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Controlled Fabrication of Multiwall Anatase TiO_2 Nanotubular Architectures

Changdeuck Bae,[†] Youngjin Yoon,[†] Hyunjun Yoo,[†] Dongil Han,[†] Jinhan Cho,[†] Byoung H. Lee,[‡] Myung M. Sung,[‡] MinGun Lee,[§] Jiyoung Kim,*[,§] and Hyunjung Shin*[,†]

[†]*School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Korea,* [‡]*Department of Chemistry, Hanyang University, Seoul 133-791, Korea, and* [§]*Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080*

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Titanium dioxide (TiO_2) is an important class of n-type semiconducting materials that shows interesting characteristics, such as photoswitchable surface wettability,[1,2] efficient photocatalytic activity,[3,4] high chemical stability,[5] bistable electrical resistance states,[6] and high electron drift mobility.[7] Nanocrystalline TiO_2 has huge potential for applications in self-cleaning surface coating,[2] dye-sensitized/hybrid solar cells,[8,9] Li-ion secondary batteries,[10,11] and nonvolatile memory devices.[6] In recent years, inorganic semiconducting one-dimensional (1D) nanostructures such as nanowires, nanorods, and nanotubes (NTs) have actively being investigated for renewable energy applications. Their attraction in this regard lies in the capacity of their 1D scaffolds to serve as charge collectors with direct pathways for charge carrier transport.[12−14] In this context, nanotubular structures of oxides, such as TiO_2 and ZnO, which are roughly twofold greater in their specific surface area in comparison with their nanowire/rod counterparts, have recently been employed in dye-sensitized solar cells.[15,16] Although nanotubes with lengths of up to several hundreds of micrometers have been produced, due to the limited areal density of the nanotube arrays, they may be insufficient for application in high-efficient devices.

We have previously fabricated single-wall oxide NTs with controlled dimensions by template-directed atomic layer deposition (ALD); related major processing issues such as selective etching of the templates, dispersion of the fabricated nanotubes, and coating of nanopores with high aspect ratio have been discussed (see our previous publications in refs 17 and 18 and others[19]). Here we report a procedure for fabricating multiwall (MW) anatase TiO_2 NTs by utilizing templated ALD synthesis in conjunction with alternating TiO_2/Al_2O_3 nanolaminate structures. Significantly increased specific surface area as well as an improved roughness factor (the ratio of real surface area over geometric surface area) can be achieved by the proposed strategy. Extraordinary etching capability through nanocapillaries with a very high aspect ratio (over 1:1000) is demonstrated in the present work.

Porous alumina membranes housing cylindrical pores were used as a template, and TiO_2/Al_2O_3 nanolaminate layers were deposited onto the template by ALD (left, Figure 1). Titanium(IV) iso-propoxide and trimethyl aluminum (UP Chemical, Korea) were used as metal reactants. Water vapor and Ar were used as an oxidant and a carrier gas, respectively. Layers of titania and alumina were deposited at 120 and 160 °C, respectively. After wet chemical etching of the sacrificial alumina layers as well as the template, MW TiO_2 NTs were obtained (right, Figure 1). With this strategy, in principle, all of the structural parameters including the diameter, length, wall thickness, interwall spacing, and number of wall layers of the MW TiO_2 NTs can be adjustable.

The fabrication began by choosing the desired nanotubular and the sacrificial layers utilized between the nanotubular layers. They should not only exhibit complete etching selectivity but also not form alloys during annealing. For example, ZnO NTs prepared by ALD on porous alumina templates cannot be separated from the template by selective etching with either acidic or alkali solutions due to their low chemical stability against alumina.[5] We thus chose TiO_2/Al_2O_3 systems for the

*Corresponding author. E-mail: hjshin@kookmin.ac.kr.

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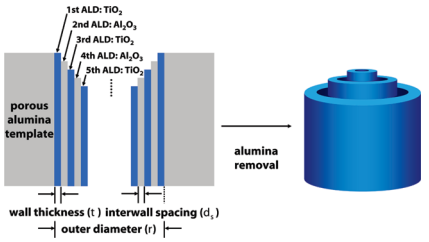

Figure 1. Schematic illustration of process to fabricate multiwall anatase TiO_2 nanotubes.

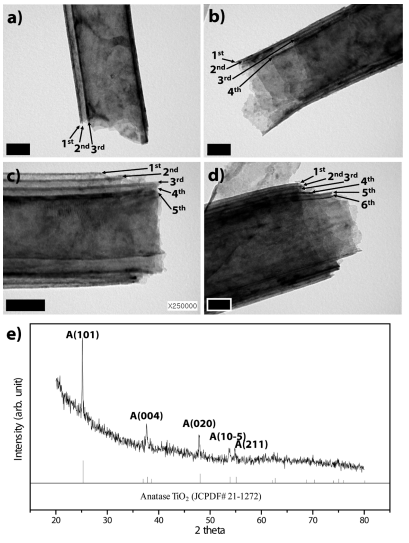

Figure 2. Series of TEM images of MW anatase TiO_2 NTs. (a−d) Triple-, quadruple-, quintuple-, and sextuple-wall NTs having 7 nm-thick and -spaced walls. Individual wall layers are indicated by black arrowheads. All scale bars = 100 nm. (e) Representative XRD results of our tubular structures, clearly showing anatase pahse.

preparation of multiwall anatase TiO_2 NTs. That is, the TiO_2/Al_2O_3 system is thermally stable, not forming any alloys with each other, and TiO_2 is chemically inert.

We first show the capability to control the number of wall layers in the fabrication of MW anatase TiO_2 NTs. Commercially available alumina membranes with 200−300 nm pore diameters were used as the template. Note that consideration of the tube lengths has been excluded from the discussion in the proof-of-concept experiments. The desired numbers of TiO_2/Al_2O_3 nanolaminates were deposited inside the alumina template by ALD. As-deposited samples were subsequently annealed at 400 °C for 1 h to crystallize the TiO_2 layers into crystalline anatase phase. The sacrificial alumina layers as well as the template were then dissolved by wet chemical etching in 1 M NaOH and 6:1 aqueous HF/NH_4F solutions, sequentially, followed by washing with pure water. A detailed description of the wet etching ability into the nanocapillaries will be provided later (Figure 3). Figure 2a−d shows a series of resulting MW anatase TiO_2 NTs with triple, up to sextuple, walls. At the broken ends of the MW NTs, individual wall layers are clearly discernible for all the nanotubes, as indicated by the black arrowheads in Figure 2. The resulting structures were identified as polycrystalline anatase phases by electron (Figure 3d) and X-ray (Figure 2e) diffraction results.

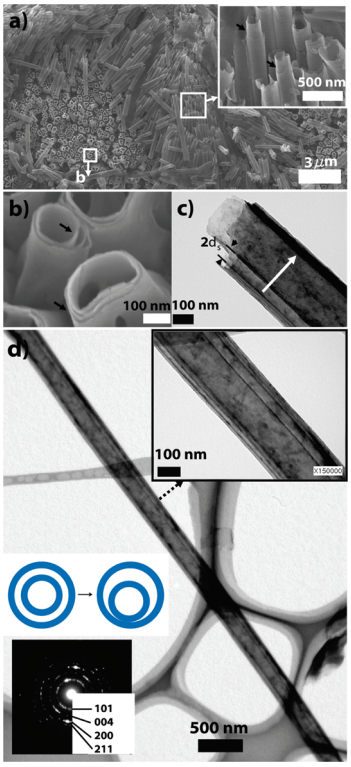

Figure 3. (a) Low-magnified SEM image of triple-wall TiO_2 NTs from 7 nm thick TiO_2 and sacrificial Al_2O_3 layers; the inset shows the layered structures, as indicated by the black arrow heads. (b) SEM of the broken ends of triple-wall NTs on an epoxy supporting film, showing that the sacrificial alumina between the TiO_2 NT walls underwent complete dissolution through the nanocapillaries. (c) TEM of a sextuple-wall TiO_2 NT with the outer quadruple walls and the inner double walls spaced by 15 nm Al_2O_3 layers, as a d_s-control experiment. (d) Low-magnified TEM image of long quintuple-wall NTs with 7 nm-thick and -spaced quadruple walls and 7 nm-thick and 15 nm-spaced inner single-wall; the left inset is a representative electron diffraction pattern, indicative of polycrystalline anatase structures, and the shifted inner wall layer in the magnified right inset is evidence of the separated TiO_2 walls as in the manner of the inset illustration.

Although the interwall spacing, d_s (as depicted in Figure 1), had been precisely controlled with the same thickness of the sacrificial alumina layers deposited by ALD, different d_s values are observed depending on the viewing angles (see Figure 2a,c for notorious examples). This could be related with capillary attraction by the etching and drying processes of the MW TiO_2 NTs with narrow nanocapillaries in their interior: When alumina is dissolved, interfaces between the etching solution and the concentrate of species dissolved from alumina are created between the inner and the outer NTs; as the area of the curved interfaces between the tubes decreases as a result of reduction of the interfacial free energy between the etching solution and the concentrate, the inner NTs move into contact on a certain side of the outer tube (see the inset illustration in Figure 3d). It is noted that the inside of MW NTs of several micrometers in length was completely, selectively dissolved via a series of capillary insertion of the etchant and subsequent diffusion-out of the etched ions in solutions, as shown in Figure 3a,d. To assess whether the sacrificial alumina layers between the TiO_2 NT walls were completely dissolved up to the root/end of the tubes, we observed the broken parts of triple-wall NT

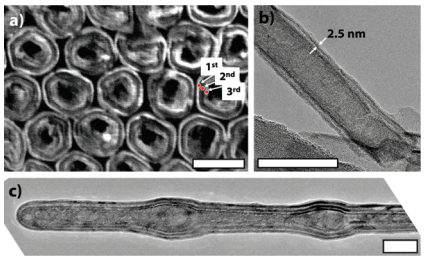

Figure 4. (a) SEM micrographs of ordered triple-wall anatase TiO_2 NTs with 7 nm-thick and -spaced walls (< 100 nm outer diameter) that have been obtained by partial chemical etching of the sacrificial alumina. (b) TEM image of double-wall TiO_2 NTs possessing 2.5 nm-thick walls separated by 4 nm. (c) TEM of a diameter-modulated triple-wall anatase TiO_2 NT released from the modulated alumina template. All scale bars = 100 nm.

arrays on an epoxy supporting film after ultrasonic treatment in water for several seconds, as shown in Figure 3b. With the successful chemical etching processes for the sacrificial alumina from the top of the tube arrays to the bottom layer,[18] MW TiO_2 NTs having several micrometers (6−8 μm) in length were prepared by dissolution through nanocapillaries spaced at 7 nm (aspect ratio, over 1:∼1000). Therefore, the different values of d_s observed in TEM measurements are attributed to shifting of the inside wall by capillary action during chemical etching and subsequent solvent drying.[18] This is further demonstrated in the d_s-control experiments. MW TiO_2 NTs with adjustable d_s can be made by introducing sacrificial layers with desired thickness between the TiO_2 walls. Figure 3c shows an example of controlled d_s, where sextuple-wall TiO_2 NTs have outer quadruple walls and inner double walls separated by d_s = 15 nm of Al_2O_3 layers. The white arrow of Figure 3c indicates the wall's movements by capillary forces, as discussed above.

We have also prepared MW nanotubular structures by using homemade alumina templates, as they not only possess higher areal density (∼10^{11} per cm^2) than that of commercially available templates (∼10^{10} per cm^2) but also can be tailored to length, interpore distance, and pore diameter (< 100 nm) with well-established methods reported in the literature.[20] Figure 4 shows examples of MW anatase TiO_2 NTs having sub-100 nm outer diameter prepared by the present strategy. Triple-wall TiO_2 NTs with 7 nm-thick and -spaced walls were fabricated (Figure 4a). With the present method, we have thus far achieved MW TiO_2 NTs having a wall thickness of as low as 2.5 nm (Figure 4b). In addition, a few approaches might be possible to create 1D nanostructures with a high degree of shape complexity, as a new nanostructural platform. We fabricated diameter-modulated MW anatase TiO_2 NTs, which have a lock-and-key geometry and allow the formation of stable MW structures in dispersion solutions without separation between each wall. A diameter-modulated alumina template with two notches was prepared by a method demonstrated recently by Lee et al.,[21] as shown in the inset of Figure 4c. Three TiO_2(7 nm)/Al_2O_3(7 nm) nanolaminate layers were deposited onto the template as demonstrated above and, after annealing, the resulting structures were released by dissolving the sacrificial alumina in NaOH and HF/NH_4F solutions. Diameter-controlled triple-wall anatase TiO_2 NTs are shown in Figure 4c. The notches seen here are apparently the template footprint.

Finally, we discuss the correlation between the roughness factor and the specific surface area of the MW anatase TiO_2 NTs, which might be of major significance for practical applications. The roughness factor is defined by the ratio of real surface area over geometric surface area, and the specific surface area is determined as the real surface area per unit mass. We estimated the roughness factor and the specific surface area for the MW TiO_2 NTs, where the calculation geometry was chosen from the values practically achievable by ALD (30 μm in length and 80 nm in outer diameter).[22] As expected, the roughness factor increases with an increase of the number of wall layers. However, the specific surface area is not enhanced simply by incorporation of the MWs, because the gradient of the specific surface area to the wall number is not steep but is exponentially decreased to the wall thickness. Considering this, we suggest that with MW NTs having thin wall layers (i.e., few nanometers), the roughness factor could reach up to ∼5000, achieving a specific surface area of ∼400 $m^2 \cdot g^{-1}$, which would be difficult to obtain with single-wall NTs.

In summary, we have introduced an important class of 1D nanomaterials by demonstrating MW anatase TiO_2 NTs prepared by the deposition of alternating TiO_2/Al_2O_3 nanolaminates onto porous alumina templates with ALD, followed by wet etching of the sacrificial alumina. The proposed structures are found to multiply the roughness factor of the anatase TiO_2 NTs by simply increasing the number of wall layers, maintaining the areal density of the nanotube arrays. The hierarchical nanostructures presented here are expected to prove useful not only as improved one-dimensional charge collectors for application in dye-sensitized solar cells, organic−inorganic hybrid solar cells, Li-ion secondary batteries, and many other devices but also as efficient photocatalysts and catalytic supports.

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