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One-pot aerosol synthesis of ordered hierarchical mesoporous core–shell silica nanoparticles

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A mixed surfactant approach has been successfully employed in an aerosol-based synthesis of spherical silica particles exhibiting a new core–shell structure where the shell and the core exhibit different ordered mesoporosity and pore sizes.

The synthesis of spray-dried spherical metal oxide particles exhibiting an ordered arrangement of mesopores has received a lot of recent attention.[1] Such materials have vast application prospects in fields such as catalysis, controlled drug release, separation, and energy conversion. The starting solution is normally a dilute ethanol–water solution containing an alkoxide precursor, a surfactant serving as the structure-directing agent, and an acid for controlling the kinetics of alkoxide hydrolysis and condensation. Both silica[1] and transition[2] metal oxide based systems have been prepared with this technique. The process is often referred to as evaporation induced self-assembly, EISA, because the different vapor pressures of the components of the synthesis mixture will lead to time-dependent changes in the relative ratios of the reactants during the drying stage.[1] Ethanol will evaporate at the fastest rate and the sol becomes progressively rich in surfactant, acid, water, and metal oxide precursor, leading to cooperative self-assembly into liquid crystalline phases. This aerosol-assisted EISA process was shown to be highly dependent on the carrying gas humidity and temperature.[3] Particles exhibiting a multimodal porosity can also be generated with this procedure if another means for pore generation is used in parallel. Thus, latex beads have been used as a template together with silica or titania precursors and surfactant in the preparation of aerosol particles exhibiting a bimodal porosity.[1b] Furthermore, spray drying of emulsions has also been utilized to synthesize silica particles exhibiting complex structures of interconnected pores with pore sizes up to 15 nm.[2] However, while the utilization of hard templates like latex beads or emulsion droplets is a straightforward means of preparing particles having a hierarchical porosity, the thus templated pores are either spherical or very interconnected networks of fairly large pores. To date, no means for a predictive synthesis of core–shell particles exhibiting a bimodal pore structure has been reported. Such a structure would be very beneficial for controlled drug release purposes, for example, where a high inner surface area can be combined with a diffusion controlling outer layer. Furthermore, a gradient in the composition of the structure-directing agents between the core and the shell could allow for a selective functionalization of the core and the shell.

In this communication we report a new strategy of synthesis which makes it possible to create such particles in a one-pot synthesis and which promises to be a versatile means of preparing porous core–shell particles with bimodal porosity. The synthesis is based on the use of a mixture of two surfactants as structure-directing agents, the non-ionic triblock-co-polymer F127 ($(EO)_{106}(PO)_{70}(EO)_{106}$, BASF, Germany) and the cationic fluorocarbon surfactant[4] IC-11 ($C_8F_{17}CH_2OHCH_2NH(C_2H_5)_2Cl$) synthesized in house. Ethanolic sols with a typical molar composition of F127 : IC-11 : Si : EtOH : H_2O : HCl of $5.7 \times 10^{-4} : 1.4 \times 10^{-2} : 1 : 25 : 5 : 0.18$, with tetraethyl orthosilicate as the silica source, were used. The sols were isotropic after surfactant dissolution and kept at room temperature before spraying. A previously described spray-drying setup[3] was operated with dry air as the carrying gas (≈ 0.1 dm^3 s^{-1} flux and $\approx 10^{10}$ particles dm^{-3}) and stabilisation was triggered by allowing the particle to remain for 1–2 s at 350 °C. The surfactants were removed by calcination at 600 °C for 5 h with a heating ramp rate of 1 °C min^{-1}. Perfectly spherical particles as those shown in the transmission electron microscopy, TEM, (Hitachi HF 2000, Japan) image in Fig. 1 were obtained.

The physical appearance and the structure of the inner part of the particles is similar to that previously reported for aerosol-generated F127–silica particles.[2] The inner pore diameter as estimated from the TEM image is about 8 nm. However, in addition to the pores in the inner parts of the particles, a thin membrane with a repeat distance of about 4 nm is clearly visible close to the particle surface. Keeping in mind the length of the hydrophobic parts of the surfactants used, it appears evident that the membrane is a result of the interaction between the IC-11 surfactant and silica, while the porosity in the inner parts of the particles results from an F127–silica interaction. It should be stressed that no regions with smaller pores could be found in the inner part of any particles. In Fig. 2 an X-ray diffraction (SAXS beamline, Elettra-synchrotron, Trieste, Italy) pattern of the same sample is shown.

Two low-angle Bragg reflections are observed, one corresponding to a *d*-spacing of 12.7 nm and another with a *d*-spacing of 3.8 nm. No crystallographic relation exists between the two reflections, and their position coincides with the two structures observed in Fig.

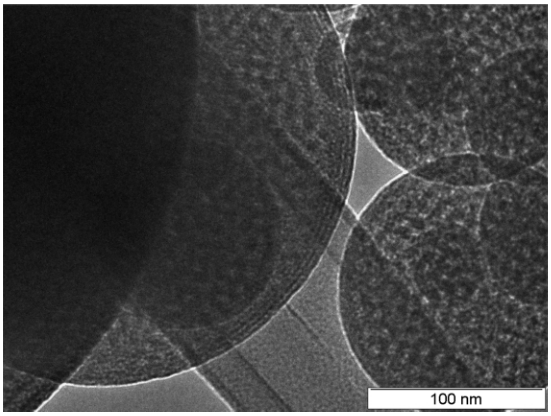

Fig. 1 TEM image of calcined spray-dried mesoporous silica particles synthesized in the presence of two surfactants. Note the thin membrane layer with a different symmetry as compared to the inner part of the particles.

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1. The intensity of the reflection appearing at about $q = 0.26\ \mathrm{nm}^{-1}$ is much lower than that of the reflection at about $q = 0.079\ \mathrm{nm}^{-1}$, since greater distances are associated with higher diffracted intensity. In addition, the membrane's diffracting planes are curved with respect to the particle surface and only a few of them seem to be composed of the diffracting domains. It should be noted that while TEM probes the local structure, XRD is a bulk technique, and the mere appearance of both structures in the XRD pattern despite the very small thickness of the membrane layer shows that the membrane is present to a large extent throughout the sample. The similar repeat distance observed by XRD and TEM could suggest that the membrane is a porous lamellar structure. However, a hexagonal phase would give a similar periodic array of stacked cylinders in the [100] direction (along the channels). An exact determination of the structure of the core cannot be made in the absence of higher order reflections in the XRD. However, lamellar planes would tend to collapse upon organic elimination. Since this is not observed by XRD or TEM, it is likely that the membrane has a hexagonal symmetry. The BET area of the core–shell particles was 390 $\mathrm{m}^2\ \mathrm{g}^{-1}$ and the pore volume 0.26 $\mathrm{cm}^3\ \mathrm{g}^{-1}$. A sharp uptake in the nitrogen sorption (Micromeritics 2010, Germany) isotherm, as shown in Fig. 3, around a relative pressure of 0.6 confirms the presence of pores with a diameter of about 5.6 nm, as determined according to the BJH algorithm from the adsorption branch of the isotherm and 6.7 nm based on the Broekhoff–DeBoer algorithm of the same branch. However, there is also an indication of another mode of pores with diameters below 4 nm, which could correspond to adsorption in smaller pores of the core. There is a large adsorption–desorption hysteresis, which is typical for non-cylindrical pore systems with a pore opening which is smaller than the inner diameter of the pore.[5] An exact determination of the pore window size based on desorption branch is not possible, since the desorption occurs at a relative pressure of about 0.42, which corresponds to the critical pressure for the instability of the meniscus of liquid nitrogen. However, one can conclude that the maximum size of the pore window in the core is about 4 nm. However, although a pronounced hysteresis would be expected for a core–shell material where the core exhibits a smaller pore size than the shell, a similar isotherm can be expected also for non-cylindrical pores with smaller pore entrances in the inner part of the material.[5] Therefore, nitrogen sorption cannot be used for an exact description of the difference in porosity between the shell and the core for the smaller mesopores, but the results are in good accordence with the results obtained by XRD and TEM. Core–shell structures are normally observed for aerosol-generated mesoporous particles, and have been ascribed to an earlier solidification of the aerosol droplet surface as compared to the inner part of the droplet.[2] However, as single structure-directing agents have been used in all previous studies, the pore size in the shell has not been reported to differ from the pore size in the bulk of the particle. Fluorocarbon-based surfactants are very surface active, resulting in very low surface-tension values ($< 18\ \mathrm{mN\ m}^{-1}$) of water for example.[6] Furthermore, phase separation has been observed at lower temperatures between hydrocarbon and fluorocarbon based surfactants.[7] A combination of a higher surface activity of the fluorocarbon surfactant micro-phase separation and solvent concentration gradient associated to the evaporation at the droplet interface may therefore be responsible for the enrichment of fluorocarbon-surfactant at the particle periphery. The structure directing agents for the pores in the core is probably a mix of IC-11 and F127 micelles, but here the longer F127 surfactant will determine the micellar diameter. However, the driving force for phase separation decreases rapidly with increasing temperature, and the absence of a bimodal porosity in the inner part of the particle can therefore be rationalized. A similar experiment performed with IC-11 and cetyltrimethylammoniumbromide, CTAB, (50 : 50 molar ratio) did not, however, lead to a similar core–shell structure as that observed for IC-11–F127, although phase separation has been observed to occur for these surfactants in solution. Therefore we postulate that the main driving force for the formation of the core–shell structure is the difference in surface activity of the surfactants in this initially highly ethanolic solution and that the effect of micro-phase separation is small. Work has been undertaken in order to verify this hypothesis.

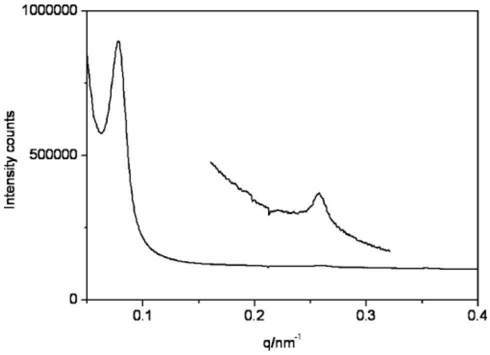

Fig. 2 Synchrotron XRD diffractogram of as-made, aerosol-generated silica synthesized in the presence of two surfactants.

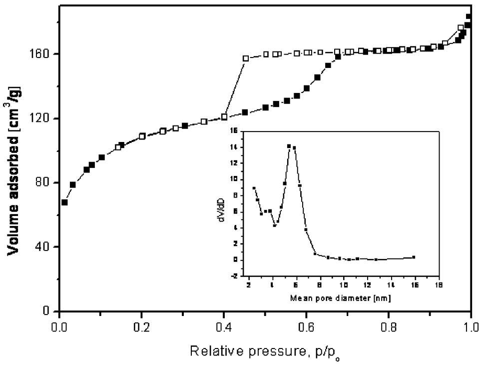

Fig. 3 Nitrogen sorption isotherm for aerosol-generated core–shell silica particles measured at 77 K. Closed symbols, adsorption; open symbols, desorption. Inset: $\mathrm{BJH_{ads}}$ pore size distribution plot.

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