Nanoparticles and Nanostructures from Direct- and Self- Assembly of Components Cleaved From Fiber Cell Walls

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Link to publications in this talk: click here
Nanocellulose

• Nanotechnology/nanomaterials: enablers for new generation products and processes.

• The graphene market continued to grow (government investments and public listings by producers). Numerous graphene-enabled products coming to the market

• Nanocellulose moved to the forefront and regulatory initiatives are multiplying.

Future Markets, Inc.
Production will likely increase by 500% at least by 2017 (Future Markets, Inc. 2012)
Assembly proteins (rosette) which produces cellulose nanofibers ~28nm

Top-down deconstruction

Bottom-up:
Nature working across $10^{10}$ scale (construction)
Fiber deconstruction

Pulp & paper

Nanofibrillar Cellulose (NFC)

Hydrolysis with strong acids

Cellulose nanocrystals (CNC)


Cellulose, 14, 539 (2007)
Cellulose, 17, 835 (2010)
Moon at al., Chem. Soc. Rev., 3941 (2011)
Cellulose, 18:1097 (2011)
Bioresources, 6, 4370 (2011)
High Volume

- Automotive (body & Interior)
- Packaging Coatings
- Hygiene and Absorbent
- Paper and packaging filler
- Plastic Film Replacement
- Paper Coatings

Low volume
- Wallboard Facing
- Insulation
- Aerospace Structure
- Aerospace Interiors
- Aerogels for Oil & Gas
- Paint-Architectural
- Paint-Special Purpose
- Paint Applications

NOVEL + Emerging Applications
- Sensors (medical, env., ind.)
- Reinforcement fiber
- Water & air filtration

Viscosity modifiers
- Purification
- Cosmetics
- Excipients
- Organic LED

Photovoltaics
- Recyclable Electronics
- 3D printing
- PhotonicFilms

Market Projections For Nanocellulose-enabled Products, J. A. Shatkin (October, 2013)
Supramolecular unit of structures ranging from “fibrils” ...

to...
spherical or ellipsoidal particles

So far as the photographs go, however, they certainly give the impression that the fibres might be regarded as ‘crystallites’ of cellulose, and this would be in harmony with those properties of this particular wall which suggest a high degree of crystallinity. The density, for example, is the highest yet recorded for cellulose (1.562) and suggests a crystalline/non-crystalline ratio of about 71 per cent. A determin-

impression is given of the presence in the wall of spherical particles, some 300 Å in diameter, linearly arranged and suggesting, therefore, a unit of smaller dimension.

Preston, R. D., Nicolai, E., Reed, R., Millard, A. (Botany Dept., Univ. Leeds) Nature, 162, 666 (1948)
Fiber deconstruction

Pulp & paper

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Microemulsion treatment: Flooding and deconstruction

Surfactant-Oil-Water Systems

Winsor phase diagrams

(a) Winsor I

(b) Winsor III

(c) Winsor II

R < 1

R = 1

R > 1
Microemulsions in CNF production

- Microfluidization not possible directly form fibers
- Microemulsions facilitates deconstruction
- Energy savings of ~50% if microemulsions are compared to single component solution
**Cellulose Nanofibrils (NFC and BC)**

- **Bioconversion**
  - Bioconversion of Cellulose
  - Cellulose, 2013
  - ACS Macro Letters, 1, 1321 (2012)
  - Biomacromolecules, 13, 3228 (2012)
  - Biomacromolecules, 14, 1637-1644 (2013)

- **Rheology modification**
  - Viscosity vs. shear rate

- **Bioactive materials**
  - Biomacromolecules, 12, 4311 (2011)
  - Biomacromolecules, 13, 2802 (2012)

- **Super-strong Hydrogels & Aerogels**
  - Cellulose 20, 2417 (2013)

- **NFC and BC**
  - J. Renewable Resources, 2013, 1, 195
  - Carbohydrate Polymers, 89, 1033-1037 (2012)

- **Composites (reinforced materials)**

- **Conductive nanopaper (+ Pyrrole, click chemistry):** 37.4 $10^{-3}$ S/cm
Aerogels: low density solid foam materials that contain ~98% air (very light, extremely strong, and excellent insulators)
Applications

High specific surface area + low density:

- Thermal/sound insulation
- Packaging
- Filters
- Nonwovens
- Absorption
- Surface chemistry and catalysis
NFC: Rheology

CNC

CNF

Viscosity (Pa*s) vs Shear rate (1/s)

- No electrolyte
- 10 mM Na
- 25 mM Na
- 50 mM Na

Viscosity (Pa*s) vs Shear rate (1/s)

- No electrolyte
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**NFC: Bioseparation**

**Biactive Cellulose:** detection, biofiltration, etc.

- **ARGET ATRP**
- **Peptide immobilization**
- **IgG adsorption**

**Poly(AMA-co-HEMA)**

- **cellulose**
- **OH group**
- **NH₂ group**
- **peptide**
- **hIgG**

**Figure:**

- **a) **Bacterial cellulose tube**
- **b) **Hollow tube**
- **c) **Pure, TEMPO-ox, CMC-modified

**Graphs:**

- **Protein adsorption (mg/m²)**
  - **IgG**
  - **BSA**

**Notes:**

- **Histidine-Tryptophan-Glycine-Tryptophan-Valine (HWRGWV)**
Nanopaper with Control of Surface Energy (lignin)

Water contact angle

<table>
<thead>
<tr>
<th></th>
<th>0L</th>
<th>2L</th>
<th>4L</th>
<th>14L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_a$</td>
<td>35.4 ± 0.5</td>
<td>48.6 ± 1.1</td>
<td>60.9 ± 4.1</td>
<td>77.7 ± 3</td>
</tr>
<tr>
<td>$\theta_r$</td>
<td>25.8 ± 1</td>
<td>25.7 ± 0.7</td>
<td>25.9 ± 1.7</td>
<td>25.8 ± 1.8</td>
</tr>
<tr>
<td>H</td>
<td>9.6</td>
<td>22.9</td>
<td>35.1</td>
<td>51.9</td>
</tr>
</tbody>
</table>

Lignin increases ~ 40° WCA and “hydrophobicity”

HYSTERESIS (H)
- Roughness
- Heterogeneity

H increases with lignin (↓roughness & ↑heterogeneity)

Roughness & Heterogeneity
Relative water absorption capacity

RWAC = $\frac{m_{\text{water}}}{m_{\text{dry solid}}} \cdot 100$

WAC = $\frac{m_{\text{water}}}{m^2}$

RWAC: 36.4 %
WAC: 19.5 g/m²

RWAC: 34.7 %
WAC: 17.4 g/m²

RWAC: 25.9 %
WAC: 15.5 g/m²

RWAC: 11.5 %
WAC: 6.5 g/m²

WAC decreases with lignin
Mechanical and Barrier properties

Graph showing strength, modulus, and strain values for Softwood, Hardwood, and Non-wood materials. The graphs include data points and error bars.

Graph on the right showing relationships between lignin content and various properties such as RWA, WAP, and OP 50% RH, with R² values provided for each relationship.
Fiber deconstruction

Cellulose, 14, 539 (2007)
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Cellulose Nanocrystals (CNC)

Spin coating

Film casting

Langmuir-Schaeffer

Shear/Convection

Coatings and anti-scratch surfaces

Biomacromolecules, 11, 2683 (2010)
Biomacromolecules, 11, 674 (2010)

Langmuir, 26, 990 (2010)
Thin Solid Films, 517(15), 4348 (2009)

Piezoelectric materials

10 Hz signal at low & high voltage: oscillation perpendicular to the $z$-direction of the image

Piezoelectric charge constant $d_{33}$ of reference 400 nm ZnO film $= 1.3 \, \text{Å/V}$.

Asymmetric CNC

Reductive amination at the reducing ends of a CNC and Ag silver NP labeling of thiol functionalized CNCs

Biomacromolecules, 12, 2788 (2011)
J. Colloid Interface Sci, 369, 202 (2012)
CNC: assemblies on solids - coatings

Film casting
Spin coating
Langmuir-Schaeffer
Shear/Convection

CNC: Energy Harvesting

- Radiation
- Thermal
- Gravitational
- Nuclear
- Magnetic
- Chemical (battery, fuel cell, fossil fuels)
- Mechanical (kinetic or vibration, elastic, fluid)

Electromagnetic, electrostatic and piezoelectric transductions

- First observations in wood: Bazhenov (1950) and Fukada (1955) [shear piezoelectric modulus d14 and d25]
- Depends on the type of wood, orientation, moisture and temperature
- Piezoelectric effect due to the chemical and asymmetric crystalline structure of cellulose fibrils.

Converse Piezoelectric Effect in Cellulose I Revealed by Wide-Angle X-ray Diffraction, Gindl et al. (2010)

278 pm/V
Dielectrophoresis of CNCs and alignment in films by electric field-assisted shear

***Bivariate map for the orientation parameter map of CNCs as a function of field strength and frequency***

**Al**

**CNCs**

**Films of aligned CNCs**

**substrate**

**induced polarization of the CNCs leads to assembly via dipolar interactions**

**Calc**
Direct Piezoelectric Effect

Induced polarization of the CNCs leads to assembly via dipolar interactions.

Films of aligned CNCs

10 Hz signal at low & high voltage: oscillation perpendicular to the z-direction of the image

Piezoelectric constant:
(2 kHz and 800 V/cm): 2.1 Å/V. Piezoelectric charge constant $d_{33}$ of reference 400 nm ZnO film = 1.3 Å/V.

Hoeger, et al., 7, 1957 (2011)
Csoka, et al., JCIS 363, 206 (2011)
Csoka, et al., ACS Macro Letters, 1, 867 (2012)
Converse Piezoelectric Effect

Preparation of dried BC

Fabrication of BCN-ZnO film

Assembly and casting evaporation

DSO measurements

Kinetic excitation

Glass slide

Support

Al upper electrode

BCN thin film

Al lower electrode
CNC: Site-specific and non-specific functionalization of cellulose nanocrystals

Synthesis mediated by TOCNCs:
Metal nanoparticle manufacture and hybrid materials

Anisotropic hybrids (Ag, Au, etc.):
Supra-colloidal self-assembly, biosensing, electro-mechanical actuation, light emitting, semiconducting/conducting

Silver NPs (site-specific)

Magnetic NPs (non site-specific)

Shape-anisotropic, magnetic responsive:
Optical sensing, protein separation, cell treatment, etc.

Proof of magnetic fluid hyperthermia

Super-strong hollow and solid μ-particles:
Light-weight component in composites, carriers + drug release, smart separation

Beads & capsules via Pickering emulsions

With the support of Dr. Leena-Sisko Johansson + Dr. Joe Campbell (XPS) and Ritva Kivelä, Marja Kärkkäinen, Anna-Leena Anttila.
Surface in aqueous medium

Coulombic repulsion between the negatively charged CNC rods tend to promote upright alignment

Flexible fixing allows CNC alignment changes

Surface after directional drying
CNC in Pickering Emulsions

Solid particles to stabilize emulsions (Ramsden (1903), Pickering (1907))

Hydrophilic particles

\[ \theta < 90^\circ \]

Hydrophobic particles

\[ \theta > 90^\circ \]

\[ R = 10 \text{ nm} - 5 \mu \text{m} \]
\[ \gamma_{ow} = 30 - 50 \text{ mN/m} \]
\[ \theta = 30^\circ - 150^\circ \]

Energy of particle desorption:

\[ E_{bulk} - E_{surface} \rightarrow \Delta E_{des} = \pi R^2 \gamma_{ow} (1 \pm \cos \theta)^2 \rightarrow \Delta E_{des} \gg kT \]
Microcapsules of Magnetic CNC-iron oxide hybrid

CNC-Cobalt ferrite-shell coprecipitation FeSO₄/CoCl₂ precursors

Styrene + 2,2'-Azobis(2,4-dimethyl) valeronitrile

Zoppe, et al. JCIS. 2012, 202
Magneto-responsive systems

Phase separation

- Purification
- Separation
- Emulsion stabilization

Optical sensing Detection (polarized lenses)

Annealing in 80°C for 48 h in magnetic field

Reinforcement in fibers
Inorganic loading for magnetic response

Magnetic fluid hyperthermia

- H = 200 Gauss
- f = 869 KHz

Shape-anisotropic: Alignment by external stimuli

- Optical sensing, protein separation, cell treatment, etc.

Lee et al. Nat. Nanotech. 2011, 418
CNC: Reinforcing fibers

PVA
- $d = 235$ nm

PCL
- $d = 210$ nm

CA
- $d = 200$ nm

Nylon

PP

PS

Lignin-CNC

Bi-component fibers (electrospinning, etc.)

... composite fibers reinforced with CNCs
Lignin-based composite fibers (90% L)

Nanofibrillar cellulose (NFC)

- Rheology modifiers, paintings, pharma, and food
- Films, packaging, barrier materials
- Composites (reinforcing)
- Biomedical materials
- Coatings
- Flexible, soft electronics
  - Circuit board base (electronic packaging)
  - Conductive/magnetic or piezoelectric films
    (sensors, actuators, RTDs)
- Bacterial Cellulose (BC)
- Cellulose Nanocrystals (CNC)
Thank you