Synthesis of monolithic meso-macroporous silica and carbon with tunable pore size

Ara Kim, Robert Black, Yong Jae Hyun, Linda Nazar and Eric Prouzet

Supplementary Information

Table SI.I : Preparation of silica porous monoliths at 20, 40 and 60°C°C

Sample	TEOS solution		LC phase	
10% NaF	For the all samples; Brij58 0.8 g H_2O 25.0 g TEOS 1.45 g	5.0 g added to LC phase	H_2O 10%NaF 90%NaCl CTPCl Cyclohexane Pentanol	0.00 g 0.009 g 0.110 g 1.00 g 3.89 g 0.80 g
50% NaF			H_2O 50%NaF 50%NaCl CTPCl Cyclohexane Pentanol	2.00 g 0.044 g 0.061 g 1.00 g 3.89 g 0.80 g
90% NaF			H_2O 90%NaF 10%NaCl CTPCl Cyclohexane Pentanol	2.00 g 0.079 g 0.012 g 1.00 g 3.90 g 0.80 g

Preparation and methods

Preparation of SLCs for SAXS analyses: 1.0 g of Cetypyridinium chloride (CtPCl) was dissolved into 2.00g of water containing 0.02 g of NaCl; 3.00 g of cyclohexane were further added under vortex stirring and an unstable white emulsion was observed; finally, different amounts of pentanol-1 (between 0.20g and 0.60g) were added dropwise under strong vortexing

Preparation of silica monoliths: A mother silica precursor solution is prepared by the hydrolysis of 1.47g of TEOS into 25 g of deionized water containing 0.8g of Brij58, a PEO-based nonionic surfactant. Five grams of this solution are further added into the different SLCs prepared with different proportions of sodium fluoride (see Table SI.I). The final amount of water is adjusted to 7 mL, and SLC phases are prepared with NaF varying between 10, 50 and 90% of the required salt amount, the total being completed with NaCl. The synthesises were also proceeded at different temperatures (20℃, 40℃, and 60℃) in a thermostated shaking bath.. All samples turned to be cloudy and viscous, and formed physical gels. As the NaF percentage increases, the sample, turns more rapidly into a gel, as a result of the silica condensation induced by NaF catalysis. The samples were further filtrated and washed with ethanol, dried at 65°C overnight and calcined at 550°C (6 hours) under air.

Preparation of carbon replicas: The carbon structures were obtained as replica of two silica porous monoliths prepared as follows.
Sample A (80% NaF: 20% NaCl) :
The silica/surfactant aqueous phase was prepared by dissolving 0.32 g of Brij58 in 10 g of deionized water (pH 2), and 0.59g of TEOS (Si(OEt)4) were added and the solution was left under stirrin under full

hydrolysis. This solution was further evaporated in a rotovapor (35°C, primary dynamic vacuum) until a 3.5 g mass loss, this mass containing water and the ethanol resulting from the hydrolysis of TEOS. In parallel, a SLC was prepared by dissolving 0.070 g of NaF and 0.025 g of NaCl, with 1 g of CTPCl, in 2 g of water (pH 2), followed by the addition of 3.9 g of cyclohexane. The two solutions were mixed together and vortexed for 5 minutes. 0.5 g of pentanol were added until the mixture becomes a white opaque gel, and the solution was let to react overnight at room temperature. The final product was freeze-dried for one day, and finally calcined for 6 h at 620°C. The remaining silica was washed and filtrered.

Sample B (20% NaF: 80% NaCl) :

The silica/surfactant aqueous phase was prepared by dissolving 0.32 g of Brij58 in 10 g of deionized water (pH 2), and 0.59g of TEOS (Si(OEt)4) were added and the solution was left under stirrin under full hydrolysis. This solution was further evaporated in a rotovapor (35°C, primary dynamic vacuum) until a 3.5 g mass loss, this mass containing water and the ethanol resulting from the hydrolysis of TEOS. In parallel, a SLC was prepared by dissolving 0.0177 g of NaF and 0.098 g of NaCl, with 1 g of CTPCl, in 2 g of water (pH 2), followed by the addition of 3.9 g of cyclohexane. The two solutions were mixed together and vortexed for 5 minutes. 0.5 g of pentanol were added until the mixture becomes a white opaque gel, and the solution was let to react overnight at room temperature. The final product was freeze-dried for one day, and finally calcined for 6 h at 620°C. The remaining silica was washed and filtrered.

Preparation of carbon replica: 2.17 g of Resorcinol, 3.17 g of a 37% Formaldehyde aqueous solution and 0.04 g of sodium carbonate were stirred in a glass vial until full dissolution. 2 g of silica (sample A or B) were added after the stirring was stopped, and the silica was left for 30 minutes up to full impregnation. Once full impregnated, the silica was extracted by filtration under vacuum, and it was left at 85°C, in a sealed vial for 3 days. The sample was then carbonized at 900°C for 2 hours under an intert argon atmosphere (heating rate of 2°C/min). After natural cooling, the silica was dissolved by HF etching in a 10% aqueous HF solution, overnight. The resulting carbon material was filtered and dried in a vacuum oven.

Methods: SEM images were obtained on a Leo 1530 microscope at an EHT of 5 kV with gold-coated samples. SAXS measurements were recorded at room temperature, on an Anton Paar SAXSess system equipped with a 2.2 kW Copper anode (λ=1.54Å) and focusing multilayer optics. Collecting flux was enhanced by linear collimation, collected over a 0 to 40 (2 theta) angular range with a 2D Imaging Plate as detector. Scattering patterns are reported as a function of the wave vector $q=2\pi/d=4\pi\sin(\theta)/\lambda$,where d is the characteristic distance. SAXS patterns were desmeared and background-extracted using SAXSquant© and OptiQuant© as the interfacing programs

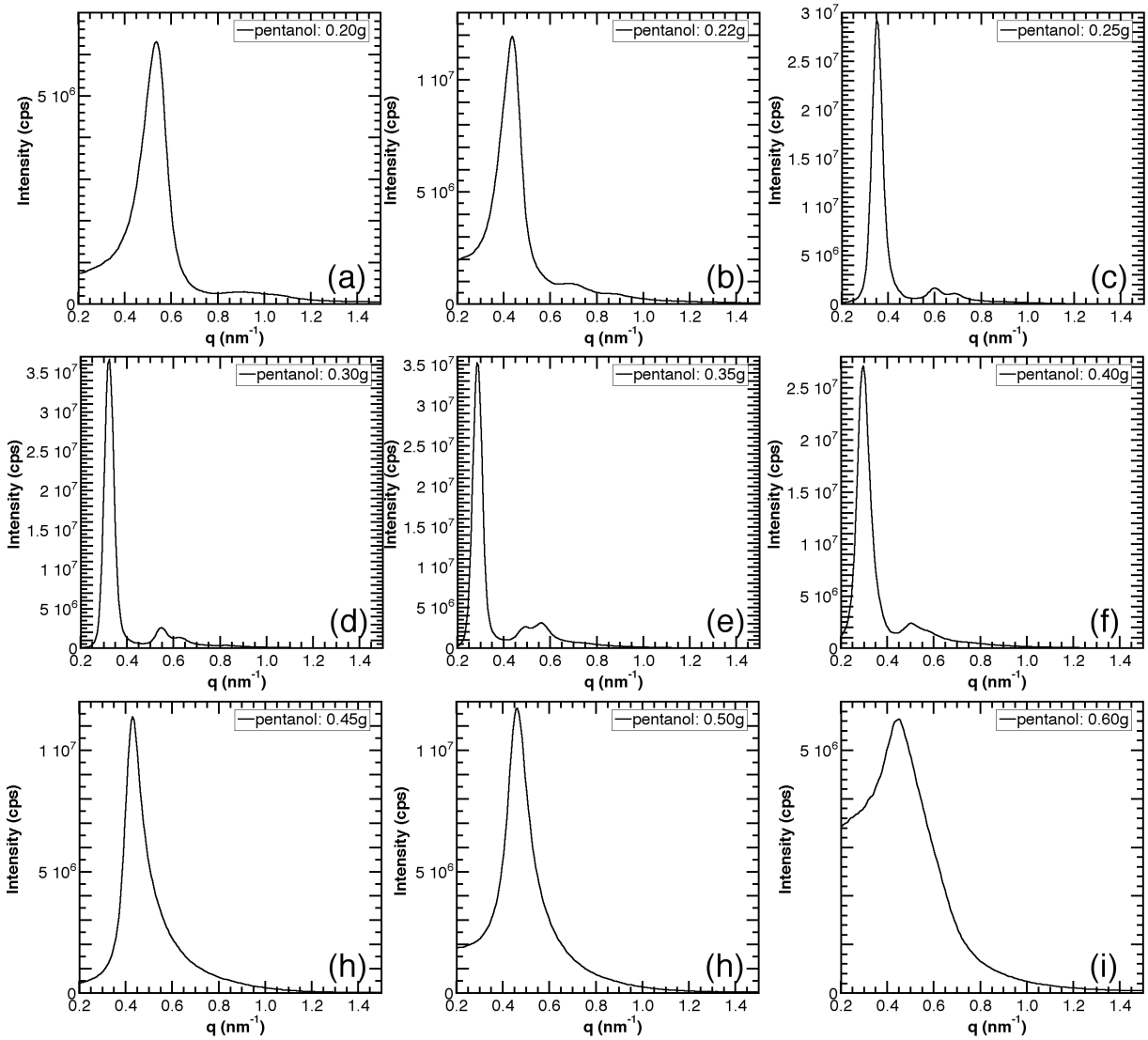

Figure SI.1 : SAXS patterns of the pure SLCs prepared with various amounts of pentanol-1 used as a co-surfactant.

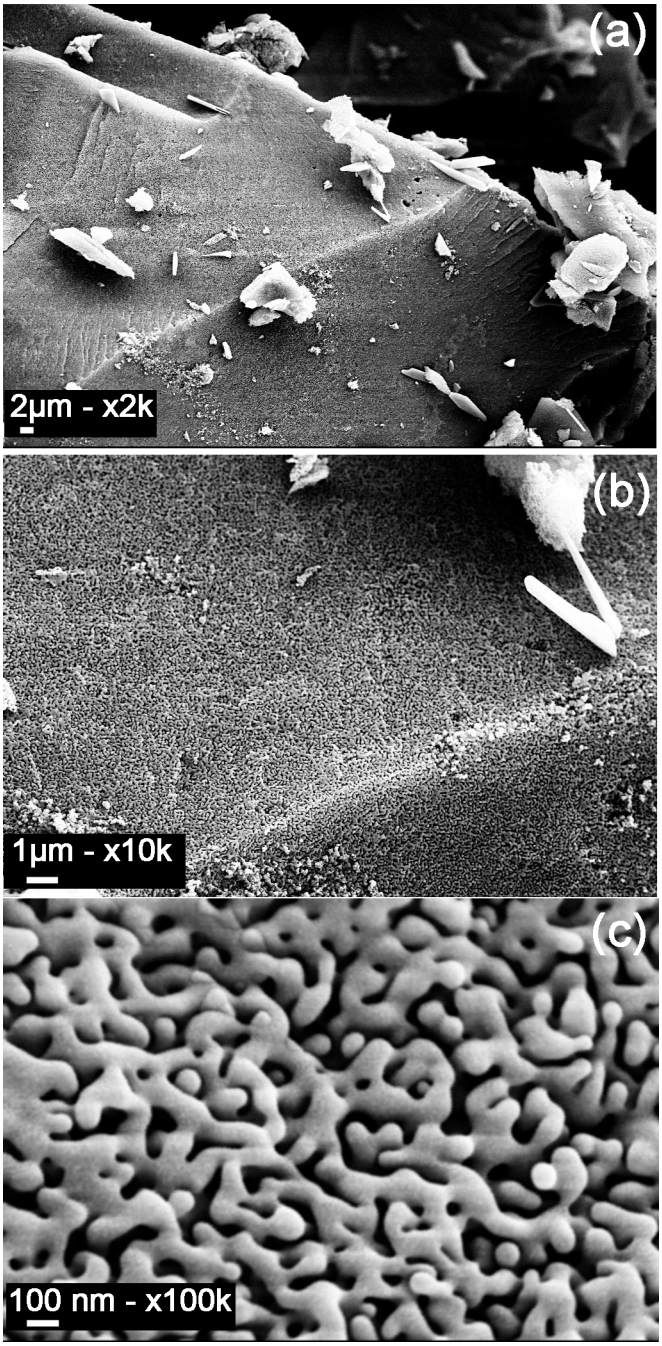

Figure SI.2 : SEM pictures of the silica sponge-like sample prepared with 50% NaF, at 40°C

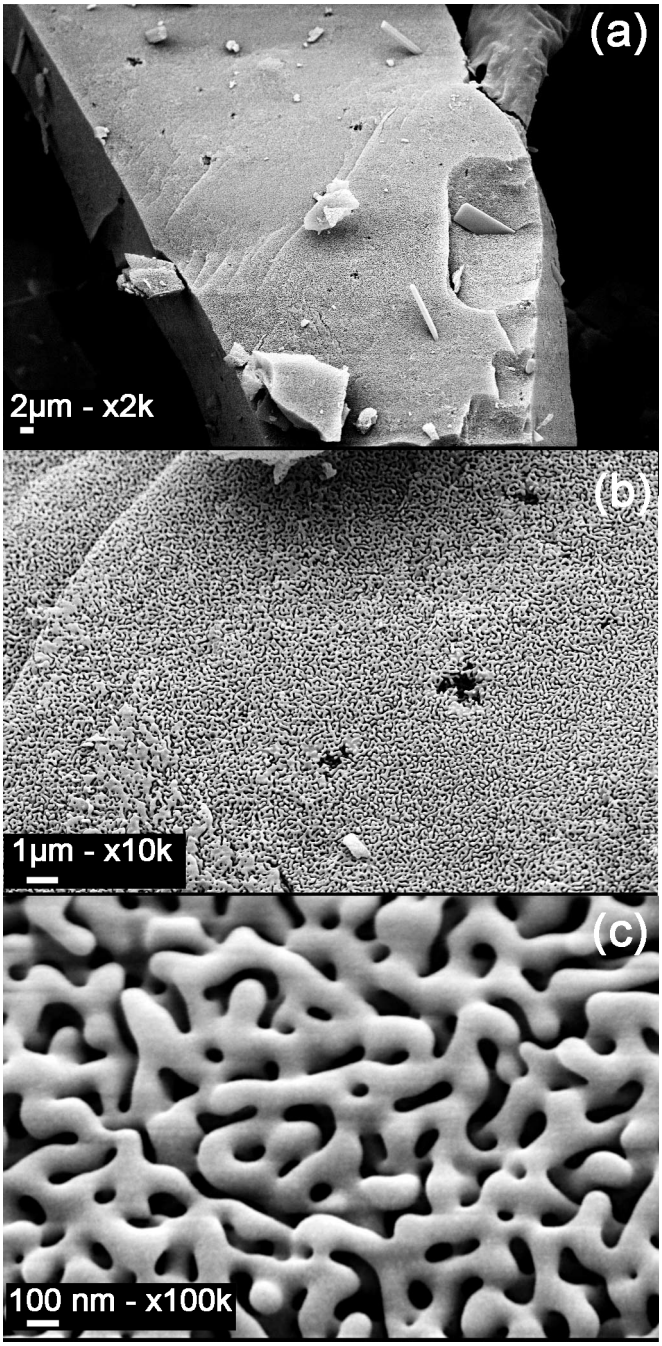

Figure SI.3 : SEM pictures of the silica sponge-like sample prepared with 50% NaF, at 60°C

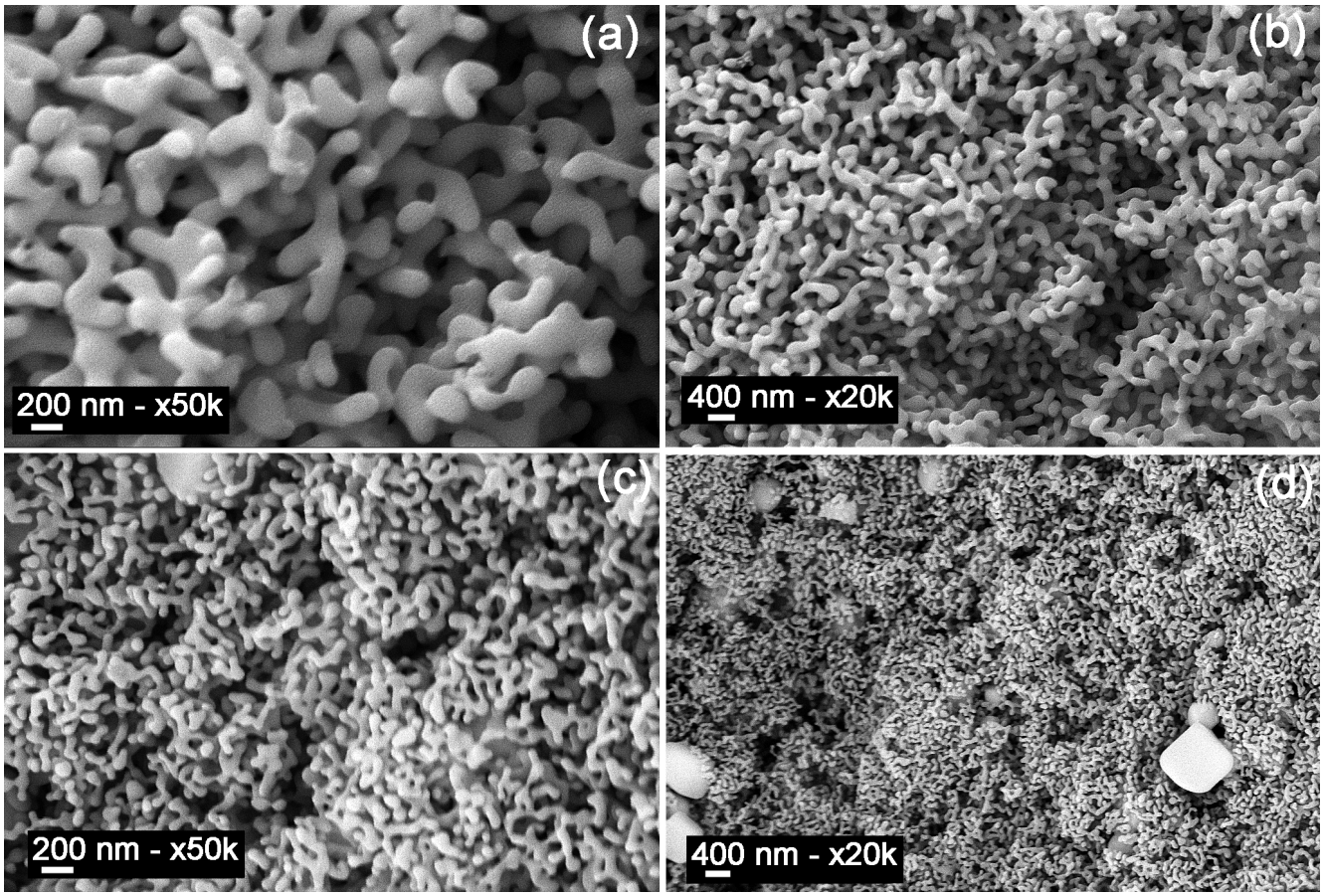

Figure SI.4: SEM pictures of the silica used for carbon replica of sample A prepared with 80% NaF and 20%NaCl (a, b), and sample B prepared with 20% NaF and 80% NaCl (c, d).

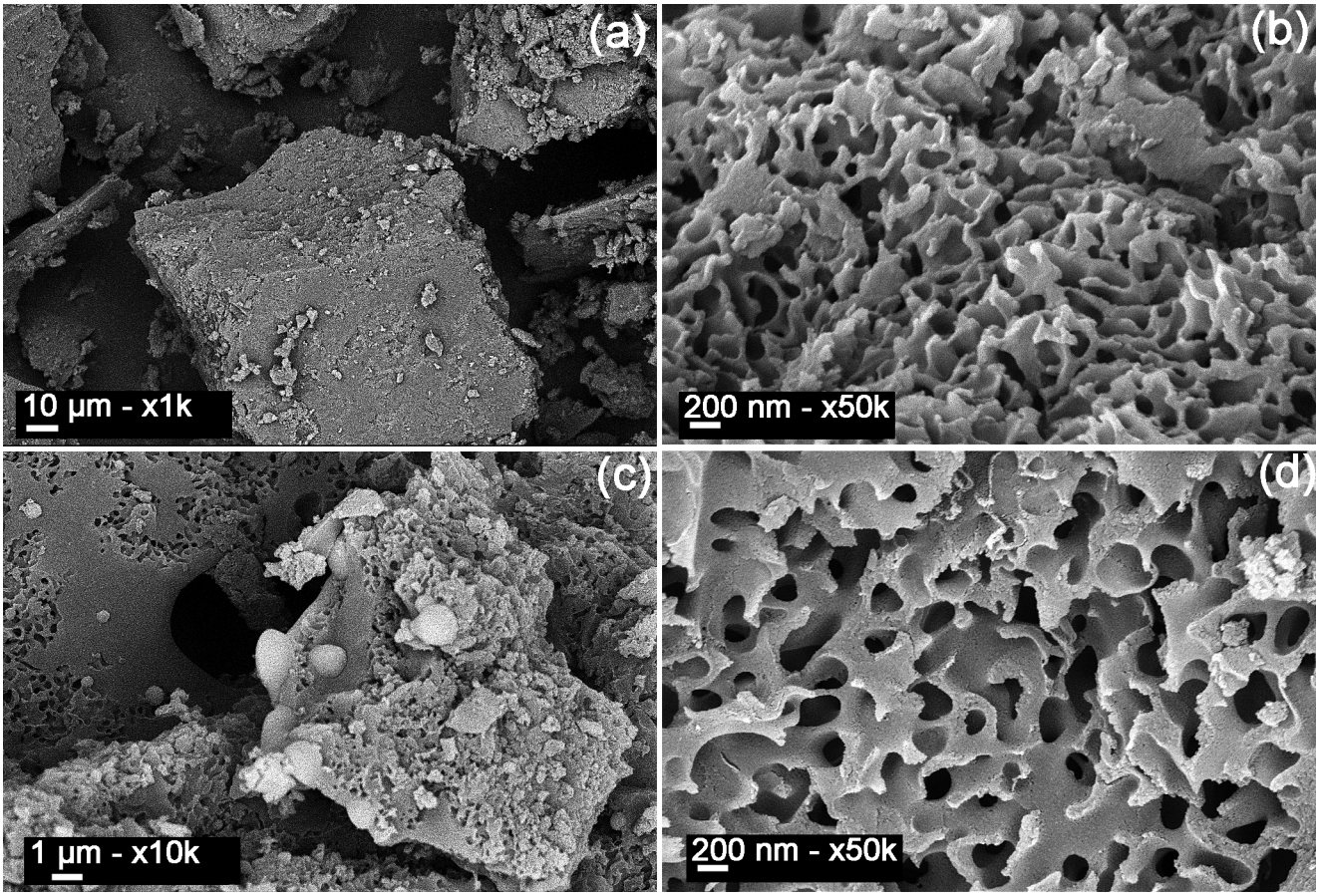

Figure SI.5 : SEM pictures of the carbon replica of sample A prepared with 80% NaF and 20%NaCl (a, b), and sample B prepared with 20% NaF and 80% NaCl (c, d).