Ultra Thin Films of Oriented Cellulose Nanocrystals by Electric Field-Assisted Convective Assembly

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Objective

- Ultra-thin films of cellulose nanocrystals (CNCs) produced by controlled assembly have gained recent attention:
  - understanding complex interactions
  - fabricating advanced materials
Self-assembly can be facilitated by:
- geometry of particles (aspect ratio)
- dimensions
- surface and intermolecular interaction forces
- their response to electric or magnetic fields
<table>
<thead>
<tr>
<th>Methods</th>
<th>Cellulose Source</th>
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## Alignment of CNXs

<table>
<thead>
<tr>
<th>Methods</th>
<th>Cellulose Source</th>
<th>Alignment evidence</th>
<th>Disadvantage</th>
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<tbody>
<tr>
<td>Electric Field</td>
<td>Tunicates and Ramie fibers</td>
<td>Electric field</td>
<td>High electric field: Voltage: 2.5 – 20V (2-10 kV/cm) Frequency: 1kHz – 2MHz</td>
<td>Bordel, D.;Putaux, J. L.; Heux, L. Langmuir, 2006, 22, 4899</td>
</tr>
</tbody>
</table>

Shear Rate with Convective Assembly
Recent advances of alignment of CNXs

- Ultra thin films of cellulose nanocrystals (CNs) can be made using (isotropic films):

  **Langmuir-Schaeffer lifting:**

  [Image of Langmuir-Schaeffer lifting process]


  **Langmuir-Blodgett lifting:**

  [Image of Langmuir-Blodgett lifting process]

Convective self-assembly:

The film is oriented

substrate: PEI treated silica wafer

particle layer

deposition plate

deposition direction

suspension meniscus

Rojas and co-workers, ACS Nano, submitted
• Aim of this presentation:
  – Demonstration of the fabrication of highly ordered structured CNC films by using:
    • electric field-assisted convective self-assembly
• Ramie fibers were used in the production of cellulose nanocrystals (CNCs)
• They were hydrolyzed with 65 % sulfuric acid at 55 °C for 30 min
• Dialysis against deionized water followed and then against Milli-Q water (for a few weeks)
• The dimensions of the CNs were 185± 25 nm in length and 6.5 ± 1 nm in width (88% CrI)
• **Dielectric**: *ability to store energy in an applied electric field* *(depend on frequency, temperature, orientation, mixture, molecular structure)*

• **Permittivity**: *interaction of a material with an electric field*

\[
\bar{\varepsilon} = \varepsilon - i \frac{\sigma}{\varepsilon_0 \omega}
\]

- \( \bar{\varepsilon} \) - how dissipative or lossy the material is
- \( R \) - how much energy from an external field is stored
Materials have an arrangement of charge carriers that can be displaced by electric fields. The charges become polarized.

To describe the complex CNC-water suspension system, the Maxwell-Wagner permittivity model must be redefined.

\[
\begin{align*}
\varepsilon_{p,MW}^*(\omega_e) &= \varepsilon_p - j \frac{\sigma_p}{\varepsilon_0 \cdot \omega_e} \\
\varepsilon_{c,MW}^*(\omega_e) &= \varepsilon_c - j \frac{\sigma_c}{\varepsilon_0 \cdot \omega_e}
\end{align*}
\]
Dipole moment: a measure of the separation of positive and negative electrical charges, a measure of the charged system’s overall polarity

\[ p_i = 4\pi a^2 b \bar{\varepsilon}_m K_i E_i \]

\[ K_i(\omega) = \frac{1}{3} \frac{(\varepsilon_p - \varepsilon_m)}{\bar{\varepsilon}_m + A_i (\varepsilon_p - \varepsilon_m)} \]

Depolarization factor

Clausius-Mossotti factor
For an ellipsoid eccentricity, the depolarization factor is given by:

\[ e = \sqrt{1 - \frac{c^2}{a^2}} \]
Dielectrophoresis: is the motion of particles due to the interaction of a non-uniform applied electric field and the moments induced in particles.
Energy of an ellipsoid particle

- with dipole moment $p$ and
- electric field $E$

$$V(\theta) = -A\mathcal{R}(p.E)$$
Calculated spectra for homogeneous prolate ellipsoids at different water and cellulose conductivities.
Rotation speed $Im[f_{CM}]$ spectra of nanocrystalline cellulose
• Probability Maxwell-Boltzmann distribution function $P$ of the orientation of ellipsoid nanocrystals in an electric field:

$$P_{MBd} = \frac{e^{-\frac{V(\theta)}{kT}}}{\int_{0}^{\pi/2} e^{-\frac{V(\theta)}{kT}} d\theta}$$

where: $k$-Boltzmann constant,

$T$-temperature
\[ O_p = \int_{0}^{\pi/2} P_{MBd} \cos2\theta \, d\theta \]
Conclusions

- Comprehensive literature review
- Polarization of CNCs
- Alignment
Thank you for your attention!