JOURNAL OF Materials CHEMISTRY Communication

Preparation of TiO_2 fibers with well-organized structures

Hiroaki Imai,*[a] Manabu Matsuta,[a] Kazuhiko Shimizu,[a] Hiroshi Hirashima[a] and Nobuaki Negishi[b]

[a]*Department of Applied Chemistry, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama, 223-8522, Japan. E-mail: hiroaki@applc.keio.ac.jp*
[b]*National Institute for Resource and Environment, Onogawa, Tsukuba 305-8569, Japan*

Received 7th June 2000, Accepted 10th July 2000
Published on the Web 24th July 2000

Ceramic textiles and wools consisting of micrometer-sized TiO_2 hollow fibers with porous walls were prepared by a chemical solution deposition technique using TiF_4 aqueous solutions.

Titanium dioxide (TiO_2) anatase is well known to find utility as a photocatalyst and an electrode in wet-type photocells.[1–5] Since a highly porous body is required for photocatalytic applications, practical catalysts are usually prepared by coating a crystalline powder with organic binders. Sol–gel techniques using organic additives have also been applied to the preparation of porous TiO_2 films.[6,7] The pore structure and the surface area of TiO_2 anatase are important for the preparation of higher performance catalysts. However, controlling of the structure of anatase powder and films is difficult using conventional methods, such as powder coating and sol–gel techniques.

Preparation of metal oxide films, such as SiO_2,[8] TiO_2,[9–11] V_2O_5,[12] and SnO_2,[13] has been achieved using direct deposition techniques in supersaturated chemical solutions. In particular, aqueous solutions of titanium tetrafluoride (TiF_4) provided TiO_2 thin films consisting of well-crystallized anatase particles, even at temperatures below 60 °C.[11] This direct deposition method is effective in the preparation of anatase photocatalysts because the deposited films are mesoscopically porous. Using this technique, coating of anatase films on various substrates with complex shapes was achieved through heterogeneous nucleation. Organic fibers, such as paper and cotton, were successfully coated with small anatase particles.[11] We also prepared anatase nanotubes using nanochannels of porous alumina membranes by a deposition technique from TiF_4 solutions.[14]

This paper describes the preparation of TiO_2 anatase textiles and wools consisting of hollow fibers using the direct deposition technique from TiF_4 solutions with organic templates. A scheme illustrating the stages involved in this technique is shown in Fig. 1. Ceramic hollow fibers were obtained by removal of the organic compounds *via* calcination in air. Although a similar technique has been employed to prepare organized carbon tubes,[15] this method has not previously been applied to the production of ceramic fibers because coating of dense ceramics on organic fibers is difficult using conventional procedures. The preparation of TiO_2 tubes was achieved by coating of dense films with the chemical solution process. In this study, crystalline TiO_2 textiles and wools were confirmed to be suitable for photocatalytic applications.

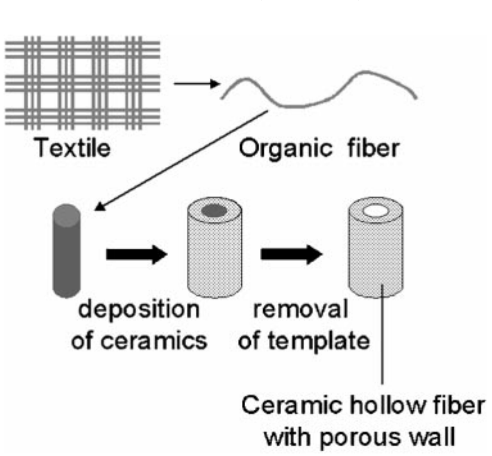

Fig. 1 Scheme for preparation of ceramic fibers by chemical solution deposition using organic fibers as a template.

Stepwise hydrolysis and dehydration of TiF_4 produces TiO_2 in aqueous solution. Crystalline TiO_2 thin films (anatase phase) have been successfully obtained on glass slides and organic polymers using solutions of pH 1–3.[11] Since solutions in this pH region gradually became supersaturated with TiO_2 produced by the stepwise reactions, thin films of crystalline TiO_2 were prepared through heterogeneous nucleation on various kinds of hydrophilic substrates. The ionic precursors were stable in solutions below pH 1. On the other hand, precipitates were predominantly produced through homogeneous nucleation above pH 3 because the solutions were highly supersaturated with TiO_2. In this work, precursor solutions were prepared by dissolving TiF_4 (Aldrich) in purified water containing ammonia. Typically, 0.74 g TiF_4 was mixed with 150 cm^3 water to prepare 0.04 M TiF_4 solutions. The pH value of the solutions was adjusted to around 2.0 by adding a small amount of 0.15 M ammonia solution. Cotton fibers, textiles and wools were immersed in the solutions, which were maintained at 60 °C for 1–24 h. Using these conditions, anatase TiO_2 coatings were successfully deposited on organic fibers. These fibers were removed by combustion at 500 °C in air, yielding the deposited TiO_2 in the form of ceramic textiles and wools. The morphology and composition of the samples were investigated using a scanning electron microscope (SEM, Hitachi S-2150) and a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700) attached to an X-ray microanalyser. Fig. 2(a) shows a microscope image of anatase textile prepared by double deposition over 24 h using woven cotton. The ceramic textile showed almost the same structure as the original template.

Fig. 2(b) and (c) show images of a hollow fiber from which the ceramic textiles are composed. The walls of the hollow fibers were found to consist of small particles 20–50 nm in diameter. The X-ray diffraction (XRD) pattern, shown in Fig. 3, of the small particles making up the hollow fibers identifies them as TiO_2 anatase. The channel diameter of the TiO_2 fibers depends on the size of the organic fiber template. The thickness of the ceramic fiber wall is controllable by changing the deposition time. A relatively thick wall of crystalline TiO_2 was required to prevent collapse of the hollow structure and shrinkage of the woven textiles during the calcination. Thus, this technique is valuable for the preparation of ceramic fibers and textiles because thick crystalline films were directly deposited on the organic

This journal is © The Royal Society of Chemistry 2000

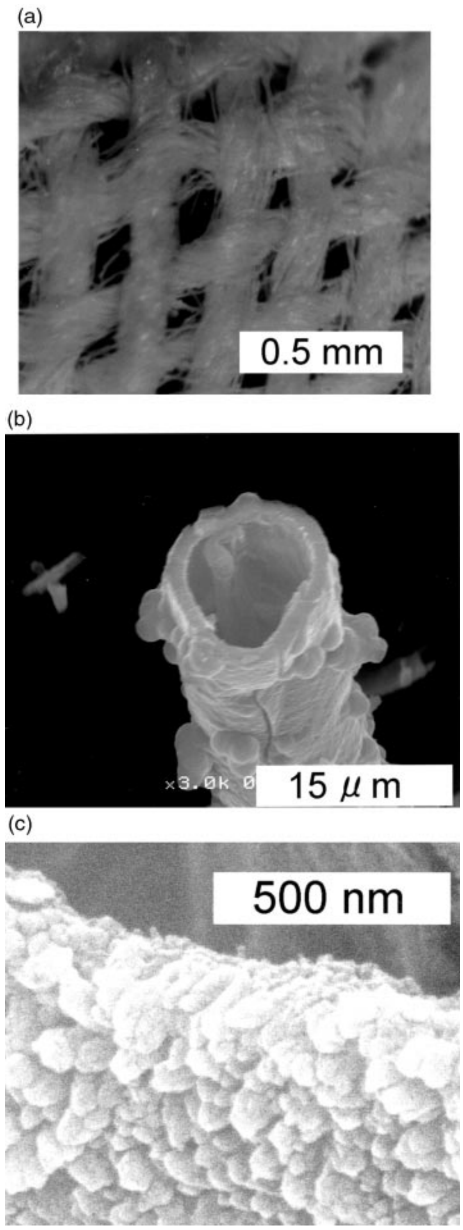

Fig. 2 Microscope images of TiO_2 textile (a), a TiO_2 hollow fiber (b), and the wall of a hollow fiber (c).

templates. The specific surface area of the deposited films was estimated to be 50–70 $m^2 g^{-1}$ by N_2 adsorption employing the BET method on a Micrometric TriStar instrument. The high specific surface area indicates that the walls of the hollow fibers are mesoscopically porous. The hierarchical structures of the ceramic textiles consisting of hollow fibers with porous walls should prove extremely beneficial for catalytic applications.

The anatase textiles were clearly produced by the deposition of anatase films consisting of small particles on the woven organic fibers. Since the shape of the anatase fibers reflected that of the original structure, the deposition must have occurred through heterogeneous nucleation on the cotton surface. The precursor solutions, supersaturated with TiO_2, directly produce crystal nuclei of anatase on the surface. The fluorine atoms bound to the titanium centres are particularly important for the direct preparation of the crystalline films, since the relatively stable Ti–F bonds suppress rapid hydrolysis and polymerization of the precursor molecules, causing

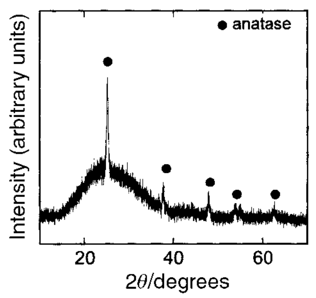

Fig. 3 A typical XRD pattern of the TiO_2 fibers, measured with Cu-Kα radiation using a Rigaku RAD-C system.

deposition of crystalline particles on the surface of the substrate through heterogeneous nucleation. As a result of the dense crystalline coatings deposited on the fibers, the morphology of the woven fibers was slightly deformed during the calcination. This suggests that the shape of the ceramic textiles could conceivably be controlled by this technique. X-Ray photoelectron spectroscopy (JEOL JPS-9000MX) on fired samples confirmed the absence of fluorine atoms in the deposited TiO_2 calcined above 300 °C in air.

The photocatalytic properties of the anatase wools were examined for the oxidation of nitrogen monoxide under UV illumination (365 nm). The anatase TiO_2 wools exhibited better performance than that with conventionally prepared coatings of anatase TiO_2 powder. The amount of nitrogen monoxide removed with the TiO_2 wools was about twice that produced using powder films. This demonstrates that anatase wools and textiles consisting of hollow fibers are applicable to conventional and advanced photocatalytic usage. Moreover, highly tailored photocatalysts could be prepared by this technique because the shape of the ceramic textiles is readily controllable by variation of the organic template.

In conclusion, TiO_2 textiles and wools consisting of hollow fibers have been prepared using a direct deposition technique with woven organic fibers as a template. Since the walls of the fibers are mesoscopically porous, the tailored structures have great potential for a wide variety of applications, such as catalysts, photocatalysts and filters.

Notes and references

1 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37.
2 I. Sopyan, S. Murasawa, K. Hashimoto and A. Fujishima, *Chem. Lett.*, 1994, 723.
3 T. Ibusuki and K. Takeuchi, *J. Mol. Catal.*, 1994, **88**, 93.
4 H. Uchida, S. Itoh and H. Yoneyama, *Chem. Lett.*, 1993, 1995.
5 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
6 N. Negishi, K. Takeuchi and T. Ibusuki, *Appl. Surf. Sci.*, 1997, **121–122**, 417.
7 K. Kato, A. Tsuzuki, Y. Torii, H. Taoda, T. Kato and Y. Butsugan, *J. Mater. Sci.*, 1995, **30**, 837.
8 H. Nagayama, H. Honda and H. Kawahara, *J. Electrochem. Soc.*, 1988, **135**, 2013.
9 S. Deki, Y. Aoi, O. Hiroi and A. Kajinami, *Chem. Lett.*, 1996, 433.
10 L. Baskaran, J. Song, Y. L. Liu, G. L. Chen and J. Graff, *J. Am. Ceram. Soc.*, 1998, **81**, 401.
11 K. Shimizu, H. Imai, H. Hirashima and K. Tsukuma, *Thin Solid Films*, 1999, **351**, 220.
12 S. Deki, Y. Aoi and A. Kajinami, *J. Mater. Sci.*, 1997, **32**, 4269.
13 K. Tsukuma, T. Akiyama and H. Imai, *J. Non-Cryst. Solids*, 1997, **210**, 48.
14 H. Imai, K. Shimizu, M. Matsuda and H. Hirashima, *J. Mater. Chem.*, 1999, **9**, 2971.
15 C. Han, J. Lee, R. Yang, H. Chang and C. Han, *Chem. Mater.*, 1999, **11**, 1806.