Preparation of Superhydrophilic Mesoporous Silica Thin Films Containing Single-site Photocatalyst (Ti, V, Cr, Mo, and W oxide moieties)

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Using a sol–gel/spin-coating method, transparent mesoporous silica thin films containing single-site photocatalyst (Ti, V, Cr, Mo, and W oxide moieties) (Me-MSTFs) could be prepared on quartz plates. All Me-MSTFs have exhibited strong hydrophilic surface properties even before UV-light irradiation and showed photoinduced superhydrophilic properties after UV-light irradiation. Among examined samples, the W-MSTF showed the highest hydrophilicity.

Design of the titanium dioxide (TiO_2) photocatalysts immobilized onto porous silica materials has attracted considerable interest for the application in various fields. In particular, the thin film materials have an ideal morphology for promising applications because of the inherent features of thin films. The TiO_2 thin film shows not only photocatalytic activities but also photoinduced surface superhydrophilicity.[1] By using the surface hydrophilic property, versatile TiO_2-based self-cleaning products such as tiles, glass, mirrors, and plastics have become commercially available. Although this surface property is very useful, the necessity of the UV-light irradiation makes application difficult. For practical use, it is important to underline that the search for new thin films exhibiting the superhydrophilic property under without UV-light irradiation.

So far, we have developed the Ti-containing mesoporous silica thin films having high surface hydrophilicity even before UV-light irradiation.[2] The single-site photocatalysts that transition metals exist in a highly dispersed state within the mesoporous silica matrix have unique and fascinating photocatalytic activities for several significant reactions.[3–8] The surface becomes more polar owing to the increase of the Brønsted acidity of the Ti site.[9] Moreover, the mesoporous structure can also enhance their hydrophilicity because of the capillary phenomenon. By the addition of transition-metal ions, such as titanium ions, within the mesoporous silica thin films, it becomes possible to design of unique surface active sites. New optically functionalized materials can be developed by combining the mesoporous silica with a highly dispersed tetrahedrally coordinated metal oxide moieties.

In this research, the mesoporous silica thin films having various metal oxide moieties (Ti, V, Cr, Mo, and W) were prepared, and we found out that the W-containing mesoporous silica thin film showed the highest hydrophilic properties among examined samples.

The W-containing mesoporous silica thin film (W-MSTF) deposited on the quartz plate (10 × 10 × 1 mm) were prepared by the sol–gel/spin-coating method using tetraethylorthosilicate (TEOS) as a silica source, aqueous ammonium paratungstate pentahydrate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$) solution as a tungsten oxide source, $C_{12}H_{25}(OCH_2CH_2)_4OH$ (Brij®30) as a structure-directing agent (SDA), hydrochloric acid and ethanol (Si + W: Brij®30:HCl:EtOH = 1.5:0.18:0.15:10 molar ratio) (Si:W = 100:x; $x = 0$ and 1). The mixture was stirred for 15 min at 298 K, dripped onto a quartz substrate, spread evenly, and spin-coated at a spinning rate of 4000 rpm for 1 min. Finally, the obtained thin film was calcined in air at 523 K for 5 h to remove the SDA from the film material. The metal oxide (Ti, V, Cr, and Mo)-MSTFs (Me-MSTF) were prepared by the same method using $Ti(OC_2H_5)_4$, NH_4VO_3, $Cr(NO_3)_6\cdot 9H_2O$, and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, as various metal oxide sources, respectively.

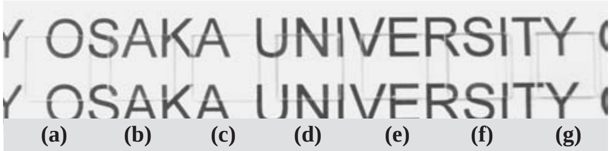

Figure 1. Sample photography of plates coated with (a) quartz plate, (b) MSTF, (c) Ti-MSTF, (d) V-MSTF, (e) Cr-MSTF, (f) Mo-MSTF, and (g) W-MSTF.

The mesoporous silica thin film (MSTF) without transition metal oxide and Me-MSTFs were transparent and well-fixed on the substrate of quartz plate. As can be seen from the photo images in Figure 1, they are colorless and completely transparent like original quartz plate.

The X-ray diffraction (XRD) patterns of the MSTF, Ti-MSTF, and W-MSTF are shown in Figure 2. These thin films exhibit a diffraction peak at around 2–4° associated with the d_{100} spacing, indicating the presence of hexagonally packed

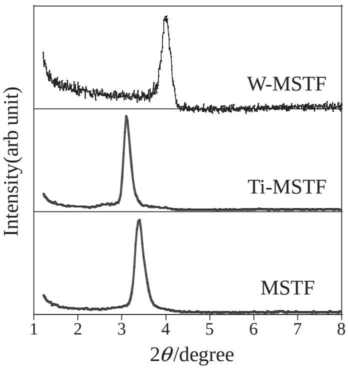

Figure 2. Low angle XRD patterns of the mesoporous silica thin film and the metal oxide (Ti and W)-containing mesoporous silica thin films.

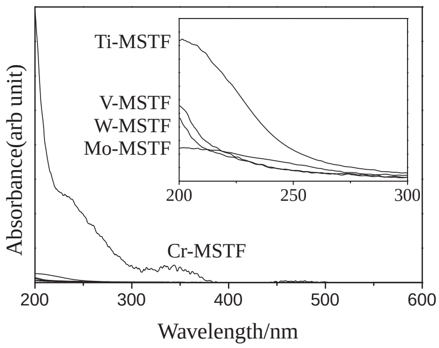

Figure 3. UV–vis spectra of the metal oxide (Ti, V, Cr, Mo, and W)-containing mesoporous silica thin films. Inset shows the UV-region spectra.

mesoporous structure. Moreover, no other peaks were observed at the higher angle, suggesting that the metal oxide moieties are highly dispersed in the silica framework. XRD patterns of V-, Cr-, and Mo-MSTF also showed the same results (Figure S1).[11]

Figure 3 shows the UV–vis absorption spectra of the Me-MSTFs, and the inset shows the region of 200–300 nm. Absorption bands of Me-MSTFs were observed in the UV wavelength region. These bands can be attributed to the ligand-to-metal charge-transfer (LMCT) band from O^{2-} to Me^{n+} ions in the tetrahedrally coordinated metal oxide moieties.[4] These results suggest that the metal oxide moieties of the Me-MSTFs exist in a highly dispersed state in the mesoporous silica matrix with the absence of octahedrally coordinated species. On the other hand, the MSTF without metal ion exhibited almost no absorption in the UV–vis range.

The Fourier-transform of W L_{III}-edge EXAFS spectrum of the W-MSTF showed a peak between 1.0 and 2.0 Å assignable to the neighboring oxygen atom (W–O bond) (Figure S2).[11] No peaks due to a W–O–W bond[10] in the second coordination sphere detectable in that of WO_3 were observed. These results suggest the presence of the isolated tungsten oxide species in this sample, as confirmed by UV–vis absorbance measurement.

To gain an insight into the surface properties of the Me-MSTFs, the contact angle of the water droplet was measured before and after UV-light irradiation (200 W mercury xenon lamp of SAN-EI ELECTRIC CO., LTD. at 60 mW/cm^2 for 2 h). The water contact angles and photo mages on the MSTF and Me-MSTFs were shown in Figures 4 and 5. The water contact angles on the Me-MSTFs before UV-light irradiation were 6, 5, 6, 11, and 3°, respectively, which were much smaller than 28° on the MSTF. From the viewpoint of practical utilization, high hydrophilicity even before UV-light irradiation is very useful. After UV-light irradiation, the water contact angles on the Me-MSTFs became extremely small values of 6° or less. Especially, the water contact angles on the W-MSTF were 3 and 1° before and after UV-light irradiation, respectively, and showed the highest hydrophilicity among examined samples. These observations revealed that the Me-MSTFs can perform the superhydrophilic property under UV-light irradiation. On the other hand, MSTF did not show significant change before and after UV-light irradiation. These results suggest that the charge transfer excited state of the tetrahedrally coordinated metal oxide moieties formed under UV-light irradiation play a significant role in the photoinduced superhydrophilic property.

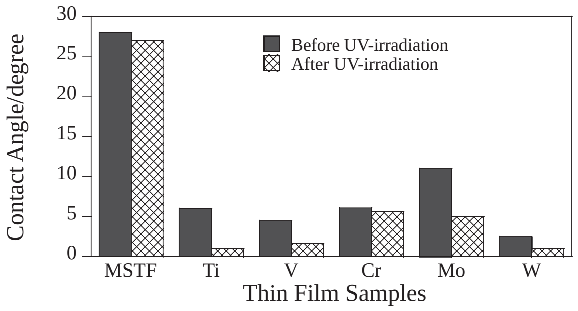

Figure 4. Contact angles of the water droplet on the metal oxide (Ti, V, Cr, Mo, and W)-containing mesoporous silica thin films.

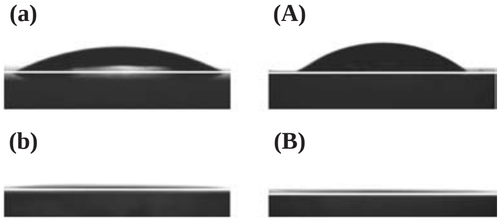

Figure 5. Photo images of water droplet before and after (capital) UV-light irradiation on (a, A) mesoporous silica thin film and (b, B) W-containing mesoporous silica thin film.

In conclusion, the metal oxide (Ti, V, Cr, Mo, and W)-containing transparent mesoporous silica thin films can be prepared on the quartz plate using the sol–gel/spin-coating method in the presence of SDA. The metal oxide species existed in a highly dispersed tetrahedral-coordination state in the mesoporous silica matrix. The Me-MSTFs have demonstrated a strong hydrophilic surface property even before UV-light irradiation. After UV-light irradiation on these thin films, the appearance of the strong superhydrophilic property was observed.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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