We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



11

Bioinspired Synthesis of Organic/Inorganic Nanocomposite Materials Mediated by Biomolecules

Xunpei Liu and Surya K. Mallapragada
Department of Chemical and Biological Engineering, Iowa State University and Ames Laboratory, Ames USA

1. Introduction

Many organisms are capable of synthesizing organic/inorganic composites for protective or support purposes, such as bones, shells, and teeth. They exert a remarkable level of molecular control on particle size, structure, morphology, aggregation, and crystallographic orientation of these organic/inorganic structured materials. These materials often hierarchically arrange from nanoscale to macroscale (Feldheim and Eaton 2007; Dujardin and Mann 2002; Mann et al. 1993; Palmer et al. 2008; Estroff and Hamilton 2001; Aizenberg et al. 2005). For example, mollusks produce shells or nacres that contain a single distinct calcium carbonate crystalline phase, such as aragonite or calcite (Addadi et al. 2006). Magnetotactic bacteria produce Fe_3O_4 or Fe_3S_4 nanoparticles with well-defined sizes and shapes to recognize magnetic fields for alignment and migration (Dennis A. Bazylinski and Frankel 2004; Komeili 2007). Marine sponges produce silica spicules that have been demonstrated to possess light-guiding characteristics and may reach lengths of up to 3 m (Aizenberg et al. 2004; Sundar et al. 2003; Cattaneo-Vietti et al. 1996). In each of the examples listed above, and in many more examples in nature (Fig.1), specialized biomolecules, such as proteins, peptides, deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and polysaccharides, have been found or are thought to play a critical role in directing the formation of these hierarchically assembled inorganic structures (Söllner et al. 2003; Müller et al. 2007). The participation of biomolecules in the nucleation and growth of crystals has attracted much research attention. Most notably, the proteins involved in directing the shape of these biomaterials have often evolved to recognize and bind selectively to one or more faces of the growing crystal. For instance, important matrix proteins involved in bone growth contain different function domains that orient the protein on hydroxyapatite nanocrystals and interact with target cell receptors (Gilbert et al. 2003). Nature has always been a source of inspiration for technical developments. Materials scientists consider the hierarchical structure of natural materials as a model for the development of new types of high-performance engineered materials (George and Ravindran 2010). The biomimetic approach could lead to the development of the controlled synthesis of inorganic nanophases, the crystal engineering of bulk solids, and the assembly of organized composite and ceramic materials (Mann et al. 1993).

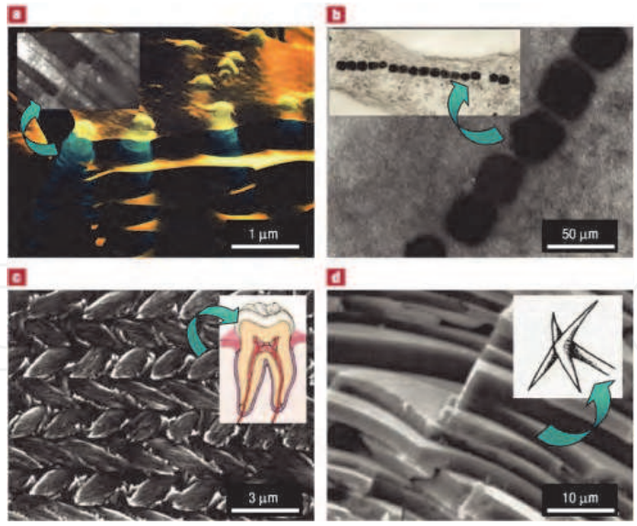


Fig. 1. a, Scanning electron microscopy (SEM) image of a growth edge of abalone (*Haliotis rufescens*) displaying aragonite platelets (blue) separated by organic film (orange) that eventually becomes nacre. (inset: transmission electron microscope (TEM) image). b, Magnetite nanoparticles formed by magnetotactic bacterium (*Aquaspirillum magnetotacticum*, inset: TEM image). c, Mouse enamel (SEM image) is a hard, wear-resistant material with highly ordered micro/nano architecture consisting of hydroxyapatite crystallites that assemble into woven rod structure (inset: schematic cross-section of a human tooth). d, SEM image of sponge spicule (with a cross-shaped apex shown in inset) has layered silica with excellent optical and mechanical properties. (Reproduced from *Nature Materials*, 2003, volume 2, issue 9, 578. Copyright © 2003 Nature Publishing Group.)

During the past decades, many inorganic crystals or hybrid inorganic/organic materials with special sizes, shapes, organization, complex forms, and hierarchies have been synthesized via bioinspired methods with the assistance of various templates, such as synthetic polymers, self-assembling peptides, proteins, and some low mass surfactant molecules (Cai and Yao 2010; Xu et al. 2007). Routine and reliable synthesis of self-assembled hybrid materials with tunable functionalities are urgently required for real-life applications and economic commercialization (Patil and Mann 2008; Gower 2008).

There are mainly two mechanisms by which organisms control the self-assembled hierarchical organic/inorganic structures. First, the organic matrix serves as template on which to form a specific mineral. Second, inorganic materials usually appear in cells at the protoplasmic surface boundary layer. Therefore, the arrangement of the biominerals is controlled by the surface tension between the cells, the vesicles, and the growing mineral (Estroff and Hamilton 2001). Recent work in the field of bioinspired synthesis has achieved varying degrees of success in both of these strategies, especially the first mechanism, in which the self-assembling organic structures are used to template the growth of inorganic materials. The structural information from the organic assembly is directly transcribed to the inorganic materials, or used to modify the morphology of the inorganic phases.

This review will focus on the recent successes in using self-assembling biomolecules as the organic matrix templates to direct and facilitate the formation of different kinds of structured organic/inorganic composite materials. The biomolecules are either natural or synthetic, including proteins, peptides, DNA, RNA, and polysaccharides.

2. The advantages of using biomolecules for bioinspired synthesis, and their sources

The use of biomolecules to direct the *in vitro* synthesis of inorganic materials is promising due to a number of reasons. The first of these potential benefits is the production of materials under mild reaction conditions (neutral pH, room temperature, aqueous solution etc.), while traditional methods require severe reaction conditions. The reduction of energy input and avoidance of harmful solvents makes bioinspired synthesis inherently "green" processing. The second major advantage of using biomolecules for materials synthesis is the elegant control on the size, shape, chemistry, and crystal structure of the inorganic product. These characteristics often impact or determine the properties of the synthesized material, making them have specific applications. Third, biomolecules offer the potential to produce materials with highly specific or multiple functions. Additionally, the large diversity of natural and synthetic biomolecules provides a high possibility of finding a biomolecule that can recognize, interact with, or direct the formation of an inorganic material (Dickerson et al. 2008).

The primary sources to obtain the biomolecules used for the bioinspired synthesis of materials include: biomolecules isolated or derived from biomineralizing organisms, biomineralizing biomolecule analogs, and peptides identified for biomineralization (Dickerson et al. 2008). Biomolecules isolated or derived from biomineralizing organisms have been widely used for biomimetic synthesis of inorganic materials, however, the use of biomineral-isolated biomolecules has several drawbacks. For example, the biomolecules may be difficult to obtain or limited by the yield, may require specialized facilities to grow, and may provide few if any opportunities to modify or engineer protein sequences. Many of these difficulties may be overcome through the recombinant expression and subsequent purification of mineralizing proteins from bacterial cells (Tahir et al. 2005). Some of the sequence characteristics native to biomineralizing proteins may also be found in readily available and inexpensive proteins, such as hen egg white lysozyme (HEWL) or bovine serum albumin (BSA), making them popular candidates for biomimetic studies (Yang et al. 2006; Shiomi et al. 2007). According to these recognized sequences, biomineralizing biomolecule analogs can be developed. The analogs are not restricted to biomolecules, for instance, synthetic polymers are also developed as templates for bioinspired inorganic synthesis (Enlow et al. 2007; Kanapathipillai et al. 2008). The development of peptide, DNA, and RNA identification, separation, and synthesis techniques provides more opportunity to design templates for the bioinspired inorganic material synthesis, for example, phage display is used for identifying peptides and systematic enrichment of ligands by exponential enrichment (SELEX) is used for recognize RNA (Feldheim and Eaton 2007).

Different types of biomolecules used in bioinspired synthesis can be broadly categorized into four categories: proteins, peptides, nucleic acids, and polysaccharides. The role of these different types of biomolecules in the bioinspired synthesis and fabrication process is discussed in greater detail using specific cases as examples in the following sections.

3. Protein-mediated bioinspired synthesis

Proteins provide functional building blocks for the development of multi-functional materials (Gajjeraman et al. 2008). The self-assembly property of proteins would allow controlled organization of the organic/inorganic interface based on molecular recognition,

resulting in hierarchical organization with desirable properties at multiple length scales. Proteins have superior specificity for target binding with complex molecular recognition mechanism (de la Rica and Matsui 2010). Through their unique and specific interactions with other macromolecules and inorganics, they process the ability to control structures and functions of biological hard and soft tissues in organisms (Sarikaya et al. 2003). In the following sections, several examples of protein-mediated bioinspired synthesis of structured organic/inorganic materials *in vitro* are highlighted.

3.1 Protein mediated hydroxyapatite (HAp) formation

Bone is a highly ordered, dynamic, and highly vascularized tissue that exhibits excellent strength, hardness, and fracture toughness. It is a biocomposite of 70% mineral (mostly nanoscale calcium phosphate crystals) and 30% organics (including collagen, glycoproteins, proteoglycans, and sialoproteins) by dry weight (Salgado et al. 2004; Hu et al. 2010; Palmer et al. 2008). Calcium phosphates, notably HAp [$Ca_{10}(PO_4)_6(OH)_2$], exhibit many levels of hierarchical structures in bone from nano to macro scales (Rey et al. 2009). Mineralized collagen fibrils are the basic building block for bone formation. More than 20 human collagens have been reported. In collagens, the amino acids glycine, proline, and hydroxyproline account for more than 50% of the amino acid composition, often presented as the Gly-X-Y repeat unit (where X and Y are either proline or hydroxyproline) (Cui, et al. 2007). Most collagens display a 67 nm periodicity due to the axial packing of the individual collagen molecules (Prockop 1995). Collagens also serve as extracellular matrix molecules for many other soft and hard tissues, such as cartilage, tendons, and ligaments.

We highlight some recent studies focused on the collagen-HAp interactions in the bioinspired synthesis of HAp composite materials. A nanocomposite of collagen and HAp was prepared in a continuous flow system, mimicking the situation *in vivo*, and resulted in a direct nucleation of HAp on the self-assembled collagen matrix. The biomineralization process of collagen and the self-organization mechanism were also analyzed. The inorganic crystals formed along the collagen fiber have similar a Ca-P ratio, crystalline degree, and carbonation extent to that observed in bone (Wang et al. 2006). Another study investigated the function of osteonectin in the formation of HAp. Osteonectin was added into the collagen solution, and results indicated that spindle-like nano-HAp could be deposited on collagen I/osteonectin and pure osteonectin (control) groups, but not on collagen II/osteonectin (Liao et al. 2009). This may help in understanding the biomineralization process in nature.

Another collagen templated HAp nanocomposite showed equal or better biocompatibility than HAp ceramics, which was known to have excellent biocompatibility. The c-axes of HAp nanocrystals were regularly aligned along collagen fibrils, which was similar to natural bone orientation. The composite promoted the osteoclastic resorption, followed by new bone formation by osteoblasts, which was very similar to the reaction of a transplanted autogenous-bone. Therefore, the HAp/collagen composite can be potentially used as an artificial bone material in medical and dental fields (Kikuchi et al. 2004).

In another study, two different bioinspired methods were used to fabricate HAp on collagen templates: dispersion of synthetic HAp in a solution of telopeptide-free collagen molecules and direct nucleation of HAp into reconstituted collagen fibers during their assembly. Composite materials obtained by direct nucleation showed similar composition, morphology, and structure to natural bone, and also indicated an intimated interaction

between the inorganic phase and protein components (Tampieri et al. 2003). This proved the template function of the collagen during the bone formation.

Proteins other than collagen are also used in bioinspired HAp synthesis. A novel human hair proteins and HAp composite was synthesized for using as a biomineral-scaffolding material. The human hair protein was soaked to a $CaCl_2$ solution for fabrication into flat films. The flat films mainly consisted of α-keratin, which could bind 3 Ca^{2+} ions per 1 keratin molecule. The composite of the human hair protein and calcium phosphate was prepared via alternate soaking processes using $CaCl_2$ and Na_2HPO_4 solutions. The diameters of deposited calcium phosphate particles were about 2–4 μm. The human hair proteins were not soluble and degraded during the soaking processes.(Fujii et al. 2009) Synthetic proteins have also been developed as templates for bioinspired synthesis. Self-assembled chimeric protein hydrogels comprising leucine zipper motifs flanking a dentin matrix protein 1 domain were developed to act as a HAp nucleator for the formation of highly oriented apatite similar to bone mineral (Gajjeraman et al. 2008).

3.2 Protein mediated magnetic materials formation

Magnetotactic bacteria form magnetite nanoparticles *in vivo* with various morphologies (Bazylinski and Frankel 2004). The magnetospirillum magneticum strain AMB-1 produces a chain of cuboctahedral magnetite nanocrystals, each surrounded by a lipid bilayer membrane (Fig.1 b). Several proteins isolated from the magnetosome membranes showed common features in their amino acid sequences, which contain hydrophobic N-terminal and hydrophilic C-terminal regions. The C-terminal regions in Mms5, Mms6, Mms7, and Mms13 contain dense carboxyl and hydroxyl groups that bind ions. Nano sized magnetic particles similar to those in magnetotactic bacteria were prepared *in vitro* by chemical synthesis of magnetite in the presence of the protein Mms6. These proteins may be directly involved in biological magnetite crystal formation in magnetic bacteria (Arakaki et al. 2003).

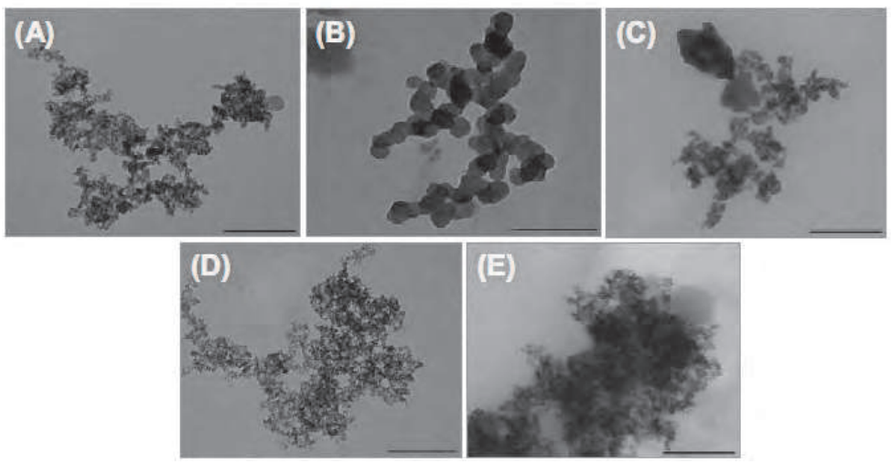


Fig. 2. TEM images of magnetite nanoparticles obtained by co-precipitation of $FeCl_2$ and $FeCl_3$: A) without protein, B) with Mms6, C) with ferritin, D) with Lnc2, and E) with BSA. Scale bars: 200 nm." at the beginning of this line. (Adapted from *Advanced Functional Materials*, volume 17, issue 6, 952. Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Similar *in vitro* synthesis of magnetite mediated by Mms6 was also achieved by other research groups. Recombinant Mms6 facilitated the formation of magnetite nanocrystals with uniform size (about 30 nm) in aqueous solution, which was verified by using TEM analysis and magnetization measurements. A polymeric gel was used to mimic the conditions at which magnetite nanocrystals were formed in magnetotactic bacteria and slow down the diffusion rates of the reagents. The nanocrystals formed in the presence of other proteins, as shown in Fig.2, did not exhibit the uniform sizes and shapes. Mms6-mediated magnetite nanoparticles demonstrated the largest magnetization values above the blocking temperature, and the largest magnetic susceptibility compared to those of the nanomaterials synthesized with other proteins. This study confirmed the hypothesis that Mms6 promotes the shape-selective formation of uniform superparamagnetic nanocrystals (T. Prozorov et al. 2007). Some inorganic magnetic materials which do not appear in living organisms, for example, cobalt ferrite ($CoFe_2O_4$) nanoparticles, were also synthesized *in vitro* by using Mms6 protein as a template. The recombinant full-length Mms6 protein or a synthetic C-terminal domain of Mms6 protein was covalently attached to self-assembling polymers (Pluronic F127) in order to template hierarchical growth of $CoFe_2O_4$ nanostructures, as shown in Fig.3. This new synthesis route enabled facile room-temperature shape-specific synthesis of complex magnetic crystalline nanomaterials with particle sizes of 40–100 nm, which were difficult to produce using conventional techniques (Tanya Prozorov et al. 2007).

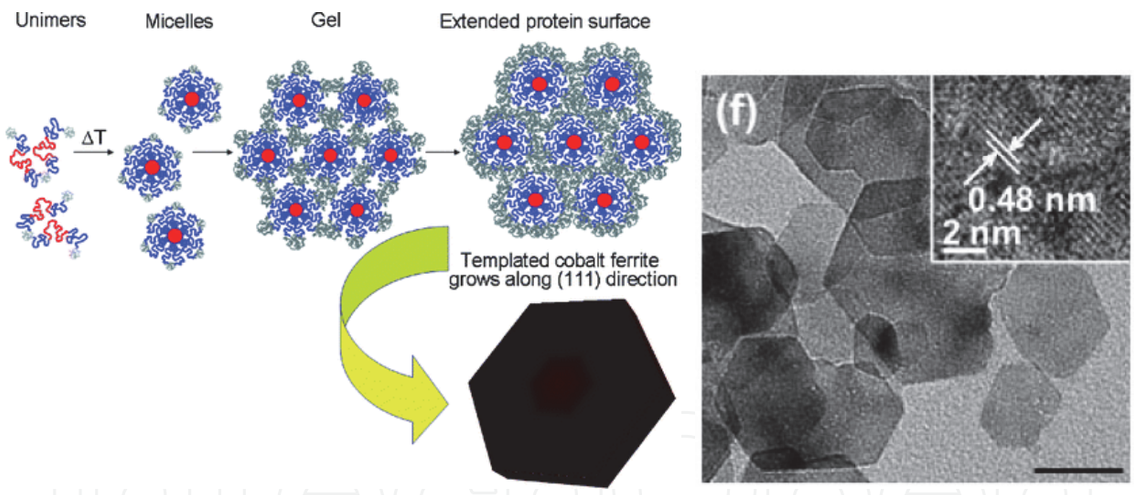


Fig. 3. Left, scheme for the protein-templated synthesis of $CoFe_2O_4$ nanocrystals in the presence of the Pluronic-conjugated recombinant Mms6 (red and blue colors stand for the Pluronic, and grey color stands for the protein); right, TEM of $CoFe_2O_4$ nanocrystals obtainedin the presence of Pluronic-conjugated c25-mms6. (Inset) High-resolution TEM image of a fragment of the central particle. (Reproduced from *ACS Nano*, volume 1, issue 3, 231. Copy right © 2007, American Chemistry Society.)

3.3 Protein mediated silica formation

Aizenberg et al. reported the structural hierarchy of biosilica observed in the hexactinellid sponge *Euplectella sp*. (see Fig.4). The hierarchical structure overcomes the brittleness of its constituent material and shows outstanding mechanical rigidity and stability (Aizenberg et al. 2005).

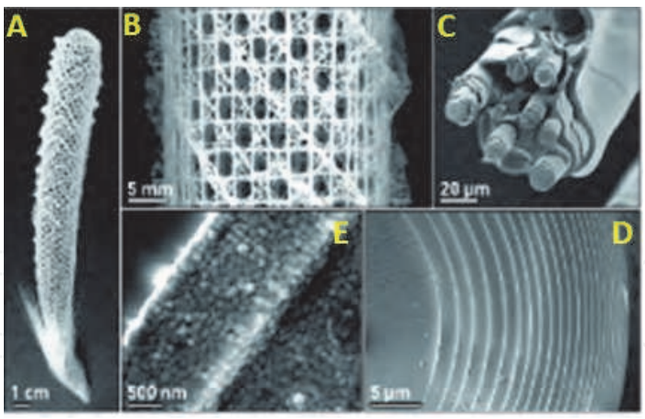


Fig. 4. Structural analysis of the mineralized skeletal system of *Euplectella sp*. (A) Photograph of the entire skeleton, showing cylindrical glass cage. (B) Fragment of the cage structure showing the square-grid lattice of vertical and horizontal struts with diagonal elements arranged in a chessboard manner. (C) SEM of a fractured and partially HF-etched single beam revealing its ceramic fiber-composite structure. (D) SEM of a cross section through a typical spicule in a strut, showing its characteristic laminated architecture. (E) Bleaching of biosilica surface revealing its consolidated nanoparticulate nature. (Adapted from *Science*, volume 309, issue 5732, 276. Copyright © 2005, American Association for the Advancement of Science.)

Silicateins, or silica proteins, were found to be enzymes (structural and catalytic proteins) that promote biosilica formation in nature (Wang et al. 2010). The silicateins exhibit catalytic activity at neutral pH and low temperature. They have also been used as templates to direct the growth of silica particles along the axial protein filament. It has been used to simultaneously catalyze and structurally direct the hydrolysis and condensation of tetraethyl orthosilicate *in vitro* to form silica (Brutchey and Morse 2008). Silicatein filaments also demonstrated the ability to form titanium dioxide, gallium oxohydroxide (GaOOH) and gamma-gallium oxide (gamma-Ga_2O_3) *in vitro*, which are three inorganic semiconductors that biological species have never naturally produced (Kröger et al. 2006; Sumerel et al. 2003; Curnow et al. 2005; Kisailus et al. 2006). An enzymatic biocatalyst from the marine sponge *Tethya aurantia*, was used to catalyze and template the hydrolysis and condensation of the molecular precursor $BaTiF_6$ at low temperature to form nanocrystalline $BaTiOF_4$ (Brutchey et al. 2006).

Amorphous silica (or silica glass) is widely used in different applications, such as membranes, columns, heat-proof materials, optical communication fibers, and catalysts in organic synthesis (Jensen et al. 2009). Silicatein from the freshwater sponge *Cauxi* catalyzed the polymerization of this type of silica *in vitro*. Briefly, the sponge shot the axial protein filament in the desired growth direction, and then silicatein polymerized a thin silica layer around the filament. However, this silica deposition inhibited the transport of the siliceous acid to the axial filament, and a new set of silicatein were shot onto the newly synthesized silica deposition. This shooting process continued until the final diameter of spicules was reached. The process is shown by Fig.5. This study offered a new route for the development of mesoporous, amorphous silica with high purity under ambient condition (Jensen et al. 2009).

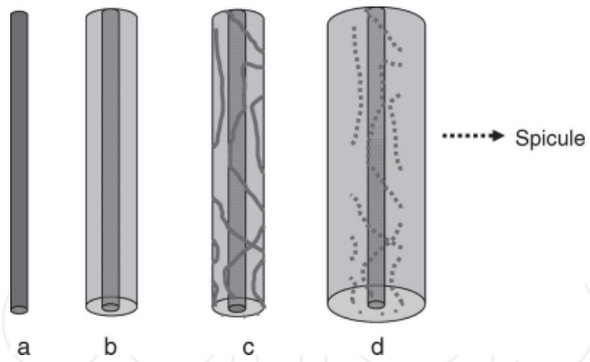


Fig. 5. Schematic illustration of the growth mechanism of amorphous silica. (Reproduced from *Journal of the Amrican Chemical Society*, volume 131, issue 7, 2720. Copy right © 2009, American Chemistry Society.)

Silicateins could be immobilized onto a template surface, while still preserving their catalytic activity. In a bioinspired approach, biosilica was synthesized on "inert" surfaces (matrices) from monomeric precursors (Tahir et al. 2004). The matrices were first functionalized with a reactive polymer that was subsequently able to chemisorb nitrilotriacetic acid (NTA), a required binder for His-tagged recombinant silicatein. Silicatein that had been immobilized onto this matrix using NTA-His tag linkage had the capability to synthesize nanoparticulate biosilica, biotitania, and biozirconia from monomeric precursors. The process is shown by Fig.6.

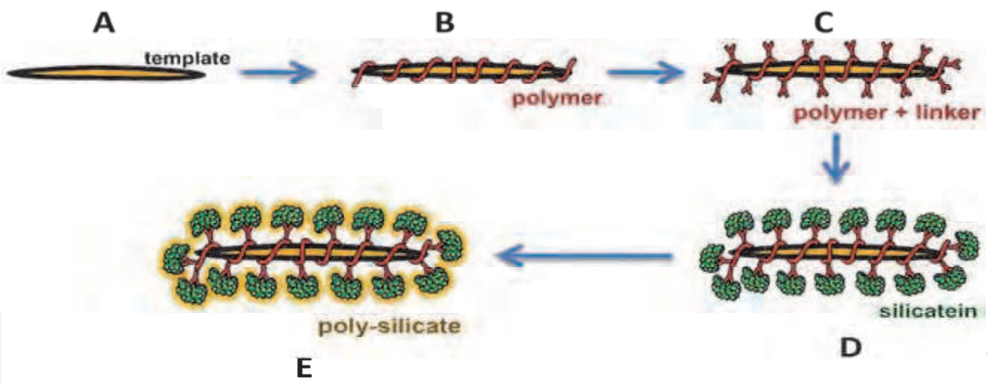


Fig. 6. The biomimetic approach: The template (A) is successively functionalized with a reactive ester polymer (B) and the NTA linker (C). (D) Recombinant silicatein is bound via His-tag and Ni^{2+} to the NTA-polymer and subsequently mediates formation and assembly of polysilica formation (E). (Adapted from *Applied Microbiology and Biotechnology*, volume 83, number 3, 408. Copyright © 2009, Springer-Verlag.)

Fungi have been used in bioinspired synthesis of inorganic materials. Silica, zirconia, and titania nanoparticles were produced by mixing the fungus *Fusarium oxysporum* with aqueous anionic complexes SiF_6^{2-}, ZrF_6^{2-}, and TiF_6^{2-}, respectively. It has been shown that the extra-cellular protein of the *Fusarium oxysporum* mediated hydrolysis of the anionic complexes. These studies introduced a facile room temperature synthesis of crystalline titania and zirconia particles, whereas calcination at 300 °C is required for crystallization of silica (Bansal et al. 2005; Bansal et al. 2004).

4. Peptide-mediated bioinspired synthesis

Peptides consist of short amino acid sequences that have less intricate functionality than proteins. Although peptides may not perform highly specialized functions compared to proteins, they can be synthesized more easily with desired amino acid sequences by well-established chemical and genetic engineering techniques. Therefore, they are widely used in the applications ranging from controlled gene and drug release, nanofabrication, biomineralization, and membrane protein stabilization to three-dimensional (3D) cell culture and tissue engineering. Peptides are designed to be folded in desired conformations, such as α-helix, β-sheet, etc. These 3D building blocks may yield supramolecular structures through self-assembly process. Moreover, the supramolecular structures can be controlled by changing the physicochemical properties of the environment such as pH, temperature, and salt content, which makes peptides versatile smart materials for the design of structured materials (de la Rica and Matsui 2010; Zhao et al. 2010).

There are several possible ways of obtaining polypeptide sequences with specific affinity to inorganics. For example, well-established *in vivo* combinatorial biology protocols, phage display, and cell-surface display have been used to identify biological ligands and to map the molecular recognition site of antibodies. Table 1 shows the specific binding affinity of peptides for various inorganic materials.

A 12-residue peptide (NPYHPTIPQSVH-GGGK-biotin: CLP12 peptide) has been identified for HAp biomineralization using phage display. The sequence responsible for the mineralizing activity resembled the tripeptide repeat (Gly-Pro-Hyp) of type I collagen. This peptide was capable of binding to single crystal HAp and templating the nucleation and growth of crystalline HAp mineral in a sequence- and composition-dependent manner. (Chung et al.). In another study, polylysine and polyleucine based block copolypeptides ($K_{170}L_{30}$) were found to form gels at very low concentrations in aqueous media. The block copolypeptides have been used as templates for forming self-assembled calcium phosphate nanocomposites. The synthesis method allowed for simultaneous formation of the self-assembled block copolypeptide gel and of the inorganic phase. The inorganic contents accounted for over 50 wt% in the nanocomposite, approaching the inorganic content in bone (Hu et al. 2009). Thermoreversibly gelling block copolymers (Pluronic F127) conjugated to hydroxyapatite-nucleating peptides (DSKSDSSKSESDSS) were used to template the growth of inorganic calcium phosphate in aqueous solutions. The inorganic phase in the organic/inorganic nanocomposite was confirmed to be HAp. This work offered a route for the development of novel, self-assembling, injectable nanocomposite biomaterials for potential orthopedic applications (Yusufoglu et al. 2008).

Self-assembling peptide amphiphiles have great potential as templates for nanofabrication. In 2001, a lipopeptide was designed and synthesized for biomineralization by the Stupp group (Hartgerink et al. 2001). In Fig.7 a and b, the C_{16} tail was connected to the N terminal of a peptide sequence which contained four cysteines, three glycines, a single phosphorylated serine and a cell adhesion ligand RGD (C_{16}–C_4G_3S(p)RGD–OH). The C_{16} tail was hydrophobic and the peptide sequences were hydrophilic. These peptide amphiphlies self-assembled into cylindrical micellar structures in aqueous phase. C_{16} acyl tails packed themselves in the center of the micelle, while the peptide sequences formed β-sheets at the outside. There were disulfide bonds that formed by cross-linking of the four cysteine residues in the middle of the molecules, making the self-assembled nanofibers robust and impervious to pH variation (Fig.7 c). The nanofibers were then used to direct the

Materials	Sequences	Size	pI	MW	Charge
Au	MHGKTQATSGTIQS	14	8.52	1446.60	+1
	SKTSLGQSGASLQGSEKLTNG	21	8.31	2050.12	+1
	QATSEKLVRGMEGASLHPAKT	21	8.60	2211.52	+1
Pt	DRTSTWR	7	9.60	920.98	+1
	QSVTSTK	7	8.75	749.82	+1
	SSSHLNK	7	8.49	771.83	+1
Pd	SVTQNKY	7	8.31	838.92	+1
	SPHPGPY	7	6.46	753.81	0
	HAPTPML	7	6.74	765.93	0
Ag	AYSSGAPPMPPF	12	5.57	1221.39	0
	NPSSLFRYLPSD	12	6.09	1395.53	0
	SLATQPPRTPPV	12	9.47	1263.46	+1
SiO2	MSPHPHPRHHHT	12	9.59	1470.63	+1
	RGRRRRLSCRLL	12	12.30	1541.89	+6
	KPSHHHHHTGAN	12	8.87	1359.43	+1
Zeolites	VKTQATSREEPPRLPSKHRPG	21	10.93	2371.68	+3
	MDHGKYRQKQATPG	14	9.70	1616.82	+2
ZnO	NTRMTARQHRSANHKSTQRA	20	12.49	2351.59	+4
	YDSRSMRPH	9	8.75	1148.26	+1
CaCO3	HTQNMRMYEPWF	12	6.75	1639.87	0
	DVFSSFNLKHMR	12	8.75	1480.90	+1
Cr2O3	VVRPKAATN	9	11.00	955.13	+2
	RIRHRLVGQ	9	12.30	1134.35	+3
Fe2O3	RRTVKHHVN	9	12.01	1146.32	+3
GaAs	AQNPSDNNTHTH	12	5.97	1335.31	0
	RLELAIPLQGSG	12	6.00	1253.46	0
	TPPRPIQYNHTS	12	8.44	1410.55	+1
ZnS	NNPMHQN	7	6.74	853.91	0

Table 1. Examples of polypeptide sequences exhibiting affinity for various inorganics. (Reproduced from *Nature Materials*, 2003, volume 2, issue 9, 581. Copyright © 2003 Nature Publishing Group.)

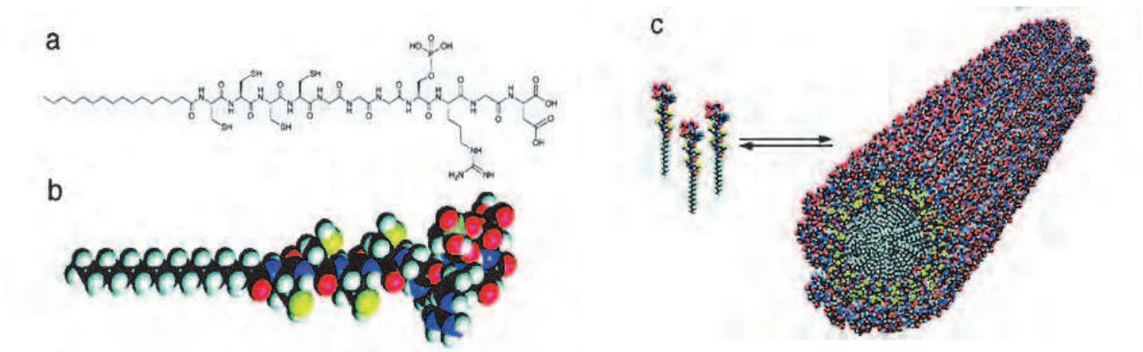


Fig. 7. (a) Chemical structure of the peptide amphiphiles. (b) Molecular model of the peptide amphiphiles. (c) Schematic model of the self-assembly of peptide amphiphiles into a cylindrical micelle. (Reproduced from *Chemical Reviews*, volume 108, issue 11, 4776. Copyright © 2008, American Chemical Society.)

mineralization of HAp. The HAp nucleated on the surfaces of the lipopeptide nanofibers and its crystals grew with their c-axes oriented along the long axes of the nanofibers. This alignment was the same as that observed between collagen fibers and HAp crystals in bone (Hartgerink et al. 2001; Zhao et al. 2010).

Shorter peptide I_3K may form nanotubes with diameters about 10 nm and lengths over 5 mm. The nanostructure from this ultra-short peptide indicated that the amphiphilicity of a peptide amphiphile can be balanced between the length of a peptide sequence and the size of hydrophobic amino acids. I_3K molecules were thought to initially interdigitate with each other through the hydrophobic interaction among the I_3 tails, forming bilayer fragments. The self-assembly was driven by the hydrophobic affinity between isoleucine residues with the I_3 tails packed in the middle and the K residues projected at the outside, facing the water. The peptide bilayer fragments then further assembled into twisted ribbons.

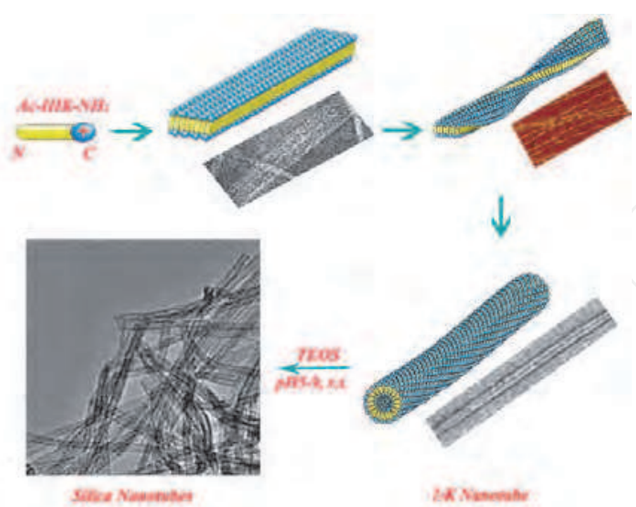


Fig. 8. A schematic representation of I_3K self-assembly process leading to the formation of peptide nanotubes which can then serve as templates for silicification. (Reproduced from *Chemical Society Reviews*, volume 39, issue 9, 3484. Copyright © Royal Society of Chemistry 2010.)

The fusion of the helical ribbons resulted in the formation of stable nanotubes, indicating the strong driving force along the main axial direction of the nanotubular structure. Fig.8 shows the self-assembling process. Because of their extreme stability against heating or exposure to organic solvents, I_3K nanotubes were used as templates for silicification from the hydrolysis of TEOS (tetraethoxysilane) precusor. The lysine groups on the inner and outer nanotube surfaces catalyzed the silicification, leading to the formation of silica nanotubes (Xu et al. 2010).

5. DNA and RNA-mediated bioinspired synthesis

DNA and RNA can self-assemble into well-defined secondary and tertiary structures at the nanoscale, which provide an ideal template for the formation of nanocrystals (Loweth et al. 1999). DNA templated gold nanoparticles have attracted much attention, as the self-assembled DNA nanostructures offer programmable scaffolds to organize the gold nanoparticles (Ding et al. 2010; Zhang et al. 2006; Wang et al. 2010). A self-assembled two-dimensional (2D) DNA nanogrid was used as a template to grow 5-nm gold nanoparticles (Au NPs) into periodic square lattices, as shown by Fig. 9. The center-to-center distance between neighboring particles was about 38 nm. These accurate controlled Au NPs distribution may find applications in nanoelectronic and nanophotonic devices (Zhang et al. 2006).

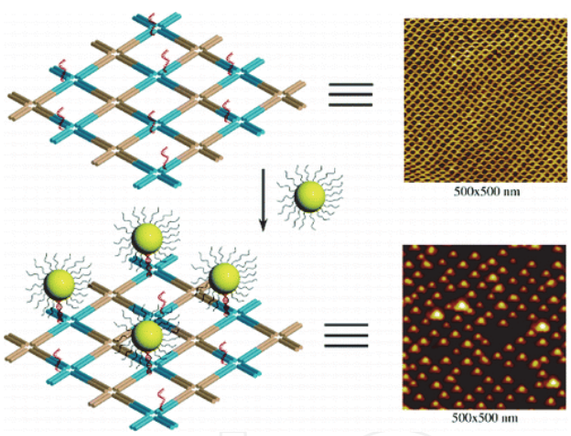


Fig. 9. Up left: the 2D DNA nanogrids with the single strand A_{15} out of the plane; up down: assembly of 5-nm Au NPs on the DNA grids. The zigzag black lines surrounding the Au NPs represent the T_{15} strands covalently linked to the surface of the particle through Au−S bonds. The right imagess are the AFM height data corresponding to each of their left. (Reproduced from *Nano Letters*, volume 6, issue 2, 248. Copyright © 2006, American Chemical Society.)

A chemically well-defined bio-core in an inorganic shell nanohybrid material was recently reported. It consisted of a DNA molecule as the bio-core with a size of 100 nm and a spherical inorganic nanoshell reassembled with exfoliated layered metal hydroxide (MH) with an overall thickness of 10 nm. The negatively charged DNA molecules can be encapsulated into a positively charged inorganic nanocavity of self-assembled MH nanosheets, as illustrated in Fig.10. Due to the pH-dependent solubility of the MH nanoshell, the DNA can be encapsulated and released, which play a crucial role in maximizing the stability of base sequence-manipulated and probe-functionalized DNA

molecules with designed information. Therefore, these hybrid materials could be used as advanced gene delivery systems and a biomedical diagnostics system for DNA-based information (Park et al. 2010).

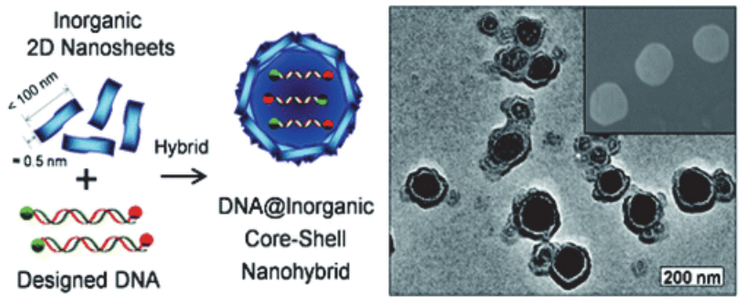


Fig. 10. Scheme, TEM and SEM image for the designed DNA@Inorganic Core−Shell nanohybrid. (Reproduced from *Journal of the American Chemical Scociety*, volume 132, issue 47, 16735. Copyright © 2010, American Chemical Society.)

A multi-lamellar structure was formed by complexes of anionic DNA and cationic liposomes self-assembly. The two-dimensional lipid sheets confined a periodic one-dimensional lattice of parallel DNA chains, as shown by Fig.11. These simple DNA-membrane templates could be used for controlled CdS crystalline synthesis. Cd^{2+} ions condensed on the DNA chains, and subsequently reacted with H_2S to form CdS nanorods. Depending on the charge of the membrane, different concentrations of Cd^{2+} ions condense onto the template, and different morphologies of CdS were formed. The degree of template overcharging was determined by the relative stoichiometry of DNA and cationic membrane lipids (Liang et al. 2004).

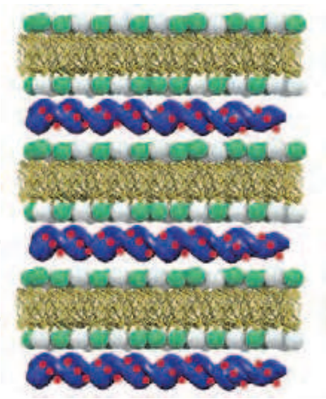


Fig.11. Schematic representation of CdS growth within DNA-membrane complexes: the Cd^{2+} ions (red balls) are organized by DNA strands (blue) in the lamellar DNA−membrane complexes (side-view). (Reproduced from *Journal of American Chemical Society*, volume 126, issue 43, 14158. Copyright © 2004, American Chemical Society.)

One kind of DNA molecules were reported to mediate the nucleation and growth of the calcium carbonate particles. $CaCO_3$ microspheres with different surface morphologies were prepared in the presence of the DNA, indicating that DNA could induce biomineralization in the biological system. It was found that the DNA concentration influenced on the surface

structures of $CaCO_3$ particles significantly. This research provided new insight into the morphological control of $CaCO_3$ and other inorganic materials (Cheng et al. 2010).
The Kelley group investigated the role of RNA secondary structure on the growth of CdS nanocrystals. They showed that a folded wild-type tRNA (wtRNA) and an unfolded mutant tRNA (mtRNA) of identical length were both able to mediate the formation of CdS during its spontaneous precipitation from solution, but they saw differences in the average nanocrystal sizes and size distributions. A narrow distribution around 6 nm diameter particles was found for particles grown with wtRNA, while mtRNA generated a bimodal distribution of 7 and 11.5 nm diameter particles. This is a good illustration that a biomolecule can affect the nanocrystal size (Ma, Dooley, and Kelley 2006).

6. Polysaccharide-mediated bioinspired synthesis

A slow but increasing interest has been developing to explore the role of polysaccharides in biomineralization, despite the fact that they have been prevalent since the early stages of evolution. Single types of polysaccharides are typically not associated with biominerals. Only hydroxylated, carboxylated, or sulfated polysaccharides, or those containing a mixture of these functional moieties, are found in biominerals (Arias and Fernández 2008). Chitin is the second most abundant natural polymer after cellulose on earth. It is a linear polysaccharide of β-(1-4)-2-acetamido-2-deoxy-d-glucose. The chemical structure of chitin is very similar to that of cellulose, with a hydroxyl group replaced by an acetamido group. Pure chitin with 100% acetylation does not exist in nature. Chitin tends to form a co-polymer with its N-deacetylated derivative, chitosan. Chitosan is a polymer of β-(1-4)-2-amino-2-deoxy-d-glucose. The chemical structures of cellulose, chitin, and chitosan are shown in Fig.12 (Meyers et al. 2008).

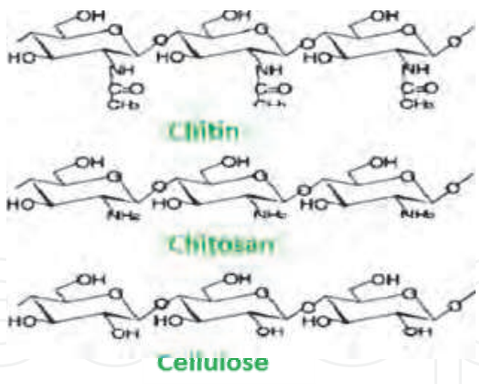


Fig. 12. Chemical structures of chitin, chitosan, and cellulose.

Chitosan composite materials have attracted much research interest in bone tissue engineering due to their minimal foreign body reactions, intrinsic antibacterial nature, biocompatibility, biodegradability, and ability to be molded into various geometries and forms. Recently, grafted chitosan natural polymer with carbon nanotubes has been incorporated to increase the mechanical strength of artificial bone (Venkatesan and Kim 2010). Laminated HAp/chitosan nanocomposites and nano-HAp/chitosan-pectin composites were prepared and showed improved strength, especially in moist environments. This combination can be expanded to other HAp-biopolymer systems, thus

offer a new insight for fabricating biomimetic nanocomposites (Li et al. 2010; Zuo et al. 2010).

Chitosan was also used as organic template to form HAp nanocrystals. Spindle shaped HAp with 30- 40 nm length and 7- 8 nm width was synthesized through the biomimetic method with chitosan as template. The spindle shaped nano HAp grew in a 0.5wt% chitosan solution for 7 days. The crystallinity of samples increased with the aging time. The HAp powders synthesized with chitosan as templates had good thermal stability up to 800 °C (He et al. 2007).

Design and synthesis of bacterial cellulose/HAp nanocomposites was reported for bone healing applications using a bioinspired approach. Bacterial cellulose with various surface morphologies (pellicles and tubes) was negatively charged by the adsorption of carboxymethyl cellulose to initiate nucleation of calcium-deficient hydroxyapatite (cdHAp). The cdHAp was grown *in vitro* via dynamic simulated body fluid treatments for 7 days (Zimmermann et al. 2011). Cellulose also used to template the growth of silica. Through *in-situ* growth of silica nanoparticles on cotton fabrics, a dual-scaled surface with nanoscaled roughness of silica and microscaled roughness of cellulose fiber was generated (Chen et al. 2010).

7. Conclusions and outlook

In summary, in the recent past, there has been remarkable progress in the development of bioinspired procedures for controlling inorganic crystal nucleation and growth, especially at the nanoscale. Biomolecules have been successfully utilized to produce a variety of self-assembled structured inorganic materials under relatively mild conditions. Biomolecules have been found to be able to direct or modify the shapes, sizes, crystal structures, and other properties of the synthesized inorganic materials. Examples of such bioinspired inorganic nanostructures include HAp, SiO_2, Fe_3O_4, CdS, TiO_2, ZrO_2, gold and silver *etc.*, which have applications in biomedical, biosensor, bioceramic, and other fields. Modern biotechnology has also enabled the construction of chimeric biomolecules with desired properties, which may be utilized to create hierarchical assembled and reinforced composite materials.

In the recent past, many biomolecules promoting materials synthesis have been identified. The number of inorganic materials that could be used for bioinspired synthesis has also been expanded. However, our fundamental understanding of these existing topics must be furthered in order to more fully harness the potential of biomolecules for material synthesis. There are also a number of interesting and powerful new concepts that have received only a little attention or remain unexplored. Design of more hierarchically self-assembled biomolecules that could template and direct the inorganic formation is also required. With the continued attention and ingenuity of researchers from diverse disciplines, the future of biomimetic materials synthesis promises to be exciting, dynamic, and rich in applications.

8. Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering. The research was performed at the Ames Laboratory. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

9. References

Addadi, Lia, Derk Joester, Fabio Nudelman, and Steve Weiner. 2006. Mollusk Shell Formation: A Source of New Concepts for Understanding Biomineralization Processes. *Chemistry - A European Journal* 12, no. 4 (1): 980-987. doi:10.1002/chem.200500980.

Aizenberg, Joanna, Vikram C. Sundar, Andrew D. Yablon, James C. Weaver, and Gang Chen. 2004. Biological glass fibers: Correlation between optical and structural properties. *Proceedings of the National Academy of Sciences of the United States of America* 101, no. 10 (March 9): 3358 -3363. doi:10.1073/pnas.0307843101.

Aizenberg, Joanna, James C. Weaver, Monica S. Thanawala, Vikram C. Sundar, Daniel E. Morse, and Peter Fratzl. 2005. Skeleton of Euplectella sp.: Structural Hierarchy from the Nanoscale to the Macroscale. *Science* 309, no. 5732 (July 8): 275 -278. doi:10.1126/science.1112255.

Arakaki, Atsushi, John Webb, and Tadashi Matsunaga. 2003. A Novel Protein Tightly Bound to Bacterial Magnetic Particles in Magnetospirillum magneticum Strain AMB-1. *Journal of Biological Chemistry* 278, no. 10 (March 7): 8745 -8750. doi:10.1074/jbc.M211729200.

Arias, José L., and María S. Fernández. 2008. Polysaccharides and Proteoglycans in Calcium Carbonate-based Biomineralization. *Chemical Reviews* 108, no. 11 (November 12): 4475-4482. doi:10.1021/cr078269p.

Bansal, Vipul, Debabrata Rautaray, Absar Ahmad, and Murali Sastry. 2004. Biosynthesis of zirconia nanoparticles using the fungus Fusarium oxysporum. *Journal of Materials Chemistry* 14, no. 22: 3303. doi:10.1039/b407904c.

Bansal, Vipul, Debabrata Rautaray, Atul Bharde, Keda Ahire, Ambarish Sanyal, Absar Ahmad, and Murali Sastry. 2005. Fungus-mediated biosynthesis of silica and titania particles. *Journal of Materials Chemistry* 15, no. 26: 2583. doi:10.1039/b503008k.

Bazylinski, Dennis A., and Richard B. Frankel. 2004. Magnetosome formation in prokaryotes. *Nat Rev Micro* 2, no. 3 (March): 217-230. doi:10.1038/nrmicro842.

Brutchey, Richard L., and Daniel E. Morse. 2008. Silicatein and the Translation of its Molecular Mechanism of Biosilicification into Low Temperature Nanomaterial Synthesis. *Chemical Reviews* 108, no. 11 (November 12): 4915-4934. doi:10.1021/cr078256b.

Brutchey, Richard L., Edward S. Yoo, and Daniel E. Morse. 2006. Biocatalytic Synthesis of a Nanostructured and Crystalline Bimetallic Perovskite-like Barium Oxofluorotitanate at Low Temperature. *Journal of the American Chemical Society* 128, no. 31: 10288-10294. doi:10.1021/ja063107g.

Cai, Yurong, and Juming Yao. 2010. Effect of proteins on the synthesis and assembly of calcium phosphate nanomaterials. *Nanoscale* 2, no. 10: 1842. doi:10.1039/c0nr00092b.

Cattaneo-Vietti, R., G. Bavestrello, C. Cerrano, M. Sara, U. Benatti, M. Giovine, and E. Gaino. 1996. Optical fibres in an Antarctic sponge. *Nature* 383, no. 6599 (October 3): 397-398. doi:10.1038/383397b0.

Chen, Xianqiong, Yuyang Liu, Haifeng Lu, Hengrui Yang, Xiang Zhou, and John H. Xin. 2010. In-situ growth of silica nanoparticles on cellulose and application of

hierarchical structure in biomimetic hydrophobicity. *Cellulose* 17, no. 6 (8): 1103-1113. doi:10.1007/s10570-010-9445-3.

Chung, Woo-Jae, Ki-Young Kwon, Jie Song, and Seung-Wuk Lee. Evolutionary Screening of Collagen-like Peptides That Nucleate Hydroxyapatite Crystals. *Langmuir* 0, no. 0 (January). doi:10.1021/la104757g. http://dx.doi.org.proxy.lib.iastate.edu:2048/10.1021/la104757g.

Cui, Fu-Zhai, Yan Li, and Jun Ge. 2007. Self-assembly of mineralized collagen composites. *Materials Science and Engineering: R: Reports* 57, no. 1-6 (August 1): 1-27. doi:10.1016/j.mser.2007.04.001.

Curnow, Paul, Paul H. Bessette, David Kisailus, Meredith M. Murr, Patrick S. Daugherty, and Daniel E. Morse. 2005. Enzymatic Synthesis of Layered Titanium Phosphates at Low Temperature and Neutral pH by Cell-Surface Display of Silicatein-α. *Journal of the American Chemical Society* 127, no. 45 (November 1): 15749-15755. doi:10.1021/ja054307f.

Dickerson, Matthew B., Kenneth H. Sandhage, and Rajesh R. Naik. 2008. Protein- and Peptide-Directed Syntheses of Inorganic Materials. *Chemical Reviews* 108, no. 11 (November 12): 4935-4978. doi:10.1021/cr8002328.

Ding, Baoquan, Zhengtao Deng, Hao Yan, Stefano Cabrini, Ronald N. Zuckermann, and Jeffrey Bokor. 2010. Gold Nanoparticle Self-Similar Chain Structure Organized by DNA Origami. *Journal of the American Chemical Society* 132, no. 10 (March 17): 3248-3249. doi:10.1021/ja9101198.

Dujardin, E., and S. Mann. 2002. Bio-inspired Materials Chemistry. *Advanced Materials* 14, no. 11 (6): 775. doi:10.1002/1521-4095(20020605)14:11<775::AID-ADMA775>3.0.CO;2-0.

Enlow, D., A. Rawal, M. Kanapathipillai, K. Schmidt-Rohr, S. Mallapragada, C.-T. Lo, P. Thiyagarajan, and M. Akinc. 2007. Synthesis and characterization of self-assembled block copolymer templated calcium phosphate nanocomposite gels. *Journal of Materials Chemistry* 17, no. 16: 1570. doi:10.1039/b613760a.

Estroff, Lara A., and Andrew D. Hamilton. 2001. At the Interface of Organic and Inorganic Chemistry: Bioinspired Synthesis of Composite Materials. *Chemistry of Materials* 13, no. 10 (October 1): 3227-3235. doi:10.1021/cm010110k.

Feldheim, Daniel L., and Bruce E. Eaton. 2007. Selection of Biomolecules Capable of Mediating the Formation of Nanocrystals. *ACS Nano* 1, no. 3 (October 1): 154-159. doi:10.1021/nn7002019.

Fujii, Toshihiro, Teppei Tanaka, and Kousaku Ohkawa. 2009. Biomineralization of calcium phosphate on human hair protein film and formation of a novel hydroxyapatite-protein composite material. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 91B, no. 2 (11): 528-536. doi:10.1002/jbm.b.31426.

Gajjeraman, Sivakumar, Gen He, Karthikeyan Narayanan, and Anne George. 2008. Biological Assemblies Provide Novel Templates for the Synthesis of Biocomposites and Facilitate Cell Adhesion. *Advanced Functional Materials* 18, no. 24 (12): 3972-3980. doi:10.1002/adfm.200801215.

George, Anne, and Sriram Ravindran. 2010. Protein templates in hard tissue engineering. *Nano Today* 5, no. 4 (August): 254-266. doi:10.1016/j.nantod.2010.05.005.

Gilbert, Michele, Cecilia M. Giachelli, and Patrick S. Stayton. 2003. Biomimetic peptides that engage specific integrin-dependent signaling pathways and bind to calcium phosphate surfaces. *Journal of Biomedical Materials Research* 67A, no. 1 (10): 69-77. doi:10.1002/jbm.a.10053.

Gower, Laurie B. 2008. Biomimetic Model Systems for Investigating the Amorphous Precursor Pathway and Its Role in Biomineralization. *Chemical Reviews* 108, no. 11 (November 12): 4551-4627. doi:10.1021/cr800443h.

Hartgerink, Jeffrey D., Elia Beniash, and Samuel I. Stupp. 2001. Self-Assembly and Mineralization of Peptide-Amphiphile Nanofibers. *Science* 294, no. 5547 (November 23): 1684 -1688. doi:10.1126/science.1063187.

He, D., X. F. Xiao, F. Liu, and R. F. Liu. 2007. Hydroxyapatite nanospindles by biomimetic synthesis with chitosan as template. *Materials Science and Technology* 23, no. 10 (10): 1228-1232. doi:10.1179/174328407X213305.

Hu, Y.-Y., A. Rawal, and K. Schmidt-Rohr. 2010. Strongly bound citrate stabilizes the apatite nanocrystals in bone. *Proceedings of the National Academy of Sciences* 107, no. 52 (December 28): 22425 -22429. doi:10.1073/pnas.1009219107.

Hu, Yan-Yan, Yusuf Yusufoglu, Mathumai Kanapathipillai, Chu-Ya Yang, YaQiao Wu, Papannan Thiyagarajan, Timothy Deming, Mufit Akinc, Klaus Schmidt-Rohr, and Surya Mallapragada. 2009. Self-assembled calcium phosphate nanocomposites using block copolypeptide templates. *Soft Matter* 5, no. 21: 4311. doi:10.1039/b904440j.

Jensen, Martin, Ralf Keding, Thomas Hö̈che, and Yuanzheng Yue. 2009. Biologically Formed Mesoporous Amorphous Silica. *Journal of the American Chemical Society* 131, no. 7 (February 25): 2717-2721. doi:10.1021/ja808847y.

Kanapathipillai, M., Y. Yusufoglu, A. Rawal, Y.-Y. Hu, C.-T. Lo, P. Thiyagarajan, Y. E. Kalay, M. Akinc, S. Mallapragada, and K. Schmidt-Rohr. 2008. Synthesis and Characterization of Ionic Block Copolymer Templated Calcium Phosphate Nanocomposites. *Chemistry of Materials* 20, no. 18: 5922-5932. doi:10.1021/cm703441n.

Kikuchi, Masanori, Toshiyuki Ikoma, Soichiro Itoh, Hiroko N. Matsumoto, Yoshihisa Koyama, Kazuo Takakuda, Kenichi Shinomiya, and Junzo Tanaka. 2004. Biomimetic synthesis of bone-like nanocomposites using the self-organization mechanism of hydroxyapatite and collagen. *Composites Science and Technology* 64, no. 6 (May): 819-825. doi:10.1016/j.compscitech.2003.09.002.

Kisailus, David, Quyen Truong, Yosuke Amemiya, James C Weaver, and Daniel E Morse. 2006. Self-assembled bifunctional surface mimics an enzymatic and templating protein for the synthesis of a metal oxide semiconductor. *Proceedings of the National Academy of Sciences of the United States of America* 103, no. 15 (April 11): 5652-5657. doi:10.1073/pnas.0508488103.

Komeili, Arash. 2007. Molecular Mechanisms of Magnetosome Formation. *Annual Review of Biochemistry* 76, no. 1 (6): 351-366. doi:10.1146/annurev.biochem.74.082803.133444.

Kröger, Nils, Matthew B. Dickerson, Gul Ahmad, Ye Cai, Michael S. Haluska, Kenneth H. Sandhage, Nicole Poulsen, and Vonda C. Sheppard. 2006. Bioenabled Synthesis of

Rutile (TiO2) at Ambient Temperature and Neutral pH. *Angewandte Chemie* 118, no. 43 (11): 7397-7401. doi:10.1002/ange.200601871.

Li, Junjie, Dunwan Zhu, Jianwei Yin, Yuxi Liu, Fanglian Yao, and Kangde Yao. 2010. Formation of nano-hydroxyapatite crystal in situ in chitosan-pectin polyelectrolyte complex network. *Materials Science and Engineering: C* 30, no. 6 (July 20): 795-803. doi:10.1016/j.msec.2010.03.011.

Liang, Hongjun, Thomas E. Angelini, Paul V. Braun, and Gerard C. L. Wong. 2004. Roles of Anionic and Cationic Template Components in Biomineralization of CdS Nanorods Using Self-Assembled DNA−Membrane Complexes. *Journal of the American Chemical Society* 126, no. 43 (November 1): 14157-14165. doi:10.1021/ja046718m.

Liao, Susan, Michelle Ngiam, Casey K Chan, and S Ramakrishna. 2009. Fabrication of nano-hydroxyapatite/collagen/osteonectin composites for bone graft applications. *Biomedical Materials* 4, no. 2 (4): 025019. doi:10.1088/1748-6041/4/2/025019.

Liu, Dan, Tao Wang, and Joseph L. Keddie. 2009. Protein Nanopatterning on Self-Organized Poly(styrene-b-isoprene) Thin Film Templates. *Langmuir* 25, no. 8 (April 21): 4526-4534. doi:10.1021/la8038957.

Loweth, Colin J., W. Brett Caldwell, Xiaogang Peng, A. Paul Alivisatos, and Peter G. Schultz. 1999. DNA-Based Assembly of Gold Nanocrystals. *Angewandte Chemie International Edition* 38, no. 12 (6): 1808-1812. doi:10.1002/(SICI)1521-3773(19990614)38:12<1808::AID-ANIE1808>3.0.CO;2-C.

Ma, Nan, Chad J. Dooley, and Shana O. Kelley. 2006. RNA-Templated Semiconductor Nanocrystals. *Journal of the American Chemical Society* 128, no. 39 (October 1): 12598-12599. doi:10.1021/ja0638962.

Mann, Stephen, Douglas D. Archibald, Jon M. Didymus, Trevor Douglas, Brigid R. Heywood, Fiona C. Meldrum, and Nicholas J. Reeves. 1993. Crystallization at Inorganic-organic Interfaces: Biominerals and Biomimetic Synthesis. *Science* 261, no. 5126: 1286 -1292. doi:10.1126/science.261.5126.1286.

Meyers, Marc André, Po-Yu Chen, Albert Yu-Min Lin, and Yasuaki Seki. 2008. Biological materials: Structure and mechanical properties. *Progress in Materials Science* 53, no. 1 (January): 1-206. doi:10.1016/j.pmatsci.2007.05.002.

Müller, Werner E G, Carsten Eckert, Klaus Kropf, Xiaohong Wang, Ute Schlossmacher, Christopf Seckert, Stephan E Wolf, Wolfgang Tremel, and Heinz C Schröder. 2007. Formation of giant spicules in the deep-sea hexactinellid Monorhaphis chuni (Schulze 1904): electron-microscopic and biochemical studies. *Cell and Tissue Research* 329, no. 2 (August): 363-378. doi:10.1007/s00441-007-0402-x.

Palmer, Liam C., Christina J. Newcomb, Stuart R. Kaltz, Erik D. Spoerke, and Samuel I. Stupp. 2008. Biomimetic Systems for Hydroxyapatite Mineralization Inspired By Bone and Enamel. *Chemical Reviews* 108, no. 11 (November 12): 4754-4783. doi:10.1021/cr8004422.

Park, Dae-Hwan, Jung-Eun Kim, Jae-Min Oh, Yong-Gun Shul, and Jin-Ho Choy. 2010. DNA Core@Inorganic Shell. *Journal of the American Chemical Society* 132, no. 47 (December 1): 16735-16736. doi:10.1021/ja105809e.

Patil, Avinash J., and Stephen Mann. 2008. Self-assembly of bio–inorganic nanohybrids using organoclay building blocks. *Journal of Materials Chemistry* 18, no. 39: 4605. doi:10.1039/b805653f.

Prockop, J D. 1995. Collagens: Molecular Biology, Diseases, and Potentials for Therapy. *Annual Review of Biochemistry* 64, no. 1 (6): 403-434. doi:10.1146/ annurev. bi.64.070195.002155.

Prozorov, T., S. K. Mallapragada, B. Narasimhan, L. Wang, P. Palo, M. Nilsen-Hamilton, T. J. Williams, D. A. Bazylinski, R. Prozorov, and P. C. Canfield. 2007. Protein-Mediated Synthesis of Uniform Superparamagnetic Magnetite Nanocrystals. *Advanced Functional Materials* 17, no. 6 (4): 951-957. doi:10.1002/adfm.200600448.

Prozorov, Tanya, Pierre Palo, Lijun Wang, Marit Nilsen-Hamilton, DeAnna Jones, Daniel Orr, Surya K. Mallapragada, Balaji Narasimhan, Paul C. Canfield, and Ruslan Prozorov. 2007. Cobalt Ferrite Nanocrystals: Out-Performing Magnetotactic Bacteria. *ACS Nano* 1, no. 3 (October 1): 228-233. doi:10.1021/nn700194h.

Rey, C., C. Combes, C. Drouet, and M. J. Glimcher. 2009. Bone mineral: update on chemical composition and structure. *Osteoporosis International* 20, no. 6 (4): 1013-1021. doi:10.1007/s00198-009-0860-y.

de la Rica, Roberto, and Hiroshi Matsui. 2010. Applications of peptide and protein-based materials in bionanotechnology. *Chemical Society Reviews* 39, no. 9: 3499. doi:10.1039/b917574c.

Salgado, António J, Olga P Coutinho, and Rui L Reis. 2004. Bone tissue engineering: state of the art and future trends. *Macromolecular Bioscience* 4, no. 8 (August 9): 743-765. doi:10.1002/mabi.200400026.

Sarikaya, Mehmet, Candan Tamerler, Alex K. -Y. Jen, Klaus Schulten, and Francois Baneyx. 2003. Molecular biomimetics: nanotechnology through biology. *Nat Mater* 2, no. 9: 577-585. doi:10.1038/nmat964.

Shiomi, Toru, Tatsuo Tsunoda, Akiko Kawai, Fujio Mizukami, and Kengo Sakaguchi. 2007. Biomimetic Synthesis of Lysozyme−Silica Hybrid Hollow Particles Using Sonochemical Treatment: Influence of pH and Lysozyme Concentration on Morphology. *Chemistry of Materials* 19, no. 18: 4486-4493. doi:10.1021/cm071011v.

Söllner, Christian, Manfred Burghammer, Elisabeth Busch-Nentwich, Jürgen Berger, Heinz Schwarz, Christian Riekel, and Teresa Nicolson. 2003. Control of Crystal Size and Lattice Formation by Starmaker in Otolith Biomineralization. *Science* 302, no. 5643 (October 10): 282 -286. doi:10.1126/science.1088443.

Sumerel, Jan L., Wenjun Yang, David Kisailus, James C. Weaver, Joon Hwan Choi, and Daniel E. Morse. 2003. Biocatalytically Templated Synthesis of Titanium Dioxide. *Chemistry of Materials* 15, no. 25 (December 1): 4804-4809. doi:10.1021/cm030254u.

Sundar, Vikram C., Andrew D. Yablon, John L. Grazul, Micha Ilan, and Joanna Aizenberg. 2003. Fibre-optical features of a glass sponge. *Nature* 424, no. 6951: 899-900. doi:10.1038/424899a.

Tahir, Muhammad Nawaz, Patrick Théato, Werner E. G. Müller, Heinz C. Schröder, Andreas Janshoff, Jian Zhang, Joachim Huth, and Wolfgang Tremel. 2004. Monitoring the formation of biosilica catalysed by histidine-tagged silicatein. *Chemical Communications*, no. 24: 2848. doi:10.1039/b410283e.

Tahir, Muhammad Nawaz, Patrick Théato, Werner E. G. Müller, Heinz C. Schröder, Alexandra Borejko, Simon Faiß, Andreas Janshoff, Joachim Huth, and Wolfgang Tremel. 2005. Formation of layered titania and zirconia catalysed by surface-bound silicatein. *Chemical Communications*, no. 44: 5533. doi:10.1039/b510113a.

Tampieri, Anna, Giancarlo Celotti, Elena Landi, Monica Sandri, Norberto Roveri, and Giuseppe Falini. 2003. Biologically inspired synthesis of bone-like composite: Self-assembled collagen fibers/hydroxyapatite nanocrystals. *Journal of Biomedical Materials Research* 67A, no. 2 (11): 618-625. doi:10.1002/jbm.a.10039.

Venkatesan, Jayachandran, and Se-Kwon Kim. 2010. Chitosan Composites for Bone Tissue Engineering—An Overview. *Marine Drugs* 8, no. 8 (8): 2252-2266. doi:10.3390/md8082252.

Wang, Xiaohong, Matthias Wiens, Heinz C. Schröder, Shixue Hu, Enrico Mugnaioli, Ute Kolb, Wolfgang Tremel, Dario Pisignano, and Werner E. G. Müller. 2010. Morphology of Sponge Spicules: Silicatein a Structural Protein for Bio-Silica Formation. *Advanced Engineering Materials* 12, no. 9 (9): B422-B437. doi:10.1002/adem.200980042.

Wang, Y., C. Yang, X. Chen, and N. Zhao. 2006. Biomimetic Formation of Hydroxyapatite/collagen Matrix Composite. *Advanced Engineering Materials* 8, no. 1-2 (2): 97-100. doi:10.1002/adem.200500220.

Wang, Zidong, Jieqian Zhang, Jonathan M. Ekman, Paul J. A. Kenis, and Yi Lu. 2010. DNA-Mediated Control of Metal Nanoparticle Shape: One-Pot Synthesis and Cellular Uptake of Highly Stable and Functional Gold Nanoflowers. *Nano Letters* 10, no. 5 (May 12): 1886-1891. doi:10.1021/nl100675p.

Xu, An-Wu, Yurong Ma, and Helmut C?lfen. 2007. Biomimetic mineralization. *Journal of Materials Chemistry* 17, no. 5: 415. doi:10.1039/b611918m.

Xu, Hai, Yuming Wang, Xin Ge, Shuyi Han, Shengjie Wang, Peng Zhou, Honghong Shan, Xiubo Zhao, and Jian R. Lu. 2010. Twisted Nanotubes Formed from Ultrashort Amphiphilic Peptide I3K and Their Templating for the Fabrication of Silica Nanotubes. *Chemistry of Materials* 22, no. 18: 5165-5173. doi:10.1021/cm101019p.

Yang, Lin, Ruimin Xing, Qingming Shen, Kai Jiang, Feng Ye, Jinye Wang, and Qiushi Ren. 2006. Fabrication of protein-conjugated silver sulfide nanorods in the bovine serum albumin solution. *The Journal of Physical Chemistry. B* 110, no. 21 (June 1): 10534-10539. doi:10.1021/jp055603h.

Yusufoglu, Yusuf, Yanyan Hu, Mathumai Kanapathipillai, Matthew Kramer, Yunus E. Kalay, P. Thiyagarajan, Mufit Akinc, Klaus Schmidt-Rohr, and Surya Mallapragada. 2008. Bioinspired synthesis of self-assembled calcium phosphate nanocomposites using block copolymer-peptide conjugates. *Journal of Materials Research* 23, no. 12 (12): 3196-3212. doi:10.1557/jmr.2008.0388.

Zhang, Junping, Yan Liu, Yonggang Ke, and Hao Yan. 2006. Periodic Square-Like Gold Nanoparticle Arrays Templated by Self-Assembled 2D DNA Nanogrids on a Surface. *Nano Letters* 6, no. 2 (February 1): 248-251. doi:10.1021/nl052210l.

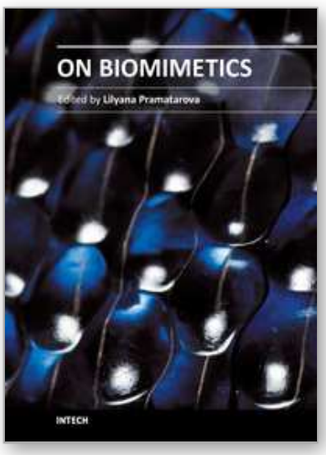
Zhao, Xiubo, Fang Pan, Hai Xu, Mohammed Yaseen, Honghong Shan, Charlotte A. E. Hauser, Shuguang Zhang, and Jian R. Lu. 2010. Molecular self-assembly and

applications of designer peptide amphiphiles. *Chemical Society Reviews* 39, no. 9: 3480. doi:10.1039/b915923c.

Zimmermann, Kristen A., Jill M. LeBlanc, Kevin T. Sheets, Robert W. Fox, and Paul Gatenholm. 2011. Biomimetic design of a bacterial cellulose/hydroxyapatite nanocomposite for bone healing applications. *Materials Science and Engineering: C* 31, no. 1 (January 1): 43-49. doi:10.1016/j.msec.2009.10.007.

Zuo, Guifu, Yizao Wan, Lei Wang, Chao Liu, Fang He, and Honglin Luo. 2010. Synthesis and characterization of laminated hydroxyapatite/chitosan nanocomposites. *Materials Letters* 64, no. 19 (October 15): 2126-2128. doi:10.1016/j.matlet.2010.06.063.

IntechOpen



On Biomimetics

Edited by Dr. Lilyana Pramatarova

ISBN 978-953-307-271-5
Hard cover, 642 pages
Publisher InTech
Published online 29, August, 2011
Published in print edition August, 2011

Bio-mimicry is fundamental idea â€˜How to mimic the Natureâ€™ by various methodologies as well as new ideas or suggestions on the creation of novel materials and functions. This book comprises seven sections on various perspectives of bio-mimicry in our life; Section 1 gives an overview of modeling of biomimetic materials; Section 2 presents a processing and design of biomaterials; Section 3 presents various aspects of design and application of biomimetic polymers and composites are discussed; Section 4 presents a general characterization of biomaterials; Section 5 proposes new examples for biomimetic systems; Section 6 summarizes chapters, concerning cells behavior through mimicry; Section 7 presents various applications of biomimetic materials are presented. Aimed at physicists, chemists and biologists interested in biomineralization, biochemistry, kinetics, solution chemistry. This book is also relevant to engineers and doctors interested in research and construction of biomimetic systems.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Xunpei Liu and Surya K. Mallapragada (2011). Bioinspired Synthesis of Organic/Inorganic Nanocomposite Materials Mediated by Biomolecules, On Biomimetics, Dr. Lilyana Pramatarova (Ed.), ISBN: 978-953-307-271-5, InTech, Available from: http://www.intechopen.com/books/on-biomimetics/bioinspired-synthesis-of-organic-inorganic-nanocomposite-materials-mediated-by-biomolecules

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License, which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen