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Synthesis, characterization and hydrophilic properties of $ZnFe_2O_4$–TiO_2 composite film

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ABSTRACT

$ZnFe_2O_4$–TiO_2 composite films have been successfully prepared via a sol–gel method and deposited on glass slides through dip coating process. The hydrophilicity of $ZnFe_2O_4$–TiO_2 composite films was investigated by the contact angles measurements under different conditions, including heat treatment temperature, molar ratios of $ZnFe_2O_4$ to TiO_2 and coating layers. The results revealed that the 7 mol% $ZnFe_2O_4$-TiO_2 composite film exhibits an excellent superhydrophilic performance with a contact angle 0°. Compared with normal glass, the self-cleaning glasses also display antifogging property. The transmittance of $ZnFe_2O_4$–TiO_2 composite films was characterized by UV–vis spectra in details. Coating layers and different molar percents of $ZnFe_2O_4$ all have impact on the light transmittance. Moreover, the structure and morphology of the $ZnFe_2O_4$–TiO_2 sample were investigated by means of X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDS) and scanning electron microscopy (SEM).

1. Introduction

Titanium dioxide (TiO_2) as a well-known photocatalytic material [1–8] is also widely used in preparation for self-cleaning glass [9]. For practical applications of TiO_2 films, high transmittance is critically important. However, TiO_2 has a large refractive index and can reflect a large portion of incident light [10]. In addition, the research focused on the wettability of TiO_2 is also studied, especially its hydrophilic property [11]. Superhydrophilic property of the surface allows water to spread completely across the surface rather than remaining as droplets [12].

$ZnFe_2O_4$ have attracted extensive attention as a multifunctional material [13–16]. Recently, pure $ZnFe_2O_4$ has been found possessing superhydrophilic properties, and the contact angle can reach 0° [17]. Thus, it is a good candidate for superhydrophilic materials. What is more, $ZnFe_2O_4$ is an efficient semiconductor photocatalyst that is sensitive to visible light [14]. Thus, the incorporation of $ZnFe_2O_4$ will probably enable the adsorption spectrum of TiO_2 to extend to longer wavelength, and its photocatalytic activity can also be improved [18–22].

In this work, we prepared the $ZnFe_2O_4$–TiO_2 composite films via a sol–gel synthesis route. The coatings are obtained by a dip-coating method for the advantages such as simplicity, controllability, reliability and reproducibility [12]. The hydrophilicity of as-prepared $ZnFe_2O_4$–TiO_2 composite films were analyzed by measurements of contact angles. We also studied the transmittance of $ZnFe_2O_4$–TiO_2 composite films as well as the antifogging property [23,24]. Moreover, the structure and morphology of the $ZnFe_2O_4$–TiO_2 powder sample were characterized.

2. Experimental

2.1. Preparation

Sol–gel method was used to prepare the $ZnFe_2O_4$–TiO_2 composite films. All the chemicals are of analytical grade and used as received. The details are as follows: $Zn(NO_3)_2$ and $Fe(NO_3)_3$ with molar ratio 1:2 were added to 20 ml of absolute ethanol under magnetic stirring. Subsequently, certain amount of tetrabutyl titanate was dissolved in the above solution. They were sealed with plastic wrap beaker, stirred for 2 h, and allowed to stand for 1 h. Then, the clear homogeneous gel was obtained. The coatings were prepared by a dip-coating method. Silicate glass plates ($25 \times 75 \times 2$ mm) are used as the support

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substrates. First, the glass plates were washed in water, acetic acid and ethanol, respectively. Then, the cleaned glass was allowed to put in the sol for 1 min, and a pulling method was used with a speed of 6 cm/min. After that, the gel coating was dried for 30 min in air. The prepared films were treated in muffle furnace for 1 h, and then cooled to room temperature. Finally, the uniform and transparent $ZnFe_2O_4$–TiO_2 composite films were obtained. The flowchart of preparation of $ZnFe_2O_4$–TiO_2 composite films was shown in Fig. 1.

For the preparation of $ZnFe_2O_4$–TiO_2 powder, the as-obtained sol was placed in air at room temperature for 4–5 days, and then into the oven at 100 °C for 30 min to form a gel. Then, the gel was ground into powder in a mortar and finally handled with a muffle furnace at different calcination temperatures to obtain the samples.

2.2. Characterization

Wetting property of the $ZnFe_2O_4$–TiO_2 composite film was evaluated by contact angle measurements performed using a sessile drop method. X-ray diffraction (XRD) spectroscopy was performed on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning step width of 0.02° and the scanning rate of 0.2° S-1 were applied to record the patterns in the 2θ range of 20–70°. The general morphology of the samples was examined using scanning electron microscopy (SEM) on a FEI QUANTA FEG 250 instrument operated at 20 kV. UV–vis diffuse reflectance spectra (DRS) of the samples were measured by using a Varian Cary 5000 UV–vis spectrophotometer. The spectra were recorded at room temperature in air from 300 nm to 800 nm. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Hydrophilicity of $ZnFe_2O_4$–TiO_2 composite film

The heat treatments have been carried out with temperature from 400 °C to 600 °C. It can be observed that more excellent hydrophilic property is obtained at high calcination temperature as shown in Fig. 2. When the heat treatment temperature reaches 600 °C, the softening deformation of glass substrate has occurred due to high temperature. Therefore, the hydrophilic property was studied at an upper temperature limit of 550 °C. The contact angle was found to decrease first and then slowly increased with the increase of $ZnFe_2O_4$ content. It is surprisingly found that the contact angle approaches to zero at 500 °C and 550 °C when the molar fraction of $ZnFe_2O_4$ is 7 mol% in $ZnFe_2O_4$–TiO_2 composite. Thus, the incorporation of $ZnFe_2O_4$ into TiO_2 significantly improved the hydrophilic properties for self-cleaning glass.

Fig. 3 shows the hydrophilic properties of 7 mol% $ZnFe_2O_4$–TiO_2 composite films calcined at 300 °C with different numbers of coating layers. The results indicated that the contact angle decreased with the increase of coating layer due to the resultant rougher surface. With further increasing the coating layer, the thickness of film reaches a certain value. The homogeneity of crystal grains in composites would be improved, which is not conducive to the hydrophilicity of the composite films.

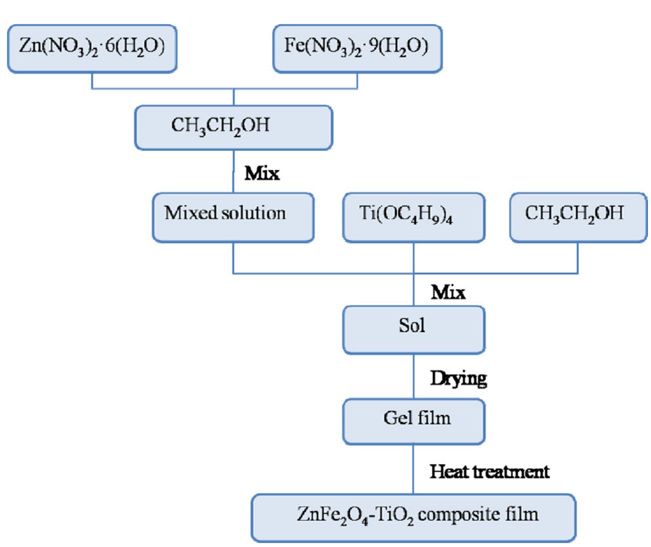

Fig. 1. Flowchart for preparation of the $ZnFe_2O_4$–TiO_2 composite films.

3.2. Antifogging property

The $ZnFe_2O_4$–TiO_2 composite film exhibits surperhydrophilicity that doubtlessly meets the requirement of antifogging coatings. Therefore, the antifogging behavior of the superhydrophilic coating was studied. The uncoated part (up in Fig. 4a and b) fogged easily while the coated part (down in Fig. 4a and b) did not fog. As water droplets are condensed at the surface, the superhydrophilicity creates a thin and transparent film of water instead of droplets. This effect is clearly shown in Fig. 4 for the coated glass slide. This result demonstrated that the $ZnFe_2O_4$–TiO_2 composite film possesses excellent antifogging property.

3.3. Optical transmittance

Fig. 5 presents the optical transmittance of $ZnFe_2O_4$–TiO_2 composite films with different molar fractions of $ZnFe_2O_4$. It can be seen that the transmittance of the composite films becomes lower with the increase of $ZnFe_2O_4$ content. Nevertheless, the transmission rates of all the $ZnFe_2O_4$–TiO_2 composite films with the molar ratios from 1 mol% to 11 mol% are beyond 85% in the visible light region, meeting the requirements for visible light transmittance of architectural glass.

As can be seen from Fig. 6, the increase of coating layers will reduce the transmittance rate. It is mainly because that the thickness of coating is close to the destructively coherent criteria of reflected light. More coating layers have much more particles in the glass surface, thus reducing the number of activated particles in the film and increasing the scattering capacity and refractive index of the film. Therefore, the visible-light transmittance capability weakened.

3.4. X-ray diffraction

The structure and the crystalline phase evolution of the sol–gel derived $ZnFe_2O_4$–TiO_2 nanostructured films were investigated by X-ray diffraction (XRD). The XRD patterns of the 7 mol% $ZnFe_2O_4$–TiO_2 powder sample at different calcination temperature were shown in Fig. 7. When the calcination temperature is 300 °C, some diffuse diffraction peaks were observed, indicating the formation of amorphous phase of TiO_2. As the temperature reaches 400 °C, we can clearly see the characteristic diffraction peaks of anatase TiO_2. With further increasing calcination temperature, a small amount of rutile TiO_2 formed. Due to the low content of $ZnFe_2O_4$, the diffraction peaks of $ZnFe_2O_4$ are not obvious compared to that of TiO_2.

Fig. 8 presents the X-ray diffraction patterns of $ZnFe_2O_4$–TiO_2 powder with different contents of $ZnFe_2O_4$. It is very important to note that the diffraction peak of rutile TiO_2 gradually appeared with the increasing the content of $ZnFe_2O_4$. When the molar fraction of $ZnFe_2O_4$ is 6 mol%, the diffraction peaks of