Template-free Hydrothermal Preparation of Mesoporous TiO_2 Microspheres on a Large Scale

Miao-Miao Ye,[1] Zhong-Lin Chen,*[1] Wen-Shou Wang,[2] Liang Zhen,[2] and Ji-Min Shen[1]
[1]*State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, P. R. China*
[2]*School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China*

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Mesoporous TiO_2 microspheres have been made on a large scale by a simple hydrothermal method without using any surfactants or templates. The products were characterized by XRD, SEM, TEM, SAED, nitrogen adsorption, and UV–vis spectroscopy. Results indicate that the TiO_2 microspheres, with a diameter of 0.8–1.2 μm, are composed of numerous TiO_2 nanocrystals with an average diameter of 5.6 nm. The average pore size, BET surface area, and optical band-gap energy of the microspheres are 4.0 nm, 185.6 m^2/g, and 3.42 eV, respectively.

The design and synthesis of inorganic materials with different nanostructures have attracted much attention because of their novel functional and size-dependent properties. Among them, TiO_2 has been extensively studied because of its extensive applications, such as photocatalysts, photovoltaic cells, gas sensors, photonic crystals, and biomaterials.[1,2] TiO_2 with different morphologies such as nanowires,[3] fan-shaped,[4] hollow spheres,[5] and microspheres,[6] has been successfully prepared via different methods. Among these nanostructures, TiO_2 microspheres with mesoporous structure have attracted significant interest owing to their high surface area and porous frameworks for the improvement of photocatalytic activity and the large diameters for the improvement of separation efficiency. Mesoporous TiO_2 was first prepared in 1995 using alkyl phosphate as a surfactant.[7] After that, many different routes for the preparation of mesoporous TiO_2 microspheres have been reported constantly. Shchukin and Caruso[8] reported the fabrication of porous TiO_2 spheres by using porous polymeric beads as templates, and the photocatalytic activity was more efficient than that of Degussa P25. Zhang et al.[9] obtained mesoporous TiO_2 solid and hollow spheres with large BET surface area via a controllable chemical route. Eiden-Assmann et al.[10] reported the fabrication of porous and nonporous monodisperse TiO_2 particles by using a sol–gel method with salt or polymer as additives. Recently, Zhong et al.[11] reported one-pot preparation of macroporous TiO_2 microspheres by the hydrolysis of titanium tetraisopropoxide in the presence of acetic acid, 2-propanol, and organic amines. However, most of the exiting methods usually use costly and/or poisonous reagents, templates, high-temperature, and complicated chemical process. Therefore, it is still a great challenge to develop a new template-free, one-step, and low-temperature method to produce mesoporous TiO_2 microspheres.

In this letter, we report the large scale preparation of mesoporous TiO_2 microspheres by a facile and low-temperature hydrothermal method without adding any surfactants or templates. In comparison with other existing preparation methods of mesoporous TiO_2 microspheres, this new approach is simple since only $Ti(SO_4)_2$ is used as the precursor without adding any other reagents and thus more suitable for industrial production.

In a typical process, 0.18 g of $Ti(SO_4)_2$ (chemical grade without further purification) was dissolved in 50 mL of distilled water, the solution (0.015 M) was then transferred to a 50-mL Teflon-lined autoclave and filled up to 80% of its capacity. The autoclave was maintained at 120 °C for 48 h and allowed to cool to room temperature. The white precipitate was collected by means of centrifugation, washed with distilled water and absolute ethanol several times, and finally dried in a vacuum at 60 °C for 8 h.

The crystalline structure of the sample was evaluated by X-ray diffraction (XRD) analyses carried out on a Rigaku D/max-rA diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å). The morphology and structure of the products were analyzed by field-emission scanning electron microscopy (SEM, Hitachi S-4700), transmission electron microscopy (TEM, Phillips Tecnai 20), and selected-area electron diffraction (SAED) at an accelerating voltage of 200 kV. The porous nature of the products was measured by the nitrogen adsorption–desorption isotherm and Barrett–Joyner–Halenda (BJH) methods on a Micromeritics ASAP 2020M accelerated surface area and porosimetry system. Absorption spectrum was measured on a TU-1901 spectrophotometer equipped with a labsphere diffuse reflectance accessory.

The XRD patterns of the uncalcined and calcined TiO_2 microspheres are shown in Figure 1. The strong and sharp diffraction peaks indicate that the obtained sample has high crystallinity. All diffraction peaks can be perfectly indexed to the anatase phase of TiO_2 (JCPDS card, 21-1272) with lattice constants $a = 3.785$ and $c = 9.513$ Å. No characteristic peaks of other impurities are detected in the XRD patterns, indicating that the TiO_2 microspheres with high purity could be obtained under current facile preparation conditions. The average crystallite size of anatase in the sample can be calculated by applying the Debye–Scherrer formula on the anatase (101) diffraction peaks. The calculated average crystallite sizes of the TiO_2 microspheres is 5.6 nm. Calcination at 500 °C for 2 h does not change the phase and composition of the TiO_2.

Figure 2a shows low-magnification SEM image of the products, which indicates that the products consist of large-scale microspheres with diameters ranging from 0.8 to 1.2 μm. High-

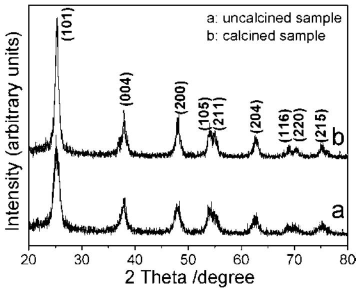

Figure 1. XRD patterns of (a) the uncalcined and (b) calcined TiO_2 microspheres.

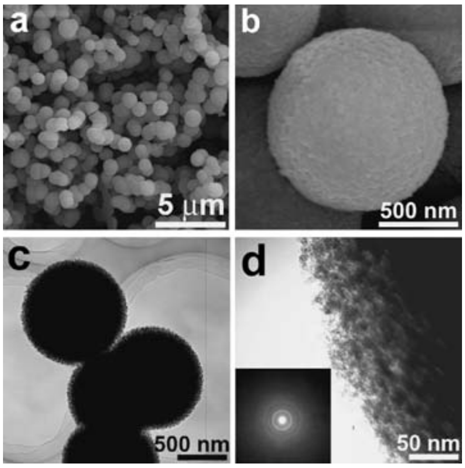

Figure 2. (a), (b) SEM and (c), (d) TEM images of the mesoporous TiO_2 microspheres. Inset: corresponding SAED pattern.

magnification SEM image (Figure 2b) shows that the surface of the TiO_2 microspheres is not smooth but is composed of numerous TiO_2 nanoparticles. Figure 2c shows a typical TEM image of the TiO_2 microspheres with an average diameter of about 1.0 µm, which is in agreement with the SEM observation. The SAED pattern taken from the selected sphere (inset in Figure 2d) indicates that the microsphere is polycrystalline, because it is composed of many tiny TiO_2 nanoparticles. The average sizes of the nanoparticles observed with TEM is almost the same to the XRD calculated size. The morphology of the TiO_2 micropheres remains unchanged when it was calcined at 500 °C for 2 h (see Figure S1).[15] Moreover, the $Ti(SO_4)_2$ concentration has an important effect on the morphology of the final products, both low (0.005 M) and high (0.05 M) $Ti(SO_4)_2$ concentration can not form microspheres. However, no significant morphology changes of the TiO_2 nanostructures were found when changing the reaction times and reaction temperatures (see Figure S2).[15]

The surface area and porosity of the mesoporous TiO_2 microspheres were investigated by using nitrogen adsorption and desorption isotherms (shown in Figure 3a). The isotherms are typical type IV-like with a distinct H_2 hysteretic loop in the range of 0.4–0.8 P/P_0, which indicate the presence of mesoporous materials according to IUPAC classification.[12] The plot of the pore size distribution (inset in Figure 3a) was determined by using the BJH method from the desorption branch of the isotherm. The average pore diameter of the TiO_2 microspheres is 4.0 nm. In addition, the mesopore size distribution is in the range of 2–8 nm, such a narrow distribution indicates great homogeneity of the pores for the TiO_2 microspheres. The BET surface area and pore volume of the microspheres are 185.6 m^2/g and 0.2265 cm^3/g, respectively.

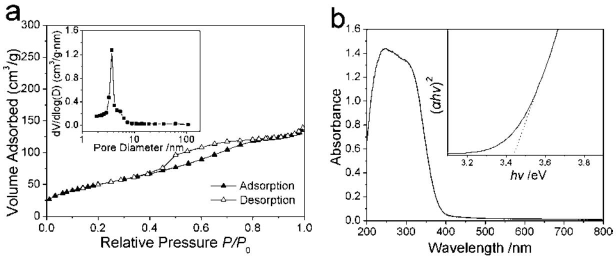

Figure 3. (a) Nitrogen adsorption–desorption isotherms of the mesoporous TiO_2 microspheres, the inset shows its BJH pore size distribution curve and (b) UV–vis absorbance spectrum of the TiO_2 microspheres, the inset shows the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$).

The optical band gap of the TiO_2 microspheres was studied by the UV–vis optical absorbance spectrum. The relationship between the absorption coefficient (α) and the photon energy ($h\nu$) can be written as shown in eq 1,[13]

$$(\alpha h\nu)^n = B(E - E_g) \qquad (1)$$

where $h\nu$ is the photon energy (E), E_g is the band gap energy, and $n = 2$, indicating that the transition is direct. Figure 3b shows the absorption spectrum of the TiO_2 microspheres. The inset shows the plots of $(\alpha h\nu)^2$ vs. $h\nu$. The band gap energy (E_g) for the TiO_2 microspheres can be calculated by extrapolating the linear portion of $(\alpha h\nu)^2$ vs. $h\nu$ plot to $\alpha = 0$. The optical band gap for the TiO_2 microspheres is 3.42 eV, which is a little higher than that of anatase TiO_2 nanoparticles with a particle size of 5–10 nm (3.36 eV).[14] The obvious blue shift of the optical band gap might be the result of the smaller average crystal size of the TiO_2 microspheres: this is the quantum-size effect.

In conclusion, we have reported a facile hydrothermal method to the large-scale preparation of mesoporous TiO_2 microspheres with a diameter of 0.8 to 1.2 µm by using only $Ti(SO_4)_2$ as the precursor. This method does not need any surfactants or templates, thus is promising for large-scale and low-cost production with high quality, and might also be useful for the synthesis of other inorganic materials. Furthermore, these mesoporous TiO_2 microspheres might be a great candidate for applications in catalysis.

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References

1 J. Yamamoto, A. Tan, R. Shiratsuchi, S. Hayase, C. R. Chenthamarakshan, K. Rayeshwar, *Adv. Mater.* **2003**, *15*, 1823.
2 M. Radecka, M. Rekas, *J. Am. Ceram. Soc.* **2002**, *85*, 346.
3 R. E. Cochran, J.-J. Shyue, N. P. Padture, *Acta Mater.* **2007**, *55*, 3007.
4 M. Ye, Z. Chen, W. Wang, L. Zhen, J. Shen, *Mater. Lett.* **2008**, *62*, 3404.
5 Z. Liu, D. D. Sun, P. Guo, J. O. Leckie, *Chem.—Eur. J.* **2007**, *13*, 1851.
6 Y. Han, G. Li, Z. Zhang, *J. Cryst. Growth* **2006**, *295*, 50.
7 D. M. Antonelli, J. Y. Ying, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2014.
8 D. G. Shchukin, R. A. Caruso, *Chem. Mater.* **2004**, *16*, 2287.
9 Y. Zhang, G. Li, Y. Wu, Y. Luo, L. Zhang, *J. Phys. Chem. B* **2005**, *109*, 5478.
10 S. Eiden-Assmann, J. Widoniak, G. Maret, *Chem. Mater.* **2004**, *16*, 6.
11 Z. Zhong, F. Chen, T.-P. Ang, Y. Han, W. Lim, A. Gedanken, *Inorg. Chem.* **2006**, *45*, 4619.
12 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, *57*, 603.
13 R. A. V. Leeuwen, C. J. Hung, D. R. Kammler, J. A. Swizer, *J. Phys. Chem.* **1995**, *99*, 15247.
14 K. M. Reddy, S. V. Manorama, A. R. Reddy, *Mater. Chem. Phys.* **2003**, *78*, 239.
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