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Relationship Between Photocatalytic Activity and Structure of TiO_2 Thin Film

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TiO_2 thin films with different crystalline structures were prepared by the CVD method. The relationship between photocatalytic activity of a TiO_2 thin film and its crystalline type was investigated. These films were characterized by XRD and AFM. Their photocatalytic properties were tested by the degradation of $NO_2{}^-$. The results showed that the crystalline structures of TiO_2 thin films are primary anatase and/or rutile when the preparation temperatures were less than 573 K and higher than 773 K respectively. When the preparation temperature was around 623 K, the structures of TiO_2 thin films were mixed crystalline structure, which showed the highest catalytic activity. When the ratio of rutile to anatase in TiO_2 thin films fell between 0.5 and 0.7, the highest catalytic activity for the degradation of $NO_2{}^-$ was found.

Key words: CVD method, TiO_2, Photocatalytic activity, Rutile, Anatase

I. INTRODUCTION

As an environmental-friendly and inexpensive catalyst, titanium dioxide (TiO_2) has been widely applied as a photocatalyst due to its chemical stability and high activity [1-18]. Compared with TiO_2 powders, TiO_2 thin films can be utilized repeatedly and regenerated easily as a photocatalyst. There are some reports about the preparation of TiO_2 thin films, in which the influence of the preparation temperature on the crystal structure of TiO_2, and the relationship between the films thickness and photocatalytic activity were studied. However, there are few studies on the relationship between the photocatalytic activity, the crystal structure and the size of crystal.

Generally speaking, there are two kinds of TiO_2 crystalline structure (anatase and rutile) that act in the photocatalytic process. The photocatalytic activity of the anatase is higher than that of the rutile [19]. It has been observed that the activity of both these crystals in single component is limited, while the mixed crystalline structures are much more active. He *et al.* studied the effect of different ratio of anatase to rutile on the photocatalytic activity, when the ratio of anatase to rutile was 7:3, the result exhibited the highest catalytic activity, much higher than that of any other type of crystal [20].

In this work, TiO_2 thin films were prepared on a glass substrate by the CVD method, and the photocatalytic activity of the TiO_2 thin films and its their crystalline composition was investigated.

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II. EXPERIMENTS

A. Main chemical reagent and instruments

The chemicals $TiCl_4$, $NaNO_2$, sulfamilic acid, sodium acetate, hydrochloric acid-1-naphthalene amic, 99.5% ethyl alcohol, were all the AR grade. Microscopy glass slides, measuring 75.5 mm×25.5 mm×1.2 mm, were used as the substate for the film deposition.

The UV lamp source, used for radiation, was a 375 W medium press mercury lamp with a characteristic wavelength of 365 nm. XRD was performed on a Y-4Q X-ray-diffraction instrument manufactured by Dandong Radio Instrument Co.. The diffraction source was a copper target, where the 2θ between 10°-70° was scanned. An AFM (Digital Instruments, USA) was used for the observation of the surface topology.

B. Preparation of TiO_2 thin films

TiO_2 thin films were prepared with $TiCl_4$ as the raw material, nitrogen as the carrying gas and glass slide as the substrate. The slide was cleaned twice with acetone and alcohol, then dried. Then it was heated by electric oven while its working voltage was controlled by a voltage-variable transformer. A thermocouple was used to measure the temperature of the slide surface. Once the temperature stabilized at the desired level, $TiCl_4$ (carried by nitrogen gas) was sprayed onto the substrate. At that point, the $TiCl_4$ hydrolyzed and thin films of TiO_2 formed on the slide. The reaction can be expressed by the following equation, where the water vapor comes from the air.

$$TiCl_4(g) + 2H_2O(g) = TiO_2(s) + 4HCl(g) \qquad (1)$$

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Different TiO_2 thin film samples were prepared in an air humility around 50% at controlled temperature of 523, 573, 623, 673, 723, 773 and 823 K, respectively.

C. The activity of photocatalytic oxidation of NO_2^-

The photocatalytic activity of the TiO_2 thin films prepared at different temperatures was studied. Five TiO_2 thin film samples, which were prepared at the same temperature, were tested for their activity in photocatalytic oxidation of NO_2^- to NO_3^-. They were placed on a culture plate with in 100 mL of NO_2^- solution 0.20 mg/L. The samples were checked to ensure that all TiO_2 thin films were upwards. Next, the culture plate was placed under the UV-light, where the absorbance (A) of the indicators (sulphanilic acid, α-naphthylamine and sodium acetate) was measured by UV-vis spectrometer at 520 nm after a period of reaction time. Finally the conversion rate of NO_2^- was calculated.

III. RESULTS AND DISCUSSION

A. The XRD of TiO_2 thin films at different temperatures

TiO_2 exists as anatase type crystal at low temperatures, while the rutile type crystal is formed at high temperatures. Generally, the phase transformation temperature is between 1073 and 1473 K. If the effect of the size effect on the nanometer particle was considered, which would make the phase transformation energy be reduced, phase transformation temperature would reduce [21-23]. So we studied TiO_2 nanometer thin films at 573 and 773 K.

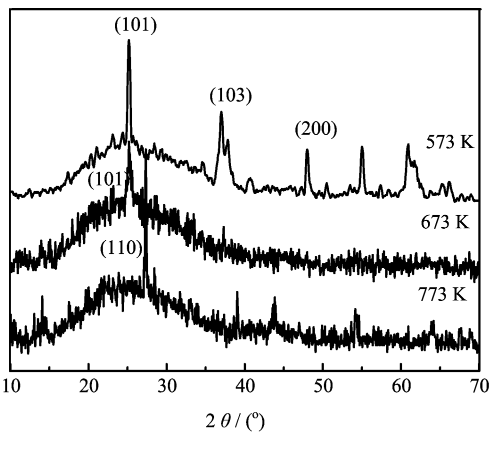

FIG. 1 XRD patterns of TiO_2 thin films prepared at different temperatures.

From Fig.1, we can see that at 573 K, TiO_2 nanometer thin films exhibit three strong diffraction peaks, whose 2θ are 25°, 37° and 48°. These correspond to the surface of (101), (103), (200) of the anatase. It is suggested that, at this time, the TiO_2 nanometer thin film is predominantly the type of anatase. At 673 K, the diffraction peak of the plane (101) is lower. While the slide temperature is 773 K, 2θ appears at a very strong characteristic diffraction angle of 27°, which corresponds to the plane (110) of rutile. The preceding analysis confirms that when the base temperature is lower than 573 K, the TiO_2 nanometer thin film is mainly composed of anatase. When the base temperature is higher than 573 K and lower than 773 K, three strong diffraction peaks which correspond to the type of anatase become lower gradually. If the temperature is higher than 773 K, the TiO_2 nanometer thin film is mainly rutile.

From Scherrer equation [24],

$$d = 0.89\lambda/(B\cos\theta) \tag{2}$$

where d is the average diameter of the particles, λ is X-ray wavelength, B is the FWHM, and θ is Bragg angle of the corresponding diffraction peak, respectively, we can calculate the sizes of microcrystal in the film for different temperature. At the temperature of 573±10, 673±10 and 773±10 K, the sizes of microcrystals in the films are 17.9, 14.9 and 22.5 nm. At higher or lower temperatures the sizes of microcrystals in the films are bigger. The smallest sizes of microcrystals appear at 673 K.

Size of crystal is an important factor that affects the TiO_2 photocatalytic activity. The smaller the particle is, the larger the number of the unit quantity particle is, and the larger the specific surface area is. Both are advantageous for the photocatalytic reaction taking place on the surface of particle. But a larger area means more opportunity for the recombination center to appear on the surface at the same time. When the compound effect acts as the main factor to influence the photocatalytic activity, the photocatalytic efficiency may be reduced, while the extent of quantization of the particle increases. So we must choose the appropriate temperature to control particle size, and then control the photocatalytic efficiency.

B. AFM observation of the TiO_2 thin films

The morphology of the TiO_2 thin films, prepared at 523 and 823 K, were observed by AFM in tapping mode. The results are shown in Fig.2. From Fig.2, we can see that TiO_2 particles are very uniform in size. The average size (15 nm) is small when the particles are prepared at 523 K. At 823 K, rutile type TiO_2 particles appear, making the surface rough and uneven. As the reaction equation (1) shows, this reaction is a strong exothermic reaction, therefore the equilibrium constant will be larger at lower temperatures. As the temperature rises, more and more rutile type TiO_2 particles appear and accumulate.

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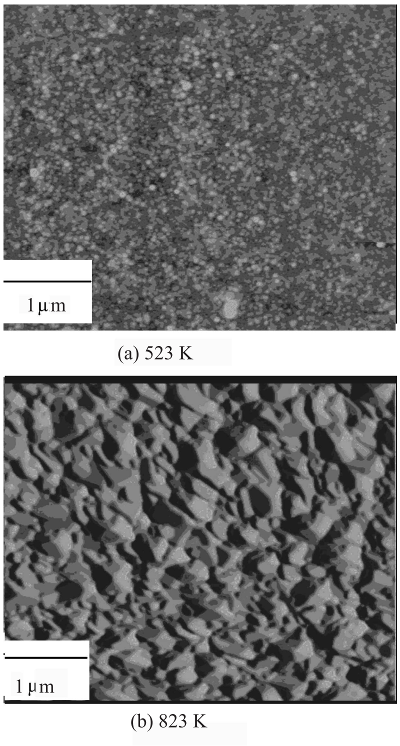

FIG. 2 AFM images of TiO_2 thin films.

C. Result of photocatalysis

Five samples, produced at five different temperature, were selected as the photocatalysts, and exposed under the UV light for 1 h. Next, the conversion of the degradtion of NO_2^- was measured for each sample. The relationship between preparation temperature and catalytic efficiency was also measured, as shown in Fig.3.

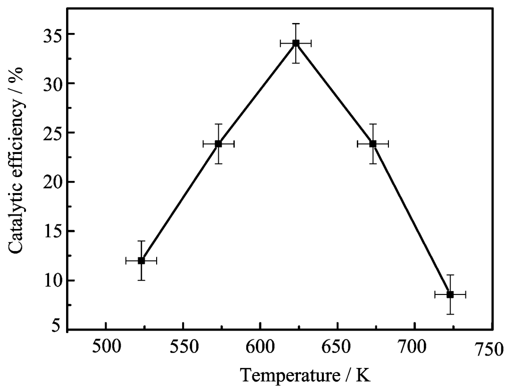

FIG. 3 The relationship between preparation temperature and catalytic efficiency.

From the Fig.3, we can see that the TiO_2 thin film prepared at 623 K has the highest photocatalytic activity. It is reported [20] that crystal type is an important factor which affects TiO_2 thin film photocatalytic efficiency. XRD conversion rate experiments show that the TiO_2 thin films prepared at 623 K are mixed crystal (anatase and rutile), and with a change of the temperature, the ratio of the two kinds of crystals in the mixed crystal will vary immediately. So we selected 623 K to produce the film used for investigating the relationship between the proportion of crystal and the catalytic activities.

Figure 4 shows the XRD patterns of each sample that was prepared at elevated temperature. When anatase and rutile coexist, the ratio of anatase in mixed crystals was calculated by the following equation [25]:

$$\omega(\mathrm{A})\% = 100/(1 + 1.265 I_{\mathrm{R}}/I_{\mathrm{A}}) I_{\mathrm{R}} \quad (3)$$

here, I_{R} and I_{A} are the strongest diffraction peaks for the rutile and the anatase, respectively.

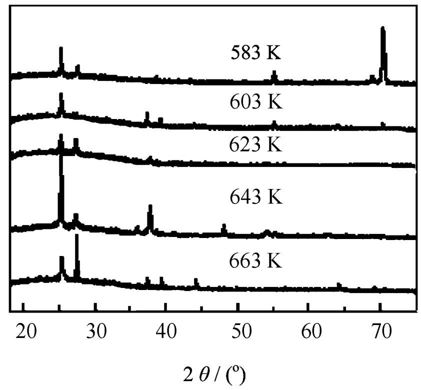

FIG. 4 XRD patterns of TiO_2 thin films prepared at different temperatures.

From the Eq.(3), we can calculate the ratio of the rutile to anatase in each sample. The relationship between catalytic efficiency and crystalline phases ratio is shown in Fig.5.

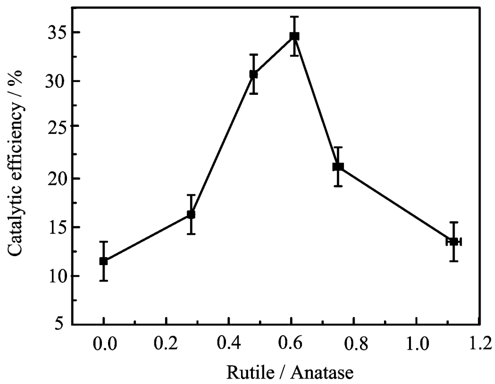

FIG. 5 The relationship between catalytic efficiency and crystalline ratio.

In Fig.5 we observe that, with the change of ratio of rutile to anatase, photocatalytic efficiency first increases

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and then decreases. When the ratio of rutile to anatase is 0.5-0.7, the TiO_2 thin film has the best photocatalytic activity to the degradation of NO_2^-.

The efficient separation of electron and hole on the surface of TiO_2 is a key process that determines the photocatalytic activity of TiO_2. In these experiments, when the anatase type of TiO_2 becomes the rutile type of TiO_2, the TiO_2 nanometer thin film has the highest activity. The possible explanation may be that when the anatase type of TiO_2 and the rutile type of TiO_2 coexist in certain proportions, the rutile type of TiO_2 appears mainly on the surface while the anatase exists inside. Rutile type of TiO_2 with lower content is an active molecule and a trap that will catch the electron and the hole, which makes the probability of the combination between the electron and positive hole much lower and separate them successfully. At the same time, this capture is reversible, rutile type of TiO_2 can release these electron and hole, then they can take part in photocatalytic reaction, which can enhance the efficiency of the photocatalytic activity. We find that the size of the particle is also an important factor that influences the photocatalytic efficiency. When the TiO_2 is a combination of rutile and anatase within certain proportions, the size is smaller than that of any one of these two types, which also makes for greater efficiency.

IV. CONCLUSION

The XRD results show that TiO_2 thin films exists mainly as anatase type crystals below 573 K and as rutile type of TiO_2 above 773 K. It is mixed crystal when it is prepared between 573 and 773 K. A TiO_2 thin film prepared at about 623 K has the highest photocatalytic activity achievable with this method. The crystal type is an important factor that influences the photocatalytic activity of TiO_2 thin film. When the ratio of rutile to anatase is between 0.5 and 0.7, the mixed crystal has the best photocatalytic activity in degradation of NO_2^-.

V. ACKNOWLEDGMENTS

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