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Biomimetic self-activated formation of multi-scale porous silica in the presence of arginine-based surfactants

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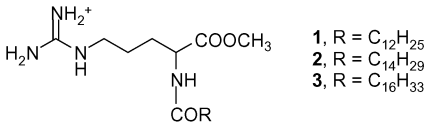
Silica polymerisation activation and structure templating using arginine-based surfactants led to bio-inspired multi-scale porous materials.

In the search for alternative strategies to design new materials, chemists have turned their attention to biomineralisation processes.[1] It has long been recognised that the formation of highly structured silica networks by the brown algae diatoms provides a striking example of multi-scale organisation of a mineral phase by organic templates.[2]

The biosilicification process in diatoms combines condensation of diluted solutions of silica precursors (*i.e.* silicic acid) and control of the morphology.[3] Different sets of proteins that could be responsible for such processes have been isolated.[4] Sumper *et al.* have shown that some proteins called silaffins were able to activate tetraethoxysilane (TEOS) condensation, leading to silica particles.[5] Stucky *et al.* used synthetic polypeptides and obtained similar results.[6] However, the main weakness of these approaches is the use of alkoxide precursors whose reactivity is different from naturally available silicic acids.[7]

We have recently reported that poly-lysine and poly-arginine were able to induce silica formation from dilute sodium silicate solutions.[8] Interestingly, these two amino acids are present in large amounts in the silaffins sequence. It has been suggested that silicate anions could interact with ammonium or guanidinium groups of the polymers. Upon adsorption, these anions are brought closer and could first condense, thus serving as the nucleation site for the gel formation. These studies underlined the importance of amino acids packing on the silica polymerisation process. However, in the presence of these two peptides, no organisation of the silica network could be observed. In this work, we have investigated the possibility of association of both silica polymerisation activation and templating effect by using surfactants derived from arginine.

Surfactants **1–3** (Scheme 1) were obtained by formation of an amide bond between the methyl ester of arginine and the corresponding fatty acids using dicyclohexylcarbodiimide (DCC) coupling, following described procedures.[9] In a typical experiment, surfactants were added to a 10 mM aqueous solution of sodium silicate (SiO_2 27%, Na_2O 10%) neutralised to pH 7 by HCl addition, in a [Si]–[surfactant] molar ratio of 10. After a few seconds, a white solid was formed. The reaction was left to proceed for 3 hours. The obtained solids were filtered, thoroughly washed with water and air-dried. Surfactant removal was performed by calcination at 500 °C.



Scheme 1 Chemical structure of arginine-based surfactants

X-Ray diffraction powder spectra of calcined powders, recorded using Cu-Kα radiation, showed an intense reflection in the 1.5–2.5 2θ range, whose maximum shifts towards low angles with surfactant chain, and a weak broad shoulder in the 3-4 2θ range, typical of a wormhole structure (Fig. 1a).[10] Corresponding d_{100}-values are gathered in Table 1, indicating an increase of the lattice parameter of about 3 Å per additional $-C_2H_4-$ group, in agreement with previous data on alkyltrimethylammonium surfactants.[11]

Nitrogen sorption experiments, illustrated for **2** in Fig. 1b, were performed to obtain specific surface area (S_{BET}), total porous volume (V_p) in STP conditions and pore diameter values (D_p) for the three solids after calcination (Table 1).[12] Pore size analysis using the BJH method indicates a bimodal distribution of primary (25–35 Å) mesopores (Fig. 1c) and secondary meso-to-macropores (100–1000 Å). It is interesting to note that the evolution of the smallest pore size with the surfactant chain length correlates well with the data obtained from XRD, thus suggesting that the wall thickness is about the same for the three solids.

Three different pore scales co-exist within these solids, as revealed by the α-plot (Fig. 1d). A first domain corresponding to micropores appears in the low-pressure domain, which accounts for 1–2% of the total pore volume. This is followed by a step indicating capillary condensation that corresponds to a

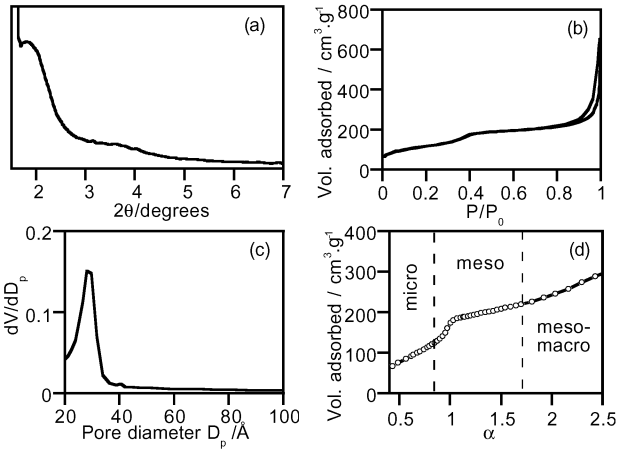


Fig. 1 (a) XRD pattern, (b) nitrogen sorption isotherm, (c) pore size distribution and (d) α-plot for porous silica formed in the presence of **2**, after calcination.‡

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Table 1 XRD d_{100} peak location; BET specific surface area (S_{BET}); total porous volume (V_p) and pore sizes (D_p) for the three calcined solids

Surfactant	d_{100}/Å	S_{BET}/m^2 g^{-1}	V_p/cm^3 g^{-1}	D_p/Å
1	45	720	1.05	25/300
2	48	510	0.95	29/600
3	51	600	1.00	34/800

primary mesoporosity, accounting for about 25% of the total pore volume (50% of the specific surface area). Finally, a third meso-to-macroporosity domain is observed for higher pressures. The absence of a plateau for P/P_0 close to 1 indicates that this corresponds to an open porosity. However, the evolution of the average pore size with the surfactant and reproducibility of these values suggest that the templates also control, at least partially, this porosity scale.

For mesoporous material formation, the use of long chain amines has already been reported by Pinnavaia *et al.* Following the S°I° pathway (with S° a neutral amine surfactant and I° an electrically neutral silica precursor), leading to wormhole frameworks.[10] In this work, the pK_a of the guanidinium group is about 11 and the amine is still highly positively charged at pH 7 whereas silica precursors are neutral ($Si(OH)_4$) or negatively charged oligomers. Therefore, both hydrogen bonding and electrostatic interactions can be expected.

Transmission electron microscopy (Fig. 2) indicates that the obtained solids consist of particles (diameter $\approx$ 50 nm) dispersed in a continuous silica network. On a smaller scale, this network exhibits the typical framework structure of wormhole mesoporous silica.[10]

Blank experiments in the absence of any added molecules or in the presence of unmodified arginine did not lead to any gelation after two weeks. This suggests that the packing of arginine heads forming the micelles outer-spheres is of primary importance, which is similar to the reported role of poly-lysine and poly-arginine chain length.[8]

Under the conditions of this work, surfactant concentrations are smaller or close to their critical micelle concentration.† Therefore, there is no significant pre-organisation of the templates and micellization should occur at the interface with the silicate species, thus leading to poorly ordered mesostructures.[15] In this context, it is noticed that porous volume remains nearly constant for the three solids whereas pore size increases with surfactant chain length. This suggests that the same amount of surfactant molecules interact with silicates during the mesoporous silica formation but that the number of micelles decreases when the chain length increases. Accordingly, thermogravimetric analysis indicates a similar Si–Surfactant molar ratio of *ca.* 5 : 1 for the three solids before calcination. Finally, XRD powder spectra of non-calcined solids exhibited the expected pore–pore correlation peak that appeared less intense than for calcined samples, corresponding d_{100} distances are about 20% larger. These data are in good agreement with previous reports for other mesoporous

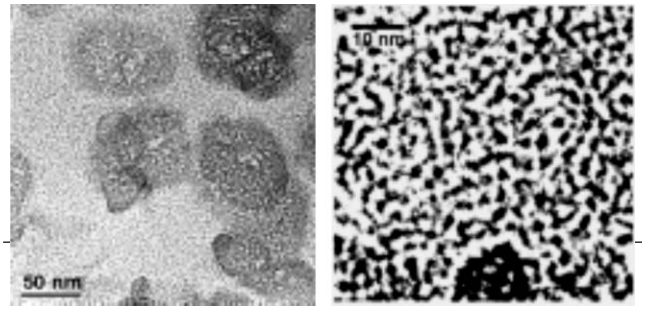
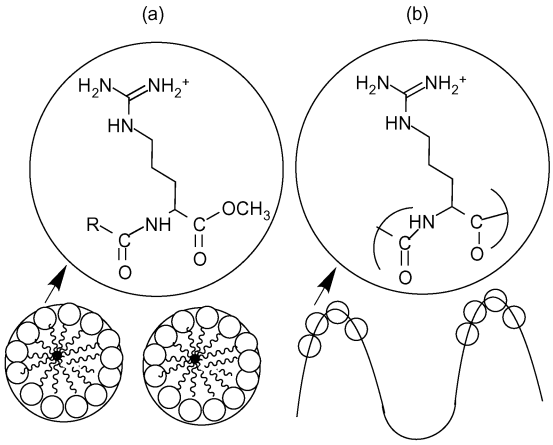


Fig. 2 Transmission electron micrographs of porous silica obtained in the presence of **1**, after calcination.



Scheme 2 Comparison of (a) arginine-based surfactant micelles and (b) arginine "patches" on silaffins peptide chains.

systems[15] and indicate that the porous framework is already substantially structured before calcination.

As illustrated in Scheme 2, a parallel can be drawn between the arginine heads organisation and the presence of lysine and arginine "patches" along the silaffins peptide chains.[5] Silica polymerisation will preferentially take place at the vicinity of positively charged amino acids sites whereas the hydrophobic or neutral area will remain poorly mineralised, thus leading to pore formation.

These bio-surfactants represent a simple model to understand silica organisation in natural systems. Such an approach allows polymerisation to be mimicked from diluted silica precursor solutions and porous organisation of the condensed phase. However, its limitation mainly lies in the use of a unique templating agent. In contrast, cells produce numerous molecules, displaying distinct functions and operating at different steps of the cell cycle. In our opinion, the vast range of reactive agents and the role of the time scale should be considered as key-parameters for future investigations of bio-inspired materials.

Notes and references

†Critical micellar concentrations (c.m.c.) values for **1** and **2** in water are reported to be 5.8 mmol L^{-1} and 2.0 mmol L^{-1}, respectively.[9a] Assuming a linear relationship between log(c.m.c) and the number of carbon atoms in the hydrophobic tail of the surfactants,[14] the c.m.c value for **3** can be estimated to be 0.6–0.7 mmol L^{-1}.

‡Pore size distributions in the 20–100 Å range were calculated using the BJH model; dV/dD_p is the derivative of the normalised adsorbed volume with respect to the pore diameter D_p. The α values were calculated using the macroporous silica LiChrospher Si-1000 as a reference.[13]

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