

Photo-induced wettability control on TiO₂ Surface

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Controlling the surface wettability of solid substrates is important in many situations. For practical applications, materials with reversible switching between high hydrophobicity (water contact angle > 150°) and high hydrophilicity (water contact angle < 5°) are particularly attractive. Recently, the reversible switching by alternation of UV light and dark storage on ZnO surface has been reported.⁽¹⁾ Comparing to ZnO which suffers from photo-corrosion and unstable under UV light, TiO₂ is a well-known photocatalyst and stable under UV light, so the wettability control on TiO₂ has attracted much attention. Here, we found that the wettability of photoetched TiO₂ surface could be reversibly switched by UV light and dark storage. This effect is believed to be due to the cooperation of the surface microstructure and the existence of bridge-site oxygen resulted by photo-electrochemical etching treatment.

Anatase TiO₂ was pressed into pellets and calcinated at 1100°C for 24 hrs. under ambient condition before reduced by calcinating at 700°C for 4 hrs. under 10% H₂/N₂ hydrogen gas stream. A copper lead wire was attached to the back of the reduced pellet with In, and was encapsulated in an insulating epoxy, working as an electrode. The photoetching was carried out by illuminating the electrodes with Hg lamp in a 0.1M H₂SO₄ aqueous solution at +1.0 V vs. Ag/AgCl reference electrode. A platinum wire was used for counter electrode. The etching quantity was controlled by monitoring the passed charges of the photocurrent by a digital coulomb meter. Fluorolalkylsilane (FAS) coating was applied to the pellet to obtain more hydrophobic surface. The microstructural investigation of photoetched surfaces was carried out by a Field Emission Scanning Electron Microscope (FE-SEM). Photoinduced hydrophilicity was evaluated by measuring water contact angles under UV irradiation.

Figure 1 shows the surface and cross sectional SEM images of the pellets before and after photoetching treatment. Obviously, microstructures were created after photoetching treatment. According to previous reports on photoetching, (100) and (110) faces were selectively exposed⁽²⁾⁽³⁾. Figure 2 shows the changes of water contact angle on the pellet under dark storage, and also under UV irradiation (127μW/cm²). On the non-treated surface, contact angle switched between 80° and 20° by UV irradiation and dark storage while on the treated surface, contact angle switched between 130° and 0°. On the photo-etched surface, both the hydrophobicity and hydrophilicity were enhanced. These results suggest that reversible switching between hydrophobicity and high hydrophilicity is due to the cooperation of the air trapped between the microstructures, favorable for hydrophobicity and bridging oxygens, favorable for hydrophilicity, exposed by photoetching. After FAS coating applied to the pellet, its surface became highly hydrophobic and gradually reverted to highly hydrophilic by UV irradiation as shown in Figure 3. We believed that high hydrophobicity is due to the surface energy decrease by applying FAS, while high hydrophilicity is due to the degradation of FAS by TiO₂ oxidative degradation power

during UV irradiation.

[References]

- (1) X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang, D. Zhu, J. Am. Chem. Soc., 126, 62 (2004)
- (2) A. Tsujiko, T. Kisumi, Y. Magari, K. Murakoshi, Y. Nakoto, J. Phys. Chem. B, 104, 4873 (2000)
- (3) T. Sugiura, T. Yoshida, H. Minoura, Electrochemistry, 67, 1234 (1999)

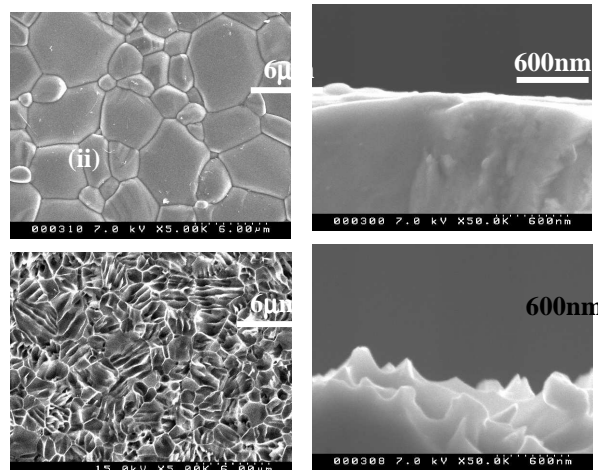


Fig.1 Surface (left) and cross sectional (right) SEM images of pellets (i) before photoetching (ii) after photoetching treatment

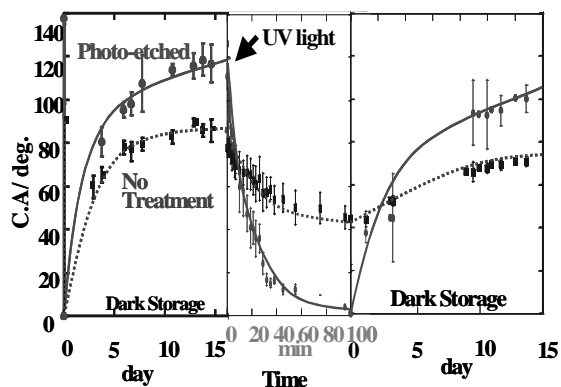


Fig.2 Changes of water contact angle of TiO₂ pellets with and without UV irradiation.

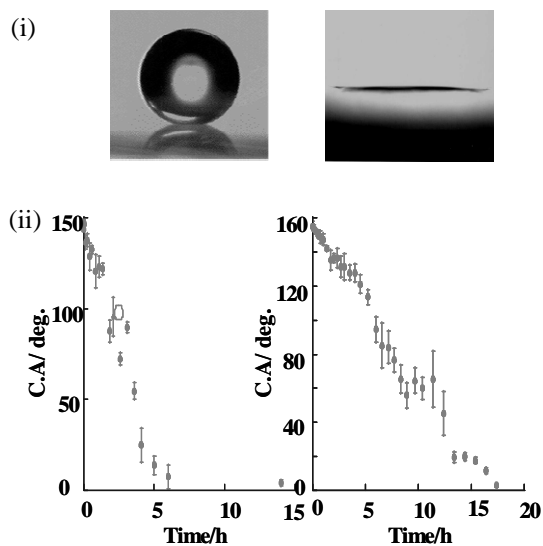


Fig.3 (i) Photographs of water droplet on FAS treated pellet before (left) and after (right) UV illumination. (ii) Changes of water contact angle of fluorolalkylsilane coated pellet under Hg lamp irradiation.