NANOCOMPOSITE THIN FILMS: Assembly, Characterizations, & Applications

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Poly(Styrene-butadiene-styrene) (SBS) offers many of the properties of natural rubber, such as flexibility, high traction, and sealing abilities, with increased resistance to heat, weathering, and chemicals.

Nanocomposite Materials

Nanotechnology R&D Priority for the forest product

- Liberating nanodimensional cellulose fibrils
- Using nanomaterials, nanosensors, and other applications of nanotechnology to improve the raw material and energy efficiency of conversion processes
- Achieving directed design of biopolymer nanocomposites
- Developing biomimetic processes for synthesizing lignocellulosic-based nanomaterials
- Utilizing self-assembly of nanodimensional building blocks for functional structures and coatings
- Exploiting the nanoscale architecture of lignocellulosics
- Biofarming lignocellulosic materials with unique multifunctional properties

NANOCOMPOSITE THIN FILMS:
Assembly, Characterizations, & Applications
Layer-by-Layer Assembly

- Spin assisted LbL
  

- Spray assisted LbL

G. Decher, et al.
Science 1997, 277, 1232.

Layer-by-Layer Assembly

Rubner and Cohen
MIT
CEN, 2005, 83(38), 34.

Kotov, U Michigan
Nature Mater. 2003, 2(6), 413.

Saraf
U Nebraska
Science, 2006, 312, 1501.
Layer-by-Layer Assembly

Cellulose Nanowire (from Tunicate), 3-4 nm, CNW/PEI LbL films, Antireflective properties

Layer-by-Layer Assembly

Employ cellulose microfibers as a support to fabricate bioactive composites with organized enzyme multilayer.

The bio activity can be tuned by varying the number of enzyme layers.

Composite LbL Nanomembrane


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With the progress of miniaturization of devices—
microphones and loudspeakers can now be
found on the tip of a pen—they need for smaller
and more versatile membranes with exceptional
mechanical properties becomes greater and greater.

One can imagine a small pressure gauge implanted in the
wall of a blood vessel transmitting information on the
blood pressure to the area in certain areas of the brain.

To realize these things, advances in the membrane
mechanical properties are needed. The mechanical
properties are dependent on the materials used,
and the ability to control the properties of the
materials is a key to the development of new
membranes.

2005, 15(5), 771
Free-standing LbL Films


Biomimetic Approach

un-cooled biological receptors with 30mK sensitivity

Free-standing LbL Thin Films

Spin-assisted LbL
Sacrificial Layer method

Freely Suspended LbL nanomembranes
Free-standing LbL Thin Films

\[ (\text{PAH-PSS})_n \text{PAH}/\text{Au}/(\text{PAH-PSS})_n \text{PAH} \]

\( n = 3, 5, 7, 9, 11, \ldots \)

C. Jiang, et al.  
Nanomechanics -- Bulging Tests

<table>
<thead>
<tr>
<th>Range</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection: 0-10 μm,</td>
<td>$\frac{1}{2} \lambda$ (~300 nm)</td>
</tr>
<tr>
<td>Pressure: 100 kPa,</td>
<td>2 Pa</td>
</tr>
</tbody>
</table>

Bulging Test

Membrane deflection

200 μm
Bulging results and elastic modulus

Mechanical parameters for different freely suspended nanomembranes

<table>
<thead>
<tr>
<th>Membrane type and Gold content</th>
<th>Fabrication method</th>
<th>Membrane diameter (μm)</th>
<th>Elastic modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9G9, 3.9% SA-LbL</td>
<td>400</td>
<td>6.6±3.3</td>
<td></td>
</tr>
<tr>
<td>9G9, 0.5% SA-LbL</td>
<td>400</td>
<td>4.3±2.0</td>
<td></td>
</tr>
<tr>
<td>9.9%, 0% SA-LbL</td>
<td>400</td>
<td>1.5±1.0</td>
<td></td>
</tr>
<tr>
<td>9G9, 4% LbL</td>
<td>N/A*</td>
<td>N/A*</td>
<td></td>
</tr>
</tbody>
</table>

* Film was broken into small piece, which cannot be transferred to holey substrate.

\[
P = \left[ C_0 \frac{E}{1 - \nu^2} \frac{h^4}{a^4} + C_1 \frac{\sigma_0 h^2}{a^2} \right] \left( \frac{d}{h} \right) + C_2 \frac{E}{1 - \nu} \frac{h^4}{a^4} \left( \frac{d}{h} \right)^3
\]

Micropattern in Nanomembrane

Gold Nanoparticle Arrays

13 nm

6 nm

1 μm

1 μm
Localized Mechanical Testing

\[ \lambda = 2\pi d \left( \frac{E_f (1 - \nu_s^2)}{3E_s (1 - \nu_f^2)} \right)^{1/3} \]

<table>
<thead>
<tr>
<th>Location</th>
<th>( \lambda ) (( \mu m ))</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With Gold</td>
<td>3.52</td>
<td>4.35</td>
</tr>
<tr>
<td>Without Gold</td>
<td>2.76</td>
<td>2.08</td>
</tr>
</tbody>
</table>

SERS in Nanomembranes

Confocal Raman microscope

Polymer Chain Behavior

Chain-like Au-NP aggregation + spreading of polymer chains

Bridging multiple nanoparticles through stretched backbones

Outstanding mechanical properties of SA-LbL films

C. Jiang, et al.  
LbL film with Silver Nanowires

Density of Silver nanowires can tune the mechanical properties of LbL thin films.

Buckling Patterns of Ag LbL Films

Buckling patterns “stop” at the location where silver nanowire appears.
3D Nanomembranes

Micro-sculptured nanomembranes

< 200 nm
Optical Grading with 3D Nanofilm

Sensitive LbL Composites Films

\[ \Delta T = \Delta P/P \]

Theoretical estimation for silicon

Gain

Projections for nanomembrane

Bulging test

AFM test

2.5 kPa

100 \mu m

Deflection (\mu m)

1E-11 to 1E-3

1E-10 to 1E-7

1E-5 to 1E-4

0.01 to 0.1

0.1 to 1

0.1 to 1

1 to 10
Micromechanical Tests

Microcavity Arrays

Half-inch wafer
64×64 cavity array
Over 4000 membranes
Uniform Thermal Behavior
Thermal Bulging

NIR Sensing Tests

Laser

CCD Camera

Light

Laser focus to 500 μm diameter

785 nm
50-150 mW
Applications for Nanofilms

- Develop multilayer ultra-thin membranes with more flexible polyelectrolyte to achieve higher sensitivity.

- Increase thermal isolation and design novel substrates for high resolution imaging application.

- Using SERS properties and design portable and sensitive chemical detector

- Infrared detector with ability to detect NIR radiations in different wavelength.

- Biological and medical application, eg. drug release and delivery.
Summary

- **Layer-by-Layer assembly**
  a versatile method in fabricating multilayer nanomembranes with a variety of nanoscale building blocks, including cellulose nanocrystals and other forest products.

- **Surface-enhanced Raman spectroscopy**
  Molecular information within the nanoscale composite thin film; confocal technique can provide spatial resolutions for composite nanomembranes

- **Free-standing LbL nanomembranes**
  with functional nanostructures are suitable for sensing applications in mechanical, thermal, and optical areas.
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