Template Synthesis of Nanostructured Materials via Layer-by-Layer Assembly†

Yajun Wang, Alexandra S. Angelatos, and Frank Caruso*

Centre for Nanoscience and Nanotechnology, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

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The layer-by-layer (LbL) templating technique has attracted significant interest as a simple, highly versatile approach that has been widely used to prepare nanostructured materials with tailored properties. The process involves the sequential deposition of species, such as polymers, nanoparticles, lipids, proteins, and dye molecules, onto various templates, which are subsequently removed to yield free-standing structures. Although fine control of the material properties (e.g., size, composition, thickness, permeability, function) is afforded by the type of species LbL-assembled, the morphology and composition of the templates also play a crucial role in determining the properties, and hence potential applications, of the materials generated. In this review, we focus on the two main classes of templates that have been employed to prepare nanostructured materials: planar and colloidal. The use of porous planar and colloidal substrates in LbL templating synthesis is also presented, as this offers opportunities to fabricate novel materials with advanced structuring. Particular emphasis will be placed on using colloidal templates of different composition (e.g., polymer, inorganic, liquid droplets, gas bubbles) and geometry (e.g., spheres, rods, fibers). The assembly routes employed to prepare a range of nanostructured materials, including films, capsules, nanotubes, nanoporous particles, and macroporous and biomimetic structures, are described, together with the potential applications of the materials in fields such as adsorption/immobilization, catalysis, drug delivery, sensing, separations, and synthesis. Future research directions of the LbL templating technique are also discussed.

1. Introduction

Since its introduction in 1991,[1] the layer-by-layer (LbL) assembly technique has rapidly expanded to become a premier method for the preparation of nanoscale films with tailored properties. Typically, the LbL process begins with the adsorption of a charged species onto a substrate of opposite charge, thereby reversing the substrate surface charge. Further layers are then deposited by the alternate adsorption of oppositely charged species onto the substrate, until the desired film thickness is achieved. The versatility of the LbL approach has allowed a broad range of materials (e.g., polymers, nanoparticles, lipids, proteins, dye molecules) to be assembled on various substrates, on the basis of not only electrostatic interactions but also hydrogen bonding, hydrophobic interactions, covalent bonding, and complementary base pairing[2–6] The properties of LbL films, such as composition, thickness, and function, can be readily tuned by simply varying the type of species adsorbed, the number of layers deposited, and the conditions employed during the assembly process. Further details of the LbL assembly technique and its applications may be found in a number of earlier reviews.[2–8]

Removal of the templating substrate following LbL film formation can give rise to free-standing nanostructured materials with different morphologies and functions. This approach, known as the LbL templating technique,[7] is the subject of the present review. Herein, we examine two main classes of templates, planar and colloidal, and within each of these classes, we consider both nonporous and porous substrates. We review a diverse array of nanostructured materials, as schematically illustrated in Figure 1: free-standing and nanoporous films (generated from solid planar supports); nanotubes (from porous membranes, rods, and fibers); capsules (from solid spheres, emulsion droplets, gas bubbles, and porous spheres); nanoporous particles (from porous spheres); macroporous materials (from crystalline arrays of colloidal particles); and biomimetic structures (from naturally occurring substrates). Throughout the review, the potential applications and future research directions of the various systems presented are also described.

2. Planar Templates

LbL assembly on planar templates typically involves solid substrates, such as quartz slides, silicon wafers, and metal electrodes. Planar substrates with defined pore structures (e.g., macroporous membranes) have also been widely employed as templates for LbL assembly.

2.1. Nonporous Planar Templates. Free-standing films can be prepared through LbL assembly on nonporous planar templates, followed by selective etching of the template surface. For example, artificial nacre (the iridescent internal layer of a mollusk shell, also known as 'mother-of-pearl') has been synthesized by assembling poly(diallyldimethylammonium chloride) (PDADMAC)/

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* Corresponding author. E-mail: fcaruso@unimelb.edu.au.

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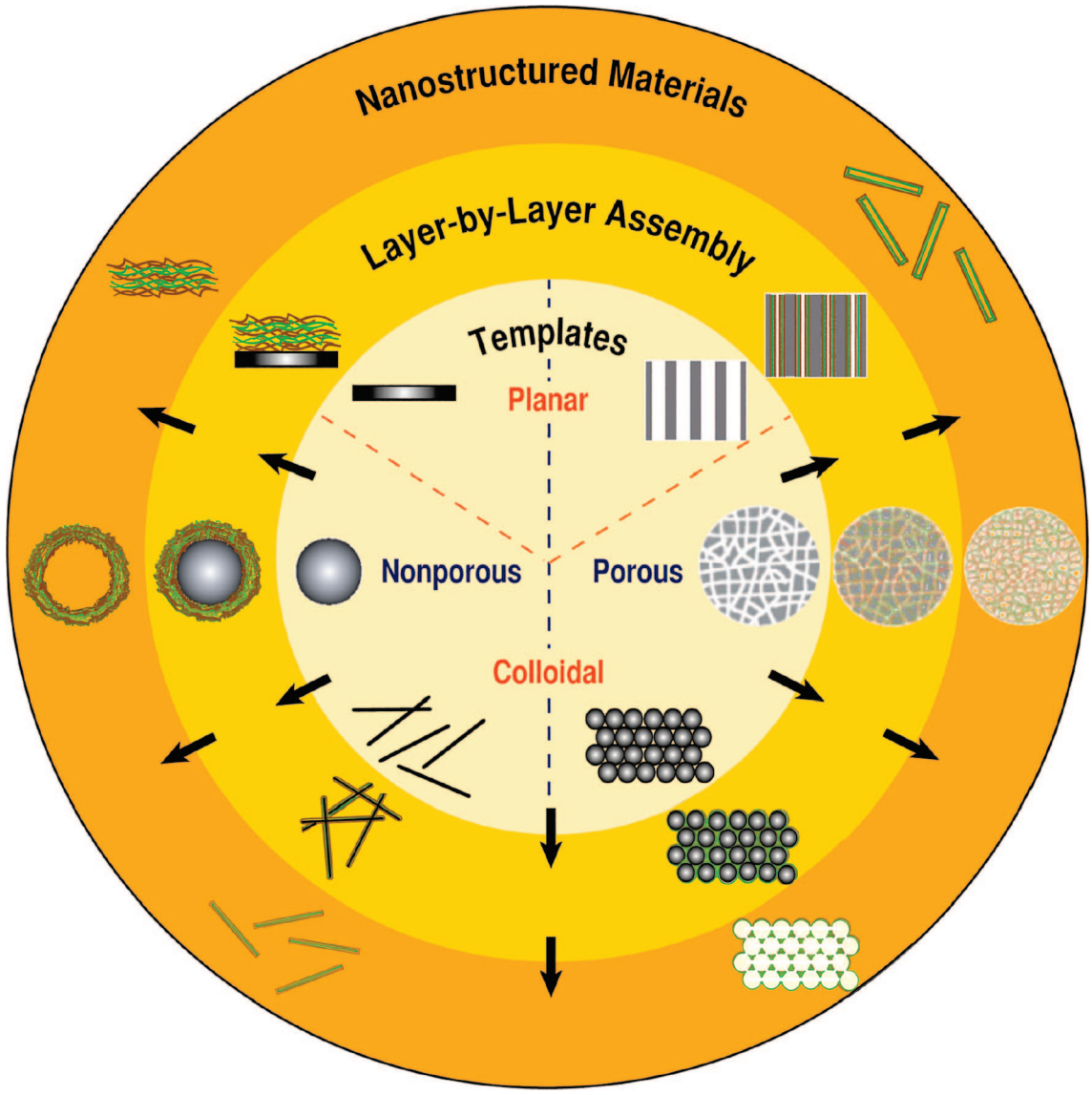

Figure 1. Schematic illustration of various nanostructured materials prepared via the LbL templating technique. The nanostructured materials depicted are (clockwise from top left): free-standing films (from nonporous planar templates); nanotubes (from porous planar templates); nanoporous particles (from porous spheres); macroporous materials (from crystalline arrays of colloidal particles); nanotubes (from nonporous rods and fibers); and capsules (from nonporous spheres). The scheme depicts the use of polymers in the LbL assembly process; however, a broad range of other species could also be used, such as nanoparticles, lipids, proteins, and dye molecules.

montmorillonite clay multilayers on silicon wafers coated with a silica layer, which was selectively dissolved with hydrofluoric acid (HF) to release the LbL films (Figure 2).[9] Mamedov and Kotov[10] have deposited alternating layers of magnetite nanoparticles and polyelectrolytes (PEs) onto glass slides coated with cellulose acetate (CA). Free-standing films were subsequently obtained by dissolving the initial CA layer with acetone. Tsukruk and co-workers[11–14] later used this approach to fabricate free-standing PE multilayer (PEM) films doped with gold nanoparticles. Layers of PEs and gold nanoparticles were assembled onto CA-coated silicon wafers, after which the LbL films were released from the solid support by using acetone to dissolve the initial CA layer. The exceptional strength of the ultrathin films obtained (elastic modulus 30–40 GPa, ultimate strain ca. 2%, ultimate tensile strength >100 MPa) renders these materials potentially suitable for a variety of different applications, ranging from gas separation, sensing, micromechanical devices, and advanced catalysis to artificial cell walls and organs. Schlenoff and co-workers used a combination of multiple polymers, deposited in several "strata", to make free-standing membranes.[15] Following PEM deposition, selective pH- or salt-induced decomposition of PE pairs resulted in controlled delamination and free-standing polymer films. In another approach, Hammond and co-workers introduced a simple "peel-off" method for the generation of free-standing PEM films.[16] Using low-energy surfaces such as Teflon and polypropylene, poly(acrylic acid) (PAA)/poly(ethylene oxide) multilayers could be easily lifted from the substrates in continuous sheets.

The selective etching technique has recently been applied to introduce porosity into LbL films.[17,18] Films comprising three different components were assembled on nonporous planar templates, after which two of the components were stabilized via cross-linking, and the third (sacrificial) component was selectively removed to produce nanopores within

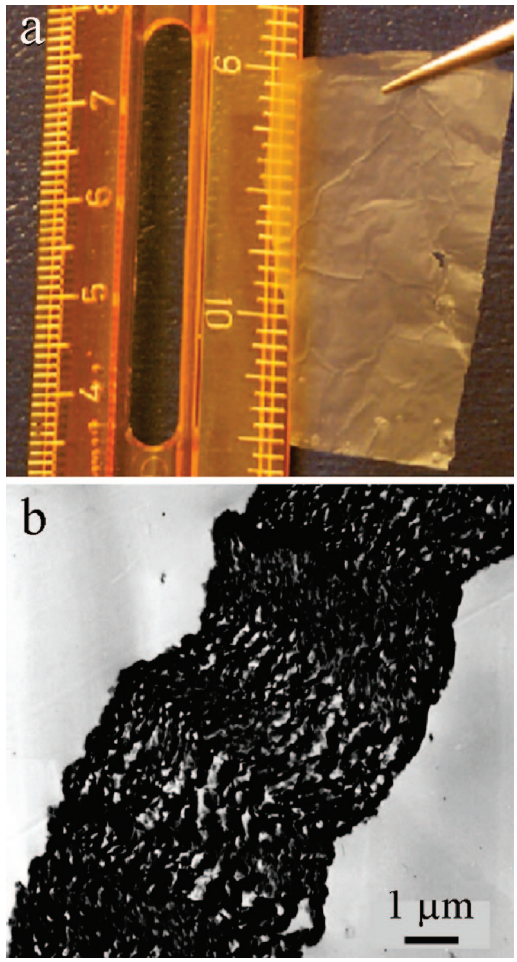

Figure 2. (a) Photograph of a free-standing film composed of (PDADMAC/montmorillonite clay)$_{50}$. (b) TEM image of a cross-section of a free-standing film composed of (PDADMAC/montmorillonite clay)$_{200}$. Reprinted with permission from ref 9. Copyright 2003 Nature Publishing Group.

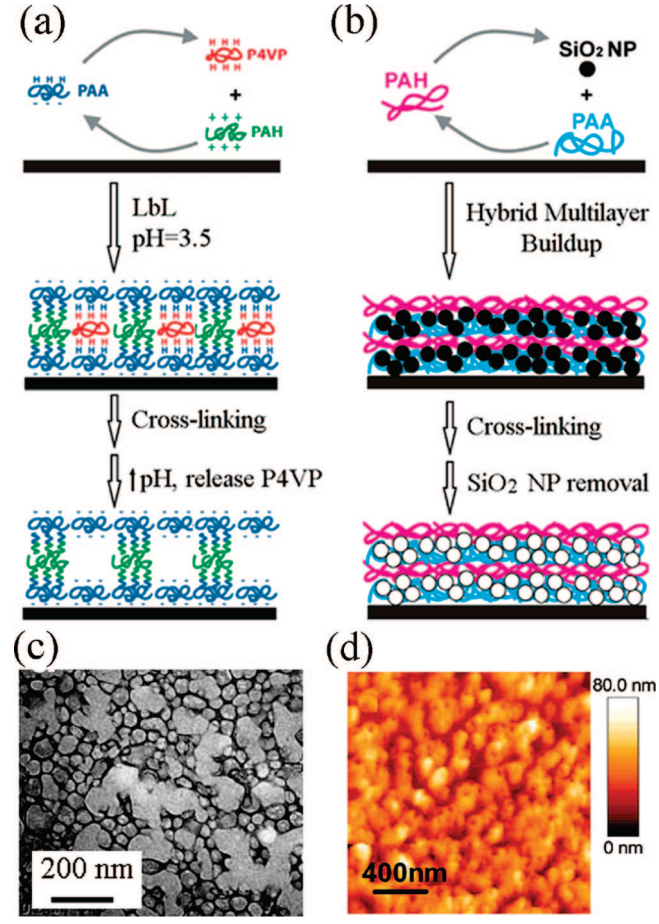

Figure 3. Schematic illustration of the preparation of nanoporous PAA/PAH films using (a) P4VP and (b) silica nanoparticles as the sacrificial components. (c) TEM and (d) AFM images of nanoporous PAA/PAH films prepared using silica nanoparticles (diameter 45 ± 5 nm) as the sacrificial component. (Image a is adapted from ref 17. Copyright 2005 Wiley-VCH. Images b−d are reprinted with permission from ref 18. Copyright 2006 American Chemical Society.

the films. Figure 3a is a schematic illustration of using a polymer as the sacrificial component.[17] First, a blend of the polycation, poly(allylamine hydrochloride) (PAH), and the hydrogen-bonding polymer, poly(4-vinylpyridine) (P4VP), was deposited in alternation with the polyanion, PAA, to produce a multilayer film. The electrostatically associated components (PAH and PAA) were cross-linked using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride. The pH was then elevated to disrupt the hydrogen-bonded components (P4VP and PAA), and hence remove the sacrificial component (P4VP), resulting in nanopores (diameter 10–50 nm) within the multilayer film. Using a similar strategy, silica nanoparticles have also been employed as the sacrificial component in the preparation of nanoporous films (Figure 3b−d).[18] In this case, a multilayer film was produced through the alternate deposition of a PAA/silica nanoparticle blend and PAH. After the PAA/PAH components were chemically cross-linked, the silica nanoparticles were decomposed via HF treatment to leave nanopores within the multilayer film, the size of which closely depended upon the diameter of the silica nanoparticles used in the LbL assembly process. Atomic force microscopy (AFM) revealed that well-defined pores of diameter ca. 25, 45, or 85 nm were introduced into the PAA/PAH films by using silica nanoparticles of diameter 25 ± 5, 45 ± 5, or 85 ± 5 nm, respectively, as the sacrificial component (Figure 3d). The increase in the film permeability upon removal of the silica nanoparticles was demonstrated by an increase in the amount of protein (bovine serum albumin) adsorbed within the nanoporous film as the bilayer number was increased. The ability to tune the protein content of the films through bilayer number is of interest for applications in biocatalysis and biosensing.

2.2. Porous Planar Templates. The use of porous planar templates for LbL assembly permits the preparation of materials with well-defined three-dimensional morphologies. For example, LbL assembly on membranes with cylindrical pores (followed by removal of the surface material and the template) gives rise to tubes (hollow cylinders). The outer diameter, length, composition, and thickness of the tubes are controlled by the pore diameter, membrane thickness, type of species deposited, and number of layers assembled, respectively. The open ends and large surface area associated with tubes renders them useful for delivery applications in particular, because they can be readily loaded with large quantities of guest species.

Nanotubes have been fabricated from polycarbonate (PC) membranes containing cylindrical pores of diameter 400 nm.[19] First, PEs and/or metal nanoparticles were LbL-

deposited within the nanopores of the template. Carborundum sand paper was then employed to remove the LbL film coating on the outer surface of the template. Finally, the PC template was decomposed with dichloromethane to yield free-standing nanotubes of defined size, wall thickness, composition, and inner and outer wall functionality.

Anodic aluminum oxide (AAO) membranes with cylindrical nanopores have also been employed as templates for the preparation of nanotubes. Ai et al.[20] LbL-coated an AAO membrane by using a syringe to inject PE solutions into the template. PEM nanotubes were obtained by wiping the LbL coating off the outer template surface, and then decomposing the template with either sodium hydroxide or phosphoric acid. To prevent the adsorption of multilayers on the outer template surface, Martin and co-workers[21] sputter-coated the faces of an AAO membrane with an ultrathin (ca. 5 nm thick) layer of gold. The subsequent α,ω-diorganophosphonate/zirconium(IV) multilayers were deposited only onto the walls of the nanopores. Without the gold precursor layer, the faces of the AAO membrane would be preferentially coated with the multilayers, and nanotubes would not be produced following removal of the template. Composite nanotubes through the LbL assembly of DNA molecules within an AAO membrane precoated with α,ω-diorganophosphonate/zirconium(IV) were also prepared.[22]

A broad range of other materials have been LbL-assembled within the cylindrical nanopores of AAO membranes to yield nanotubes. Tian et al.[23] reported protein/PE nanotubes fabricated from cytochrome C and poly(sodium 4-styrenesulfonate) (PSS). Cyclic voltammetry measurements indicate that the biochemical and electrical activities of the protein component are retained in the nanotubes. Protein/lipid nanotubes can be prepared via the sequential adsorption of protein and L-*R*-dimyristoylphosphatidic acid from aqueous or chloroform solutions.[24] The incorporation of lipid components could lead to biocompatible/biodegradable nanotubes that may serve as drug/gene delivery vehicles, bioreactors, or biosensors. Nanotubes composed of only protein have been synthesized from solutions of human serum albumin (HSA) (pI ca. 4.8) at pH 3.8 (positively charged protein solution) and pH 7.0 (negatively charged protein solution).[24] The HSA nanotubes are smooth, ca. 30 nm thick (which accounts for their high flexibility), ca. 60 μm in length, and exhibit good stability (Figure 4). The preparation of cross-linked protein nanotubes involves alternately immersing the AAO membrane in solutions of protein and glutaraldehyde, the latter acting as the cross-linking agent to bind the protein layers together.[23,25] It has been observed that the enzymatic activity of cross-linked protein nanotubes increases as the wall thickness increases. Fluorescent nanotubes have been fabricated from polyethyleneimine (PEI) and perylene-3,4,9,10-tetracarboxylic dianhydride, the electrical and optical properties of which are preserved after covalent bonding to PEI within the nanotubes.[26] Bai and co-workers[27] have reported the synthesis of arrays of nanotubes made from titania and titania-based composites (titania/cadmium sulfide, titania/gold).

Recently, macroporous CA membranes comprising interconnected fibers were employed as templates for the preparation of inorganic nanotubes.[28] After LbL assembly and calcination, an inorganic membrane with a three-dimensional framework of interconnected nanotubes was obtained. This high-surface-area material is expected to find application in the areas of adsorption, separation, and catalysis.

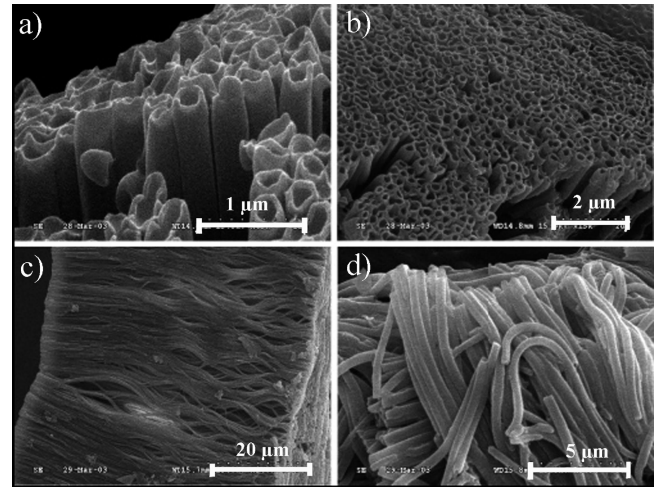

Figure 4. SEM images of HSA nanotubes prepared via the LbL deposition of oppositely charged HSA within an AAO membrane, followed by removal of the surface material and the template. The HSA nanotubes: (a) are smooth, with a wall thickness of ca. 30 nm; (b) are ordered; (c) are ca. 60 μm in length; and (d) are highly flexible. Reprinted with permission from ref 24. Copyright 2005 American Chemical Society.

3. Colloidal Templates

3.1. Nonporous Colloidal Templates. *3.1.1. Spherical Colloids.* Capsules in the nanometer to micrometer regime are important for a range of different applications, including the encapsulation and controlled release of substances (e.g., drugs, genes, dyes, inks, cosmetics, pesticides, food stuffs), catalysis, and sensing. A versatile means of preparing capsules is the LbL colloid-templating technique,[3–7,29,30] which involves the deposition of LbL films onto the outer surface of colloidal particles that are subsequently removed via chemical or thermal means. This method permits unprecedented control over capsule properties (e.g., size, composition, thickness, permeability, function) through the choice of the sacrificial colloids and the film components.

Predominantly, solid spheres of polystyrene (PS), melamine formaldehyde (MF), or silica with diameters between 0.1 and 5 μm have been employed as templates for the LbL preparation of capsules. Each of these sacrificial cores has certain limitations associated with their application. The use of PS particles requires solvents such as tetrahydrofuran to effect template removal, and where polymer coatings are used on PS particles, swelling of the PS cores during removal can lead to rupturing of the polymer capsules.[31] MF particles are chemically decomposed under acidic conditions (pH ca. 1.5), and some of the oligomers produced during MF dissolution are often retained within the polymer capsule walls.[32,33] Although the decomposition of silica particles typically involves the use of HF, this is a relatively efficient process, and ammonium-fluoride-buffered HF solutions at mild pH can be used in the presence of biological materials (e.g., DNA, proteins) without significantly affecting bioactivity.[34] Gold nanoparticles have also been used as templates

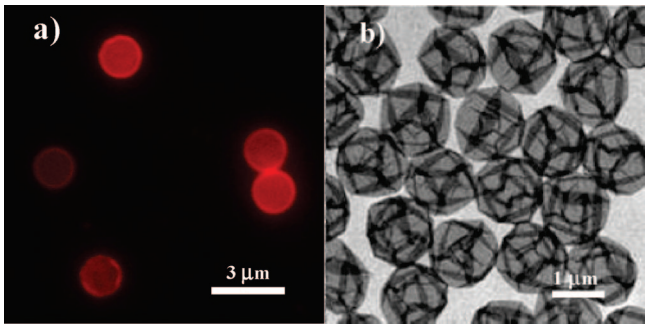

Figure 5. (a) CLSM and (b) TEM images of capsules prepared via the LbL assembly of $(PSS/PAH)_4$ on MF particles, followed by removal of the template. The capsules in image a were stained with rhodamine 6G to permit visualization via CLSM. Image b is reprinted with permission from ref 43. Copyright 2005 American Chemical Society.

for the LbL preparation of capsules. In these cases, the gold nanoparticles are efficiently removed upon exposure to potassium cyanide.[35–38]

The vast majority of capsules prepared from these templates have been assembled by the alternate deposition of positively and negatively charged polymers, where electrostatic forces govern the multilayer buildup. Recently, polymer capsules prepared via covalent bonding and complementary base pairing have also been reported.[39–42] Such polymer capsules retain the spherical shape of the original particle templates when dispersed in solution, as depicted in Figure 5a for PSS/PAH multilayer capsules prepared from MF particle templates. However, when air-dried onto a substrate, these capsules adopt a collapsed structure that resembles deflated balloons (Figure 5b).[43]

The biocompatibility/biodegradability of the shell is a key requirement in the use of polymer capsules for in vivo applications (e.g., drug/gene delivery). Biocompatible capsules have been prepared from various polymer pairs, such as poly(L-lysine)/poly(L-glutamic acid),[34] chitosan/dextran sulfate,[44] poly(DL-lactic acid)/poly(DL-lactic-*co*-glycolic acid),[45] chondroitin sulfate/poly(L-arginine),[46] and dextran sulfate/protamine.[47] Biodegradable capsules have been prepared from polymer multilayers that are cross-linked through disulfide bonds.[48] Such capsules show great promise as delivery vehicles because they are stable at physiological pH but undergo disassembly (and hence release their cargo) in response to thiol/disulfide exchange (a process that occurs naturally within cells by means of proteins). Recently, Such et al. reported the preparation of single-component (PAA) capsules by click chemistry.[40] The pH-responsive behavior of these click capsules, together with their potential for postfunctionalization, render them suitable for applications such as targeted drug/gene delivery, biosensing, and biocatalysis.

The shells of polymer capsules have been modified with various species, including poly(ethylene glycol), lipids, antibodies, and nanoparticles, to control the behavior of the capsules in biological environments.[43,49–57] For example, the interaction between breast cancer cells and polymer capsules with different outer layers has been investigated to determine the effect of capsule surface properties on cellular uptake.[57] Confocal laser scanning microscopy (CLSM) data showed that the capsules were mostly internalized into the cytoplasm

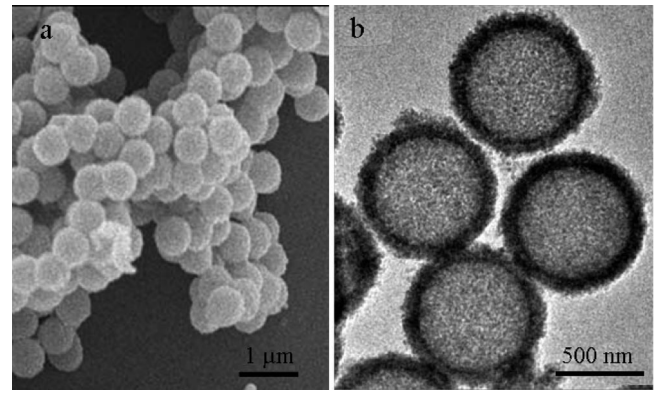

Figure 6. (a) SEM image of titania capsules prepared via the deposition of (PDADMAC/PSS/PDADMAC/titania nanoparticle)$_4$ on PS particles, followed by calcination to remove the organic material. (b) TEM image of silica capsules prepared via the deposition of (PDADMAC/silica nanoparticle)$_3$ on PS particles, followed by calcination to remove the organic material. Image a is reprinted with permission from ref 58. Copyright 2001 American Chemical Society. Image b is reprinted with permission from ref 31. Copyright 1998 American Association for the Advancement of Science.

of the cells, rather than into the cell nuclei. The targeting and uptake of polymer capsules biofunctionalized with antibodies that bind specifically to the tumor-associated markers on colorectal cancer cells has been reported.[54] Polymer capsules doped with magnetic nanoparticles have been targeted to breast cancer cells using a flow channel system and a magnetic field,[55] while controlled release has been achieved from polymer capsules doped with gold nanoparticles upon irradiation with near-infrared laser light.[43]

Inorganic capsules possess a number of advantages over polymer capsules, namely, superior mechanical and thermal stabilities. They can be fabricated from either preformed nanoparticle building blocks or inorganic molecular precursors. Inorganic capsules have been prepared via the alternate deposition of PDADMAC and nanoparticles (silica, titania) onto PS particles, followed by calcination to remove the organic components (the template and the PE) (Figure 6).[31,58] Both the diameter and the shell thickness of inorganic capsules can be controlled through the number of nanoparticle layers deposited. The calcination process leads to sintering of the nanoparticles, which enhances the mechanical strength of the capsules. Thus, inorganic capsules retain the spherical shape of the original particle templates upon drying (Figure 6), unlike polymer capsules, which adopt a collapsed structure after drying (Figure 5b).

A range of other nanoparticle building blocks have been employed to assemble inorganic capsules via the LbL colloid-templating technique, including metals (gold, silver),[59,60] oxides (clay, zeolite, magnetite),[61,62] semiconductors (cadmium telluride), and composites (gold-coated silica nanoparticles, octa(3-aminopropyl)aminosilsesquioxane-capped silver nanoparticles).[63,64] The use of zeolite nanocrystals to prepare zeolite capsules is attracting considerable interest because the ordered porosity of the shells renders the capsules selectively permeable. However, the relatively low mechanical strength of zeolite capsules limits their application. In an attempt to improve the structural stability of zeolite capsules, Valtchev et al.[65] have subjected PS particles coated with zeolite nanocrystals to hydrothermal crystallization.

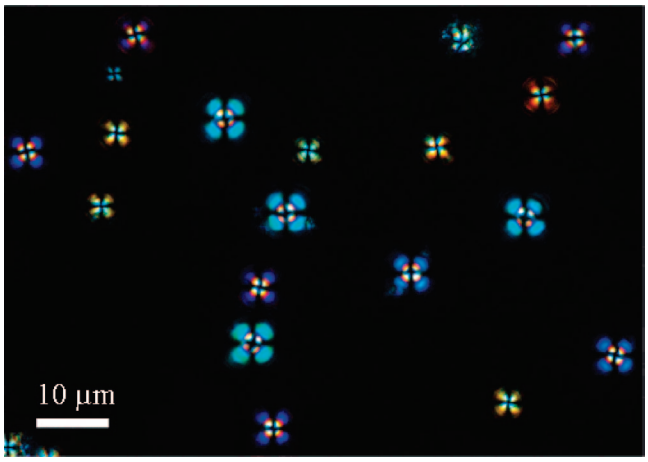

Figure 7. Cross-polarized image of 5CB droplets LbL-coated with $(PAH/PSS)_7$, and then exposed to SDS. Reprinted with permission from ref 70. Copyright 2006 American Chemical Society.

Several inorganic molecular precursors have also been used to prepare inorganic capsules via the LbL colloid-templating technique. For example, titania capsules were obtained by coating PS particles with alternate layers of the water-stable titanium precursor, titanium(IV) bis(ammonium lactato) dihydroxide (TALH), and PDADMAC, after which the template and the polycation were decomposed by calcination.[66] Alternatively, metal oxide capsules were fabricated by first adding the water-sensitive alkoxide precursor, lithium niobium(V) ethoxide, to PEM-coated PS particles (which had undergone solvent exchange to remove the majority of the water component) and then calcining the coated particles.[67] The presence of trace amounts of adsorbed water within the PEM shell results in hydrolysis/condensation of the precursor, and hence the formation of inorganic/PE coatings, the thickness of which is defined by the number of preassembled PEMs.

The LbL colloid-templating technique has also been extended to liquid droplets. For example, three-layer polymer membranes (comprising lecithin, chitosan, and pectin, or lactoglobulin, carrageenan, and gelatin) have been deposited onto corn oil droplets dispersed in water.[68,69] More recently, PEM films have been assembled at the interfaces of thermotropic liquid crystal (LC) droplets of 4′-pentyl-4-cyanobiphenyl (5CB) dispersed in an aqueous phase.[70] The bipolar-to-radial ordering transition of the LCs upon exposure to surfactant (sodium dodecyl sulfate, SDS) was 2 orders of magnitude slower for the coated droplets than for the naked droplets (Figure 7). This shows that PEMs influence the interactions between LCs and analytes and hence can be used to tune the sensing properties of LC emulsions. PEM capsules were obtained when the LC cores of the coated droplets were removed with ethanol, thereby demonstrating that emulsion droplets are an effective template for the facile preparation of capsules. Ferri et al.[71] have adsorbed PEs onto a charged amphiphilic lipid monolayer at the aqueous/air interface of a single pendant drop. The PEMs were deposited inside the pendant drop by alternately changing the polycation and polyanion solutions injected and withdrawn from the coaxial capillaries on which the drop was formed. Lipid-based capsules prepared in this way could potentially be used as drug/gene delivery vehicles. Difficulties in separating excess PE from liquid droplets can present challenges in their utilization for the generation of capsules. Further, the creation of high-quality, small, and monodisperse droplets is still a challenge, especially in applications where sub-100 nm capsules with relatively narrow size distributions are required.

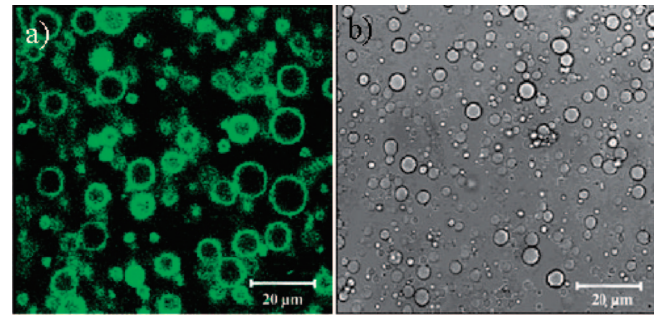

Figure 8. CLSM images of air-filled $(PAH/PSS)_6$ capsules in (a) the fluorescence mode (signal arises from FITC-labeled PAH) and (b) the bright-field mode. Reprinted with permission from ref 72. Copyright 2005 Wiley-VCH.

Another template currently being explored for the preparation of capsules is gas bubbles. Shchukin et al.[72] have employed detergent-coated air bubbles as templates for the formation of PEM microcapsules with a gaseous interior (Figure 8). The PEMs stabilize the air microsuspension against collapse by preventing air dissolution in the aqueous media. The coated air bubbles can be easily treated and transferred from one solution to another by filtration or centrifugation. A key advantage of using gas bubbles as templates for the preparation of capsules is that the core removal stage is eliminated; however, the relatively low stability of naked bubbles and the polydispersity of bubbles may limit their application.

3.1.2. High-Aspect-Ratio Colloids. One approach to preparing tubes involves using porous planar templates (see section 2.2). In an alternative approach, nonporous high-aspect-ratio particles (e.g., rods, fibers) are employed as templates. The use of high-aspect-ratio particles avoids issues with pore blockage and nonuniform pore coating that can be associated with membrane templates, particularly when the infiltrating macromolecules are comparable in size to the membrane pore size. Mayya et al.[73] applied the LbL assembly technique to coat the surface of nickel nanorods (average diameter ca. 65 nm, length ca. 1.5 μm) with eight layers of PDADMAC/PSS. PEM nanotubes were subsequently obtained by using dilute hydrochloric acid to remove the template. Similarly, titania-based nanotubes have been prepared via the alternate deposition of TALH and PDADMAC onto nickel nanorods, followed by hydrolysis of the TALH component (through heating under reflux), and decomposition of the template.[73] Zeolite microtubes have been fabricated via LbL assembly of zeolite nanocrystals and PDADMAC on carbon microfibers, coupled with removal of the organic material (the template and the polycation) by calcination (Figure 9).[74] The inner diameter (several micrometers) and length (tens of micrometers) of the microtubes were determined by the outer diameter and length, respectively, of the carbon microfibers employed as the template. Furthermore, the composition and thickness of the microtube walls were governed by the type of zeolite nanocystals used (e.g., silicalite-1, titanium silicalite-1, beta) and the number of deposition cycles

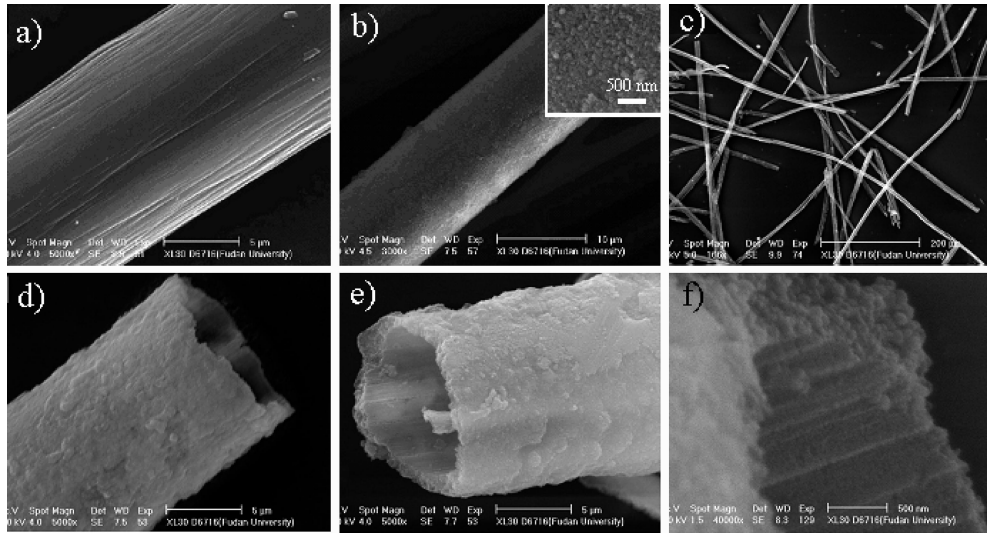

Figure 9. SEM images of (a) a carbon microfiber, (b) a carbon microfiber LbL-coated with (PDADMAC/silicalite-1)$_8$, and zeolite microtubes prepared by LbL-coating carbon microfibers with (c, d) (PDADMAC/silicalite-1)$_8$, (e) (PDADMAC/silicalite-1)$_{12}$, and (f) (PDADMAC/beta)$_{10}$/(PDADMAC/titanium silicalite-1)$_8$, followed by calcination to remove the organic material. Reprinted with permission from ref 74. Copyright 2000 Chemical Society of Japan.

performed, respectively. The alternate deposition of different types of zeolite nanocystals gave rise to concentric microtubes, where the composition at the inner microtube surface differed from that at the outer microtube surface. PEM microtubes have been prepared from electrospun PS microfibers with very high aspect ratios (>1 × 10^5:1).[75] After the PS microfibers were coated with PAH/PSS multilayers, the PS template was decomposed with tetrahydrofuran to yield PAH/PSS microtubes.

3.2. Porous Colloidal Templates. Porous particles have attracted significant interest in recent years. An advantage of using such templates is that the highly porous interior of the particles can be exploited to encapsulate various materials. Examples include mesoporous silica (MS) particles[44,48,76–82] and calcium carbonate particles,[83,84] both of which can be decomposed under conditions that do not significantly affect the activity of biomaterials loaded within the templates (i.e., a HF/ammonium fluoride buffer at pH 5.0 and ethylenediaminetetraacetic acid at pH 7.5 are typically used to decompose MS particles and calcium carbonate particles, respectively, when the templates are loaded with biomaterials). The high surface areas (up to ca. 1500 m^2 g^{-1}), high nanopore volumes (up to ca. 2 cm^3 g^{-1}), and homogeneous nanopore structures of MS particles have been exploited to encapsulate a variety of species, such as proteins, low-molecular-weight drugs, and nanoparticles. For example, MS particles have been employed as templates to prepare PEM capsules with high, uniformly distributed loadings of catalase (40 mg mL^{-1}) and lysozyme (185 mg mL^{-1}).[34,76,77] MS particles have also been used to fabricate zeolite capsules loaded with metal, metal oxide, carbon, and polymer particles.[79–81] Palladium nanoparticle-loaded zeolite capsules exhibit high activity, stability, and reusability as microreactors for catalyzing a series of Heck coupling reactions.[81] In addition, MS particles play an important templating role in the molecular beacon (MB) approach to measuring capsule permeability.[82] This method involves immobilizing MBs inside MS particles, encapsulating the MB-loaded MS particles within the LbL film to be probed, and then incubating the encapsulated MB-loaded MS particles with DNA target sequences of different lengths. Permeation of the DNA targets through the capsule shell causes the immobilized MBs to open because of hybridization of the DNA targets with the complementary loop region of the MBs, resulting in an increase in the MB fluorescence. Diffusion coefficients ranging from 1 × 10^{-19} to 1 × 10^{-18} m^2 s^{-1} have been obtained for DNA targets (15–60 bases in length) through PSS/PAH multilayer films.

Recently, MS particles have been used as templates to prepare nanoporous polymer spheres (NPSs) for application in various areas, such as delivery, adsorption/immobilization, separation, and synthesis. In the preparation of NPSs from the weak PE pair, PAA and PAH,[85] the polyanion (PAA) is first deposited within the nanopores of amine-functionalized (positively charged) MS particles. The infiltration of PAA into amine-functionalized MS particles has been studied in detail as a function of the PAA molecular weight, nanopore size, and solution conditions (pH, ionic strength).[86] Next, cross-linking (via chemical or thermal means) is used to selectively form amide bonds between the carboxylic acid groups of the PAA and the primary amine groups of the template, thereby stabilizing the adsorbed PAA molecules. The particles are then exposed to the polycation (PAH), after which cross-linking is again performed to bond the carboxylic acid groups of the PAA with the primary amine groups of the PAH. Finally, the template is removed using dilute HF (10 wt %). NPSs are obtained provided two or more PE layers have been deposited within the template. Electron microscopy indicates that the NPSs exist as individual particles with no obvious signs of aggregation (Figure 10). The homogeneous distribution of pores (diameter 10–50 nm) within the NPSs is evident from high-magnification scanning electron microscopy (SEM) images of the particles (Figure 10c) and high-magnification transmission electron microscopy (TEM) images of ultramicrotomed sections (ca. 90 nm thick slices) of the particles (Figure 10f). The accessibility of the nanopores to proteins was demonstrated by the strong, uniform fluorescence observed from the NPSs after incubation in fluorescein isothiocyanate (FITC)-labeled lysozyme. Because of the homogeneous porosity and abundance of functional groups within the NPSs, they possess a high

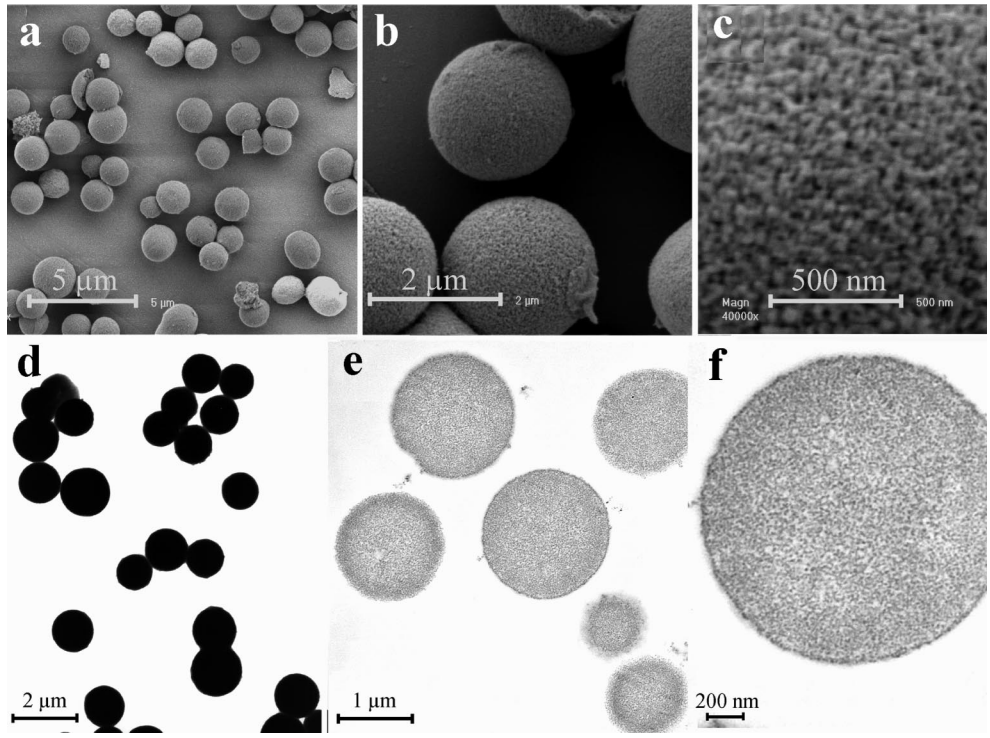

Figure 10. (a−c) SEM and (d−f) TEM images of NPSs prepared via the deposition of cross-linked $(PAA/PAH)_2$/PAA within amine-functionalized MS particles, followed by removal of the template. Images e and f show ultramicrotomed sections (ca. 90 nm thick slices) of the NPSs. The variation in the particle diameters in image e is a consequence of the ultramicrotoming process. Reprinted with permission from ref 85. Copyright 2005 Wiley-VCH.

capacity for protein sequestration (e.g., $(PAA/PAH)_2$/PAA NPSs yield lysozyme loadings of ca. 470 mg mL^{-1}) and exhibit great potential for pH-responsive protein loading/release.[87]

A range of NPSs with different compositions (and hence functions) can be fabricated by simply varying the species LbL-assembled within the MS particle templates.[87] For example, nanoporous protein-based particles (NPPs) have been prepared by infiltrating PEs into MS particles preloaded with proteins, thereby forming a protein/PE complex within the template.[88] The stability of the protein/PE complex (held together primarily by electrostatic interactions) was further enhanced through the formation of amide bonds between the carboxylic acid groups of the PE and the primary amine groups of the protein. Following this cross-linking process, leakage of the protein from the template was negligible, and the activity of the protein was largely retained (e.g., catalase activity was ca. 75%). NPPs were obtained after the template was removed using a HF/ammonium fluoride buffer at pH 5.0 to preserve the protein activity. Typically, the NPPs have a very high protein content (ca. 80 wt %), and they range in diameter from 1.6 to 2.4 μm, which corresponds to a size reduction of ca. 20% relative to the template. The disordered array of pores (diameter 10–50 nm) within the NPPs can be seen in high-magnification TEM images of ultramicrotomed sections of the particles. Nanoporous protein-based fibers have also been prepared by this method, using MS fibers as the template.[88]

Crystalline arrays of colloidal particles (e.g., silica, latex) represent another porous template. In this case, removal of the template following LbL assembly yields three-dimensional ordered macroporous (3DOM) materials, commonly referred to as "inverse opals".[89–96] For example, 3DOM zeolite membranes have been fabricated by LbL-coating of a crystalline array of MS particles (diameter ca. 1.2 μm) with silicalite-1 nanoparticles (diameter ca. 60 nm), followed by hydrothermal treatment.[94] Figure 11 shows cross-sections (at different magnifications) of a 3DOM zeolite membrane (thickness ca. 140 μm), the periodic structure of which extends areas up to 100 μm^2. The macropores are interconnected via "windows" (100–140 nm in size), and the macropore walls consist of a dense packing of nanoparticles (thickness ca. 200 nm). A bioreactor was subsequently prepared through the LbL assembly of PEs and catalase within the 3DOM zeolite membrane; the loading and activity of the enzyme were found to vary linearly with the membrane thickness. The LbL assembly technique has also been used to modify 3DOM titania membranes with multilayers of PAH and cadmium telluride nanocrystals.[95] Similarly, Lee et al.[96] have modified 3DOM hydrogel membranes (pore diameter 25–30 μm) through the deposition of clay/PDADMAC multilayers (Figure 12). Coating with clay particles renders the surface biocompatible and rough (on the nanoscale). Thus, the surface of the 3DOM hydrogel membranes were switched from being cell-repulsive to cell-adhesive following the deposition of ten clay/PDADMAC layers. It was found that floating cells are partially entrapped in the macropores, residing in close proximity to the cells adhered to the membrane walls. Using this approach, one can efficiently simulate differentiation niches for different components of hematopoietic systems, such as T-, B-, and stem cells.

Crystalline arrays of LbL-coated colloidal particles have also been employed as templates for the preparation of 3DOM materials. For example, a 3DOM composite material composed of interconnected hollow spheres was fabricated by infiltrating a titania precursor into a crystalline array of PE/silica nanoparticle-coated colloidal particles, and then

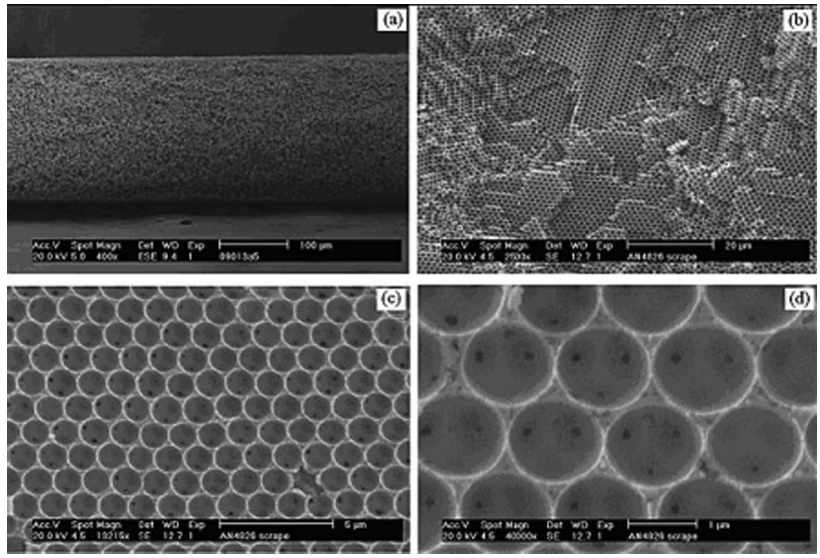

Figure 11. SEM images of a 3DOM zeolite membrane prepared by LbL-coating a crystalline array of MS particles with silicalite-1 nanoparticles, followed by hydrothermal treatment. Images a−d are cross-sections of the membrane at different magnifications. Reprinted with permission from ref 94. Copyright 2004 Wiley-VCH.

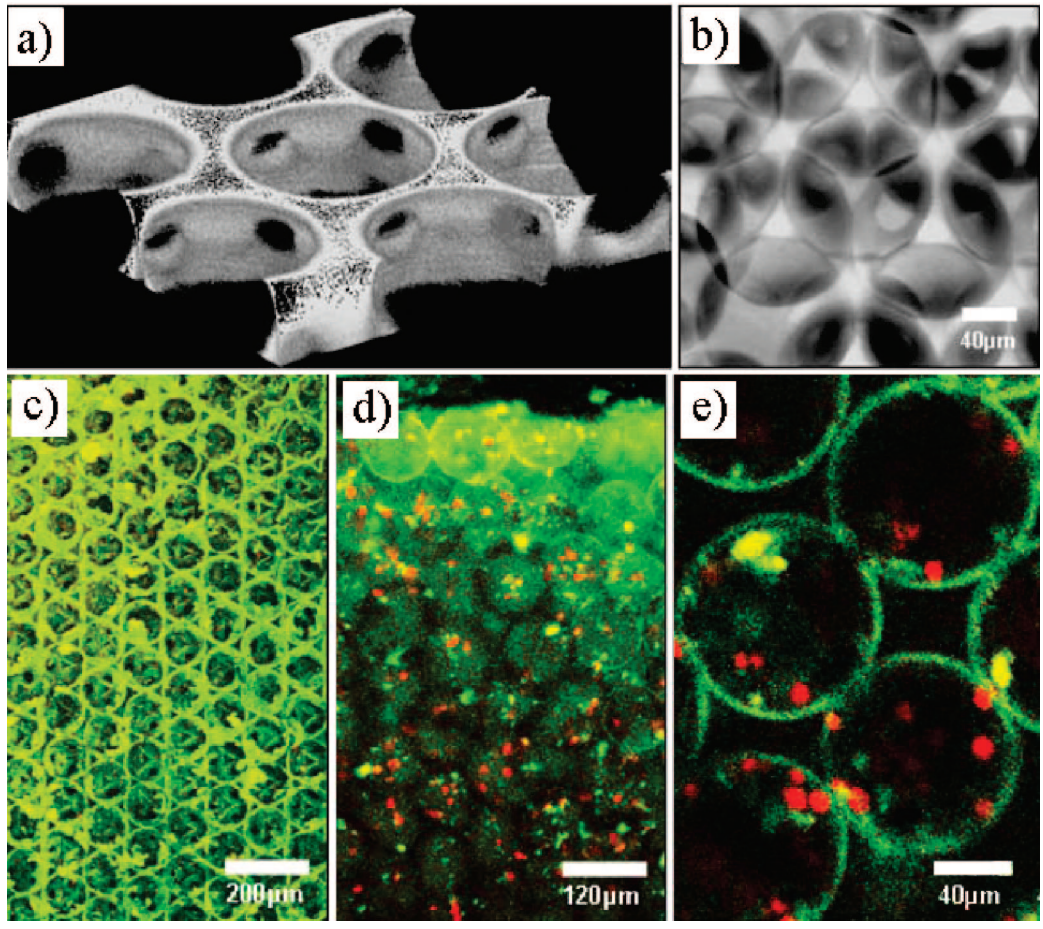

Figure 12. CLSM images of a fluorescent 3DOM hydrogel scaffold: (a) a three-dimensional reconstruction of serial z-section images taken in 0.5 μm steps, showing the organization of the main pores and interconnected channels of the scaffold without shape deformation; and (b) three-dimensional overlapping images of serial z-section images of 160 μm interval with 5 μm step size. CLSM images of cocultured 3DOM hydrogel scaffolds (the green and red regions correspond to thymic epithelial cells and monocytes, respectively): (c) a bottom area image showing that the surface of the scaffold was densely covered with thymic epithelial cells, and that most of the monocytes around the edge of the scaffold were released; (d) a cross-sectional image (after cutting the cocultured scaffold with a razor blade) showing decreasing thymic epithelial cell density moving to the inside of the scaffold, monocytes distributed through the whole scaffold, and a similar number of cells entrapped at each pore; and (e) a lateral section image of 80 μm in depth. Reprinted with permission from ref 96. Copyright 2006 Royal Society of Chemistry.

removing the organic material via calcination.[97] The thickness of the macropore walls (which is relatively difficult to control when arrays of "bare" colloids are used as templates) could be readily tuned by simply varying the number of

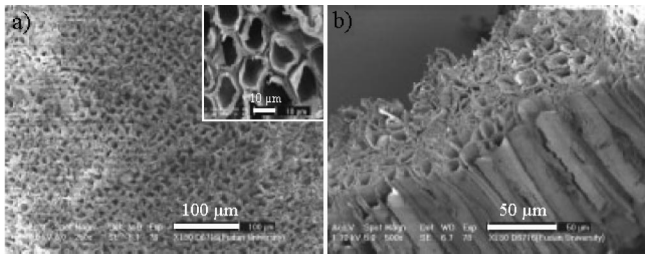

Figure 13. SEM images of (a) a cross-section and (b) the side view of a self-standing zeolitic tissue prepared from a cedar template. The inset shows the original cedar cells. Reprinted with permission from ref 101. Copyright 2002 Wiley-VCH.

layers deposited onto the colloids. 3DOM zeolite monoliths have been formed by centrifuging PE/silicalite nanoparticle-coated PS colloids into a crystalline array, and then using calcination to remove the organic components.[98] Crystalline arrays of MS particles LbL-coated with zeolite seeds have also been employed as templates for the preparation of 3DOM zeolite monoliths,[99] into which various species have been loaded by infiltrating the MS particles prior to the LbL coating.[100]

4. Naturally Occurring Templates

Many of the nanostructured materials currently under development draw their inspiration from structures found in nature. This approach is based on mimicking the supramolecular architecture of natural structures to prepare complex materials with highly sophisticated morphologies and functions. An early example of LbL templating biological cells involves gluteraldehyde-fixed echinocytes. The cells were first coated with a PDADMAC/silica nanoparticle multilayer film and then removed via treatment with a highly oxidizing solution to produce hollow organic/inorganic structures whose morphology resembles that of the original cell templates.[7] This example effectively illustrates how the LbL templating technique can be used to closely replicate the sophisticated structures of natural materials.

Dong et al.[101] developed an interesting method for the preparation of hierarchically structured porous zeolite materials from wood tissue templates. First, the wood tissue (e.g., cedar, bamboo) was seeded with a layer of zeolite nanocrystals via the LbL-assembly of PDADMAC and zeolite nanocrystals on the template. Following hydrothermal treatment to stabilize the zeolite nanocrystals deposited, calcination was performed to remove the organic components (the template and the polycation). The structure of the wood tissue template is clearly evident in the morphology of the zeolite material produced (Figure 13).

Another naturally occurring substance that has been employed extensively as a template is diatomite, which typically comprises highly porous disk-like particles (pore diameter 300–500 nm). Zeolite materials with good chemical/mechanical stability have been prepared via the LbL-assembly of PDADMAC and zeolite nanocrystals on diatomite.[102] The morphology and porosity of the template are well-preserved following the deposition of the PDADMAC/zeolite nanocrystal multilayers and the partial conversion of the amorphous silica component to hierarchically structured zeolite (by treatment with amine vapor).[103] After cobalt(II) ions were immobilized within the zeolite/diatomite composite, this material was used to separate histidine-containing biomolecules through immobilized metal ion affinity chromatography.[104] Recently, Rosi et al.[105] exploited the sequence-specific assembly properties of DNA to fabricate hierarchically structured materials via the LbL-coating of diatomite templates with DNA-functionalized gold nanoparticles.

5. Conclusions and Outlook

This review has highlighted some of the recent advances in the preparation of nanostructured materials via the LbL templating technique. A diverse array of systems was examined: free-standing and nanoporous films, capsules, nanotubes, nanoporous particles, and macroporous and biomimetic structures. These systems illustrate that the simple, yet highly versatile LbL assembly method can be combined with the template synthesis approach to yield complex assemblies, the structures and properties of which may be readily controlled through the choice of the LbL components and the template. We expect that, with further development, the nanostructured materials discussed herein will play an important role in a range of different applications, including adsorption/immobilization, catalysis, drug/gene delivery, sensing, separation, and synthesis. Furthermore, we anticipate that a variety of novel nanostructured materials will emerge as further progress is made in LbL templating synthesis. For example, LbL films have also been successfully assembled on mobile planar substrates[106,107] and patterned planar substrates.[108–114] Although removal of these templates following LbL assembly has not yet been shown, use of these (in particular patterned) planar substrates offers the possibility of preparing free-standing materials with highly sophisticated morphologies and functions. Recent advances in the preparation of patterned colloids[89,115–117] will also provide opportunities to introduce new levels of control and complexity in colloidal materials prepared via LbL colloid-templating.

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