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 ($\theta_w$) of the fresh TiO$_2$ film is 0°. 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. $\theta_w = 0^\circ$). During storage in air ambience, the surface carbon concentration (C%) increases remarkably, correspondingly, $\theta_w$ also increases. In temperature programmed desorption (TPD) test for 17-d-stored sample, the species CH$_3$CO 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$_2$H$_5$)$_4$ ethanol sol (content of Si(C$_2$H$_5$)$_4$ 3.95 (weight percent), adjusted to pH = 0.2 by HNO$_3$), then with ten layers of Ti(n-C$_4$H$_9$)$_4$ ethanol sol (content of Ti(n-C$_4$H$_9$)$_4$ 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°C for 0.5 h, then temperature was raised to 530°C 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 i o s 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 $\theta_w$ of fresh TiO$_2$ surface was determined. After ca. 0.3 h since the $\theta_w$ 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 $\lambda = 365$ 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.](image)

2.2 Change of hydrophilicity

The fresh TiO$_2$ film coated on glass is super-hydrophilic, i.e. $\theta_w = 0^\circ$. Fig. 2(a) is the dependence of $\theta_w$ on storage time ($t$). In the first stage, the sample glass was placed in a closed ves-