

SUPERHYDROPHILIC AND SUPERHYDROPHOBIC SURFACES WITH PHOTOCATALYTIC ACTIVITY

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We have recently found that UV illumination of TiO₂ materials can produce a highly amphiphilic surface [1]. The production of such a unique surface is attributed to the formation of a microstructured distribution of hydrophilic and oleophilic phases [1]. We have explained the existence of hydrophilic sites in terms of the photoreduction of Ti⁴⁺ sites on the hydrophobic TiO₂ surface to the Ti³⁺ oxidation state [1]. It is necessary to clarify the mechanism for the change of the wettability of TiO₂ surface. In the present work, we have extensively investigated the conversion of the surface wettability. On the basis of results from X-ray photoelectron spectroscopy (XPS) as well as contact angle measurements, the mechanism of the surface reactions has been analyzed.

We used TiO₂(110) single crystals for this study. Experiments have been conducted under different environmental conditions: (1) ambient condition (295 K, RH 80%, in air); (2) O₂ atmosphere (295 K, RH < 10%). When UV illumination of 40 mW/cm² was carried out under ambient conditions, water contact angle of the surface quickly decreased with irradiation time. However, when UV illumination was carried out in O₂ atmosphere water contact angle of the surface dropped at first, followed by a plateau of slow decay and eventually saturated at 35°. This indicates that the existence of O₂ gas greatly blocked the hydrophobic-to-hydrophilic surface wettability conversion.

XPS spectra were acquired for a (110) surface upon UV illumination in air. The spectra were collected with photoelectrons taking off from the surface at 15°, 45°, and 75°, respectively, after the surface was exposed to UV light of 40 mW/cm² for 30 min in air. The Ti 2p spectrum scarcely changes with the electron emission angle, whereas significant differences exist among the spectra of O 1s obtained at the three angles. With decrease of the takeoff angle, a shoulder band appears at 1.5 eV lower than the O 1s band, and is maximized at the angle of 15°. This shoulder band corresponds to dissociative water.

It was concluded that UV light caused the photoreduction of surface Ti⁴⁺ to Ti³⁺ at definite sites, leading to preferential adsorption of dissociative water on top.

The superhydrophobic surfaces will be presented in the talk.

[1] R. Wang, K. Hashimoto, A. Fujishima et al., *Nature*, **388**, 431 (1997).

[2] R. Wang, K. Hashimoto, A. Fujishima et al., *Adv. Mater.*, **10**, 135 (1998).