoparticles were controllable by changing the composition of the precursor solution. The foamy morphology of titania was confirmed to be suitable for photochemical purification of organic impurities in air and water, which is ascribed to high accessibility for the molecules and high transparency of the titania foams for UV light.

References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37.
- [2] P. Hoyer, H. Masuda, *J. Mater. Sci. Lett.* 15 (1996) 1228.
- [3] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Hiihara, *Langmuir* 14 (1998) 3160.
- [4] H. Imai, Y. Takei, K. Shimizu, M. Matsuda, H. Hirashima, *J. Mater. Chem.* 9 (1999) 2971.
- [5] S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai, *Chem. Mater.* 12 (2000) 1523.
- [6] H. Imai, M. Matsuda, K. Shimizu, H. Hirashima, N. Negishi, *J. Mater. Chem.* 10 (2000) 2005.
- [7] T. Sugiura, T. Yoshida, H. Minoura, *Electrochem. Solid-State Lett.* 1 (1998) 175.
- [8] R.A. Caruso, M. Antonietti, M. Giersig, H.-P. Hentze, J. Jia, *Chem. Mater.* 11 (2001) 13.
- [9] R.A. Caruso, M. Giersig, F. Willig, M. Antonietti, *Langmuir* 14 (1998) 6333.
- [10] S. Matsushita, T. Miwa, A. Fujishima, *Chem. Lett.* 26 (1997) 925.
- [11] T. Ota, M. Imaeda, H. Takase, M. Kobayashi, N. Kinoshita, T. Hirashita, H. Miyazaki, Y. Hikichi, *J. Am. Ceram. Soc.* 83 (2000) 1521.
- [12] A. Imhof, D.J. Pine, *Adv. Mater.* 11 (1999) 311.