Self-assembly TiO_2 Hierarchical Hollow Microspheres with Rutile Nanorods by Template-free Hydrothermal Method

Yanfeng Zhang,[1] Xiaohui Feng,[1] Hui Liu,[1] Cici Wang,[1] Jingze Liu,*[2] and Yu Wei*[1]
[1]*College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050016, P. R. China*
[2]*College of Life Science, Hebei Normal University, Shijiazhuang 050016, P. R. China*

(Received August 4, 2008; CL-080757; E-mail: weiyu@mail.hebtu.edu.cn, Liujingze@mail.hebtu.edu.cn)

Hierarchical TiO_2 hollow microspheres composed of rutile nanorods were directly prepared by a simple, efficient, facile, and template-free hydrothermal method with $TiCl_4$ solution in the presence of hydrochloric acid.

Inorganic hollow nanostructures have attracted considerable attention owing to their potential applications in optical, electronic, magnetic, catalytic, and sensor devices.[1–3] Among various synthesis methods, template-directed approaches have been demonstrated to be effective for preparing hollow microspheres. Various methods using hard templates (e.g., polymer latex and anodic aluminum oxide templates) or soft templates (e.g., supramolecular, ionic liquids, surfactant, and organogel) have been extensively investigated.[4–6] However, the used surfactants or polymers have to be removed to create the hollow interiors, which limits their potential applications. Therefore, it is highly desired to develop a facile and template-free route for the preparation of inorganic hollow nanostructures.

Hollow TiO_2 microspheres are a very important multifunctional material because of potential uses in diverse fields such as optical materials, photocatalysts, and catalysts.[7–10] Recently, TiO_2 microspheres with mesoporous core–shell structures have been prepared with a combination of wet and solid-state reactions.[11] Hollow anatase TiO_2 nanospheres have been obtained in the presence of thiourea and urea under hydrothermal conditions.[12] Dandelion-like TiO_2 microspheres have been prepared using $TiCl_3$ in a saturated NaCl solution.[13,14] Although several methods have been reported, it is necessary to develop an efficient and surfactant-free method to prepare hollow TiO_2 microspheres. In this letter, we report a simple and efficient route to fabricate TiO_2 hollow microspheres using $TiCl_4$ and hydrochloric acid.

In a typical experiment, 10 mL of $TiCl_4$ was added to 90 mL of distilled water in a conical flask which is emersed in ice water. Then the concentration of titanium tetrachloride was determined by titration method. Certain amounts of the above solution, 16.7 mL of hydrochloric acid and some distilled water were placed to a beaker. The final concentration of $TiCl_4$ and hydrochloric acid are 1.0 and 2.0 M, respectively. After stirring at room remperature for 20 min, 80 mL of transparent mixing solution was put into a Teflon-lined stainless steel autoclave of 100-mL capacity. After being sealed, the autoclave was put into a muffle furnace, heated at 180 °C for 5 h and then allowed to cool to ambient temperature. The white precipitate was filtered, washed with distilled water several times followed by drying at 60 °C for 10 h.

The phase structures of the obtained samples were examined by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer with Cu Kα radiation. The morphology of the sample was observed by scanning electron microscopy (SEM) on a Hitachi 570 and field-emission SEM (FESEM) on a Hitachi S-4800. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken by field emission transmission electron microscopy on a Philips Tecnain F30. UV–vis diffuse reflectance spectrum (UV–vis DRS) was recorded on a Hitachi U-3010 spectrophotometer. The nitrogen adsorption and desorption isotherms at 77 K were determined using a Micrometrics ASAP2020.

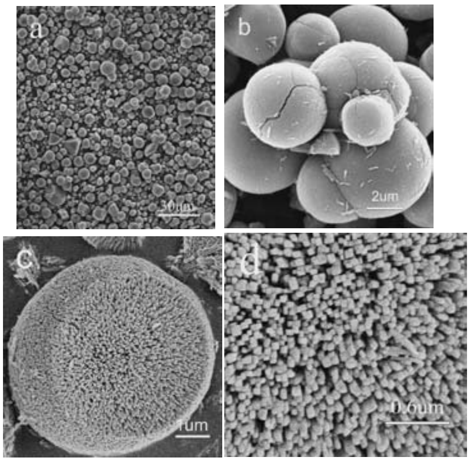

Figure 1. (a) The typical SEM image of the overall TiO_2 microspheres (preparation condition: $[TiCl_4] = 1.0\,M$, $[HCl] = 2.0\,M$, 180 °C, 5 h). (b) High-magnification SEM image. (c) FESEM image of a TiO_2 microsphere. (d) The higher magnification FESEM image of part of (c).

Figure SI-1 shows the XRD pattern of the prepared sample.[18] All of the diffraction peaks can be assigned to the rutile TiO_2 (JCPDS file No. 21-1276). Figures 1a and 1b give the SEM images of the sample. The average diameter of titania spheres was ca. 6 µm. The self-assembly was verified by FESEM, as shown in Figures 1c and 1d. Interestingly, the titania nanorods organized into ordered spherical assemblies. The titania microspheres with hollow interior were further verified by FESEM and TEM images of spheres broken by ultrasonic, as shown in Figure 2. The TEM image shows a reduced electron density in the inter region of the titania spheres, also suggesting that microspheres with hollow interiors were obtained. Figure 2b shows that the titania spheres are composed of rutile titania nanorods in 10–30 nm diameter and 50–400 nm length. HRTEM image gives lattice image of a nanorod crashed by ultrasonic. The distance between the adjacent lattice fringes can be assigned to the interplanar distance of rutile $TiO_2(110)$, $d_{110} = 3.25\,\text{Å}$, indicating single-crystalline nature of rutile titania nanorod.

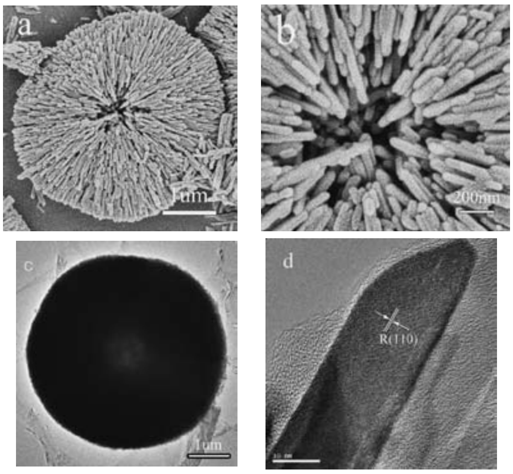

Figure 2. (a) The typical FESEM image of a TiO_2 microsphere crashed by ultrasonic (preparation condition: $[TiCl_4] = 1.0\,M$, $[HCl] = 2.0\,M$, 180 °C, 5 h). (b) The higher magnification image of the hollow interior of (a). (c) TEM image of a TiO_2 microsphere. (d) High-resolution image.

By varying the reaction conditions, we find that the added amount of hydrochloric acid, reaction temperature, and time play important roles in the formation of titania hollow microspheres. The preparation conditions of hollow titania microspheres are: the molar ratio of $HCl:TiCl_4 \geq 2$, the reaction temperature from 160 to 200 °C, the reaction time $\geq$5 h. To investigate the formation mechanism of hollow microspheres, the effect of reaction time on the morphology of the sample was studied. Figure SI-2 illustrates the morphology evolution of hollow titania microspheres.[18] When the reaction time is shorter (1–4 h), the titania microspheres are solid spheres without hollow interior, which are composed of numerous thinner and longer nanorods.

When the reaction time extended to 5 h, the microspheres evolved to hollow interior structure. And the titania nanorods became thicker and shorter. This phenomenon can be further confirmed by the XRD patterms of the samples prepared at different times (Figure SI-3).[18] With the reaction time extending, the diffraction peaks become sharper and narrower, indicating the improvement of crystallinity and the crystal grain growth of rutile titania nanorods. In addition, no precipitation can be collected when the reaction time is 40 min. When the reaction time is 50 min there are little powders with a morphology of microsphere composed of nanoorods (Figure SI-4).[18] It indicates that the microspheres form rapidly as soon as the reaction occurs. A hollow effect is clearly observed with longer reaction time (24 h, Figures SI-2g and SI-2h).[18] According to the experiment results, we think the morphology formation and evolution of microspheres seem to be as follows: In the initial stage, driven by the minimization of the total energy of the system, the primary titania particles are aggregated together with a sphereical appearance. Under the high-temperature and high-pressure conditions, it is helpful to form rod-like rutile titania. Due to some acid added to the reaction system (Figure SI-5),[18] the concentration of hydrogen ions is much larger. When the rutile titania nanorods form, the hydrogen ions are adsorbed to the surface of titania particles. Simultaneously, it is ineluctable the hydroxy is adsorbded to the surface of titania particles owing to the molecular polarity. The titania nanorod is aligned with another rod through hydrogen bonds formation between the adsorbed hydrogen ions and hydroxy group. When the rutile titania microspheres self-assemble, the long rod-like of titania particles evolve to short rod-like ones with hollow interior by the Ostwald ripening, which means crystallites grow at the expense of smaller ones.[15–17] While further work is needed to clearly understand the formation mechanism of the self-assembled titania hollow microspheres, we believe that the formation process of titania hollow structures can be expressed by Figure SI-6.[18]

Figure SI-7 shows the UV–vis DRS of titania hollow microspheres.[18] The spectra implies that the titania microspheres display strong absorbance for UV light (200–420 nm). The photocatalytic activity of the sample was evaluated by photocatalytic decolorization of aqueous Methyl Orange solution (Figure SI-8).[18] Generally, rutile titania was thought to have poor photocatalytic activity. However, the as-prepared rutile titania hollow microspheres show obvious activity. And the microspheres have a BET surface area of $18.5\,m^2/g$, 14.2 nm pore-size distribution (Figure SI-9).[18]

In summary, we have demonstrated a simple method for the convenient preparation of titania microspheres with hollow interiors by template-free hydrothermal method. It is shown that the addition of hydrochloric acid, reaction temperature, and time play important roles in the preparation of titania hollow microspheres. This titania hollow microspheres composed of well-aligned nanorods will possibly provide various applications, such as drug-delivery carriers, catalysis, photocatalysis, and nanoreactors. This simple and efficient method will open up new avenues for the controlled fabrication of other metal oxide hollow microspheres architecture.

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References and Notes

1 H. Yu, J. Yu, S. Liu, S. Mann, *Chem. Mater.* **2007**, *19*, 4327.
2 B. Liu, H. C. Zeng, *J. Am. Chem. Soc.* **2004**, *126*, 8124.
3 G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418.
4 Y. Sun, Y. Xia, *Science* **2002**, *298*, 2176.
5 J. Yuan, W.-N. Li, S. Gomez, S. L. Suib, *J. Am. Chem. Soc.* **2005**, *127*, 14184.
6 J. H. Jung, H. Kobayashi, K. J. C. van Bommel, S. Shinkai, T. Shimizu, *Chem. Mater.* **2002**, *14*, 1445.
7 A. M. Collins, C. Spickermann, S. Mann, *J. Mater. Chem.* **2003**, *13*, 1112.
8 H. Yoshitake, T. Sugihara, T. Tatsumi, *Chem. Mater.* **2002**, *14*, 1023.
9 T. Nakashima, N. Kimizuka, *J. Am. Chem. Soc.* **2003**, *125*, 6386.
10 Y. Li, C. Song, Y. Hu, Y. Wei, Y. Wei, *Chem. Lett.* **2006**, *35*, 1344.
11 H. G. Yang, H. C. Zeng, *J. Phys. Chem. B* **2004**, *108*, 3492.
12 C.-W. Guo, Y. Cao, S.-H. Xie, W.-L. Dai, K.-N. Fan, *Chem. Commun.* **2003**, 700.
13 X. Feng, J. Zhai, L. Jiang, *Angew. Chem., Int. Ed.* **2005**, *44*, 5115.
14 X. Bai, B. Xie, N. Pan, X. Wang, H. Wang, *J. Solid State Chem.* **2008**, *181*, 450.
15 R. Li, Z. Luo, F. Papadimitrakopoulos, *J. Am. Chem. Soc.* **2006**, *128*, 6280.
16 M. Epifani, J. Arbiol, E. Pellicer, J. R. Morante, *Chem. Mater.* **2007**, *19*, 4949.
17 J. Li, H. C. Zeng, *J. Am. Chem. Soc.* **2007**, *129*, 15839.
18 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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