Porous Solids from Rigid Colloidal Templates: Morphogenesis**

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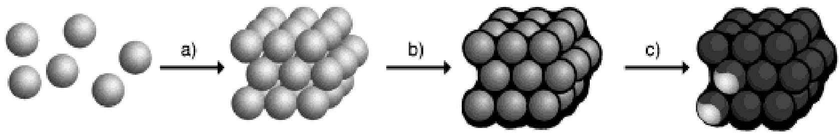
The creation of nanoporous inorganic and organic solids through the exploitation of colloidal objects as templates is a new development in materials science which recently has been receiving great attention and coverage in top-rank journals. The reasons for this trend are obvious: To generate novel materials with improved properties, modern research is increasingly focusing on structuring matter on a nanometer-length scale rather than producing molecularly new species. The formation of porosity on the length scale of a few nanometers is a comparably simple method of creating new properties in old—that is, chemically well known—materials. Furthermore, the exploration of "nanospace" possesses an undeniable aesthetic attraction.

In modern approaches towards porous ceramic nanostructures, surfactants are used to stabilize the interface between inorganic and organic matter; therefore they are superbly suited as structure-directing porogens. The synthetic pathways[1, 2] are now sufficiently understood to allow predictable production of a large variety of inorganic pore systems. This is not always the case for organic porous polymer gels, as the principle of casting the "soft" amphiphile template into an organic polymer gel fails. The dimension of organic pore systems prepared in organized surfactant media is all too often located on the length scale of microns instead of a few nanometers. The successful synthesis of porous organic polymers from supramolecular assemblies has been reported for polymerizable surfactants,[3] but the templating mechanisms here are far more complicated and sensitive to phase disruption than in the case of inorganic mesoporous nanostructures: Nanostructured polymers are difficult to make by direct templating of supramolecular aggregation structures. The often observed structural phase changes result mainly from macroscopic demixing, because the amphiphile aggregate structure is too soft.

This simple conclusion leads to an equally simple consequence, namely, the use of rigid colloidal templates, where solid objects of nanoscale dimensions act as structure-directing media. Besides structural integrity throughout the polymerization process, the main prerequisite for a successful templating of a "colloidal crystal" (i.e., the ordered arrangement of particles) is the sufficient compatibility of the template with the polymer precursor. Individual compatibility problems can even be addressed by adding amphiphiles or cosurfactants to stabilize the resulting interface. In this context the use of organic colloidal templates (i.e., polymer latex spheres) has particular potential, because modern heterophase polymerization techniques allow the synthesis of latices of almost any size and with a rich variety of surface functionalities.

The general method of rigid-colloid templating occurs in three stages (Scheme 1), namely, the assembly of nanosized spherical objects into a more or less regular array (a), filling the interstitial volumes of this colloidal crystal with a precursor mixture and polymerization (b), and finally removal of the template (c). In contrast to classical procedures, rigid colloidal templating can be applied to the synthesis of inorganic and organic polymers (IP and OP); inorganic as well as organic templates (IT and OT) can be used to prepare ordered porous solids.



Scheme 1. The synthesis of porous solids from rigid colloidal templates occurs in three steps: a) assembly of colloidal particles into a regular array, b) impregnation of template with monomer(s) and polymerization, and c) removal of the template.

The most regular pore systems are produced by the OT–IP approach. Here the interstitial volumes within a layer of monodisperse, densely packed, polymer latices (between 0.2 and 1 μm in diameter) are filled with a siliceous sol–gel precursor, which solidifies there.[4] The colloidal crystal is obtained by simply densifying a latex dispersion on a filter membrane. Since in the OT–IP approach the templating colloidal crystal is not intrinsically compatible with the growing inorganic polymer, it is necessary to create compatibility by adsorbing a surfactant layer on the template surface. A similar approach has been reported for the synthesis of other porous ceramic oxides.[5, 6] Here the crystallization of monodisperse latex spheres is achieved by pouring a latex

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dispersion through a paper-covered filter funnel, where it forms a colloidal crystal. The sol–gel synthesis of titania, zirconia, and alumina within this polymer layer produces a 1:1 cast of the latex assembly. The macropore size is directly related to the diameter of the latex particles used to displace the growth of the inorganic ceramic oxide, commonly between 300 and 400 nm. Achieving compatibility by an additional surfactant is not necessary, as the alcohol formed by the hydrolysis of the ceramic precursor sufficiently mediates between the two materials. This procedure works equally well for the templating of synthetic poly(styrene) opal, which after removal of the organic matter leaves a "crystal of air spheres" in titania.[7]

But how about using the rigid templates for the generation of organic nanostructures? In addition to structural integrity and compatibility, a further prerequisite to be fulfilled by a suitable template is its facile removal from the organic polymer. And if an organic template can be removed from an inorganic cast, an inorganic template must surely be separable from its organic replica. Indeed, the principle of the rigid colloidal template can be reversed: The production of a cross-linked polymer within the continuous, three-dimensional pore system of a suitable mesoporous silica object (IT–OP) and subsequent dissolution of the inorganic matrix with hydrofluoric acid affords the organic polymer replica without any detectable loss of order.[8]

The most recent development in colloidal templating, however, is the use of silica spheres as templates for the generation of porous organic polymers.[9] In analogy to the crystallization of latex spheres, monodisperse silica particles can be assembled into colloidally crystalline pellets. Slight sintering of the pellet causes the nanosized spherical entities to partially sinter and fuse, thus rendering additional stability to the template. The impregnation of this inorganic template with a mixture of monomer and radical initiator preserves its structure as an organic cast. By this route, it is possible to create rigid as well as flexible porous polymers with pore diameters between 15 and 35 nm. The pore size can be chosen freely through the appropriate chemical composition of a copolymer, because the extent of shrinkage of each copolymer depends linearly on the monomer fraction. Although the control over the pore size is reliable, it is only given for a particular chemistry: Not all monomers will show exactly the same behavior, so that either the chemical composition of the polymer or the pore size can be chosen freely. However, having mapped a master curve, there is a high degree of control of surface functionality and pore size.

By using the OT–OP route, three-dimensional porous poly(urethane) membranes with pore diameters around 0.5 μm are obtained by filling the voids between densely packed poly(styrene) particles with a photocurable prepolymer.[10] Photopolymerization and subsequent dissolution of the template affords a highly ordered porous polymer film consisting of a three-dimensional network of spherical pores interconnected by circular "windows": Such films are promising candidates for separation processes and are discussed in context with photonic devices.

Finally, reproduction of the three-dimensional periodicity of colloidally crystallized silica spheres (opal) in nonpolymer solids has been reported.[11] Here the production of regularly structured porous carbon morphologies (glassy carbon, graphite, and diamond) was achieved by either steeping the inorganic matrix in a precursor or by chemical vapor deposition (CVD) and subsequent heat treatment. As in the IT–OP approach, the inorganic template can be removed by extraction.

One drawback of rigid colloidal templating may be the fact that only spherical pores can be generated, as the controlled synthesis of nonspherical nanoparticles and their colloidal crystallization is not sufficiently established. Also, the connectivity of these pores cannot be adjusted in order to provide individually designed diffusion pathways. Nevertheless, templating of rigid colloidal aggregates is a versatile alternative for the generation of meso- and macroporous solids, whenever soft amphiphilic aggregate structures fail to do their job.

So far, the main objective of rigid-colloid casting has been morphogenesis, the preparation and utilization of a novel template in order to address still existing problems of porous nanostructure design. Now the question arises: "what now?". In this context it is to be hoped that the application-orientated future of these beautiful structures is not going to let us wait long. There is a vast number of potential applications ranging from robust catalysts and supports over size- and shape-selective membranes to photovoltaic devices. These materials are the first template-synthesized nanostructures with periodicities in the range of optical wavelengths and are therefore promising candidates as photonic crystals.[12]

Scientists have established this inventive, simple, and very successful methodology of shaping matter, and this is the time to address the technological aspects and to bench-test the many predicted uses of the "porous nanostructure". The author has the pleasure of looking forward to finding this documented in top-rank journals soon.

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