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Photocatalytic and Hydrophilic Properties of TiO_2/Fe_2O_3 Composite Films

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Abstract

TiO_2/Fe_2O_3 composite thin films were prepared on common glass substrates by sol-gel processing and dip-drawing method. The effect of Fe_2O_3 content on the photocatalytic and hydrophilic properties of composite films was studied. The results indicate that the photocatalytic activities of composite TiO_2 films are superior to that of pure TiO_2 film, and the film containing 0.5% Fe_2O_3 has the best photocatalytic activity. The hydrophilicity is difference with variant Fe_2O_3 content, the films containing 0.05%~0.1% Fe_2O_3 have the best hydrophilicity and their contact angles are 0°.

1. Introduction

The super-hydrophilic and photocatalytic properties of TiO_2 thin film have attracted a great deal of attention in recent years [1,2]. By the irradiation of UV light, TiO_2 film not only can break down organic compounds, but also spreads the water flatly on its super-hydrophilic surface and makes it easily to keep the surface self-cleaning. There have been some research papers about improving the photocatalytic activity and super-hydrophilic properity of TiO_2 thin films recently. A. Fujishima et al. [3] have discussed the current progress in the area of TiO_2 photocatalysis, and presented photoinduced superhydrophilic phenomenon involving TiO_2 and its applications. T. Watanabe et al. [4] have been evaluated photoinduced hydrophilic conversion on the different crystal faces of rutile single crystal and also polycrystalline anatase titanium dioxide to clarify the dependence of the crystal structure on the photoinduced hydrophilic conversion. However, the super-hydrophilic property of composite TiO_2/Fe_2O_3 film has not been reported yet. Composite TiO_2/Fe_2O_3 nanometer thin films were prepared via sol-gel method on the soda-lime glasses in this paper, and the photocatalytic and hydrophilic properties were studied.

2. Experiments

Precursor solutions for TiO_2/Fe_2O_3 composite films were prepared by the following method. Tetranbutyl titauate was dissolved in ethanol. After stirring vigorously for 30min at room temperature, HNO_3 was added dropwise to the solution to adjust pH=3.5, and then distillated water was added dropwise to the solution with a burette under stirring. The resultant alkoxid solution was kept stirring for hydrolysis reaction for 4h, resulting in the TiO_2 sol. The chemical composition of the beginning alkoxid solution was $(C_4H_9O)_4Ti:C_2H_5OH:H_2O$=1:82:3 in mole ratio. On the other hand, $FeCl_3 \cdot 6H_2O$(AR) was dissolved in ethanol. After stirring and refluxing vigorously for 1h at 90℃, distillated water was added dropwise to the solution with a burette under stirring. The solution was kept stirring for hydrolysis reaction for 6h, resulting in the Fe_2O_3 sol. The chemical composition of the beginning solution was $FeCl_3:C_2H_5OH:H_2O=1:66:3$ in mole ratio. Then TiO_2 sol and Fe_2O_3 sol was mixed in proportion as $Fe_2O_3:TiO_2$=0.05%, 0.1%, 0.25%, 0.5%, 1%, 2.5%, 20% (mole ratio), respectively. Then composite TiO_2/Fe_2O_3 sols containing different amount of Fe_2O_3 were prepared. TiO_2/Fe_2O_3 films formed on the substrates were prepared from the sol solutions by dipping-withdrawing at room temperature. The withdrawal speed was 3mm/s. The thickness of TiO_2/Fe_2O_3 films was adjusted by repeating the cycle from dipping to heat treatment. The substrates coated with TiO_2/Fe_2O_3 composite gel films and the corresponding composite xerogel were dried with infrared light and then heat-treated together at different temperature for 60min in air using an electric oven.

The TiO_2/Fe_2O_3 powder which was heat-treated at 450℃ was characterized by X-ray diffraction instrument (Type D/maxⅢ, Japan). The hydrophilic properties of various TiO_2/Fe_2O_3 films were evaluated by measuring the contact angle for water of TiO_2/Fe_2O_3 thin films with a contact angle device (Type JC2000A, China). The photocatalytic activity of the composite films was evaluated by measuring the photocatalytic decolorization of aqueous methyl orange. The method is as following: pure TiO_2 film and TiO_2/Fe_2O_3 composite films were placed in aqueous methyl orange which the initial concentration is 46mg/l in quartz cells, respectively. A ultra-violet lamp (30W) was used as a light source. The averaged intensity of UV irradiance was 78 $\mu W/cm^2$ by measuring with a UV irradiance meter (Model UV-A, China), wavelength range is 320-400nm, and peak wavelength is 360nm. The concentration of methyl orange was determined by UV-VIS8500 spectrophotometer (wavelength range 200-1100nm, China). All the films had been illuminated before measuring by natural light for 30min after being placed in dark for 24h.

3. Results and Disscission

Fig.1 shows the XRD patterns of pure TiO_2 and composite TiO_2/Fe_2O_3 ($Fe_2O_3:TiO_2$= 20%) powders which have been heat-treated at 450℃ together with the corresponding TiO_2 and TiO_2/Fe_2O_3 films. It indicates that the constituents detected on composite TiO_2/Fe_2O_3 are TiO_2 and Fe_2O_3, respectively, and the crystal form of TiO_2 detected on pure TiO_2 and composite TiO_2/Fe_2O_3 are all confirmed to be anatase. The patterns also show that the diffraction peak width of TiO_2/Fe_2O_3 is broader than that of pure TiO_2, so the average diameter of the former is smaller than that of the latter. It indicates that the rate of TiO_2 particle growth is decreased because of the existence of a small amount of Fe_2O_3. There might be two reasons for above phenomenon, one is that the containing variant Fe_2O_3 particle cannot be normal growth because the charge distribution on the surface of TiO_2 is changed owning to the existence of Fe-iron; the other is that the growth of TiO_2 particle in composite sol is impeded for Fe_2O_3 particle admixing among TiO_2 particles.

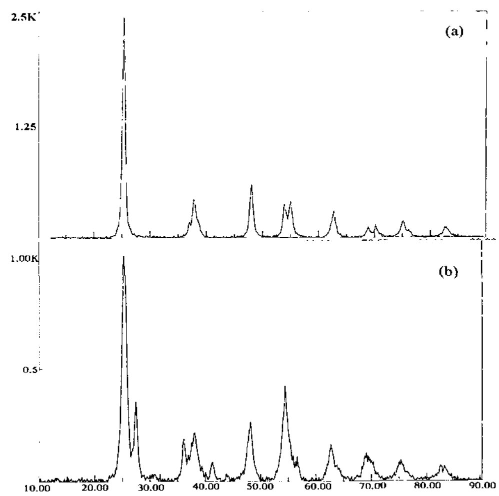

Fig. 1. XRD patterns of TiO_2 powder
(a) Containing 0 Fe_2O_3
(b) Containing 20% Fe_2O_3

Fig. 2 shows the results of photocatalytic decolorization of methyl orange degraded by TiO_2/Fe_2O_3 films containing different amount Fe_2O_3 (3 coating cycle times, heat-treated at 450℃, after 30min illuminated by ultraviolet lamp). From Fig. 2, we can see that the photocatalytic activities of all TiO_2/Fe_2O_3 composite films are higher than that of pure TiO_2 film. This phenomenon is attributed to the decreasing in recombination of photoinduced carriers in TiO_2/Fe_2O_3 composite films, because the conduction band energy level of Fe_2O_3 is 0eV and that of TiO_2 is -0.25eV which result in photoinduced electrons easily transfer from the surface of TiO_2 to the surface of Fe_2O_3 when Fe_2O_3 and TiO_2 are compound. It is found that the photocatalytic activity increases with Fe_2O_3 content in the films until it is 0.5%, then the activity decreases.

The contact angle for water of TiO_2/Fe_2O_3 thin films (3 coating cycle times, heat-treated at 450℃) was listed in table 1. It is found that the contact angle for water on pure TiO_2 film is 2.5°, the contact angles for water on the TiO_2/Fe_2O_3 films which the proportion is Fe_2O_3:TiO_2=0.05%, 0.1%, respectively, are 0°, and the contact angles on the TiO_2/Fe_2O_3 films in which the proportion is Fe_2O_3:TiO_2=0.25%, 0.2%, 0.3%, respectively, increase in turn. The results indicate that a little doping of Fe_2O_3 can improve the hydrophilicity of TiO_2 film, which is probably attributed to the increase in the amount of hydroxyl of the composite films. The optimal proportion for superhydrophilicity is Fe_2O_3: TiO_2=0.05%−0.1%.

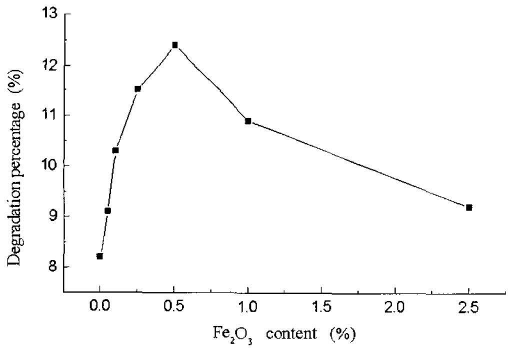

Fig. 2. Decolorization of methyl orange degraded by TiO_2/Fe_2O_3 films containing different amount Fe_2O_3.
(3 coating cycle times, heat-treated at 450℃)

Table 1 Contact angle on the surface of TiO_2/Fe_2O_3 composite films containing variant Fe_2O_3

Fe_2O_3/TiO_2 (%)	0	0.05	0.1	0.25	0.5	1	2.5
Contact angle (°)	2.5	0	0	3.5	5.5	10	15

4. Conclusions

The TiO_2/Fe_2O_3 composite coating films are prepared from precursor solutions added with different amount Fe_2O_3 on soda lime glasses by sol-gel method. The super-hydrophility and photocatalytic property of the composite films are studied. It shows that the hydrophilic property and photocatalytic activity of TiO_2/Fe_2O_3 composite films are superior to pure TiO_2 film. The contact angle for water of the TiO_2/Fe_2O_3 composite films is 0° as the amount of Fe_2O_3 in the films is 0.05% - 0.1% and heat-treated at 450℃. The photocatalytic activity of the composite films is the best as the containing of Fe_2O_3 in the films is 0.5%.

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