

Figure 3. a) HRTEM image of ZrO_2 nanotubes fabricated in PC templates with 200 nm pores. The fabricated nanotubes are 200 nm in diameter. b) AFM topographic image shows that the fabricated ZrO_2 nanotubes are about 12 μm long.

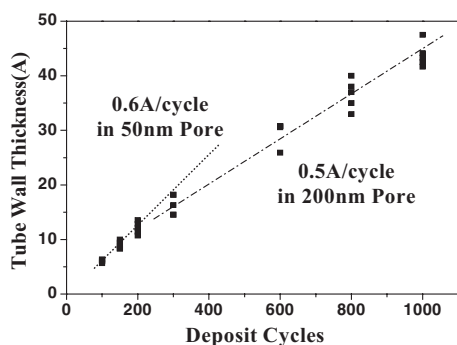


Figure 4. Plot of the growth rate of wall thickness showed a linear dependence on the coating cycles in the TiO_2 nanotubes. Growth rates of the wall thickness were 0.6 and 0.5 $\text{\AA}/\text{cycle}$ for PC templates with 50 and 200 nm pores, respectively.

structures. Contact-angle analysis was performed using a model A-100 Ramé-Hart NRL goniometer to measure water contact angles under ambient conditions using the Sessile drop method.

Received: October 13, 2003
Final version: March 5, 2004
Published online: July 5, 2004

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Facile Route to Silver Nanotubes**

By Liangti Qu, Gaoquan Shi,* Xufeng Wu, and Bin Fan

One-dimensional (1D) nanostructured materials have attracted increasing attention in recent years, mainly due to their potential applications in mesoscopic physics and the fabrication of nanometer-scale devices.^[1] Nanotubular materials, for example, are expected to find uses as the paths for gases and fluids or reservoirs for catalysts, and they also have potential applications in fuel cells, sensors, and separation systems.^[2] A series of nanotubes, including metals (e.g., Au, Pt),^[3] inorganic compounds (e.g., TiO_2 , WS_2),^[4] and polymers (e.g., polyaniline, polythiophene),^[5] have been prepared. Si-

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[**] This work was supported by the National Natural Science Foundation of China (50225311, 20374034, 50373023) and the National Basic Research Foundation (2003CB615700).

multaneously, synthesis strategies based on hydrothermal reactions, replacement reactions, and surfactant-assisted or porous template (polymer or anodic alumina porous membrane)-assisted growth techniques have been developed.

Silver is one of the most extensively studied and applied metals, and its nanostructures with morphologies of wires, rods, spheres, cubes, triangular plates, and dendrites have already been fabricated.^[3a,6] However, heretofore little work concerned the synthesis of 1D silver nanotubular structures. Silver nanotubes (Ag NTs) are useful as nanosized electrodes, catalysts, and substrates for surface-enhanced Raman spectroscopy, etc.^[7,8] Recently, Rubinstein and coworkers presented a procedure for preparing silver nanotubes.^[9] The process involved letting a colloid solution of nanometer-scale Ag particles enter the pores of a surface-modified nanoporous alumina membrane, followed by spontaneous coalescence of the surface-confined nanoparticles to yield solid Ag NTs. In this approach, a previously modified porous alumina membrane and nanometer-sized silver particles were used as the template and precursor, respectively. More recently, Kijima et al. utilized a lyotropic mixed-surfactant liquid crystal as the template for generating Ag NTs, and the resulting materials cohered into a dense aggregate.^[10] Thus, the preparation of Ag NTs with well-defined size via a facile route still remained a challenge. Here we report a simple route to synthesize arrays of Ag NTs using pristine porous alumina membranes as the templates. The Ag NTs were prepared by absorption of AgNO₃ solution in the pores of the templates, followed by drying and decomposition of the salt at high temperatures.

Porous alumina membranes with pore diameters in the range of 200–350 nm (see Experimental section) were used as the templates. Figure 1 presents schematically the fabrication of the Ag NTs. First, the porous template was immersed in a 10–15 M AgNO₃ solution for 30 min with slight heating. Thus, the pores of the alumina membrane were filled with AgNO₃ solution due to capillary interactions. After the excess AgNO₃ solution on the membrane surfaces had been removed by blowing nitrogen gas and wiping with filter paper, the AgNO₃-filled template was dried at 80–100 °C to evaporate the solvent. As a result, solid AgNO₃ adhered to the pore walls of the template. Then, the salt-filled template was heated at 500 °C in an ambient pressure furnace for 30 min. The AgNO₃ in the nanopores of the template decomposed into metallic silver and gaseous products. Finally, Ag NTs were freed from the template by dissolving the alumina membrane with 1.0 M KOH aqueous solution and then washed with distilled water.

Figure 2 shows typical scanning electron microscopy (SEM) images of the Ag NTs released from the templates. As can be seen from this figure, fibril products were obtained (Fig. 2a). The diameters of the fibrils are in the range of 200–350 nm, which agrees with the pore sizes of the alumina template. The tubular morphology of the fibrils is clearly demonstrated in Figures 2b,c. The open ends of the fibrils, indicated by the arrows (Fig. 2c), demonstrate the hollow structure of the resulting product, which is confirmed by the high-magnification im-

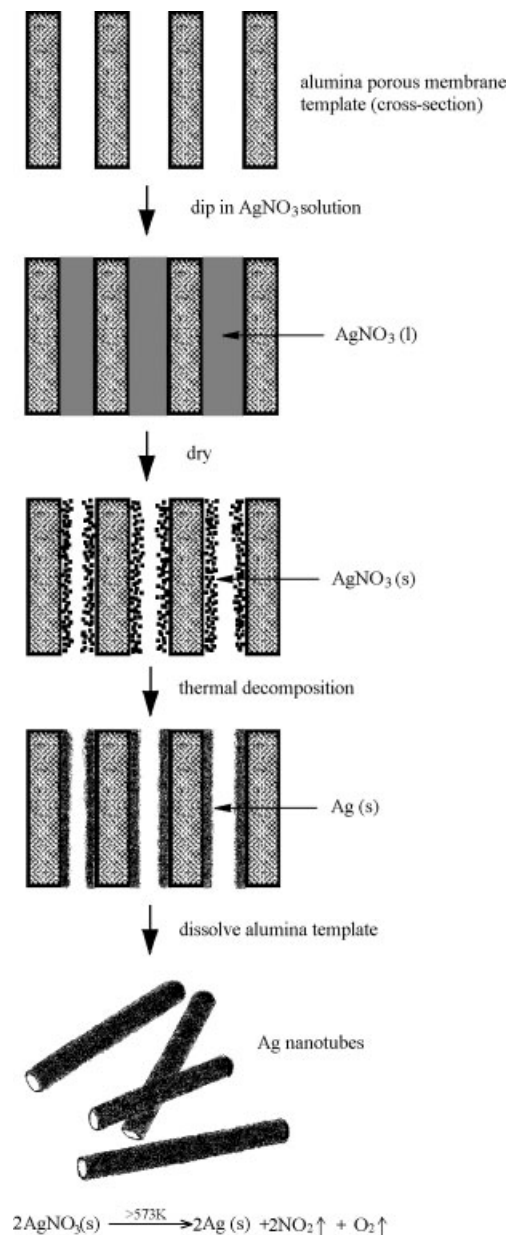


Figure 1. Scheme of fabrication of the Ag nanotubes (dimensions are not to scale).

age of a fibril end shown in Figure 2d. Thus, the fibrils are Ag nanotubes. The walls of the tubules are composed of coalesced Ag nanoparticles (about 10–20 nm) and their thickness is around 50 nm. The hollow structure can be further proved by the SEM image of a sonicated sample. As shown in Figure 2e, the hollow structure can be clearly observed from the tube broken by ultrasound vibration.

A transmission electron microscopy (TEM) image of an individual Ag NT is shown in Figure 3a. There are pale and dark regions distributed along the tube, however, its hollow interior is not clearly reflected because the silver wall is thick and the nanoparticles in the wall are compactly coalesced

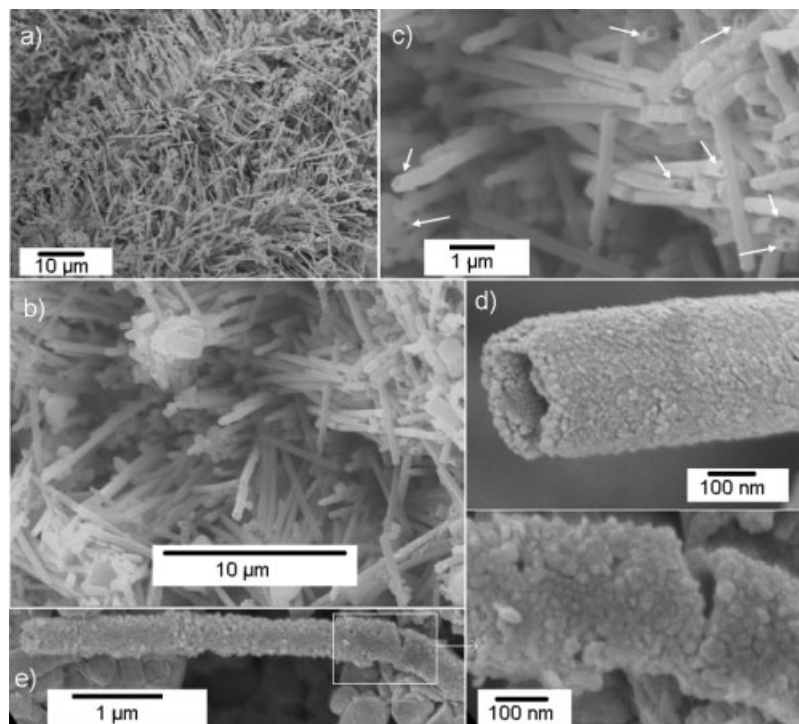


Figure 2. SEM images of Ag NTs (a–d) and a broken tube (e) shown at different magnifications.

together. The microscopic electron diffraction (ED) pattern of this Ag NT indicates the single-crystalline nature of the nanoparticles forming the nanotube (inset in Fig. 3a). The typical wide angle X-ray diffraction (XRD) pattern of the obtained Ag NTs clusters presents sharp diffraction peaks corresponding to the cubic structure of metallic silver, indicating the formation of highly crystalline silver.

The morphology of the resulting silver products depends strongly on the concentration of the AgNO_3 aqueous solution precursor. When the AgNO_3 concentration was lower than 5 M, silver nanoparticles (about 10–20 nm) cohered sparsely on the inner wall of the nanopores of the template (Fig. 4a, left), and only silver nanoparticles were observed (Fig. 4a, right). When a 7.0 M AgNO_3 solution was used, silver nano-

particles were orderly assembled along the pore walls at a high density (Fig. 4b). As the salt concentration increased to 10 M, some neighboring nanoparticles coalesced together to form tubular structures (Fig. 4c). These results are in good agreement with the fact that the walls of Ag NTs are made of nanoparticles (Figs. 2d,e). When a 15 M AgNO_3 solution was used, large arrays of tubular structures were formed (Fig. 4d, left) and clusters of Ag NTs (about 10–40 μm in length) were generated (Fig. 4d, right).

In conclusion, arrays of Ag NTs with diameters in the range of 200–350 nm can be synthesized by a simple template-assisted procedure. The decomposition of solid AgNO_3 within the pores of an alumina membrane led to the formation of Ag NTs. The walls of the Ag NTs were composed of densely

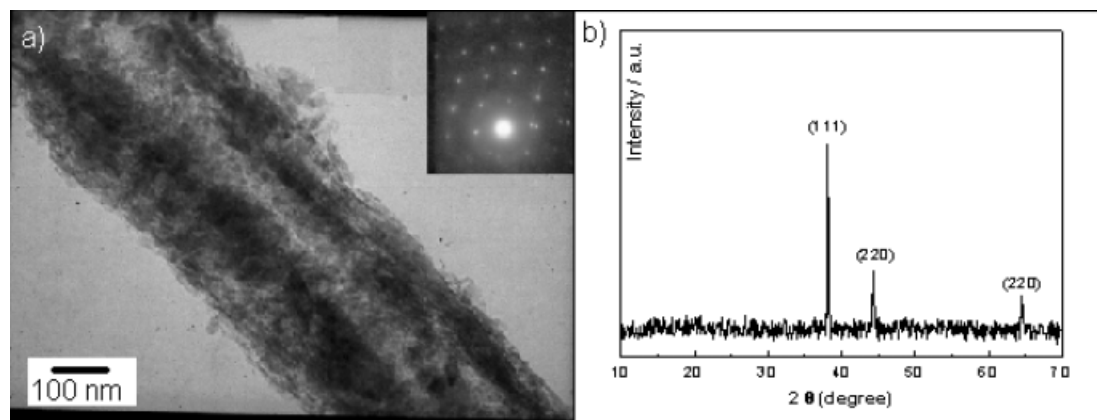


Figure 3. a) TEM image of a single Ag NT and the corresponding convergent beam electron diffraction pattern (inset). b) XRD pattern of the clusters of Ag NTs.

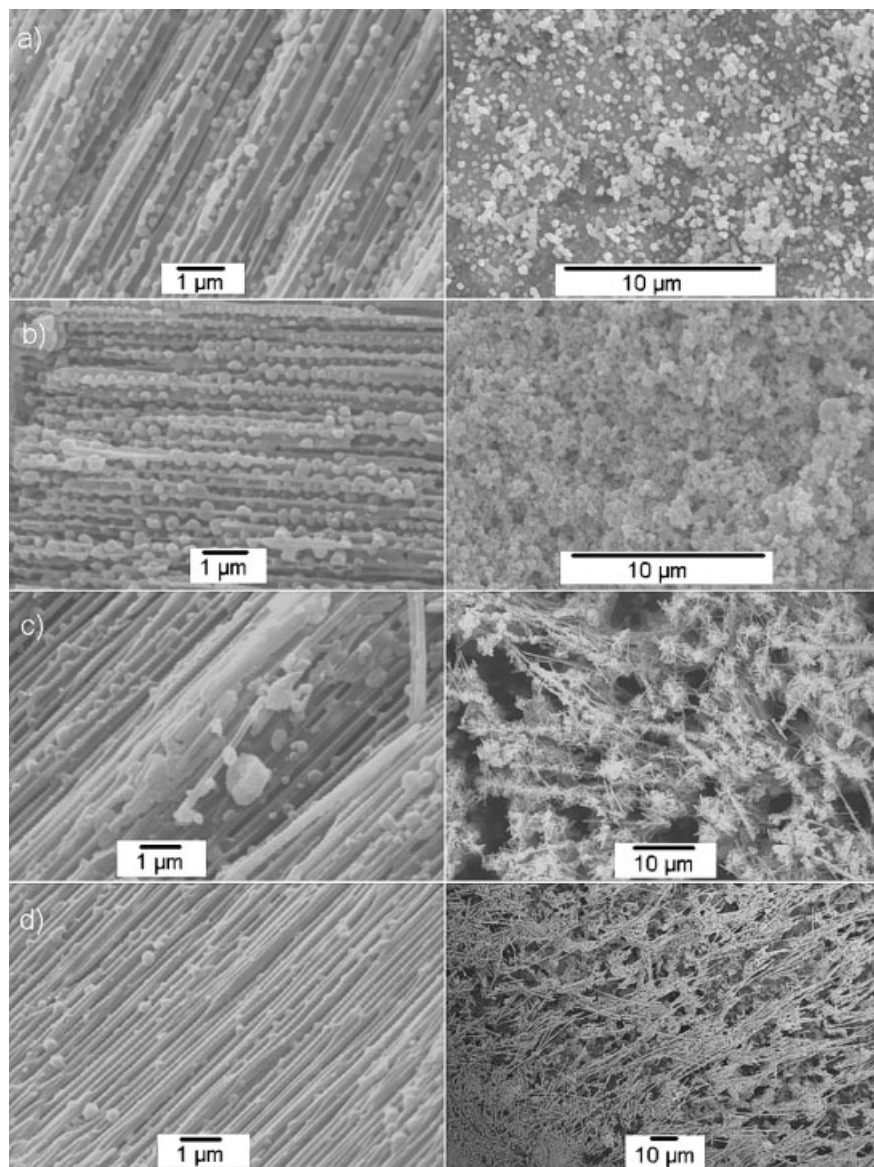


Figure 4. SEM images of the cross sections of AgNO_3 -filled nanoporous templates after decomposition of the salt (left) and the resulting products released from the templates (right). The concentrations of AgNO_3 solution used to fill the nanopores of the templates were ≤ 5 M (a), 7.0 M (b), 10 M (c), and 15 M (d).

coalesced crystalline silver nanoparticles with diameters of 10–20 nm.

Experimental

Materials: Porous alumina membranes (Anodisc 25) with pore diameters in the range of 200–350 nm (most of them are 220 ± 20 nm, $>85\%$, according to the SEM images of the template) and thickness of 60 μm were purchased from Whatman International Ltd (England). AgNO_3 with purity higher than 99.8% was a product of Beijing Chem. Fact. (Beijing, China). Both were used as received.

Synthesis of Ag NTs: A porous alumina membrane was immersed in a saturated aqueous solution of AgNO_3 (~ 15 M) for about 30 min

and heated slightly. As a result, the pores of the membranes were fully filled with the solution. Then, the wetted template was dried at 80–100 $^\circ\text{C}$ for about 30 min. After drying, the template with the salt was heated to 500 $^\circ\text{C}$ and kept in an ambient pressure furnace for about 30 min. Finally, the Ag NTs were released by dissolving the alumina membrane in 1.0 M KOH for over 8 h and collected by filtration after washing repeatedly with distilled water.

Instrumentation: The SEM images were taken using a JSM-6700 F scanning electron microscope (JEOL, Japan) at 3.0 kV. TEM images and electron diffraction (ED) patterns of the Ag NTs were recorded on a model 800 transmission electron microscope (Hitachi, Japan) at an accelerating voltage of 200 kV. X-ray diffraction (XRD) was performed on a D8-advance X-ray diffractometer (Bruker, Germany) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$ Å). The data were collected over the range $10^\circ \leq 2\theta \leq 70^\circ$ in steps of 0.02° with a count time of 1 s.

Received: January 13, 2004

Final version: April 7, 2004

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