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Characteristics modification of TiO_2 thin films by doping with silica and alumina for self-cleaning application

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Self-cleaning hydrophilic and hydrophobic properties of TiO_2-based thin films on glass substrates have been investigated in this study. The addition of SiO_2 into TiO_2 can increase the wettability of films and maintain the hydrophilic state for a long time even in the dark. The contact angle of water on deposited films containing 15% SiO_2 is less than 2° after 2 h of UV illumination. These TiO_2–SiO_2 films exhibit excellent antifogging characteristics. Meanwhile, TiO_2–Al_2O_3 films possess high water repellent ability and the photo-induced self-cleaning can take place even in visible light. The TiO_2 thin film containing 33% of Al_2O_3 shows a high hydrophobic state with a water contact angle of 73° after being irradiated with sunlight for 2 h. A comparison of hydrophilic TiO_2–SiO_2 and hydrophobic TiO_2–Al_2O_3 films demonstrates the ability to modify the TiO_2 thin film properties for self-cleaning applications.

Keywords: TiO2; hydrophilic; hydrophobic; modification capability

1. Introduction

In practice, cleaning the surfaces of buildings made of materials like tiles or glass panels causes considerable troubles, including concerns for the operator's safety, and takes a lot of time [1,2]. Therefore, there is a need for a material that has self-cleaning properties. Since the discovery of photo-stimulated water splitting on TiO_2 electrodes by Fujishima and Honda three decades ago, extensive research has been carried out on TiO_2 for the purpose of solar energy conversion and environmental cleanup [3]. Among a myriad of applications of TiO_2, the self-cleaning surfaces utilising sunlight and natural rainfall to keep the surface clean are one of the most interesting and attractive, drastically reducing time, cost and energy for maintenance [4]. TiO_2, excited by the UV part in the sunlight spectrum, can decompose organic contaminants adhering to the surface [4]. There are two main properties for self-cleaning materials: the so-called super-hydrophilicity and

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super-hydrophobicity [2]. The super-hydrophilic property of TiO_2 stimulated by UV light allows water to spread completely on the surface rather than remaining in the shape of droplets [3]. The result is that TiO_2-coated glass and tiles have antifogging and self-cleaning abilities. However, the photo-induced super-hydrophilicity rapidly vanishes when the surface is stored in the absence of UV exposure [5]. It was found out that by adding SiO_2 the contact angle becomes low immediately after production, and that the hydrophilic state remains good even in a dark place [5]. On the contrary, hydrophobicity is a low-wettability state where surfaces have contact angles of about 100° [2]. This is illustrated by the well-known Lotus effect, beautifully visible on the great leaves of the lotus plant. In that case, the adhesion of water, as well as particles on the surface, is extremely reduced. Water on super-hydrophobic surfaces will immediately take the shape of droplets. The contaminant particles on the surface will adhere to the droplet and are removed from the rough surface when the droplets roll off [2]. Tadanaga *et al*. [6] have studied super water-repellent Al_2O_3 coating films on polymer with contact angles of 150°. A combination of Al_2O_3 and TiO_2 materials has been reported by Celik *et al*. [7]. In Celik's work, properties of TiO_2 were modified by introducing Al dopant into the TiO_2 lattice. This work showed the feasibility of improving the photo catalytic activity of TiO_2 under visible light [7].

In this study, we have investigated the effects of doping with SiO_2 on the hydrophilic property of TiO_2 as well as the effects of doping with Al_2O_3 on the hydrophobicity of films. Sol-gel method is used to fabricate thin films due to its advantages: good homogeneity, ease of composition control and good optical properties. In particular, the sol-gel process is very efficient in producing thin and transparent multi-component oxide layers on various substrates such as stainless steel plates, alumina plates, glass panels and ceramic tiles. This work contributes to the comprehension of using modified TiO_2 as self-cleaning materials.

2. Experimental procedures

2.1. *Film preparation*

2.1.1. *TiO_2–SiO_2 films*

Titanium tetraisopropoxide (TTIP) and tetraethylorthosilicate (TEOS) were used as precursors for titania and silica, respectively. First, TEOS was hydrolysed in an aqueous HCl solution, and then the TTIP ethanol mixture (1 mol TTIP per 20 mol ethanol) was slowly introduced dropwise. The molar ratio of Si/Ti in the solutions was varied from 0% to 30%. Polyethylene Glycol (PEG 600) was also added into the solution to control the film porosity and hence increase the specific surface area. Thin film deposition was performed by spin coating of the solution at room temperature, with a spinning rate of 3000 rpm for 30 s. After each layer was deposited, the film was annealed at 250°C on a hotplate for 10 min. The procedure from coating to drying was repeated three times to achieve a film thickness of about 150 nm. The films were then calcinated at 500°C in a furnace for 2 h. Finally, the fabricated films were irradiated by a 20 W Osram 360 nm wavelength UV light.

2.1.2. *TiO_2–Al_2O_3 films*

TiO_2–Al_2O_3 nanoparticles were prepared by sol-gel method. Aluminum chloride ($AlCl_3 \cdot 6H_2O$) powder was dissolved in isopropanol and glacial acetic acid. Titanium isopropoxide (TTIP) was then added into the mixture. The obtained solution was stirred for 1 h at room temperature in air in order to yield a transparent and homogeneous solution. Spin coating was used to prepare films with thickness of 150 nm. The heat treatment was similar to the treatment for TiO_2–SiO_2.

2.2. *Characterisation of film structure and morphology*

The TiO_2-based films on glass substrates were characterised by various analytical tools. Crystalline structures of the films were identified by X-ray diffraction using Cu-Kα radiation (Siemens Kristalloflex diffractometer). The FT-IR spectra were recorded on KBr disc using a Brucker TENSOR 37 FT-IR spectrophotometer. The optical transmittance was measured using Jasco UV-vis V530 double beam spectrophotometer in the wavelength range from 190 to 1100 nm. Surface morphology of the films was evaluated by Scanning Electron Microscope (Jeol JMS-6480LV) and Atomic Force Microscope (Nanotech Electonica SL). A Veeco Dektak 6M surface profilometer was used to evaluate the films' thickness.

2.3. *Characterisation of hydrophilic and hydrophobic properties*

Surface hydrophilicity and hydrophobicity of films were quantified by measuring the water contact angle. The measurement was performed at 25°C within an environmental chamber equipped with an OCA-20 Dataphysic. This goniometer is connected to a video camera. Several deionised water droplets of 1.0 mL volume were spread onto the samples and contact angles of those droplets were measured at different positions of the thin film surface for statistical purpose. The samples were then stored in the dark under ambient conditions in an open atmosphere. The water contact angles were periodically measured using the previously mentioned procedure in order to study the effects of natural aging on the film wettability.

3. Results and discussion

3.1. *X-ray diffraction*

3.1.1. *TiO_2–SiO_2 films*

The XRD diagrams of TiO_2–SiO_2 films with different amount of SiO_2 are illustrated in Figure 1. After 2 h of annealing at 500°C, the XRD diagram indicates the obtention of pure TiO_2 film with all peaks corresponding to anatase phase with high intensity. The Bragg's reflection at about 25.4°, 38° and 48° corresponds to (101), (004) and (200) tetragonal crystal planes of anatase. With an increase in the SiO_2 content, peaks intensity decreases significantly (15% mol SiO_2 as shown in Figure 1(b)) and the film is nearly amorphous with 30% SiO_2 addition. It is obviously seen that SiO_2 has a suppressive effect on the development of TiO_2 crystallisation.

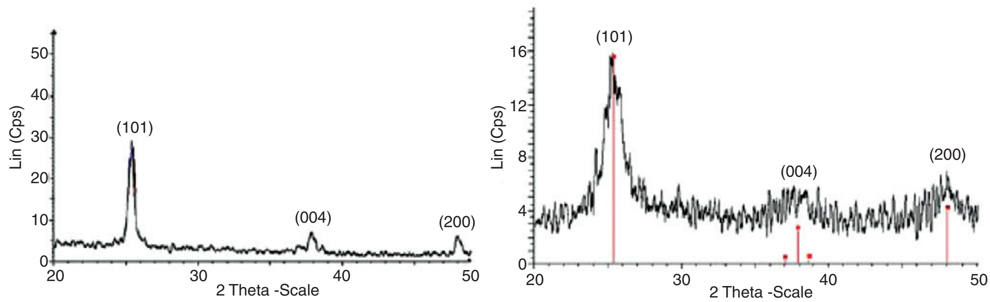

Figure 1. XRD diagrams of (a) pure TiO_2 and (b) 85%TiO_2–15%SiO_2 thin films on glass substrate annealed at 500°C in 2 h.

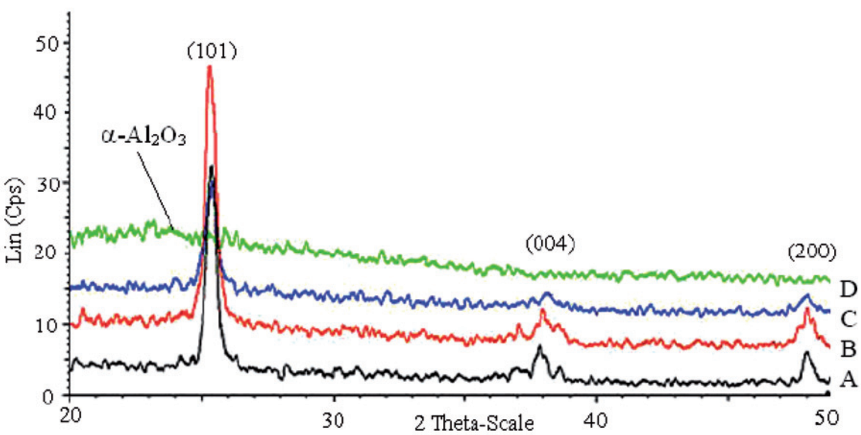

Figure 2. XRD diagrams of TiO_2–Al_2O_3 thin films on glass substrates with (A) 0.00, (B) 6.54, (C) 15.3 and (D) 33.3 mol% of Al_2O_3 after annealing at 500°C for 2 h in air.

3.1.2. *TiO_2–Al_2O_3 films*

The phase identification of TiO_2–Al_2O_3 films on glass slide substrates was performed after annealing the films in air at 500°C for 2 h. Figure 2 shows the XRD diagrams of these films, with different Al_2O_3 contents of 0.00, 6.54, 15.3 and 33.3 mol%. Anatase phase of pure TiO_2 having tetragonal structure was strongly observed at 500°C as explained elsewhere [6]. It can be seen that the peaks at 2θ of 25.4°, 38.0° and 48.0° assigned to (101), (004) and (200) lattice planes of TiO_2 were also visible. Additional peak of corundum α-Al_2O_3 was identified at $2\theta = 24°$. These results are in good agreement with the work of Celik *et al.* [7].

3.2. *Optical properties of TiO_2-based films on glass substrates*

3.2.1. *TiO_2–SiO_2 films*

The optical transmittance spectra of TiO_2–SiO_2 films on glass substrates are shown in Figure 3. The transmittance within the visible and near infrared region is higher than 85% including the glass substrates, which reveals the excellent optical properties

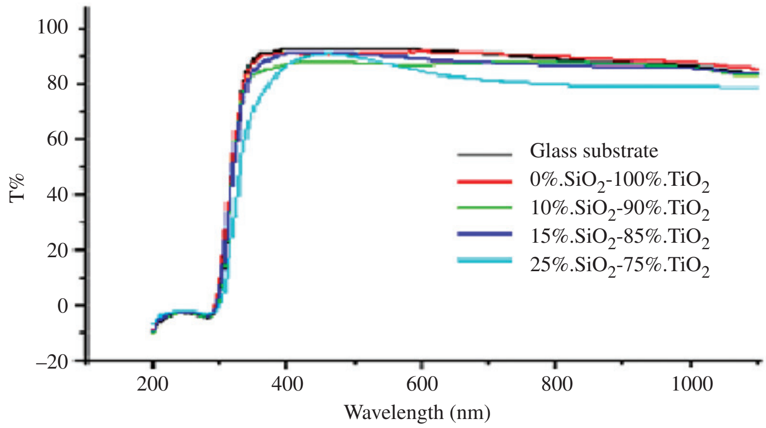

Figure 3. UV-vis spectra of TiO_2–SiO_2 films with different amount of SiO_2.

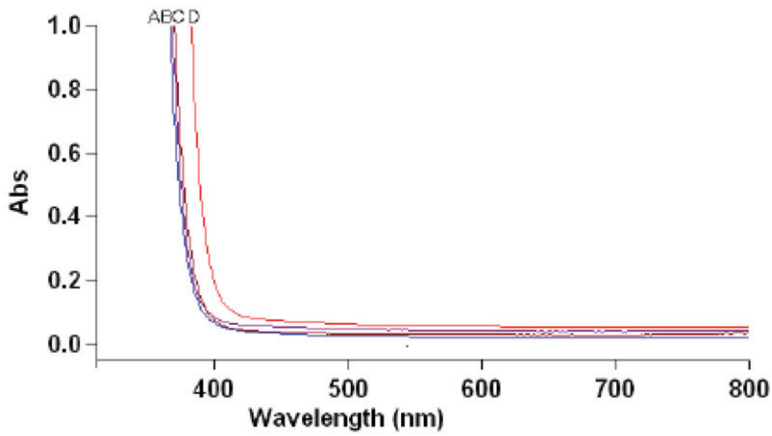

Figure 4. UV-vis spectra of TiO_2–Al_2O_3 thin films on glass substrates with (A) 0.00, (B) 6.54, (C) 15.3 and (D) 33.3 mol% of Al_2O_3.

of TiO_2–SiO_2 produced in this study. The transmittance decreases slightly when SiO_2/TiO_2 ratio increases. In all cases, the films show sharp absorption edge in ultraviolet region at a wavelength of about 300 nm. It is known that TiO_2 is a semiconductor oxide and its anatase phase has an optical band gap of 3.2 eV (385 nm). The blue shift of about 85 nm in the spectra is considered as a result of quantum confinement effect [8,10].

3.2.2. *TiO_2–Al_2O_3 films*

Figure 4 illustrates the UV-vis absorption of TiO_2–Al_2O_3 films. There are sharp absorption edges in the wavelength of around 380–420 nm. From these results, it is noteworthy to indicate that by increasing the Al_2O_3 content in TiO_2 films, the cut-off wavelength can move into the visible region (at 420 nm with 33.3 mol% Al_2O_3). For this reason, the presence of Al_2O_3 can improve the photo catalytic activity of TiO_2 under visible light.

3.3. *Surface morphology studies*

3.3.1. *TiO_2–SiO_2 films*

As far as the geometry of a surface is concerned, the hydrophilic properties are well known to be enhanced by fine roughness. Therefore, controlling surface microstructure of the films is a way to improve the hydrophilic property [5]. In this work, we have added PEG 600 into the solution to control the film porosity and hence increase the specific surface area. Figure 5 shows the SEM images of 85% TiO_2–15% SiO_2 films derived from coating solutions including 3% and 5% PEG. When the weight percentage of PEG is low (Figure 5(a)), the distribution of PEG in the solution is not good and big clusters are formed [11,12]. The subsequent decomposition of PEG by heat treatment creates large pores with different diameters in TiO_2–SiO_2 films. When the PEG content increases to 5% (Figure 5(b)), the dispersion of PEG in solution becomes better, which prevents the agglomeration of big clusters in solution and results in creation of many small and uniform pores in TiO_2–SiO_2 film. Therefore, the addition of PEG results in an increase of specific surface area and thus enhances the photo catalytic properties of films.

Figure 6 shows AFM images of 85% TiO_2–15% SiO_2 films, indicating that the particle sizes and film roughness decreased according to the increase in PEG quantity. The surface roughness (rms) decreases from 11.19 to 8.02 nm and 2 nm with the addition of PEG from 1% to 3% and 5%, respectively. However, when the PEG content is larger than 5%, the films become highly porous and their mechanical properties decrease

3.3.2. *TiO_2–Al_2O_3 films*

Figure 7 shows SEM micrographs of TiO_2–Al_2O_3 films on glass substrate with different contents of Al_2O_3. Depending on Al_2O_3 content of the coatings, microstructure of TiO_2–Al_2O_3 films slightly changes. Generally speaking, the presence of Al_2O_3 improves surface

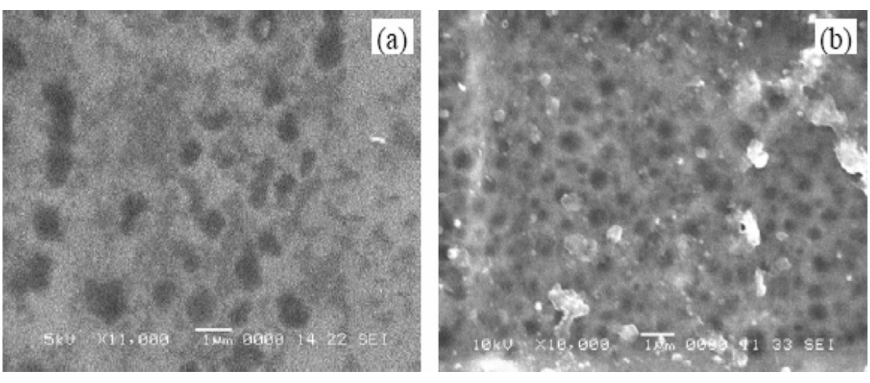

Figure 5. SEM images of (a) 3% and (b) 5% PEG SiO_2–TiO_2 films.

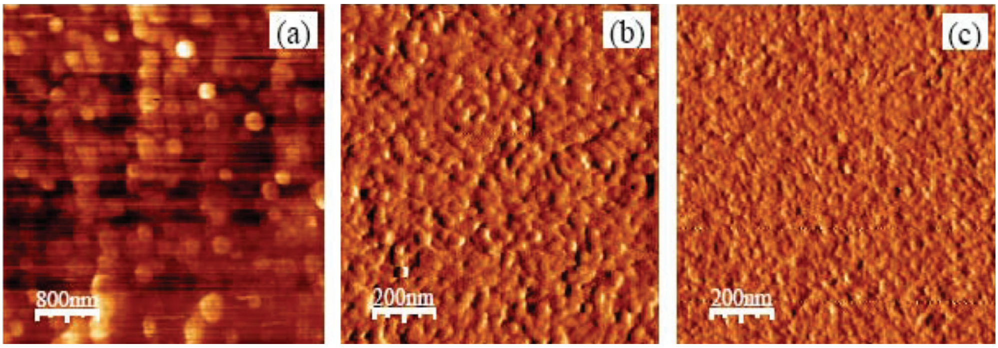

Figure 6. AFM images of (a) 1%, (b) 3% and (c) 5% PEG TiO_2–SiO_2 films.

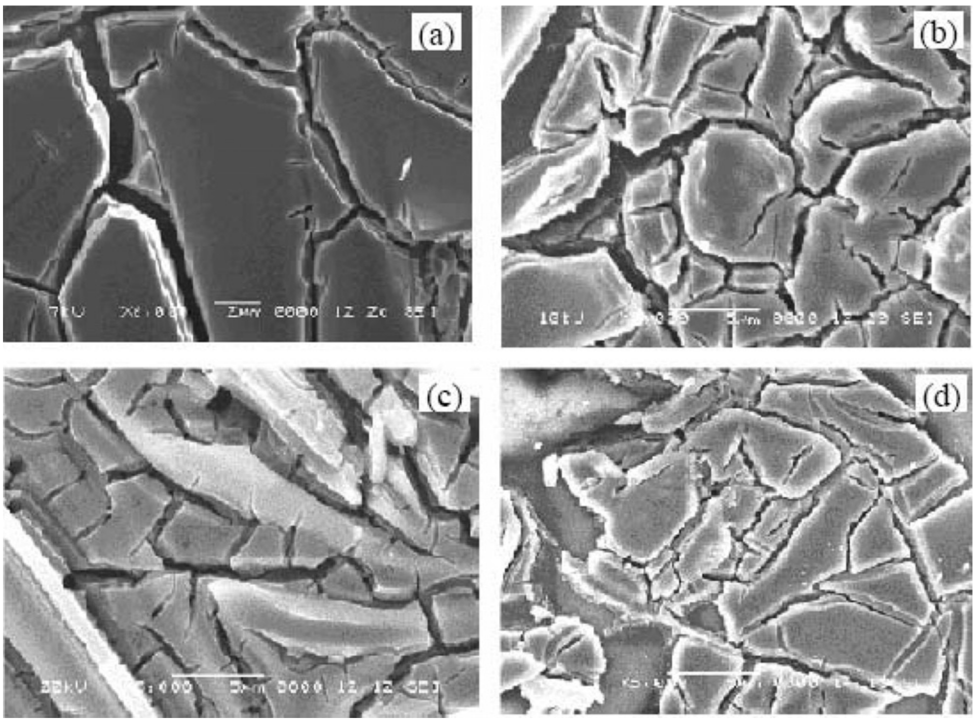

Figure 7. SEM images of TiO_2–Al_2O_3 films with (a) 0%, (b) 6.54%, (c) 15.3% and (d) 33.3% of Al_2O_3.

morphology of the films. The microstructure of pure TiO_2 film in Figure 7(a) reveals large cracks throughout the coatings. As shown in Figure 7 (b)–(d), many small channels separating large islands were found. When the content of Al_2O_3 increases, the coating structure becomes more continuous and homogeneous (Figure 7(d)).

We also observed the roughness of these thin films by AFM (Figure 8). The 3D-images of TiO_2–Al_2O_3 thin films exhibit a microgranular and flat surface. AFM investigations

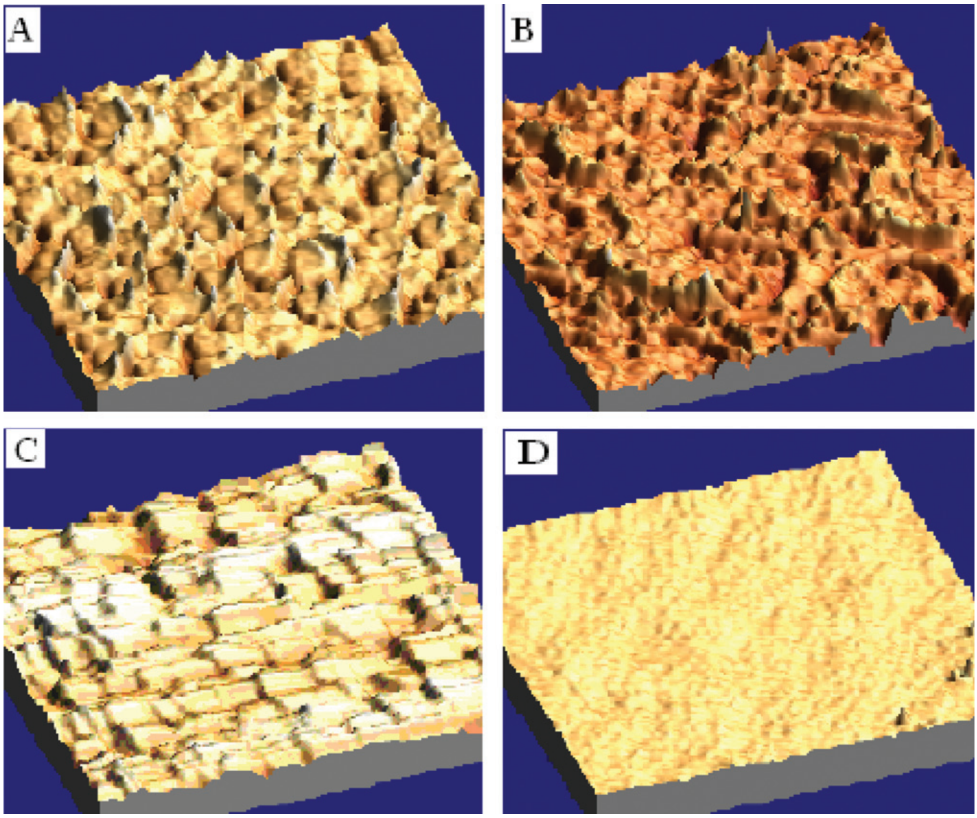

Figure 8. AFM images of TiO_2–Al_2O_3 films with (a) 0%, (b) 6.54%, (c) 15.3% and (d) 33.3% of Al_2O_3.

of these samples indicate surface roughness of 7.52, 5.12, 4.25 and 2.82 nm for Al_2O_3 doping of 0.00%, 6.54%, 15.3% and 33.3%. The higher the Al_2O_3 content is, the flatter the thin film surface becomes.

3.4. *Photo-induced hydrophilic and hydrophobic properties*

3.4.1. *TiO_2–SiO_2 films*

Figure 9 illustrates the dependence of photo-induced change in the water contact angle of TiO_2–SiO_2 films with different concentrations of SiO_2 after 2 h of UV irradiation and then kept overnight in a dark place. The contact angle of pure TiO_2 sample is about 11° and is less than 2° for 15% SiO_2–85% TiO_2 sample. After keeping these samples in a dark place for 12 h, the contact angle goes up from 11° to 27° for samples with only TiO_2, and from 2° to 7° for samples with 15 mol% SiO_2 addition. The results show that with 15 mol% SiO_2 addition, the water contact angle of the film increases very slowly and can maintain the super-hydrophilic state for a long time in the dark.

It is known that with the increase is chemically absorbed –OH groups on the surface, the hydrophilic property of films is enhanced. To explain the chemical effect of SiO_2 on the

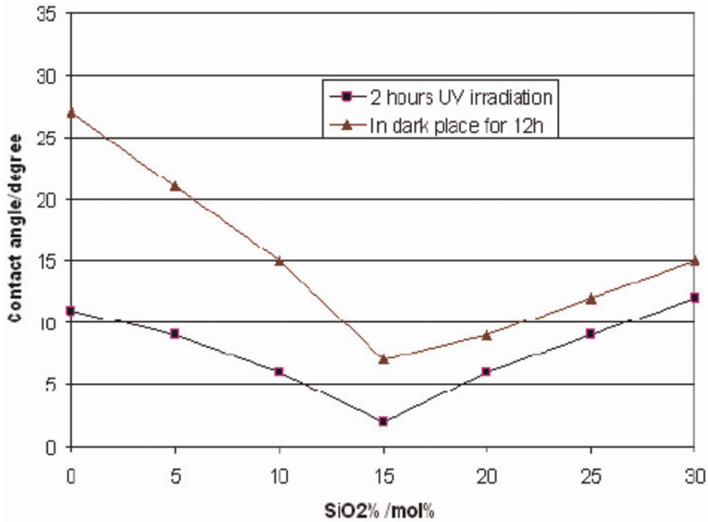

Figure 9. Dependence of photo-induced change in the water contact angle of TiO_2–SiO_2 films.

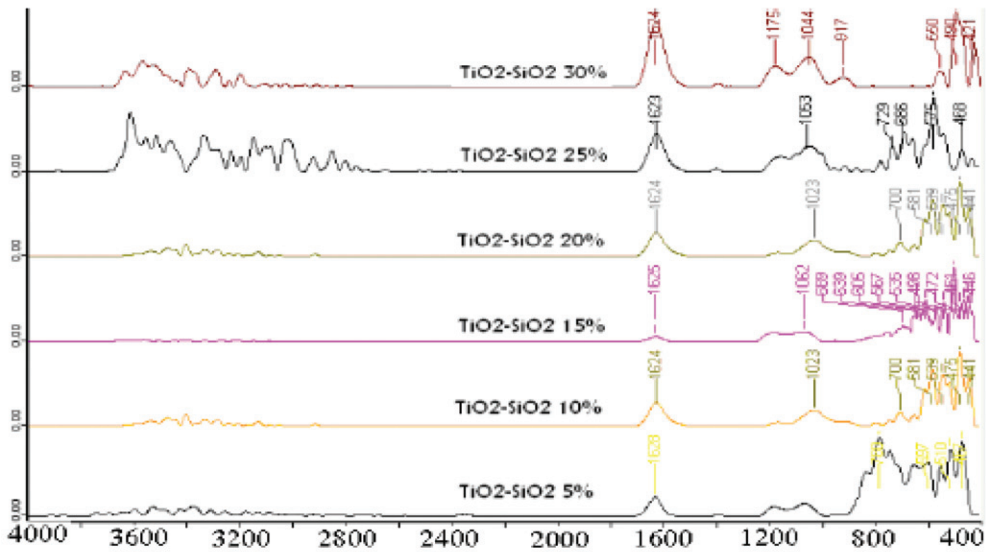

Figure 10. FTIR spectra of TiO_2–SiO_2 powders with different molar ratios of SiO_2.

wettability of TiO_2, we also investigated the FT-IR spectra of films with different amount of SiO_2 annealed at 500°C for 2 h (Figure 10). There is a broad absorption in the range of 3800–2800 cm^1 centred at 3400 cm^{-1} which corresponds to the stretching vibration of hydroxyl groups in the absorbed water or of titanium hydroxide. The absorption peak at 1624 cm^{-1} is due to the bending vibration of absorbed H_2O. It is worth noting that the higher the percentage of SiO_2 in the TiO_2 films, the higher the intensity of the 1624 cm^{-1}

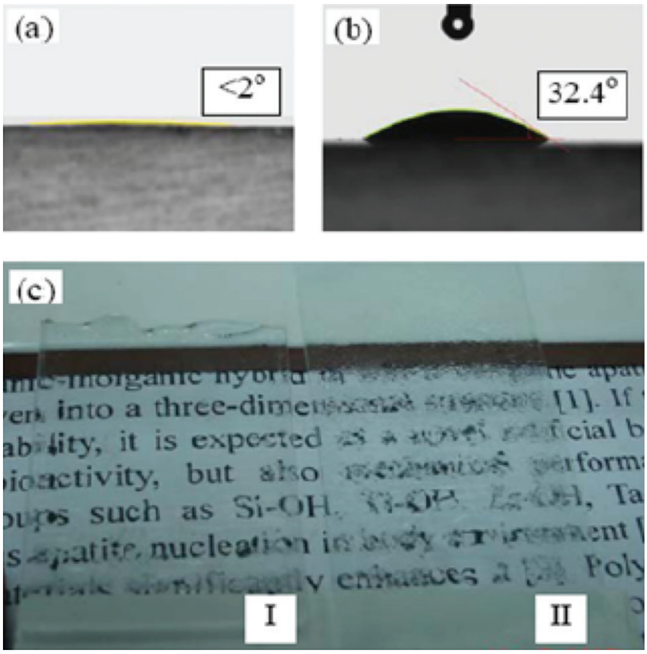

Figure 11. Contact angles between water (a) 15%SiO_2–85%TiO_2 film/glass substrate, (b) bare glass substrate after 2 h UV irradiation and (c) their antifogging effect.

peak. This can be attributed to the increase of –OH group on the surface. The Si–O–Si bonds appear near 1050 cm^{-1} [5] and these peaks increase with the increase of SiO_2 content. A small peak in the range 910–945 cm^{-1} is characteristic of Si–O–Ti bond and the intensity increase with the increase of SiO_2. The peak of Ti–O–Ti bonds are near 500 and 440 cm^{-1}. This peak decreases when the amount of SiO_2 increases. These FT-IR studies indicate that the addition of SiO_2 into the TiO_2 can enhance the wettability of this material, hence increase and maintain the antifogging and self-cleaning ability of TiO_2–SiO_2 thin films even in dark place.

To investigate the antifogging ability of the film coatings, hot or cold water vapour was applied onto the surface of the films. Figure 11(c) shows the result of this test. With the TiO_2–SiO_2 coated glass sample (I), we can read the text behind the TiO_2–SiO_2 coated glass very clearly, whereas the letters behind the glass substrate sample without coating (II) cannot be read. This result shows excellent antifogging ability of TiO_2–SiO_2 films produced in this work. These transparent self-cleaning TiO_2 films on glass substrates have a high potential for practical applications such as mirrors, window glasses, windshields of automobiles, etc.

3.4.2. *TiO_2–Al_2O_3 films*

Contact angles between water and the bare TiO_2 and TiO_2–Al_2O_3 films on glass substrates were investigated under sunshine irradiation (Figure 12). After being exposed to sunlight for 2 h, the bare TiO_2 film shows a contact angle of 16.7° to be compared with the 73° of

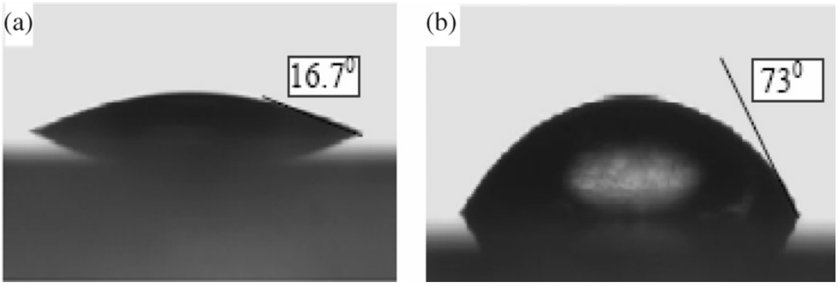

Figure 12. Contact angles between (a) water and pure TiO_2 and (b) 33% Al_2O_3–67% TiO_2 films on glass substrate after 2 h of sunshine irradiation.

33% Al_2O_3–67% TiO_2 sample. The more the Al_2O_3 content in TiO_2 films, the higher the hydrophobicity becomes. In the case sample with 33.3% Al_2O_3 is exposed to irradiation for 2 h, the contact angle approaches 100°. These results show that TiO_2–Al_2O_3 thin films exhibit water repellent property similar to that of polyvinylcloride (PVC) resin [6].

4. Conclusion

In this work, we have successfully fabricated hydrophilic TiO_2–SiO_2 and hydrophobic TiO_2–Al_2O_3 thin films on glass substrates that demonstrate the capability of TiO_2 properties modification. These films exhibit good optical and mechanical properties as well as excellent adhesion to glass substrates. For TiO_2–SiO_2, the contact angle of film with 15% SiO_2 addition is less than 2° and the film can maintain a super-hydrophilic state for a long time in dark places, thus exhibiting excellent antifogging capability. The addition of SiO_2 into TiO_2 retards or inhibits the crystallisation of the anatase phase. A suitable amount of PEG can create many small and homogeneous pores in the films, the consequence of which is the increase of specific surface area and hence an enhancement of the photo catalytic properties of the films. On the contrary, TiO_2 films with 33.3% Al_2O_3 possess high water repellent property. The contact angle is 73° after exposure to sunlight and 100° after UV irradiation. This work demonstrates the feasibility of improving the photo catalytic activity of TiO_2–Al_2O_3 films under visible light.

Acknowledgements

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