

## ARTICLE

**Fabrication and Photocatalysis of TiO<sub>2</sub> Flower-like Nanostructures**Yan-zong Wang<sup>a,b</sup>, Xun Hong<sup>a,b</sup>, Guan-zhong Wang<sup>a,b\*</sup>, Xiao-ping Wang<sup>a,b</sup>*a. Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, China;**b. Department of Physics, University of Science and Technology of China, Hefei 230026, China*

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TiO<sub>2</sub> nanostructures were fabricated by a reaction of Ti foils in H<sub>2</sub>O<sub>2</sub> solution at mild temperature. Porous TiO<sub>2</sub> nanostructures, well-adhered to Ti foil surfaces, were formed at 80 °C in 10 min, and then flower-like and rod nanostructures formed in succession after a longer reaction time. Samples prepared at 80 °C for 4 h are amorphous, and anatase-dominated crystal phase emerged in the sample prepared for as long as 10 h. Almost pure anatase phase were obtained in TiO<sub>2</sub> nanostructures by annealing the samples at a temperature of 300 °C. Photocatalysis of the TiO<sub>2</sub> nanostructures was characterized by the degradation of RhB dye molecules in an aqueous solution exposed to ultraviolet light. Results show a 7 cm<sup>2</sup> annealed TiO<sub>2</sub> flower-like nanostructure having the degradation rate of RhB as fast as 29.8 times that of the dye solution exposed to ultraviolet light alone.

**Key words:** TiO<sub>2</sub> nanostructure, Photodegradation, RhB solution**I. INTRODUCTION**

Recently TiO<sub>2</sub> nanomaterials has received much attention in many applications such as optical devices, biomaterials, solar cells, sensors and photocatalysis [1], because of its inexpensive, non-toxic, chemical stability and other desirable physical and chemical properties. Since Fujishima and Honda discovered the photocatalytic splitting of water on TiO<sub>2</sub> electrodes in 1972 [2], more and more researchers are investigating on treating wastewater and other environment problems by using TiO<sub>2</sub> as a photocatalyst. Now many researchers are interested in understanding the basic process of photocatalysis and how to enhance the photocatalytic efficiency. Because photocatalytic reactions mostly take place on the surface of TiO<sub>2</sub>, it is important to get a large effective surface area for higher photocatalytic efficiency. When a TiO<sub>2</sub> particle reaches nanosize, its large surface ratios and decreasing of carrier recombination probability, induced by photogenerated electron and hole pairs can quickly reach to the surface of the nanosize particle, increases significantly the photocatalytic efficiency. Therefore, many studies are devoted to nanocrystalline TiO<sub>2</sub> photocatalysts, which include unsupported suspended TiO<sub>2</sub> powders [3] and the form of TiO<sub>2</sub> immobilized on substrates [4]. Though the suspended powders have higher photocatalytic efficiency because of the large surface area of catalyst available for reaction, it is difficult to separate them from the treated wastewater and use them again. Also, they tend to aggregate at high concentrations [5]. A photocatalyst immobilized on the substrate can avoid the above prob-

lems, so it has been the subject of extensive research recently. Immobilized photocatalyst has been prepared by the sol-gel method [6], hydrothermal method [7], electrodeposition [8] and so on. Chen *et al.* have prepared ultrafine powders with different morphologies by a method of Ti-H<sub>2</sub>O<sub>2</sub> oxidation-hydrothermal growth [9,10]. In this paper, we present the fabrication of TiO<sub>2</sub> nanostructures by a reaction of Ti foils in H<sub>2</sub>O<sub>2</sub> solution under mild temperature of 80 °C and the effect of reaction time on the different nanostructures. In a relatively short time a high surface-to-volume ratio amorphous flower-like nanostructure was prepared. Pure anatase nanostructure can be obtained with high catalytic activation at relatively low annealing temperature. By prolonging the reaction time to 10 h, crystalline flower-like nanostructure was produced. This research also investigated the photocatalytic activation of flower-like TiO<sub>2</sub> nanostructures.

**II. EXPERIMENTS**

TiO<sub>2</sub> flower-like nanostructures were prepared from Ti foils (99.3% in purity, 0.1 mm in thickness, purchased from General Research Institute for Nonferrous Metals, Beijing, China). Ti foils were degreased in an ultrasonic bath in acetone and alcohol successively, etched by dilute HF solution for 1 min, rinsed with deionized water and dried by nitrogen gas flow. Then the Ti foils were put in 50 mL H<sub>2</sub>O<sub>2</sub> (30%) to prepare TiO<sub>2</sub> nanostructures at 80 °C. The preparation time was 10 min, 1, 4, 10 and 24 h, respectively. After the reaction was sustained for a given time, the sample was naturally cooled in H<sub>2</sub>O<sub>2</sub> solution to room temperature. Then the sample was taken out from the solution, rinsed with deionized water, and dried in air. Some samples were annealed at 300, 450 and 600 °C in air to investigate the

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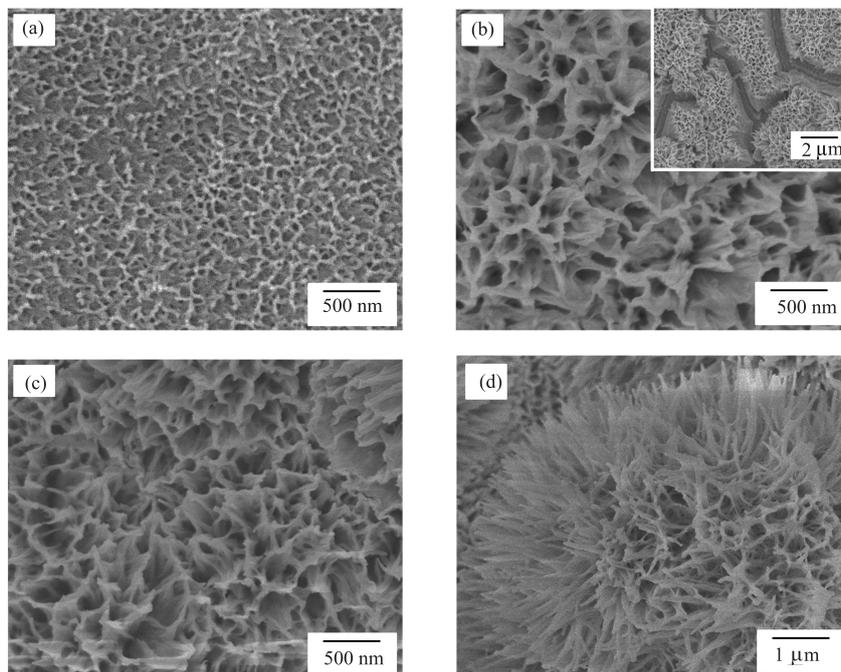


FIG. 1 SEM images of flower-like nanostructures prepared at 80 °C by a reaction of Ti foils in  $\text{H}_2\text{O}_2$  solution for (a) 10 min, (b) 4 h, (c) 10 h and (d) 24 h. Inset in (b) is the SEM image of the sample prepared for 4 h and annealed at 450 °C for 3 h in air.

annealing effect on  $\text{TiO}_2$  microstructures and improve the crystallization of the sample for a photocatalysis experiment. The photocatalysis experiment was carried out with a 7  $\text{cm}^2$  annealed  $\text{TiO}_2$  flower-like nanostructure sample 450 °C in 50 mL RhB solution (initial concentration of 0.01 mmol/L). A 200 W high-pressure mercury lamp illuminated the  $\text{TiO}_2$  nanostructure sample in the solution at 30 cm distance. The solution was stirred continuously during the reaction, and the beaker was coated with glass foils. During the photocatalysis experiment, the temperature of the solution was about 40 °C.

Morphologies of the  $\text{TiO}_2$  nanostructures were characterized by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F). The crystal structure was characterized by X-ray diffraction using Mo radiation ( $\lambda=0.70930$  Å) (MAC MXPAHF). The concentration of RhB solution was monitored with a UV-Vis spectrophotometer (Hitachi U4100) at a wavelength of 554 nm.

### III. RESULTS AND DISCUSSION

#### A. Formation of nanostructures and crystal phases

SEM images of the  $\text{TiO}_2$  nanostructures prepared in  $\text{H}_2\text{O}_2$  solution at 80 °C for 10 min, 4, 10 and 24 h are shown in Fig.1. The sample prepared for 10 min is porous, as shown in Fig.1(a). The pores are probably due to the gel formed from Ti and  $\text{H}_2\text{O}_2$  reac-

tion filled with  $\text{O}_2$  that came from the decomposition of  $\text{H}_2\text{O}_2$  [11,12]. As the concentration of the Ti-peroxide in the solution increased as the result of Ti and  $\text{H}_2\text{O}_2$  reaction, the gel was gradually formed on the porous nanostructure surface, and then produced flower-like nanostructures, as shown in Fig.1(b). The formation of titania gel nanostructures reduced the Ti-peroxide concentration in the solution and resulted in the petals of the nano-flowers growing thin at the ends, as shown in Fig.1(c). Finally, titania nanorods were formed on the petals of the nano-flowers when the reaction time is as long as about 24 h, as shown in Fig.1(d). Inset in Fig.1(b) is the SEM image of the sample prepared for 4 h and annealed at 450 °C for 3 h in air. The SEM image shows cracks in the sample due to gel dehydration and shrinking after the annealing. However, no evidence indicates any change of the nanostructures. The XRD patterns of a sample prepared at 80 °C for 4 h and annealed at different temperature for 3 h are shown in Fig.2. For comparison, another sample prepared at 80 °C for 10 h is also shown in Fig.2. From the XRD patterns, there is no evidence of  $\text{TiO}_2$  crystal phase in the flower-like nanostructure sample prepared for 4 h, but the sample became anatase phase (PDF number 84-1286) dominated after the sample annealed at 300, 450, and 600 °C, respectively. There are only peaks corresponding to anatase phase for the sample annealed at 300 °C. The peaks corresponding to rutile phase (PDF number 76-0326) emerged for the sample annealed at 450 °C, and their intensity increased for the sample an-

nealed at 600 °C. The rutile phase could come from the oxidation of Ti substrate (PDF number 44-1294) and the transition of anatase phase. Polycrystalline phase, mainly anatase phase, emerged in the sample prepared for 10 h without any annealing, which can be explained by a dissolution precipitation mechanism and a result of the ageing process [13].

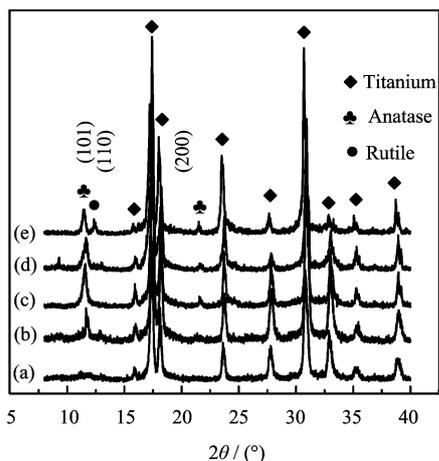


FIG. 2 XRD patterns of flower-like nanostructures prepared at 80 °C for (a) 4 h and (b) 10 h, and the sample prepared for 4 h annealed in air at (c) 300 °C, (d) 450 °C and (e) 600 °C.

### B. Photodegradation of RhB solution

Dye RhB (0.01 mmol/L) photocatalytic degradation was chosen to investigate the photocatalytic activation of the flower-like TiO<sub>2</sub> nanostructure. In order to avoid the effect of H<sub>2</sub>O<sub>2</sub> on experimental result and increase the photocatalytic activation of the TiO<sub>2</sub>, the sample annealed at 450 °C was used as photocatalytic material [14]. Figure 3 shows the time-dependent UV-Vis absorbance spectrum of RhB solution containing a flower-like nanostructure sample (7 cm<sup>2</sup>) after UV irradiation. The maximum absorption peak at 554 nm corresponding to RhB molecule almost disappears after about 5 h of UV irradiation, as shown in Fig.3. This result indicates that the RhB molecules have been degraded due to the destruction of the dye chromogen. The efficiency of the degradation processes was evaluated by monitoring the absorbance at the maximum absorption wavelength. If we define  $c$  and  $c_0$  as the concentration of the solution at detection time and initial stage respectively, we can use  $c/c_0$  in place of  $A/A_0$  by the Lambert-Beer law that the normalized concentration of the solution equals the normalized maximum absorbance. Here  $A$  and  $A_0$  are absorbance at the maximum absorption wavelength of the solution at detection time and initial stage. From Fig.3, the photocatalytic degradation of RhB by the flower-like nanostructure sample with UV irradiation

follows the pseudo-first-order reaction [15],

$$\ln\left(\frac{c_0}{c}\right) = kt \quad (1)$$

where  $k$  is the apparent photodegradation rate constant, which is 0.77/h in this experiment. As a comparison, UV light photocatalytic degradation of dye RhB without TiO<sub>2</sub> was carried on at same experimental setup. The photodegradation rate is 0.0258/h when the dye solution exposed to ultraviolet light alone. Therefore, we can conclude that the 7 cm<sup>2</sup> annealed TiO<sub>2</sub> flower-like nanostructure sample increases photodegradation rate by 29.8 times compared with the dye solution exposed to ultraviolet light alone. From Fig.3(b), the degradation speed seems to decrease gradually with time, which could be due to the solvent evaporating in the photocatalytic process.

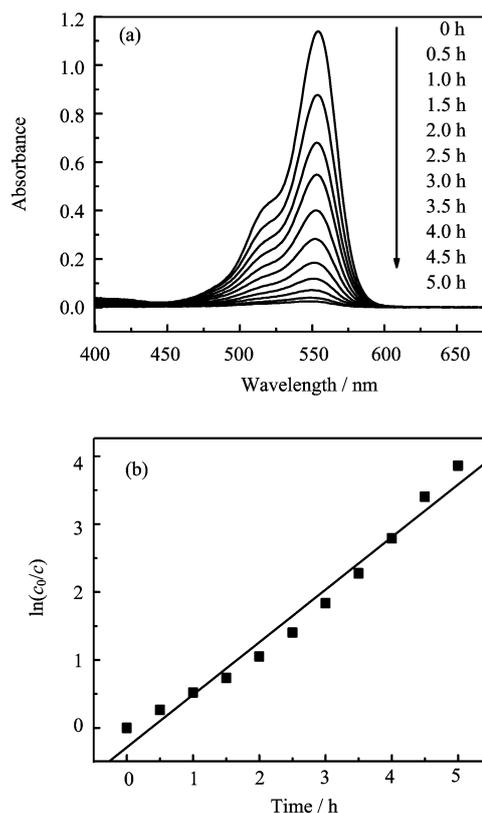


FIG. 3 (a) Absorption spectra of RhB solution catalyzed by an annealed TiO<sub>2</sub> flower-like nanostructure sample with UV-light irradiation for different times. (b) Time dependence of  $\ln(c/c_0)$ .

### IV. CONCLUSION

Flower-like and other TiO<sub>2</sub> nanostructures were prepared by the Ti and H<sub>2</sub>O<sub>2</sub> reaction at mild temperature. The morphology of the nanostructures varied with reaction time. Porous structure was formed in the sample at

beginning of the Ti foil reaction with  $\text{H}_2\text{O}_2$ , then flower-like structure formed after 4 h, and finally thin nanorods formed on the petal of the nano-flowers after 24 h. The samples prepared shorter than 3 h were amorphous, but crystal anatase phase was found in the sample prepared for 10 h. Through a 300 °C annealing process, anatase dominated phase flower-like  $\text{TiO}_2$  nanostructure was obtained. However, rutile phase emerged in the sample annealed at 600 °C. Photocatalytic results show an annealed  $\text{TiO}_2$  flower-like nanostructure ( $7 \text{ cm}^2$ ) having a degradation rate of RhB dye molecules in an aqueous solution exposed to ultraviolet light as fast as 29.8 times that of the dye solution exposed to ultraviolet light alone.

## V. ACKNOWLEDGMENTS

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- [1] A. L. Linsebigler, G. Q. Lu and J. T. Yates, *Chem. Rev.* **95**, 735 (1995).
- [2] A. Fujishima and K. Honda, *Nature* **37**, 238 (1972).
- [3] K. Tanaka, K. Padermpole and T. Hisanaga, *Water Res.* **34**, 327 (2000).
- [4] R. W. Matthews, *Water Res.* **25**, 1169 (1991).
- [5] H. Hidaka, T. Shimura, K. Ajisaka, S. Horikoshi, J. C. Zhao and N. Serpone, *J. Photochem. Photobio. A: Chem.* **109**, 165 (1997).
- [6] A. Yasumori, K. Ishizu, S. Hayashi and K. Okada, *J. Mater. Chem.* **8**, 2521 (1998).
- [7] J. Yang, S. Mei and J. M. F. Ferreira, *J. Am. Ceram. Soc.* **83**, 1361 (2000).
- [8] C. Natarajan and G. Nogami, *J. Electrochem. Soc.* **143**, 1547 (1996).
- [9] Y. T. Qian, Q. W. Chen, Z. Y. Chen, C. G. Fan and G. Zhou, *J. Mater. Chem.* **3**, 203 (1993).
- [10] Q. W. Chen, Y. T. Qian, Z. Y. Chen, G. I. Zhou and Y. H. Zhang, *Mater. Lett.* **22**, 77 (1995).
- [11] S. Komarneni, R. Roy and E. Breval, *J. Am. Ceram. Soc.* **68**, C-41 (1985).
- [12] P. Tengvall, H. Elwing and I. Lundstrom, *J. Colloid Interface Sci.* **130**, 405 (1989).
- [13] D. S. Seo, J. K. Lee and H. Kim, *J. Cryst. Growth* **233**, 298 (2001).
- [14] J. M. Wu, T. W. Zhang, Y. W. Zeng, S. Hayakawa, K. Tsuru and A. Osaka, *Langmuir* **21**, 6995 (2005).
- [15] I. K. Konstantinou, T. M. Sakellarides, V. A. Sakkas and T. A. Albanis, *Environ. Sci. Technol.* **35**, 398 (2001).