A New Strategy to Synthesize TiO_2-hollow Spheres Using Carbon Spheres as Template

Weihua Shen, Yufang Zhu, Xiaoping Dong, Jinlou Gu, and Jianlin Shi*
State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding-xi Road, Shanghai 200050, P. R. China

(Received February 22, 2005; CL-050230)

The TiO_2-hollow spheres with uniform shell and diameter have been synthesized using carbon sphere as template, which has abundant –OH groups in its surface hydrophilic layer, and the titanium source was modified into this layer by the covalent –O–Ti bonding.

Titanium dioxide is an important metal-oxide semiconductor that has various applications in many fields, such as solar cells, gas sensing, catalyst supports, and wastewater purifications.[1–3] Its unique photocatalytic character makes it suitable for the oxidations of the organic pollutions from wastewater or drinking water supplies. Mesoscopic hollow spherical particles or capsules are useful in a number of areas. For example, they can serve as the extremely small container applied in catalysis, delivery of drugs, development of artificial cells, and protection of active biological reagent. In the recent years, more and more attention has been paid to fabricate core/shell composite materials and capsules with varied structural, catalytic, and optical properties using sphere polymer, silica, metal, and semiconductor as templates.[4–10] Previously, a hydrothermal synthesis route of colloidal carbon sphere with tunable diameter using glucose as carbon source was developed by Y. Li et al.,[11] and it is demonstrated that the surface of this carbon has relatively high reactivity, because of the abundant hydroxyl group remaining on the outer surface of those carbon spheres. Using this carbon sphere as template, the carbon core–noble metal shell structure was synthesized by the surface-redox reaction,[11] semiconducting Ga_2O_3- hollow spheres were prepared by the physical adsorption of the Ga source cation,[12] and WO_3-hollow spheres had also been prepared.[13] Hereby, we present a new strategy to synthesize TiO_2-hollow spheres with ultrathin crystal shell composed of nanoparticle.

The colloidal carbon-sphere template was synthesized similarly to the procedure described in the literature.[11] Typically, 1 M glucose solution was transferred to a Teflon-lined autoclave, sealed and maintained at 170 °C for 10 h. The dark-brawn product was collected by centrifugation at 8000 rpm for 20 min, washed with distilled water and ethanol for several times, respectively, and dried at 70 °C in vacuum. The carbon/TiO_2 composite was prepared as follows: 0.2 g of as-prepared carbon sphere template was redispersed in 50 mL of toluene by the ultrasonic treatment. To this homogeneous suspended solution, 5 mL of titanium tetraisopropoxide was added, and this solution was refluxed in a silicone oil bath at 120 °C for 20 h. After cooled to the room temperature, the resulting product was collected by centrifugation and washed with the toluene for three times, dried in vacuum at 70 °C, and hydrolyzed at 70 °C under saturated water vapor for 10 h. To obtain the titanium dioxide-hollow sphere, the as-prepared carbon–titanium dioxide composite was calcined in air at 450 °C for 2 h. A reference sample was heated under vacuum at 450 °C for 2 h and this sample was named as TiO_2/C-v.

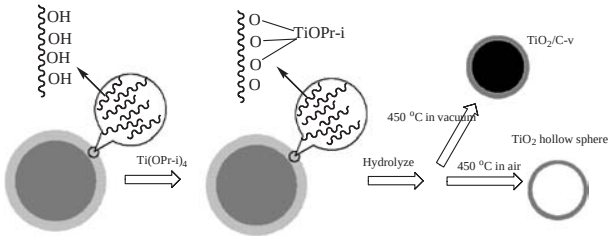

Figure 1. Schematic mechanism for the formation of TiO_2-Hollow sphere using carbon sphere as template.

Figure 1 shows the schematic process for the formation of TiO_2-hollow spheres. In this synthesis strategy, the template used was the carbon spheres prepared by dehydrating glucose under the hydrothermal condition. According to the literature,[11,12] the surface of the spheres has a distribution of –OH and C=O groups similar to that of polysaccharide, which make it easy to modify the surface with heteroatom. The FTIR spectrum (not shown) of the as-prepared carbon sphere confirms that –OH and C=O organic groups exist on the as-prepared carbon sphere. When the carbon spheres were dispersed in the titanium tetraisopropoxide toluene solution, the isopropoxide group can exchange with the –OH on the surface layer to generate isopropanol, and the titanium source was modified into the hydrophilic layer by the covalence of –O–Ti.

The XRD patterns of the samples of three different stages were illustrated in the Figure 2. It can be seen that the XRD pattern of the as-prepared carbon/TiO_2 composite only shows a broad peak 2θ at about 15–25° which is considered the diffraction peak of amorphous carbon, and no TiO_2 characteristic peaks were detected. After thermal treatment under vacuum at 450 °C for 2 h, TiO_2 of this composite crystallized, and the TiO_2/C-v sample shows well-discerned characteristic peaks of the anatase phase with little broadening in the XRD pattern. However, the XRD pattern of the hollow spherical TiO_2, which was calcined in air at 450 °C to burn off carbon shows hybrid crystalline phase of anatase and a little amount of rutile. This evidence suggests that the crystallization of TiO_2 is inhibited by the organic substance at the surface layer of the carbon spheres under the hydrolyzed condition, and the thermal treatment in the vacuum causes the further dehydration and shrinkage of carbon spheres because of the loose structure of the carbon spheres, which lead the TiO_2 in the surface layer to concentrate and crystallize. The small amount of rutile phase of the hollow sphere TiO_2 may be formed by the local overheating owing to the carbon burning. According to the Scherrer equation, the crystallite sizes of the TiO_2/C-v and the hollow-sphere TiO_2 are 16 nm and 20 nm, respectively (the crystallite size of hollow-sphere TiO_2 is calculated by the anatase form XRD diffraction peak). The weight lose is 86.7%

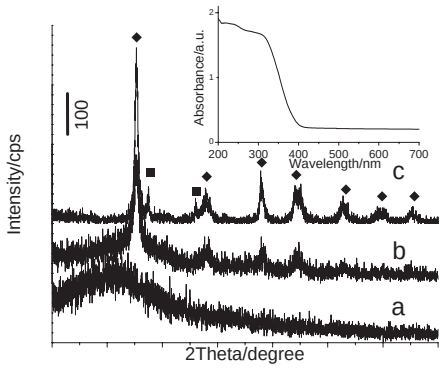

Figure 2. Powder XRD patterns of a) the as-prepared TiO_2/carbon sphere composite, b) the TiO_2/C-v, and c) the TiO_2-hollow spheres (◆ represent the anatase phase, and ■ represent the rutile phase) obtained using Rigaku D/MAX-2550V X-ray diffractometer with Cu target (40 kV, 40 mA), and the inset is the UV–vis absorbance of the TiO_2-hollow spheres.

estimated from the process of calcinations. The UV–vis absorbance curve of the TiO_2-hollow spheres was performed in the inset of Figure 2, the absorption bands of this hollow spheres are very close to that of the bulk materials.

A typical FE-SEM image of the as-prepared carbon sphere template is shown in the Figure 3A. Perfect sphere morphology with uniform particle size can be seen. The size of the carbon spheres is about 500 nm. It has been reported that the particle size can be controlled by adjusting the parameters of the concentration, temperature, and hydrothermal time.[11] In our experiment, the carbon spheres of 500 nm diameter were used as template. The typical TEM image of the hollow-sphere TiO_2 is shown in the Figure 3B. It can be see that the diameter of the TiO_2-hollow sphere is obviously smaller than the carbon template, and the shrinkage ratio is about 40%. The thickness of the TiO_2 shell is about 18 nm estimated from the TEM image, which matchs well with the calculated size of the TiO_2 crystallite size by the XRD pattern ≈20 nm, and the outer surface is a little irregular. The selected area electron diffraction (inset of the Figure 3B) confirms the polycrystalline nature of the TiO_2-hollow spherical shell. The N_2 sorption measurement under 77 K reveals that the TiO_2-hollow spheres possesses a specific surface area of 56.6 m^2/g calculated with the BET method, also suggesting that the shell of the TiO_2-hollow sphere is composed of the TiO_2 nanoparticle. It is meaningful for the hollow spheres to act as a carrier for host–guest material such as a carrier for metal, CdSe, etc. and for drug delivery system.

In summary, we have successfully synthesized the TiO_2-hollow spheres with uniform shell and diameter, using the carbon spheres as template by a new strategy. The shell thickness is about 18 nm, composed of TiO_2 nanoparticles. This strategy provides a simple and cheap method to prepare TiO_2-hollow spheres and probably other oxides hollow spheres.

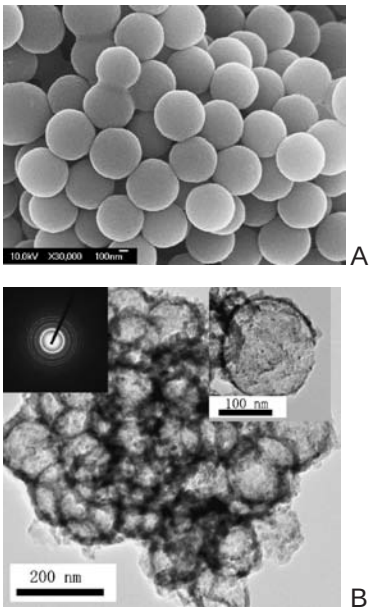

Figure 3. (A) Typical SEM image of the carbon-sphere template acquired on JSM-6700F field emission scanning electron microscope, (B) typical TEM image of the TiO_2-hollow sphere obtained on 2100F electron microscope operated at 200 kV, the inset present the selected area electron diffraction (SAED) and the ampliative TEM image.

References

1 N. G. Park, G. Schlichthorl, J. van de Lagemaat, H. M. Cheong, A. Mascarenhas, and A. J. Frank, *J. Phys. Chem.*, **103**, 3308 (1999).
2 K.-N. P. Kumar, K. Keizer, A. J. Burggraaf, and T. Okubo, H. Nagamoto, *J. Mater. Chem.*, **3**, 923 (1993).
3 J. C. Yu, L. Zhang, and J. Yu, *Chem. Mater.*, **14**, 4647 (2002).
4 H. Fudouzi and Y. Xia, *Adv. Mater.*, **15**, 892 (2003).
5 A. Dong, Y. Wang, Y. Tang, N. Ren, Y. Zhang, and Z. Gao, *Adv. Mater.*, **14**, 1506 (2002).
6 Z. Yang, Z. Niu, Y. Lu, Z. Hu, and C. C. Han, *Angew. Chem., Int. Ed.*, **42**, 1943 (2003).
7 Y. Yin, Y. Lu, B. Gates, and Y. Xia, *Chem. Mater.*, **13**, 1146 (2001).
8 H. Zeng, J. Li, Z. L. Wang, J. P. Liu, and S. Sun, *Nano Lett.*, **4**, 187 (2004).
9 H. J. Hah, J. I. Um, S. H. Han, and S. M. Koo, *Chem. Commun.*, **2004**, 4012.
10 G. Büchel, K. K. Unger, A. Matsumoto, and K. Tsutsumi, *Adv. Mater.*, **10**, 1036 (1998).
11 X. Sun and Y. Li, *Angew. Chem., Int. Ed.*, **43**, 597 (2004).
12 X. Sun and Y. Li, *Angew. Chem., Int. Ed.*, **43**, 3827 (2004).
13 X. Li, T. Lou, X. Sun, and Y. Li, *Inorg. Chem.*, **43**, 5442 (2004).

Published on the web (Advance View) May 21, 2005; DOI 10.1246/cl.2005.840