

Template-Directed Assembly Using Nanoparticle Building Blocks: A Nanotectonic Approach to Organized Materials

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There are a number of strategies available for extending the length scale of structural organization in inorganic materials. Those that involve the assembly of inorganic nanoparticles into materials with higher-order architecture are collectively termed *nanotectonics*. In this review, we highlight one possible approach that involves the template-directed assembly of preformed nanoparticle building blocks. The inspiration for the use of preformed particles arises in part from studies of certain biomineral structures, some general aspects of which are summarized. Several synthetic examples of the use of template-directed approaches in nanotectonics are described in detail.

A central objective of biomimetic materials chemistry is to develop new strategies for the synthesis of materials and composites that exhibit the organizational and functional specificity exemplified by biological minerals such as bones, shells, and teeth.^{1,2} The synthesis of hierarchically ordered inorganic frameworks is of potential interest in various fields including catalysis,³ separation techniques,⁴ and materials chemistry.⁵ Some progress has been made toward developing biomimetic approaches to the formation of inorganic materials with controlled size, shape, orientation, and polymorphic structure.^{6,7} Current research is also investigating routes to the synthesis of inorganic materials with complex form,^{8,9} and higher-order hybrid assemblies,^{10–13} more reminiscent of the hierarchical structures seen in Nature. In particular, interest is now focused on introducing structural hierarchy and chemical functionality to improve the range of properties and applications in a wide range of materials.

There are a number of strategies available for extending the length scale of structural organization in inorganic materials. As described in this review, one possible strategy involves the use of *preformed* building blocks to construct complex multilevel structures. In general, the construction of organized materials from crystalline building modules represents a higher-order process in crystal science and, for this reason, has been referred to as “crystal tectonics”.¹⁴ Likewise, here we use the term, *nanotectonics*, to refer specifically to the use of preformed nanoparticle building blocks in the assembly of inorganic materials with higher-order architecture. As a general guideline, several approaches in nanotectonics can be identified (Figure 1). These include the shape-directed assembly¹⁵ and programmed assembly¹⁶ of nanoparticles comprising surface attached molecules,

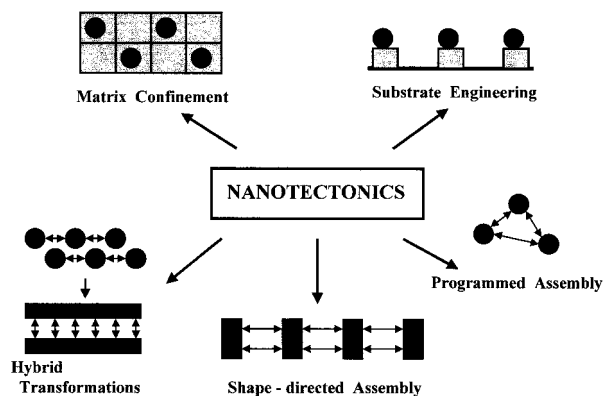


Figure 1. Schematic illustrating various nanotectonic strategies for assembling preformed nanoparticles into higher-order architectures.

ligands, and recognition sites, as well as the formation of complex hybrid nanostructures by in situ transformation of unstable nanoparticle-based precursors.¹⁷ Alternatively, as discussed in this paper, template-directed methods can be used in which preformed nanoparticles are spatially confined within the organized interiors of extended organic matrixes (matrix confinement), such as bacterial superstructures, polymer sponges, and colloidal crystals,¹⁸ or on the surfaces of organic substrates (substrate engineering), such as coated polymer beads¹⁹ or bacterial membranes.²⁰ Because the inspiration for the use of preformed particles has come in part from studies of certain biomineral structures, in the next section we summarize some general aspects of biomineral tectonics before describing in detail several synthetic examples of the use of template-directed approaches in nanotectonics.

Biomimetic Tectonics

Organisms produce mineral hard parts with complex, multilevel architectures.²¹ For example, certain types of

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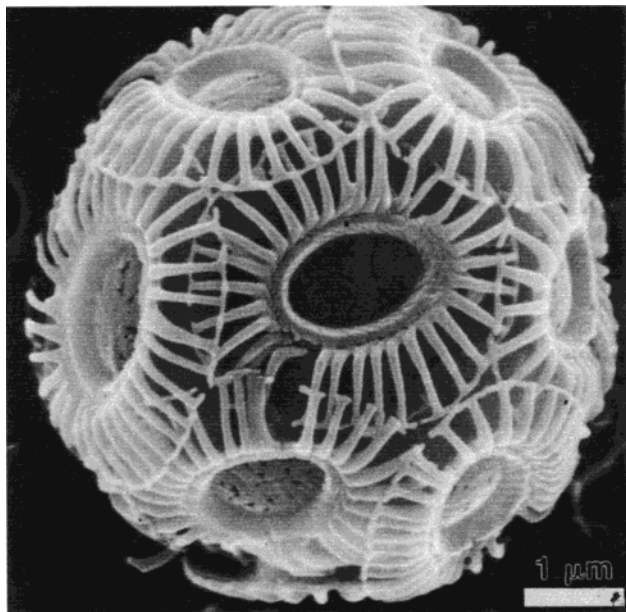


Figure 2. SEM image of a coccosphere of *Emiliana huxleyi*. Each of the interlocking scales (heterococcoliths) consists of a simple elliptical arrangement of morphologically complex single crystals of calcite.

algae, referred to as coccolithophores, produce elaborate calcified scales with several levels of structural organization (Figure 2). These unicellular organisms have been investigated in detail, and the studies demonstrate how remarkable levels of control over the size, shape, polymorph purity, and crystallographic orientation of calcite crystals can be achieved in biomineralization.²² Moreover, it is well established that studies on these and similar organisms have enabled a number of strategies to be identified and mimicked in synthetic materials chemistry and crystal engineering.^{6,7}

In recent years, some of the emphasis on coccolithophores has now shifted to how the calcified biominerals are constructed into higher-order architectures. For example, although morphologically complex, the component calcite crystals shown in Figure 2 are arranged in a simple elliptical pattern to produce the calcite scales (heterococcoliths), which in turn are organized into a hollow shell, referred to as the coccosphere, on the surface of the cell. Intriguingly, in some species another group of calcite structures, termed holococcoliths, is produced during a different stage in the life cycle (Figure 3). Holococcoliths are thought to result from extracellular mineralization rather than the highly controlled intracellular biomineralization responsible for heterococcolith formation.²³ In both cases, the net result is the production of calcified scales with species-specific elaborate arrangements of calcite crystals, although the holococcoliths have comparatively simple morphological forms.

Foraminifera are also unicellular algae, which produce inorganic exoskeletons (tests) that exemplify two extremes in modes of skeletal construction. Most suborders of the foraminifera secrete mineralized shells by a highly controlled intracellular biomineralization process. At the other extreme, one suborder, the *agglutinating* foraminifera, form wall structures by the cementing together of foreign particles, such as sand grains and sedimentary particles, onto an organic membrane (Fig-

ure 4). Some species are very selective, collecting particles of specific size, shape, and composition while others collect any grain in the appropriate size range.²⁴ For example, *Astrammmina rara* is grain-size selective, specifically arranging particles such that smaller ones fill the gaps between larger particles on the outer surface only.²⁵ *Trochammmina pacifica* is also grain-size selective, choosing progressively larger particles as chamber size increases through ontogeny.²⁶ In contrast the mineral particles in the test of *Astrorhiza limicola* are similar in size and proportion to those in the surrounding sediment.²⁷ The process of agglutination is not restricted to foraminifera; other protozoa, such as tintinnids and xenophyophores,²⁸ and higher organisms, such as polychaete worms,²⁹ form agglutinated structures. It is presumed that this mode of construction, i.e., cementing together preformed building blocks, offers certain advantages for these organisms as opposed to secreting a biomineralized shell per se.

Studies on agglutinated structures in biomineralization suggest that similar modes of construction should be possible in materials synthesis, provided that appropriate building units, connectors, and scaffolds can be established. Here we focus on the combination of nanoparticles and extended organic templates as the basis for a nanotectonic approach to organized materials.

Template-Directed Construction: Matrix Confinement

In this review we pay particular attention to the template-directed assembly of inorganic nanoparticles into ordered three-dimensional (3-D) materials rather than thin films or membranes or discrete colloids. Building 3-D structures is a particular challenge in biomimetic materials chemistry. Conceptually, the simplest way of producing such structures is to build inside or on a preorganized extended template (scaffold) using building blocks that represent a significant volume fraction of the composite structure.

Templated mineralization can be used to produce ordered materials at a range of length scales. For example, there is considerable interest in the production of inorganic framework materials containing well-defined pore networks. In general, strategies for synthesizing these materials rely on using templates, the size and nature of which dictate the pore architecture. Microporous materials are prepared using molecular templates³⁰ while at the meso length scale supramolecular aggregates are required.³¹ We have previously demonstrated how supracellular templates can be used to extend the length scale of 3-D inorganic patterning into the micrometer scale (see below).^{18a,d,32} Subsequently various other strategies, most notably the use of colloidal crystal and emulsion templates,^{33–35} have been employed.

In many cases, these strategies use molecular precursors that infiltrate and react within confined but structured spaces patterned within the interior of the organic matrix. For nano- and mesoscale structures, this approach generally works well, provided that there is sufficient chemical and interfacial complementarity between the organic and inorganic components. Indeed, methods have been further developed to produce hier-

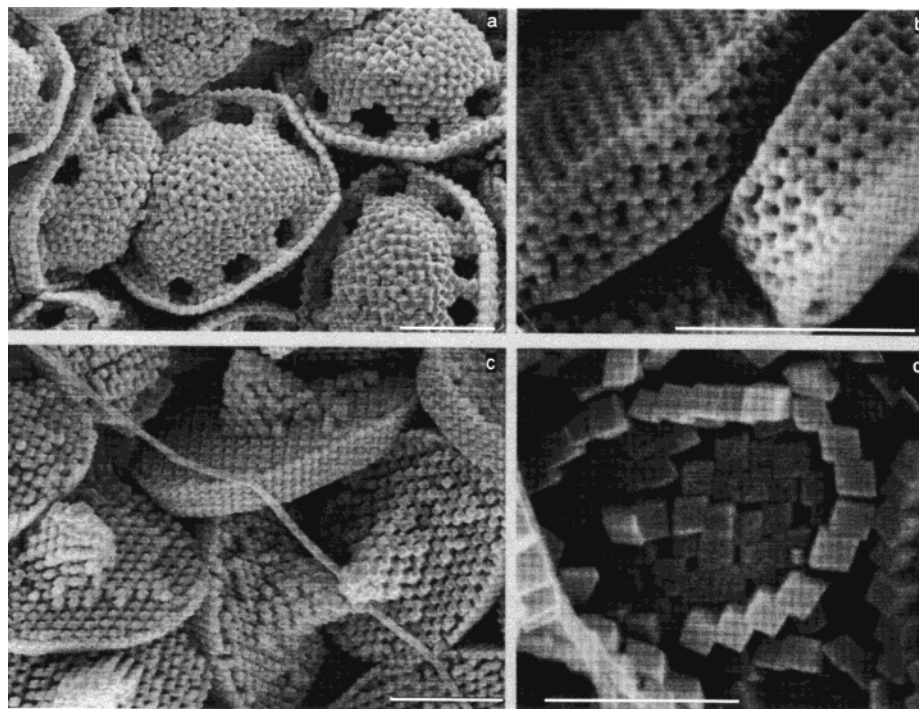


Figure 3. SEM images of four different holococcolith ultrastructures, scale bars = 1 μm . All consist of relatively complex arrangements of simple rhombohedral calcite crystals.



Figure 4. Light microscopy image of the agglutinating foraminifera *Saccammina sphaerica*. The shell is constructed by the cementing together of preformed particles scavenged from the local sediment.

archical silica-based materials containing bimodal-sized pore networks by dual templating procedures.^{32,34,36} However, inorganic mineralization of ordered structures extending beyond 100 nm can be difficult to achieve at high volume fractions because the supersaturation level attainable within the template is too low to produce a stable replica of the void space. One possibility is to use flow, rather than batch processing; for example, the continuous flow of alkoxide precursors through a latex colloidal crystal “membrane” has been used to construct inorganic frameworks with coherent micrometer-scale organization.³³

Alternatively, the use of nanoparticles provides a more general approach that extends the range of

inorganic components beyond ceramic materials produced from alkoxide precursors. Moreover, a wide variety of chemical and physical properties can be predefined and high-volume space filling within 3-D macroporous templates can be achieved. In general, the successful confinement of nanoparticles within organic matrixes requires inorganic building blocks of uniform size and shape, as well as structurally extended templates with physical and structural properties that enable high infiltration, compaction, and consolidation. Several examples of template-directed approaches in nanotectonics are now discussed.

Bacterial Superstructures. Organized bacterial superstructures in the form of macroscopic threads can be produced from a mutant strain of the bacterium *Bacillus subtilis* that has a cylinder-shaped cell, 0.8 μm in diameter and 4 μm in length. In fluid cultures, the mutant strain, which exhibits suppressed cell separation, can only grow by elongation at constant diameter along the cylinder axis to produce long multicellular filaments that intertwine to form weblike structures (Figure 5a). Drawing these web structures from the culture medium results in compaction of the individual filaments at the fluid–air interface to give a bacterial thread, often several decimeters long and 0.1–0.2 mm wide.^{37,38} The air-dried thread consists of a superstructure of multicellular filaments aligned parallel to the thread axis and arranged in a pseudo-hexagonal-packed configuration, reminiscent of the organization of cylindrical surfactant micelles in the H_1 liquid-crystal lyotropic phase, albeit on a length scale 2 orders of magnitude greater (Figure 5b). A typical bacterial thread can contain in excess of 10^{10} cells and 50 000 filaments arranged as a cell \rightarrow filament \rightarrow thread hierarchy of cylindrical building units.³⁹

In recent studies, the reversible swelling of unmineralized threads in the presence of preformed inor-

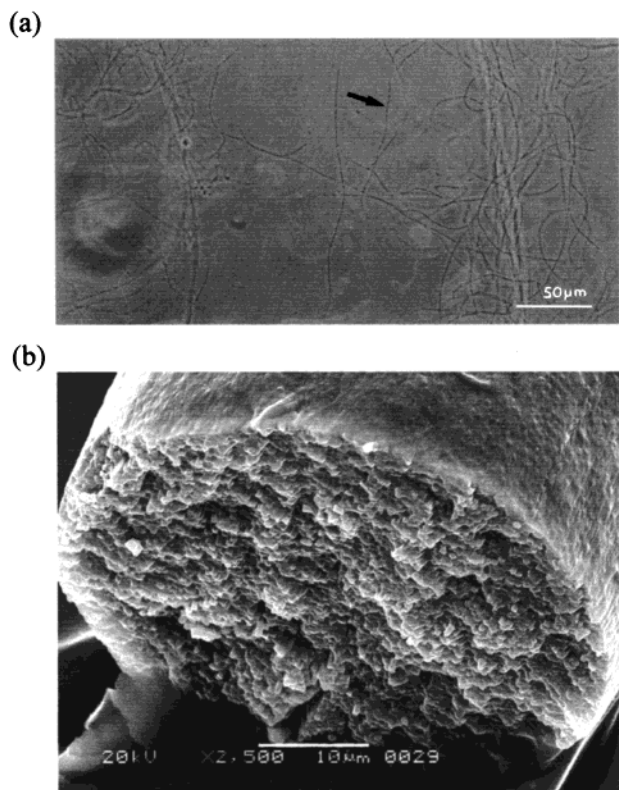


Figure 5. (a) Light microscopy image of bacterial web culture showing multicellular filaments (arrow). (b) SEM of a fractured bacterial thread in cross section showing co-aligned multicellular filaments.

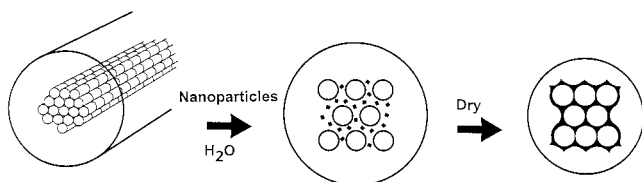


Figure 6. Schematic diagram illustrating process of nanoparticle infiltration into supercellular, swellable bacterial templates.

organic nanoparticles has been exploited in the fabrication of organized bacterial mineral composites.^{18a,d,32} The objective was to exploit the underlying organization of the thread as a template for producing composites with an extended, ordered microstructure. This was achieved by loading the bacterial thread with colloidal suspensions of nanoparticles, followed by air-drying to consolidate the inorganic mineral and replicate the interfilament spaces in the form of a continuous inorganic framework. For example, preformed ceramic (SiO₂), magnetic (Fe₃O₄), and semiconducting (CdS) inorganic nanoparticles were incorporated into macroscopic threads of *Bacillus subtilis* by reversible swelling of the superstructure in colloidal sols (Figure 6).^{18a,32} Inorganic patterning of the interfilament spaces was influenced by the surface charge of the nanoparticles used. Negatively charged silica and magnetite colloids gave good infiltration and replication of the bacterial superstructure such that the air-dried mineralized fibers consisted of a close packed array of 0.5 μm diameter multicellular bacterial filaments, each of which was coated with a 30–70 nm thick layer of aggregated nanoparticles. In both cases, repulsive forces between the nanoparticles and

cell membranes (which are also negatively charged due to the predominance of carboxylic acid groups) facilitated infiltration throughout the swollen organic superstructure. When the thread was redrawn from the sol, nanoparticles trapped between or adhering to the bacterial filaments were retained and consolidated within the interfilament spaces on drying. In contrast, neutral ligand-capped CdS nanoparticles, although internalized to some extent, were preferentially localized at the surface of the thread, and positively charged sols of TiO₂ did not penetrate the swollen fiber at all. The latter were deposited on the external surface of the macroscopic bacterial thread to produce a coherent surface coating with uniform thickness.

Formation of a continuous wall structure from the entrapped nanoparticles requires particle–particle aggregation and fusion into an extended network that does not collapse on removal of the organic matrix. This was achieved for amorphous silica nanoparticles, which produced intact inorganic fibers with ordered macroporous channels after the bacterial template was removed by calcination. In contrast, bacterial threads infiltrated with crystalline magnetite nanoparticles did not produce stable porous inorganic replicas of the multicellular superstructure because the nanoparticles remained only loosely associated even after calcination.

Recent studies have used superstructured bacterial threads for the synthesis of a hierarchical silica-based material containing micropores and macropores.^{18d} For this, a stable aqueous dispersion of preformed monodisperse zeolite nanoparticles was infiltrated into the organized bacterial matrix. The zeolite used was TPA-silicalite-1, nanoparticles of which were synthesized from clear solution by reflux of an aqueous solution containing tetraethyl orthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH), followed by repeated centrifugation and washing. The resulting colloidal dispersion had a pH of between 10 and 11 and consisted of particles with a net negative charge and a mean particle diameter of ca. 50 nm. When immersed in this suspension, the bacterial thread swelled without loss of structural integrity, and on air-drying a composite fiber was produced. Calcination above 600 °C removed both the molecular (TPA⁺) and micrometer-scale (supercellular) templates to produce a white macroporous inorganic fiber (Figure 7) that consisted of an organized array of ca. 0.5 μm diameter channels aligned approximately perpendicular to the long axis. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) data confirmed that the walls were composed of crystalline, microporous silicalite.

A similar hierarchical material was prepared by infiltration of the bacterial superstructure with incipient MCM-41 synthesis mixtures that we inferred to consist of small nanoparticles and clusters. In this case, an ordered macroporous fiber with channel walls of periodic mesoporous silica was obtained after calcination.³² Recently, stable colloidal dispersions of MCM-41 and organo-functionalized MCM-41 nanoparticles have been prepared,⁴⁰ and these are currently under investigation as building blocks in the nanotectonic assembly of hierarchical silica materials.

In summary, these studies demonstrate that in the longer term, it should be possible to integrate biotech-

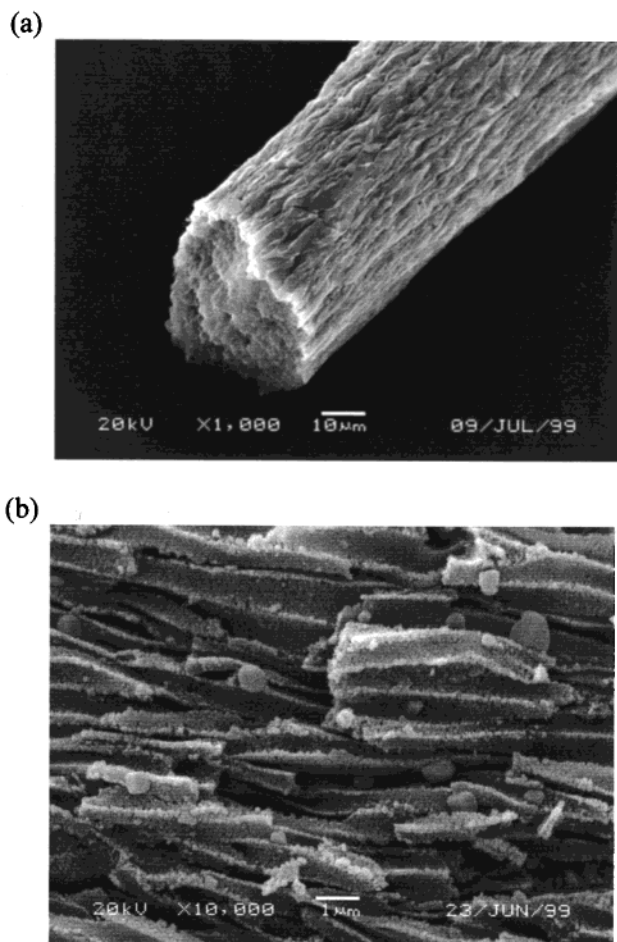


Figure 7. SEM images of a macroporous zeolite fiber formed by bacterial templating using silicalite nanoparticle building blocks: (a) intact zeolite replica after calcination; (b) higher magnification image of a fiber fractured longitudinally, revealing the co-aligned internal channels surrounded by walls of aggregated silicalite nanoparticles.

nological and materials chemistry processes for the fabrication of a wide range of hybrid materials exhibiting patterned microstructures and morphological complexity. The microarchitecture and the chemical and physical properties of the biological template are pre-defined by the bacterial matrix; specifically, a mutant form of *Bacillus subtilis* was engineered (by removal of the appropriate enzyme) such that cell separation was suppressed. Complex macroporous topologies are also possible in synthetic materials, and in this regard, monolithic polymer gels that exhibit reversible swelling and tunable chemical properties appear to be good candidates as organized templates in nanotectonics.^{18c} We discuss some recent examples in the next section.

Polymer Sponges. Bicontinuous polymeric gels have been used as templates for the in situ mineralization of magnetite⁴¹ and titanium alkoxide polymerization.⁴² In collaboration with Professor M. Antonietti and colleagues (MPI, Golm), we have used functionalized polymer gels, produced using acrylic acid-based copolymers with different proportions of carboxylic acid and hydroxyl functionalities, in association with colloidal suspensions of preformed magnetite (Fe_3O_4) or titanium dioxide (TiO_2) nanoparticles, to prepare three-dimensional inorganic monoliths with spongelike texture. The three-dimensional channel system of these swellable

polymeric templates is of key importance for the flow-derived mass transport of the nanoparticle building blocks. In comparison, conventional unstructured gels such as agarose or gelatine cannot be used in this way. Furthermore, unlike the bacterial superstructures previously described, synthetic copolymer gels can be tailored in architecture, functionality, and physical properties⁴³ to complement the colloidal properties of a wide range of inorganic building blocks. For example, the degree of swelling in the gels used is dependent on the nature of the response to changes in the local environment, in particular pH. This is predominantly determined by the electrostatic repulsion between ionizable groups and therefore by the carboxylic acid content of the copolymers. However, changes in the balance of functionalities can also influence the gel structure, so judicious adjustment of various parameters may be required to optimize the infiltration, compaction, and consolidation of inorganic colloids in the spongelike organic matrix.

Monolithic copolymer gels with bicontinuous macroporous structures were synthesized by copolymerization of a mixture of acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA) monomers in aqueous solutions containing the surfactant Brij 56. Gels containing either 10 or 20 wt % AA showed a good swelling response to immersion in nonacidic aqueous solutions; however their microstructure was significantly different. The 20 wt % AA copolymer gel showed a much greater degree of interconnectivity and homogeneous spongelike texture compared with the 10 wt % AA gel which consisted of interlinked globular particles (Figure 8). With these gels, some general properties could be exploited to produce homogeneously loaded inorganic-polymer hybrid materials by a single-step immersion in aqueous sols of inorganic nanoparticles. The swelling behavior of the gels was determined by the nature of the comonomers used and the corresponding porous architecture. By introduction of acidic functionalities, gels were produced that swelled significantly at high pH, such that nanoparticle dispersions stable under these conditions (e.g., Fe_3O_4) could be used to infiltrate the polymer structure within 24 h. In contrast, when acidic suspensions of TiO_2 nanoparticles were used, the absence of swelling resulted in slow infiltration and the time scale for composite formation was increased from days to weeks.

Stable monolithic inorganic inverse replicas of the polymer gel template were achieved using ceramic nanoparticles such as SiO_2 and TiO_2 , which formed continuous wall structures at low sintering temperatures (Figure 9a) due to condensation of the surface hydroxyl groups between neighboring particles. The use of silica-coated inorganic nanoparticles might therefore circumvent some of the limitations observed for materials such as magnetite—namely, the low degree of particle-particle fusion and mechanical stability of the inorganic replica (Figure 9b)—by facilitating the construction of continuous walls after calcination in structures prepared from core-shell nanoparticles.

Further studies are required to optimize the loading and broaden the range of materials that can be assembled using template-directed nanotectonics. The flexibility of the approach allows various properties of

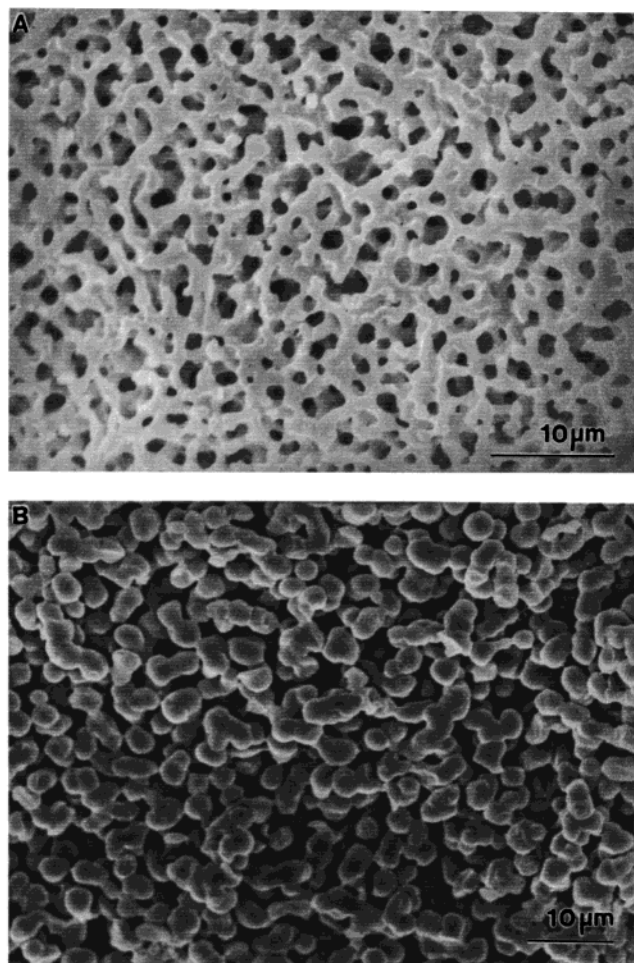


Figure 8. cryo-SEM images of bicontinuous copolymer gels showing composition-dependent microstructure: (A) 80 wt % 2-hydroxyethyl methacrylate (HEMA), 20 wt % acrylic acid (AA); (B) 90 wt % HEMA, 10 wt % AA.

the components of the hybrid structures to be tailored. For example, other functional residues, such as phosphonic or sulfonic acid, can be introduced into the gel structure by using suitable comonomers (e.g., vinyl phosphonic acid or 2-acrylamido-2-methyl-1-propane-sulfonic acid, respectively). Similarly, it should also be possible to change the nature of the “structural” polymer. However, finding the balance between structural and functional properties may be nontrivial. For example, preliminary experiments using *n*-isopropylacrylamide (NIPAM)/acrylic acid gels indicated that although the as-synthesized monolithic gels were homogeneous and mechanically stable, on dipping into a magnetite suspension the gels swelled but tended to disintegrate. Scanning electron microscopy at cryogenic temperature (cryo-SEM) revealed that the polymer walls consisted of nanoparticles weakly linked by thin strands of polymer, thus explaining the observed mechanical instability on swelling. The results emphasize the sensitivity of gel architecture to initial monomer composition. Experiments to obtain stable NIPAM/AA gels are ongoing, particularly because the thermosensitive reversible swelling properties of the template should result in hybrid materials with novel properties.

In conclusion, swellable polymer gel templates could have general use for the controlled organization of preformed inorganic nanoparticles into hybrid compos-

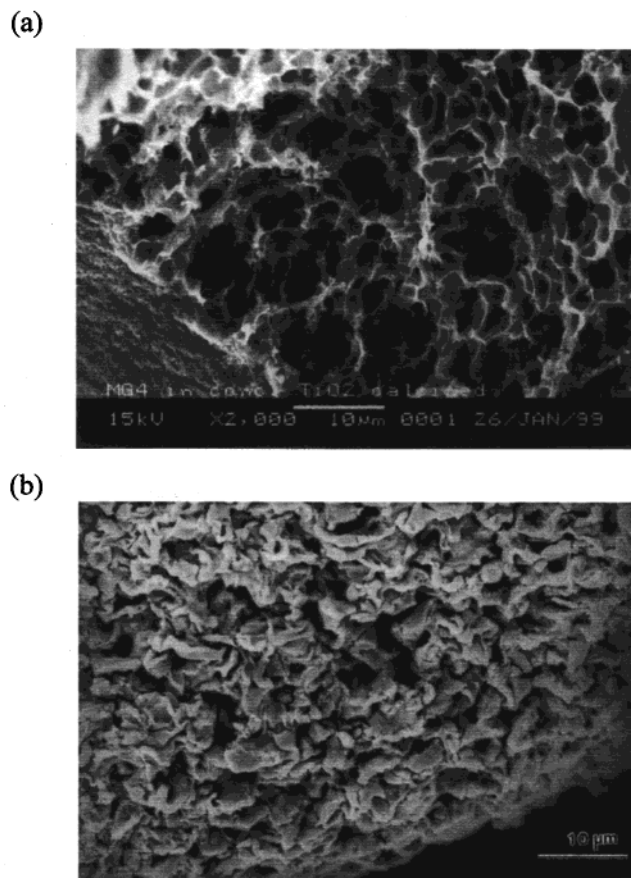


Figure 9. SEM images of macroporous interconnected structures after calcination of monoliths formed by polymer gel templating (20 wt % AA) using (a) a titania nanoparticle dispersion (pH 1.6) for 7 weeks and (b) a magnetite nanoparticle dispersion (pH 9.6) for 24 h.

ites that can be subsequently transformed into ceramic monoliths with macroporous structure. This strategy is wide ranging as the structure and composition of the polymer gel phase, and the surface chemistry and nature of the inorganic nanoparticles can be systematically varied. For example, a variety of functional silica-based dispersions, including amorphous, mesoporous, microporous, and core-shell nanoparticles are available as building blocks for nanotectonic assembly.

Other Matrixes. Velev and co-workers have used a flow-based system to infiltrate latex colloidal crystal templates with gold sols. Subsequent removal of the template at elevated temperatures resulted in sintering of the gold particles to produce a stable inorganic replica with high periodicity.^{18b,33c} Similarly, semiconductor quantum dots⁴⁴ and ceramic⁴⁵ nanoparticles have been infiltrated into silica and latex colloidal crystals, respectively. Although very regular, the architecture of the extended template is usually restricted to a simple close-packed arrangement of spheres, limiting the types of porous structures available by this approach.

Rather than an extended organic template, Seshadri and Meldrum used the highly porous magnesian calcite sea urchin skeleton, which has a periodic minimal surface structure, as an inorganic template for inorganic deposition.^{18e} The bicontinuous structure was infiltrated with a gold paint, and then the calcium carbonate template was removed by comparatively mild acid treatment. The thickness of the metallic phase could be

varied such that all the void space was filled or, alternatively, only a thin gold coating was produced on the calcite structure. After template removal, this produced either an inverse or positive replica, respectively, of the biomineralized architecture.

Template-Directed Construction: Substrate Engineering

One major limitation in the aforementioned examples is that the preformed nanoparticles are randomly arranged with respect to each other within the organized spaces of the template and show no registry with the template itself. This is not unexpected given that the particles are isotropic and being used via repulsive interactions predominantly for space filling. Thus, although complicated macro-organized templates can be replicated, at the local (meso-) scale the ordering is random. This is analogous to the use of concrete in building, where complex shapes can be generated quickly by pouring and setting in a suitable mold. In contrast, the more laborious "bricks and mortar" approach, which involves an intimate interfacial association between the components, gives rise to ordering across a range of length scales.

One method for introducing a certain degree of local scale ordering is "layer-by-layer" assembly. This approach to substrate engineering was first developed on 2-D surfaces and involves the sequential absorption of oppositely charged entities such as polyelectrolytes, biomolecules, and nanoparticles to produce multilayer films of controlled thickness.⁴⁶ Recently, the process was extended to spherical polymer templates that were coated with thin polyelectrolyte and hybrid polyelectrolyte-nanoparticle multilayer films to produce core/shell particles. Subsequent dissolution of the polymer beads produced hollow polyelectrolyte or inorganic shells with controlled diameter and thickness.^{19,47} Progress in the production of this new class of colloidal materials has been recently reviewed by Caruso.⁴⁸

By combining this strategy with molecular templating and self-assembly, it has been possible to produce a hierarchical silica material by sequential construction.⁴⁹ Alternating layers of preformed TPA-silicalite-1 nanoparticle "building blocks" and oppositely charged polyionic "cement" were sequentially absorbed onto sub-micrometer spherical latex particles to produce nanostructured composite zeolite shells of controlled thickness (Figure 10). The average thickness of each zeolite-polyelectrolyte layer pair was determined to be 39 nm by transmission electron microscopy measurements. These prefabricated micrometer size core/shell particles were then assembled into close-packed macroscopic structures by centrifugation. Subsequent calcination removed the organic components of the zeolite framework, composite shell, and latex template to produce the hierarchical silica monolith (Figure 11). The continuous wall structure around the ordered macropores consisted of a dense array of crystalline microporous silicalite nanoparticles that contained disordered mesopores associated with the interparticle voids. Using this strategy, in which the latex bead acts as both template and porogen, should allow both pore diameter and wall thickness to be tailored in the macrostructure.

For example, Figure 12a shows a sample in which smaller latex particles (460 nm diameter) were coated

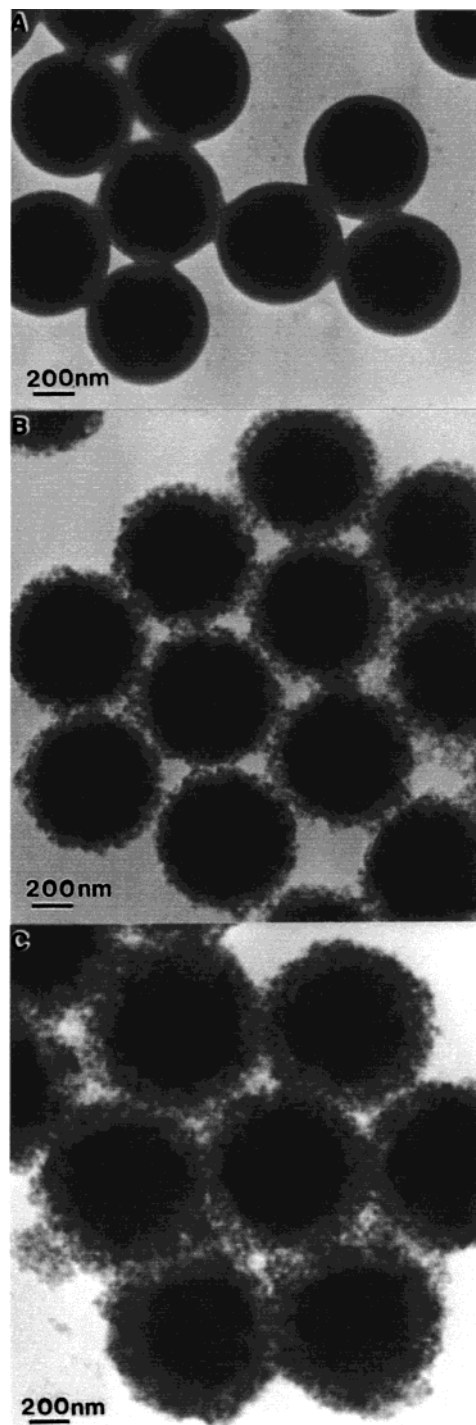


Figure 10. TEM images of 640 nm latex beads coated with alternating layers of silicalite nanoparticles and oppositely charged polyelectrolytes: (A) zero-, (B) two-, and (C) five-layer pairs.

with five layers of zeolite nanoparticles. Aggregates of the core/shell particles form during the process, resulting in subsequent zeolite and polyelectrolyte layers being built up around dimers and trimers etc., such that after centrifugation and calcination a bicontinuous, macroporous zeolite was produced (Figure 12b). Such structures could be very useful in catalysis and separation because of their increased accessibility compared with the "closed shell" periodic macroporous structures shown in Figure 11.

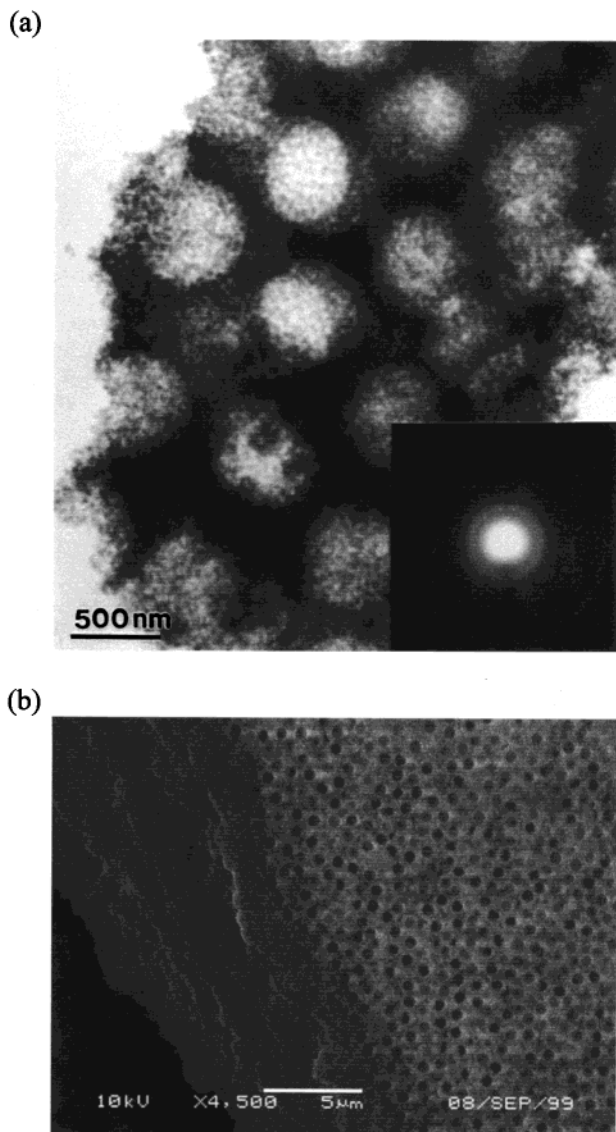


Figure 11. (a) TEM image from a fragment. (b) SEM image from a monolithic sample of a hierarchical silica material formed by calcination of a close packed assemblage of latex particles precoated with multilayers of zeolite nanoparticles.

A key aspect of the strategy is that core-shell structures are exploited as a combined building block and porogen (sacrificial template) for the construction of the hierarchical structure. This is in marked contrast with the matrix confinement approaches previously discussed^{18,33,34} that involve the infiltration of preformed templates such as colloidal crystals, polymer gels, or ordered superstructural templates, to prepare hierarchical materials. These methods have the disadvantage that the wall thickness is often limited by the void spaces of the organic matrix, which often cannot be readily adjusted. In comparison substrate engineering facilitates the construction of precoated templates and their subsequent assembly into extended structures. It should therefore be possible to fine-tune both the thickness and composition of the wall structures comprising the macroporous monoliths, by using multistep procedures.

Conclusions

The examples outlined above illustrate some early stages in the evolution of template-directed strategies

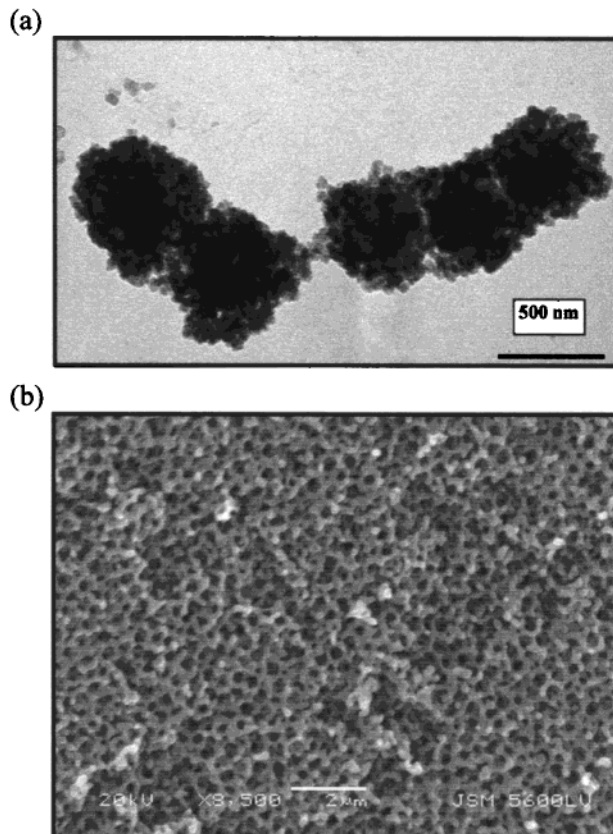


Figure 12. (a) TEM image of 460 nm latex beads, coated with five layer pairs of zeolite/PE, showing aggregated particles. (b) SEM image of the bicontinuous, macroporous structure obtained after centrifugation and calcination of the core/shell sample shown in (a).

to control the construction of preformed inorganic particles in nanotectonic approaches to organized matter. The use of bacterial or polymer architectures demonstrate how swellable templates with regular structure can confine the aggregation of inorganic building blocks using nonspecific repulsive interactions. Similarly, static colloidal crystal or biomineral templates can control colloidal aggregation by matrix confinement. Although the inorganic structures are organized at the micrometer length scale, the component nanocrystals are randomly arranged. The layer-by-layer sequential assembly of nanoparticles onto sacrificial substrates introduces further control over the construction process, to produce micrometer-sized core/shell particles that can be further assembled into higher order structures.

Finally, we note that besides template-directed approaches, there are various other strategies available in nanotectonics for introducing structural organization into the local arrangement of nanoparticles (see Figure 1). For example, patterned substrates containing sufficient informational content to induce regiospecific binding and site-specific deposition, would greatly facilitate the "brick-and-mortar" approach. This method has been used recently to induce the assembly of periodic superlattices of gold nanoparticles on bacterial S-layers.²⁰ It may also be possible to improve nanoparticle ordering by programming the inorganic surfaces. The coupling of the particles then occurs for example by specific biomolecular interactions, such as DNA hybridization, biotin-streptavidin conjugation, or anti-

body–antigen coupling, located between the nanoparticle surfaces.¹⁶ The shape of the nanoparticles is also likely to have a major influence in the ordering process; for example in bacterial threads, elongated nanoparticles could be preferentially aligned along the thread axis.

Furthermore, by combining different constructional strategies, which operate on different length scales, in a simple stepwise manner, it should be possible to prepare hierarchical materials with several layers of embedded structure. As the variety of protocols increase, the choice of building modules and templates will be made retrospectively, so that a wide range of complex multilevel structures should become accessible by a rational approach based on materials *retrosynthesis*.

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