New nano-architectures of mesoporous silica spheres analyzed by advanced electron microscopy

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Since the discovery of MCM materials, ordered mesoporous materials have attracted a great deal of attention from a wide research community. Each of these materials demonstrates typical pore sizes, different wall thicknesses and a specific pore arrangement. Accurate control of the morphology of these materials is one of the major issues for many applications.

Using template-containing silica micro spheres as a precursor, novel ordered mesoporous silica nanoparticles with a narrow pore size distribution and high crystallinity have been synthesized by various hydrothermal merging processes. Several architectures like chains, dumbbells, triangles, squares and flowers have been discovered. The linking mechanisms of these interacting silica spheres leading to the formation of ordered nano-structures are studied by SEM, HRTEM, HAADF-STEM and electron tomography (3D-ET). A plausible model is presented for several merging processes [1].

Spherical silica particles (SSPs) can be considered as one of the first examples of such “nano-architecture” for mesoporous materials [2]. These SSPs consist of a mixture of the MCM-48 and the MCM-41 structure, with bundles of MCM-41 growing on the surface of a truncated MCM-48 nucleus acting as the core of the SSP (Fig. 1a). These bundles grow pseudo-epitaxially and doing so translate the symmetry of the cubic facets onto the surface of the SSP. The spherical particles, although having a roughly hexagonal pore arrangement at the surface, reflect the cubic crystallographic symmetry and will preferentially merge other particles having a suitable epitaxial orientation.

HRTEM shows the merging behaviour of the SSPs (Fig. 1). A nanoparticle structure consisting of two merged SSP’s is displayed in Fig. 1b. The structure is definitely different from the anisotropic particles reported previously. The Fourier transforms (FT) taken from the two separated cores of upper and bottom SSPs show that the particles exhibit hexagonal symmetry and are oriented parallel to each other. The upper left FT (Fig. 1b) consists of two patterns, rotated 30° with respect to each other, suggesting a 30° grain boundary inside the upper SSP (see inserted filtered image). The fact that both crystal cores have a related structural orientation suggests a non-random connection mechanism between the two, in agreement with the proposed structural model of SSPs [2]. This fixed relationship between SSPs can be translated to larger structures. The formation of a quadruplet structure comprised of SSPs is displayed in Fig. 1c and provides further proof for the “cubic core” model. The quadruplet exhibits a square shape as well as a square shaped nanopore in the centre. Electron tomography results are shown in Fig.1d-h and not only confirm the combined presence of external and internal merging SSPs of various architectures, but also confirm that the angles between the merging points fit the cubic symmetry of the SSPs.

On top of the chain architectures and symmetry determined packing architectures, morphology changes to individual SSPs prior to merging can also be obtained through precise tailoring of the hydrothermal treatment. Examples of these morphology changes are displayed in Fig. 2: several SSPs can be merged into ring-shaped architectures (Fig. 2a) or into e.g. a triple-point with pores from all three SSPs running to a central surface-core at the connection point (Fig. 2b). The cores of the SSPs no longer appear to be centrally located inside the SSP spheres. The TEM images clearly demonstrate that upon merging, two SSPs display a merger of “surface-cores” (see inset to Fig. 2a). Further hydrothermal treatment leads to the formation of “flower-type” SiO2 structures, as displayed in Fig. 2c. This flower-type structure has an open morphology, with pores bundles only growing under certain crystallographic orientations, which are likely related to the MCM-48 core. This results in the absence of pore bundles in a range of ~ 30° solid angle surrounding the flower core.
The core size and the pore length of the merged surface-core are not significantly different in these SSPs from the core in standard SSPs with a central truncated cubic MCM-48 core (Fig. 1a). The only difference is that in the present example, SSP bundles did not grow equally from all facets, which points to a structural and/or surface difference in the facets from which the bundles. To explain this open flower structure demonstrating specific growth directions, we present a structural model.

References


Figure 1. HRTEM image of (a) a single SSP; (b) two connected particles, the FT of both cores and a filtered, enlarged image of the 30° boundary are given as inset; (c) interconnected nanoparticles forming a square. (d) Tomographic reconstruction of the spherical particles. Slices through the tomographically reconstructed volume (orthoslices) showing two linearly attached particles ((e) & (f)), a triangular formation (g) and a surface-core connection (h).

Figure 2. HRTEM images of different nanoparticle architectures. In (a) and (b), the particles demonstrate the presence of outer connections through a surface-core. Particles connected into a ring-type structure are visible in (a) while particles forming a triple point connection can be seen in (b). In (c) flower-type structures have formed.