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Preparation of Transparent Particulate MoO_3/TiO_2 and WO_3/TiO_2 Films and Their Photocatalytic Properties

Kang Yong Song, Myun Kyu Park, Young Tae Kwon, Hyun Woo Lee,
Won Jo Chung, and Wan In Lee*

*Department of Chemistry and Center for Chemical Dynamics, Inha University,
Inchon 402-751, Korea*

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By monolayer coverage of highly acidic semiconductors, such as MoO_3 and WO_3 on the surface of TiO_2 nanoparticles (Degussa P25), the stability of colloidal suspensions in aqueous solution can be greatly improved. The average diameter of agglomerated MoO_3/TiO_2 and WO_3/TiO_2 particles in aqueous suspension is only 85−110 nm, respectively, which is about one-fifth to one-fourth of that of pure TiO_2 suspension. The optically transparent photocatalytic films have been prepared with deposition of these colloidal suspensions. The colloidal particles in aqueous solution and the prepared transparent photocatalytic films were characterized with TEM, SEM, AFM, and other spectroscopic techniques. It has also been found that the photocatalytic activity of WO_3/TiO_2 film is 2.8−3 times that of pure TiO_2 film in decomposing gas-phase 2-propanol, while MoO_3/TiO_2 film is less effective.

Introduction

It has been known that TiO_2 demonstrates one of the highest photocatalytic activities among the semiconductors for the elimination of organic pollutants in aqueous solution or in the gas phase.[1−8] Especially, TiO_2 photocatalysts in thin film form have promising application for the decomposition of gas-phase pollutants or as a self-cleaning smart material. Moreover, the TiO_2 surface shows super-hydrophilic character with an irradiation of light. Hence, the TiO_2 thin films coated on a window glass, a light bulb, ceramic tiles, or a wall can purify the polluted air in the room and can self-clean or defog their surfaces.[9−12] For these industrial applications, the preparation of optically transparent TiO_2 films in a large area and the improvement of their photocatalytic activity would be crucial tasks. In addition, TiO_2 films should be fabricated at low temperature because those films are in general applied on the soda-lime glass, which has a very low softening point. So far, many techniques, such as MOCVD, sputtering, and sol−gel methods, have been applied for the preparation of transparent TiO_2 films.[13−15] TiO_2 films with high photocatalytic activity and great uniformity can be obtained by MOCVD or sputtering techniques. However, these methods have high costs, and the preparation of films in a large area is technically difficult. The sol−gel method is an economical process, but heat treatment at temperatures higher than 450 °C is essential for the elimination of organic components and for the achievement of a crystallized TiO_2 phase with reasonably high photocatalytic activity.

In this work, we report a novel method for preparing transparent TiO_2 films having enhanced photocatalytic efficiency at low temperature. We have modified the surface of commercial TiO_2 particles with highly acidic metal oxides. These particles are well-dispersed in aqueous solution and can be applied for the coating of uniform photocatalytic films. In general, colloidal particles in solution should be smaller than about 150 nm in diameter to avoid the scattering of visible light in the range of 400−700 nm. Commercial TiO_2 particles, such as Degussa P25, which is prepared by the flame hydrolysis of $TiCl_4$ in a hydrogen/oxygen flame, are about 25 nm in diameter. Hence, the preparation of transparent TiO_2 films by the coating of suspended Degussa P25 particles is basically possible. However, the individual TiO_2 particles in the suspension are heavily agglomerated to decrease the surface energy, and the agglomerated particles are hardly broken by physical suspending methods, such as ultrasonication or ball milling. It has been found that the average size of agglomerated TiO_2 particles in a colloidal solution is

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* To whom correspondence should be addressed. Tel.: +82-32-863-1026. Fax: +82-32-867-5604. E-mail: wanin@inha.ac.kr.

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≈400−500 nm, though the size can be varied more or less depending on the suspending method.

Wahl et al. prepared nanostructured TiO_2 films with the coating of Degussa P25 TiO_2 particles suspended in a mixture of dimethlyformamide and poly(vinylidene-fluoride).[16] However, their films were very porous, and the surface was too rough to be a transparent film. In the present work, we modified the surface of Degussa P25 with MoO_3 and WO_3. The prepared MoO_3 /TiO_2 (or WO_3/TiO_2) particles are much more stably suspended in water, and their average colloid sizes in the suspension are notably decreased, compared with those of pure TiO_2. The surface of films derived from these suspensions has been characterized, and their photocatalytic activities have also been evaluated.

Experimental Section

A commercial form of TiO_2 (Degussa P25; particle size of 25 nm; surface area of 47 m^2/g) was chosen as the standard particle. MoO_3/TiO_2 (or WO_3/TiO_2), the TiO_2 particle whose surface was modified with MoO_3 (or WO_3), was prepared by the incipient wetness method as described below. TiO_2 was suspended in a dilute ammonia solution dissolved with a stoichiometric amount of ammonium paramolybdate (Aldrich) and dried in a water bath under stirring conditions. It was then heat-treated at 400 °C for 2 h in flowing oxygen. For the preparation of WO_3/TiO_2, TiO_2 powder was suspended in ammonia solution with tungstic acid (Aldrich). It was dried and subsequently heat-treated at 450 °C for 2 h in oxygen.

The Lewis surface acidity of prepared samples was evaluated by titrating 0.5 g of each sample suspended in benzene with 0.1 N *n*-butylamine benzene solution, using methyl red as an indicator.[17]

The surface-modified photocatalytic powders were primarily ultrasonicated in water, and they were then subsequently suspended by a typical ball-milling technique. That is, 2 g of each powder sample was suspended in 60 mL of water; 0.4 g of cetyltrimethylammonium bromide and 40 mL of zirconia balls at 0.2-mm diameter were also added, and the mixtures filled in a polypropylene vessel were then milled for 48 h by rotating the vessel at 60 rpm.

The average diameters of agglomerated TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 particles in suspended aqueous solution were estimated with a particle size analyzer (Zeta Master, Malvern Co.). The prepared particles were also examined by a high-resolution TEM technique. One milligram of TiO_2, WO_3/TiO_2, and MoO_3/TiO_2 particles was dispersed in 50 mL of methanol and a drop of suspension was spread on a holey amorphous carbon film deposited on a Ni grid (JEOL Ltd.). The prepared sample was then examined in a Philips CM30 transmission electron microscope operated at 250 kV.

The prepared colloidal suspensions were employed for the fabrication of photocatalytic films. Suspended solution (0.4 M) (2.0 g of TiO_2 in 60 mL) was spin-coated on Pyrex glass (2 × 2 cm^2) at 1800 rpm. The thickness of film per each spin-coating process was about 30 nm. The coated TiO_2 films were then baked at 120 °C. After several coating and baking cycles, the films were finally heat-treated at 300 °C for 2 h in an oxygen environment.

The prepared transparent TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 films at 150-nm thickness were tested as photocatalysts for the decomposition of 2-propanol in the gas phase. The gas reactor system used for this photocatalytic reaction is described elsewhere.[18] The net volume of gastight reactor was 200 mL, and a TiO_2 film was located in the center of the reactor. The whole area of the TiO_2 film (2 × 2 cm^2) was irradiated by a 300-W Xe lamp through the 2-in. diameter silica window on the reactor. After evacuation of the reactor, a stoichiometric amount of 2-propanol and water vapor was added (the molar concentrations are 200 and 400 ppm, respectively). The reactor pressure was then controlled to 700 Torr by the addition of oxygen gas. Under these conditions, 2-propanol and H_2O remained in the vapor phase. The gas mixtures in the reactor were magnetically convected during the irradiation. After the irradiation every 30 min, 0.5 mL of gas sample in the reactor was automatically picked up and sent to a gas chromatograph (Young Lin M600D) by using an autosampling valve system (Valco Instruments Inc. A60). For the detection of CO_2, a methanizer was installed between the GC column outlet and FID detector.

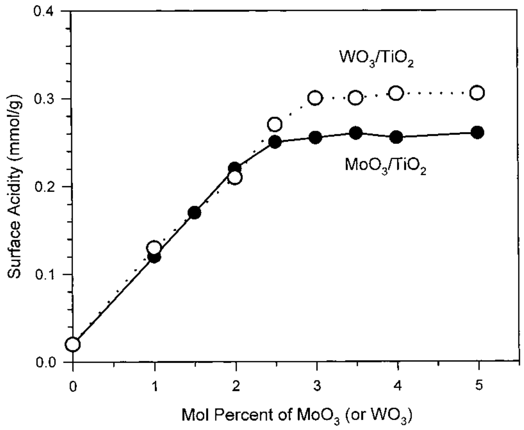

Figure 1. Change of Lewis surface acidity for the MoO_3/TiO_2 and WO_3/TiO_2 particles with the increase in MoO_3 and WO_3 concentration. MoO_3 and WO_3 were coated on the surface of TiO_2 by the incipient wetness method.

Results and Discussion

Characterization of MoO_3/TiO_2 and WO_3/TiO_2 Particles. Because MoO_3 is much more acidic than TiO_2, the Lewis surface acidity of MoO_3/TiO_2 will be increased with increasing concentration, until the surface of TiO_2 is saturated with the coverage of MoO_3. As shown in Figure 1, the Lewis surface acidity of MoO_3/TiO_2 was increased steadily, until it reached a plateau level at ≈2.5 mol % of MoO_3. This indicates that at least 2.5 mol % of MoO_3 is needed for the saturation coverage of the TiO_2 surface. It has been reported that the saturation coverage of MoO_3 on TiO_2 is a density of ca. 4×10^{14} Mo atoms/cm^2 of TiO_2, and this corresponds to about half the theoretical monolayer capacity.[19−22] It is suggested that each Mo cation binds a couple of $-Ti-O^-$. The density of ca. 4×10^{14} Mo atoms/cm^2 of TiO_2 corresponds to 2.4 mol % of MoO_3 for Degussa P25 with a surface area of 47 m^2/g. Therefore, from our surface acidity result and the reports in the literature, it is deduced that MoO_3 preferentially covers the surface of TiO_2 as a monolayer rather than as clusters. The MoO_3/TiO_2, in the composition of Mo:Ti = 2.5:97.5 in mol %, was used for the preparation of a colloidal suspension in this work.

The change of Lewis surface acidity of WO_3/TiO_2 as a function of WO_3 concentration was also described in

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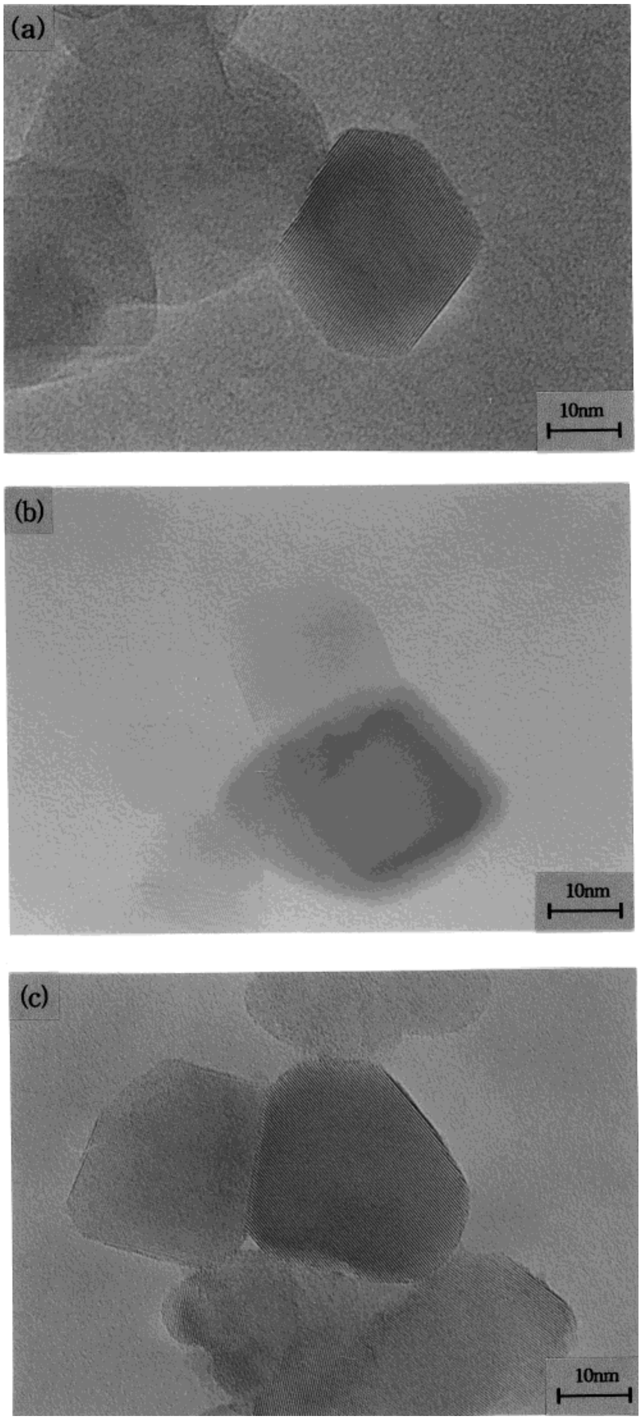

Figure 2. TEM images of TiO_2 (a), MoO_3/TiO_2 (b), and WO_3/TiO_2 (c) particles. TiO_2 is Degussa P25. MoO_3/TiO_2 and WO_3/TiO_2 were prepared by the incipient wetness method.

Figure 1. The increase of its Lewis surface acidity was halted at ≈3 mol % of WO_3 in WO_3/TiO_2. In the literature, it was reported that 3.4 mol % of WO_3 is necessary to cover the surface of Degussa P25 with saturation coverage.[23] It is also indicated that WO_3 preferentially covers the surface of TiO_2 as a monolayer until it reaches saturation coverage, in the same manner that MoO_3 behaves. The WO_3/TiO_2 sample (W:Ti = 3.0:97.0 in mol %) was then used for the preparation of a colloidal suspension.

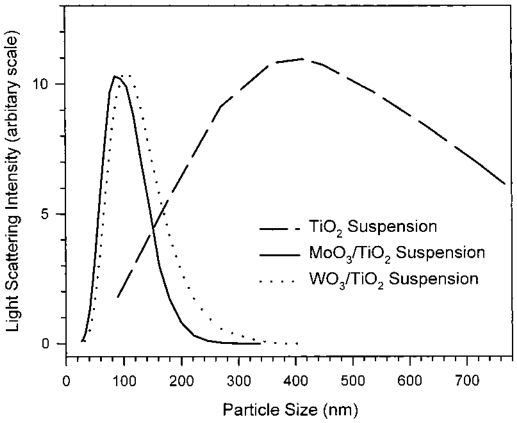

Figure 3. Particle size distributions for the TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 colloids suspended in aqueous solution. Peak analysis was done by the volume of particle.

The high-resolution TEM images in Figure 2 indicate that the TiO_2 particles (Degussa P25) are about 25 nm in diameter. The uniform lattice fringes observed over an entire TiO_2 particle indicate that the individual particle consists of a single grain. The MoO_3/TiO_2 and WO_3/TiO_2 particles also showed lattice fringes similar to those observed in pure TiO_2 particles, and no MoO_3 or WO_3 clusters were found around the TiO_2. This suggests that MoO_3 or WO_3 are uniformly dispersed on the surface of TiO_2.

Characterization of Colloidal Particles in Aqueous Suspensions. Aqueous suspensions of pure TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 were prepared by a ball-milling method. TiO_2 (2 g) (MoO_3/TiO_2 or WO_3/TiO_2) suspension in 60 mL of water, 40 mL of zirconia balls at 0.2-mm diameter, and 0.4 g of cetyltrimethylammonium bromide were added to a polypropylene bottle. After 2 days of the ball-milling procedure, the sizes of the agglomerated colloids in the suspended solutions were estimated with a particle size analyzer. In the pure TiO_2 colloidal suspension, the particle size in volume average was 460 nm, as shown in Figure 3. This indicates that a colloidal particle contains 6×10^3 of individual TiO_2 particles on average. On the other hand, those of MoO_3/TiO_2 and WO_3/TiO_2 were 85 and 110 nm, respectively, and this suggests that the mean numbers of individual particles contained in each colloid are only 40 and 85.

The shapes of ball-milled particles were also analyzed by TEM microscopy; 0.1 g of each TiO_2 and MoO_3/TiO_2 ball-milled suspension was diluted in 100 mL of H_2O and a drop of suspension was then dropped on a holey amorphous carbon film deposited on a Ni grid. TEM images in Figure 4a,b show the shape of ball-milled TiO_2 and MoO_3/TiO_2 particles. When compared with the images in Figure 2, the size of each particle was not appreciably changed. In addition, a uniform lattice fringe was observed over an entire particle. This indicates that the colloidal particles are not fragmented nor combined during the ball-milling procedure. Figure 5a−c shows low-magnification images of ball-milled TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 particles spread on an amorphous carbon film. In the case of TiO_2, particles were agglomerated to large lumps. In contrast, the MoO_3/TiO_2 particles were uniformly spread over the carbon film and each agglomerated cluster consisted of

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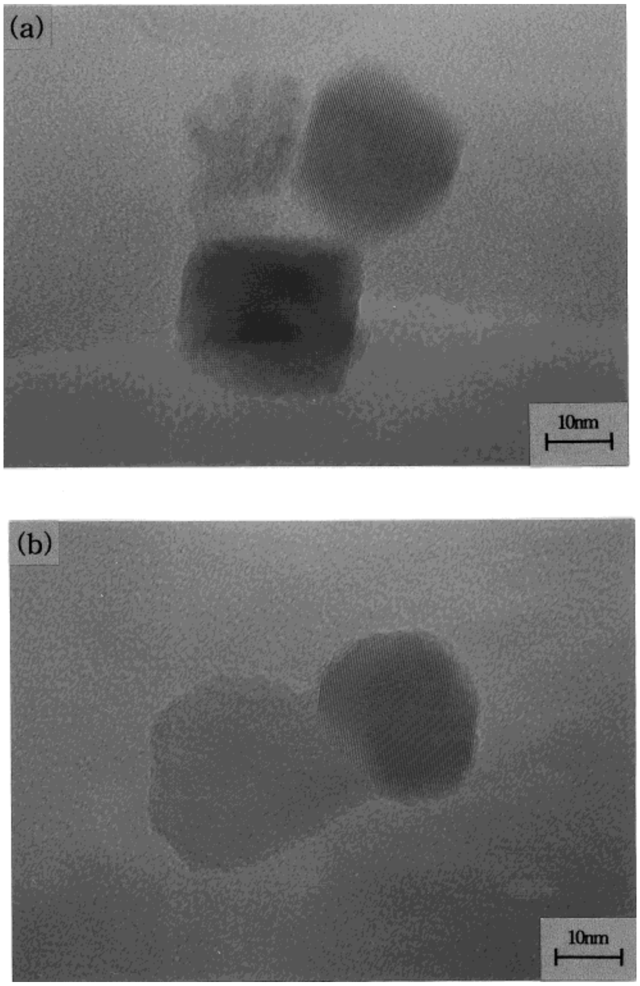

Figure 4. TEM images of ball-milled TiO_2 (a) and MoO_3/TiO_2 (b) particles.

≈30 particles on average. This is consistent with the average particle size data obtained by the light-scattering method.

Role of MoO_3 and WO_3 in Stabilizing Colloidal Suspension. As we have described, by the coverage of MoO_3 or WO_3 on their surfaces, the TiO_2 particles were well-suspended in aqueous solution, and the stability of the colloidal suspension was greatly improved. It is speculated that MoO_3 (or WO_3) on the surface of TiO_2 may accommodate more surfactant molecules, or substantially the surface of MoO_3/TiO_2 (or WO_3/TiO_2) has much more hydrophilic character, compared with that of TiO_2.

The adsorbed amount of surfactant for the ball-milled colloidal particles was determined by the following experiment. The ball-milled TiO_2 suspension was filtered through a 20-nm-size microfilter and washed several times with distilled water. The collected particles were dried and the weight was measured. The samples were then burned at 600 °C for 2 h in oxygen. The weight decrement during the calcination would be tantamount to the amount of the adsorbed cetyltrimethylammonium bromide onto TiO_2 particles. It was found that a 5% weight decrease was observed for pure TiO_2 particles, with a 5% weight decrease for MoO_3/TiO_2 and 6% for WO_3/TiO_2. This indicates that the number of surfactants covering the surface of MoO_3/TiO_2 and WO_3/TiO_2 is virtually the same as that of TiO_2 within measurement error, even though the Lewis surface acidity is greatly different.

The filtered particles obtained from ball-milled suspensions were washed by 0.1 N HCl aqueous solutions several times. The washed samples were then vacuum-dried and the weight changes were measured. The weight losses were coincident with the adsorbed amount of surfactants, which indicates that all the adsorbed surfactants were eluted out by ion-exchange reaction. Thus, it is suggested that surfactants are bound to colloidal particles as a form of ion pair [presumably, a kind of electrostatic interaction between dangling oxygen anions on a TiO_2 (MoO_3 or WO_3) surface and $C_{14}H_{28}(CH_3)_3N^-$]. The above result indicates that the stability of MoO_3/TiO_2 and WO_3/TiO_2 colloids in aqueous solution does not originate from the accommodated surfactant molecules, but from the highly acidic and hydrophilic character of MoO_3 and WO_3.

As indicated by particle size measurements, the colloidal size of MoO_3/TiO_2 in an aqueous suspension is relatively smaller than that of WO_3/TiO_2, even though WO_3 is slightly more acidic than MoO_3. This would be responsible for the solubility of MoO_3 in aqueous solution, different from WO_3. The soluble surface may induce ultra-hydrophilic properties for the MoO_3/TiO_2 particles.

Characterization of Transparent Photocatalytic Films. The suspended TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 particles were then used as coating solutions for the deposition of thin films on Pyrex substrates. For the test of film uniformity, the reflectance spectra in the range of 900−300 nm for the TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 thin films at about 150-nm thickness were obtained by a UV−visible spectrometer. In principle, an optically transparent film differs greatly in reflectance value between the constructive and destructive interference fringes. As illustrated in Figure 6, the interference fringes of MoO_3/TiO_2 and WO_3/TiO_2 films stand in much greater contrast than those of pure TiO_2 films. Especially, the interference pattern of MoO_3/TiO_2 film was as good as that of films obtained by a typical sol−gel process or MOCVD technique.

The surface morphologies of prepared films with 150-nm thickness have been characterized by FESEM, as shown in Figure 7. The surface of TiO_2 film derived from pure TiO_2 suspension looked rough and porous. The size of grains was the same as that of individual TiO_2 particles. On the other hand, MoO_3/TiO_2 and WO_3/TiO_2 films presented a much more uniform surface than pure TiO_2 film. Their surface also looked dense like a film prepared by the MOCVD or sol−gel method. Figure 7d shows the cross-sectional view of the MoO_3/TiO_2 film. No void was observed among the grains, and the roughness of the surface was estimated to be no greater than the size of the individual particles. The surface roughness of TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 films was also observed by AFM, as shown in Figure 8. The average roughness of pure TiO_2 film was 51 nm, while that of MoO_3/TiO_2 and WO_3/TiO_2 films was only 19 and 25 nm, respectively. The roughness result of MoO_3/TiO_2 film is consistent with that obtained from the SEM cross-sectional image.

Photocatalytic Activities of Transparent TiO_2, WO_3/TiO_2, and MoO_3/TiO_2 Thin Films. We evaluated

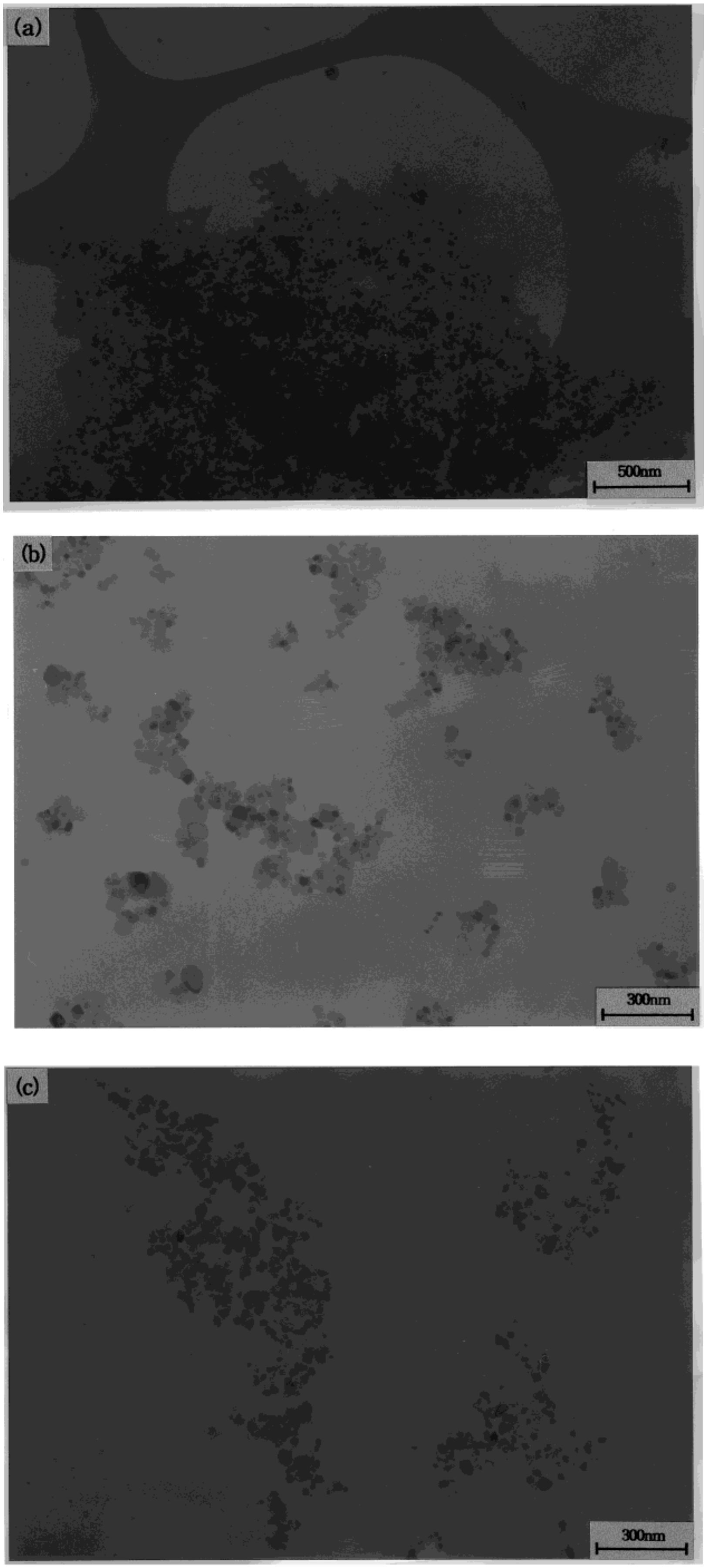

Figure 5. TEM images for TiO_2 (a), MoO_3/TiO_2 (b), and WO_3/TiO_2 (c) suspensions spread on amorphous carbon films.

the photocatalytic activities of pure TiO_2, WO_3/TiO_2, and MoO_3/TiO_2. Because the photocatalytic activity is greatly dependent on the thickness of film, the thickness of each photocatalytic film was fixed to 150 nm in this work,

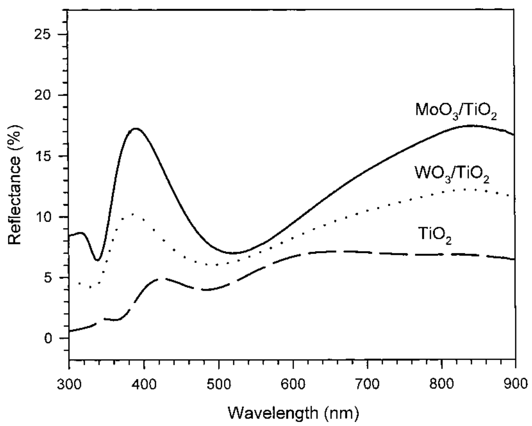

Figure 6. Reflectance spectra of TiO_2, MoO_3/TiO_2, and WO_3/TiO_2 films at about 150-nm thickness.

for the comparison of photocatalytic activity. 2-Propanol was utilized as a model compound for the photocatalytic decomposition of gas-phase pollutant. 2-Propanol is primarily decomposed to acetone and then finally decomposed to CO_2. Thus, the photocatalytic activity was estimated by two methods. First, the decomposition of 2-propanol to acetone was monitored. Figure 9 describes the decomposition rates of 2-propanol with pure TiO_2, WO_3/TiO_2, and MoO_3/TiO_2 films as a function of irradiation time. The amount of remaining 2-propanol after 45 min of irradiation with TiO_2 film was tantamount to that with WO_3/TiO_2 film after 15 min of irradiation. This suggests that the decomposition rate of 2-propanol with WO_3/TiO_2 film is $\approx$3 times that with pure TiO_2 film. Second, the amount of CO_2 evolved was evaluated. Figure 10 describes the amount of CO_2 evolved with the pure TiO_2 and WO_3/TiO_2 films as a function of irradiation time. It was found that the CO_2 evolved in 60-min of irradiation with WO_3/TiO_2 films was 2.8 times that with pure TiO_2. As we have indicated, WO_3 is much more acidic than TiO_2. Thus, WO_3 has a higher affinity for chemical species having unpaired electrons. This would be an important factor in determining the high photocatalytic activity of WO_3/TiO_2.

Different from WO_3/TiO_2 film, MoO_3/TiO_2 film was not effective in decomposing 2-propanol, as described in Figures 9 and 10. The amount of remaining 2-propanol after 45 min of irradiation with MoO_3/TiO_2 film was similar to that with pure TiO_2 film after 15 min of irradiation. This indicates that the decomposition rate of 2-propanol with MoO_3/TiO_2 is only one-third of that with pure TiO_2 film. At the same time, the CO_2 evolved after 60 min of irradiation with MoO_3/TiO_2 films was 26% of that with pure TiO_2. It was found that the MoO_3/TiO_2 film turned pale-blackish during the photocatalytic oxidation reaction of 2-propanol. We examined the change of carbon concentration and oxidation state of Mo on the surface of MoO_3/TiO_2 films before and after the photocatalytic oxidation reaction with X-ray photoelectron spectroscopy (XPS). The measured composition of carbon on the surface of MoO_3/TiO_2 increased to 8 to 13 mol %. The XPS spectra in Figure 11 show that the binding energies of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ for the as-prepared MoO_3/TiO_2 sample are 232.3 and 235.5 eV, respectively, while those for the sample after reaction are 232.5 and 235.7 eV, which are typical binding energies for MoO_3. The slight increase in binding energy suggests that at least MoO_3 is not reduced during the

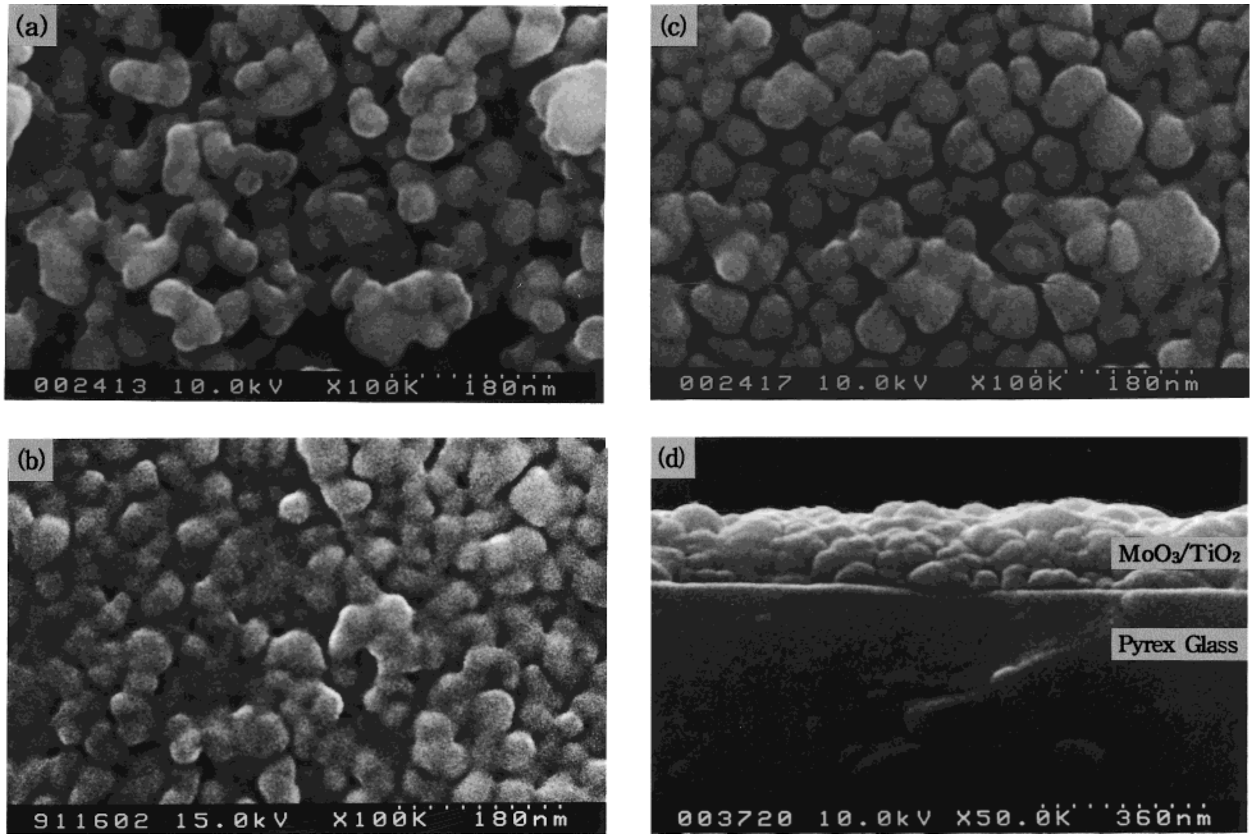

Figure 7. Field emission SEM images of TiO_2 (a), MoO_3/TiO_2 (b), and WO_3/TiO_2 (c). A cross-sectional image of MoO_3/TiO_2 film is shown in (d).

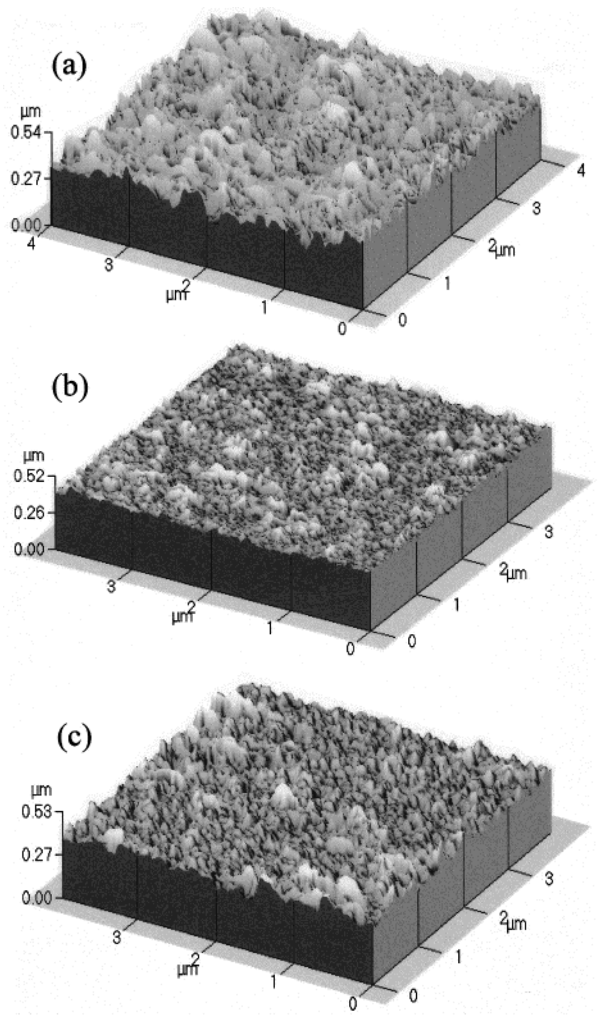

Figure 8. AFM images of TiO_2 (a), MoO_3/TiO_2 (b), and WO_3/TiO_2 (c) films at 150-nm thickness.

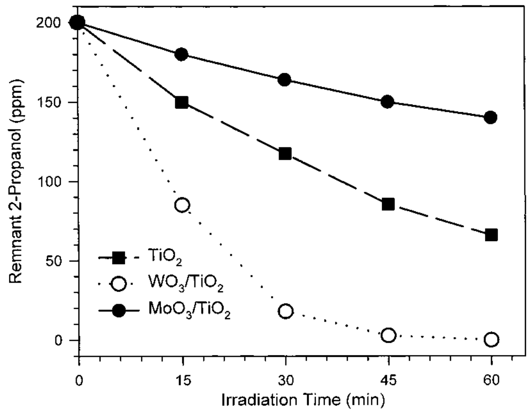

Figure 9. Gas chromatogram recorded for the remaining 2-propanol as a function of irradiation time (2-propanol: 200 ppm; H_2O: 400 ppm; O_2: 690 Torr).

photocatalytic oxidation reaction. We believe that a kind of carbon soot is formed on the film surface that may block the photocatalytic reaction. However, the carbon soot can be eliminated by irradiation with Xe light for several hours. The reason MoO_3/TiO_2 film shows low photocatalytic activity is not clear at this moment, but it is considered that a kind of dehydrogenation reaction has preferentially occurred on the surface of MoO_3/TiO_2 film.

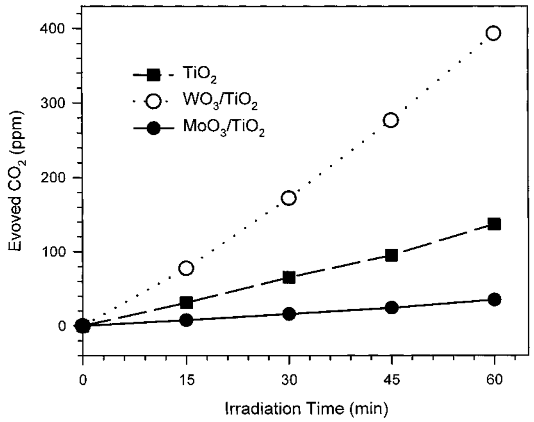

Figure 10. Photocatalytic oxidation rate of 2-propanol to CO_2 with irradiation time (2-propanol: 200 ppm; H_2O: 400 ppm; O_2: 690 Torr).

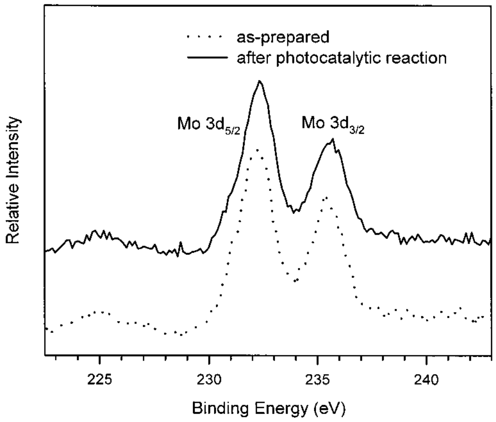

Figure 11. XPS spectra of Mo 3d for the MoO_3/TiO_2 films before and after the photocatalytic oxidation of 2-propanol in 1 h.

Conclusions

With surface modification with MoO_3 or WO_3, the TiO_2 nanoparticles become much more hydrophilic, and they can be more stably suspended in aqueous solution. The average diameter of agglomerated MoO_3/TiO_2 and WO_3/TiO_2 particles in the colloidal suspension is 85 and 110 nm, respectively, while that of pure TiO_2 suspension is 460 nm. It is believed that an excellent dispersibility in aqueous solution originates from the high hydrophilicity of MoO_3 and WO_3.

MoO_3/TiO_2 and WO_3/TiO_2 films obtained by the spin-coating of suspended solutions are optically transparent, and their average surface roughnesses are only 19 and 25 nm, respectively. In addition, WO_3/TiO_2 films are greatly effective for the photocatalytic decomposition of 2-propanol in the gas phase. The decomposition rate of 2-propanol and the amount of CO_2 evolved after 60 min of irradiation with WO_3/TiO_2 films is 3 and 2.8 times greater, respectively, compared with those of pure TiO_2. On the other hand, MoO_3/TiO_2 film was not effective in decomposing 2-propanol. It is considered that a dehydrogenation reaction has preferentially occurred on the surface of MoO_3/TiO_2 film.

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