Reversible Wettability Switch of Large Area TiO_2 Films

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On the large area nanoporous TiO_2 films with an average pore diameter of 80 nm, reversible wettability switch between high hydrophobicity [contact angle (CA) about 137°] and high hydrophilicity (CA $< 10°$) was achieved by UV light irradiation and dark storage in alternation.

Wettability is a very important property depending on the surface free energy of chemical composition as well as the geometrical structure of solid surface.[1,2] Recently, reversible switch between hydrophobicity and hydrophilicity has been attracted extensive interest for the development of smart devices. Some stimuli-responsive organic compounds have been investigated by surface modification.[3–7] Among these external stimulus, light is one of the best candidates because it can be controlled easily, remotely and accurately. Therefore, it is of great importance to develop a photoinduced switch between hydrophobicity and hydrophilicity on a semiconductor surface. Jiang et al. reported the aligned ZnO nanorod films with reversible superhydrophobicity to superhydrophilicity transition which was intelligently controlled by alternation of UV illumination and dark storage.[8,9]

Titanium dioxide (TiO_2) has attracted more attentions for its potential application as a photocatalyst, photovoltaic material, gas sensor, etc.[10,11] Since the discovery of photoinduced water splitting on TiO_2 electrodes in 1972,[12] Fujishima et al. reported that the UV illumination of TiO_2 film produced a superhydrophilic surface with a water contact angle (CA) of zero degree from a hydrophilic surface of CA $= 30°$.[13–15] However, no work about TiO_2 film with reversible photoinduced switch between hydrophobicity and hydrophilicity has been reported till now. In the present study, we demonstrated for the first time a reversible transition on the nanoporous TiO_2 film from high hydrophobicity to high hydrophilicity by the illumination of UV light and dark storage, respectively.

A nanoporous TiO_2 film with large area was prepared according to the modified anodic oxidation procedure.[16] High purity titanium foil (99.9%) with a thickness of 0.5 mm was obtained from Alfa Aesar Inc. The foil was rinsed with acetone and air-dried in preparation for etching before anodic oxidation. The well-cleaned foil was activated in a mixture solution of nitric acid/hydrofluoric acid (w:w = 10%:5%) until bubbles occurred over the surface. Finally, the activated titanium foil was dipped in hydrofluoric acid (0.2%) with a two electrode system constructed with a silicon sheet acting as the counter electrode. The distance between two electrodes was controlled to 5 cm. After 2-h anodic oxidation under a constant voltage of 20 V in 0.2% HF solution, the TiO_2 film exhibited clearly brown surface when illuminated by white light, which indicated the formation of a highly ordered porous structure. Figures 1a and 1b are typical field-emission scanning electron microscopy (FE-SEM) top-images of the TiO_2 film at low and high magnifications, respectively, showing the relatively regular nanostructures on a large scale. The average diameter of the pores is about 80 nm and the distance between pores (pore wall) is about 20 nm. The pore depth of TiO_2 film is about 60 nm observed from the atom force microscopy (AFM, see Supporting Information). Such a size of the pores is suitable for absorbing air into the nanopores of TiO_2 film to construct an air-trapped surface. The result of X-ray photoelectron spectroscopy (XPS) measurement (see Supporting Information) shows that the nanoporous surface is mainly composed of TiO_2 with 1.9% molar ratio of F/(Ti + O). Unfortunately, for the strong diffraction of Ti substance, diffraction peaks of TiO_2 were not observed from XRD, suggesting that TiO_2 may be amorphous.

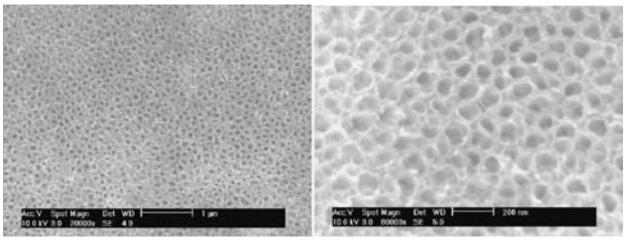

Figure 1. FE-SEM top-images of the nanoporous TiO_2 film at low (a) and high (b) magnifications, respectively.

The wettability of the TiO_2 film was characterized by the measurement of the water CAs on its surface. The water contact angle was measured on the OCA 20 (Dataphysics Co., Germany) by the sessile drop method. The water droplets (about 4 µL) were introduced using a microsyringe and the images were captured by CCD. The CAs measurements were performed at five different points for each sample within an experimental error of ±1°. Before measurement, all sample were treated with 5.0×10^{-5} Pa vacuum for 24 h to move off small molecules which may be absorbed by the surface. When water droplet is placed on the nanoporous TiO_2 film, it makes dry contact. The measured water CA on this TiO_2 film is about 137° (see Figure 2a), which is the highest water CA for TiO_2 films to our best knowledge.[13] Generally speaking, the water drop is inclined to remain a sphereical shape to maintain the smallest surface. In the present case, the water did not fill the inner pores on this roughness surface. To thoroughly understand high hydrophobicity of the TiO_2 surface, theoretical considerations are necessary. The contact angle on the composite surface (θ_r) can be expressed by eq 1.[17]

$$\cos\theta_r = f_1 \cos\theta - f_2 \qquad (1)$$

Here, θ_r and θ are the contact angles on the nanoporous TiO_2 surface and on the flat TiO_2 surface, respectively; f_1 and f_2 are the fractions of the TiO_2 solid surface and air in contact with liquid, respectively (i.e., $f_1 + f_2 = 1$). Given the water CAs of the nanoporous TiO_2 surface ($\theta_r = 137°$) and on the flat TiO_2

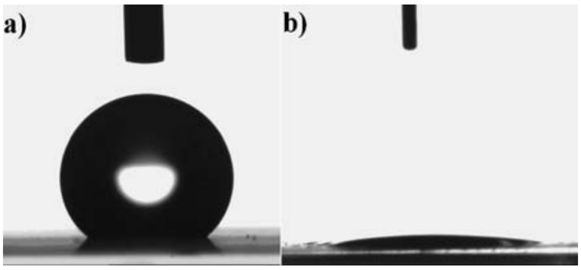

Figure 2. Photographs of water droplets on the anodically oxidized TiO_2 film before (a) and after (b) UV irradiation for 2 h.

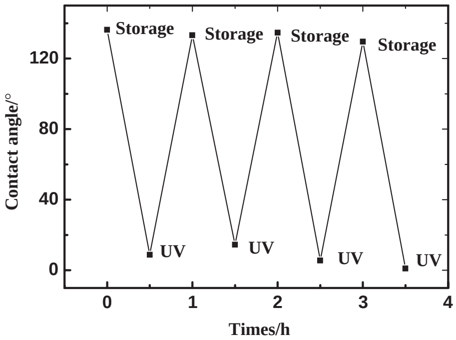

Figure 3. Reversible hydrophobic-to-hydrophilic transtition of the nanoporous TiO_2 film between UV illumination and dark storage.

surface ($\theta = 36°$), f_2 is calculated to be 0.85 according to the eq 1, which indicates that the fraction of air in the surface is high and that the achievement of high hydrophobic TiO_2 film is mainly a result of air trapped in the nanoporous structure.

Importantly, after UV (obtained from a 200 W SHG200 UV lamp with a filter centered at 365 ± 10 nm) illumination for 2 h, the water droplet on the TiO_2 film spreads immediately, resulting in a water CA of about 9° (see Figure 2b). Therefore, the high hydrophilic surface was obtained. This result suggests that the wettability changes from hydrophobicity to hydrophilicity. Sakai et al.[18] reported that the reconstruction of the surface hydroxyl groups under UV irradiation, that is, one OH group doubly coordinated to Ti atoms converts to two OH groups singly coordinated to each Ti atom, caused the photoinduced hydrophilic conversion. The hydrophobicity of TiO_2 film was obtained again after the UV-illuminated film was stored in the dark for about one week. The alternation between hydrophobicity and hydrophilicity is reversible for many times, exhibiting a good reversibility of the surface wettability (shown in Figure 3). Generally, oxygen atoms gradually replaced the hydroxyl when the UV-illuminated film was stored in the dark, because the hydroxyl was energetically unstable and the oxygen adsorption is thermodynamically favored. As a result, the surface was back to its original state and became highly hydrophobic.

In conclusion, we fabricated the nanoporous TiO_2 film by a simple and highly reproducible method and made it transition between high hydrophobicity and high hydrophilicity controlled by UV light and dark storge alternatively.

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References

1 R. N. Wenzel, *Ind. Eng. Chem.*, **28**, 988 (1936).
2 A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, **40**, 546 (1944).
3 K. Ichimura, S. K. Oh, and M. Nakagawa, *Science*, **288**, 1624 (2000).
4 J. Lahann, S. Mitragotri, T. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai, and R. Langer, *Science*, **299**, 371 (2003).
5 L. Liang, X. Feng, J. Liu, P. C. Rieke, and G. E. Fryxell, *Macromolecules*, **31**, 7845 (1998).
6 S. H. Anastasiadis, H. Retsos, S. Pispas, N. Hadjichristidis, and S. Neophytides, *Macromolecules*, **36**, 1994 (2003).
7 X. Yu, Z. Q. Wang, Y. G. Jiang, F. Shi, and X. Zhang, *Adv. Mater.*, **17**, 1289 (2005).
8 X. J. Feng, L. Feng, M. H. Jin, J. Zhai, L. Jiang, and D. B. Zhu, *J. Am. Chem. Soc.*, **126**, 62 (2004).
9 H. Liu, L. Feng, J. Zhai, L. Jiang, and D. B. Zhu, *Langmuir*, **20**, 5659 (2004).
10 A. Heller, *Acc. Chem. Res.*, **28**, 503 (1995).
11 M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
12 A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
13 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, and T. Watanabe, *Nature*, **388**, 431 (1997).
14 R. Wang, N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, *J. Phys. Chem. B*, **103**, 2188 (1999).
15 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, and T. Watanabe, *Adv. Mater.*, **10**, 135 (1998).
16 J. Choi, R. B. Wehrspohn, J. Lee, and U. Gösele, *Electrochim. Acta*, **49**, 2645 (2004).
17 A. W. Adamson and A. P. Gast, “Physical Chemistry of Surfaces,” 6th ed., Wiley, New York (1997), pp 358–359.
18 a) N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, *J. Phys. Chem. B*, **107**, 1028 (2003). b) R. D. Sun, A. Nakajima, A. Fujishima, T. Watanabe, and K. Hashimoto, *J. Phys. Chem. B*, **105**, 1984 (2001).