

Photocatalysis and Photoinduced Hydrophilicity of Various Metal Oxide Thin Films

Masahiro Miyauchi,[†] Akira Nakajima,[‡] Toshiya Watanabe,^{*,†} and Kazuhito Hashimoto^{*,†}

Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan, and Advanced Systems of Technology Incubation, 2-8-1 Honson, Chigasaki-shi, Kanagawa 253-8577, Japan

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Thin films of various metal oxides were prepared on glass substrates by a wet process to determine their photocatalytic ability to decompose adsorbed dye and to evaluate their photoinduced hydrophilicity under UV illumination. The metal oxides used in this study are classified into four categories based on their behavior over the two photochemical reaction: (1) active in both photocatalytic oxidation and photoinduced hydrophilicity (TiO₂, SnO₂, ZnO); (2) only active in photocatalytic oxidation (SrTiO₃); (3) only active in photoinduced hydrophilicity (WO₃, V₂O₅); (4) and inactive over both processes (CeO₂, CuO, MoO₃, Fe₂O₃, Cr₂O₃, In₂O₃). X-ray photoelectron spectroscopy revealed that oxygen defect sites were produced by Ar⁺ bombardment on the surface of metal oxides, showing photoinduced hydrophilicity. These results indicate that photoinduced hydrophilicity is not induced by the photocatalytic oxidation of organic compounds adsorbed on the surface, but is based on structural changes of the metal oxide surfaces.

Introduction

From the discovery of photoinduced water splitting on titanium dioxide (TiO₂) electrodes in 1972,¹ TiO₂ has been widely studied because of its potential industrial applications.^{2–10} When UV light is illuminated on TiO₂, electron and hole pairs are generated and they reduce and oxidize adsorbates on the surface, respectively, producing radical species such as OH• and O₂^{•−}.^{11,12} These radicals decompose most organic compounds; thus, much research has been conducted on TiO₂ with the intention to study its application to water and air purification.^{13,14} In addition to these studies of conven-

tional TiO₂ photocatalysis, we previously reported another intriguing phenomenon: the surface of TiO₂ becomes highly hydrophilic with a water contact angle (θ) of nearly 0° under UV illumination.¹⁵ This phenomenon has already found application in various industrial items such as self-cleaning exterior tiles and anti-fogging mirrors.¹⁶ The mechanism of photoinduced hydrophilicity in TiO₂ has been intensively investigated.^{17–21} On the basis of our recent studies, this phenomenon is considered to be a result of structural changes of the TiO₂ itself, which proceed in a different fashion than in conventional photocatalytic oxidation reactions.²²

In addition to the TiO₂ photocatalyst, other metal oxides, such as SnO₂,²³ ZnO,²⁴ WO₃,^{25,26} CdS,^{27,28} Fe₂O₃,²⁵

* To whom correspondence should be addressed. E-mail: kazuhito@fchem.chem.t.u-tokyo.ac.jp; watanabe@fchem.chem.t.u-tokyo.ac.jp.

[†] University of Tokyo.

[‡] Advanced Systems of Technology Incubation.

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Table 1. Preparation Methods for Thin Films of Various Metal Oxides.

	starting materials	concentration of solution	coating method
TiO ₂	alkoxide solution (NDH510C, HihonSoda Co. Ltd.)	5.0 wt %	spin
SnO ₂	SnO ₂ sol (S-8, Taki Chemical Co. Ltd.)	5.0 wt %	spin
ZnO	aqueous solution of Zn(CH ₃ COO) ₂	0.66 wt %	spray pyrolysis
WO ₃	aqueous ammonia solutions of H ₂ WO ₄	2.0 wt %	spin
SrTiO ₃	alkoxide solution (DSRIT150, Gelest Co. Ltd.)	5.0 wt %	spin
V ₂ O ₅	aqueous solution of VCl ₃	0.78 wt %	spray pyrolysis
CeO ₂	CeO ₂ sol (A-1, Nissan Chemical Industries Co. Ltd)	5.0 wt %	spin
CuO	aqueous solution of CuCl ₂	2.0 wt %	spin
MoO ₃	molybdenum pentaethoxide dissolved in IPA	2.0 wt %	spin
Fe ₂ O ₃	iron tri-isopropoxide dissolved in IPA	2.0 wt %	spin
Cr ₂ O ₃	aldoxide solution (SYM-CR015, High Purity Chemetals)	0.78 wt %	spin
In ₂ O ₃	indium tri-isopropoxide dissolved in IPA	5.0 wt %	spin

and SrTiO₃²⁹ have been studied to determine their photocatalytic oxidation properties. Few studies, however, have been performed to determine the photoinduced hydrophilic properties of metal oxides other than TiO₂.^{21,30,31} The possibility of controlling the surface wettability of TiO₂ has motivated increasing interest in studying changes in the photoinduced wettability of other photocatalyst materials. In the present study, we have evaluated the photocatalytic ability to decompose organic compounds and the photoinduced hydrophilicity of various metal oxides such as TiO₂, SnO₂, ZnO, WO₃, SrTiO₃, V₂O₅, CeO₂, CuO, MoO₃, Fe₂O₃, Cr₂O₃, and In₂O₃.

Experimental Section

Preparation of Thin Films. Thin films of various metal oxides were prepared on Pyrex glass substrates by a wet process. Prior to thin film coating, substrates were degreased ultrasonically in ethanol for 30 min and then rinsed thoroughly with distilled water. Table 1 lists the preparation method and liquid starting material for each film. Samples coated by the spin-coating method were calcined at 500 °C for 30 min in air. For the spray pyrolysis method, pure nitrogen was used as the carrier gas, and the temperature of substrates was maintained at 500 °C while applying the starting liquid (Table 1). After spraying, these samples were calcined at 500 °C for 30 min in air. The thickness of these films was about 500 nm. Prepared films were stored in the dark under clean air.

Characterization. Crystal phases of the thin films were evaluated by X-ray diffraction with Cu K α rays (XRD: model RINT-2100, Rigaku Co., Tokyo, Japan). Ultraviolet–visible (UV–vis) absorption spectra of the thin films were recorded on a spectrophotometer (UV-3100, Shimadzu Co., Kyoto, Japan). The binding energy of each element was measured by X-ray photoelectron spectroscopy (XPS: model 5600, Perkin-Elmer) following Ar⁺ ion bombardment, using standard Mg K α X-rays. Photoelectrons were collected at a takeoff angle of 45°. Ar⁺ ion bombardments were all performed using the same ultra-high-vacuum chamber, with a 2.0-kV beam voltage of bombardment.

Photocatalytic Decomposition of Methylene Blue. Films were dipped in an aqueous solution of 1.0×10^{-3} mol/L methylene blue at room temperature for 1 h. After dipping, they were stored in the dark for 2 h to dry the adsorbed dye, while dye adsorbed on the opposite side of the coated surface was wiped off. Ultraviolet radiation with an intensity of 2.0 mW/cm² was produced by a 10-W cylindrical black light bulb

Table 2. Crystal Structures and Optical Absorption Edges of Metal Oxide Films.

	crystal phase	optical absorption edge
TiO ₂	anatase	380 nm
SnO ₂	rutile	385 nm
ZnO	wurtzite	396 nm
WO ₃	ReO ₃ structure	460 nm
SrTiO ₃	perovskite	380 nm
V ₂ O ₅	like ReO ₃ structure	568 nm
CeO ₂	fluorite	440 nm
CuO	wurtzite	N. D.
MoO ₃	ReO ₃ structure	443 nm
Fe ₂ O ₃	corundum	620 nm
Cr ₂ O ₃	corundum	N. D.
In ₂ O ₃	scandium oxide structure	482 nm

(BLB: Toshiba Co., Tokyo, Japan) with light intensity measured by an UV radiometer (UVR- 2, Topcon Co., Tokyo, Japan). The decomposition of dye on the films was quantitatively evaluated following UV illumination using the peak absorbance value of methylene blue, which ranged from 550 to 600 nm. Before each absorbance measurement, thin films were stored in the dark for 2 h to reconvert reduced methylene blue of the leuco form (LMB) into its initial state.³² By this procedure, changes in absorbance values can be ascribed to the level of methylene blue decomposition from the oxidation reaction. The absorbance value was measured on a UV–vis spectrometer (UV-1200, Shimadzu, Co., Kyoto, Japan).

Surface Wettability under UV Illumination. Measurements of the water contact angle 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 $\pm 1^\circ$. UV illumination was provided by the same method described above.

Results and Discussion

Crystal phases of the prepared films determined by XRD are summarized in Table 2. All samples exhibited polycrystalline phases with good crystallinity. Figure 1 depicts the energy levels of the valence and conduction bands at a pH of 7 (versus the normal hydrogen electrode (NHE)) along with the band-gap energies of these metal oxides. These data were adapted from the literature.^{33–39} Wavelengths at the optical absorption edges were analyzed by UV–vis spectra, which are

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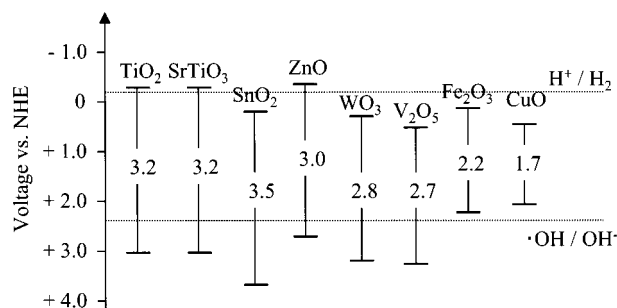


Figure 1. Diagram depicting the redox potentials of valence and conduction bands and band-gap energies for various metal oxides estimated at pH 7. The redox potential positions of H^+/H_2 and OH^-/OH^\bullet at pH 7 are also illustrated.

shown in Table 2. Absorption edges of TiO_2 and $SrTiO_3$ were found at 380 nm, corresponding to a band-gap energy of 3.2 eV.^{40–42} Absorption edges of ZnO and WO_3 were observed at 396 and 460 nm, respectively. These absorption edges correspond to the band gaps of ZnO (3.0 eV)^{43,44} and WO_3 (2.8 eV).^{45,46} Copper oxide and Cr_2O_3 did absorb visible light; however, their adsorption edges were unable to be clearly determined. All metal oxides were found to absorb UV light between 300 and 400 nm produced by a black light bulb.

Photocatalytic oxidative activities of the metal oxides under UV illumination were evaluated by analysis of the decomposition rate of methylene blue adsorbed on the film surfaces in air. Figure 2 shows the changes in the absorbance values of methylene blue. Among the metal oxides, TiO_2 , $SrTiO_3$, and ZnO exhibited strong oxidizing powers, while SnO_2 showed only a small amount of oxidizing activity. The remaining metal oxides, however, did not decompose methylene blue under UV illumination. Tin oxide decomposed dye completely under longer UV illumination of 24 h, while the remaining metal oxides except TiO_2 , $SrTiO_3$, and ZnO did not. It has been reported that methylene blue adsorbed on TiO_2 can be oxidized by holes directly or by OH^\bullet radicals.⁴⁷ The quantum efficiency for photocatalytic water splitting on $SrTiO_3$ anodes is as high as that on TiO_2 anodes;^{48–50} thus, it is expected that they exhibit similar photocatalytic oxidizing activities for the decomposition of methylene blue.³⁰ Although ZnO is known as a photocorrosive material, a number of studies have reported its strong oxidative ability in the decomposition of organic compounds.²⁴ Because valence bands of TiO_2 , $SrTiO_3$, and ZnO lie at deep levels, photogenerated holes have strong enough oxidizing power to create OH^\bullet radicals, which decompose most organic compounds. Positions of the conduction bands for these

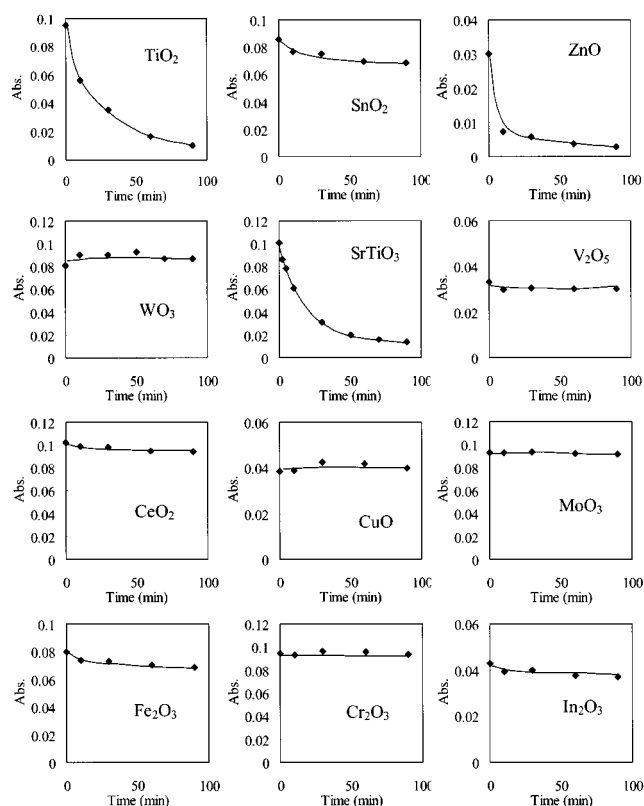


Figure 2. Change of absorbance values of methylene blue adsorbed on surfaces under UV illumination. UV illumination, 2.0 mW/cm², under ambient conditions: 295 K, relative humidity (RH), 60%, air.

metal oxides are high enough to reduce oxygen molecules adsorbed on the surface. As for TiO_2 , $SrTiO_3$, and ZnO , it is expected that photogenerated electrons and holes are effectively separated and that the holes have a strong oxidizing ability. Therefore, it is reasonable that methylene blue adsorbed on these metal oxide films can be completely bleached under UV illumination. In contrast, the valence bands of Fe_2O_3 and CuO are situated at +2.2 and +2.0 V (versus NHE at pH 7),³⁴ which are more negative than the redox potential necessary for the generation of OH^\bullet radicals. These materials cannot create OH^\bullet radicals and thus have a smaller amount of oxidative activities. In contrast, metal oxides such as SnO_2 , WO_3 , and V_2O_5 also showed limited oxidizing ability, even though the valence bands of these metal oxides are deep enough to create OH^\bullet radicals that decompose most organic compounds. This is because their conduction bands are lower than those of TiO_2 , $SrTiO_3$, and ZnO ,^{34,51} and the photogenerated electrons of these metal oxides are not high enough to be trapped by adsorbates such as oxygen molecules on the surface. Therefore, it is suggested that the efficiencies of charge separation in these metal oxides are low, leading to their inability to decompose methylene blue. In this way, the basis for the reduced photocatalytic oxidation activities is roughly explained by the position of valence and conduction bands, while the surface morphology, crystallinity, and optical absorption property also play an important role.

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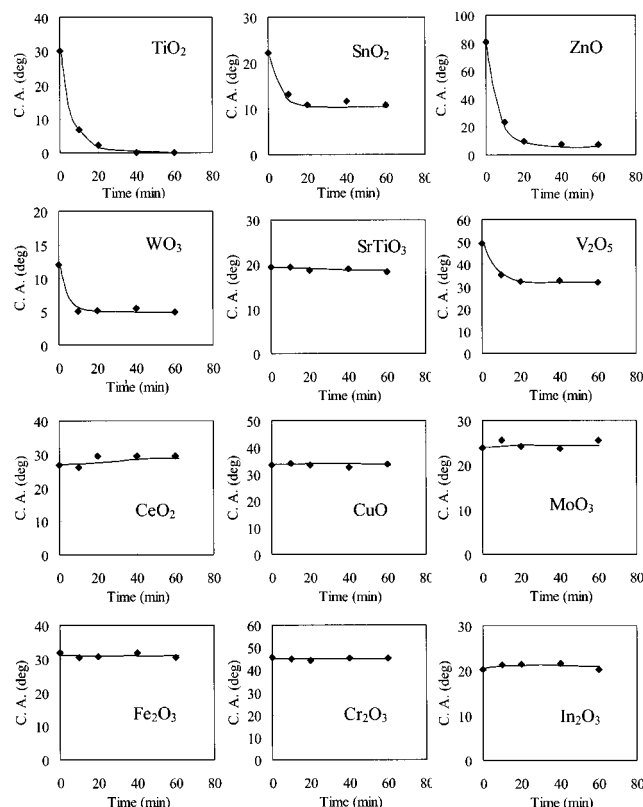


Figure 3. Change of the water contact angle under UV illumination. UV illumination, 2.0 mW/cm², under ambient conditions (295 K, RH 60%, air).

Figure 3 shows changes in the water contact angle of various metal oxides under UV illumination. Among these metal oxides, TiO₂, SnO₂, ZnO, WO₃, and V₂O₅ exhibited hydrophilic conversions on the surface. In particular, the surfaces of WO₃ and V₂O₅ became hydrophilic under UV illumination, even though they did not decompose any methylene blue. Furthermore, the SrTiO₃ film did not become hydrophilic, even though it exhibited strong oxidizing ability in decomposing dye adsorbed on its surface. These results indicate that photoinduced hydrophilicity is not explained simply by the removal of organic adsorbates by a photocatalytic decomposition process.

The mechanism of the photoinduced hydrophilic reaction has been intensively studied for TiO₂ and ZnO photocatalysts.^{15–22,31} On the basis of our previous studies, photoinduced hydrophilicities of these materials are considered to be due to structural changes of the surfaces, which differ completely from conventional photocatalytic oxidation reactions. Recent FT-IR (SEI-RAS), XPS, and TDS studies have revealed that the reconstruction of surface hydroxyl groups of TiO₂ occurs under UV illumination⁵² and the total amount of surface hydroxyl groups increases.⁵³ In addition, we recently reported that the reconstruction of hydroxyl groups of the TiO₂ surface is attributable to photogenerated holes.²² Photogenerated holes are trapped at surface lattice oxygen atoms, causing a dissociation of their bonds with titanium atoms, followed by the adsorption

of water molecules at these sites. On the basis of these results, it is supposed that the bonding strength between metal ions and oxygen ions is important for photoinduced hydrophilicity. Metal oxides exhibiting photoinduced hydrophilic conversions in this study (TiO₂, SnO₂, ZnO, WO₃, V₂O₅) are known as n-type metal oxides with oxygen vacancies. Oxygen vacancies are easily created in these materials by heating under oxygen at reduced pressures or under atmospheres of hydrogen or other reducing gases.^{54,55} In particular, TiO₂, WO₃, and V₂O₅ are known to create shear planes, called the Magneli phase, when they are annealed in hydrogen.^{56–58} This phase is described in terms of the elimination of planes of oxygen ions with accompanying crystallographic shear. Besides annealing under a reducing gas atmosphere, Ar⁺ ion bombardment,^{59–61} electron beam exposure,^{61,62} and high-energy UV light in an ultra-high vacuum⁶³ can create surface oxygen vacancies on these materials. The adsorption behavior of water molecules on defect-containing TiO₂ single-crystal surfaces has been studied extensively,^{59,64–68} and it has been reported that water molecules adsorb dissociatively on surface defect sites. We believe that agreement between the surface oxygen vacancies and the wettability conversion is not accidental.

To discuss the creation of defects on the surfaces of various metal oxides, we measured XPS after Ar⁺ ion bombardment on the surface of TiO₂, SrTiO₃, and WO₃. Figure 4 shows changes of the XPS spectra before and after Ar⁺ ion bombardment. These spectra were broadened by the Ar⁺ ion bombardment, indicating that oxygen vacancies were created and electrons were trapped by the metal species. These films became highly hydrophilic with a contact angle of 0° after Ar⁺ ion bombardment for 1 min. Noticeably, SrTiO₃ films were more stable under Ar⁺ ion bombardment than TiO₂ or WO₃ films. These results indicate that defect sites on TiO₂ and WO₃ can be created more easily than those on SrTiO₃. On the basis of these results, it is reasonable that the surface of SrTiO₃ does not become hydrophilic under UV illumination at intensities up to 2.0 mW/cm², owing to its crystal stability against UV illumination, whereas the surfaces of TiO₂ and WO₃ become hydrophilic, suggesting that UV illumination on TiO₂ or WO₃ causes the dissociation of atomic bonds between oxygen

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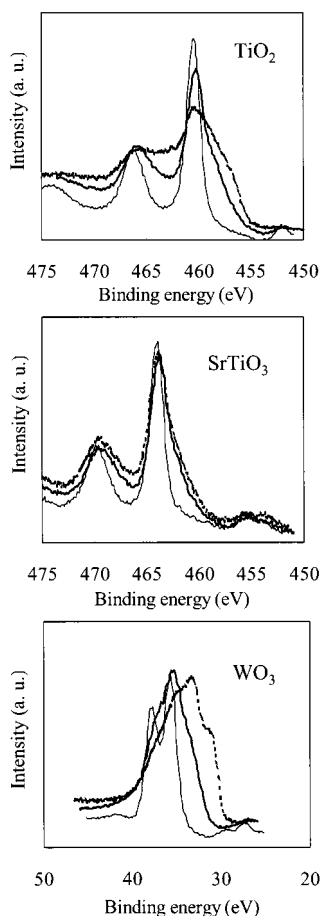


Figure 4. X-ray photoelectron spectroscopy for TiO_2 , SrTiO_3 , and WO_3 films. The analyzed band of TiO_2 and SrTiO_3 was the Ti 2p orbital, while for WO_3 the W 4f orbital was used. Thin solid line: before Ar^+ ion bombardment. Thick solid line: after Ar^+ ion bombardment for 1 min. Dashed line: after Ar^+ ion bombardment for 5 min. The beam voltage of Ar^+ ion bombardment was 2.0 kV.

and metal atoms in the surfaces of these oxides, followed by the adsorption of a water molecule at these defect sites. We also evaluated the XPS spectra of these metal oxides after UV illumination in ambient air; however, no changes in the XPS spectra were detected. This is a result of the reduced metal species donating electrons to adsorbed oxygen molecules in air and reconverting to their stoichiometric states.

As mentioned above, photoinduced hydrophilicity is considered to result from surface structural changes. This reaction involves changes at the topmost layer of metal oxides, which should not require a high quantum

efficiency in comparison to the photocatalytic oxidation process. Therefore, it is reasonable that the surfaces of WO_3 and V_2O_5 become hydrophilic under UV illumination, while they cannot decompose dye adsorbed on the surface.

At present, details of the surface states under UV illumination and quantum efficiencies of various metal oxides are unclear. For the strict comparison of rate constants or quantum efficiencies of photochemical reactions on the films prepared in this study, further investigation will be required under the constant photon adsorption condition. However, the current study offers a fundamental understanding of the mechanism of the photoinduced hydrophilic reaction.

Conclusions

The surfaces of TiO_2 , SnO_2 , and ZnO exhibited both surface reactions of photoinduced hydrophilicity and photocatalytic oxidation of methylene blue dye. The surface of SrTiO_3 , however, did not become hydrophilic under UV illumination, even though it rapidly decomposed methylene blue adsorbed on its surface. In contrast, the surfaces of WO_3 and V_2O_5 exhibited photoinduced hydrophilicity, while they did not decompose methylene blue dye at all. These results indicate that photoinduced hydrophilicity is not explained simply by the removal of organic adsorbates by a photocatalytic decomposition process. Photoinduced hydrophilicity is considered to be caused by some structural changes at the surface, that is, photogenerated holes diffuse to the surface of metal oxides and are trapped at surface lattice oxygen atoms, followed by the dissociative adsorption of a water molecule at these defect sites. Consequently, our XPS results after Ar^+ bombardment reveal that defect sites can be easily created on the metal oxides, which indicates their photoinduced hydrophilicizing ability.

At present, details of the surface states of various metal oxides under UV illumination are unclear, and they are currently under intensive investigation. The present study, however, is quite valuable as it can be applicable not only from a scientific standpoint but also from an industrial one. Furthermore, the candidates of applicable photocatalysts have now been expanded from TiO_2 to a number of additional metal oxides, adding vast importance to future study.

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