The formation of gigantic hollow silica spheres from an $\text{EO}_{76}-\text{PO}_{29}-\text{EO}_{76}/\text{butanol}/\text{ethanol}/\text{H}_2\text{O}$ quaternary system†

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Gigantic hollow silica spheres with a hierarchical intra- and inter-particle porosity were obtained from an $\text{EO}_{76}-\text{PO}_{29}-\text{EO}_{76}/\text{butanol}/\text{ethanol}/\text{H}_2\text{O}$ quaternary system, which is unique in its extremely rapid silica condensation and in the resulting hierarchical morphology.

The preparation of mesoporous silicas with controlled morphology is receiving increasing attention due to their potential applications as catalyst supports, sorbents, compartments for the storage and release of (bio)molecules, etc.1 Mesoporous materials with controlled pore structures have been prepared through templating routes making use of a variety of surfactant systems based on low molecular weight compounds2 as well as on amphiphilic polymers.3 Recently also much effort has been directed towards the synthesis of hollow silica spheres using a variety of synthetic techniques including the templating by vesicles, polymer particles, calcium carbonate nanoparticles, but also through the use of acoustic cavitation, electrically forced liquid jets and of a two-step based method.4

Previously, we have shown the fabrication of uniformly shaped silica hollow spheres with a well defined layer structure via an emulsion based templating route using the polymeric surfactant $\text{EO}_{76}-\text{PO}_{29}-\text{EO}_{76}$.5 This pluronic-type block copolymer acts not only as a stabilizing agent for the emulsion droplets, but its PEO segments also catalyse the condensation of silica on the aggregate surface. In our search for new approaches to generate well defined silica morphologies through the directed precipitation of silica we found that using a mixture of $\text{EO}_{76}-\text{PO}_{29}-\text{EO}_{76}/n$-butanol/ethanol/water led to the rapid precipitation of silica particles that assemble to form large spherical aggregates. In this communication we describe how this system can be used to generate gigantic hollow silica spheres with diameters up to tens of micrometres.

In a typical synthesis procedure,6 0.5 g of $\text{EO}_{76}-\text{PO}_{29}-\text{EO}_{76}$ was first dissolved in 25 g of deionized water, to which 4 ml of 1 M HCl was added under stirring. The copolymer solution was then added to a mixture of 75 g of butanol and 25 g of ethanol, which appeared transparent with no phase separation visible. When a diluted aqueous sodium silicate solution was added drop-wise (5 ml, 6.75% SiO$_2$, w/w) under vigorous stirring, the solution turned turbid nearly immediately and the pH value was then adjusted to 5.2 with a dilute NaOH solution (0.1 M). After 24 h of aging at room temperature (RT), the white powders were collected by filtration, washed and dried at 80 °C. The removal of organic species from the as-prepared products was achieved by calcination in air at 550 °C for 4 h.

SEM revealed that a mixture of spherical particles and big spherical aggregates of the same particles was formed (Figs. 1(a) and (b)). High magnification micrographs indicated that these spherical aggregates were composed of closely aggregated small particles, nevertheless they revealed the fusion among these particles (Fig. 1(c)) and a smooth internal surface (Fig. 1(d)). Transmission electron microscopy (TEM) performed on the calcined samples revealed that the small particles contained pores with dimensions of 3–5 nm (Fig. 2).

BET analysis revealed a type IV nitrogen physiosorption isotherm with a steep increase in nitrogen uptake at high relative pressure $p/p_0 = 0.9–1.0$ and a wide hysteresis loop at $p/p_0 = 0.1–0.9$, typical for a mesoporous solid with bigger pores (Fig. 3(a)).

† Electronic supplementary information (ESI) available: Effect of molar ratio and temperature on product morphology and in-situ monitoring of the gigantic hollow spheres by optical microscopy and SAXS. See http://www.rsc.org/suppdata/jm/b4/b413363c/  
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Fig. 1 SEM micrographs of as-made gigantic hollow silica spheres. (a) Overview, (b) a close view, (c) the fusion of the small particles, (d) the smooth internal surface. Scale bars (a) 10 μm, (b) 5 μm, (c) 2 μm and (d) 1 μm.
Indeed, the Barrett–Joyner–Halenda (BJH) method\(^7\) used to calculate the pore size distribution (Fig. 3(b), inset) indicated that the as-made samples had a bimodal pore structure: smaller pores with a diameter of 4 nm (as observed with TEM, vide supra) and bigger pores of approximately 40 nm in diameter. The 4 nm pores are typical in the bulk synthesis of silicas templated by EO\(_{76}-\)PO\(_{29}-EO\(_{76}\) and are therefore assigned to the pore structure of small particles.\(^5\) The bigger pores most probably are the voids that are left between the clustered particles (Figs. 1(c) and (d)). The MAS \(^{29}\text{Si}\) NMR spectrum (99 MHz; 45° excitation; 120 s interscan delay; 12 kHz sample rotation rate) showed that the majority of silicon coordination states were Q\(_4\) (\(\sim -110\) ppm) and Q\(_3\) (\(\sim -101\) ppm). This is surprising as it points to a relatively high degree of cross-linking, thereby suggesting a rather effective condensation during the extremely rapid precipitation reaction (Fig. 4). The as-made solid sample was further investigated by USAXS (ultra-small angle X-ray scattering). The obtained scattering curve showed a transition point at ca. 1 \(\mu\)m. This is in good agreement with the observed dimensions of the smaller particles. The observed slope of \(-3.2\) between the length scales of 1 \(\mu\)m and 30 nm (see electronic supplementary information (ESI)\(\dagger\)) is characteristic for spheres with a roughened surface and confirms the SEM and TEM analysis (Figs. 1 and 2).

The formation of these gigantic hollow spheres was monitored by optical microscopy of samples taken at different time intervals. Within only two min after the addition of the sodium silicate gigantic hollow spheres with diameters up to 30 \(\mu\)m were observed, together with a large amount of isolated silica particles with submicron sizes. In the following 5 h the small particles completely agglomerated into the larger spheres as was concluded from the fact that only the latter could still be observed (see ESI\(\dagger\)). Also SEM studies showed that in the early stages of the reaction (\(<0.5\) h) the majority of the silica was present as isolated silica particles (diameters \(\sim 300-2000\) nm), whereas 8 h later the product was composed mainly of gigantic hollow spheres with a smooth internal surface, suggesting that the fusion of silica particles is a slow process. Our attempts to monitor the reaction with time resolved SAXS were hampered by the fact that during the preparation of the sample cell (\(<5\) min) the reaction had proceeded such that the scattering profiles remained unchanged for 4 h except for a slight intensity change at high \(q\) region, corresponding to the consumption of nanometre-sized silica components. These results suggest that the smaller particles are indeed formed very rapidly during the very first stages of the reaction and that the aggregation to form the large spheres is a rather slow process that takes several hours.

The formation mechanism of such hierarchically hollow spheres is still under investigation. In the present butanol-based emulsions, the droplets are expected to be kinetically unstable and under these conditions a process of dynamic exchange of materials between the water droplets is known to occur.\(^8\) Furthermore, due to the partial miscibility of the different components in the butanol-ethanol–H\(_2\)O system the materials exchange through the interface will also...
be significant. Dynamic light scattering analysis reveals that the EO$_{86}$–PO$_{29}$–EO$_{86}$–PO$_{29}$–butanol/ethanol/H$_2$O quaternary system has emulsion-like droplets with an average diameter of 250 nm. When sodium silicate solution was titrated into the quaternary system, the size of the droplets quickly increased up to over 1000 nm in 5 min, while the silica precipitates appeared visible by the eye within half an hour. The possible mechanism maybe as shown in Fig. 5. When the silicate solution was added, the 250 nm-sized water droplets quickly swelled because of the increase of ionic strength. Silica condensed in the enlarged water droplets around the micelles of EO$_{86}$–PO$_{29}$–EO$_{86}$, an efficient silica mineralization template. The removal of the block copolymer from the interface will correspondingly reduce the stability of the droplets. Upon collision these flexible droplets can fuse with each other to form a bigger droplet (over 1000 nm) with a smaller surface area. Due to the slightly hydrophobic nature of crosslinked silica the silica nanoparticles will stay at the interface of droplets. With the reaction proceeding, the silicates that remained in the water pool will then continue to condense and gradually deposit onto these nanoparticles smoothing the internal surface of the resulting shell. As a consequence of this process big hollow spherical particles with smooth internal surfaces and shells composed of the smaller micrometre-sized particles will be formed.

In conclusion, gigantic silica hollow spheres composed of small spherical particles with smooth internal surface and a hierarchical intra- and inter-particle porosity have been fabricated using the quaternary EO$_{86}$–PO$_{29}$–EO$_{86}$–PO$_{29}$–butanol/ethanol/water system, which is unique in its extremely rapid precipitation process and in the resulting gigantic hollow sphere structures. These intriguing morphologies in a way mimic the hierarchical structure of biogenic silica in diatoms which makes them also interesting, e.g. for application as catalyst supports.

Fig. 5  Schematic representation of a possible formation mechanism for gigantic silica hollow spheres. The figure depicts the swelling and fusion of polymer stabilized aqueous droplets upon the addition of sodium silicate and the subsequent growth and fusion of silica particles at the organic–aqueous interface.

### Notes and references

6. Gigantic hollow spheres were prepared in the presence of EO$_{86}$–PO$_{29}$–EO$_{86}$ (analytical grade; Aldrich-Sigma #41 232-5) as a structure directer. The sodium silicate solution (27 wt.% SiO$_2$ 8 wt.% Na$_2$O, analytical grade, Merck) was diluted 4-fold prior to use. When the solvent composition was changed no hollow spheres were obtained. Increasing...
the reaction temperature leads to the formation of spherical aggregates with similarly large diameters, but built-up from particles with larger diameters (see ESI†).
