

Supplementary Data

Impact of molar ratio of butanol, ethanol and water on the product morphology

Fig. 1 shows the morphology of the silica spheres prepared at different ratio of BuOH: H₂O: EtOH which indicates that other than the gigantic silica hollow spheres shown in the context, silica particles with curved surface and hollow spheres can be obtained, too.

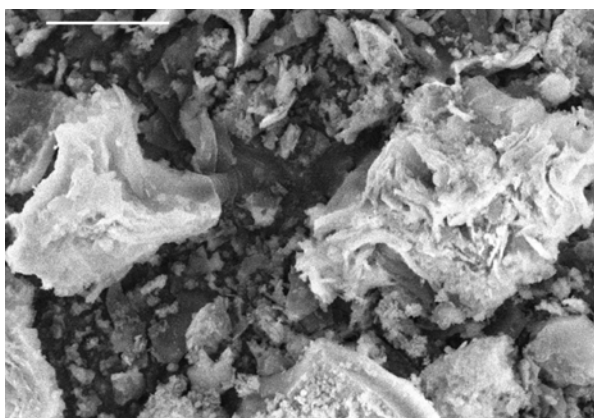


Fig. 1a SEM micrograph of as-made sample. Molar ratio of BuOH: H₂O: EtOH = 75: 25: 0 (scale bar 10 μ m)

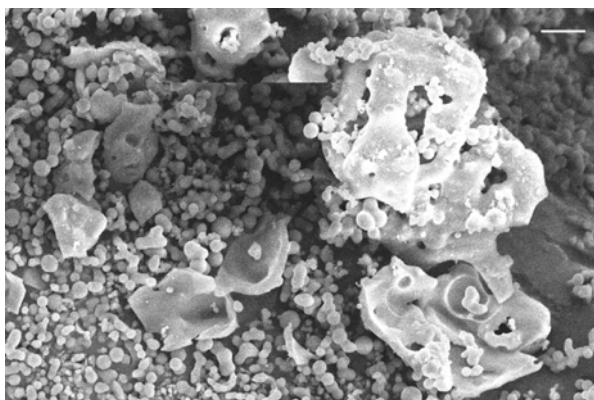


Fig. 1b SEM micrograph of as-made sample. Molar ratio of BuOH: H₂O: EtOH = 33: 33: 33 (scale bar 10 μ m)

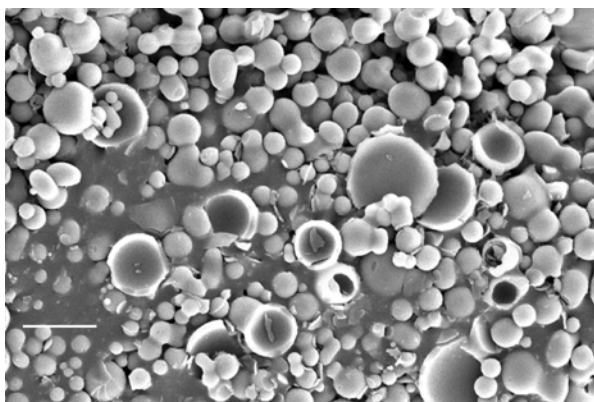


Fig. 1c SEM micrograph of as-made sample. Molar ratio of BuOH: H₂O: EtOH = 20: 60: 20 (scale bar 10 μ m)

Impact of synthesis temperature on the product morphology

Temperature is an important factor on the product morphology. At low temperature (4 °C) the condensation proceeds quite slow (picture not shown), while the sample prepared at 80 °C was composed of big particles, probably due to the fast condensation (Fig. 2).

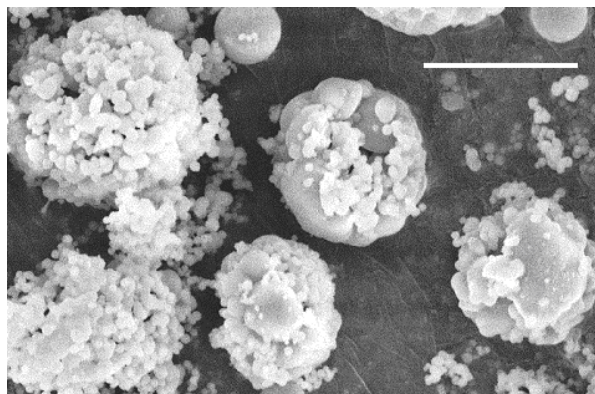


Fig. 2 SEM micrograph of gigantic hollow silica spheres at 80 °C (scale bar 10 μ m).

In-situ monitoring of the formation of gigantic hollow silica spheres by optical microscopy

The formation of gigantic silica hollow spheres was studied by optical microscopy as shown in Fig. 3. Two minutes after the addition of sodium silicate solution, small particles ca. ~ 1 μm in diameter could be observed (Fig. 3a). 30 minutes later large amount of gigantic spheres formed in size of ca. 20-60 μm (Fig. 3b). After five hours the gigantic spheres turned more opaque while the small particles almost disappeared (Fig. 3c).

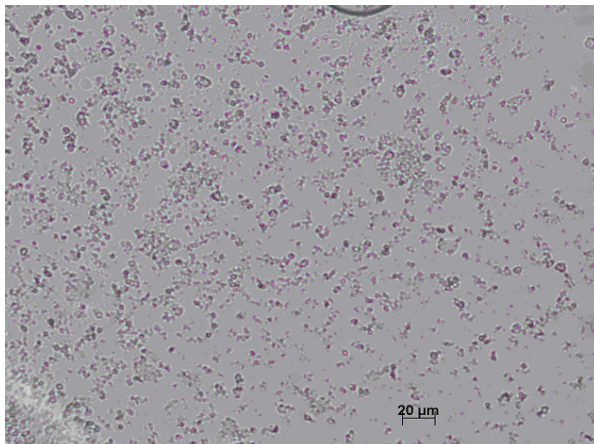


Fig. 3a Optical micrograph of as-made gigantic hollow silica spheres, 2 minutes after the addition of sodium silicate solution.

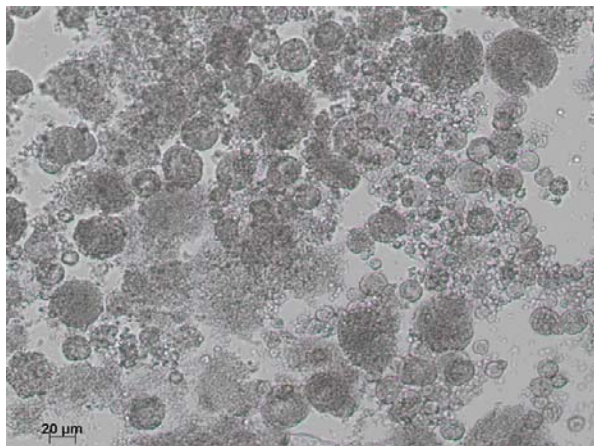


Fig. 3b Optical micrograph of as-made gigantic hollow silica spheres, 30 minutes after the addition of sodium silicate solution.

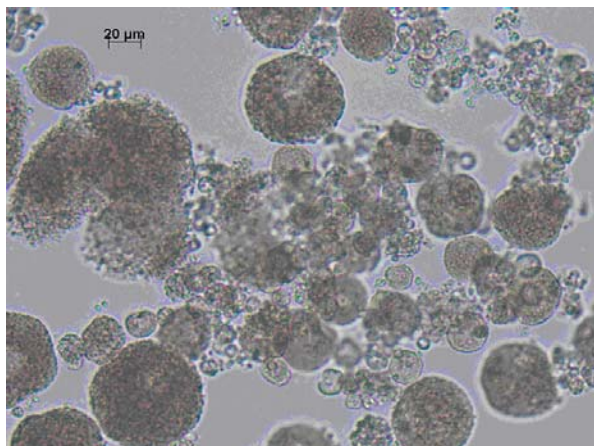


Fig. 3c Optical micrograph of as-made gigantic hollow silica spheres, 300 minutes after the addition of sodium silicate solution.

In-situ monitoring of the formation of gigantic silica hollow spheres by SAXS

The reaction was further monitored with time resolved SAXS. During the preparation of the sample cell (~ 5 min) the reaction had already proceeded so the scattering profiles remained unchanged for 4 hours except for a slight intensity change at high q region, corresponding to the consumption of nanometer-sized silica components.

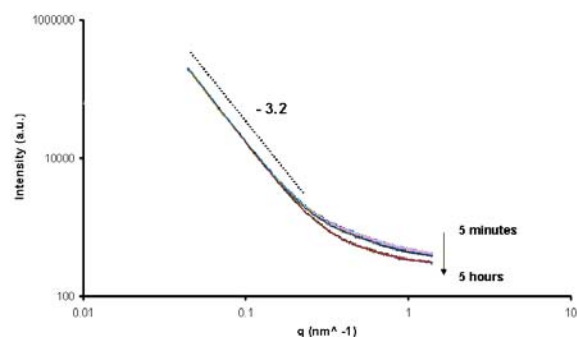


Fig. 4 *in-situ* SAXS spectra of the formation of gigantic silica spheres.

USAXS spectrum of the as-made gigantic silica hollow spheres

The as-made solid sample was investigated by USAXS using a Bonse-Hart camera, which showed a transition point at ca. 1 micron and a slope of -3.2 between the length scale of 1 micron and 30 nm that is characteristic for spheres with a roughened surface.

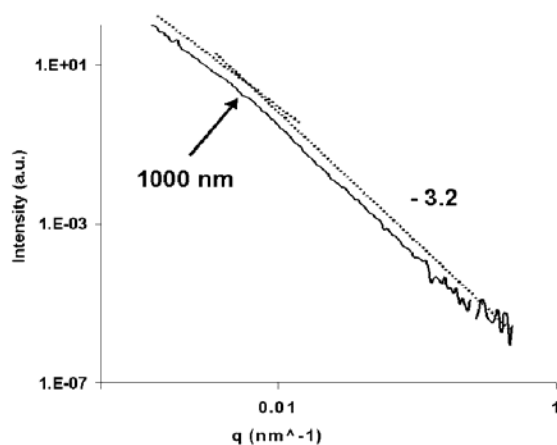


Fig. 5 USAXS pattern of as-made gigantic hollow silica spheres.