NANOCHEMISTRY

A Chemical Approach to Nanomaterials

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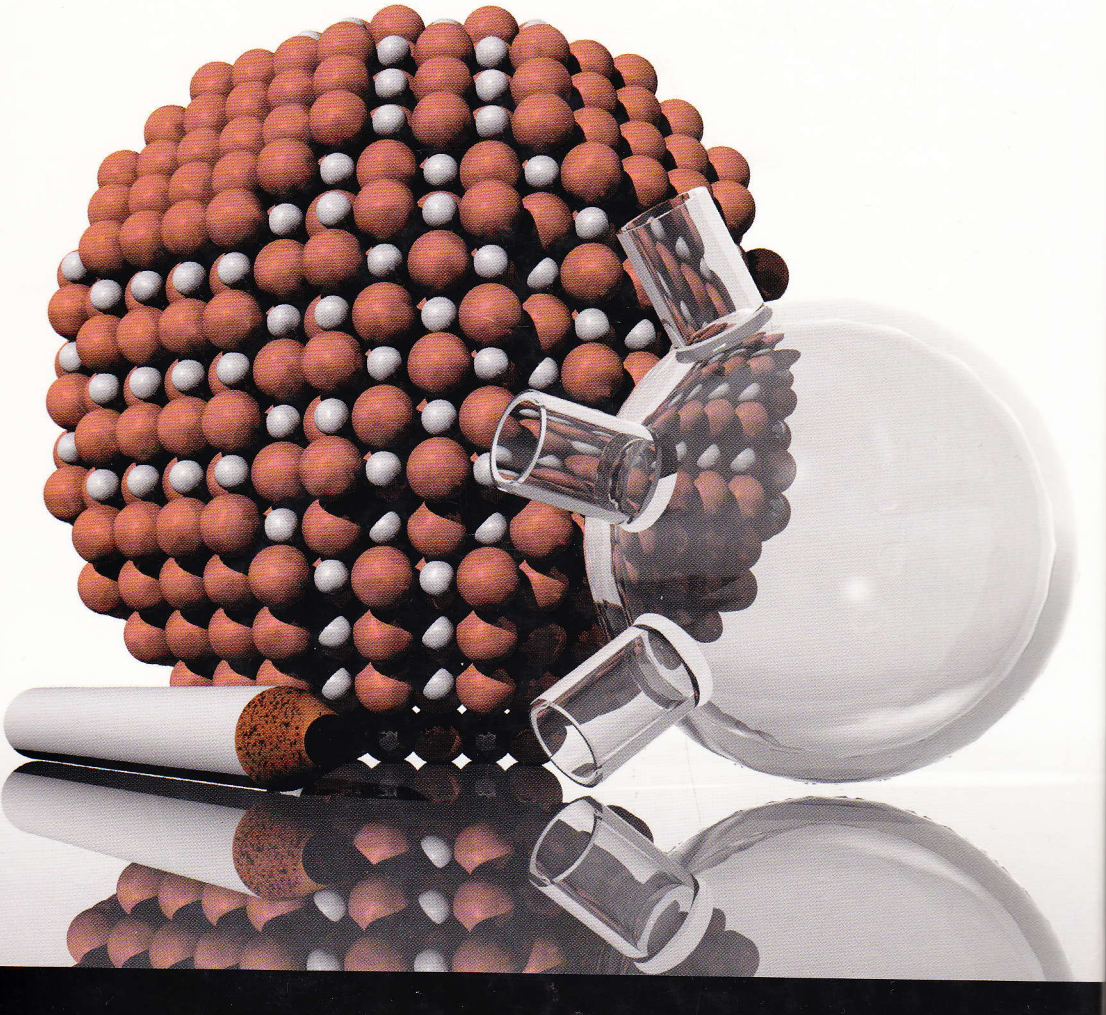

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CHAPTER 1

Nanochemistry Basics

> *"We are like dwarfs on the shoulders of giants, so that we can see more than they."*
> *Bernard of Chartres, 12th century*

1.1 Materials Self-Assembly

When thinking about self-assembly of a targeted structure from the spontaneous organization of building blocks with dimensions that are beyond the sub-nanometer scale of most molecules or macromolecules, there are five prominent principles that need to be taken into consideration. These are: (i) building blocks, scale, shape, surface structure, (ii) attractive and repulsive interactions between building blocks, equilibrium separation, (iii) reversible association–dissociation and/or adaptable motion of building blocks in assembly, lowest energy structure, (iv) building block interactions with solvents, interfaces, templates, (v) building-blocks dynamics, mass transport and agitation.

A challenge for perfecting structures made by this kind of self-assembly chemistry is to find ways of synthesizing (bottom-up) or fabricating (top-down) building blocks not only with the right composition but also having the same size and shape. No matter which way building blocks are made they are never truly monodisperse, unless they happen to be single atoms or molecules. There always exists a degree of polydispersity in their size and shape, which is manifest in the achievable degree of structural perfection of the assembly and the nature and population of defects in the assembled system. Equally demanding is to make building blocks with a particular surface structure, charge and functionality. Surface properties will control the interactions between building blocks as well as with their environment, which ultimately determines the geometry and distances at which building blocks come to equilibrium in a self-assembled system. Relative motion between building blocks facilitates collisions between them, whilst energetically allowed aggregation de-aggregation processes and corrective movements of the self-assembled structure will allow it to attain the most stable form. Providing the building blocks are not too strongly bound in the assembly it will be able to adjust to an orderly structure. If on the other hand the building blocks in the assembly are too strongly interacting, they will be unable to adjust their relative positions within the assembly and a less

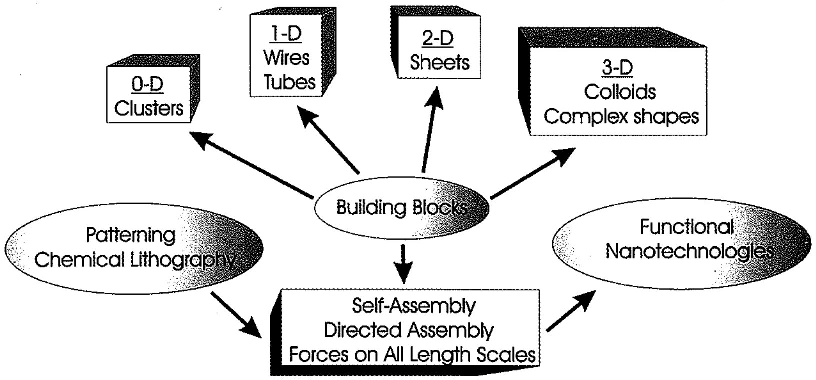

Figure 1.1 *A flowchart delineating the factors that must be considered when approaching the self-assembly of a nanoscale system*

ordered structure will result. Dynamic effects involving building blocks and assemblies can occur in the liquid phase, at an air/liquid or liquid/liquid interface, on the surface of a substrate or within a template co-assembly.

As this text describes, building blocks can be made out of most known organic, inorganic, polymeric, and hybrid materials. Creative ways of making spheres and cubes, sheets and discs, wires and tubes, rings and spirals, with nm to cm dimensions, abound in the materials self-assembly literature. They provide the basic construction modules for materials self-assembly over all scales, a new way of synthesizing electronic, optical, photonic, magnetic materials with hierarchical structures and complex form, which is the central theme running throughout this chapter. A flowchart describing these main ideas is shown in Figure 1.1.

1.2 Big Bang to the Universe

At the beginning it is said that nothing self-assembled into everything. An energetic singularity, where all symmetry and forces were one, transformed in time to all that we know today about our universe. This is the "ultimate in materials self-assembly over 'all' scales": From the smallest, densest most energetic form of matter to an expanding and seemingly infinite universe built from a diversity of materials, comprised of organic and inorganic molecules, polymers and networks, large and small, cast through the construction tool kit of chemistry, physics and biology as lifeless abiological and living biological systems.

1.3 Why Nano?

Nano-, a prefix denoting a factor of 10^{-9} has its origin in the Greek *nanos*, meaning dwarf. The term is often associated with the time interval of a nanosecond, a billionth of a second, and the length scale of a nanometer, a billionth of a meter or 10 Å. In its broadest terms, nanoscience and nanotechnology congers up visions of making, imaging, manipulating and utilizing things really small. Feynman's prescient nanoworld "on the head of a pin" inspires scientists and technologists to venture into this uncharted nano-terrain to do something big with something small. It excites investors and corporations, governments and policy makers to gamble on nanoscience breakthroughs and create new nanotechnologies.

While early theoretical concepts and experimental results for nano-size materials and devices appeared five decades ago, it is rather recent scientific developments that have inspired a resurgence of activity in the field. The stimulus for this growth can be traced to new and improved ways of making and assembling, positioning and connecting, imaging and measuring the properties of nanomaterials with controlled size and shape, composition and surface structure, charge and functionality, for use in the macroscopic real world.

1.4 What do we Mean by Large and Small Nanomaterials?

It was not so long ago in the world of molecules and materials that 1 nm (1 nm = 10 Å) was considered large in chemistry while 1 μm (1 μm = 1000 nm = 10,000 Å) was considered small in engineering physics. Matter residing in the "fuzzy interface" between these large and small extremes of length scales emerged as the science of nanoscale materials and has grown into one of the most exciting and vibrant fields of endeavor, showing all the signs of having a revolutionary impact on materials as we know them today.

In our time, "nano" has left the science reservation and entered the industrial technology consciousness and public and political perception. Indeed, bulk materials can be remodeled through bottom-up synthetic chemistry and top-down engineering physics strategies as nanomaterials in two main ways, the first by reducing one or more of their physical dimensions to the nanoscale and the second by providing them with nanoscale porosity (Figure 1.2). When talking about finely divided and porous forms of nanostructured matter, it is found that "nanomaterials characteristically exhibits physical and chemical properties different from the bulk as a consequence of having at least one spatial dimension in the size range of 1–1000 nm".

It is the "synthesis, manipulation and imaging of materials having nanoscale dimensions, the study and exploitation of the differences between bulk and

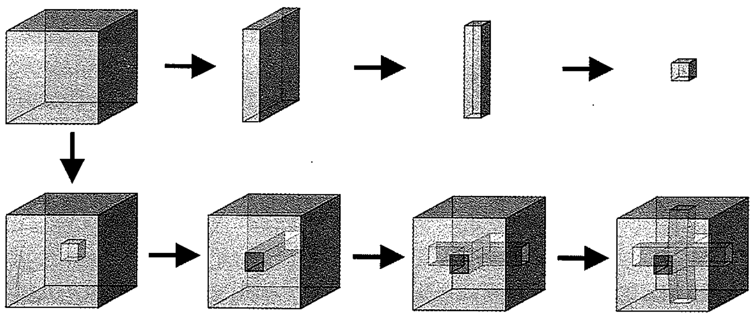

Figure 1.2 *Dividing matter to the nanoparticle and nanoporous state*

nanoscale materials, and the understanding and utilization of nanomaterials scaling laws by interdisciplinary scientists, that drive contemporary endeavors in nanoscience and nanotechnology." It is an astute awareness of the unique attributes of nanoscale matter and the tremendous opportunities for discovery and innovation that abound in the field of nanoscience, that provides much of the inspiration for researchers working in the field of nanomaterials.

1.5 Do it Yourself Quantum Mechanics

The formalism underpinning the scaling laws of materials with size tunable properties is couched in the physics language of "quantum size effects," (QSE). The Schrödinger wave equation is solved for an electron and hole in a box having either 1D, 2D or 3D and spatial dimensions of the order of the Bohr radius of the electron, hole or exciton (electron–hole pair). In this intermediate size range between molecular and bulk matter, called the nanoscale, individual energy states of molecules and continuous energy bands of solids become discrete and their energy separations display an analytic dependence on the spatial dimension of the material. This is expressed in a scheme of the type shown in Figure 1.3, which represents the "transformation of the electronic density of states (DOS) of valence and conduction bands in metals and semiconductors from continuous to discrete to individual in bulk, quantum-confined and molecular states of matter."[1] As the dimensionality of quantum-confined matter changes from that of a 2D quantum well, to a 1D quantum wire and finally a 0D quantum box, the DOS correspondingly alters from the parabolic shape of the 3D bulk material, first to a 2D stepped parabola, then to a 1D inverse stepped parabola and eventually to a 0D discrete form.

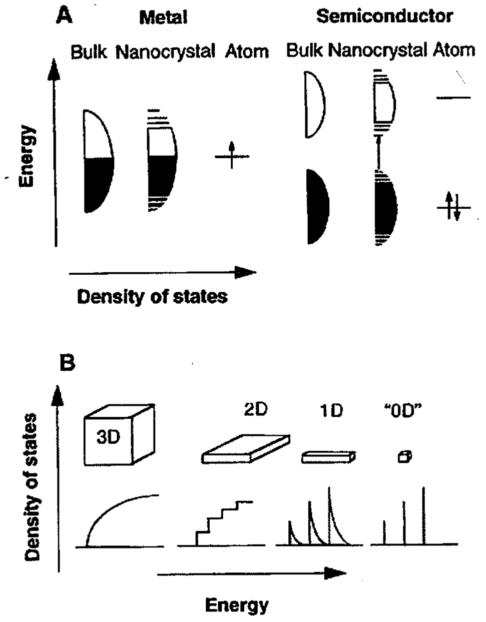

Figure 1.3 *Relation between bulk, quantum confined and molecular states of matter* (Reproduced with permission from Ref. 1)

The challenge in materials chemistry is to understand how the properties of nanomaterials scale with physical dimension because different properties scale in distinct ways with size. Thus, electronic band gaps scale differently to melting points and magnetization and so forth. The point is that in chemical approaches to the preparation and assembly of well-defined nanostructures into functional and integrated systems of nanocomponents, it is vital to appreciate how the properties of materials scale with size in order to target the right combination of materials compositions and length scales to achieve a desired objective.

1.6 What is Nanochemistry?

With nanoscience being the discipline concerned with making, manipulating and imaging materials having at least one spatial dimension in the size range 1–1000 nm and nanotechnology being a device or machine, product or process, based upon individual or multiple integrated nanoscale components, then what is nanochemistry? In its broadest terms, the defining feature of nanochemistry is the utilization of synthetic chemistry to make nanoscale building blocks of different size and shape, composition and surface structure, charge and functionality. These building blocks may be useful in their own right. Or in a self-assembly construction process, spontaneous, directed by templates or guided by chemically or lithographically defined surface patterns, they may form architectures that perform an intelligent function and portend a particular use.

1.7 Molecular vs. Materials Self-Assembly

The driving forces for molecule organization are quite varied and can be ionic, covalent, hydrogen, non-covalent and metal–ligand bonding interactions, which may result in structures and properties not found in the individual components. This is Jean Marie Lehn's supramolecular chemistry, the science of molecule-based assemblies.

Materials self-assembly chemistry transcends that of molecular assembly. It is distinct solid-state materials chemistry where building blocks and their assemblages are unconstrained by scale and not restricted to just chemical bonding forces. The way to view materials self-assembly over "all" scales, the subject of this text, is in terms of a map of bonding forces that operate between building blocks and over different length scales. The forces responsible for materials self-assembly at length scales beyond the molecular include capillary, colloidal, elastic, electric, magnetic and shear. In a self-organizing system of materials construction units like nanoclusters, nanorods or nanosheets, a particular architecture forms spontaneously with a structural design, which is determined by the size and shape of individual nanocomponents and map of bonding forces between them. The system proceeds towards a state of lower free energy and greater structural stability.

1.8 What is Hierarchical Assembly?

A feature of self-assembly is hierarchy, where primary building blocks associate into more complex secondary structures that are integrated into the next size level in the hierarchy. This organizational scheme continues until the highest level in the hierarchy is reached, as illustrated hypothetically in Figure 1.4. These hierarchical constructions may exhibit unique properties that are not found in the individual components. Hierarchy is a characteristic of many self-assembling biological structures and is beginning to emerge as a hallmark of materials self-assembly that encompasses multiple length scales.

1.9 Directing Self-Assembly

Self-assembly of molecules and materials may be directed by templates. Directed self-assembly of building blocks, which may involve structure-directing additives, often molecular and organic, in addition to the constituent building units, is considered to be distinct from spontaneous self-assembly. The template in this building block auto-construction process can serve to fill space, balance charge and direct the formation of a specific structure. For instance, microporous aluminosilicates called zeolites are templated by single molecules while mesoporous silicas are templated by assemblies of molecules like block copolymers or lyotropic liquid crystals. In this definition, template assembly is synonymous with co-assembly and distinct from self-assembly. Template directed assembly, may also involve the intervention of a lithographically or otherwise patterned substrate planar or curved, where spatially defined hydrophobic–hydrophilic, electrostatic, hydrogen bonding, metal–ligand or acid–base interactions between substrate and building blocks guide the assemblage into a predetermined architecture. A case in point concerns patterns of hydrophobicity that have been used to organize non-polar polymers into microlens arrays. A lithographically defined relief pattern carved in the surface of a substrate may also be used to direct building block assembly within, an example being the alignment and packing of nanorods in substrate nanowells. The direction of the assembly process may also be driven by the involvement of a porous template that has been patterned at the nanoscale. One such template is a nanochannel membrane made of polymers, silicon and alumina used to replicate nanowires.

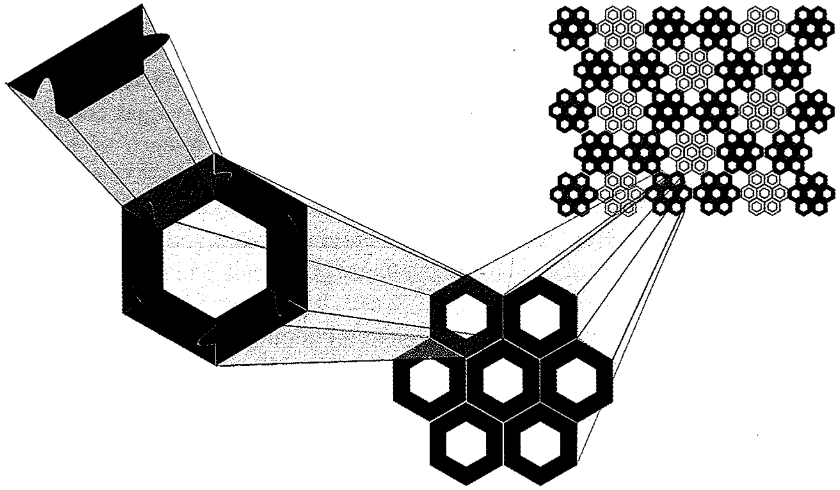

Figure 1.4 *A hypothetical hierarchical system, exhibiting distinct building rules at different length scales*

1.10 Supramolecular Vision

Jean Marie Lehn (Figure 1.5) had a vision of supramolecular chemistry, which unveiled a world far beyond the molecule.[2,3] It introduced to chemistry how molecular recognition can lead to the self-assembly of supramolecular materials. Lehn's construction kit consisted of complementary organic and inorganic molecules that recognize one another through lock and key types of intermolecular interactions to spontaneously form molecular assemblies. The driving forces for this molecular organization are quite varied and can be ionic, covalent, non-covalent, coordination and hydrogen bonding interactions, which may result in structures and properties not found in the individual components. Therefore, self-assembly as a route to materials has its roots firmly in organic chemistry where the ability to make molecules of almost any shape and functionality lends itself well to designing complementary interactions. However, it was realized relatively quickly that self-assembly is a very general principle, one which relies on reversible interactions and a balance of attractive and repulsive forces. Self-assembly, therefore, encompasses

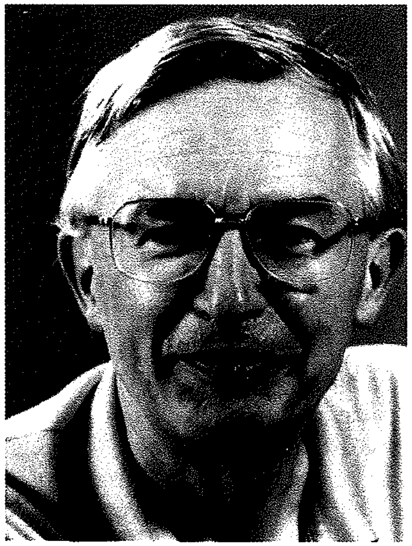

Figure 1.5 *Jean-Marie Lehn, pioneer of supramolecular chemistry* (Reproduced with permission from research group website: www.isis.u-strasbg.fr/supra/)

all scales, with the possibility of a completely rational and predictable route to materials.[4] The self-assembly approaches to materials we attempt to illustrate in this book attest to this fact.

1.11 Genealogy of Self-Assembling Materials

It is often interesting, and always valuable, to trace the genealogy of a new branch of chemistry. One can argue that materials self-assembly had its beginnings with the observation by Pieter Harting that organics are somehow involved in the organization of inorganics in biomineral formation.[5] Harting found that the mixing of calcium ions with carbonate and phosphate under quiescent conditions in organic concoctions, such as albumen, blood, mucus and bile, produced calcareous concretions with natural form. The synthetic morphologies of Harting were published in 1873 and can be considered to predate biomimetic inorganic materials chemistry by more than a century (Figure 1.6). Harting had stumbled into organic-mediated mineralization without much knowledge of organic or inorganic chemistry, crystal nucleation, growth and tectonics.

Harting made his breakthrough at a time when there was a revolt from morphology and a movement to separate organic from inorganic chemistry, just at a point in his work when they most needed to unify. The zeitgeist, or prevailing view, of Harting's time was not conducive to the emergence of biomimetic inorganic chemistry as a field, or to templated materials synthesis for that matter, and it had to await developments in molecular recognition, self-assembly, templating, biochemistry, solid-state chemistry and biomineralization. Harting hoped that his synthetic morphology would lead to a new field just as important as Wöhler's organic chemistry.[6] Harting's aspirations lay dormant until reawakened by the discovery over a century later of inorganic liquid crystals and their mineralization to inorganics. These could be produced with morphologies and surface patterns that resembled self-made shapes and designs found in nature's biominerals.[7]

While Harting was experimenting with biomimetics in the laboratory, Ernst Haeckel was on a field trip with his friends aboard the H.M.S. Challenger during which time he discovered thousands of different kinds of sculpted silica microskeletons mineralized by single cell marine organisms known as the radiolaria.[8] His personal etcher Nitsche documented in meticulous artistic detail a myriad of filigree skeletal patterns produced by these simple organisms. Reproductions of Haeckel's exquisite drawings of radiolarian microskeletons continue to adorn the walls of museums and homes (Figure 1.7). The growth, form and biological function of the tiny lace-like radiolarian skeletons remains both an enigma and a delight to scientists and artists alike. In MacKay's recent translation of *Crystal Souls: Studies of Inorganic Life*, the last book written by Haeckel, it seems that a tenuous connection may have been made between the organic liquid crystals discovered by Reinitzer and Lehmann, and the morphogenesis of the radiolarian microskeletons.[9] Haeckel surmised that there was a relation between the organization of liquid crystals and the way silica was ordered into spectacular patterns by the radiolarian. The forethought of Haeckel in this century old work is

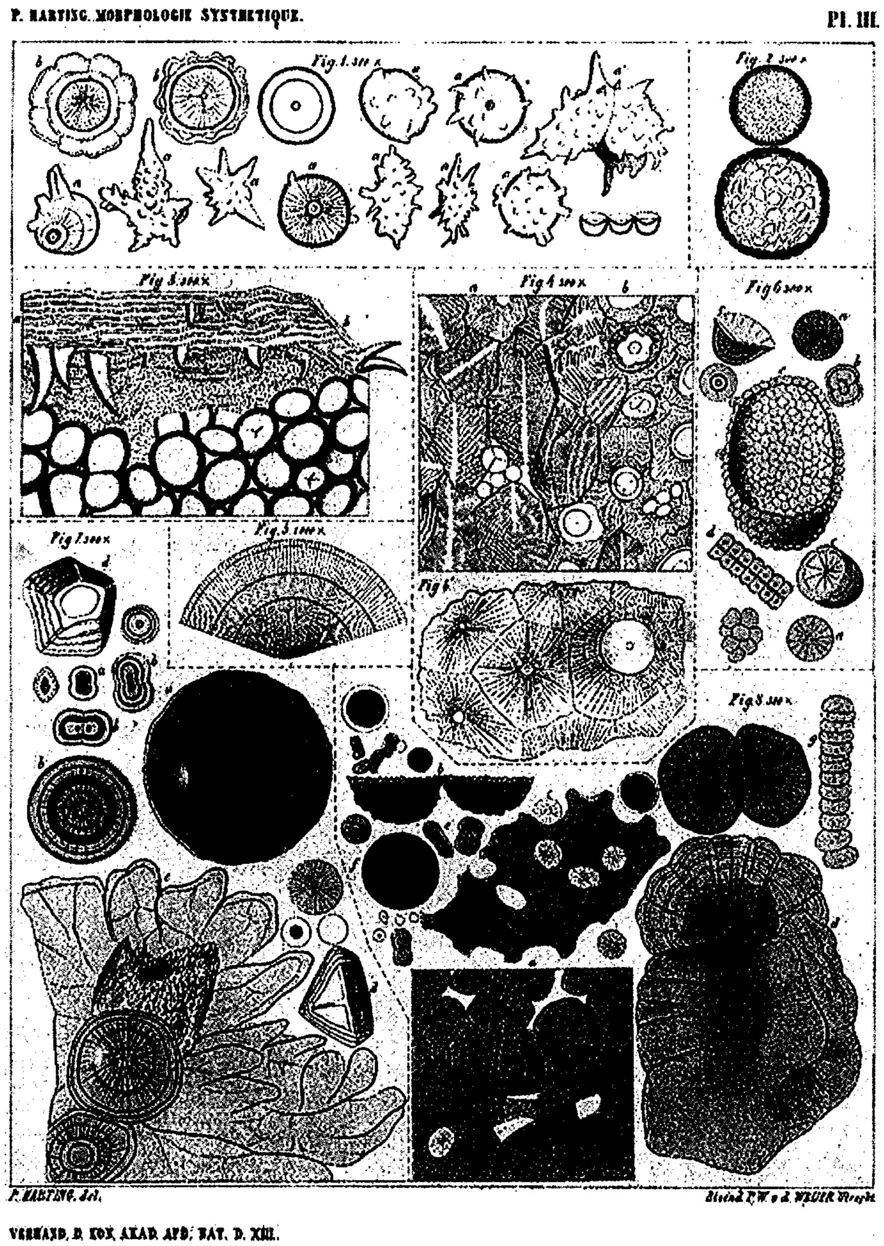

Figure 1.6 *Image of synthetic morphologies produced by Pieter Harting, hand-drawn by himself in 1872*

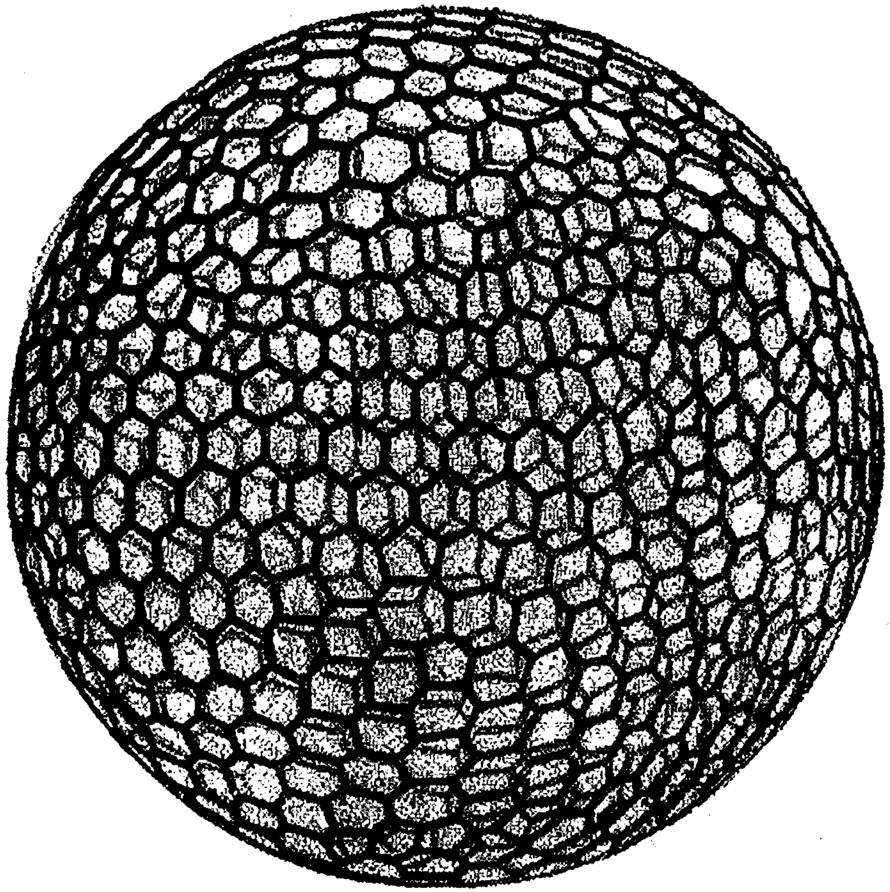

Figure 1.7 *Sketch of a radiolarian discovered by Ernst Haeckel* (Reproduced with permission from Ref. 11)

remarkable when placed in the context of supramolecular templating, especially the polymerization of silicate and phosphate liquid crystals to create silica and aluminophosphate "replica" materials with complex and natural form.[10]

The connection of this early thinking about the importance of interfaces between organics and inorganics is intriguing when placed in the light of the classic 1917 text of D'Arcy Thompson, *On Growth and Form* (Figure 1.8).[11] He was the first to apply physico-geometrical principles to explain the morphogenesis of biominerals. His view of diatoms and radiolarians was that a contiguous assembly of close-packed cells, alveoli or bubbles, functioned as a template to direct the deposition of silica. By localizing the biosilicification process to spaces within the protoplasmic froth, a mineralized copy of the templating interfaces could be formed. In retrospect, this can be seen to be a paradigm for using organics to template microporous (small molecule organics), mesoporous (micelles, liquid crystals, block-copolymers), and macroporous (microemulsions, vesicles, colloidal crystals) materials.

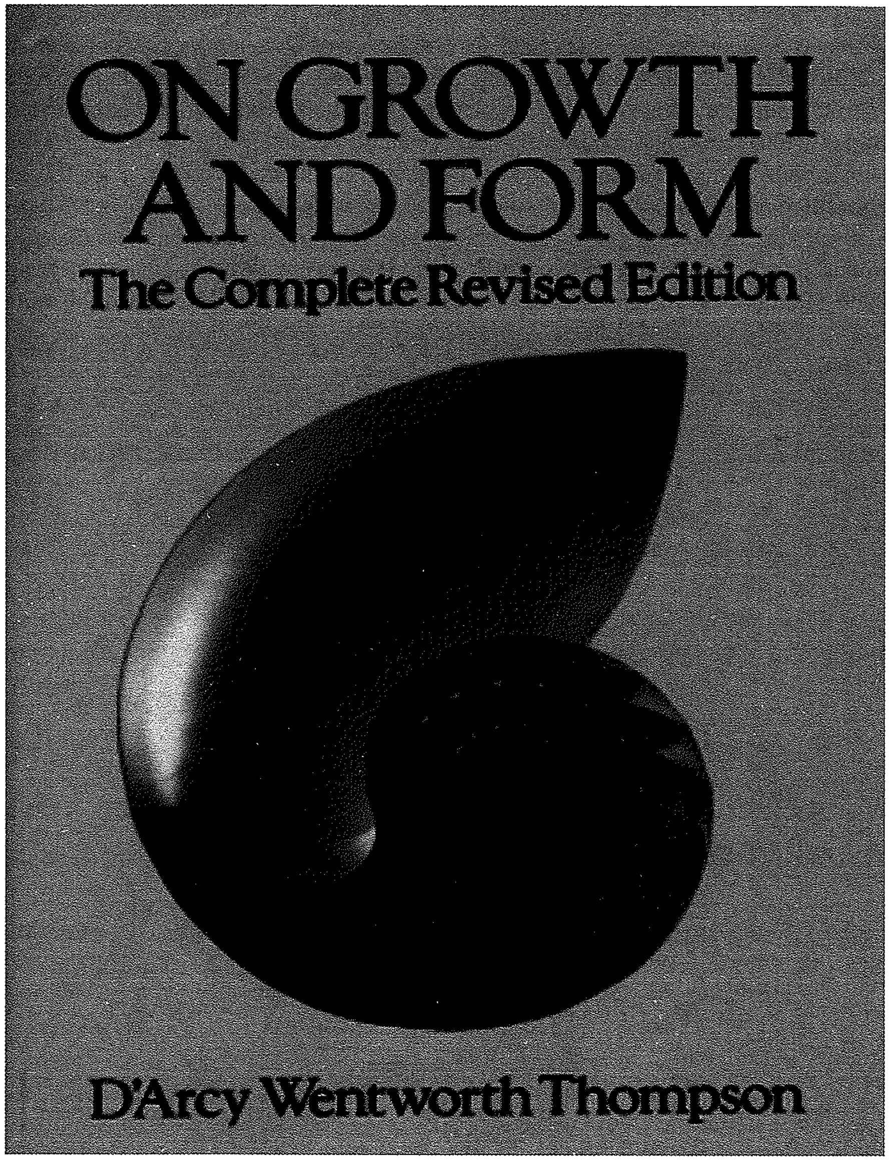

Figure 1.8 *On growth and form, the groundbreaking text by D.W. Thompson* (Reproduced with permission on from Ref.11)

1.12 Unlocking the Key to Porous Solids

Emil Fischer's 1894 lock-and-key principle, molecules recognizing one another through site-selective binding, spawned fundamental studies of intermolecular forces and cooperative interactions.[12] The complementary hydrogen bonding, electrostatic and hydrophobic interactions between organic molecules underpins recognition events, self-assembly, replication and catalytic processes in biology. Nowhere is this more clear than in Watson–Crick hydrogen bonded base pairs in the DNA double helix, the complementary nature of transfer RNA in protein synthesis, and the exquisite substrate selectivity in enzyme action. In a similar vein, Richard Barrer recognized that complementary interactions involving quaternary alkylammonium cations and silicates/aluminates were able to direct the assembly of crystalline microporous alumino-silicates called zeolites (Figure 1.9).[13] These types of minerals are also naturally occurring, and their name translates to "boiling stones" since their large volume of adsorbed moisture can be released upon heating. Such microporous materials could act as hosts to selectively recognize adsorbed molecules or catalyze the reaction of organic guests based on their size and shape.[14] Barrer's organic molecule templating of zeolites can be considered to have set the stage for the development of template-based synthesis of inorganic materials, which led to the emergence of materials self-assembly chemistry. In particular, Charles Kresge showed that the length scale of templating porous solids can be increased far beyond the small molecule.[15,16] Moreover, Edith Flanigen and Robert Bedard demonstrated that the compositions of porous solids may be extended from traditional aluminosilicate zeolites and silicate molecular sieves to encompass a large portion of the periodic table.[17,18] Throughout much of this work, the underlying theme of organics directing inorganics to create composite materials remains essentially the same.

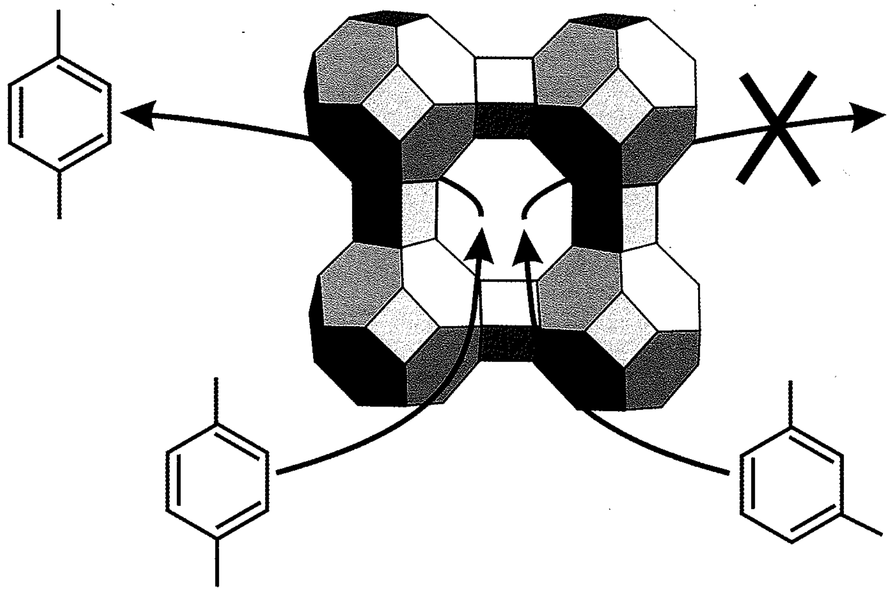

Figure 1.9 *A zeolite's crystalline aluminosilicate framework assembles around an organic template molecule providing pores after its removal. Some molecules, such as linear para-xylene, can permeate through the small pores, while more bulky molecules, such as meta-xylene, are excluded due to their size*

Self-assembly of specifically designed molecular and cluster building blocks often under exceeding gentle conditions, called soft chemistry, has also led to a diversity of open-framework solids, far beyond what is possible with microporous oxides like the zeolites and molecular sieves.[19,20] Open-framework materials (Figure 1.10)[21] now include metal phosphates, cyanides, halides, nitrides, sulfides and selenides, as well as metal interconnected heterocyclic ligands like porphyrins[22] and bipyridyls. The chemical and structural diversity of this class of materials is constantly expanding. Their open structures are aesthetically appealing because of the chemical

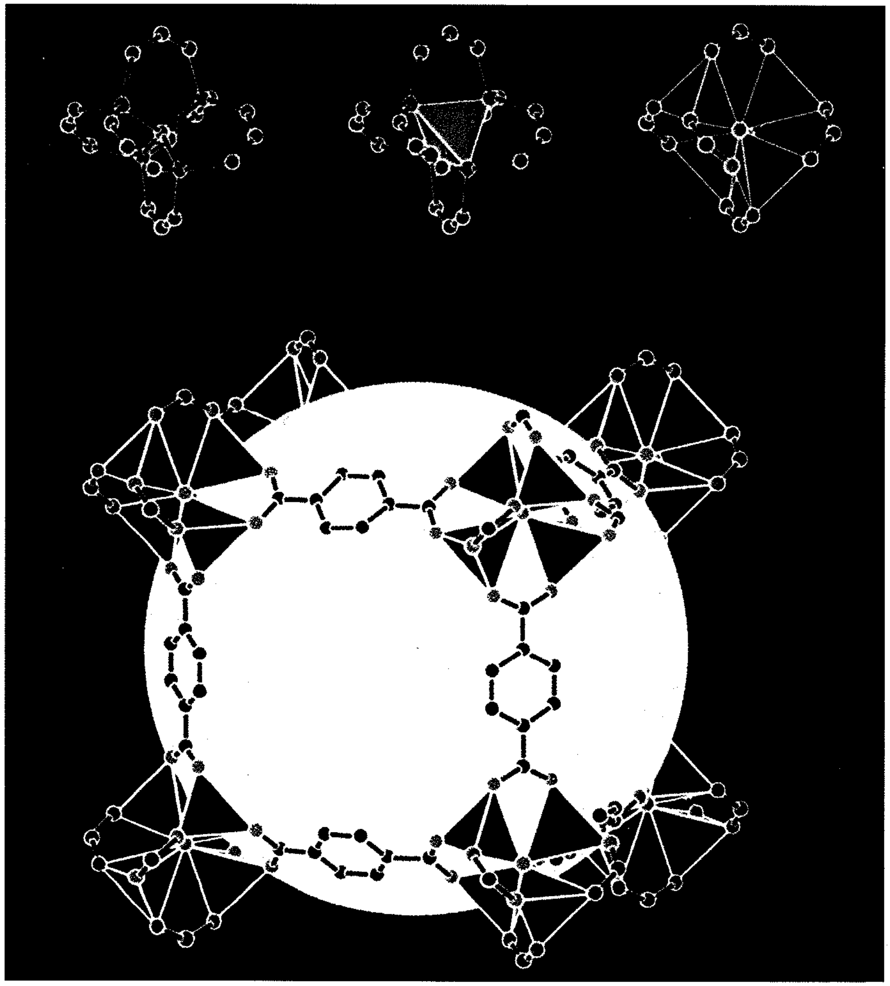

Figure 1.10 *The top of this figure shows a central tetra-zinc core used to build a framework by connecting these clusters through dicarboxylate linkages. The resulting porous solids can have very large accessible surface areas, shown as the large white sphere*
(Reproduced with permission from Ref. 21)

and stereochemical control potentially attainable in their construction. The majority use metal–ligand bonding to link the individual components into crystalline frameworks containing spacious cavities and channels.[23,24] The internal voids can account for greater than 50% of the volume of the crystal. Disordered template, water or solvent molecules may occupy the void spaces. Spaces in one framework may be filled by one or more independent framework. This creates crystalline entangled structures known as self-interpenetrating networks,[25,26] a phenomenon which reduces expected surface areas. The frameworks can be cationic, anionic or neutral, allowing size, shape and chemically selective ion exchange and adsorption. Linking of modules may facilitate guest or temperature induced angular distortions of the framework, which can have profound impacts on various properties such as electronic coupling.[27] As a result, open-framework materials display flexibility and expand in size to accommodate adsorbed guests, thereby making the material interesting for separation, catalysis and sensing applications.[28]

Both oxide and non-oxide porous frameworks offer interesting opportunities for host–guest inclusion chemistry aimed at creating composite materials.[29–31] Guests may be atomic, ionic, molecular, cluster or polymeric. The periodic array of channels and cavities within these porous solids allows assembly of novel kinds of materials, examples being metal and semiconductor clusters, wires and superlattices thereof, buckyminsterfullerene (buckyballs, a carbon allotrope with formula C_{60}) arrays, aligned chromophores, vectorial electron transport chains, and photosynthetic mimics.[32] Nanochemistry of this type is pointing the way to quantum electronic, photonic and data storage materials for advanced devices.

1.13 Learning from Biominerals – Form is Function

Hientz Lowenstam is considered to be the father of biomineralization. He first proposed his theory of organic matrix mediated mineralization in the 1970s.[33–39] A personal account of the thinking behind his discovery involves a fascinating encounter with a chiton (sea urchin) while he was sitting at a water pool in the Grand Bahama Banks. Lowenstam noticed that the chiton created chevron marks in the rocks as it fed by scraping off algae attached to the rock. He reasoned that the radula (teeth on the tongue of the chiton) must be harder than the rock in order to make marks in this hard mineral (Figure 1.11).

Returning to the laboratory, he found that the radula were comprised of magnetite, which proved the mineralization process that created them occurred intracellularly. Although it took a decade for his proposal to be accepted, it is now the basis for all mineralization processes in biological systems. In a classic 1981 *Science* magazine article, Lowenstam documented about 60 minerals that are formed biologically and classified the phyla amongst which they are distributed. Most biominerals are composed of calcium carbonate, phosphate and oxalate, silica and iron oxides and much has been reported on the biorganic and bioinorganic chemistry responsible for nucleation, growth and form of biominerals.

Pioneering biomineralization and biomimetic research from the groups of Steve Wiener and Lia Addadi,[40–44] Robert Williams,[45–47] Stephen Mann,[48–53] Galen Stucky and Daniel Morse[54–57] have provided a wealth of information on the role of the organic matrix in biological and abiological mineralization processes. Proteins have been extracted from biominerals, and amino-acid sequencing and site-selective mutagenesis have identified nucleation sites on the protein that may be responsible for mineralization.[58,59] The use of many of these extracted proteins in synthetic systems can lead to unusual crystal forms and morphologies resembling those in natural systems,[60–66] giving further indication of their role in the biomineral matrix. The picture emerging from these studies is that complementary interactions between the organic matrix and the mineralizing inorganic, involving matching of charge, stereochemistry and geometry, establish the site of nucleation, growth and generation of mineral shape.[49,67–69] In essence, the organic functions as a blueprint that carries programmed information for the synthesis of materials with natural form and a biological function.

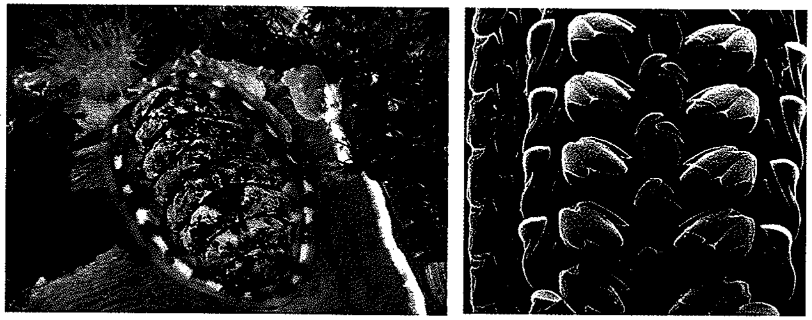

Figure 1.11 *The chiton, left, a primivite marine mollusk. Chiton radula, right, composed of biomineralized iron oxide, are hard enough to scrape algae-covered rocks* (Left image reproduced with permission from Jon Gross photography. Right image reproduced with permission from www.personal.dundee.ac.uk/~amjones/chitintr.htm)

It has been said that the outstanding problem in biology is the form problem.[70,71] In biomineralization and biomimetic chemistry, the form problem is morphogenesis, the origin and control of a shape. Biomineralization centers on the idea that organics control the nucleation, growth and form of inorganics, and it is this process that creates hierarchical composite structures with unique chemical and physical properties. Conversely, biomimetic chemistry aims to exploit the principles of biomineralization in order to synthesize novel materials where form controls function and utility (Figure 1.12).[72,73] As mentioned before, nature is frugal in her choice of inorganic materials, however, the mineralized designs and diversity of naturally occurring forms have only recently been seriously challenged by synthesis. The chemical bonding of biominerals is not unusual, and varies from amorphous covalent networks found in silica forms to multi-crystalline ionic lattices in calcareous shapes. In molecular terms, it is relatively easy to comprehend the early stages of self-organization, molecular recognition, and nucleation that precede the morphogenesis of biomineral form, however, it is not obvious how complex shapes emerge and how, in turn, they can be copied synthetically.

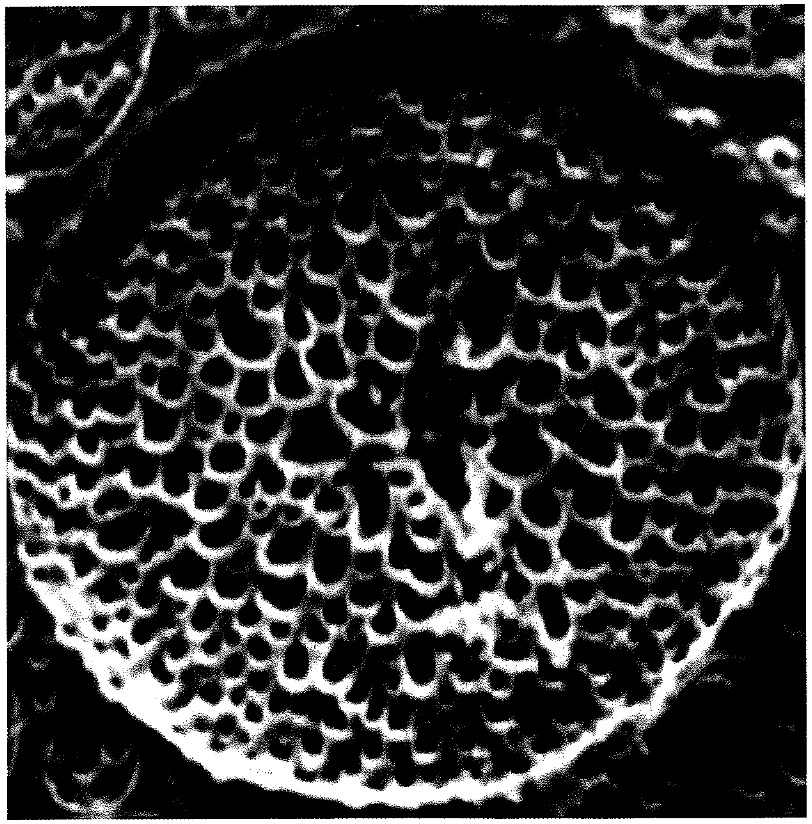

Figure 1.12 *Synthetic morphology resembling biomineralized systems*

Biological materials display hierarchical organization of structure.[74] At each level of this hierarchy, distinctive building rules are apparent. Some of these levels do not demand periodicity in the strict definition of ideal crystals, and their description requires a break from standard crystallography. The traits of biological minerals are manifested in an astonishing array of curved shapes, surface patterns and hierarchical order. These are not the characteristics of conventional crystals with their limited range of polyhedral habits and similar rules of construction from atoms to bulk.[75] Nature has learned how to replace the Platonic concept of arranging atoms in a pre-existing framework of planar symmetry elements, by the idea that local interactions between atoms can introduce long-range order and curvature into materials. It is all a matter of balance: it is energetically favorable for atoms to lay in a classical crystal unless other interactions bring the non-classical shapes to a lower free energy.

1.14 Can You Curve a Crystal?

Bernal showed how a shift from the theory of exact equivalence and long-range order in the perfect crystal, to quasi-equivalence and short-range order in biological crystals is necessary for curved shapes to emerge.[76] To expand upon the idea, the symmetry elements of the 230 space groups determine the number of ways that identical atoms can be arranged in an infinite array. Here the underlying space pattern of the primitive unit cell dictates the shape of a crystal. To deal with a system whose shape does not conform to this stereotype, it is necessary to abandon the idea that the environment of every lattice site has to be identical for order to emerge, and to consider ways of introducing curvature into crystallography and rounded form into solid-state chemistry. MacKay's "flexicrystallography" is a mathematical construct founded upon minimal surfaces with which to formalize these topological ideas.[77] The concept of minimal surfaces has also been used in architecture, and made famous by Antoní Gaudí's *Sagrada Familia* church in Barcelona (Figure 1.13).

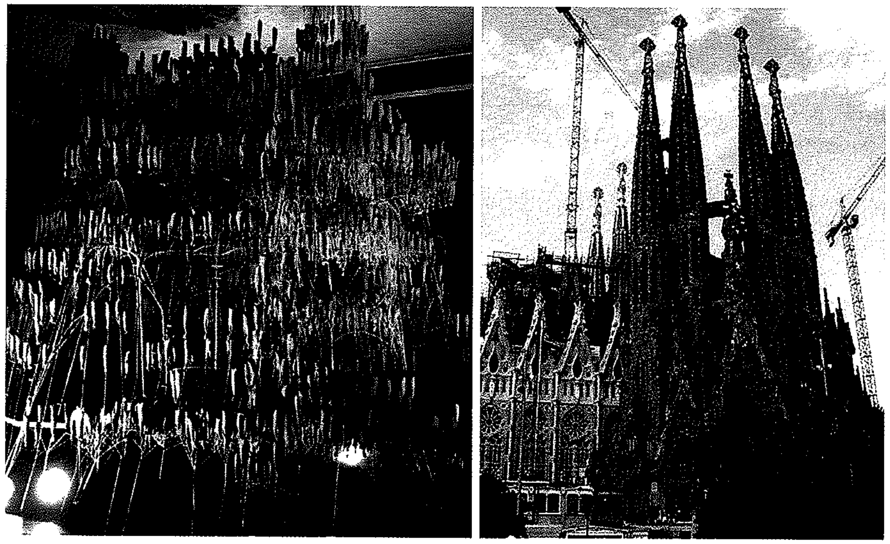

Figure 1.13 *Introducing curvature into crystals allows a break from traditional crystallography. The concept of minimal surfaces has been used quite famously by the architect Antoní Gaudí, who used a model built of hanging strings with weights (upside down on the left) to calculate the exact curvatures needed to support the weight of the massive Sagrada Familia church in Barcelona, right*
(Left image reproduced with permission from http://www.hawbaker.org/1/public Right image reproduced with permission from wikipedia, the free encyclopedia, http://en.wikipedia.org)

1.15 Patterns, Patterns Everywhere

In 1952, stimulated by the visual imagery of natural shapes, Alan Turing developed a theory of how patterns can appear spontaneously in chemical reaction–diffusion systems far from equilibrium.[78] Turing's contributions proved relevant to the understanding of morphogenesis, and suggested to developmental biologists that

Figure 1.14 *Pattern formation in nature: seashell stripes*
(Reproduced with permission from Daniel Guerin Photography)

these kinds of chemical processes might be responsible for the appearance of complex patterns in nature. The appearance of regular stripes in clouds is an example of non-equilibrium pattern formation, demonstrating that order might also arise from more than well understood, chemical interactions. Since the publication of Turing's influential work there has been intense activity on the mathematical modeling of patterns in a diversity of biological and non-biological systems.[79] Excellent examples can be found in Meinhardt's book on *The Algorithmic Beauty of Sea Shells*, in which the pigment patterns found on mollusk shells are mathematically modeled using differential equations that describe various kinds of activator–inhibitor reaction–diffusion systems (Figure 1.14).[80] Ball's recent text, *The Self-Made Tapestry*,[81] is a scholarly exploration of pattern formation in the natural world, from bubbles, waves, bodies and branches to breakdown, fluids, grains and communities. Ball's obsession with materials and patterns can be considered to represent a 21st century revival of D'Arcy Thompson's classic text *On Growth and Form.*[11]

1.16 Synthetic Creations with Natural Form

As mentioned earlier, about a century ago Haeckel in his book *Crystal Souls* wrote that the properties of organic liquid crystals were somehow connected with radiolarian microskeletal forms. A century later it has been found that the polymerization of silicate and phosphate liquid crystals can produce silica and aluminophosphate morphologies with natural form.[82] By natural form, we imply the visual perception of a class of objects that share particular features typically associated with biological shapes. Features such as curvature, hierarchy and complexity are not exclusive to biological shapes, but the fact that they are observed in so many biological systems makes the synthetic systems interesting, potentially from a fundamental point of view. However, form is not sufficient. Just as an understanding of the evolution of organic soft-matter in living systems depended on a molecular level understanding of DNA and its interaction with proteins, the biomineral problem demanded at least the same level of comprehension of the involvement of inorganic ions and solids in biological systems.

Kresge's discovery of supramolecular templating of mesoporous silica materials and the authors' work on synthetic shape and patterns based upon the mineralization of inorganic liquid crystals has stimulated interest in morphosynthesis in materials chemistry.[51,67,83–85] Inorganic liquid crystals, especially the unique kind of self-organization and mineralization they exhibit, provide a new tool for enhancing the understanding of the form problem. While morphogenesis was originally motivated by Darwinian theories of evolution, morphosynthesis is driven by the evolution of a materials society. The control of morphology through biomimetic inorganic chemistry is expected to play a central role in the development of new materials, products and processes, where form controls function and utility. Motivation derives from the notion that the control of morphology is the mainstay of materials science, particularly for tuning mechanical, thermal acoustical, magnetic, electronic, optical, and catalytic properties of materials. By evaluating the multiplicity of forms we can self-assemble synthetically, we can catalog an array of parts which could be used in the designs of future nano-devices. A synthetic seashell is shown in Figure 1.15, and is one of a myriad shapes achievable through chemical means.

Kresge's synthesis of mesostructured inorganics (2–10 nm length scale) involves the polymerization of an inorganic liquid crystal formed from a templating mesophase, creating its inorganic replica. This represents a new approach to materials synthesis, a paradigm shift in materials chemistry, and ushers in an exciting new era of materials research. The synthetic methodology has been generalized to

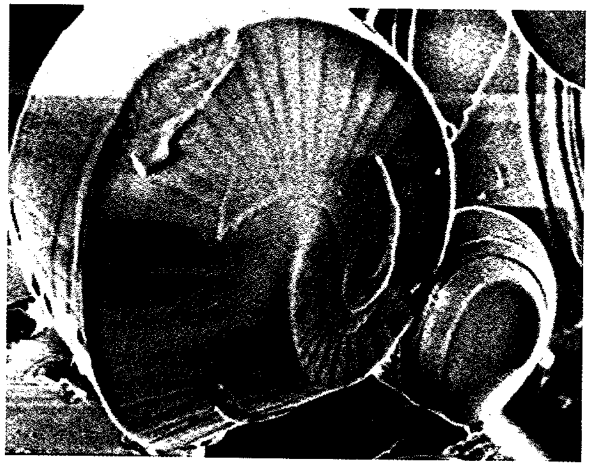

Figure 1.15 *Synthetic seashell from a liquid crystal templated aluminosilicate*

include diverse kinds of supramolecular[86] (surfactant) and macromolecular[87] (block-copolymer) templates.[88] In addition, purely inorganic liquid crystals such as niobate nanotubules can also be used as templates.[89,90] This approach has provided silica and organosilica materials with structural features in the range of 2–35 nm, modular mesostructures that assemble from cluster building blocks, compositions that pervade a good part of the periodic table, electrical properties that can be insulating, semiconducting or metallic, and morphologies and surface patterns that may span three spatial dimensions.

1.17 Two-Dimensional Assemblies

If we pass from materials self-assembly in three dimensions to that in two dimensions, we find there is also a natural progression of concepts and methods behind its development, using layer-by-layer deposition of mono- and multilayer films. This research direction can be traced through seminal work of Langmuir and Blodgett,[91] Sagiv, Nuzzo, Whitesides, Decher, Mallouk and Marks on self-assembly of controlled architecture films at air, liquid and solid interfaces. Irving Langmuir, while working at General Electric Schenectady, developed a generalized theory of adsorption for solid and liquid surfaces based on the idea of satisfying unsaturated surface valency forces.[92] Following up on the lead provided by Lord Rayleigh's theory of wave motion[93] and Agnes Pockels' "kitchen sink" surface tension measurements of oil on water,[94] he developed the Langmuir film balance to measure the properties of monolayer surface films at the boundary between air and water. He confirmed the films were one molecule thick, recorded pressure–area isotherms, and obtained the sizes and shapes of organic molecules even before the advent of X-ray diffraction. Katherine Blodgett in 1935 working with Langmuir at GE developed monolayer film transfer to different supports and built multilayer assemblies. The Langmuir-Blodgett (LB) technique lay dormant until after the Second World War, at which point a surge of interest developed as the commercial potential of all types of thin films in electronics and optics became apparent. This coincided with the advent of transistors, integrated circuits, the computer-communication revolution, and the thrust towards nanotechnology and ultimately molecular electronics.[95] One of those chiefly responsible for arousing worldwide interest in the uses of Langmuir–Blodgett assemblies was Hans Kuhn, starting in the late 1960s at the University of Marburg. He confirmed several important aspects of these films such as their stability, defect levels, and ability to make them with molecular scale patterning.[96]

Repetitive transfer of LB surfactant monolayers provided a rational approach to known thickness of LB multilayer films. Through judicious selection of the structure of the surfactant and due cognizance of interactions between surfactants, it proved possible to create a wide variety of LB multilayer film architectures with structure and composition designed for a particular function. A surfactant is an amphiphile, bearing two chemically distinct termini, and understanding the chemical composition of the substrate permits one to know both how the surfactant will orient with respect to it, as well as which end the surfactant will expose to further bind with a properly chosen counterpart. Two-dimensional supramolecular chemistry of this genre has provided access to ferromagnetic,[97] ferroelectric,[98] semiconducting,[99] dielectric,[100] non-linear optical,[101,102] electroactive[103] and photosensitive[104] multilayers, in which the spacing between active centers in the film can be controlled with angstrom precision. Such control over the separation of chemical species was of pivotal importance for understanding certain details of the surface enhanced Raman effect[105] as well as aspects of energy and electron transfer.[106,107]

The thermal fragility inherent in organic-based LB films could be circumvented by directly anchoring organic moieties to a substrate. Pioneering experiments by Sagiv[108] demonstrated that alkoxysilanes bearing long-alkane chains were able to anchor to surface hydroxyls and spontaneously self-assemble into close-packed well-ordered films. This methodology provided a rational approach to the synthesis of mono and multilayer functional organic surfaces. Marks and others expanded upon this lead to create designer organic surfaces, noteworthy being aligned chromophoric assemblies for second harmonic generation.[109] Mallouk devised a synthetic approach to inorganic LB-like films[110] (Figure 1.16). The method involved initial attachment of α,ω-alkanehydroxyphosphonate to glass or an α,ω-alkanethiophosphonate to gold surfaces. This was followed by the sequential assembly of Zr^{4+} and α,ω-bis-alkanephosphonates to give well-ordered zirconium organophosphonate multilayer films.

Self-assembled LB films of this type display higher thermal and mechanical stability than their purely organic LB counterparts. The methodology allows precise control of film thickness and porosity, substituents on the alkane, nature of the metal ion connector and distance between active sites. Numerous device concepts based on inorganic LB films have been brought to practice, including chiral separation, second harmonic generation, vectorial electron transport and chemical sensing.

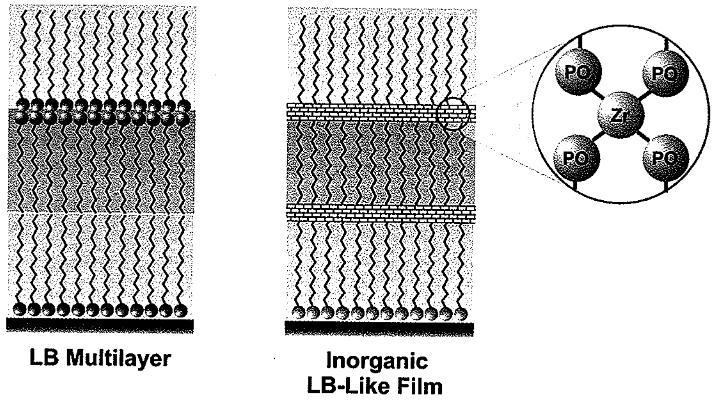

Figure 1.16 *Langmuir–Blodgett films are formed through the repetitive transfer of amphiphile monolayers, left. Inorganic LB-like films can be synthesized from diphosphonates and metal ions, right*

Decher developed a simple and elegant yet extremely powerful approach to the formation of controlled architecture multilayer polymer films based upon the layer-by-layer self-assembly of oppositely charged polyelectrolytes to create an electrostatically bound superlattice[111–114] (Figure 1.17). The method begins with the anchoring of a primer layer such as 3-aminopropyltrimethoxysilane to hydroxyl groups on the surface of glass or silicon. In aqueous solution, the amine groups are protonated and the primer layer develops an overall positive charge. This facilitates the adsorption from solution of a monolayer of a polyanion, such as poly(styrenesulfonate). The process of polyanion adsorption on the primer layer, and as a consequence the formation of an electrical double layer due to dissociation into the aqueous phase of some fraction of countercations, serves to create a sufficient excess of surface negative charge[115] to allow the subsequent adsorption of a monolayer of a polycation such as poly(allylaminehydrochloride). This method of depositing single layers of polyelectrolytes of alternating charge can be repeated several times to produce multilayer polymer films that exhibit an impressive degree of regularity in the interlayer repeat distance.[116] Decher's technique allows the construction of functional polyelectrolyte electrostatic superlattices one layer at a time in which the individual polymer layers can be electrically insulating, semiconducting or metallic and may contain photo-, redox or optically active components. In fact, further investigations have shown that this method is even more versatile than previously thought. The materials to be layered are not limited to polymer electrolytes, but effectively to any species bearing several charged groups such as colloids of various types,[117] viruses[118] and large proteins.[119] The versatility of the method for building designer multilayers is proving to be of considerable scientific and technological interest.[120]

In a creative extension of this research, Mallouk[121–123] and others[124] applied Decher's technique, layer-by-layer deposition of polyelectrolyte films of alternating charge, to the self-assembly of electrostatic superlattices comprised of exfoliated charged lamellae of layered metal phosphonates, oxides or sulfides in combination with for example, polymers, clusters, coordination compounds and bioinorganics.

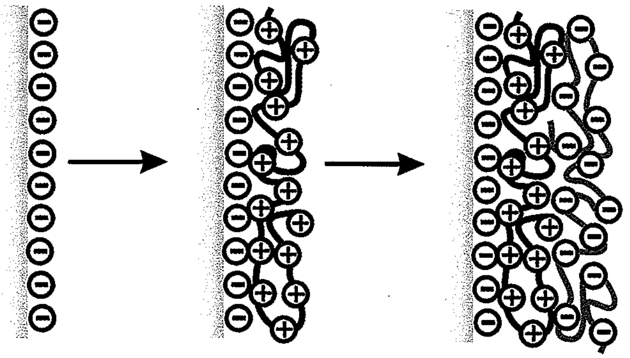

Figure 1.17 *Iterative formation of layer-by-layer electrostatic multilayers by alternately dipping in solutions of polycations and polyanions*

This bricks-and-mortar, materials self-assembly chemistry provides a simple and elegant way to assemble inorganic and organic components into controlled thickness multilayer composite films for a range of perceived device applications. For instance, by assembling monodispersed gold nanoclusters between thin oxide layers, single electron transistor (SET) and coulomb blockade behavior have been demonstrated.[125] The method may also provide access to high dielectric constant oxide thin films for the gate electrode in next generation, smaller and faster field effect transistors. Another intriguing application of designer electrostatic superlattices involves control over the abrasion resistance of surfaces. This has been achieved by coating a surface with an ultra-hard composite nanolaminate that is constructed of alternating monolayers of colloidal zirconium oxide and polyallylaminehydrochloride.[126] These tough organic–inorganic composite films are assembled in a slow "serial" process, one layer at a time, but with the ultimate control in composition.

1.18 SAMs and Soft Lithography

Nuzzo noticed how long chain alkanethiolates could self-assemble on gold surfaces to give well-ordered monolayer films, self-assembled monolayers, now affectionately known as SAMs.[127,128] Whitesides effectively expanded upon the SAM methodology to develop soft lithography.[129] This technique makes use of a patterned elastomer made of polydimethylsiloxane (PDMS), as a mask, stamp or mold. With this simple process, high quality patterns and structures can be created with lateral dimensions from about 5 nm to 500 mm, in two- and three-dimensions, that cannot easily be achieved by photolithography. Figure 1.18 shows square drops of colored water held in this shape by hydrophobic lines surrounding them.[130] Whitesides' strategy for patterning and shaping materials over different length scales and dimensions embraces chemical concepts of self-assembly, templating and crystal engineering, together with soft lithographic techniques of microcontact printing and micromolding. It is an alternative non-photolithographic microfabrication method to complement photolithography, where feature size is limited by optical diffraction. As well, the short wavelength radiation required for photolithographically defining smaller and smaller designs necessitates prohibitively expensive and complex facilities and technologies.

While soft lithography circumvents in theory the diffraction limits of 2D photolithography, in practice the PDMS structures need to be templated upon some fabricated pattern. Usually the pattern is cast from a photolithographically patterned master, thereby imposing onto soft lithography the same size constraints as photolithography, but smaller features can be accessed by fabricating a master through e-beam, UV or X-ray lithography. Even though very fine lithography may be expensive, the master can be repeatedly used and the cost per PDMS replica becomes quite small. Soft lithography provides access to topologically complex 3D objects for building micromachines and electrical circuits, accommodates a wide range of materials, and enables a rational surface chemistry. Soft lithography is easily accessible to chemists interested in experimenting with reliable, convenient

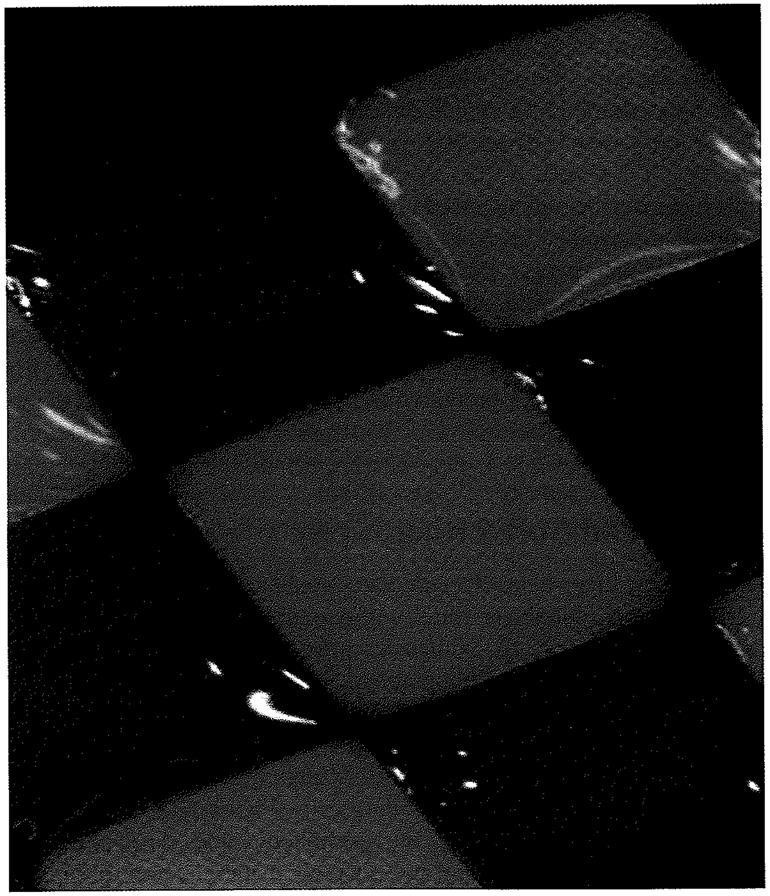

Figure 1.18 *Square drops of water through soft lithography* (Reproduced with permission from Ref. 130)

and inexpensive methods for patterning planar or curved surfaces with organic, inorganic, polymer, liquid crystal, ceramic or biological structures. Whitesides' research illustrates the potential of soft lithographic procedures in a wide range of areas, from microelectronics to optics, microanalysis to sensors, microelectromechanical systems to cell biology. It is abundantly clear that the utility of soft lithography in diverse areas of chemistry, for rapid and low cost patterning and shaping of materials, will definitely increase in the near future. It is an indispensable component of the new materials self-assembly chemistry for the next millennium.

1.19 Clever Clusters

The self-assembly of organic monolayer films on planar substrates is analogous to their assembly on a monodisperse nanocluster, the curved cousin of the plane. In these systems nanocluster nucleation, growth and stabilization is achieved through capping with organic ligands, surfactants and polymers. The idea of capping clusters with organics can be traced to synthetic work of Steigerwald and Brus that concerned the formation of narrow size distribution metal chalcogenide clusters in reverse micelles, and their stabilization by capping with surface thiolates.[131] Also Bentzon showed that the thermal decarbonylation of iron pentacarbonyl in the presence of oleic acid led to surfactant-capped iron oxide nanoclusters,[132] that had such a narrow size distribution that they spontaneously assembled into 2D and 3D capped cluster superlattices. The magnetic properties of periodic arrays of superparamagnetic and ferromagnetic, capped nanocluster films are expected to be most interesting especially in the context of high density, magnetic data storage media. In principle, every cluster in a perfect array could be individually addressed, leading to a storage density approaching the theoretical limits of magnetism.[133]

These breakthroughs set the stage for an elegant series of experiments by Bawendi and Alivisatos on the nucleation and growth of monodispersed zinc and cadmium chalcogenide nanoclusters, capped with a phosphine oxide surfactant.[134] Extraordinary control over cluster size and width of the distribution, often better than a single atomic layer, was feasible by controlling the cluster nucleation and growth using the phosphineoxide as a dual-purpose solvent and capping agent (Figure 1.19). It was also found that polydisperse samples could be size selected to an extremely narrow distribution by several cycles of precipitation from a good solvent by addition of a non-solvent. Cluster films supported on SAMs[135] and cluster supercrystals[136] could be obtained using this synthetic technique. Access to size

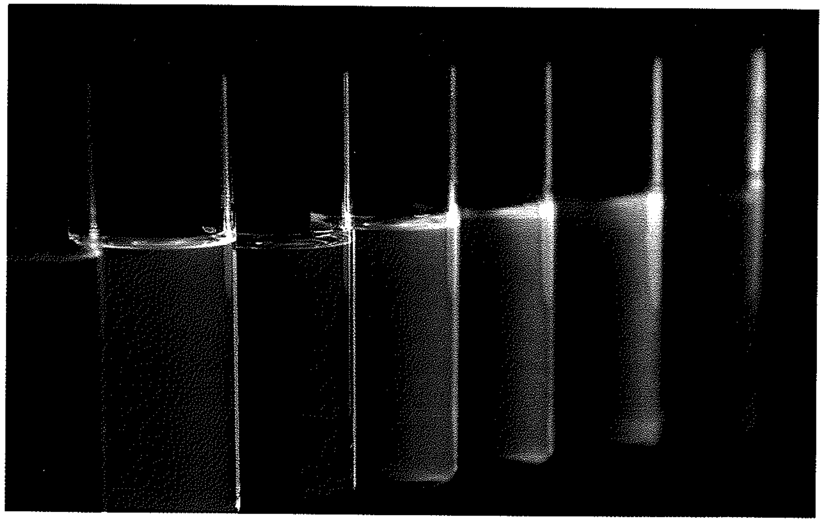

Figure 1.19 *Solutions of CdSe nanoparticles of different sizes under UV light, showing size-dependent emission properties* (Courtesy of Prof. G.D. Scholes)

tunable and monodispersed capped semiconductor clusters opened up a myriad of exciting opportunities in cluster science. These include establishment of scaling laws for cluster physical properties,[137,138] such as melting points,[139] phase transitions,[140] phonon and electronic energies,[141] and magnetic relaxation times. It also enabled the development of electroluminescent cluster-based devices,[142,143] SETs,[144,145] and the study of single clusters using near field optical[146] and laser scanning confocal spectroscopy.[147,148] Significantly, a biological rather than an optoelectronic application may emerge from this kind of research. It centers on the selective fluorescent labeling of biological materials with brightly emissive and appropriately end-functionalized capped II–VI semiconductor clusters of different size.[149] Specific sites in biological specimens have been tagged with this new class of "inorganic dyes." They have the benefit of narrower emission, higher luminescent yield and greater photochemical stability than currently used organic dye labels.

Gold colloids are not new. Nearly two centuries ago, Michael Faraday was generating deeply colored gold colloids using gold tetrachloroaurate and white phosphorus.[150] The use of citric acid as a reductant was successfully applied in the 1950s,[151,152] and is still used by researchers today. However, Whyman's phase-transfer reductive synthesis[153] and Whetten's aerosol cluster beam synthesis[154] of alkanethiolate capped gold nanoclusters opened the way to a rational surface chemistry of gold nanocrystals with the study of 3D versions of SAMs on metal surfaces. This work spawned refined synthetic methods for improving the dispersity of the system to the point that alkanethiolate gold clusters are sufficiently single sized to allow them to be crystallized into well-ordered ensembles, such as cluster wires, rings, mono and multilayer films and crystals,[155] and inverse colloidal crystals using a variety of templating and patterning techniques.[156] Numerous studies have detailed the size-scaling physical properties[157] and behavior of these gold "designer molecules."[158] Some interesting properties include preferred (magic) cluster sizes and shapes, faceting of the clusters, interdigitated-bunching of the chains of the capping alkanethiolates, defects and order–disorder transitions of capped cluster supercrystals, QSEs on optical and electrochemical properties, charge-transport through a single cluster, and SET behavior.[159]

1.20 Extending the Prospects of Nanowires

Lieber, Yang and Xia, amongst others, have made great strides with the synthesis of semiconductor and metal nanowires using vapor and solution phase preparative strategies.[160] A wide range of nanowire compositions with controlled length, diameter, doping and surface structure, charge and functionality, have been reported. These nanowires are often found to grow as oriented single crystals. Diameter dependent QSEs on the electronic band gap have been observed for single crystal silicon nanowires. Interesting new chemistry and physics is beginning to emerge on prototype semiconductor nanowire devices based on single and crossed nanowire architectures. Demonstration nanowire devices like diodes, transistors, light emitting diodes, logic circuits, lasers and sensors, have been described.

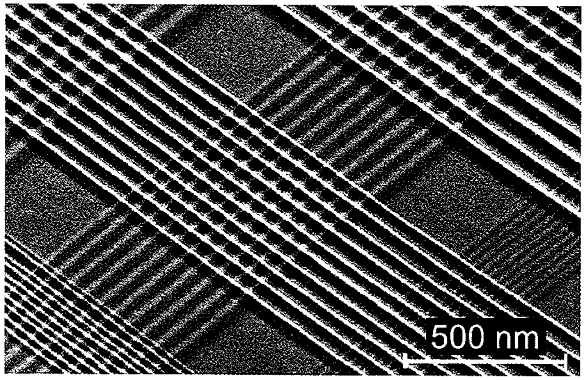

Figure 1.20 *Ultra-small pitch wire arrays made by superlattice templating* (Reproduced with permission from Ref. 161)

A grand challenge with nanowire building blocks is self-assembly into functional architectures that can form the basis for the development of nanoscale electronic, optoelectronic and photonic circuitry with exceedingly high densities of nanowires. These densities can only be achieved if the pitch between nanowires is also nanoscale, a feat that has recently been achieved by Heath, Lieber, Rogers, and Williams using bottom-up directed self-assembly and top-down microfabrication techniques investigated in Chapter 5. A crossed nanowire array made by Heath *et al.* using a creative directed self-assembly technique is shown in Figure 1.20.[161]

1.21 Coercing Colloids

Self-assembled materials have moved well beyond the 10 nm length scale with the advent of synthetic microspheres having extraordinarily narrow size distributions (less than about 2–3% polydispersity).[162] The ability to synthesize monodispersed latex and silica microspheres by heterogeneous emulsion polymerization[163] and sol–gel chemistry,[164] respectively, with diameters in the 50 nm–3 μm range provides a new class of materials with a range of exciting applications in chemistry and physics (Figure 1.21).[165] They can be crystallized into structurally well-ordered colloidal crystals, films and patterns, which can serve as templates to make inverted replica colloidal crystals with a wide range of compositions. One of the most appealing properties is that these periodic dielectric lattices are 3D photonic crystals, the optical analog of the electronic semiconductor.[166] This realization has spawned tremendous interest in them as miniature optical devices for all-optical circuits in telecommunications. Many other exciting opportunities are emerging for colloidal and inverted colloidal crystals, which take advantage of their ordered porosity and the "structural colors" that emerge from the interference of light with a microstructure, rather than absorption of light by a chromophore. Some of these opportunities include solar cells which amplify light absorption, batteries

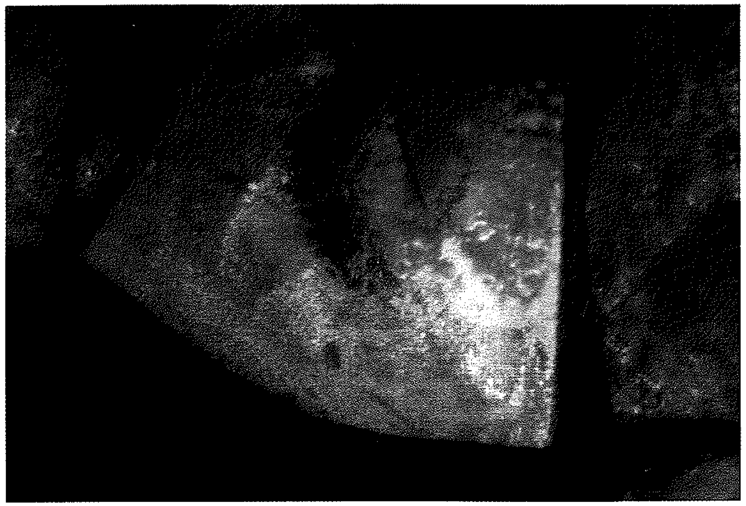

Figure 1.21 *"Inverse opal" photonic crystal made of titania, templated by an array of polystyrene spheres*
(Reproduced with permission from Ref. 165)

which change color as they discharge, chemical sensors with a multiple color-based readout, and paper-thin full color video displays.

Preparing colloidal crystals and films can be achieved using Stokes sedimentation,[167] electrophoresis[168] or evaporation induced self-assembly.[169] Microsphere epitaxy with a lithographically micropatterned substrate has been used to direct the crystallization of close-packed as well as non-close-packed colloidal crystal films.[169] Crystallization of microspheres as monolayer films has been exploited for lithographic patterning of surfaces[170] and for projection lithography,[171] while micromolds[172] and surface relief patterns[173] enable microsphere assembly and control over the size, morphology and orientation of colloidal crystals.

SAM and micromolding in capillary (MIMIC) soft lithographic patterning techniques have been combined with surfactant-based supramolecular templating to synthesize periodic mesoporous silica materials with micron scale designs.[175] Materials of this type exhibit hierarchical order with structural organization over nanometer and micrometer length scales.

Hierarchical synthesis of this genre has been elevated to an even higher level of structural complexity by utilizing a creative combination of micromolding together with colloidal crystal and triblock-copolymer templating (Figure 1.22).[176,177] Microchannels are used to template microspheres, the voids between them in turn template an ordered microphase separated triblock-copolymer,[178] and this polymer finally templates the formation of an ordered oxide. This strategy provides access to inorganic materials with micron scale designs of periodic macroporous crystals having walls composed of ordered mesoporous oxides such as silica, titania and niobia with nanometer scale pores. Here we have an inorganic sol–gel-block-copolymer mesophase (10 nm length scale)[179] that is infiltrated into the interstitial spaces of an organized array of latex spheres (100 nm length scale) in a decorated mold (1000 nm length scale) which yields after polymerization a composite organic–inorganic material with hierarchical construction and ordering over three distinct length scales.

Soft lithographic patterning and colloidal crystal templating over multiple length scales is producing structures with complex texturing of a type that have never been seen before in materials chemistry. Yet we cannot think too highly of ourselves, for hierarchy of this genre is the hallmark of Nature's biomineral constructions. This can be seen in the delicate ornate microskeletons of the single-cell marine organisms known as the diatoms. Nature in this case also makes use of organic molds and templates to shape and decorate silica over many length scales in a single body. In a microscopy image of the diatom *Cymbela Mexicana,* the hierarchical assembly is clearly visible (Figure 1.23). Silica frustules are sculpted in the 1000 nm size range, and these are permeated with 100 nm dimension ordered macropores and 10 nm scale periodic mesopores. Seeing these beautiful constructions is quite humbling, for it shows us our crude, albeit impressive, imitations for what they truly are. At the same time, they do show us the prospects of what we may achieve one day, and while this is not always heartening it invariably presses us to even greater scientific heights.[180]

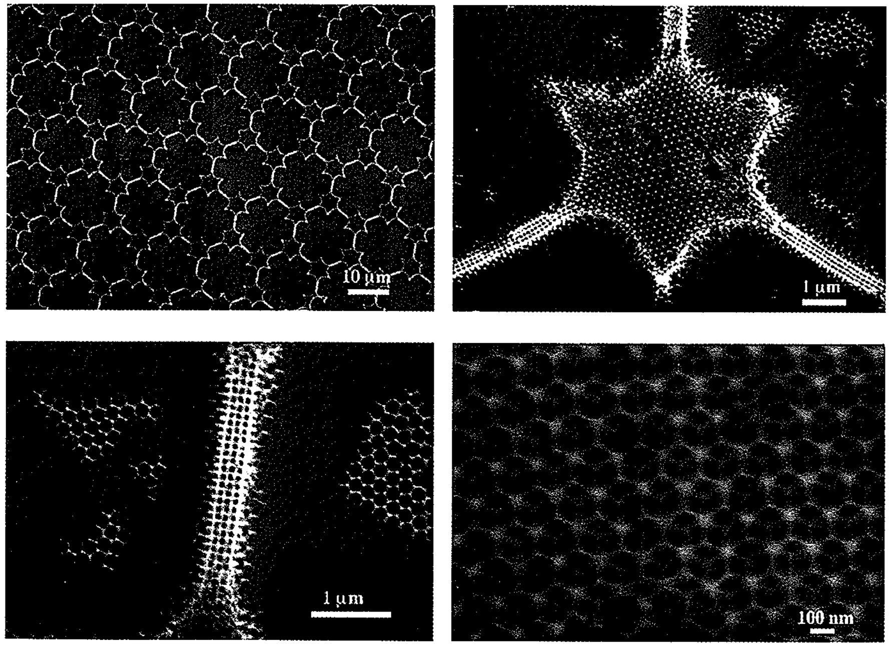

Figure 1.22 *Hierarchically ordered oxide through a combination of microchannel, microsphere, and block-copolymer templating*
(Reproduced with permission from Ref. 176)

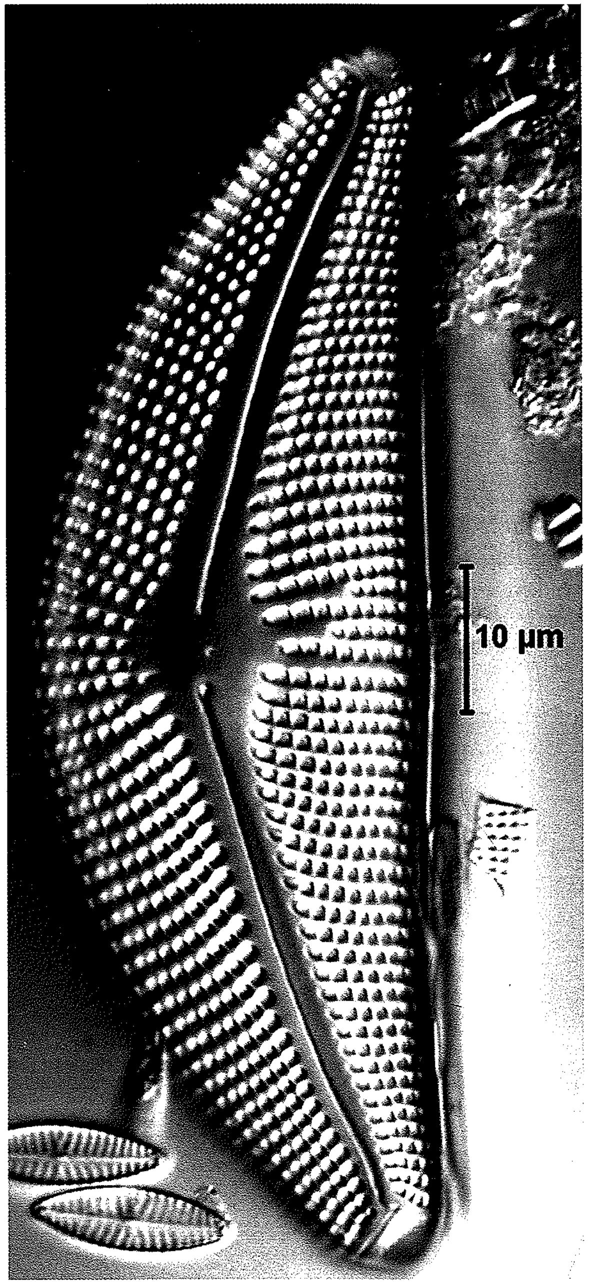

Figure 1.23 *Microstructure of siliceous diatom,* Cymbela Mexicana, *observed by microscopy*
(Reproduced with permission from www.diatom.acnatsci.org/AlgaeImage)

1.22 Mesoscale Self-Assembly

Continuing the theme of length scales it is interesting to look at a recent and fascinating example of 3D materials self-assembly of millimeter scale geodesic objects and examine why this type of research is scientifically very important and where it is likely to find utility in the future. Currently, microfabrication based on photolithography is inherently a 2D technology. New architectures envisaged for future microelectronic, optoelectronic, photonic and microelectro-mechanical devices such as photonic band-gap crystals, biomimetic structures and neural-type computers, necessitate 3D microfabrication schemes. A primitive yet pivotal 3D self-assembly demonstration experiment has amalgamated a creative combination of three elements, namely: (a) spherical templating by a drop of liquid dispersed in a non-miscible liquid (b) capillary-based self-assembly at the interface of the spherical droplet and surrounding liquid of hexagonally shaped gold platelets with a central hole having surfaces that are made selectively hydrophobic and hydrophilic by coating with alkanethiols or silica, respectively, and finally (c) welding together of the gold hexagons into a mechanically robust "micro-geodesic" dome by microelectrodeposition of silver (Figure 1.24). While the open spherical lattice generated by this strategy is comprised of structural objects with no particular function, the demonstration provides compelling proof of concept for

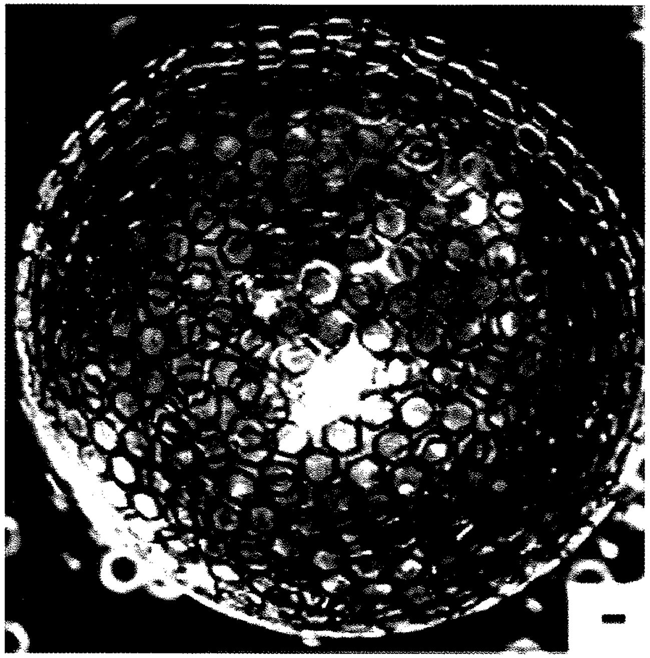

Figure 1.24 *Micron-sized self-assembled geodesic dome assembled onto a drop of water in heptane, the scale bar showing 1* µm
(Reproduced with permission from Ref. 181)

the feasibility of constructing topologically complex 3D microstructures through self-assembly.[181] The future success of this approach necessitates the use of individual or collections of functional objects that spontaneously organize and make connections with themselves and the outside world to generate fully integrated and practical electronic, optical, chemical or mechanical systems. Exciting demonstrations from Whitesides' group, which show convincingly that this can be done, have appeared in droves in the literature and will be explored further in later chapters.

Clearly, the toolbox of materials self-assembly chemistry has been greatly expanded since the work of Harting, Haeckel and Thompson. The newly acquired ability to synthesize hierarchical materials built of individual parts with tunable compositions and dimensions with designed surface structure, charge and functionality suggests that it should be possible in the near future to self-assemble components and interconnects of fully integrated and functional electronic, optical, mechanical, fluidic and chemical systems in a parallel procedure and over all length scales.

1.23 Materials Self-Assembly of Integrated Systems

Simple, elegant and robust attributes of self-assembly are now being combined with powerful methods of inorganic and solid-state chemistry to create materials with unprecedented structures, compositions and morphologies. This is facilitating purely synthetic approaches to hierarchical systems with components integrated over multiple length scales. By combining self-assembly and microfabrication, it has become feasible to organize and connect organic, inorganic and polymeric chemical components with well-defined functions into integrated electronic, photonic, mechanical, analytical and chemical systems for a future nanotechnology.[182] Motivation is being driven by the notion that complex systems in biology, physics, engineering and chemistry are generally based on hierarchical building principles, that is, smaller units are assembled into larger ones, which in turn are organized at a higher dimension. This construction process is continued until the highest level of structural complexity in the hierarchy has been attained.

The hallmark of an integrated system is the assembly of components into an architecture that performs a certain functional task. In the cell of a higher green plant the photosynthetic chloroplast (a hierarchical solar cell) and the ATP-producing mitochondrion (a hierarchical energy converter) are perhaps two of the most impressive examples of integrated chemical systems. Within the body of a computer, atoms are assembled into insulators, semiconductors, metals, and dopants. These form gates, active layers, sources, drains, junctions, metal leads and contacts. These in turn are the building blocks that constitute the transistors, diodes and capacitors of the integrated circuits, millions of which comprise circuit boards and subassemblies of an integrated microelectronic system. Familiar integrated chemical systems include heterogeneous catalysts, photoelectrochemical cells, solid-state lithium batteries, hydrogen–oxygen fuel cells, instant color photographic film, sensors and chromatographic stationary phases.

The ability to self-assemble organic, inorganic and polymeric materials over all length scales and spatial dimensions has taken synthetic chemistry to a level of structural complexity that approaches biology and engineering physics. Synthetic strategies can now be devised for organizing, patterning and connecting functional chemical components into architectures that were not previously possible. Demonstrated examples include layer-by-layer assembly of a thin film Zener diode from conducting polymers and semiconductor nanoclusters,[183] Metal-Insulator-Metal Nanocluster-Insulator-Metal (MINIM) SET,[184] a multicolor pixel voltage-controllable semiconductor nanocluster-luminescent polymer light emitting diode,[185] an all-plastic field effect transistor driven light emitting diode,[186] and a high density rechargeable graphite oxide nanoplatelet-polyelectrolyte lithium ion battery[187] (Figure 1.25). These few early examples demonstrate the power and versatility of a materials self-assembly approach to integrated systems.

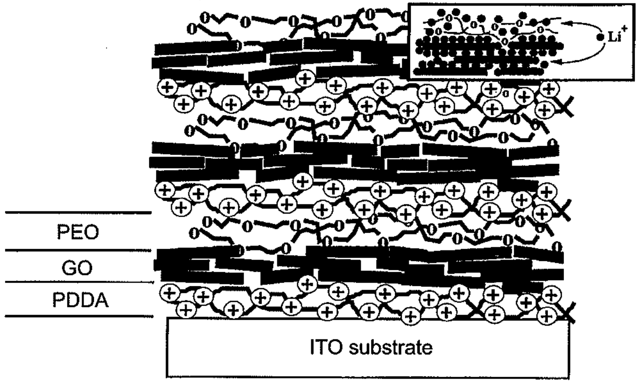

Figure 1.25 *Layer-by-layer self-assembled lithium battery*
(Reproduced with permission from Ref. 187)

In the chapters that follow, the materials self-assembly theme will be expanded upon by introducing various classes of nanoscale building blocks, and referring to pioneering case studies in the literature where building block chemistry over multiple length scales has led to new and interesting architectures. These novel architectures, often unachievable by any other means, have novel and exciting structure–property–function relations, which may lead to utility and a niche in the materials world of this new millennium.

1.24 References

1. A.P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, *Science*, 1996, **271**, 933.
2. J.M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, Germany, 1995.
3. J.M. Lehn, Supramolecular chemistry, *Science*, 1993, **260**, 1762.
4. A. Stein, S.W. Keller and T.E. Mallouk, Turning down the heat: design and mechanism in solid-state synthesis, *Science*, 1993, **259**, 1558.
5. P. Harting, *Natuurkd. Verh. Koninkl. Acad.*, 1873, **13**, 1.
6. F. Wöhler, On the artificial production of urea, *Ann. Phys. Chem.*, 1828, **12**, 253.

7. S. Mann and G.A. Ozin, Synthesis of inorganic materials with complex form, *Nature,* 1996, **382**, 313.
8. E. Haeckel, *Art Forms in Nature*, Prestel-Verlag, Munich, 1998.
9. E. Haeckel, translated by A.L. Mackay, Crystal souls, *Forma*, 1999, **14**, 1–146.
10. S. Oliver, A. Kuperman, N. Coombs, A. Lough and G.A. Ozin, Lamellar aluminophosphates with surface patterns that mimic diatom and radiolarian microskeletons, *Nature*, 1995, **378**, 47.
11. D.W. Thompson, *On Growth and Form*, 1992, complete revised edition; Dover Publications, New York, p. 708.
12. These thoughts are outlined in Emil Fischer's 1902 Nobel speech: www.nobel.se/chemistry/laureates/1902/fischer-lecture.pdf
13. R.M. Barrer, Zeolite synthesis: an overview, *NATO ASI Ser., Ser. C: Math. Phys. Sci.*, 1988, **231** (*Surf. Organomet. Chem.: Mol. Approaches Surf. Catal.*), 221.
14. R.M. Barrer, Zeolite inclusion complexes, *Inclusion Compd.*, 1984, **1**, 191.
15. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, *Nature,* 1992, **359**, 710.
16. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, A new family of mesoporous molecular sieves prepared with liquid crystal templates, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
17. S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan and E.M. Flanigen, Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
18. E.M. Flanigen, Zeolites and molecular sieves: a historical perspective, *Studies in Surface Science and Catalysis*, 2001, vol. 137 (*Introduction to Zeolite Science and Practice*, 2nd edn), p. 11.
19. A.K. Cheetham, G. Ferey and T. Loiseau, Open-framework inorganic materials, *Angew. Chem. Int. Ed.*, 1999, **38**, 3268.
20. O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi and J. Kim, Reticular synthesis and the design of new materials, *Nature*, 2003, **423**, 705.
21. H. Li, M. Eddaoudi, M. O'Keeffe and O.M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework, *Nature*, 1999, **402**, 276.
22. M.E. Kosal, J.H. Chou, S.R. Wilson and K.S. Suslick, A functional zeolite analogue assembled from metalloporphyrins, *Nat. Mater.*, 2002, **1**, 118.
23. N.L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O.M. Yaghi, Advances in the chemistry of metal-organic frameworks, *Cryst. Eng. Commun.*, 2002, **4**, 401.
24. O.M. Yaghi, H.L. Li, C. Davis, D. Richardson and T.L. Groy, Synthetic strategies, structure patterns, and emerging properties in the chemistry of modular porous solids, *Acc. Chem. Res.*, 1998, **31**, 474.
25. S.R. Batten, Coordination polymers, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 107.

26. M. Fujita, Y.J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, Interpenetrating molecular ladders and bricks, *J. Am. Chem. Soc.*, 1995, **117**, 7287.
27. G.J. Halder, C.J. Kepert, B. Moubaraki, K.S. Murray and J.D. Cashion, Guest-dependent spin crossover in a nanoporous molecular framework material, *Science*, 2002, **298**, 1762.
28. P.H. Dinolfo and J.T. Hupp, Supramolecular coordination chemistry and functional microporous molecular materials, *Chem. Mater.*, 2001, **13**, 3113.
29. O.M. Yaghi, G.M. Li and H.L. Li, Selective binding and removal of guests in a microporous metal-organic framework, *Nature*, 1995, **378**, 703.
30. A. Stein, Advances in microporous and mesoporous solids – highlights of recent progress, *Adv. Mater.*, 2003, **15**, 763.
31. F. Schuth and W. Schmidt, Microporous and mesoporous materials, *Adv. Mater.*, 2002, **14**, 629.
32. M.W. Anderson, J.M. Shi, D.A. Leigh, A.E. Moody, F.A. Wade, B. Hamilton and S.W. Carr, The confinement of buckminsterfullerene in one-dimensional channels, *Chem. Commun.*, 1993, (6), 533.
33. H.A. Lowenstam, Goethite in radular teeth of recent marine gastropods, *Science*, 1962, **137**, 279.
34. K.M. Towe, H.A. Lowenstam and M.H. Nesson, Invertebrate ferritin: occurrence in Mollusca, *Science*, 1963, **142**, 63.
35. H.A. Lowenstam, Opal precipitation by marine gastropods (Mollusca), *Science*, 1971, **171**, 487.
36. H.A. Lowenstam, Lepidocrocite, an apatite mineral, and magnetite in teeth of chitons (Polyplacophora), *Science*, 1967, **156**, 1373.
37. H.A. Lowenstam and D.P. Abbott, Vaterite, mineralization product of the hard tissues of a marine organism (Ascidiacea), *Science*, 1975, **188**, 363.
38. H.A. Lowenstam, Minerals formed by organisms, *Science*, 1981, **211**, 1126.
39. H.A. Lowenstam and S. Weiner, On biomineralization, Oxford University Press, Oxford, UK, 1989.
40. L. Addadi and S. Weiner, Interactions between acidic proteins and crystals: stereochemical requirements in biomineralization, *Proc. Natl Acad. Sci. USA*, 1985, **82**, 4110.
41. L. Addadi and S. Weiner, Control and design principles in biomineralization, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 153.
42. G. Failini, S. Albeck, S. Weiner and L. Addadi, Control of aragonite or calcite polymorphism by mollusk shell macromolecules, *Science*, 1996, **271**, 67.
43. L. Addadi and S. Weiner, Biomineralization: crystals, asymmetry and life, *Nature*, 2001, **411**, 753, 755.
44. L. Addadi, E. Beniash and S. Weiner, Assembly and mineralization processes in biomineralization: strategies for forming biological composite materials, *Supramol. Org. Mater. Des.*, 2002, 1.
45. R.J.P. Williams, An introduction to biominerals and the role of organic molecules in their formation, *Philos. Trans. R. Soc. London Ser. B: Biol. Sci.*, 1984, **304**, 411.
46. S. Mann, J.P. Hannington and R.J.P. Williams, Phospholipid vesicles as a model system for biomineralization, *Nature*, 1986, **324**, 565.

47. C.C. Perry, J.R. Wilcock and R.J.P. Williams, A physicochemical approach to morphogenesis: the roles of inorganic ions and crystals, *Experientia*, 1988, **44**, 638.
48. E. Dujardin and S. Mann, Bio-inspired materials chemistry, *Adv. Mater.*, 2002, **14**, 775.
49. S. Mann, The chemistry of form, *Angew. Chem. Int. Ed.*, 2000, **39**, 3392.
50. S. Mann, Biomineralization and biomimetic materials chemistry, *Biomimetic materials chemistry*, VCH, New York, NY, 1996, pp. 1–40.
51. S. Mann and G. Ozin, Synthesis of inorganic materials with complex form, *Nature*, 1996, **382**, 313.
52. S. Mann, D.D. Archibald, J.M. Didymus, T. Douglas, B.R. Heywood, F.C. Meldrum and N.J. Reeves, Crystallization at inorganic–organic interfaces: biominerals and biomimetic synthesis, *Science*, 1993, **261**, 1286.
53. S. Mann, Molecular tectonics in biomineralization and biomimetic materials chemistry, *Nature*, 1993, **365**, 499.
54. M. Fritz, A.M. Belcher, M. Radmacher, D.A. Walters, P.K. Hansma, G.D. Stucky, D.E. Morse and S. Mann, Flat pearls from biofabrication of organized composites on inorganic substrates, *Nature*, 1994, **371**, 49.
55. J.N. Cha, K. Shimizu, Y. Zhou, S.C. Christiansen, B.F. Chmelka, T.J. Deming, G.D. Stucky and D.E. Morse, Learning from biological systems: novel routes to biomimetic synthesis of ordered silica structures, *Mater. Res. Soc. Symp. Proc.*, 2000, **599** (*Mineral. Nat. Synth. Biomater.*), 239.
56. J.N. Cha, G.D Stucky, D.E. Morse and T.J. Deming, Biomimetic synthesis of ordered silica structures mediated by block copolypeptides, *Nature*, 2000, **403**, 289.
57. H.C. Lichtenegger, T. Schoeberl, M.H. Bartl, H. Waite and G.D. Stucky, High abrasion resistance with sparse mineralization: copper biomineral in worm jaws, *Science*, 2002, **298**, 389.
58. M.A. Cariolou and D.E. Morse, Purification and characterization of calcium-binding conchiolin shell peptides from the mollusk, *Haliotis rufescens*, as a function of development, *J. Comp. Physiol. B*, 1988, **157**, 717.
59. X.Y. Shen, A.M. Belcher, P.K. Hansma, G.D. Stucky and D.E. Morse, Molecular cloning and characterization of lustrin A, a matrix protein from shell and pearl nacre of *Haliotis rufescens*, *J. Biol. Chem.*, 1997, **272**, 32472.
60. N. Kroger, R. Deutzman and M. Sumper, Polycationic peptides from diatom biosilica that direct silica nanosphere formation, *Science*, 1999, **286**, 1129.
61. G. He, T. Dahl, A. Veis and A. George, Nucleation of apatite crystals in vitro by self-assembled dentin matrix protein 1, *Nat. Mater.*, 2003, **2**, 552.
62. Y.C. Liou, A. Tocilj, P.L. Davies and Z.C. Jia, Mimicry of ice structure by surface hydroxyls and water of a beta-helix antifreeze protein, *Nature*, 2000, **406**, 322.
63. A. Berman, L. Addadi and S. Weiner, Interactions of sea-urchin skeleton macromolecules with growing calcite crystals: a study of intracrystalline proteins, *Nature*, 1988, **331**, 546.

64. J.N. Cha, K. Shimizu, Y. Zhou, S.C. Christiansen, B.F. Chmelka, G.D. Stucky and D.E. Morse, Silicate in filaments and subunits from a marine sponge direct the polymerization of silica and silicones in vitro, *Proc. Natl Acad. Sci. USA*, 1999, **96**, 361.
65. G. Falini, S. Albeck, S. Weiner and L. Addadi, Control of aragonite or calcite polymorphism by mollusk shell macromolecules, *Science*, 1996, **271**, 67.
66. A.M. Belcher, X.H. Wu, R.J. Christensen, P.K. Hansma, G.D. Stucky and D.E. Morse, Control of crystal phase switching and orientation by soluble mollusc-shell proteins, *Nature*, 1996, **381**, 56.
67. G.A. Ozin, Morphogenesis of biomineral and morphosynthesis of biomimetic forms, *Acc. Chem. Res.*, 1997, **30**, 17.
68. G.K. Hunter, Interfacial aspects of biomineralization, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 430.
69. L.A. Estroff and A.D. Hamilton, At the interface of organic and inorganic chemistry: bioinspired synthesis of composite materials, *Chem. Mater.*, 2001, **13**, 3227.
70. B.C. Goodwin, The life of form. Emergent patterns of morphological transformation, *C.R. Acad. Sci., Ser. III*, 2000, **323**, 15.
71. B.C. Goodwin, What are the causes of morphogenesis?, *Bioessays*, 1985, **3**(1), 32.
72. B. Bensaude-Vincent, H. Arribart, Y. Bouligand and C. Sanchez, Chemists and the school of nature, *New J. Chem.*, 2002, **26**, 1.
73. M. Sarikaya, H. Fong, D.W. Frech and R. Humbert, Biomimetic assembly of nanostructured materials, *Mater. Sci. Forum*, 1999, **293** (*Bioceramics*), 83.
74. National Research Council, *Hierarchical Structures in Biology as a Guide for New Materials Technology*, National Academy Press, Washington, DC, 1994.
75. C. Giacovazzo, G. Artioli, D. Viterbo and G. Ferraris, *Fundamentals of Crystallography*, Oxford University Press, Oxford, 2002.
76. J.D. Bernal, Symmetry and genesis of form, *J. Mol. Biol.*, 1967, **24**, 379; J.D. Bernal and C.H. Carlisle, Range of generalized crystallography, *Sov. Phys. Cryst. USSR*, 1969, **13**, 811.
77. A.L. Mackay, Flexicrystallography: curved surfaces in chemical structures, *Curr. Sci.*, 1995, **69**, 151.
78. A.M. Turing, The chemical basis of morphogenesis, *Bull. Math. Biol.*, 1990, **52**, 153. (Reprinted from: A.M. Turing, Chemical basis of morphogenesis, *Trans. Roy. Soc.*, 1952, **B237**, 37.)
79. J.N. Weiss, Z.L. Qu and A. Garfinkel, Understanding biological complexity: lessons from the past, *FASEB J.*, 2003, **17**, 1.
80. H. Meinhardt, *The Algorithmic Beauty of Seashells*, Springer, Berlin, 1995.
81. P. Ball, *The Self-Made Tapestry: Pattern Formation in Nature*, Oxford Press, Oxford, 2001.
82. N. Coombs, D. Khushalani, S. Oliver, G.A. Ozin, G.C. Shen, I. Sokolov and H. Yang, Blueprints for inorganic materials with natural form: inorganic liquid crystals and a language of inorganic shape, *J. Chem. Soc.-Dalton Trans.*, 1997, 3941.

83. S. Oliver, A. Kuperman, N. Coombs, A. Lough and G.A. Ozin, Lamellar aluminophosphates with surface patterns that mimic diatom and radiolarian microskeletons, *Nature*, 1995, **378**, 47.
84. H. Yang, N. Coombs and G.A. Ozin, Morphogenesis of shapes and surface patterns in mesoporous silica, *Nature*, 1997, **386**, 692.
85. S.M. Yang, I. Sokolov, N. Coombs, C.T. Kresge and G.A. Ozin, Formation of hollow helicoids in mesoporous silica: supramolecular origami, *Adv. Mater.*, 1999, **11**, 1427.
86. J. Rathousky, M. Zukalova and A. Zukal, Supramolecular templating: a new strategy for the synthesis of mesoporous molecular sieves, *Chem. Listy*, 1997, **91**, 413.
87. C. Goltner-Spickermann, Nanocasting of lyotropic liquid crystal phases for metals and ceramics, *Colloid Chem. 1 Top. Curr. Chem.*, 2003, **226**, 29.
88. A. Stein, *The Role of Surfactants and Amphiphiles in the Synthesis of Porous Inorganic Solids*, ed. J. Texter, Marcel Dekker, New York, 2001, p. 819.
89. F. Camerel, J.C.P. Gabriel and P. Batail, Synthesis of a mesoporous composite material prepared by the self-assembly of mineral liquid crystals, *Chem. Commun.*, 2002, **17**, 1926.
90. J.C.P. Gabriel, F. Camerel, B.J. Lemaire, H. Desvaux, P. Davidson and P. Batail, Swollen liquid-crystalline lamellar phase based on extended solid-like sheets, *Nature*, 2001, **413**, 504.
91. G.G. Roberts, Langmuir–Blodgett films, *Contemp. Phys.*, 1984, **25**, 109.
92. www.nobel.se/chemistry/laureates/1932/langmuir-lecture.html
93. www.nobel.se/physics/laureates/1904/strutt-bio.html
94. M.E. Derrick, Profiles in chemistry: Agnes Pockels, 1862–1935, *J. Chem. Ed.*, 1982, **59**, 1030.
95. R.P. Feynman, famous "Plenty of room at the bottom" speech: www.its.caltech.edu/~feynman/plenty.html
96. H. Kuhn, Present status and future prospects of Langmuir–Blodgett film research, *Thin Solid Films*, 1989, **178**, 1.
97. C. Mingotaud, C. Lafuente, J. Amiell and P. Delhaes, Ferromagnetic Langmuir–Blodgett film based on Prussian blue, *Langmuir*, 1999, **15**, 289.
98. A.V. Bune, V.M. Fridkin, S. Ducharme, L.M. Blinov, S.P. Palto, A.V. Sorokin, S.G. Yudin and A. Zlatkin, Two-dimensional ferroelectric films, *Nature*, 1998, **391**, 874.
99. K.K. Kan, G.G. Roberts and M.C. Petty, Langmuir–Blodgett film metal-insulator semiconductor structures on narrow-band gap semiconductors, *Thin Solid Films*, 1983, **99**, 291.
100. C.D. Fung and G.L. Larkins, Planar silicon field-effect transistors with Langmuir–Blodgett gate insulators, *Thin Solid Films*, 1985, **132**, 33.
101. D.W. Kalina and S.G. Grubb, Langmuir–Blodgett films of non-centrosymmetric azobenzene dyes for non-linear optical applications, *Thin Solid Films*, 1988, **160**, 363.
102. I.R. Girling, S.R. Jethwa, R.T. Stewart, J.D. Earls, G.H. Cross, N.A. Cade, P.V. Kolinsky, R.J. Jones and I.R. Peterson, 2nd-order non-linear optical effects in Langmuir–Blodgett films, *Thin Solid Films*, 1988, **160**, 355.

103. J.S. Facci, P.A. Falcigno and J.M. Gold, Characterization of electroactive Langmuir–Blodgett monolayers of (ferrocenylmethyl)dimethyloctadecylammonium sulfate at gold and air water interfaces, *Langmuir*, 1986, **2**, 732.
104. M. Suzuki, Photosensitive polyimide Langmuir–Blodgett films derived from 4-(17-octadecenyl)pyridine and polyamic acid, *Thin Solid Films*, 1989, **180**, 253.
105. A. Otto, I. Mrozek, H. Grabhorn and W. Akemann, Surface-enhanced Raman scattering, *J. Phys.: Condens. Matter.*, 1992, **4**, 1143.
106. D.M. Adams, L. Brus, C.E.D. Chidsey, S. Creager, C.R. Kagan, P.V. Kamat, M. Lieberman, S. Lindsay, R.A. Marcus, R.M. Metzger, M.E. Michel-Beyerle, J.R. Miller, M.D. Newton, D.R. Rolison, O. Sankey, K.S. Schanze, J. Yardley and X.Y. Zhu, Charge transfer on the nanoscale: current status, *J. Phys. Chem. B*, 2003, **107**, 668.
107. M. Fujihara, Photoinduced electron-transfer and energy-transfer in Langmuir–Blodgett films, *Adv. Chem. Ser.*, 1994, **240**, 373.
108. L. Netzer and J. Sagiv, A new approach to construction of artificial monolayer assemblies, *J. Am. Chem. Soc.*, 1983, **105**, 674.
109. S. Yitzchaik and T.J. Marks, Chromophoric self-assembled superlattices, *Acc. Chem. Res.*, 1996, **29**, 197.
110. H. Lee, L.J. Kepley, H.G. Hong and T.E. Mallouk, Inorganic analogs of Langmuir–Blodgett films – adsorption of ordered zirconium 1,10-decanebisphosphonate multilayers on silicon surfaces, *J. Am. Chem. Soc.*, 1988, **110**, 618.
111. G. Decher, Fuzzy nanoassemblies: toward layered polymeric multicomposites, *Science*, 1997, **277**, 1232.
112. G. Decher and J.D. Hong, Build up of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces, *Makromol. Chem.-Macromol. Symp.*, 1991, **46**, 321.
113. G. Decher and J.D. Hong, Build up of ultrathin multilayer films by a self-assembly process. 2. Consecutive adsorption of anionic and cationic bipolar amphiphiles and polyelectrolytes on charged surfaces, *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.*, 1991, **95**, 1430.
114. G. Decher, J.D. Hong and J. Schmitt, Build up of ultrathin multilayer films by a self-assembly process. 3. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces, *Thin Solid Films*, 1992, **210**, 831.
115. J.B. Schlenoff and S.T. Dubas, Mechanism of polyelectrolyte multilayer growth: charge overcompensation and distribution, *Macromolecules*, 2001, **34**, 592.
116. J. Schmitt, T. Grunewald, G. Decher, P.S. Pershan, K. Kjaer and M. Losche, Internal structure of layer-by-layer adsorbed polyelectrolyte films – a neutron and X-ray reflectivity study, *Macromolecules*, 1993, **26**, 7058.
117. N.A. Kotov, I. Dekany and J.H. Fendler, Layer-by-layer self-assembly of polyelectrolyte-semiconductor nanoparticle composite films, *J. Phys. Chem.*, 1995, **99**, 13065.

118. Y. Lvov, H. Haas, G. Decher, H. Mohwald, A. Mikhailov, B. Mtchedlishvily, E. Morgunova and B. Vainshtein, Successive deposition of alternate layers of polyelectrolytes and a charged virus, *Langmuir*, 1994, **10**, 4232.
119. Y. Lvov, K. Ariga and T. Kunitake, Layer-by-layer assembly of alternate protein polyion ultrathin films, *Chem. Lett.*, 1994, **12**, 2323.
120. M. Schonhoff, Self-assembled polyelectrolyte multilayers, *Curr. Opin. Colloid Interface Sci.*, 2003, **8**, 86.
121. C. Guang, H.G. Hong and T.E. Mallouk, Layered metal phosphates and phosphonates – from crystals to monolayers, *Acc. Chem. Res.*, 1992, **25**, 420.
122. S.W. Keller, H.N. Kim and T.E. Mallouk, Layer-by-layer assembly of intercalation compounds and heterostructures on surfaces – toward molecular beaker epitaxy, *J. Am. Chem. Soc.*, 1994, **116**, 8817.
123. M.M. Fang, D.M. Kaschak, A.C. Sutorik and T.E. Mallouk, A "mix and match" ionic–covalent strategy for self-assembly of inorganic multilayer films, *J. Am. Chem. Soc.*, 1997, **119**, 12184.
124. E.R. Kleinfeld and G.S. Ferguson, Stepwise formation of multilayered nanostructural films from macromolecular precursors, *Science*, 1994, **265**, 370.
125. D.L. Feldheim, K.C. Grabar, M.J. Natan and T.E. Mallouk, Electron transfer in self-assembled inorganic polyelectrolyte/metal nanoparticle heterostructures, *J. Am. Chem. Soc.*, 1996, **118**, 7640.
126. Y.J. Liu, A. Rosidian and R.O. Claus, Mechanical properties of electrostatically self-assembled Al_2O_3–ZrO_2 nanocomposites prepared at room temperature, *J. Cluster Sci.*, 1999, **10**, 421.
127. C.D. Bain, E.B. Troughton, Y.T. Tao, J. Evall, G.M. Whitesides and R.G. Nuzzo, Formation of monolayer films by the spontaneous assembly of organic thiols from solution onto gold, *J. Am. Chem. Soc.*, 1989, **111**, 321.
128. A.R. Bishop and R.G. Nuzzo, Self-assembled-monolayers: recent developments and applications, *Curr. Opin. Colloid Interface Sci.*, 1996, **1**, 127.
129. Y.N. Xia and G.M. Whitesides, Soft lithography, *Angew. Chem. Int. Ed.*, 1998, **37**, 551.
Quote [illegible]
130. N.L. Abbott, J.P. Folkers and G.M. Whitesides, Manipulation of the wettability of surfaces on the 0.1-micrometer to 1-micrometer scale through micromachining and molecular self-assembly, *Science*, 1992, **257**, 1380.
131. M.L. Steigerwald, A.P. Alivisatos, J.M. Gibson, T.D. Harris, R. Kortan, A.J. Muller, A.M. Thayer, T.M. Duncan, D.C. Douglass and L.E. Brus, Surface derivatization and isolation of semiconductor cluster molecules, *J. Am. Chem. Soc.*, 1988, **110**, 3046; M.L. Steigerwald and L.E. Brus, Semiconductor crystallites – a class of large molecules, *Acc. Chem. Res.*, 1990, **23**, 183.
132. M.D. Bentzon, J. Van Wonterghem, S. Mrup, A. Thölen and C.J.W. Koch, Ordered aggregates of ultrafine iron-oxide particles – super crystals, *Philos. Mag. B*, 1989, **60**, 169.
133. D.A. Thompson and J.S. Best, The future of magnetic data storage technology, *IBM J. Res. Dev.*, 2000, **44**, 311.

134. C.B. Murray, D.J. Norris and M.G. Bawendi, Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
135. V.L. Colvin, A.N. Goldstein and A.P. Alivisatos, Semiconductor nanocrystals covalently bound to metal-surfaces with self-assembled monolayers, *J. Am. Chem. Soc.*, 1992, **114**, 5221.
136. C.B. Murray, C.R. Kagan and M.G. Bawendi, Self-organization of CdSe nanocrystallites into 3-dimensional quantum-dot superlattices, *Science*, 1995, **270**, 1335.
137. P. Alivisatos, Colloidal quantum dots. From scaling laws to biological applications, *Pure Appl. Chem.*, 2000, **72**, 3.
138. G. Schmid, Large clusters and colloids – metals in the embryonic state, *Chem. Rev.*, 1992, **92**, 1709.
139. A.N. Goldstein, C.M. Echer and A.P. Alivisatos, Melting in semiconductor nanocrystals, *Science*, 1992, **256**, 1425.
140. S.H. Tolbert and A.P. Alivisatos, Size dependence of a first-order solid–solid phase-transition – the wurtzite to rock-salt transformation in CdSe nanocrystals, *Science*, 1994, **265**, 373.
141. U. Banin, Y.W. Cao, D. Katz and O. Millo, Identification of atomic-like electronic states in indium arsenide nanocrystal quantum dots, *Nature*, 1999, **400**, 542–544; L. Brus, Electronic wave-functions in semiconductor clusters – experiment and theory, *J. Phys. Chem.*, 1986, **90**, 2555; L. Brus, Size dependent development of band-structure in semiconductor crystallites, *New J. Chem.*, 1987, **11**, 123.
142. V.L. Colvin, M.C. Schlamp and A.P. Alivisatos, Light-emitting-diodes made from cadmium selenide nanocrystals and a semiconducting polymer, *Nature*, 1994, **370**, 354.
143. S. Coe, W.K. Woo, M. Bawendi and V. Bulovic, Electroluminescence from single monolayers of nanocrystals in molecular organic devices, *Nature*, 2002, **420**, 800.
144. D.L. Klein, R. Roth, A.K.L. Lim, A.P. Alivisatos and P.L. McEuen, A single-electron transistor made from a cadmium selenide nanocrystal, *Nature*, 1997, **389**, 699.
145. R.P. Andres, T. Bein, M. Dorogi, S. Feng, J.I. Henderson, C.P. Kubiak, W. Mahoney, R.G. Osifchin and R. Reifenberger, "Coulomb staircase" at room temperature in a self-assembled molecular nanostructure, *Science*, 1996, **272**, 1323.
146. M. Nirmal, B.O. Dabbousi, M.G. Bawendi, J.J. Macklin, J.K. Trautman, T.D. Harris and L.E. Brus, Fluorescence intermittency in single cadmium selenide nanocrystals, *Nature*, 1996, **383**, 802.
147. J. Tittel, W. Gohde, F. Koberling, T. Basche, A. Kornowski, H. Weller and A. Eychmuller, Fluorescence spectroscopy on single CdS nanocrystals, *J. Phys. Chem. B.*, 1997, **101**, 3013.
148. S. Empedocles and M. Bawendi, Spectroscopy of single CdSe nanocrystallites, *Acc. Chem. Res.*, 1999, **32**, 389.

149. W.J. Parak, D. Gerion, T. Pellegrino, D. Zanchet, C. Micheel, S.C. Williams, R. Boudreau, M.A. Le Gros, C.A. Larabell and A.P. Alivisatos, Biological applications of colloidal nanocrystals, *Nanotechnology*, 2003, **14**, R15.
150. M. Faraday, Experimental relations of gold (and other metals) to light, *Philos Trans. R. Soc.*, 1857, **147**, 145.
151. J. Turkevich, P.C. Stevenson and J. Hillier, A study of the nucleation and growth processes in the synthesis of colloidal gold, *Discuss. Faraday Soc.*, 1951, **11**, 55.
152. J.W. Slot and H.J. Geuze, A new method of preparing gold probes for multilabeling cytochemistry, *Eur. J. Cell Biol.*, 1985, **38**, 87.
153. M. Brust, M. Walker, D. Bethell, D.J. Schiffrin and R. Whyman, Synthesis of thiol-derivatized gold nanoparticles in a 2-phase liquid–liquid system, *Chem. Commun.*, 1994, **7**, 801.
154. R.L. Whetten, J.T. Khoury, M.M. Alvarez, S. Murthy, I. Vezmar, Z.L. Wang, P.W. Stephens, C.L. Cleveland, W.D. Luedtke and U. Landman, Nanocrystal gold molecules, *Adv. Mater.*, 1996, **8**, 428.
155. P. Mulvaney and L.M. Liz-Marzan, Rational material design using Au core-shell nanocrystals, *Coll. Chem. 1* (*Top. Curr. Chem.*), 2003, **226**, 225.
156. A.E. Saunders, P.S. Shah, M.B. Sigman Jr., T. Hanrath, H.S. Hwang, K.T. Lim, K.P. Johnston and B.A. Korgel, Inverse opal nanocrystal superlattice films, *Nano Lett.*, 2004, 1943.
157. T. Castro, R. Reifenberger, E. Choi and R.P. Andres, Size-dependent melting temperature of individual nanometer-sized metallic clusters, *Phys. Rev. B*, 1990, **42**, 8548.
158. G. Schmid and B. Corain, Nanoparticulated gold: syntheses, structures, electronics, and reactivities, *Eur. J. Inorg. Chem.*, 2003, **17**, 3081.
159. M.M. Alvarez, R.L. Whetten, S.W. Chen, R.S. Ingram, M.J. Hostetler, J.J. Pietron, R.W. Murray, T.G. Schaaff and J.T. Khoury, Gold nanoelectrodes of varied size: transition to molecule-like charging, *Science*, 1998, **280**, 2098.
160. Y.N. Xia, P.D. Yang, Y.G. Sun, Y.Y. Wu, B. Mayers, B. Gates, Y.D. Yin, F. Kim and Y.Q. Yan, One-dimensional nanostructures: synthesis, characterization, and applications, *Adv. Mater.*, 2003, **15**, 353.
161. N.A. Melosh, A. Boukai, F. Diana, B. Gerardot, A. Badolato, P.M. Petroff and J.R. Heath, Ultrahigh-density nanowire lattices and circuits, *Science*, 2003, **300**, 112.
162. Y.N. Xia, B. Gates, Y.D. Yin and Y. Lu, Monodispersed colloidal spheres: old materials with new applications, *Adv. Mater.*, 2000, **12**, 693.
163. H. Kawaguchi, Functional polymer microspheres, *Prog. Polym. Sci.*, 2000, **25**, 1171.
164. P. Dong, Advances in preparation and application of monodisperse colloidal silica particles, *Prog. Natl Sci.*, 2000, **10**, 575.
165. J.E.G.J. Wijnhoven and W.L. Vos, Preparation of photonic crystals made of air spheres in titania, *Science*, 1998, **281**, 802.
166. J.D. Joannopoulos, P.R. Villeneuve and S.H. Fan, Photonic crystals: putting a new twist on light, *Nature*, 1997, **386**, 143.

167. R.C. Salvarezza, L. Vazquez, H. Miguez, R. Mayoral, C. Lopez and F. Meseguer, Edward–Wilkinson behavior of crystal surfaces grown by sedimentation of SiO_2 nanospheres, *Phys. Rev. Lett.*, 1996, **77**, 4572.
168. M. Trau, D.A. Saville and I.A. Aksay, Assembly of colloidal crystals at electrode interfaces, *Langmuir*, 1997, **13**, 6375. M. Holgado, F. Garcia-Santamaria, A. Blanco, M. Ibisate, A. Cintas, H. Miguez, C.J. Serna, C. Molpeceres, J. Requena, A. Mifsud, F. Meseguer and C. Lopez, Electrophoretic deposition to control artificial opal growth, *Langmuir*, 1999, **15**, 4701.
169. P. Jiang, J.F. Bertone, K.S. Hwang and V.L. Colvin, Single-crystal colloidal multilayers of controlled thickness, *Chem. Mater.*, 1999, **11**, 2132.
170. A. van Blaaderen, R. Ruel and P. Wiltzius, Template-directed colloidal crystallization, *Nature*, 1997, **385**, 321.
171. C.L. Haynes and R.P. Van Duyne, Nanosphere lithography: a versatile nanofabrication tool for studies of size-dependent nanoparticle optics, *J. Phys. Chem. B*, 2001, **105**, 5599.
172. J.C. Love, D.B. Wolfe, H.O. Jacobs and G.M. Whitesides, Microscope projection photolithography for rapid prototyping of masters with micron-scale features for use in soft lithography, *Langmuir*, 2001, **17**, 6005.
173. E. Kim, Y.N. Xia and G.M. Whitesides, Two- and three-dimensional crystallization of polymeric microspheres by micromolding in capillaries, *Adv. Mater.*, 1996, **8**, 245.
174. A. Arsenault, S.B. Fournier-Bidoz, B. Hatton, H. Miguez, N. Tetrault, E. Vekris, S. Wong, S.M. Yang, V. Kitaev and G.A. Ozin, Towards the synthetic all-optical computer: science fiction or reality? *J. Mater. Chem.*, 2004, **14**, 781.
175. M. Trau, N. Yao, E. Kim, Y. Xia, G.M. Whitesides and I.A. Aksay, Microscopic patterning of orientated mesoscopic silica through guided growth, *Nature*, 1997, **390**, 674.
176. P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B.F. Chmelka, G.M. Whitesides and G.D. Stucky, Hierarchically ordered oxides, *Science*, 1998, **282**, 2244.
177. P. Yang, A.H. Rizvi, B. Messer, B.F. Chmelka, G.M. Whitesides and G.D. Stucky, Patterning porous oxides within microchannel networks, *Adv. Mater.*, 2001, **13**, 427.
178. O.D. Velev, T.A. Jede, R.F. Lobo and A.M. Lenhoff, Porous silica via colloidal crystallization, *Nature*, 1997, **389**, 447.
179. D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka and G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science*, 1998, **279**, 548.
180. H. Arribart and B. Bensaude-Vincent, Chemists' defiance: imitating the beauty of living things, *Recherche*, 1999, **325**, 56.
181. W.T.S. Huck, J. Tien and G.M. Whitesides, Three-dimensional mesoscale self-assembly, *J. Am. Chem. Soc.*, 1998, **120**, 8267.
182. A.J. Bard, *Integrated Chemical Systems: a Chemical Approach to Nanotechnology*, Wiley, New York, NY, 1994.

183. T. Cassagneau, T.E. Mallouk and J.H. Fendler, Layer-by-layer assembly of thin film Zener diodes from conducting polymers and CdSe nanoparticles, *J. Am. Chem. Soc.*, 1998, **120**, 7848.
184. D.L. Feldheim, K.C. Grabar, M.J. Natan and T.E. Mallouk, Electron transfer in self-assembled inorganic polyelectrolyte/metal nanoparticle heterostructures, *J. Am. Chem. Soc.*, 1996, **118**, 7640.
185. V.L. Colvin, M.C. Schlamp and A.P. Alivisatos, Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer, *Nature*, 1994, **370**, 354.
186. H. Sirringhaus, N. Tessler and R.H. Friend, Integrated optoelectronic devices based on conjugated polymers, *Science*, 1998, **280**, 1741.
187. T. Cassagneau and J.H. Fendler, High-density rechargeable lithium-ion batteries self-assembled from graphite oxide nanoplatelets and polyelectrolytes, *Adv. Mater.*, 1998, **10**, 877.

Nanofood for Thought – Nanochemistry, Genealogy, Materials Self-Assembly, Length Scales

1. Discuss connections between D'Arcy Wentworth Thomson's ideas on morphogenesis of porous siliceous microskeletons of radiolaria in biology and template directed self-assembly of periodic nanoporous forms of silica in the materials chemistry laboratory.
2. In the context of nanochemistry briefly explain with examples what is meant by (a) self-assembly, (b) co-assembly, (c) template directed self-assembly, (d) colloidal assembly, (e) inverse colloidal assembly, (f) soft lithography, (g) cluster superlattice, (h) electrostatic superlattice, (i) hierarchical structure, (j) nanocomposite, (k) periodic mesostructure and (l) topotactic metamorphosis.
3. Amplify upon the statement: "Self-assembly enables the diversity of chemistry to be combined with the complexity of biology to create materials that auto-construct over 'all' length scales and this represents a new frontier in solid-state chemistry".
4. In a few sentences delineate the key scientific developments in the 20th century that enabled solid-state chemistry, as we know it today.
5. What were the key breakthroughs that enabled today's nanoscience?
6. Where did the term "self-assembly" first appear in the scientific literature?
7. Why is it important to realize that not all nanomaterials are small? Describe such a "large" nanomaterial with size-tunable properties in the micron range.
8. Which seminal contributions of Pieter Harting and Heinz Lowenstam can be cited to support the consensus that they are, respectively, the fathers of biomimetic inorganic chemistry and biomineralization?
9. Why is curvature an important concept in materials chemistry and biology? Why is curvature becoming particularly relevant in materials self-assembly chemistry?
10. What can you accomplish with inorganic Langmuir–Blodgett multilayer film that would be impossible with the organic analog?
11. Discuss the different classes of nanostructures that can be synthesized. How could each of these classes of structures be useful in nano-devices?