Bioinspired synthesis of hierarchical macro-mesoporous titania with tunable macroporous morphology using cell-assemblies as macrotemplates†

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Received (in Cambridge, UK) 27th April 2009, Accepted 4th June 2009
First published as an Advance Article on the web 30th June 2009
DOI: 10.1039/b908294h

Cell-assemblies with different cell shapes were used as macrotemplates in the bioinspired synthesis of hierarchical macro-mesoporous titania with tunable macroporous morphology and enhanced photocatalytic performance.

Porous materials are known to feature large surface areas and connected pore channels, which can be used in numerous applications including catalysis, sorbents, separations, fuel cells, microelectronics, sensors, and medical diagnosis.[1] Recently, hierarchical pore materials with macropores along with micro- and/or mesopores have gained significant attention since they combine the advantages of all the pore systems.[2] The presence of macropores can act as a transport system for liquids and gases, thus increasing the accessibility of the smaller pores, especially improving the flow rates at high back pressure. These smaller pores with high surface area will greatly enhance the host–guest interactions, selectivity, and catalytic or ion-exchange properties.[3]

Hierarchical porous materials can be prepared by a single surfactant route,[4] macroscopic phase separations,[5] and even a template-free assembly,[6] however, a dual templating method was proved to be the most effective. This is because the hierarchical porous morphology and size can be varied easily by independently changing the shape, size and assembly of the hierarchical templates.[7] Currently, mesoporous structures are widely synthesized by using surfactants as templates,[8] and the three-dimensional arrays of macropores are made using macrotemplates such as polymer spheres,[9] silica beads,[10] emulsions,[11] inorganic salts[12] and ice crystals.[13]

Hierarchical porous structures are also found in nature, *i.e.* lungs of animals and leaves of trees,[14] which accelerate air and solar energy exchange.[15] To take advantage of this, much effort has been devoted to the bioinspired synthesis of porous materials using biotemplates, such as diatoms,[16] wood,[17] sea urchins,[18] bacterial superstructures,[19] bio-cellulose,[20] and cuttlebone.[21] However, the restrictions of these biotemplates such as fixed morphology and low availability render them unfeasible, leaving the abundant synthesis of porous materials with tunable macroporous morphology an unresolved challenge.

Cells are the basic organizational units of all known living organisms. In nature, cells have ample functionalities, properties and structures, making them facile and economic for widespread use.[22] Mimicking the natural cell-assembly process to synthesize porous materials with tunable macroporous morphology may be a novel and effective route. Possible advantages of the bioinspiration and biomimetics concept include: enhanced adsorption and/or photocatalytic efficiency, reduced energy consumption, and improved ecological harmlessness.[23]

Here, cell-assemblies with different cell shapes (spherical *Saccharomyces cerevisiae* cells (Fig. 1a) for sample A, baculiform *Stenotrophomonas acidaminiphila* cells (Fig. 1d) for sample B, filamentous *Grifola frondosa* cells (Fig. 1g) for sample C) are formed into macrotemplates by freeze drying of the fixed cells with glutaraldehyde.[24] A surfactant/titania sol–gel mixture (PEG 1500/tetraethoxide) is then introduced into the preformed macrotemplates. Once the reaction is completed, the surfactant and cell templates are removed by calcination (ESI†).

Fig. 1 shows the scanning electron microscopy (SEM) images of the cell-assembled macrotemplates and the corresponding titania materials that are synthesized by using them. The porous materials exhibit relatively homogeneous and uniform macropores with spheroidal, baculiform, and worm-like porous shapes, respectively. As expected, the macroporous morphologies resemble the parent macrotemplates and vary with the macrotemplate shapes, demonstrating that the macroporous structure morphology can be easily controlled by choosing the morphology of the cells. Since in nature cells have ample variety of shapes and sizes, this novel cell-assembly template method makes it possible to synthesize macroporous materials with diversified porous morphology and tuned pore sizes.

The pores of the titania network are significantly smaller when compared to the size of the cells used as macrotemplates, indicating a considerable shrinkage during template removal. For example, sample A uses cells of 3–4 μm and forms pores with diameters about 0.7–1.6 μm, sample B uses 3.5–4.5 μm cells to form pores with sizes about 0.6–1.2 μm, and sample C has pores with diameters about 1.1–4.0 μm when cells with sizes 2.9–3.7 μm are used. To our surprise, for sample C, we observed some pores that exceeded the sizes of the templates. This may be because *Grifola frondosa* cells are filamentous and

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† Electronic supplementary information (ESI) available: Synthesis and characterization details, XRD patterns, photocatalytic activity measurement. See DOI: 10.1039/b908294h

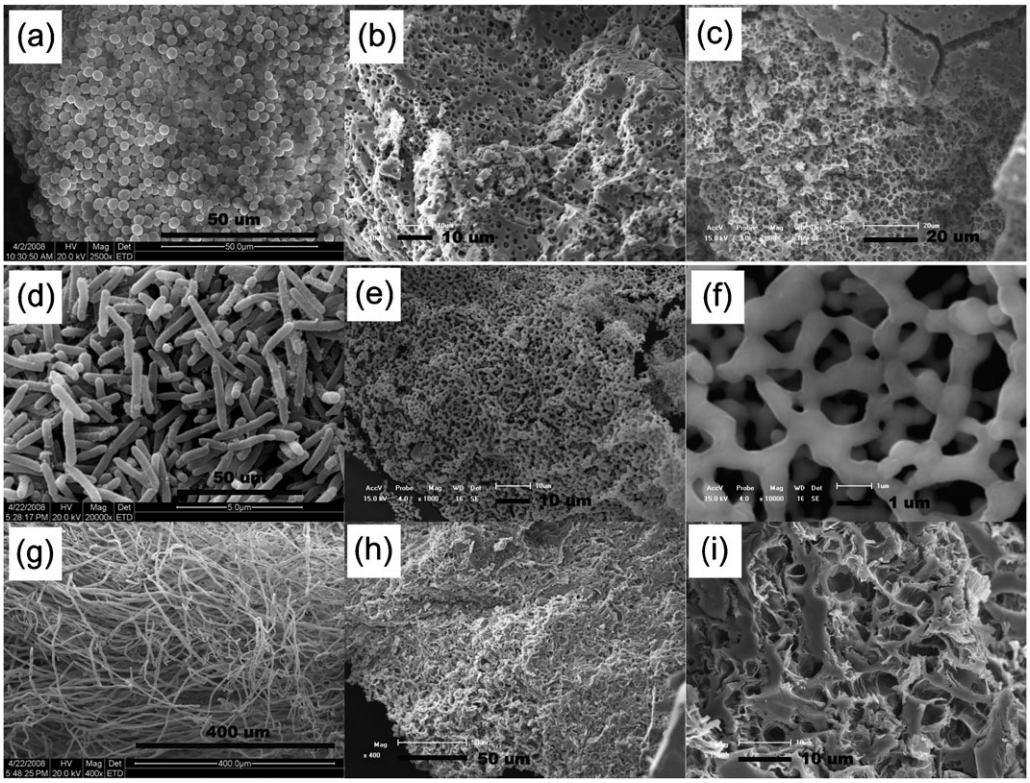

Fig. 1 SEM images of the fixed and freeze-dried cell-assemblies (a, d, and g) and the titania materials using cells assembled as macrotemplates (b, c for sample A; e, f for sample B; and h, i for sample C).

during the titania incorporation some of them twist and bundle with each other to increase the template width by double or more. Specifically, Fig. 1c shows that inner macropores pack together and in some cases interconnect to each other. Fig. 1e and Fig. 1f reveal that the baculiform macroporous structures are almost three-dimensionally uniform and are interconnected from surface to interior, which is due to a suitable aspect ratio, flexibility of the bacteria cells and proper assembly of the cells. For sample C, the large aspect ratio and soft features of filar fungi cells make it hard to maintain the original shape after the titanium precursor immission and worm-like macropores with a wide range of pore sizes are formed.

As it is known, cell walls contain some functional groups, such as amino groups, hydroxyl groups and carboxylic groups. They may interact with the metal precursor, anchoring the precursor molecules to the surface of the cells where aggregation and coating may easily occur.[25] However, direct filling of the spaces between macrotemplates without functional groups, *i.e.* polystyrene spheres, could also yield organized frameworks; a more detailed study of the mechanism of this cell-assembly method is underway. Since the mesostructure components are introduced after the formation of the macrotemplate and the two macro- and mesotemplates do not interfere, the macroporous and mesoporous structures, with pores of different shapes and sizes, can be modulated independently.

The typical mesoporous structures of the macro-mesoporous titania are verified by a transmission electron microscopy (TEM) image, N_2 adsorption–desorption isotherms and the corresponding pore-size distribution curve for sample B in

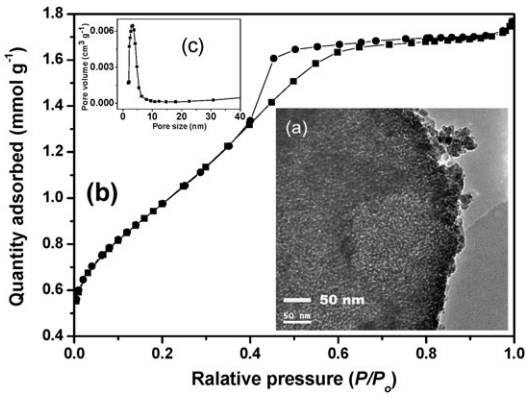

Fig. 2 TEM image (a), N_2 adsorption–desorption isotherms (b) and the corresponding pore-size distribution curve (c) of the macro-mesoporous titania sample B.

Fig. 2. The TEM image also reveals the presence of a disordered worm-like mesoporous structure formed by the agglomeration of titania nanoparticles. Fig. 2c conforms a narrow pore-size distribution range with a maximum at 3.1 nm, whilst the Brunauer–Emmett–Teller (BET) surface area is 96 m^2 g^{-1}. The X-ray diffraction patterns (ESI†) of the macro-mesoporous titania and the mesoporous titania without using cells as macrotemplates are both consistent with the standard data for anatase phase titania (JCPDS No. 21-1272). There is no significant change of the peak intensities and width after using the macrotemplate, which indicates that the formation of the macroporous structure does not change the crystallinity and the crystallite size (*ca.* 10 nm, see ESI†) of titania.

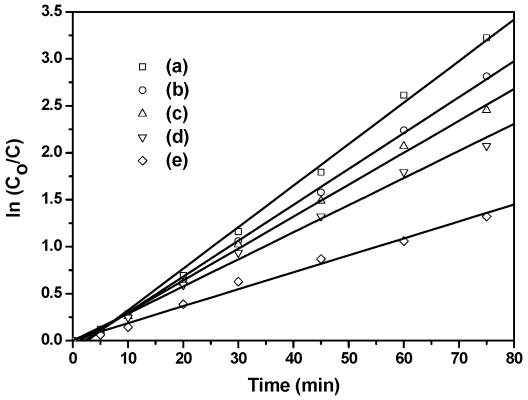

Fig. 3 $\ln(C_0/C)$ as a function of UV irradiation time with different TiO_2 photocatalysts: (a) nanoparticle titania, (b) sample B, (c) sample A, (d) sample C, (e) mesoporous titania.

The photocatalytic performance of the macro-mesoporous titania was evaluated by degrading methylene blue (MB) under UV irradiation (ESI†) in comparison with the mesoporous titania without using cells assembled as macro-templates and the anatase nanoparticles with similar particle size (*ca.* 10 nm)[26] (Fig. 3). Sample B showed higher photocatalytic activity with an apparent rate constant (k) of 0.03821 min^{-1}, compared to 0.03401 min^{-1} for sample A, and 0.02886 min^{-1} for sample C. The k value of mesoporous titania decreased to 0.01803 min^{-1}. By keeping the crystallite phase, size and mesoporous morphology for all the tested samples almost the same, we were able to conclude that the fundamental reason behind the difference in photocatalytic performance is purely down to the macroporous morphology. The presence of a macroporous structure in hierarchical macro-mesoporous titania enhances the photocatalytic activity, which is also in agreement with the theoretical studies reporting that these structures permit facile fluid transport and greatly increase the catalytic efficiency.[27] Therefore, we believe that an optimal catalyst should combine large pores (enabling high substance flow rates) with smaller pores (ensuring high substrate–substance contact) in a connected network.[28] Besides, hierarchical macro-mesoporous titania are comparable to nanoparticles (k = 0.0442 min^{-1}) in terms of their photocatalytic properties, but at the same time they retain their structures in liquid phase. Thus, they can easily be collected and reused proving that they are more economical and convenient to apply in industrial applications.[29]

In conclusion, the procedure of assembling cells as macroporous templates is shown to provide a facile bioinspired method for the synthesis of hierarchical macro-mesoporous titania with tunable macroporous morphology and enhanced photocatalytic activity. This is also a simple and facile technique that can be used to prepare many types of metal oxide porous materials with good control over the pore size and morphology.

We gratefully acknowledge the financial support of the National Basic Research Program of China (2009CB623502), National Natural Science Foundation of China (20573059, 20777039) and International S&T Cooperation Program of China (2007DFA90720). We would also like to thank Mr Zefang Wang and Ms Yongxin Jin for the cell cultures and valuable discussions. Our deepest gratitude goes to Dr Cafer T. Yavuz and Dr Yifeng Shi for their help in writing and in-depth discussions on the mechanism.

Notes and references

1 M. E. Davis, *Nature*, 2002, **417**, 813; Z. Y. Yuan and B. L. Su, *J. Mater. Chem.*, 2006, **16**, 663.
2 A. Stein, F. Li and N. R. Denny, *Chem. Mater.*, 2008, **20**, 649; K. Nakanishi and N. Tanaka, *Acc. Chem. Res.*, 2007, **40**, 863.
3 E. S. Toberer and R. Seshadri, *Adv. Mater.*, 2005, **17**, 2244; F. Iskandar, A. B. D. Nandiyanto, K. M. Yun, C. J. Hogan, K. Okuyama and P. Biswas, *Adv. Mater.*, 2007, **19**, 1408.
4 Z. Y. Yuan, A. Vantomme, A. Leonard and B. L. Su, *Chem. Commun.*, 2003, **13**, 1558.
5 T. Amatani, K. Nakanishi, K. Hirao and T. Kodaira, *Chem. Mater.*, 2005, **17**, 2114.
6 A. Collins, D. Carriazo, S. A. Davis and S. Mann, *Chem. Commun.*, 2004, **5**, 568.
7 Z. Y. Wang and A. Stein, *Chem. Mater.*, 2008, **20**, 1029.
8 D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
9 C. Li and L. M. Qi, *Angew. Chem., Int. Ed.*, 2008, **47**, 2388; H. Maekawa, J. Esquena, S. Bishop, C. Solans and B. F. Chmelka, *Adv. Mater.*, 2003, **15**, 591.
10 G. J. Lee and S. I. Pyun, *Carbon*, 2005, **43**, 1804.
11 H. F. Zhang, I. Hussain, M. Brust and A. I. Cooper, *Chem. Commun.*, 2006, **24**, 2539.
12 W. Yue, A. N. Kulak and F. C. Meldrum, *J. Mater. Chem.*, 2006, **16**, 408.
13 D. Y. Zhao, P. D. Yang, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 1174.
14 M. S. Gordon, *Animal Physiology: Principles and Adaptation*, Macmillan, New York, 3rd edn, 1997.
15 K. R. Stern, S. Jansky and J. E. Bidlack, *Introductory Plant Biology*, McGraw-Hill, New York, 9th edn, 2003.
16 E. G. Vrieling, T. P. M. Beelen, R. A. van Santen and W. W. C. Gieskes, *J. Biotechnol.*, 1999, **70**, 39.
17 A. G. Dong, Y. J. Wang, Y. Tang, N. Ren, Y. H. Zhang, J. H. Yue and Z. Gao, *Adv. Mater.*, 2002, **14**, 926.
18 J. Aizenberg, D. A. Muller, J. L. Grazul and D. R. Hamann, *Science*, 2003, **299**, 1205.
19 S. A. Davis, S. L. Burkett, N. H. Mendelson and S. Mann, *Nature*, 1997, **385**, 420.
20 D. Y. Zhang and L. M. Qi, *Chem. Commun.*, 2005, **21**, 2735.
21 E. Culverwell, S. C. Wimbush and S. R. Hall, *Chem. Commun.*, 2008, **9**, 1055.
22 A. Bruce, J. Alexander, L. Julian, R. Martin, R. Keith and W. Peter, *Molecular Biology of the Cell*, Garland Science, New York and London, 2002.
23 C. Sanchez, H. Arribart and M. M. G. Guille, *Nat. Mater.*, 2005, **4**, 277.
24 F. M. Morel, R. F. Baker and H. Wayland, *J. Cell Biol.*, 1971, **48**, 91.
25 B. Bohme, T. Vandenbos, D. P. Cerretti, L. S. Park, U. Holtrich, H. RubsamenWaigmann and K. Strebhardt, *J. Biol. Chem.*, 1996, **271**, 24747.
26 L. D. Li, X. H. Sun, Y. L. Yang, N. J. Guan and F. X. Zhang, *Chem.–Asian J.*, 2006, **1**, 664.
27 T. Dogu, *Ind. Eng. Chem. Res.*, 1998, **37**, 2158.
28 J. G. Yu, Y. R. Su and B. Cheng, *Adv. Funct. Mater.*, 2007, **17**, 1984.
29 D. Beydoun, R. Amal, G. K. C. Low and S. McEvoy, *J. Phys. Chem. B*, 2000, **104**, 4387.

