Synthesis of ordered macroporous SiO_2 in supercritical CO_2 using 3D-latex array templates

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Ordered macroporous SiO_2 membranes were produced by the decomposition of silicon alkoxides in supercritical carbon dioxide ($scCO_2$) using 3D-latex arrays as templates.

The synthesis of structured porous ceramic materials has important applications in catalysis, chromatography, separation, biomaterials, microelectronics and photonic materials.[1,2] Many methods to produce porous materials in the liquid phase are quite time consuming (involving multi-step syntheses or ageing), generate large quantities of polluted aqueous waste streams, and can be very energy intensive (particularly in the drying steps), rendering them environmentally unfriendly. The development of faster and more sustainable methods of synthesis, as well as the improvement of the properties of the material is a field of constant activity.

Monodisperse latex microspheres of controlled size and variable composition can be arranged in three-dimensional (3D) ordered arrays. These materials have been used as templates for structured porous material including inorganic oxides, carbons, metals and polymers.[1,3–6] We have recently reported the synthesis of SiO_2 and TiO_2 ordered macroporous materials by reaction of sodium silicate and titanium tetraisopropoxide (TTIP) solutions, respectively, into 3D-latex arrays.[5,6] The polymeric template was infiltrated by the precursor using suction or capillary forces. Here we report for the first time the impregnation and reaction of silicon alkoxide precursors into 3D-ordered latex arrays in $scCO_2$.

$scCO_2$ is an attractive medium for the synthesis of ceramic materials because it is non-flammable, non-toxic, inexpensive and it has easily accessible critical parameters (T_c = 31 °C, P_c = 73.8 bar).[7] Large quantities of metal alkoxides can be dissolved in $scCO_2$ at moderate temperature and pressure.[8] At the same time, the transport properties of $scCO_2$ (low viscosity, high diffusivity relative to liquids and very low surface tension) promote infiltration in complex geometries and mitigate mass transfer limitations common to liquid phase processes. Compressed gases are also highly soluble in polymers, decreasing the glass transition temperature of the polymer. CO_2 is a gas at ordinary pressure and can be eliminated completely upon depressurisation.

These properties have been previously exploited and both amorphous and structured porous ceramic materials have been produced in $scCO_2$. Loy *et al.*[9] reacted tetramethylorthosilicate (TMOS) and 1,4-bis(triethoxysilyl)benzene directly in $scCO_2$ at 35–45 °C and 414 bar using 13–36% formic acid and obtained, in each case, large surface area silica aerogels.[9] Pai *et al.* have shown the preparation of mesoporous silicate films in $scCO_2$ using microphase separated block-copolymer.[10] Films were prepared by infusion and selective condensation of tetraethylorthosilicate (TEOS) in $scCO_2$ at 60 °C and 120 bar within the hydrophilic blocks of the polymer which contained the catalyst *p*-toluenesulfonic acid. Wang *et al.* have recently produced hollow silica spheres with large mesopore wall structure, reacting TEOS in CO_2-in-water emulsion in the presence of block copolymers.[11] Wakayama and Fukushima have used carbon fibres to produce ceramic and metallic porous materials in $scCO_2$.[12,13] Impregnation and reaction of TEOS and TTIP on the surface of the carbon fibres was carried out without any catalyst at 120–150 °C and 260 bar in $scCO_2$. After calcination or oxidation of the template, a ceramic structured material was obtained.

Herein we report the synthesis of ordered macroporous ceramic materials in $scCO_2$. Materials were prepared using 3D-latex arrays of polystyrene (PS) latex particles decorated with different hydrophilic groups on their surface as the template. The monomers 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), methacrylic acid (MA), acrylic acid (AA) and itaconic acid (IA) were reacted with styrene (S) (variable ratios between 1 : 9 and 1 : 14 with excess S) by emulsion copolymerisation in water following a procedure previously described.[5] After dialysis of the suspension for four weeks against water, latex particles were redispersed in solutions of monochloroacetic acid (ClAcH) or benzosulfonic acid (BSA), of different concentrations. 3D-Latex arrays were prepared by evaporation of the solvent, membrane filtration or centrifugation. The materials were dried under air at room temperature or at 45 °C in an oven. Some samples were further dried under vacuum at 70 °C. In all cases membranes appeared iridescent to visible light reflecting the 3D-ordering of the template. These materials are often called opals because of their opalescence (colour change depending on the view angle).

Experiments were performed in a *ca.* 70 ml custom-made stainless-steel high-pressure reactor. Three small glass vials were placed inside the reactor, each containing: (1) pieces of 3D-latex arrays of variable thickness (1–5 mm), (2) TEOS and (3) H_2O. Factors controlling the stability of the polymeric membranes in pure $scCO_2$ have been previously studied.[14] In most experiments liquid reactants were used in excess. To prevent contact of the reactants during gas filling, a perforated stainless-steel plate was place inside the reactor above the open vials. The reactor was immersed in a thermostatic bath at 40 °C and filled with CO_2 using a high-pressure syringe pump (Isco, Inc. Model 260D) up to 85 bar. Materials were kept at these conditions for 2–18 h. The

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depressurization time was varied between 10 min and 3 h. Reacted materials were calcined at 500 °C for 4 h. Calcination of the materials obtained from templates which had not been treated with acid, did not render any significant solid residue. On the contrary, reactions on those templates treated with ClAcH or BSA gave bluish-white coloured solid residues (inverse opals). Reaction was very sensitive to the surface composition and acid concentration. SiO_2 loading after calcination represented only 4–7 wt% of the polymeric template. The materials were characterized using FTIR, SEM, TEM and N_2 adsorption.

Fig. 1 shows a SEM picture of a PS–MA–IA 3D-latex array (monomer ratios 52 : 1 : 2) before reaction with TEOS. Monosized 350 nm round particles self-organize in 3D-ordered arrays of particles. Pictures reveal a fcc packing of particles together with some less ordered regions. Experimentally, 3D-ordering of functionalized PS particles is better than ordering of bare PS particles.

The presence of the organic acid (catalyst) on the particle surface was investigated by FTIR. Spectra of the polymeric templates showed bands ascribed to the corresponding homopolymers. The coincidence of functional groups in ClAcH and the latex particles obscured the identification of ClAcH by FTIR. The membranes impregnated with BSA, however, showed a band due to the sulfonic acid group at 1128 cm^{-1}. FTIR spectra of the samples infused and reacted in $scCO_2$ showed broad and intense SiO_2 bands (1000–1250 cm^{-1}) superimposed on those of the template. After calcination, only SiO_2 bands were observed.

Fig. 2 shows a SEM picture of an inverse opal obtained from the reaction of TEOS on a PS–MA–IA 3D-latex array impregnated with BSA 0.01 M in $scCO_2$. The material was reacted in $scCO_2$ at 40 °C and 85 bar for 4 h and further calcined at 500 °C for 4 h. The SEM picture shows an ordered macroporous material which replicates the structure of the original template. SEM shows holes among the hollow spheres as well as seams between adjacent spheres. Reaction of the precursor at these conditions seems to take place only at the particle surface.

3D-Ordering of the porous material is confirmed by TEM. Fig. 3 shows TEM pictures of the same sample displayed in Fig. 2, along the [111] and [100] projections, showing the close packing of the voids after calcination of the template. TEM picture of the sample along the [111] projection shows that both tetrahedral and octahedral holes are empty, as expected if the precursor reacts only at the surface of the template. The empty octahedral sites are apparent in the [100] projection. The wall thickness of the material produced in $scCO_2$ at 40 °C and 85 bar is 7.5–10 nm. The TEM picture of the [111] projection also reveals a small gap, 5–10 nm long, between adjacent particles. Most spheres are not in contact, in contrast to the close packing of hollow SiO_2 spheres. Nevertheless, relatively large fragments of porous material have been obtained after calcination, which suggests that some binding between particles maintains the 3D-structure.

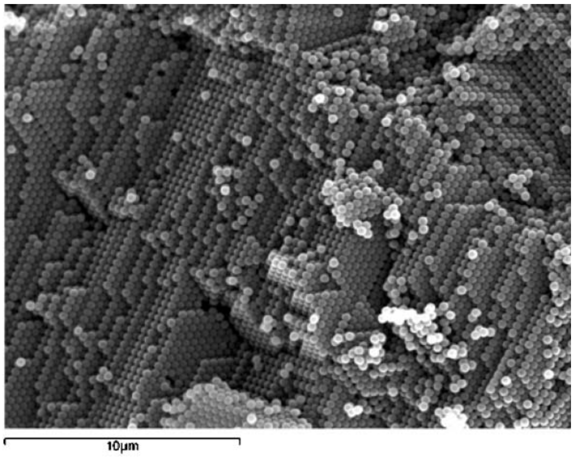

Fig. 1 SEM picture of the PS–MA–IA 3D-latex array used as template. Scale bar = 10 μm.

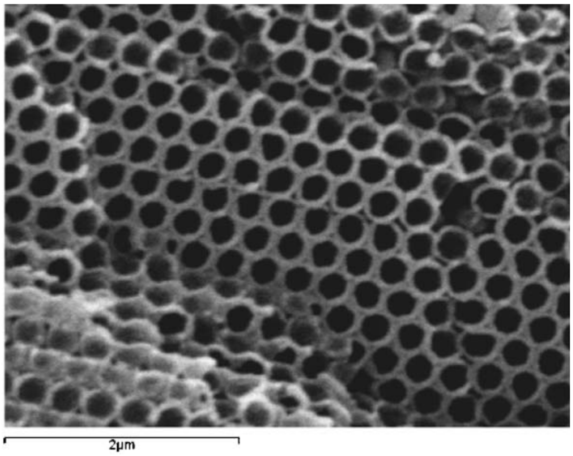

Fig. 2 SEM picture of an inverse opal produced by condensation of TEOS in $scCO_2$, using the template shown in Fig. 1. Scale bar = 2 μm.

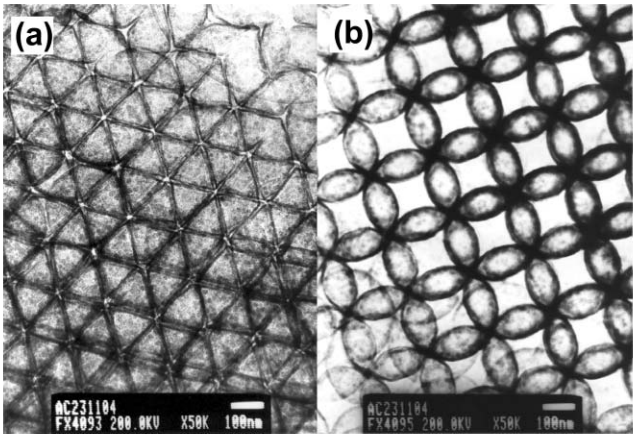

Fig. 3 TEM picture of an inverse opal produced by condensation of TEOS in $scCO_2$, using the template shown in Fig. 1: (a) [111] projection and (b) [100] projection. Scale bars = 100 nm.

For comparative purposes a piece of PS–MA–IA 3D-latex array impregnated with BSA 0.2 M was infused by capillarity with a solution of TEOS : H_2O : EtOH of ratio 1 : 4 : 4.5. After 18 h the sample was calcined at 500 °C for 4 h. Although infusion in the liquid phase has not been optimized, experiments indicate that the reaction proceeds with filling of tetrahedral and octahedral holes and that there is not space between voids. In contrast materials obtained in $scCO_2$ resembled those produced by the slow evaporation of silica coated single polymer particles on a surface.[15]

Another interesting result of the SEM and TEM analysis is that the contraction of the structure after condensation is rather small.

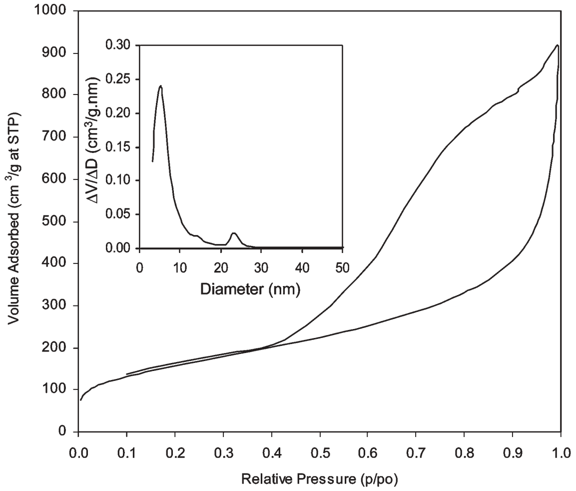

Fig. 4 BET adsorption isotherm of an inverse opal produced by condensation of TEOS in $scCO_2$. Inset shows the distribution curve for the desorption branch.

The distance between pore centers in the calcined material determined by SEM and TEM is close to 300 nm. Considering the size of the original latex particles, the shrinkage of the network after condensation represents only 14%. In contrast, the shrinkage of the network when the reaction is performed in liquid phase is close to 25%. The smaller shrinkage observed when the reaction is performed in $scCO_2$ is related to the high solubility of ethanol in the solvent.[16] Ethanol dissolves in $scCO_2$ as it is being produced, assisting the fast drying of the gel and driving hydrolysis and condensation reactions towards products.

The N_2 adsorption isotherm of the calcined material produced in $scCO_2$ (Fig. 4) is of type IV and displays a hysteresis loop which suggests pores interconnected through narrow openings.[17] Analysis of the adsorption branch of the isotherm using the BJH method for a cylindrical pore model gives a broad pore size distribution from 150 nm to the lowest mesopores. Analysis of the distribution curve obtained from the desorption branch (shown in Fig. 4 as an inset) shows a maximum at *ca.* 5 nm and other smaller relative maxima between 10 and 30 nm. SEM and TEM pictures show macropores shaped by the template, mesopores due to the presence of interconnected teatrahedral and octahedral holes and, at these conditions, smaller mesopores between adjacent hollow SiO_2 spheres. The mesopore system can be described as interconnected channels of quasi-circular cross section and variable diameter. The variable pore diameter justifies the broad pore size distribution obtained from the adsorption branch.[18] During desorption, evaporation happens through the openings formed by two or three neighbouring hollow spheres. From TEM, the spacing between two spheres is 5–10 nm and the diameter of the window formed by 3 spheres is 20–25 nm. These values match closely the maxima observed in the distribution curve. The gap between two adjacent spheres can be due to the small, but noticeable, shrinkage of the network upon condensation. Furthermore, the ceramic wall must present meso and microporosity. BET area and external area (obtained from the *t*-plot) are 570 $m^2\ g^{-1}$ and 403 $m^2\ g^{-1}$, respectively. The large external area compared to the geometrical area calculated from the template suggests mesoporosity in the walls, which would contribute to the maximum observed in the desorption curve. The difference between the BET area and the external area indicates microporosity.

N_2 adsorption analysis of the material produced by sol-gel reaction in liquid medium also showed a type IV isotherm with a much narrower hysteresis loop. In this case the BET area was only 92 $m^2\ g^{-1}$ and the external area was 31 $m^2\ g^{-1}$ (close to the geometrical one).

To summarize, a new method to produce ordered macroporous ceramics by sol-gel reaction of silicon alkoxides in $scCO_2$ using 3D-latex array templates is reported. Macroporous SiO_2 membranes were produced in $scCO_2$ at 40 °C and 85 bar. Controlling the surface composition of the template is crucial. Synthesis can be carried out under other temperature and pressure conditions, yielding materials of different porosity. Other silicon precursors such as TMOS can be also used. Currently, we are exploring the potential of our technique for synthesising other macroporous materials.

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