HIERARCHICALLY ORDERED COLLOIDAL CRYSTALS: FABRICATION, STRUCTURES, AND FUNCTIONS

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ABSTRACT

Marrying nanochemistry with optics has opened a new gateway to design and fabricate novel nanostructures that can interact with light in unprecedented manners. Self-assembled colloidal photonic crystal is one of the emerged nanostructured photonic materials, which possess well-defined, highly ordered structure and periodicities of light wavelength. Various 2D and 3D ordered structures have been fabricated through self-assembly methods by employing latex colloidal particles, or functionalized latex particles with more sophisticated structural features such as core-shell and anisotropy. The unique ordered structure and light-interactive properties have afforded them versatile functionalities in light manipulation, catalysis, sensing, and light harvesting. In this book chapter, we review recent research progress on hierarchical colloidal photonic crystals: the preparation methods, structural properties and applications. By introducing a hierarchy of interconnected structures at different length scales, the surface-to-volume ratio can be dramatically increased and the materials properties tailored accordingly. Moreover, the band-gap features of the photonic crystals may also be adjusted by the structure hierarchy.

INTRODUCTION

Colloidal crystals are a kind of periodically structured lattices assembled from monodisperse colloidal particles [1]. They appear as analogous entities to atomic crystals but with constituents in the size range of several nanometers to several micrometers. The

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prerequisite to their formation is the monodispersity of colloidal particle size, which is enabled by the increased control of particle size and shape in synthesis. The formation of these ordered structures in general is facilitated by intermolecular and surface forces as opposed to covalent forces or ionic bonds in atomic crystals.

In this chapter, we focus our attention on the colloidal crystals made of spheres of several hundred nanometers. Because this periodicity range matches with light wavelength, these colloidal crystals can diffract light in UV, visible, and near-infrared regions, and prevent light from being transmitted in a range of frequencies known as the photonic bandgap (PBG) [2, 3]. Subsequently, they are also referred to as colloidal photonic crystals (CPC). Photonic crystals have been first theoretically proposed by Yablonovich [2] and John [3] and gradually experimentally proven and demonstrated as a fascinating material for guiding, confining and manipulating light at low energy losses, which leads to their strong potential in optoelectronics, all-optic devices, and sensing [4–6]. Physicists first employed microfabrication methods such as drilling to obtain 2D structures with periodic contrast in dielectric constants, which are generally capital cost intensive and laborious. When chemists made the link between photonic crystals and self-assembled colloidal crystals, it has raised significant hope in developing self-assembly into an effective parallel production method for 2D and 3D photonic crystals [7–9].

Self-assembled CPCs often refer to the inverse porous structures; the monodisperse particle packings serve as sacrificial template to allow infiltration and solidification of a second material that is of high reflective index or possesses other desired properties. Ordered porous networks through colloidal templates alone is a topical subject in its own right [10]. However, self-assembly also implies minimum free energy, which means most structures obtained from self-assembly are of face centered cubic (fcc) or hexagonal close-packed (hcp) lattice symmetry. These kinds of crystal structures require the refractive index of the backbone material to be greater than 2.8 in order to have complete photonic band gap [11]. Overcoming the fcc structure limit and forming diamond lattice has been one of the key challenges in colloidal self-assembly [12]. The other very active area in CPC research has been the exploration of ways to impart various functionalities to the material by utilizing the structural regularities. Hierarchically ordered colloidal crystal (HOCC) represents one of the promising routes serving for both objectives.

HOCCs are self-organized structures combining features of several hierarchical ordering characteristic length scales. Hierarchically ordered porous structures are widely present in nature, e.g., diatoms, bones and lungs. The open, interconnected pores of different sizes are orderly arranged. They offer efficient transport of fluids for facilitating molecular-level biophysicochemical processes, typically using macropores to enhance the mass transport and meso- and micropores to enlarge the surface area for reactions. Yang et al. [13] have first demonstrated this concept by combining copolymer templating (~10 nm), latex sphere templating (~100 nm) and micromolding (~µm), and fabricated hierarchically ordered oxides. Recent years have seen significant progress of this concept and the categorical shift of colloidal crystallization from thermodynamics-driven to well-controlled assembly through hierarchical organization [14]. HOCCs also offer great potential for the design of new materials and devices for various applications due to the interconnected cavities at different length scales, increased specific surface area and higher density of reactive sites. Given the importance and strong potential of this field, this chapter intends to provide a brief account of the recent progress on HOCCs, fabrication strategies, their properties and potential applications.
FABRICATIONS AND APPLICATIONS OF HOCCs

Building on extensively studied fabrication methods for colloidal crystals [10, 15, 16], a major challenge in the synthesis of HOCCs is on how to introduce other feature hierarchical length scales, particularly on the nanoscale.

The general fabrication strategy for functional colloidal crystals is through colloidal templating [10]: first, self-assemble colloidal crystal from monodisperse silica or latex submicron spheres; second, it is infiltrated with the precursor of a targeted material, followed by polymerization or solidification; subsequent removal of the sphere-assembly template results in an inverse structure with ordered and interconnected macropores of hundreds nanometers in size.

The meso- and micro-size features are mostly introduced by surfactants, amphiphilic block copolymers, multiple-size colloidal particles, anisotropic colloid particles, ionic liquids, and/or pre-functionalized constituent particles.

1. Block Copolymer and Surfactant Templating

Similar to surfactants, amphiphilic block copolymers consist of at least two segments with different chemical natures. While the size of surfactants or surfactant micelles is more comparable to micropores (<2 nm) different to surfactants, amphiphilic copolymers can cover a length scale from several nanometers to a couple of tens nanometers, therefore, they are more suitable for being used as mesopore (2 – 50 nm) templates. Since surfactant templating is relatively mature, here we place more emphasis on block copolymer templating. Because of the difference in interface activity between the two kinds of polymer segments with their surroundings, block copolymers tend to self-organize into ordered structures such as lamellar, cylindrical and vesicular to reduce the interfacial energy between the immiscible blocks and to maximize the chain conformation entropy. Their polymeric nature affords versatility and diversity in both chemistry and geometry to this class of materials [17].

Therefore, block copolymers have been broadly explored in 2 dimensional (2D) and 3 dimensional (3D) nanopatterning. Yang et al. [13] investigated for the first time the hierarchical templating combination of top-down and bottom-up fabrication methods. They produced 3D HOCCs by concurrently or sequentially combining micromolding, colloidal self-assembly with polystyrene (PS) spheres and cooperative assembly of hydrolyzed inorganic species and amphiphilic block copolymers. In a typical sequential process, latex particles were first self-assembled in a pattern imposed by a silicon mold. Then, a drop of sol-gel-block copolymer precursor solution was introduced into the patterned colloidal crystal, followed by gelation. Subsequent calcination removed both latex particle and block copolymer templates.

Figure 1 shows the electron microscopic images of the resultant silica structure at different length scales.
In this process, while the silicon mold provided the macro-scale patterning and latex particles self-assembled into ordered structure on hundreds nanometer scale, block copolymer, here Pluronic F127 (EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}), also self-organized with regularity in the interstitial voids among the latex particles, affording mesopores to the final silica film.

Silica-based hierarchically ordered macro-/meso-, macro-/micro- or macro-/meso-/microporous structures have since been fabricated through colloidal templating with sol-gel in combination with surfactants, or liquid crystals, or ionic liquid, or block copolymers [18-20]. Among these efforts, Villaescusa et al. have shown that when a good control is applied over the filling fraction of the meso- or microporous guest material by employing the right infiltration method, the optical functionality conferred by the colloidal particle regular packing can be well preserved for the HOCCs[20]. In addition, Chmelka and coworkers have also demonstrated that the catalytic selectivity of meso-macroporous bimodal aluminosilica materials is higher than microporous zeolite beta and mesoporous SBA-15, owing to the improved diffusive resistance to mass transfer [21].

These successes in silica-based porous materials have naturally led to strong interests in synthesising hierarchically ordered porous carbon materials, because of the usefulness of porous carbon in separation, catalysts and catalyst supports, electrodes, sensors, super capacitors, batteries, gas storage, and many other applications [22 - 25]. Stein and coworkers [26] prepared hierarchically ordered biomodal porous carbon with macropores of 200 – 400 nm and mesopores of 2.8 nm by a multistep templating method combining colloidal templating and nanocasting. As Figure 2 illustrates, their procedure involves: 1. Preparation of 3D ordered mesoporous silica replica by infiltrating a sol of nonionic oligomer surfactant (Brij 56, C\textsubscript{18}H\textsubscript{33}EO\textsubscript{10}) and tetramethyl orthosilicate into a PMMA colloidal crystal and calcinations; 2. Infiltration of the macro-/mesoporous silica replica with phenol resin precursor as a carbon source; 3. Pyrolysis of the composite sample and removal of silica scaffolds by hydrofluoric acid (HF). It should be appreciated that where the surfactants were applied, various blockcopolymers can substitute depending on the requirement of the mesopore size.

By introducing mesopores into the skeleton structure, the surface area has reached >1200 m\textsuperscript{2}/g in contrast to 20 m\textsuperscript{2}/g for a macropore only structure. However, such a multiple templating procedure is highly laborious. Zhao and coworkers have developed an organic–organic self-assembly between block copolymers and phenolic resin precursors as a direct templating approach to ordered mesoporous carbons with various pore structures [27, 28].
This technique typically involves the following procedures as illustrated in Figure 3: a. polymerizing phenol and formaldehyde in alkaline condition to form the low-molecular-weight phenolic resol; b. mixing low-molecular-weight resol with PEO-PPO-PEO triblock copolymer in an ethanolic solvent and thermally polymerizing the resol; c. evaporating the solvent, which induces self-assembly of block copolymer to ordered structure, hence ordered assembly of resol nanoparticles.

The copolymer template can be removed by calcination at 350–450 °C and carbonization of resol precursor takes place when calcination over 600 °C. Studies have shown that the formed mesostructures are highly stable and can be retained at a temperature as high as 1400 °C under nitrogen atmosphere [29].
This organic-organic mesopore formation method has been neatly combined with colloidal templating and a facile synthesis method for producing hierarchically ordered macro-/mesoporous carbon materials was developed [29]. As shown in Figure 4, a mixture of F127 triblock copolymer and resol is infiltrated into a preformed silica colloidal crystal by a sol-gel process. Subsequent sol evaporation induces ordered vesicle formation on silica sphere surface as well as in the voids among silica spheres. After carbonization and etching off silica template, a carbon-based HOCC is obtained. Owing to the copolymer template size, Deng et al. [27] obtained ~11 nm mesopores within the matrix of hundreds nanometer macropores, which makes the materials more compatible when dealing with large molecules such as biomolecules.

It needs to be stressed that copolymers alone can create post-mesoscale structures in the macropores of colloid crystals and their inverse structures. These pores provide strong spatial confinement to copolymer self-organization, which may break the symmetry of a structure, thus
allow the copolymers to demonstrate new behavior [30-32]. Ozin, Manners and coworkers [33] have systematically studied the various mesoscale structures that lamella- and cylinder-forming diblock copolymers in silica colloidal and inverse colloidal crystals. 3D confined geometries such as octapods and tetrapods, core-multishell, golf ball; belt hexagonal packed spheres were observed when the ratio of 3D interspacing distance over the equilibrium periodicity of the diblock copolymer microphase separation \((D/L_0)\) varied, where \(D\) stands for interspacing distance and \(L_0\) denotes the copolymer characteristic equilibrium period.

The previous examples have shown block copolymer templating can afford a mesoporous structure in the backbone of the ordered macroporous framework. Questions also arise as to the possibility of introducing mesostructures on the inner walls of the inverse colloidal crystal. The motivations are two-folds: 
\(a\). from fundamental research point of view, it is highly interesting to understand the self-assembly of block copolymers on surface in confined geometry as opposed to the case of filling the entire confined space; 
\(b\). from application point of view, the mesostructures on the walls of macropores are most accessible sites for reactants, hence, by introducing mesostructures only on the macro pore walls it is highly probable to generate materials with similar functionalities but of higher mechanical strength.

As a versatile surface patterning template, block copolymer can self-assemble into well-defined nanostructures such as hexagonally ordered cylinders or stripe-like lamella, which are highly interesting for 2D ordered patterning of nanoparticles [34] and proteins [35] with several to tens nanometer inter-distance as well as synthesis of nanofibrils [36]. By wetting a pre-formed silica inverse colloidal crystal with a PS-\(b\)-PMMA solution as illustrated in Figure 6, Fu et al. [37] have obtained hierarchically ordered 3D arrays of block copolymer hollow spheres with nanostructured shells and nanopatterns on inner walls. We have produced unique copolymer-coated silica inverse colloidal crystals and their daughter hollow copolymer sphere arrays (by etching away silica with HF solution), owing to the fact that solution wetting method generated a thin layer of the block copolymer solution on the silica walls of inverse colloidal crystal templates and thus created thin block copolymer films on the internal surface of templates after solvent evaporation. By systematically varying the symmetry of the diblock copolymers PS-\(b\)-PMMA, Fu et al. [37] have observed intriguing copolymer patterns as shown in Figure 6 compared with their behavior under un-confined conditions. Together with the data on varying \(D/L_0\), this study showed that the interplay among copolymer microphase separation, geometrical confinement imposed by template macropores and the additional free surface between polymer and air adds more complexity to copolymer self-organization, in turn provides additional routes for forming hierarchically ordered functional materials.

2. Multiple-Size Particle Templating

Co-deposition of colloidal particles of different diameters also presents an effective and facile fabrication approach to HOCCs. Jonas and coworkers [38] reported for the first time the preparation of hierarchical ordered structure by vertical lifting co-deposition of PS particles (465 nm), PMMA particles (84 nm), and silica nanoparticles (6 nm), which resulted in macropores of two distinct sizes (460 and 80 nm) with interconnecting holes of 140 and 25 nm, as shown in Figure 7.
Figure 6. (a) Concentration dependence of shell thickness and the SEM images of, after removal of silica templates, (b) the 3D arrays of hollow PS-b-PMMA spheres and the annealed hollow spheres of (c) S125-PMMA50, (e) S450-MMA182, and (g) S1037-MMA322. The PS-rich domains appear bright and the PMMA-rich domains appear dark in the SEM images. The schemes in (d), (f), and (h) represent the schematic cross-section view of the nanostructured shells observed in (c), (e), and (g) [37].

The entire procedure only requires two steps, a. co-crystallization of template and matrix particles, and b. template removal, which is simple and elegant. As shown by our vis-NIR spectroscopy characterization (Figure 7), the colloidal crystals formed by multiple-size templating method possess distinct pseudo stop bands as mono-colloidal crystals.

Li, Zhao and co-workers [39] have further improved the co-crystallisation technique. We found that the multiple-size co-crystallization can take place by horizontal deposition, therefore, the technique can readily prepare centimetre-size binary and ternary colloidal crystals without requirement of any sophisticated equipment, as illustrated in Figure 8.
Hierarchically Ordered Colloidal Crystals

Figure 7. Schematic and SEM image of multiple-size particle templating of hierarchically ordered binary colloidal particles and vis-NIR spectra [38].

Figure 8. Horizontal deposition method for fabrications of HOCCs [39].

The uniform distribution of the small particles in the voids of large particle packing has been attributed to the combined ‘halo effect’ in colloidal suspension [40] and void constriction effect [39]. The operational window of utilizing the void constriction effect in forming HOCC was found to be around $0.154 < \text{diameter ratio} < 0.225$.

HOCCs can also be prepared by contact printing with pintool plotter [41], which makes it highly promising for protein array application. Kingshott and co-workers [42] have employed the binary colloidal crystal packing for highly ordered mixed protein patterns by first coating
the two sizes colloidal particles with different proteins before mixing and co-crystallisation. This work has provided a new concept on utilising the hierarchically ordered binary system.

On the utilisation of binary inverse colloidal crystals, Cai et al. [43] have demonstrated the advantage of the hierarchically ordered structure. TiO$_2$ inverse colloidal crystals have been prepared by multisize-particle (1 µm and 170 nm polystyrene spheres) cocrystallisation. In this study, TiO$_2$ was introduced by infiltrating the pre-formed binary colloidal crystals with a TiO$_2$ precursor, which was prepared by adding titanium isopropoxide to a mixture of trifluoroacetic acid and of hydrochloric acid under vigorously stirring. Photo-active anatase TiO$_2$ inverse structure was formed upon calcination at 500ºC as shown in Figure 9. By varying the small to large particle number ratio, the surface areas of HOCCs were altered. Tests on benzoic acid degradation under UV irradiation (Figure 10) showed that the TiO$_2$ HOCCs have exhibited enhanced photo-activity, mostly attributed to their increased surface area [43].

In the application field of photocatalysis, so far the slow photon effect in photonic crystals has been underutilised in HOCC. It has been observed first by Imhof et al. [44] that at the frequency edges of the stop bands of photonic crystals, photons propagate with strongly reduced group velocity, hence, they are called slow photons. Ozin and coworkers [45] have shown that slow photons in photonic crystals can significantly increase the interaction of light with TiO$_2$. By reducing the group velocity of light at energies near the edge of the photonic stop-band, a higher probability of absorption can be achieved and the photodegradation efficiency of TiO$_2$ doubled [45]. Therefore, there is still plenty of room to further improve HOCCs for the applications of photocatalysis and solar cells.

Multisize-particle co-crystallisation strategy has also been employed in preparation of hierarchically ordered porous carbon. Wu and co-workers [46] co-crystallised colloidal particles of two sizes (large polystyrene spheres and small silica particles) in sucrose solution as shown in Figure 11.

![Figure 9. FETEM images of TiO$_2$ binary inverse opals with different porous structures. The number ratios of small to large spheres are (a-d) 2, 2, 4, and 8. (e, f) High-resolution TEM images showing the TiO$_2$ crystal lattice [43].](image-url)
Figure 10. Photodegradation of Benzoid Acid using TiO$_2$ HOCCs and TiO$_2$ nanoparticles [43].

Figure 11. Schematic illustration for the preparation of hierarchically ordered porous carbon [46].

The sucrose in the interstitial voids was then turned into partially graphitized frameworks, which were shown as very good support for Pt-Ru alloy catalyst in direct methanol fuel cells. Their work has further confirmed the simplicity and versatility of this method for preparation of useful HOCC functional materials.

It is worth mentioning that in a theoretical study conducted by Wan et al. [47], binary inverse colloidal crystals show wider photonic band gaps compared to their mono-inverse
colloidal crystal counterparts. The increased width is dependent on the distribution density of the small voids resulting from the smaller particle templates.

3. Directed Assembly from Pre-Functionalised Colloids

The third promising HOCC fabrication route is through directed assembly from pre-functionalised colloids or colloidal clusters.

The aforementioned two classes of methods have focused on thermodynamics-controlled self-assembly, primarily mediated by van der Waals force, electric double layer repulsions as well as capillary forces [48]. The new exploratory approach is to devise the colloidal particles into true atom analogues, which are capable of mimicking molecular self-assembly through covalent and non-covalent interactions to build designer materials for specific applications. As illustrated by Wang and co-workers in Figure 12 [14], colloidal particles can be first either decorated with nematic materials or functionalised to mimic molecular structures before self-organising through directed assembly into cluster structures, which then can be further assembled into super lattice structures. The final superlattice structure is determined by the functionality of the colloidal particle and the cluster spatial arrangement.

Nelson [49] has theoretically postulated that spherical colloidal particles coated with liquid crystals or other materials can exhibit nematic degrees of freedom, which may form composite materials that exhibit point defects with sp and sp³ valences. Zhang et al. [50] have decorated PS spheres with gold dots analogous to sp valence. A leading work produced by Pine and co-workers [51] has shown that by employing emulsions colloidal particles can be assembled into clusters due to the confinement of dispersant droplets, which illuminates a new pathway to building designer materials from hierarchically organized colloids.

Figure 12. Schematic diagram illustrating various strategies for the generation of hierarchically organized colloidal particle structures [14].
CONCLUSIONS AND OUTLOOK

Colloidal crystals and hierarchically ordered colloidal crystals have captured significant interests from research community, owing to their beauty, simplicity and usefulness. Besides being a good analogue system to atoms [52], colloids have shown fascinating self-organization behavior as summarized in this chapter. HOCCs will remain as an active area in the coming years with research focuses shifting more towards directed self-assembly of pre-functionalized colloids with designer materials in mind. The tunabilities in photonic, electronic and magnetic properties [53-56] still require further explorations to exhibit their full potential.

REFERENCES


NinoK