DALTON PERSPECTIVE

Crystal tectonics: Chemical construction and self-organization beyond the unit cell†

Stephen Mann,* Sean A. Davis, Simon R. Hall, Mei Li, Katja H. Rhodes, Wayne Shenton, Sébastien Vaucher and Baojian Zhang

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK. E-mail: s.mann@bris.ac.uk

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Crystal tectonics involves the chemical-based construction and self-assembly of organized materials from solid-state building blocks, such as inorganic nanoparticles. This Perspective describes, through a series of examples, how the architectural complexity of materials with higher-order structure can be controlled by organic templating, inter-particle molecular recognition and mesophase transformation. It is shown how the coupling of synthesis and self-assembly over multiple length scales is leading to new horizons in the chemistry of organized matter.

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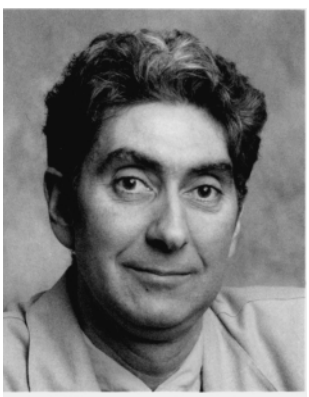
Traditionally, inorganic chemists view crystallography with a practical eye intent on describing crystal structures in terms of local coordination geometries and their concomitant implications for bonding and reactivity. With the dramatic increase in the number of high resolution structures and the expanding capability of computer analysis, data banks are now mined for the extraction of collective and generic properties, such as structural correlations (crystal systematics)[1] and constructional motifs (crystal engineering).[2] These retrospective evaluations of description and structure have significantly extended our knowledge of crystal science and offer much intellectual and technological promise. Combined with the established approaches to solid-state reactivity (crystal chemistry),[3] we now have a concerted

Stephen Mann is currently Professor of Chemistry and Director of the Centre for Organized Matter Chemistry at the University of Bristol. He received his D.Phil. from the University of Oxford in 1982 and was professor in the School of Chemistry, University of Bath, between 1990 and 1998. Professor Mann has published over 200 scientific papers and received several awards, including the Corday–Morgan Medal (RSC, 1993), Vinci of Excellence Trophy (1996), Max Planck Research Prize (1998) and RSC Interdisciplinary Award (1999). He is currently on the editorial and advisory board of numerous journals including Advanced Materials, Angewandte Chemie, *and* Chemistry of Materials. *His current research is concerned with the biomimetic synthesis, characterization and emergence of complex forms of organized matter across extended length scales. He enjoys family life, running half marathons (slowly), and playing electric guitar (badly).*

Sean Davis was born in Carmarthen, Wales in 1970. He received his BSc and PhD degrees from the University of Bath, UK. He is currently working as a Research Associate in Electron Microscopy at the University of Bristol. His research interests are the study of biominerals and the templated assembly of inorganic nanoparticles.

Simon Hall was born in 1969 in Stratford-Upon-Avon. He graduated from the Open University with Honours in chemistry in 1997, and joined the research group of Professor Mann in the same year. He is currently studying for a PhD, where his research interests are in template-directed nanoscale syntheses, biomimetic chemistry, and crystallographic studies on the phylum 'Bryozoa'.

Mei Li received her BSc degree of chemistry from Jilin University in 1982 after which she was a research assistant at Beijing Forestry University. She was appointed to a lectureship at Beijing Forestry University from 1987 to 1994. She pursued her M.Phil. degree in molecular biology at the University of Wales Swansea from 1995 to 1997. Currently she is pursuing her PhD degree under the supervision of Professor Mann at the University of Bristol. Her current research interests are in the synthesis, characterization and self-assembly of nanoscale materials in micelles and microemulsions, and organization of inorganic nanoparticles using biological connectors.



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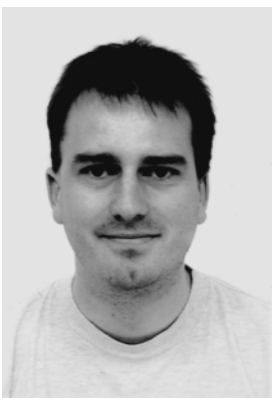

Simon Hall

Mei Li

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multi-pronged approach to the study of materials with nanoscale periodicity.

If there is a cloud on this new horizon it arises from the long-acknowledged fact that the processes of crystallization remain empirically based and subject to serendipity and "green fingers". Furthermore, current theories of nucleation, crystal growth and morphology, documented in detail in many physical chemistry texts,[4] are not generally considered part and parcel of new research areas such as crystal engineering. This is unfortunate because the integration of structure (energetics) and mechanism (kinetics) is fundamental to the "crystal-structure synthesis" paradigm at the heart of crystal engineering. For example, supramolecular synthons[5] may orchestrate the bulk lattice interconnectivity, but they first need to be incorporated into the propagating front of the nucleus. As the surface of the nucleus is dynamic, unstable and probably disordered or relaxed away from the bulk lattice, specific surface-binding configurations will lower the interfacial energy and direct the nucleation pathway towards the adoption of certain crystal structures. The stability and precise placement of molecular aggregates ("pre-synthons"?) in the transient clusters present during nucleation might for example explain the structural origin of polymorphism. In this regard, computer modelling of synthon stability as a function of crystal volume and lattice relaxation would be interesting because although the surface/edge energies are relatively unimportant in bulk crystal structures they become dominant at the nanometre dimensions that are typical of the nucleation stage. The unit cell may be the smallest repeat unit of the bulk crystal but it is unlikely that it corresponds to the first structure formed during the crystallization process.

The important interplay between structure and process illustrates that although the unit cell remains an icon of chemical crystallography, it is the means by which this repeating pattern proliferates that gives rise to useful materials such as crystals, nanoparticles, colloids, porous solids, polytypes, superlattices and ordered defect structures. This is not to deny the influence of crystal structure on function, but rather to emphasize that structure and morphology beyond the unit cell are often pre-eminent in determining the success of crystalline materials in industrial applications. Owing to thermodynamic constraints, the crystal structure is to a certain extent immutable and not readily accessible to manipulation, whereas repetition of the unit cell building block is susceptible to a wide range of modifications in the crystallization process. In recent years, chemists have exploited this for the synthesis of crystalline materials with increasing levels of higher-order organization beyond the construction of the unit cell (Fig. 1).

The lowest level of this hierarchy involves the control over nucleation and growth, for example by chemically functionalized surfaces and soluble additives, respectively, to produce oriented crystals[6–8] or modifications in crystal habit.[9–12] These studies emphasize that crystallization is analogous to a self-assembly process involving precise interfacial molecular recognition. Although curtailed to some extent by symmetry restrictions, crystal faces are nevertheless susceptible to a wide range of interfacial interactions that produce reproducible habit modifications in the equilibrium form and crystallographic alignment of nuclei on substrates with appropriate chemical complementarity. Increased levels of complexity have been introduced into crystalline materials using novel approaches involving templating, "morphosynthesis" and patterning of crystal architectures (Fig. 1). In these materials, proliferation of the unit cell building block is directed to such an extent by external fields that the resulting crystal architecture bears little or no resemblance to the underlying Bravais lattice. That is, the symmetry that describes the nanoscale periodicity is not manifest in the macroscopic form. The chemistry of materials with complex form has recently been reviewed in detail,[13–16] and is therefore not discussed in this article. Instead, we discuss a further level of organization in crystal science in which individual crystals, perhaps with unusual

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Katja Rhodes was born in Reading in 1977. She received her MChem degree from UMIST in 1998. She is currently studying for her PhD at the University of Bristol under the supervision of Professor Mann. Her research interests lie in the field of nanostructured organic/inorganic composite architectures.

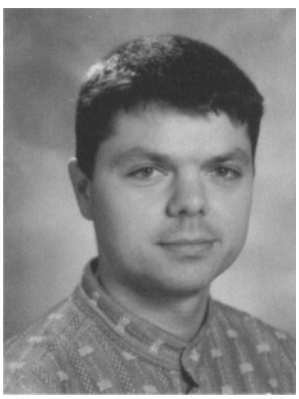
Wayne Shenton, born in Stoke-on-Trent, Staffordshire, studied Chemistry and Biochemistry at the University of Leeds, UK from 1992 to 1995. He obtained his PhD Thesis in the group of Professor Mann at the University of Bath, UK in 1999, where he carried out research on the use of various biomolecules, including viruses, enzymes and antibodies, for the fabrication of novel bio-inorganic materials. His current research at the University of Bristol concerns the synthesis of quantum dots using hollow protein macromolecules resembling ferritin.

Sébastien Vaucher was born in Neuchâtel (Switzerland) in 1970. He obtained his diploma in chemistry from the University of Neuchâtel in 1993. He joined the Tokyo Institute of Technology for one year. After completing his PhD back at the University of Neuchâtel in 1998, he moved to Bristol as a post-doctoral fellow. His interest is mainly centred around the higher-order synthesis of supramolecular materials.

Baojian Zhang was born in Changchun, Jilin Province, P. R. China, in 1951. He received his MSc at the Northeast Normal University (Changchun) in 1985, where he became an Associate Professor in 1993. Currently he is carrying out his PhD at the University of Bristol. His research interests include heteropoly-oxometalate chemistry and zeolite-based materials by template-directed synthesis.

Katja Rhodes

Wayne Shenton



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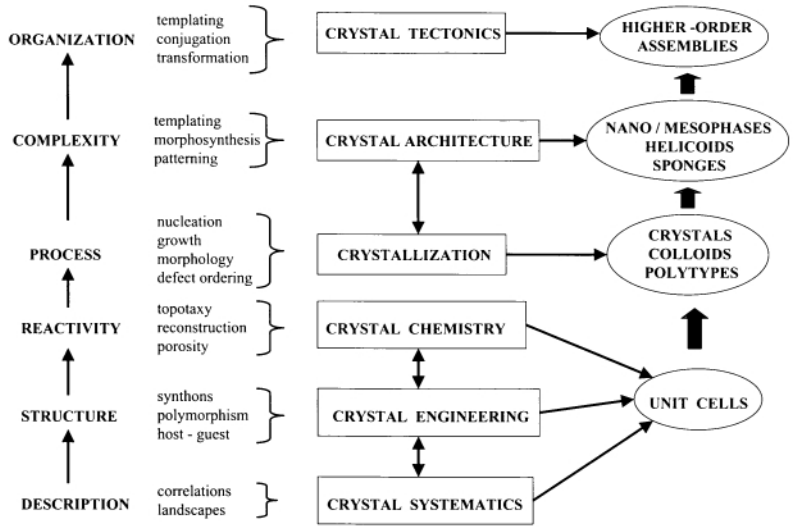

Fig. 1 Beyond the unit cell: levels of organization in crystal science.

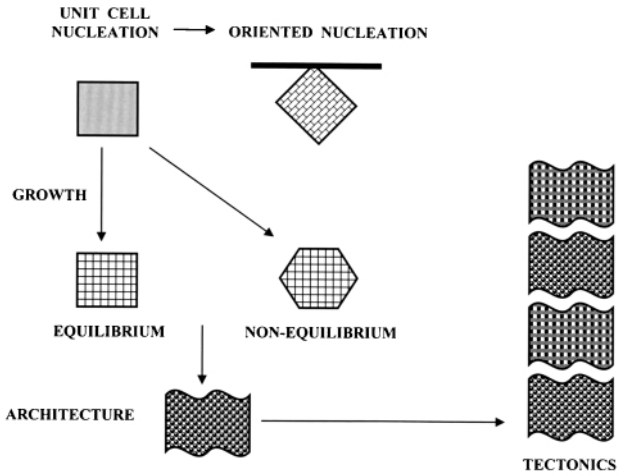

Fig. 2 Inter-relationships between crystallization (nucleation, growth, morphology), crystal architecture (complex form) and crystal tectonics (higher-order assembly). Levels of complexity, organization and informational content tend to increase as the length scale is extended.

architecture, are assembled into higher-order arrays and superstructures (Fig. 2). The construction of ordered materials from preformed building blocks, *crystal tectonics* (Gr. *tekton*, a builder), is an important aspect of the chemistry of organized matter and should lead to a variety of functional materials for use in nanoelectronics, catalysis and magnetic storage.

Crystal tectonics

The study of crystal tectonics is being inspired in part by investigations of certain biological minerals which have higher-order structures that originate from the organized assembly of preformed mineral building blocks in association with organic structures such as phospholipid vesicles. The involvement of vesicles appears to be a general feature of many biomineralization processes.[17] The vesicles are secreted and assembled prior to biomineralization and function as membrane-bounded reaction environments for inorganic deposition. In some organisms, groups of vesicles are used spatially to pattern and organize the mineral crystals into arrays and superstructures. For example, an elliptical ring of vesicles is assembled prior to the formation of elaborate calcium carbonate structures called coccoliths.[18] Each vesicle acts as the nucleation and mineralization site for the growth of a single Z-shaped calcite particle such that the resulting structure consists of a continuous ring of discrete but interlocked crystallites (Fig. 3). Similarly, magnetite crystals in

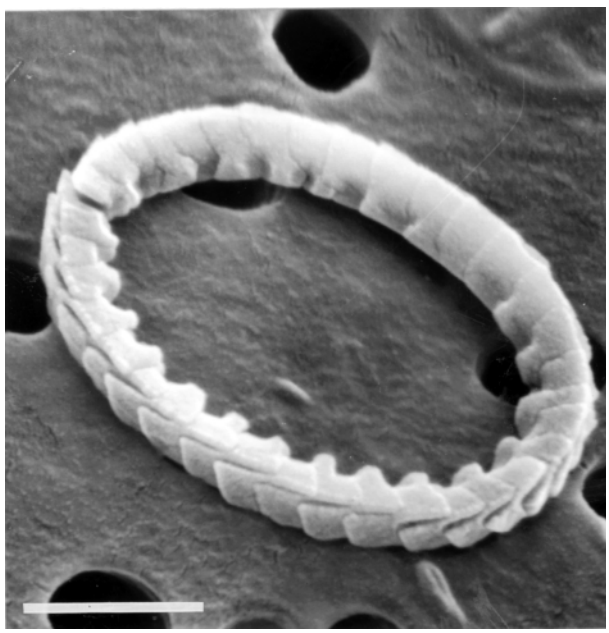

Fig. 3 SEM image of the initial stage of coccolith biomineralization in the alga *Emiliania huxleyi*. Each calcite crystal in the interlocked ring is crystallographically aligned and spatially discrete. Scale bar = 0.5 μm.

magnetotactic bacteria are sequentially synthesized along a linear chain of vesicles so that the cells contain a permanent magnetic dipole for navigation in the geomagnetic field.[19] In other unicellular organisms curved silica fibres are shaped in elongated vesicles and then transported through the cell membrane to the extracellular space where they are used as rod-shaped building blocks for the construction of a basket-like framework.[20]

A central aim of crystal tectonics is chemically to construct materials with long-range organization that exceeds the simple close-packed geometry of colloidal crystals and emulates the complexity and functionality of biomineralized structures, but with a technological rather than biological bias. To control long-range ordering, sufficient informational content has to be included in the solid-state building blocks or external medium, or both. We illustrate this principle below by a number of examples taken from our recent work. The overarching idea is to use preformed inorganic nanoparticles in association with organic self-assembly to prepare materials by direct, synergistic or emergent constructional processes (Fig. 4). We show that certain organic structures can be used to prepare inorganic replicas with nanoparticle constituents by direct templating.

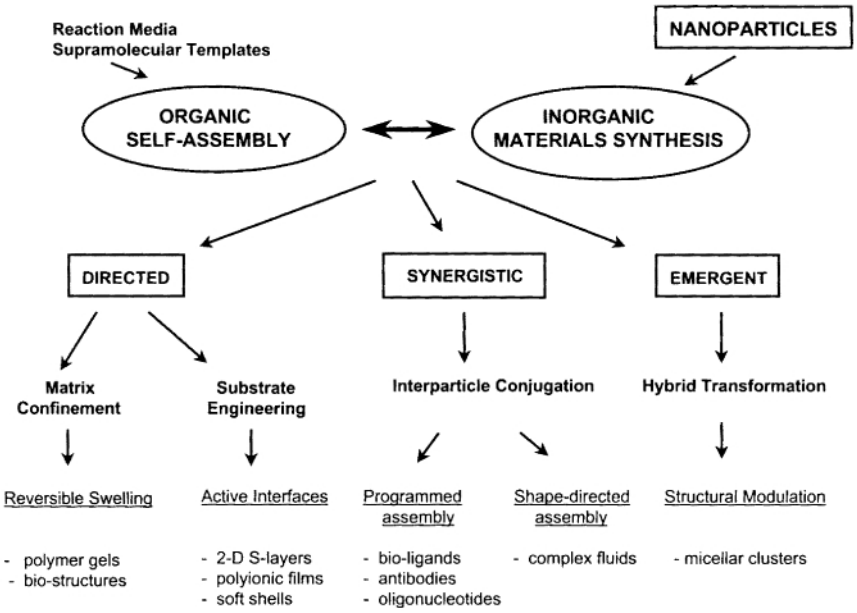

Fig. 4 Chemical approaches in crystal tectonics.

Alternatively, surface ligands attached to individual nanoparticles can be used to couple the inorganic building blocks in solution into superstructures. We also describe how reactions within the confined nanoscopic water droplets of water-in-oil microemulsions can produce shaped nanoparticles that spontaneously self-assemble into linear chains and rectangular superlattices through hydrophobic interactions arising from surface-adsorbed surfactant molecules. Finally, we show that aggregates of metastable hybrid mesophases, such as surfactant–inorganic micellar clusters, can structurally transform with time into complex architectures with higher levels of organization.

Template-directed construction

Organic substrates with 2-D or 3-D architecture can be used as templates for the spatial patterning and placement of inorganic nanoparticles to produce ordered arrays and microstructures. The simplest case involves the infiltration of a porous organic matrix with preformed nanoparticles such that the inorganic replica is patterned through confinement in the structured void spaces of the template. Moreover, if the surfaces of the organic substrate can be chemically and spatially functionalized to provide site-specific binding, then it should be possible selectively to direct the assembly of nanoparticle arrays within the patterned matrix.

Matrix confinement. Infiltration of an organic template such as a polymer gel with inorganic nanoparticles is often curtailed by preferential deposition of an impermeable surface coating. This can be circumvented through the use of an organic template with reversible swelling properties such that the nanoparticles diffuse by capillary forces into the hydrated matrix. Moreover, the nanoparticles become trapped and consolidated within the patterned void spaces by shrinkage during drying. For example, macroscopic bacterial threads with an ordered superstructure consisting of a pseudo-hexagonal arrangement of long multicellular cylindrical filaments undergo significant swelling when hydrated in the presence of colloidal sols of silica[21] or zeolite (silicalite)[22] nanoparticles (Fig. 5). The large increase in void volume between the multicellular filaments results in extensive infiltration of the bacterial superstructure, particularly for negatively charged nanoparticles because these are electrostatically repelled from the highly anionic bacterial cell walls. The particles therefore reside primarily in the interstitial void spaces of the superstructural template and permeate

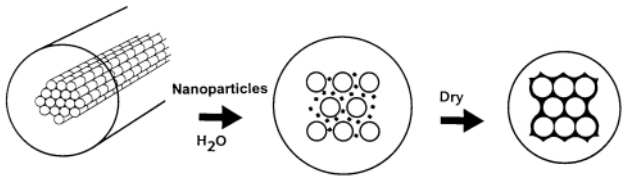

Fig. 5 Scheme showing template-directed construction of organized macroporous inorganic frameworks using bacterial templates with supercellular organization (drawing on the left) and inorganic nanoparticles as building blocks.

deep into the bacterial thread. On drying the thread contracts and large increases in ionic strength occur within the interfilament regions. This shields the surface charge on the inorganic nanoparticles such that a continuous mineral framework is formed by particle–particle aggregation. Subsequent thermal decomposition of the bacterial template produces an intact inorganic fibre with ordered 0.5 μm macroporous channels lined by 100 nm wide walls of coalesced nanoparticles (Fig. 6). Using silicalite nanoparticle building blocks, this results in a hierarchically ordered zeolite fibre consisting of macroporous channels surrounded by nanoporous walls.

A similar approach has been developed to prepare interconnected 3-D macroporous frameworks of coalesced magnetite or titania nanoparticles by incorporation of nanoparticles into swellable sponge-like block copolymer gels.[23] In other studies, 3-D colloidal crystals consisting of close packed polymer latex beads have been used as porous templates for the infiltration and fusion of gold nanoparticles.[24] The resulting ordered macroporous materials could have important applications as photonic devices.

Substrate engineering. The use of bacterial or polymer architectures for the template-directed assembly of inorganic nanoparticles illustrates how preformed solid-state building blocks can be integrated into regular spatial structures by matrix confinement of colloidal aggregation. Although these structures exhibit order at the micrometre scale, the particles themselves are randomly coalesced. It should be possible to prepare analogous materials comprising ordered nanoparticles if substrates engineered with appropriate surface binding sites can be found. As a start towards this goal, we have used a biomolecular template in the form of a 2-D protein crystal with site-specific periodicity to fabricate highly organized arrays of gold nano-

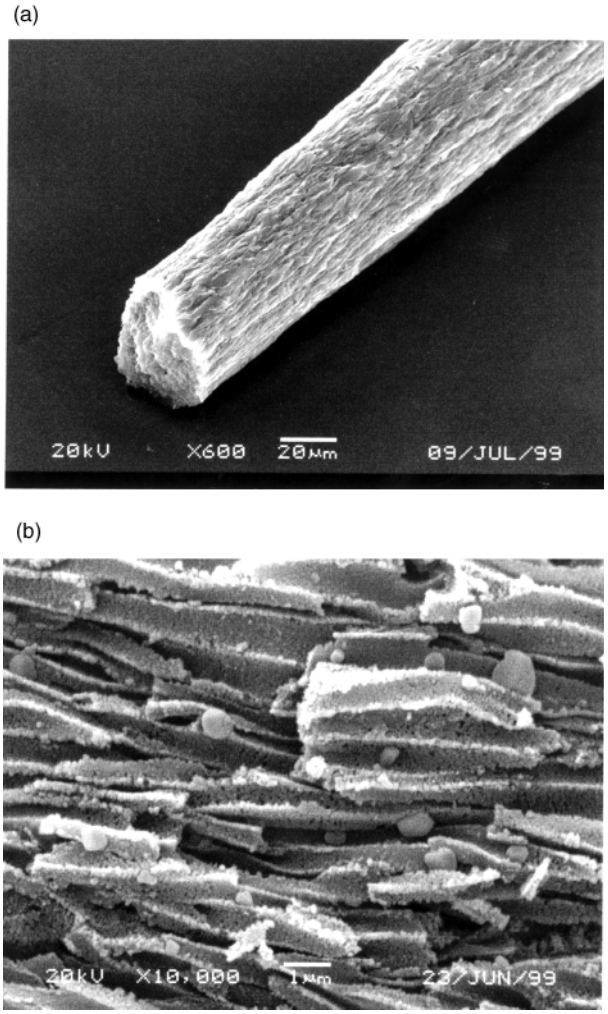

Fig. 6 SEM images of (a) macroporous zeolite fibre formed by bacterial templating using silicalite nanoparticle building blocks, scale bar = 20 μm, (b) longitudinal fracture of the zeolite fibre showing internal channels surrounded by walls of coalesced silicalite nanoparticles, scale bar = 1 μm.

particles.[25] Crystalline sheets of the surface (S)-layer protein present in the cell wall of the bacterium *Deinococcus radiodurans* are readily assembled from multiple copies of a single protein (M_r = 106000) that crystallize as a *p6* array of hexamers.[26] The native S layer exists as a 1:1 complex with an outer membrane-bound 5′-exonuclease, in which the nuclease macromolecules are electrostatically bound specifically at the tip of cone-shaped protrusions arranged in a hexagonal lattice of unit cell length 18 nm.[27] The site-specific binding of these macromolecules on the patterned S-layer inner surface suggests that analogous processes could be employed with inorganic nanoparticles (Fig. 7).

Indeed, when self-assembled S layers were mounted on hydrophobic TEM grids and exposed to an aqueous dispersion of uniform-sized gold nanoparticles, regular superlattices were patterned across the hydrophilic outer surface of the bio-crystal (Fig. 8). The superlattices were formed only for negatively charged gold nanoparticles that were smaller than the S-layer lattice parameter. Positively charged gold nanoparticles were not organized across the biomolecular substrate, even when the particle size was less than the S-layer lattice constant. Significantly, increases in nanoparticle size did not effect the centre-to-centre spacing (18 nm) but reduced the inter-particle contact distances proportionately (Fig. 8b and c). The results indicate that electrostatic binding of the nanoparticles is highly site-specific and in 1:1 register with the periodicity of the S-layer template. It seems feasible that the nanoparticles bind specifically at the positively charged ends of channels that are exposed on the

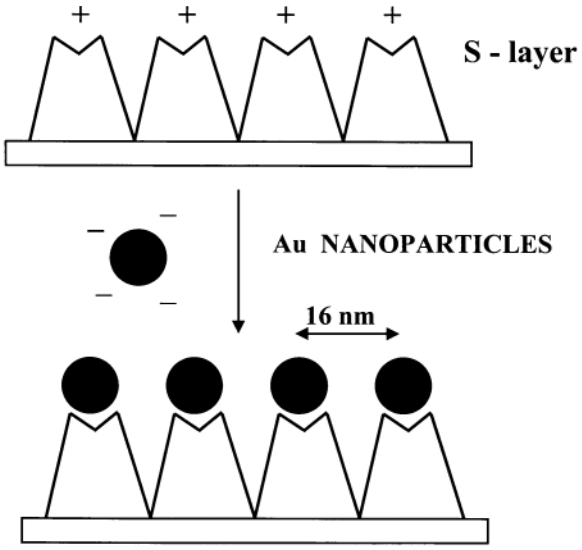

Fig. 7 Schematic illustrating the use of bacterial membrane 2-D crystals (S layers) in the assembly of periodic superlattices of gold nanoparticles.

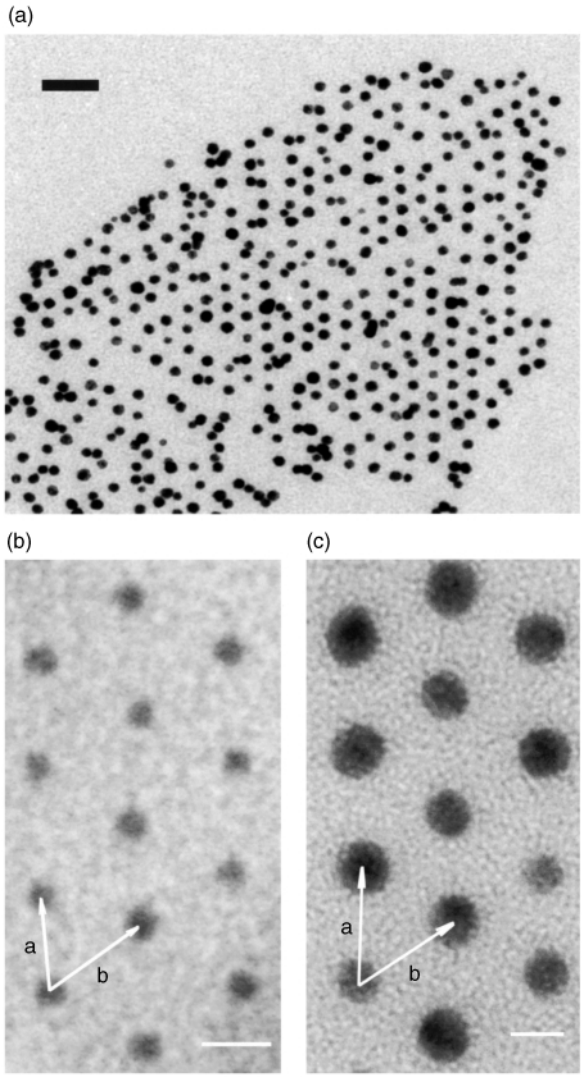

Fig. 8 TEM micrographs of S-layer templated gold nanoparticle superlattices. (a) Low magnification image showing single crystal domain with defects, scale bar = 40 nm. (b) and (c) 2-D hexagonal arrays of 5 and 10 nm gold nanoparticles with interparticle contact distances of *ca.* 12 and 7 nm, respectively. Vectors *a* and *b* show an average centre-to-centre spacing of 18nm in both cases. Scale bars = 10 nm.

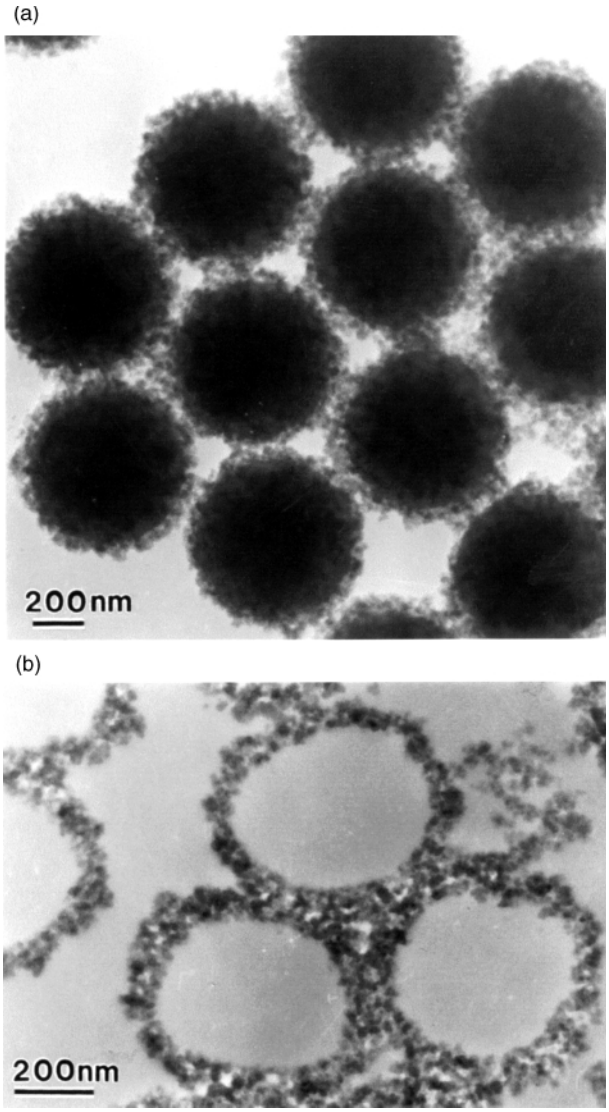

Fig. 9 TEM micrographs of polyelectrolyte–zeolite shells assembled on latex bead templates (a) before and (b) after removal of the template. The image in (b) is recorded after thin sectioning of the hollow zeolite spheroids. Scale bars = 200 nm.

hydrophilic outer surface of the S-layer crystal. The ability to template materials with constant superlattice symmetry but variable interparticle contact distances could have important applications in the study of basic quantum phenomena, such as coulomb blockade[28] and single charge tunneling[29] events.

To date, it has not been possible to incorporate this degree of nanoparticle ordering into three dimensions by template-directed construction, although nanoparticles can be assembled onto the surface of curved substrates by strong electrostatic interactions.[30] For example, hierarchically structured hollow zeolite shells have been prepared by a layer-by-layer deposition process that involves the alternate adsorption of a cationic polyelectrolyte followed by negatively charged silicalite nanoparticles onto the surface of 640 nm diameter polystyrene beads.[31] Repeating this procedure several times produces nanostructured composite shells of controlled thickness that can be calcined to remove the latex template or assembled into close-packed structures, or both. The resulting materials consist of zeolitic spheroids with nano-, meso- and macro-porosity (Fig. 9). Although the individual nanoparticles remain intact they are not ordered on the polyelectrolyte template because of the absence of periodicity in the electrostatic binding sites. It might be possible to increase the degree of nanoparticle ordering by using amphiphilic macromolecules such as block copolymers that undergo micro-phase separation of hydrophilic and hydrophobic domains when absorbed onto the curved surface of the latex bead.

Interparticle conjugation

It should be possible to build elaborate higher-order structures from preformed nanoparticles endowed with sufficient informational content that their surfaces couple in solution along specific directions. At least two factors need to be considered in this approach to vectorial interparticle conjugation. First, interactions between the surfaces should be programmable in the sense that the nanoparticles contain specific recognition properties so that the process is selective but reversible; this limits the number of non-specific interactions and reduces the accumulation of "errors" in the construction process. Secondly, the assembly process must be constrained to specific directions if periodic or regular superstructures are to be prepared.

Programmed assembly by molecular recognition. The highly specific recognition properties of antibodies and antigens make them excellent candidate molecules for the ligand-induced assembly of preformed nanoparticles in solution. For example, if an antibody such as IgE is raised against a molecule containing a dinitrophenyl (DNP) group (anti-DNP IgE) and then chemisorbed onto 12 nm gold nanoparticles, the particles can reversibly be aggregated by addition of a molecule (antigen) that consists of a double-headed DNP functionality (Fig. 10).[32] Clearly, the interparticle cross-linking can only occur if both DNP headgroups can bind antibodies on adjacent nanoparticles, so a spacer chain of at least eight carbon atoms is required (the binding sites are often buried in the protein molecule). With this *caveat*, the aggregation process is highly specific and reversible (Fig. 11). For example when the DNP-DNP antigen is added to a gold nanoparticle dispersion containing chemisorbed antibodies with highly specific binding sites for the small molecule biotin (anti-biotin IgG antibodies) no precipitate is observed. Similarly, a sol containing two populations of different gold nanoparticles with either surface-adsorbed anti-DNP IgE or anti-biotin IgG is only aggregated in the presence of a synthetic DNP-biotin antigen with a 19 atom spacer (Fig. 10).[32]

Similar approaches have been developed in which protein–substrate or oligonucleotide complementary pairs are used to induce the reversible aggregation of inorganic nanoparticles. For example, when single-stranded oligonucleotides with complementary base sequences are attached to gold nanoparticles the crystallites selectively aggregate.[33,34] This pioneering approach is versatile and has the potential to be highly specific in controlling the distances between the aggregated nanoparticles. Another possibility is to exploit the non-covalent binding of biotin to the protein streptavidin ($K_a = 10^{14}$ dm^3 mol^{-1}) in the reversible cross-linking of biotinylated gold nanoparticles.[35] Streptavidin is a tetrameric protein structure with four biotin binding sites so it is an efficient connecting unit for three-dimensional aggregation.

The direct attachment of biotin derivatives to nanoparticles is limited by the surface chemistry of the inorganic phase, but this can be circumvented if the nanoparticles are encapsulated in a protein or lipid shell that can routinely be functionalized with biotin surface groups. For example, iron oxide particles prepared within the 8 nm cavity of the protein ferritin are organized into network structures by biotinylation of the 60 to 70 exposed lysine residues on the surface of the protein shell, followed by conjugation in solution with streptavidin (Fig. 12).[36] A flexible hexanoate spacer is incorporated into the covalent linkage to access the four high affinity biotin binding sites in streptavidin. This works well if there are both free and bound biotin groups on the protein surface. If too much streptavidin is added then all the binding sites are saturated and no cross-linking of the protein shells can occur. A balance between primary and secondary coupling of the biotinylated

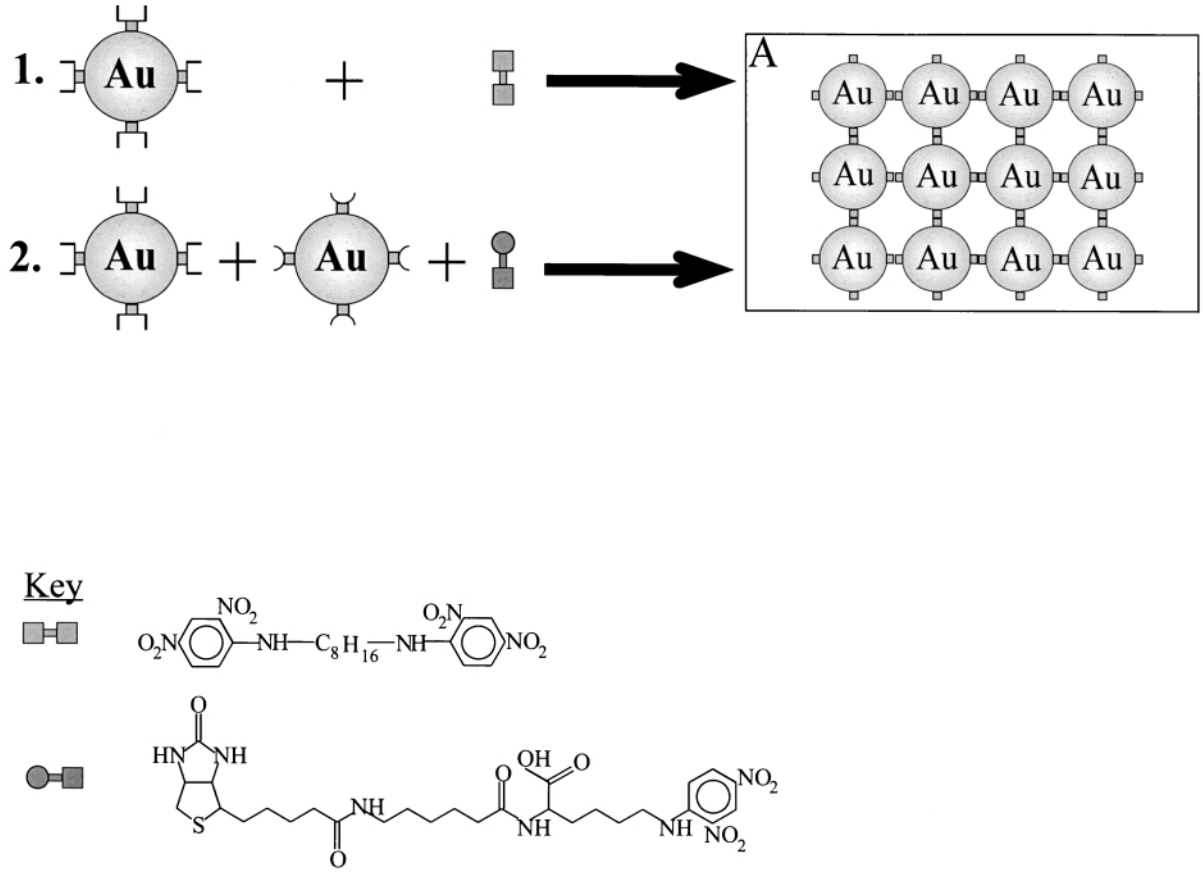

Fig. 10 Schematic representation showing possible approaches to the programmed assembly of organized metallic materials using antibody–antigen cross-linking of gold nanoparticles. The structures shown are idealized; in reality the materials are highly disordered. (1) Gold nanoparticles with surface-attached anti-DNP IgE antibodies and DNP-DNP antigen connector. (2) Gold nanoparticles with either surface-attached anti-DNP IgE or anti-biotin IgG antibodies and DNP-biotin antigen.

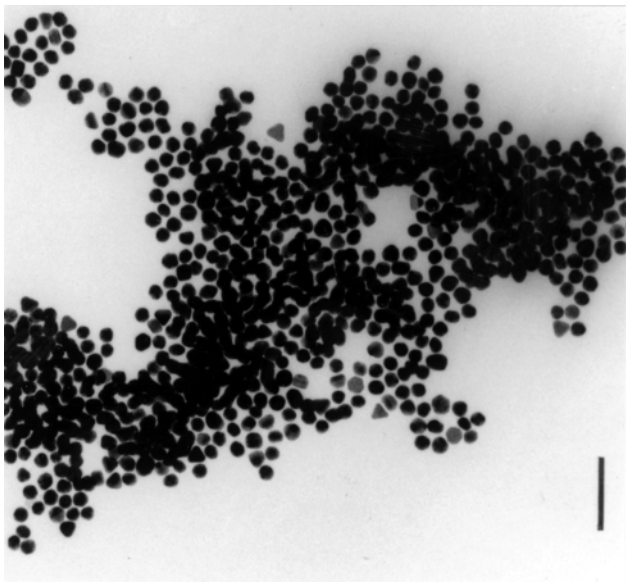

Fig. 11 TEM micrograph showing aggregated Au/anti-DNP antibody nanoparticles formed after addition of a soluble DNP-DNP double-headed antigen. Scale bar, 60 nm.

groups to the binding sites of free streptavidin and streptavidin–ferritin complexes, respectively, is therefore required to achieve aggregation of the protein-encapsulated nanoparticles. These interactions become co-operative rather then competitive when approximately 10% of the surface biotin groups are involved in primary coupling.

Shape-directed assembly. Although the above examples illustrate the enormous potential for programmed assembly in crystal tectonics, at the current time no ordered superstructures have been produced. This is principally due to the fact that only spherical nanoparticles have been used with the consequence that the aggregation process is isotropic. Clearly, combining the surface recognition chemistry with nanoparticles of specific shape, for example gold nanorods,[37] should provide some degree of vectorial control over construction. Moreover, if the shape is related to the underlying crystallographic symmetry, several different crystal faces can be expressed at the nanoparticle surface. This raises the possibility of programming an individual nanoparticle with two or more different recognition surfaces because different faces may have different affinities for the surface binding of ligands, antibodies and oligonucleotides.

Confined reaction media such as water-in-oil microemulsions can be used to synthesize nanoparticles with well defined geometric shape.[38,39] For example, hydrophobic Prussian blue nanoparticles with uniform cubic shape and size can routinely be synthesized from reactions within nanoscale water droplets formed in reverse microemulsions prepared from the anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT).[40] Growth of the nanoparticles within the restricted reaction field is controlled by a multi-step process involving slow photoreduction of aqueous $[Fe(C_2O_4)_3]^{3-}$ to iron(II) ions that subsequently react with $[Fe(CN)_6]^{3-}$ ions to produce nuclei and clusters of Prussian blue encapsulated within the water droplets. Crystals of the molecular magnet grow by further exchange and fusion between microemulsion droplets to produce regular 16 nm size nano-cubes that are surrounded by a shell of surfactant molecules. Although the highly hydrophobic surface properties of surfactant-capped inorganic nanoparticles have previously been used to prepare superlattice structures by solvent evaporation,[41–44] these are invariably limited to hexagonally close-packed arrays because spherical nanoparticles are employed. In contrast, the Prussian blue nanocrystals self-

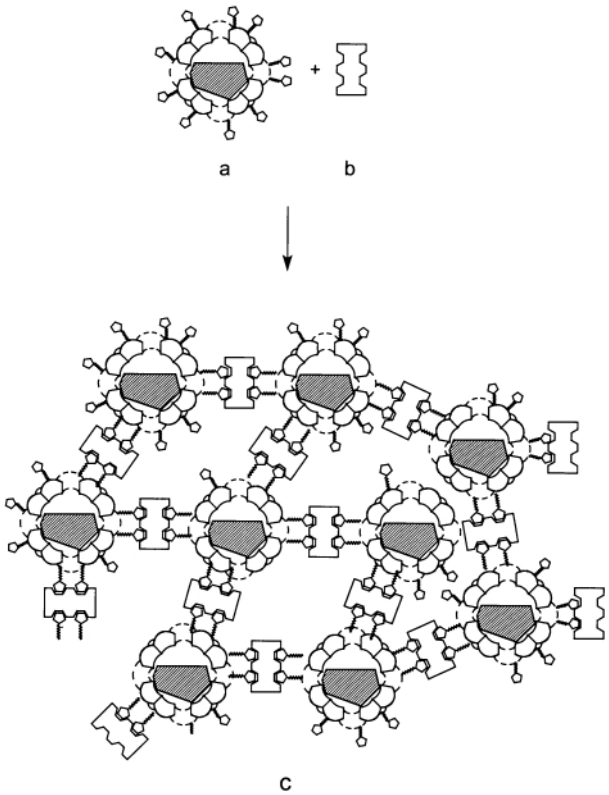

Fig. 12 Controlled aggregation of iron oxide nanoparticles in biotinylated ferritin using streptavidin connectors: (a) biotinylated ferritin; (b) streptavidin; (c) organized product.

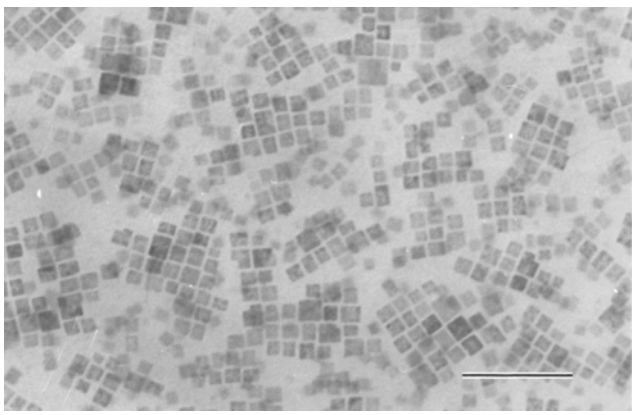

Fig. 13 TEM image showing cubic-shaped Prussian blue nanoparticles and self-assembled square superlattices of cell length 16 nm. The crystals were synthesized in AOT microemulsions. Scale bar = 100 nm.

assemble into well-ordered 2- and 3-D cubic superlattices due to the facetted nature of the nanoparticle surface (Fig. 13).

Although the informational content of surfactant-capped nanoparticles is negligible compared with the high fidelity recognition properties of Au–antibody[32] or Au–oligonucleotide[33,34] colloids, the exposed hydrophobic tails can strongly be interacting and therefore exploited in interparticle conjugation under certain conditions. The key factors appear to be high nanoparticle shape anisotropy and strong pinning of the surfactant molecules onto a subset of the crystal faces.[45] In these circumstances, the hydrophobic driving force for aggregation is enhanced by interdigitation of the immobilized alkyl chains present on smooth faces of relatively large surface area. A stable bilayer is thus formed between certain faces of adjacent particles, and this process becomes directional and self-sustaining. Moreover, because nanoparticle synthesis in microemulsions is spatially constrained by the membrane boundary but interfacially active *via* membrane fusion, these processes

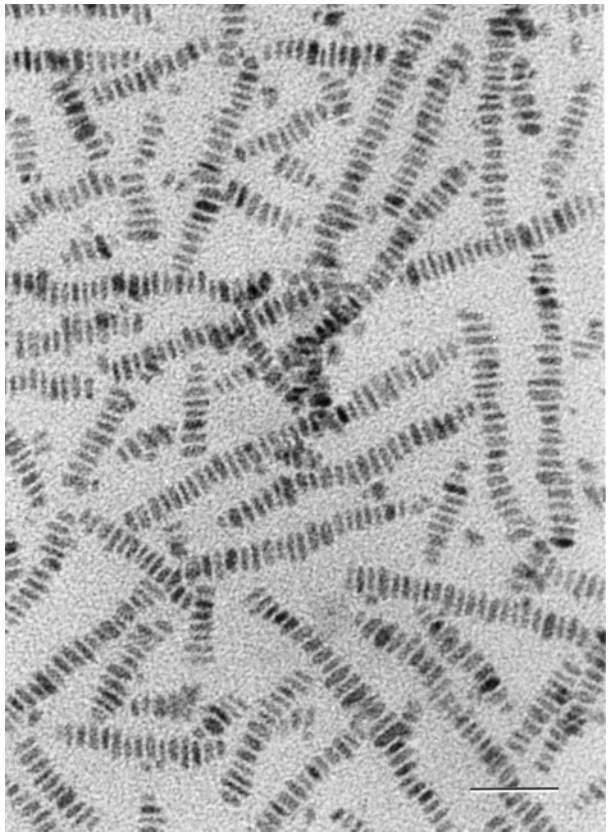

Fig. 14 TEM image showing ordered chains of surfactant-coated prismatic $BaSO_4$ nanoparticles prepared in AOT microemulsions. Scale bar = 50 nm.

can be coupled *in situ* to produce superstructures direct from the reaction medium.

For example, linear chains of prismatic nanoparticles are synthesized in solution from a mixture of $Ba(AOT)_2$ reverse micelles and NaAOT microemulsions containing encapsulated sulfate (or chromate) anions.[45] The reverse micelles are about 2 nm in diameter and consist of a spherical cluster of *ca.* 10 Ba^{2+} ions strongly associated with the sulfonic acid headgroups of the surfactant, along with water of hydration. The microemulsions are larger (4.5 nm across) as they contain bulk aqueous Na_2SO_4 or Na_2CrO_4 at a water to surfactant molar ratio, $w = 10$. When mixed together the two reaction fields interact so that the constituents are slowly exchanged and $BaSO_4$ or $BaCrO_4$ nanoparticles nucleate and grow within the surfactant-bounded aqueous environments.

Discrete spherical nanoparticles are only formed when the anion concentration is two to five times that of the Ba^{2+} cations. Under these conditions the surface charge on the $BaSO_4$ or $BaCrO_4$ crystals is negative (a surface excess of anions) so there is minimal interaction with the sulfonate headgroups and crystal growth in the droplets is unperturbed. Moreover, the surfactant membrane remains fluid and not susceptible to interparticle bilayer aggregation. In contrast, when the surface charge of the nanoparticles is close to neutral ($[Ba^{2+}]:[SO_4^{2-}]$ (or $[CrO_4^{2-}]$) = 1.0 : 1), remarkable linear chains of aggregated $BaSO_4$ or $BaCrO_4$ nanoparticles are formed spontaneously in the microemulsion reaction media (Fig. 14). The colloidal chains are 50 to 500 nm in length and consist of uniform-sized rectangular prismatic crystals ($16 \times 6.8 \times 6$ nm at $w = 10$) spaced at regular intervals of 2 nm and preferentially aligned with the long axis of each particle perpendicular to the chain direction.

The prismatic shape implies that crystal face-specific interactions with the sulfonate headgroups occur during growth, and this is consistent with the surface charge being no longer negative. In addition, immobilization of the surfactant

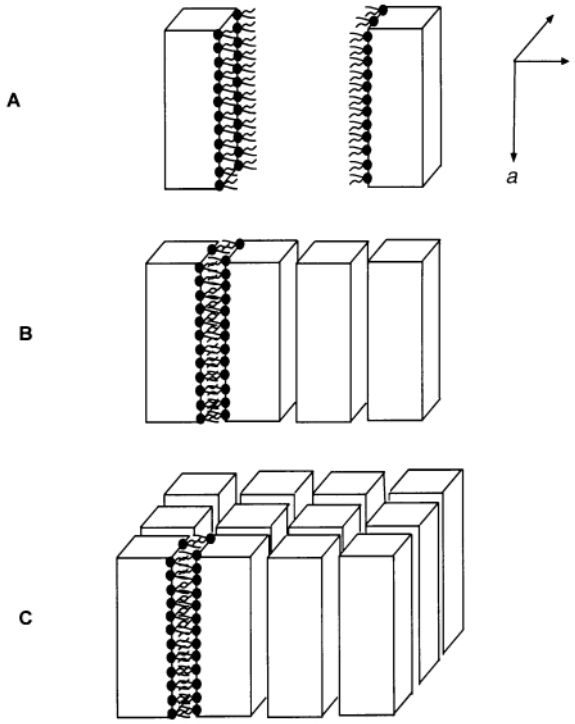

Fig. 15 Proposed model for the shape-directed, surfactant-mediated self-assembly of nanoparticle chains and superlattices in micro-emulsions. (A) Surfactant-coated prismatic $BaCrO_4$ nanoparticles; for clarity, only one face is shown with associated surfactant molecules. (B) Interdigitation of the surfactant monolayers on the largest side face induces preferential aggregation normal to the prism long axis (crystallographic *a* axis). (C) Aggregation in 2-D proceeds as the chains develop in length and number.

molecules on the crystal faces increases the free energy of the membrane and provides a driving force for bilayer formation associated with interparticle aggregation (Fig. 15). This process occurs *in situ* and specifically along one direction because there are two sets of side faces that differ in surface area. Thus, aggregation is directed along the axis perpendicular to the larger side face because this maximizes the hydrophobic–hydrophobic interactions between the crystals and lowers the free energy of the surfactant–nanoparticle superstructure. With time, the chains interact and precipitate from the micro-emulsion in the form of a 2-D rectangular superlattice that contains regularly spaced nanocrystallites separated by a distance of 2 nm (Fig. 15). The superstructure, which contains approximately 30% by weight of surfactant, forms by secondary interactions between surfactant molecules on the exposed side faces of the chains so that the long axis of each prismatic crystal is aligned perpendicular to the plane of the superlattice.

Transformation-directed construction

The construction of higher-order structures by alignment of hydrophobic nanoparticles with anisotropic shape highlights the important interplay between the onset of membrane instability and crystal growth in reaction media such as water-in-oil microemulsions. Both processes are influenced by the extent of surfactant adsorption, which is determined by the surface charge of the growing nanoparticles. Increasing the level of interaction results in modifications of crystal habit and surfactant-induced aggregation. A further possibility is to increase the level of surface adsorption to such an extent that the surfactant molecules inhibit the crystallization process within the micelles such that metastable clusters of a surfactant–inorganic biphase are produced.

For example, amorphous $BaSO_4$–AOT nanoparticles, less than 4 nm in diameter, are synthesized when a molar excess of cations is used in the microemulsion reaction system described

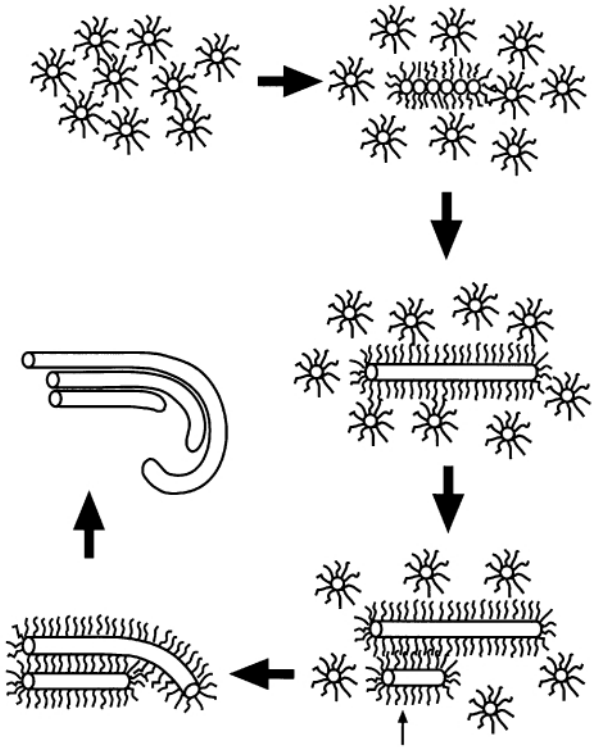

Fig. 16 Proposed model for the transformation of disordered $BaSO_4$–surfactant nanoparticles into coiled bundles of $BaSO_4$–surfactant nanofilaments. See text for details.

in the previous section.[46] In this case, however, the surface charge is highly positive so the AOT molecules are so strongly adsorbed that they cap the inorganic surface during nucleation and prevent barite crystallization. As before, pinning of the surfactant onto the inorganic surface induces interparticle aggregation but no ordered superstructures are initially formed because of the absence of shape anisotropy. However, the hybrid nanoparticles are both structurally metastable and interfacially interactive, with the consequence that coiled bundles of crystalline $BaSO_4$–AOT nanoscopic threads, often several micrometres in length, are produced over periods of days by linear coalescence and structural transformation (Fig. 16).[45–47] The clusters first aggregate into a linear array that fuses together to give a single 5 nm wide crystallographically aligned inorganic filament. The structural reconstruction originates from the strong coupling between the increase in inorganic lattice energy and reduction in membrane curvature that specifically accompanies linear association. Moreover, the structure propagates along one direction because surfactant molecules at the tips are readily displaced compared with those assembled along the filament edges.

With time, other filaments are nucleated parallel to the original thread to produce a small bundle of co-aligned inorganic nanofilaments held together by surfactant bilayers. The locking in of new filaments by surfactant interdigitation generates a bending force in the non-attached segment of the longer primary thread. This results in the coiling of the bundle into a characteristic spiral-shaped structure several hundred nanometres in size that becomes self-terminating at one end because further addition of the primary nanoparticles is prevented by spatial closure (Fig. 17a). The final angle of rotation is dependent on the number of secondary nucleation events that occur on the internal edge of the primary filament. As the number of co-aligned filaments increases as the structures grow away from the terminus, the bending energy decreases and the bundle becomes straight. However, two further structural modulations can occur as the bundles extend in length. First, dissipation of strain energy arising from lateral packing pressure causes some bundles to splay outwards into cone-shaped

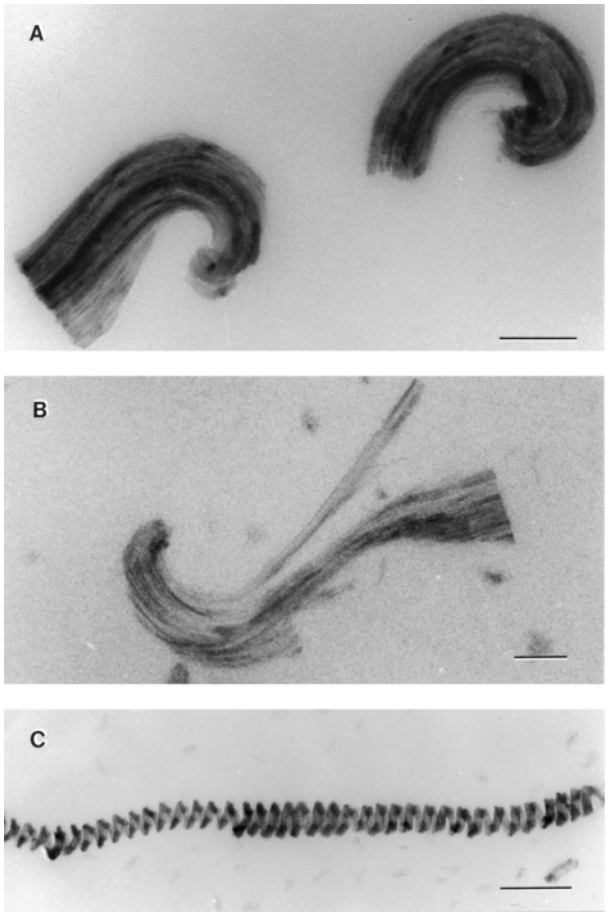

Fig. 17 TEM images of $BaSO_4$–surfactant higher-order structures assembled by transformation-directed construction. (A) Intermediate stage of transformation showing spiral-shaped bundles and uni-directional outgrowth, scale bar = 100 nm. (B) Later stage of growth showing splaying and twisting of filament bundle and formation of cone-shaped outgrowths, scale bar = 100 nm. (C) Helical filament with 40 nm pitch. Scale bar = 200 nm.

growth ends (Fig. 17b). Secondly, if the strain energy is low and the bundle is relatively thin, then differences in rigidity along the bundle can induce twisting of the filaments. This can arise from the lateral fusion and compaction of filaments by displacement of the AOT bilayers, and takes place initially in the older coiled end of the bundle. Since the twisting is not associated with any stress field or elastic deformation it can propagate throughout the length of the bundle as the filaments coalesce to produce a single crystal helicoid (Fig. 17c).

Conclusion

The study of periodicity at the nanoscopic level is a springboard for the chemistry of higher-order complexity, form and organization. In this respect, the emergence of inorganic crystal engineering offers rich possibilities in designing the basic building blocks and their interconnectivity, but a focus only on structure is limited without an understanding of the processes by which crystallization takes place. The chemical manipulation of nucleation and growth leads to control over orientation and habit, and ultimately to the synthesis of complex form, superstructures and organized arrays. Inorganic chemists are centrally placed to have a pivotal role in the synthesis and characterization of order beyond the unit cell, and forge the development of new fields such as crystal architecture and crystal tectonics.

In this paper we have highlighted recent work in crystal tectonics to illustrate the scope of inorganic chemistry in encompassing scales from the molecular to macroscopic. We have focused on a number of examples from our laboratory that in general involve the use of crystalline nanoparticles that were synthesized prior to the organizational process. This multi-step method can be circumvented, however, for example in the spontaneous assembly of linear chains of $BaSO_4$ or $BaCrO_4$ prismatic nanoparticles, suggesting that it should be possible to develop a chemistry of organized materials based on "synthesis-with-construction" which operates interactively across multiple length scales. Thus, a future goal of our work is to develop strategies for coupling nanoparticle synthesis and higher-order assembly, such that the transformation from molecular reactants to nanoparticles to organized matter is coordinated in time and space.

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