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Effect of surface microstructure on the photoinduced hydrophilicity of porous TiO_2 thin films

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The relationship between photoinduced hydrophilicity and surface microstructure of porous TiO_2 thin films has been investigated. Porous TiO_2 thin films on soda-lime glass were prepared by the sol–gel method from alkoxide solutions containing polyethylene glycol (PEG). These materials were characterised by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and UV-Vis transmittance measurements. The larger the amount of PEG used in preparing the thin films, the larger was the pore size produced from the thermal decomposition of PEG. This generated also a relatively rough thin film surface with a strong affinity for hydroxyl groups. This study proves that suitable surface microstructures can enhance the photoinduced super-hydrophilic properties of porous TiO_2 thin films and hinder the conversion from a hydrophilic to a hydrophobic state. Among the porous TiO_2 thin films tested, the one with a PEG to TiO_2 mass ratio of 12.5% exhibited the best photoinduced super-hydrophilic property and the slowest conversion rate from the hydrophilic to a hydrophobic state.

1. Introduction

Titanium dioxide photocatalysis has long been a subject of interest ever since Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes in 1972.[1] Recently, the application of TiO_2 has been focused on purification and treatment of water and air, which is an important aspect in environmental protection.[2–4] However, there is an intrinsic drawback with the conventional powder catalysts. A post-treatment separation step is required in such a slurry type system. The coating of catalysts as thin films will overcome this limitation and extend its industrial applications. Therefore, TiO_2 thin film photocatalysts have received a great deal of attention.[5–10]

A discovery on TiO_2 amphiphilic surfaces was reported by Wang *et al.* in 1997: UV illumination of TiO_2 polycrystal or single crystal materials can generate surfaces that display 0° contact angle for both water and oily liquids.[11–14] The mechanism of the photoinduced hydrophilicity and hydrophobicity of TiO_2 has been intensively investigated by many researchers.[11–20] Studies by IR, XPS and AFM revealed that the concentration of OH groups on the surface of a TiO_2 thin film increases upon UV illumination, Ti^{4+} ions on TiO_2 surfaces are reduced to Ti^{3+} ions and the characteristics of charge transfer between Ti ions and adsorbents such as hydroxyl ions and/or oxygen can be altered by UV radiation. UV illumination can also produce unique hydrophilic and hydrophobic microdomain structures on the surface. When TiO_2 thin films are irradiated by UV light, their water contact angle decreases gradually, and finally becomes almost zero. However, a typical non-porous TiO_2 thin film cannot maintain this hydrophilic state. As soon as the thin film is placed in the dark, the water contact angle increases. From a practical point of view, it is desirable for the contact angle to remain low or rise only very slowly in the dark. In order to obtain these characteristics, we should investigate the influence of surface microstructure on the photoinduced hydrophilic property of thin films. It is well known that the wettability of solid surfaces with liquids is governed not only by the chemical properties of the surfaces but also by their geometry.[21–24] As far as the geometry of a surface is concerned, the hydrophilic properties are known to be enhanced by fine roughness.[21–23] Therefore, the control of the microstructure of the surfaces of thin films is a way to improve their hydrophilic properties. Of course, the chemical properties of the surfaces is another important factor which affects the hydrophilic properties.[22–24] With an increase in chemically adsorbed –OH on the surface, the polar properties and hydrophilicity of the surface are enhanced.[22–23] Very recently, Lee *et al.* and Miyauchi *et al.* have reported the influence of surface morphology and composition on photoinduced super-hydrophilic properties.[24,25] However, to our knowledge, the effect of surface microstructure on the photoinduced hydrophilic property of sol–gel derived porous TiO_2 thin films has not been reported yet.

In the present work, transparent porous anatase TiO_2 nanometer thin films were prepared on soda-lime glass by the sol–gel method, and characterised by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), UV-Vis spectrophotometry and X-ray diffraction (XRD). The mechanism of the photoinduced hydrophilic properties of porous TiO_2 thin films is also discussed.

2. Experimental

2.1. Preparation

Precursor solutions for porous TiO_2 thin films were prepared by the previously described method using tetrabutylorthotitanate, ethanol, water, diethanolamine and PEG with an average molecular weight of 2000.[8] Tetrabutylorthotitanate (17.0 ml) and diethanolamine (4.8 ml) were dissolved in ethanol (67.3 ml). After stirring vigorously for 2 h at room temperature, water (0.9 ml) and ethanol (10.0 ml) were mixed together and added to the solution. The molar ratio of water to the

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alkoxide was 1. A set of five thin films were prepared by adding 0, 0.25, 0.5, 1.0 and 2.0 g PEG in 100 mL precursor solutions. The PEG to TiO_2 mass ratios in the films were calculated to be 0, 6.25, 12.5, 25.0 and 50%, respectively. The solutions containing various amounts of PEG were transparent and light yellow. Glass slide plates (75 mm × 25 mm × 1.5 mm) were used as the support substrates. They were carefully cleaned by using ultrasonic treatment with base, aqueous acid solution, distilled water and alcohol, consecutively, and dried at 100 °C. The TiO_2 thin films were prepared by a dip-coating method. The withdrawal speed was 1 mm s^{-1}. Gel thin films were dried at 100 °C for 60 min and then carefully heat-treated in air. The temperature was elevated rapidly (6 °C min^{-1}) to 520 °C and kept at 520 °C for 1 h. The PEG contained in the gel coating films decomposed completely at 520 °C. The thickness of the TiO_2 coating films was adjusted by repeating the cycles from withdrawing to heat treatment.

2.2. Characterisation

Surface roughness and morphologies of TiO_2 thin films were evaluated by atomic force microscopy (AFM: Nano Scope 3a, Digital Instruments Inc., Santa Barbara, CA) in the contact mode using conventional silicon nitride cantilevers under ambient conditions (*i.e.* 295 K, relative humidity [RH]: 50%, air). Crystalline phase of films was measured by X-ray diffraction (XRD: RINT-2100, Rigaku Co. Tokyo, Japan). UV-Vis spectra of films were obtained using a UV-Visible spectrophotometer (UV-160A, Shimadzu, Japan). TiO_2 thin films were analyzed by X-ray photoelectron spectroscopy (XPS), using a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh-vacuum (UHV) chambers; the pressure in the chambers during the experiments was about 10^{-7} Pa. A Mg Kα X-ray source was used. The analyzer was operated at 20 eV pass energy for high-resolution spectra and 50 eV for survey spectra. The X-ray photoelectron spectra were referenced to the C_{1s} peak ($E_b = 284.80$ eV) resulting from the adventitious hydrocarbon (*i.e.* from the XPS instrument itself) present on the sample surface.

2.3. Contact angle

The sessile drop method was used for contact angle measurements with a contact angle meter (Cam-Micro, Tantec Inc., USA). The experimental error of the measurements was $\pm 1°$. The droplet size used for the measurements was 5 μL. Water droplets were placed at five different positions for one sample and the average value was adopted as the contact angle. The water contact angles (θ) for freshly prepared TiO_2 thin films and porous TiO_2 thin films were about 15° and 3°, respectively. However, when these samples were stored in the dark for 3 months, the water contact angles increased to 20–40°. In order to change these TiO_2 films to their photoinduced superhydrophilic states, the films were illuminated by a 15 W 365 nm UV lamp (Cole-Parmer Instrument Co.). Integrated UV intensity in the range 310–400 nm was measured by a UV radiometer (UVX, UVP Inc., California, USA). The intensity of the UV light striking the films was 540 ± 10 μW cm^{-2}. The hydrophilic property of TiO_2 thin films was evaluated by examining the contact angle for water of various TiO_2 thin films.

3. Results and discussion

3.1. Thickness, crystalline phase and transmittance of TiO_2 films

At a pulling speed of 1 mm s^{-1}, the average film thickness per coating cycle was measured to be about 0.08 μm from the second coating onwards, while the first coating thickness was about 0.15 μm. This is considered to be simply due to the fact that the films from the second coating onwards were deposited on the material formed just before, while the first one was coated directly on to a glass substrate that has very different surface properties.[22–23] XRD results revealed that the crystalline phase of the porous TiO_2 thin films was pure anatase. Fig. 1 shows that the transmittance of TiO_2 films prepared with larger quantities of PEG is lower than that with smaller amounts. The transmittance of a TiO_2 film prepared from the precursor solution containing 2.0 g PEG by one coating cycle is very low, due to the scattering of light by pores with diameters in the range of 200–500 nm in the film. This indicates that the difference in transmittance among the samples is related to the difference in the size and number of pores in the films.

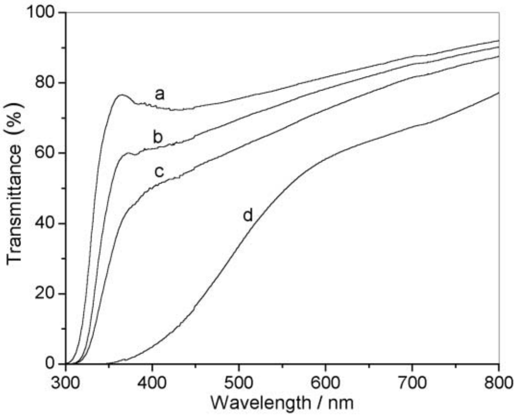

Fig. 1 Transmittance of TiO_2 thin films prepared by 1 coating cycle and using precursor solutions containing: (a) 0.25 g, (b) 0.5 g, (c) 1.0 g and (d) 2.0 g PEG.

3.2. Surface morphologies and roughness of TiO_2 films

It was found that the surface morphologies and roughness of porous TiO_2 films were obviously different with increasing amounts of PEG in precursor solutions. Fig. 2 shows the AFM three-dimensional images of the surface of porous TiO_2 thin films prepared from precursor solutions containing (a) 0 g, (b) 0.5 g, (c) 1.0 g and (d) 2.0 g PEG by one coating cycle. It was observed that TiO_2 films prepared from the precursor solution without PEG (Fig. 2a) had granular microstructure and flat texture with the lowest surface roughness. On the other hand, different surface microstructure and roughness developed in TiO_2 films prepared from precursor solutions with PEG. There were many fine pores produced in the films because PEG contained in the gel films decomposed completely at 520 °C. The size of the pores was related to the amount of added PEG. The diameters of the pores were tens of nm, 100–250 nm, 200–500 nm for the films prepared from precursor solutions containing 0.5, 1.0 and 2.0 g PEG. It is also clearly seen that the surface roughness of the films increases with an increasing amount of PEG. Therefore, it may be concluded that the larger the amount of added PEG, the larger the surface roughness and the size of pores produced in the resultant films. The degree of surface roughness of TiO_2 thin films was quantitatively characterised by AFM. The roughness data (R_{rms}) of these films are shown in Table 1.

3.3. XPS measurements

Fig. 3 shows the high resolution XPS spectra of the O1s region, taken on the surface of the prepared TiO_2 films from precursor solutions containing (a) 0 and (b) 0.5 g PEG by ten coating cycles. The O1s region is composed of several peaks. The main peak is attributed to the Ti–O in TiO_2. The other four oxygen peaks can be assigned to the Ti–O bonds of Ti_2O_3, the hydroxyl groups, the C–O bonds and the adsorbed H_2O, respectively. Table 2 lists the results of curve fitting of XPS spectra for five film samples. The contribution of each type of oxygen is expressed by r_i (%). It is interesting to note that the hydroxyl

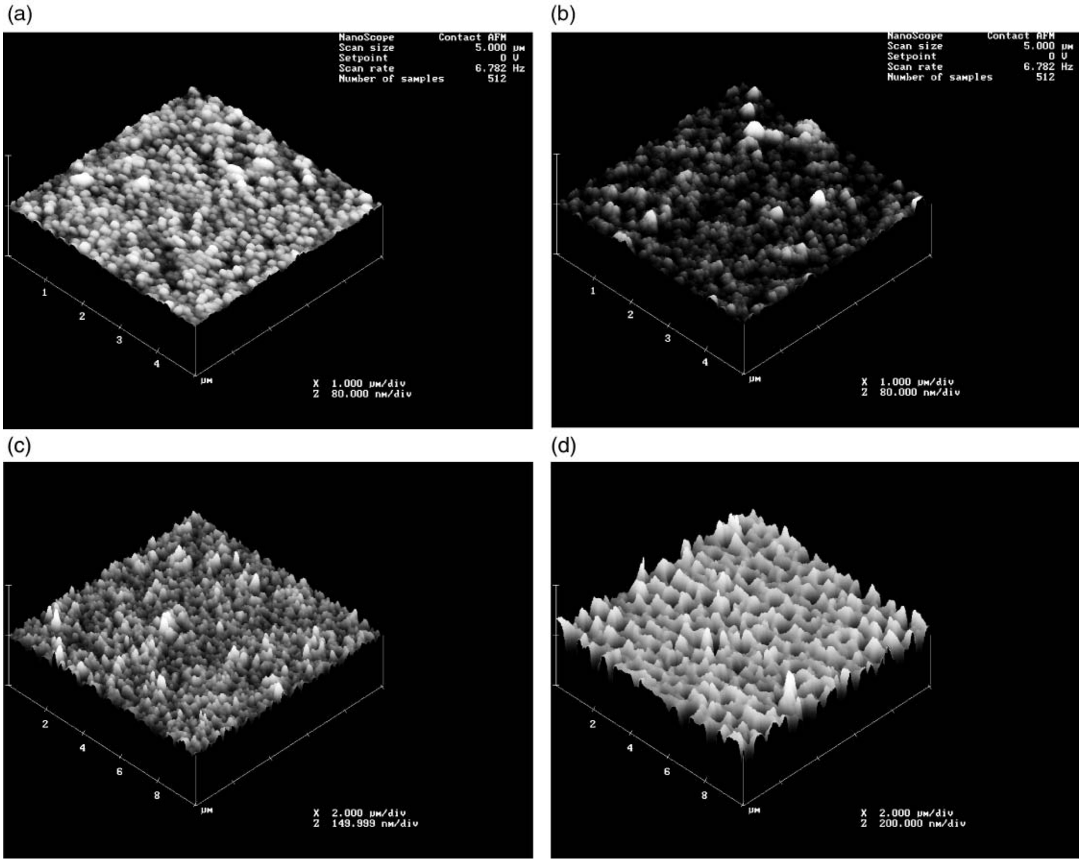

Fig. 2 AFM 3D images of the surface of TiO_2 thin films prepared from precursor solutions containing (a) 0 g, (b) 0.5 g, (c) 1.0 g and (d) 2.0 g PEG by 1 coating cycle.

content in the films prepared with PEG is greater than that without PEG. Moreover, the hydroxyl content increases with increasing amounts of PEG added and this trend levels off at about 0.5 g by weight of PEG. The difference in the hydroxyl content among the films can be explained by the difference in size and numbers of pores. Water vapor is more readily adsorbed onto thin films with relatively large pores. Hydroxyl groups existing in the films are attributed to the chemisorbed H_2O, and some H_2O is also physically absorbed on the surface of TiO_2 films. It can be seen from Table 2 that there is no obvious difference in the amount of physically adsorbed H_2O among the TiO_2 films. This is due to the fact that H_2O physically adsorbed on TiO_2 is easily desorbed under the ultra-high vacuum conditions of the XPS system. Generally, with an increase in the amount of chemisorbed –OH on the surface of TiO_2 thin films, van der Waals forces and hydrogen bonding interactions between H_2O and –OH are increased. Water can easily spread across the surface and the hydrophilic property will be enhanced.[22–23] The C–O bonds in the films are attributed to organic residues (*e.g.* alcohol and unhydrolyzed alkoxide groups) and inorganic carbonate.[26] Ti_2O_3 may be formed by the reduction reaction from organic radicals introduced by precursors during heat-treatment. The organic material during oxidation draws oxygen from the surrounding

Table 1 Effects of the amount of the added PEG on roughness data and water contact angles of TiO_2 thin films

	a	b	c	d	e
Amount of PEG/g	0	0.25	0.5	1.0	2.0
R_{rms}/nm	1.18	2.75	6.74	13.75	41.96
$^a\theta/°$	15	5	<3	<3	<3
$^b\theta/°$	40	35	21	27	30

[a]Freshly prepared TiO_2 thin films. [b]After storage in the dark for 3 months.

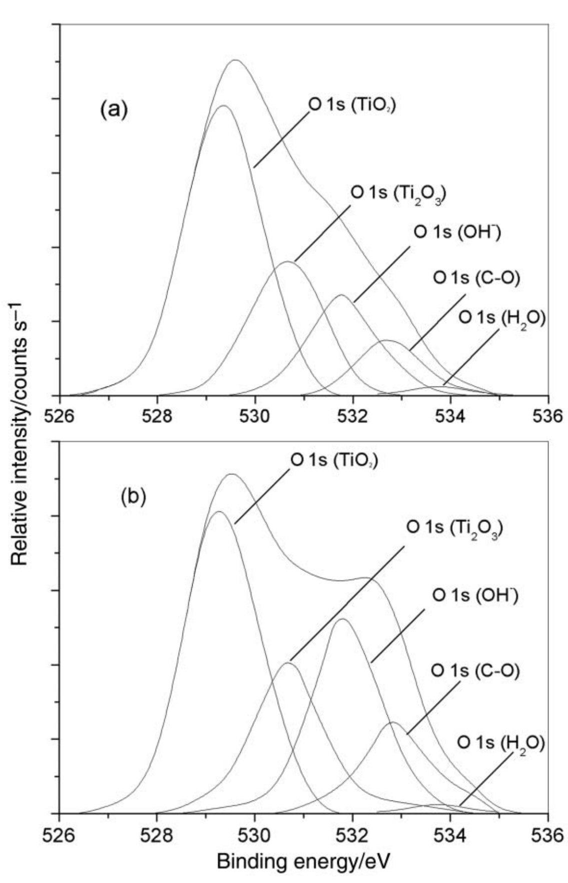

Fig. 3 High resolution XPS spectra of the O1s region, taken on the surface of the TiO_2 thin films prepared from precursor solutions (a) without additives and (b) containing 0.5 g PEG by repeating the cycle 10 times.

Table 2 Results of curve-fitting of the high resolution XPS spectra for the O1s region: r_i (%) represents the ratio of $A_i/\sum A_i$ (A_i is the area of each peak)

Sample		O1s (TiO_2)	O1s (Ti_2O_3)	O1s (OH)	O1s (C–O)	O1s (H_2O)
a	E_b/eV	529.4	530.6	531.9	532.8	534.0
	r_i (%)	43.3	32.0	12.7	10.2	1.8
b	E_b/eV	529.6	530.8	531.9	532.9	534.1
	r_i (%)	48.4	22.9	17.2	10.0	1.4
c	E_b/eV	529.5	530.8	531.9	532.9	534.0
	r_i (%)	41.3	19.7	25.7	11.6	1.7
d	E_b/eV	529.5	530.7	531.9	532.9	534.0
	r_i (%)	40.4	19.8	26.0	12.0	1.8
e	E_b/eV	529.6	530.7	531.9	532.9	534.2
	r_i (%)	38.0	19.7	26.4	13.9	2.0

[a] Samples a, b, c, d and e were prepared by 10 coating cycles from the precursor solutions containing 0 g, 0.25 g, 0.5 g, 1.0 g and 2.0 g of PEG, respectively.

atmosphere and layer network, which would reduce some Ti(IV) to Ti(III).[8,27]

3.4. Photoinduced super-hydrophilic properties of TiO_2 thin films

Table 1 shows the results of contact angle measurements for water on the as-prepared TiO_2 thin films without UV illumination. It had been found that the contact angles for water on the porous TiO_2 films decreased with increasing amounts of PEG.[22,23] However, as the amount of PEG reached 0.5 g in 100 ml, the contact angles for water on the porous TiO_2 thin films did not decrease further. The TiO_2 thin film prepared from the precursor solution without PEG had the greatest contact angle because its hydroxyl content and surface roughness were smallest and water could not easily enter the interior region of the thin films. The TiO_2 thin film prepared from the precursor solution containing 2.0 g PEG had larger pores and surface roughness than the other thin films, and also the hydroxyl content of the thin film was greater. Therefore, its contact angle with water was low. It should be noted, however, that its transmittance was the lowest due to the scattering of light by the increased number and size of pores homogeneously distributed in the TiO_2 thin film. Such poor transparency would limit its use as a self-cleaning glass. The TiO_2 thin films prepared from the precursor solution containing 0.5 g PEG had almost the same hydroxyl content as those prepared with 1.0 g and 2.0 g PEG. Although the size of the pores and the surface roughness of the former were smaller than those of the latter, the small pores with larger capillary force would attract water into the pores and lead to a low contact angle. As a result, their contact angles were almost the same. The transmittance of the former was much greater than that of the latter, therefore, the former would do better as a self-cleaning glass. These results revealed that both small and large pores in TiO_2 thin films would lead to low contact angles.

All the porous TiO_2 thin films freshly prepared by the sol–gel method showed hydrophilic properties, but when hydrophilic porous TiO_2 thin films were stored in dark rooms in the air, the water contact angle of TiO_2 films tended to increase gradually up to certain saturation contact angle values. For example, the contact angle for water of porous TiO_2 films prepared from the precursor solution containing 2.0 g PEG increased up to about 30° when stored in a dark room for three months. Fortunately, the hydrophilicity could be fully recovered to the original state by UV illumination again.[11,25]

In order to evaluate the photoinduced hydrophilicity of TiO_2 thin films, we measured the changes of water contact angle of five thin films under illumination by a 15 W UV lamp for 120 min and then stored in the dark room for 7 days. Fig. 4 showed the characteristics of cyclic change of contact angle about the hydrophobic↔hydrophilic state of the films. It can be seen from Fig. 4 that the inter-conversion speed of hydrophobic↔hydrophilic state of the films was different from specimen to specimen. The surface of thin films (a), (b) and (c) became highly hydrophilic with a water contact angle of 0° under 540 $\mu W\ cm^{-2}$ UV illumination within 120 min. However, films (d) and (e) did not become highly hydrophilic. Further investigation found that there was an optimum amount of added PEG in the precursor solution for increasing the photoinduced hydrophilicity of the film. Fig. 5 shows the hydrophilization rate ($\Delta\theta$) in the first 10 min *versus* the amount of PEG in the precursor solutions. As shown in Fig. 5, with an increase in the amount of PEG in the precursor solutions, the rate of becoming hydrophilic increased. The hydrophilization rate was the highest at 0.5 g PEG, and it dropped drastically at 1.0 g and 2.0 g. This may be due to the fact that when the amount of PEG was 0.5 g, film (c) contained a lot of surface hydroxyl groups and small surface micropores. Usually, hydroxyl groups and micropores of films can adsorb and fix water, and small micropores in films can also produce a two-dimensional capillary phenomenon. This would result in a

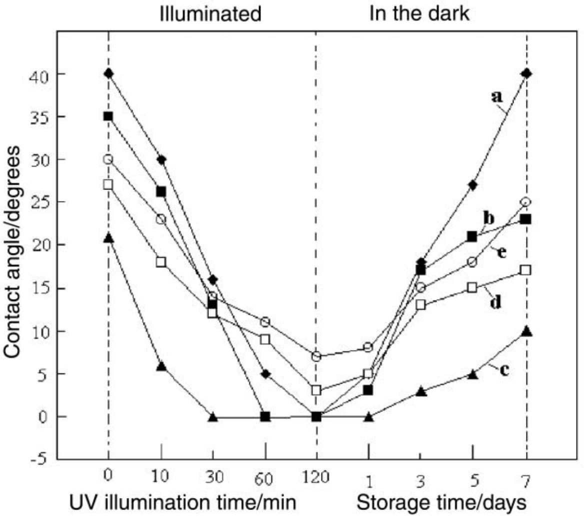

Fig. 4 Changes in the contact angle when illuminated by UV light for 120 min and subsequently stored in a dark room for 7 days. Samples a, b, c, d and e were prepared by 10 coating cycles from the precursor solutions containing (a) 0 g, (b) 0.25 g, (c) 0.5 g, (d) 1.0 g and (e) 2.0 g PEG, respectively.

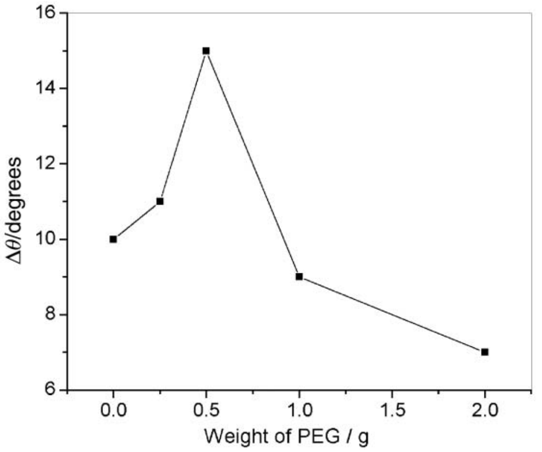

Fig. 5 Rate of becoming hydrophilic *versus* the amount of added PEG in the precursor solution. The rate of becoming hydrophilic was estimated by subtraction of the water contact angle ($\Delta\theta$) in the first 10 minutes under 540 $\mu W\ cm^{-2}$ UV illumination under ambient conditions (*i.e.* 295 K, RH: 50%, air).

more rapid change of the surface to the super-hydrophilic state. Although films (d) and (e) had more surface hydroxyl groups and larger surface roughness as compared to films (a), (b) and (c), the diameters of the micropores in films (d) and (e) were larger. Therefore, their two-dimensional capillary action was weaker. Moreover, light could not penetrate as far from the surface due to the scattering by more numerous pores of larger size distributed in films (d) and (e).[8] The intensity of light irradiance greatly decreased in the interior region. Under this condition, fewer oxygen vacancies and Ti^{3+} ions could be formed as shown in the following mechanism:[11–14,28–29]

$$TiO_2 + 2h\nu \rightarrow 2h^+ + 2e^- \tag{1}$$

$$O^{2-} + 2h^+ \rightarrow 1/2O_2 + \square \text{ (oxygen vacancy)} \tag{2}$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+} \text{ (surface trapped electron)} \tag{3}$$

The decrease in light intensity coupled with a weak capillary action would slow down the conversion from a hydrophobic to a hydrophilic state.

It can be seen from Fig. 4 that the conversion kinetics of five thin films were obviously different, and film (c) showed the slowest conversion. This was due to the fact that film (c) contained a lot of surface hydroxyl groups and small surface micropores that adsorbed and trapped water. Fig. 6 shows the rate of becoming hydrophobic ($\Delta\theta$) for samples stored in the dark for 7 days *versus* the amount of PEG. The pure TiO_2 film exhibits the highest rate of becoming hydrophobic because it has the lowest surface roughness and hydroxyl content. The rate of becoming hydrophobic reaches a minimum with the sample of 0.5 g PEG, and it goes back up when extra PEG is added. Thin films prepared from 1.0 g and 2.0 g PEG contain relatively large pores. Water evaporates more easily from larger pores resulting in a higher conversion rate from the hydrophilic to the hydrophobic state.

4. Conclusions

Transparent porous TiO_2 thin films with different surface microstructures were prepared on soda-lime glass substrates from precursor solutions containing PEG by the sol–gel method. The surface microstructure and photoinduced super-hydrophilic property of the TiO_2 films thus obtained were investigated as a potential self-cleaning glass. The results showed that the surface roughness and hydroxyl content of TiO_2 thin films increased with increasing amount of added PEG in the precursor solution. Suitable surface microstructures could enhance the photoinduced super-hydrophilic properties of porous TiO_2 thin films and hinder the conversion from the hydrophilic to the hydrophobic state. When the mass ratio of PEG to TiO_2 is kept at 12.5%, the resulting porous TiO_2 thin films showed better photoinduced hydrophilic properties and a slower conversion rate from the hydrophilic to the hydrophobic state. Many factors, such as the pore size and number in TiO_2 films, surface roughness and the amount of –OH in TiO_2 films, influenced the inter-conversion rate of the hydrophobic↔hydrophilic state of TiO_2 thin films.

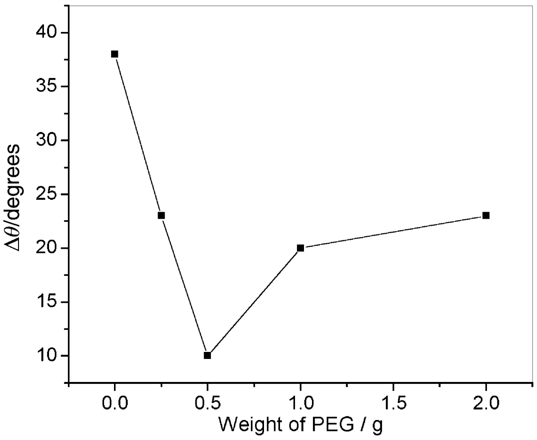

Fig. 6 Rate of becoming hydrophobic *versus* the amount of added PEG in the precursor solution. The rate of becoming hydrophobic was estimated by addition of the water contact angle ($\Delta\theta$) in the dark for 7 days under ambient conditions (*i.e.* 295 K, RH: 50%, air).

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