LETTER

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One-pot synthesis of a high-surface-area zirconium oxide material with hierarchically three-length-scaled pore structure

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A new type of hierarchically three-length-scaled porous zirconium oxide material with high BET surface area of > 900 m^2 g^{-1}, having a uniform macroporous (300–500 nm) structure of a supermicroporous (1.5 nm) nanoparticle (~25 nm in size) assembly with irregular mesovoids (20–60 nm) in the macroporous walls, was prepared by a simple one-pot method in the presence of alkyltrimethylammonium surfactant, which should be significant for practical applications in multiple fields including catalysis and separation.

Materials with high and multi-scale porosity and high surface area play key roles in industrial processes, from catalysis and surface chemistry to gas storage, purification and separation. Various synthetic pathways, including exo-templating and endo-templating strategies, have been developed to create porous and high-surface-area inorganic materials.[1,2] Many metal oxides, such as ZrO_2,[3,4] TiO_2,[5,6] CeO_2,[7] and Al_2O_3,[8] have been synthesised, owing to their great potential applications in the field of catalysis. However, the design of high-surface-area materials with multi-scaled porous structures still remains an experimental challenge.

Zirconium oxide is of particular interest because of its ion exchange, redox, and acid-basic properties. Much effort has been devoted to the synthesis of mesoporous zirconia materials using supramolecular templating techniques with cationic quaternary ammonium surfactants,[3,9–13] anionic surfactants,[14–17] primary amines,[18–20] non-ionic surfactant[21] and block copolymers.[22] However, the surface areas of these previously reported mesoporous zirconias rarely exceed 700 m^2 g^{-1}.[3,9–22] Pacheco *et al.*[23] synthesised microporous zirconias using anionic (Niaproof 4) and nonionic (Tergitol 7) surfactants; their surface areas were only in the range of 100–250 m^2 g^{-1}. Antonelli[4] synthesised sulfated meso- and microporous zirconias by using chelating carboxylate surfactants; their surface areas were on the order of 400–650 m^2 g^{-1}.

Practical approaches require the preparation of mesoporous materials having hierarchical porous structures at different length scales in order to achieve highly organised functions.[24,25] Several groups have reported the preparation of macroporous materials with microporous or mesoporous walls by dual templating methods with the utilisation of colloidal polymer latex,[25–28] starch gel,[29] inorganic salts,[30] emulsions[31] or vesicles[32] as templates for creating the macropores. A simple method for the synthesis of hierarchical bimodal mesoporous-macroporous zirconias by a single surfactant templating method has also been developed recently; the surface area could reach 700 m^2 g^{-1}.[33,34] This method is quite facile without the need for polymeric spheres or vesicles to act as a template that generates the macroporous structure. On the other hand, a porous structure having three orders of length scale is of great interest for bulk chemical applications. Suzuki *et al.*[24] synthesised mesoporous silica foams with hierarchical trimodal pore structure (macrovoids and two kinds of mesopores ranging around 3 and 40 nm) by the self-assembly of surfactant micelles, silica nanoparticles and air bubbles. Sen *et al.*[35] prepared hierarchically micro-meso-macroporous silicas with ordering on three different scales in the presence of multiple templates of polystyrene latex spheres, triblock copolymers and co-surfactants (butanol or pentanol). In this letter, we report the synthesis of hierarchically porous zirconia materials with ordering on three different length scales by a simple one-pot method in the presence of a single surfactant (see Experimental) and extend their surface areas to over 900 m^2 g^{-1} This novel zirconium oxide material, due to its extremely high surface area and the hierarchically trimodal porous structure, can find new applications, such as a bioactive ceramic.

The synthesised zirconia particles are mainly tens of micrometers in size with a regular array of macropores, as shown in the SEM image of Fig. 1(a). The diameters of the macropores range from 300 to 500 nm. The macropores are uniformly distributed in the particles [Fig. 1(b)], similar to with those obtained previously for macroporous oxides of niobium[32] and zirconium.[33,34] The regularity of the macropores can be confirmed by the cross-sectional TEM image in Fig. 1(c). A careful observation shows that the macroporous walls are composed of nanoparticles of about 25 nm in size, and the small irregular voids ranging between 20 and 60 nm are the interparticle spaces resulting from the aggregation of these nanoparticles. These mesovoids are randomly distributed in the macroporous walls. The high-magnification TEM images also reveal that these nanoparticles are mesostructured with a disordered wormhole-like assembly of accessible meso-/micropores [Fig. 1(d)]. This kind of wormhole-like meso(micro)structure was previously observed in silica- and alumina-based mesostructured material synthesised by using non-ionic surfactants.[36]

Fig. 2 shows the X-ray diffraction patterns of the synthesised samples. The wide-angle diffraction only gives a broad feature in the 2θ range of 20–40°, which indicates that the zirconia frameworks possess amorphous walls. One single broad diffraction peak is present in the low-angle region, suggestive of the packing of regularly sized ZrO_2 nanoparticles, giving the mesovoids. This is consistent with the TEM analysis.

Fig. 3 shows the typical nitrogen adsorption-desorption isotherm of the synthesised material. The isotherm is of type IV, according to the IUPAC classification. A high BET (Brunauer–Emmet–Teller) surface area of 903 m^2 g^{-1} is obtained from this material with the total pore volume of 1.01 cm^3 g^{-1}. (Although the specific surface area determined by the BET method, based on the assumption of uniform monolayer-

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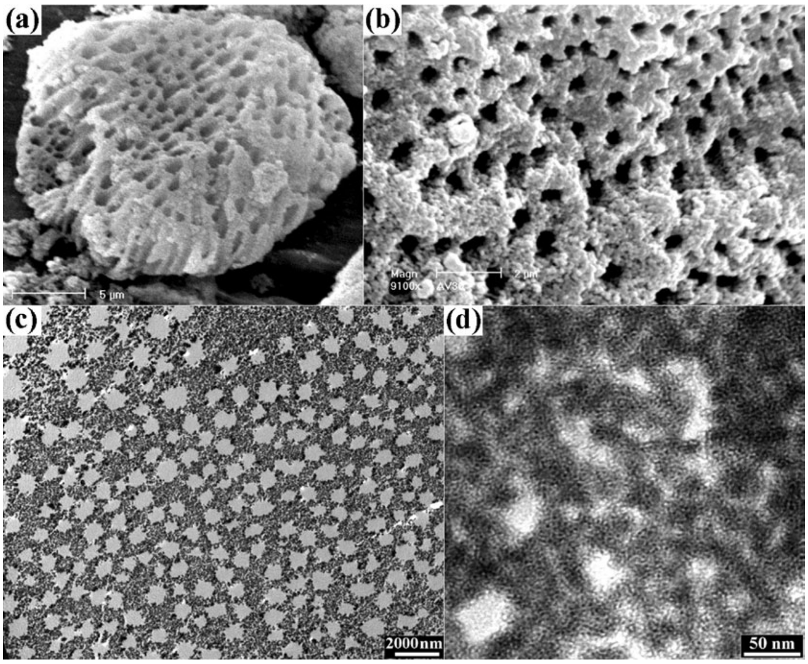

Fig. 1 (a, b) SEM images of the synthesised zirconia particles showing uniform macroporosity; (c) low-magnification TEM image of a cross-section of the synthesised zirconia showing the uniform macropore structure with mesovoids in the walls; (d) high-magnification TEM image of a region of the macropore walls, showing the assembly of zirconia nanoparticles into wormhole-like supermicropores with irregular mesovoids.

multilayer formation with the absence of micropores, may be slightly overestimated for hierarchical porous materials, we used the BET method here for the sake of simplicity. The BET surface area value presented here is still informative.) The adsorption isotherm exhibits a high uptake of N_2 at low relative pressure (P/P_0), indicating the presence of supermicropores with a pore size if the range of 1–2 nm (between micropore and mesopore size). The analysis of the pore size distribution by the Barret–Joyner–Halenda method from the adsorption branch of the isotherm reveals a narrow pore size distribution centred at 1.5 nm (Fig. 3). At relative pressures higher than 0.85, a strong increase in nitrogen adsorbed volume is observed, evident of an appreciable amount of secondary porosity, that is the large mesopores or the interparticle porosity. This secondary porosity can be attributed to the mesovoids observed in the macroporous walls. The macropores, confirmed by TEM and SEM images, are too large to be measured by N_2 adsorption analysis. Therefore, TEM and SEM observations and N_2 adsorption analysis reveal that the current material exhibits the trimodal pore structure of a micro-meso-macroporous system.

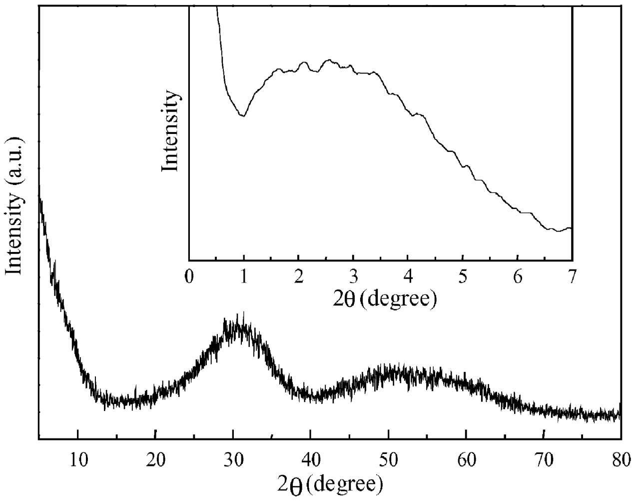

Fig. 2 XRD patterns of the synthesised zirconia material. Inset is the low-angle diffraction pattern.

This hierarchical structure is synthesised at a high concentration of surfactant CTMABr with a high surfactant-to-Zr ratio. It is known that the pore size of mesostructured zirconias will decrease with increasing surfactant concentration, and zirconias with a pore size of about 1.8 nm can be prepared at low surfactant concentration (*e.g.*, Surf : Zr ratio of 0.33).[34] Although the role of surfactant molecules in the creation of macroporous structures remains unclear, it is reasonable on the basis of previous[13,33,34] and present observations to believe that the supermicropores of the current zirconia are induced by surfactant molecules. Since the hydrolysis and precipitation rates of the zirconium alkoxide are very fast, nanometer-sized particles of supermicrostructured surfactant–zirconia composite with surface hydroxyl groups could form as soon as the Zr precursor is added to the surfactant micellar solution. The unconsumed surfactant molecules cover the nanoparticles of the supermicrostructured surfactant–zirconia composition due to the affinity between the hydroxyl groups of the nanoparticles and the hydrophilic heads of the surfactant molecules.[24] The presence of surfactant molecules surrounding the surface improves the size homogeneity and promotes the gentle assembly of the nanoparticles, driving the formation of the mesovoids (interparticle spaces) in the aggregation of the nanoparticles. Meanwhile, a large amount of propanol molecules are generated quickly by the hydrolysis and condensation of

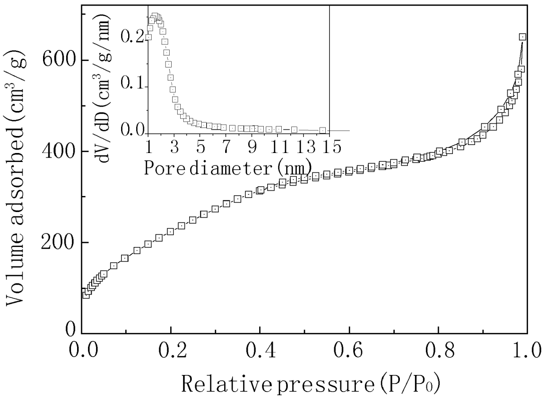

Fig. 3 N_2 adsorption-desorption isotherms of the synthesised zirconia and (inset) the corresponding BJH adsorption pore size distribution.

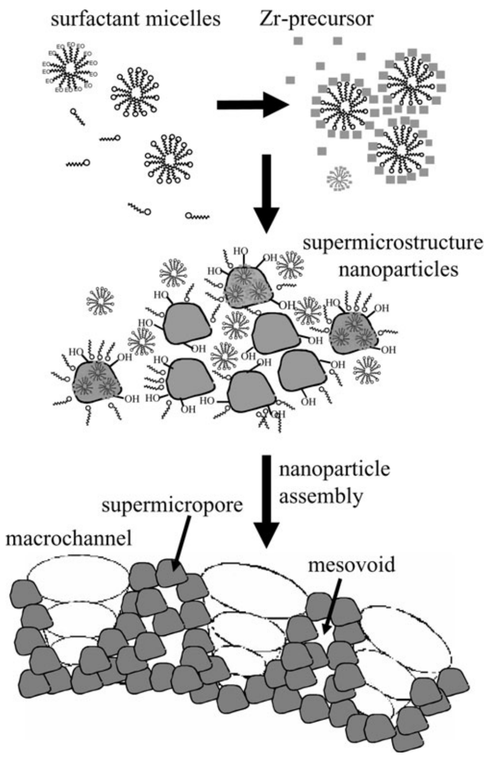

Fig. 4 Schematic representation for the formation of hierarchical supermicro-meso-macroporous zirconia.

zirconium propoxide, which might produce microphase-separated domains of ZrO_2 nanoparticles and water/alcohol channels which are the initiators of the macrochannels.[37,38] Thus, a hierarchical structure of uniform macrochannels with mesovoids in the walls of a supermicrostructured nanoparticle assembly would form during the synergistic packing of the surfactant–zirconia nanoparticles. The existence of a very high surface area should be compatible with this pore architecture of three-length-scaled ordering. The proposed mechanism for the formation of such a hierarchical trimodal pore structure of zirconia is illustrated in Fig. 4.

In conclusion, a hierarchically supermicro-meso-macroporous zirconium oxide with high surface area has been prepared for the first time by a simple one-pot synthetic pathway using only a single surfactant as the directing agent of supermicropores and mesovoids. The significant asset of the hierarchically three-length-scaled pore system and the exceptionally high surface area allow easy molecular diffusion to the reaction sites, especially in catalysis. Therefore, this novel material may find potential applications in multiple fields, such as catalysis, adsorption, separation, chemical sensors and solid oxide fuel cell electrode materials, as well as bioactive ceramics.

Experimental

In a typical preparation, a 15 wt % micellar solution of cetyltrimethylammonium bromide (CTMABr) was prepared by dissolving CTMABr in an aqueous acidic solution (pH = 2) at 40 °C under stirring for at least 3 h. An appropriate amount of zirconium propoxide [$Zr(OC_3H_7)_4$] was added dropwise into the above solution to give a surfactant : Zr molar ratio of 1.65. After further stirring for 1 h, the mixture was transferred into a Teflon-lined autoclave and heated at 60 °C for 2 days. The product was filtered by Soxhlet extraction over ethanol for at least 30 h in order to remove the surfactant species, and then dried at 60 °C in vacuum. No trace of a C–H stretch was observed in the infrared spectrum of the product, indicating a template-free material. Characterisation was performed by XRD (Philips PW 1820 with Cu-K_α radiation), N_2 adsorption analysis (Micrometrics Tristar 3000), SEM (Philips XL-20 at 15 keV) and TEM (Philips TECNAI-10 at 100 keV).

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References

1 F. Schüth, *Angew. Chem., Int. Ed.*, 2003, **42**, 3604.
2 T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633.
3 M. J. Hudson and J. A. Knowles, *J. Mater. Chem.*, 1996, **6**, 89.
4 D. M. Antonelli, *Adv. Mater.*, 1999, **11**, 487.
5 S. Cabrera, J. El Haskouri, A. Beltran-Porter, D. Beltran-Porter, M. D. Marcos and P. Amoros, *Solid State Sci.*, 2000, **2**, 513.
6 H. Yoshitake, T. Sugihara and T. Tatsumi, *Chem. Mater.*, 2002, **14**, 1023.
7 D. Terrible, A. Trovarelli, J. Llorca, C. de Leitenburg and G. Dolcetti, *J. Catal.*, 1998, **178**, 299.
8 T. Z. Ren, Z. Y. Yuan and B. L. Su, *Langmuir*, 2004, **20**, 1531.
9 U. Ciesla, S. Schacht, G. D. Stucky, K. K. Unger and F. Schüth, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 541.
10 U. Ciesla, M. Fröba, G. Stucky and F. Schüth, *Chem. Mater.*, 1999, **11**, 227.
11 J. S. Reddy and A. Sayari, *Catal. Lett.*, 1996, **38**, 219.
12 J. A. Knowles and M. J. Hudson, *J. Chem. Soc., Chem. Commun.*, 1995, 2083.
13 J. L. Blin, R. Flamant and B. L. Su, *Int. J. Inorg. Mater.*, 2001, **3**, 959.
14 G. Pacheco, E. Zhao, A. Garcia, A. Sklyarov and J. J. Fripiat, *Chem. Commun.*, 1997, 491.
15 G. Pacheco, E. Zhao, A. Garcia, A. Sklyarov and J. J. Fripiat, *J. Mater. Chem.*, 1998, **8**, 219.
16 M. S. Wong and J. Y. Ying, *Chem. Mater.*, 1998, **10**, 2067.
17 G. Larsen, E. Lotero, M. Nabity, L. M. Petkovic and D. S. Shobe, *J. Catal.*, 1996, **164**, 246.
18 N. Ulagappan, V. N. Raju and C. N. R. Rao, *Chem. Commun.*, 1996, 2243.
19 Y.-Y. Huang, T. J. McCarthy and W. M. H. Sachtler, *Appl. Catal. A*, 1996, **148**, 135.
20 D. J. McIntosh and R. A. Kydd, *Microporous Mesoporous Mater.*, 2000, **37**, 281.
21 V. Idakiev, L. Ilieva, D. Andreeva, J. L. Blin, L. Gigot and B. L. Su, *Appl. Catal. A*, 2003, **243**, 25.
22 (*a*) P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature (London)*, 1998, **396**, 152; (*b*) P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 2813.
23 G. Pacheco, E. Zhao, E. D. Valdes, A. Garcia and J. J. Fripiat, *Microporous Mesoporous Mater.*, 1999, **32**, 175.
24 K. Suzuki, K. Ikari and H. Imai, *J. Mater. Chem.*, 2003, **13**, 1812.
25 P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides and G. D. Stucky, *Science*, 1998, **282**, 2244.
26 B. Lebeau, C. E. Fowler, S. Mann, C. Farcet, B. Charleux and C. Sanchez, *J. Mater. Chem.*, 2000, **10**, 2105.
27 M. Antonietti, B. Berton, C. Göltner and H. Hentze, *Adv. Mater.*, 1998, **10**, 154.
28 B. T. Holland, L. Abrams and A. Stein, *J. Am. Chem. Soc.*, 1999, **121**, 4308.
29 B. J. Zhang, S. A. Davis and S. Mann, *Chem. Mater.*, 2002, **14**, 1369.
30 D. Zhao, P. Yang, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 1174.
31 Z. Y. Yuan, T. Z. Ren and B. L. Su, *Adv. Mater.*, 2003, **15**, 1462.
32 D. M. Antonelli, *Microporous Mesoporous Mater.*, 1999, **33**, 209.
33 J. L. Blin, A. Léonard, Z. Y. Yuan, L. Gigot, A. Vantomme, A. K. Cheetham and B. L. Su, *Angew. Chem., Int. Ed.*, 2003, **42**, 2872.
34 Z. Y. Yuan, A. Vantomme, A. Léonard and B. L. Su, *Chem. Commun.*, 2003, 1558.
35 T. Sen, G. J. T. Tiddy, J. L. Casci and M. W. Anderson, *Angew. Chem., Int. Ed.*, 2003, **42**, 4649.
36 S. A. Bagshaw, E. Prouzet and T. J. Pinnavia, *Science*, 1995, **269**, 1242.
37 A. Collins, D. Carriazo, S. A. Davis and S. Mann, *Chem. Commun.*, 2004, 568.
38 T. Z. Ren, Z. Y. Yuan and B. L. Su, *Chem. Phys. Lett.*, 2004, **388**, 48.