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Communications

Photoinduced Surface Reactions on TiO_2 and $SrTiO_3$ Films: Photocatalytic Oxidation and Photoinduced Hydrophilicity

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From the discovery of photoinduced water splitting on titanium dioxide (TiO_2) electrodes in 1972,[1] TiO_2 has attracted many researchers due to its potential usage in industry.[2,3] The strong oxidation power of the photogenerated holes, the chemical inertness, and nontoxicity of TiO_2 have made it a superior photocatalyst and thus it has been extensively studied first in powder form and then in film form.[4−9] In recent years, environmental cleanup has become one of the most active topics in photocatalysis.[10−12] Conversely, we have found that the UV illumination of TiO_2 produces a highly hydrophilic surface, exhibiting a water contact angle of zero degree.[13,14] On the basis of investigations with friction force microscopy (FFM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS), we have suggested that these hydrophilic surfaces are caused by a surface structural change on TiO_2, the production of surface oxygen vacancies, leading to preferential adsorption of water.[14−16] Here we compare photoinduced processes proceeding on TiO_2 and strontium titanate ($SrTiO_3$) films. Like TiO_2, $SrTiO_3$ is known as an efficient photocatalyst for the production of gaseous hydrogen from water and for the decomposition of various organic compounds.[17−20] Moreover the electronic structure of $SrTiO_3$ resembles that of TiO_2, i.e., the valence and conduction bands of these metal oxides consist mainly of O-2p-like orbitals and Ti-3d-like orbitals, respectively, with band gaps of about 3 eV.[21−23] It is also reported that the $SrTiO_3$ surface is composed of Ti−O, and no Sr^{2+} ions are exposed.[24,25] However, it should be noted that the crystal structure of $SrTiO_3$ is neither rutile nor anatase, but is perovskite which contains only corner-sharing TiO_6 octahedra, not edge-shared octahedra.

Both TiO_2 and $SrTiO_3$ polycrystalline films were prepared on SiO_2-coated glass plates, by a spin-coating method and using commercial alkoxide solutions [NDH-510C (Nihon Soda, Ltd.) for TiO_2 and DSRT150 (GELEST, Inc.) for $SrTiO_3$, respectively], followed by a calcination at 500 °C for 30 min in air. Such coating steps were repeated twice, yielding thin films of $\sim$350 nm. XRD showed sharp diffraction patterns of anatase and perovskite for TiO_2 and $SrTiO_3$, respectively. The UV−vis spectra showed that the main absorption edges for both TiO_2 and $SrTiO_3$ are situated at $\sim$380 nm, corresponding to a band gap of 3.2 eV.

The activities of photocatalytic oxidation of these films were determined by the decomposition rate of methylene blue adsorbed on the film surface. The amounts of the dye adsorbed on the surface were evaluated by measuring the average absorbance of the film in the range

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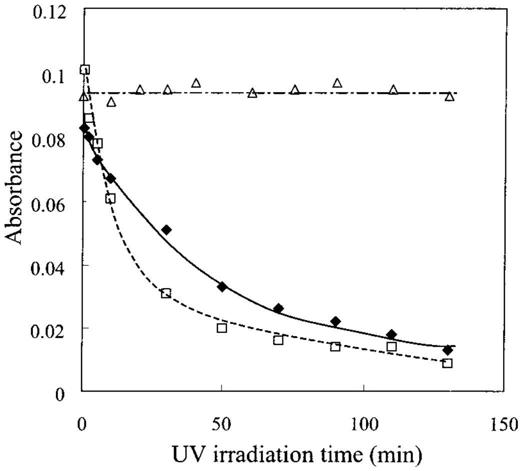

Figure 1. Time dependence of absorbance under UV irradiation of methylene blue adsorbed on TiO_2 (—◆—), on $SrTiO_3$ (--□--), and on an uncoated glass substrate (-•-△-•-). UV irradiation was 1 mW/cm^2 under ambient conditions (i.e., 295 K, relative humidity (RH), 60%, air).

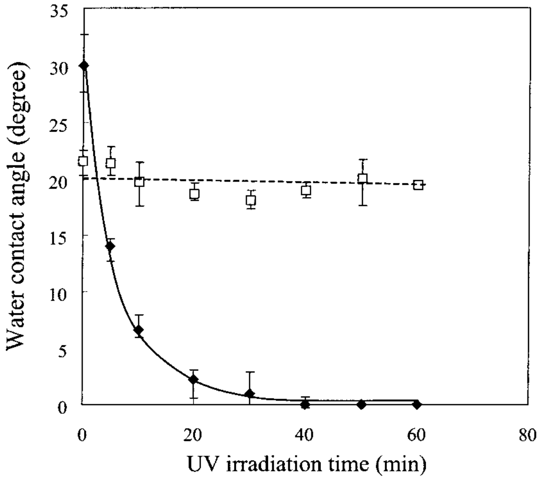

Figure 2. Time dependence of water contact angle under UV irradiation of TiO_2 (—◆—), and $SrTiO_3$ (--□--). UV irradiation was 1 mW/cm^2 under ambient conditions (i.e., 295 K, RH 60%, air).

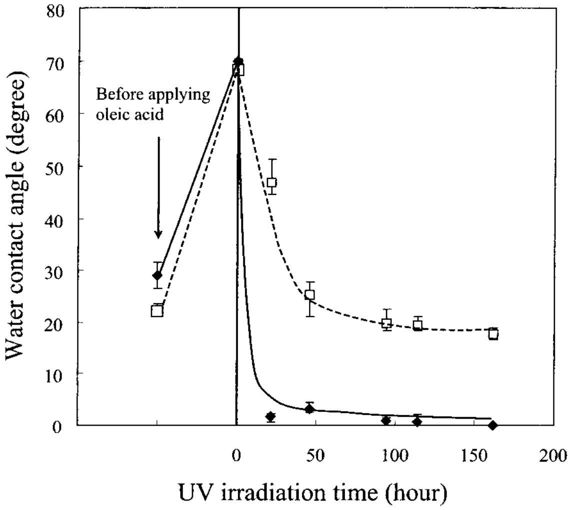

Figure 3. Time dependence of water contact angle under UV irradiation after applying oleic acid to the surfaces of TiO_2 (—◆—), and $SrTiO_3$ (--□--). UV irradiation was 1 mW/cm^2 under ambient conditions (i.e., 295 K, RH 60%, air).

between 550 and 600 nm. Figure 1 shows the absorbance changes due to the photocatalytic oxidation of methylene blue on these films. Although methylene blue on the glass substrate was stable under the UV irradiation, it was decomposed on both the TiO_2 and $SrTiO_3$ substrates. The decomposition rate on $SrTiO_3$ is slightly higher than that on TiO_2.

The irradiation of semiconductor photocatalysts with photons having energies greater than the band gap gives rise to excited-state electrons in the conduction band and holes in the valence band. It is known that photogenerated electrons and holes in both TiO_2 and $SrTiO_3$ react with oxygen and water, producing various radicals such as $HO_2^\bullet$ and $OH^\bullet$, respectively, which decompose organic compounds adsorbed on the surface eventually to CO_2 and H_2O.[26,27] It has been also reported that the photocatalytic quantum efficiency on $SrTiO_3$ is as high as that of TiO_2.[17−19] Therefore, it is reasonable that they have similar photocatalytic oxidation activities for the decomposion of methylene blue.

The photoinduced hydrophilicities of these films were evaluated by measuring the change of the water contact angle on the surfaces. Figure 2 shows the change of the water contact angle on these films under UV irradiation. Whereas the TiO_2 film surface became very hydrophilic with a contact angle of nearly zero degrees after 60 min irradiation, the $SrTiO_3$ surface did not change its wettability, exhibiting the constant contact angle of ∼20°. The further irradiation of $SrTiO_3$ for 48 h did not change the contact angle. Thus, it is clear that $SrTiO_3$ does not become hydrophilic under UV irradiation, even though it has a similar photocatalytic oxidation power to TiO_2. These results indicate that the high photoinduced hydrophilicity of TiO_2 is not based on the photocatalytic oxidation of organic compounds adsorbed on the surface but on structural changes on the surface.

To discuss the photoinduced hydrophilic effect more definitively, the following experiment was carried out. Figure 3 shows the change of water contact angle under UV irradiation after applying oleic acid to the film surface. Just after applying oleic acid, both TiO_2 and $SrTiO_3$ surfaces were converted to a hydrophobic state (with contact angles of ∼70°) due to the hydrophobic property of oleic acid adsorbed on the surfaces. When UV light was irradiated on the $SrTiO_3$ surface, the water contact angle decreased to ∼20°, which was the same value as the water contact angle before applying oleic acid. As a result of the conventional photocatalytic oxidation processes, surface adsorbed oleic acid is decomposed and removed, reproducing the initial clean surface. For the TiO_2 surface, however, the water contact angle decreased to 0°, which is lower than the initial value (∼30°), showing that the highly hydrophilic surface of TiO_2 is not simply attributed to the effect of the photocatalytic oxidation power.

On the basis of our previous studies, the photoinduced hydrophilicity peculiar to TiO_2 is attributed to some structural changes at the surface,[13−16] which is different from the photocatalytic oxidation process. Photogenerated electron−hole pairs can lead to the reduction and oxidation of TiO_2 surface itself, resulting in the conver-

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sion of Ti^{4+} sites to Ti^{3+} sites, and oxygen vacancies are created at the surface as follows:

$$TiO_2 \xrightarrow{h\nu} e^- + h^+$$

$$O(O)^{2-} + 2h^+ \rightarrow V(O) + {}^1/_2O_2$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+}$$

This is essentially the same surface redox process as those induced by Ar^+ ion sputtering,[28,31] electron beam exposure,[31,32] and high-energy UV light.[33] The produced oxygen vacancies are presumably favorable for water adsorption.[28−30] Usually water molecules are dissociatively adsorbed on defect sites to form singly coordinated or doubly coordinated surface hydroxyls,[37,38] and as a result, a highly hydrophilic surface is formed.

On $SrTiO_3$ surfaces, the topmost atomic layer is mostly composed of Ti−O, and no Sr^{2+} ions are exposed after annealing in air[24] or etching in HF solution.[25] It is reported that oxygen vacancies on $SrTiO_3$ surfaces can be created by Ar^+ ion sputtering[34−36] when the material is heated under ultrahigh vacuum.[36] However, our recent results on X-ray photoelectron spectroscopy for Ti^{2p} after Ar^+ bombardment suggest that defect sites on TiO_2 are created much more easily than $SrTiO_3$. Therefore, the present results indicate that the UV irradiation at intensities up to 1 mW/cm^2 does not create oxygen vacancies at the $SrTiO_3$ surface, due to its crystal stability versus UV irradiation.

In the present study, we have evaluated photocatalytic activities and photoinduced wettabilities for TiO_2 and $SrTiO_3$ films. Although both types of films had almost the same photocatalytic oxidation activity, photoinduced wettabilities of these films showed different phenomena. The photoinduced hydrophilicity peculiar to TiO_2 is not caused by the photocatalytic oxidation of organic compounds adsorbed on the surface. The highly hydrophilic surface of TiO_2 is ascribed to photogenerated Ti^{3+} defect sites that are favorable for dissociative water absorption. The yield of this photoinduced hydrophilic reaction is not clear at the present time. It is noted that this reaction involves a surface structural change, which should not require a high quantum efficiency as compared to conventional photocatalytic oxidation. This mechanism is now being examined in more detail.

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