Preparation of Titanium−Silicon Binary Oxide Thin Film Photocatalysts by an Ionized Cluster Beam Deposition Method. Their Photocatalytic Activity and Photoinduced Super-Hydrophilicity

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Titanium−silicon binary oxide thin films of differing TiO_2 content were prepared by using an ionized cluster beam (ICB) deposition method using multi-ion sources under a dry preparation process. From the results of UV−vis absorption measurements, binary oxide thin films with low TiO_2 content showed much higher transmittance as compared with the pure TiO_2 thin film, indicating that the Ti−oxide species of these Ti−Si binary oxide thin films exist in a highly dispersed state within the SiO_2 matrices. Ti K-edge XAFS measurements revealed that such binary oxide thin films with low TiO_2 content (less than 20%) showed only a sharp preedge peak attributed to the highly dispersed Ti−oxide species which are different from the peaks of anatase TiO_2 thin films. Moreover, they were found to exhibit much higher and more efficient photocatalytic reactivity for the decomposition of NO into N_2 and O_2 under UV light irradiation than the pure TiO_2 thin films.

Introduction

TiO_2 thin films coated on various substrates such as glasses, tiles, and various architectural materials have been reported to show a super-hydrophilic property in which the contact angle of water droplets on the surface of the TiO_2 thin films can attain zero degree during UV light irradiation, so that TiO_2 thin films have attracted much attention as photofunctional materials for an anti-fogging, antibacterial, and stain-proofing agents.[1−5] In fact, we can now see many products utilizing these TiO_2 thin film photocatalysts in practical applications. However, various improvements are necessary, for example, the addition of SiO_2 fine particles[6] or the deposition of the SiO_2 thin layer[7] onto the surface of the TiO_2 thin films, to retain super-hydrophilicity even under dark conditions for an extended period of time. Ti−Si sol−gel films prepared by using a mixed solution of tetraethoxysilane (TEOS) and titanium tetraisopropoxide (TTIP) have been reported to include the 4-fold coordinated Ti species.[8,9] However, TTIP is easily hydrolyzed by water vapor in air to form TiO_2 aggregates much faster than TEOS forms SiO_2 aggregates, so that it is very difficult to control the gelation process to prepare binary oxide thin films in which SiO_2 and TiO_2 domains mix well with each other. The addition of SiO_2 to the TiO_2 thin film using a dip coating process[6] or a very thin and porous SiO_2 layer coating onto the TiO_2 thin films[7] have been also reported as efficient ways to enhance the super-hydrophilic properties because the added SiO_2 particles or a SiO_2 layer coating on the TiO_2 thin films work as a means to store water molecules even under dark condition.

Ti−Si binary oxide powder having low TiO_2 content prepared by a sol−gel method has been reported to include the 4-fold coordinated Ti−oxide species highly dispersed within the SiO_2 matrices, showing a unique and characteristic photocatalytic performance for the hydrogenation of unsaturated hydrocarbons with H_2O, the decomposition of NO into N_2, O_2, and N_2O, as well as the reduction of CO_2 with H_2O to produce CH_3OH and CH_4 under UV light irradiation.[10−18] Ti−B binary oxide thin films prepared by using an ionized cluster beam (ICB) deposition apparatus equipped with a multi-ion source have also been reported to show much higher photocatalytic performance for the decomposition of NO and photoinduced super-hydrophilic property under UV light irradiation.[19]

In this paper, we will deal with the preparation of Ti−Si binary oxide thin films including the highly dispersed 4-fold coordinated Ti-oxide species within the SiO_2 matrices by applying an ICB deposition method using multi-ion sources. The relationship between the photocatalytic performance for the decomposition reaction of NO under UV ($\lambda > 270$ nm) light irradiation and the local structures of the Ti-oxide species in these binary oxide thin films having different TiO_2 contents will also be discussed by analyses of UV−vis absorption and Ti K-edge XAFS measurements. Furthermore, to discuss the surface wettability of these Ti−Si binary oxide thin films, the contact angles of the water droplets were measured in ambient conditions using a contact angle meter.

Experimental Section

Ti−Si binary oxide thin films were prepared by an ionized cluster beam (ICB) deposition apparatus equipped with a multi-ion source. A schematic diagram of this procedure is shown in Figure 1. For the ion-source materials of TiO_2 and SiO_2, metallic titanium grains (High Purity Chemicals Corp.; grade, 99.99%; size, 5−10 mm) and silicon monoxide (SiO) grains (Furu-uchi Chemicals Corp.; grade, 99.99%; size, 5−10 mm) were used, respectively. The quartz substrates (size, 10 mm × 10 mm × 1 mm) were ultrasonically cleansed in acetone for 15 min, dried at 373 K for half a day, and then calcined in air at 723 K for 5

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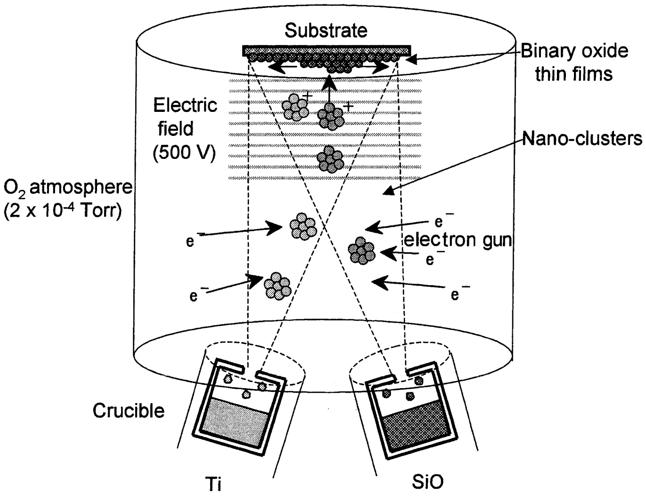

Figure 1. Schematic diagram of an ionized cluster beam (ICB) deposition method using Ti and SiO ion sources.

h in order to obtain a clean surface before the deposition process of these thin films.

The metallic Ti and SiO as the source materials were heated to approximately 2200 K in each crucible, and Ti and SiO vapors were each introduced into the high vacuum chamber. At this time, the Ti metal and SiO clusters reacted with sufficient amounts of O_2 molecules (oxygen pressure, 2×10^{-4} Torr) in the vacuum chamber to produce stoichiometric TiO_2 and SiO_2 clusters. These TiO_2 and SiO_2 clusters ionized by electron beam irradiation were then accelerated by an electric field (acceleration voltage, 500 V) and bombarded onto the substrate to form Ti−Si binary oxide thin films. The Ti/Si ratio, the film thickness, and the deposition rate (about 0.1 nm/s) could be strictly and easily controlled by monitoring their parameters with a quartz film thickness meter (Inficon) during the deposition process. The temperature of the substrate was kept at 623 K in order to obtain a good crystallinity and strong adhesion of the thin film onto the substrates.

The resulting transparent Ti−Si binary oxide thin films were characterized by various spectroscopic means such as XRD (Rigaku, RINT-1200) and UV−vis absorption (Shimadzu, UV-2200A) measurements at room temperature. To investigate the local structures of the Ti−oxide species in the SiO_2 matrices, the Ti K-edge XAFS spectra of these thin films were obtained in the fluorescence mode at 295 K at the BL-7C facility of the Photon Factory at the National Laboratory for High Energy Physics (KEK−PF) in Tsukuba. A Si(111) monochromator was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The normalized spectra were obtained by a procedure described in previous publications.[20,21]

The photocatalytic properties of these Ti−Si binary oxide thin films were investigated by carrying out the photocatalytic decomposition of NO under UV light ($\lambda > 270$ nm) irradiation. Pretreatment and photocatalytic reactions for the decomposition of NO were carried out using the same procedure shown in previous papers. UV ($\lambda > 270$ nm) light irradiation was carried out with a 100 W high-pressure Hg lamp (Toshiba, SHL-100 UVQ-2) through a color filter (Toshiba Glass, UV-27). The contact angles of the water droplets on these binary oxide thin films were measured under ambient conditions using a contact angle meter (Kyowa Interface Science Co. Ltd., CA-X) at 295 K. The procedures for UV light irradiation were the same as that for the photoreactions described above.

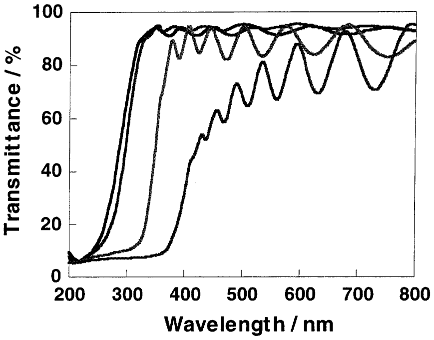

Figure 2. UV−vis transmittance spectra of Ti−Si binary oxide thin films prepared by an ICB deposition method using Ti and SiO ion sources. The amount of TiO_2 (left to right): (a) 6.6, (b) 9.5, (c) 50.1, and (d) 100%.

Results and Discussion

Figure 2 shows the UV−vis absorption spectra of the Ti−Si binary oxide thin films (film thickness, 700 nm) with different TiO_2 contents measured by the transmittance method. The SiO_2 thin film deposited on the quartz substrate did not show any significant absorption in measurable ranges (200−800 nm) due to a similar refractive index of the SiO_2 thin film and quartz substrate, so that the absorption spectra of these binary oxide thin films could be attributed to the Ti−oxide species. The TiO_2 thin films were found to show clear interference fringes in visible light regions typical of the absorption spectra of thin films, indicating that highly transparent and uniform films could be formed on the substrate. On the other hand, as the TiO_2 content decreased, the intensity of the interference fringes was found to decrease as well. From these results, it could be expected that the Ti−oxide species do not have a long-range order and exist as small clusters highly dispersed within the SiO_2 matrixes. In the XRD patterns of the Ti−Si binary oxide thin films with lower Ti content, no peaks attributed to anatase and/or rutile TiO_2 could be observed. These XRD results were in good correspondence with that of the UV−vis absorption measurements. A remarkable shift in the absorption edge toward shorter wavelength regions could be seen along with the decrease in the TiO_2 content. The absorption peak of the binary oxide thin film having a TiO_2 content of 6.6% was observed at around 220−250 nm. The absorption peak of the highly dispersed and 4-fold coordinated Ti−oxide species incorporated within the zeolite frameworks has been reported to be observed at around 220−230 nm.[22−26] Therefore, these binary oxide thin films can be also expected to include the highly dispersed and 4-fold coordinated Ti−oxide species. These shifts in the absorption edge are explained by the quantum size effect arising from the presence of ultrafine Ti−oxide species dispersed within the SiO_2 matrixes.

To investigate the local structures of the Ti−oxide species included in these Ti−Si binary oxide thin films, the Ti K-edge XAFS spectra were measured at the BL-7C facility of High Energy Physics in Tsukuba. Figure 3 (left side) shows the XANES spectra of the binary oxide thin films with different TiO_2 contents. In the spectra with low TiO_2 content (less than 10%), only a sharp preedge peak could be observed at 4.97 keV which is attributed to the highly dispersed Ti−oxide species that differs from that of anatase TiO_2 thin films. As the TiO_2 content increased, the intensity of the sharp preedge peaks was found to decrease, indicating that the highly dispersed ultrafine Ti−oxide species aggregate to form small clusters containing a part of the TiO_6 octahedrons. Figure 3 (right side) also shows the Fourier transforms of the EXAFS oscillation of these binary

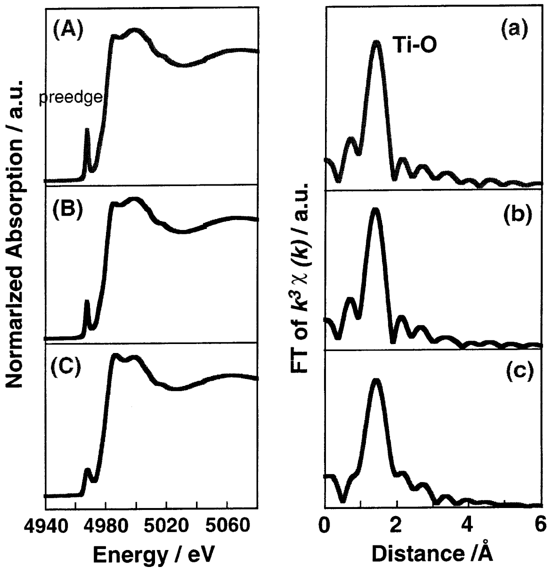

Figure 3. XANES (A−C) and Fourier transforms of EXAFS (a−c) of the Ti−Si binary oxide thin films prepared by an ICB deposition method using Ti and Si ion-sources. The amount of TiO_2 (top to bottom): 6.6, 9.5, and 50.1%.

TABLE 1: Results of the Curve Fitting of Fourier Transforms of EXAFS Data for the Ti−Si Binary Oxide Thin Films

TiO_2 contents (%)	shell	R^a (Å)	CN^b	σ^c (Å)
6.6	Ti−O	1.81	4.3	0.0001
9.5	Ti−O	1.82	4.4	0.0001
50.1	Ti−O	1.85	4.9	0.0056
100	Ti−O	1.93	6.0	0.0089

[a] Bond distance. [b] Coordination number. [c] Debye−Waller factor.

oxide thin films. In every spectra, a strong peak at around 1.6−1.7 Å attributed to the neighboring O atoms (Ti−O) can be seen in the first coordination sphere; however, a peak at around 2.8−3.0 Å attributed to the Ti atoms (Ti−O−Ti) could not be observed in the second coordination sphere. These results clearly indicate that no aggregated TiO_2 species exist although ultrafine Ti−oxide clusters including the 4-fold coordinated Ti−oxide species are highly dispersed within the SiO_2 matrixes. Furthermore, the results of the curve fitting in the Fourier transforms of the EXAFS data for these binary oxide thin films were collected, as shown in Table 1. The Ti−O bond distance of the highly dispersed 4-fold coordinated Ti−oxide species incorporated within the zeolite framework at the atomic level has been reported to be about 1.78 Å. The Ti−O bond distance in these Ti−Si binary oxide thin films was found to be slightly longer at 1.81−1.82 Å. These results indicate that the Ti−oxide species in these Ti−Si binary oxide thin films exist not as a completely isolated tetrahedral TiO_4 unit incorporated within the SiO_2 matrixes at the atomic level but as highly dispersed ultrafine Ti−oxide clusters including the 4-fold coordinated Ti−oxide species.

UV light (λ > 270 nm) irradiation of these Ti−Si binary oxide thin films in the presence of NO were found to lead to the photocatalytic decomposition of NO with an evolution of N_2 and O_2. Figure 4 shows the reaction time profiles of the photocatalytic decomposition of NO on the Ti−Si binary oxide thin film having a TiO_2 content of 6.6% under UV light irradiation. This photoreaction to evolve N_2 was found to proceed with a good linearity against the light irradiation time which ceased under dark conditions. These results clearly indicate that these Ti−Si binary oxide thin films including the highly dispersed Ti−oxide species work efficiently as a photocatalyst under UV light irradiation as is the case with pure TiO_2 thin films.

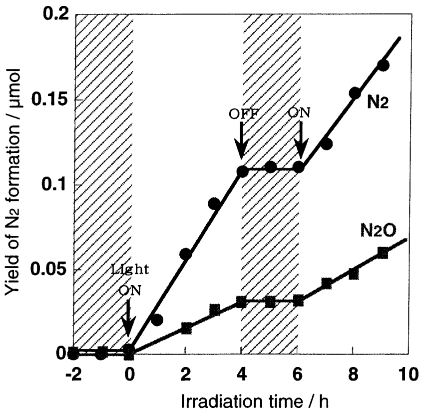

Figure 4. Reaction time profiles of the photocatalytic decomposition of NO on Ti−Si binary oxide thin film (TiO_2 content, 6.6%), under UV light irradiation (λ > 270 nm) at 275 K.

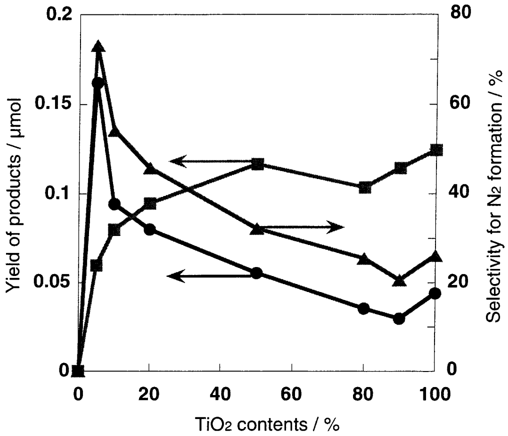

Figure 5. Effect of the TiO_2 content on the production yields of N_2 (circle plots) and N_2O (square plots) and the selectivity for N_2 formation (triangle plots) in the photocatalytic decomposition of NO on Ti−Si binary oxide thin films under UV light irradiation (λ > 270 nm) at 275 K.

The photocatalytic reactivity and selectivity of N_2 formation for the decomposition of NO were found to strongly depend on the local structures of the Ti−oxide species. Figure 5 shows the effects of the TiO_2 content on the production yields of N_2 and N_2O as well as on the selectivity for N_2 formation in the photocatalytic decomposition of NO. As the TiO_2 content in these binary thin films was lessened, the amount of N_2 formation increased, whereas in contrast, the amount of N_2O formation decreased, resulting in the higher selectivity for N_2 formation. The amount of N_2 produced on the Ti−Si binary oxide thin film prepared by an ICB deposition method and having a TiO_2 content of 6.6% for the photocatalytic decomposition of NO under UV light irradiation for 7 h was 2 times greater as compared to the pure TiO_2 thin films which were also prepared by an ICB deposition method.

Furthermore, the relationship between the selectivity for N_2 formation in the photocatalytic decomposition of NO under UV light irradiation (circle plots) and the coordination number of the Ti−oxide species determined by XAFS measurements (square plots) as well as the wavelength of the absorption edge determined by the UV−vis absorption spectra (diamond plots) can be seen in Figure 6. The tendency toward selectivity for N_2 formation in the photocatalytic decomposition of NO was

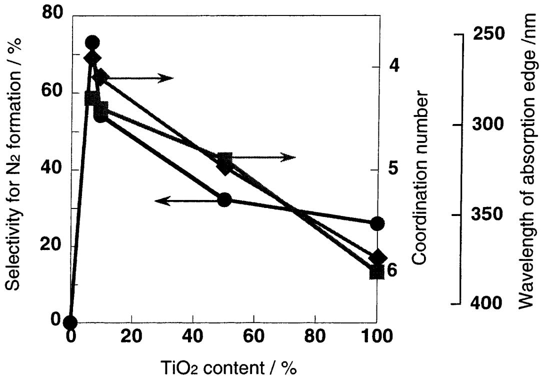

Figure 6. Relationship between the selectivity for N_2 formation (circle plots) in the photocatalytic decomposition of NO and the coordination number of the Ti−oxide species (square plots) as well as the wavelength of the absorption edge (diamond plots).

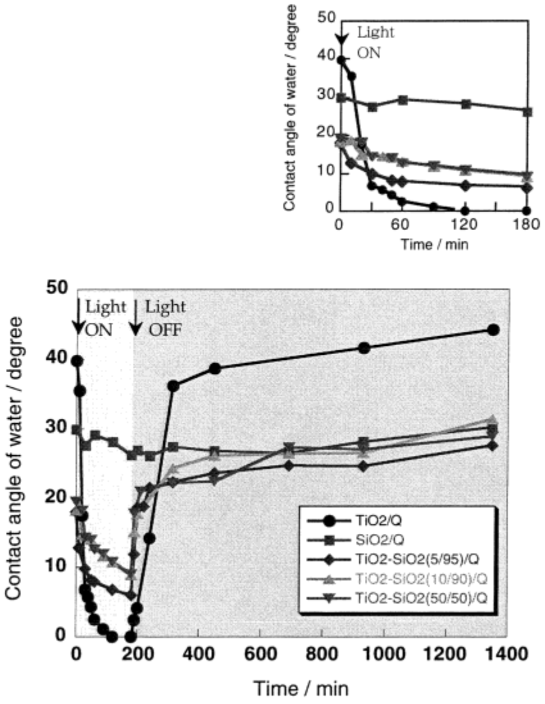

Figure 7. Time courses of the changing in the contact angles of the water droplets on Ti−Si binary oxide thin films having different TiO_2 contents.

found to be in good correspondence with the coordination numbers of the Ti−oxide species. In other words, Ti−Si binary oxide thin films having low TiO_2 content contain a tetrahedral TiO_4 unit incorporated within the SiO_4 matrixes. These results clearly indicate that the highly dispersed ultrafine Ti−oxide species included with the tetrahedral TiO_4 units play a very important role in the formation of N_2 and O_2 in the photocatalytic decomposition of NO under UV light irradiation. However, as the absorption edge of these Ti−Si binary oxide thin films with low TiO_2 content shifts toward shorter wavelength regions, it is necessary for these thin films with highly dispersed Ti−oxide species to be irradiated by UV light having much shorter wavelengths.

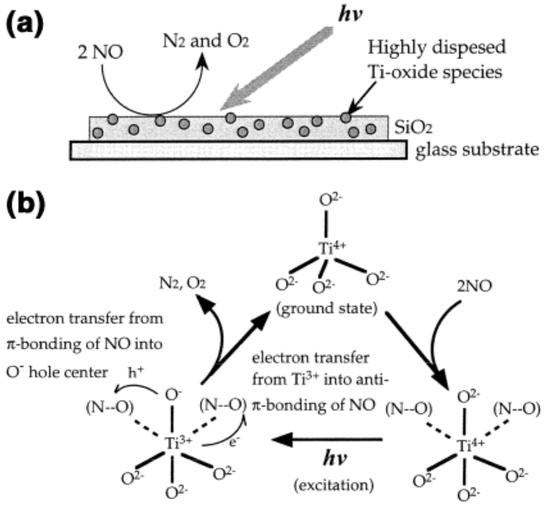

Figure 8. (a) Model of Ti−Si binary oxide thin films having highly dispersed Ti−oxide species. (b) The reaction mechanism of the photocatalytic decomposition of NO into N_2 and O_2 on the 4-fold Ti−oxide species.

To discuss the surface wettability of these Ti−Si binary oxide thin films, the contact angles of water droplets were measured under UV light irradiation under ambient conditions. Figure 7 shows the time courses of the contact angles of water droplets on these thin films when the samples were irradiated by UV light for 3 h and then kept in the dark for 19 h. The inserted figure also shows the detailed time courses under UV light irradiation. The initial contact angle of the water droplets of about 40−50° on the TiO_2 thin films before light irradiation could reach less than 10° by UV light irradiation of only about 30 min, while retaining its super-hydrophilicity during irradiation. On the other hand, the initial contact angles of the water were found to be slightly smaller than those on pure TiO_2 thin films, gradually lessening with the UV irradiation time and saturating at around 10°. However, because only the SiO_2 thin films did not show any response to UV light irradiation, these changing in the surface wettability on these Ti−Si binary oxide thin films under UV light irradiation could be associated with the existence of the highly dispersed Ti−oxide species. Thus, these results indicate that the highly dispersed Ti−oxide clusters including the tetrahedral Ti−oxide species exhibit photoinduced super-hydrophilic properties under UV light irradiation as in the surface of TiO_2 thin films. However, the slower photoresponses of these Ti−Si binary oxide thin films are explained by the much longer distances between each Ti−oxide clusters because the Ti−oxide species are highly dispersed within the SiO_2 matrixes. Furthermore, because the surface of SiO_2 originally exhibits the hydrophilic property, the contact angles of water droplets before light irradiation and after saturation in dark conditions were found to be small when compared to the pure TiO_2 thin films.

Conclusions

Ti−Si binary oxide thin films having different TiO_2 contents were successfully prepared by applying an ionized cluster beam (ICB) deposition method using multi-ion sources as a dry process. From the results of UV−vis absorption measurements, the transmittance of these binary oxide thin films with low Ti content was found to be much higher than that of the pure TiO_2 thin film, indicating that the Ti−oxide species in the Ti−Si binary oxide thin films are highly dispersed within the SiO_2 matrixes, as shown in Figure 8a. The results of Ti K-edge XAFS measurements showed the existence of the highly dispersed Ti−oxide species having a tetrahedral local structure which is different from the octahedral structure of anatase TiO_2. These characteristic tetrahedral Ti−oxide species were also found to exhibit more efficient photocatalytic reactivity and higher selectivity for N_2 formation in the decomposition of NO under

UV light irradiation as compared to the pure TiO_2 thin films. The simultaneous interaction of two NO molecules on one 4-fold Ti−oxide species plays a very important role in the high selective decomposition of NO into N_2 and O_2 as the decomposition mechanism proposed for the highly dispersed Ti−oxide species (Figure 8b). Furthermore, these highly dispersed Ti−oxide species were found to show photoinduced hydrophilic conversion under UV light irradiation as could be observed with the pure TiO_2 thin film photocatalysts.

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