

Design and fabrication of monodisperse hollow titania microspheres from a microfluidic droplet-template†

Xiuqing Gong, Limu Wang and Weijia Wen*

Received (in Cambridge, UK) 5th May 2009, Accepted 9th June 2009

First published as an Advance Article on the web 26th June 2009

DOI: 10.1039/b908932b

We report a facile microfluidic methodology to fabricate monodisperse hollow titania microspheres with a tunable surface morphology.

Titania microspheres are of particular interest, owing to their diversified applications that include photocatalysts, photovoltaic materials, paint pigments, abrasives and filters, among others.^{1–3} Typical applications in photocatalytic reactions and photovoltaic efficiencies require low material density, high surface area, and high light-trapping and conversion efficiency.^{4–6} Such properties are expected from hollow structures, and so fabrication of hollow titania microspheres and control of surface morphology have attracted enormous scrutiny.^{7–9} Previous studies have shown that hollow titania microspheres can be synthesized by either layer-by-layer polyelectrolyte-mediated deposition,^{10,11} colloidal-particle templating^{12–17} or spray-drying.^{18,19} However, these approaches are either technically demanding or time consuming; for example, templating methods require the preparation of well-dispersed colloidal suspensions and subsequent removal of the sacrificial template by calcination or chemical etching. An alternative to the preparation of inorganic hollow microspheres is the use of a metal alkoxide as a precursor and emulsion droplets as soft templates. Yet the presence of bulk water in those sacrificial droplets hampers their application to the more reactive titanium metal alkoxides. Several research groups have developed methods to solve this problem; for example, Collins *et al.*²⁰ used polar formamide to initiate the hydrolysis of titanium ethoxide in the emulsion; Nakashima *et al.*²¹ emulsified the alkoxide in an ionic liquid. Unfortunately, the monodispersity of the products resulting from the use of formamide to control the hydrolysis was found to be inadequate, and the ionic liquid requisite to the latter methodology is difficult to obtain.

Here, we introduce a facile microfluidic method in microsphere surface morphology, tailored to control the water diffusion from the water droplets, whereby hydrolysis between titanium alkoxide and water droplets was controlled to continuously form hollow titania gel microspheres in one step without surfactants or sacrificial core materials (Fig. 1a). The microfluidic method, directing the flow of microlitre volumes along microscale channels, offers the advantages of fast mixing

and reaction, and cessation of the reaction at specific stages.²² Basically, there are two microfluidic flow regimes, continuous flow and segmented flow,²³ wherein segmented flow has won more popularity in micro-material synthesis,^{24–30} for example, Eun *et al.* recently reported the formation of titanium alkoxide droplets in aqueous solution (O/W) by a microfluidic method, but the resultant microspheres were smooth without feasible control of surface morphology.³¹

A simple microfluidic reactor with flow focusing geometry (MFF)³² was first fabricated on a polydimethylsiloxane (PDMS) substrate by soft lithography.^{33,34} The microfluidic reactor has 5 inlets and a long serpentine flowing channel. Into the microfluidic chip are introduced three flow phases: phase 1, water in glycerol; phase 2, titanium tetrabutoxide (TBT) dissolved in hexadecane; and phase 3, butanol mixed with viscous paraffin oil (Fig. 1a, left panel). Phase 1 is first sheared into droplets by phase 2 through MFF geometry. The hydrolysis of TBT takes place to form a thin titania gel shell around the droplets as soon as the droplet is formed (Fig. 1b, left panel). After the shell is formed, phase 3, as carrier fluid, carries the microspheres flowing inside the channel and determines the flow rate inside the channel (Fig. 1b, dashed frame in left panel). In the triple phase system, the phase boundary line initially formed between phase 2 and phase 3 disappears as the

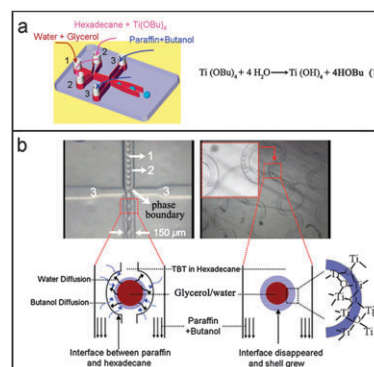


Fig. 1 (a) Schematic diagram of a microfluidic reactor (left panel). Channels 1, 2, and 3 correspond to phases 1, 2, and 3, respectively. The right panel shows the hydrolytic reaction between TBT and water. (b) Phase 1 (water and glycerol) is first sheared into droplets by phase 2 (hexadecane and TBT). Phase 3, paraffin and butanol (as carrier fluid) then convey the droplets inside the channel (dashed frame in left panel). When the droplets flow inside the channel, the interface between phases 2 and 3 disappears and the butanol can diffuse through them (dashed frame in right panel). The TBT will react with the water diffused from the droplets, driven by the “dewetting” effect of butanol. A gel microsphere with a glycerol core is thus formed. Images are captured from real time video.

Department of Physics and KAUST-HKUST Micro/Nano-fluidics Joint Laboratory, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.
E-mail: phwen@ust.hk

† Electronic supplementary information (ESI) available: Details of materials preparation, measurements and fluorescence detection. See DOI: 10.1039/b908932b

hexadecane is gradually dissolved into the paraffin, which allows the butanol previously dissolved in paraffin to diffuse through the hexadecane (Fig. 1b, dashed frame in right panel). The effect of butanol is to absorb water from the droplets as the solubility of *n*-butanol in water is 9.1 ml per 100 ml at room temperature, referred to as “dewetting” in our previous work.³⁵ The contact angle of phase 2 on the PDMS substrate is 25.6°; of phase 3, 34.8°, and of phase 1, 89.8°. This indicates that phases 2 and 3 and their mixture have a higher affinity for the PDMS channel than the phase 1 water droplets, thus enabling the droplets to be fully surrounded by TBT in hexadecane in their flow.^{36,37} As the microspheres flow inside the serpentine channel, further hydrolysis occurs, and the droplets are transformed into gel-like microspheres. After that, a quench step is introduced to cease the hydrolysis reaction.

To better understand the process of gel microsphere formation, we labeled phase 1 with fluorescent rhodamine B (red color) and phase 2 with fluorescein isothiocyanate (FITC, green color). Because the rhodamine B dissolved in water can move with the water diffusion, the shell of the gel was distributed both with rhodamine B and FITC (Fig. 2a and b). Accordingly, we could detect a hydrolytic reaction area with the hybrid colors, rhodamine B (red) and FITC (green), as seen in Fig. 2c. The core-shell structure was also confirmed by the distribution of the fluorescent intensity (inset in Fig. 2c). 3D imaging of the fluorescent microspheres further proves that the fluorescent microsphere has a surface with hybrid colors, red and green (Fig. 2d).

The content of butanol is critical in the surface morphology control. To prove it, three volume fractions were used in our experiments: no butanol, 1 v/v% butanol, and 2 v/v% butanol (Fig. 3). It is seen that if no butanol was added, the particles had relatively smooth surfaces (Fig. 3a), whereas if 1 v/v% or 2 v/v% butanol was added, rougher surfaces were obtained (Fig. 3c and e). When butanol is added, water has the potential to dissolve into butanol which leads to the continuous diffusion of water from the inside of the droplet to the outside. Water can migrate through the gel network of the titania shell and out to the surface where the hydrolysis takes place. As the

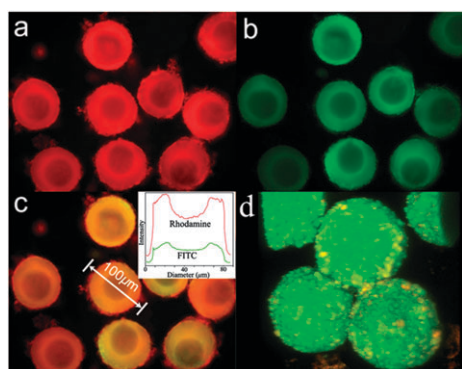


Fig. 2 Titania gel microspheres with both red rhodamine fluorescence (a) and green FITC fluorescence (b) distributed on the shell. The superposition of (a) and (b) demonstrates a mixing reaction area of water and TBT (c). The distribution of fluorescent intensity as shown in the inset indicates a core-shell structure of microspheres in (c). (d) 3D imaging of the fluorescent microspheres corresponding to (c).

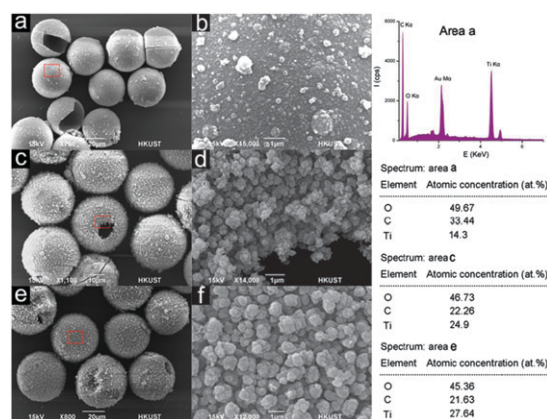


Fig. 3 (a) SEM image of titania gel microspheres prepared without adding butanol. (b) SEM image of the magnified surface labeled in red in (a); (c) titania gel microspheres prepared with 1 v/v% butanol added and its corresponding magnified surface (d); (e) with 2 v/v% butanol added and its corresponding magnified surface (f). The composition of the particle surface is measured by EDX (right upper panel). The detailed Ti atomic contents measured by EDX are listed in the right lower panel. The holes in the microspheres are the result of partial collapse during the sample treatment.

migration is more or less hampered by the gel network, the hydrolytic reaction is no longer simultaneous and uniform around the microsphere. This makes the growth of big granules and the formation of rough surfaces possible (Fig. 3b, d and f), with higher titanium contents on the surfaces as measured by EDX (Fig. 3, right panel).

However if we directly put 2-butanol in the TBT/hexadecane phase, the hydrolytic reaction is too fast to be controlled, because of the high reactivity of titanium alkoxide, the hydrolytic product can easily block the channel. To slow down the reaction rate, we put 2-butanol in another phase, paraffin. Thus, the longer diffusion time of 2-butanol through the two phases delays the water absorption and decreases the hydrolytic rate, allowing more time to control the hydrolytic process when the droplets flow inside the microfluidic channel. From the EDX, it is found that there is more carbon in the selected area when no butanol is added than with the addition of butanol, this may be caused by the unreacted TBT. Because the hydrolysis of TBT consists of multiple reactions, more water will lead to deeper hydrolysis of TBT and loss of more organic content from the TBT molecules in the form of HOBu. As a result, if less butanol is added, the gel microspheres are mainly composed of TiO_2 and other forms of hydrolytic products of TBT.

Fig. 4a reveals more distinctly the hollow structure with a shell thickness of 2 μm . An interesting phenomenon is that the inner wall of the microsphere was pocked with nanopores of about 100 nm diameter (Fig. 4b), which might have resulted from the effective diffusion of water through the gel microspheres. It is possible to convert gel microspheres to the crystal state without shell collapse. We annealed gel microspheres in a furnace to temperatures of 500 $^\circ\text{C}$, 650 $^\circ\text{C}$, and 900 $^\circ\text{C}$ to determine the calcination process and found that under 900 $^\circ\text{C}$ temperature treatment, titania microspheres can still maintain the hollow structure though some microspheres collapse as shown in the SEM images of Fig. 4c and d. The surface was

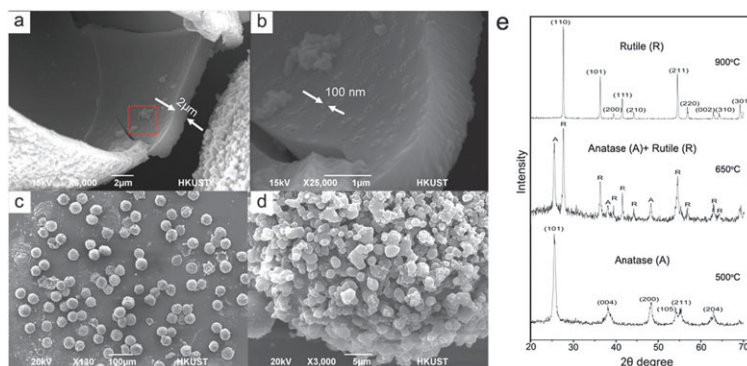


Fig. 4 (a) SEM image of a damaged microsphere revealed the hollow structure of titania, in which the thickness of the shell is about 2 μm , (b) the magnified image of the red framed area in (a) indicates that the inner wall of the microsphere was pocked with nanopores of about 100 nm diameter. The picture is correspondent to the sample in Fig. 3a and b. (c) SEM image of a titania microsphere after being calcined at 900 $^{\circ}\text{C}$, (d) magnified surface morphology of particles in (c), (e) XRD patterns of titania gel microspheres calcinated at 500 $^{\circ}\text{C}$, 650 $^{\circ}\text{C}$, and 900 $^{\circ}\text{C}$. The microspheres can change from anatase to rutile phase under heat treatment. The picture is correspondent to the sample in Fig. 3e and f.

found to contain bigger granular size and many pores, which may be caused by the fusion of small particles and the removal of organic components during combustion.^{19,38} Furthermore, the XRD pattern (Fig. 4e) shows that titania can crystallize into anatase (JCPDS File No. 21-1272) and rutile (JCPDS File No. 21-1276) structures after 2 h of annealing treatment in air at 500 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$, respectively. From the XRD results, the phase transition from anatase to rutile seemed to occur at about 650 $^{\circ}\text{C}$ where diffraction of both phases was observed and was consistent with previously reported results based on sol gel precursors.³⁸

This publication is based on work partially supported by award no. SA-C0040/UK-C0016, made by King Abdullah University of Science and Technology (KAUST), Hong Kong, RGC grants HKUST 603608 and 602007. The work was also partially supported by the Nanoscience and Nanotechnology Program at HKUST.

Notes and references

- A. Fujishima, T. Inoue and K. Honda, *J. Am. Chem. Soc.*, 1979, **101**, 5582.
- B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
- I. Najeh, A. Salim, S. A. Bagshaw, A. Bittar, T. Kemmitt, A. J. McQuillan, A. M. Mills and M. J. Ryan, *J. Mater. Chem.*, 2000, **10**, 2358.
- T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, *Langmuir*, 1998, **14**, 3160.
- Y. Yu and D. Xu, *Appl. Catal., B*, 2007, **73**, 166.
- E. Beyers, P. Cool and E. F. Vansant, *Microporous Mesoporous Mater.*, 2007, **99**, 112.
- H. Li, Z. Bian, J. Zhu, D. Zhang, G. Li, Y. Huo, H. Li and Y. Lu, *J. Am. Chem. Soc.*, 2007, **129**, 8406.
- Y. Kondo, H. Yoshikawa, K. Awaga, M. Murayama, T. Mori, K. Sunada, S. Bandow and S. Iijima, *Langmuir*, 2008, **24**, 547.
- J. G. Xu, S. W. Liu and H. G. Yu, *J. Catal.*, 2007, **249**, 59.
- F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 1998, **282**, 1111.
- F. Caruso, *Adv. Mater.*, 2001, **13**, 740.
- Z. Zhong, Y. Yin, B. Gates and Y. Xia, *Adv. Mater.*, 2000, **12**, 206.
- F. Caruso, *Chem.-Eur. J.*, 2000, **6**, 413.
- P. Jiang, J. F. Bertone and V. L. Colvin, *Science*, 2001, **291**, 453.
- R. A. Caruso, A. Susa and F. Caruso, *Chem. Mater.*, 2001, **13**, 400.
- Z. J. Liang, A. Susa and F. Caruso, *Chem. Mater.*, 2003, **15**, 3176.
- K. Kamata, Y. Lu and Y. Xia, *J. Am. Chem. Soc.*, 2003, **125**, 2348.
- J. Zhu, S. Xu, H. Huang, J. Zhu and H. Chen, *Adv. Mater.*, 2003, **15**, 156.
- X. Wang and P. Xiao, *J. Mater. Res.*, 2005, **20**, 796.
- A. Collins, C. Spickermann and S. Mann, *J. Mater. Chem.*, 2003, **13**, 1112.
- T. Nakashima and N. Kimizuka, *J. Am. Chem. Soc.*, 2003, **125**, 6386.
- Y. Song, J. Hormes and C. Kumar, *Small*, 2008, **4**, 698.
- A. Günther and K. F. Jensen, *Lab Chip*, 2006, **6**, 1487.
- D. Dendukuri, D. C. Pregibon, J. Collins, T. A. Hatton and P. S. Doyle, *Nat. Mater.*, 2006, **5**, 365.
- J. B. Edel, R. Fortt, J. C. deMello and A. J. deMello, *Chem. Commun.*, 2002, 1136.
- A. Hassan, O. Sandre, V. Cabuil and P. Tabeling, *Chem. Commun.*, 2008, 1783.
- S. Xu, Z. Nie, M. Seo, P. Lewis, E. Kumacheva, H. Stone, P. Garstecki, D. Weibel, I. Gitlin and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2005, **44**, 724.
- S. Poe, M. Cummings, M. Haaf and D. Mcquade, *Angew. Chem., Int. Ed.*, 2006, **45**, 1544.
- J. Kim, A. Utada, A. Fernández-Nieves, Z. Hu and D. A. Weitz, *Angew. Chem., Int. Ed.*, 2007, **46**, 1819.
- G. M. Whitesides, *Nature*, 2006, **442**, 368.
- T. H. Eun, S. H. Kim, W. J. Jeong, S. J. Jeon, S. H. Kim and S. M. Yang, *Chem. Mater.*, 2009, **21**, 201.
- S. L. Anna, N. Bontoux and H. A. Stone, *Appl. Phys. Lett.*, 2003, **82**, 364.
- S. Takeuchi, P. Garstecki, D. B. Weibel and G. M. Whitesides, *Adv. Mater.*, 2005, **17**, 1067.
- Y. Xia and G. M. Whitesides, *Annu. Rev. Mater. Sci.*, 1998, **28**, 153.
- X. Gong, S. Peng, W. Wen, P. Sheng and W. Li, *Adv. Funct. Mater.*, 2009, **19**, 292.
- F. C. Chang and Y. C. Su, *J. Micromech. Microeng.*, 2008, **18**, 065018.
- M. Seo, Z. Nie, S. Xu, M. Mok, P. C. Lewis, R. Graham and E. Kumacheva, *Langmuir*, 2005, **21**, 11614.
- X. Jiang, T. Herricks and Y. Xia, *Adv. Mater.*, 2003, **15**, 1205.