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The Biomimetic Mineralization Closer to a Real Biomineralization

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1. Introduction

In view of the huge timeframe Nature has to optimize and perfect functional materials to survive during the evolution and natural selection, as a result, biominerals, the organic-inorganic hybrid materials are formed through biomineralzation, one of the most important processes for the organisms to produce for a variety of purposes, including mechanical support, navigation, protection, and defense (Lowenstam & Weiner, 1989; Stupp, et al., 1993; Weiner & Addadi, 2003). These biomaterials are generally molded into specifically designed devices with fascinating properties of superior materials properties and environmentally friendly synthesis and biocompatibility (Xu, et al., 2007) , in which the structure, size, shape, orientation, texture, and assembly of the constituents are precisely controlled over several hierarchy levels. Therefore, the understanding and ultimately mimicking of the processes involved in biomineralization may provide new approaches to the fabrication of specialized organic-inorganic hybrid materials, in other words, nature provides a perfect model for people to design and fabricate novel materials with special structures and functions through the biomimetic mineralization method (Mann, 2000).

Based on these ideas a rapidly developing research field has evolved, which can be summarized as bioinspired or biomimetic materials chemistry (Mann, 1995; Cölfen & Yu, 2005), is meanwhile already an important branch in the broad area of biomimetics (Mann, et al., 1993; Davis, et al., 2001; Cölfen, 2003; Meldrum, 2003; Yu & Cölfen, 2004). As the research is continuously developed, the main aim to mimic the syntheses of these biominerals, is not only to emulate a particular biological architecture or system, but also to abstract the guiding principles and ideas and use such knowledge for the preparation of new synthetic materials and devices (Dujardin & Mann, 2002). During the past decades, exploration as well as application of these bio-inspired synthesis strategies has resulted in the generation of complex materials with specific size, shape, orientation, composition, and hierarchical organization (Archibald & Mann, 1993; Antonietti & Göltner, 1997; Yang, et al., 1997; Li, et al., 1999; Estroff & Hamilton, 2001; Jones & Rao, 2002; Cölfen & Mann, 2003; Dabbs & Aksay, 2003; Aizenberg, 2004). The human efforts in the fields of chemistry and materials science have led to the development of a complementary set of inorganic and hybrid materials with special characteristics. However, by mimicking the design and synthesis of, e.g., biomaterials, to date no synthetic materials have evolved that show properties which are superior to those found in their natural counterparts (Sommerdijk & With, 2008). It is

evident that the understanding and ultimately the mimicking of the processes involved in biomineralization has been a motivation for humans to copy Nature and to adapt ideas from Nature to achieve functional, aesthetic, and societal value (Mann, 2000; Xu, et al., 2007), and it still has a long way to go. A proper biomimetic system closer to a real environment and process of biomineralization is necessary to both understand the mechanism of biomineralization and instruct materials synthesis using biomimetic mineralization approaches (Towe, 1990).

Many methods have been established to study and mimic the biomineralization process with the aim to synthesize superstructures that mimic natural biominerals and to gain an insight into the biomineralization mechanism. Among these approaches, as shown in Fig. 1, organic Langmuir monolayer (b) has an obvious structural feature of approximation to half of the bilayer structure of a biomembrane (a), as a result, organic Langmuir monolayer has been often used as a convenient model to approach the two-dimensional structure of biomembrane (Stine, 1994; Gzyl-Malcher & Paluch, 2008). For this, Langmuir monolayer usually can serve as an ideal model system for simulating and studying biomacromolecules and biomacromolecule-controlled mineralization at the air-water interface. Therefore, it has been widely used as the organic templates in the research of biomimetic mineralization to guide the growth of inorganic crystals with special structural features and to better understand the interface nature of organic-mineral interface and what occurs at the interface between organic molecules and inorganic materials (Mann, et al., 1988; Heywood & Mann, 1992; Heywood, 1992; Mann, et al., 1993; Heywood & Mann, 1994; Mann & Ozin, 1996; Mann, 2001; Zhang, et al., 2004; Amos, et al., 2007; Popescu, et al., 2007; Pichon, et al., 2008).

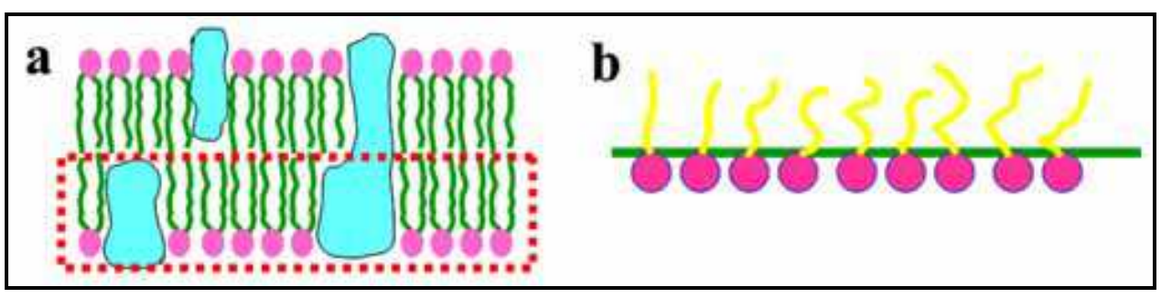

Fig. 1. The schematic diagrams of a biomembrane (a) and a Langmuir monolayer (b).

There has been so much biomimetic mineralization research in the past several decades using many kinds of Langmuir monolayer template system, such as small organic molecules, polymers, cells of organisms and so on. However, the proteins, the most important and the most frequently presented matrix in the biomineralization process of organisms, have not been researched enough in the biomimetic mineralization in a manner of Langmuir monolayer.

On the other hand, in the usual research of biomimetic mineralization, the regulation of organic Langmuir monolayer on the nucleation and growth of inorganic materials has been researched extensively as the important foundation of biomimetic synthesis. However, as an equally important factor for the special structural features of the biominerals in the real environment and process of biomineralization, the kinetic control of inorganic crystals growth in the biomimetic mineralization system has not gotten due diligence.

Fortunately, these two problems have attracted more and more attention in the recent years. The protein Langmuir monolayer and the kinetic control factor has been gradually

introduced into the systems in order to make the biomimetic mineralization much closer to a real environment and process of biomineralization, which on the one hand provides a perfect model for biomineralization research; on the other hand, more opportunities to get inorganic materials with special structural features can also be obtained through introducing more conditions of controlling on the basis of a usual organic template system, providing an effective experimental method for controllable fabrication of functional materials. So in this chapter, particular emphasis is placed on what has been accomplished in the research on both the biomimetic mineralization of calcium carbonate under a protein, especially bovine serum albumin (BSA) Langmuir monolayer and the novel biomimetic interface system named dual-template approach in which the inorganic materials are grown under a Langmuir monolayer in the presence of kinetic control generated from ammonia diffusion.

2. Biomineralization and biomimetic mineralization of calcium carbonate under a protein Langmuir monolayer

2.1 Biomineralization and biominerals

Biomineralization is the process by which living organisms secrete inorganic minerals in an organized fashion with exceptional physical properties, by virtue of finely controlled microstructure, morphology, and hierarchical organization of the minerals and accompanying organic material (DiMasi, et al., 2003; Xu, et al., 2007). It is already a rather old process in the development of life, which was adapted by living beings probably at the end of the Precambrian more than 500 million years ago (Wood, et al., 2002). There are more than 60 biologically formed minerals identified, examples include iron and gold deposits in bacteria and other unicellular organisms, silicates in algae and diatoms, carbonates in diatoms and nonvertebrates, and calcium phosphates and carbonates in vertebrates (Boskey, 2003).

Biominerals formed through biomineralization process are highly optimized materials with remarkable structural features and functional properties, which attracted a lot of recent attention. Fig. 2 shows three kinds of typical biominerals: combination coccosphere (a), the silica wall of the marine benthic diatom Amphora coffeaeformis (b), and a part of the skeleton of a brittlestar Ophiocoma wendtii (c). Obviously, the abilities to design and construct those inorganic materials with specified atomic structure, size, shape, orientation, and number of defects and to integrate these architectures into functioning devices is an important foundation for the survival of the organisms. These inorganic biominerals provide a wonderful and peerless foundation for advances in technologies that rely on the devices' electrical, optical, magnetic, and chemical outputs. Their formation and impressive properties have inspired chemists to take a biomimetic approach to the synthesis of materials. However, assembly methods that allow simultaneous control of these features at lengths from the nanometer scale to the macroscale is still extremely difficult to replicate synthetically for scientists and engineers. The ability to build architectures with such control would consequentially bring many new areas of technology—some already enumerated in the literature and others the outcomes of unanticipated surprises that are the direct consequences of the precision in assembly (Davis, 2004).

If there were constructors that could sequester inorganic ions from water, accumulate and concentrate them to produce architectures controlled over length scales from nanometers to tens of centimeters, and do all of this in a matter of hours at ambient temperatures (Davis,

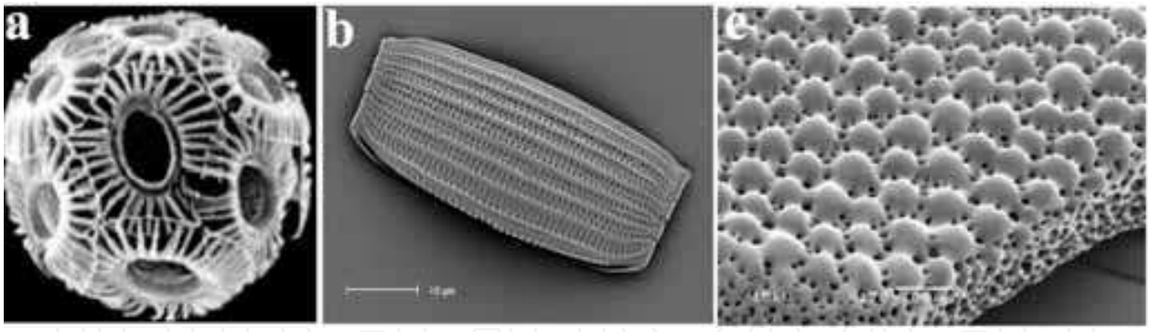

Fig. 2. Selection of biomineral structures. Each of them performs a specific function. a: Coccoliths calcite plates on the exterior of a single celled coccolithophorid alga, Emiliania huxleyi. Coccoliths are thought to provide protection against grazing, improve buoyancy, and scatter light to protect against damage from intense UV as well as improving light capture for species at depth (Cusack & Freer, 2008) (from Ref (Young, et al., 1999) with permission). b: Intricate walls. Scanning electron micrograph of the silica wall of the marine benthic diatom Amphora coffeaeformis. Note the ornate structure, patterning, and porosity of the silica wall (from Ref (Wetherbee, 2002) with permission of professor Richard Wetherbee). c: Scanning electron micrograph (SEM) of a part of the skeleton of a brittlestar Ophiocoma wendtii (Ophioroidea, Echinodermata). The entire structure (the mesh and the array of microlenses) is composed of a single calcite crystal used by the organism for mechanical and optical functions (Aizenberg, et al., 2001) (from Ref (Aizenberg, et al., 2003). (Reprinted with permission from AAAS).

2004), obviously, they will present an excellent model and bring a bright future for material science. In fact, such constructors are not inventions of science fiction novels but rather unicellular microalgae called diatoms with highly sculpted walls of silica. Because living cells must constantly interact with their environment, the diatom walls have myriad openings (such as pores and slits) that facilitate such exchanges (Aizenberg, Muller et al., 2003). The intricate patterns and symmetries (Fig. 2b) are species-specific and genetically determined (Pickett-Heaps, et al., 1990). And Kröger et al. (Kröger, Lorenz et al., 2002) have also found that silaffins have been implicated in the biogenesis of diatom biosilica and are crucial for the formation of these diatom walls. It is also found by Aizenberg et al. (Aizenberg, et al.,, 2001) that certain single calcite crystals (Fig. 2c) used by brittlestars for skeletal construction (Wainwright, et al., 1976; Lowenstam & Weiner, 1989) are also a component of specialized photosensory organs, conceivably with the function of a compound eye. The analysis of arm ossicles in Ophiocoma (Hendler & Byrne, 1987) shows that in light-sensitive species, the periphery of the labyrinthic calcitic skeleton extends into a regular array of spherical microstructures that have a characteristic double-lens design to minimize spherical aberration and birefringence and to detect light from a particular direction. The optical performance is further optimized by phototropic chromatophores that regulate the dose of illumination reaching the receptors. These structures represent an excellent and astonishing example of a multifunctional biomaterial with both mechanical and optical functions (Aizenberg, et al., 2001). It illustrates a remarkable example of organisms, through the process of evolution, to optimize one material for several functions, and provides new ideas for the fabrication of smart materials (Mann & Ozin, 1996; Belcher, et al., 1998).

Biological materials constitute most of the body of plants and animals around us. They allow cells to function, eyes to capture and interpret light, plants to stand up to the light and animals to move or fly. This multitude of solutions has always inspired mankind to make materials and devices, which simplify many of our day-to-day functions (Fratzl, 2007). However, the design strategies of biominerals are not immediately applicable to the design of new engineering materials, since there are some remarkable differences between the strategies common in engineering and those used by nature (Fratzl, 2007). Firstly, the range of choice of elements in natural materials is much less than that in manmade materials. Natural materials consist of relatively few constituent elements that are used to synthesize a variety of polymers and minerals, but human use many more elements. Secondly, manmade materials usually require high temperatures for fabrication but biological organisms have no access to them. For example, the diatom silica walls and single calcite crystals of skeleton of brittlestar with high degree of complexity and hierarchical structures are just achieved under mild physiological conditions. Meanwhile, nature grows both the material and the whole organism using the principles of biologically controlled self-assembly according to a recipe stored in the genes, rather than being fabricated according to an exact design, which is usually the basic principle for manmade materials (Fratzl, 2007). Therefore, the improved understanding of biomineralization process will unambiguously lead to the creation of better technologies (Davis, 2004). For example, some structures produced by biomineralization have superior properties to those of man-made counterparts. Nacre, the mother-of-pearl layer found on the inner surface of shells, has fracture toughness approximately 3000 times that of the synthetic analogue aragonite (Zaremba, et al., 1996). Nacre is composed of thin (circa 30 nm) layers of a protein-polysaccharide intercalated between 0.5-μm-thick layers of aragonite tablets. The weak interface between the organic and inorganic layers is thought to dissipate the energy of crack propagation and thus strengthen the composite structure. Recently, Much et al. (Munch, et al., 2008) emulate Nature's toughening mechanism through the combination of two ordinary compounds, alumina oxide and polymethylmethacrylate, into ice-template structures whose toughness can be over 300 times that of their constituents. This sophisticated architecture provides clues as to how man-made structures can be improved. It should be mentioned that biological structures are a constant source of inspiration for solving a variety of technical challenges in materials science (Jeronimidis & Atkins, 1995). Careful investigation of a biological system serving as the model is necessary for biomimetic materials research, as the elementary step, the design and construction of biomimetic mineralization system closer to native biomineralization process is a promise and important way to understand basic mechanism of biomineralization and get man-made materials with structural and functional features closer to the biominerals.

2.2 Biomimetic mineralization of calcium carbonate under a bovine serum albumin (BSA) Langmuir monolayer

The basic building blocks available to evolution when deciding skeletal structure are just Ca^{2+} and HCO_3^- or HPO_4^{2-}, this dichotomy is resolved when vertebrates evolve utilizing phosphate and (most) invertebrates evolve utilizing carbonate (Cusack & Freer, 2008). However, Nature has created a staggering diversity of perfect structures in the carbonate zone and continuing evolutionary masterpieces in the vertebrates using so limited fundamental building blocks. The secret to this diversity is the inclusion of organic materials, such as protein, carbohydrate and lipid as the thread to stitch together

complicated structures from a simple cloth through biomineralization process (Cusack & Freer, 2008). Just as mentioned above, the success of diatoms in processing silica results from specific interactions at the organic-inorganic interface, between highly modified peptides called silaffins and silica (Kröger, et al., 2002). It is the variety of biomineral ultrastructures and chemical compositions, in combination with the organic components that ultimately determines the physical and material properties of these biocomposites, facilitating the specific functions (Cusack & Freer, 2008).

In pursuit of comparable synthetic materials, the processes by which minerals nucleate from solution in the presence of organic species have been under intense study in recent years, because it is clear that the organic matter controls and defines the end product in biomineralization (DiMasi, et al., 2003). One of the most challenging scientific problems is to gain greater insight into the molecular interactions occurring at the interface between the inorganic mineral and the macromolecular organic matrix. Many studies have been devoted to the putative mechanisms underlying the formation of highly organized mineral structures in molluscs and similar organisms. Due to the various experimental difficulties of observing crystal growth in living molluscs, scientists have sought out suitable model systems for mimicking biomineralization processes to reflect the mineral/matrix interactions active at the atomic or molecular level of structural complexity (Fricke & Volkmer, 2007). Seminal contributions were made by Mann and Heywood, who studied the controlled nucleation and crystallization of $CaCO_3$ under Langmuir monolayers of stearic acid (Mann, et al., 1988), which should be considered as extremely important work, as it placed the use of Langmuir monolayer studies, a technique well established in the field of physical chemistry in past century, now in the context of biomineralization. Importantly, the work noted that partially compressed Langmuir monolayers were optimal in inducing crystal formation, which was related to the possibility that the stearate molecules would adopt a Ca-induced local ordering resulting in a configuration tailored for nucleation of these crystals. This paper clearly is the onset for a large number of papers using Langmuir monolayers to study the nucleation of calcium carbonate and other minerals (Sommerdijk & With, 2008). As a general advantage, the biomimetic mineralization system using Langmuir monolayer as organic template allows for creating conveniently a smooth and clean interface and for depositing a measured quantity of amphiphilic molecules in a highly controlled way, the average area per molecule can be easily adjusted by a movable barrier, and the surface pressure is monitored by a pressure sensor. In many cases it is straight-forward to obtain a first approximation model to half of the bilayer structure of a biomembrane. All of these features make it possible to research precisely the structural relation between the organic matrixes and inorganic crystals. $CaCO_3$ is not only one of the most abundant biominerals, but also the mineral of choice for fundamental studies on template–mineral interactions due to its sensitivity to template effect (Dey, et al., 2010). Therefore, the model system of crystallization of calcium carbonate underneath Langmuir monolayer is often regarded as a straight-forward experimental approach toward biomimetic mineralization (Fricke & Volkmer, 2007).

Although the mechanisms by which organisms generate mineral crystals are not well understood, there is widespread belief that proteins play important roles. Thus, biomineralization can be seen as an interfacial phenomenon in which (usually extracellular) proteins interact with nascent crystals in order to control their growth (Hunter, et al. 2010), and Calcium carbonate grown under a Langmuir monolayer of protein should be a perfect model closer to a real biomineralization to get more insight on the mechanisms of

biomineralization. As mentioned above, as one of the most important substances in the organisms, proteins are often implicated in the biomineralization. Proteins both collect and transport raw materials, and consistently and uniformly self- and co-assemble subunits into short- and long-range-ordered nuclei and substrates (Lowenstam & Weiner, 1989; Sarikaya, et al., 2003). Whether in controlling tissue formation, biological functions or physical performance, proteins are an indispensable part of biological structures and systems. A simple conclusion is that next-generation biomimetic systems should include proteins in synthesis, assembly or function (Bayley & Cremer, 2001; Sarikaya, et al., 2003). And proteins have widely been used for preparation of inorganic materials by biomimetic method. Comprehensive reviews on the synthesis of inorganic nanomaterials mediated by proteins assemblies (Behrens, 2008) and peptides (Chen & Rosi, 2010) have been given by Behrens and Chen et al., respectively. On the other hand, it is also important and necessary that proteins are introduced in the mineralization mimic and biomimetic syntheses research in appropriate manner closer to the real biomineralization process because of the special features of proteins, e.g., the large diversity of natural and synthetic proteins and their adjustability provide high probability that proteins recognize, interact with, and direct the formation of many inorganic materials. More importantly, the motivation and advantage using protein Langmuir monolayer as organic template for biomimetic mineralization is that it is easy to realize the structural changes of the protein molecules by simply controlling the surface pressure, which provides a great convenience for researching the influence of structural changes of protein molecules on the structural formation of biominerals.

Bovine serum albumin (BSA) is a popular candidate for biomimetic studies because some of the sequence characteristics is native to biomineralization proteins, at the same time, it is in readily available and inexpensive (Dickerson, et al., 2008). Xue et al. (Xue, et al. 2009) researched the templated crystallization of calcium carbonate nanoparticles beneath the Langmuir monolayer of bovine serum albumin (BSA). Through researching the area–time curve of BSA Langmuir monolayer on the supersaturated $Ca(HCO_3)_2$ solution subphase, they found that it takes about 18 min for the BSA Langmuir monolayer to be compressed to a surface pressure of 15 mN m^{-1}, and the area between the two barriers decreases as much as 26% during keeping the surface pressure at 15 mN m^{-1} for 1 h, which means the area per molecule has a 26% decrease during the crystallization of calcium carbonate. Such a decrease is closely related to the structural flexibility of the BSA Langmuir monolayer. The interaction between the BSA molecules and the Ca^{2+} ions in the subphase solution can affect the structure self-regulation of the BSA monolayer along with the formation of the inorganic crystal. Simultaneously, the structure self-regulation of the BSA monolayer affects in turn the formation of the inorganic crystal as well. The formation of the $CaCO_3$ crystals beneath the BSA Langmuir monolayer can be thought as a mutual-correlating, influencing, and adjusting process, where the key worth of special emphasis is that the structural flexibility of the BSA Langmuir monolayer helps to provide enough room for the $CaCO_3$ crystals to modulate and self-regulate their structure. BSA molecule contains charged amino acids such as 41 aspartic acids, 58 glutamic acids, and 60 lysine arrayed along certain directions at the interface between the BSA Langmuir monolayer and subphase solution. In addition to the putative BSA cation-binding by Asx residues, the presence of Lys and Arg residues may provide active sites for interaction with carbonate counterion. These acidic and basic residues, in conjunction with Ser and Glx residues, also provide active sites for hydrogen-

bonding with water, and the presence of Gly residues generate considerable flexibility along the protein backbone (Xue, et al., 2009). The BSA molecules usually tend to have α-helix conformation when being spread onto the air/water interface. The Ca^{2+} ions in (104) plane has the similar structure of orthogonal repeat units to the α-helix conformation, which provides convenience for their structural regulation to grow along the (104) plane, while the template and structural adaptability play a key role in the oriented crystallization of $CaCO_3$ (Xue, et al., 2009). In the experiments, the transformation of calcium carbonate from unstable amorphous calcium carbonate (ACC) phase to stable calcite crystals was also observed, indicating a multistep crystallization process found in other biomimetic mineralization of calcium carbonate crystals (Xu, et al., 1998; Pouget, et al., 2009).

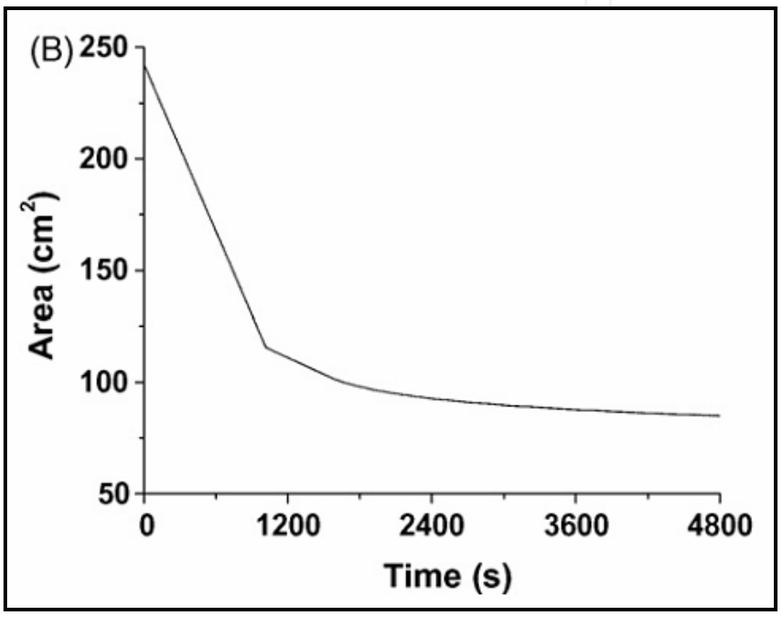

Fig. 3. The area–time curve of BSA Langmuir monolayer compressed and kept for 60 min on calcium bicarbonate solution subphase (from (Xue, et al., 2009) with permission).

Aside from the BSA Langmuir monolayer, some factors such as pH, temperature, and supersaturation degree also play key roles in controlling the growth and morphologies of $CaCO_3$ crystals. As one of the thermodynamic driving forces, the supersaturation degree is the most decisive parameter for crystallization process and has a different subphase concentrations. The influence of different subphase concentrations on the growth process and morphology evolution of calcium carbonate crystals under a BSA Langmuir monolayer was investigated (Xue, et al. 2009). The morphologies of the $CaCO_3$ crystals grown under the BSA Langmuir monolayer experienced a great evolution from disk-like calcite particles with an average diameter of 0.75 μm at a subphase concentration of 2.5 mM (Fig. 4a, b), to bowknot-like calcite particles formed at 5.0 mM (Fig. 4c, d), and to hexagonal-shaped morphology with a size of 16–18 μm at 7.5 mM (Fig. 4e, f). The result shows that the concentration is a key factor for the structural control in the biomimetic mineralization systems. Certainly, further work is needed to reveal the role of the BSA Langmuir monolayer and subphase concentration in the nucleation and growth process of calcium carbonate in more details (Xue, et al., 2009).

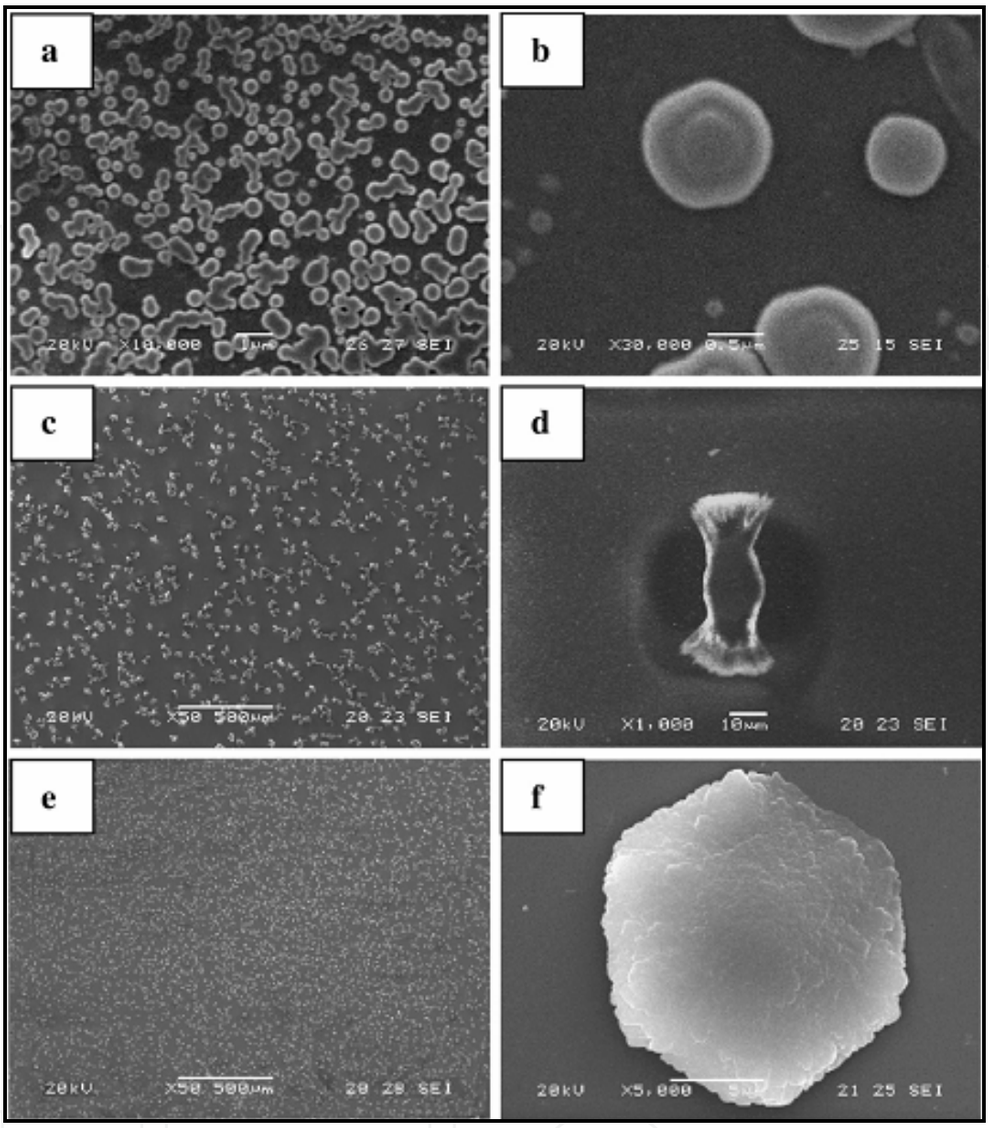

Fig. 4. SEM images of calcium carbonate formed at different subphase concentrations: (a and b) 2.5 mM, (c and d) 5.0 mM, (e and h) 7.5 mM from ref (Xue, et al., 2009) with permission.

3. Biomimetic mineralization in the presence of kinetic control from ammonia diffusion

Biomimetic synthesis inspired from biomineralization has recently been attracting more and more attention as a green and environment-friendly method, developing to be a multi-disciplinary hot spot. In the usual research of biomimetic mineralization, the regulation of organic Langmuir monolayer on the nucleation and growth of inorganic materials is considered and researched as the important foundation of biomimetic synthesis. However, as an equally important factor for the special structural features of the biominerals in a real biomineralization, the kinetic control of inorganic crystals growth has not gotten enough attention.

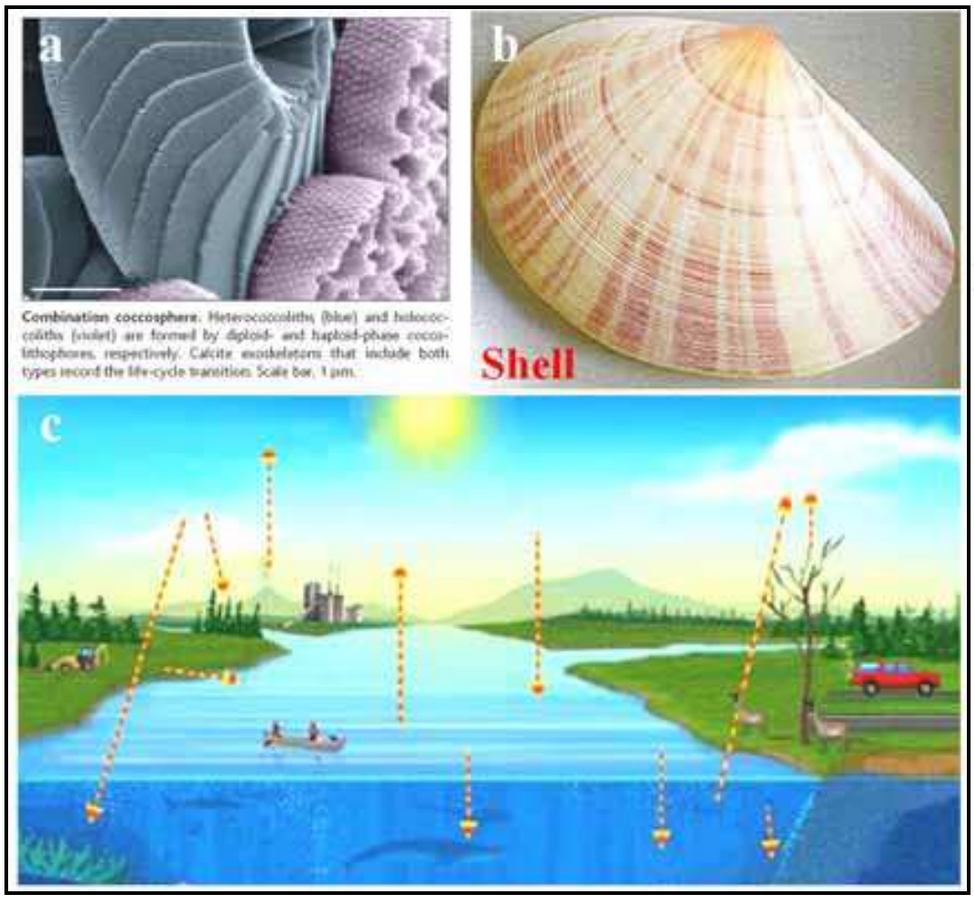

Fig. 5. Calcite of coccosphere (a) (from (Davis, 2004) with permission), shell (b), schematic circle diagram of carbon dioxide in nature (c).

In fact, the growth of natural inorganic biominerals is also regulated by the kinetic control except of the regulation of organic matrix that is emphasized in the usual biomineralization and biomimetic research. As shown in Fig. 5, both the calcite of coccosphere (a) (Davis, 2004) and shell (b) show perfect structural features. What's the most important, they both present specific properties, e.g., nacre, the mother-of-pearl layer found on the inner surface of shells, has fracture toughness approximately 3000 times that of the synthetic analogue aragonite, and such a mechanical capacity results from the organic components and its special formation (Zaremba, et al., 1996). While the special formation results from the kinetic control as well as the genetic regulation and the participation of organic components. Fig. 5c is a schematic circle diagram of carbon dioxide in nature. Statistics show that the carbon dioxide concentration in the atmosphere is much less than that of human emissions and a large part of carbon dioxide is absorbed by the oceans (Ridgwell, et al., 2003). Carbonic anhydrase exists in the body of many sea creatures can catalyze the transformation reaction between carbon dioxide and hydrogen carbonate. Under the nucleation and growth control of the organic matrix, the calcium ions in the body combine with the hydrogen carbonates and finally form those biominerals with sophisticated architecture and special properties. In such a process, the slow catalysis of transformation from carbon dioxide to hydrogen carbonate plays a key role on the structures of inorganic crystals. Obviously, the

environment and the speed of such a process have important influence on the formation and growth of inorganic biominerals. Clams, oysters and some other microbes are through this process for synthesis of shells and other hard minerals.

These natural examples indicate that the kinetic control plays an important role on the formation of special morphological and structural features for these biominerals. Therefore, more attention should be paid to the kinetic control factors in the biomimetic mineralization research. If a kinetic control can be introduced into the biomimetic growth system on the basis of regulation effect of organic template through designing novel and suitable biomimetic interface system, one hand, the biomimetic synthesis can be much closer to a real biomineralization environment, providing a perfect model for biomineralization mimic research; on the other hand, more opportunities to get inorganic materials with special structural features can also be obtained through introducing more conditions of controlling on the basis of a usual organic template system, providing an effective experimental method for controllable fabrication of functional materials. So it is meaningful for both understanding biomineralization phenomena and instructing biomimetic synthesis of inorganic functional materials.

Nanocrystalline TiO_2 (Sumerel, et al., 2003) and Ga_2O_3 (Kisailus, et al., 2005) were fabricated using a biomimetic synthesis method where silicatein, a catalytically active, structure-directing enzyme (Morse, 1999), was used as a catalyst and template for the hydrolysis and subsequent polycondensation of water stable molecular complexes of titanium and gallium to form nanocrystalline TiO_2 (Sumerel, et al., 2003) and Ga_2O_3 (Kisailus, et al., 2005), respectively. Ferroelectric $BaTiO_3$ nanocrystals were also synthesized by using an assembly of bola-amphiphile peptide, a linear type of peptide monomer with two amide head groups connected by a hydrocarbon tail group (Nuraje, et al., 2006). When a solution of the peptide monomers was added to the $BaTi(O_2CC_7H_{15})[OCH(CH_3)_2]_5$ precursor, ring-shaped peptide assemblies and tetragonal $BaTiO_3$ crystals were formed. During this process, the peptides were self-assembled into nanorings simultaneously as the precursor was hydrolyzed inside the cavity of the assembly. As the cavity size of the nanorings was a function of the pH value, the diameter of the particles could be varied from 6 to 12 nm. The surface chemical structure as well as the confinement effect of the peptide nanorings was likely to induce the unusual crystallization of the tetragonal $BaTiO_3$ nanoparticles (Nuraje, et al., 2006). By using the similar method, β-Ga_2O_3 semiconductor crystals that are known to be kinetically unfavoured to grow under ambient conditions, were successfully synthesized (Lee, et al. 2007). Where, the peptide assembly captured primary GaOOH particles, mineralized them into β-Ga_2O_3 crystals by its catalytic functions, and then fused them to grow monodisperse, single-crystalline, 50 nm particles in the cavity of the peptide assembly. It was suggested that the carboxyl groups of the peptide which were hydrogen-bonded with neighbouring amines catalyzed the hydrolysis of the gallium precursor (Behrens, 2008). Inspired by that some protein filaments shown in vitro to catalyze the hydrolysis and structurally direct the polycondensation of metal oxides at neutral pH and low temperature, Kisailus et al. (Kisailus, et al., 2006) designed and fabricated a bifunctional self-assembled monolayer surfaces containing the essential catalytic and templating elements by using alkane thiols microcontact-printed on gold substrates. The interface between chemically distinct self-assembled monolayer domains provided the necessary juxtaposition of nucleophilic (hydroxyl) and hydrogen-bonding (imidazole) agents to catalyze the hydrolysis of a gallium oxide precursor and template the condensed product to form GaOOH and the defect spinel, γ-Ga_2O_3. These methods use the similar principles borrowed from biomimetic synthesis

routes (Sumerel, et al., 2003; Kisailus, et al., 2005; Schwenzer, et al., 2006): 1) slow catalysis of synthesis from molecular precursors provides the opportunity for kinetic control; and 2) crystal growth is vectorially regulated by a template, operating in concert with kinetic control to provide spatial and temporal control of crystal polymorph, orientation and morphology. And the results indicate that the kinetic control can provide an opportunity to get the materials with special structural features.

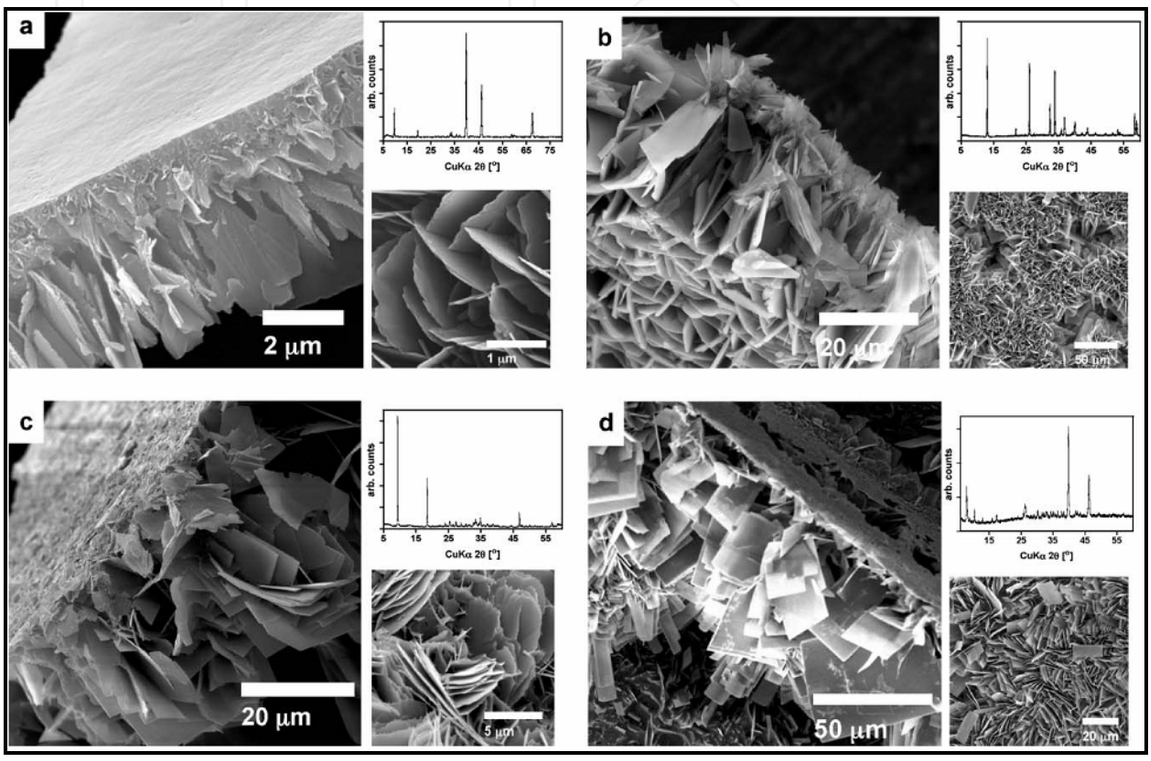

Fig. 6. Morphological and crystallographic characterization of metal hydroxide and phosphate thin films. Scanning electron microscopy (SEM; side- and bottom-view) images and XRD patterns of (a) $Co_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (hydrotalcite-like structure), (b) $Cu_2(OH)_3(NO_3)$ (rouaite structure), (c) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (hydrotalcite-like structure) and (d) $Mn_3(PO_4)_2 \cdot 7H_2O$ (switzerite structure). Peaks at 39.7° and 46.2° in the XRD spectra of (a) and (d) result from the Pt holder of the instrument (from ref (Schwenzer, et al., 2006) *Reproduced by permission of The Royal Society of Chemistry*).

However, Morse et al. (Schwenzer, et al., 2006) believe that protein filaments that catalyzed and templated synthesis of nanocrystalline TiO_2 (Sumerel, et al. 2003) and Ga_2O_3 (Kisailus, et al. 2005) will incorporate the carbon impurities and degrade the performance of the materials for device applications that require high purity materials. In order to prevent the carbon impurities originating from the use of organic template, at the same time to capture the advantage of the slow catalysis and anisotropic, vectorial control of biocatalytic crystal growth, they developed a low-temperature, solution-based method employing the slow diffusion of ammonia vapor as a catalyst or hydrolysis of metal-containing molecular precursors. The diffusion through a solution of molecular precursor can establish spatially and temporally regulated gradient of the catalyst, while the vapor–liquid interface serves as

a nucleation template. The resulting vectorially controlled combination of the molecular precursor and hydrolysis catalyst at room temperature yields a nanostructured thin film at the vapor–liquid interface. The diffusion of the basic catalyst (ammonia) into the aqueous solution creates a pH gradient that determines the morphology of the growing film, resulting in a unique structure of the film. Nanostructured $Co_5(OH)_8Cl_2 \cdot 3H_2O$, $Co_5(OH)_8(NO_3)_2 \cdot 2H_2O$, $Co_5(OH)_8SO_4 \cdot 2H_2O$, $Cu_2(OH)_3(NO_3)$, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, $Mn_3(PO_4)_2 \cdot 7H_2O$ (Schwenzer, Roth et al., 2006) and ZnO (Kisailus, et al., 2006) thin films were prepared by this kinetically controlled vapor-diffusion method as shown in Fig. 6.

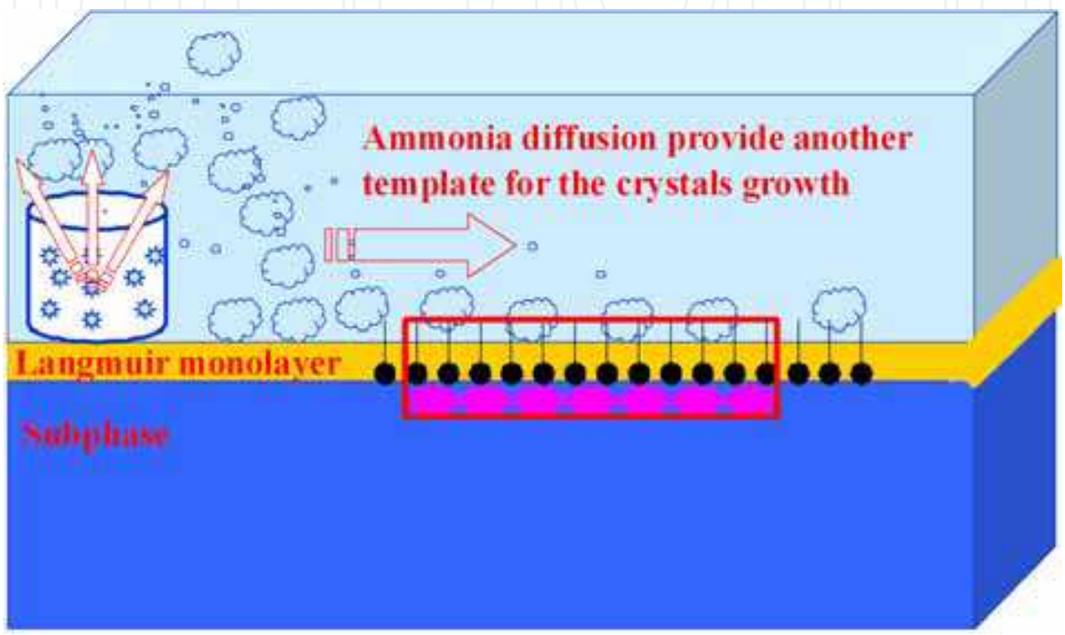

Fig. 7. Schematic diagram of the dual-template approach. A Langmuir monolayer is used as organic template; and the kinetic control of the hydrolysis degree of the molecular precursor, the species and concentration ratio of the cations and anions at the vapor-liquid interface is also realized through the pH value gradient, concentration gradient of reactants, and surface tension gradient generated from the vapor-diffusion and decided by the mode and the rate of ammonia diffusion, which directly influences the nucleation rate and crystal growth mode. The vapor-liquid interface generated from ammonia diffusion provides template information for the crystal growth, which is used as a kinetic template, and the system is named as dual-template approach. Obviously, it is much closer to a real biomineralization process.

Although hydrogen sulfide gas is widely used to fabricate PbS (Wang, et al., 1987; Zhao, et al., 1992; Zhu, et al., 1992; Tassoni & Schrock, 1994; Yang & Fendler, 1995; Mukherjee, et al., 1997; Shenton, et al., 1999; Ni, et al., 2004; Lu, et al., 2005) and CdS (Lianos & Thomas, 1987; Wang & Mahler, 1987; Facci, et al., 1994; Cui, et al., 2005; Lu, et al., 2005) nanoparticles, it only served as a gas reactant, which is completely different from the concept that ammonia used as a catalyst dissolves in an aqueous metal salt solution to initiate hydrolysis. It should be noted that Morse et al., (Schwenzer, et al., 2006) for the first time, put forward the concept that the vapor-liquid interface generated by the vapor-diffusion of catalyst (ammonia) can work as the nucleation template (Hu, et al., 2009). However, as shown in Fig. 6, the

morphologies of the thin films obtained by the vapor-liquid interface template method are not very uniform, furthermore, their crystallographic orientation is random, the reason of which is the absence of organic matrix templates in synthetic conditions. Additionally, as mentioned above, it has been proved that Langmuir monolayers as organic matrix templates can play a key role in controlling morphology and crystallinity of the products in many biomimetic processes (Mann, et al., 1988; Heywood & Mann, 1992; Mann, et al., 1993; Yang, et al., 1995; Estroff & Hamilton, 2001; DiMasi, et al., 2002; With, 2008). Considering the nucleation effect of the vapor-liquid interface template and the matrix role of the organic template, we think that the combination of both templates will construct uniform morphological and well-oriented thin films at ambient temperature. With this consideration in mind, we developed a combination strategy of the vapor-liquid interface nucleation template and the organic matrix template, which was named as dual-template approach, and the schematic diagram is shown in Fig. 7 (Hu, et al., 2009). The experimental results proved that this dual-template approach was rather effective in the preparations of uniform morphological and well-oriented thin films of pure or doped metal hydroxide nitrates. The most important characteristic of our developed dual-template approach is the synergetic effect of the vapor-liquid interface nucleation template and the organic matrix template.

Firstly, the effect of organic matrix template in the dual-template system on the crystals growth is investigated. Fig. 8a shows the TEM image of crystals formed under a BSA Langmuir monolayer template at the surface pressure of 15 mN m^{-1} for 2 h. Individual nanosheets crystals can be observed in Fig. 8a, large area nanosheets are uniformly distributed on the substrate and some crystals stand while some lie, which is further confirmed by SEM images (Fig. 8d-8e). Their lengths and widths are ca. 2−4 μm and ca. 200−300 nm, respectively. The pattern of selected area electron diffraction (SAED) (Fig. 8b), recorded at the rectangular area shown in Fig. 8a, shows 6-fold symmetry and confirms that nanosheets are highly ordered single crystal structure. A high-resolution TEM image (HR-TEM) shown in Fig. 8c presents good crystallinity, and clear well-defined lattice fingers are in good agreement with the SAED pattern taken at the same area shown in Fig. 8b (Hu, et al., 2009).

It is remarkable that an interesting phenomenon in the recent publication, Casse et al. (Casse, et al., 2008) has found that even a rather flexible matrix like the block copolymers film at the vapor-liquid interface not only leads to uniform particles with identical particle sizes, but also can act as a tool for the 2D arrangement of the resulting particles in a near-crystalline order in a distorted hexagonal lattice. Regulating mineralization on the atomic (crystal phase) and the nanoscopic (particle size and shape) scale in the reported work is often encountered in the case that inorganic crystals are mineralized under organic matrix templates. Those mineralized inorganic crystals usually adopt a preferred orientation along a specific plane, even a single crystal structure at the atomic scale, meanwhile, display a uniform particle size and shape at the nanoscopic scale, just as the results shown in Fig. 8. However, it is seldom observed for the 2D arrangement of the resulting particles in a near-crystalline order. The main reason for the phenomenon is perhaps due to a special stage of balance between the nucleation and the growth of calcium phosphate at a very low concentration and a suitable pH value of the subphase, such conditions make the nucleation and growth process of minerals well-defined. In our recent work, we have also found that our dual template approach can lead to a 2D aggregation of crystals with a special fractal structure. In a word, these works give an implication that the organic matrix templates can realize an effective control for the mineralization of inorganic crystals, which provides us a

good model for biological mineralization and an opportunity to obtain a series of inorganic materials with special structural features.

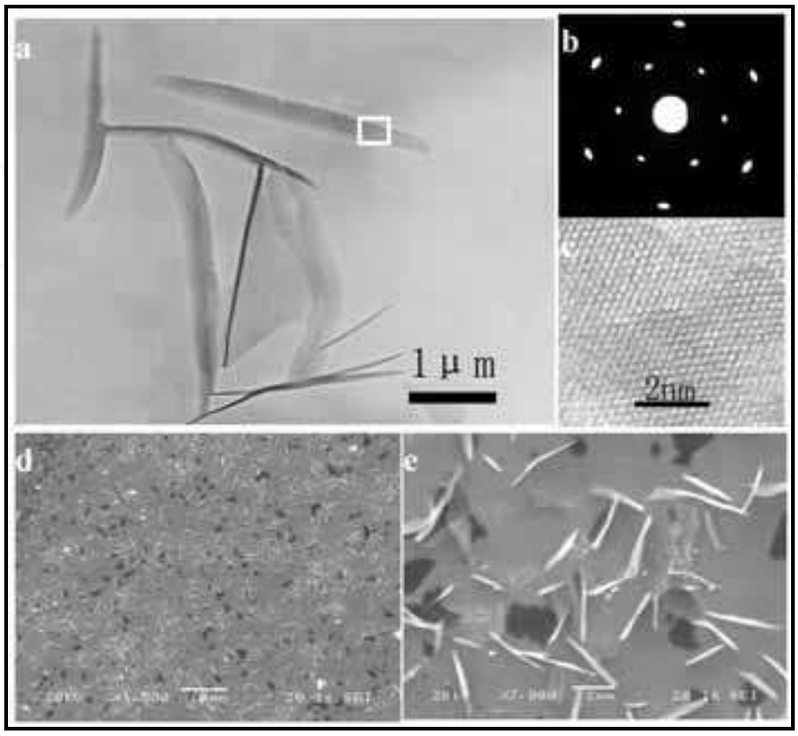

Fig. 8. TEM image (a), SAED pattern (b), HR-TEM image (c), and SEM images (d and e) of the nanosheets grown under the BSA Langmuir monolayer for 2 h at surface pressure of 15 mN m−1. The scale bars in a: 1μm, c: 2 nm, d: 10 μm and d: 2 μm (from ref (Hu, et al., 2009) *Reproduced by permission of The Royal Society of Chemistry*).

However, when the vapour-liquid interface template generated by the kinetically controlled vapor-diffusion of ammonia exists together with the organic matrix template on the surface of the subphase, it is notably different from the situation when only organic matrix template is present. The TEM images of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ films formed at 2 h under a BSA Langmuir monolayer at surface pressure of 15 mN m^{-1} in the presence of ammonia diffusion are shown in Fig. 9. Compared with Fig. 8, Fig. 9 shows a continuous film other than the individual nanosheets in the presence of ammonia. It is obvious that the vapor-liquid interface template generated by the kinetically controlled vapor-diffusion of ammonia plays a key role in the formation of the thin films. The diffusion through a solution of molecular precursor [$Zn(NO_3)_2 \cdot 6H_2O$] establishes a spatially and temporally regulated gradient of the catalyst (ammonia), to control the supersaturation of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ through the formation of complexes (Kisailus, et al., 2006), while the vapor–liquid interface serves as the nucleation template (Schwenzer, et al., 2006; Hu, et al., 2009). Such a template as assistant of the BSA organic template directs crystal growth where there are no nanosheets induced by BSA Langmuir monolayer (like the blank areas in Fig. 8a). The co-operation effect between the vapor-liquid interface template and the organic template directs the growing materials to adopt a continuous film morphology, in contrast, the competition effect between the two templates leads to the morphological differences between nanosheets in the films and those

as shown in Fig. 8a. The inset in Fig. 9b is the ED pattern of films, indicating a polycrystallinity structure. In comparison with Fig. 8 and Fig. 9, it is easy to see that the organic template favors to the formation of individual single-crystal nanosheets whereas the dual template is propitious to the construction of continuous polycrystalline films, but there exist still some single-crystal domains in polycrystalline films. This observation confirms that co-operation and competition (synergetic effect) of the dual template at the interface lead to the structure containing single-crystal domains in the polycrystalline films (Hu, et al., 2009).

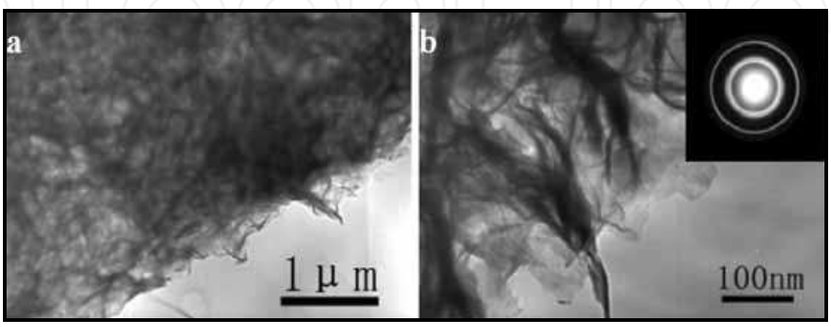

Fig. 9. TEM images of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ thin films formed at 2 h in the presence of dual template. The scale bars are 1 μm in a, 100 nm in b. The insets in b, is the corresponding ED pattern (from ref (Hu, et al., 2009) *Reproduced by permission of The Royal Society of Chemistry*).

Through changing the composition of subphase solutions, $Co_5(OH)_8(NO_3)_2 \cdot 2H_2O$, and Co-doped $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ thin films were also successfully prepared using such a method, indicating the dual-template biomimetic mineralization system can be a promise method for preparing many other kinds inorganic thin films. The Fig. 10 and Fig. 11 are the SEM images and XRD patterns of the thin films, respectively. Obviously, the products shows a much more uniform morphology than that of ref (Kisailus, et al., 2006; Schwenzer, et al., 2006) and a preferred orientation along (200) plane.

The uniform surface morphologies and the preferred orientation along (200) plane of the films are ascribed to the special structural features of the materials and the synergetic effect of the dual template in the novel biomimetic system. As for $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, as we know, it consists of layered sheets with octahedrally coordinated Zn^{2+} ions in the brucite layer, one quarter of which are replaced by two tetrahedrally coordinated Zn^{2+} ions located above and below the plane of the octahedrally coordinated Zn^{2+} ions (Stählin & Oswald, 1970; Biswick, et al., 2007). The nitrates anions are located between the sheets and do not directly coordinate to the zinc atoms. There are only zinc atoms in the (200) plane, which indicates that the (200) plane is a polar plane. When BSA molecules are spreaded on the surface of $Zn(NO_3)_2$ solution, the Zn^{2+} are strongly attracted by the negative charge of BSA Langmuir monolayers through electrostatic interactions, therefore, the nucleation along the (200) plane is facilitated because of the strong polarity of (200) plane. Furthermore, it has been proposed that structural flexibility in the organic monolayer plays an important role in the orientation growth of inorganic crystals (Cooper, et al., 1998). A cooperative interaction between the organic templates and inorganic phases leads to local re-arrangement of the Langmuir films during the nucleation stage. Here, the interactions between the BSA molecules and Zn^{2+} ions in the subphase solution make the monolayer self-regulate its structure during the formation of the inorganic crystals; meanwhile, the formation of

inorganic crystals is also influenced by the self-regulation of the monolayer, which should be a synergetic process of adapting each other and adjusting each other. What's the most important is that the structural flexibility of BSA monolayer provides a probability for the regulating and adjusting. All of those factors above lead to the decrease of the interfacial energy and improve the preferred orientation along the (200) plane. As for $Co_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and Co-doped $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, a similar situation takes place.

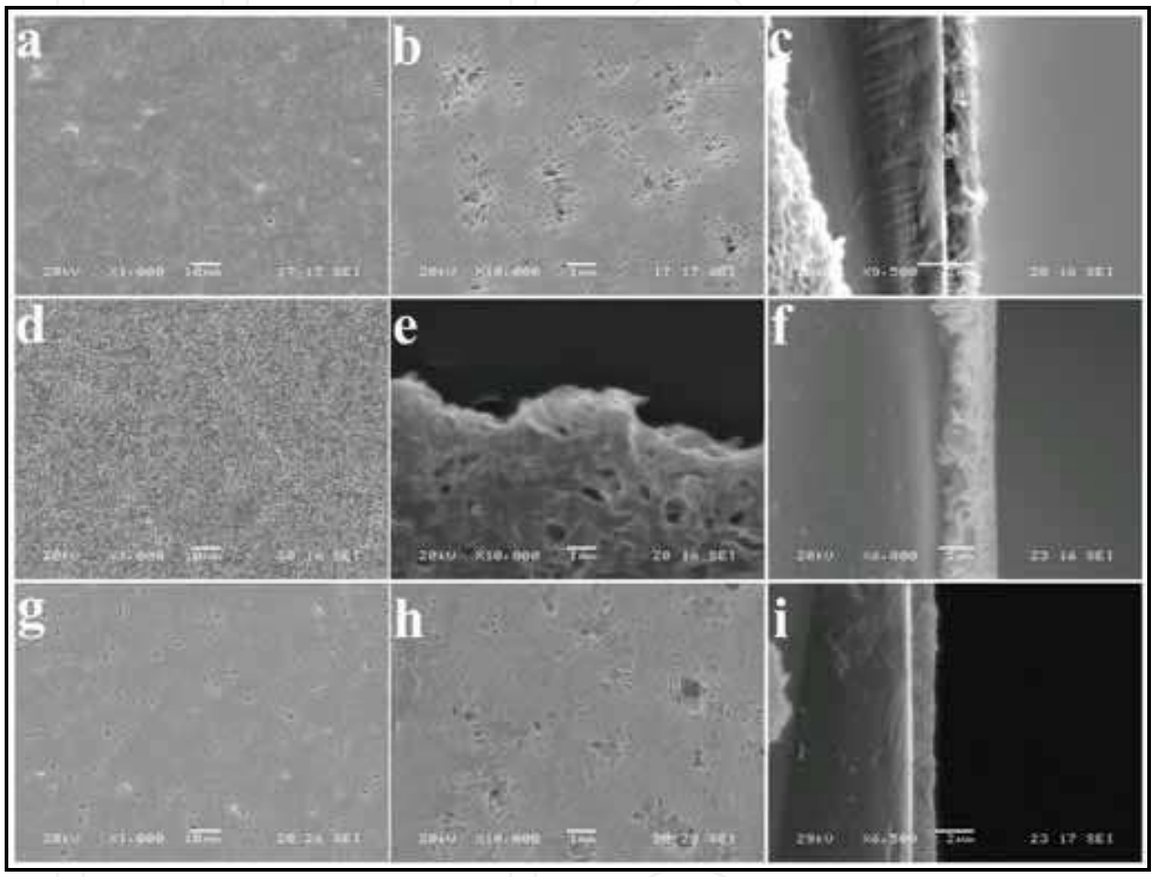

Fig. 10. SEM images of the films obtained at 2 h in the presence of dual template: top view in different magnification of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (a and b), $Co_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (d and e), and Co-doped $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ thin films (g and h); side view of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (c), $Co_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (f), and Co-doped $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ thin films (i). Scale bars are 10 μm in a, d, g; 1 μm in b, e, h; and 2 μm in c, f, I, respectively (from ref (Hu, et al., 2009) *Reproduced by permission of The Royal Society of Chemistry*).

In a word, such a dual-template approach make the usual biomimetic mineralization system only using Langmuir monolayer as organic template closer to a real biomineralization process, which captures the advantages of both the vapor-liquid interface generated by the vapor-diffusion of catalyst (ammonia) served as the other nucleation template providing a kinetic control and the crystal growth regulated by the organic matrix template providing control of crystal structures and morphologies (Sumerel, et al., 2003; Hosono, et al., 2005; Kisailus, et al., 2005). The regulation effect of Langmuir monolayer on the crystal growth was realized in the novel interface system, meanwhile, the kinetic control of materials was

also realized through the pH value gradient, concentration gradient of reactants, and surface tension gradients generated from the vapor-diffusion. The novel biomimetic interface system unambiguously influenced the growth mode and habit of inorganic crystals, being a promise method for realizing structural controllable fabrication of inorganic functional materials at room temperature.

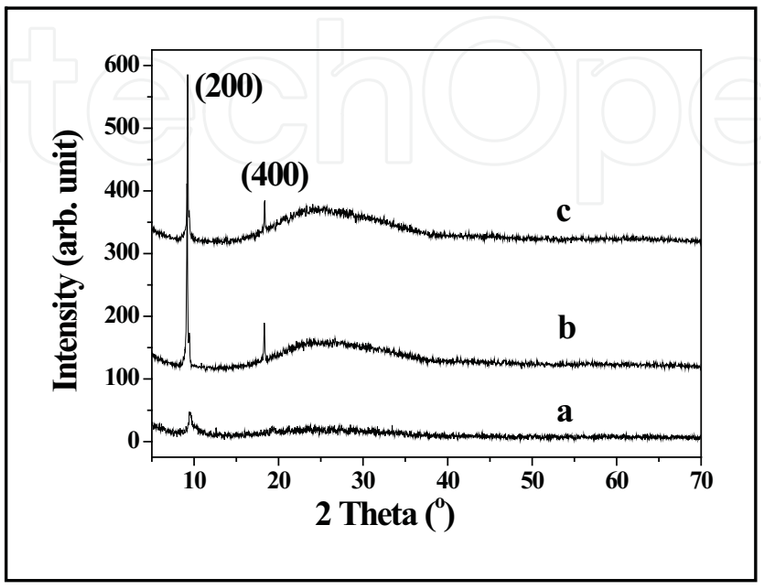

Fig. 11. XRD patterns of the films formed under BSA Langmuir monolayer at surface pressure of 15 mN m^{-1} at 2 h on the surfaces of 0.03 M Co^{2+} solution (a), 0.03 M Zn^{2+} solution (b) and 0.03 M Zn^{2+}/Co^{2+} mixed solution (c) in the presence of ammonia diffusion (from ref (Hu, et al., 2009) *Reproduced by permission of The Royal Society of Chemistry*).

4. Conclusion

How do mussels form their shells? Why is a sea-urchin spine so mechanically stable? Can we grow teeth in the test-tube? Why is bone hard as well as elastic? These questions are still mainly unresolved (Becker, et al., 2003). Biomineralization processes can form biominerals with delicate structures and various functions, attracting peoples to strive to understand molecular mechanisms of the assembly of inorganic materials. Obviously, the elucidation of the mechanisms for the formation of these composite materials will lead to new strategies for assembling other inorganic-organic composites and bring a bright future for materials science (Bensaude-Vincent, et al., 2002). Although many researches of biomineralization mimic and biomimetic mineralization have been carried out from disciplinary of biology, chemistry, crystallography and materials science, our understanding on the essence of biomineralization is still very limited.

It is well known that biomineralization takes place at a biomembrane interface, so an appropriate mimic model of biomembrane is indispensable for exploring the secret in Nature. As an approximation to half of the bilayer structure of a biomembrane, organic Langmuir monolayers can usually serve as a convenient model to approach the two-dimensional structure of biomembranes through easy control, and therefore, Langmuir monolayer is an ideal model interface for biomimetic mineralization and has been widely

used as the organic templates in the research of biomimetic mineralization to guide the growth of inorganic crystals with special structure, size, and morphology. Meanwhile, although the mechanisms by which organisms generate mineral crystals are not well understood, there is widespread belief that proteins play important roles. So proteins should be paid more attention in the biomimetic mineralization research, especially in a manner of Langmuir monolayer. The large diversity of natural and synthetic proteins and their adjustability provide high probability that proteins recognize, interact with, and direct the formation of many inorganic materials. At the same time, it is easy to realize the structural changes of the protein molecules by simply controlling the surface pressure of a protein Langmuir monolayer, which provides a great convenience for researching the influence of structural changes of protein molecules on the structural formation of biominerals. As an equally important factor for the special structural features of the biominerals in the real biomineralization, the kinetic control of inorganic crystals growth in the biomimetic mineralization system has not gotten due diligence. The kinetic control of the hydrolysis degree of molecular precursor, the species and concentration ratio of the cations and anions at the vapor-liquid interface is also realized through the pH value gradient, concentration gradient of reactants, and surface tension gradient generated from ammonia diffusion. So, the dual-template interface system introducing the kinetic control generated from ammonia diffusion into a usual biomimetic mineralization interface of only a protein Langmuir monolayer should be a preliminary ideal biomimetic mineralization interface system, it is still faraway from but much closer to a real biomineralization process.

If one day we want to be able to manufacture materials with hierarchical structures similar to those of nature, learning from a real biomineralization process is important and necessary. The design and construction of biomimetic mineralization system closer to the real environment and process of biomineralization should be undoubtedly a promise way, which on the one hand provides a perfect model for biomineralization research; on the other hand, more opportunities to get inorganic materials with special structural features can also be obtained through introducing more conditions of controlling, providing an effective experimental method for controllable fabrication of functional materials. It is meaningful for both deepening the understanding on the mechanism of biomineralization and promoting the ability of fabricating materials using biomimetic mineralization approach.

5. Acknowledgments

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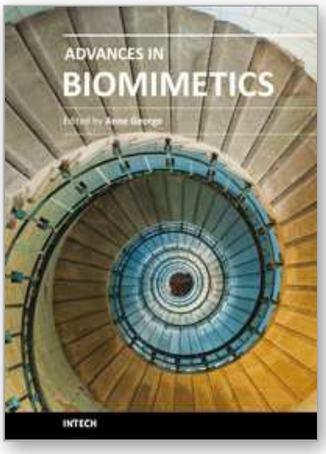

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The interaction between cells, tissues and biomaterial surfaces are the highlights of the book "Advances in Biomimetics". In this regard the effect of nanostructures and nanotopographies and their effect on the development of a new generation of biomaterials including advanced multifunctional scaffolds for tissue engineering are discussed. The 2 volumes contain articles that cover a wide spectrum of subject matter such as different aspects of the development of scaffolds and coatings with enhanced performance and bioactivity, including investigations of material surface-cell interactions.

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