

Preparation of Highly Ordered Cubic Mesoporous WO₃/TiO₂ Films and Their Photocatalytic Properties

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Highly ordered cubic mesoporous WO₃/TiO₂ thin films were prepared by spin coating via an evaporation-induced self-assembly (EISA) process, employing metal alkoxides as inorganic precursors and Pluronic F127 as a structure-directing agent. With the incorporation of WO₃ into TiO₂, the ordering of the mesopore structure has been appreciably improved. That is, the presence of 2–6 mol % WO₃ retards the crystallization to the anatase phase, and this leads to the relative stabilization of the mesopore structure. The characterization results suggest that the majority of incorporated W species are located at the surface of the mesopore wall instead of doping into the TiO₂ lattice. For the prepared cubic mesoporous WO₃/TiO₂ thin films, the photocatalytic activity in decomposing 2-propanol in the gas phase was optimized at 4 mol % of WO₃ concentration. Its photocatalytic activity was 2.2 times that of a mesoporous TiO₂ film and 6.1 times that of a nonporous TiO₂ film derived from a typical sol–gel method. The enhanced photocatalytic activity of WO₃/TiO₂ is ascribed to the increase in surface acidity.

Introduction

Recently, the fabrication of mesoporous TiO₂ has drawn considerable attention due to the variety of its potential applications such as photocatalysts,¹ electrochromic devices,² photovoltaics,³ host–guest chemistry,⁴ and luminescent devices.⁵ The so-called evaporation-induced self-assembly (EISA) process, initiated by Brinker's group, has realized a facile fabrication of mesoporous TiO₂ in thin film form.^{6–11} With solvent evaporation, the concentration of the surfactant in the sol solution begins to exceed the critical micelle concentration, and the self-assembly procedure is triggered at the same time.^{12–14} The 2D-hexagonal or 3D-cubic mesophase of TiO₂ can be selectively controlled by a subtle

adjustment of the initial sol composition as well as the aging condition during the EISA process.

One of the promising applications of these mesoporous TiO₂ films would be their use as photocatalysts in decomposing pollutants or in generating hydrogen by water splitting.^{15,16} Despite their low crystallinity, the mesoporous TiO₂ structures can be an efficient photocatalyst due to their ultrahigh surface area and greatly organized pore structures. In most cases, mesoporous TiO₂ has been studied for the decomposition of pollutants in aqueous solution.^{17–19} However, they would be more efficient in the treatment of gas-phase organic pollutants since the mass transfer of pollutant molecules into the mesopore of TiO₂ is regarded as a rate-determining step in the photocatalytic reaction and fast diffusion is expected for gas-phase reactants. It is also expected that the cubic mesoporous film would offer higher photocatalytic efficiency than the hexagonal one since the mesopore channels of cubic mesostructures are open on the surface of the film regardless of the mesophase orientation, whereas those of hexagonal mesophases are parallel to the substrate and are not open on the film surface.

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Previously, we modified the surface of TiO₂ nanoparticles (Degussa P25) with WO₃.^{20,21} The TiO₂ nanoparticles covered with a monolayer of WO₃ were much less agglomerated and more stably suspended in aqueous solution. Furthermore, the photocatalytic activity in decomposing gaseous 2-propanol was greatly improved owing to the dramatic increase in surface acidity. Similar results have also been observed by several other research groups.^{22–24} Thus, it is expected that the WO₃-incorporated TiO₂ (WO₃/TiO₂) in the form of a mesoporous structure can further enhance photocatalytic efficiency.

The preparation of TiO₂-based composite mesoporous materials is currently attracting attention.^{25–29} For example, Bartl et al. thermally post-treated Cd²⁺-doped TiO₂ films with sulfur or selenium vapor. Then the synthesized mesoporous CdS/TiO₂ and CdSe/TiO₂ thin films showed an enhanced sensitivity to visible light.^{25,26} Grosso et al. synthesized several mesoporous TiO₂-based binary metal oxide thin films with high thermal stability such as SrTiO₃ and Co_{0.15}-Ti_{0.85}O_{1.85} dielectric materials.²⁷ Frindell et al. reported that the addition of Ce(III) improves the long-range ordering of mesoporous TiO₂ films.²⁹ Lu et al. reported WO₃/TiO₂ mesoporous films applicable to bio-photoelectrodes.³⁰ However, the prepared mesoporous film had a wormlike structure, and the precise analysis of the composite structure was not provided.

In this paper, we report a facile and reproducible method for the preparation of highly ordered transparent cubic mesoporous WO₃/TiO₂ thin films with various compositions of WO₃. In the previous report, we indicated that the mesophases of TiO₂ thin films were selectively controlled by the speed of spin coating during the EISA process.³¹ The cubic mesoporous TiO₂ thin films were obtained by spin coating at a low rpm, while the 2-D hexagonal mesoporous films were prepared at a high spin-coating speed. In the present work, the structure of cubic mesoporous WO₃/TiO₂ films derived by this method was fully characterized by XRD, TEM, XPS, Raman and UV–visible spectroscopy, and surface acidity measurement. WO₃/TiO₂ thin films were then tested as photocatalysts in decomposing gas-phase organics, and the role of WO₃ in photocatalytic behavior was also discussed.

Experimental Section

Preparation of Cubic Mesoporous TiO₂ and WO₃/TiO₂ Films and Nonporous TiO₂ Film. Cubic mesoporous TiO₂ and WO₃/TiO₂ thin films were derived from the mixed metal alkoxides in stoichiometric ratio stabilized in an acidic ethanol solution containing triblock copolymer. The preparation method was based on our previous report on mesoporous TiO₂ thin films.³¹ In a typical experiment, titanium tetraisopropoxide (TTIP, 97%, Aldrich) was dissolved and stabilized in ethanol solution acidified with aqueous HCl for 10 min at room temperature. Tungsten(V) pentaethoxide (95%, Gelest), stabilized by 2 equiv of 2,4-pentadione, was then added with vigorous stirring. After the solution was stirred for an additional 10 min, the resultant W–Ti sol was added to the Pluronic F127 (Aldrich) ethanol solution dropwise. The molar ratio of the final composition in the Ti–W sol was as follows: (Ti + W)/F127/HCl/H₂O/ethanol = 1:0.005:1.75:10:25. The transparent sol was aged under mild agitation for 3 h and then deposited on a precleaned Pyrex glass (2.5 × 2.5 cm²) substrate by spin coating. The spin speed was raised to 600 rpm with an acceleration of 300 rpm/s, and it was then maintained for 5 s. The resulting films were aged for 3 days in a closed chamber, the relative humidity (RH) of which was maintained at 60% by a saturated Mg(NO₃)₂ aqueous solution. The removal of F127 used as a liquid-crystal template was carried out by heating at 400 °C for 4 h (ramping rate: 1 °C/min) in air. The thickness of each calcined film was controlled to 300–320 nm.

For the comparison, TiO₂ films without the pore structure were prepared by a typical sol–gel method. TTIP (0.020 mol) was dissolved in 10 mL of *n*-propanol, and 0.040 mol of 2,4-pentadione was then added dropwise while cooling. An additional 14 mL of *n*-propanol and 1 mL of 0.1 M nitric acid were then added and stirred for 4 h to prepare the 0.8 M Ti-sol solution. The prepared Ti-sol was deposited on a Pyrex substrate by spin coating at 2000 rpm for 20 s, and the coated film was subsequently baked at 150 °C. After three coating and baking cycles, the resultant film was calcined at 400 °C for 4 h to obtain a nonporous anatase TiO₂ film with a 300 nm thickness.

Characterization of Mesoporous WO₃/TiO₂ Thin Films. X-ray diffraction (XRD) patterns for the TiO₂ and WO₃/TiO₂ films were obtained by using a Rigaku Multiflex diffractometer with a monochromated high-intensity Cu K α radiation. XRD scanning was performed under ambient conditions over the 2 θ region 0.8–4° at the rate of 0.1°/min (20 kV, 10 mA) and 20–60° at 2°/min (30 kV, 20 mA), respectively.

For the observation of prepared mesoporous thin films by TEM (Hitachi S-4500 transmission electron microscope operated at 250 kV), the samples were peeled off from the substrate, and the collected flakes were gently dispersed in methanol. The suspension was then dropped on a holey amorphous carbon film deposited on a Ni grid (JEOL Ltd.).

The optical transmissions for the films were recorded by a UV–visible spectrophotometer (Perkin-Elmer Lambda 40) in the wavelength range of 200–800 nm. Raman spectra were recorded on a FT Raman spectrophotometer (Bruker, RFS-100/S) equipped with a room-temperature InGaAs diode detector. The 514.5 nm line from the Ar⁺ laser beam was used as an exciting source. The output of the incident laser power was about 130 mW, and the resolution of the spectra was 2 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) analyses of the mesoporous WO₃/TiO₂ thin films were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below 5 × 10⁻⁹ Torr at room temperature. Photoemission spectra were recorded by a Sigma Probe Instrument (Thermo VG, U.K.) equipped with a standard monochromatic Al K α excitation source ($h\nu = 1486.6$ eV). The pass

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energy and step size of low-resolution XPS scan were performed at 50 and 10 eV, respectively. For the high-resolution XPS scan, the parameters above were adjusted to 20 and 0.1 eV. The binding energy (BE) scale was calibrated by measuring a C 1s peak at 284.5 eV from the surface contamination. The resultant XPS spectra were simulated by assuming the photoelectron peaks as Gaussian line shape.

For the measurement of surface acidity, each mesoporous film was prepared in a large area and was scraped to obtain a 0.1 g of sample. The 0.1 g mesoporous sample was suspended in doubly distilled benzene and then titrated with 0.03 N *n*-butylamine benzene solution, using methyl red as an indicator whose endpoint lies between pH 4.8 and 5.9.

Measurement of Photocatalytic Activity. Cubic mesoporous TiO₂ and WO₃/TiO₂ thin films 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.³² A mesoporous film was located in the center of a gastight reactor with a net volume of 200 mL. With injection of 1.6 and 3.2 μ L of liquid 2-propanol and water, respectively, their partial pressures in the reactor were adjusted to 2 and 16 Torr, respectively. The total pressure of the reactor was then controlled to 700 Torr by adding 682 Torr of oxygen gas. The gas mixtures in the reactor were magnetically convected during the irradiation. The mixture of UV and visible light, which was generated from a 300 W Xe lamp equipped with a water filter to cut off infrared, was used as the irradiation source. On the surface of the photocatalytic film, the overall light intensity was 1.0 W/cm². After irradiation for a certain period of time, 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). The evolved CO₂ and remnant 2-propanol were detected by a methanizer installed between the GC column outlet and the FID detector.

Results and Discussion

The long-range ordering of the mesopore structure for the WO₃/TiO₂ composite films was analyzed by small-angle XRD patterns, as indicated in Figure 1a. The fwhm's of the (200) peak for the pure TiO₂ and 2, 4, 6, and 8% WO₃/TiO₂ films are 0.184, 0.157, 0.148, 0.172, and 0.202°, respectively. The (200) peak of the 4% WO₃/TiO₂ mesoporous film is considerably more narrow, and its peak intensity is twice that of the pure TiO₂ film. This indicates that the ordering of the mesopore structures can be notably improved by the incorporation of WO₃. Also the (110) and (111) peaks, which were obscure in the pure mesoporous TiO₂ film, were clearly resolved for 2 and 4% WO₃/TiO₂ films. From the relative positions of these diffraction peaks, the prepared mesostructures were determined to be the *Im* $\bar{3}m$ 3D cubic phase.^{1,5,7} A further increase in WO₃ over 4 mol % decreased the ordering of the mesopore array. Wide-angle XRD patterns obtained from several WO₃/TiO₂ films are shown in Figure 1b. Regardless of the WO₃ concentration, they were shown as pure anatase without impurity phases. However, the intensity of the (101) peak at 25.6° gradually decreased, and its peak width was broader with an increase in WO₃ compositions in the TiO₂ mesoporous film. Obviously, the incorporation of WO₃ hindered the crystallization of TiO₂

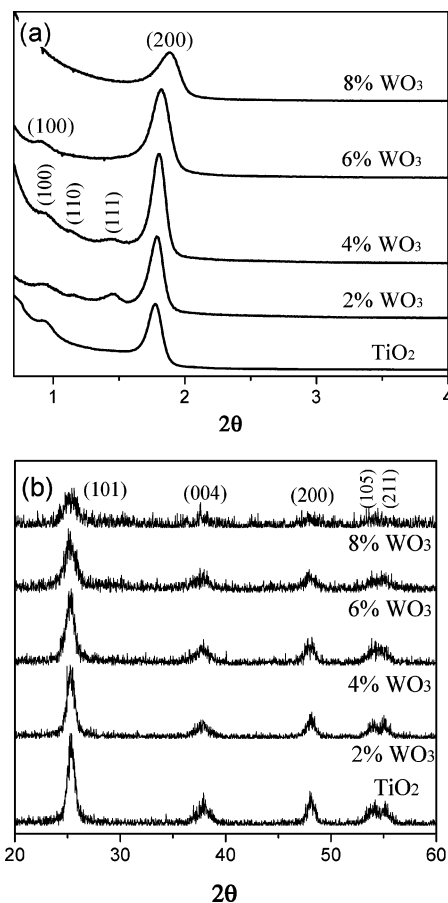


Figure 1. Small-angle (a) and wide-angle (b) XRD patterns for the mesoporous WO₃/TiO₂ thin films calcined at 400 °C.

during the calcinations at 400 °C. In general, the mesopore structures are becoming distorted or collapsed while crystallizing at the calcination temperature, and this lowers the long-range ordering of the mesopores, as commonly observed in the formation of bulk mesoporous transition metal oxides. Thus, we suggest that the improvement of long-range ordering for the mesoporous WO₃/TiO₂ film is caused by the comparatively low crystallinity.

TEM images for several mesoporous WO₃/TiO₂ films calcined at 400 °C are shown in Figure 2. The films containing 2, 4, and 6 mol % of WO₃ had highly ordered cubic mesoporous structures. The *d*(100) of the cubic mesopore was estimated at 10.0 nm, which corresponds to the result of 10.03 nm determined from the XRD patterns. On the other hand, the ordering of mesopores for the film containing 8 mol % of WO₃ was not so high. Its mesophase was regarded as a mixture of the cubic and wormlike structure. The overall trend of long-range ordering as a function of WO₃ concentration was consistent with the results of small-angle XRD.

Figure 3 shows the UV–visible spectra indicating the transparency of the mesoporous WO₃/TiO₂ films in a thickness of about 300 nm. All the mesoporous films showed higher transmittance than 80% over the entire visible light range, which would be caused by their high porosity and surface uniformity. However, the transmittance of the WO₃/TiO₂ films was gradually decreased with an increase in incorporated WO₃. The segregated amorphous WO₃ domains

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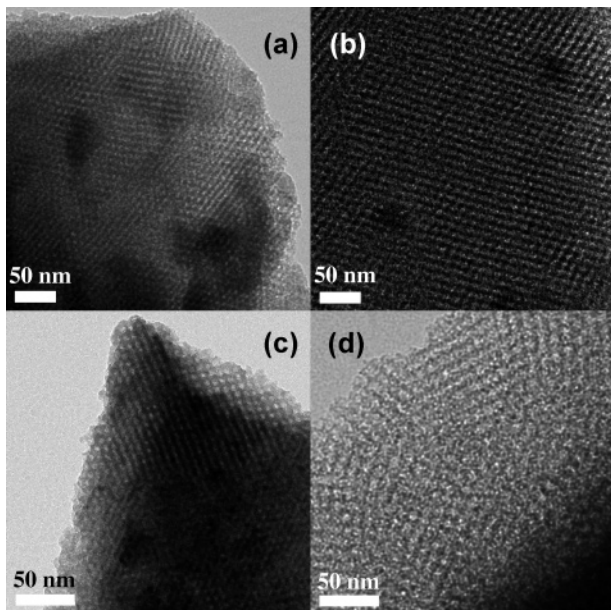


Figure 2. TEM images for several mesoporous WO_3/TiO_2 thin films calcined at 400°C . The concentrations of WO_3 are 2 (a), 4 (b), 6 (c), and 8 (d) mol %.

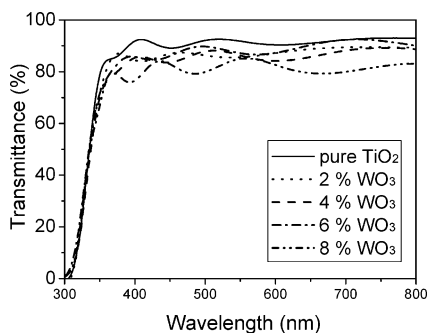


Figure 3. Transmittance spectra obtained by a UV-visible spectrophotometer for the cubic mesoporous TiO_2 and several WO_3/TiO_2 thin films calcined at 400°C .

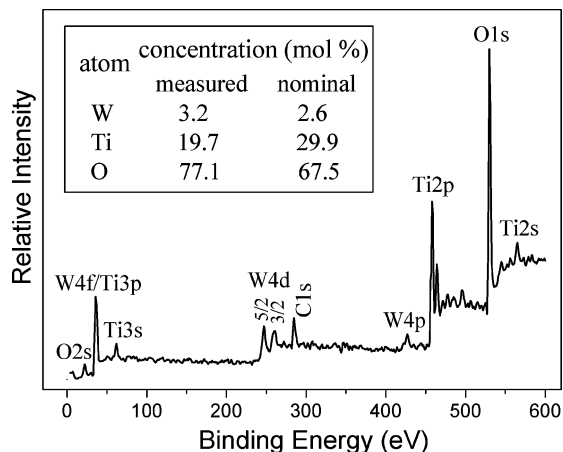


Figure 4. XPS survey spectrum of the mesoporous 8 mol % WO_3/TiO_2 thin films calcined at 400°C .

on the surface of TiO_2 mesopores or in the grain boundaries could be responsible for this loss in transmittance.

XPS measurements were performed to elucidate the surface chemical composition and the oxidation state for the mesoporous WO_3/TiO_2 thin films. Figure 4 shows the XPS survey spectrum for the mesoporous 8 mol % $\text{WO}_3/92$ mol % TiO_2 film calcined at 400°C . The XPS peaks indicate

Table 1. XPS Analysis Result for the Cubic Mesoporous TiO_2 and WO_3/TiO_2 Thin Films

peaks	TiO_2	4% WO_3	8% WO_3	
Ti 2p _{3/2}	458.50	458.44	458.37	
Ti 2p _{1/2}	464.28	464.00	463.89	
Ti 3p		37.04	37.10	
O 1s	(Ti-O)	529.96	529.89	529.81
	(-OH)	531.33	531.95	532.01
	(C-O)	532.78	533.01	533.06
	(H ₂ O)		534.26	534.30
W 4f _{7/2}		35.22	35.27	
W 4f _{5/2}		37.42	37.47	

that the WO_3/TiO_2 films contain Ti, W, O, and trace amounts of carbon, which originates from the residual carbon in the mesoporous film and the adventitious hydrocarbon in the XPS instrument itself. The determined concentration of W was 1.8 times higher than that of the nominal one, suggesting that relatively more W species are present on the surface of the mesoporous film (see inset of Figure 4). Figure 5 shows the high-resolution XPS spectra of Ti 2p, O 1s, and W 4f, which were taken on the surfaces of pure TiO_2 and 4 and 8% WO_3/TiO_2 mesoporous thin films, respectively. With the incorporation of W species, the intensity of Ti 2p was considerably decreased. This also suggests that relatively more W species are present on the surface of the mesopore structure. In addition, the binding energy of Ti 2p was slightly decreased as indicated in Figure 5a and Table 1. The slight decrease in binding energy suggests that some of Ti^{4+} is converted to a lower oxidation state, such as Ti^{3+} . As shown in Figure 5b, the O 1s band has been greatly modified with the introduction of the W species. For the pure mesoporous TiO_2 , three oxygen contributions were taken into account. The peak at 529.96 eV was assigned to the oxygen bound to Ti, while the other peaks were related to the hydroxyl groups (BE = 531.33 eV) and the oxygen in C-O or C=O bonds (BE = 532.78 eV), respectively. On the other hand, the O 1s region of WO_3/TiO_2 was considerably broader and was fitted with four peaks. The peak at 529.8–529.9 eV contained contributions from both the Ti-O and W-O, which have similar binding energies. Besides the -OH and C-O peaks, an additional O 1s peak at around 534.26–534.30 eV appeared. This was assigned to the adsorbed H_2O on the surface of WO_3/TiO_2 mesoporous films. Also, the intensity of the -OH peak was considerably increased, compared to that of the pure mesoporous TiO_2 films. This clearly indicates that the mesoporous WO_3/TiO_2 composite thin films calcined at 400°C have more hydroxyl groups as well as surface-adsorbed water. As shown in Figure 5c, the determination of the exact peak positions of W 4f_{7/2} and 4f_{5/2} was difficult because of the overlap with the Ti 3p peak. However, their positions are virtually the same as those of pure WO_3 , suggesting that the oxidation state of the incorporated tungsten species is +6.

The Raman spectra of the mesoporous WO_3/TiO_2 thin films with different molar ratio calcined at 400°C are shown in Figure 6. The bands at ca. 147, 196, 397, 516, and 639 cm^{-1} originate from the anatase phase of TiO_2 . By introducing WO_3 , an additional broad band appeared at ~ 975 cm^{-1} . This was assigned to a terminal W=O stretching band which

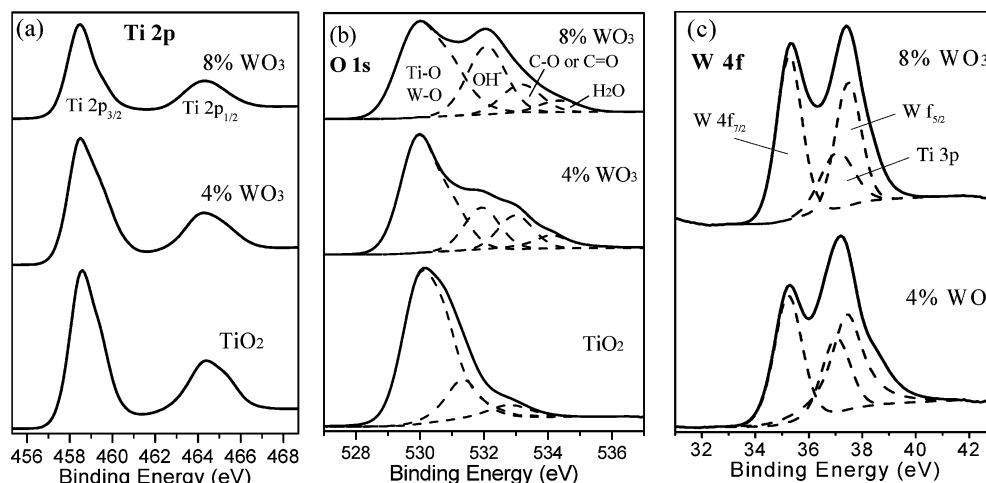


Figure 5. High-resolution XPS spectra and simulated Gaussian line shapes of Ti 2p (a), O 1s (b), and W 4f (c) region taken on the surface of pure TiO₂ and 4 and 8 mol % WO₃/TiO₂ mesoporous thin films.

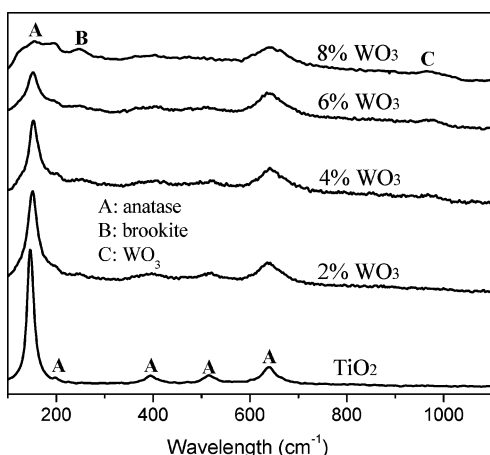


Figure 6. Raman spectra of several mesoporous WO₃/TiO₂ films calcined at 400 °C.

is common for all types of tungsten trioxide hydrates.^{23,33,34} This supports the XPS result that adsorbed H₂O is contained in the WO₃/TiO₂ samples. However, the O–W–O stretching band at $805 \pm 5 \text{ cm}^{-1}$, the main peak of crystallized monoclinic or orthorhombic WO₃, did not appear at all. This suggests that most of the incorporated WO₃ is highly dispersed over the TiO₂ mesoporous structure without forming large crystallized structures at 400 °C.

With an increase in incorporated WO₃, the bands from the anatase phase were gradually decreased in intensity and became broader. This is ascribed to the lower crystallinity of the anatase phase and is consistent with the results of the XRD patterns. In the Raman spectra, a weak peak at 246 cm^{-1} , considered to be originated from the brookite phase, which was not resolved by XRD, appeared. Its peak intensity increased with a corresponding increase in WO₃ concentration. Presumably, the incorporation of WO₃ in TiO₂ promotes the evolution of the brookite phase, while suppressing the formation of the anatase phase.

The photocatalytic activities of cubic mesoporous TiO₂ and WO₃/TiO₂ films of 300 nm thickness were evaluated.

2-Propanol was utilized as a model compound for the photocatalytic decomposition of a gas-phase pollutant. It was initially decomposed to acetone and then finally mineralized to CO₂ and H₂O. Thus, the photocatalytic activity was estimated in two ways. First, the decomposition of 2-propanol was monitored, as shown in Figure 7a. The photocatalytic decomposition was plotted as irradiation time vs $\ln[c]$, with the approximation of first-order kinetics.²⁰ That is, the photocatalytic reaction can simply be described by $-d[c]/dt = k_r[c]$, where $[c]$ is the concentration of gaseous 2-propanol, t is the irradiation time, and k_r is the overall rate constant. Here, we defined the photocatalytic activity as k_r . Compared with the nonporous film derived from the spin coating of Ti-sol solution, the cubic mesoporous pure TiO₂ films presented 2.7 times greater photocatalytic activity in decomposing 2-propanol. The increase in photocatalytic activity despite the low crystallinity for the mesoporous structure would be due to the ultrahigh surface area of the mesoporous TiO₂. By the incorporation of WO₃ into the TiO₂ mesoporous structure, the photocatalytic activity was even more enhanced. The photocatalytic activity was maximized at 4 mol % of WO₃, and a further increase over 4% rapidly decreased its efficiency. The 4 mol % WO₃/TiO₂ cubic mesoporous film demonstrated 2.2 and 6.1 times greater photocatalytic efficiency than the pure cubic mesoporous TiO₂ film and the nonporous TiO₂ films, respectively. In evolving CO₂, a similar trend was observed, but the increment was relatively lower, as described in Figure 7b. It was found that the CO₂ evolved in 60 min of irradiation with 4 mol % mesoporous WO₃/TiO₂ films was 1.5 times greater than that with the pure mesoporous TiO₂ films. Likewise, it was 2.8 times greater than that with the nonporous TiO₂ films.

Figure 8 shows the acidity of mesoporous WO₃/TiO₂ as a function of the WO₃ composition. By the incorporation of WO₃, the surface acidity of the resultant mesoporous structures was considerably increased due to the highly acidic nature of WO₃. For the initial addition of WO₃, especially, the increment was very large. That is, by the introduction of 1 and 2 mol % WO₃, the surface acidity went up from 0.13 to 0.22 and 0.30 mmol/g, respectively. However, with a higher concentration of WO₃ over 6 mol %, the surface

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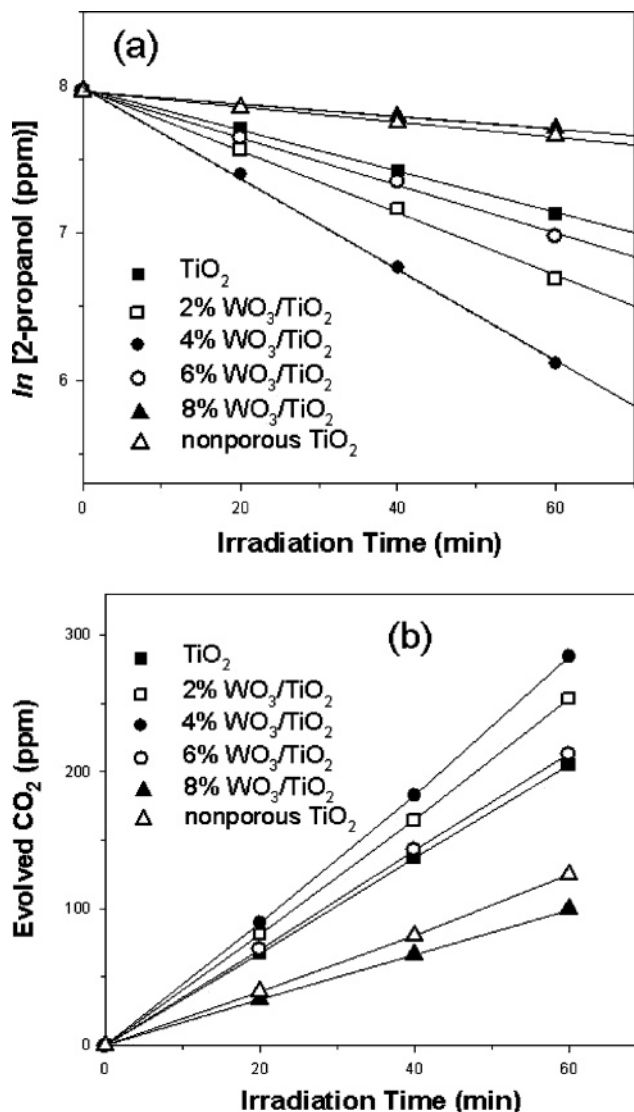


Figure 7. Photocatalytic decomposition rate of 2-propanol to acetone (a) and evolution rate of CO₂ (b) with several cubic mesoporous and nonporous films.

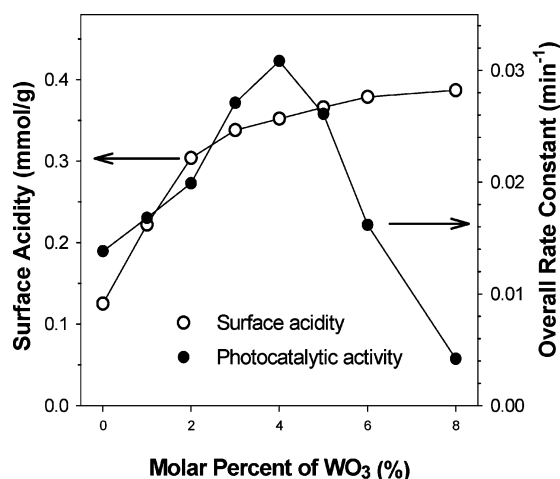


Figure 8. Surface acidity and photocatalytic activity of the mesoporous WO₃/TiO₂ thin films as a function of WO₃ concentration.

acidity was not appreciably changed. In Figure 8, the trend of photocatalytic activity as a function of WO₃ composition is also illustrated. The photocatalytic activity in decomposing 2-propanol was optimized in the range of 3–5 mol % of

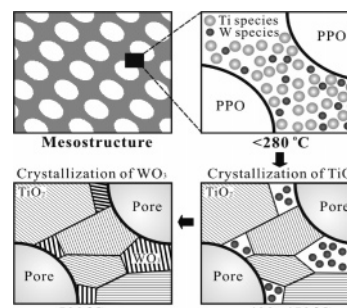


Figure 9. A scheme for the formation of the mesostructured WO₃/TiO₂ binary system during the heat treatment.

WO₃, where the surface acidity reached a plateau region. This result was similar to our previous reports on the surface modification of TiO₂ particles with WO₃.^{20,21}

With the introduction of WO₃, the increase in surface area was not appreciable. The surface area of the cubic mesoporous TiO₂ film was 114 m²/g, while that of the WO₃/TiO₂ films containing 2–8 mol % of WO₃ was 120–130 m²/g. Thus, the enhancement of photocatalytic activity was not caused by the increase in surface area. As was reported previously, we believe that it is mainly due to the increase in surface acidity with the introduction of WO₃.^{19–22} That is, as analyzed by the O 1s XPS spectra, the WO₃/TiO₂ thin films can adsorb a greater amount of organic molecules and OH⁻ or H₂O, which are necessary to initiate the photocatalytic reaction.

The crystallization of TiO₂ during the formation of the mesoporous structure by the EISA process has been delayed markedly compared to that of films derived by the typical sol–gel method. Several groups have reported that the mesoporous TiO₂ films calcined at 350 °C remained in the amorphous phase,^{10,18,30} and that the phase transition to anatase was not complete even at 400 °C. By the addition of the W species, the crystallization of TiO₂ is further suppressed, as shown by the XRD data (Figure 1b). In general, a solid solution between TiO₂ and WO₃ can be formed with a heat-treatment temperature higher than 700 °C.^{35,36} Even in this case, the level of WO₃ doping is lower than 1 mol %. Furthermore, it is well-known that the crystallization temperature of WO₃ is higher than that of TiO₂.²³ During the aging and drying steps in the EISA process, the Ti and incorporated W species are assumed to be mixed up uniformly, even though the complete mixing at the atomic level is not confirmed with the different reactivity and kinetics between the Ti and W precursors. With the subsequent heat treatment reaching up to 400 °C, TiO₂ itself will be crystallized first without forming a solid solution with WO₃. Thus, the remaining W species would be expelled to the grain boundary of the TiO₂ crystallites or to the surface of the mesopores, as suggested in Figure 9. Since the surface area of the mesopore is very large and the thickness of the wall is less than 7 nm, which is smaller than the typical grain size of TiO₂, the majority of WO₃ would be located on or near the surface of a mesopore. At a low concentration of

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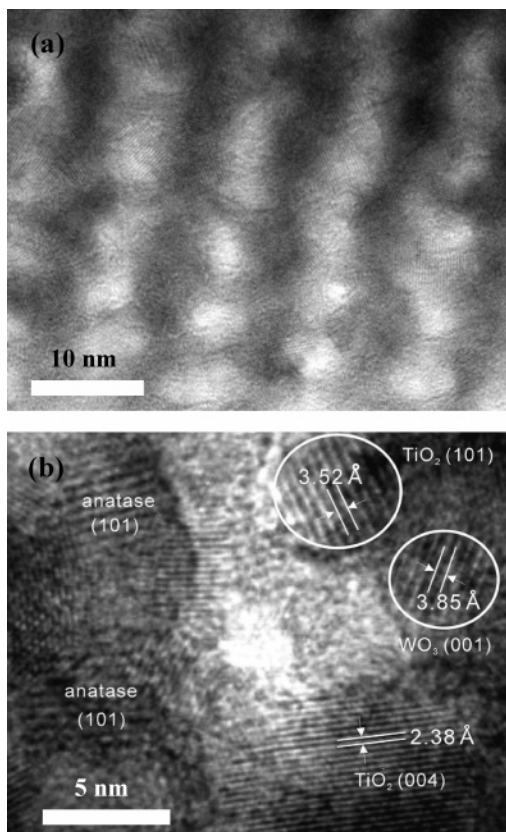


Figure 10. Representative HRTEM images for cubic mesoporous 6 mol % WO₃/TiO₂ thin films calcined at 400 °C (a) and 500 °C (b).

WO₃, it is expected that WO₃ preferentially binds to the surface of the TiO₂ grains with a high binding affinity between the TiO₂ and WO₃. Thus, most of the WO₃ exists in a form of highly dispersed molecular species on the surface of the TiO₂ mesopore. If the concentration of WO₃ is high, the extra WO₃ will be segregated by itself. This is clearly supported by the surface acidity result in which the surface acidity of WO₃/TiO₂ was dramatically increased with the initial addition of WO₃, whereas it was not appreciably increased at the higher concentrations of WO₃ over 4 mol %. In this circumstance, the state of WO₃ would be the mixtures of highly dispersed molecular species, clusters, and segregated domains with low crystallinity.

To monitor the definite morphology of the incorporated WO₃ in the mesostructure, the cubic mesoporous WO₃/TiO₂ thin films containing 6 mol % of WO₃ were examined by high-resolution TEM. As shown in Figure 10a, the crystallinity of the cubic mesoporous film calcined at 400 °C was not high enough for a structural analysis. For the observation of the crystallized structure of WO₃, the same mesoporous sample was heat-treated at 500 °C, but the identification of the WO₃ phase by TEM was still very difficult since the WO₃ is not sufficiently crystallized at this temperature and is presumably well-dispersed as small clusters along the surface or grain boundaries of TiO₂. After several trials done and errors incurred, a crystallized WO₃ grain was monitored in a certain area around a mesopore, as indicated in Figure 10b. The fringe spacing of 3.85 Å was indexed to the (001) plane of the orthorhombic WO₃ phase.

Conclusions

In this work, we have synthesized transparent and highly ordered cubic mesoporous WO₃/TiO₂ thin films by the EISA process. We found that the introduction of 2–6 mol % WO₃ in TiO₂ mesoporous structures hinders the crystallization of the anatase phase, but the long-range ordering of the mesostructure was appreciably more organized. The characterization data for the films annealed at 400 °C indicate that the incorporated W species exist as WO₃ and that the majority of the WO₃ are located around the surface of mesopores instead of doping into TiO₂ lattice. This is because WO₃ and TiO₂ do not form a solid solution at this temperature and the crystallization temperature of WO₃ is relatively higher than that of TiO₂. By the incorporation of WO₃ the photocatalytic activity in decomposing gaseous 2-propanol was enhanced, and it was maximized at 4 mol % of WO₃. The enhanced photocatalytic activity of WO₃/TiO₂ was ascribed to the increased surface acidity which was induced by the WO₃ present on the surface of the mesopores.

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