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Bacterial templating of zeolite fibres with hierarchical structure

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Ordered macroporous zeolite fibres are prepared from the infiltration of swollen bacterial supercellular threads with as-synthesized silicalite nanoparticles.

There is considerable interest in the production of inorganic materials containing frameworks with well defined pore networks. In general, strategies for synthesising these materials rely on the use of templates, the size and nature of which dictate the pore dimensions and architecture. Microporous (nanoporous) materials, such as zeolites, are prepared using molecular templates[1] whilst mesoporous solids, for example MCM-41 silicas, are structured by supramolecular aggregates.[2] We have previously demonstrated how supercellular templates can be used to extend the length scale of 3D inorganic patterning into the micrometre dimension.[3,4] For example, we were able to prepare MCM-41 silica-based fibres containing hierarchically organized pore structures at the meso- and micro-metre scale.[3] Subsequently, various other strategies, most notably the use of colloidal crystal templates,[5] have been employed to prepare ordered macroporous inorganic oxide structures by infiltration of the void spaces with alkoxide or inorganic precursors.[6] Both meso-[6] and micro-scopic[7] pores have been introduced into the macroporous architecture using a dual templating procedure.

Here, we report the synthesis and characterization of hierarchically structured zeolite fibres containing ordered pores at the nano- and micro-scopic length scale. In contrast to our previous work, in which we used *in situ* precipitation from a MCM-41 synthesis mixture,[3] here we use a stable aqueous dispersion of preformed zeolite nanoparticles as building blocks for the infiltration of a bacterial supercellular thread by reversible swelling. Silicalite nanoparticles are aggregated specifically within the organized micro-architecture, which consists of long multicellular filaments (0.5 μm in diameter) aligned parallel to the thread axis and arranged in a pseudo-hexagonally packed configuration.[8] Subsequent thermal decomposition of the bacterial template produces an intact zeolite fibre with ordered macroporous channels lined by 100-nm wide walls of coalesced silicalite nanoparticles. Because each nanoparticle consists of a periodic structure of intersecting nanoporous channels, the porous architecture is hierarchically ordered.

TPA-silicalite-1 nanoparticles were synthesized from clear solution by reflux of an aqueous solution containing tetraethylorthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) followed by repeated centrifugation and washing.† The resulting colloidal suspension was stable in deionized water at pH values between 10 and 11. Dynamic light scattering gave a mean hydrodynamic radius of 57 nm for the as-synthesized TPA-silicalite. This was in close agreement with transmission electron microscopy (TEM) which showed that the sample consisted of discrete nanoparticles with irregular surface texture and narrow particle size distribution (47 ± 10 nm) (Fig. 1). Significantly, the mean particle size was lower than that previously reported (95 nm),[9] possibly due to the reduced temperature (80 *cf.* 98 °C) and water content used in our synthesis mixture. High magnification TEM images suggested that the individual nanoparticles were constructed from aggregates of smaller primary clusters, and this was consistent with TEM analysis of the early stages of crystallization, which showed a predominance of 10 nm-size silicalite particles in samples extracted 24 h after the start of the reaction.

The crystallinity of the particles was confirmed by electron diffraction, XRD and FTIR spectroscopy. Powder X-ray diffraction (PXRD) patterns of the as-synthesized-TPA-silicalite-1 samples showed an orthorhombic lattice with broadened reflections and *d* spacings (d_{hkl} = 1.13 nm {011}, 1.00 nm {200}, 0.385 nm {501}, 0.373 nm {033}, 0.366 nm {133}) consistent with the PDF data base.[10] Corresponding FTIR spectra showed typical Si–O–Si framework bands, including the characteristic double ring vibration at *ca.* 550 cm^{-1}.[11] The sample also showed a shoulder at 960 cm^{-1} and bands at 2980 and 1380–1470 cm^{-1}, attributable to Q^3 Si–OH groups and TPA^+, respectively.[11,12] Thermogravimetric analysis gave a total weight loss of 20% that included the desorption of water and TPAOH (< 260 °C). The weight loss between 260 and 600 °C was 12% owing to decomposition of occluded TPA–OSi and loss of TPA^+ framework counter ions. This value was consistent with a theoretical value of 11.7 wt% for four TPA^+ cations per unit cell.

Bacterial threads‡ were swollen without loss of structural integrity in silicalite sols and air-dried to produce composite fibres consisting of a semi-ordered matrix of multicellular filaments embedded in a continuous framework of zeolite nanoparticles. The reversible swelling procedure gave good infiltration of the inter-filament spaces throughout the macroscopic fibre, and produced a highly compacted network of silicalite nanoparticles after air-drying. The composite fibres were calcined at 600 °C to remove the molecular (TPAOH) and supercellular (bacteria) templates. Thermogravimetric analysis gave a total weight loss of 75%, corresponding to removal of water, TPAOH and the bacteria template. The remaining inorganic phase was in the form of an intact white silicalite fibre with a macroporous internal structure (Fig. 2). Significantly, the replica consisted of an organized array of *ca.* 0.5 μm-wide channels that were oriented approximately parallel to the fibre axis [Fig. 2(c)]. The channel walls were *ca.* 100 nm thick as

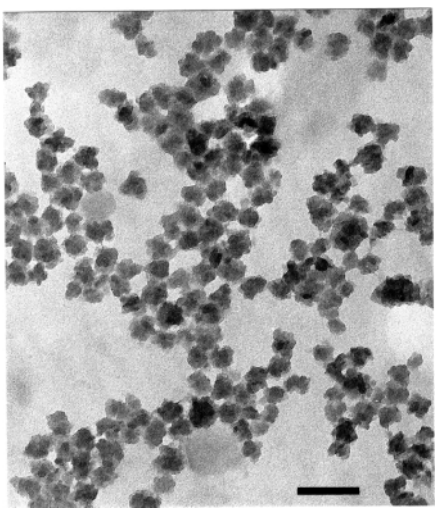

Fig. 1 TEM image of as-synthesized silicalite nanoparticles used as building blocks for the construction of porous zeolite fibres, scale bar = 100 nm.

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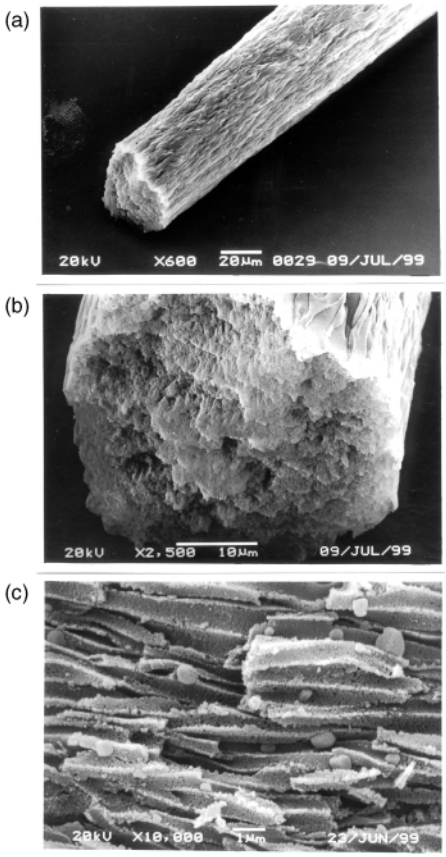

Fig. 2 SEM micrographs of silicalite-infiltrated bacterial thread after calcination at 600 °C: (a) intact zeolite replica, scale bar = 20 μm. (b) Fractured fibre tip showing the channel-like architecture, scale bar = 10 μm. (c) High magnification image of a thread fractured longitudinally, showing the continuous zeolite wall structure enclosing co-aligned channels, 0.5 μm in width, scale bar = 1 μm.

determined by SEM measurements. TEM images of lightly ground samples indicated that the wall structure consisted of closely packed aggregates of 50 nm sized silicalite nanoparticles. Corresponding electron diffraction data on the particles were consistent with crystalline silicalite. XRD patterns on the bulk calcined thread showed reflections with increased intensities, indicating an increase in the crystallinity of the nanoparticles compared with the as-synthesized zeolite. FTIR spectroscopy showed the characteristic double-ring vibration band at *ca.* 550 cm^{-1}, but no shoulder at 960 cm^{-1}, indicating almost complete condensation of the Si–OH groups in the calcined product.

Our results indicate that silicalite nanoparticles can be infiltrated into the ordered void spaces of a bacterial template where they can be used as building blocks for the construction of a macroporous inorganic framework. The mechanism responsible for high-fidelity inorganic replication of the bacterial superstructure has been described previously for macroporous fibres prepared from amorphous silica colloids.[3] The same considerations, such as surface-charge repulsion between the bacterial cell walls and the silicalite nanoparticles at high pH, and ionic strength-induced aggregation on deswelling, are likely to be responsible for the irreversible coalescence and compaction of the zeolite nanoparticles into the patterned architecture. Removal of both molecular (TPA^+) and micrometre-scale (multicellular filaments) templates by thermal degradation affords a zeolite fibre with hierarchical porosity that might have technological advantages owing to the high surface area and unidirectionality of the patterned architecture. Porous zeolite threads could also be aligned in thin films or flow tubes for separation processes or catalysis. By changing the template, it should also be possible to produce more complex macroporous zeolite monoliths by nanoparticle infiltration of patterned organic materials exhibiting reversible swelling. For example, recent studies indicate that sponge-like block copolymer gel templates can be used to prepare interconnected macroporous frameworks of coalesced magnetite or titania nanoparticles.[13]

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Notes and references

† TPA-silicalite nanoparticles were synthesized from clear solutions following a modified version of the method described by Persson *et al*.[9] Tetraethylorthosilicate (16.0 g; Aldrich, > 98%) was added to 27.32 g of 1.0 M aqueous solution of tetrapropylammonium hydroxide (TPAOH; Aldrich) in a polypropylene bottle. The reactant mixture (molar composition: 9 TPAOH : 25 SiO_2 : 354 H_2O : 100 EtOH) was stirred for 24 h at room temp. to allow hydrolysis of the TEOS. The colourless solution obtained was heated under reflux in a preheated paraffin oil bath at 80 °C for 96 h without stirring. The colloidal particles produced were sedimented by centrifugation (12000 rpm) and washed by resuspending in deionized water. This process was repeated until the final pH of the suspension was 10–11. At this pH the particles have a net negative surface charge, and the dispersion is stable for several months. Dynamic light scattering and zeta potential measurements were performed on suitably diluted solutions, using a Brookhaven Instruments ZetaPlus particle sizer. Specimens for TEM were prepared by depositing a drop of the suspension onto carbon-coated, formvar-covered copper grids. Powder samples for XRD, FTIR and TGA were prepared by air drying the suspension.

‡ Macroscopic bacterial threads were produced from cell cultures of mutant FJ7 strain of *Bacillus subtilis* by methods described elsewhere.[8] Infiltration of the bacterial superstructure was achieved as follows. The tip of a 3–5 cm long prewashed bacterial thread was held by reverse tweezers and the fibre dipped into the washed silicalite colloidal solution (pH 10–11, 1–4% w/w) for at least 3 h at room temp. The swollen fibre was then very slowly withdrawn from the colloidal solution and allowed to dry in air. During the dipping process, the tweezers were held so that the tip of the thread was not immersed in the colloidal solution. This aided recovery of the intact mineralized fibre. Calcined materials were prepared by heating the composite fibres in a Carbolite furnace to a temperature of 600 °C at a rate of 2 °C min^{-1}. Samples were kept at 600 °C for at least 2 h before cooling to room temperature.

SEM and EDXA were carried out using a JEOL JSM5600LV instrument operated at 5 keV for uncoated samples or at 20 keV for gold-coated samples. The samples were mounted onto Al stubs, using carbon sticky pads. TGA was performed on a Netzsch TG209 instrument at a heating rate 5 °C min^{-1} from room temperature to 800 °C in a nitrogen atmosphere with flow rate 90 ml min^{-1}. The TGA residues were collected and used for PXRD and FTIR measurements. Powder X-ray diffraction studies were carried out on a Siemens D500 diffractometer with Cu-Kα_1 radiation, in the 2θ range 5–60°. FTIR spectra were recorded on a Bruker IFS 25 spectrophotometer using KBr pellets in the range 400–4000 cm^{-1}. For TEM and SAED analysis the calcined fibres were ground, dispersed in deionized water and then deposited on carbon-coated, formvar-covered copper grids.

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