Research News

Structured Porous Materials via Colloidal Crystal Templating: From Inorganic Oxides to Metals**

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The formation of nanostructured materials by using colloidal crystals as templates is a relatively new but rapidly growing area of materials science. Colloid crystalline templates are three-dimensional close-packed crystals of submicrometer spheres, whose long-ranged ordered structure is replicated in a solid matrix, to yield materials with ordered pores. These materials hold promise for use as photonic crystals, advanced catalysts, and in a variety of other applications. Here we review the wide range of materials that have been made following the original synthesis of structured porous silica. This method has been recently modified to produce porous metals.

1. Introduction

Materials with spatially ordered features on the nano-meter scale have current and future potential applications in optical information processing and storage, advanced coatings, catalysis, and other emerging nanotechnologies. Colloidal crystals are a promising class of such materials formed via self-assembly of particles ranging in size from nanometers to micrometers into crystalline arrays. This long-range ordering of the colloidal particles results in a number of distinctive and potentially useful characteristics such as optical diffraction and photonic bandgaps, maximal packing density, and high surface/volume ratio. However, dried colloidal crystals are very brittle and may disperse in water. Any practical device thus requires that the crystal either be fixed in place or replicated by another more ro-bust material. Indeed, Nature's opals are an example of "fixing", whereby a colloidal crystal of silica spheres is made into a solid material after the voids between the par-ticles are infiltrated by hydrated silica.

A variety of structures similar to natural opals have been synthesized recently. One approach for creating novel ma-terials, highlighted here, is to replicate the colloidal crystal structure in a durable matrix. In this method, the colloidal crystals serve as templates, with the voids infiltrated by ma-terial that solidifies in place without disrupting the order of the crystal. The original colloidal particles are subsequently

removed, leaving behind a new type of material whose pores preserve the most valuable property of the colloidal crystal, namely its long-ranged periodic structure (Fig. 1).
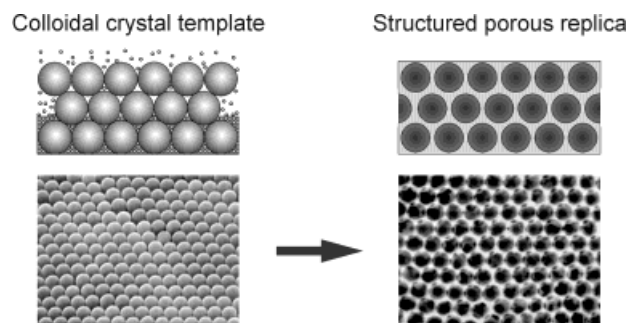

Fig. 1. Schematic of the replication of colloidal crystal structure into porous materials.

2. Basics and Modifications of the Colloidal Crystal Templating Method

The method has by now been used to make porous mate-rials from a wide variety of precursors and templates. A summary of the different modifications is given in Table 1. Our procedures for forming porous silica or porous gold il-lustrate the methods; Figure 2 shows the schematic outline.

Synthesis of porous silica was the first example of artifi-cial replication of a colloidal crystal by a stable and durable silica matrix.[1] The templates are formed by filtering a dis-persion of latex particles (diluted to 0.1 vol.-%) slowly through a smooth polycarbonate membrane. As the parti-cles concentrate above the membrane, they crystallize, and the crystal grows outwards as new particles are brought to its surface by the incoming flux. The latex layer is then

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Table 1. Summary of the published methods for synthesis of porous materials via colloidal crystal templates (in approximate order of appearance).

Material	Infused via	Template	Assembled via	Removed by	Reference
SiO_2 (Silica)	Surfactant induced polymerization	Polystyrene latex	Filtration	Calcination	Velev et al. (1997, 1998) [1]
TiO_2 (Titania), ZrO_2, SiO_2	Sol-gel hydrolysis	Oil emulsion droplets	Centrifugation	Calcination	Imhof and Pine (1997) [2]
TiO_2, ZrO_2, Al_2O_3, zeolites, many others	Hydrolysis	Latex	Filtration or centrifugation	Calcination or dissolution	Holland et al. (1998, 1999) [5]
TiO_2	Hydrolysis	Latex	Centrifugation	Calcination	Wijnhoven and Vos (1998) [6], Yin and Wang (1999) [22]
Polyurethane	UV induced polymerization	Latex	Deposition in a thin cell	Dissolution in toluene	Park and Xia (1998) [7], Gates et al. (1999) [8]
Polymers – DVB, EDMA, PMMA, etc.	Heat or UV induced polymerization	Silica microspheres	Drying, pressing	Dissolution in HF	Johnson et al. (1999) [9], Jiang et al. [23]
SiO_2, Nb_2O_5, TiO_2, ZrO_2, WO_3, etc.	Hydrolysis	Surfactant assemblies, latex, PDMS mold	Filling of mold channels	Calcination	Yang et al. (1998) [11]
Graphite, glassy carbon, diamond	Pyrolysis, chemical vapor deposition	Silica	Sedimentation, drying, sintering	Dissolution in HF	Zakhidov et al. (1998) [10]
Semiconductor CdSe nanocrystals	Particle infusion	Silica	Sedimentation, drying, fusion	Dissolution in HF	Vlasov et al. (1999) [12]
TiO_2, SiO_2	Particle infusion	Latex	Sedimentation, drying	Calcination	Subramania et al. (1999) [13], Subramanian et al. (1999) [13]
NiO, Metallic Ni	Salt precipitation, H_2 reduction	Latex	Centrifugation	Calcination	Yan et al. (1999) [14]
Ni, Cu, Ag, Au, Pt	Seeding, electroless deposition	Silica	Deposition in vertical film	Dissolution in HF	Jiang et al. (1999) [15]
Au	Particle infusion	Latex	Filtration	Calcination or dissolution in $CHCl_3$	Velev et al. (1999) [16]
Semiconductor CdSe and CdS	Electrodeposition	Latex, silica	Sedimentation	Dissolution in toluene or HF	Braun and Wiltzius (1999) [18]

washed with a solution of cationic surfactant, which makes the method insensitive to the type of the latex used. In particular, either positively or negatively charged microspheres can be used to make templates. After this washing, the cavities between the particles are mineralized by infusion with 0.5 M aqueous solution of $Si(OH)_4$, and polymerization is initiated by the surfactant. Finally the latex/silica composites are dried, and calcined at 450 °C. The organic components of the material burn out during calcination, leaving behind porous low-density silica flakes.

Scanning electron microscopy (SEM) reveals large three-dimensional ordered arrays of spherical cavities, which are organized in monocrystalline domains with different orientations. The domain organization of the original colloidal crystal is repeated both on the surface and throughout the bulk (Fig. 3a), so the material is a negative replica of the crystal template. Hexagonal arrays (corresponding to randomly stacked hexagonal close-packed planes, rhcp, and face-centered cubic, fcc, packing) predominate on the surface, although square arrays (which may correspond to a body centered cubic, bcc, packing) are seen occasionally (Fig. 3). Some of the domains include more than a thousand identical pores in almost perfect hexagonal lattices in the first visible layer.

A major advantage of this template method is that the dimensions of the pores are set by the size of the latex beads, and so can be varied easily. We have produced structured materials with pore sizes ranging from ca. 150 nm to 1 μm. Thermogravimetric analysis of the calcination process shows an estimated porosity of 78 vol.-%, which is close to that expected for a material with close-packed ordered spherical pores (≈74 %).

Other workers have produced a variety of interesting inorganic and organic materials using different colloidal crystal templates and infusion schemes. Concurrently with our work, Imhof and Pine described how crystal-like assembles formed from densely packed monodisperse non-aqueous emulsion droplets can serve as templates for the formation of porous titania, zirconia, and silica.[2] Even though the method yields pore ordering and uniformity that are not as good as those given by the latex crystals, the templates are easy to obtain and so have technological potential. Other types of materials from simple, though somewhat disordered, templates have been reported by Davis et al.[3] and Antonietti et al.[4]

Holland et al.[5] have designed a straightforward way to use latex colloidal crystals for the formation of porous titania, alumina, and zirconia via the sol–gel technique. They have pushed the method further to produce structures from a wide variety of chemical compositions, including oxides of W, Fe, Sb, Zr/Y, aluminophosphates, silicates, zeolites, and others.[5] The first study to specifically target the formation of a material with photonic crystal properties, dense porous titania, is reported by Wijnhoven and Vos.[6] The high refractive index of the titania is a prerequisite for the remarkably wide reflectance peak produced by the calcined structure, even though it does not possess a full photonic bandgap.

The use of latex colloidal crystals as templates for the formation of porous polyurethane membranes has been demonstrated by Park and Xia.[7,8] Porous polymers have also been synthesized by Johnson et al.[9] who have used microspheres below 100 nm in diameter, thereby closing the gap of pore sizes between those attainable via colloidal crystal templating and those found in the now conventional mesoporous MCM materials templated by surfactant assemblies.
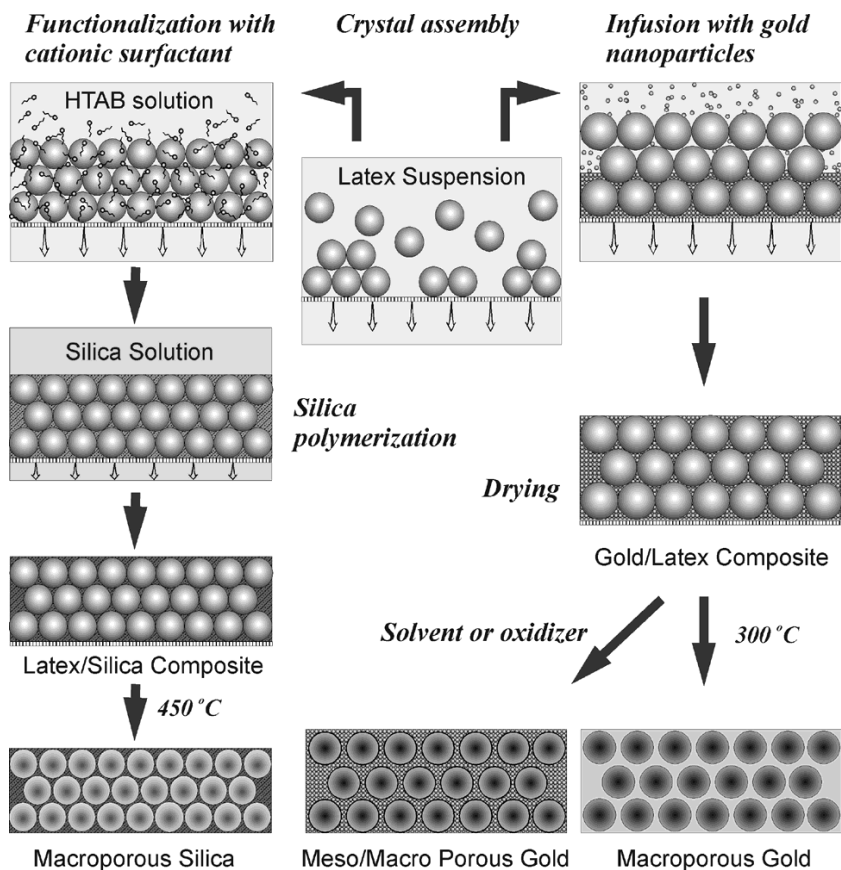
Fig. 2. Schematic of methods for preparation of porous silica (left branch) and gold (right branch).

material from semiconductor CdSe quantum dots. Similar methods have been used to make silica and titania structures,[13] and by us for the formation of porous gold as described below.

Porous structured metals may have important technological applications, particularly in electronics and optoelectronics. So far, reported procedures for fabrication of metallic structures avoid the direct infusion of a heat-resistant crystal with a molten metal. Such a method has several technical problems as a result of the required high temperatures and pressures, although it is possible that this approach will be developed. Yan et al.[14] have synthesized porous Ni by impregnation of the template with a Ni salt, followed by thermal decomposition and reduction in hydrogen atmosphere. Jiang et al.[15] have synthesized a variety of porous metals via electroless deposition into silica crystals functionalized with gold nanocrystals.

In the low-temperature "wet" method developed in our laboratory,[16] both the colloidal crystal and a templated gold structure are assembled in situ from nanoparticle suspensions. The procedure is shown in the right hand side branch of Figure 2. The pore size of the filter membrane is small enough to retain both the latex and the gold particles, while still allowing a reasonably high flux of water. The mesoscopically porous gold structure in the cavities of the latex crystals is formed by deposition from suspension of 15–25 nm colloidal gold particles. Two alternative procedures are used to remove the latex beads from within the composite, and they yield porous metal with different properties. The first procedure is calcination at 300 °C, in which case the final products are flakes with the distinct yellow color of metallic gold. Alternatively, the latex templates can be removed by chemical oxidation or solvent dissolution of the polystyrene beads at room temperature. The resulting materials are brownish metallic flakes. Both of these metallic materials exhibit brightly colored reflections at appropriate angles of incident illumination and are highly conductive. Examples of the discrete morphology of these materials and their hierarchical porosity are given in Figure 3d–f.

Formation of structured porous carbon with remarkable optical properties via crystalline templates from silica spheres has been reported by Zakhidov et al.[10] The carbon "inverse opals" are conductive, show intense opalescence from the ordered arrays of holes, and may have a photonic bandgap in the infrared region. Yang et al.[11] demonstrated how colloidal crystal templating can be used together with other templates to create hierarchically ordered porous oxides on three scales. In this case, the smallest ordered pores (~10 nm) are formed by self-assembled surfactant block copolymers, in analogy with the MCM materials. The midranged ordered pores (~100 nm) are templated by arrays of ordered latex microspheres, and the final longest feature surface patterns (~1 μm) are created by molding with a poly(dimethylsiloxane) stamp.

A major modification of the colloidal crystal method, which also leads to a material with a hierarchical porosity on both a mesoscopic and macroscopic scales, is to fill the interstices of the colloidal template with structures made from smaller colloidal particles. This approach has the advantage of synthesis at room temperature without complex chemistry. The size of the large pores can be manipulated by changing the diameter of the templating particles, while the size of the small pores and the overall specific surface area are determined by the size of the small particles. This approach was first used by Vlasov et al.[12] to form porous

3. Potential Applications

In just a few years the fabrication of porous materials using colloidal crystal templates has become a rapidly growing field. As shown in Table 1, nearly all classes of inorganic and organic materials and metals have been tem-
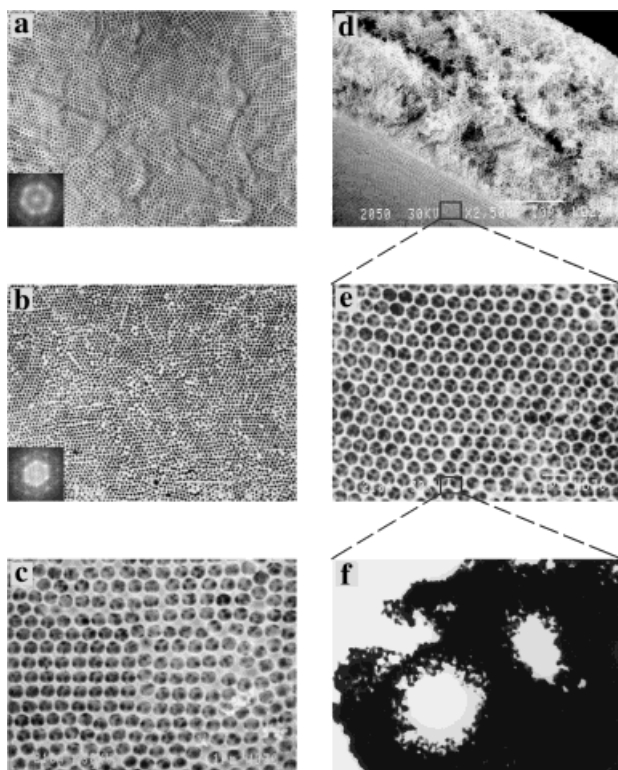
ADVANCED MATERIALS

Fig. 3. Electron micrographs at different magnifications illustrating the structure of the porous materials. a) Low-magnification SEM picture of the surface of porous silica. b) Low-magnification picture of a metallic sample. c) A square array in a metallic sample formed using 1 μm templates. d) Low magnification SEM across the edge of a metallic flake. e) SEM of the surface of a metallic flake. f) TEM illustrating the internal porosity and demonstrating that the Au structure is assembled from nanoparticles.

plated into porous ordered structures. The creation of these structures is a fascinating and intellectually challenging problem, but interest in these materials also arises from their wide array of potentially usable applications. The most "visible" of these applications is as photonic crystals.

Photonic crystals are structures with three-dimensional periodicity on a length scale comparable to that of light. Such structures could increase the internal efficiency of light emitting diodes and be used in optical processing devices as miniature waveguides, or mirrors, thereby acting as analogs to conductors and insulators in electric circuits.[17] Micromachining methods to make photonic structures are expensive, so the formation of similar materials via self-assembly and templating is economically attractive. The structured porous materials discussed here can possess the desired full photonic bandgap when created out of a matrix with high refractive index.[6,12,13,17,18] Such materials have not yet been synthesized, even though recent advances in creating structures via electrochemical growth of semiconductors[18] appear very promising. Another technological obstacle will be the formation of defectless crystals of specific structure and orientation, which in principle can be achieved via assembly onto pre-formatted surfaces.[19]

Another promising direction for future research is the templated formation of thin supported porous layers mounted on solid substrates. Thin semi-transparent films from porous metals may have interesting transmission properties arising from the surface plasmons in the metallic layers,[20] and could find applications, e.g., as substrates for surface-enhanced Raman scattering (SERS). Recently, we have been able to modify the method shown in the right branch of Figure 2 to form two-dimensional structured metallic layers only 1–3 pores thick on a glass substrate. The samples are semi-transparent and show colors by diffraction. Such two-dimensional colloidal templates also hold hope for surface processing of materials.[21]

Apart from photonic crystal and optical applications, the three-dimensional porous materials have potential applications in advanced catalysis, where the hierarchical porosity combines efficient transport and high surface area. Both the bulk and surface chemistry of the materials can be modified to the desired composition.[5] Interesting catalytic and other applications could be based on the ability of the method to form membranes or composite metallic/dielectric structures. This new field is clearly far from exhausting its store of novel ideas and possibilities.

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