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Nanoparticle Shaping

Shaping Mesoporous Silica Nanoparticles by Disassembly of Hierarchically Porous Structures**

*Fan Li, Zhiyong Wang, and Andreas Stein**

Self-assembly is a simple but efficient way towards 3D nanostructured materials with different morphologies. One example involves the fabrication of opal-like colloidal crystals through the natural assembly of monodisperse latex spheres that form close-packed arrays with interconnected voids.[1] By using such colloidal crystals as templates, inverse opal structures can be produced.[2] During this process, the structural ordering of the close-packed monodisperse spheres is inherited by a three-dimensionally ordered macroporous (3DOM) structure, which is a replica of the void space in the opal crystal. As the voids in the opal lattice are also highly ordered, one can consider the resulting 3DOM skeleton to be constructed from certain basic building blocks. This consideration suggests a new strategy towards nanoparticle synthesis, namely the disassembly of 3DOM materials to prepare monodisperse nanoparticles with predefined morphologies. Herein, we report the implementation of this strategy for the synthesis of mesoporous silica nanocubes and their carbon or polymer replicas whose shapes and sizes are solely determined by a colloidal crystal template.

Silica nanoparticles with mesoporosity are of great interest owing to their potential applications in enzyme encapsulation,[3a] drug delivery,[3b] and as cell markers.[3c] They can also serve as basic building blocks for hierarchical porous structures[4a] and as hard templates for porous structures with other compositions.[4b,c] Typically, their preparation involves spontaneous nanoparticle growth with supramolecular templating in which nanoparticles are formed by emulsion reactions,[5a] quenching,[5b] or confinement within micelles,[5c] whereas mesophases are realized by templating with surfactants or block copolymers.[6a] Because these methods involve complex interactions between precursors and surfactant templates, process optimization to obtain discrete and monodisperse products can be challenging. Monodispersity can be destroyed by particle aggregation, which diminishes the benefits of nanoscopic sizes.[5a] Furthermore, although different morphologies have been observed for the resulting materials,[5b,6] little shape control has been achieved owing to the amorphous nature of silica. In the synthesis presented herein, a silica skeleton with hierarchical porosity was first formed through a surfactant and polymer sphere dual-templating system. The three-dimensionally ordered structure was then disassembled to obtain a bimodal dispersion of silica nanocubes and nanospheroids whose specific shapes and sizes were dictated by the colloidal crystal template. This approach can be quite versatile, and by choosing specific templates, nanoparticles with different morphologies may be obtained.

Monodisperse poly(methylmethacrylate) (PMMA) spheres were synthesized by emulsion polymerization and assembled into ordered colloidal crystal templates with a largely face-centered cubic (fcc) structure.[7] An aqueous mixture of nonionic surfactant (Brij 56, $C_{16}EO_{10}$), tetraethyl orthosilicate (TEOS), and oxalic acid was infiltrated into the template (see the Supporting Information). Brij 56 forms a lyotropic liquid-crystal phase, which, in this case, served as the structure-directing agent for the mesostructure.[8] This mesophasic precursor mixture infiltrated and adopted the shape of the interstitial space between PMMA spheres after gelation. Similar dual-templating syntheses employing both polymer sphere templates and surfactants have previously been used to create hierarchically structured silica with both macropores and mesopores.[9] However, in our experiment, after the decomposition of the template during calcination at 550 °C, a further structural transformation (disassembly) occurred and a bimodal dispersion of silica nanoparticles ($\approx$119 nm and 55 nm) was obtained (Figure 1a). The larger particles have a

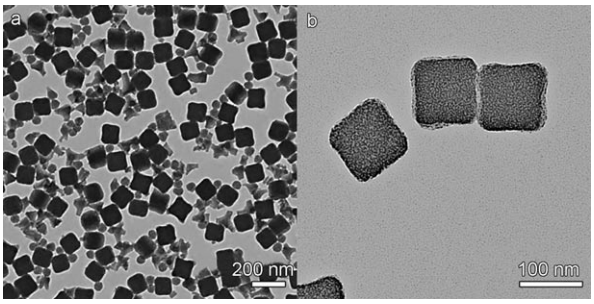

Figure 1. a) TEM image of the bimodally dispersed silica particles prepared through disassembly of 3DOM silica. A few replicas of the tetrahedral holes are visible among the smaller particles, although a larger fraction of these particles have transformed to more spherical shapes. b) A higher-magnification view of the monodisperse silica nanocubes produced from the octahedral holes after centrifugation. Wormholelike mesoporosity can be clearly seen.

[*] F. Li, Z. Wang, Professor A. Stein
Department of Chemistry
University of Minnesota
Minneapolis, MN 55455 (USA)
Fax: (+1) 612-626-7541
E-mail: stein@chem.umn.edu

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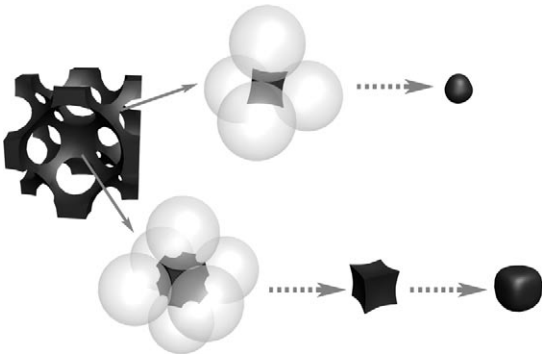
cubic shape and can be separated through density-gradient centrifugation (Figure 1b).

The disassembly process is illustrated in Scheme 1. In an fcc array of spheres, octahedral (O_h) and tetrahedral (T_d) voids exist between the spheres with a theoretical ratio of 1:2



Scheme 1. Illustration of the disassembly of the 3DOM structure.

(O_h/T_d). The silica precursor infiltrated these voids and formed an inverse replica of the template. So correspondingly, the 3DOM structure can be considered to be built up from these two basic units (O_h and T_d), which are interconnected through narrow necks. The disassembly occurs first by thinning of the necks, followed by complete disconnection of the skeleton at the narrowest connection points. Hence the two types of basic units were obtained as discrete nanoparticles. Later, these units gradually developed into cubic and spheroidal shapes to minimize their surface-to-volume ratios.

The relative sizes of the PMMA spheres and the synthesized bimodal particles can be calculated from a simplified model (see the Supporting Information), in which the PMMA phase is considered to be an assembly of hard spheres that do not deform, and the volume of the silica phase is conserved after the disassembly of the 3D skeleton. Based on this calculation, the ratios of the polymer sphere diameters, the edge lengths of the larger silica cubes, and the diameters of the smaller silica spheres would be 1:0.511:0.368 (PMMA/O_h/T_d)

This proposed transformation was evaluated by scanning electron microscopy (SEM) image analysis. An SEM image of 1670 particles showed a number ratio of larger cubes (O_h) to smaller spheroids (T_d) of 533:1137, that is, relatively close to the theoretical ratio of 1:2 (see the Supporting Information). The particle size ratios determined by SEM were PMMA/O_h/T_d = 1:0.327:0.151. Although the PMMA sphere deformation was not considered in the above calculation, this ratio still indicates quite a large volume reduction during the calcination, confirming that shrinkage occurred during the disassembly process. The spheroidal particles exhibited more shrinkage than the nanocubes. This can be explained by the fact that the tetrahedral unit, with half the number of necks of the octahedral unit ($T_d = 4$; $O_h = 8$), has only one-fifth the volume of the octahedral unit and as such, greater relative shrinkage is not unexpected for the tetrahedra. The sizes of the mesoporous silica particles correlated linearly with the diameters of the PMMA spheres (see the Supporting Information). Therefore, direct particle size control is easily achieved through the choice of template dimensions.

This special morphological transformation is attributed to the rapid condensation between remaining silanol groups. When two Si–OH groups are replaced by one Si–O–Si bond, the average atomic distance is reduced in the local structure. Overall, this effect results in a structural contraction to minimize the surface-to-volume ratio and the total free energy.[10] Typically, this causes sintering effects between silica gel particles with nearly spherical shapes.[11] However, the 3DOM structure, as an inverse replica of the sphere array, has a very large internal surface area of negative curvature, a very unstable situation, and it can easily be subject to a large contraction upon calcination. Under the appropriate conditions (those used for syntheses of 3DOM materials), the extensive three-dimensional interconnectivity of the 3DOM structure and, to some extent, the hindering effect from the PMMA template residue, allow the extended skeleton to remain intact. When the contraction exceeds a certain limit, the 3DOM structure can no longer be maintained and breaks down at its weakest points. Thus a disassembly process occurs as illustrated in Scheme 1. In comparison, template removal by toluene/ethanol extraction results in a typical 3DOM material (see the Supporting Information).

An aging step (at 50 °C) between infiltration and calcination is critical for the disassembly process. For short aging times (< 3 h), no structural transformation occurs. The resulting material has an opalescent appearance and a typical 3DOM structure is produced (Figure 2a). Partial disassembly is observed in samples aged for a few hours but less than two days (Figure 2b). Complete disassembly could be achieved after calcination with virtually no remaining 3DOM structure only after a sufficient time of aging (at least 48 h; Figure 2c). ^{29}Si magic-angle spinning (MAS) NMR spectra (Figure 3) show that this behavior is related to the difference in the degree of condensation. Initially, the silica phase contained primarily Q^2 and Q^3 sites (silicate tetrahedra condensed through two or three oxygen bridges, respectively, with two or one hydroxy groups remaining), whereas the fraction of Q^4 sites (completely condensed silicate tetrahedra) increased

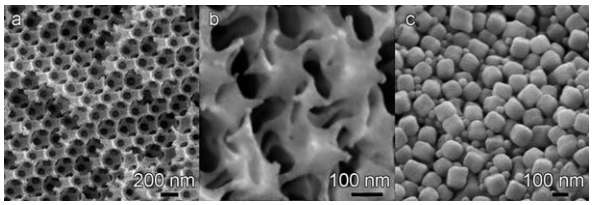


Figure 2. a) 3DOM silica structure of the sample calcined immediately after infiltration of the colloidal crystal template. b) Intermediate structure with incomplete disassembly from a sample that had been aged for approximately 6 h after template infiltration. c) A fully developed sample after disassembly in which both cubes with rounded corners and smaller, near-spherical particles coexisted in a ratio of approximately 1:2. This sample had been calcined after it had aged in the template for 48 h.

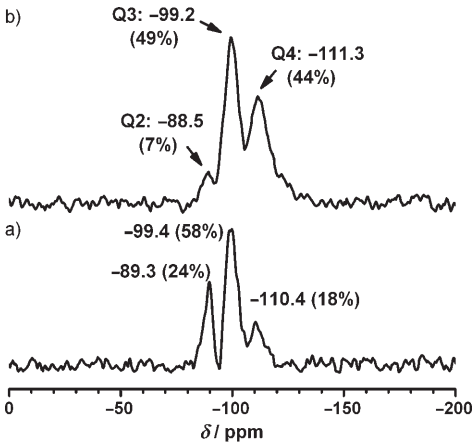


Figure 3. ^{29}Si MAS NMR spectra of a PMMA/precursor composite sample characterized immediately after infiltration of the colloidal crystal (a) and a sample characterized after aging for 48 h in the colloidal crystal (b).

significantly after aging. These data suggest that the disassembly requires both a relatively high degree of condensation to form a more rigid network and a significant number of hydroxy groups remaining. Without sufficient condensation, contraction forces during calcination are evenly dissipated, whereas a more rigid network ensures that forces can accumulate sufficiently to break the weakest points in the structure, that is, the necks.

Furthermore, oxalic acid is essential as a catalyst for the disassembly process. Much weaker morphological transformations were observed when a stronger acid (HCl) was employed under the same conditions. As a weak acid, oxalic acid may provide a lower but longer-lasting acidic environment owing to a low degree of dissociation.[12] Thus, it may influence the silicate network by controlling the condensation rate. In fact, it has been used as a drying-control chemical additive to prevent cracking during the preparation of sol–gel glasses. It sharpens micropore size distributions during drying so that capillary forces are reduced and spread more evenly.[13] Furthermore, although no chemical bonding between oxalic acid groups and the silicate network was detected by ^{29}Si MAS NMR spectroscopy, the oxalic acid can remain within the templated material in solid form before subliming at higher temperatures. It is likely that its presence may separate some internal silanol groups and preserve bonding possibilities for condensation at a higher temperature. This may also facilitate the disassembly as it is a thermodynamically favorable but kinetically demanding process.

Aggregation is a major problem in syntheses of silica nanoparticles. It occurs largely by condensation of silanol groups on the surface of individual particles.[4a,14] In our synthetic route, hydrolysis and condensation proceed within the confinement of polymer spheres. At the stage when polymer spheres disappear and discrete nanoparticles form by disassembly of the 3DOM structure (calcination at 550 °C), drastic dehydration has eliminated most silanol groups[11] so that particle aggregation becomes much less likely.

The incorporation of mesoporosity is evident from TEM, which reveals wormlike pores (Figure 1b). The small-angle X-ray scattering pattern shows only one reflection peak corresponding to a *d* spacing of 4.2 nm, indicative of a lack of long-range order (see the Supporting Information). This absence of mesophase ordering indicates that the specific shape of the nanoparticle was not induced by the crystalline mesostructure as observed before,[6a,b] and further confirmed the templating–disassembly mechanism. The mesoporosity within the silica nanocubes was characterized by N_2 sorption. A reversible type-IV isotherm with a sub-step at low pressure was observed (see the Supporting Information). A BET surface area of $1018\,m^2\,g^{-1}$ and a mesopore volume of $0.624\,cm^3\,g^{-1}$ were calculated from the desorption branch. Despite the drastic morphological change, the mesoporous structure was preserved during this process, consistent with previous observations that surfactant-templated mesopores can survive up to 1000 °C.[15]

Complete replication of the mesoporous silica nanocubes by both carbon and PMMA was achieved and could expand the range of possible applications (Figure 4). The carbon replica was prepared through a chemical vapor deposition

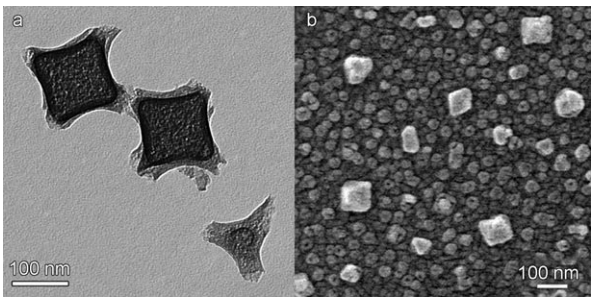


Figure 4. a) TEM image of carbon replicas of the mesoporous silica nanoparticles prepared by CVD of a phenol-formaldehyde resin. b) SEM image of PMMA replicas of the mesoporous silica nanoparticles prepared by in situ polymerization of MMA monomers. The larger cubes are the replica particles supported on an etched silicon surface.

technique modified from that of Lee et al.[16] A vapor mixture of phenol and paraformaldehyde was deposited in the mesopore channels within $AlCl_3$-pretreated nanoparticles and polymerized there. The resulting phenolic resin was carbonized by heating in nitrogen at 850 °C. The PMMA replication was realized following work by Sozzani et al.[17] MMA monomer liquid was infiltrated into the mesopores under reduced pressure and polymerized in situ with heating for 24 h at 80 °C. In both cases, silica was finally removed by HF etching. These two distinct methods demonstrated the versatility of the mesoporous silica nanocubes and the other fragments as hard templates for different compositions.

In summary, mesoporous silica nanocubes and spheroids were prepared based on the disassembly of ordered hierarchically porous structures. The degree of silica condensation determined the morphological transformation and oxalic acid played a key role in this process. The facile hard-templating strategy provided vigorous control over shape and size and

minimized the agglomeration effect common in traditional hydrothermal syntheses. Moreover, the "bottom-up and top-down" strategy represented by the combination of colloidal crystal templating and disassembly of the 3DOM structure brings new insight into nanoparticle synthesis, greatly extending the capability for functional material design. Based on polymer templates with different shapes or packing patterns, it may be possible to prepare more complicated and specific nano-objects for a wide range of applications. As this structural transformation is an intrinsic property of the 3DOM structure, we believe it may also be extended to other 3DOM materials under appropriate conditions. The exploration of different structural features with a variety of materials is under investigation.

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