Biomineral-inspired Materials Chemistry

- ***Valuable insights into the scope of materials chemistry and the inorganic-organic interface***

Biominerals

We have seen how minerals are highly controlled in structure, composition, shape and organization

These properties are directly related to many areas of materials chemistry

- *Inorganic-Organic composites*
- *Nanomaterials*
- *Funsctional materials and interfaces*
- *Oriented crystals*
- *Materials with complex morphologies*
- *Organized assemblies*
- *Hierarchical materials*

Biomimetics

- *Biological concepts*
- *Biological molecules and matrices*
- *Biological systems*

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SYNTHESIS

Concepts and Strategies

- *Supramolecular assemblies prior to biomineralization* → *Spatial confinement of chemical reactions and their materials products*
- *Interfacial molecular recognition* → *Template-directed control of nucleation and architecture*
- *Vectorial regulation of biomineral morphogenesis and pattern formation* → *Approaches to the morphosynthesis of inorganic materials in complex form*

Synthesis in confined reaction spaces

The ability of supramolecular compartments such as phospholipid vesicles to control the spatial dimensions of many biominerals suggests that analogous systems should be available and exploitable in synthetic materials chemistry across a range of length scales

Examples

Organic boundaries in biomineralization and their biomimetic counterparts in spatially confined materials synthesis

Biomineralization	Biomimetic synthesis
Phospholipid vesicles	Synthetic vesicles
Ferritin	Artificial ferritins
Cellular assemblies	Bacterial threads
Macromolecular frameworks	Polymer sponges

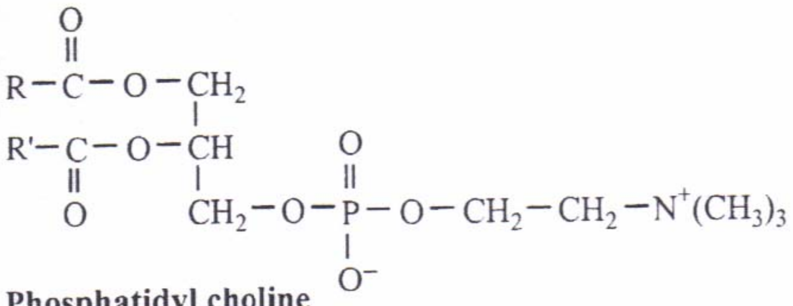
Examples

Table 9.3 Biomineral-inspired approaches to the synthesis of inorganic nanoparticles and composites in confined spaces

Approach	Product	System	Materials
Boundary-organized reaction spaces	Surfactant-coated clusters	Reverse micelles	CdS, $BaSO_4$
		Microemulsions	Pt, Co, metal borides Fe_3O_4, $CaCO_3$
	Membrane-bounded nanoparticles	Vesicles	Pt, Ag, CdS, ZnS Ag_2O, FeOOH, Fe_3O_4, Al_2O_3 Ca phosphates
	Artificial proteins	Ferritin	MnOOH, UO_3, FeS, Fe_3O_4 CdS
		Viroid cages	Tungstates
	2-D nanoparticle superlattices	Porous S-layers	Ta/W, CdS, Au
Internally organized extended structures	Mineral–organic mesostructures	Lipid bilayer films	CdS, Fe_3O_4
		Multilamellar vesicles	SiO_2
	Bacteria–mineral fibres	Bacterial threads	SiO_2, zeolites
	Polymer–mineral composites	Copolymer sponges	Fe_3O_4, TiO_2
		Polyethylene oxide gels	CdS
		Collagen gels	Ca phosphates

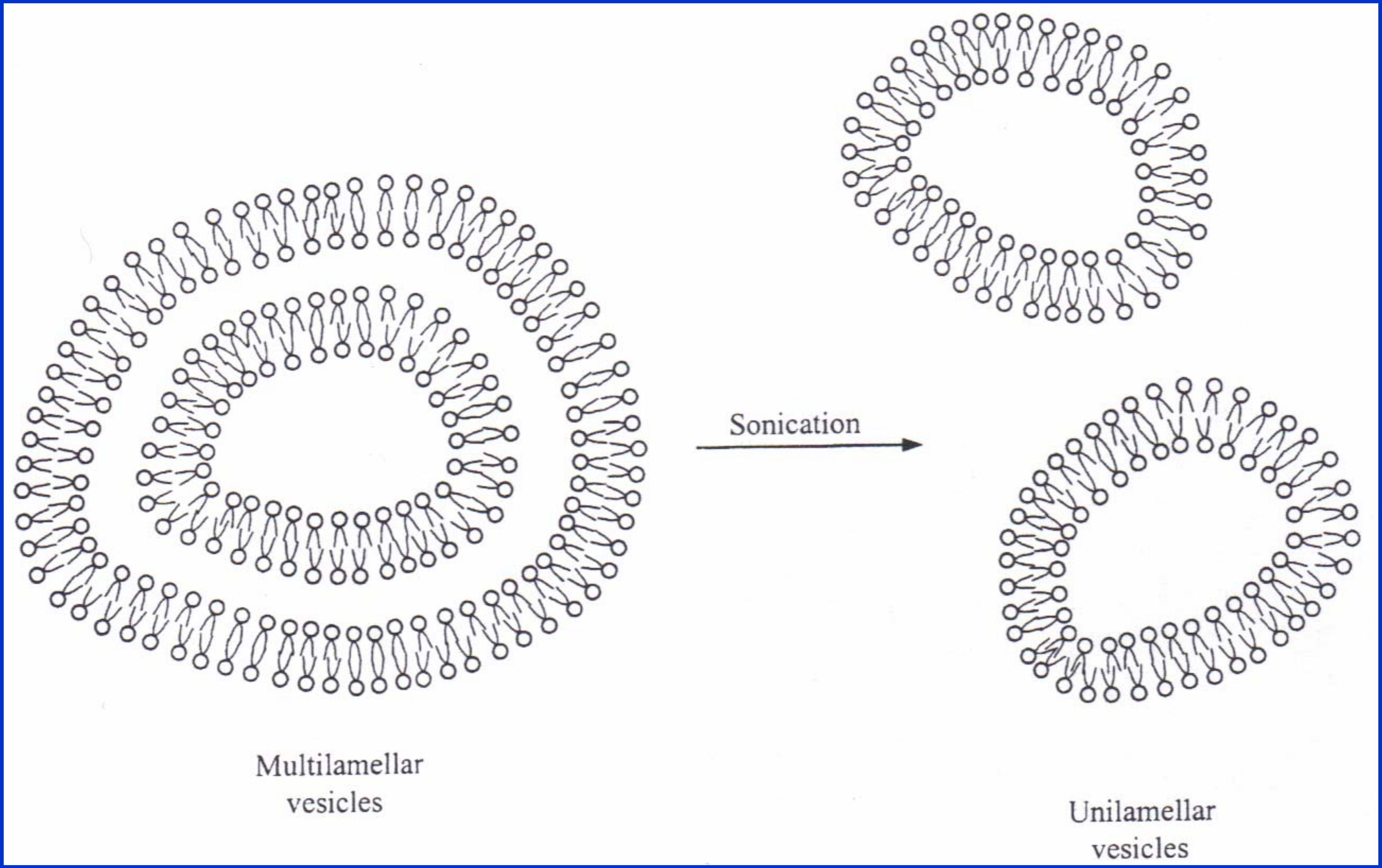
Synthesis Vesicles

In the lab synthetic vesicles can be prepared by sonicating aqueous dispersions of phospholipid molecules, such as phosphatidyl choline

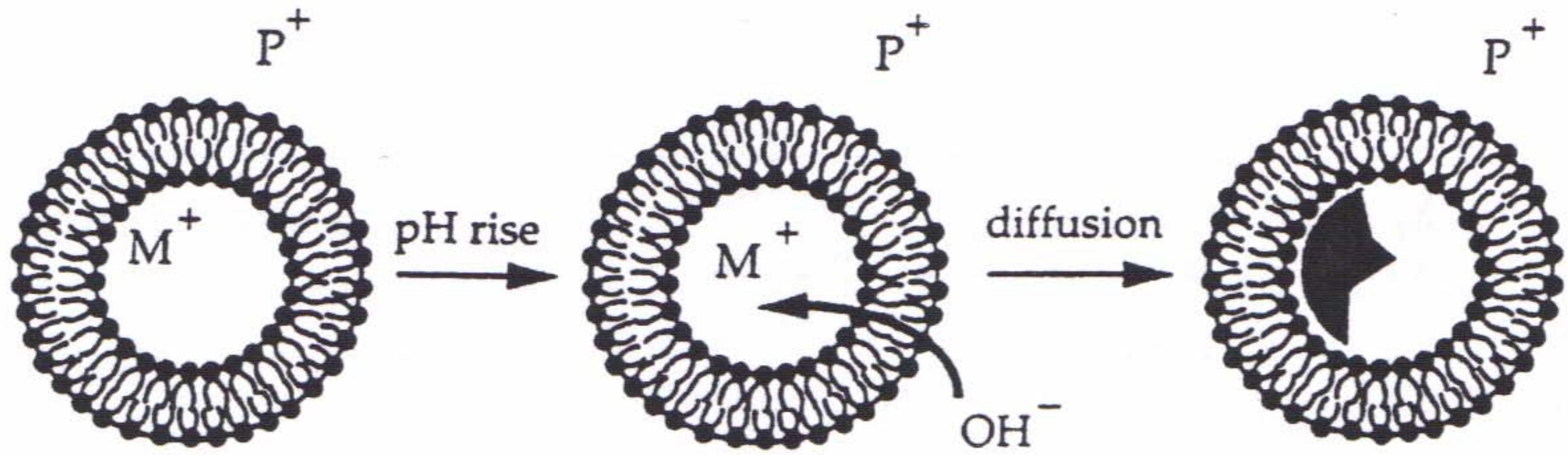


Phosphatidyl choline

Multilamellar and Unilamellar Vesicles

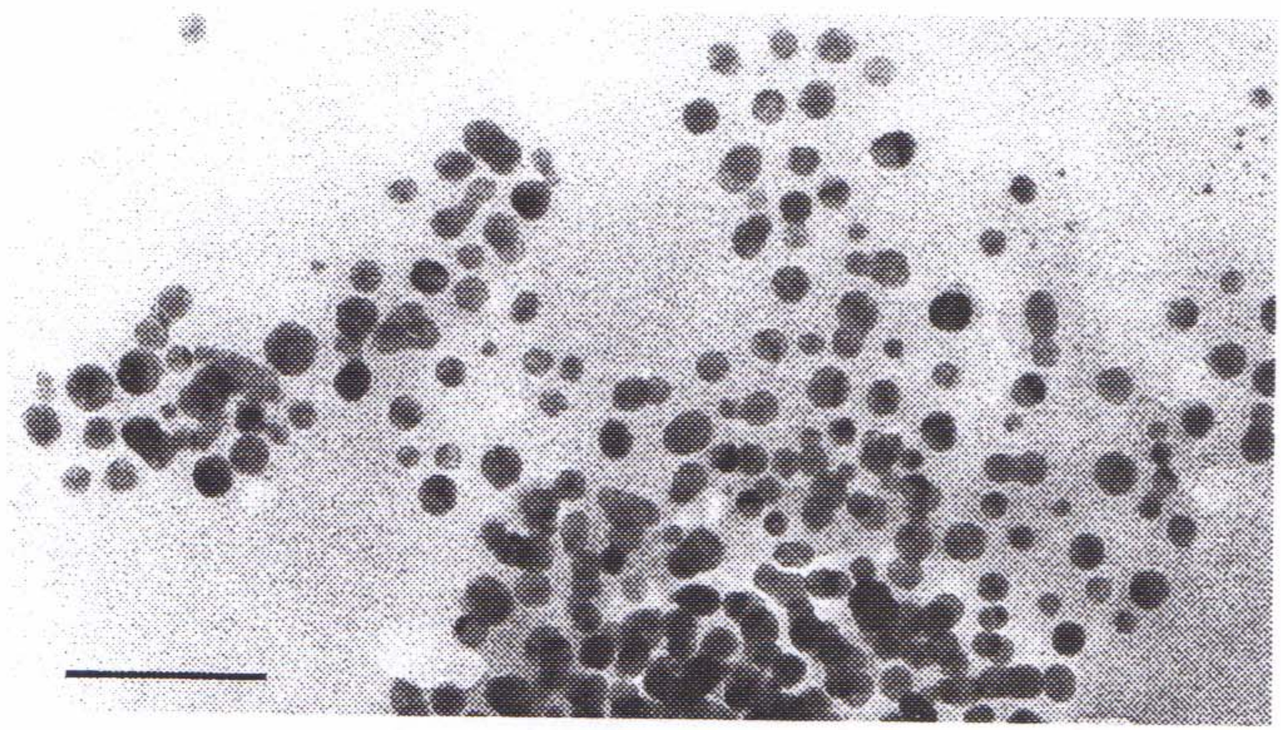


Formation of metal oxide nanoparticles



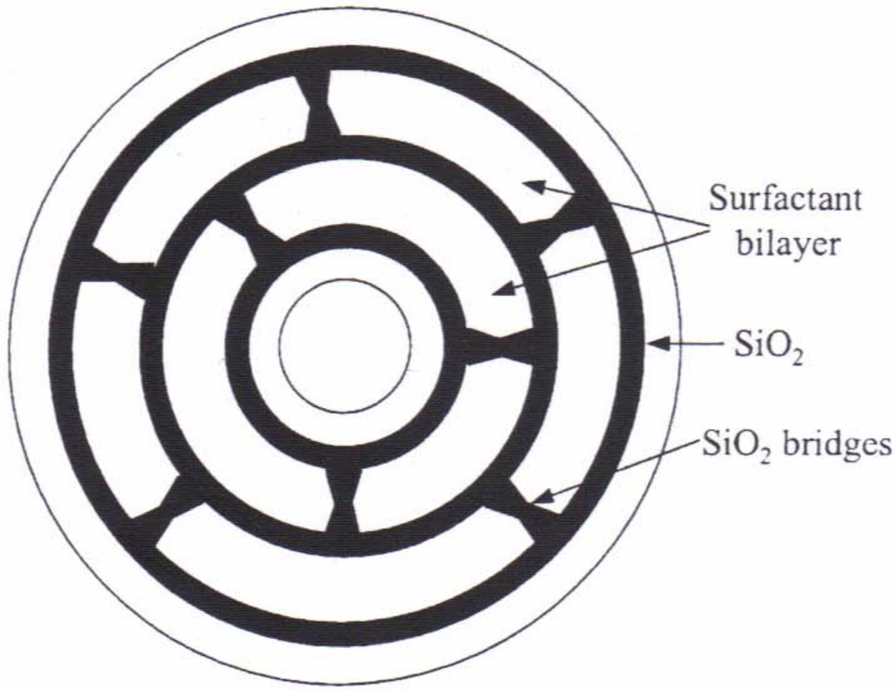
Formation of metal oxide nanoparticles within unilamellar vesicles. Metal cations (M^+) are encapsulated and reacted with OH^- ions that diffuse through the bilayer membrane. Inert cations (P^+) are required to maintain electroneutrality.

Formation of metal oxide nanoparticles



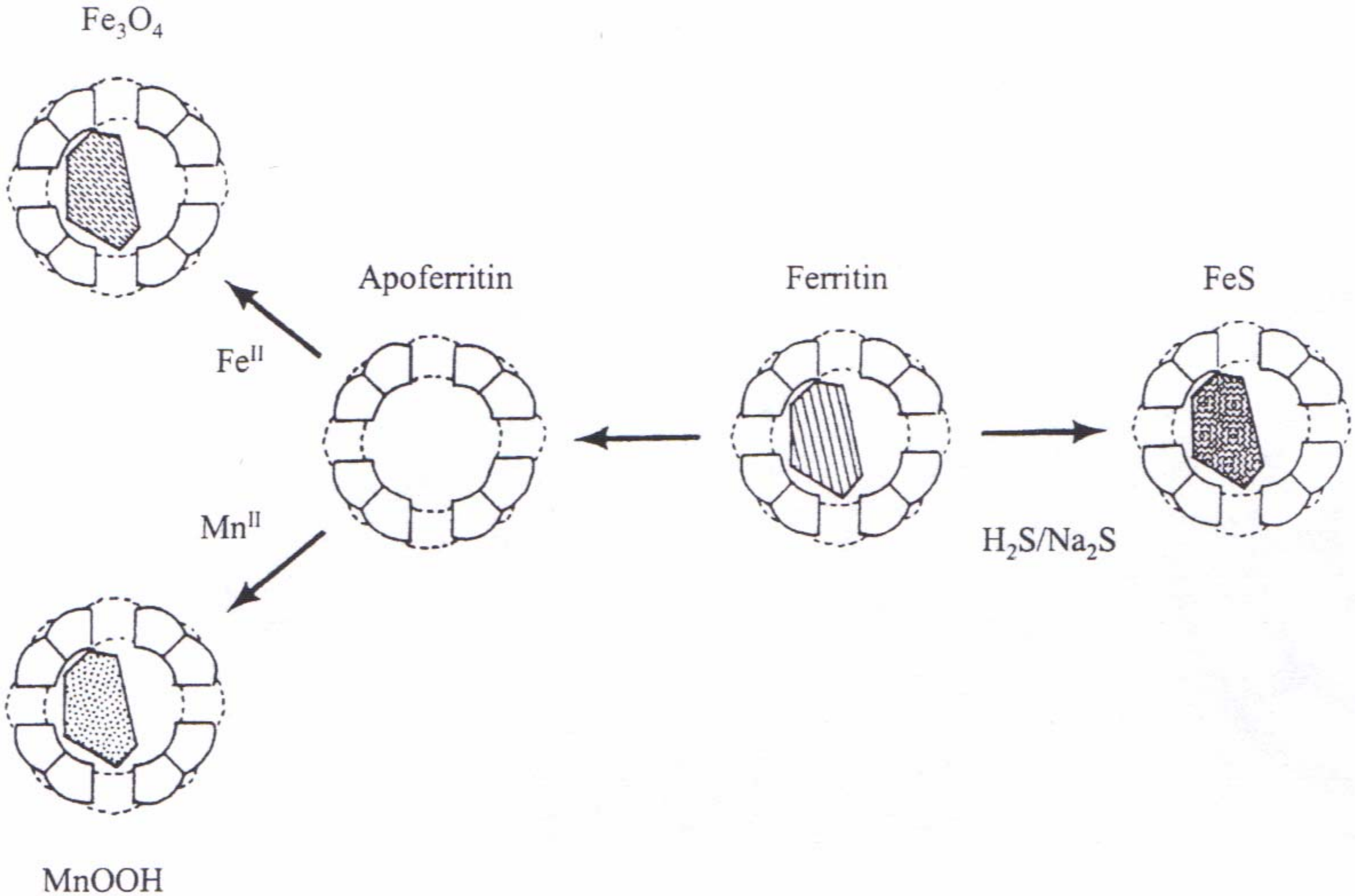
Ag_2O nanoparticles prepared inside phosphatidyl choline unilamellar vesicles. Scale bar, 75 nm.

Organized nanostructures from mutilamellar vesicles



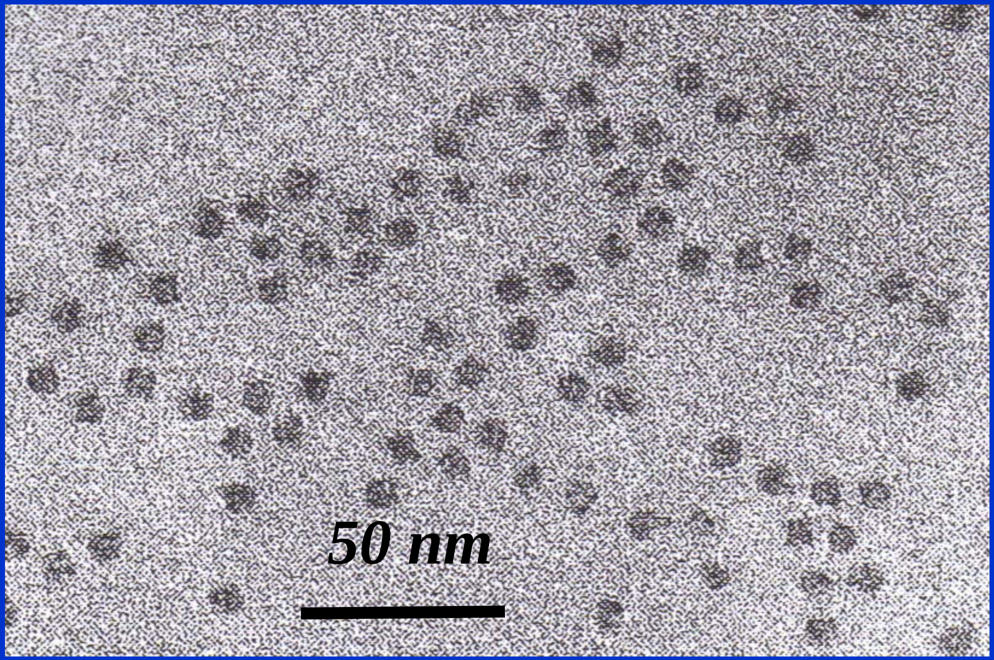
Silica mineralization in multilamellar vesicles and formation of an onion-like inorganic–organic nanocomposite.

Artificial Ferritins



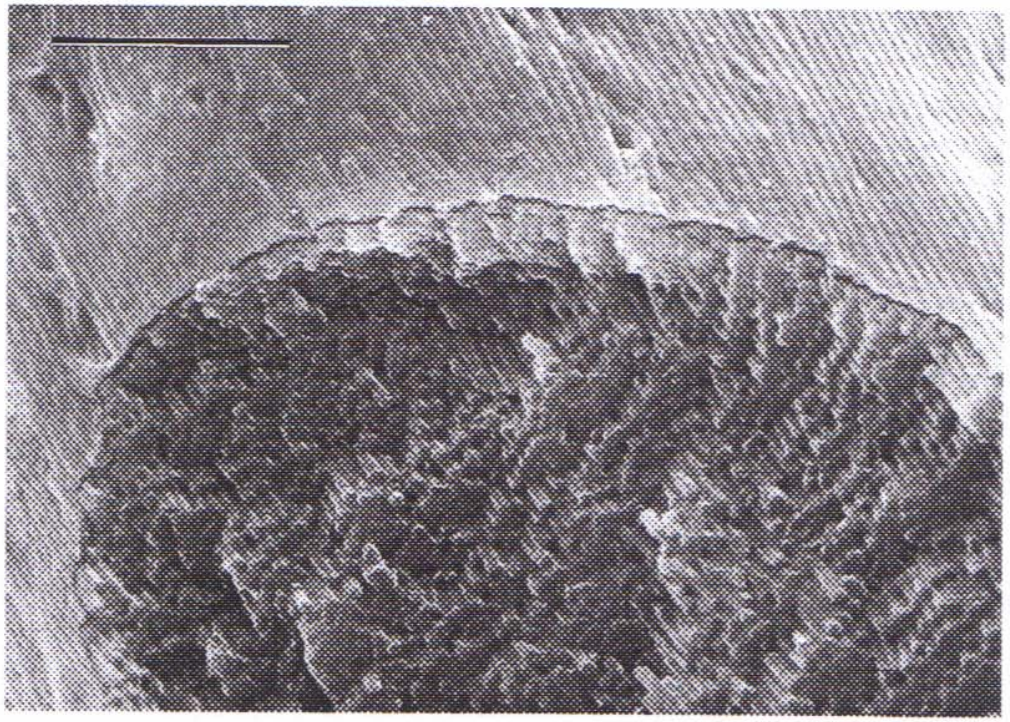
Biomimetic synthesis of artificial ferritins.

Artificial Ferritins for the synthesis of MnOOH



Bacterial Threads

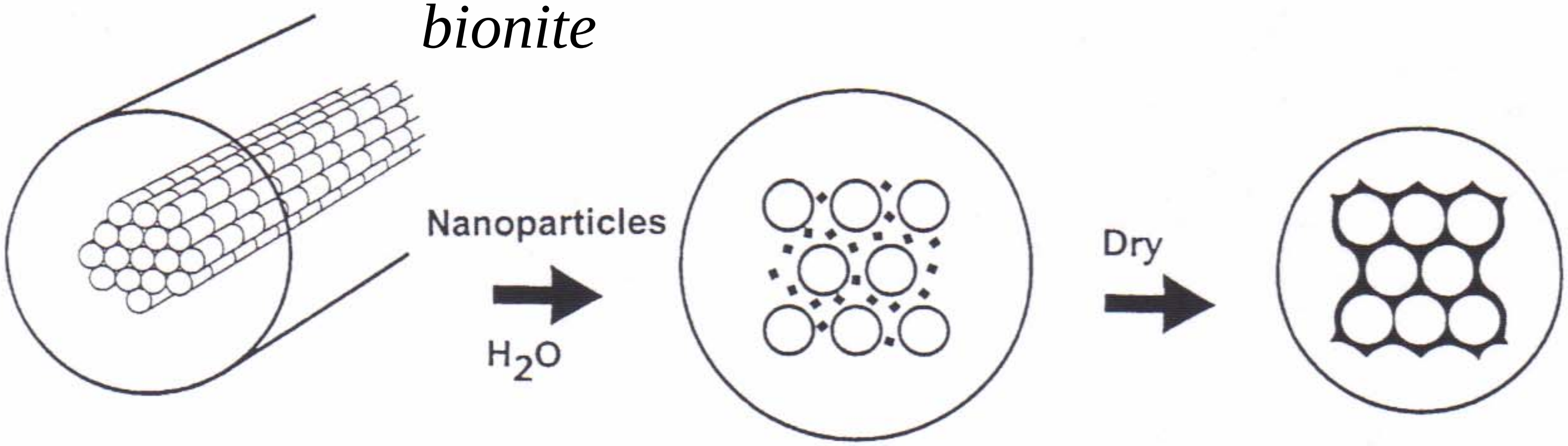
Bacillus subtilis



Sectioned bacterial thread showing internal hexagonal superstructure of coaligned multicellular filaments. Scale bar, 10 μm.

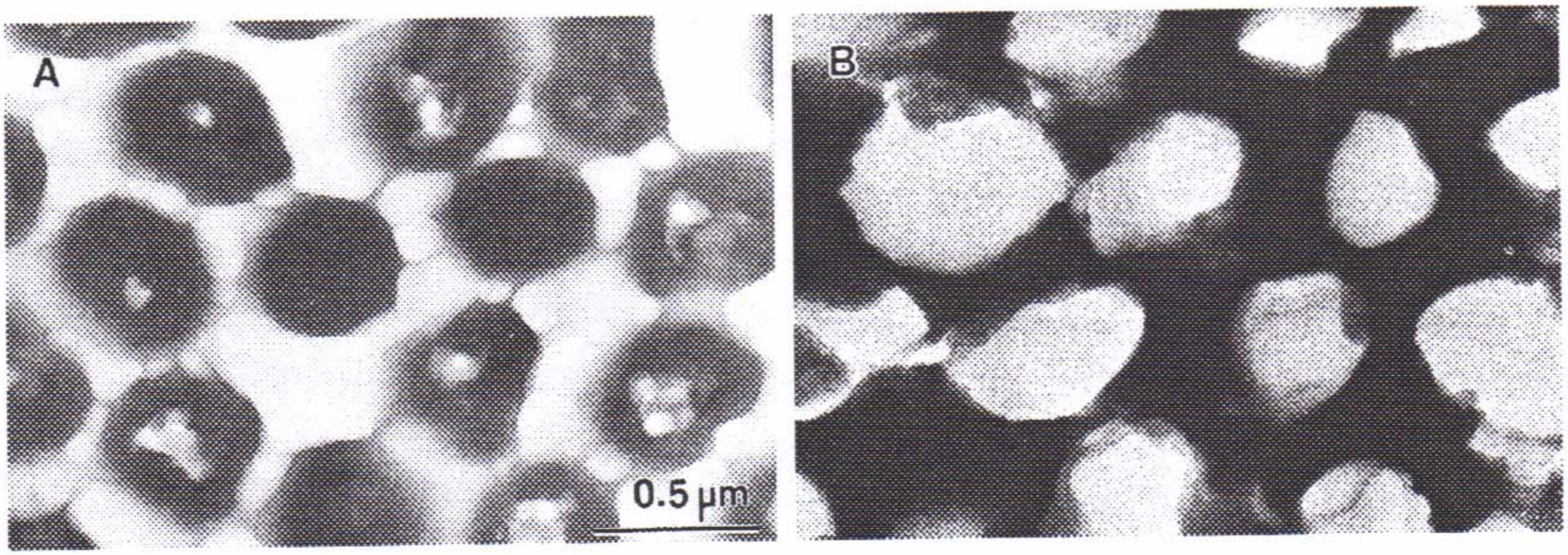
Bacterial threads for materials synthesis

bionite



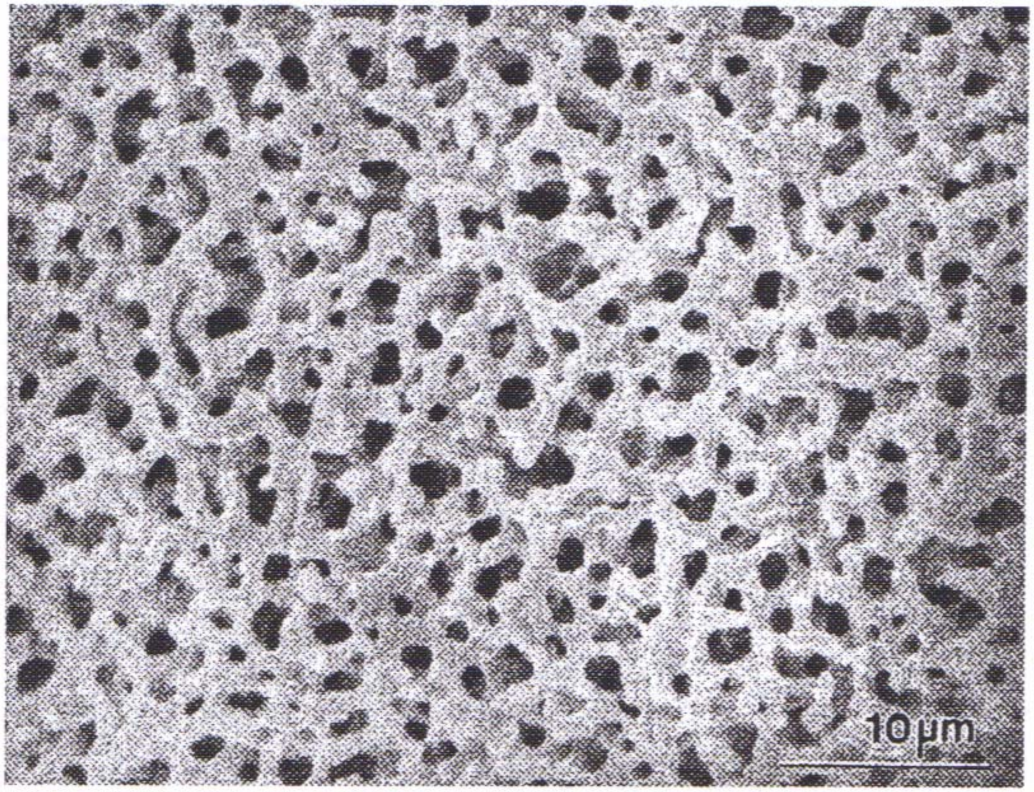
Mineralization of bacterial superstructure using inorganic nanoparticles and reversible swelling.

Bacterial threads

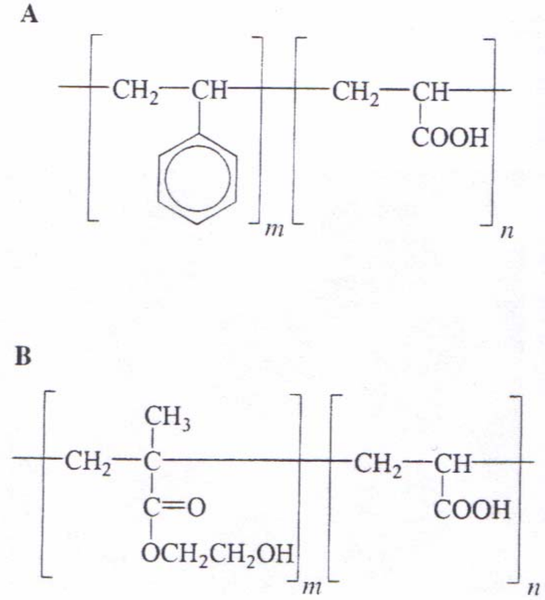


Cross-section of bacterial thread: (A) before mineralization showing end-on view of the multicellular filaments and interfilament spaces; (B) after mineralization showing continuous silica walls between the entrapped filaments. Scale bar, 0.5 μm in both micrographs.

Polymer Sponges



Polymer sponge. Scale bar, 10 μm.



Copolymers: (A) styrene and acrylic acid; (B) 2-hydroxyethyl methacrylate and acrylic acid.

Template-directed materials synthesis

Table 9.4 Biomineral-inspired approaches to the organic template-directed synthesis of inorganic materials

Approach	Product	System	Materials
Nucleation on biomineral matrices	Organized composites	β-Chitin/acidic macromolecules	$CaCO_3$, Ca phosphates
		Cuttlebone β-chitin	SiO_2
Nucleation on 3-D structures	Mineral–organic cylinders/tubes	Lipid tubules	Cu, Ni, Al_2O_3, Fe oxides, Au
		Viroid tubules	CdS, PbS, SiO_2, Fe oxides
		Bacterial rhapidosomes	Pd
		Bacterial fibres	$CaCO_3$, CuCl, Fe oxides
Nucleation on thin films	Oriented crystals	Langmuir monolayers	NaCl, $CaCO_3$, $BaSO_4$, PbS $CaSO_4$, $CuSO_4$
		Polyaspartate/polystyrene	$CaCO_3$
	Surface coatings	Self-assembled monolayers	TiO_2, zeolites
		Polyacrylate films	Fe oxides, $BaTiO_3$