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Extension of endurance of superhydrophilicity in Cassie-Baxter law by epitaxial growth of SiO_2 overlayers on a rutile TiO_2(110) surface

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Deposition of SiO_2 on TiO_2 has been widely known as one of the most effective methods to enhance the water wettability of TiO_2-related materials. We examined the hydrophilicity of the TiO_2(110) surfaces covered by SiO_2 monolayers [1]. The SiO_2 monolayers epitaxially grew as rectangular patches, and the hydrophilicity of the surface was enhanced with the coverage of the SiO_2 monolayers. The hydrophilicity of the SiO_2 monolayer was attributed to the high density of surface OH groups on the basis of structural and compositional analysis. In this work, we focused on the durability of the hydrophilicity of the SiO_2-covered TiO_2(110) surface in laboratory air.

TiO_2(110) wafers were placed in a quartz case and annealed at 1273 K in an electric furnace to fabricate the SiO_2 monolayer. The coverage of the SiO_2 monolayer was controlled by changing the annealing time. The TiO_2 wafers were analyzed by non-contact atomic force microscopy (NC-AFM), and X-ray photoemission spectroscopy (XPS). Water contact angle (WCA) measurement was conducted to examine the conversion from superhydrophilic to less hydrophilic for samples exposed to air after UV light (400 mW/cm^2) irradiation.

The WCA for a surface annealed for 6 h at 1000 °C without the UV was 16°, covered with SiO_2 patches of 15 % area ratio around step lines of the TiO_2. The WCAs after annealed for 24 and 48 h for 44% and 74% area ratio were 11° and 5°, respectively. The WCA approached to 0° (superhydrophilic) after annealed for 72 or more, almost fully covered with the SiO_2. Figure 1 shows a summary of the changes of WCA of SiO_2/TiO_2 surface with different area ratios of SiO_2 during air exposure for 0, 2, 4, 6, 8, 10, 12 and 24 h after UV light irradiation for 2 min. All samples showed superhydrophilic just after the irradiation. The WCA, however, increased with time possibly owing to contamination covering except the area ratio of 0%. By covering with the SiO_2, the endurance of hydrophilicity can be extended. The change of cosine WCA is always linearly proportional to the decrease in TiO_2 area ratio. This was satisfied with Cassie-Baxter law for a surface consisting of two components with different WCAs, expressed as the following equation:

$$\cos\theta_R = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (1)$$

θ_R, θ_1, θ_2 are contact angles of the composite surface, one component surface, and the other component surface, respectively. f_1 and f_2 are the area ratio of one and the other component on the surface. For our data, θ_2 for the SiO_2 can be regarded as 0°. To our knowledge our result shows the new finding for the validity of Cassie-Baxter law down to nanoscale with two component patches.

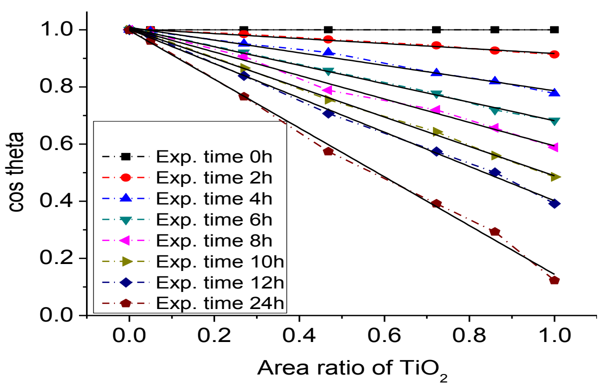

Fig. 1: Change of cos θ_R (WCA) for SiO_2 deposited on rutile TiO_2(110) versus the area ratio of bare TiO_2 region (not covered with the SiO_2 overlayer) to the total surface area at 0, 2, 4, 6, 8, 10, 12 and 24 hours after UV light irradiation in air.

Reference

[1] Tu Tran Uyen Le, et al.: J. Phys. Chem. C **117** (2013) 23621.