



ISSN 2278 – 0211 (Online)

Advances in Molecular Biomimetics

Sivaprakash Arul

Lecturer, Department of Chemistry, Loyola College, Chennai, Tamil Nadu, India

Abstract:

Biomimetic material synthesis gained more interest in the recent years. Biomimetic material synthesis can be done by mimicking the natural processes to produce materials in a controlled manner. Biomimetic synthesis requires complete understanding of interactions behind the biomolecules and material surface. In this article, I describe the current progress in biomimetic synthesis in both experimental and simulations mode and classify this information in following perspectives: biomimetic system with template; progress in molecular simulations; materials development based on simulation; intelligent biomimetic system; and bioinspired systems. In addition, synthesis, simulations, principles and relationships are discussed, and the challenges and directions for further development are considered.

Keywords: Nanomaterials, Biomimetic synthesis, Simulations, Bioinspired materials

1. Introduction

The concept of learning from nature traced back a few thousand years ago until the term biomimetics was suggested by Schmitt in 1960^[1-4]. The term was used to investigate the formation of biologically produced substances and materials (such as enzymes or silk) and processes (photosynthesis and protein synthesis), specifically for synthesizing similar products by synthetic mechanisms that mimic natural ones. In recent years, biomimetics or bioinspired materials gained more attention and taking lessons from nature and extend research in many fields, such as robotics^[5], bioelectronics^[6], medicine, catalysis^[7], self cleaning^[8], material science, and energy. With an increase in miniaturization of the objects of nano sized plays a big role in nanofabricated structures and microfluidic technologies. It requires in depth understanding of tools from nanotechnology.

Nanotechnology is a study of manipulation of nano sized materials in space and time with substantial amount of detail. Increasing demand of quantitative details in the biological experiments, biologists resort to knowledge offered by physics, chemistry, and nanotechnology. Biomimetic synthesis of nanomaterials is the fastest and interesting area in the branch of biomimetics. It can be classified into areas: functional biomimetic synthesis and process biomimetic synthesis. Functional biomimetic synthesis aims to mimic nature materials/structures/systems to create artificial systems such as bones and artificial organs. In case of process biomimetic synthesis is a kind of synthesis method, that attempts to prepare artificial materials/substances by mimicking synthesis process. For example, by mimicking protein synthesis process, many nanostructures like dendrimer, cubes, 2D arrays, 3D AuNP tubes, pyramids have been assembled in vitro.

Organism contain a lot of information about biological processes, such as molecular assembly, recognition, and template regulation. With advanced recognition biomineralization involves elementary biological processes. Synthesis of nanomaterials can be conducted by mimicking biological processes in vitro. Biomimetic synthesis uses animal structures such as butterfly wings^[9], sea-urchin skeletons, beetles, silk-fibrin filaments, spider silk, and eggshell membranes^[10]. Butterfly wings has several colors and patterns due to their periodic pattern and are widely exploited for biomimetic synthesis. Notably, Zhang's group prepared ZnO^[11] and ZrO₂ photonic crystals and Fe₃O₄ magnetophotonic crystals with a 3D network using butterfly wings.

Cells can also be used for the biomimetic synthesis of nanomaterials. Red blood cells (RBCs) show biological responses to chemical agents, and four distinct morphologies, stomatocytes, echinocytes, spherocytes, discocytes, can be obtained. These asymmetric RBC shapes can be used as anisotropic composites and inorganic particles using a process of silica bioreplication. As a result, due to the adjustable shapes of RBCs, the internal structure/porosity of the obtained mesoporous material can be tuned.

2. Biomimetic Synthesis via Liquid Membranes

Recent employment of liquid membranes such as emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs). Emulsion liquid membranes successfully employed to create biomimetic system. Surfactant is a crucial factor for synthesis of nanomaterials/nanostructures that influences crystal nucleation and growth. Wu co-workers demonstrated the ELM system to synthesize range of quantum dots, such as CdS, HgSe, and ZnSe, which shows quantum confinement that is different from bulk materials.

An assembly of ZnSe quantum dots into 2D orthohexagonal ZnSe single-crystal slices (Fig 1A, B) was observed in an ELM biomimetic system. Using ELM system flower like BaCrO₄ superstructures can be obtained in ELM system (Fig 1C). Rare earth oxide composite phosphors can be obtained in an ELM system and facilitate the route for designing composite structures and components via control of the transport rate and charge ratios. Composite structure CoFe₂O₄ was prepared using ELM system (Fig 1D). Wu co-workers successfully applied SLMs, a type of monodisperse liquid membrane, for the synthesis of nanostructures/nanostructures. ZnS chain-like nanospheres, CdS hollow/solid nanospheres, bunched PbMoO₄ nanobelts, and Cd(OH)₂ nanowires were synthesized using SLM biomimetic system. SLM can be employed to mimic the transmembrane transport process of biomembrane via mobile carriers in a liquid membrane and offers an inorganic–organic interface for crystal nucleation and growth. SLM biomimetic synthesis may provide a new route for metastable crystal synthesis. It was reported that abnormal structure conversion of CaCO₃ from calcite to vaterite using an SLM system. Initial calcite is formed by biomimetic system (Fig 2A), but it is gradually transformed into vaterite (Fig 2B, C, D)

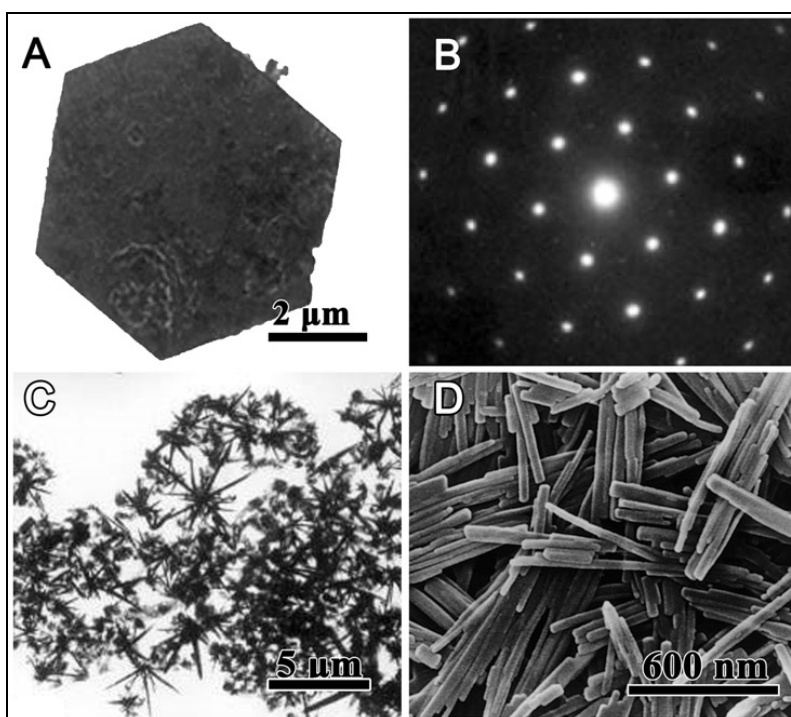


Figure 1: A) TEM image of one orthohexagonal ZnSe slice. B) SAD of orthohexagonal ZnSe slice C) TEM images of a BaCrO₄ superstructure. D) SEM image of a composite Co–Fe oxalate. Reproduced with permission [12].

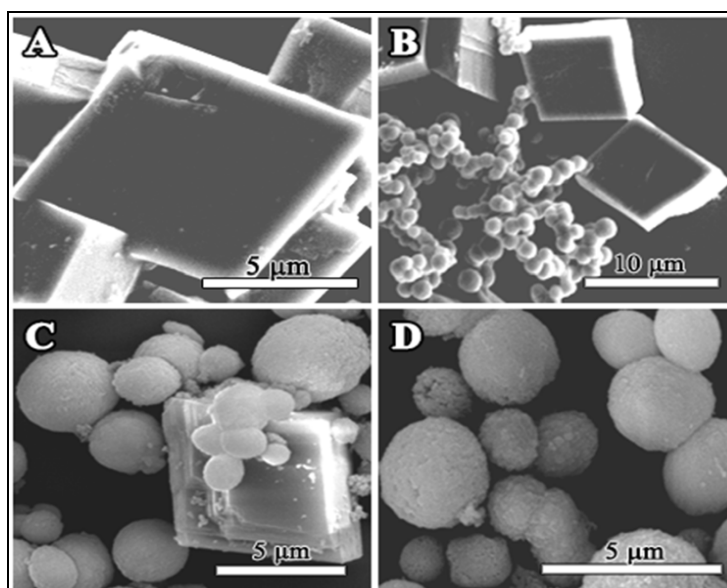


Figure 2: SEM images of abnormal polymorph conversion of CaCO₃ in SLM system for 5 min (A), 30 min (B), 4 h (C), 60 h (D). Reproduced with permission [13].

3. Protein Templated Biomimetic Synthesis

Proteins are the primary source of regulators in living organisms. Both soluble and insoluble proteins can influence the crystal morphology during biomineralization. Insoluble proteins act as template for crystal nucleation and growth, and soluble proteins can adsorb preferentially to specific facets and influence the oriented growth of crystals. In vitro, these effects can be mimicked to either probe the mechanism of biomineralization or to synthesize complex nanostructures and functional inorganic nanomaterials.

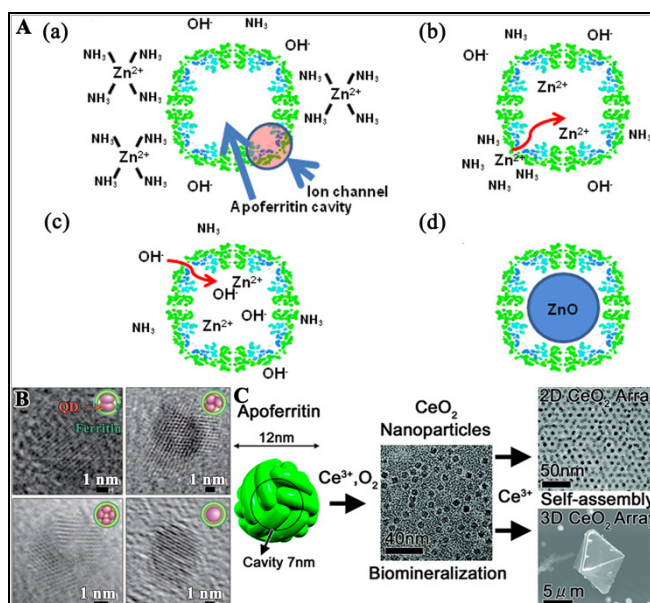


Figure 3: Apoferritin is used as a template for biomimetic synthesis. Reproduced with permission [14–16].

Apoferritin is a ubiquitous protein in living organisms and serves as an iron-storage protein that maintains iron homeostasis in cells. Apoferritin is a 24 polypeptide subunits, exhibiting a spherical structure with a diameter of 12 nm and an internal cavity of 7 nm. Studies have shown that the biomineralization reaction in apoferritin helps nucleation and crystal growth through a multistep process involving the uptake of Fe II, oxidation to Fe III (Fig 3). Studies also showed that heat shock proteins, and DNA-binding proteins, have a similar capacity as apoferritin, in that they can be used as nanoreactors for the biomimetic synthesis of nanomaterials.

4. Simulations Assist Biomimetic Synthesis

Current computational methods to examine structural, chemical, and physical properties underlying interactions between the inorganics and organic molecules. Quantum mechanical calculations enable the analysis of the geometry of molecules, conformers, and clusters of molecules with a focus on electron density, orbital geometry, chemical reactions, and transition states, whereas molecular dynamics and monte carlo simulations reveals structure, conformations, binding energy [17, 18]. Several force fields were built to study the interface (Fig 4).

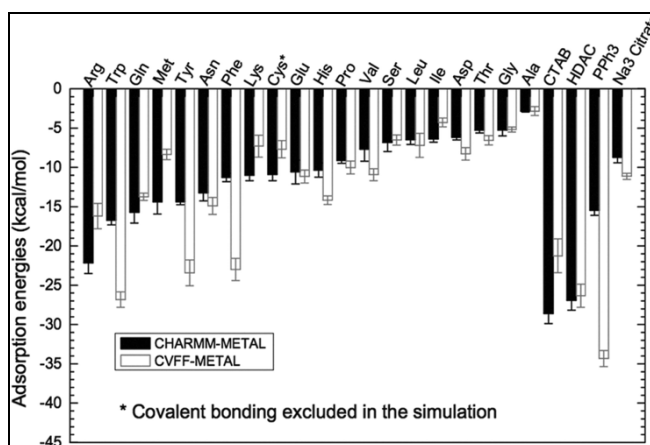


Figure 4: Computed adsorption energies of the natural amino acids on gold(111) surfaces in solution using CHARMM-INTERFACE and the CVFF-INTERFACE force field. Reproduced with permission from [19]

Phage display derived peptides affinity has also been studied computationally on silicon[20]. Authors designed novel peptide with

enhanced properties from the simulation knowledge that is used as template for greater adhesion (Fig 5) [21] .

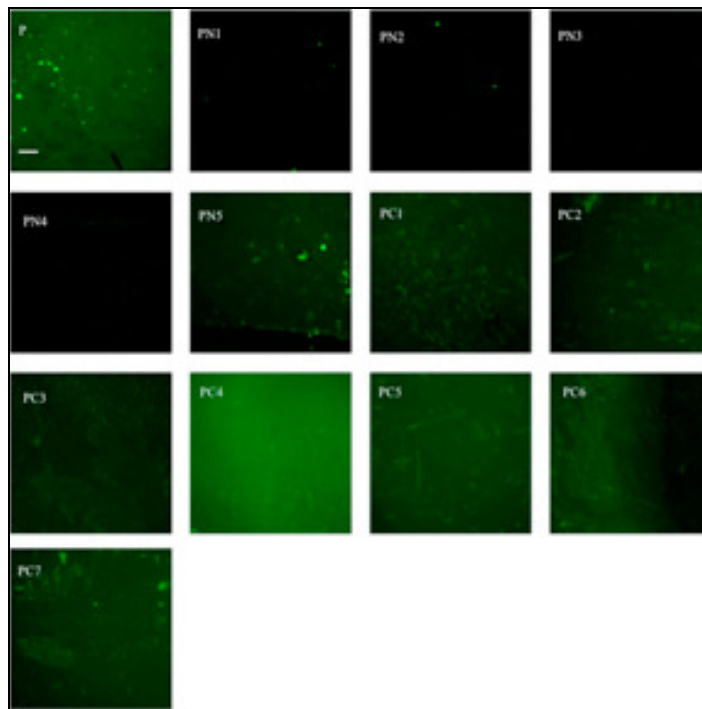


Figure 5: Engineered peptides for greater adhesion to substrate. Reproduced with permission from [21]

5. Conclusion

In conclusion, only a few methods for used to develop biomimetic synthesis were reviewed. There is no doubt that biomimetic synthesis will lead to develop novel materials with predictive properties. Many researchers tend to use bioinspired and biomimetic approaches to address fundamental material synthesis. Nature mimicking materials have greater precision compared to classical trial and methodologies. Simulations on the other hand can provide quantitative trends in interactions and help design binding molecules for each class of materials, allowing the formulation of materials-specific concepts with predictive character.

6. References

- i. P Fratzl andFG Barth (2009) Biomaterial systems for mechanosensing and actuation, *Nature* 462, 442–448
- ii. Y Bar-Cohen (2006) Biomimetics—using nature to inspire human innovation, *Bioinspiration & Biomimetics*.
- iii. C Sanchez, H. Arribart, and M. Guille (2005) Biomimetism and bioinspiration as tools for the design of innovative materials and systems, *Nature materials*. 4, 277–288.
- iv. T Douglas (2003) A bright bio-inspired future, *SCIENCE-NEW YORK THEN WASHINGTON*.
- v. R Pfeifer, M Lungarella, and F Iida (2007) Self-organization, embodiment, and biologically inspired robotics, *science*.
- vi. M Ma, L Guo, DG Anderson, and R Langer (2013) Bio-inspired polymer composite actuator and generator driven by water gradients, *Science*.
- vii. L Que and WB Tolman (2008) Biologically inspired oxidation catalysis, *Nature*.
- viii. J Meng, P Zhang, and S Wang (2015) Recent progress of abrasion-resistant materials: learning from nature, *Chem. Soc. Rev* 45(2):442
- ix. J Han, H Su, D Zhang, J Chen, and Z Chen (2009) Butterfly wings as natural photonic crystal scaffolds for controllable assembly of CdS nanoparticles, *Journal of Materials Chemistry*, 19(46), 8741-8746
- x. Q Dong, H Su, W Cao, D Zhang, Q Guo, and Y Lai (2007) Synthesis and characterizations of hierarchical biomorphic titania oxide by a bio-inspired bottom-up assembly solution technique, *Journal of Solid State Chemistry*. 180(3), 949-955.
- xi. Y Chen, X Zang, J Gu, S Zhu, H Su, and D Zhang (2011) ZnO single butterfly wing scales: synthesis and spatial optical anisotropy, *Journal of Materials Chemistry* 21(17), 6140-6143
- xii. T Hirai, J Kobayashi, and I Komazawa (1999) Preparation of acicular ferrite fine particles using an emulsion liquid membrane system, *Langmuir* 15(19), 6291-6298
- xiii. QS Wu, DM Sun, HJ Liu, and YP Ding (2004) Abnormal polymorph conversion of calcium carbonate and nano-self-assembly of vaterite by a supported liquid membrane system, *Cryst. growth Des* 4, 717-720.
- xiv. M Okuda, Y Suzumoto, and I Yamashita (2011) Bioinspired synthesis of homogenous cerium oxide nanoparticles and two- or three-dimensional nanoparticle arrays using protein supramolecules, *Crystal Growth & Design* 11(6), 2540-2545
- xv. M Naito, K Iwahori, A Miura, and M Yamane (2010) Circularly polarized luminescent CdS quantum dots prepared in a protein

- nanocage, *Angewandte Chemie International Edition*, 49, 7006-7009
- xvi. Y Suzumoto, M Okuda, and I Yamashita (2012) Fabrication of zinc oxide semiconductor nanoparticles in the apoferritin cavity, *Crystal Growth & Design* 12(8), 4130-4134
- xvii. S. Ramakrishnan, M. Martin, T. Cloitre, L. Firlej, F. Cuisinier, and C. Gergely (2013) Insights on the Facet Specific Adsorption of Amino Acids and Peptides toward Platinum, *Journal of Chemical Information and Modeling*. 53, 3273–3279.
- xviii. S.K. Ramakrishnan, M. Martin, T. Cloitre, L. Firlej, and C. Gergely (2015) Design rules for metal binding biomolecules: understanding of amino acid adsorption on platinum crystallographic facets from density functional calculations., *Physical chemistry chemical physics : PCCP*. 17, 4193–8.
- xix. RB Pandey, RJ Berry, BL Farmer, RR Naik, and H Heinz (2011) Adsorption mechanism of single amino acid and surfactant molecules to Au {111} surfaces in aqueous solution: design rules for metal-binding molecules, *Soft Matter*, 7, 2113-2120
- xx. SK Ramakrishnan, M Martin, and T Cloitre (2014) Molecular mechanism of selective binding of peptides to silicon surface, *Journal of Chemical Information and Modeling*. 54 (7), 2117–2126
- xxi. S.K. Ramakrishnan, S. Jebors, M. Martin, T. Cloitre, V. Agarwal, A. Mehdi, J. Martinez, G. Subra, and C. Gergely (2015) Engineered Adhesion Peptides for Improved Silicon Adsorption., *Langmuir : the ACS journal of surfaces and colloids*. 31, 11868–74.