Materials Science

DOI: 10.1002/anie.200501337

The Fabrication and Switchable Superhydrophobicity of TiO_2 Nanorod Films**

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Titanium dioxide (TiO_2) is an important material that is used in many industrial applications related to photo-splitting of water,[1] photocatalysis,[2] photovoltaic devices,[3] etc. Since the discovery[4] of photoinduced superhydrophilicity (water contact angle (CA) $< 10°$) on a hydrophilic TiO_2 surface in 1997, many research efforts[5–8] have been devoted to exploring this photosensitive mechanism with the aim of manipulating the surface wettability to a larger extent in virtue of the good light, thermal, and chemical stability and better biocompatibility of TiO_2 than of other organic or inorganic materials. However, its wettability has only been tuned in a limited region thus far.

In the past several years, inspired by the surface-topography-induced superhydrophobicity of lotus leaves[9,10] and water striders' legs,[11] various films that exhibit superhydrophobic properties have been fabricated.[12–19] On the other hand, superhydrophilic surfaces have been realized by taking advantage of a 2D[4] or 3D[20] capillary effect. Very recently, several stimuli-responsive, smart, interfacial materials that can be switched between superhydrophilicity and superhydrophobicity by combining the geometrical morphology of

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[**] We thank the State Key Project for Fundamental Research and the Special Research Foundation of the National Natural Science Foundation of China for continuing financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

the surface with a change of surface chemistry have been reported.[21–23] Herein, we report on the creation of superhydrophobic surfaces consisting of inorganic nanorods fabricated from hydrophilic TiO_2, and further demonstrate that their wettability can be reversibly switched between superhydrophobicity and superhydrophilicity. The mechanism involves the cooperation of the micro- and nanoscale hierarchical surface structures, the orientation of the crystal planes, and the surface photosensitivity.

The TiO_2 nanorod films were deposited on glass substrates by a low-temperature hydrothermal approach. Typically, aqueous solutions of titanium trichloride supersaturated with NaCl were heated to 160 °C for 2 h. The films deposited on glass wafers used as substrate were rinsed thoroughly with deionized water and ethanol, dried at room temperature, and stored in the dark for two weeks. Figure 1 a shows a typical field emission scanning electron microscopy (FE-SEM) image of the as-synthesized nanorod films. Many papillae can be found on the surface in a random pattern with diameters ranging from 2 to 6 μm. Each of these papillae is composed of nanorods with uniform diameters of 30 to 60 nm. As can be seen from the magnified image of a single papilla (Figure 1 b), the nanorods grow radial to the substrate and are self-assembled into micro- and nanoscale hierarchical structures.

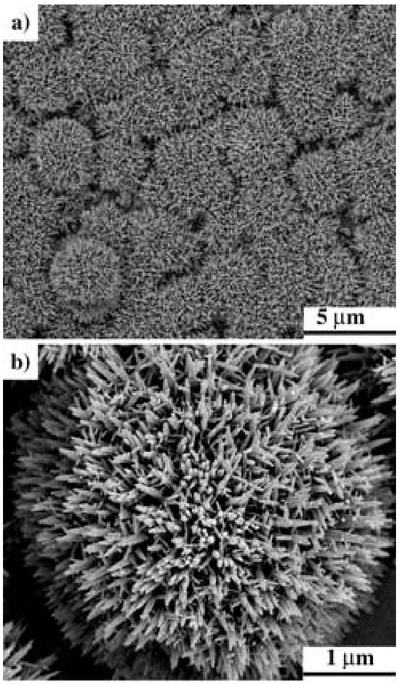

Figure 1. a) Low-magnification FE-SEM image of a TiO_2 nanorod film deposited on a glass wafer; b) morphology of a single papilla at high magnification.

According to the X-ray diffraction (XRD) pattern of the as-prepared TiO_2 films, the nanorods can be classified as having a standard tetragonal rutile structure (space group $P4_2/mnm$; JCPDS file no. 21-1276). The peaks are relatively broad compared with those of the bulk material, thus corroborating the small crystal size. In contrast to the standard pattern, the XRD profiles clearly exhibit an enhanced peak for the (110) reflection and a comparatively low diffraction intensity for (101) and (111) (see Supporting Information), which indicates that the growth of the nanorods has a preferred orientation. The samples were then dispersed onto a transmission electron microscopy (TEM) grid for further detailed structure analysis. Figures 2 b and c show the high-resolution TEM images of the side and top surfaces, respectively, of the nanorod wall shown in Figure 2 a at low magnification. It can be seen that the nanorod is well crystallized with clear lattice fringes parallel to the wall. The inter-plane distance of 0.325 nm for the (110) planes perpendicular to the rod axis can be readily resolved. Combined with the XRD data and SEM images, such features imply that the nanorods grow along the (110) crystal plane with a preferred orientation in the (001) direction.

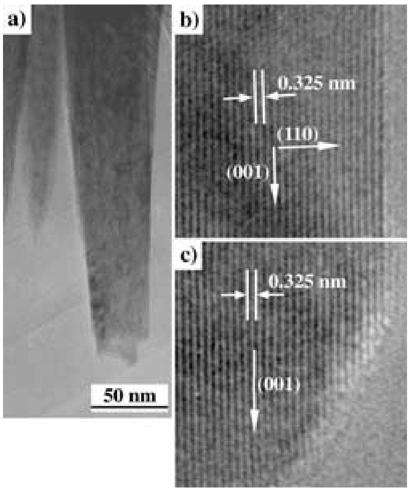

Figure 2. TEM image of a single TiO_2 nanorod (a). High-resolution TEM images of a nanorod wall at the side surface (b) and at the top surface (c) of the nanorod.

The wettability of the films was evaluated by contact angle (CA) measurements. The rutile form of TiO_2 is a hydrophilic material with a water CA of 72 and 74° on smooth single crystal (110) and (001) surfaces, respectively.[6] As shown in Figure 3 a (left), the water CA of the as-prepared rough TiO_2 nanorod films is large ($(154\pm1.3)°$), that is, the as-prepared films show superhydrophobicity. This result indicates that the surface structure strongly affects the wetting behavior. There are two equations in the literature that describe the water CA on rough surfaces. One is Wenzel's law,[24] $\cos\theta_f = r\cos\theta_w$, where θ_f and θ_w are, respectively, the water CA on a rough and smooth surface and r is the surface roughness. For $\theta_w < 90°$, it can be seen that an increase of r will result in a smaller CA, and water will fill the grooves below the droplet. However, the high water CA of the as-prepared films indicates that the water droplet does not penetrate the trough but is suspended on the sharp nanorod films, and that an air pocket might be formed on the surface.

The apparent contact angle θ_f can be described by another equation, first formulated by Cassie and Baxter,[25] which is generally valid for heterogeneous surfaces composed of air and a solid with superhydrophobicity, $\cos\theta_f = f_s\cos\theta_w - f_v$,

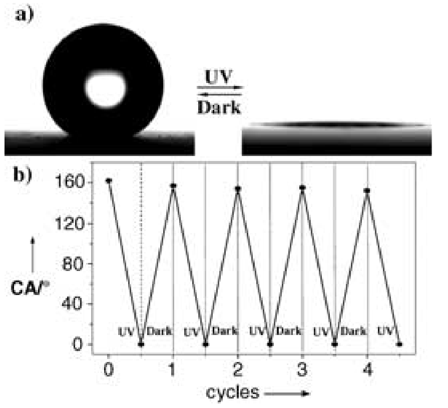

Figure 3. a) Photographs of a spherical water droplet with a CA of (154 ± 1.3)° (left) and a flat water film with a CA of 0° (right) before and after the films were exposed to UV illumination, respectively; b) reversible superhydrophobicity/superhydrophilicity transition of the as-prepared films by alternating UV irradiation and storage in the dark.

where f_s and f_v are the area fractions of the projecting solid and air on the surface, respectively ($f_s + f_v = 1$). The large fraction of air trapped in the films forms a cushion at the film–water interface that prevents the penetration of the water droplet into the grooves. All these results indicate that the preferred orientation of the (001) crystal plane of TiO_2 nanorods and the micro- and nanoscale hierarchical surface structures result in a significant change of the wetting behavior from hydrophilic to superhydrophobic.

When the as-prepared films were exposed to UV light, their surface superhydrophobicity transformed into superhydrophilicity; this remarkable surface wettability transition can be tuned reversibly. Figure 3a shows the change of the water CA when the films are irradiated with UV light (obtained from a 500-W high-pressure Hg lamp with a filter centered at (365 ± 10) nm) for 2 h. The spherical water droplet spreads out on the film with a CA of about 0°. After the UV-irradiated films were placed in the dark for two weeks, their superhydrophobicity was obtained again. This process was repeated for several cycles; a good reversibility of the surface wettability was observed (Figure 3b). TiO_2 is a photosensitive material,[5] and when the film is irradiated with UV light the photogenerated hole reacts with lattice oxygen to form surface oxygen vacancies, to which water molecules kinetically coordinate. This improves the surface hydrophilicity greatly. For the as-prepared multiscale rough surface, the water droplet will fill the grooves along the nanorods and replace the trapped air. This results in a water CA of about 0°. After the hydroxy group adsorption, the surface transforms into an energetically metastable state, and the adsorbed hydroxy groups can gradually be replaced by atmospheric oxygen[6] when the films are placed in the dark. Subsequently, the surface evolves back to its original state, and the surface wettability converts from superhydrophilic to superhydrophobic again.

In conclusion, TiO_2 nanorod films with special micro- and nanoscale hierarchical surface structures have been prepared. A remarkable, controllable surface wettability that shows reversible superhydrophobicity/superhydrophilicity, which is a challenge in surface chemistry, is observed on this inorganic oxide nanorod film. The cooperation of the hierarchical surface microstructures, the orientation of the crystal planes, and the surface photosensitivity are considered to be responsible for this behavior.

Experimental Section

The films were synthesized by hydrothermal treatment of an aqueous titanium trichloride (0.15 M) solution supersaturated with NaCl. The solution was placed in a Teflon-lined autoclave. Thoroughly cleaned glass wafers were used as substrates and immersed in the solution. The mixture was then heated to (160 ± 2) °C for 2 h. The as-deposited films were rinsed with deionized water and ethanol, dried at room temperature, and stored in the dark. The structure and morphology of the product was investigated by FE-SEM (JSM-6700F, Japan), HRTEM (Tecnai F30, Japan), and powder XRD (diffractometer D/max2500 using $Cu_{K\alpha}$ radiation). Water CAs were measured with an OCA20 (DataPhysics, Germany) at ambient temperature.

Received: April 18, 2005

Keywords: hydrophilicity · hydrophobicity · nanostructures · surface chemistry · titanium

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