Synthesis, wettability and optical properties of $x\text{TiO}_2-(1-x)\text{SiO}_2$ composite thin films

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Abstract. $x\text{TiO}_2-(1-x)\text{SiO}_2$ composite thin films with $x=1.0, 0.9, 0.7, 0.5$ were dip-coated on glass substrates by sol-gel method. The effects of composition on the microstructure, wettability and optical properties were investigated by X-ray diffraction (XRD), contact angle tester and ultraviolet visible spectrophotometer. Results showed that only the anatase diffraction peaks of $\text{TiO}_2$ were found in composite materials. With the increase of $\text{SiO}_2$ concentration, the crystallization degree of the composite material decreased slightly. The hydrophilicity was enhanced after coating on glass substrates. The water contact angle of $\text{TiO}_2$ film was the smallest in all the films. All the composite films were transparent in visible wavelength. And the average transmittance of $0.5\text{TiO}_2:0.5\text{SiO}_2$ was highest. The sharp decrease of transmittance was observed in the transmittance spectra, which was related to absorption of photos by electron in valence band.

1. Introduction

$\text{TiO}_2$ is a low cost, corrosion resistant, non-toxic and chemical stable semiconductor photocatalyst. It has been widely studied for using in solar cells, self-cleaning, biomaterials and self-sterilizing. While, the large band gap and photogenerated electron-hole recombination rate limit the application filed of $\text{TiO}_2$. Several methods have been used to reduce the band gap and improving the efficiency of photogenerated electron-hole separation by adjusting the composition and microstructure. Most popular used method is to dope materials with transition metal$^{[1]}$, noble metal$^{[2-4]}$, non-metal$^{[5, 6]}$ and carbon materials$^{[7]}$. However, the doping modification affects the anatase structure and electron state of $\text{TiO}_2$.

Another modification method is to prepare composite material. Preparation and properties of $\text{TiO}_2$ composite has attracted a great deal of attention in recent years. $\text{ZnO}^{[8]}$, carbon quantum dots$^{[9]}$, $\text{C}_3\text{N}_4$ $^{[10]}$, $\text{WO}_3^{[11]}$, $\text{TiN}^{[12]}$ and $\text{SiO}_2^{[13-15]}$ have been used to prepare $\text{TiO}_2$ composite materials. The heterostructure formed in the interface can capture electron and extended the lifetime of the photogenerated carriers.

Although many studies have been reported about $\text{TiO}_2-\text{SiO}_2$ composite thin films, the correlation between composition and wettability, optical properties have not yet been reported. In this work, $\text{TiO}_2-\text{SiO}_2$ composite thin films with different $\text{SiO}_2$ concentration were fabricated on glass substrates by sol-gel dip-coating method. The effect of composition on the microstructure, wettability and optical properties were investigated. The results can be used as a reference for $\text{TiO}_2$ matrix composites.
2. Experimental
For TiO\textsubscript{2} sol, tetrabutyl titanate (TBOT) was used as titanium source, ethanol as solvent, nitric acid as acid catalyst and water as hydrolysis agent. The molar ratio of TBOT/ethanol/nitric acid/H\textsubscript{2}O was 1:20:1.5:1. In the experiment, tetrabutyl titanate was added to half of ethanol and stirred for 30 min, which was named solution A. Nitric acid and water were added to the other half of ethanol, which was named solution B. In the stirring, the solution B was gradually added to the solution A. The mixed solution was stirred for 1 hour to obtain TiO\textsubscript{2} sol. In the xTiO\textsubscript{2}-(1-x)SiO\textsubscript{2} (x=0.9, 0.7, 0.5) sol, partial tetraethoxy silane (TEOS) was used instead of tetrabutyl titanate (TBOT).

The films were deposited on glass substrates (25×25×2 mm). Prior to deposition, the substrates were cleaned in an ultrasonic cleaner with acetone, ethanol and distilled water for 10 min each. The films prepare process parameter by dip coating were as follows: the withdraw speed was 2000 μm/min, and the immersion time was 60 s. The wet films were dried at 100 °C for 10 min and heat treated at 300 °C for 30 min in the muffle furnace. In order to increase the thickness of the films, the coating-heating process was repeated twice. TiO\textsubscript{2}-SiO\textsubscript{2} films were annealed at 500 °C for 60 min.

To study the effect of composition on the microstructure of TiO\textsubscript{2}-SiO\textsubscript{2} composite materials, the powders were prepared by the corresponding sol. The sintering process of the powders was consistent with that of the films.

Structure of the fabricated TiO\textsubscript{2}-SiO\textsubscript{2} composite powders were characterized by X-ray diffraction (XRD) using a Cu Kα1 (λ=1.5418 Å) X-ray radiation source in Bragg–Brentano (θ–2θ) configuration. The wettability of the composited films were evaluated by measuring the contact angle of a water droplet on the film surface. The transmittance spectra of the composite films were measured by ultraviolet visible spectrophotometer in the wavelength from 200 to 1100 nm.

3. Results and discussion
3.1. Optical properties of TiO\textsubscript{2}-SiO\textsubscript{2} sol
The stability of sol is very important for the preparation of high-quality films by sol-gel method. The experimental environment (temperature, humidity, etc.) and preparation process parameters determined the stability of the sol. In our experiment, the effect of solution concentration and PH value on the stability of sol was studied. The light yellow transparent sol was obtained and can be placed over three months at room temperature (about 25 °C) and humidity of about 45%. The transmittance spectra of xTiO\textsubscript{2}-(1-x)SiO\textsubscript{2} sol with x=1.0, 0.9, 0.7, 0.5 were showed in figure 1. All of the sol were high transparent in visible wavelength range.

![Fig. 1 Transmittance spectra of TiO\textsubscript{2}-SiO\textsubscript{2} sol](image)

3.2. Microstructure of TiO\textsubscript{2}-SiO\textsubscript{2} composite materials
Figure 2 gives the XRD patterns of TiO\textsubscript{2}-SiO\textsubscript{2} powders. All the diffraction peaks were well matched with the tetragonal TiO\textsubscript{2} anatase phase. The diffraction peak index was marked in the figure according
to the JCPDS card (No: 84-1286). No other diffraction peaks were observed in TiO$_2$-SiO$_2$ composite materials. And the angle of antase phase diffraction peak has not changed with the addition of SiO$_2$. This means that there is no bonding structure between TiO$_2$ and SiO$_2$ in the composite materials. The diffraction background for 0.5TiO$_2$-0.5 SiO$_2$ was enhanced, especially from 15 to 30°. It may be related to the formation of amorphous SiO$_2$.

3.3. Wettability and optical properties of TiO$_2$-SiO$_2$ composite thin films

The wettability of material surface was characterized by water contact angle measurements. 3 mL water droplet were applied to define the wettability of TiO$_2$-SiO$_2$ composite thin films by measuring contact angles. The results were shown in figure 3. The water contact angle decreased and the hydrophilicity increased after coating on glass substrates. TiO$_2$ has the smallest water contact angle. The contact angle increased with the increase of SiO$_2$ content. This may be related to composition and the degree of crystallization of the films.

![Fig. 3 Water contact angle of glass and TiO$_2$-SiO$_2$ thin film](image1)

![Fig. 4 Transmittance spectra of TiO$_2$-SiO$_2$ thin films on glass substrate](image2)

The transmittance was measure by normal incidence in the wavelength of 200-1100 nm. Transmittance spectra of TiO$_2$-SiO$_2$ composite thin films with different composition were shown in figure 4. It can be seen that all the samples were high transmittance in visible and near-infrared regions. 0.5TiO$_2$-0.5SiO$_2$ film has the highest average transmittance. Three interference fringes can be revealed in TiO$_2$-SiO$_2$ composite films except TiO$_2$ film. This was related the thickness of the films [8]. A strong absorption region was observed in wavelength below 360 nm. It was due to the photons with high energy (short wavelength) can be absorbed by electrons in the valence band. The electron that absorbs energy in the valence band can transition to the conduction band. The electron-hole pair was formed.
and the properties of the thin films were changed.

4. Conclusion

$\mathrm{xTiO}_2-(1-x)\mathrm{SiO}_2$ ($x=1.0, 0.9, 0.7, 0.5$) composite powder and films were prepared by sol-gel dip-coating method. The composite materials were crystallized with anatase structure. As the content of $\mathrm{SiO}_2$ increase, the crystallization degree of the composite materials decreased. The composition and crystallization degree of the films affect wettability. The contact angle of $\mathrm{TiO}_2$ was smallest. The composite films were highly transparent in the visible region and strongly absorbed in the ultraviolet region. $0.5\mathrm{TiO}_2-0.5\mathrm{SiO}_2$ film has the highest average transmittance in the composite films.

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