

Preparation of nanoporous titania photocatalyst with high photocatalytic activity using metatitanic acid

QINGLIN YANG*, JINGNAN ZHANG, QIN WANG, LIN GUO, LEI JIANG

School of Chemistry and Environment, Beijing University of Aeronautics and Astronautics, Beijing 100191, China

High photocatalytic activity nanoporous titanium oxide (TiO₂) was prepared at low temperature by simple chemical method, using low-cost metatitanic acid and sodium hydroxide as raw materials. The XRD pattern shows that the phase composition of titania is anatase and the crystallite size is around 10 nm. From SEM, TEM images and BET analysis, the nanoporous TiO₂ aggregates display mesoporous structure and the surface area of the sample is 231.28 m²·g⁻¹. The FTIR spectrum of the porous TiO₂ aggregates shows no other bands in the spectrum except Ti-O vibrating and the surface adsorbed water and the hydroxyl groups. The photocatalytic activity of the sample is about 4 times of P-25 by decomposing the methylene blue under UV light irradiation through photocatalytic test.

(Received April 4, 2011; accepted June 9, 2011)

Keywords: Titanium Oxide, Photocatalyst, Photocatalytic Activity, Porous Materials, Metatitanic Acid

1. Introduction

As one of the most popular photocatalyst, Titanium oxide possesses relatively abundant resource, large annual consumption, stable chemical properties, good acid/alkali resistance and appropriate band gap [1]. It is widely applied in gas sensors, purification of air and water, preparation of solar cells as well as antibacterial and self-cleaning coatings [2-3]. Recently, there are many achievements on titania photocatalyst research, but it still can not meet the needs of practical application. One of the most important causes is how to obtain high photocatalytic activity photocatalyst which limits its application. Nowadays how to adopt cheap and simple methods to synthesize high powered nanosized titanium oxide has already become one of the difficulties in photocatalytic practice ability.

In recent years, preparation of two or three dimension porous materials has attracted more attention, because it has great applied foreground in separation materials, catalyst, catalyst support, immobilized enzyme, photonic crystals and so on. Meantime, a number of methods have been used to prepare nanoporous Materials, such as selective etching method[4], surfactant template method[5-6], crystal templating method and so on[7-8]. The porous materials that have larger surface area and narrow pore size distribution are the optimum catalytic materials[9-10]. Among those, nanoporous titania has attracted much attention because of its high surface-to-volume ratio, which of great importance in photocatalysis, photosplitting water, and solar energy conversion. Therefore, worldwide research activity based on nanoporous titania has ensued[11-12]. Most of the

proposed syntheses of nanoporous titania by precipitation depend on controlling the high reactivity of Ti(IV) by the addition of stabilizing agents[13]. In our work, a simple, chemical precipitation method without employing any organic or inorganic templates was used to produce nanostructured TiO₂ aggregates with porous walls, using cheap metatitanic acid as raw material.

2. Experimental procedure

2.1 Synthesis

A simple preparation of the porous TiO₂ aggregates was performed as follows. Typically, metatitanic acid (50 g, Beijing Chemical Co.) and sodium hydroxide (105 g, Beijing Chemical Co.) were dissolved in distilled water (200 mL). The mixture was stirred for 2 h at 95 °C. The reaction formula of metatitanic acid with concentrated NaOH can be written as follows (Equation.1):



The white powders were collected by means of filtrated, washed with deionized water, and dried in an oven at 80 °C for 12 h. The Na₄TiO₄, when treated with deionized water, converted to H₄TiO₄ (Equation.2):



The products were obtained by adding hydrochloric acid (pH=1) to the white powder and stirred at room temperature for 4 h, then filtrated, washed with deionized

water and dried in an oven. The TiO_2 can be achieved to the following equation (Equation.3):



2.2 Characterization

The composition of the products was characterized by means of powder X-ray diffraction using a D/MAX2200PC diffractometer with $\text{CuK}\alpha$ radiation. The morphologies were observed by using a JEOL JSM-5800 field emission scanning electron microscope and a JEM-2100F transmission electron microscope. The nitrogen adsorption-desorption isotherm at 77 K was measured by a NOVA 2200e Surface Area & Pore Size Analyzer after sample was vacuum dried at 573 K. Infrared spectra on pellets of the samples mixed with KBr were recorded on an AVATAR 360 FTIR spectrometer at a resolution of 4 cm^{-1} . The concentration of the samples was kept around 0.2 %. Visible spectrometry (Shanghai Precision & Scientific Instrument Co. LTD, 722-N) was used to monitor the absorbency of methylene blue as a function of illumination time.

2.3 Measurement of photocatalytic activity

Through experiment, the maximum absorption length of methylene blue which was 663 nm could be measured. Photodegradation of methylene blue under irradiation of UV resource was evaluated by absorbance under the maximum wave length. A cylindrical Pyrex flask was used as the photoreactor vessel. The aqueous system containing methylene blue (MB, 4 mg/L, 200 mL) and the porous TiO_2 aggregates (20 mg) was magnetically stirred in the dark for 30 min to reach the adsorption equilibrium of MB, and then exposed to UV light from an Ultraviolet lamp (254 nm, 15 W). Commercially available TiO_2 (Degussa P25) was adopted as the reference with which to compare the photocatalytic activity under the same experimental conditions. A 6 mL aliquot was sampled at various time intervals and centrifuged before analysis. After measuring the absorbency of methylene blue, the ratio of practical concentration (c_t) and original concentration (c_0) was used to measure the catalytic effect (M), $M=c_t/c_0$.

3. Results and discussion

The structural characterization of nanoporous TiO_2 was performed from XRD. Fig. 1 shows the XRD pattern for the nanoporous TiO_2 aggregates obtained from simple chemical method. The strong sharp diffraction peaks of the samples are in good agreement with an anatase phase (JCPDS file No. 21-1272). The average crystal size of the sample (D in nanometers) has been estimated by Scherrer's formulation: $D=0.89\lambda/B(2\theta)\cos\theta$, in which $B(2\theta)$ is the width of the XRD peak at half-peak height in radians, λ is the X-ray wavelength in nanometers, and θ is the angle between the incident and diffracted beams in

degrees. The crystal size of the porous TiO_2 aggregates is estimated to be around 10 nm.

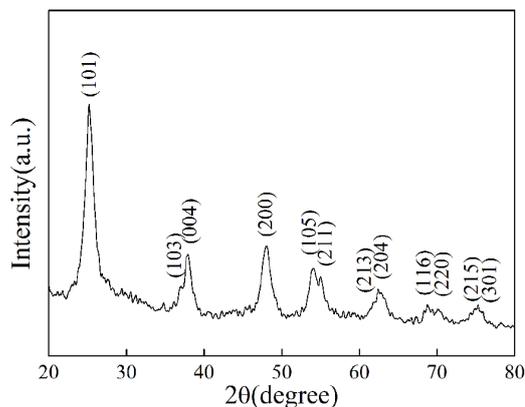


Fig.1. XRD pattern of the nanoporous TiO_2

Field emission scanning electron microscopy (FE-SEM) analyses were performed to examine the morphology of the as-prepared samples. Fig. 2 shows the FE-SEM images of the nanoporous TiO_2 aggregates at different magnifications. It indicates that the aggregates are composed of a large quantity of nanoparticles and have loose porous structure.

It can also see the morphology of the aggregates is mesoporous sphericity. These nanoparticles agglomeration and the diameter of the aggregates are from hundreds of nanometers to several micrometers. The mesoporous structure of the TiO_2 nanoparticle aggregates can be seen

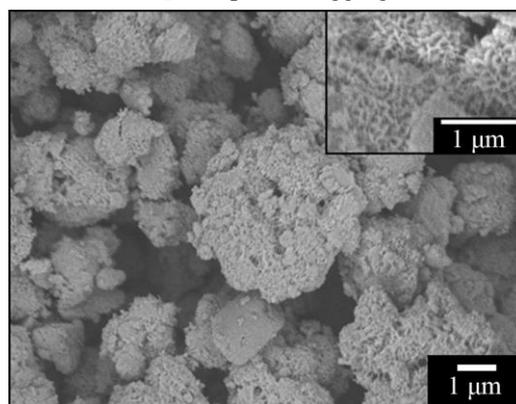


Fig.2. SEM images of the sample. The inset shows enlarged SEM image of the nanoporous aggregates.

more easily from FE-SEM images recorded at a higher magnification (inset in Fig. 2), which shows a unique porous surface of the sample. The porous structure of the TiO_2 nanoparticle aggregates was further confirmed by means of TEM as shown in Fig. 3. A typical TEM image (90 nm) of the aggregates is presented in Fig. 3, in which the interior of the aggregate is clearly visible. From the higher magnification (10 nm) (inset in Fig. 3), we can see the particle size is about 10 nm, which is consistent with the result of XRD. Fig. 4 shows the schematic illustration

of synthesis of nanoporous TiO_2 aggregates. The molecule of H_4TiO_4 would be destroyed so that TiO_2 can be obtained. In this process, the abounding hydroxyls in H_4TiO_4 associate with each other to form large molecule, so the prepared TiO_2 shows soft aggregates, this can be testified by SEM and TEM.

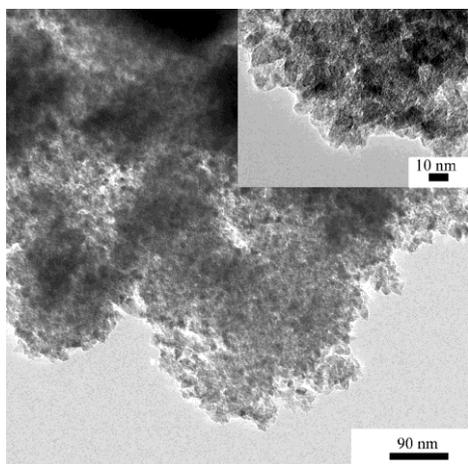


Fig. 3. TEM images of the sample. The inset shows enlarged TEM image of the sample. low-magnification (a) and high-magnification (b.)

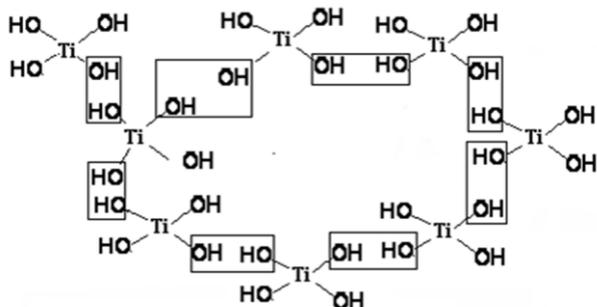


Fig. 4. Schematic illustration of synthesis of nanoporous TiO_2 aggregates.

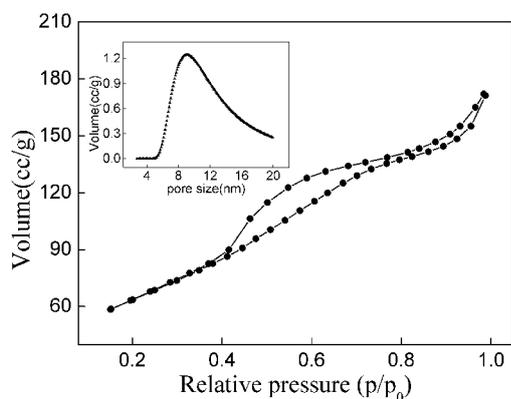


Fig. 5. Nitrogen adsorption and desorption isotherms of titania nanoporous aggregates. Inset shows the pore size distribution determined from the desorption branch.

The surface area and porosity of the nanoporous TiO_2 aggregates were investigated through nitrogen adsorption and desorption isotherms. Fig. 5 shows the isotherm of typical type IV-like with a type H2 hysteric loop, which indicates the presence of mesoporous materials according to IUPAC classification[14]. The plot of the pore size distribution (inset in Fig. 5) was determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm and is relatively narrow with an average pore diameter of 9.1 nm; this shows that these TiO_2 aggregates clearly have mesoporous structure. The BET specific surface and pore volume of the nanoporous aggregates are about $231.28 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.09081 \text{ cm}^3 \cdot \text{g}^{-1}$ respectively, and the pore size distribution was 6~20 nm. The result suggests that the nanoporous aggregates mainly originated from the interstices between the interconnected titania, in good agreement with the result of SEM and TEM[15].

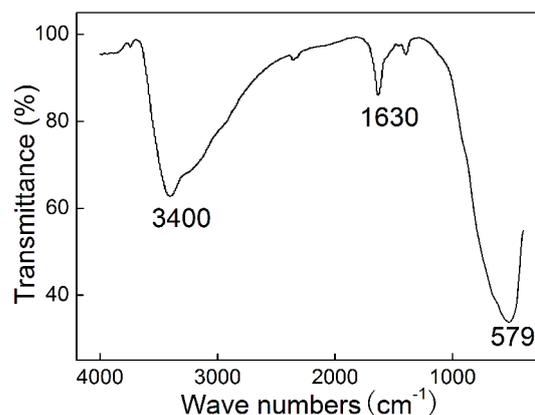


Fig. 6. FT-IR spectrum of the sample.

The FT-IR spectrum of the nanoporous TiO_2 aggregates is shown in Fig. 6. The absorbances under 1000 cm^{-1} originate from TiO_2 [16]. The two peaks at 3400 and 1630 cm^{-1} correspond to the surface adsorbed water and the hydroxyl groups[15]. The surface hydroxylation is very advantageous for the photocatalytic activity of the anatase phase crystals, because it provides higher capacity for oxygen adsorption[17]. There are no other bands in the spectrum, which indicates that no precursor residues reside in the nanoporous TiO_2 aggregates after washing the sample with distilled water.

The degradation of methylene blue (MB) was selected as a test-reaction to verify the photocatalytic activity of synthesized TiO_2 samples. The initial concentration of MB was 4 mg/L. Typically, MB solutions display maximal absorbance under 663 nm which was ascertained by experiments.

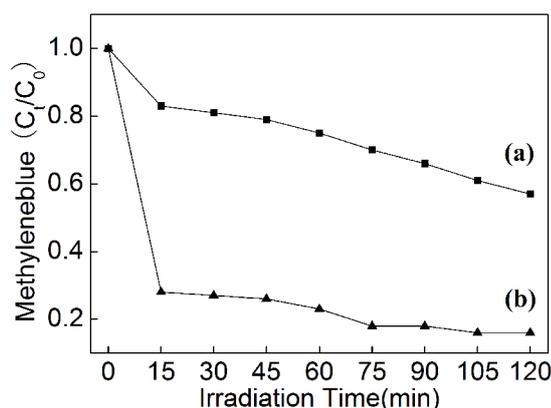


Fig.7. Photodegradation of methylene blue in the presence of (a) P-25 and (b) prepared titania.

Fig. 7 illustrates the photodegradation of methylene blue in the presence of nanoporous titania aggregates and commercial P-25. It suggests that the photocatalytic activity of the sample is about 4 times of P-25 by decomposing the methylene blue under UV light irradiation through photocatalytic test. From the trend of the photocatalytic curve, we can see the degradation of MB is 75 % in the presence of the prepared samples, and 25 % of P-25 in the first 15 min. After 75 min, the degraded effect of prepared sample is 85 % while only 30 % of P-25. Several factors, including the total surface area, crystal composition, crystal phase, and catalyst morphology contribute to the altered catalytic performance. Anatase is usually believed to be more photocatalytically active than the rutile. Among the TiO₂ samples used for photocatalysis study, the samples are found to be the most active to catalyze the photodecomposition of MB. This is because both TiO₂ samples possessed the larger surface area and higher content of anatase phase. Meanwhile, the high photocatalytic activity of the prepared TiO₂ samples resulted from the abounding hydroxyl of its surface which can be seen through the analysis of FT-IR.

4. Conclusions

Spheric nanoporous aggregates of anatase titania were successfully prepared by using metatitanic acid as raw material. The aggregates were established through the action among hydroxide groups of H₄TiO₄, the average crystal size of the particles is 10 nm; the surface area is 231.28 m²·g⁻¹, pore volume is 0.09081 cm³·g⁻¹, and the pore size distribution is 6 ~ 20 nm. The photocatalytic activities of the sample are about 4 times of P-25 by decomposing the methylene blue under UV light irradiation. The high photocatalytic activity of these TiO₂ aggregates is related to the larger surface area, smaller

crystal size, and highly porous structure.

Acknowledgments

The authors would like to acknowledge the National Center for Nanoscience and Technology Coordination Laboratories for the SEM measurements.

References

- [1] A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photoch. Photobio. C: Photoch. Rev.* **1**, 1 (2000)
- [2] O. Carp, C. L. Huisman, A. Reller, *Prog. Solid State Chem.* **32**, 33 (2004)
- [3] S. Bae, E. Shim, J. Yoon, H. Joo, *Sol. Energy Mater. Sol. Cells.* **92**, 402 (2008)
- [4] R. C. Furneaux, W. R. Rigby, A. P. Davidson, *Nature* **337**, 147 (1989)
- [5] G. Widawski, M. Rawiso, B. Francois, *Nature* **369**, 387 (1994)
- [6] Z. F. Liu, Z. G. Jin, W. Li, J. J. Qiu, *Mater. Lett.* **59**, 3620 (2005)
- [7] J. H. Moon, S. Kim, G. R. Yi, Y. H. Lee, S. M. Yang, *Langmuir* **20**, 2033 (2004)
- [8] P. N. Bartlett, J. J. Baumberg, P. R. Birkin, M. A. Ghanem, M. C. Netti, *Chem. Mater.* **14**, 2199 (2002)
- [9] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **359**, 710 (1992)
- [10] F. Kleitz, W. Schmidt, F. Schuth, *Micropor. Mesopor. Mat.* **44**, 95 (2001)
- [11] X. B. Chen, S. S. Mao, *Chem. Rev.* **107**, 2891 (2007)
- [12] X. B. Chen, *Chin J Catal* **30**, 839 (2009)
- [13] T. Y. Peng, D. Zhao, K. Dai, W. Shi, K. Hirao, *J. Phys. Chem. B* **109**, 4947 (2005)
- [14] Z. Y. Liu, D. D. Sun, P. Guo, J. O. Leckie, *Chem. Eur. J.* **13**, 1851 (2007)
- [15] J. C. Yu, L. Z. Zhang, J. G. Yu, *Chem. Mater.* **14**, 4647 (2002)
- [16] Z. Ding, G. Q. Lu, P. F. Greenfield, *J. Phys. Chem. B* **104**, 4815 (2000)
- [17] Z. Y. Liu, X. Quan, H. B. Fu, X. Y. Li, K. Yang, *Appl. Catal. B* **52**, 33 (2004)

*Corresponding author: yangql@buaa.edu.cn