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Biomimetics : A Route for the Synthesis of Novel Materials

P. RAMACHANDRARAO
National Metallurgical Laboratory, Jamshedpur – 831007

ABSTRACT

The performance of smart / intelligent materials is dependent on the close interplay between structure, organisation and dynamics. These can be tailored to make advanced materials meet specific requirements. An attempt has been made to summarise recent advancements in understanding the synthesis of inorganic intelligent materials through such tailormade processes in Nature. The growth of the science of biomimetics, where endeavours are made to copy and learn from Nature, is traced.

***Keywords** : Biomimetics, Nanocrystalline materials, Biomineralisation, Structural hierarchy, Novel materials.*

INTRODUCTION

Advanced materials are becoming increasingly tailormade to meet specific requirements. The performance of smart materials/intelligent materials is dependent on close interplay between structure, organisation and dynamics. The miniaturisation of electronic devices has resulted in the development of nanocrystalline materials and devices. It is now well understood that the extremely small size gives nanoscopic (<1.5 nm) and mesoscopic (1.5-100 nm) materials many unusual properties as a result of quantum-mechanical and Coulomb-charging effects [1,2]. The former effect arises as a result of the wave-like nature of electrons; the crystals are too small to have continuous energy bands even when they have an identifiable crystal structure. The Coulomb-charge effect is a consequence of the fact that the addition of an extra electron to the conducting sphere exceeds the mean thermal energy. Consequently, thermal fluctuations in the total charge are suppressed. These effects are now beginning to place a lower limit on the size of microelectronic devices. Scientific curiosity has stimulated the study of structures which reach these limits in one-, two- or three-dimensions. Demand for the synthesis of nanocrystalline materials is driven both for the exploitation of the unusual physical, chemical, mechanical and other properties and by the need to have a better understanding of the origin of such properties.

SYNTHESIS OF NANOCRYSTALLINE MATERIALS

Currently nanocrystalline materials are synthesised through physical or chemical vapour deposition, plasma processing, sputtering, inert gas condensation, spark erosion of solids, ball milling, electrodeposition, rapid solidification and solution chemistry [2]. Many of these methods are time consuming and reproducibility of the properties of the product is also difficult. Solution chemistry enables one to control the synthesis at a molecular level and is cost effective. In the light of these advantages the chemical strategy for the synthesis of nanostructures is gaining ground rapidly. Currently four strategies are adopted for the synthesis of large molecules and assemblies [3]. These are briefly enumerated below.

Controlled Formation of Covalent Bonds

Also known as sequential covalent synthesis, this approach generates arrays of covalently linked atoms of definite composition, shape and connectivity. Synthesis of vitamin B_{12} is a good example of this method. Considerable difficulties are, however, encountered in engineering individual bonds and significant progress needs to be made to extend the technique for the synthesis of nanostructured materials.

Covalent Polymerisation

This is a simple and effective strategy for the generation of polymers from monomers which react with themselves. Formation of polyethylene from ethylene is an outstanding example of synthesis by this route. The simplicity of the process is in itself a limitation. Creation of well organised three dimensional structures is difficult and requires an understanding of noncovalent interactions in the system

Self-Organisation

This is the route responsible for the formation of liquid crystals, molecular crystals, micelles, Langmuir-Blodgett films, emulsions *etc.* Weak bonds such as the van der Waals, hydrogen and ionic bonds play a major role in driving the structure to settle for a thermodynamically stable and organised configuration.

Molecular Self-Assembly

In this route for the synthesis of an aggregate of a large number of molecules, use is made of all the above strategies. Initially some intermediate molecular

Table 1 : Some minerals found in living organisms [from Mann [4]]

Mineral	Formula	Organism/Function
Calcium carbonate		
Calcite	$CaCO_3$	Algae/Exoskeletons Tribolites/Eye lens
Aragonite	$CaCO_3$	Fish/Gravity device Molluscs/Exoskeleton
Amorphous	$CaCO_3.nH_2O$	Plants/Ca store
Calcium phosphate		
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	Vertebrates/Endoskeletons, teeth
Octa-calcium phosphate	$Ca_8H_2(PO_4)_6$	Vertebrates/precursor phase in bone
Calcium Oxalate		
Whewellite	$CaC_2O_4.H_2O$	Plants/Ca store
Weddellite	$CaC_2O_4.2H_2O$	Plants/Ca store
Sulphates		
Gypsum	$Ca\ SO_4$	Jelly fish larvae/ gravity device
Barite	$Ba\ So_4$	Algae/Gravity device
Celestite	$SrSO_4$	Acantharia/Cellular support
Iron oxides		
Magnetite	Fe_3O_4	Bacteria/Magnetoaxis
Goethite	a–FeOOH	Limpets/Teeth
Ferrihydrite	$5FE_2O_3.9H_2O$	Animals & Plants/ Fe storage
Silicon dioxide		
Silica	$SrSO_4$	Algae/ Gravity device

structures are generated through sequential covalent bonding, these molecules are then made to form larger aggregates through noncovalent linkages such as hydrogen bond and van der Waals interaction. Several copies of these aggregates are then put together in an ordered fashion.

SYNTHESIS IN NATURE

It is now recognised that nature employs well controlled solution chemistry techniques in the synthesis of over 40 different minerals or inorganic compounds in living organisms as shown in Table 1 [4]. These are salts of calcium, barium, strontium, silicon and iron with the phosphate and carbonates of calcium being the most abundant. Biomineralisation or the formation of these minerals from the body fluids occurs due to a co-operative interaction between the organic membranes and the inorganic chemicals. The resulting crystals of the minerals are characterised by extremely reproducible size, shape and orientation. Often, they also have unusual crystal structures. These minerals in turn form hierarchical and complex forms such as spirals, skeletons, spheroids *etc.* Besides utilising them to form such structures, nature employs these minerals in an extremely effective fashion to perform diverse functions. For example, a single mineral *viz.,* calcium carbonate, may serve, in different organisms, the purpose of forming the eye lens, being a gravity balance device, providing defence against predators or for making love darts. In order to achieve this versatility, continuity and reproducibility, the process of biomineralisation is extremely well controlled. We are beginning to understand these processes and duplicate them in lifeless laboratory systems. These attempts at imitating nature have given birth to a field of scientific endeavour called *biomimetics.* In order to understand the techniques being developed in this area, it is instructive to understand the process of biomineralisation.

BIOMINERALISATION

In biological systems, the formation of inorganic crystals and structures based on them occurs in enclosures which result from a partitioning of the biological space to provide the necessary environment. The reaction 'chamber' is formed by supramolecular pre-organisation. This is achieved by either self-assembly of protein cages and lipid vesicles or the formation of extended protein -polysaccharide networks. The first of these methods enables intracellular crystallisation while the latter leads to intercellular crystallisation. The self-assembly is driven by the existence of hydrophobic-hydrophilic interactions in amphiphilic molecules in aqueous environments. For example, if molecules of phospholipids having a polar head group and a non-polar hydrocarbon tail and held together by weak van der Waals force are placed in water, they will organise themselves into forms which minimise the contact of their tails with water. The polar heads of the molecule are attracted to the water by electrostatic and hydrogen bond interactions. Some of the resulting assemblies are shown in Fig.1. The biological space enclosed by the formation of micelles, vesicles, tubules *etc.,* (Fig.2) provides a controlled environment within which parameters such as supersaturation, pH, complexation, ionic strength *etc.,* can be controlled. The control is exercised by selective ion diffusion through the vesicle membrane. The physical constraint imposed by the vesicle determines the size of the mineral crystal formed. Thus, the iron storage protein, ferritin, consists of a cage formed by the self-assembly of 24 peptide subunits and has a cavity measuring 8 nm. Iron oxide consisting of only about 4500 iron atoms can form inside this cage [5]. In unicellular organisms, there seems to be no greater interaction between the constraining organic molecule and the mineral. In multicellular organisms, however, the organic

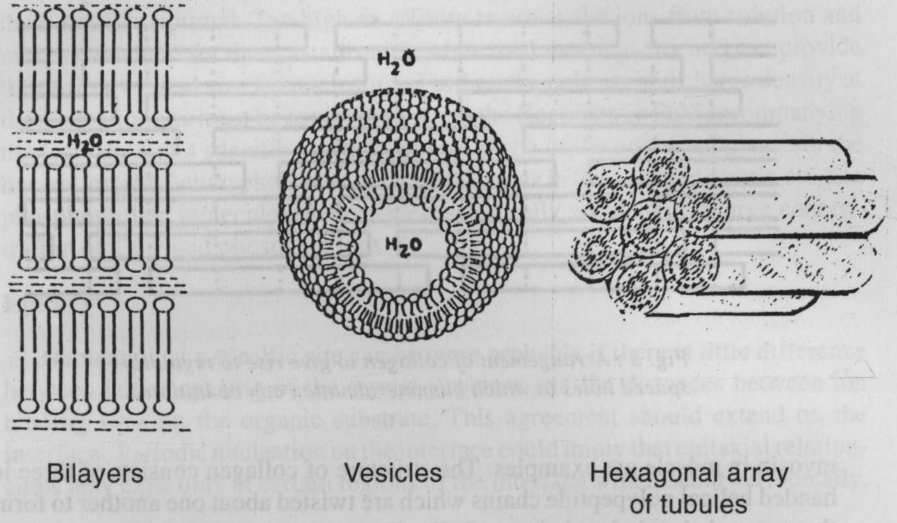

Fig. 1 : Various shapes that can be synthesized from organic molecules having a hydrophilic head and hydrophobic tails.

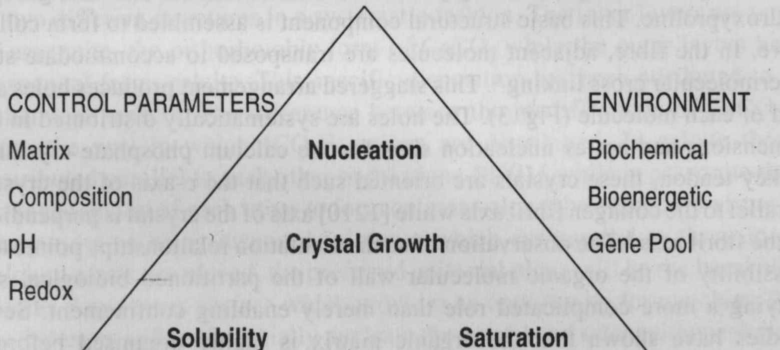

Fig. 2 : Partitioned biological space and control of various processes in biomineralisation.

interface appears to control the crystallographic orientation. The orientation of calcium phosphate crystals in bone is an example and will be discussed later.

When relatively large structures of biominerals such as bones and teeth are to be formed, the pre-organised organic frame works have to be constructed on a considerably larger scale. This is achieved by the use of polymeric organic matter such as fibrous proteins. Collagen in tendons, keratin in nails, horn and feathers,

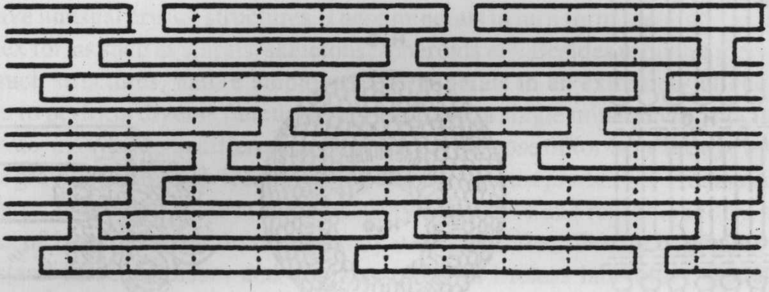

Fig. 3 : Arrangement of collagen to give rise to regularly spaced holes in which biomineralisation can be initiated.

myosin in muscle are examples. The structure of collagen consists of three left handed helical polypeptide chains which are twisted about one another to form a three stranded right handed superhelix. Each polypeptide chain is composed of glycine, proline, alanine and hydroxyproline. The three chains are held together by hydrogen bonding between glycine side chains and between -OH groups of hydroxyproline. This basic structural component is assembled to form collagen fibre. In the fibre, adjacent molecules are transposed to accommodate strong intermolecular cross linking [6]. This staggered arrangement produces holes at the end of each molecule (Fig .3). The holes are systematically distributed in three dimensions and act as nucleation sites for the calcium phosphate crystals. In turkey tendon, these crystals are oriented such that the *c*-axis of the crystal is parallel to the collagen fibril axis while [1210] axis of the crystal is perpendicular to the fibril axis [4].The observation of such orientation relationships points to the possibility of the organic molecular wall of the partitioned biological space playing a more complicated role than merely enabling confinement. Several studies have shown that the organic matrix is highly organised before the nucleation of the inorganic crystal [7,8]. The acidic and hydrophobic molecules are so arranged as to be able to provide sites which have some form of molecular complimentarity at the interface. Polarity, charge and stereochemical relationships are tailored to make nucleation extremely site specific. The specificity arises in three distinct ways which are discussed below.

Electrostatic considerations

In order to nucleate the crystal, a site on the organic matrix must attract the required number of atoms of the inorganic material to be nucleated such that the critical nucleus can be formed. It should also be able to bind these to itself for further growth. The capacity to localise the required ions and the ability to bind them must be optimal. Too high an affinity removes the ions from solution and makes them inert for the crystallisation while too low a capacity may not provide the desired critical size for nucleation. Further, the polarity and charge density at the nucleation site must be complimentary to the electrostatic field accompanying the formation of a specific crystallographic plane of the nucleated phase. In the nucleation of calcium phosphate in bone, the holes in the collagen matrix contain phosphoprotein molecules that can electrostatically accumulate a large concentration of Ca^{2+} and phosphate ions.

Epitaxy

Nucleation at a specific site can be more probable if there is little difference between lattice spacing of the crystal structure and the distances between ion binding sites on the organic substrate. This agreement should extend on the interface . Periodic nucleation on the interface could imply that epitaxial relationships may exist only at certain regions of the interface which occur periodically.

Stereochemical Requirements

It has been observed that in shells of many species, calcium carbonate occurs in two different structures in a systemátic fashion. The inner layers are made up of aragonite, the orthorhombic form of $CaCO_3$ while the outer layers have its hexagonal form, calcite. This specific disposition has been attributed to stereochemical aspects. The difference between the modifications of $CaCO_3$ arise from the way in which $[CO_3]^{2-}$ anions are distributed. In calcite these are distributed parallel to each other in the plane {0001} while in aragonite they are arranged on top of each other to form columns along the *c*-axis. By virtue of the oxygen atoms being disposed in planes which are parallel to those in which calcium atoms are placed, the preferred epitaxial plane will be the basal plane of calcite. Any matrix surface which provides an opportunity for matching the Ca-Ca distances will preferentially nucleate the crystal and select either calcite form or aragonite form depending upon the anion orientations.

Cellular Processing

Three dimensional organisation of the organic matrix polymers such as collagen in bone is only one of the ways for the creation of larger structures through biomineralisation . In many organisms, cellular intervention takes place to bestow unusual shapes and textures to the crystals and their assemblies. Such processes have been observed in diatoms which have a siliceous exoskeleton. During the preorganisation regime, large areolar vesicles are secreted and attached to the membrane wall. These vesicles are arranged into a thin polygonal foam. Silica deposition vesicles are now formed with microtubules around the boundary spaces of the areolar vesicles. Mineralisation of the microtubular vesicles then occurs to yield an open geometric mesh of mesopores. The mineralised walls thicken by the extension of the silica deposition vesicle in association with endoplasmic reticulum. The process is repeated after the areolar vesicles detach themselves from the cell membrane wall. The process continues until the pores become nanosized. Intracellular events thus play an important role and give rise to organisational motifs.

Larger scale organisation is also influenced by constraints of crystal growth. For example, whenever the crystal exhibits a preferential growth direction, as discussed in the case of calcite in bones, the vesicles are elongated in the direction of rapid growth and yield elongated architectures. In other instances, the vesicular morphology dominates and the crystal forms are not easily related to the underlying crystal structure. Examples are also known where some structures are built, transported and reorganised to meet specific needs of the organism. Examples are provided below.

Growth of Bacterial Magnetite

Magnetotactic bacteria synthesise and assemble magnetite (Fe_3O_4) crystals into linear chains to maintain a magnetic dipole along the cell axis in order to orient themselves in the geomagnetic field . For example, a 3 mm long cell of *A. magnetotacticum* has about 20 intracellular particles forming a chain along the length of the cell. Each particle has a diameter of about 40-50 nm [9]. These cells synthesise the magnetite under microaerobic conditions after concentrating iron to the extent of 20-30,000 times in their surroundings. Electron microscopic and Mossbauer studies of the cells have shown that the crystallisation of the magnetite occurs in localised regions of the cell. Initially an amorphous gel of hydrated iron oxide is formed and the magnetite crystals nucleate and grow into the amorphous region. The resultant crystals often have a single domain and possess an octahedral morphology. The crystals exhibit a texture and align themselves with the [111] direction parallel to the chain axis.

Crystal Assembly in Coccoliths

Coccoliths are the calcite plates formed in unicellular phytoplanktonic algae. Extensive studies on sediments in the seas have shown that the mechanism of crystal nucleation and assembly has not changed in over 200 million years implying that nature has found the optimum route for their synthesis and that the underlying mechanisms are simple enough to be reproduced without faults. The coccolith grows by the assembly of a ring of single crystals of calcite that alternate in orientation. The complex structures produced are characteristic of the genus and are sufficiently reproducible in each case to enable classification of the species. The entire process of constructing the complex coccolith morphology from single crystals of calcite involves seven stages [10].

The various examples and mechanisms discussed so far clearly bring out the three stages in biomineralisation *viz.*, supramolecular preorganisation, interfacial recognition and cellular processing. It is now being recognised [7] that the first two steps enable us to synthesise nanocrystals, while supramolecular organisation coupled with cellular processing can help in microstructural fabrication. Interfacial recognition and cellular processing will enable crystal engineering. Biomimetic strategies being explored are based on this understanding.

STRUCTURAL HIERARCHY AND DESIGN IN NATURE

The formation of crystals of minerals and their organisation is but one of the fascinating aspects of nature's materials synthesis. The distribution of the crystals also meets the additional requirements of imparting desired mechanical and other properties to living organisms. Mattheck [11] has highlighted this aspect in a recent review and emphasised that millions of years of ruthless selection procedures have left only those biological structures that have adapted to the demands. These are also endowed with adaptive mechanisms that are responsive to changing needs. A study of trees and bones, both of which carry loads, has indicated that biological load bearing structures optimise to ensure constant stress distribution. Thus, trees detect local increase in stresses through the cambium and heal by forming locally thick tree rings while bones can both increase the thickness in high stress areas and shrink in areas where the stress is subcritical. The response of biological load bearing structures to external stresses is thus characterised by the effort to maintain a constant stress.

Natural evolution has also enabled biological structures to tailor their microstructure. It is observed that bamboo, which is a composite material, is reinforced by fibres. They are distributed unevenly across the cross section. Fibre density is high at the periphery and low in the inner regions. Similar behaviour is observed in corn. In barley columns on the other hand the number of honeycomb cells is higher on the outside than inside. Such gradients enable these tall and slender structures to withstand high bending stresses generated during high winds. Besides the entire assemblage of the important constituents has a hierarchy of scales. The cellulose fibres in bamboo are mesoscopic while the cellular structures are microscopic. The vascular bundle sheath has dimensions in the domain of 1-100 mm while the diameter of the bamboo and the distance between it's nodes can be several tens of centimetres [12]. This wide variation in the structural component size imparts the much needed flexibility and strength.

LEARNING FROM NATURE

Studies on biomineralisation have emphasised the following aspects :

a) biominerals are generated by the replication of patterned organic aggregates
b) under constant vesicular shape, the inorganic pattern produced is a transcription of the self-assembled organic architecture
c) it is possible to form continuous structures by confining the mineralisation to interstitial spaces in vesicular foams through cellular mediation.

Attempts are now being made in the area of biomimetics to use this knowledge in developing newer strategies/ modifying existing methodologies for materials synthesis. These have been enumerated by Mann and Ozin [13] and can be grouped into the following categories.

Transcriptive Synthesis

The final form of the inorganic structure assembled from crystals of the mineral corresponds closely to the self assembled organic structure. Much of the information required for the formation of the inorganic crystals is present in the interface. Nucleation and growth of the crystals at the interface lead to mineralisation and replication of the organic preform. Simple tubular, lamellar, mesoporous and thin film structures can be formed by this route. The rate controlling step is often the transport of the ions through the wall of the vesicle and this form of synthesis yields relatively low volume fractions of the mineral.

Synergistic Synthesis

As the name implies a certain synergistic interaction takes place between the organic and inorganic constituents present in the reaction media. The initial self-assembled system and that resulting from the mineralisation coadapt. Mesoporous silica and metal oxide phases are known to be synthesised in this fashion. The extent to which coadaptation occurs is controlled by thermodynamic and kinetic considerations and is sensitive to the stoichiometry and chemical potentials of the reactants. It has been observed that at a high supersaturation of silicate species, phase separation occurs through the formation of amorphous silica while too low concentrations result in soluble phases. It is at intermediate concentrations that lamellar, hexagonal and cubic arrays are stabilised.

Metamorphic Reconstruction

In this form of synthesis, the replica formed from the coassembly undergoes changes which are relatively small. Very often the reorganisation is driven by surface energetic considerations. Larger changes in the form and scale of the replicated patterns may also occur if the self organised reaction environment can undergo restructuring during inorganic crystallisation. This process of coassembly→replication→reconstruction is found to be operative in the formation of microskeletal calcium phosphate.

As can be seen, some of these methods are already in vogue while others are a result of the study of biomineralisation. We shall now illustrate the strategies being adopted with a few examples.

Synthesis of Iron Sulphide with the Aid of Ferritin

Meldrum *et al.,* [5] used the iron storage protein for the synthesis of iron sulphide. In their experiments H_2S was bubbled through a suitably buffered solution (pH = 8.5) of ferritin. The solution turned black within 20 s and no precipitation was observed in the solution. Similar changes were observed on the addition of sodium sulphide at a pH of 8.0. Electron microscopy revealed that, in both cases, iron sulphide was formed within the supramolecular cages of ferritin. Precipitation with the aid of H_2S was rapid and the crystals were irregular while they were spherical at the end of a slow reaction with Na_2S. This successful attempt at using biological molecules for the production of nanometric inorganic crystals is a new approach and confirms that some of the biological routes can be imitated in the laboratory.

Production of Semiconducting CdS

Using a liquid-crystalline phase as a template, Braun *et al.,* [14] synthesised ~100 nm particles of CdS in an organic phase consisting of hexagonally close-packed tubules of self assembled amphiphiles. The organic phase was formed by using oligoethylene oxide oleyl ether and water. Initially the organic phase was doped with a 0.1M cadmium diacetate dihydrate and H_2S was allowed to flow through. On diffusion of H_2S into the tubules of the organic phase, CdS and acetic acid are formed. Such semiconductor-organic composites, when tailored suitably, are expected to have applications in the area of photosynthesis and photocatalysis.

With a view to mimic biosynthetic mechanisms, Bianconi *et al.*[15], chose polyethyleneoxide as the polymer matrix. Cadmium was added in the form of $CdCl_2$.

Recently, Dameron *et al.*[16], reported the synthesis of monodispersed CdS particles of 2 nm using yeasts [*Candida glabrata* and *Schizosacharomyces pombe*] cultured in the presence of cadmium salts. These yeasts used the commonly occurring γ-glutamyl peptides and these experiments have raised the hope of synthesising quantum crystals with size dependent and discrete excited electronic states.

Mesolamellar Aluminophosphates

It is to be noted how some organisms synthesise elaborate exoskeletons whose length scales may extend upto millimetres. Recently, Oliver *et al.*[17], reported the synthesis of lamellar aluminophosphate structures that imitate natural exoskeletons using self assembled organic templates. The model proposed by them to explain the observed microstructure has many common features when compared with biomineralisation.

Hollow Porous Shells of Calcium Carbonate

Walsh *et al.*[18], developed hollow spherical shells of a honeycomb architecture using oil–water–surfactant microemulsions and micron-sized polystyrene beads as substrate for the emulsion. The bicontinuous microemulsion was supersaturated with calcium bicarbonate and a surfactant at the oil-water interface. A few drops of the emulsion were spread on a metallic substrate and washed with hot chloroform or hexane followed by drying in air . Scanning electron microscopy showed that extensive networks of a honeycomb microstructure made up of aragonite. The interspersed pores were irregular and columnar. Their geometry could be manipulated by varying the water to oil ratio. Hollow spheres of $CaCO_3$ could be fabricated by coating the emulsion on polystyrene spheres. A hierarchy of structures could thus be produced with the carbonate being crystalline at the unit cell level, cellular at the mesophase level and spherical at the microscopic level.

In this process of generating periodic structures with the aid of surfactant/inorganic materials, the electrostatic complementarity between the organic ions in solution, the charged head groups of the surfactant and the inorganic ions is the key to the assembly process. Huo *et al.*[19], have studied the principles underlying the synthesis of mesostructured surfactant/inorganic biphase areas and identified four different path ways. These are

a) direct condensation of anionic inorganic species with a cationic surfactant

b) condensation of a cationic inorganic material with an anionic surfactant

c) condensation of cationic inorganic species with cationic surfactant d` condensation of anionic inorganic species with anionic surfactant.

In the last two cases it is necessary to have solution species that have a charge opposite to that of the surfactant. They can be formed from Cl^-, Br^-, Na^+, K^+ such that species of the type $Su^+ Cl\text{-}Na^+$ or $Su^- Cl^- Na^+$ where Su stands for the surfactant formed. They confirmed the possibilities with aid of a variety of surfactants including lipids and zwitterionic types. It was concluded that temporal and spatial control of the biphase and interface assembly processes in cooperative templating is essential for the production of periodic arrays.

It has been found [20] that freshly cleaved mica can also be used as a template for the production of mesoporous silica. Mica consists of double layers of tetrahedral SiO_4/AlO_6 building blocks sandwiching a single layer of octahedral AlO_6 units. When cleaved the surface exposes flat tetrahedral base with the overall surface having hexagonal symmetry. Under acidic conditions the surface offers anchoring sites for SiOH for binding to silica -surfactant micellar precursor species. Further reactions lead to the formation of the mesoporous film.

CONCLUSION

An attempt was made to briefly summarise the recent attempts at understanding the synthesis of inorganic materials in living organisms and trying to reproduce the methodologies under laboratory conditions. Considerable success has been achieved in this direction and novel techniques and materials are being continuously explored and synthesised respectively. Growing interest in nanostructured materials for microelectronic applications and continuing demand for the production of mesoporous structures for catalytic and molecular sieve applications is driving research in this area. Materials scientists have the added interest due to the existence of hierarchical structures ranging from crystal structure at the smallest level to microstructure at the microlevel through periodic organisation at the mesoscale. Biomimetics as a science has taken firm route and will bring together biologists, chemists and materials scientists for the synthesis of intelligent materials.

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