ELSEVIER

Current Opinion in Colloid & Interface Science 5 (2000) 56–63

Current Opinion in Colloid & Interface Science

www.elsevier.nl/locate/cocis

Colloidal crystals as templates for porous materials

Orlin D. Velev*, Abraham M. Lenhoff

Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

Abstract

Close-packed colloidal crystals are promising precursors for novel materials, but only after appropriate methods are developed to fix their structure. A wide range of advanced materials has recently been synthesized by replicating the structure of colloidal crystals into durable solid matrices. Such materials with structured pores have promise as photonic crystals, catalysts, and membranes, and in a variety of other applications. This paper reviews the methods used in the formation of these materials and likely future trends in the field.

Keywords: Colloidal crystals; Porous materials; Templates

1. Synthesis strategies

The long-range ordering of particles in the structure of colloidal crystals results in a number of unique potentially useful properties, such as optical diffraction and photonic band gaps, maximal packing density and high surface/volume ratio. However, the materials obtained after the particulate arrays are dried are very brittle and can be re-dispersed in water. A fascinating example of how colloidal crystals can be turned into a durable material with remarkable properties is provided by the natural opals, which are formed when the voids between ordered sediments of silica particles are infiltrated by hydrated silica, which then solidifies.

A variety of artificial structures based on colloidal crystals have been synthesized recently using the 'fixing' concept suggested by the opals. The primary focus of this paper is to review recent advances in creating novel materials by replicating the structure of colloidal crystals into durable matrices. In this approach (Fig. 1), the colloidal crystals are assembled in order to serve as templates, the voids of which are infiltrated by material that solidifies there. The original colloidal particles are subsequently removed, leaving behind a new material with pores that preserve the most valuable property of the colloidal crystals — the long-ranged periodic structure. A major advantage of the colloidal crystal template method is the ability to control the dimensions of the pores easily by varying the size of the beads in the templates.

Latex and silica microspheres are the two major types of particles that are usually used for the colloidal crystal assembly, as they can be obtained both highly monodisperse and relatively cheaply. Central to the materials synthesis is the design of procedures for assembling the crystals and subsequently infusing them with appropriate media. A summary of the crystallization methods used by different investigators is represented in Fig. 2. The simplest method is gravitational sedimentation of the particles, usually combined with drying of the suspension from above. The process can be accelerated and the quality of the materials can be improved via centrifugation (Fig. 2b).

* Corresponding author. Tel.: +1-302-831-8919; fax: +1-302-831-1048.

E-mail address: velev@che.udel.edu (O.D. Velev).

1359-0294/00/$ - see front matter
PII: S1359-0294(00)00039-X

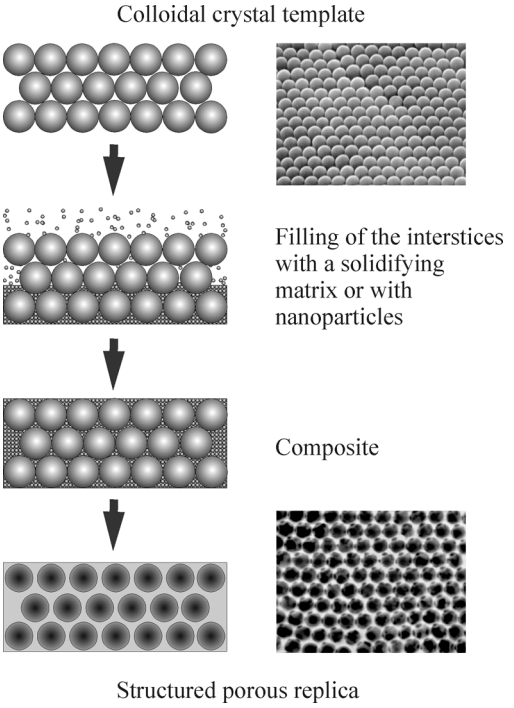

Fig. 1. Schematic of the general procedure for replicating the structure of colloidal crystals into porous materials.

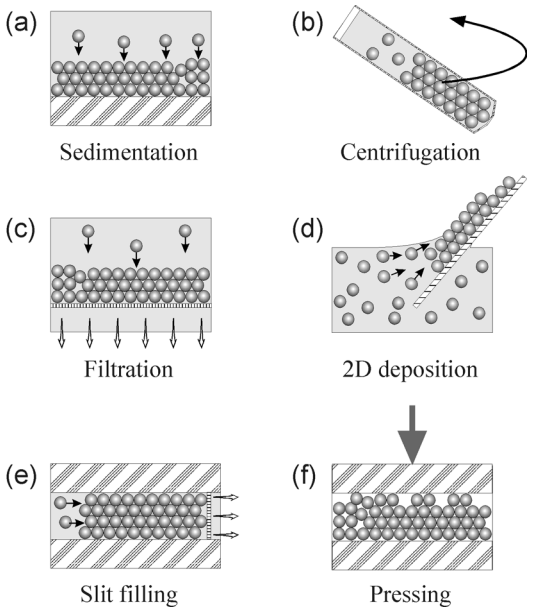

Fig. 2. Schematics of methods used for assembling the colloidal crystalline templates.

Another way to speed the process up is by filtration (Fig. 2c), which also allows easy washing and subsequent infusion with different media. Of certain interest is the formation of crystalline sheets of specific thickness, for which the convective assembly method [2–4] (Fig. 2d) has been used after recent modifications and improvements [5]. Colloidal crystals can also form when the particles are confined in the thin film between two solid boundaries [1]. This approach has also recently been used to assemble closely packed crystals, by filtering suspensions into a thin slit between two solid plates (Fig. 2e) [6,7]. Finally, ordered structures between solid surfaces can be formed by pressing and compaction of particles in the dry state (Fig. 2f).

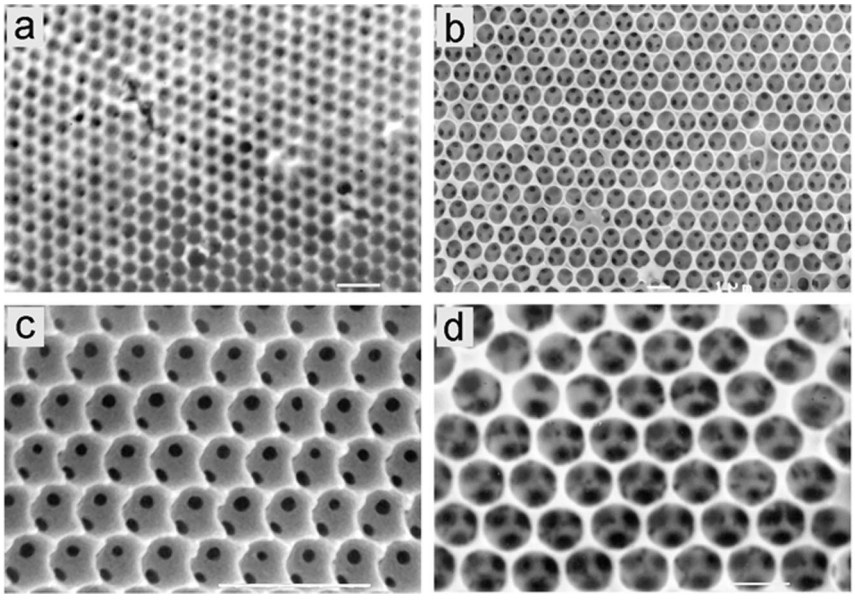

Fig. 3. Scanning electron micrographs illustrating the similarity in the structure of materials formed from different precursors. (a) Porous silica sample, reprinted with permission from Velev et al. [11]; (b) Porous polymer membrane, photo courtesy of Gates et al. [30]; (c) Inverse opal from phenolic resin, photo courtesy of Zakhidov et al. [33]; (d) Sample of metallic gold similar to those in Velev et al. [35]. Scale bars = 1 μm.

In all of the above methods, the transition to the ordered state is induced by the increased concentration of the particles in the vicinity of a flat surface. The phases formed are usually built up of polycrystalline domains in different orientations, for several reasons: (i) nucleation tends to occur concurrently at many locations; (ii) the high friction within the arrays inhibits re-arrangement; and (iii) impurities are present that distort the lattice. The typical lattice types in these domains are randomly-stacked hexagonal close-packed planes (r.h.c.p.), and face-centered cubic (f.c.c.) [8,9]. Square arrays, which may correspond to body centered cubic (b.c.c.) packing, are formed occasionally in the interstices between the growing hexagonal domains, or in films of thickness commensurate with a discrete number of squarely packed layers [1]. The growth of defectless crystalline templates with desired symmetry and orientation is one of the major challenges in the field. One way to achieve this may be the use of micropatterned surfaces to promote epitaxial-like growth [10•].

The solidified structure in the pores between the microspheres can be formed by, for example, polymerization [11•,12•] or sol-gel hydrolysis [13•,14•,15•] of a liquid precursor. More recently, structures have been grown via electroless or electrochemical deposition [16•,17•] or precipitation [18•]. A conceptual extension of the method that avoids complex chemistry is to fill the interstices of the colloidal template with smaller colloidal particles [19•], which also leads to a structure with a hierarchical porosity on both mesoscopic and macroscopic scales. The size of the large pores can be manipulated via 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.

In the final step of the process, the colloidal crystal templates are removed from the composite material either by calcination or by chemical or physical dissolution. The pores left in place of the particles are arranged in ordered three-dimensional arrays that represent a negative replica of the original colloidal crystal (Fig. 1). The morphology of the structures is broadly similar irrespective of the type of solid matrix used (Fig. 3). The various materials synthesized to date are reviewed below, grouped by their chemical composition and hence potential function.

2. Materials based on inorganic oxides

The first demonstration of replicating the ordered structure of colloidal crystals into a stable matrix yielded structured porous silica [11•,20]. The templates were assembled by filtering diluted suspensions of latex microspheres through smooth membranes. The surfaces of the microspheres were functionalized by adsorption of cationic surfactant from solution, which served to initiate the polymerization of $Si(OH)_4$ to solid silica after the crystal was subsequently infused with aqueous silica solution [20]. The latex particles were removed from the composite via calcination. The products of the mineralization are porous low-density silica flakes (Fig. 3a). The range of pore sizes obtained by varying the size of the latexes used, 150 nm to 1 μm, is typical for such materials.

In a separate leading study, Imhof and Pine [13•] described how colloidal crystal-like assemblies of densely packed monodisperse non-aqueous emulsion droplets can serve as templates for the formation of porous titania, zirconia and silica. The pores are less ordered and uniform than with latex microspheres, but the method has technological potential due to the use of simple easily obtained templates. In addition, the sol-gel alkoxide hydrolysis method employed for depositing the oxide matrix had later proved useful with latex particle templates. The formation of macroporous materials from simple but generally disordered templates has also been reported by Davis et al. [21] and Antonietti et al. [14•].

The versatility of the principle has been demonstrated both in the range of materials made and in the ability to design specific functional and structural characteristics into them. Holland et al. [15•] assembled latex crystals by both filtration and centrifugation (Fig. 2a,b) and used them as templates for porous titania, alumina and zirconia via the sol-gel technique. This group has adapted the method further to form structures of a wide variety of chemical compositions, including oxides of W, Fe, Sb, Zr/Y, aluminophosphates, silicates, carbonates, zeolites and others [18•,22•,23]. Doping of porous titania with metals such as Co has also been reported [24•].

The first study specifically to target the formation of a material with photonic crystal properties, dense porous titania, was that of Wijnhoven and Vos [25•]. The templates are assembled via centrifugation, and the titania structure is formed by the sol-gel method. The high refractive index of the titania is a prerequisite for a remarkably wide reflectance peak of the calcined structure, although the samples obtained do not display a full photonic band gap.

Greater structural complexity has been attained by complementing the colloidal crystal templates with other templating techniques to create hierarchically ordered porous oxides [26•]. The smallest ordered mesopores (~ 10 nm) are formed by templating by surfactant block copolymers analogously to the MCM materials templated by surfactant assemblies. The mid-ranged ordered pores (~ 100 nm) are templated by the arrays of latex microspheres in the colloidal

crystals. The largest features (~ 1 μm) are created by molding with a PDMS master.

Porous silica and titania have also been assembled from nanoparticles. In the direct methods formulated by Subramania et al. [27] and Subramanian et al. [28], the latex particles are mixed with TiO_2 or SiO_2 nanoparticles. The latex is crystallized via drying and sedimentation, during which process the inorganic nanoparticles fill the interstices in the crystal. The simplicity of this method and its potential for scaling up make it attractive for practical applications.

3. Structured porous polymers

The use of colloidal crystals as templates for forming porous polyurethane membranes was first demonstrated by Park and Xia [12•,29]. The latex templates are assembled by injection and accumulation between solid plates (Fig. 2e). The polyurethane precursor is UV-polymerized and the latexes are removed by selective dissolution in toluene, leaving structures analogous to those in Fig. 3b. These authors later extended the fabrication procedure to silica spheres [30•]. Johnson et al. [31•] synthesized porous polymers using microspheres < 100 nm in diameter, closing the gap of pore sizes attainable via colloidal crystal templating and the conventional mesoporous MCM materials. The templates in this case were assembled via pressing in the solid state (Fig. 2f). Finally, Jiang et al. [32] modified the convective assembly method (Fig. 2d) to prepare free-standing, optically active porous films from a wide variety of polymers.

4. Materials from carbon and semiconductors

Zakhidov et al. [33•] have developed procedures for using crystalline templates to form a family of structured porous carbons with remarkable optical properties. The templates are artificial opals assembled from SiO_2 microspheres, which are embedded into carbon phases by three alternative routes: (i) by infiltrating the crystals with phenolic resin, removing the microspheres, and pyrolyzing the resin structure to glassy carbon; (ii) by chemical vapor deposition (CVD) of graphitic carbon; and (iii) by diamond-seeded CVD from plasma. The carbon 'inverse opals' obtained are highly conductive, show intense opalescence from the ordered arrays of holes and may have a photonic band gap in the infrared region.

Structured porous semiconductors are of significant interest because of the quantum 'dots' and 'wells' they display and because their high refractive index holds promise for use in photonic crystals. Vlasov et al. [19•] were the first to assemble a secondary structure from nanoparticles and prepare a porous material from semiconductor CdSe quantum dots. The effective refractive index of the material assembled is, however, lower than that or solid semiconductors due to the presence of air in the pores between the nanocrystals. The problem of creating an optically dense, continuous, semiconductor structure is solved in the electrochemical method reported by Braun and Wiltzius [17•]. Here, the template crystals of latex or silica microspheres are assembled via sedimentation onto conductive indium tin oxide (ITO) electrodes, and then CdSe and CdS are grown electrochemically in their interstices via electrodeposition. Structures made by this approach should display deep photonic band gaps and good mechanical stability.

5. Structured porous metals

Due to the importance of metals in technological applications, structured porous metals may find application in a variety of areas, particularly electronics and optoelectronics. The direct infusion of a heat-resistant crystal with a molten metal presents technical problems due to the high temperatures and pressures required. Although such methods may be reported in the future, the methods published to date create the metallic structure via alternative procedures. Yan et al. [34•] assembled latex crystals by centrifugation and impregnated the template with a nickel salt that was then oxidized to NiO and finally reduced to metallic Ni in a hydrogen atmosphere. The highly porous nickel obtained can be useful in catalysis and in electrochemical electrodes.

Using a totally 'wet' approach, Jiang et al. [16•] synthesized a variety of porous metals by electroless deposition. Silica colloidal crystals were assembled in thin wetting films (Fig. 2d) and functionalized with gold nanocrystals that provide the nucleation sites for electroless deposition. The method has been used to form samples from Ni, Cu, Ag, Au and Pt, which have remarkable optical properties due to the long-ranged ordered porous structure on the surface.

Our wet method [35•] produces a templated gold structure assembled entirely from a suspension of gold nanoparticles. This is made possible by assembling the latex crystal by filtration through a membrane of pore size small enough to retain both the latex as well as the gold particles subsequently added, while still allowing a reasonably high flux of water. Thus, a mesoscopically porous gold structure is grown in the interstices of the latex crystals. Two alternative procedures are used to remove the latex beads from the composite, yielding porous metal with different properties. One procedure is calcination at 300°C,

which leads to some melting and fusion of the nanoparticles, so that only the larger pores templated by the polymer beads are preserved. Alternatively, a hierarchical mesoporous–macroporous structure is created when the latex templates are removed by chemical oxidation or solvent dissolution at room temperature. Both of these metallic materials exhibit brightly colored reflections in incident illumination and are highly conductive. Examples of the discrete morphology of these samples and their hierarchical porosity are shown in Fig. 4.

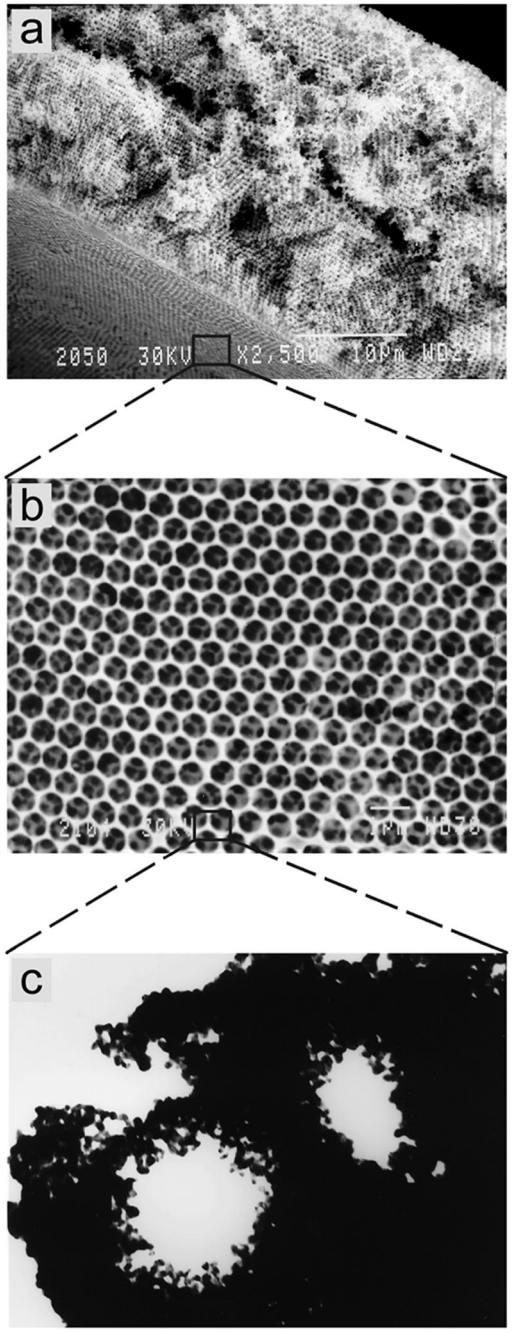

Fig. 4. Electron micrographs at different magnifications, illustrating the hierarchical structure of the meso-macroporous material assembled from metallic nanoparticles. (a) Low magnification SEM across the edge of a metallic flake; (b) A representative area on the surface; (c) TEM demonstrating that the structure is assembled from nanoparticles. Adapted with permission from Velev et al. [35].

6. Current challenges and future directions

In just a few years the fabrication of porous materials using colloidal crystal templates has become a rapidly growing area in nanomaterials. As shown here, nearly all classes of organic and inorganic materials and metals have already been templated into porous ordered structures. The design and synthesis of these structures is a fascinating, intellectually challenging problem, but the interest in these materials is also rooted in their wide array of potentially usable applications.

First, the method has produced materials with closely spaced pores of sizes from < 100 to > 1000 nm, a range that cannot be obtained by the earlier techniques such as templating via surfactant micelles and liquid crystals. The uniformity and the interconnection of the densely packed pores make some of these materials usable as efficient filtration membranes [30•]. The three-dimensional materials of hierarchical porosity have potential applications in advanced catalysis, where the larger pores allow rapid mass transport, while the small ones provide high surface area. Promising directions are the synthesis of silicates with zeolitic microporous frameworks [23] and doping and modification of the bulk and surfaces of the pore walls [22•,24•]. Theoretical research on the dynamics of formation of such materials is under way [36]. Interesting catalytic and other applications can be foreseen by modifying the method to form membranes and layers of alternating chemical composition and by implanting catalytic particles within the pores. An additional level of structural complexity can be obtained via subsequent disassembly [37] or reverse templating [38].

Second, the long-ranged ordering of the submicrometer pores opens a wide variety of potential applications in areas such as optical information processing and storage, advanced coatings and emerging nanotechnologies. The most ‘visible’ of these applications is as photonic crystals. Such structures, with three-dimensional periodicity on a length scale comparable to that of light, could be used to make microscopic lasers and efficient light emitting diodes, and be used as miniature waveguides or mirrors in optical processing devices [39–42]. The alternative micromachining methods for creating photonic structures are expensive, and the formation of similar materials via self-assembly and templating is a lucrative undertaking. It has been shown that the structured porous materials

discussed here can possess the desired full photonic bandgap when created from a matrix with high refractive index [17•,19•,42]. The synthesis of such structures is still a challenge, as few materials have such a high refractive index and it is necessary to grow these in a continuous manner [17•]. Another obstacle that has been solved in principle [10•], but still remains a technological challenge, is the growth of defectless colloidal crystals of desired symmetry and orientation.

A major direction that warrants exploration is the use of colloidal crystals as templates in fabricating supported thin films and for surface modification of materials. One topic that has been relatively well studied previously is the use of thin colloidal crystals as non-lithographic masks for forming surface patterns via deposition of metal through the layers [43–47]. Two-dimensional colloidal templates have recently been used in preparing porous TiO_2 surfaces with enhanced photocatalytic activity [48•]. Thin semitransparent films from porous metals may have interesting transmission properties arising from the surface plasmons in the metallic layers [49•,50,51]. Recently, we have been able to modify the method for preparing porous metals so as to form two-dimensional structured metallic layers only 1–3 pores thick deposited on a glass substrate, which are semitransparent and show colors by diffraction [52]. One promising application of such structured porous metallic films is as substrates for surface enhanced Raman spectroscopy (SERS) [53–55], where the cheap and simple assembly method has significant advantages over the microfabrication techniques used at present [55]. Given the interest and the strongly competitive research in this field, exciting new ideas and practical applications are likely to emerge rapidly in the future.

Acknowledgements

Our research referred to here has been performed with the essential collaboration of Peter Tessier, Raul Lobo and Eric Kaler. The partial financial support of the Department of Chemical Engineering, University of Delaware, is acknowledged.

References and recommended reading

- • of special interest
- •• of outstanding interest

[1] Pieranski P. Colloidal crystals. Contemp Phys 1983;24:25–73.

[2] Denkov ND, Velev OD, Kralchevsky PA, Ivanov IB, Yoshimura H, Nagayama K. Mechanism of formation of two-dimensional crystals from latex particles on substrata. Langmuir 1992;8:3183–3190.

[3] Denkov ND, Velev OD, Kralchevsky PA, Ivanov IB, Yoshimura H, Nagayama K. 2-Dimensional crystallization. Nature 1993;361:26.

[4] Dimitrov AS, Nagayama K. Continuous convective assembling of fine particles into two-dimensional arrays on solid surfaces. Langmuir 1996;12:1303–1311.

[5] Jiang P, Bertone JF, Hwang KS, Colvin VL. Single-crystal colloidal multilayers of controlled thickness. Chem Mater 1999;11:2132–2140.

[6] Park SH, Qin D, Xia Y. Crystallization of mesoscale particles over large areas. Adv Mater 1998;10:1028–1032.

[7] Park SH, Xia YN. Assembly of mesoscale particles over large areas and its application in fabricating tunable optical filters. Langmuir 1999;15:266–273.

[8] Pusey PN, van Megen W, Bartlett P, Ackerson BJ, Rarity JG, Underwood SM. Structure of crystals of hard colloidal spheres. Phys Rev Lett 1989;63:2753–2756.

[9] Zhu JX, Li M, Rogers R et al. Crystallization of hard-sphere colloids in microgravity. Nature 1997;387:883–885.

[10] • van Blaaderen A, Ruel R, Wiltzius P. Template-directed colloidal crystallization. Nature 1997; 385:321–4.

The authors demonstrate how colloidal crystals of desired symmetry and orientation can be grown epitaxially onto microfabricated substrates. This approach may be crucial for growing defectless crystals for photonic applications.

[11] • Velev OD, Jede TA, Lobo RF, Lenhoff AM. Porous silica via colloidal crystallization. Nature 1997; 389:447–8.

One of the first two pioneering papers to present the concept, and the first to use long-ranged ordered templates from solid microspheres (see also ref. 13).

[12] • Park SH, Xia YN. Fabrication of three-dimensional macroporous membranes with assemblies of microspheres as templates. Chem Mater 1998; 10:1745–7.

The first synthesis of porous polymers via colloidal crystal templates.

[13] • Imhof A, Pine DJ. Ordered macroporous materials by emulsion templating. Nature 1997; 389:948–51.

The second pioneering paper to show the proof-of-concept via assemblies of emulsion droplets and inorganic oxides formed via alkoxide hydrolysis.

[14] • Antonietti M, Berton B, Göltner C, Hentze H-P. Synthesis of mesoporous silica with large pores and bimodal pore size distribution by templating of polymer lattices. Adv Mater 1998; 10:154–159.

A simple method to template macroporous materials with latex beads, albeit without long-range ordering of the pores.

[15] • Holland BT, Blanford CF, Stein A. Synthesis of macroporous minerals with highly ordered three-dimensional arrays of spheroidal voids. Science 1998; 281:538–40.

The first paper to present a range of structured metallic oxides formed via microsphere templating and alkoxide hydrolysis.

[16] • Jiang P, Cizeron J, Bertone JF, Colvin VL. Preparation of macroporous metal films from colloidal crystals. J Am Chem Soc 1999; 121:7957–8.

This paper introduced electroless metal deposition as a route to the synthesis of a variety of porous structured metals.

[17] • Brown PV, Wiltzius P. Electrochemically grown photonic crystals. Nature 1999; 402:603–604.

The electrochemical deposition of semiconductors allows the formation of dense materials with high refractive index, and is one possible route to photonic crystals with full band gap.

[18] • Yan HW, Blanford CF, Holland BT, Smyrl WH, Stein A. General synthesis of periodic macroporous solids by templated salt precipitation and chemical conversion. Chem Mater 2000; 12:1134–41.

The precipitation method allows the synthesis of materials with a new range of chemical compositions.

[19] Vlasov YA, Yao N, Norris DJ. Synthesis of photonic crystals
• for optical wavelengths from semiconductor quantum dots. Adv Mater 1999; 11:165–69.

The first group to demonstrate the formation of porous semiconductors via assembly of nanoparticles in the interstices of the templating colloidal crystal.

[20] Velev OD, Jede TA, Lobo RF, Lenhoff AM. Microstructured porous silica obtained via colloidal crystal templates. Chem Mater 1998;10:3597–3602.

[21] Davis SA, Burkett SL, Mendelson NH, Mann S. Bacterial templating of ordered macrostructures in silica and silica-surfactant mesophases. Nature 1997;385:420–423.

[22] Holland BT, Blanford CF, Do T, Stein A. Synthesis of highly
• ordered, three-dimensional, macroporous structures of amorphous or crystalline inorganic oxides, phosphates and hybrid composites. Chem Mater 1999; 11:795–805.

The method has been extended to materials with a wide range of precursor chemistry.

[23] Holland BT, Abrams L, Stein A. Dual templating of macroporous silicates with zeolitic microporous frameworks. J Am Chem Soc 1999;121:4308–4309.

[24] Yin JS, Wang ZL. Template-assisted self-assembly and cobalt
• doping of ordered mesoporous titania nanostructures. Adv Mater 1999; 11:469–72.

The chemistry of the pore walls can be modified via metal ion doping from solution to create materials with potential applications in catalysis.

[25] Wijnhoven JEGJ, Vos WL. Preparation of photonic crystals
• made of air spheres in titania. Science 1998; 281:802–804.

The first group specifically to target the formation of materials with high refractive index for photonic crystal applications.

[26] Yang PD, Deng T, Zhao DY et al. Hierarchically ordered
• oxides. Science 1998; 282:2244–46.

As many as three templating techniques, including colloidal crystals, have been used simultaneously to form materials with three levels of hierarchical structure, from the nanometer to the sub-micrometer region. An important illustration of how the colloidal crystal template approach is likely to complement and interface other templating and processing methods in the future.

[27] Subramania G, Constant K, Biswas R, Sigalas MM, Ho K-M.
• Optical photonic crystals fabricated from colloidal systems. Appl Phys Lett 1999; 74:3933–35.

Synthesis of inorganic oxide materials via assembly of nanoparticles (see also ref. 19).

[28] Subramanian G, Manoharan VN, Thorne JD, Pine DJ. Ordered macroporous materials by colloidal assembly: A possible route to photonic bandgap materials. Adv Mater 1999;11:1261–1265.

[29] Park SH, Xia YN. Macroporous membranes with highly ordered and three-dimensionally interconnected spherical pores. Adv Mater 1998;10:1045–1048.

[30] Gates B, Yin Y, Xia YN. Fabrication and characterization of
• porous membranes with highly ordered three-dimensional periodic structures. Chem Mater 1999; 11:2827–2836.

Synthesis of a variety of porous polymer membranes and characterization of their permeability for potential filtration applications.

[31] Johnson SA, Ollivier PJ, Mallouk TE. Ordered mesoporous
• polymers of tunable pore size from colloidal silica templates. Science 1999; 283:963–5.

Extension of templated polymers to materials with pores in the sub-100 nm region, bridging the gap in the pore sizes attainable via colloidal crystal and surfactant liquid crystal templating.

[32] Jiang P, Hwang KS, Mittleman DM, Bertone JF, Colvin VL.
• Template-directed preparation of macroporous polymers with oriented and crystalline arrays of voids. J Am Chem Soc 1999; 121:11630–7.

Polymer films with remarkable optical properties prepared from thin crystalline layers formed via convective assembly.

[33] Zakhidov AA, Baughman RH, Iqbal Z et al. Carbon struc-
• tures with three-dimensional periodicity at optical wavelengths. Science 1998; 282:897–901.

Extension of the method to porous structures of glassy carbon, graphite and diamond.

[34] Yan HW, Blanford CF, Holland BT, Parent M, Smyrl WH,
• Stein A. A chemical synthesis of periodic macroporous NiO and metallic Ni. Adv Mater 1999; 11:1003–6.

The first synthesis of porous metal based on the precipitation-reduction technique (see also ref. 23).

[35] Velev OD, Tessier PM, Lenhoff AM, Kaler EW. A class of
• porous metallic nanostructures. Nature 1999; 401:548.

Simple synthesis of hierarchical, meso-macroporous structured metal via assembly of nanoparticles (see also ref. 19).

[36] Zhang LH, Van Tassel PR. Theory and simulation of adsorption in a templated porous material: hard sphere systems. J Chem Phys 2000;112:3006–3013.

[37] Zhong ZY, Yin YD, Gates B, Xia YN. Preparation of mesoscale hollow spheres of TiO_2 and SnO_2 by templating against crystalline arrays of polystyrene beads. Adv Mater 2000; 12:206–209.

[38] Colvin VL et al. Personal communication. 2000.

[39] Yablonovitch E. Inhibited spontaneous emission in solid-state physics and electronics. Phys Rev Lett 1987;58:2059–2062.

[40] Joannopoulos JD, Meade RD, Winn JN. Photonic crystals: molding the flow of light. Princeton: Princeton University Press, 1995.

[41] Krauss TF, De La Rue RM. Photonic crystals in the optical regime — past, present and future. Progr Quant Electron 1999;23:51–96.

[42] van Blaaderen A. From the de Broglie to visible wavelengths: manipulating electrons and photons with colloids. MRS Bull 1998;23:39–43.

[43] Deckman HW, Dunsmuir JH. Natural lithography. Appl Phys Lett 1982;41:377–379.

[44] Hulteen JC, Van Duyne RP. Nanosphere lithography — a materials general fabrication process for periodic particle array surfaces. J Vac Sci Technol A 1995;13:1553–1558.

[45] Boneberg J, Burmeister F, Schafle C et al. The formation of nano-dot and nano-ring structures in colloidal monolayer lithography. Langmuir 1997;13:7080–7084.

[46] Burmeister F, Schafle C, Keilhofer B et al. From mesoscopic to nanoscopic surface structures: lithography with colloid monolayers. Adv Mater 1998;10:495–497.

[47] Hulteen JC, Treichel DA, Smith MT, Duval ML, Jensen TR, Van Duyne RP. Nanosphere lithography: size-tunable silver nanoparticle and surface cluster arrays. J Phys Chem B 1999;103:3854–3863.

[48] Matsushita SI, Miwa T, Tryk DA, Fujishima A. New me-
• sostructured porous TiO_2 surface prepared using a two-dimensional array-based template of silica particles. Langmuir 1998; 14:6441–7.

Two-dimensional colloidal crystals used to template hexagonal arrays of mesopores on the surface of TiO_2 films, enhancing their photocatalytic activity.

[49] Ebbesen TW, Lezec HJ, Ghaemi HF, Thio T, Wolff PA.
• Extraordinary optical transmission through sub-wavelength hole arrays. Nature 1998; 391:667–9.

The remarkable optical properties of the holey metallic structures

suggest one area where metallic materials synthesized via colloidal crystal templates could find application.

[50] Ghaemi HF, Thio T, Grupp DE, Ebbesen TW, Lezec HJ. Surface plasmons enhance optical transmission through subwavelength holes. Phys Rev B 1998;58:6779–6782.

[51] Pendry J. Applied physics — playing tricks with light. Science 1999;285:1687–1688.

[52] Tessier PM, Velev OD, Kalambur AT, Rabolt JF, Lenhoff AM, Kaler EW. Assembly of gold nanostructures templated by colloidal crystals and application to surface enhanced Raman spectroscopy. 2000; submitted.

[53] Vo-Dinh T. Surface-enhanced Raman spectroscopy using metallic nanostructures. Trend Anal Chem 1998;17:557–582.

[54] Freeman RG, Grabar KC, Allison KJ et al. Self-assembled metal colloid monolayers — an approach to SERS substrates. Science 1995;267:1629–1632.

[55] Kahl M, Voges E, Kostrewa S, Viets C, Hill W. Periodically structured metallic substrates for SERS. Sensor Actuat B-Chem 1998;51:285–291.