

Morphosynthesis of macrocellular mesoporous silicate foams

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Silicate macroskeletons which have both templated mesoporosity and open-cell macrovoid structures have been prepared in monolithic form at near ambient temperatures from continuous metastable foams of non-ionic alkylpolyethylene oxide surfactants under aqueous, neutral pH reaction conditions.

The controlled synthesis of inorganic frameworks exhibiting very large pores and complex macroscale forms is an area of intense scientific and technological effort for potential applications in catalysis, molecular sieving and biomaterials.¹ Assemblies of both charged and uncharged amphiphilic molecules are known to interact with inorganic precursors to form complex architectures in the inorganic phase.^{2,3} However, void size control of such porous compositions has generally been restricted to the micro- and meso-scales between 0.3 and 30 nm diameter.^{4,5} Recent work by the groups of Ozin, Stucky and Mann have produced materials that display porosity and morphology on the supermeso- and macro-scales.^{6–8} Ozin reported the morphosynthesis of SBA-2 materials into complex rod, disc, swirl and top shapes,⁶ while Stucky described the templating and shaping of supermesoporous oxides.⁷ The morphosynthesis of silica and calciferous materials displaying open skeletal frameworks have been reported by Mann and coworkers.⁸ The voids created by the amorphous silica, calcium phosphate or carbonate skeletons are of the order of micrometres and thus begin to approach structures with void dimensions and compositions desirable for bioceramic applications.⁹ Possible technological drawbacks of these materials are that they are obtained as precipitated particles, the solid phases are non-porous and that they are synthesised in frozen, complex bicontinuous microemulsions over long reaction times. The use of biliquid foam structures to prepare transition metal oxide films from super-saturated precursor solutions has also been reported.¹⁰ Ceramic foams of various metal oxide compositions are well known in industrial applications and are generally prepared by slurry coating a ceramic powder, for example alumina and zirconia, onto the surface of a fibrous polymer support which is then removed through calcination.

In an effort to simplify the microemulsion synthesis system and to produce materials with larger macrovoids, we replaced the unstable biliquid microemulsion with a metastable surfactant foam system. This was with the goal of replicating, in an inorganic silica phase, the three dimensional macrostructured foam under ambient and benign reaction conditions. Here we describe the sol-gel synthesis of novel silica and metallo-silicate materials that exhibit both open macroporous skeletal networks of amorphous silica and templated mesoporosity within the solid skeleton. These novel macrostructured mesoporous silica foam materials, which we label MMSF, are formed directly from tetraethoxyorthosilicate (TEOS) or TEOS plus a basic metal salt, solubilised within the water-rich film of an alkylpolyethylene oxide (PEO) based nonionic surfactant foam.¹¹ The reaction conditions are almost identical to those previously reported for [Si]- and [M]-MSU-X mesostructure syntheses.^{†12,13} The appearance of these products suggests that void size control over length scales¹⁴ of differing orders of magnitude can be achieved in a single, simple synthesis medium. The MMSFs have added novelty over most existing

macrostructured materials in that they can be formed in monolithic shapes with, in principle, no limit to their dimensions.

X-Ray diffraction (XRD) patterns[‡] of the hydrothermally treated and calcined MMSFs (Fig. 1) exhibit single peak d_{100} reflections at low angle. No higher angle reflections and hence long-range symmetry were indicated, suggesting that the solid part of the MMSF material is amorphous with a regular repeating pore motif. The single reflection XRD patterns are identical to those obtained from [M]-MSU-X mesostructures and thus suggest that a pore structure exists that is similar to the three dimensional disordered worm-like pore arrays exhibited by [M]-MSU-X materials.^{13–15} Nitrogen sorption isotherms[‡] of hydrothermally treated/calcined monolithic samples indicate the presence of well defined large mesopores. The adsorption branch displays a strong capillary condensation step indicative of mesopores with well defined diameters (Fig. 2) while the desorption branch exhibits some hysteresis as a result of the high partial pressure of adsorption. We therefore conclude that the solid silicate phase that makes up the MMSF material, is itself mesoporous and furthermore, the analytical data indicate that the solid skeleton of MMSF is at the mesoscopic level, identical to hydrothermally treated [M]-MSU-X powders¹⁵ exhibiting surface areas between 800 and 900 m² g⁻¹, pore volumes of ca. 1.0 mL g⁻¹ and pore diameters between 20 and 40 nm depending upon template dimensions, synthesis temperatures and length of hydrothermal treatment. Optical photographs[‡] of sections of MMSF monoliths display the macrovoid nature of the MMSF materials that distinguish them from existing [M]-MSU-X materials which are produced only as powders. These images suggest that a true macrostructured skeletal material is assembled from both skeleton-like silica filaments or struts [Fig. 3] and surface-like structures and not agglomerations of silica particles. The open-cell nature of the MMSF was demonstrated by the absorption of a brightly

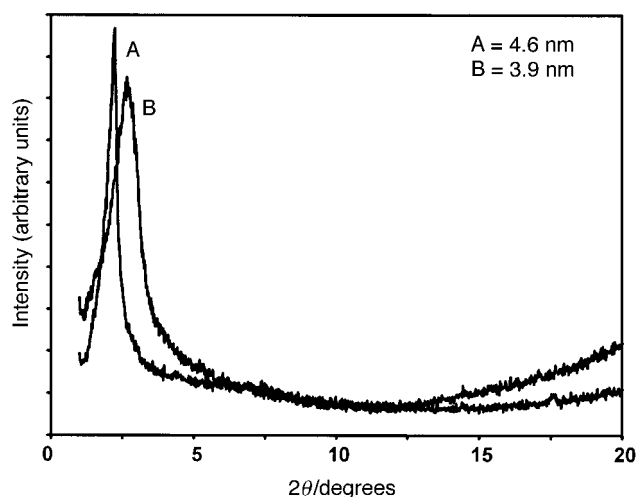


Fig. 1 XRD patterns of a representative macrostructured mesoporous silica foam MMSF prepared from Triton N-101 surfactant. (A) after hydrothermal treatment for 72 h, (B) hydrothermally treated and calcined at 600 °C 4 h in air.

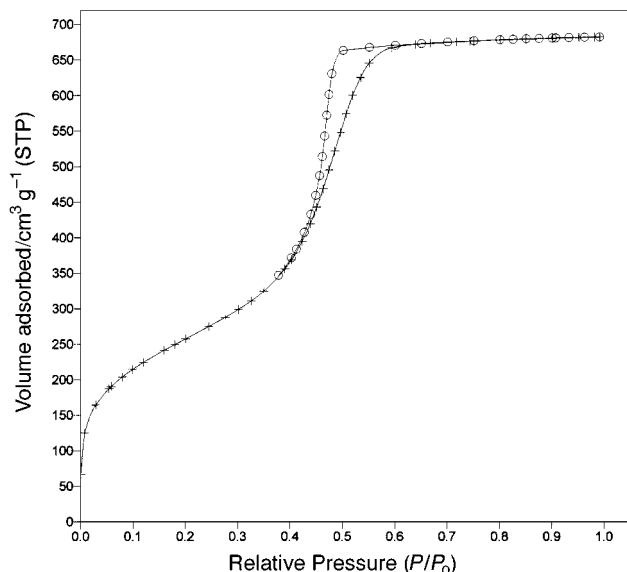


Fig. 2 Nitrogen sorption isotherms of MMSF after hydrothermal treatment and calcination; (+) adsorption, (O) desorption.

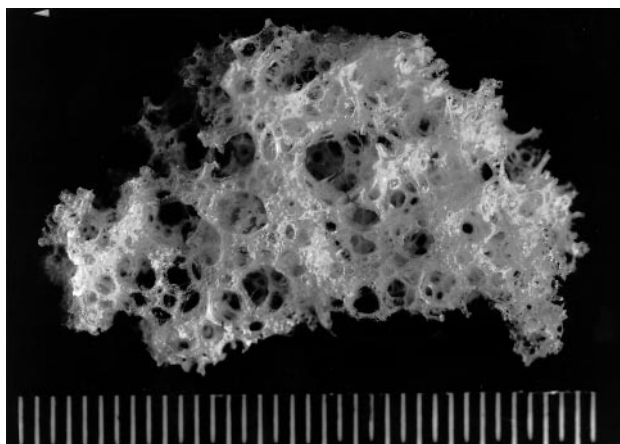


Fig. 3 Optical photograph of hydrothermally treated and calcined MMSF exhibiting macrocellular form. Scale divisions are 0.5 mm.

coloured aqueous dye solution into a monolithic sample *via* capillary action. The photographs presented indicate that the macrovoids range in diameter from hundreds of microns to 1–2 mm, the smaller end of this scale being ideal for application in artificial bioceramic bone implant technologies.⁹ Currently the MMSF materials are brittle and exhibit only limited fracture resistance. Improvement of the compressive and tensile strengths is being pursued.

A perhaps surprisingly simple mechanism of formation of the MMSFs is proposed. Minimum surface spherical bubbles make up the surfactant foam, their diameters being determined by the rate and mode of agitation of the surfactant emulsion. Upon TEOS addition, the water immiscible $\text{Si}(\text{OC}_2\text{H}_4)_4$ monomers are progressively solubilised through hydrogen bonding between the surfactant PEO head-group of micelle structures and the alkoxide species. The PEO micellar corona solvates the TEOS monomers, transports them throughout the foam film and the strong H-bonding therein induces polarisation of the Si–OR bond and subsequent hydrolysis and condensation.¹² In the initial stages of reaction the rate of film drainage is high and no stable foam results. As hydrolysis and condensation of the TEOS proceed, the viscosity within the foam film increases and drainage from the film slows, allowing a stable, interconnected open cell foam to be maintained.¹⁶

The synthesis route described here is very simple, low cost, environmentally benign and able to be modified in many ways

so that varied product engineering is possible. Development of the MMSF structures, compositions and physical properties is continuing. The author thanks Industrial Research Ltd. for funding through the Non-Specific Output Fund as part of a contract with the New Zealand Foundation for Research, Science and Technology.

Notes and references

† *Experimental*: in a typical MMSF synthesis, TEOS is added to a dilute 5–10 wt% solution of a non-toxic, inexpensive non-ionic surfactant (*e.g.* Triton N-101 nonyl-PEO₁₀), at 24–30 °C and at neutral pH. Metallosilicate analogues may be prepared by adding a basic metal salt solution [*e.g.* $\text{Al}_2(\text{SO}_4)_3$, TiOSO_4 , ZrOCl_2 , $\text{VO}(\text{SO}_4)_2$] to the TEOS, before addition to the surfactant emulsion. This causes pre-hydrolysis of the TEOS and formation of water soluble Si–O–M units.¹⁴ In the step that separates [M]-MSU-X synthesis from MMSF synthesis, the surfactant/TEOS emulsion is then stirred rapidly at 750–1000 rpm with a magnetic stirrer whose length is 60–75% of the width of the reaction vessel thereby creating turbulence within the vessel. Hydrolysis of the TEOS is catalysed by hydrogen bonding with the PEO¹³ surfactant headgroup. As this hydrolysis proceeds spherical bubbles aggregate to form an organic/inorganic composite foam which adopts the dimensions of the reaction vessel. After 16–24 h, stirring is arrested and the foam composite is allowed to age under static conditions for 24–48 h. The solid foam monolith that results may then be removed from the vessel and dried, taking care to avoid cracking caused by drying too quickly. The as-prepared MMSFs may then be hydrothermally treated at 100–150 °C and/or calcined at 450 °C for 4 h in air to yield an inorganic silicate foam. Calcination without hydrothermal treatment invariably induces cracking in the MMSF monoliths. Hydrothermal treatment¹⁵ improves the cross-linking within the amorphous silica, the mesopore diameters and also the fracture resistance. MMSF yields are typically 80–90% in Si while the remainder of the SiO_2 is retrieved as precipitated templated [M]-MSU-X. Foam bubble sizes and hence final macrovoid dimensions may be modified by changing the turbulence within the reaction vessel. This can be achieved by moderation of the stirring speed or by substituting different shaped magnetic stirrer followers and is the subject of continued investigation.

‡ *Characterisation*: XRD patterns were measured on a Philips PW 1700 series APD diffractometer equipped with an automatic variable divergence slit and Co-K α radiation ($\lambda = 0.179026$ nm). Nitrogen sorption isotherms were obtained with a Micromeritics ASAP 2010 sorptometer at –196 °C. Surface areas were calculated using the BET model while pore size distributions were calculated using the BJH model. Optical photographs were obtained with a Nikon Multiphot type A camera equipped with a 65 mm Macro Nikkor lens using incident lighting and T-Max 100 black and white film.

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