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Highly Hydrophilic TiO_2 Surface Induced by Anodic Potentials

Jeromerajan Premkumar†

Research Center for Advanced Science and Technology,
The University of Tokyo, 4-6-1 Komaba,
Meguro-ku, Tokyo 153-8904, Japan

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Semiconductor-based photocatalysts have attracted much attention after the invention of the photoinduced decomposition of water molecules on TiO_2 electrodes.[1] One of the important applications using the photocatalyst is photodegradation of organic molecules and much of the research work has been focused in the direction of water and air purification.[2,3] Most of the research experiments have focused on TiO_2, which showed high sensitivity and chemical stability under UV light irradiation conditions.[4−8] Another interesting application of TiO_2 photocatalysis is to various building materials such as ceramic tile and glass. Those materials coated with TiO_2 film can decompose organic strains and microorganisms on the surfaces, showing self-cleaning and antibacterial function under UV light. In addition, it was found out that the TiO_2 surface becomes highly hydrophilic under UV light irradiation.[6] This wettability change is also originated in the photogenerated holes produced in TiO_2. This highly hydrophilic phenomenon has already been applied in various industrial items such as self-cleaning, exterior tiles, and antifogging mirrors.[9] However, application of this intriguing property has been limited to outdoor use so far since the wettability requires UV illumination approximately as intense as natural sunlight. Hydrophilic transformation of TiO_2 and nitrogen doped TiO_2 films (anatase) are analyzed under lower anodic potentials (in the presence of light)[10,11] as well as cathodic polarization (TiO_2 amorphous).[12] Here, we found that such super-hydrophilic property is obtained even in dark conditions by applying higher anodic oxidation potential. It was found out that the TiO_2 surface reached a super-hydrophilic state, by applying anodic oxidation potentials of higher than 3.2 V under dark conditions in aqueous solution. At the potential of 3.2 V, one electron receives the energy of 3.2 eV, which corresponds to the band-gap energy of TiO_2.

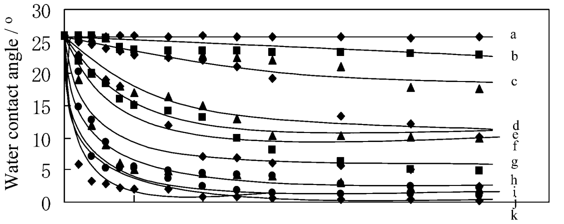

Figure 1. Changes in the electro-induced hydrophilic conversion of the TiO_2 film surface at various applied potentials time under (a) 1.0 V, (b) 2.0 V, (c) 3.0 V, (d) 3.1 V, (e) 3.2 V, (f) 3.3 V, (g) 3.5 V, (h) 3.7 V, (i) 3.9 V, (j) 4.0 V, and (k) 5.0 V in 0.01 M sodium sulfate solution in dark conditions.

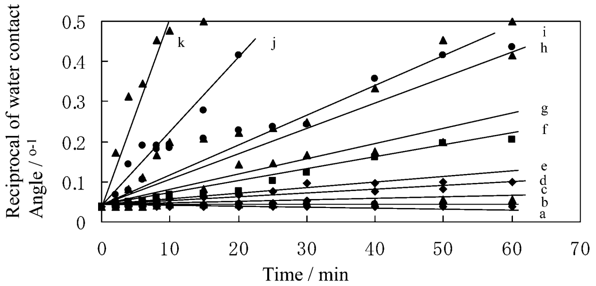

Figure 2. Reciprocal of water contact angle with time; the conditions are the same as in Figure 1.

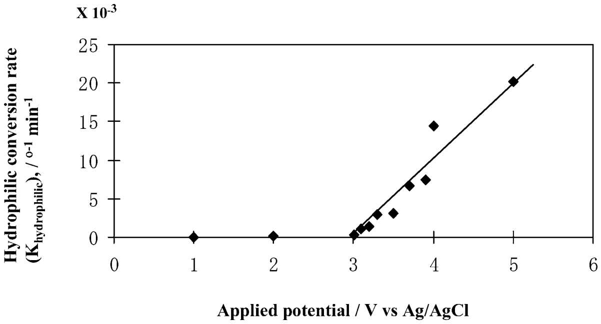

Figure 3. Plot of the hydrophilic conversion rate versus the applied potential of TiO_2 film in 0.01 M sodium sulfate solution under dark conditions.

Conducting SnO_2 plates were used as substrates for the preparation of thin polycrystalline TiO_2 films. The polycrystalline thin films were prepared by a sputtering method. The details were described elsewhere.[13] The thickness (200 nm) and roughness (2.6 nm) were measured by focused laser microscopy and AFM observations, respectively. The obtained TiO_2 films were transparent with whitish color. The optical absorption spectrum of the film had good agreement with the earlier reports. A homemade quartz cell with a single compartment and a three-electrode fitting arrangement was used for electrochemical experiments and it was connected

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† Present address: Department of Chemistry, Faculty of Science, 3 Science Drive 3, National University of Singapore, Singapore 117543.

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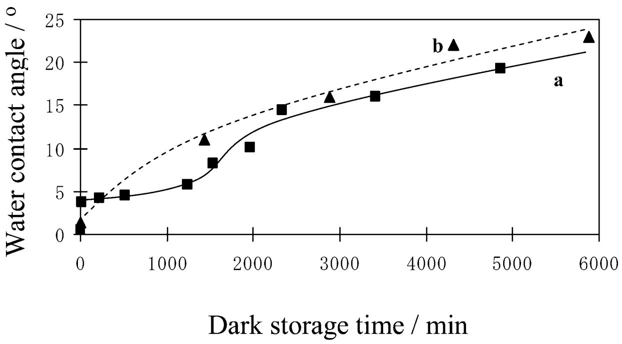

Figure 4. Development of hydrophobic character in TiO_2 film when it is kept in dark conditions. Initially, the film is converted into a super-hydrophilic state by (a) applying 5.0 V for 60 min in dark conditions and (b) irradiation with UV light for 60 min.

with the potentiostat (Hokuto Denko HSV 100 Automatic Polarization System). The working, reference, and counter electrodes were TiO_2 thin film, Ag/AgCl, and platinum wire, respectively. Sodium sulfate (0.01 mol dm^{-3}) was used as the supporting electrolyte. The sample's hydrophilicity was determined by the water contact angle on the surface using a commercial water contact angle meter (Kyowa Interface Science, CA-X). While the water contact angle was being measured, each time at least five time measurements were carried out and the average value was used. After the TiO_2 thin film was prepared, it was kept for a long period of time (about 3 months time) in the dark conditions at room temperature (25 °C). Then the water contact angles were measured and it was discovered that the values of the water contact angle were more than $60 \pm 1°$. Before the experiments were done, the TiO_2 film was dipped into the aqueous solution and the water contact angle was measured. The water contact angle changed to $26 \pm 1°$. This value did not change even after the film was kept for a long time in the aqueous solution, and thus we used this value as the initial contact angle.

Figure 1 shows the development of hydrophilicity on the TiO_2 film surface with application of various anodic oxidation potentials in aqueous media. When high anodic potentials (more than 3.2 V) were applied, the water contact angle became less than 5°. In contrast, when the applied potential was less than 3.2 V, almost no super-hydrophilic conversion was observed. The reciprocal of the water contact angle plotted against the applied potential time gives the straight line as shown in Figure 2 and that the slope of the straight lines can be defined as the apparent rate constant for the hydrophilic conversion ($K_{\mathrm{hydrophilic}}$).[14] In Figure 3 are plotted the apparent rate constants defined in this way versus the TiO_2 electrode potential. It should be noted that the conversion rates at potentials more positive than +3.2 V sharply increased.

The rate for the reverse process, that is, the high hydrophilic state to the less hydrophilic state in the dark, was also investigated. The change of the contact angle in the dark after undergoing super-hydrophilic conversion by applying 5.0 V is shown in Figure 4a. The high hydrophilic surface produced by an applied potential gradually converted to a less hydrophilic state in several hours. In comparison, we have done the experiments of TiO_2 film using UV light irradiation (2 mW/cm^2) alone (Figure 4b), which were comparable with those obtained by high anodic oxidation potentials ($>$3.2 V).

The X-ray photoemission spectrum (XPS) shows (given as electronic Supporting Information) the increase in the surface hydroxyl group (shoulder peak between 532 and 534 eV in O 1s spectra) and the decrease in the surface carbon content on the surface of the potential-induced super-hydrophilic TiO_2. As was reported previously, the increase in the surface hydroxyl group is responsible for the conventional UV light-induced hydrophilicity on TiO_2,[6–8] and thus it is expected that a similar phenomenon occurred under the high anodic potential in aqueous electrolyte media. It is also reported that the holes play a major role in the formation of the surface hydroxyl group of TiO_2.[14] Based on these observations, the present hydrophilic conversion process can be explained as follows. When the TiO_2 electrode was applied by positive potential of more than 3.2 V in which one electron receives the energy of more than 3.2 eV, exceeding the band gap energy of TiO_2, it is considered that electrons were moved from a valance bond to a conduction band by the tunneling effect and that holes (h^+) were generated at the surface as shown in Figure 5. The holes

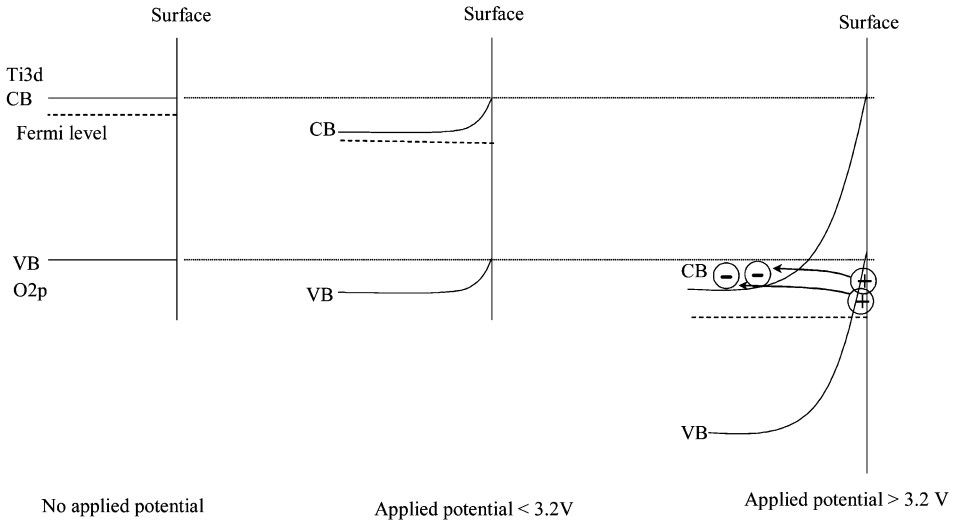

Figure 5. Schematic explanation of the development of super-hydrophilicity by applying anodic oxidation potentials.

formed the surface hydroxyl group of TiO_2, and it led to the super-hydrophilicity.

In summary, the super-hydrophilicity on the TiO_2 surface even without using UV light was achieved by applying high anodic oxidation potentials. The results of hydrophilic and hydrophobic conversions obtained by applied anodic oxidation potentials were comparable with those obtained by UV light irradiation. This kind of electro-induced hydrophilic technique may have potential applications in the future in dark conditions or indoor arrangements. Arising from cleaning (super-hydrophilic) effects, they may be used in lenses of medical devices for invasive procedures.

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Supporting Information Available: X-ray photoemission spectrum (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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