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Preparation, Microstructure and Photocatalytic Performance of the Anatase Nano-TiO_2 Thin Film

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The anatase nano-TiO_2 thin films with different layers were prepared on the ordinary glass slides using sol-gel method. The photocatalytic activity of the thin films and the microstructure were investigated. The results showed that the optimum annealing temperature for anatase nano-TiO_2 was 500 ºC and TiO_2 particles were spherical in shape and dispersed uniformly on the surface of the thin films. The films have good adhesion with the glass substrate. Moreover, the nano-TiO_2 particles on the surface have the trend to grow large with the increase of film layers. The prepared thin films have good light transmission rate and the absorption threshold has an obvious red shift with the increase of film layers. Furthermore, the thin films have high photocatalytic activity and the photocatalytic decolourization rate of acidic black 10B can reach 80 % in 120 min over 6-layer thin film.

Key Words: Nano-TiO_2 thin film, Microstructure, Photocatalytic activity, Degradation.

INTRODUCTION

Nano-TiO_2 has been widely used in many fields, such as treating with wastewater, purifying air, solar battery, gas sensors, packaging material, coating material, *etc.*[1]. So far, the major research contents of nano-TiO_2 include preparation, microstructure, macro-property and application[2-4]. Nano-TiO_2 thin film has characteristics of efficiency, stability and easy recovery compared with nano-TiO_2 powders, so it can be used in a flow system of photocatalysis[5,6]. Therefore, the preparation and study of high efficiency nano-TiO_2 photocatalytic thin film has become an important subject in the field of photocatalytic technology.

Sol-gel method is one of the simple wet-chemical preparation methods. Because the formulation of sol is easy to be controlled, the doping is easy to be carried out and thin film can be prepared on the substrates with different shapes[7]. This method has been most commonly used for the preparation of nano-TiO_2 thin film. But the composition, structure, orientation and thickness of nano-TiO_2 thin film are different with the different formulation and process parameters[8,9]. Therefore the research workers are devoted time to solve the problem of how to prepare nano-TiO_2 with powerful adhesion, densified uniform and good performance.

In this paper, the anatase nano-TiO_2 thin films with different layers were prepared on the ordinary glass flake using sol-gel method. The structure of the anatase nano-TiO_2 thin films was characterized by scanning probe microscopy and XRD and the relationship between the microstructure of the thin films and their photocatalytic activity were discussed.

EXPERIMENTAL

Preparation of sol-TiO_2 and nano-TiO_2 powder: A certain amount of $Ti(OC_4H_9)_4$ and $NH(C_2H_5O)_2$ were first dissolved in anhydrous ethanol under stirring for 2 h. Then a small amount of distilled water was added drop by drop with stirring for 1 h. Finally 1 mL $C_5H_8O_2$ was added dropwise to the mixture, continuing stirring for 1 h. After aging for 24 h, a clear and translucent light yellow sol-TiO_2 was obtained with viscosity 2.6 mpa·s. Then the sol-TiO_2 was separated to two parts, one is for the film forming process, the other was put into a vacuum drier to make it become dry gel under 100 ºC. The dry gel was put into muffle furnace and kept for 1 h under different annealing temperatures to obtain nano-TiO_2 powder.

Film forming process: The glass slides (38 mm × 26 mm) for film forming was cleaned by acetone, hydrochloric acid, distilled water and ultrasonic. The sol was filmed on the cleaned glass slide using spin coating method by the KW-4A Spin coating machine. Then the glass slide was put into oven drying for 15 min at 100 ºC. The film with differen layers could be obtained by repeating this process. Finally, the sample was put into muffle furnace with a temperature programming function and heated to 500 ºC, then kept for 1 h. After natural cooling, nano-TiO_2 film was gained on glass slide.

Photocatalytic activity test: Photocatalytic activity test was carried out under 20 W ultraviolet lamp (wavelength was 2537 Å). Every time, two pieces of glass slides (size of 38 mm × 26 mm) with different coating layers were put into the 90 mm petri dish with 50 mL dye wastewater which contained 20 mg/L acidic black 10 B simulation. In this procedure, the coating layers faced to the ultraviolet lamp, which is 7 cm far from the bottom of petri dish. The dye wastewater was stirred by constant aeration. At suitable intervals, the supernatant was taken into cuvette to measure the absorbance, then the decolourization rate was calculated by the following formula, $D = (A_0 - A)/A_0 \times 100$ %, where A_0 and A stand for the absorbance of dye solution before and after photocatalytic treatment respectively. According to the change of decolourization rate, photocatalytic activity of nano-TiO_2 thin films with different layers was evaluated.

Instrument: Y2000 X-ray diffractometer with CuK_α radiation (λ = 1.54178 Å,30 kV × 20 mA); 5500 scanning probe microscopy; TU-1900 UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Effect of the annealing temperature on the crystal structure of TiO_2: There are three kinds of TiO_2 crystal structures including anatase, rutile and brookite. The anatase (band gap: 3.2 ev) was found to have the best photocatalytic activity[1,10]. Considering that the nano-TiO_2 film prepared by spin-coating method was very thin, it would show too weak signal in conventional X-ray diffractometer. Furthermore, in this work, coating film was carried out on the amorphous glass slide, which would affect the intensity of diffraction peak. Therefore, the crystalling phase transition of dry gel at different annealing temperature was analyzed indirectly by the powders with the same components as the film and under same heat treatment process.

Fig. 1 shows the XRD patterns of TiO_2 powders treated by different annealing temperature. It can be seen that there are some weaker and wider diffraction peaks for anatase phase (A) under the heat treatment at 400 ºC. Then the intensity of diffraction peak increases with the heat treatment temperature and the diffraction peaks become very sharp at 500 ºC, showing the higher degree of crystallization. Furthermore, the distinct peaks of rutile phase (R) can be obtained at 550 ºC expect for the characteristic peak of anatase phase, indicating that part of anatase phase has transformed into rutile phase. When the annealing temperature increases to 650 ºC, the transformation is accomplished along with the disappearance of anatase phase peak. Therefore, in order to obtain the anatase nano-TiO_2 thin films with high photocatalytic activity, 500 ºC is the most appropriate temperature. Moreover, the particle size of anatase TiO_2 is about 18 nm, which was calculated from Scherrer formula.

Scanning probe microscopy analysis for the surface of nano-TiO_2 thin films: Scanning probe microscopy is one of the most powerful microanalysis methods for studying the surface morphology of thin films. In order to obtain accurate results, the 3000 nm range of thin film surface was scanned by contacting mode (Si probe). Roughness (RMS) for the thin film surface was obtained through the instrument software standard formula. The surface morphology and corresponding three-dimensional diagram of two- and six-layer TiO_2 film are shown in Fig. 2.

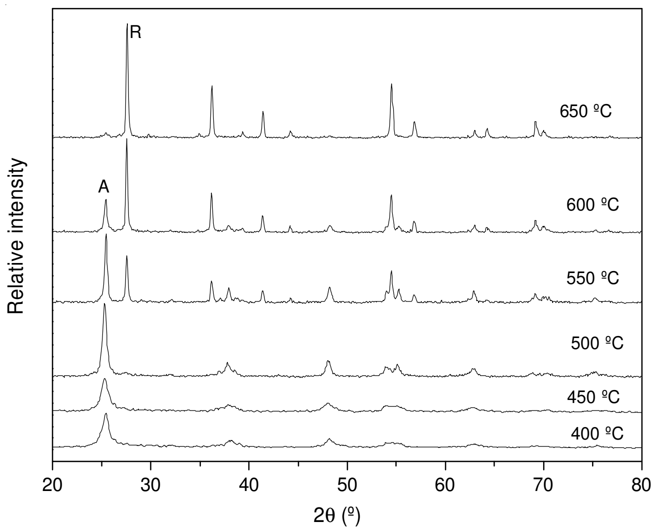

Fig. 1. XRD patterns of TiO_2 different anneal temperature

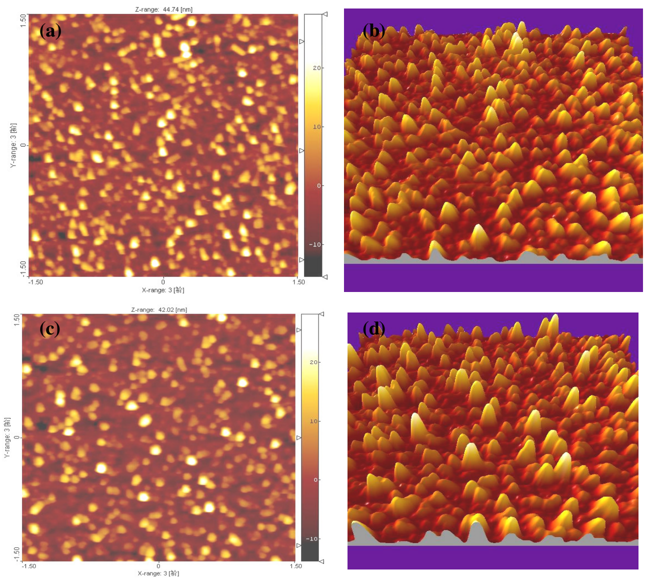

Fig. 2. Surface and corresponding three dimension map of TiO_2 film; (a) two-layer surface (b) two-layer surface three dimension (c) six-layer surface (d) six-layer surface three dimension

The spherical TiO_2 particles on the glass substrate surface look just like islands, are relatively evenly distributed. The thin dense film has good cohesion with the glass substrate. From three-dimensional diagram, it is concluded that as-prepared TiO_2 thin film is one of undulating granular films, but the undulation is relatively small. Some of the larger grain particles can be found, forming large protuberance and having the trend to grow large. The RMS of the two-layer thin film is 57 nm and partical size is about 20 nm, whereas the RMS of the six-layer thin film is 63 nm and partical size is about 26 nm. Comparing with the two conditions, the feature of thin films is essentially unchanged but the nano-TiO_2 particles on the surface have the evident trend to grow large with the increase of the amount of film layers[11,12].

UV-VIS spectra analysis for the films: In order to determine the transmittance spectra of TiO_2 films, taking the uncoated glass slide as reference material. The transmittance spectra of 2-, 4- and 6-layer TiO_2 thin films are shown in Fig. 3, it can be seen that the films are more transparent in the visible region. And the transmittance of the films in the visible high band (650 nm-800 nm) decreases with the increase of coating layers. This phenomenon results from the diffraction or refraction within the film. However, the transmittance below 400 nm declines sharply, which is due to the interband transition absorption of TiO_2 in UV-VIS band. Besides, with the increase of the coating layers, the absorption threshold of film shifts to long wavelength, *i.e.*, red shift, which is attributed to the difference in grain size of TiO_2. According to the quantum size effect, the smaller the grain size of TiO_2, the wider the band gap. It can be inferred that the thicker the film, the greater TiO_2 grain, which is consistent with the result of scanning probe microscopy analysis. It should be noted that all the films with different layers show regular uplift peak at 450 nm-600 nm band. This may be due to the interference occurred between the films and substrate[13].

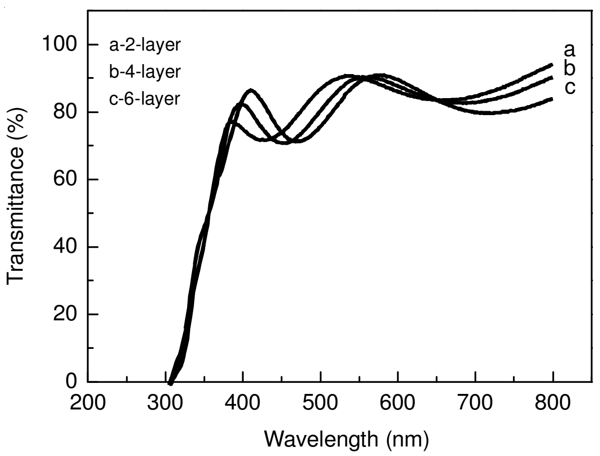

Fig. 3. Transmittance spectra of TiO_2 thin films with different layers

Photocatalysis activity of Nano-TiO_2 thin film: The relationship between the degradation rate and time in different layer film are shown in Fig. 4. The results show that photocatalytic degradation ability is enhanced with the increase of coating layers, however, the enhanced rates slow down gradually. The photocatalytic activity of 4-layer film is 11 % higher than that of 2-layer film and that of 5-layer film is 4.3 % higher than that of 4-layer film and that of 6-layer film is 2.58 % higher than that of 5-layer film in 120 min. The reason is that the loading of catalyst is too low when the film layer is fewer, so that the utilization of UV-light energy is low and the effective photon energy can not be totally converted into chemical energy, which leads to the slow reaction rate. With the increase of film layers, more nano-TiO_2 particles participate in the reaction. Therefore, the energy efficiency can be improved, leading to the increase of photocatalytic activity[14,15]. The decolouring rate of acidic black 10B is 80 % in 120 min on 6-layer film, but the increasing trend slows down after 120 min.

Photocatalytic activity of the film is not increased as the film thickness has been increased. When the TiO_2 film achieves a certain thickness, the intensity of UV-light through the film will decline sharply, which make nano-TiO_2 in deeper layer can not conduct photocatalysis totally. Moreover, when the thickness exceeds the optimum value, the light electrons and holes can not effectively spread to the surface, so the photocatalytic activity dropped sharply.

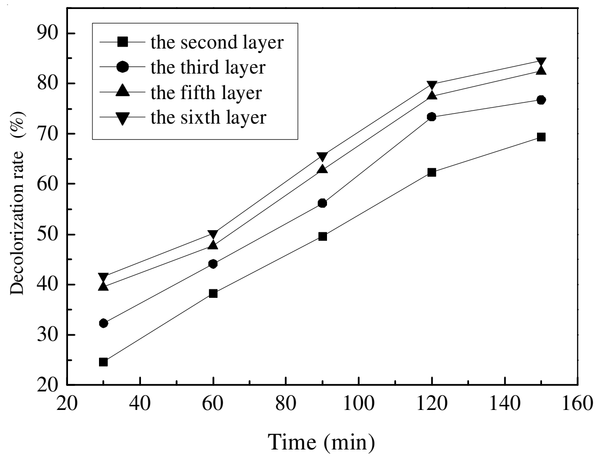

Fig. 4. Denpendence of degradation of acid black 10 B on photocatalytic properties of nano-TiO_2 films with different layers

Conclusion

(1) The anatase nano-TiO_2 thin films with different layers were prepared on glass slides using the spin coating method. The phase transition of gel under different temperatures were investigated and 500 ºC was found to be the optimum annealing temperature.

(2) The prepared films have better light transmission rate than the traditional ones. Furthermore, the red shift of the film absorption threshold can be found with the increase of the layers of film. This is beneficial to broaden the spectral response range of the film, leading to the improvement of photocatalytic activity.

(3) TiO_2 particles on the surface of film are nearly spherical, relatively uniform. The film has good adhesion with the glass substrate and belonges to the dense film. There are no obvious changes in film morphology with the increase of film layers, but the sizes of nano-TiO_2 particles increase gradually in small ranges. In addition, the surface presents some island shape protuberants, leading to the increase of the specific surface area of film. It is conducive to the photocatalytic reaction.

(4) The prepared films have shown high photocatalytic performance. The decolouring rate of acidic black 10 B can reach 80 % in 120 min over the six-layer film.

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