Replication of anisotropic dispersed particulates and complex continuous templates

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Anisotropic nano-, micro- and mesoscale natural and synthetic structures possess a unique combination of physical properties due to a complex balance of steric factors and intermolecular interactions at multiple length scales. Utilizing such structures as templates for conformal replication allows reproduction of their unique shapes and properties into different synthetic materials. This review is devoted to the recent progress made on anisotropic microstructures suitable as sacrificial templates as well as techniques currently used for their precise replication into various materials. We present an overview of synthetic strategies used for the replication of both dispersed particulates and continuous templates with a number of recent examples of anisotropic organic and inorganic replicas presented. Strategies for generating adequate robust replicas and their expected assembling behavior are also briefly discussed.

1. Introduction

Nature provides numerous examples where anisotropic shapes and directional interactions are crucial to biological functioning and higher-order organization of anisotropic building blocks. For example, bacteria are found to have a variety of shapes, including ellipsoids, rods and spirals which are selectively recognized by white blood cells.[1] Human red blood cells are able to pass through the spleen due to their highly compliant disk-like shape. Oblate particles are predicted to adhere to vascular endothelium more effectively than spherical particles of the same volume.[2] The irregular shape of thrombocytes assists their rolling on vascular endothelium in hemostasis.[3] The most important step in drug delivery, ingesting foreign materials by white blood cells, is dictated by shape.[4] Other complex and anisotropic biological examples include unique photonic properties of butterfly wings,[5] superhydrophobicity of lotus leaves,[6] enhanced fluid and air flow sensing of fish and spider hairs,[7,8] and antireflective properties of fly eyes.[9] Such intriguing shape-dependent behavior in biological objects encourages scientists to learn from nature and create organized structures with unique shapes in order to control properties and functions of synthetic structures.[10,11]

Anisotropic microstructures of unique shapes bring advantages that are difficult to achieve through traditional microstructures with surface-tension driven round shapes. For instance, benefits of using non-spherical carriers for targeted drug delivery are predetermined by cellular internalization and vascular dynamics.[12] Recent studies have shown that transport, life-time and interactions of particles with cells are strongly

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dependent on shape and spatially-specific intermolecular interactions.[13]

Anisotropic micro- and nanoparticles have been also demonstrated to serve as building blocks for assembly into hierarchical synthetic structures with useful properties.[14–17] Assembly of such anisotropic structures is governed by the spatially and orientationally dependent balance of attractive forces (such as hydrogen bonding, electrostatic attraction between oppositely charged ligands, or dipole–dipole interactions) and repulsive forces (such as steric forces and electrostatic repulsion).[18] Selective facet functionalization of anisotropic building blocks produces chemically heterogeneous particles. "Adding" shape and interaction anisotropy to the particles extends the possible assemblies to complex motifs.

For example, gold-tipped tetrapods[19] should have the propensity to forming open three-dimensional (3D) arrays through attractive van der Waals interactions at the tips and restrictions on the symmetry of spatial packing of tetrapods.[20] Self-assembly of gold nanorods terminated with polystyrene (PS) brushes shows that the evolution of structures occurs through competition between the side-to-side and end-to-end aggregation (Fig. 1).[21] As a result, complex chain-like, smectic-like or globular aggregates can be formed by appropriate selection of solvents and ligands attached to the side and end facets of the nanorods (Fig. 1).

A variety of replication techniques have been developed to mirror unique shapes and morphology of various structures (Scheme 1). Hollow replicas of various complex shapes are of great interest because of their unique characteristics such as low specific density, high specific surface area, variable curvature, enhanced catalytic and binding activities, potential ion storage, complex refractive index and complex plasmon coupling.[22–25] Hollow replicas have been utilized as microcontainers for encapsulating materials such as therapeutics, fluorescent markers, and field-responsive agents applicable for drug delivery and biomedical imaging.[26] For example, Zhu *et al.* achieved stimuli-controlled drug release from hollow silica particles with mesoporous walls by capping the pores with polyelectrolyte multilayers.[27] Sokolova *et al.* reported fabrication of multishell calcium phosphate particles loaded with DNA for delivering genetic materials to cells.[28] Chen *et al.* reported the use of gold nanocages as optical imaging contrast agent for optical coherence tomography.[29]

This review discuses some recent results on the preparation of anisotropic dispersed particulates and the construction of synthetic replicas of such stand-alone structures as well as complex continuous templates that can be used as molds for conformal and robust replication. The review is limited to synthetic and biological templates with characteristic anisotropic dimensions ranging from upper nanoscale to lower mesoscale length scale (from ∼100 nm to several tens of a micron). We aim

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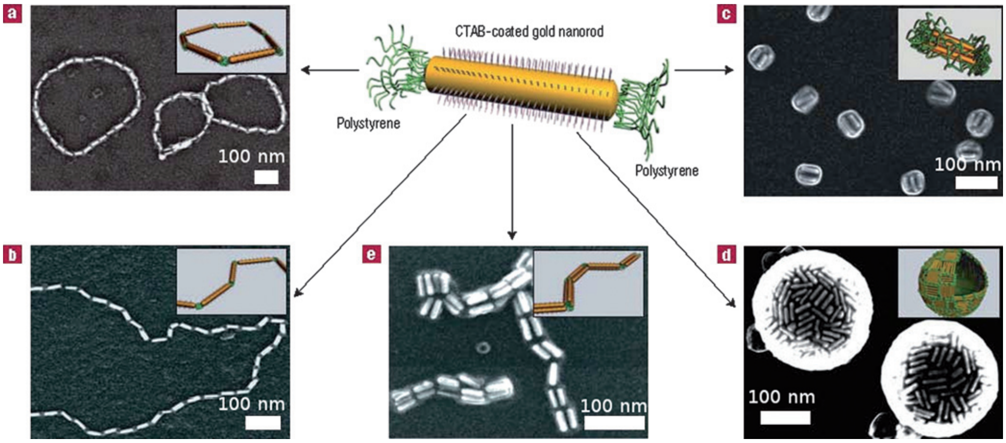
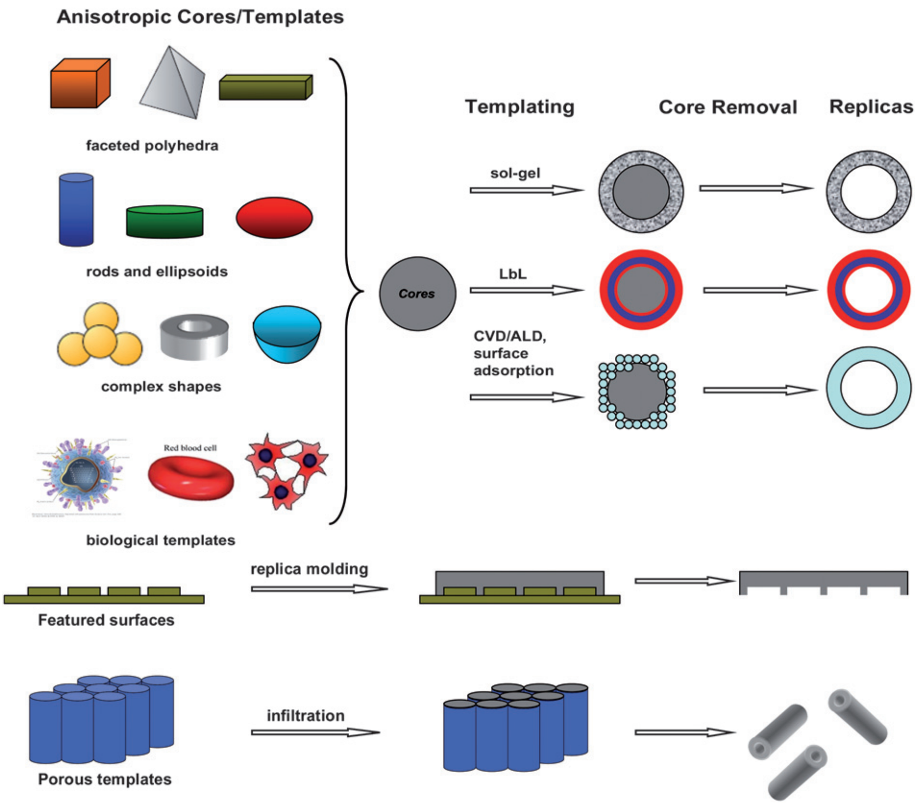


Fig. 1 An amphiphilic gold nanorod carrying a double layer of CTAB along the longitudinal side (the {100} facet) and polystyrene molecules grafted to both ends. (a–e): SEM images of the self-assembled nanorod structures: rings (a) and chains (b) self-assembled in dimethyl formamide–water mixture at water contents of 6 and 20 wt%, respectively, side-to-side aggregated bundles of nanorods (c) and nanospheres (d) self-organized in tetrahydrofuran–water mixture at water contents of 6 and 20 wt%, respectively, and bundled nanorod chains obtained in the ternary dimethyl formamide–tetrahydrofuran–water mixture at a weight ratio of liquids 42.5 : 42.5 : 15 (e). The insets show corresponding schematic diagrams of the nanorod assemblies. Reprinted by permission from Macmillan Publishers Ltd. from ref. 21, copyright 2007.



Scheme 1 Schematic of anisotropic cores/templates and possible replication pathways.

at selected developments in this field rather than its comprehensive coverage and examine new techniques applied for reproducing of anisotropic shapes and surface morphologies.

2. Dispersed particulates and replicas

Activities in this area have been long focused on the use of spherical templates due to easy fabrication routines based upon colloidal approaches governed by minimization of surface tension.[22] To date, there is a relatively narrow choice of monodisperse non-spherical particles with well-defined shapes suitable to serve as sacrificial anisotropic templates.

Preparation of anisotropic hollow replicas with assistance of sacrificial cores/templates introduces significant technical challenges such as, for example, formation of a uniform conformal coating around surfaces with large variation in curvature and the deficiency of anisotropic dispersed particulate templates with appropriate dimensions. Another challenge in the replication approach is the preservation of the shape of the replicates after core removal and even after drying. Similar to spherical templates, the material used to coat the anisotropic templates should be stable under the harsh conditions employed for core removal, such as high acid concentration or high temperature. An additional requirement for the core properties includes easy dissolution under conditions when an organic shell would remain stable. For example, pH is critical for stability of hydrogen-bonded multilayer shells deposited on an inorganic core, and etching the core at low pH is preferred. In replication of microstructures, their stability under local stresses and during the pulling-off routine is the critical issue. Considering these contradictory requirements, only a limited number of anisotropic cores/templates can be indeed utilized for desired replication with some of them discussed below.

2.1. Anisotropic inorganic particles

Spherical polymer and inorganic microparticles obtained *via* a variety of colloidal and nucleation routines have been the focus of long-standing research (Fig. 2A).[30] However, only recently, a variety of easily dissolvable and highly anisotropic inorganic colloids of different shapes, compositions and functionalities have been introduced as prospective sacrificial templates for replication, including cubes,[31] peanuts,[32] dimers,[33] rods,[34] and tetrahedra.[35]

These microparticles can be fabricated by using various approaches.[36–38] The simplest method that satisfies the requirements is the preparation of calcite cores, which are not-toxic, can be easily obtained and selectively dissolved at acidic and neutral pH.[39,40] Specifically, 3 μm cubic calcium carbonate particles can be prepared by the precipitation reaction of sodium carbonate with calcium chloride in water in the presence of polyacrylic acid at 80 °C (Fig. 2B).[41] Uniform rhombohedral microcrystals of cadmium carbonate can be synthesized by aging a mixture of cadmium chloride solutions in the presence of urea at 80 °C for 24 h (Fig. 2C).[42] Another example of shaped colloids is tetrahedral microcrystals of SnS that can be formed by thermally decomposing tin chloride and elemental sulfur in a primary amine solvent (Fig. 2D).[35]

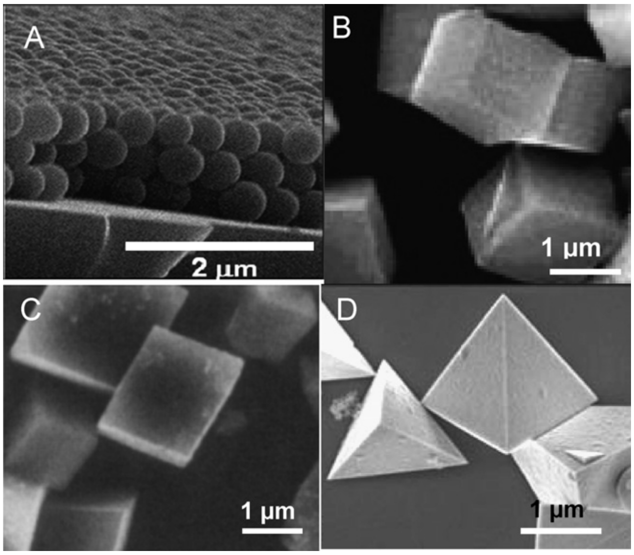


Fig. 2 Templates with well-defined shapes. (A) Traditional silica spheres, adapted with permission from ref. 30, copyright 2005, American Chemical Society. (B) Cubic calcium carbonate particles, adapted with permission from ref. 31, copyright 1993, American Chemical Society. (C) Rhombohedral cadmium carbonate particles, reprinted from ref. 41, copyright 2004, with permission from Elsevier. (D) Tetrahedral SnS microcrystals. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA, reproduced with permission from ref. 35.

These precipitation approaches for producing anisotropic inorganic particles are readily scalable but often lack fine control of particle size and monodispersity. In addition, these methods are limited in the variety of produced shapes mostly to those listed above.

2.2. Anisotropic organic particles

Despite much success in the synthesis of inorganic microcrystals, the preparation and shape control of anisotropic microstructures from organic compounds have not yet been widely reported, despite the fact that they may offer great variety and flexibility in molecular design. One recent example includes 2,5,8,11-tetra-*tert*-butylperylene (TBPe) crystals with cubic, truncated cubic, or

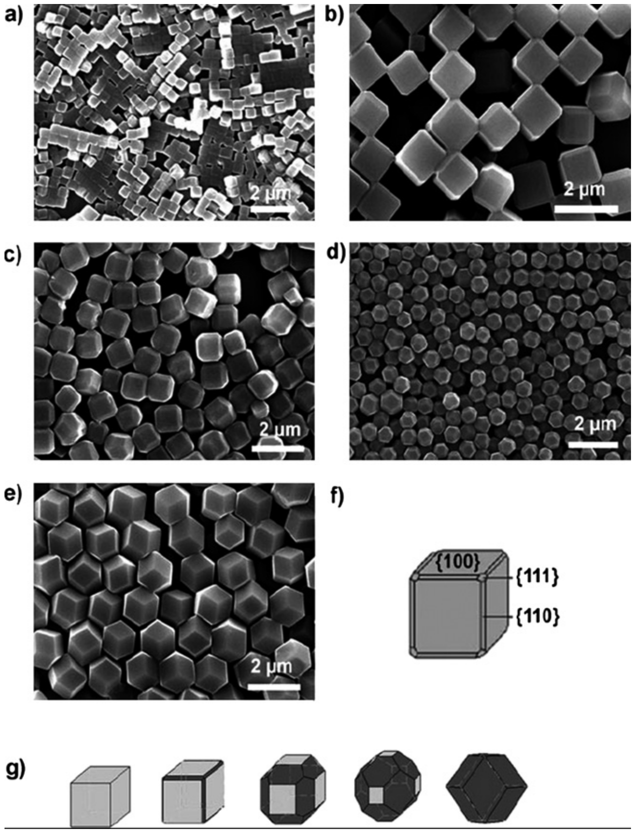


Fig. 3 SEM images of TBPe polyhedral particles formed under different conditions: (a) Cubes, (b) truncated cubes, (c) intermediate shape, (d) truncated rhombic dodecahedra, (e) rhombic dodecahedron. (f) Unit cell of the cubic lattice. (g) Geometrical particle shapes determined by the ratio of the growth rate in the (100) and (110) directions. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission from ref. 43.

rhombic dodecahedral shapes prepared by a surfactant-assisted process (Fig. 3).[43] The precise shape control in this case was achieved by changing the solvent composition or solubility of TBPe with the assistance of a surfactant, which altered the growth rate in the (100) direction relative to that in the (110) direction.

The preparation of anisotropic polymer colloidal particulates has been a challenging task for a multiple phase colloidal process. This is caused by the minimization of the interfacial free energy usually resulting in spherical microparticles.[44] However, despite this challenge a variety of easily dissolvable anisotropic polymeric colloids have recently been prepared, including ellipsoids,[45] corpuscle-shaped,[46] and tetrahedral particles.[47] In most cases, anisotropic microparticles are fabricated by fine tailoring the colloidal procedure developed for spherical colloids. For example, dimers and multiplets, ellipsoidal particles, spheres with holes, snowman-like, disk-like and pear-like particles all can be fabricated from microspheres by seeded polymerization[48] or self-assembly of complex structures.[49] A popular pathway to form anisotropic polymer colloids is a so called "lost-wax" approach, which involves deformation of the polymer template to achieve elliptical particles.[50] The other methods to prepare non-spherical particles include colloidal lithography[51] and interference lithography.[52]

2.3. Particles with anisotropic surface properties

Particles with biphasic chemical composition and anisotropic surface properties present a new type of microparticles known as two-face Janus particles.[53,54] Janus particles display interesting assembling behavior since they possess both the physical and chemical properties of each phase.[55–58] Assemblies of Janus particles result in minimized interfacial energy and spontaneous aggregation of particles into clusters.[59] Moreover, Janus particles prepared by selective polymer coating of inorganic particles can be used to obtain half-shells upon the release of inorganic cores. Such half-shells present a new class of anisotropic replicas of spherical particles. An impressive number of methods have been developed to fabricate Janus particles with two-face composition.[60–63] The most popular method of selective functionalization is based on toposelective surface modification and template-directed assembly. Most popular procedures include masking of one hemisphere during the surface modification or microcontact printing.[60]

One example presented here describes Janus particles fabricated by toposelective plasma polymerization and layer-by-layer (LbL) assembly on microspheres (silica and titania), which are partially embedded into a sacrificial polymer layer (Fig. 4).[64] By varying the thickness of the sacrificial polymer layer, the masked areas of the spheres can be adjusted. The plasma coating remained firmly attached to the particles as the sacrificial layer was dissolved and the Janus particles were released. The coverage areas of the particles with the polymerized coatings can vary in a wide range: from very low to a high ratio. Finally, the plasma polymerized coatings covering the microspheres can be released producing robust highly crosslinked half-shells (Fig. 4).

2.4. Complex shape particles by interference lithography

The excellent control over the geometrical parameters offered by interference lithography (IL) has been exploited for the fabrication of microparticles with complex shapes. Yang and co-workers have demonstrated the synthesis of monodisperse anisotropic colloids (disc- to rod-like) with fine control over the dimensions and the aspect ratio.[52] A sacrificial polyimide layer was employed to release an array of cylindrical posts resulting in individual anisotropic colloidal particles.

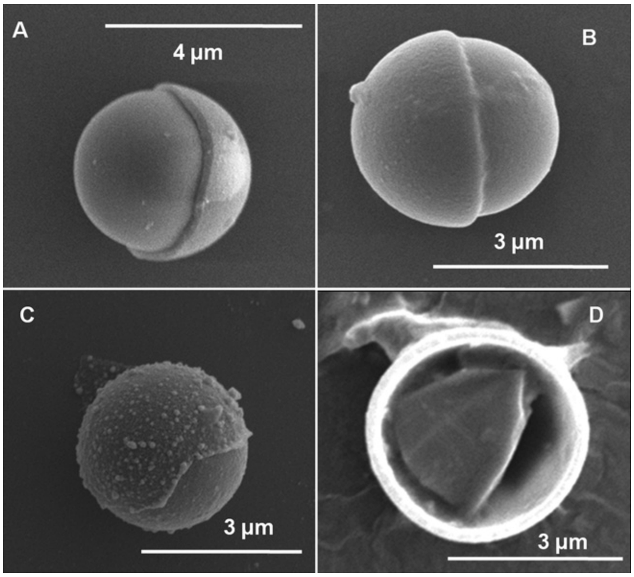


Fig. 4 SEM images of (A, B) Janus particles with coverage of particles with plasma polymerized acrylonitrile on silica microspheres; (C) Janus particles with coverage of particles with LBL-Ag shell on titania microspheres; (D) plasma polymerized half-shell obtained upon release of inorganic cores.

Thomas and co-workers have extended the IL approach to fabrication of complex "multivalent" submicron particles (Fig. 5).[65] Colloidal microparticles with complex concave shapes were obtained by cleaving highly porous connected structures. The highly complex shape sprouts from the ability of the IL to control geometry such as symmetry and volume fraction in a 3D lattice. The technique involves continuous decrease in the volume fraction of the connected IL structure, which eventually pinches off the thin connecting struts and yields disconnected anisotropic particles (Fig. 5).

Combining stop-flow lithography with phase mask lithography enabled the fabrication of microparticles with complex shape such as triangles with internal periodicity.[66] The precise shape is controlled by the microscope projection lithography and the continuous processing under laminar flow of the precursors in microfluidic devices.

2.5. Particle replication in nonwetting template

Monodisperse and well-shaped particles ranging from the nanometre to micrometre size regime can be produced by a method called particle replication in nonwetting template (PRINT), recently introduced by DeSimone *et al.* (Fig. 6).[67] In this method, a liquid, which can be any organic or inorganic material, is evenly distributed over the perfluoropolyether mold using a roller (Fig. 6). Then, the liquid is solidified (*e.g.*, photochemically or by thermal curing), followed by harvesting the

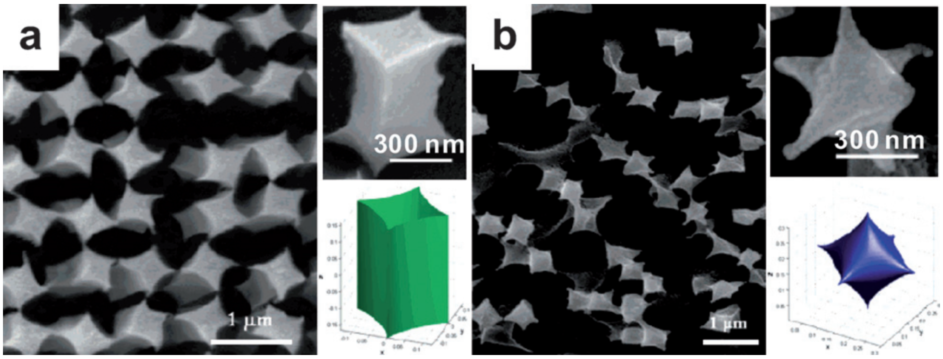


Fig. 5 SEM images of 3D structures after UV/ozonolysis. Lower insets show the single unit cell with the calculated light intensity distributions corresponding to the SEM images. The upper insets are magnified individual "4-valent" (a) and "6-valent" (b) particles very similar to the theoretical model in the lower insets. Reprinted with permission from ref. 65, copyright 2007 American Chemical Society.

particles from the mold by dissolving a sacrificial adhesive layer. This approach allows the fabrication of very monodisperse microparticles with controlled dimensions and an infinite variety of shapes, which could serve as sacrificial cores. Another significant advantage of PRINT is flexibility in chemical composition, and surface functionality. However, this method requires significant efforts to scale up and produce sufficient quantity of particles.

2.6. Biological particulate templates

Biological materials and structures present a relatively new inspiration for the design of functional materials *via* replication.[68] Many organisms synthesize inorganic structures with ordered features and this approach can be utilized to fabricate synthetic replicas. The encapsulation of cells and other cellular materials may have itself important applications in biotechnology and medicine, because the surrounding shell protects the interior from external influences. The use of biological templates has opened a way towards biomimetical structures, such as artificial cellular structures as will be briefly discussed below.

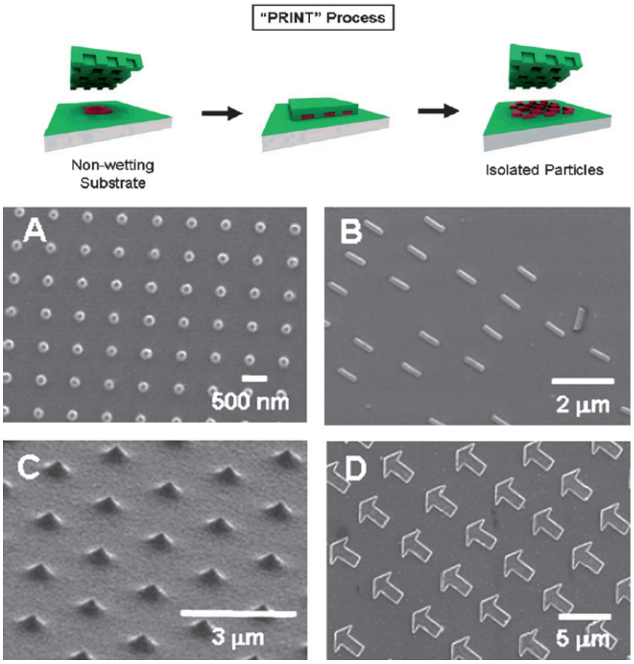


Fig. 6 Process of fabrication of shape-specific microparticles and SEM images of (A) 200 nm trapezoidal PEG particles; (B) 200 nm × 800 nm bar PEG particles; (C) 500 nm conical PEG particles that are <50 nm at the tip; (D) 3 µm arrow-shaped PEG particles. Reprinted with permission from ref. 67, copyright 2005 American Chemical Society.

2.7. Methods for replication of dispersed particulates and examples of replicas

Templating against colloidal particles is the most effective and widely used method for the preparation of hollow anisotropic replicas with various shapes similarly to that developed for round colloidal particles.[22] In this method, the particulate template is coated with a thin layer of selected material to form a core–shell structure followed by removal of the template *via* selective etching in a solvent or thermal decomposition in air. This selective removal results in the formation of hollow particles whose shape and interior size are determined by the template selected. Along with sol–gel coating, various other methods have been utilized for the shell-fabricating step, including grafting techniques,[69] chemical vapor deposition,[70] atomic layer deposition,[71] surface adsorption,[72] deposition of preformed colloids,[73] and LbL approach.[74] In this section we focus on methods that have been utilized to replicate anisotropically shaped cores.

2.7.1. Sol–gel templating. Mesoscopic hollow particles of non-spherical shapes can be synthesized by templating a sol–gel precursor solution against an array of particles. For example, ceramic egg-shell-like hollow replicas were generated from ellipsoidal particles.[75] The resulting egg-shell-like hollow particles had a well-controlled void size that was determined by the dimensions of the template. Chen and co-workers have demonstrated the use of hematite particles as templates to create various ellipsoidal hollow replicas.[32] First, Fe_2O_3@SiO_2 core–shell particles were synthesized by base-catalyzed hydrolysis of tetraethylsiloxane on hematite cores. Next, polymerization of pyrrole was performed around as-prepared Fe_2O_3@SiO_2 composite spheres to form sandwich multilayer core–shell particles. Silica, silica/polypyrrole, polypyrrole ellipsoidal hollow capsules and polypyrrole ellipsoidal hollow capsules with movable hematite cores were obtained after the selective removal of the hematite, $Fe_2O_3@SiO_2$ cores or silica middle shell of the sandwich ellipsoids respectively.

Peanut-shaped hematite colloids have been prepared by several groups[32,76] and used recently by Liddell and co-workers as templates to create hollow shells (Fig. 7).[77] To synthesize the core hematite particles, a condensed ferric hydroxide gel was aged under hydrothermal conditions. A silica shell was then grown onto the hematite surface using modified sol–gel chemistry followed by core removal through selective etching using concentrated hydrochloric acid. The resulting silica peanut-shaped replicas were organized under confinement into an aperiodic crystal structure, in which particle lobes tile a triangular lattice while their orientations uniformly populate the symmetry-defined directions (Fig. 6). This study demonstrated that simple anisotropic replicas can be constructed using non-spherical colloids.

2.7.2. "Quasi-template" method. Preparation of octahedral silica nanocages have been recently demonstrated in a novel one-step approach by Lou *et al.* (Fig. 8).[78] To accomplish this strategy, a solution of H_2PtCl_6 is added to a mixture of ethanol–H_2O/ammonia containing tetraethylorthosilicate and amino-propyltrimethoxysilane (APTMS). Surface functionalization with amino groups from APTMS plays an important role for subsequent deposition of silica on the obtained $(NH_4)_2PtCl_6$ quasi-template. This "quasi-template" method has several important advantages over conventional template strategies. First, the quasi-templates though insoluble in the original ethanol–H_2O reaction mixture are easily removed by washing with water. Moreover, the template is generated *in situ*, which renders pre-synthesized hard templates unnecessary, thus allowing structures with a wider range of sizes, and of high purity to be readily synthesized. Furthermore, the quasi-template itself serves as the precursor to noble-metal nanoparticles, which can yield controlled Pt-functionalized products by simple calcination.

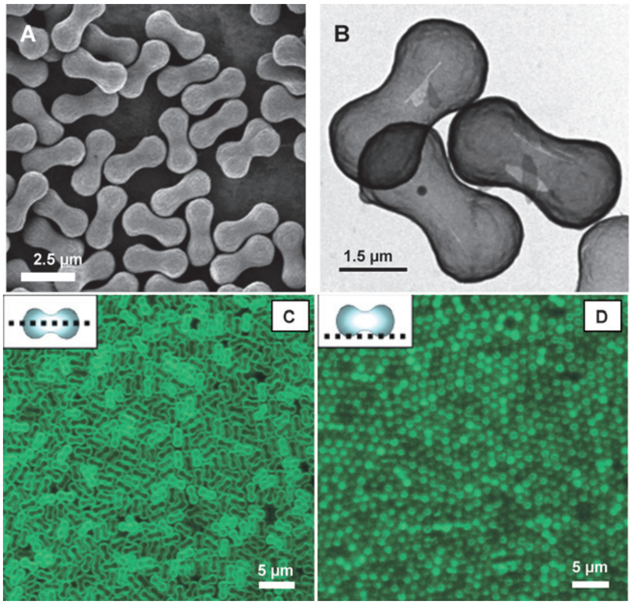


Fig. 7 (a) SEM image of monodisperse hematite colloids from which hollow particles were templated. (b) Transmission electron microscopy (TEM) micrograph of hollow silica replicas. (c) Confocal optical image of a dense monolayer of anisotropic colloids taken across the equatorial plane (inset, schematic view). (d) Triangular ordering of the lobes is revealed when an image is captured at a focal plane that just grazes the particle lobes (inset, schematic). Reproduced from ref. 77 by permission of The Royal Society of Chemistry, copyright 2008.

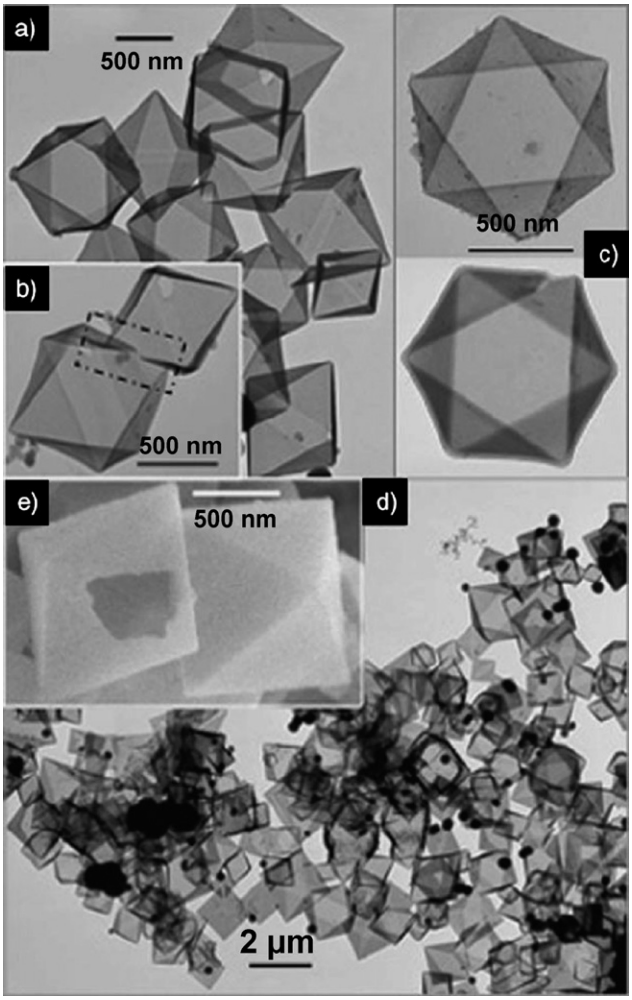


Fig. 8 (a–d) TEM and (e) SEM images of octahedral silica nanocages after intensive washing to remove Pt salt. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission from ref. 78.

2.7.3. Layer-by-layer approach. LbL assembly is one of the prominent methods to build ultrathin polymer micro- and nanoshells with nanometre-level control over composition, thickness and tunable chemical functionality.[79,80] In this method, multilayer structures are formed on various cores through a sequential adsorption of appropriately matched species—biological molecules, polymers, organic molecules and nanoparticles—able to interact *via* electrostatic interactions, hydrogen-bonding or produce covalent bonds during LbL assembly.

LbL-treated colloidal particles have been extensively exploited to fabricate thin-shell spherical microcapsules after the subsequent dissolution of the core (Fig. 9A).[81–83] Hollow complex LbL microcapsules can be used for encapsulation/release of delicate biomaterials such as enzymes. To achieve a sustained separation of several components within confined compartments of a single capsule entity, capsule-in-capsule technology was suggested.[84] In this approach, calcium carbonate microparticles as a novel category of template have been recently considered. Due to high porosity, the calcium carbonate spherical template provides excellent loading capacities for biological materials along with the easy removal of the core. Fabrication of the capsule-in-capsule structure involves utilization of complex core of two concentric calcium carbonate compartments that can be independently loaded with biopolymers. The resulting ball-in-shell particles can be employed for the fabrication of novel multi-compartment microcontainers.

Anisotropically shaped LbL-assembled hollow structures have high potential as stimuli-responsive microcarriers for drug delivery application due to shape-dependent interactions of particles with cells. As a part of a hollow container, ultrathin hydrogel walls are capable of controlling directional permeability, and therefore site-dependent loading and release of macromolecules to/from such containers in response to environmental pH variations.

There are few examples where anisotropic microcapsules have been constructed from anisotropic geometries considering the need to stabilize thermodynamically unfavorable shapes with sharp edges.[85–87] One of the earliest examples of such an attempt was the alternate deposition of poly(styrene sulfonate) (PSS) and poly(allyl amine hydrochloride) (PAH) polymer layers on surfaces of cubic enzyme crystals.[88] The formation of the $(PSS/PAH)_4$ shell around the core particle was achieved under conditions when the enzyme crystals were insoluble. The size and shape of the template crystals were retained during the LbL coating. However, after the enzyme core was solubilized and washed away in the pH range of $4 > pH > 6$, the resultant hollow multilayer shells did not show any shape memory leaving behind almost spherical hollow polymer shells.[89] This transformation is due to the high osmotic pressure built up within the LbL microcapsule because of high concentration of dissolved enzyme. Indeed, when the same polyelectrolyte pair was applied to rhombohedral cadmium carbonate cores, no significant differences was found for hollow shells left after $CdCO_3$ dissolution at slightly acidic pH.[88,90]

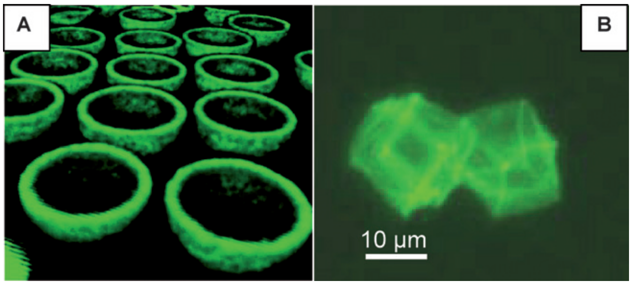


Fig. 9 (a) Confocal microscopy image of hollow polymer capsules produced on spherical silica particles through the LbL approach. Reprinted with permission from ref. 83, copyright 2008 American Chemical Society. A fluorescence optical microscopy image of hollow $(PEI/PMAA)/(PVPON/PMAA)/(PEO/PMAA)_3$ hybrid hydrogen-bonded capsules (b) after core dissolution. Reprinted with permission from ref. 40, copyright 2005 American Chemical Society.

LbL multilayers based on hydrogen-bonding were also demonstrated to have sufficient structural strength and integrity to maintain the original form of a template particle in solution after core removal.[40] Cubic-shaped LbL microcapsules can be fabricated by the deposition of poly(methacrylic acid)/poly(*N*-vinylpyrrolidone) (PMAA/PVPON) or PMAA/poly(ethylene oxide) (PMAA/PEO) multilayers from pH 3.5 solutions onto 10 μm cubic $CdCO_3$ particles. Remarkably, the original shape of the template particles was demonstrated to be perfectly preserved including well-defined sharp edges despite the ultrathin walls of the resultant capsule (less than 20 nm) (Fig. 9B). Moreover, these anisotropic hollow polymer capsules possess a pH-sensitivity and can be quickly dissolved under neutral or basic conditions.

Anisotropic microcapsules of a cubic shape with the capsule walls made *via* the LbL approach have been recently demonstrated by Paunov *et al.*[39] Nano-cotton fibers derived from sulfuric acid hydrolysis of cellulose carried negative surface charge and were combined with positively charged PAH on to needle-like aragonite and rhombohedral calcium carbonate crystals (Fig. 10). The geometry of the template was well-reproduced in the polymer shell after the crystal template dissolution. A drastic reinforcement of the polymer shell with cotton microfibers was demonstrated. A single-layer shell was robust enough to sustain the cubic hollow structure (Fig. 10).

Various biological structures with multiple-length scale dimensions have been utilized as templates for LbL-based anisotropic replicas. For example, red blood cells of discoid or echinocytic shapes were coated with $(PAH/PSS)_5$ LbL shell (Fig. 11).[91,92] After core removal by the (NaCl + NaOCl) solution, the distinctive shape of the original templates was still preserved. Similarly, *E. Coli* bacteria chemically stabilized with

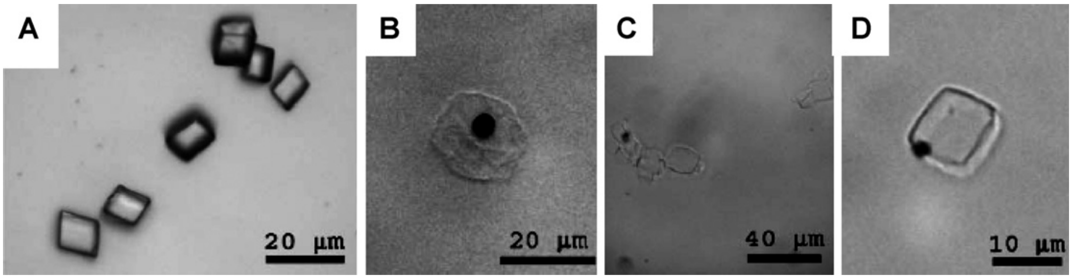


Fig. 10 Optical microscopy image of calcite crystals coated with one layer of PAH/nano-cotton fibers (A). Optical microscopy image of the microcapsules with a single composite layer of PAH and nano-cotton fibers (B) and similar images of microcapsules with two composite layers of PAH and nanocotton fibers (C, D). Reproduced from ref. 39 by permission of The Royal Society of Chemistry, copyright 2007.

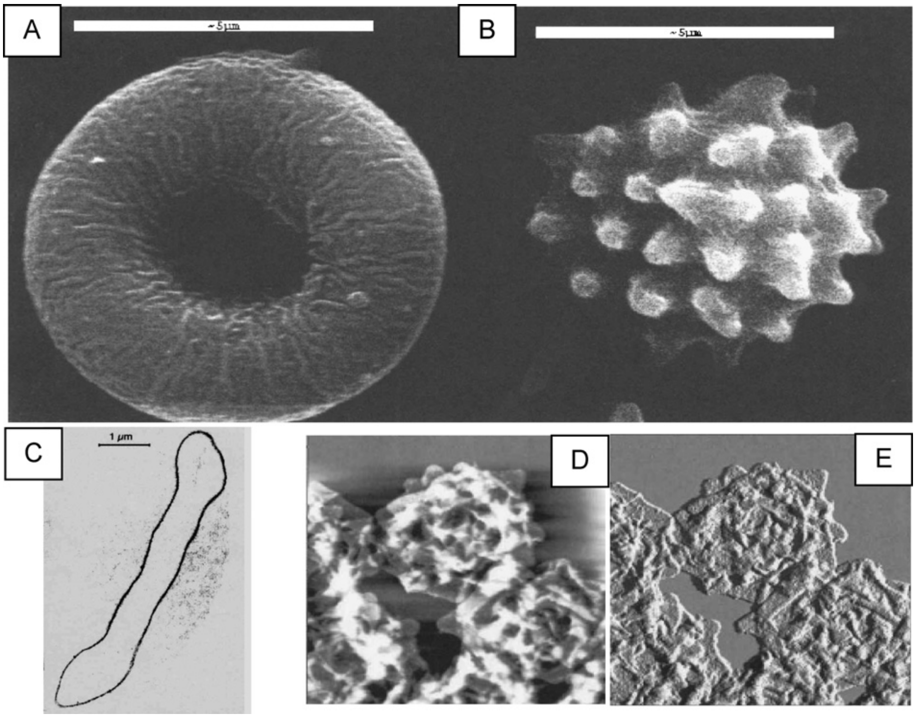


Fig. 11 SEM image of fixed discoid and echinocytic RBC with $(PAH/PSS)_5$ polyelectrolyte layers (A, B). TEM image of the polyelectrolyte shell obtained after the digestion of the discoid blood cell (C) resembles the shape and size of the original template. AFM images of polyelectrolyte shells formed on echinocytes (D, E). The shell walls are composed of $(PAH/PSS)_5$. The images were taken in the contact (D) and tapping modes (E). Reprinted from ref. 91 by permission of the publisher (Taylor & Francis's Group), copyright 2001.

glutaraldehyde crosslinker were used as templates for the fabrication of the $(PSS/PAH)_5$-based hollow cell replicas.

Hybrid multilayers of silica nanoparticles and poly(diallyldimethylammonium chloride) (SiO_2/PDDA) were used to replicate the glutaraldehyde-fixed crenated red blood cells.[85] Corresponding hollow microcapsules obtained after the cell-core was destroyed by a deproteinizer, mimicked the original shape including the fine secondary structure, such as sharp nanoscale spikes of the original template.

Conformal and continuous titania coatings were generated on biosilica templates, *Aulacoseira* diatom frustules through the LbL approach.[93] The silica diatom frustules were exposed in an alternating manner to a titania-forming protein, protamine, and then to an aqueous titania precursor to build up a conformal titania coating (Fig. 12). After pyrolysis at 500 °C, a conformal, continuous crystalline titania coating was achieved. Removing the silica templates resulted in free-standing complex titania microstructures with morphologies replicated from diatom templates.

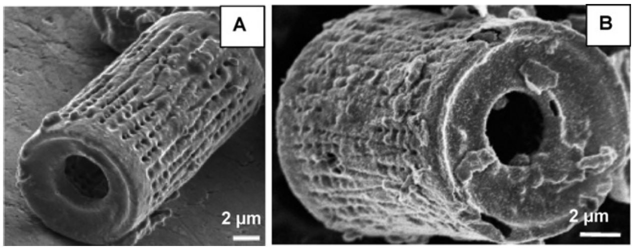


Fig. 12 SEM images of an *Aulacoseira* frustule (A) and a complete frustule-derived titania structure (B) after 12 cycles of protamine/TiBALDH LbL assembly, at 500 °C for 2 h treatment, and selective silica dissolution. Reprinted with permission from ref. 93, copyright 2009 American Chemical Society.

Despite the success in producing replicated capsules of anisotropic templates with perfectly mirrored shape and size of the initial templates, the hollow LbL structures do not yet possess the mechanical strength to retain those features in a dry state. A combination of materials, *e.g.*, reinforced hybrid organic–inorganic nanocomposites, or a combination of methods, such as the LbL approach and the mineralization, are yet to be explored to yield the desired combination of properties.

3. Continuous templates and replicas

Replication of 3D periodic structures into high-index inorganic materials or metals can result in photonic and plasmonic structures. Various dry and wet methods such as atomic layer deposition, chemical vapor deposition, sol–gel process, electrodeposition, and biomolecule mediated chemical reduction have been employed to realize the inorganic replicas.[94–97] This section discuses some complex continuous templates that have been recently developed and utilized for replication. Synthetic molding of biological continuous templates is also considered in this section.

3.1. Microfabrication techniques

The widely used techniques for replication of continuous periodic structures are based on molding of topographically patterned substrate, called masters. The masters are fabricated using photolithography with an appropriately chosen photosensitive material. Casting and curing a prepolymer (*e.g.*, to make polydimethylsiloxane, PDMS) against a master generates an inverse replica of the master. Peeling the PDMS from the master forms the "stamp" or "mold". Multiple stamps can be formed from a single master. The soft nature of the stamp provides added processing capabilities, such as patterning on curved surfaces.

Soft lithography refers to a set of methods for fabricating or replicating structures using elastomeric stamps. For example, fluorinated elastomeric molds are utilized in the imprint lithographic technique (PRINT), described above, to fabricate distinct anisotropic particles. Soft lithography offers a simple and low-cost surface patterning with high versatility.[98] The technique has been proven to be the easily accessible microfabrication method applicable to various synthetic and biological materials under regular lab conditions.[99–101] This field pioneered by Whitesides in the late 1990s has been fully covered in a number of thorough reviews.[102,103] Therefore, here we will not discuss this topic extensively but rather briefly mention related microfabrication techniques, since they are one of the first examples of synthetic replication of continuous structures.

3.2. Microprinting and microfluidic techniques

PDMS stamps are utilized in microprinting techniques to replicate surface patterns of molecules onto the surface of a substrate. Contact printing is a direct patterning method where a molecular "ink" that is soaked in a PDMS stamp is transported to the substrate surface by diffusion with the aid of conformal contact. In a molding process a polymer layer is molded into the features of the polymer master.[104] Moreover, patterns of different surface functionalities can be further used for the selective deposition of inorganic materials.[98] The capability of the method has been demonstrated by the fabrication of patterned structures from a variety of functional materials, metallic and magnetic nanoparticles, organic semiconductors, biomolecules and cells.[105,106] The patterns can be used to adhere proteins or cells on predefined locations of a substrate or within a microfluidic channel. For instance, metal-binding peptide solution was pre-patterned on a solid substrate with the aid of the PDMS-based microchannels, which resulted in a stripped array of polygonal silver nanoparticles.[107] The silver nanoparticles were selectively deposited in regions containing the peptide and not in the surrounding areas or between the microchannels thus replicating the original pattern (Fig. 13). The fabrication of gold nanoparticles at specific locations can be achieved through a polypeptide-induced reduction.[108] In a similar way, titania nanoparticles were obtained on patterned silaffin-topped surfaces.[109] Striped LbL films have been prepared by transferring gold nanoparticles and carbon nanotubes with capillary transfer lithography.[110,111]

3.2. Porous alumina templates

Hollow nanostructures with tailored dimensions can be obtained by templating a porous material with suitable pore size.[112] This process includes the infiltration of a polymer into open anisotropic cavities, then the polymer is solidified within the cavity, and finally the replicated polymeric material is achieved by removing initial template. For example, anodized alumina with pore diameters ranging from few tens of nanometres to a few hundred nanometres is a popular "natural" (not microfabricated in traditional way) template which is extensively employed as a template for the fabrication of inorganic and organic nanostructures. Numerous methods such as infiltration from melt, spin assisted infiltration from solution, vacuum assisted infiltration and electrodeposition have been employed for the fabrication of polymer replicas.[113–115] Russell and co-workers have observed a transition from partial to complete wetting with increasing annealing temperature, resulting in the formation of replicas of either nanorods or nanotubes.[113] Complete wetting of the cylindrical pores with the polymer melt resulted in long nanotubes while partial dewetting resulted in short nanorods.[116]

The fabrication of ordered nanostructures was extended to block copolymers, which enables the phase separation in highly confined state, resulting in core–shell nanotube or nanorod structures.[117,118] Wang *et al.* fabricated diblock copolymer nanorods by infiltration of a polymer melt and investigated the topology of nanorods at different pH values.[119] The responsive nanorods exhibited a change in the topology to the mesoporous state upon exposure to acidic environment. Using a spin assisted approach, Chang *et al.* have demonstrated the fabrication of high aspect ratio nanotubes from responsive block copolymer, polystyrene-*block*-poly (2-vinylpyridine) (PS-*b*-P2VP) combined with *in situ* grown gold nanoparticles (Fig. 14).[120] Owing to the pH-sensitive nature of P2VP block, which exhibits a coil to globule transition above pH 3.6, the PS-*b*-P2VP-gold nanoparticles nanotubes show reversible changes in topology and optical properties. Reversibly swellable nanotubes comprised of multilayers of poly(allylamine hydrochloride) and

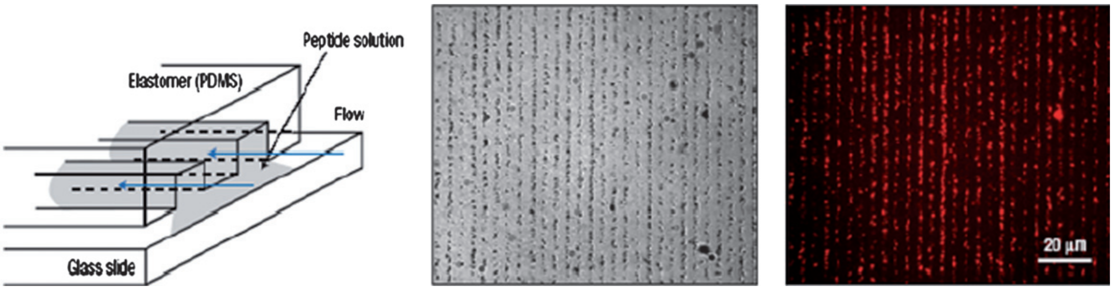


Fig. 13 *In situ* reduction of periodic array of silver nanoparticles on a peptide-patterned substrate with patterned microfluidic flow. Adapted by permission from Macmillan Publishers Ltd., ref. 107, copyright 2002.

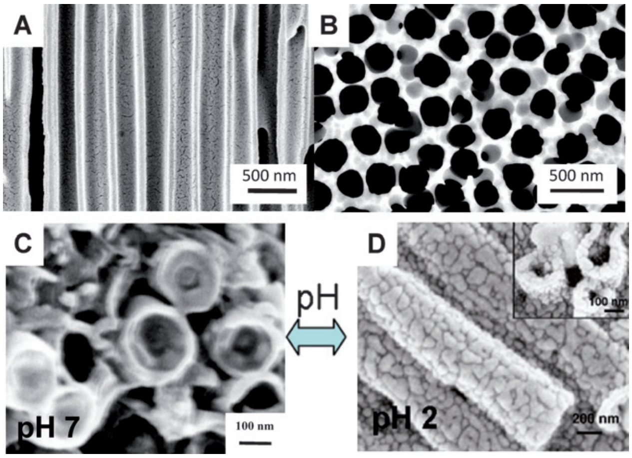


Fig. 14 SEM images of initial alumina membranes: side view (A) and top view (B). SEM images showing the reversible topology changes in the produced nanotubes with external pH due to the pH responsive nature of the P2VP domain (C and D). Reprinted with permission from ref. 120, copyright 2009 American Chemical Society.

poly(acrylic acid) have also been fabricated by utilizing porous alumina as templates.[121]

3.3. Colloidal crystal templates

One of the widely studied types of complex 3D replicas of microparticles is the inverse replicate of the face-centered cubic (fcc) opaline templates[30,122] prepared by colloidal crystal templating.[123] To prepare such structures, void spaces between spherical particles (*e.g.*, PS latexes or silica colloids), are infiltrated by fluid followed by its solidification. Removal of these particles produces the highly ordered porous solids or the inverse opal structure (Fig. 15).[124] Silica particles are removed by etching with hydrofluoric acid and polymer spheres by dissolution in appropriate solvent or by calcination. The resulting inverse replica contains uniform spherical voids that are interconnected through windows at the points where the original spheres touched (Fig. 15).[125] Inverse opals are used as photonic crystals due to their regular periodicity of low and high dielectric constant materials.[126]

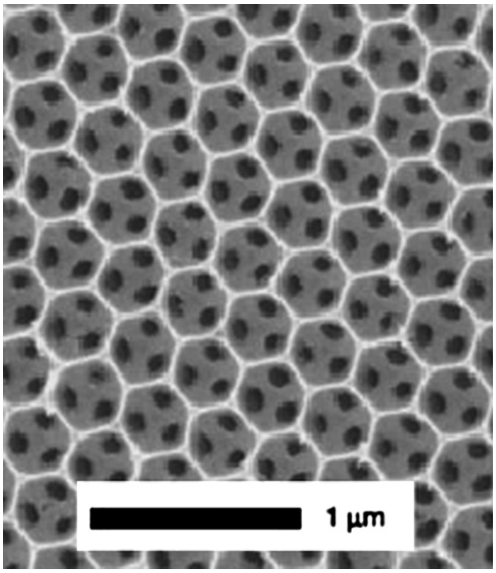


Fig. 15 SEM image of the (111) face of a titania inverse opal. Adapted by permission from Macmillan Publishers Ltd., ref. 125, copyright 2004.

A variety of materials have been used to prepare inverse opals,[124] beside silica,[127,128] such as alumina, titania, zirconia[9,129–131] and gold.[132,133] The general preparation scheme consists of (i) deposition of polymer spheres on a porous support[127,129] or inside a capillary[130,131] from an aqueous or ethanol solution; (ii) filling the voids with a silica precursor (tetraethoxysilane); (iii) drying; (iv) removal of the polymer spheres by soaking in toluene or calcination at 500 °C. To prepare gold inverse opals, silica colloidal crystals have been used with silica colloids surface-modified with 3-mercaptopropyltrimethoxysilane, followed by decorating with 5 nm gold nanoparticles and electroless deposition of gold.[132]

In addition to the infusion of colloidal crystal templates with a precursor, two alternate assembly processes for inverse opals have been developed. One method is based on simultaneous co-assembly of small nanoparticles with larger colloidal spheres. The small nanoparticles fill the voids in the templating structure resulting in similar structures to those described above.[73,134,135] This method allows compositional homogeneity of the structured product if nanoparticles of a desired composition are prepared before templating. The other alternate route involves the preparation of core–shell structures that are assembled into a colloidal crystal followed by removal of the cores.[136,137] This method provides good control over the wall thickness of the ordered porous material.

Inverse opals can serve as suitable molds to create spherical particles with uniform, predetermined diameters. In this case, the inverse opal can be infiltrated with precursors for the target spheres and removed to obtain the replica structure, often an interconnected array of solid spheres arranged in an opal structure. For example, the inverse opal method was used for the fabrication of well-ordered carbon microspheres by infiltration of phenolic resin into silica inverse opal structure and subsequent carbonization (Fig. 16).[138] This approach has been also used to synthesize spherical colloids of various oxides, sulfides, halides, carbides, metals, silicon, polymers, liquid crystals and wax.[50,139–145]

Colloidal crystals from non-spherical particles such as those discussed above have the potential for producing inverse opals which have higher complexity, asymmetric unit cells, and anisotropic properties, which cannot be achieved with traditional spherical particles. However, the self-assembly of the anisotropic building blocks remains a challenging task because control over uniform particle orientation during the assembly is required. A few examples of such colloidal crystals include asymmetric dimer colloids and mushroom-like colloids.[146,147] Colvin and co-workers have shown that polymer inverse templates can be uniformly deformed to produce ellipsoidal inverse opals, which can be used to generate anisotropic particle arrays.[50]

3.4. Interference lithographical templates

IL allows fabrication of periodic patterns with open architectures and fine dimensions (sub-micrometre) using coherent beams of light as was mentioned above.[148–151] Crucial to their use as ordered templates is the fact that this technique affords control over feature size and geometry in a wide range.

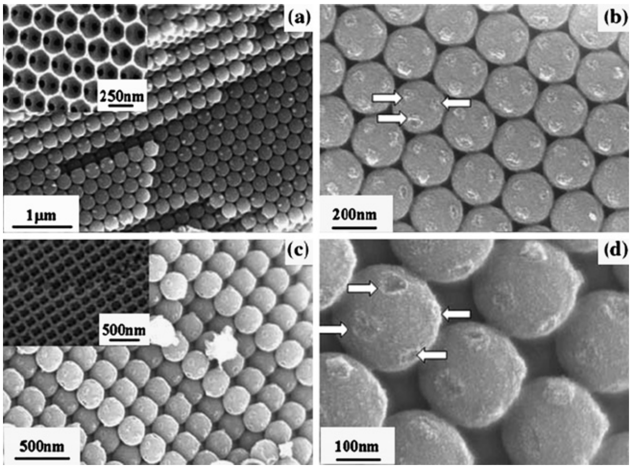


Fig. 16 Microparticle arrays with hcp (a, b) and fcc (c, d) structures. Insets show the corresponding silica inverse opal. The arrows indicate the contact points with the neighboring carbon microparticles. Reprinted with permission from Springer Science + Business Media from ref. 138, copyright 2007.

Replica molding has been employed to fabricate ordered structures from non-photoresist materials such as PDMS, polyurethane (PU), and responsive block-copolymers such as PS-*b*-P2VP.[152–155] Replica molding involves the fabrication of positive resist (which is soluble in organic solvents) by a single exposure followed by crosslinking (Fig. 17). Subsequently, the open 3D network structure is completely filled with reactive monomer *via* vacuum assisted infiltration, and cured. Finally, a second flood exposure to UV light is done to make the template easily soluble in a dilute basic solution leaving a negative replica of the periodic structure. This way, 3D bicontinuous PDMS elastomeric structures were demonstrated.[153]

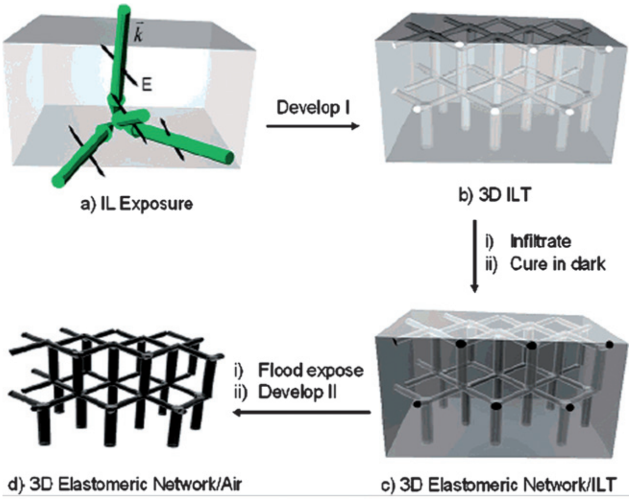


Fig. 17 Schematic illustration showing the replication process for the fabrication of 3D continuous elastomeric network/air structure. (a) Exposure by interference lithography. Large arrows show the direction of the beam while small arrows show the direction of polarization of each beam. (b) 3D interference lithography template (ILT) fabricated on positive resist. (c) 3D elastomeric network/ILT structure from the replication of the PDMS onto the ILT. (d) 3D elastomeric network/air structure after flood exposure under UV lamp and subsequent removal of template in a water-based developing solution. Reprinted with permission from ref. 153, copyright 2010 American Chemical Society.

Capillary transfer lithography[110] was used to reproduce a square array of air cylinders formed by interference lithography in SU8 photoresist (Fig. 18). Initially PDMS negative replica of the 2D organized porous IL structure was fabricated by pouring a mixture of pre-polymer and curing agent followed by curing. The negative replicas obtained, were then used for the fabrication of organized structures from other polymers (Fig. 18). The remarkable similarity between the original structures and their replicas proves excellent replication of surface topology (Fig. 18).

Near complete filling of diamond-like IL polymer structures with titania precursors through the electrodeposition method has been demonstrated.[96] At the early stage of electrodeposition, a thin titania seed layer (55 nm thick) was conformally deposited on the surface of the IL structure, after which the deposition occurred preferentially from the template bottom layer. Subsequent removal of the polymer template resulted in an inverse titania crystal with unusual photonic properties. In a different approach, gentle metallization of the porous IL structures was attained by biomediated formation of gold nanoparticles.[97]

3.5. Replication of continuous biological templates

Direct replication of biological structures, known as bioreplication, can be used to create complex synthetic replicas which not only mimic unique morphologies of biological materials but also can inherit their morphology-related functionalities such as self-cleaning ability of lotus leaves, anisotropic wetting of rice leaves, or antireflective properties of cicada eyes.[6,156,157] Alternatively, Aizenberg and co-workers have recently reported fabrication of high-aspect-ratio nanostructured surfaces inspired by the echinoderm skin, gecko foot and superficial neuromasts in fish and amphibians by a soft-lithographic method.[158–160]

The superhydrophobic and self-cleaning properties induced by surface roughness are widely known in natural structures, including plant leaves, butterfly wings and water strider legs.[156] Replication of the complex hierarchical topography of leaves of the Agave plant (*Agave attenuate*) was achieved with excellent precision using two soft lithographic techniques, replica molding and nano-imprinting (Fig. 19).[161] The Agave leaves were used as a structured biological template to transfer their characteristic morphological patterns to artificial surfaces to endow them with superhydrophobic properties without traditional tedious multi-step microfabrication (Fig. 19).

Phase-separation micromolding was applied to replicate surfaces of the plant leaves.[162] In comparison to regular replica molding when PDMS is used for the replication, this technique allows a straightforward structuring of a broad range of copolymers and biodegradable polymers. Anisotropic surface structure of the rice leaf was replicated in surface morphology of Hyflon film by using this technique. As a result, a reproduced artificial rice leaf had even better anisotropic wettability compared to that of the natural rice leaf. Moreover, the contact angle measured in the direction parallel to the grooves was shown to be 160° compared to 140° for the natural rice leaf.

Inorganic structures can yield hard and high-temperature replicas of biological templates. Such inorganic replicas can combine enhanced mechanical properties offered by the hard

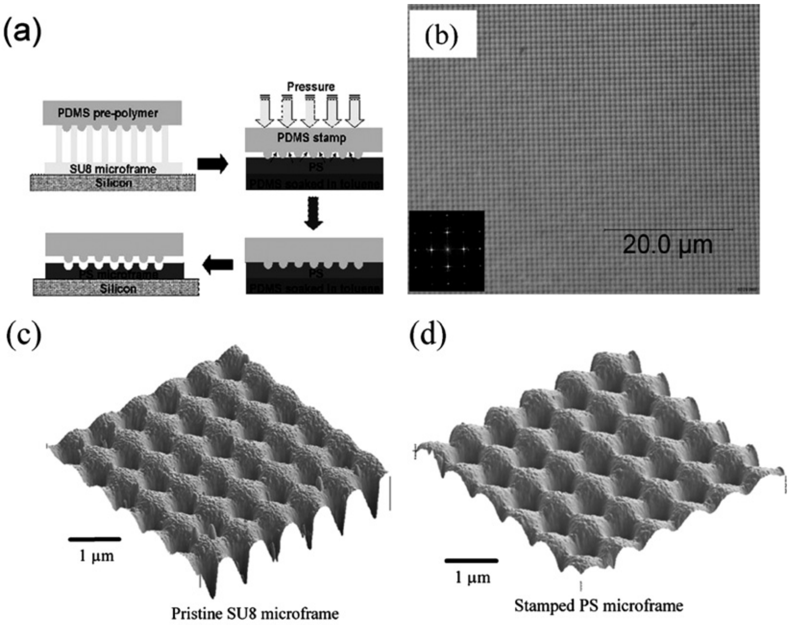


Fig. 18 (a) Schematic of the capillary transfer lithography using IL structures as masters; (b) Optical image of the PDMS stamp showing the large scale uniformity. AFM images of (c) pristine SU8 structure and (d) stamped PS structure showing identical topographical features down to the nanoscale. Reproduced from ref. 155 by permission of the PCCP Owner Societies.

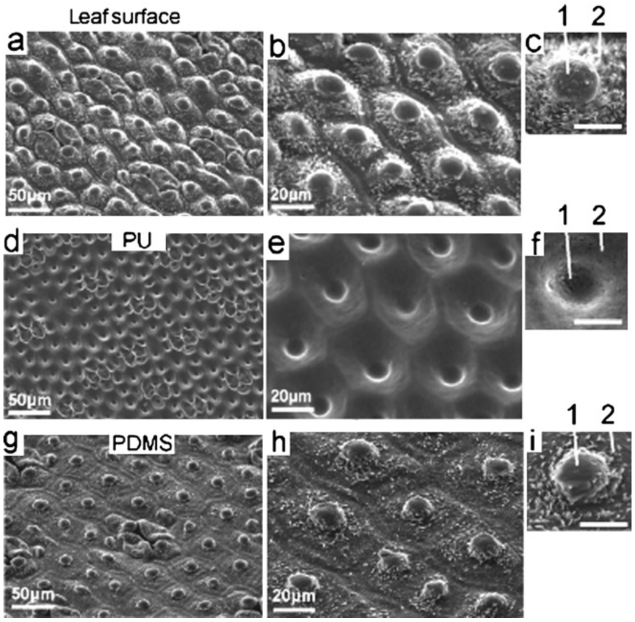


Fig. 19 SEM Images of *Agave* leaf surface and the corresponding replicas showing the replication process. Leaf surface (a–c), PU negative (d–f) and PDMS positive (g–i) replicas. Papillae structures with micro (1) and nanofeatures (2) are marked. Reprinted with permission from ref. 161, copyright 2008.

material with optical, chemical and biochemical properties. Thus, titania replicas of *Morpho* butterfly wing scale structures were obtained through multi-step sol–gel replication.[5] After 40 cycles of the biotemplate exposure to a mixed titania–tin alkoxide solution and water, followed by firing at 450 °C, rutile titania-based nanocrystalline structures retained the micro- and nanoscale features of the chitin templates.

4. Conclusions and outlook

In the past decade, considerable progress has been achieved in the fine replication of complex synthetic and biological objects including dispersed particulates and continuous structures. Replication of exotic shapes would bring advantages due to generation of complex replicas with unusual physical properties and ability to guided assembly in complex 3D structures. For instance, as we discussed here, polymer-based replicas might allow controlled and directed release of loaded material through selective surface modification.

A variety of anisotropic dispersed particulates have been synthesized and used as sacrificial templates compatible with common replication routines. Some of the recent replication approaches shown here include sol–gel templating, *in situ* generated templating and LbL assembly. In addition to dispersed particulates, continuous templates such as porous inorganic structures, microfabricated periodic masters, anisotropic inorganic microcrystals, colloidal crystals and biological structures are widely utilized.

The literature survey conducted here shows that highly scalable techniques for producing high-quality replicas are still limited due to the technical problems discussed above. This is probably the most critical issue for further developments of this approach and for exploring prospective applications. Further development of novel synthetic routes toward new anisotropic and complex shapes is also desired in order to achieve uniquely shaped replicas at multiple length scales.

Another significant challenge in the fabrication of complex replicas from polymeric materials is their ability to maintain the inherited shape under stresses imposed by capillary forces or osmotic pressure to maintain their shape under variable environmental conditions. Most of current replicas are not robust enough to be handled or utilized *e.g.*, for further manipulation such as change of solvent, chemical modification, drying, or transferring to different substrate. On the other hand, hollow replicas based on inorganic materials possess such important properties as mechanical strength and stability sufficient to withstand such challenges. We suggest that introducing inorganic components into a flexible matrix to create hybrid organic–inorganic replicas might result in stabilization of the complex replicated anisotropic structures without compromising their compliance, functionality, tunability and permeability.

Although preparation of periodic continuous microfabricated templates and their replication has been intensively explored over the past decade, there are a number of challenges in this area to be addressed. For example, fabrication of "photoresist" masters for elastomeric molds is expensive, limited in resolution, restricted mostly to planar substrates, does not allow easy fabrication of 3D structures, and is incompatible with many very compliant organic and biological materials.

As we showed here, interference lithography enables the fabrication of templates with a high degree of complexity which can render unique dispersed and continuous structure to the polymeric replicas which are unachievable by many traditional methods. However, the technique is not free of certain shortcomings which should be addressed in future research. Fabrication of nearly defect-free and complex 3D IL structures involves in a tedious and time-consuming optical alignment of multiple optical beams. The functionalized materials, which can be employed, are limited and the inception of new materials requires painstaking optimization. Recent development such as phase mask lithography provides complex 3D structures and this approach obviates the need for optical alignment of the beams in 3D space. We believe that phase mask lithography is a viable platform for obtaining complex 2D and 3D structures and is likely to be embraced by a broader scientific community.

Porous alumina has served as an excellent template for obtaining one-dimensional high-aspect ratio polymeric structures such as nanowires, nanotubes, and more importantly for understanding the nanoscale confinement effects in these systems. Whereas the technique offers excellent control over the size of the cylindrical structures, the control over the shape of these structures is limited. Future developments in this area will critically depend on the ability to produce reproducible porous alumina membranes with finely tailored pore shape, gradient in diameter along thickness and controllably modulated pore diameter along the thickness. In fact there are some recent reports using hard anodization approaches, where the pore diameters could be modulated along the thickness of the porous alumina membranes.[163] These PAMs are expected to serve as unique templates for the fabrication of polymer structures with controlled variation in the degree of confinement.

Anisotropy in shapes and interactions might promote hierarchical organization into complex structures which is an important prospective for anisotropic structures discussed here. Indeed, as suggested by de Gennes, the hierarchical assembly can be tailored by the design of multifaceted microparticles with directional interactions from diversely functionalized hemispheres.[60] The dual nature of chemical interactions could be used in hierarchical assembly, a subject for experimental study exploiting Janus particles.[164,165] The assemblies of Janus particles into ordered and pre-determined clusters represent an intriguing example of complex behavior of anisotropic structures and can be themselves potentially used as complex templates for replication. In fact, tailored assemblies of Janus particles have been recently considered by Granick *et al.*,[59,166] who suggested a simple model for predicted interfacial energy, and spontaneous aggregation of Janus particles into clusters with well-defined aggregation numbers (Fig. 20).[166] Moreover, mismatch in cross-sectional area such as that possible for Janus particles in Fig. 4 might results in additional strong contribution of steric factors which might promote, *e.g.*, antiparallel packing of neighbouring particles.

Replication of anisotropic templates also opens new opportunities for creation of complex assemblies with anisotropic surface properties which may lead to guided assembly of complex architectures. For example, polymer replicas of complex templates such as hollow microcapsules with anisotropic shapes or asymmetric surface charge distributions are expected to exhibit anisotropic properties such as direction-dependent interaction with targeted surfaces and directionally-dependent release profiles. Glotzer *et al.*[14,167,168] suggested that directional interactions combined with steric confinements may result in chain-like organization strings, double strings, sheets and rings,

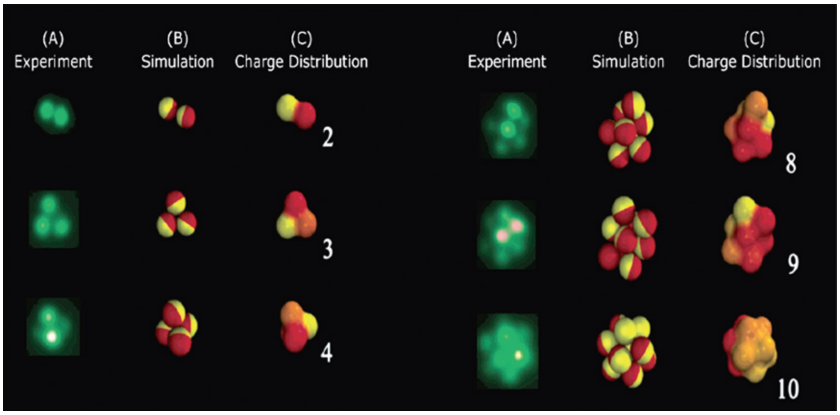


Fig. 20 Fluorescence images and computer simulations of the self-assembled discreet clusters of Janus particles with positive and negative charges on the two hemispheres. Reprinted with permission from ref. 166, copyright 2010 American Chemical Society.

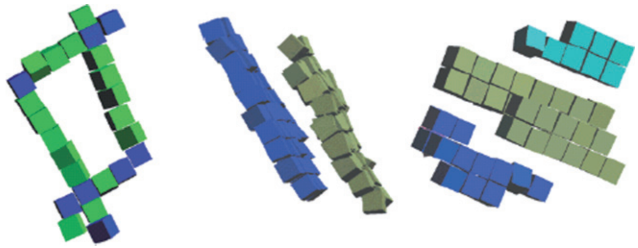


Fig. 21 Self-assembled chain-like aggregation of cubic nanocrystals from simulation snapshots. Cubes within the same structures are colored the same. Reprinted with permission from ref. 168, copyright 2010 American Chemical Society.

all assemblies controlled by fine balance between face-to-face contacts and dipole interactions (Fig. 21). Although such assemblies are rarely observed for traditional colloidal particles, anisotropic building blocks are excellent candidates for rational design of complex hierarchical materials.

Acknowledgements

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