

Biomimetic Synthesis of Calcium Carbonate Films.

Introduction

- There have been increasing recent efforts in search of biomimetic processing strategies to produce inorganic thin films.
- These efforts have focused on exploring the promoting effect of templates on crystal nucleation and growth.
- Several categories of such approaches can be discerned, according to the nature and structural complexity of the templates employed.

- The first approach focuses on the *in vitro* or *in vivo* functions of the biological matrix.
- These investigations have yielded valuable information on how matrix proteins can affect biomineral formation.
- However, due to their formidable structural complexity, much work is yet to be done to illustrate the nature of these biological systems

- **The second approach** uses synthetic polymeric analogues as substrates for the deposition of polycrystalline inorganic materials.
- Calcium carbonate has been deposited on model polymeric substrates and even inorganic polymer surfaces
- Iron oxides and tin oxide were deposited on sulfonated polystyrene films. Cadmium sulfide and titanium oxide were assembled on absorbed polyelectrolyte surfaces and hydroxyapatite was also deposited on polymers.
- A major problem with this method is that the macromolecule surface is usually too rough and complicated to allow an understanding of the interfacial interactions at a molecular level.

- The third approach has made use of the well-ordered two-dimensional structure of a self-assembled film on a solid substrate or a Langmuir film at the air/water interface as the nucleating template.
- Calcium carbonate, iron oxides, cadmium or zinc sulfide, hydroxyapatite, and zirconium oxides have been grown under such amphiphilic monolayers.
- Though this method has provided important insight into the relationships between the structure of the substrate and the overgrowing crystals, most amphiphiles used seem to be structurally too fluid to simulate the biogenic control exhibited by natural matrix proteins.

- A recent approach has employed synthetic supramolecular assemblies to offer semirigid templates for calcium carbonate crystallization.
- For example, the function of the acidic glycoprotein matrix could be mimicked in vitro with a supramolecular assembly of porphyrin amphiphiles.

- None of the approaches so far have exerted control over the mineral growth in the direction perpendicular to the template with respect to parallel deposition.
- To produce an extended two-dimensional structure, lateral growth should be favored over normal growth.
- A template alone is apparently insufficient to fulfill this requirement. Nature, on the other hand, has offered many examples of minerals forming well-ordered thin-film structures such as calcium carbonate. Highly oriented aragonite tablets are found in the molluscan nacreous layers.

- Ordered to a less extent but highly laminated as well are calcitic thin layers existing in both the foliated calcite layers of mollusk and the semi-nacre of brachiopods.
- Although different detailed mechanisms have been proposed for the growth and orientation of these thin laminar structures, a controlled inhibition of mineral growth, either by generating preformed organic compartment or by releasing inhibitive organic substances, has been a common feature.
- The interplay of mineral growth initiation and cessation, administered by the interlaminar organic matrix, has played a critical role in determining the two-dimensional structure .

- Various acidic proteins extracted from biological minerals have shown the remarkable ability to inhibit crystal growth or to modify crystal habit.
- In different extracts, both specific and nonspecific protein–mineral interface interactions have been identified.
- On the basis of specific interactions, small molecules or small peptides have been "tailor–made" to affect crystal morphology by inhibiting the growth of particular crystal faces.

- Films formed through a multistage assembly process, during which an initial amorphous deposition was followed by a phase transformation into the ultimate crystalline phase.
- The orientation of the crystalline phase was controlled by the porphyrin template during the phase transformation.
- The template–inhibitor–biomineral interaction and a new mechanism for synthesizing ceramic thin film under mild conditions.

- Synthetic anionic polypeptide analogues and anionic non-peptide polymers have also been found to be potent inhibitors or habit modifiers of inorganic crystallization.
- A similar mechanism by adsorption onto the surfaces of the growing crystals, thus controlling their growth rate and habit through the strength and selectivity of this adsorption.
- Poly(acrylic acid), for example, is well-known to prevent calcium carbonate from scaling.

Biomimetic Synthesis

- Preparation at air/subphase interfaces by promoting mineral deposition with amphiphilic porphyrin templates, coupled with growth inhibition by the use of poly(acrylic acid).
- Films formed were found to have a biphasic structure containing both amorphous and crystalline calcium carbonate.
- The crystalline regions were identified to be calcite oriented with the (00.1) face parallel to the porphyrin monolayer at the air/subphase interface.

- Biologically mineralization features an orchestrated balance among various controlling factors such as spatial delineation, template promotion, crystal growth modification and cessation, and so on.
- Highly ordered calcium carbonate lamellae formed in the nacreous layers of mollusk (aragonite), the foliated calcitic layers of mollusk (calcite), or the semi-nacre of brachiopods (calcite) are excellent examples.
- Mimicking the interplay of template promotion and growth inhibition utilized in biomineralization.
- Synthesized macroscopic and continuous calcium carbonate thin films

CaCO₃ crystallization with monolayer

- The Ca(HCO₃)₂ subphase was prepared by bubbling CO₂ gas into Milli-Q deionized water in the presence of CaCO₃ for 2 h. Excess solid CaCO₃ was removed by filtering, and the filtrate was purged with CO₂ for another hour.
- The freshly prepared Ca(HCO₃)₂ was immediately mixed with sodium polyacrylate (MW2,100, Fluka) solution. Then, a porphyrin monolayer was deposited onto the surface of the subphase from a chloroform solution of the amphiphilic tricarboxyphenylporphyrin iron(III) –oxo dimers as a template for the CaCO₃ film formation.
- The whole system was then left undisturbed at 22 C while CaCO₃ formation took place through the slow, spontaneous loss of CO₂ from the Ca(HCO₃)₂ solution beneath the porphyrin monolayer.

Film characterization

- Films were picked up by dipping and subsequently withdrawing substrates through the surface film or by touching the film from above with substrates.
- The dipping technique enabled a view of the side that was facing the template while the latter method afforded a perspective of the flip side (i.e. the side facing the subphase) of the film. After being picked up, all the samples were naturally dried in the air and stored in desiccators at room temperature.
- Films picked up on various substrates were examined by optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersion X-ray analysis (EDS), thermogravimetric analysis and differential scanning calorimetry (TGA/DSC), and infrared spectroscopy (IR).

Observations

- Under the scanning electron microscope (SEM), the two sides of the film were different. One side was rough while the other side was smooth.
- Based upon the deposition method used, the smooth side corresponded to the side facing the porphyrin monolayer and the rough side corresponded to the growth front in the solution.
- The smooth side appeared flat. A view of the cross section of the film showed that the region close to the smooth side was condensed and the region close to the rough side was more particulate .
- Measurements taken at different sites from different segments of the film indicates that a continuous and homogeneous growth.
- Depending upon the experimental conditions such as temperature, inhibitor concentration, and the time period allowed for film growth, the thickness of different films could range from 0.4 to 0.6 μm , similar to that of the calcite laminae formed by many organisms.