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Synthesis of large-pore phenylene-bridged mesoporous organosilica using triblock copolymer surfactant†

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Periodic mesoporous benzene-silicas with large pores of 6.0 to 7.4 nm in diameter are synthesized using triblock copolymer as a template. These mesoporous materials have a well-defined hexagonal rod morphology and high thermal stability up to 823 K in air.

A new class of organic-functionalized mesoporous material synthesized from a bridged organosilica precursor $(R'O)_3Si–R–Si(OR')_3$ has recently been reported.[1–5] The new class of materials contains bridging organics as an integral component of the silicate framework, and extensive research has been conducted toward extending the variety of bridging organics[5] and potential applications, including catalysts,[6] templates for nano-cluster synthesis[7] and selective adsorbents.[8] Currently, research is focused on expanding the pore size of these organic-bridged mesoporous materials[9–13] for the immobilization and encapsulation of large molecules. Large-pore mesoporous organosilicas have been successfully synthesized using triblock copolymer as a structural directing agent instead of alkyltrimethylammonium surfactants. To the best of the authors' knowledge, ethane ($–CH_2–CH_2–$) bridged mesoporous materials are the only materials that have been synthesized using a non-ionic block copolymer. However, the functionality of the ethane group is limited. By comparison, phenylene ($–C_6H_4–$) bridged mesoporous materials are highly functional and suitable for further chemical modification, and have the great advantage of the formation of molecular-scale periodicity in the pore walls.[14] Sulfuric acid functionalized phenylene bridged mesoporous materials in particular have potential applications as solid acid catalysts and electrolytes for fuel cells.[14,15] This report presents the first synthesis of large-pore phenylene-bridged mesoporous materials with well-defined external morphology using a non-ionic surfactant.

Phenylene-bridged mesoporous materials were synthesized from a 1,4-bis(triethoxysilyl)benzene (BTEB) precursor in the presence of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer template (Aldrich, M_{av} = 5800, P123) under acidic conditions. In a typical synthesis, 0.99 g of P123 was dissolved in 36 ml of distilled water and added to 200 μl of hydrochloric acid (36 wt%). BTEB (1.01 g) was added to the solution and then stirred for 1 h at 273 K. The mixture was then heated at 312 K for 20 h with stirring, and followed by aging in a closed vessel at 373 K for 24 h. The white precipitate was recovered by filtration and washed with water repeatedly to yield mesoporous material. The molar composition of the reaction mixture was $BTEB : P123 : HCl : H_2O = 1 : 0.034 : 0.48 : 400$. To improve structural ordering, the material was subsequently treated by heating a synthesized sample dispersed in water at 373 K for 72 h.[16,17] The surfactant was removed by solvent extraction with ethanol followed by calcination at 523 K in air.

XRD analysis (Fig. 1) of the products with and without post-synthesis treatment revealed well-defined patterns with three clear peaks in the low-angle region ($2\theta < 5$), which are assigned to (10), (11) and (20) with two-dimensional hexagonal symmetry. The unit cell dimensions of the hexagonal lattice ($a = 2/\sqrt{3} \times d_{10}$) are 10.4 and 10.7 nm. The post-treated sample (Fig. 1b) exhibits a better-defined pattern, indicating the effectiveness of this post-synthesis treatment for improving the structural ordering. This is the first organic hybrid mesoporous material prepared using a non-ionic surfactant that exhibits such a highly ordered mesostructure. The XRD pattern on the post-treated sample includes a very broad peak centered around 2θ = 12° with a d-spacing of 0.8 nm, suggesting periodicity in the pore walls as a result of organization of phenylene-silica moieties. However, the degree of periodicity is still significantly lower than that of phenylene-bridged materials prepared using an alkyltrimethyl-ammonium surfactant under basic conditions.[14]

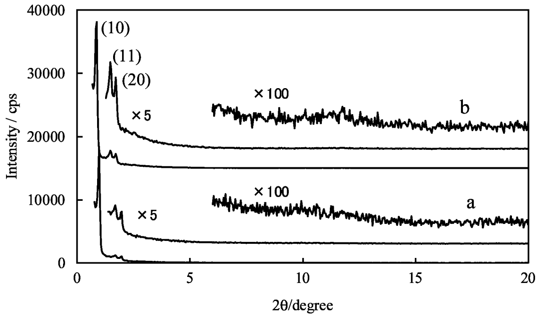

Fig. 1 XRD patterns of (a) phenylene-bridged mesoporous material (surfactant free) and (b) post-synthesis treated material (surfactant free).

Nitrogen adsorption isotherms (Fig. 2) reveal a steep increase in adsorption at P/P_0 = 0.60–0.75 due to capillary condensation of nitrogen in the mesopores, indicating a highly mesopore structure. The BJH pore diameter, BET surface area, and pore volume were calculated from the adsorption isotherms (Table

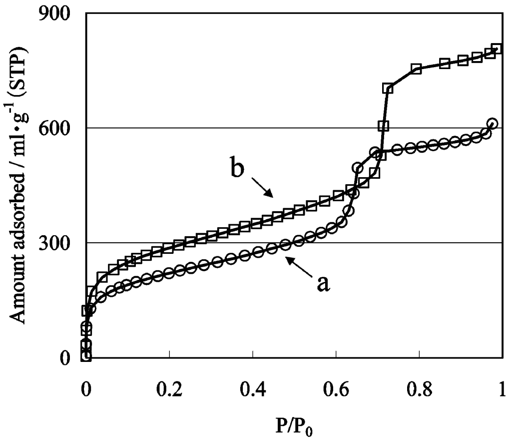

Fig. 2 Nitrogen adsorption isotherms of (a) phenylene-bridged mesoporous material (surfactant free) and (b) post-synthesis treated material (surfactant free).

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† Electronic supplementary information (ESI) available: Fig. S1–3, ^{29}Si MAS NMR, ^{13}C MAS NMR spectra and TGA for the phenylene bridged mesoporous material with post-synthesis treatment. See http://www.rsc.org/suppdata/cc/b2/b207825b/

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Table 1 Pore sizes, surface areas and pore volumes of phenylene-bridged mesoporous materials

Post-synthesis treatment	Pore diameter (BJH)/nm	BET specific surface area/ $m^2 g^{-1}$	Pore volume	
			Micropore/ ml g^{-1}	Mesopore/ ml g^{-1}
None	6.0	792	0.08	0.69
373 K, 72 h	7.4	1029	0.16	0.93

1). The larger pore size and pore volume exhibited by the post-treated sample is the typical effect of post-synthesis treatment and is also observed in MCM-41 materials. The pore walls include slight microporosity due to penetration of the polyethylene oxide chains of the triblock copolymer template into the hydrophilic pore walls during synthesis. This microporosity is typical for mesoporous silica SBA-15 prepared using triblock copolymer.[18]

FE-SEM[19] (Fig. 3a) reveals the product to consist of rod-like elements with diameter of 0.1–1 μm and length of 2–20 μm. The enlarged image (Fig. 3b) shows that the rods have a hexagonal cross-section. In addition, transmission electron microscopy (TEM[20]) (Fig. 3c) reveals that the channels run parallel with the rods. These results indicate that the sample has a highly ordered mesostructure with a single-crystal morphology. The external morphologies of the post-treated and as-synthesized sample appear almost identical. We have only a few examples of the formation of a single-crystal morphology for mesoporous materials prepared using triblock copolymer.[21–23] The pore-wall thickness, calculated by subtracting the pore diameter from the unit cell constant, is 3.3 nm, which is in agreement with the value estimated from the TEM image (Fig. 3c). Thick walls such as these are also observed for mesoporous silica SBA-15 prepared using triblock copolymer.

The ^{29}Si MAS-NMR spectrum of the present phenylene-bridged mesoporous material includes three signals at −61.5, −70.6 and −78.0 ppm, assigned to Si species covalently bonded to carbon atoms of T^1 [$\mathit{Si}C(OH)_2(OSi)$], T^2 [$\mathit{Si}C(OH)(OSi)_2$] and T^3 [$\mathit{Si}C(OSi)_3$], respectively, confirming the full framework linkage of these organic groups. The absence of SiO_4 species such as Q^3 [$\mathit{Si}(OH)(OSi)_3$] and Q^4 [$\mathit{Si}(OSi)_4$], which produce signals between −90 and −120 ppm, confirms that no carbon–silicon bond cleavage of the BTEB molecules occurred during synthesis. The T^3/T^2 peak intensity ratio is about 0.65, which is smaller than that observed for mesoporous benzene-silica prepared using alkyltrimethylammonium,[5] but similar to the Q^4/Q^3 ratio of mesoporous silica SBA-15. The ^{13}C NMR spectrum includes a signal at 133.1 ppm with side bands due to phenylene carbon. The combined results of NMR analysis therefore indicate that the framework is a covalently bonded network of $O_{1.5}Si–C_6H_4–SiO_{1.5}$ units. Furthermore, this mesoporous benzene silica has extremely high thermal stability. In thermogravimetric analysis, the walls retained the benzene groups up to 823 K, which is about 50 K higher than that of mesoporous benzene-silica prepared using alkyltrimethylammonium.[14]

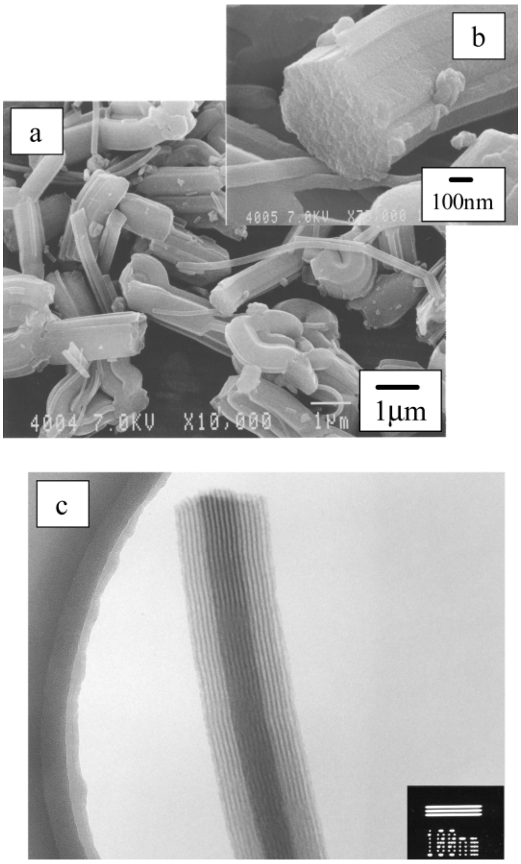

Fig. 3 FE-SEM (a,b) and TEM (c) images of phenylene-bridged mesoporous material with post-synthesis treatment (surfactant free).

In summary, phenylene-bridged mesoporous organosilica with large pore size was synthesized using triblock copolymer. The mesoporous materials have a well-defined external morphology consisting of hexagonal rods, and high thermal stability. The materials are expected to be used as host materials for enzyme fixation and optical applications.

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