Effect of Surface Structure on Wettability of TiO_2 Nanofibrils Prepared in Aluminum Oxide Template

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Porous anodic alumina (PAA) with regular channel structure was chosen as a template, and highly ordered TiO_2 nanofibrils arrays were fabricated within the pores of PAA by a sol–gel process. A series of TiO_2 nanostructures obtained after the TiO_2/Al_2O_3 composite film was treated with the NaOH for different times. Contact angle measurements indicated that the surface structure strongly affected the wetting behavior of the TiO_2 nanofibrils. The wettability of the surface changed from hydrophilic to hydrophobic when the structure of aligned nanofibrils with end tips was obtained.

In recent years, there has been increasing interest in the fabrication of one-dimensional nanostructures because of their potential applications in many fields, such as nanodevices, drug delivery, and nanosensor and microelectronics,[1–5] due to its particular structure and properties. Porous anodic alumina (PAA) template has been become an important membrane for the fabrication of one-dimensional nanomaterials in the last decade,[6–10] because it has regular cylindrical pores and its aspect raio can be adjusted by varying the oxidation conditions.

As a well-known optoelectronic semiconductor with photocatalytic activities, TiO_2 has potential applications in electronics, photocatalytic solar cells, gas sensors, and high-performance photocatalysts.[11–13] We prepared TiO_2 nanofibrils in the channels of PAA by sol–gel process. And it was found that the anatase-phase TiO_2 nanofibrils were uniform and had similar size to that of PAA.

The wettability of a solid surface is very important and affected by both the chemical composition and the geometric microstructure of the surface.[14–16] Herein, we report the relationship of wettability vs. surface microstructures of the highly porous TiO_2/Al_2O_3 composite nanostructures. The surface structures varied when the TiO_2/Al_2O_3 was treated with a NaOH aqueous solution for different times. The CA measurements further demonstrate that the wetting behavior of TiO_2 nanofibrils was strongly affected by the surface structure. As a result, the structure of aligned TiO_2 nanofibrils is propitious to obtain hydrophobic surface, on which a very large fraction of air was captured. Surface modification was not necessary in the fabrication process, so it provided a new way to control the wettability of nanostructured surfaces by changing the air fraction of the aligned nanofibrils.

The PAA template with a thickness of 20 μm and pore diameters of 100 nm in our experiment was obtained by a two-step anodizing process.[17] TiO_2 nanofibrils were prepared using a sol–gel process in the PAA. The TiO_2 sol used here was prepared by titanium *n*-butoxide, acetylacetone (ACAC), distilled water, and ethanol at a mole ratio of 1:1:3:20.[6] The anodic alumina structures was first immersed in ethanol for 10 min and then dipped into the TiO_2 sol at for 20 min. The TiO_2 sol on the surface of the PAA was washed away with ethanol. After drying at room temperature for more than 30 min, the TiO_2/Al_2O_3 was heated in air in a muffle furnace at 100 °C for 1 h and 400 °C for 2 h, at a rate of 2 °C/min. Then, a series of TiO_2 nanostructures obtained after the TiO_2/Al_2O_3 composite film was immersed in 3 M NaOH at 30 °C for 2, 4, 6, 8, 10, 14, and 18 min, respectively.

Two-step anodization results in uniform arrangement of pores in the PAA, which is seen in Figure 1a.The almost perfect hexagonal porous arrays can be observed. The diameter of the pores is 100 nm and the pore density can be as high as $1.0 \times 10^{10}\,cm^{-2}$. Figure 1b showed that the TiO_2 nanofibrils are uniform and have relatively straight morphologies and smooth surface. The diameters of TiO_2 nanofibrils are about 90 nm which is consistent with the pore diameter of PAA.

Figure 2 shows the XPS survey spectra from TiO_2 nanofibrils deposited in the PAA template. A clear Ti signal is present at 458.37 eV ($2p_{3/2}$) and a relatively small peak at 464.3 eV

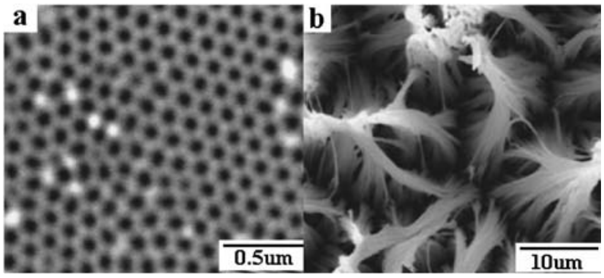

Figure 1. The SEM images of the PAA template and the TiO_2 nanofibrils. (a) Top surface structure view of PAA, (b) TiO_2 nanofibrils after PAA dissolved partly.

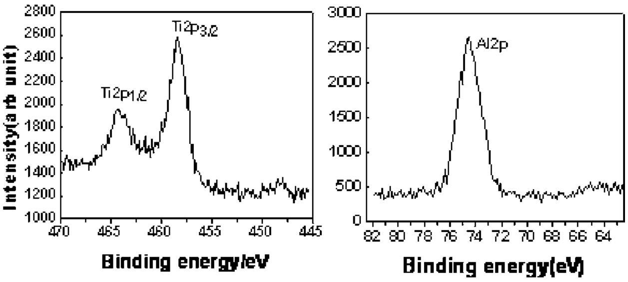

Figure 2. XPS spectra of the TiO_2/Al_2O_3 composite film: a) Ti 2p, b) Al 2p.

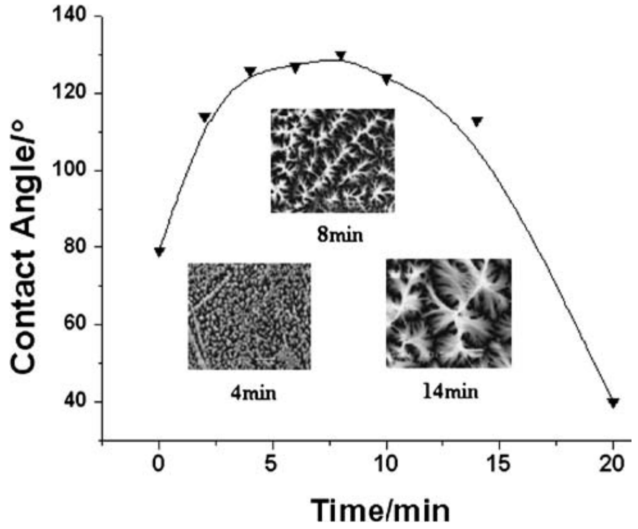

Figure 3. The relationship between water CA and immersion time.

($2p_{1/2}$), which agree with reference values for bulk TiO_2.[18] This suggests that titanium atoms in TiO_2 nanofibrils are positively charged by the formation of direct bonds with oxygen. The peak of binding energy of Al 2p in Figure 2b, lies at approximately 74.5 eV, corresponding to characteristic regions of alumina.

Figure 3 displays the relationship between water contact angle (CA) and immersion time. The three SEM micrographs showed the different TiO_2 nanofibrils structures obtained when TiO_2/Al_2O_3 film were treated with 3 M NaOH at 30 °C for 4, 8, and 14 min. It can be concluded that the water CA of the surface changed in the form of a parabola with increase of immersion time. The wetting behavior of the surface varied from hydrophilic to hydrophobic at the same time.

The surface of the TiO_2 nanofibrils can be regarded as a composite surface consisting of nanofibrils and air. The contact angle on the surface is described by the Cassie eq 1:[19] $\cos\theta_f = f_s \cos\theta_w - f_v$, where θ_f and θ_w are the contact angles on TiO_2 nanofibrils with a rough surface and on native TiO_2 film with a smooth surface, f_s and f_v are the area fractions of the TiO_2 nanofibrils and of the air in the grooves between individual nanofibrils, respectively.[20,21] When TiO_2/Al_2O_3 film was treated with 3 M NaOH at 30 °C for different time, in the beginning, the smooth surface is merely hydrophobic. With dissolving time increase, the top of the alumina template gradually dissolved and an aligned TiO_2 nanofibrils forest with end tips was obtained. This kind of surface is rough enough, and air can be trapped in the space between individual nanofibrils, forming a cushion to prevent water droplets from penetrating into the slots of the forest.[18,21] The water CA (θ_f) of the equation rose in this case with increasing f_v. When dissolving time was 8 min, the CA value reached a maximum 130°, and the wettability of the surface changed from hydrophilic to hydrophobic. After dissolving in NaOH for 14 min, the bottom of the alumina template had dissolved. The TiO_2 nanofibrils lean against each other and gather together into bundles of nanofibrils because of losing the support of the PAA. The CA decreases with f_v decreasing, and the wettability tends to be hydrophilic again.

In conclusion, the highly ordered TiO_2 nanofibril arrays have been fabricated within the pores of PAA with a sol–gel process. And a series of TiO_2 nanostructures obtained after the TiO_2/Al_2O_3 composite film was treated with 3 M NaOH for different times. Contact angle measurements indicated that the surface of TiO_2 nanofibril structures strongly affected the wetting behavior. A hydrophobic surface was obtained when the structure of the aligned TiO_2 nanofibrils with end tips existed. This may provide a new method to get a hydrophobic surface from other inorganic oxide materials by making a high-density nanorod structure.

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