Photoinduced Hydrophilic Conversion of TiO₂/WO₃ Layered Thin Films

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The photoinduced hydrophilicity of TiO₂ films with underlying WO₃ layers (TiO₂/WO₃ layered thin film) was evaluated. Although the top surface was fully covered by TiO₂, the presence of the WO₃ layer enhanced the hydrophilic conversion rate under a 10-W cylindrical fluorescent light bulb. When the TiO₂ and WO₃ layers were separated by an insulating layer, the surface did not become highly hydrophilic under the same light bulb. On a TiO₂/WO₃ layered film the photocatalytic oxidation of methylene blue adsorbed onto the surface and the photocatalytic reduction of silver nitrate in an aqueous solution were investigated under a 10-W cylindrical black light bulb. The oxidation reaction was enhanced by the presence of the WO₃ layer, however the reduction reaction was not. These results indicate that the photogenerated charge carriers can transfer between the TiO₂ and WO₃ layers, i.e., photogenerated holes accumulate in the TiO₂ layer, whereas electrons accumulate in the WO₃ layer. Because of the efficient charge separation, a TiO₂/WO₃ layered film formed on a grounded electroconductive substrate displayed a higher hydrophilicizing rate than when coated onto an insulating substrate. It was also demonstrated that visible light passing through the TiO₂ layer could excite WO₃. Thus, visible light can be used for the hydrophilic reaction in the present TiO₂/WO₃ system.

Introduction

When TiO₂ is illuminated with UV light, electron and hole pairs are generated, and they reduce and oxidize adsorbates on the surface, respectively. These reactions are known as photocatalysis,[1–6] and much research has been conducted on these reactions from a viewpoint of applications for water and air purification,[7–12] antibacterial agents,[13,14] and self-cleaning surfaces of various substrates coated with TiO₂.[15]

Besides these conventional TiO₂ photocatalytic reactions, another intriguing phenomenon we have previously reported is that the surface of TiO₂ becomes highly hydrophilic with a water contact angle (θ) of 0 degrees under UV illumination.[16] The mechanism of this photoinduced hydrophilicity of TiO₂ has been thoroughly investigated.[17–23] This phenomenon is explained as a structural change in the TiO₂ surface that arises from a process different from conventional photocatalytic oxidation reactions.[24] On the basis of our recent studies, the photoinduced hydrophilicity of TiO₂ is initiated by holes which react with surface lattice oxygen atoms,

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followed by the dissociative adsorption of a water molecule at those defective sites.[25]

The photoinduced hydrophilicity of a TiO_2 surface is quite interesting from both a scientific and an industrial standpoint. This phenomenon is already applied in various industrial items such as self-cleaning exterior tiles and anti-fogging mirrors.[26] However, current applications are limited to outdoor use because a large UV source like the sun is required for the wettability conversion.

A lot of research has focused on improving the activity of TiO_2 photocatalysts. It has been reported that the efficiency of a photocatalytic reaction is improved in heterogeneous semiconductor systems because the recombination of photogenerated charge carriers is suppressed due to vectorial transfers of the photogenerated charges between the different types of semiconductor particles.[27] Various heterogeneous semiconductor systems, such as CdS/TiO_2,[27,28] TiO_2/SnO_2,[29-33] WO_3/WS_2,[34] TiO_2/ZnO,[35] TiO_2/WO_3,[28,36-42] have been investigated. These studies have been concerned mainly with the photocatalytic oxidation of organic compounds or photocatalytic water splitting. Recently, we have focused on the heterogeneous TiO_2/WO_3 system due to the highly sensitive photoinduced hydrophilic reactions. The band gap of TiO_2 is 3.2 eV, which is too large to be excited by visible light. In contrast, the band gap of WO_3 is 2.8 eV and both the upper edge of the valence band and the lower edge of the conduction band of WO_3 are lower than those of TiO_2. Thus, WO_3 can be excited by illumination with visible light and the photogenerated holes can be transferred from WO_3 to TiO_2. Consequently, we have reported a TiO_2/WO_3 film, composed of tungsten trioxide (WO_3) particles deposited onto a TiO_2 layer that becomes highly hydrophilic with exposure to regular indoor lights such as fluorescent light bulbs.[43]

This paper investigates the photoinduced hydrophilic conversion of a TiO_2 film prepared on a WO_3 film coated onto a glass substrate. The charge-transfer process between these two semiconductors and the effect of visible light excitation on the WO_3 layer on the hydrophilic conversion of the TiO_2 surface will be discussed.

Experimental Section

Preparation of Thin Films. Pyrex glass plates (7059, Corning) and indium−tin oxide (ITO) coated glass plates (P070E-R-PX, Nippon Glass Sheet Glass Co., Tokyo, Japan) were used as substrates for preparing the thin films. The conductivity of ITO was $5.0 \times 10^3 \ S \cdot cm^{-1}$. Prior to coating the films, these substrates were ultrasonically degreased in ethanol for 30 min and were then thoroughly rinsed with distilled water. Tungsten trioxide thin films were constructed on the substrates by a spin coating method, using aqueous ammonia solutions of tungsten acid (H_2WO_4, Wako Pure Chemical, Co., Tokyo, Japan). Tungsten acid was dissolved in aqueous ammonia with a concentration of 5.0 wt %, and substrates were spun at 1500 rpm for 10 s. These samples were then calcined in a furnace at 500 °C for 30 min. Afterward, they were dipped into a titanium tetraisopropoxide solution (NDH-510C, Nihon Soda Co., Tokyo, Japan), and were slowly removed from the solution at a fixed rate of 15 cm/min under dry nitrogen. These samples were calcined at 500 °C for 30 min.

WO_3/TiO_2 layered thin films where a WO_3 film formed on a TiO_2 film that was coated onto a glass substrate were prepared. Additionally, $TiO_2/SiO_2/WO_3$ films, in which a silica layer was inserted between the TiO_2 and WO_3 layers, were prepared by coating silica onto WO_3 films before adding the TiO_2 coating. The silica was coated by the dip-coating method using a commercial alkoxide solution (NDH-500A, Nihon Soda Co., Tokyo, Japan) and calcined at 500 °C for 30 min. In the case of ITO coated glass substrates, a copper wire was attached to the ITO with silver paste.

Lattice parameters were evaluated with powdered samples that were prepared from the dried aqueous ammonia solutions of tungsten acid and from the hydrolyzed titanium tetraisopropoxide solution. These powders were crushed and calcined at 500 °C for 30 min in air before and after mixing.

Characterization. Surface morphologies and cross sections of the thin films were observed using a scanning electron microscope (SEM model S-4200, Hitachi Co., Tokyo, Japan). The surface was scanned with an Auger electron probe and the cross section was scanned with probing reflected electrons. The crystal phases of the thin films were evaluated by the grazing angle method of X-ray diffraction with Cu Kα rays (XRD model RINT-2100, Rigaku Co., Tokyo, Japan). The incident angle was fixed at 0.5° and 2 θ was scanned in the range of 10−60°. To determine the lattice parameters, the diffraction patterns of the powdered samples, which were prepared from the same starting materials as the TiO_2/WO_3 thin films, were evaluated by a step scan method with a silicon powder as an internal standard. Lattice parameters were calculated using a program that was installed in the software of the Rigaku diffractometer.

The ultraviolet−visible absorption spectra of the thin films were recorded on a spectrophotometer (UV-3100, Shimadzu Co., Kyoto, Japan). The absorption coefficient (α%) was obtained by measuring the transmittance (*T*%) and reflectance (*R*%) of the thin films, where $\alpha = 100 - (T + R)$.

Evaluation. The contact angle measurements were performed at room temperature (~295 K) using a commercial contact angle meter (CA-X, Kyowa Interface Science, Saitama, Japan), with an experimental error of ±1 degree. A 10-W fluorescent light bulb (Toshiba Co., Tokyo, Japan) was the source of illumination. Both a 10-W black light bulb (Toshiba Co., Tokyo, Japan) and a 150-W xenon lamp (LA-150Xe,

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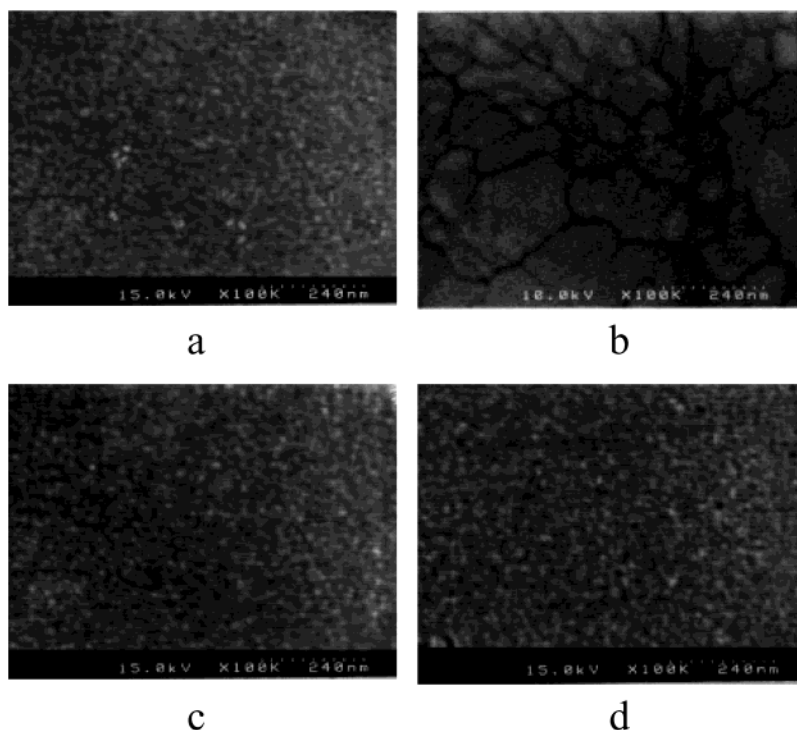
Figure 1. SEM images of the film surfaces: (a) TiO$_2$/Pyrex glass; (b) WO$_3$/TiO$_2$/Pyrex glass; (c) TiO$_2$/WO$_3$/Pyrex glass; and (d) TiO$_2$/SiO$_2$/WO$_3$/Pyrex glass films. Images were scanned by probing for Auger electrons.

Hayashi Watch-Works Co. Ltd., Tokyo, Japan) were used for simultaneously illuminating with UV and visible light. The VIS lamp was used in conjunction with an optical fiber coupler, which employed an UV cutting filter (Y-43, Toshiba Co. Ltd., Tokyo, Japan) and an IR cutting filter (V-40, Toshiba Co. Ltd., Tokyo, Japan). Integrated UV intensity in the range between 310 and 400 nm was measured with a UV radiometer (UVR-2, Topcon Co., Tokyo, Japan).

The photocatalytic oxidation activity of the thin films was evaluated by observing the decomposition of adsorbed methylene blue dye when exposed to air. Films were soaked for 1 h in an aqueous solution of 1.0×10^{-3} mol/L methylene blue at room temperature, and then were stored in the dark for 2 h for the adsorbed dye to dry. The dye that adsorbed on the opposite side of the coated surface was then wiped off. Ultraviolet radiation with an intensity of 1.0 mW/cm^2 produced by a 10-W cylindrical black light bulb (BLB, Toshiba Co., Tokyo, Japan) was used to illuminate the films. The light intensity was measured with an UV radiometer (UVR-2, Topcon Co., Tokyo, Japan). The peak absorbance value of methylene blue spanning from 550 to 600 nm determined the decomposition of the dye on the films. To reconvert the reduced methylene blue of the leuco form (LMB) into its initial state, the thin films were stored in the dark for 2 h before each absorbance measurement.[44] Using this procedure, changes in absorbance can be ascribed to the decomposition of the methylene blue by the oxidation reaction. Absorbances were measured with a UV−Vis spectrometer (UV-1200, Shimadzu, Ltd.).

The photocatalytic reduction of the thin films was evaluated by measuring the amount of Ag deposited on the surface in an aqueous silver nitrate solution under UV illumination. Thin films were immersed in a 6.0×10^{-3} mol/L AgNO$_3$ (Wako Pure Chemical, Co., Tokyo, Japan) aqueous solution (200 mL). N$_2$ was bubbled through the solution for 30 min, then ultraviolet light from a 10-W cylindrical black light bulb (BLB, Toshiba) with an intensity of 1.0 mW/cm^2 illuminated the films. The light intensity was measured with an UV radiometer (UVR-2, Topcon Co., Tokyo, Japan). After the Ag was deposited, the

thin films were thoroughly washed with pure water and dried in clean air. The amount of Ag deposited on the film surface was measured by X-ray photoelectron spectroscopy (XPS, model 5600, Perkin-Elmer), using standard Mg Kα X-rays with a takeoff angle of 45°. The photoelectrons of Ti-2p, Ag-3d, and C-1s orbitals were recorded. The C-1s peak of hydrocarbon contamination at 284.8 eV was used as an internal reference for the absolute binding energies. The integrated peak areas of Ti-2p and Ag-3d were calculated after subtracting the nonlinear background. Quantitative analysis of Ag coverage was based on the peak area multiplied by sensitivity factors supplied by Perkin-Elmer, taking into account the geometric configuration of the apparatus.

Results and Discussion

Figure 1 shows SEM images of the surfaces of thin films. Regardless of the underlying material, the TiO$_2$ surfaces (Figure 1a, c, and d) exhibited nearly identical surface morphologies without cracks or pinholes. The diameters of TiO$_2$ particles were approximately 30 nm. Figure 1b shows the surface of the WO$_3$/TiO$_2$/Pyrex glass system, and the diameter of WO$_3$ particles ranged from 100 to 200 nm. Figure 2 shows SEM images of the cross sections. Each semiconductor portion was laminated with a clear interface, and heterogeneous portions such as the reaction products or mixed phase were not observed. The thicknesses of the TiO$_2$, SiO$_2$, and WO$_3$ layers were 75, 40, and 70 nm, respectively.

Figure 3 shows the XRD patterns of the TiO$_2$/WO$_3$/Pyrex glass and the TiO$_2$/SiO$_2$/WO$_3$/Pyrex glass thin films. The crystal structures of TiO$_2$, SiO$_2$, and WO$_3$ were the anatase, amorphous, and triclinic phases, respectively. The lattice parameters of TiO$_2$ are nearly identical in the TiO$_2$/WO$_3$ and TiO$_2$/SiO$_2$/WO$_3$ films. Chang et al. reported the phase diagram of a TiO$_2$−WO$_3$ system and concluded that a solid solution was not formed between TiO$_2$ and WO$_3$.[45] The TiO$_2$/WO$_3$ and TiO$_2$/SiO$_2$/WO$_3$ systems have nearly identical half widths

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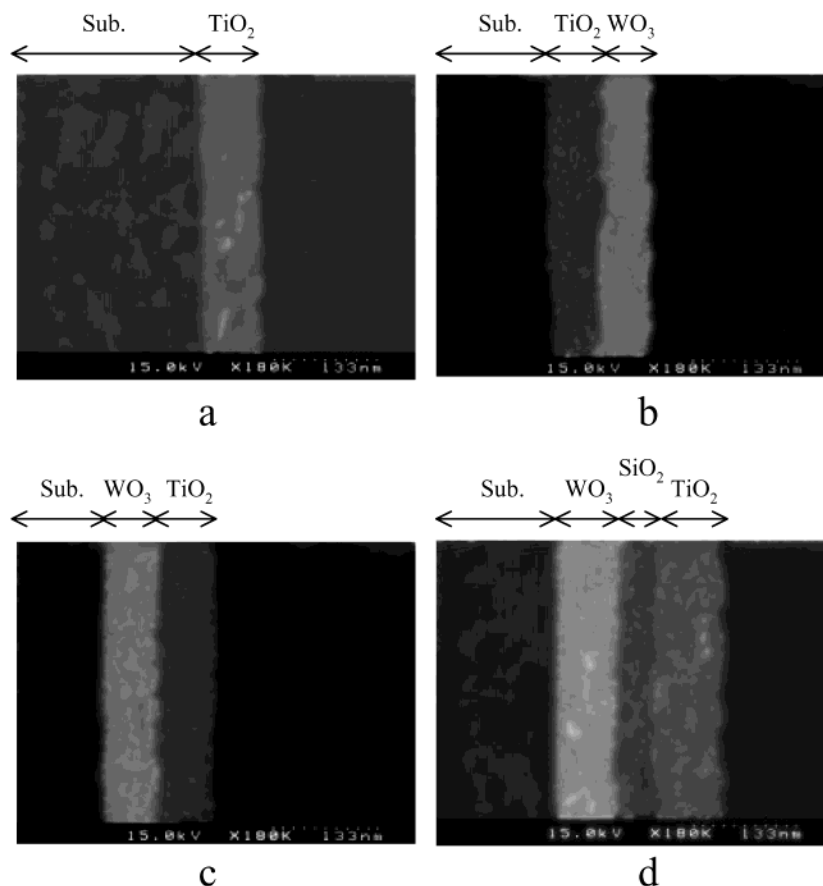
Figure 2. SEM images of the cross-sections of the films: (a) TiO_2/Pyrex glass; (b) WO_3/TiO_2/Pyrex glass; (c) TiO_2/WO_3/Pyrex glass; and (d) TiO_2/SiO_2/WO_3/Pyrex glass films. Images were scanned by probing for reflected electrons.
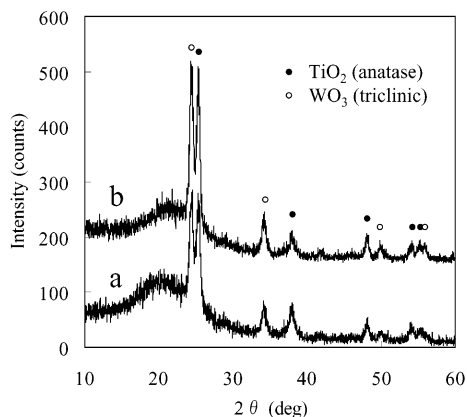

Figure 3. X-ray diffraction patterns by the grazing angle method for the thin films. The angle of incidence was fixed at 0.5°, and 2θ was scanned in the range of 10°−60°. (a) TiO_2/WO_3/Pyrex glass; and (b) TiO_2/SiO_2/WO_3/Pyrex glass films.
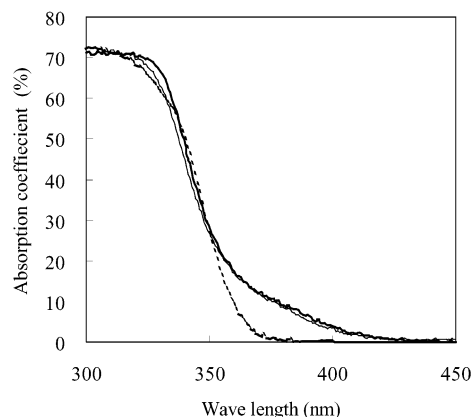

Figure 4. UV−Vis spectra of the thin films. The absorption coefficient (α%) was obtained by the equation $\alpha = 100 - (T + R)$, where T is transmittance (%), and R is reflectance (%) Thick solid line, TiO_2/WO_3/Pyrex glass film; thin solid line, TiO_2/SiO_2/WO_3/Pyrex glass film; dotted line, TiO_2/Pyrex glass film.

of the TiO_2 peaks, which suggests the crystallinity of TiO_2 between these two films was the same.

Figure 4 shows the absorption spectra of the TiO_2/ Pyrex glass, the TiO_2/WO_3/Pyrex glass, and the TiO_2/ SiO_2/WO_3/Pyrex glass films, respectively. The absorption of the thin films containing a WO_3 layer started around 440 nm, whereas that of the TiO_2 began around 380 nm. These absorption edges correspond to the band gaps of WO_3 (2.8 eV) and TiO_2 (3.2 eV), respectively.[46,47]

The photoinduced hydrophilicity of these films was evaluated by illuminating them with a fluorescent light bulb. Figure 5 shows the changes in the water contact angle under a fluorescent light bulb. It is clear that the TiO_2/WO_3 film became highly hydrophilic, whereas the others did not. This indicates that the photoinduced hydrophilic reaction of the TiO_2 surface was enhanced by the presence of WO_3 under the TiO_2 layer. The photoinduced hydrophilic reaction of the TiO_2 surface was inhibited when a layer of SiO_2 separated the TiO_2 and WO_3 layers.

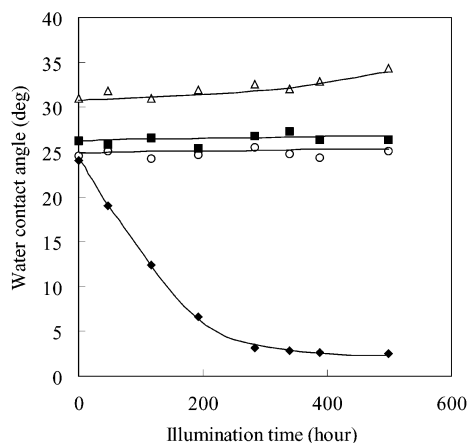(45) Chang, Y. L. L.; Scroger, M. G.; Phillips, B. J. *Less-Common Metals* **1967**, *12*, 53.

Figure 5. Changes in the water contact angle under an UV intensity of 10 μW/cm^2 illuminated by a 10-W fluorescent light bulb: (○) TiO$_2$/Pyrex glass; (△) WO$_3$/TiO$_2$/Pyrex glass; (◆) TiO$_2$/WO$_3$/Pyrex glass; and (■) TiO$_2$/SiO$_2$/WO$_3$/Pyrex glass films.
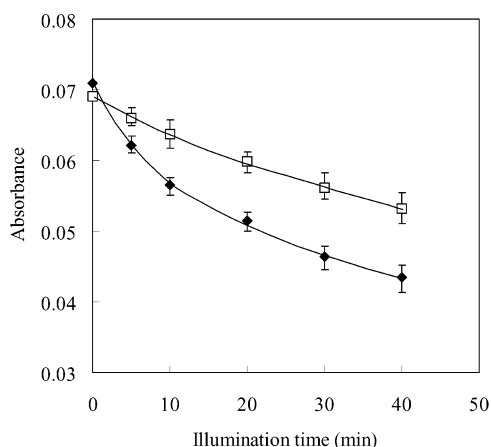
Figure 6. Photocatalytic decomposition of methylene blue adsorbed on the film surface in air: (◆) TiO$_2$/WO$_3$/Pyrex glass film; and (□) TiO$_2$/SiO$_2$/WO$_3$/Pyrex glass film. UV illumination was provided by a 10-W black light bulb with an UV intensity of 1.0 mW/cm^2.

The decomposition rate of methylene blue adsorbed on the film surfaces determined the activity of the photocatalytic oxidation in these films. Figure 6 shows the absorbance changes of methylene blue under UV illumination using a cylindrical black light bulb. The initial absorbances of methylene blue on these films exhibited almost the same value ($\sim$0.07), thus the amounts of methylene blue adsorbed on these films were nearly identical. During the first 20 min of UV illumination the decomposition rate of the dye on the TiO$_2$/WO$_3$ film was greater than that on the TiO$_2$/SiO$_2$/WO$_3$ film, but after 20 min the decomposition rates were nearly identical. The decomposition rate depends on the amount of dye, and as the illumination time is increased, the amount of dye absorbed onto the film becomes smaller. Therefore, the oxidation ability should be determined by comparing the initial decomposition rates upon illuminating.[48] Similar to the photoinduced hydrophilic conversion, the presence of an underlying
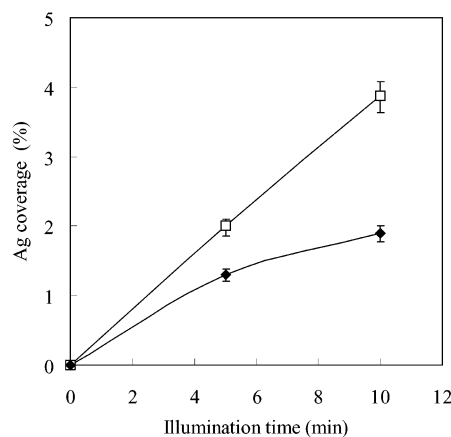
Figure 7. Time dependence of Ag deposition on the film surfaces in an aqueous silver nitrate solution under UV illumination: (◆) TiO$_2$/WO$_3$/Pyrex glass and (□) TiO$_2$/SiO$_2$/WO$_3$/Pyrex glass films. UV illumination was provided by a 10-W black light bulb with an UV intensity of 1.0 mW/cm^2.

WO$_3$ layer enhanced the photocatalytic oxidation reaction on the TiO$_2$ surface.

We also compared the rates of the photocatalytic reduction on these films under UV illumination. Figure 7 shows the changes in Ag coverage on the film surface by the photocatalytic reduction. The Ag deposition rate for the TiO$_2$/WO$_3$ film was lower than that for the TiO$_2$/SiO$_2$/WO$_3$ film. Unlike the photoinduced hydrophilicity and photocatalytic oxidation, the presence of a SiO$_2$ layer between the TiO$_2$ and WO$_3$ layers enhanced the photocatalytic reduction of the TiO$_2$ surface. In other words, the presence of a WO$_3$ layer directly beneath the TiO$_2$ layer retards the photocatalytic reduction on the TiO$_2$ surface.

Extensive studies on the mechanisms of the photocatalytic oxidation and photocatalytic reduction have been conducted. It is known that the photogenerated holes in TiO$_2$ react with water, producing OH· radicals, which oxidize organic compounds adsorbed on the surface to produce CO$_2$ and H$_2$O.[49,50] It is also known that the photogenerated electrons in TiO$_2$ react with Ag$^+$ ions in aqueous solutions, leading to reduced Ag deposits onto the TiO$_2$ surface.[51] On the other hand, the photoinduced hydrophilicity of TiO$_2$ is attributed to structural changes at the surface caused by the photogenerated holes. Photogenerated holes diffuse to the surface of TiO$_2$ and react with surface lattice oxygen atoms, which is followed by the dissociative adsorption of a water molecule at those defective sites.[16-24] During the photoinduced hydrophilicizing process, photogenerated electrons are transferred to adsorbed oxygen molecules and they do not play an important role in the hydrophilic process.[25] Therefore, both the photoinduced hydrophilicity and the photocatalytic oxidation reactions are caused by holes, which are diffused to the surface, whereas the photocatalytic reduction is caused by electrons. Our experimental results indicate that the presence of an underlying WO$_3$ layer enhances surface reactions associated with holes, but does not enhance

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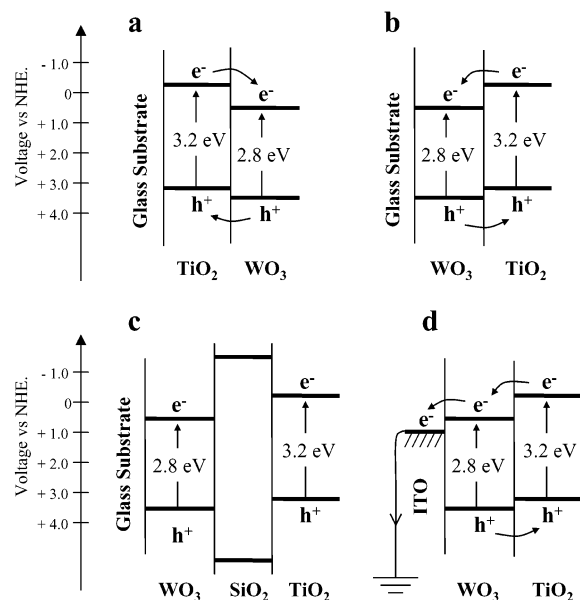(51) Ohtani, B.; Okugawa, Y.; Nishimoto, S.; Kagiya, T. *J. Phys. Chem.* **1987**, *91*, 3550.

Figure 8. Energy diagrams for the thin films: (a) WO$_3$/TiO$_2$/glass; (b) TiO$_2$/WO$_3$/glass; (c) TiO$_2$/SiO$_2$/WO$_3$/glass; and (d) TiO$_2$/WO$_3$/ITO coated glass films.

Figure 9. Changes in the water contact angle under a 10-W fluorescent light bulb with an UV intensity of 10 μW/cm^2: (○) TiO$_2$/WO$_3$/Pyrex glass; (△) TiO$_2$/WO$_3$/ITO coated glass films, where ITO was an open circuit; and (◆) TiO$_2$/WO$_3$/ITO coated glass film, where ITO was grounded.

surface reactions associated with electrons. These results also indicate that the photogenerated charge carriers can transfer between the TiO$_2$ and WO$_3$ layers. Figure 8 shows schematic illustrations of band energies for the following (a) WO$_3$/TiO$_2$/Pyrex glass, (b) TiO$_2$/WO$_3$/Pyrex glass, and (c) TiO$_2$/SiO$_2$/WO$_3$/Pyrex glass systems. Both the valence and conduction bands of WO$_3$ have larger positive potentials than those of TiO$_2$.[52,53] The photogenerated electrons initially created in TiO$_2$ are transferred to WO$_3$, whereas the holes generated in WO$_3$ are transferred to TiO$_2$. Therefore, it is reasonable that the TiO$_2$/WO$_3$ system (Figure 8b) exhibits a high hydrophilicizing rate, but the WO$_3$/TiO$_2$ system (Figure 8a) does not. When the insulating SiO$_2$ layer is between the TiO$_2$ and WO$_3$ layers (Figure 8c), a photogenerated charge carrier cannot transfer from one layer to another.

The photoinduced hydrophilicity of TiO$_2$/WO$_3$ layered films formed on an ITO coated glass plate was evaluated in order to discuss the elimination process of electrons in the WO$_3$ layer within the TiO$_2$/WO$_3$ system. Despite using different substrate materials, variations were not observed in either the crystallinity or morphology of TiO$_2$. Figure 9 shows the changes in the water contact angle under a 10-W fluorescent light bulb. The TiO$_2$/WO$_3$ film formed on an ITO coated glass exhibited a higher hydrophilicizing rate than the film formed on a Pyrex glass substrate. Furthermore, the hydrophilicizing rate was enhanced when the ITO was grounded. These results indicate that when the substrate is an insulator, electrons are transferred to the WO$_3$ layer and are consumed by the reduction of adsorbed oxygen molecules at the edge of the WO$_3$ film.[54] As for the electroconductive ITO substrate, electrons accumulated in the WO$_3$ layer can be injected into the electrocon-
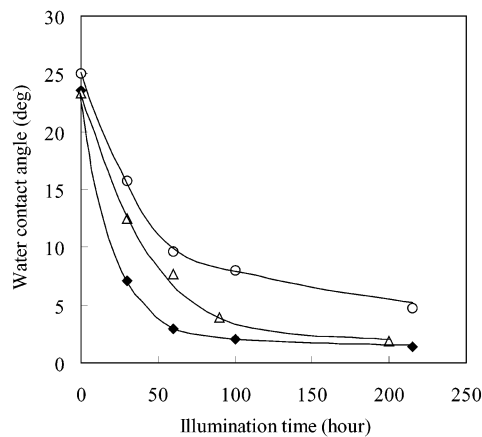
ductive layer of the substrate. These electrons located in the electroconductive layer can be transferred to the edge of the film and trapped by oxygen molecules absorbed there. As shown in Figure 8d, when the electroconductive layer is grounded, electrons injected in the electroconductive layer are effectively eliminated. Consequently, a greater efficiency of charge separation is induced and the hydrophilic reaction of the TiO$_2$ surface is enhanced. In this study, ITO coated glass was used as an electroconductive substrate. Enhancement of the hydrophilic reaction is also expected with other electroconductive materials, which form ohmic contact with WO$_3$.

As shown in the optical absorption spectra (Figure 4), tungsten trioxide can absorb visible light. It is expected that visible light can initiate the hydrophilic conversion of the TiO$_2$ surface. To investigate the effects of exciting the WO$_3$ layer with visible light, the wavelength dependence of the hydrophilic conversion was evaluated using both UV and VIS light sources. The spectra of these light sources are shown in the inset of Figure 10. The wavelength of UV light ranged from 320 to 410 nm, and that of VIS light ranged from 410 to 500 nm. Changes in the water contact angle were evaluated by illuminating with UV radiation and by simultaneously illuminating with UV and VIS light. The results are shown in Figure 10. Similar hydrophilic properties were exhibited by both TiO$_2$ films whether illuminating with UV radiation or with both UV and VIS radiation because TiO$_2$ cannot be excited by VIS illumination. However, the layered TiO$_2$/WO$_3$ film became more hydrophilic under simultaneous UV and VIS radiation than with only UV radiation. These results indicate that the photogenerated holes excited by visible light in the WO$_3$ layer can be transferred to the TiO$_2$ layer, and these holes react with the surface lattice oxygen atoms of TiO$_2$. In other words, visible light can be used to initiate the hydrophilic conversion of the TiO$_2$ surface in a TiO$_2$/WO$_3$ layered film. Consequently, when illuminating with a fluorescent light bulb, which contains both UV and VIS light, the surfaces of the TiO$_2$/WO$_3$ layered films become highly hydrophilic. However, the surface of the TiO$_2$/WO$_3$ films did not become hydrophilic when illuminating with only VIS light. The

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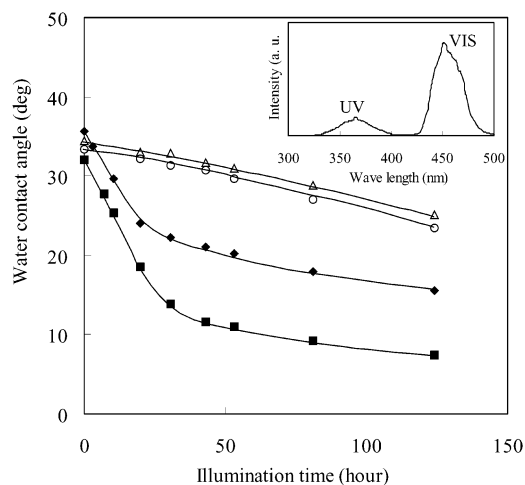
Figure 10. Wavelength dependence on photoinduced hydrophilicity: (○) TiO_2 with UV illumination; (△) TiO_2 with UV and VIS illumination; (◆) TiO_2/WO_3 with UV illumination; and (■) TiO_2/WO_3 with UV and VIS illumination. The inset shows spectra of the UV and VIS light sources. UV and VIS illuminations were provided by a 10-W black light bulb and a 150-W Xenon lamp with an optical fiber coupler, which employed UV and an IR cutting, respectively.

hydrophilic conversion of the heterogeneous TiO_2/WO_3 films requires radiation in the UV region, indicating that the excitation of TiO_2 is indispensable. The reason why excitation of TiO_2 is indispensable to this process remains unclear, but one possible explanation is that the band bending of TiO_2 is well-suited for charge transfer between the TiO_2 and WO_3 layers during the photoexcitation process of TiO_2.

Conclusion

The surface of the TiO_2 films formed above a WO_3 layer became highly hydrophilic when illuminated with a 10-W fluorescent light bulb, which had an UV intensity of 10 $\mu W/cm^2$. The enhancement of the hydrophilic conversion of the TiO_2/WO_3 layered system can be explained by the following two effects. (1) Charge transfer occurs between the TiO_2 and WO_3 layers. The photogenerated holes accumulate at the surface of TiO_2, whereas electrons accumulate within the WO_3 layer. (2) Visible light passing through the TiO_2 layer can excite WO_3, which produces electron−hole pairs. These photogenerated holes in the WO_3 layer can be used to initiate the surface reactions of TiO_2.

The layered TiO_2/WO_3 thin films produce a highly hydrophilic surface even with indoor lights, such as fluorescent light bulbs. These films may be applied as coatings on indoor products requiring antifogging and self-cleaning properties.