Surfactant-assisted synthesis of unprecedented hierarchical meso-macrostructured zirconia

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A surfactant-assisted one-step synthesis route was developed, leading to the formation of a very high surface area (600 m² g⁻¹) of zirconia and unprecedented hierarchical meso-macroporous structure with wormhole-like mesoporous walls and a novel, uniform assembly of macropores ranging in size from 300 to 500 nm.

The fabrication of hierarchically-ordered porous structures at multiple scales has recently attracted considerable attention for both fundamental and practical reasons.[1,2] Mesoporous oxide materials with macroporous structures are of much interest as potential catalysts and sorbents, partly because the textural mesopores and intrinsic interconnected pore systems of macrostructures should be able to efficiently transport guest species to framework binding sites. The combination of surfactant templating techniques[3] and colloidal crystal templating methods[4] allows the construction of hierarchically bimodal mesoporous-macroporous silicas.[5] Sponge-like silica membranes with three-dimensional meso-macrostructures were synthesised from an electrolyte phase of block copolymer/silica systems, though inorganic salt crystals inevitably grew along with the silica membrane.[6] Antonelli[7] reported the synthesis of macro-mesoporous niobium oxide by means of a NaCl-promoted vesicle templating method using a niobium ethoxide/amine gel. In this communication, we describe a simple method to synthesise a novel hierarchical structure of meso-macroporous zirconia in one step using a single surfactant. This method does not require polymeric spheres to generate the macropore structure nor does salt need to be added to form templatable vesicles.

Zirconia is an important functional material. Much research has focused on the synthesis of mesoporous zirconia by using a surfactant, such as cetyltrimethylammonium bromide (CTMABr), as the structure-directing template agent.[8] However, the mesoporous zirconias that have been reported have typically yielded macroscaled particles of fairly random shape. The mesoporous zirconia synthesised in this work exhibits an unusual morphology of macroporous structure.† The particles have a size of tens of micrometers with one flat but dense layer with a smooth surface (Fig. 1). Above this layer, a regular array of macropores occurs. In size, the macropores range from 300 to 500 nm. The hollow macrochannels are practically parallel to each other and perpendicular to the flat dense layer of the monolithic particles. A view of the monolithic particles' profiles shows that these macrochannels extend throughout almost the whole particle. Such a macroporous structure is unprecedented and quite different from those previously reported, including the structures of vesicle-templated and latex sphere-templated macroporous oxide materials.[4,7] The particles containing such a macrostructure have a good yield of over 60%, which is estimated by SEM observations. A TEM image of a cross-sectional zirconia specimen also reveals that the macroporous framework is composed of accessible mesopores with a disordered wormhole-like array (Fig. 1e).

Fig. 2 shows the X-ray diffraction (XRD) patterns of the synthesized meso-macrostructured zirconia. The presence of a single broad diffraction peak in the low-angle range is indicative of a disordered mesostructure with no discernible long-range order in the mesopore arrangement — this is consistent with the TEM image. No significant diffraction in the wide-angle range except a broad feature in the 2θ range of 20–40° was observed, which indicates that the zirconia frameworks possess amorphous walls.

Representative nitrogen adsorption–desorption isotherms and the corresponding pore size distributions are shown in Fig. 3. A strong uptake of N_2 due to capillary condensation occurs in a relative pressure (P/P_0) range of 0.14–0.40 and reaches a plateau at P/P_0 of 0.80. This kind of isotherm indicates that the final materials belong to the mesoporous family. The pore size
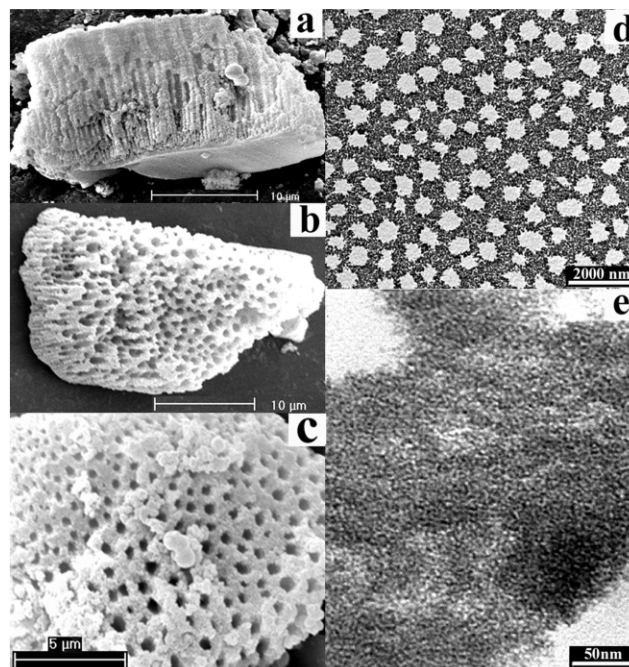

Fig. 1 (a–c) SEM images of the synthesised meso-macroporous zirconia particles; (d) low-magnification TEM image of a cross-section of meso-macrostructured zirconia along the macrochannel direction; (e) high-magnification TEM image of the macroporous structure, showing that the macrostructure framework is composed of wormhole-like mesopores.
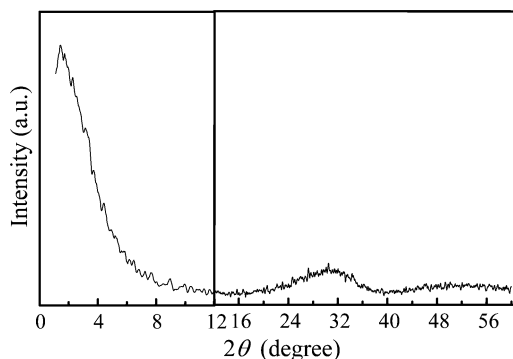

Fig. 2 XRD pattern of the synthesised meso-macrostructured zirconia.
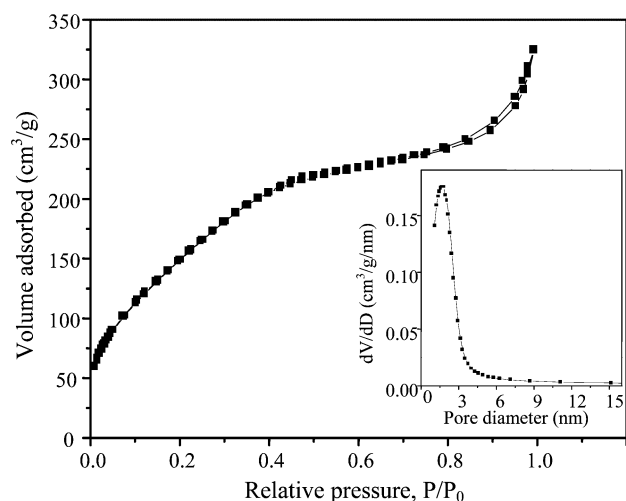
Fig. 3 N_2 adsorption–desorption isotherms of the meso-macrostructured zircona. The corresponding pore size distribution curve (insert) is obtained from the adsorption branch of the isotherm using the BJH (Barrett–Joyner–Halenda) method.

Fig. 4 Schematic representation of meso-macrostructure formation.

distribution curve obtained by the BJH method using the adsorption branch of the isotherm is centered at about 1.8 nm. The macropores, confirmed by SEM and TEM images, are too large to be measured by N_2 adsorption analysis. The BET surface area is 600 m^2 g^{-1} with a pore volume of 0.510 cm^3 g^{-1}.

The synthesis of such a well-structured zirconia with mesoporous walls separating the parallel macrochannels can be performed in a wide range of experimental conditions, having a good reproducibility with a yield of 40 to 90%. Only one surfactant of CTMABr is needed to direct the production of meso-macrostructure. The variation of the molar ratio of surfactant to zirconium from 0.5 to 10, or the ratio of water to zirconium from 20 to 300 did not affect the formation of the meso-macrostructure, though the surface area of the production could vary within the range of 518 to 670 m^2 g^{-1} while the mesopore size could vary within the range of 1.8 to 2.5 nm. The precipitation rate is known to be very fast when the ratio between the concentration of water and zirconium is higher than 4.[9] Thus, hydrolysis and condensation occurred as soon as $Zr(OC_3H_7)_4$ was added to the micellar solution of surfactant, and the primary particles of mesostructured surfactant/zirconia composite were formed with a large number of surface hydroxyl groups due to incomplete condensation. Meanwhile, the surfactant molecules in the solution can be adsorbed onto the surface of primary particles to form a bilayer structure at the interface. The further aggregation of these primary hybrid particles and surfactant molecules could result in the vesiculation of bilayer structures and the formation of supermicelles by the coalescence of multiple micelles and the inter-aggregate interactions.[10–12] This cooperative self-assembly process would lead to the production of an ordered array of macrochannels (Fig. 4). The removal of the surfactant species then gives a hollow macroporous structure with mesoporous walls. Of course, the possibility of emulsion templating in the formation of macroporous structure cannot be fully excluded, though it is being increasingly questioned,[13] and surfactant–inorganic structures with a vesicular architecture have been well-documented.[10–13] Some complementary studies on understanding the formation mechanism and the regulation of the orderliness of mesopore-composed macroporous walls are thus being carried out.

The meso-macrostructured zirconia network with open and accessible pores can be well-preserved after calcination at 300 °C, indicating the high thermal stability. The macropore structure can even be preserved after calcination at 500 °C, though the mesostructure has been damaged due to sintering, which is revealed by XRD, SEM and N_2 adsorption analysis.

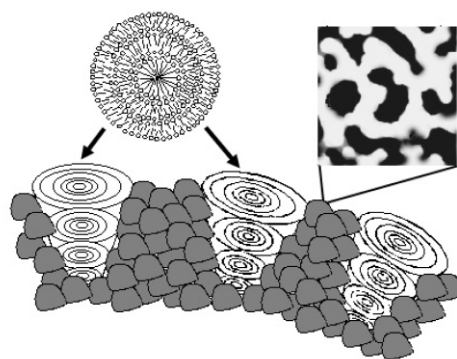This hierarchical meso-macrostructured material should be significant for its applications in catalysis and separation technology. It can also be employed in the design of inorganic membranes which may be applied in various domains such as process filtration, cell culture, and biomolecule separation and storage. Additionally, it can be used as templating material for the inverted synthesis of new advanced materials such as nanotubes and nanowires. Functionalisation of this material by chemical modification of the internal pore surface may lead to more practical applications.

Notes and references

1 I. Soten and G. A. Ozin, *Curr. Opin. Colloid Interface Sci.*, 1999, **4**, 325.
2 P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides and G. D. Stucky, *Science*, 1998, **282**, 2244.
3 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; D. Zhao, J. Feng, Q. Huo, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
4 B. T. Holland, C. F. Blanford and A. Stein, *Science*, 1998, **281**, 538; S. H. Park and Y. Xia, *Adv. Mater.*, 1998, **10**, 1045.
5 M. Antonietti, B. Berton, C. Göltner and H. Hentze, *Adv. Mater.*, 1998, **10**, 154; R. A. Caruso and M. Antonietti, *Adv. Funct. Mater.*, 2002, **12**, 307; B. Lebeau, C. E. Fowler, S. Mann, C. Farcet, B. Charleux and C. Sanchez, *J. Mater. Chem.*, 2000, **10**, 2103.
6 D. Zhao, P. Yang, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 1174.
7 D. M. Antonelli, *Microporous Mesoporous Mater.*, 1999, **33**, 209.
8 B. T. Holland, C. F. Blanford, T. Do and A. Stein, *Chem. Mater.*, 1999, **11**, 795; U. Ciesla, M. Fröbe, G. Stucky and F. Schüth, *Chem. Mater.*, 1999, **11**, 227.
9 L. Davies, L. Daza and P. Grange, *J. Mater. Sci.*, 1995, **30**, 5087.
10 S. Oliver, A. Kuperman, N. Coombs, A. Lough and G. A. Ozin, *Nature*, 1995, **378**, 47.
11 P. T. Tanev and T. J. Pinnavata, *Science*, 1996, **271**, 1267.
12 Z. Y. Yuan, J. Q. Liu, L. M. Peng and B. L. Su, *Langmuir*, 2002, **18**, 2450.
13 A. Lind, B. Spliethoff and M. Lindén, *Chem. Mater.*, 2003, **15**, 813.