

Fabrication of mesoporous core-shell structured titania microspheres with hollow interiors†

Chang-Wen Guo, Yong Cao,* Song-Hai Xie, Wei-Lin Dai and Kang-Nian Fan*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China. E-mail: yongcao@fudan.edu.cn; Fax: 86-21 65641740; Tel: 86-21 65643792-5

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Thermally stable mesoporous core-shell structured titania microspheres with well-defined hollow interiors were directly prepared by a novel hydrothermal precipitation of TiCl_4 in the presence of urea and ammonium sulfate.

The synthesis of nanostructured inorganic materials with hierarchical morphologies has attracted considerable attention in the field of catalysis, separation technology, microelectronic devices, and biomaterials engineering.^{1–6} In particular, the design and fabrication of spherical materials with hollow interiors have attracted considerable attention in recent years because of their potential uses as low-density capsules for controlled release of drugs, dyes, and inks, development of artificial cells, protection of proteins, enzymes, and DNA, and catalysis.^{7–13} A variety of hollow particles comprised of metals, ceramics and inorganic-hetero-composites with various diameters and wall thickness have been fabricated. So far, most of the systems reported for the formation of hollow spherical materials were based on template-assisted processes involving the replication of organized reaction fields such as emulsion foams,^{14,15} emulsion droplets and bicontinuous microemulsions,^{16–18} followed by the removal of the template materials by calcination or solvent etching. However, all above methods generally require the use of surfactants or polymers which have to be removed to create the hollow interiors. Moreover, these materials are usually unstable, and hence limited in their potential applications. In this communication, we report a novel simple and non-surfactant approach to synthesize stable core-shell structured titania microspheres with hollow interiors by a hydrothermal precipitation of titanium chloride (TiCl_4) with urea in ethanol/water solution in the presence of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). The method includes the following steps: (1) formation of a homogeneous ethanol/water solution of TiCl_4 , urea, and ammonium sulfate; (2) a subsequent hydro-

thermal precipitation of the above reaction mixture. The microspheres synthesized show no agglomeration and do not collapse even after calcination at 600 °C for 6 h. In addition, the core-shell titania sphere is mesoporous with a narrow pore size distribution in the nm range. The titania spheres were also thermally stable and had high surface area. These characteristics make it potentially useful in applications like controlled release capsules for drugs, dyes, cosmetics and inks, artificial cells, catalysts, and fillers.

It is well known that solvent-control and electrolytes addition can be used to control the macroscale topology of titania with tailored properties by adjusting the aggregation behavior of titanium species.^{18,19} The present procedure to prepare the mesoporous titania microspheres with core-shell structure is as follows: Certain amounts ammonium sulfate and urea were dissolved in a dilute aqueous solution of TiCl_4 under ice-water bath and then combined with equal amounts of ethanol. The molar composition of $\text{TiCl}_4:\text{H}_2\text{O}:\text{EtOH}:(\text{NH}_4)_2\text{SO}_4:\text{CO}(\text{NH}_2)_2$ was 1:86:24:1:46. After stirring for 2–4 h, a transparent solution was obtained. The mixture was transferred into an autoclave of 200 ml capacity and, after sealing, the autoclave was heated and maintained at 368 K for 5 h, and then allowed to cool to ambient temperature. The resultant slurry was filtered, twice washed with distilled water and subsequently washed carefully three times with absolute ethanol followed by vacuum-drying at 353 K. Calcination of the dried titania sample was conducted on a muffle oven at 773 K in air for 3 h.

SEM analyses (Philips-XL-30) were performed to examine the morphology of the titania microspheres. It is worth noting that the titania spheres produced by calcining at 773 K were intact and maintained the three-dimensional spherical nature of particles with an average diameter of ca. 3 μm (Fig. 1(a)). The core-shell nature with hollow interior of the titania spheres was verified by SEM examination of deliberately broken spheres (the insert in Fig. 1(a)). The TEM image (Fig. 1(b)) shows a reduced electron density of the spheres in the middle region of the titania spheres, suggesting that core-shell structured spheres with hollow interiors were obtained. A wall thickness of approximately 60–80 nm is estimated by TEM (JEOL-2011)

† Electronic supplementary information (ESI) available: Experimental details, *in situ* XRD data and thermal evolution of the textural properties of the mesoporous core-shell titania spherical samples. See <http://www.rsc.org/suppdata/cc/b2/b212845d/>

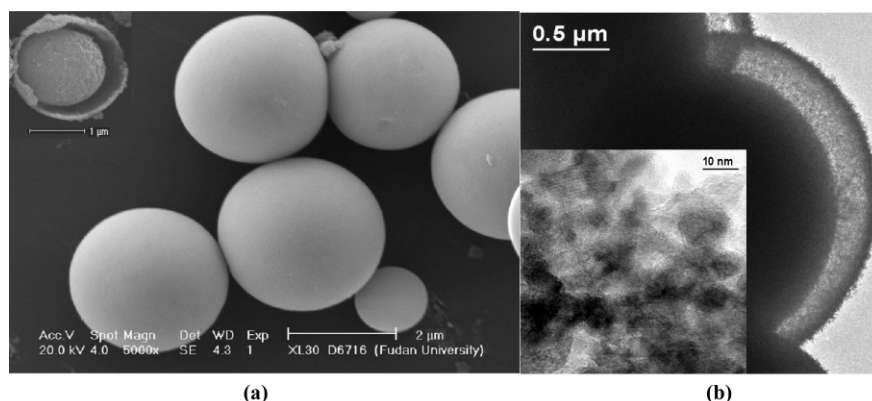


Fig. 1 SEM and TEM images of the mesoporous titania microspheres with hollow interiors after calcination at 450 °C. The higher magnification image in inset (b) displaying the crystalline nature (anatase) of the titania nanoparticles that make up the shell of the titania microspheres.

(from the dark ring around the perimeter of the hollow spheres) for the titania microspheres. High resolution TEM (the insert in Fig. 1(b)) showed that the shell of the core-shell titania spheres were comprised of connected crystalline titania nanoparticles approximately in 8–10 nm diameter, with a lattice spacing consistent with the anatase phase (0.352 nm).

On the other hand, we found that the present preparation methodology could lead to the formation of well-defined mesophases in the core-shell structured titania microspheres. The porosity of the titania materials have been investigated using nitrogen adsorption–desorption isotherms. Fig. 2 gives the nitrogen adsorption–desorption isotherm of the 450 °C calcined sample, it shows type IV-like isotherm with an inflection of nitrogen adsorbed volume at $P/P_0 = 0.45$ (type H₂ hysteresis loop), indicating the presence of well-developed mesoporosity in the fibrous samples. A typical value for the specific surface area according to the BET method is 139.7 m²g⁻¹ (Micromeritics TriStar System). The insert to Fig. 2 shows the pore-size distribution plots calculated using the BJH (Barrett–Joyner–Halenda) equation from the adsorption branch of the isotherm. The pore size distribution (PSD) measurements show that the spherical titania sample had pronounced mesoporosity of a very narrow pore-size distribution with an average pore diameter at ca. 4.0 nm.

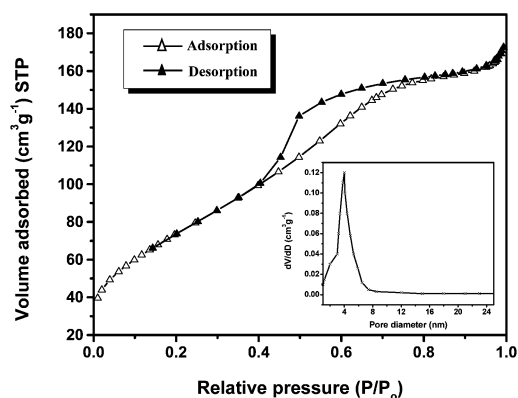
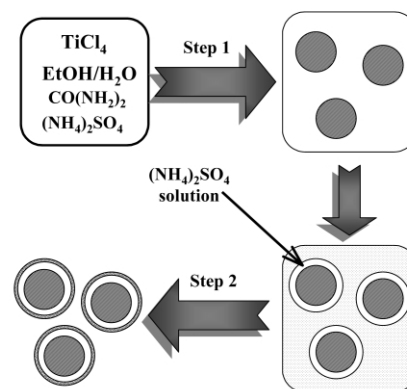


Fig. 2 Nitrogen adsorption/desorption isotherms and the corresponding pore size distribution (inset) for the calcined titania microspheres.

In order to examine the processing parameters that control the morphology and structural properties of the spherical titania samples, factors affecting the hydrolysis–polycondensation process including the amount of ammonium sulfate and urea additive, EtOH/H₂O ratio, reaction temperature and time were investigated. By varying these parameters, we find that the preparation parameters display vital importance in the final formation of titania. It is found that the presence of ethanol as a co-solvent and the use of ammonium sulfate as a dispersing agent are essential for the final formation of spherical titania particles with well-developed mesoporosity and hollow interiors. In addition, a critical dependence of the average diameter of the titania spheres as a function of the concentration of the ammonium sulfate ($< 0.5 \text{ mol L}^{-1}$) in the reaction system is also observed (ESI†). While further work is needed to fully understand the mechanism of the formation of these core-shell structured titania spheres with hollow interiors, we believe that the hollow structures of the titania materials are associated with a two-step precipitation of the titania species from the reaction systems (Scheme 1). In this respect, the presence of ammonium sulfate can behave as an electrolyte and thus modify the zeta potential of spherical poly-condensed titania species generated at the initial stage of the hydrolysis reaction.²⁰ The hollow interiors may therefore be created due to the subsequent precipitation of the titania species onto the ammonium sulfate-



Scheme 1

stabilized spherical titania surrounded by the ammonium sulfate dissolved EtOH/H₂O solutions in the reaction systems.

In summary, we have demonstrated a new method for the convenient preparation of thermally stable core-shell structured titania microspheres with hollow interiors by using a novel hydrothermal precipitation technology. Owing to their large specific area, stability and surface permeability, the spheres with hollow interiors can be used possibly in catalysis, separation technology and optonic electronics. Although the mechanism of the formation of the hollow titania microspheres with core-shell structures is not clear and is still under investigation, this work presents an easy method to fabricate titania materials with tailored microstructures.

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Notes and references

- I. L. Radtchenko, G. B. Sukhorukov, N. Gaponik, A. Kornowski, A. L. Rogach and H. Mohwald, *Adv. Mater.*, 2001, **13**(22), 1684.
- C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- H. Yang, N. Coombs and G. A. Ozin, *Nature*, 1997, **386**, 692.
- D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
- P. V. Braun, P. Osenar and S. I. Stupp, *Nature*, 1996, **380**, 325.
- J. Liu, Y. Shin, Z. Nie, J. H. Chang, L. Q. Wang, G. E. Fryxell, W. D. Samuels and G. J. Exarhos, *J. Phys. Chem. A*, 2000, **104**, 8328.
- Hollow and Solid Spheres and Microspheres: Science and Technology Associated with their Fabrication and Application*, ed. D. L. Wilcox, Sr., M. Berg, T. Bernat, D. Kelleman, J. K. Cochran, Jr., *MRS Proc.*, Vol.372, Materials Research Society, Pittsburgh, PA, 1994.
- E. Mathlowitz, J. S. Jacob, Y. S. Jong, G. P. Carino, D. E. Chickering, P. Chaturvedi, C. A. Santos, K. Vijayaraghavan, S. Montgomery, M. Bassett and C. Morrell, *Nature*, 1997, **386**, 410.
- H. Huang and E. E. Remsen, *J. Am. Chem. Soc.*, 1999, **121**, 3805.
- D. L. Wilcox and M. Berg, *Mater. Res. Soc. Symp. Proc.*, 1995, **372**, 3.
- Z. Y. Zhong, Y. D. Ying, B. Gates and Y. N. Xia, *Adv. Mater.*, 2000, **12**, 206.
- R. Rengarajan, P. Jing, V. Colvin and D. Mittleman, *Appl. Phys. Lett.*, 2000, **77**, 3517.
- D. Y. Wang and F. Caruso, *Chem. Mater.*, 2002, **14**, 1909.
- D. Walsh and S. Mann, *Nature*, 1995, **377**, 320.
- A. Imhof and D. J. Pine, *Nature*, 1995, **389**, 948.
- D. Walsh, J. D. Hopwood and S. Mann, *Science*, 1994, **264**, 1576.
- M. Ohmori and E. Matijevic, *J. Colloid Interface Sci.*, 1992, **150**, 594.
- S. D. Sims, D. Walsh and S. Mann, *Advanced Materials*, 1998, **10**, 151.
- J. L. Look and C. F. Zukoski, *J. Am. Chem. Soc.*, 1992, **75**, 1587.
- W. Janusz, A. Sworska and J. Szczypta, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 1999, **152**, 223.