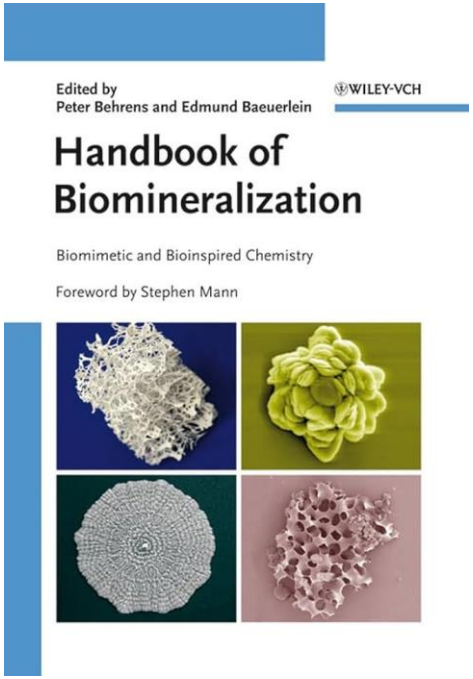
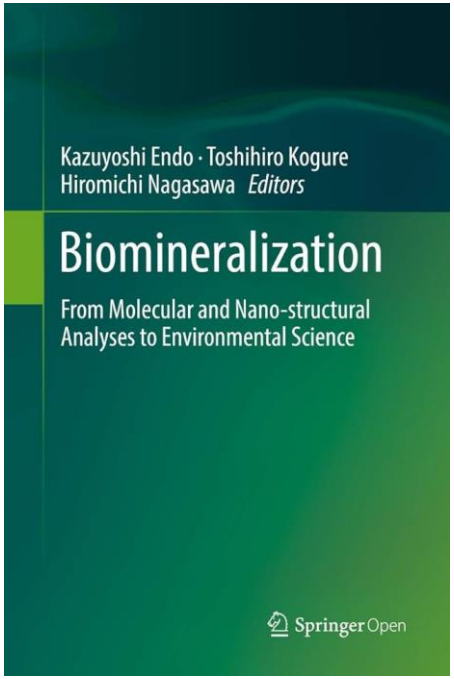
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Amorphous Materials

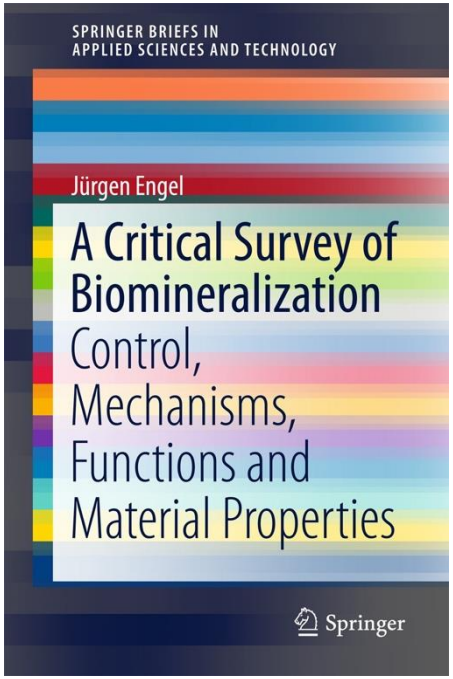
16: Biomineralization of Amorphous Materials

Juejun (JJ) Hu

References


Edited by
Peter Behrens and Edmund Baeuerlein
WILEY-VCH
Handbook of Biomineralization
Biomimetic and Bioinspired Chemistry
Foreword by Stephen Mann


Kazuyoshi Endo · Toshihiro Kogure
Hiromichi Nagasawa Editors
Biomineralization
From Molecular and Nano-structural Analyses to Environmental Science
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APPLIED SCIENCES AND TECHNOLOGY
Jürgen Engel
A Critical Survey of Biomineralization
Control, Mechanisms, Functions and Material Properties
Springer

Outline

- Introduction to biomineralization
  - Examples: mollusk shells, crustacean exoskeleton, bone and teeth, biosilica
- Microstructural evolution and kinetics of biomineralization
  - Hierarchical microstructures
  - Transient amorphous precursors
- Applications inspired by biomineralization
  - Bioinspired structural materials
  - Diatom-based sensing and drug delivery
  - Biomineralization processes in chemical synthesis and dental therapies

Biologically controlled mineralization

- Formation of inorganic solids by living organisms
- Hierarchical structure: organic matrix + inorganic phase



Source: public domain

Hexactinellid (glass sponge)



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Mollusk shells



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Bones in vertebrates



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Diatom frustules

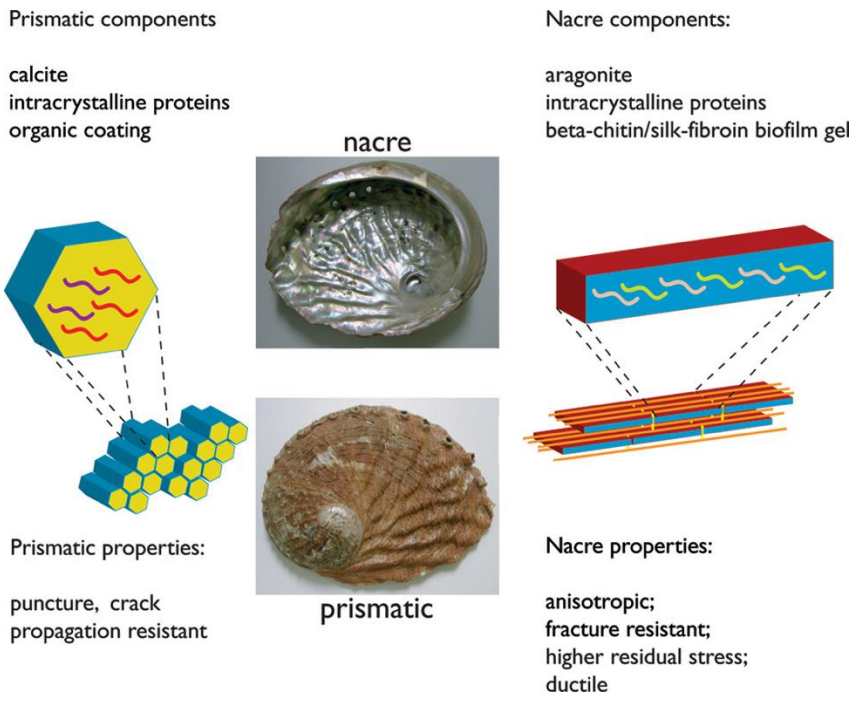
Mollusk Shells



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Mollusk Shells

- Calcite or aragonite crystals (> 95% by weight) with an organic matrix (~ 5%)
  - Calcite: prismatic layer
  - Aragonite: nacre layer
- **Amorphous calcium carbonate (ACC)**: a transient precursor in shell formation
  - Reduces interfacial energy barriers, allowing rapid formation of uniform mineral layers
  - Crystal phase controlled by matrix proteins

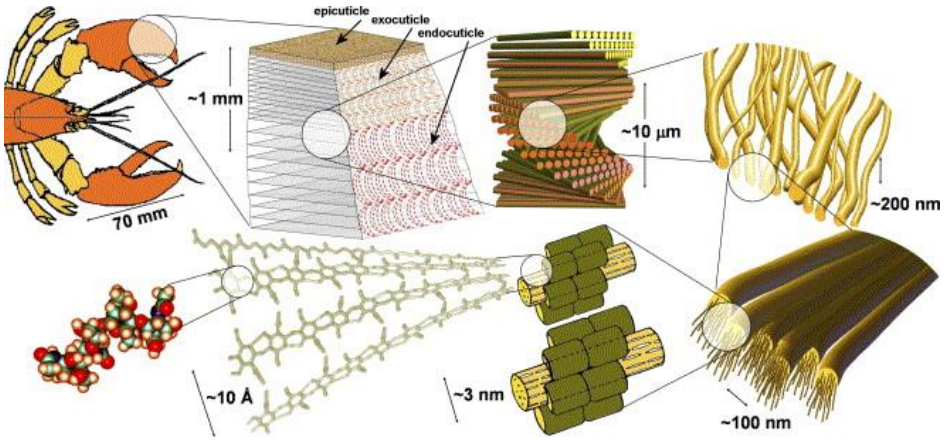


Chem. Rev. **108**, 4455 (2008)

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Crustacean exoskeleton

- Composition: chitin, proteins, and minerals (most commonly ACC and calcite)
- Hierarchical architecture
  - Millimeter scale: layered mineralized composite
  - Micron scale: helicoidal Bouligand stacking
  - Nanometer scale: chitin fibrils wrapped in protein
- Mechanical properties
  - Crack resistance
  - Enhanced toughness
  - Near-isotropic strength
  - Flexibility

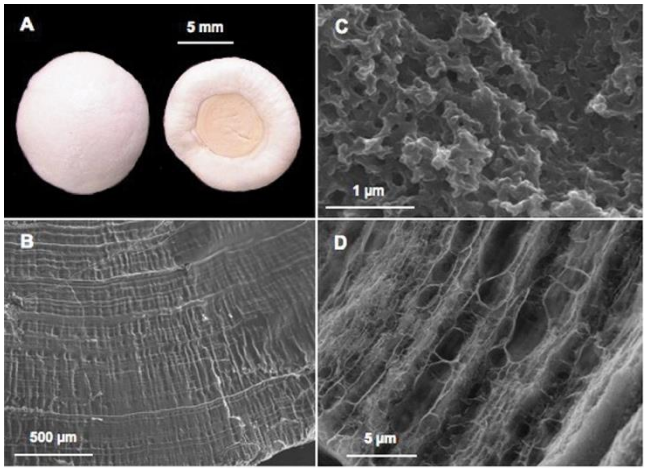


Acta Mater. **53**, 4281 (2005)

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Crustacean exoskeleton

- Molting: a process of shedding hard exoskeletons to facilitate growth
- Calcium balance
  - Terrestrial and freshwater crustaceans store large amounts of calcium to minimize calcium loss due to molting
  - Gastrolith: ACC and amorphous calcium phosphate in an organic matrix



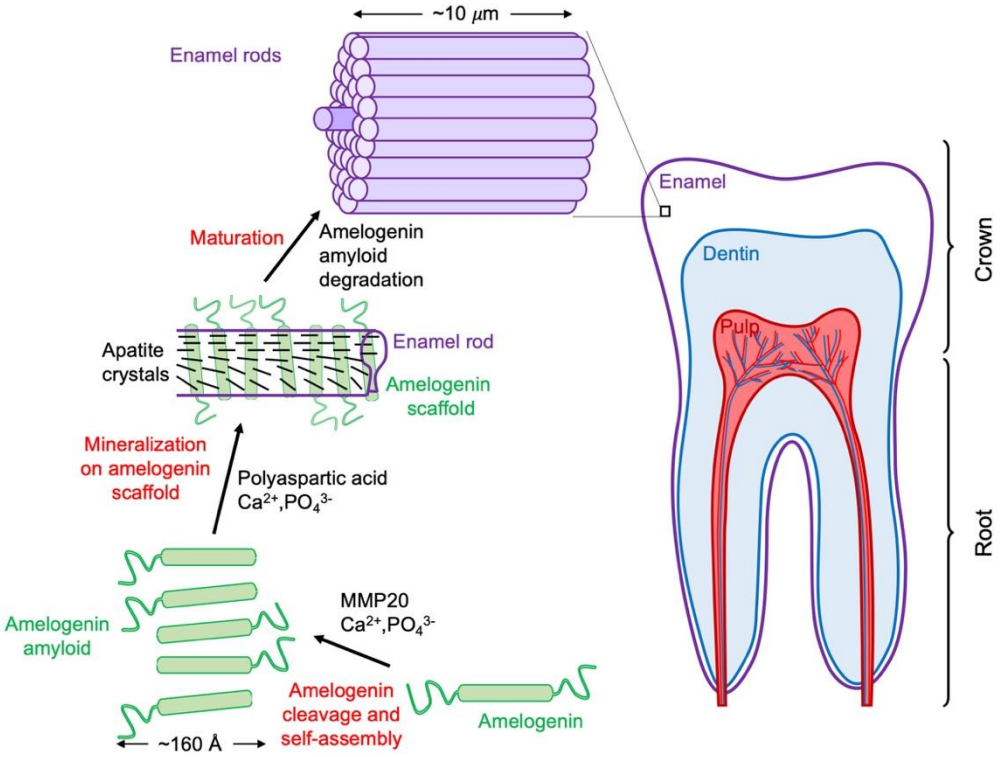
Zookeys **176**, 103 (2012)

A Pair of gastroliths from the crayfish *Cherax quadricarinatus*; **B** Internal striated structure visible on natural fracture after slight acetic acid decalcification; **C** Ultrastructure well visible after natural fracture and high magnification: the mineral is precipitated as nanospheres; **D** Organic matrix network revealed after acetic acid decalcification.

Figure in Luquet, Gilles. (2012). Biomineralizations: Insights and prospects from crustaceans. ZooKeys. 176. 103-21. 10.3897/zookeys.176.2318. License: CC BY 4.0.

Bone and teeth of vertebrates

- Composition
  - Mineral phase: calcium phosphate primarily as hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]
  - Organic matrix: mainly collagen type I (in bone & dentin) or non-collagenous proteins (in enamel)
  - Water phase: providing hydration

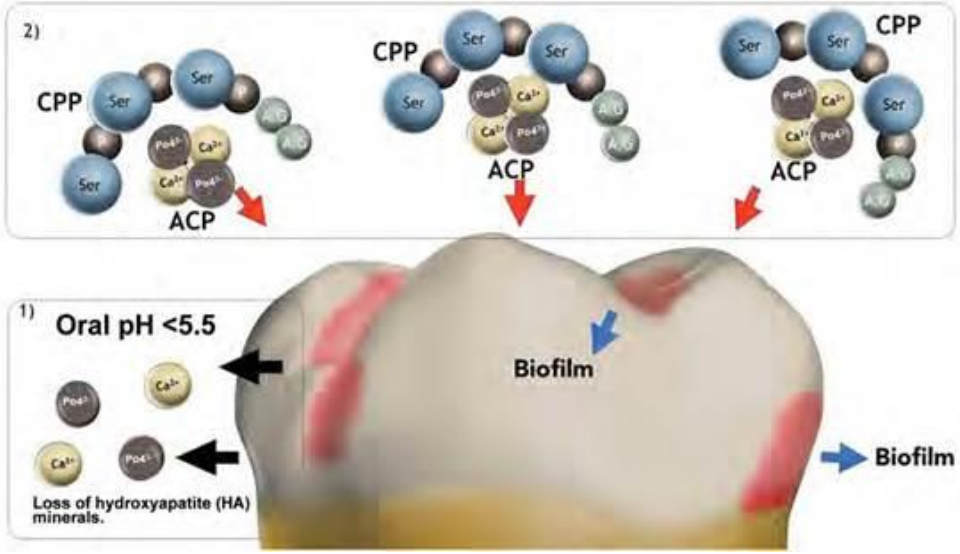


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Bone and teeth of vertebrates

- Amorphous calcium phosphate (ACP)
  - Act as precursors for crystalline hydroxyapatite
  - Provide shape flexibility: fill small gaps and coat collagen fibrils evenly before crystallization
  - Allow controlled transformation and support nucleation



Casein phosphopeptide-amorphous calcium phosphate nanocomplex (CPP-ACP) in dentistry: state of the art, *Rev. Fac. Odontol. Univ. Antioq* **30**, (2019)

Madrid-Troconis, C. C., & Perez-Puello, S. del C. (2019). Casein phosphopeptide-amorphous calcium phosphate nanocomplex (CPP-ACP) in dentistry: state of the art. Revista Facultad De Odontología Universidad De Antioquia, 30(2), 248–263. https://doi.org/10.17533/udea.rfo.v30n2a10

Silica mineralization: diatoms and glass sponges

- Skeletons made of hydrated amorphous silica ($SiO_2 \cdot nH_2O$)
- Use organic molecules to guide silica formation, shape, and patterning
  - Silaffins in diatoms: induce silica precipitation and interact with other molecules to create self-organized silica nanostructures

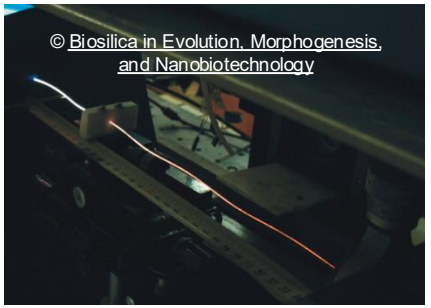


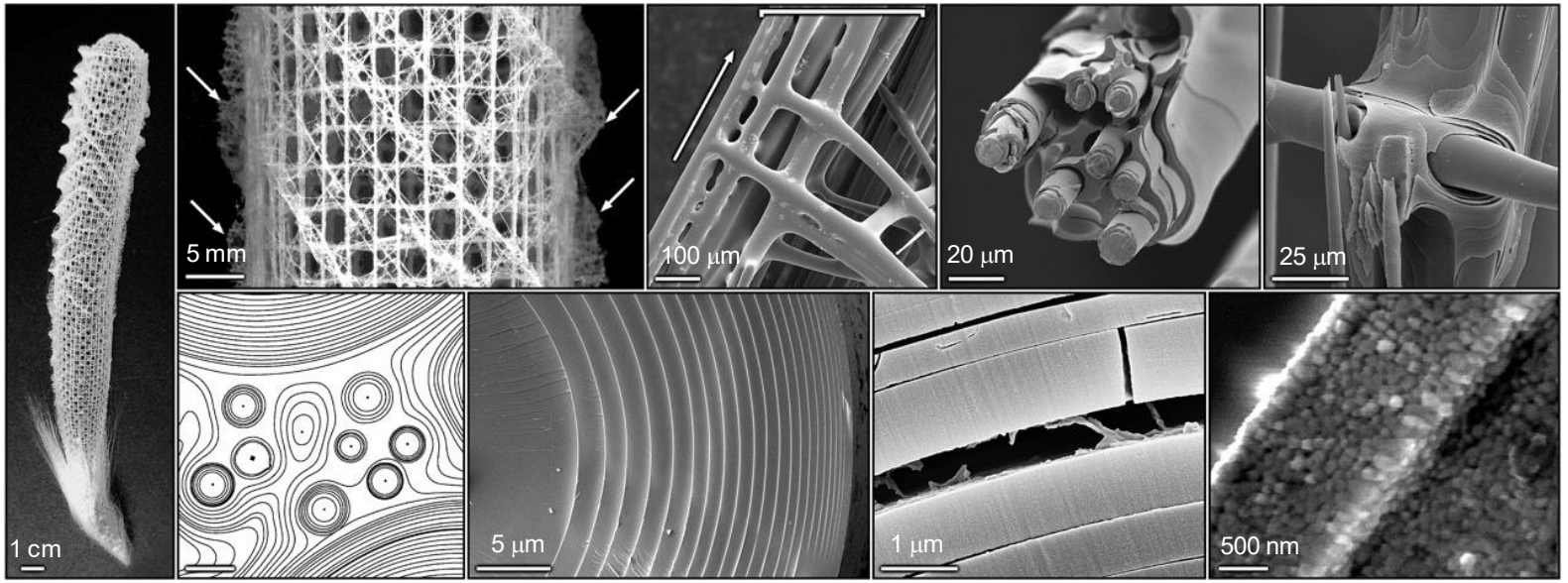
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  - Silicateins in sponges: protein catalysts and scaffolds that assemble silica into long, layered spicules

Hierarchical structure of glass sponge spicule

- Core-shell architecture
  - Protein-rich central core surrounded by concentric layered amorphous silica shells with thin organic interlayers



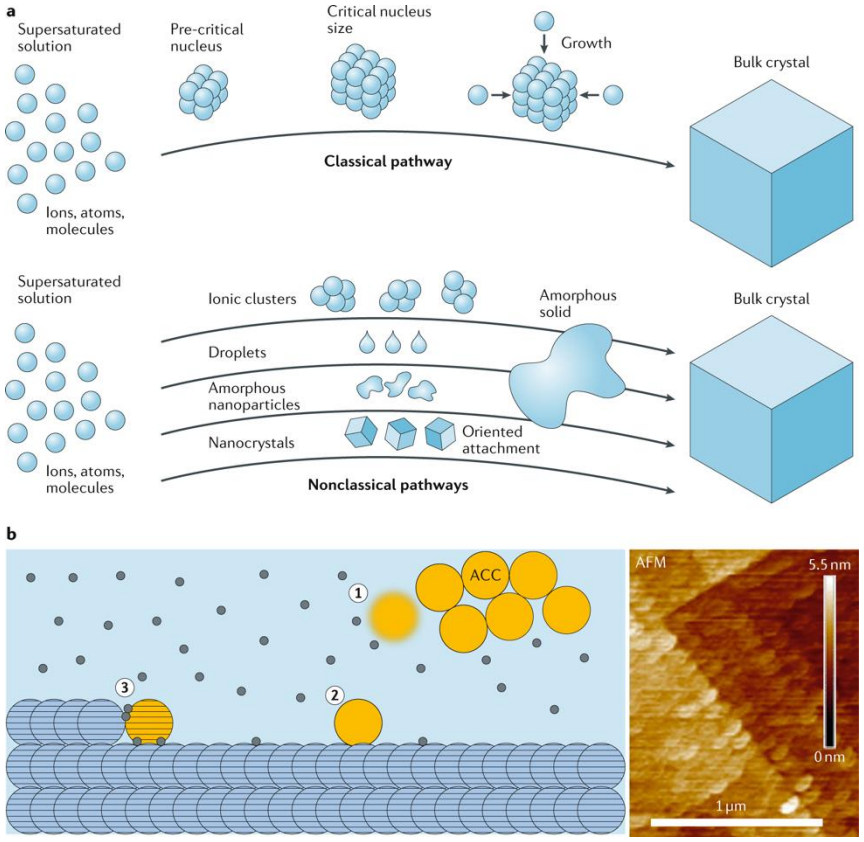


Science **309**, 275 (2005)

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Transient amorphous phases: amorphous first, crystalline later

- Lowering nucleation barrier
  - Ostwald step rule
  - Reduced interfacial energy
  - Providing preferential nucleation sites via organic matrices
- Solution phase infiltration and deposition
- Crystallization by particle attachment

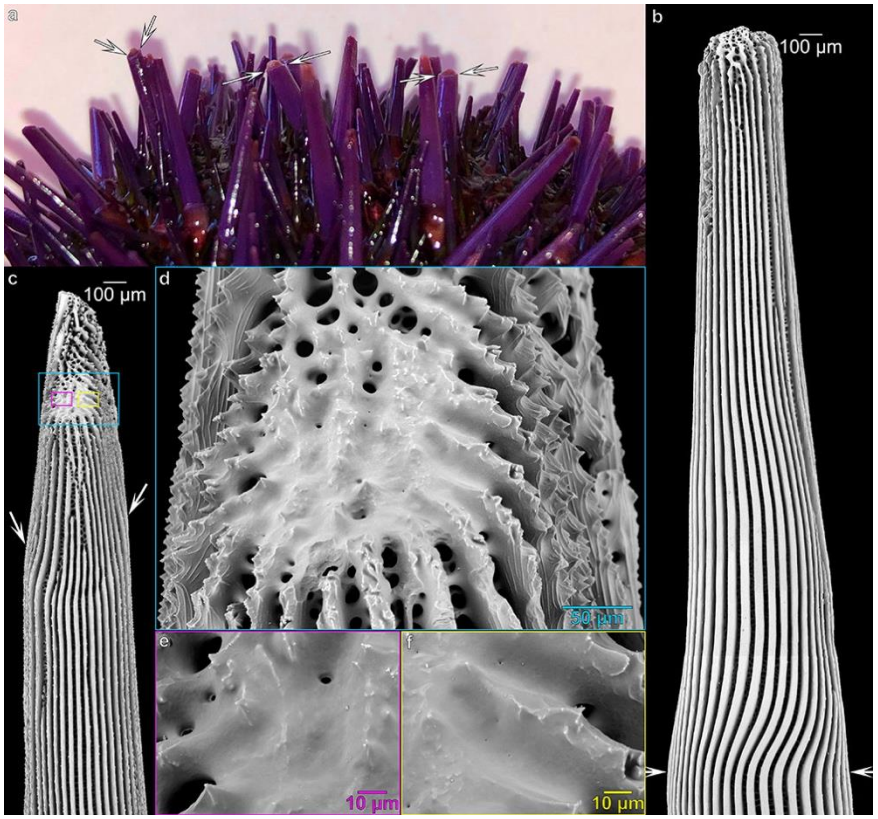


Nat. Rev. Chem. **5**, 93 (2021)

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Transient amorphous phase stabilization

- Organic macromolecules (proteins, polysaccharides)
- Small ions: Mg^{2+} in ACC
- Water and hydration shells
- Confinement by organic templates
- Example: Mg^{2+}-rich, hydrated ACC stabilized by SM50 protein in sea urchin spicules before transforming into **single-crystalline** calcite

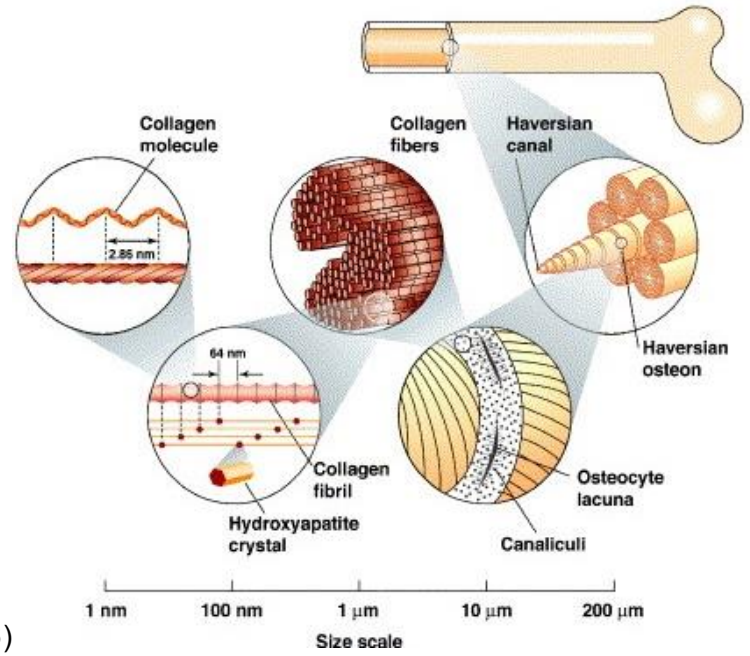


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Hierarchical microstructural evolution

- Formation of amorphous precursor phase
- Assembly into mesoscale scaffolds
  - The amorphous precursor is transported and deposited into organic scaffolds
- Controlled local transformation into nanocrystals
- Nanocrystal alignment along the organic matrix
- Nanocrystals assemble into macroscopic structures



Hierarchical structure of human cortical/compact bone

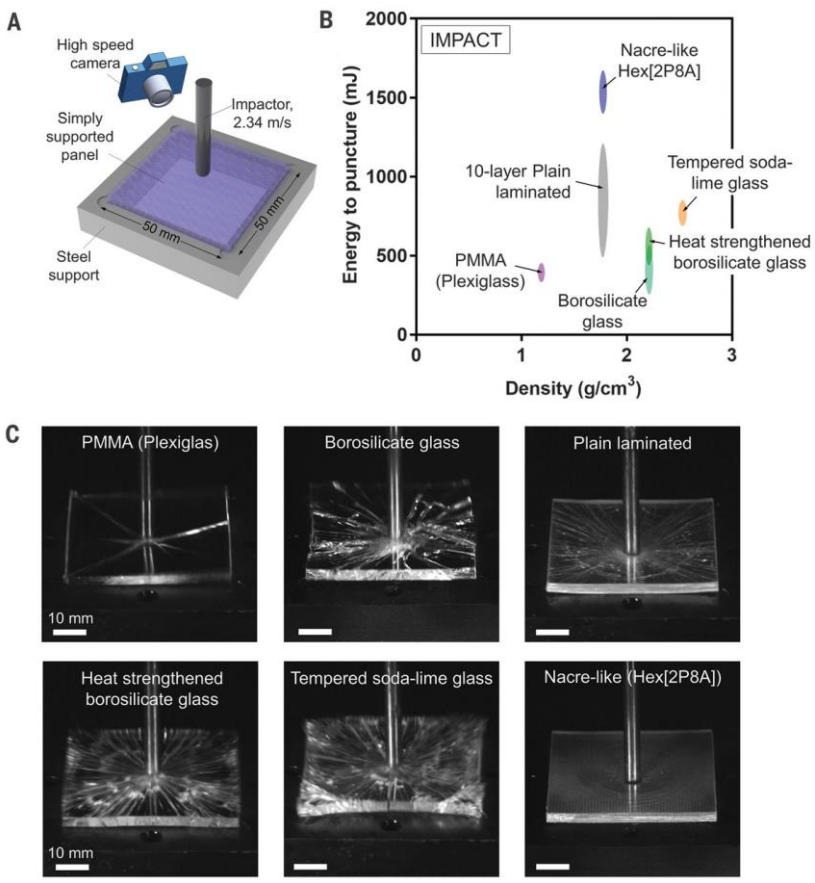
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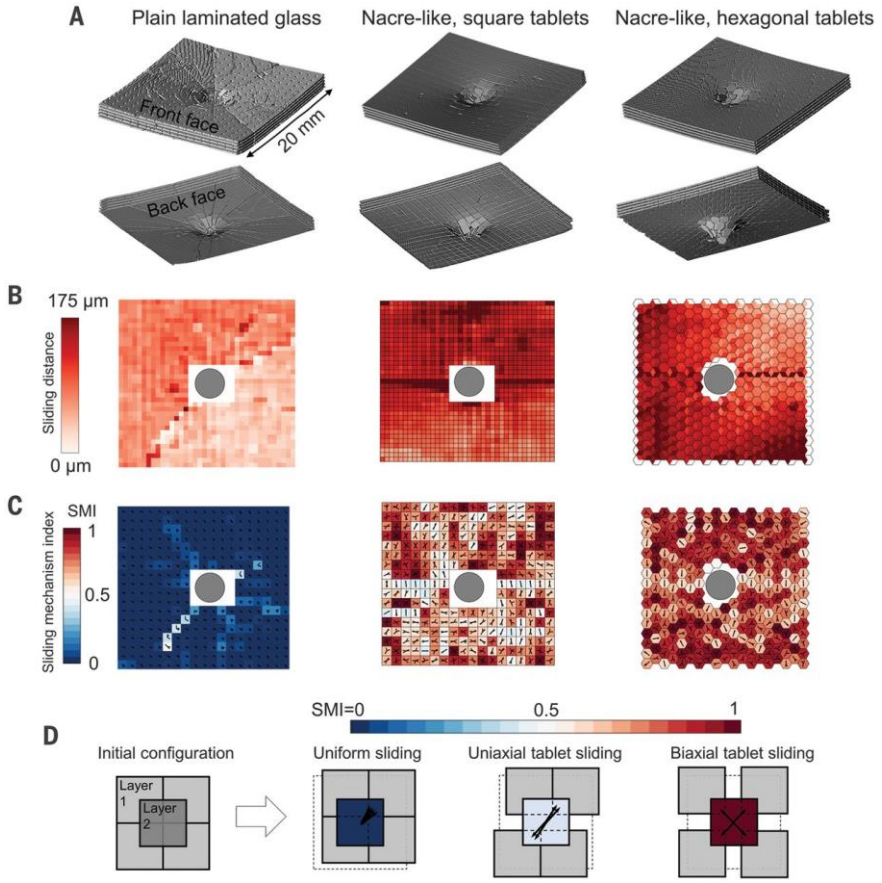
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Amorphous materials in hierarchical microstructural evolution

- Shape molding flexibility
  - Can fill irregular or nanoconfined spaces
- Avoidance of brittle failure
  - Premature crystal nucleation would create internal stresses and cracks
- Kinetic control
  - Organisms can “freeze” the amorphous phase at desired times or locations
- Hierarchical integration
  - Once the amorphous phase transforms, it connects nanoscale, microscale, and macroscale order seamlessly

Bioinspired composites: nacre-inspired glass

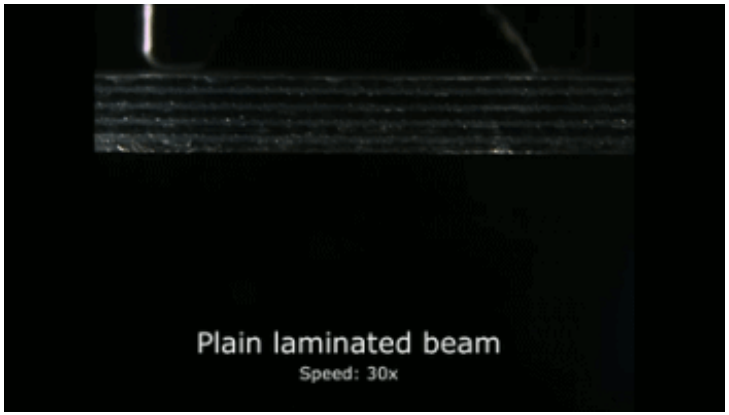


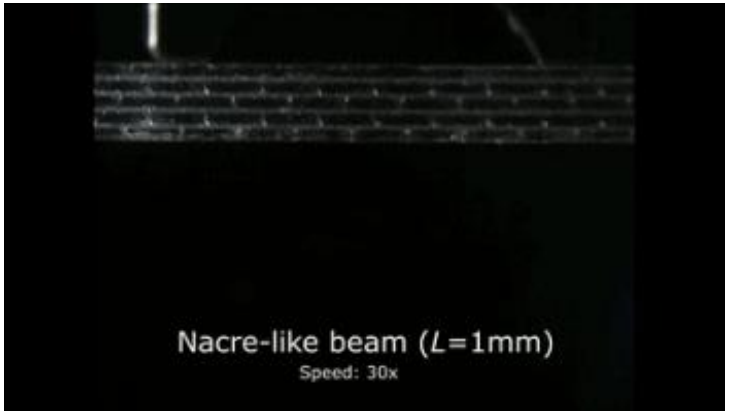


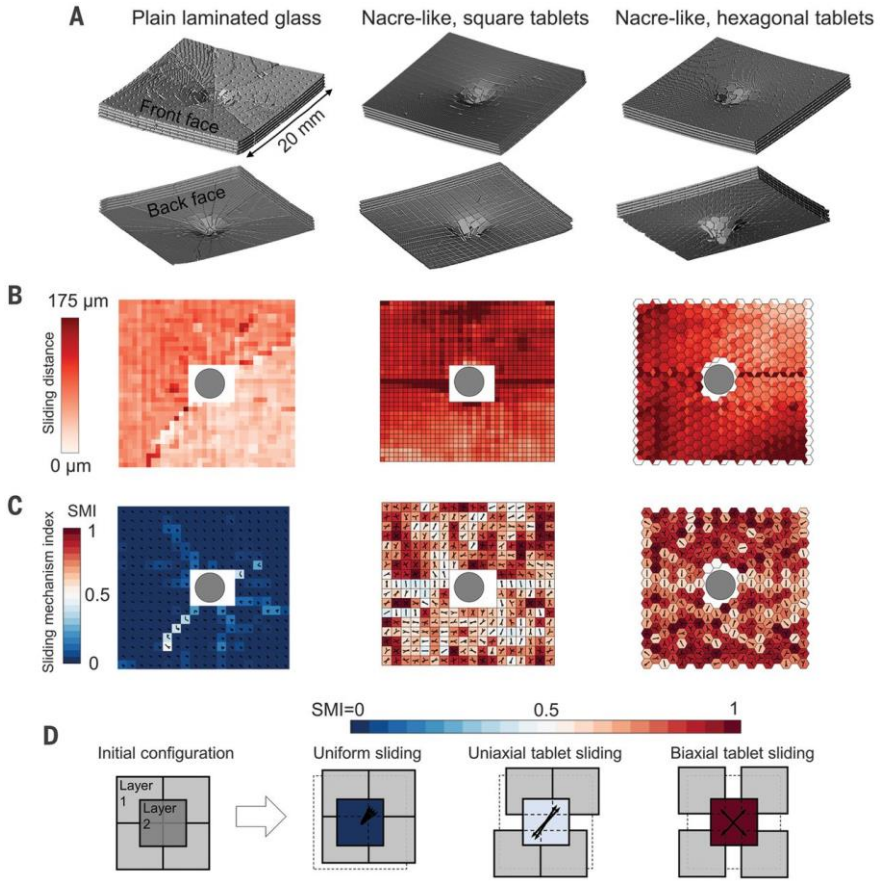
Science **364**, 1260 (2019)

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Bioinspired composites: nacre-inspired glass





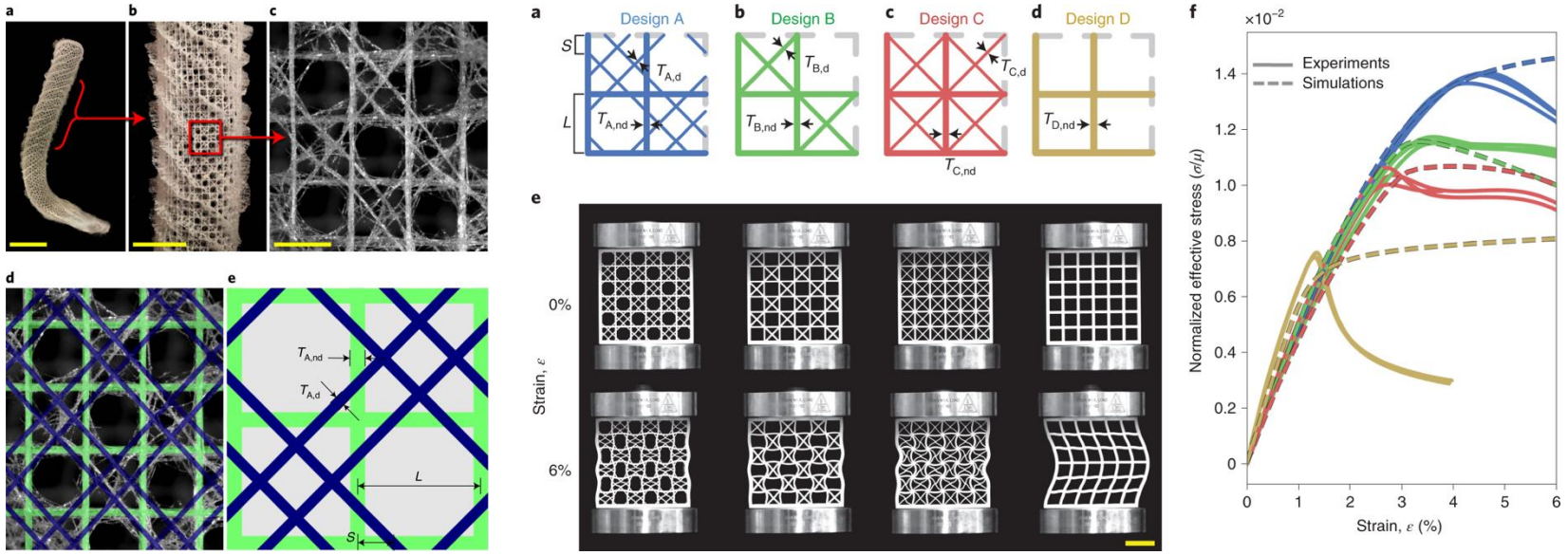


Science **364**, 1260 (2019)

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Sponge-inspired buckling-resistant lattices

- Silica skeleton of *Euplectella aspergillum* consists of a square grid overlaid with a double set of diagonal bracings
- The diagonal reinforcement strategy achieves the highest buckling resistance for a given amount of material

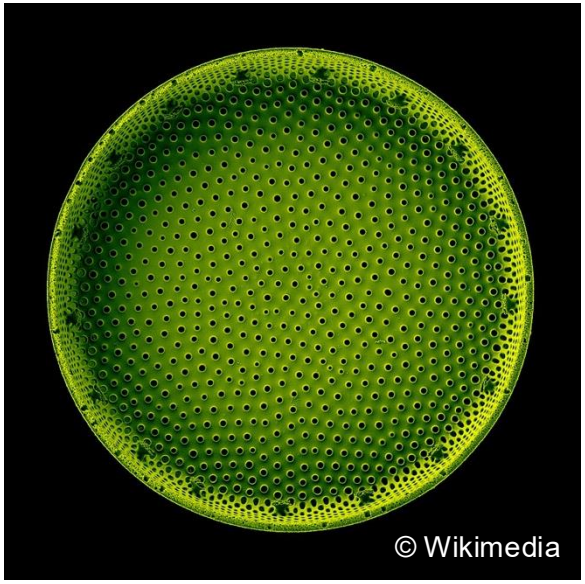


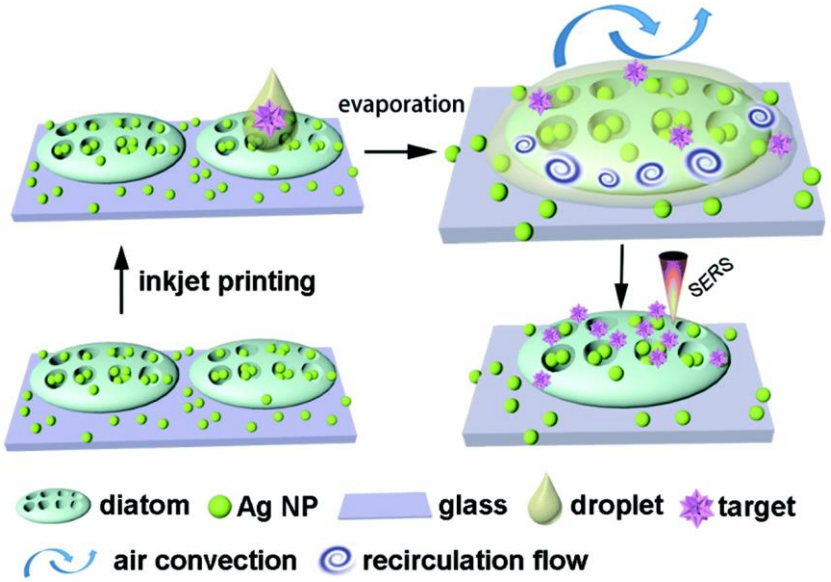
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Diatom-based single-molecule sensors

- Dual enhancement by diatom biosilica
  - Hydrophilic surface pulls droplets inward during drying
  - Porous structure amplifies SERS hot-spot intensity



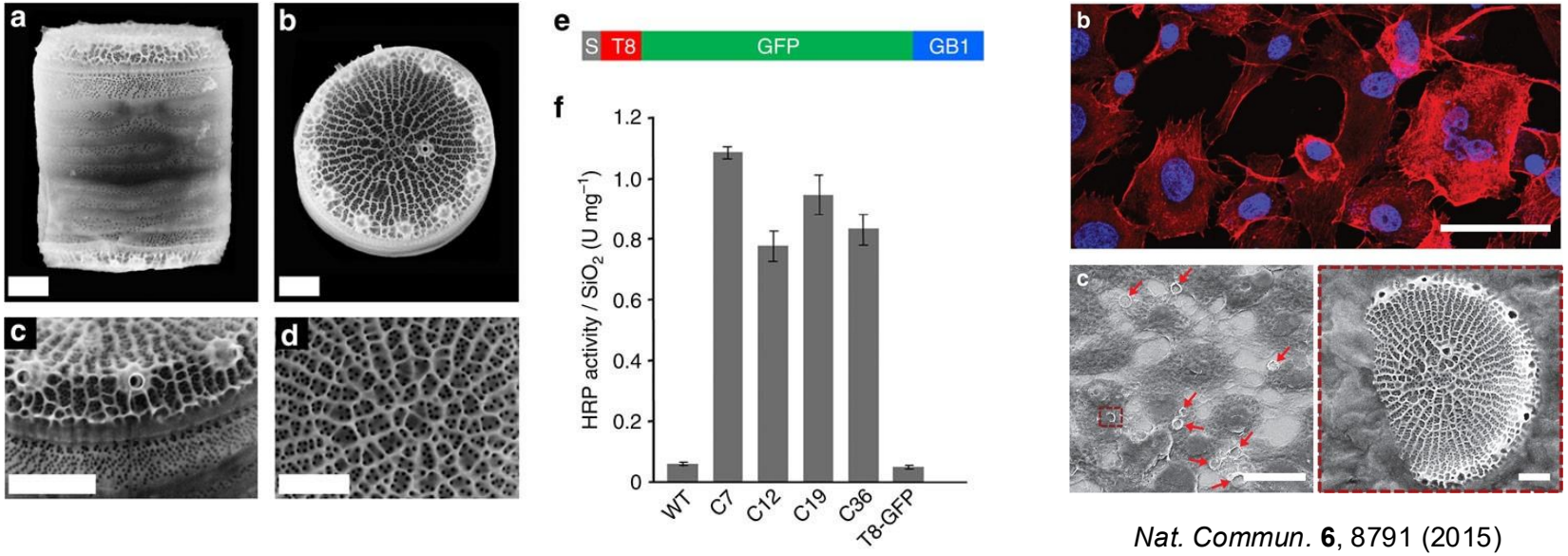


Nanoscale **8**, 17285 (2016)

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Diatom-based drug delivery

- Targeted drug delivery using genetically engineered diatom
  - Genetically engineered diatoms display GB1 protein domain on their silica shells, enabling the binding of IgG antibodies
  - Hydrophobic drugs loaded into cationic liposomes, which electrostatically adsorbed onto negatively charged biosilica

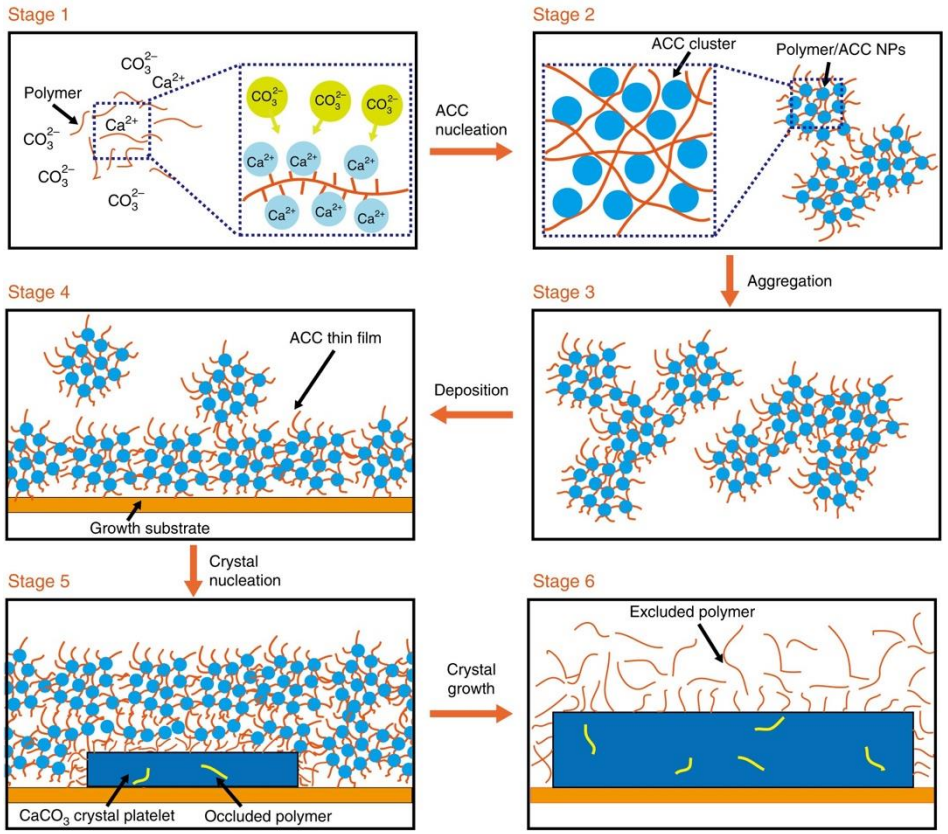


Nat. Commun. **6**, 8791 (2015)

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Polymer-induced liquid precursor (PILP)

- Adding polyionic polymers to a solution supersaturated with mineral ions
- Polymers interact with the mineral ions, stabilizing them in liquid-like amorphous clusters
- Infiltration into organic or porous matrices
- The precursor dehydrates and solidifies
- The matrix guides the alignment and orientation of the crystals formed



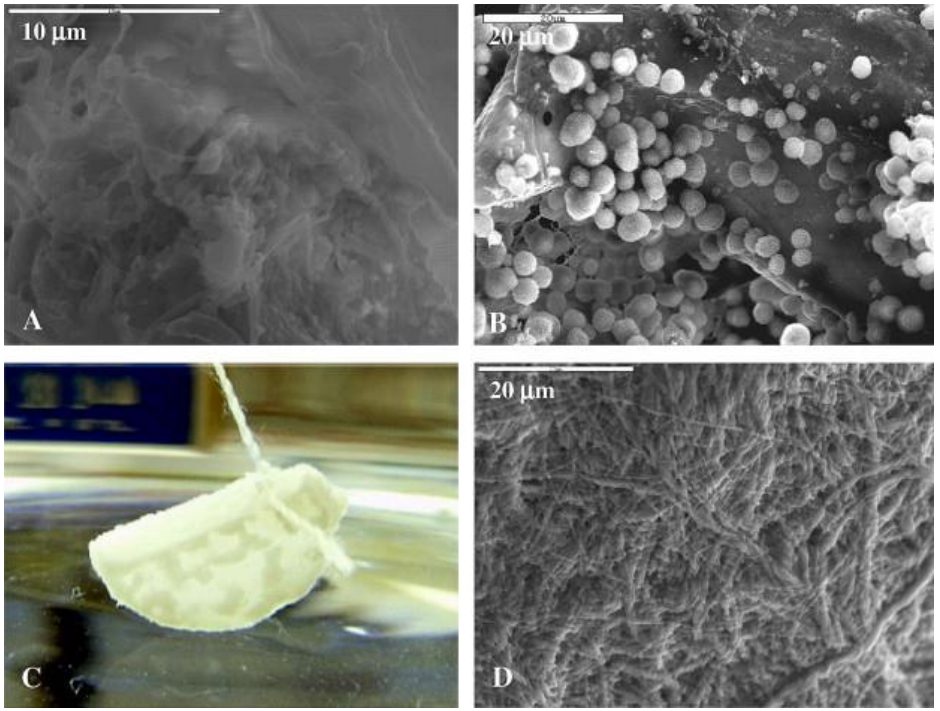
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Mineralization of collagen sponges mimicking bone structures

- Develop bone-like collagen-hydroxyapatite (HA) composites using the PILP process to mimic natural bone nanostructure
- PILP achieved intrafibrillar infiltration of HA via capillary action within collagen fibrils
- Nanocrystals aligned along the collagen fibril long axis ([001] direction) matching native bone

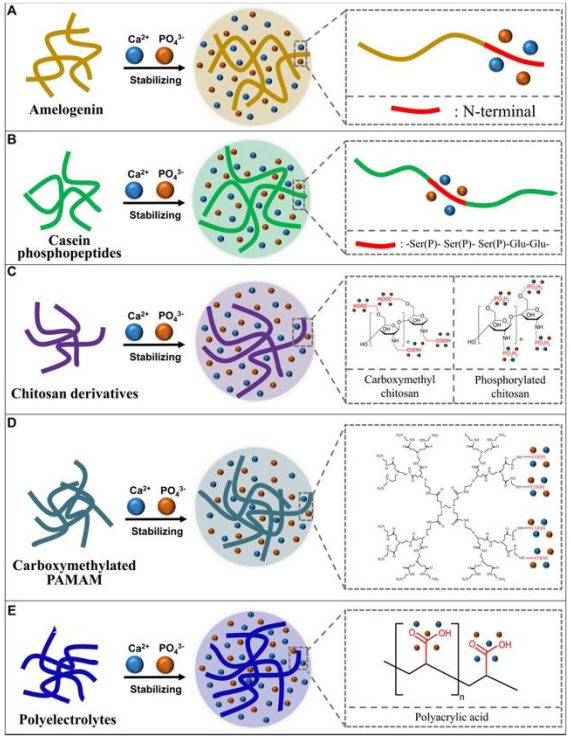
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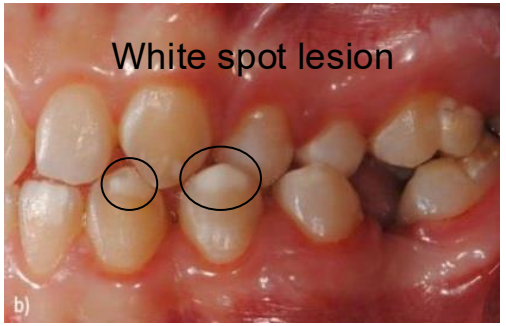


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ACP-based enamel remineralization

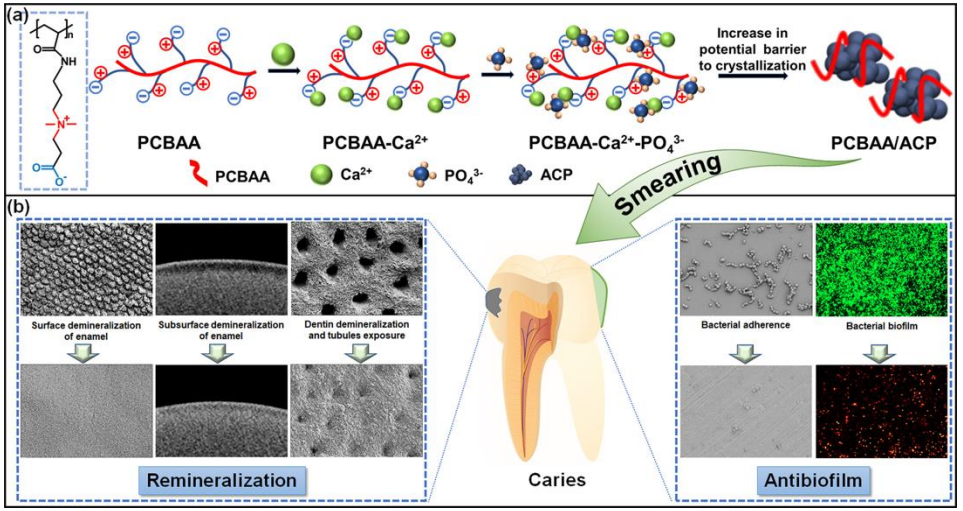
- ACP deposition, infiltration, and phase transformation into hydroxyapatite crystals
- Stabilization of ACP





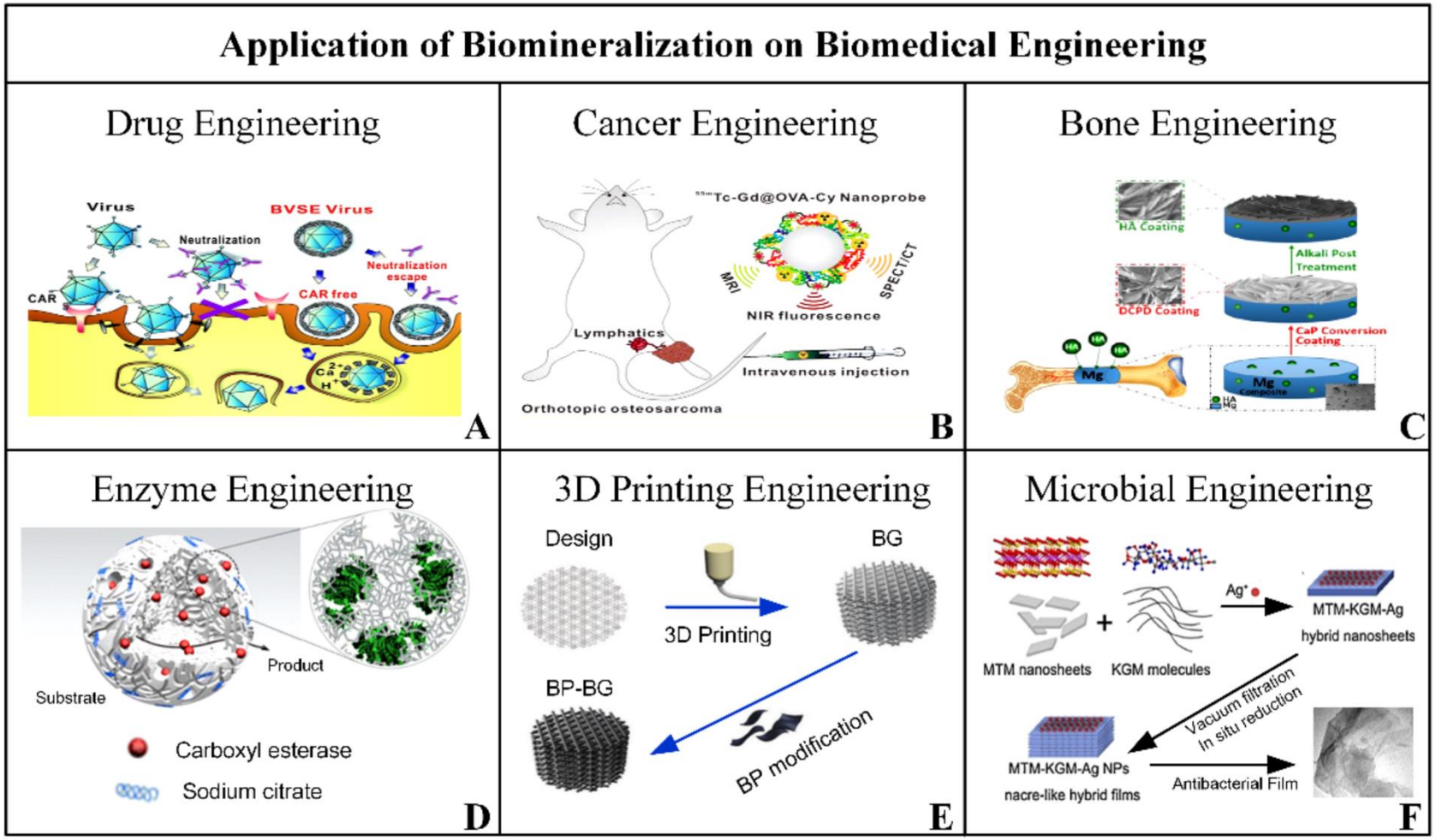
Renata Pereira, Bruna Guerra Silva, Débora Alves Nunes Leite Lima, Giselle Maria Marchi, Flávio Henrique Baggio Aguiar. Esthetic Approach for Treatment of Molar Incisor Hypomineralization: A Case Report. Dental Research and Oral Health 2 (2019): 062-072. License: CC BY 4.0.

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Minerals **9**, 68 (2019)

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3.071 Amorphous Materials
Spring 2025

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