

Hydrophilic property of SiO₂-TiO₂ overlayer films and TiO₂/SiO₂ mixing films^①

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Abstract: The photo-induced hydrophilicity of SiO₂ overlayer on TiO₂ films prepared by sol-gel method was investigated by means of contact angle measurement, XPS, UV-VIS and FTIR spectra. The results show that, compared with the TiO₂ film without SiO₂ overlayer, when the TiO₂ film is thoroughly covered by SiO₂ overlayer, the hydrophilicity and the sustained effect are enhanced. It is found that the significant growth of the OH⁻ group occurs in the surface of SiO₂ overlayer. The different mechanism of enhanced hydrophilicity between SiO₂ overlayer on TiO₂ films and TiO₂/SiO₂ mixing films was analyzed. The result suggests that the photo-generated electrons created in the interface between TiO₂ and SiO₂ tend to reduce the Ti(IV) cation to the Ti(III) state, and the photogenerated holes transmit through the SiO₂ layer to uppermost surface efficiently. Once the holes go up to the surface, they tend to make the surface hydrophilic. The stable hydrophilicity of SiO₂ overlayer which adsorbs more stable OH groups, enhances the sustained effect, i. e. the super-hydrophilic state can be maintained for a long time in dark place.

Key words: TiO₂; SiO₂; super-hydrophilic property; overlayer films; sol-gel method

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1 INTRODUCTION

The photocatalytic activity of TiO₂ is very useful not only in environmental purification by decomposition of organic substances but also in the material industry such as mirrors and glasses owing to its self-cleaning and antifogging effects^[1-5]. The antifogging effect has been attributed to the photo-induced hydrophilic or amphiphilic surfaces^[6-8].

The superhydrophilic property of the surface allows water to spread completely across the surface rather than remaining as droplets. The TiO₂-coated glasses are antifogging and self-cleaning. The transparent self-cleaning TiO₂ thin films on glass substrates have a high potential for practical applications such as mirrors, window glasses, and windshields of automobiles.

For the thin film consisting of only TiO₂, the contact angle of water almost becomes zero during UV irradiation. However, it was found that the contact angle goes up and is restored early comparatively in a dark place. It is desirable that the contact angle rises slowly in a dark place, and maintains low for a long time. It was found that by adding SiO₂, the contact angle of water was low after production, and the maintenance of hydrophilicity in a dark place was also good^[9-14].

The effect and mechanism of SiO₂ addition on

the photo-generated hydrophilicity of TiO₂ films obtained from sol solutions were studied^[14]. In order to further investigate the enhanced photo-induced hydrophilicity of TiO₂ film affected by SiO₂, the SiO₂/TiO₂ overlayer films were designed, which are TiO₂ film overlaid with SiO₂ films. The different effects and mechanism of enhanced photo-induced hydrophilicity between the SiO₂/TiO₂ overlayer films and the TiO₂-40% SiO₂ mixing films (TiO₂ films with SiO₂ addition) are discussed, which will give hints to develop a new type of photo-induced hydrophilic films.

2 EXPERIMENTAL

Tetraethylorthosilicate (TEOS) was hydrolyzed in ethanol and water solution containing certain amount of HCl for 1 h to obtain SiO₂ sol solution (TEOS: H₂O: C₂H₅OH: HCl = 1: 0.2: 20: 0.2 in molar ratio). Tetrabutyl titanate was dissolved in a solution of ethanol and water and stirred for 30 min, then HCl catalyst was added to obtain TiO₂ precursor solution (TBOT: H₂O: C₂H₅OH: HCl = 1: 0.5: 58: 0.5 in molar ratio).

Glass plates (25 mm × 75 mm × 2 mm) were used as the support substrates. The coatings were prepared on the supports by a dip-coating method.

The gel coatings were dried at 250 °C for 30 min

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and then heat-treated in air. The temperature was elevated slowly ($2\text{ }^{\circ}\text{C}/\text{min}$) to $600\text{ }^{\circ}\text{C}$ and kept at $600\text{ }^{\circ}\text{C}$ for 1 h. The thickness of the films was increased by repeating the cycles from withdrawing to heating. The sample for characterizing repeated 2 dipping cycles for TiO_2 , and 1 cycle for SiO_2 . The average thickness of the films was calculated by the mass increase of the films. The schematic structure of the films is shown in Fig. 1.

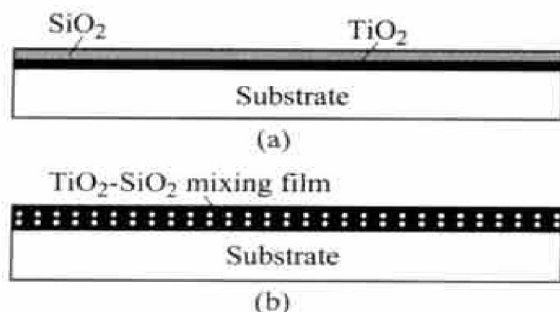


Fig. 1 Schematic structure of $\text{SiO}_2/\text{TiO}_2$ overlayer films and $\text{TiO}_2\text{-SiO}_2$ mixing films

- (a) — SiO_2 overlayer on TiO_2 films;
(b) — $\text{TiO}_2/\text{SiO}_2$ mixing film

The TiO_2 films with 40% SiO_2 addition, which is effective for reduction of the contact angle of water, were chosen as the counterpoint. The preparation method and performance of mixing $\text{TiO}_2\text{-40\% SiO}_2$ films were remarked in Refs. [13, 14].

The samples were characterized by ultraviolet-visible spectrophotometer (UV-VIS), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). The hydrophilic property of the mixing films was evaluated by measuring the contact angle for water droplets.

3 RESULTS

3.1 Thickness and component of surface

The thickness of $\text{SiO}_2/\text{TiO}_2$ overlayer is 170 nm, in which TiO_2 is 130 nm thick, and SiO_2 is 40 nm thick. The thickness of $\text{TiO}_2\text{-40\% SiO}_2$ mixing film is 130 nm. The XPS spectrum of SiO_2 -overlaid films is shown in Fig. 2, in which no $\text{Ti } 2p$ peak is observed. This means that the TiO_2 film is thoroughly covered by the SiO_2 overlayer.

3.2 FTIR spectra

Fig. 3 shows the FTIR spectra of the films. A broad absorption peak is observed at $3\,000\text{--}3\,800\text{ cm}^{-1}$, which is assigned to the stretching modes of O-H bands and related to the surface absorbed water^[14]. The peak at about $1\,600\text{ cm}^{-1}$ is attributed to the bending vibration of H-O-H bond, which is assigned to the chemisorbed water. The peak at about 440 cm^{-1} is due to the stretching vibration of Ti-O

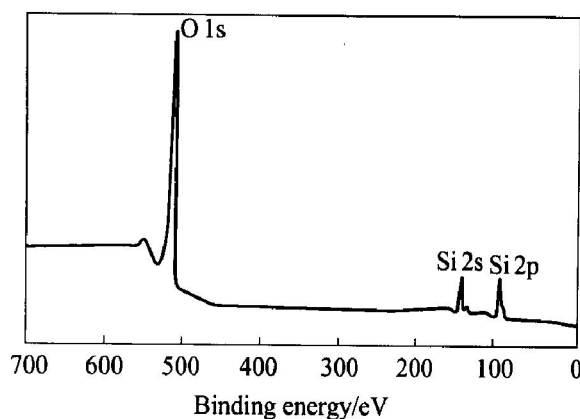


Fig. 2 XPS spectrum of SiO_2 overlayer

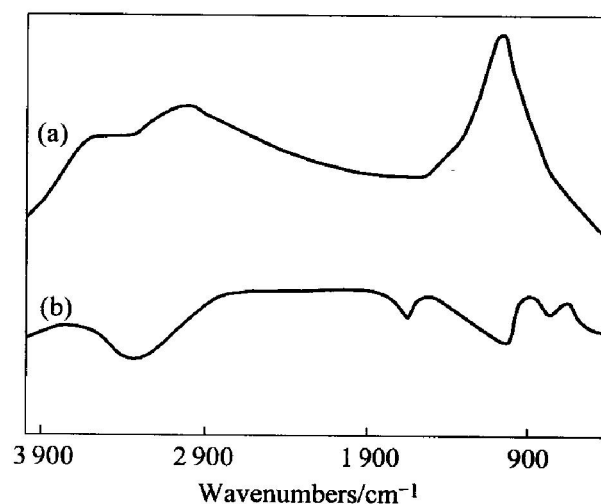


Fig. 3 FTIR result of TiO_2 films without SiO_2 overlayer (a) and with SiO_2 overlayer (b)

O-Ti and Ti-O bands. As can be seen in Fig. 3 (b), the intensities of the absorption peaks at $3\,000\text{--}3\,800\text{ cm}^{-1}$ and at about $1\,600\text{ cm}^{-1}$ increase. The absorption peak at about 800 cm^{-1} is ascribed to the vibration of amorphous SiO_2 . As can be seen, with SiO_2 overlaid films, the intensities of the absorption peaks of OH groups or water increase, indicating that the uppermost surface of SiO_2 overlayer on TiO_2 films has the capability of absorbing water in air.

3.3 UV-VIS spectra

Fig. 4 shows the UV-VIS spectra of soda lime glass substrate and soda lime glass coated TiO_2 films, TiO_2 films with SiO_2 overlayer, and $\text{TiO}_2\text{-40\% SiO}_2$ mixing films, respectively.

As can be seen from Fig. 4(a), the absorption edge of soda lime glass is about 280 nm. This is caused by the adsorption of soda lime glass, because SiO_2 has no adsorption edge in ultraviolet band. The absorption edge for the samples is about 330 nm.

The transmittance of the soda lime glass is the highest and reaches 90% over the visible light region, and drops to about 70% with the pure TiO_2 film.

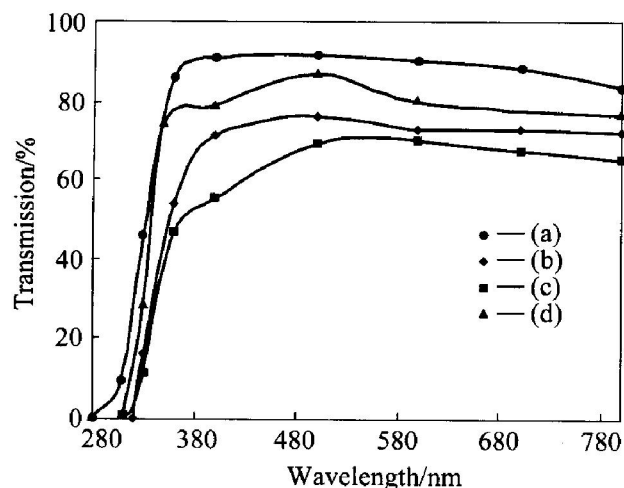


Fig. 4 UV-VIS transmission spectra of soda lime glass (a); coated TiO₂, 2 cycles (b); TiO₂ with 1 cycle of SiO₂ overlayer (c); and TiO₂-40% SiO₂ mixing film, 2 cycles (d)

The transmittance of the mixing films containing 40% SiO₂ is about 80%, which can be partially attributed to the fact that the TiO₂ crystalline size in mixing films is smaller than that in pure TiO₂ film, resulting in the decreasing of light scattering^[13, 14].

3.4 Sustained efficiency of hydrophilicity of films

The contact angle measurements were made in air using the sessile-drop method. A droplet was injected on the surface using 1 μ L micro-injector. Assuming that the geometry of the sessile drop is a spherical section, the contact angle can be estimated by measuring the spreading diameter of the contact circle using reading-microscope.

To evaluate the sustained efficiency of hydrophilicity, the water contact angle measurements of films stored in a dark room were carried out every day for 5 days. The samples used in this experiment were prepared to be hydrophilic (about 3°–5° of water contact angle) by 5 h UV light irradiation, respectively.

The photo-induced hydrophilic SiO₂/TiO₂ overlayer films possess another significant property. Fig. 5 shows the sustained efficiency of hydrophilicity of the photo-induced hydrophilic films during storage in a dark room for 5 days. The water contact angle of the TiO₂ film without SiO₂ overlayer increases right away after storing in a dark room (Fig. 5(a)). However, as shown in Fig. 5(b), TiO₂ film with SiO₂ overlayer, exhibiting the enhanced photo-induced hydrophilicity, shows greater sustained efficiency of the hydrophilicity than the TiO₂ film without SiO₂ overlayer. Within 24 h, the contact angle of water is almost unchangeable. From the second day, it rises slowly. It is demonstrated that the thorough coverage of TiO₂ film by SiO₂ overlayer greatly improves the sustained efficiency of hydrophilicity. The TiO₂-SiO₂ mixing film also shows good sustained efficiency of

hydrophilicity, as shown in Fig. 5(c), which is slightly weaker than that of SiO₂-TiO₂ multilayer films.

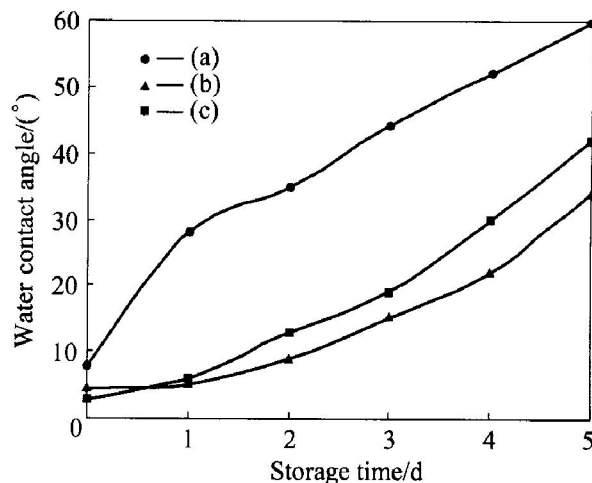


Fig. 5 Sustained effect of photo-induced hydrophilicity of TiO₂ film without SiO₂ overlayer (a), TiO₂ film with SiO₂ overlayer (b), and TiO₂-SiO₂ mixing films (c)

4 DISCUSSION

The contact angle of water maintains low for a long time in dark place both for SiO₂/TiO₂ overlayer films and for TiO₂-40% SiO₂ mixing films, which may be resulted from different mechanism.

Because TiO₂ is a semiconductor, UV light can excite pairs of electrons and holes. The electrons tend to reduce the Ti(IV) cations to the Ti(III) state, and the holes oxidize the O²⁻ anions. In the process, oxygen atoms are ejected, creating oxygen vacancies. Water molecules can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic^[3]. For TiO₂-SiO₂ mixing films, the adsorbed OH groups by TiO₂ diffuse to SiO₂ surface, which enhances the sustained efficiency of hydrophilicity of the mixing film. In addition, the complex oxide of TiO₂-SiO₂ enhances the surface acidity that results in the increasing of the hydroxyl content in the mixing films. So the hydrophilicity and the capability to the absorbed water of the mixing films are increased and can be maintained for a long time in dark place.

However, the mechanism of enhanced hydrophilicity of SiO₂/TiO₂ overlayer films is not the case related above. SiO₂ is an insulator that does not possess photocatalytic properties, so variation in photo-induced hydrophilicity must be due to the interaction between SiO₂ and TiO₂ in the interface. The above experiments show that the enhanced hydrophilicity is attributed to the growth of stable OH group in the uppermost surface and the adsorption of water on the surface attracted by the OH group.

Tada et al.^[15] explained the improved photocatalytic activity with SiO_x monolayer coverage of TiO_2 particles. The phenomenon could be attributed to the increase in the electrostatic attraction of adsorbates to the surface, which was caused by the interfacial charge transfer through the tunneling effect. In general, porous monolayer coverage may exhibit tunneling effect, but the SiO_2 overlayer has thoroughly covered the TiO_2 films and seems little tunneling effect. On the other hand, the electrons and holes generated in the interface between TiO_2 and SiO_2 can transfer to the upper surface without tunnels. So the enhanced hydrophilicity for $\text{SiO}_2/\text{TiO}_2$ overlayer films may be due to other reasons.

The hydroxyl radical, which will produce SiOH group, must be generated in the uppermost surface of the SiO_2 overlayer by UV light irradiation. The photo-generated holes in the TiO_2 layer can transmit through the SiO_2 layer to uppermost surface. Maybe the amorphous SiO_2 structure makes the hole easier to move through the SiO_2 film to the uppermost surface, which can separate a pair of photoelectron and hole away, and decrease the rate of recombination of the pair and keep holes longer.

So we can deduce the reason of the increased hydrophilicity for $\text{SiO}_2/\text{TiO}_2$ overlayer films. The photo-generated electrons in the interface between TiO_2 and SiO_2 tend to reduce the Ti(IV) cations to the Ti(III) state, and the photo-generated holes transmit through the SiO_2 layer to uppermost surface. Once the holes go up to the surface, they can dissociate water adsorbed on the surface and produce stable OH groups, which tend to make the surface hydrophilic. The bonding energy of SiOH is thought to be more stable than TiOH . The stable hydroxyl groups on the surface can result in the increasing of super-hydrophilicity and the capability of holding absorbed water, which means that the super-hydrophilic state of the $\text{TiO}_2/\text{SiO}_2$ multilayer films can maintain for a long time in dark place.

In addition, in order to achieve enough photocatalytic effect, the semiconductor such as TiO_2 is needed to form a charge space layer on the surface, which separates a pair of photoelectron and hole away, and decreases the rate of recombination of the pair^[16]. The SiO_2 overlayer can enlarge the charge space layer in the interface between TiO_2 and SiO_2 layers to keep holes longer. The photo-induced hydrophilicity can be also improved by the enlargement of a charge space layer and the efficiency of holes to reach the uppermost surface.

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