

Fabrication of TiO_2 Tubules by Template Synthesis and Hydrolysis with Water Vapor

Sihoon Lee,^{*,†} Chanseok Jeon,[‡] and Yoonchang Park[‡]

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208 and Department of Chemistry, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon, Kyungki-do, South Korea 440-746

Received March 30, 2004. Revised Manuscript Received June 29, 2004

TiO_2 nanostructures are prepared using a template method involving synthesis of TiO_2 within pores of a nanoporous membrane. In this study, template synthesis is accompanied by hydrolysis by water vapor in the preparation of TiO_2 nanotubes. These TiO_2 nanotubules are prepared within the pores of an alumina template membrane. Characterization of the TiO_2 tubules is accomplished by infrared spectroscopy (IR), UV–Vis spectrometry (UV), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmittance electron microscopy (TEM). TiO_2 nanotubule diameters of ca. 50 and 200 nm were found. The 50-nm-diameter nanotubules were polycrystalline of anatase, and the 200-nm-diameter nanotubules had a thickness of 10 nm. This new method based on template synthesis and hydrolysis by water vapor can fabricate smaller TiO_2 nanotubules easier than sol–gel template synthesis.

Introduction

Titanium dioxide nanostructures (tubules or fibrils) are known for their catalytic properties^{1–3} and are used as electrodes for solar cells.⁴

Titanium dioxide alone is an important metal-oxide semiconductor. It has many important applications in pigments, catalysts, supports, ceramics, inorganic membranes, and wastewater purification.^{5–7} Its unique photocatalytic properties make it suitable for the oxidation of organic pollutants and other contaminants from wastewater or drinking water supplies.^{8–11} Titanium dioxide has long been known to possess photocatalytic activity.

When TiO_2 is illuminated with light at <390 nm, it generates electron/hole pairs to employ titania as a photocatalyst. The valence band potential is positive enough to generate hydroxyl radicals at the surface, and the conduction band potential is negative enough to

reduce molecular O_2 . The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of the TiO_2 resulting in complete oxidation to CO_2 .

Sol–gel chemistry has recently evolved into a general and powerful approach for preparing inorganic materials.^{12,13} This method typically entails hydrolysis of a solution of a precursor molecule to obtain first a suspension of colloidal particles (the sol), and then to form a gel composed of aggregated sol particles. The gel is then thermally treated to yield the desired material. Martin et al. reported fabrication of TiO_2 nanofibrils with diameters of 22 nm by sol–gel template synthesis.¹⁴

In the synthesis of TiO_2 nanostructures by the template method, the membrane is dipped into the titania sol obtained through sol–gel hydrolysis. The size of tubular TiO_2 is limited by the size of titania sol. To date, the size of titania sol developed is ca. 5 nm.¹⁵

However, there are effective ways to decrease the size of tubular TiO_2 . Titanium alkoxide can be used as a dipping solution instead of titania sol. Since titanium alkoxide is molecularly smaller than titania sol polymer, titanium alkoxide can synthesize smaller tubular TiO_2 .

The hydrolysis of titanium alkoxide followed by condensation is involved in this sol–gel process.¹⁶



In pursuit of smaller TiO_2 tubules, titanium alkoxide with the addition of 2,4-pentanedione (acetylacetone)

- * To whom correspondence should be addressed. E-mail: sonate@hanmir.com.
- † University of South Carolina.
- ‡ Sungkyunkwan University.
- (1) Zheng, Y. Y.; Pang, J. B.; Qiu, K. Y.; Wei, Y. *Microporous Mesoporous Mater.* **2001**, *49*, 189.
- (2) Zhao, J.; Wang, Z.; Wang, L.; Yang, H.; Zhao, M. *Mater. Chem. Phys.* **2000**, *63*, 9.
- (3) Moret, M.; Zallen, R.; Vijay, D. P.; Desu, S. B. *Thin Solid Films* **2000**, *366*, 8.
- (4) Grant, C. D.; Sewartberg, A. M.; Smestad, G. P.; Kowalik, Y.; Tolbert, L. M.; Zhang, J. Z. *J. Electroanal. Chem.* **2002**, *522*, 40.
- (5) Ollis, D. F.; Pelizzetti, E.; Serpone, N. *Environ. Sci. Technol.* **1996**, *5*, 1523.
- (6) Solomon, D. H.; Hawthorne, D. G. *Chemistry of Paints And Fillers*; Wiley: New York, 1983; Chapter 2.
- (7) Kumar, K.-N. P.; Keizer, K.; Burggraaf, A. J. *J. Mater. Chem.* **1993**, *3*, 1141.
- (8) Fotou, G. P.; Pratsinis, S. E. *J. Aerosol Sci.* **1995**, *26*, 227.
- (9) Jung, K. Y.; Park, S. B. *Appl. Catal. A* **2002**, *224*, 229.
- (10) Bems, B.; Jentoft, F. C.; Schlogl, R. *Appl. Catal. B* **1999**, *20*, 155.
- (11) Hermann, J. M.; Guillard, C.; Disdier, J.; Lehaut, C.; Malato, S.; Blanco, J. *Appl. Catal. B* **2002**, *49*, 189.

(12) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*; Academic Press: New York, 1990.

(13) O'Regan, B.; Moser, J.; Anderson, M.; Grätzel, M. *Nature* **1991**, *335*, 737.

(14) Lakshmi, B. B.; Dorhout, P. K.; Martin, C. R. *Chem. Mater.* **1997**, *9*, 857.

(15) Hsu, J. P.; Nacu, A. *Langmuir* **2003**, *19*, 4448.

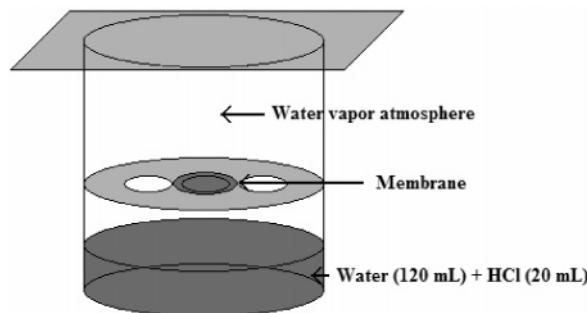


Figure 1. Scheme of water vapor reactor.

was used as precursor. 2,4-Pentanedione was used to chelate titanium alkoxide, to form a monomeric complex.¹⁷ The chelation of 2,4-pentanedione inhibited hydrolysis of titanium alkoxide. Control of the rate of hydrolysis was necessary to synthesize TiO₂ tubules because rapid hydrolysis of titanium alkoxide obstructs the synthesis of TiO₂ tubules. Vacuum filtration was used to remove the center regions of titanium alkoxide filled pores. The remaining titanium alkoxide left coating the walls of the pores was then hydrolyzed by water vapor. Previous researchers obtained the tubular TiO₂ by immersing the membrane template into the titania sol for a brief period at 15 °C.^{14,18} However, this method only fabricated TiO₂ tubules with diameters of 200 nm.

The method above could fabricate smaller tubular TiO₂ efficiently at room temperature.

Experimental Section

Materials. Titanium isopropoxide (97%), 2,4-pentanedione (99+%), 2-propanol (99+) and hydrochloric acid (36.5%) were obtained from Aldrich and used as received. Purified water was obtained by passing house-distilled water through a Milli-Q (Millipore) water purification system. The alumina template membranes (Anodisc 47) with 200- and 20-nm diameter pores were obtained from Whatman Corp.

Synthetic Methods. All experiments were conducted in an argon filled glovebox (water-free atmosphere).

Titanium isopropoxide (5 mL) was added to 25 mL of 2-propanol (mole ratio [Ti⁴⁺]/[2-propanol] = 1:20), and one equiv of 2,4-pentanedione (1.7 mL) was added to this solution (mole ratio [Ti⁴⁺]/[2,4-pentanedione] = 1:1). The solution was stirred for 3 h at room temperature (298 K). The alumina template membrane was dipped into this solution for 1 min. After removal from the solution, vacuum (vacuum pump) was applied to the bottom of the membrane until the entire volume of the solution was pulled through the membrane.

To hydrolyze the titanium isopropoxide inside the membrane pores by water vapor, a reactor was set up as shown in Figure 1. A solution of 20 mL of 1 M HCl and 120 mL of deionized water was added to the bottom of the reactor. The membrane was placed on top of the solution for 24 h. The membrane was air-dried for 60 min at room temperature, and then placed in a furnace (in air) with a temperature ramp of 2 °C h⁻¹ to 673 K for 2 h. The temperature was then decreased at a ramp rate of 2 °C h⁻¹ to room temperature (298 K).

Infrared (IR) Spectroscopy. The chelation of titanium isopropoxide with 2,4-pentanedione and formation of a monomeric complex was confirmed by obtaining an IR spectrum of titania sol. The infrared spectrometer used was a Nicolet FT-IR 205.

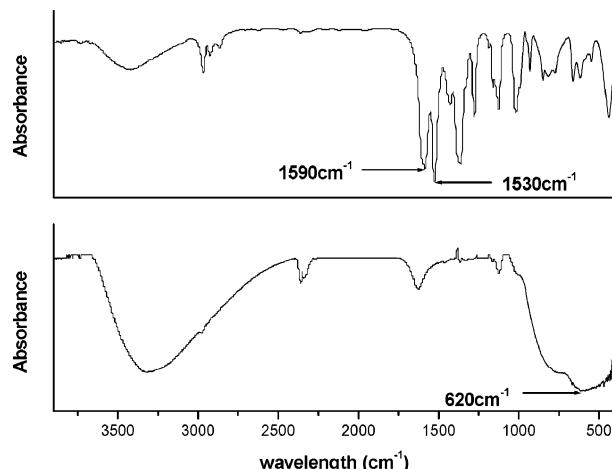


Figure 2. FT-IR spectra of titanium isopropoxide after (top) and before (bottom) the addition of 2,4-pentanedione.

UV–Visible (UV) Spectroscopy. To confirm the band gap of TiO₂ tubules, the UV spectrum of TiO₂ tubules was obtained by an HP 8453 spectrometer.

X-ray Diffraction Patterns (XRD). X-ray diffraction patterns were recorded by a Rigaku model DMAX-33 (Cu K α , Ni filter, 35 kV-15 mA) in the range 10–60° (2 θ).

Scanning Electron Microscopy (SEM). Scanning electron microscopic (SEM) images of the TiO₂ tubules were obtained. One surface of the membrane was polished and removed by sandpaper. The membrane was glued (using Torr-Seal Epoxy, Varian) to a piece of glass plate (Corning) with the polished side face up. The resulting composite was immersed into 6 M aqueous NaOH for several minutes to dissolve the alumina membrane. This yielded an ensemble of TiO₂ tubules or fibrils that protruded from the glass surface like the bristles of a brush. 10 nm of Au was sputtered onto the surface using an Anatech sputter coater. The resulting sample was imaged using a Phillips XL30 FE-ESEM microscope.

Transmission Electron Microscopy (TEM). To obtain transmission electron microscopy (TEM) images of the TiO₂ tubules, both surfaces of membrane were polished and removed by sandpaper. A piece of the resulting membrane was immersed into 6 M aqueous NaOH for several minutes to dissolve the alumina membrane. This solution was well dispersed by using an ultrasonic cleaner (Branson 2510). A drop of the solution was placed onto a carbon-film-coated TEM grid and allowed to dry. When dry, the freed TiO₂ nanotubes were imaged using a JEOL TEM 3010 microscope.

Results and Discussion

Chelation of Titanium Isopropoxide by 2,4-Pentanedione (IR). Titanium isopropoxide was modified by the addition of 2,4-pentanedione (acetylacetone) to hydrolyze titanium isopropoxide slowly. Chelation of titanium isopropoxide by 2,4-pentanedione was confirmed by infrared spectroscopy (IR).

Figure 2 shows the IR spectra of titanium isopropoxide (bottom) and titanium isopropoxide with addition of 2,4-pentanedione (top). Several peaks between 2800 and 3000 cm⁻¹ are assigned to ν (C–H) of methyl groups of isopropoxy and acetylacetone groups. Several peaks at approximately 1000 cm⁻¹ are assigned to (C–O) of isopropoxy groups bound to titanium. This shows isopropoxy groups already bound to titanium. When 2,4-pentanedione was added to titanium isopropoxide, the peak at approximately 1700 cm⁻¹ that arises from the ketone form of 2,4-pentanedione disappears. Also, the broad peak at 1610 cm⁻¹ that arises from C–O and C–H stretching mode from the enol form of 2,4-pen-

(16) Yoko, T.; Hu, L.; Kozuka, H.; Sakka, S. *Thin Solid Film* **1996**, 283, 188.

(17) Livage, J.; Sanchez, C. *J. Non-Cryst. Solids* **1992**, 145, 11.

(18) Hulteen, J. C.; Martin, C. R. *J. Mater. Chem.* **1997**, 7, 1075.

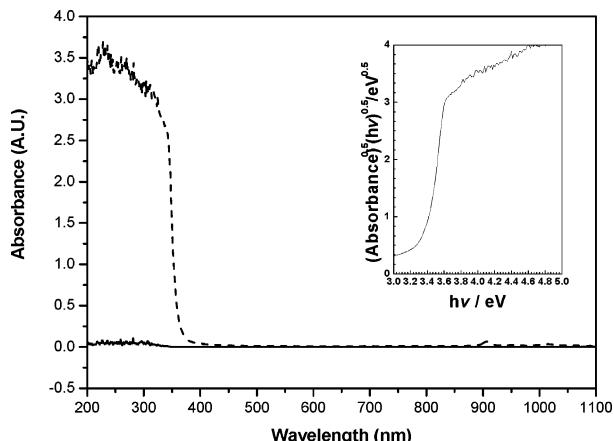


Figure 3. UV–Visible spectra of the 200-nm-diameter TiO_2 tubules: (dashed line) TiO_2 tubules and (solid line) standard deviation. Insert: Variation of $(\text{absorbance})^{0.5}(h\nu)^{0.5}$ with excitation energy ($h\nu$) for the TiO_2 tubules to identify indirect transitions.

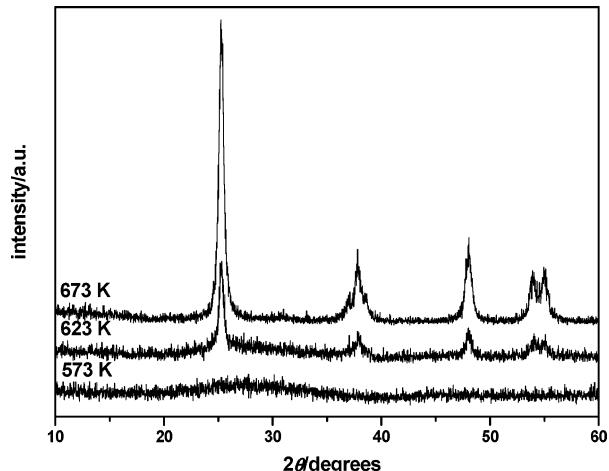


Figure 4. X-ray diffraction patterns of TiO_2 crystallites obtained after sintering the colloidal solution at several temperatures.

tanedione is shifted and separated into two peaks, 1590 and 1530 cm^{-1} . These two peaks are assigned to (C–O) and (C–H) of acetylacetonato-groups- bound titanium, respectively.¹⁹

These results confirm that 2,4-pentanedione chelated with titanium isopropoxide, and a stable monomeric complex ($Ti(Acac)(iPrO_3)_3$) was formed.¹⁷

Chelation of titanium isopropoxide by 2,4-pentanedione aids in hydrolyzing titanium isopropoxide slowly, and synthesizing TiO_2 tubules easily.

Band Gap of TiO_2 Tubules (UV–Vis). Figure 3 shows a UV–visible spectrum of the TiO_2 tubules prepared in the 200-nm-diameter pore alumina membrane. An absorbance below $\lambda \approx 370$ nm was observed. These spectra were processed to obtain the band gap energy, E_g , from the expression corresponding to indirect gap semiconductors (insert in Figure 3)

$$\alpha(h\nu)h\nu \propto (h\nu - E_g)^2$$

Here α is the absorption coefficient (cm^{-1}) and $h\nu$ (eV) is the energy of excitation. From this plot, a value of E_g

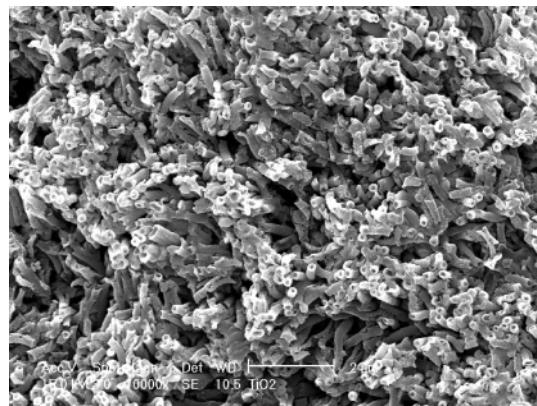


Figure 5. SEM images of the TiO₂ tubules prepared in the alumina membrane with 200-nm-diameter pores. All experiments were conducted at 298 K.

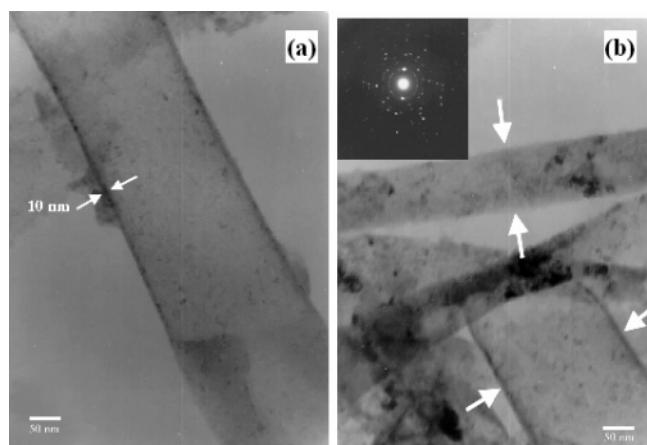


Figure 6. TEM images of TiO_2 tubules: (a) prepared in the alumina membrane with 200-nm-diameter pores; and (b) prepared in the alumina membrane with 20-nm-diameter pores. All experiments were adopted vacuum filtration at 298 K. Upper square is the electron diffraction pattern corresponding to the selected area (SAED).

of 3.28 eV is obtained for the TiO_2 tubules, which is ascribed to bulk anatase TiO_2 (3.18 eV).²⁰ Therefore, it was confirmed that the form of TiO_2 tubules is anatase.

Crystallographic Characterization of TiO_2 (XRD).

Crystallographic characterization was performed with XRD. It is difficult to measure TiO_2 nanostructures directly, so the titania sol with 2,4-pentanedione was placed in a furnace (in air) with a temperature ramp of $50\text{ }^{\circ}\text{C h}^{-1}$ to 573, 623, and 673 K. The titania sol was heated at these temperatures (573, 623, and 673 K) for 2 h, and then the temperature was decreased to room temperature at a ramp rate of $30\text{ }^{\circ}\text{C h}^{-1}$. From the XRD patterns shown in Figure 4, two forms gave either anatase or amorphous structures. Peaks are observed at values of 2θ equal to 25.6, 38.1, 48.2, and 54.7° that correspond to the anatase structure. The sample calcined at 573 K was an amorphous form, and samples calcined at 623 and 673 K were anatase forms. It was confirmed that template-synthesized TiO_2 tubules were anatase structure. Addamo et al. obtained an anatase TiO_2 calcined at 573 K.²¹ The different results are caused by calcination time. Our samples were calcined

(20) Serpone, N.; Lawless, D.; Khairutinou, R. *J. Phys. Chem.* **1995**, 99, 16646.

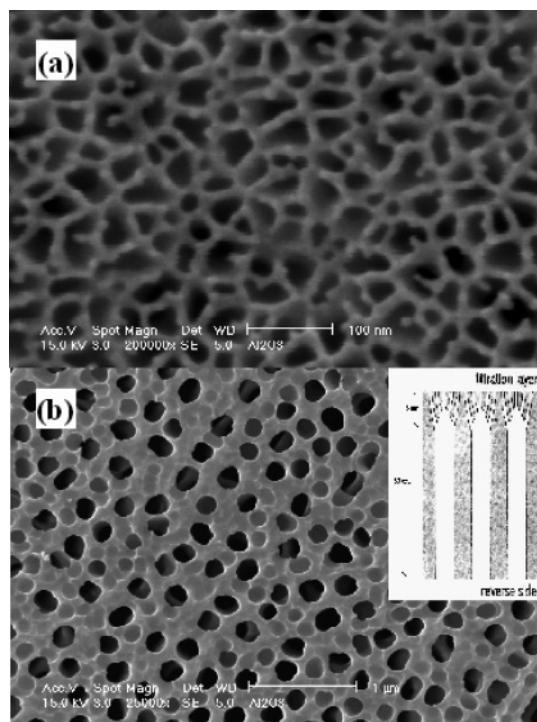


Figure 7. SEM images of commercial Whatman anodisc (20 nm): (a) top view; and (b) bottom view.

for 2 h. Otherwise other researchers calcined TiO₂ for 24 h. When an experiment was carried out with same conditions (24-h calcination time, 573 K), same results (an anatase TiO₂) were obtained.

Morphological Characterization of TiO₂ Tubules. Figure 5 shows SEM images of the TiO₂ tubules prepared in the alumina membrane with 200-nm-diameter pores. In all cases the TiO₂ tubules were 50 μm long (the thickness of the alumina membrane) and had external diameters of 200 nm (the diameter of the pores). These results show that the previous method with water vapor is one by which TiO₂ tubules can be prepared easily at room temperature.

Figure 6a shows a TEM image of the TiO₂ tubules obtained after dissolving the 200-nm alumina membrane. The thickness of the TiO₂ tube was 10 nm. Figure 6b shows a TEM image of the TiO₂ tubules obtained

(21) Addamo, M.; Augugliaro, V.; Paola, A. D.; Garcia-López, E.; Loddo, V.; Marci, G.; Molinari, R.; Palmisano, L.; Schiavello, M. *J. Phys. Chem. B* **2004**, *108*, 3303.

after dissolving the 20-nm diameter pore alumina membrane. TiO₂ tubules with variable diameters (50–200 nm) were observed. TiO₂ tubules had external diameters of larger than 20 nm (the diameter of the pores).

These results were consistent with the structure of the commercial Whatman anodisc membrane used in this experiment, which has a 20-nm diameter at the top of membrane (Figure 7a) and a ca. 200-nm diameter at the bottom of membrane (Figure 7b). The upper square of Figure 7b shows the selected area electron diffraction pattern (SAED) from the center of the tubule bundle. The data show that the tubules are highly crystalline anatase-phase TiO₂ and polycrystalline TiO₂.²²

Since the fabrication of TiO₂ tubules with diameter of 50 nm was confirmed, this method is a promising candidate for the fabrication of smaller TiO₂ tubules.

Conclusions

The template method has become a very simple yet powerful process for the synthesis of TiO₂ nanostructures.

The TiO₂ nanotubes fabricated by template synthesis and water vapor hydrolysis were polycrystalline and anatase. Chelation of titanium isopropoxide by 2,4-pentadiene was confirmed by FT-IR. When an alumina template with pores of 20-nm diameter was used, 50-nm diameter TiO₂ tubules were observed. This difference between the diameter of the template pores and the TiO₂ tubules was due to the nonuniform pores of the commercial alumina membrane, which have a diameter of 20 nm at the top of the membrane and a diameter of 200 nm at the bottom of the membrane. If an alumina membrane with uniform pores of 20-nm diameter is used, uniform 20-nm TiO₂ tubules will be fabricated. Our results show that smaller TiO₂ tubules can be fabricated easily through hydrolysis by water vapor at room temperature using template synthesis.

This method can be used in applications of photocatalyst and in electrodes of solar cells since it fabricates the largest surface area of TiO₂. There is also possibility of controlling the size of TiO₂ tubules.

CM049466X

(22) Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*; Wiley-Interscience: New York, 1974.