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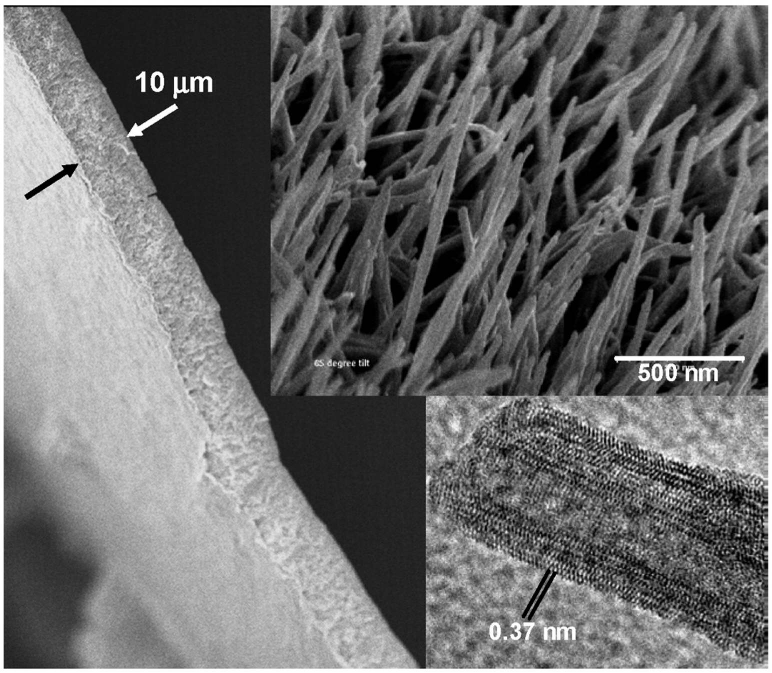

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Large Oriented Arrays and Continuous Films of TiO_2-Based Nanotubes

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Titanium oxide (TiO_2) and materials derived from TiO_2 are widely investigated for applications in photovoltaic cells, batteries, separations, sensing, optical emissions, photonic crystals, catalysis and photocatalysis, selective adsorption, ion exchange, ultraviolet blockers, smart surface coatings, and as functional filling materials in textile, paints, paper, and cosmetics. Recently, TiO_2-based nanotubes began to attract wide attention because of their potentials in many areas such as highly efficient photocatalysis[1] and photovoltaic cells.[2,3] Mainly, two approaches were reported for preparing titania nanotubes in powdery forms, one using a templating synthesis[2,4] and the other using a hydrothermal reaction.[5−7] However, thin films and coatings of oriented nanostructures are often more desirable for applications involving catalysis, filtration, sensing, photovoltaic cells, and high surface area electrodes. In this paper, we report for the first time a one-step, templateless method to directly prepare large arrays of oriented TiO_2-based nanotubes and continuous films. These novel nanostructures can also be easily prepared as conformal coatings on a substrate.

In our synthesis, the nanotubes were formed on a substrate that was seeded with TiO_2 nanoparticles, rather than in the bulk solution. We first prepared a dilute TiO_2 suspension by dispersing 1.0 g of Degussa P25 TiO_2 powder in 20 g of deionized (DI) H_2O. After 5 min of sonication, the suspension was centrifuged for 1 min at 1000 rpm to remove coarse particles and aggregates. TiO_2 nanoparticles were deposited on a titanium (Ti) foil (99.999% pure) through dip coating from this TiO_2 suspension. The Ti foil containing the predeposited TiO_2 nanoparticles was then reacted with an alkaline solution in a sealed Teflon reactor, containing 10 mL of 10 M NaOH solution. The reaction temperature ranged from 95 to 160 °C. After the reaction, the Ti foils, covered with the newly formed film, were removed, soaked and washed with DI H_2O, and then dried in air.

Figure 1 shows the scanning electron microscopy images (SEM) of the films made of oriented nanotubes. After 6 h of reaction, a uniform film of nanotubes formed on the Ti substrate surface (Figure 1a). The oriented texture of the film could be better seen from a tilted sample (Figure 1b). A high magnification SEM image of the tilted sample reveals that most nanotubes are vertically aligned (Figure 1c). These nanotubes are about 12 nm in diameter, in line with the results reported in the literature.[5−7] Samples reacted for less than 6 h also show similar oriented nanostructures, but these films contain halfway curled nanofoils (arrows) as well as fully grown nanotubes (Figure 1d). This result suggests that nanotube formation involves folding of sheetlike structures, but literature results also revealed different pathways of how this folding can take place.[7]

After 20 h of the reaction, the nanotubes grew very long in length, and a continuous film, 10 μm in thickness, formed (Figure 2a). This film can be easily removed from the substrate as a free-standing film (the inset in Figure 2a). In contrary, the nanotubes formed in short time reactions (as shown in Figure 1) strongly adhere onto the substrate. A high magnification SEM image shows that the long nanotubes formed after long time reactions could no longer retain their vertical alignment atop the film (Figure 2b). However, the vertically aligned nanotubes were still observed near the film base (Figure 2c).

Figure 3 shows some high resolution transmission electron microscopy (HRTEM) images of the typical nanotubes. Most of the nanotubes are open-ended (Figure 3a). However, some close-

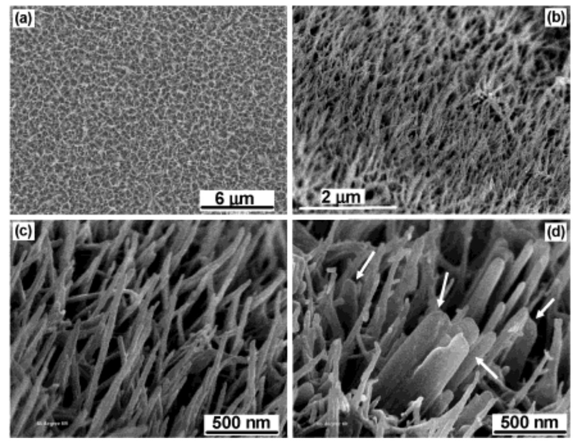

Figure 1. SEM images of large arrays of oriented TiO_2-based nanotubes prepared at 150 °C. (a) A low magnification, face-on SEM image of the films after 6 h of reaction. (b) A low magnification SEM image of a 60° tilted sample after 6 h. (c) A high magnification SEM image of (b). (d) Curled foils (arrows) in transition to nanotubes after 3 h.

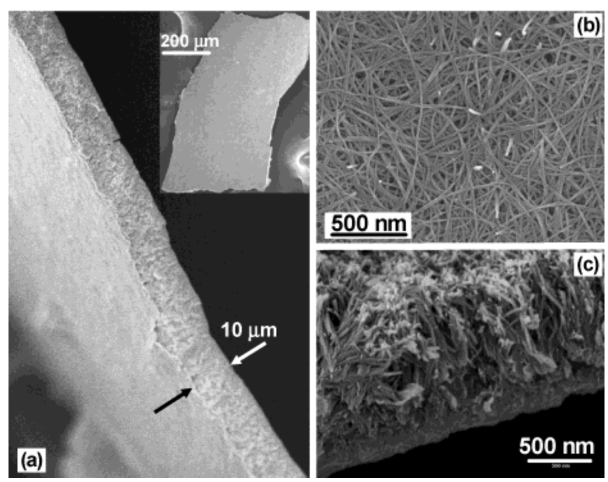

Figure 2. Continuous nanostructured films after 20 h of reaction at 150 °C. (a) A cross-section image of the free-standing film. The inset is a low magnification face-on image of the detached film. (b) Top view of the film made of long nanotubes. (c) A cross-section image of oriented nanotubes near the substrate.

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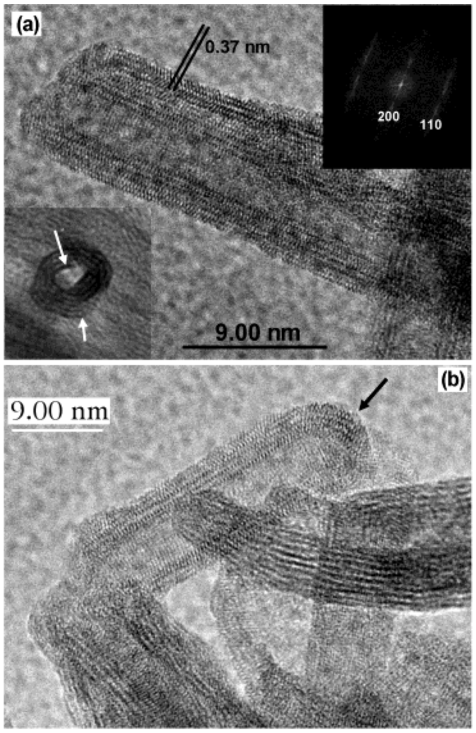

Figure 3. High-resolution TEM images of the nanotubes. (a) An open nanotube. The inset on the left is a cross-section image. The inset on the right is the Fourier transformation of the TEM image. (b) A close-ended nanotube.

ended nanotubes were observed occasionally (Figure 3b). The nanotubes are made of multilayered sheets. The outer diameter (OD) of the nanotube is about 12 nm, and the inner diameter (ID) of the nanotube is about 3.7 nm. The interlayer spacing is about 0.78 nm. The fine fringe perpendicular to the tube orientation is 0.37 nm. The left inset confirmed that the tubes are made of folded sheets, as indicated by the arrows that point to terminal sheets. In the literature, both anatase[5a,6f] and titanate[7b,c] were used to explain the crystalline structure of the TiO_2-based nanotubes. The X-ray diffraction patterns and the high-resolution TEM results we obtained were similar to those reported by Chen and Du et al.,[7b,c] who suggested a $H_2Ti_3O_7$ structure (monoclinic, $C2/m$, $a = 1.603$, $b = 0.375$, $c = 0.919$ nm, $\beta = 101.45°$). The Fourier transformation pattern (right inset in Figure 3a) is indexed according to this titanate structure.

The oriented TiO_2-based nanotubes and films are an exciting addition to a fast growing family of oriented nanowires and nanorods, including carbon nanotubes,[8,9] ZnO nanorods,[10] and conductive polymer nanowires.[11] The seeded growth method should be applicable to different substrates, as we have demonstrated in other systems.[11] Because of the unique chemical, electronic, and optical properties, we expect to find wide applications for this new class of oriented nanostructures.

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