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Reason for the loss of hydrophilicity of TiO_2 film and its photocatalytic regeneration

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Abstract TiO_2 film was prepared on soda-lime glass by sol-gel method. The water contact angle (θ_w) of the fresh TiO_2 film is 0^o. During storage in air, the surface of TiO_2 film is gradually converted to the hydrophobic state. XPS and ITD results reveal that it is due to the adsorption of organic contaminants on TiO_2 surface in air ambience. The lost hydrophilicity of TiO_2 film can be regenerated by UV illumination.

Keywords: TiO_2 film, hydrophilicity, water contact angle, photocatalysis.

Since Wang et al. published the paper “Light induced amphiphilic surfaces”[1,2], the study on the antifogging of glass coated with a thin TiO_2 film arose out of extensive interest [3—7]. Such research was also done in our laboratory[6,7]. In our experiments, we found that the fresh TiO_2 film itself is superhydrophilic (i.e. $\theta_w = 0°$). During storage in air ambience, the surface carbon concentration (C%) increases remarkably, correspondingly, θ_w also increases. In temperature programmed desorption (TPD) test for 17-d-stored sample, the species CH_3CO can be detected. All the results show that the hydrophilic-to-hydrophobic change of TiO_2 film surface is due to the adsorption of volatile organic compounds (VOCs) in air ambience. The lost hydrophilicity of TiO_2 film can be regenerated by photocatalytic decomposition of the adsorbed VOCs under UV illumination.

1 Experimental

1.1 Preparation of TiO_2 film

The washed glass (6 cm × 6 cm) was firstly dip-coated with a layer of $Si(C_2H_5)_4$ ethanol sol (content of $Si(C_2H_5)_4$ 3.95 (weight percent), adjusted to pH = 0.2 by HNO_3), then with ten layers of $Ti(n\text{-}C_4H_9)_4$ ethanol sol (content of $Ti(n\text{-}C_4H_9)_4$ 7.46 (weight percent), adjusted to pH = 0.9 by HNO_3). After drying in air, the glass was annealed in muffle furnace at 300℃ for 0.5 h, then temperature was raised to 530℃ and kept for 2 h. The sample of glass coated with a clean TiO_2 film was attained when it was cooled.

1.2 Characterization of TiO_2 film

The UV-Vis spectrum was taken on a He λ ios α UV-Vis spectroscopy. Surface morphology was observed using an SII model SPA 400 atomic force microscope (AFM). Contact angles were performed on a model CA-A contact angle instrument. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Model ESCALAB 210 X-ray photoelectron spectrometer. The binding energy was calibrated by the C1s (E_b = 284.6 eV). The relative surface atomic concentrations of elements were calculated by a computer using the XPS sensitive factor. After ca. 0.3 h since the annealed glass sample was cooled, the θ_w of fresh TiO_2 surface was determined. After ca. 0.3 h since the θ_w determination was accomplished, the XPS analysis was conducted.

1.3 TPD test

A quartz reactor (inner diameter 10 mm, height 140 mm) was used in TPD tests. The TPD products were analyzed by an ion trap detector (ITD, Finnigan Mat model 700), composed of ion trap mass spectrometer and operated at scan range M (charge-mass ratio) of 10—200, scan rate is 2 per second, helium flow rate of 50 mL • min^{-1}.

1.4 UV illumination

A 200 W high pressure Hg lamp was used as the light source. The distance between light source and glass sample surface is 14 cm and the light intensity for λ = 365 nm is 3 mW/cm^2.

2 Results and discussion

2.1 Light absorption and morphology

Fig. 1(a) is the absorption spectrum of TiO_2 film (background of the glass substrate has been deducted), which shows that the onset absorption ($\lambda_{onset} \approx$ 360 nm) is evidently blue-shifted. The AFM morphology of TiO_2 film is shown in fig. 1(b), which gives a surface structure composed by grains with ca. 55 nm average size and ca. 3.4 r/min roughness.

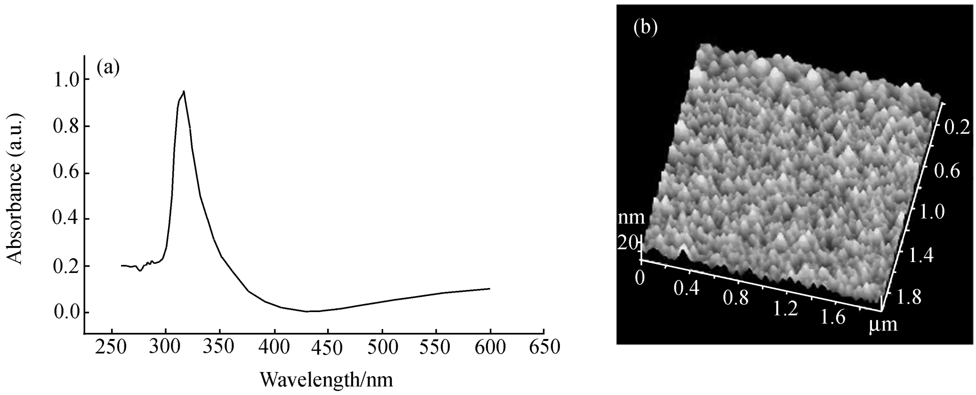


Fig. 1. The UV-Vis spectrum and AFM image of TiO_2 film. (a) UV-Vis spectrum; (b) AFM image.

2.2 Change of hydrophilicity

The fresh TiO_2 film coated on glass is super-hydrophilic, i.e. θ_w = 0°. Fig. 2(a) is the dependence of θ_w on storage time (t). In the first stage, the sample glass was placed in a closed vessel containing unpurified air and in the second stage, it was placed in the open environment of our laboratory. Obviously, the rate of θ_w increase for the first stage is slower than that of the second stage. Another sample glass placed in a vessel was filled with purified air (by 0.5 nm molecular sieve, activated carbon and silica gel), the θ_w varied only from 0° to (2±1°) in 8-d time interval (fig. 2(b)). The above results suggest that the change of θ_w could be related to the adsorption of air contaminants on TiO_2 surface. The saturated adsorption of acetone on fresh TiO_2 film can also cause the θ_w to increase from 0° to 51°. After evacuation at 130 Pa for 40 h, the θ_w remains unchanged (fig. 2(c)), which means that the adsorption of acetone on TiO_2 surface is irreversible.

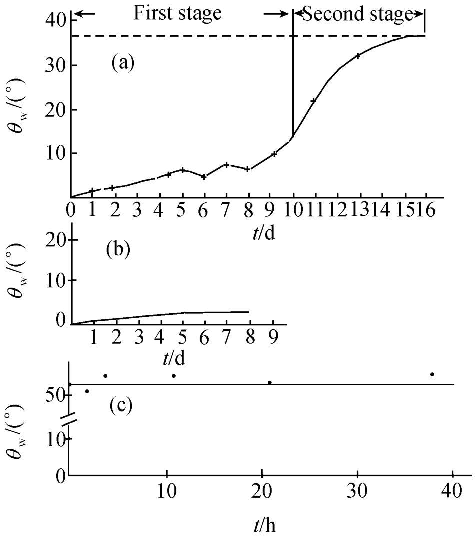
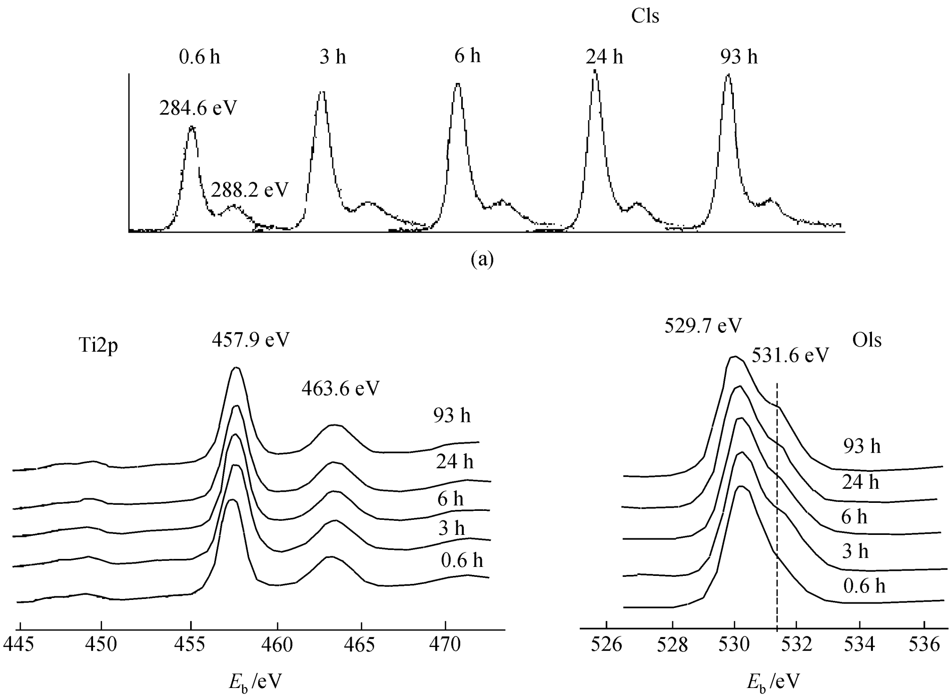


Fig. 2. Dependence of θ_w on time for TiO_2 film. (a) In air ambience; (b) in purified air; (c) desorption test for adsorbed acetone under vacuum condition.

2.3 XPS analysis

2.3.1 Fresh TiO_2 film. Except Ti and O, there are C, Na, Si, Ca and Cl elements on the fresh TiO_2 surface. Their relative atomic concentrations are Ti 16.6%, O 46.9%, C 16.0%, Na 12.1%, Si 4.6%, Ca 2.7% and Cl 0.27%. Na and Ca elements are stemmed out of soda lime glass substrate by thermal diffusion. Before XPS analysis, the fresh sample glass has contacted with ambient air for ca. 0.6 h, so the C element can come from the adsorption of air contaminants.

2.3.2 Change of surface carbon concentration. The XPS spectra of C1s at different stored times shown in fig. 3(a) indicate that there are two kinds of carbon species. Their binding energies (E_b) are 284.6 and 288.2 eV respectively (ΔE_b = 3.6 eV). The C1s peak at 288.2 eV can be assigned to the carboxyl carbon, 284.6 eV to the alkyl carbon[8,9] according to the observed E_b of acrylic acid adsorbed on TiO_2(001)[8] and that of acetic acid/propanoic acid adsorbed on TiO_2(001)[9]. The dependence of C% and θ_w on stored time (t) is shown in table 1 and figs. 4(b) and (a). Compared fig. 4(b) with (a), there clearly exists a corresponding relationship between C%-t and θ_w-t. At t = 0.6 h, though surface carbon content reaches ca. 16%, θ_w is zero, which suggests that the low-level carbon content on film surface does not affect the water spreading completely over the surface. At the time interval of 0.6—6 h, θ_w rises steeply with the increasing of surface carbon content. At $t > 6$ h, accompanying the increase of surface carbon content to slow down, the change of θ_w is also reduced and then approaches to a steady value (43±1)°. After storing for 17 d, the θ_w still remains at (42±1)°, while another sample stored in a closed vessel filled with



(a)

(b)

(c)

Fig. 3. Dependence of C1s, Ti2p, O1s spectra on time. (a) C1s spectra; (b) Ti2p spectra; (c) O1s spectra.

purified air (by 0.5 nm molecular sieve, activated carbon and silica gel) for 17 d, the θ_w is only $(1 \pm 1)^\circ$ (see table 1). The above results strongly support that the hydrophilic-to-hydrophobic change of TiO_2 film surface is due to the surface contamination by organic compounds. This phenomenon can be illustrated by thermodynamic theory of surface wetting action[10]. The clean metal oxide surface has high surface energies (500—5000 mN/m), and many low surface energy liquids (e.g. H_2O, liquid paraffins) can spontaneously spread over their surfaces, i.e. $-\Delta G = \gamma_{sg} - \gamma_{sl} - \gamma_{lg} > 0$, where ΔG is surface free energy change, γ_{sg} the solid-gas interface energy, γ_{sl} the solid-liquid interface energy, and γ_{lg} the liquid-gas interface energy. After contamination by some organic compounds, the surface energy of metal oxide is lowered, and then, the low surface energy liquid is never again to spread over its surface but can form drops. According to Young's equation

$$\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}},$$

where θ is liquid contact angle, the greater the θ, the worse the wetting power of liquid on solid surface.

2.3.3 Ti2p, O1s spectra. In fig. 3(b) , E_b (Ti2p$_{3/2}$) = 457.9 eV, E_b(Ti2p$_{1/2}$)= 463.6 eV, and FWHM of Ti2p$_{3/2}$ peaks =1.65 eV are typical for Ti^{4+}. The peak position of Ti2p$_{3/2}$ and Ti2p$_{1/2}$ did not

Table 1 The change of relative surface atomic concentrations and θ_w with stored time

Relative surface atomic concentration (%)	Stored time/h					Remark
	0.3—0.6	3	6	24	93	
C	16.4	22.0	23.0	25.2	24.6	stored in air for 402 h θ_w = (42±1)° stored in a closed vessel filled with purified air for 17 d θ_w = (1±1)°
O(1)	48.0 (14.9)	49.8 (17.4)	48.7 (16.3)	48.5 (16.5)	48.8 (17.8)	
Ti	16.3	14.8	15.0	14.6	13.5	
Na,Si,Ca	19.4	13.6	13.3	11.7	13.1	
θ_w	0°	17°	30°	38°	43°	

Values in brackets are relative surface oxygen concentration for E_b = 531.6 eV.

change during storage, which indicates that the valence state of titanium remains constant, but its surface concentration slightly decreases (see table 1). Along with the stored time prolonging, the O1s peak gradually widens and the shoulder becomes evident (fig. 3(c)). After deconvolution, there are two O1s peaks. E_b = 531.6 eV peak represents the carboxyl oxygen, 1.9 eV greater than crystal lattice oxygen peak (E_b = 529.7 eV)[9]. During storage the surface concentration of carboxyl oxygen increases while the surface concentration of crystal lattice oxygen has some reduction (table 1).

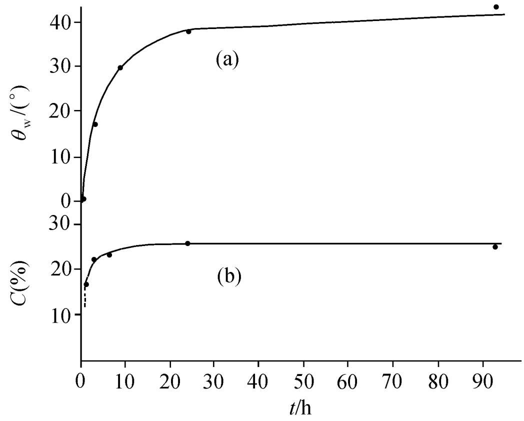


Fig. 4. Dependence of C% and θ_w on time. (a) θ_w-t; (b) C%-t.

It is well known that the clean surfaces of metal oxides are very easily to adsorb the foreign compounds in air ambiance, such as H_2O and low-level volatile organic compounds (VOCs) arising from various channels. The dissociative adsorption of H_2O on TiO_2 surface forms two types of OH$^-$, i.e. acid and base sites, which are as well as the adsorption centers for VOCs[11]. Kurtz et al.[12] have proved that the saturation coverages of dissociative adsorption of H_2O are independent of the initial concentration of its surface oxygen vacancies on TiO_2 (110), however, the rate of dissociative adsorption is higher on defective surfaces. Falconer et al.[13] gave the evidence that the surface oxygen vacancies produced by UV illumination will be replenished by air oxygen at room temperature. The dissociative adsorption of H_2O cannot change the hydrophilic property of TiO_2 surface [14], of course, the adsorption of VOCs can.

2.4 Products of ITD

For further verifying the adsorption of VOCs on TiO_2 film, the TPD tests for the 17-d-stored sample and reference sample (i.e. freshly prepared TiO_2-coated glass) were conducted in high purity He flow. The desorption products were analyzed by ITD. Subtracting the signal counts of reference sample (fig. 5(a)) from that of 17-d-stored sample (fig. 5(b)) at desorption temperature T = 470℃, the amount of M = 43 and 12 species in 17-d-stored sample is larger than that in reference sample (indicated by positive bars in fig. 5(c)). The TPD test of 17-d-stored sample was conducted immediately after the TPD test of reference sample, so the M = 14 to 34 species (indicated by negative bars) were mainly originated from the TPD quartz reactor. Figs. 5(d) and (e) are the TPD results of M = 43 for reference sample and 17-d-stored sample respectively. Subtracting fig. 5(d) from fig. 5(e), we can obtain fig. 5(f). M = 43 is the species CH_3CO, which can be produced in mass analysis of some chemicals, such as CH_3COOH, $CH_3COOC_2H_5$, CH_3CHO, and $CH_3(CO)CH_3$[15]. So we guess that the adsorbed VOCs from the ambient air of our laboratory were mainly the CH_3CO group containing organic compounds (acetone, ethyl acetate etc. have been proved to be contaminants for clean TiO_2 surface [6]). The above results are in accordance with the XPS results in sec. 2.3.

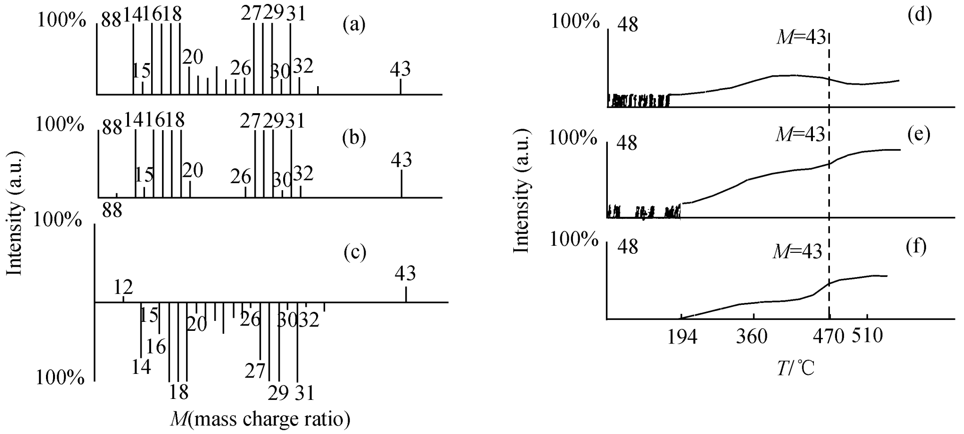


Fig. 5. Results of temperature-programmed desorption (TPD) products analyzed by ion trap detector. (a) Signal intensities of reference sample at desorption temperature T = 470℃; (b) signal intensities of 17-d-stored sample at desorption temperature T = 470℃; (c) (b) – (a); (d) TPD curve of reference sample(M = 43); (e) TPD curve of 17-d-stored sample (M = 43); (f) (e)–(d).

2.5 Photocatalytic regeneration

TiO_2 is a good photocatalyst. Once the clean TiO_2 surface was contaminated by VOCs, under UV illumination, the VOCs will be photocatalytically decomposed to recover the cleanliness of TiO_2 surface while the hydrophilicity will be regenerated (see fig. 6 cycling tests). Fig. 6(I) is θ_w-t curve for the first run test, which was conducted in a laboratory not the same as that in sec. 2.3. Storing for 60 d at room temperature, the θ_w reached to a steady value (23°). After 5 h UV illumination, θ_w lowered to ca. 6°. The curves for the second and third run tests are shown in figs. 6(II) and (III). Their steady θ_w values were 30° and 28°, respectively, and after 5 h UV illumination, θ_w lowered to ca. 5° for the second run test. The initial rate of θ_w increase $(d\theta_w/dt)_{t=0}$ for the first run was different from that of the second run and the third run. The latter is $4^{\circ} \cdot h^{-1}$, ca. 60 times higher than the former $0.06^{\circ} \cdot h^{-1}$, which is possibly resulted from the enhancement of adsorption activity of organic contaminants on TiO_2 surface after UV illumination. The concentration and kinds of air contaminants in our laboratory would be different at different times, which could be the reason of the different steady θ_w values of the above test runs. But the differences of steady θ_w values are much smaller than that of $(d\theta_w/dt)_{t=0}$, indicating that the adsorption of contaminants on TiO_2 surface is of approximate monolayer and independent of the initial adsorption rate. As for the θ_w only lowered to 5^o under UV illumination, it might be due to that there existed the photoadsorption of air contaminants accompanied with the photocatalytic decomposition of the adsorbed contaminants on TiO_2 surface. When the rates of such two processes become equal, the θ_w never again decreases.

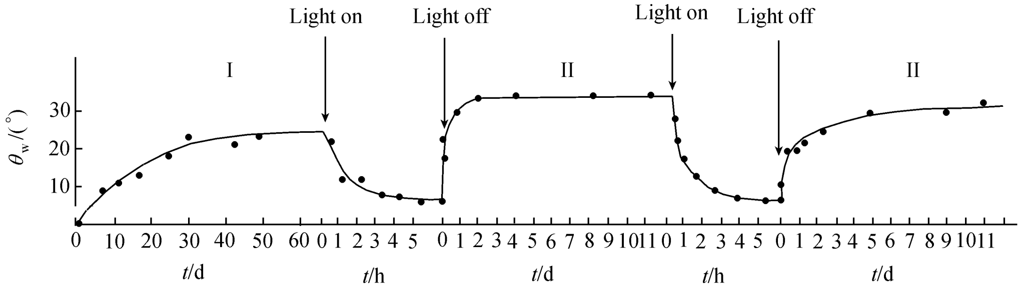


Fig. 6. Photoregeneration of the hydrophilicity of contaminated TiO_2 film.

3 Conclusions

(i) The superhydrophilicity of clean TiO_2 film is its intrinsic property and the loss of the hydrophilicity in air ambience is due to the adsorption of organic contaminants.

(ii) The lost hydrophilicity of TiO_2 film can be regenerated under UV illumination, but the θ_w only can be lowered to ca. 5°. It might be due to that there exists the photoadsorption of air contaminants accompanied with the photocatalytic decomposition of adsorbed contaminants on TiO_2 surface. When the rates of such two processes become equal, the θ_w never again decreases.

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