Crystallisation at Interfaces

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Crystal growth at interfaces fundamental to biological crystal growth

Complex ⇒ look at model systems

• Langmuir Monolayers

• Self Assembled Monolayers (SAMs)

• Patterned SAMS
Precipitation of CaCO$_3$ under Langmuir Monolayers

Monolayers spread on supersaturated calcium bicarbonate solution. CaCO$_3$ precipitates under the monolayer on loss of CO$_2$

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 (g) + \text{H}_2\text{O}
\]

Range of long-chain amphiphilic monolayers examined:

<table>
<thead>
<tr>
<th>Stearic Acid (SA)</th>
<th>Octadecylamine (ODA)</th>
<th>Eicosyl Sulphate (ES)</th>
<th>Eicosyl Phosphonate (EP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{16}\text{COOH}$</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{17}\text{NH}_2$</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{19}\text{OSO}_3\text{Na}$</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{17}\text{OPO}_3\text{H}_2$</td>
</tr>
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</table>

The crystal polymorph and orientation was selected according to the monolayer structure
Stearic acid (SA) Monolayers

\([\text{Ca}^{2+}] = 9 \text{ mM}, \text{ oriented calcite formed}\)

2 morphological forms \(\Rightarrow\) Type-I and Type-II

Both plate-like at early stages, nucleated from (1-1.0) plane \(\Rightarrow\) realignment occurred during growth

\([\text{Ca}^{2+}] = 4.5 \text{ mM} \Rightarrow\) oriented Type-I vaterite crystals were produced

Type I - capped rhombohedral plates

Type II - related triangular morphology
Crystal Orientation:

- Orientation of crystals under SA monolayers due to stereochemical and geometric matching

- The monolayer has a hexagonal lattice with $a \approx 5 \text{ Å} \Rightarrow$ the carbonate-carbonate spacing is $4.69\text{Å}$ in the (1-1.0) face of calcite and a close epitaxial match occurs in two directions

Open circles: Ca ions in (1-10) face calcite

Filled circles: close-packed stearic molecules
Stereochemical Effects

• The stereochemistry of the monolayer headgroups is also essential in directing nucleation ⇒ other planes eg. (0001) offer a similar geometric match

The orientation of the carboxylate groups in the SA monolayer mimics the rows of perpendicular carbonate ions in the (1−1.0) calcite face, but not in the (0001) face
n-Eicosyl Sulphate and n-Eicosyl Phosphonate Monolayers

• Sulphate and phosphonate headgroups have a trigonal symmetry

• Sulphate monolayer, immature crystals were pseudo-hexagonal in form, nucleated from a (0001) face

⇒ developed to a trigonal pyramidal morphology

• Phosphonate gave similar results

Orientational Effect of Monolayer?

Approximate geometric match between:

- Hexagonal array of Ca\(^{2+}\) ions in the (0001) calcite face,
  \(a = 4.96\,\text{Å}\),
- Hexagonal packing of the headgroups in the sulphate,
  \(a = 5.5\,\text{Å}\)
- Hexagonal packing of the headgroups in the phosphonate
  \(a = 5.2\,\text{Å}\)

However, STEREOCHEMICAL RECOGNITION is probably the overriding factor determining the orientation.

The monolayer headgroups have a trigonal symmetry \(\Rightarrow\) mimics the planar carbonate ions in the (0001) face of calcite.
Calcite Precipitation under Acidic Polydiacetylene Films

• Previous monolayers showed control of CaCO₃ crystal orientation normal to the monolayer
  → no control in the plane of the monolayer

• Langmuir-Schäfer films of acidic polydiacetylene - highly organised and structure well defined - carboxyl groups exposed

• Calcite crystals with either rounded or triangular morphologies formed ⇒ co-aligned within single domains of the PDA films.

• Crystals nucleated from an (01.2) plane

• $a$-axis parallel to the polymer backbone direction.

Both the crystal and p-PDA polymer have a periodicity of $\approx 5\text{Å}$ along the $a$-axis

⇒ the carboxy groups along the polymer backbone fit closely to the calcite crystal structure.
What Factors Control the Crystal Orientation?

• **Stereochemistry of the carboxylate groups also important in selecting the (01.2) crystal face.**

• The (01.2) face comprises alternating planes of Ca$^{2+}$ ions and CO$_3^{2-}$ ions that are tilted 28° to the normal of the (01.2) plane.

• This orientation is closely matched by the 30° tilt of the side chains and carboxylate groups on the polymer.

The stereochemical match thus uniquely selects for the (01.2) plane, rather than, eg. the (0001) face, which offers a similar geometric, but poor stereochemical match.
Interfacial Electrostatics Guiding the Crystallization of CaCO$_3$ under Monolayers of Calixarenes and Resorcarenes

Monolayers of above macrocyclic compounds offer different surface charge densities – investigate CaCO$_3$ growth under these

Volkmer, Fricke, Agenab and Mattay J. Mater. Chem. 2004, 14(14), 2249-2259
• Both macrocycles form monolayers on water and $Ca^{2+}$ containing subphases

• At zero pressures show coexistence of LC/LE phases

• Featureless isotherms suggest no long range order
Aragonite crystals precipitate under a compressed monolayer of (1), $\pi = 20$ - $25 \text{ mN m}^{-1}$

At low pressures, $p = 0$ - $2 \text{ mN m}^{-1}$, fraction of vaterite and (1-10) oriented calcite increases

Monolayers of (2) support uniformly (012) oriented calcite at low pressures, non-oriented calcite crystals at higher pressures
How can the Orientational Effect of the Monolayer be Interpreted?

• Macrocycles (1) and (2) differ greatly in the molecular surface area

• Molecular structures vary greatly

• Oriented calcite growth occurs at low pressures where monolayer is in a liquid condensed phase

Any geometric match seems very unlikely...
• Monolayers of (2), and many other structurally different amphiphiles support (012) oriented calcite:

⇒ Occurs at a surface pressure where the average density of carboxylate residues is 2.00-2.44 \( \text{CO}_2^- \text{ nm}^{-2} \)

Monolayers of (1), support aragonite formation

⇒ Occurs at surface pressures where the average density of carboxylate residues is 4.65-5.00 \( \text{CO}_2^- \text{ nm}^{-2} \)
⇒ also in keeping with other studies

Results strongly indicate that non-directional interfacial electrostatics is the dominant effect in template-directed \( \text{CaCO}_3 \) growth under Langmuir monolayers
Summary

EPITAXIAL MECHANISMS CAN operate to provide orientation of crystals
⇒ see TOTAL orientation effects by highly organised p-PDA monolayers
⇒ Geometric matching is NOT ESSENTIAL for oriented growth

INTERFACIAL ELECTROSTATICS – ion binding and dipole moments
- appear to be important

STEREOCHEMISTRY – can be a dominating effect. Can observe orientation where NO ordering of monolayer

(001) oriented calcite on PAH/PSS film (104) (NON) oriented calcite on glass
Crystallisation on Self Assembled Monolayers (SAMs)

- Offer a simple and flexible method to produce a solid state organic thin film
- The surface chemistry is defined by the SAM terminal group
- Demonstrated to offer high degree of control over crystal nucleation and orientation

SAMs can be easily patterned to direct crystal growth on to designated areas
CaCO$_3$ Deposition on Functionalised SAMs

$\omega$-terminated alkanethiols on gold and silver thin films

$\Rightarrow$ highly effective in controlling the orientation of deposited calcite crystals,
## Orientation Effects

<table>
<thead>
<tr>
<th>Thiol</th>
<th>Au</th>
<th>Ag</th>
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<tbody>
<tr>
<td>$\text{HS(} \text{CH}<em>2\text{)}</em>{15}\text{CO}_2\text{H}$</td>
<td>(015)</td>
<td>(102)</td>
</tr>
<tr>
<td>$\text{HS(} \text{CH}<em>2\text{)}</em>{11}\text{OH}$</td>
<td>(104)</td>
<td>(103)</td>
</tr>
<tr>
<td>$\text{HS(} \text{CH}<em>2\text{)}</em>{11}\text{SO}_3\text{H}$</td>
<td>(10 12)</td>
<td>(107)</td>
</tr>
<tr>
<td>$\text{HS(} \text{CH}<em>2\text{)}</em>{11}\text{PO}_3\text{H}_2$</td>
<td>planes oriented at $24^\circ$ with respect to the $c$-axis</td>
<td>planes oriented at $\approx 40^\circ$ to the $c$-axis</td>
</tr>
<tr>
<td>$\text{HS(} \text{CH}<em>2\text{)}</em>{11}\text{N(} \text{CH}_3\text{)}_3\text{Cl}$</td>
<td>non-oriented/ inhibited crystallisation</td>
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</tr>
<tr>
<td>$\text{HS(} \text{CH}<em>2\text{)}</em>{15}\text{CH}_3$</td>
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- The $\text{CO}_2\text{H}$, $\text{OH}$ and $\text{SO}_3\text{H}$ SAMs selectively nucleate calcite from one plane only.

- For the $\text{PO}_3^-$ headgroup, the monolayer selects only the angle that the $c$-axis makes with the substrate.
• Lattice structure of SAMs is the same for a given metal

• No lattice match occurs between the metal lattice and the calcite nucleating plane.

The calcite nucleation face is determined by the structure, chemical character and coordination number of the monolayer headgroup
In all cases of oriented nucleation, the Au and Ag substrates induced nucleation from faces differing in orientation by 15-20°, identical to the difference in the tilt angle of the thiol molecules on Au and Ag.

Match of CO$_2$H orientation of SAM headgroup and CO$_3^-$ groups in calcite nucleating face

Match of CO$_2$H groups in SAM and Ca ions
Summary

• **Lattice match** between SAM and nucleating crystal planes **DOES NOT APPEAR** to be responsible for oriented nucleation

• **Orientation of functional groups** in the SAM precisely matched the orientation of carbonate groups in the nucleating crystal face

• **Matching of symmetry of functional group** alone cannot be responsible for orientation - cf. \( \text{SO}_3\text{H}^- \) and \( \text{PO}_3\text{H}_2^- \)

**Benefit of SAMs** ⇒ can selectively nucleate a wide range of orientations ⇒ can make systematic changes in the structure
Oriented Nucleation on SAMS with Alkyl Chains of Differing Parity

Calcite grown on -COOH terminated SAMs with odd/even alkyl chains

Ag substrates ⇒ orientation of terminal group constant

Au substrates ⇒ terminal group adopts 2 different orientations for odd and even chains

• Crystal orientation constant on Ag SAMs (012)
• (013) Oriented on odd-chain SAMs on Au
• (113) Oriented on even-chain SAMs on Au

Alignment of -CO₂H groups on SAMs with the carbonate groups in calcite for a) odd (and even) chain length SAMs on Ag, b) odd chain length SAMs on Au, c) even chain length SAMs on Au, NP=(113).

The CO bonds in the surface carboxylate groups are parallel to the CO bonds in the carbonates in the nucleated calcite crystals.
Patterning Crystal Growth

One of major advantages of SAMs ⇒ can be patterned in 2D

Generates patterns of SAMs with contrasting endgroups
Oriented Crystal Growth on Patterned SAMs

Patterned SAMs enable periodic arrays of discrete crystals with controlled densities, location, size and orientation to be produced.

Variation of the density and sizes of features on the stamp, the concentration of the crystallising solution and the SAM terminal groups gives control over the:

- Location of crystal growth
- Density of crystal growth
- Number of crystals nucleating within a given region
- Orientation of the crystals

Localised crystallisation occurs due to diffusion-limited nucleation

- Crystals nucleate first on the areas of hydrophilic \(-\text{CO}_2\text{H}\) thiols

- Transport of ions to the growing crystals reduces the concentration of ions in the adjacent hydrophobic areas
  \[\Rightarrow\text{prevents non-specific nucleation within a characteristic distance of the interface.}\]

- Variation of the size and periodicity of patterns and the concentration of the crystallising solution therefore offers control over crystal patterning.
Summary

Orientational Control

• **Geometric Match** – doesn't appear to be overriding effect

• **Stereochemical Match** – evidence quite convincing!

Control by SAMs...

• Orientation between Au substrate and crystals indicates the structural relationship between the SAM and calcite crystals

• Match of $CO_2H$ orientation of SAM headgroup and $CO_3$-groups in calcite nucleating face

Electrostatics...

“Non-directional interfacial electrostatics is the dominant effect in template-directed $CaCO_3$ growth under Langmuir monolayers”