PennState College of Engineering | CHEMICAL ENGINEERING

Nanoengineering Cellulose for Environmental & Biomedical Applications

***Amir Sheikhi**, Ph.D.*

Assistant Professor
Chemical Engineering
Biomedical Engineering (Courtesy)
The Pennsylvania State University

sheikhi@psu.edu

Bio-Soft Materials Laboratory (B-SMaL): www.sheikhilab.com

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Pennsylvania State University
University Park, PA, USA, April 16, 2020

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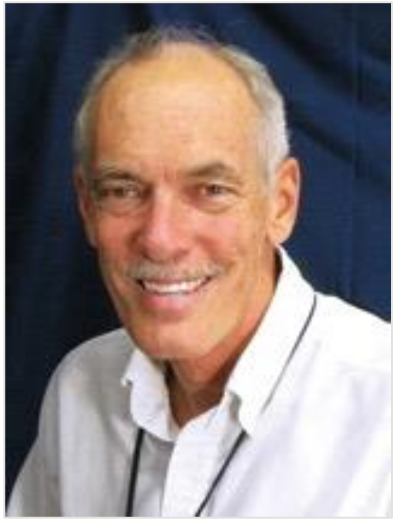
Introductions



Mike
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PennState

Trevor Thornton
Professor

ASU

Introductions

Presenter

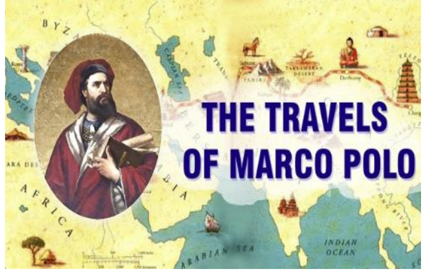
Amir Sheikhi
Assistant Professor
Chemical Engineering

PennState

Amir Sheikhi

EDUCATION

BS: University of Tehran, Chemical Engineering
MS: University of Tehran, Chemical Engineering
PhD: McGill University, Chemical Engineering
PDF: McGill University, Chemistry
PDF: Harvard-MIT Health Sciences and Technologies, Engineering in Medicine
PDF: UCLA, Bioengineering

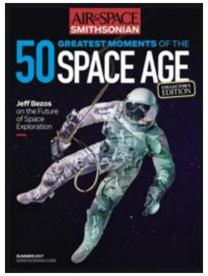


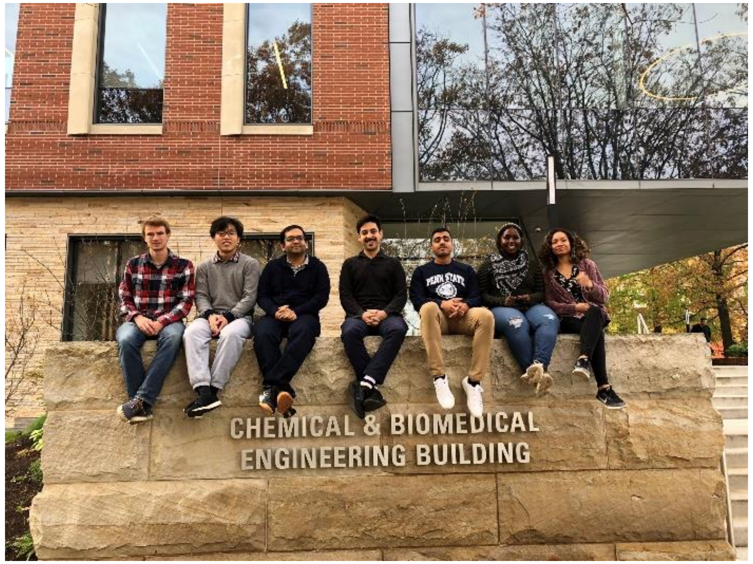
Research Keywords

Experimental Soft Materials
Biomaterials
Living Materials
Environment
Tissue Engineering and Regeneration
Bioseparation

FUN FACT(S) about ME

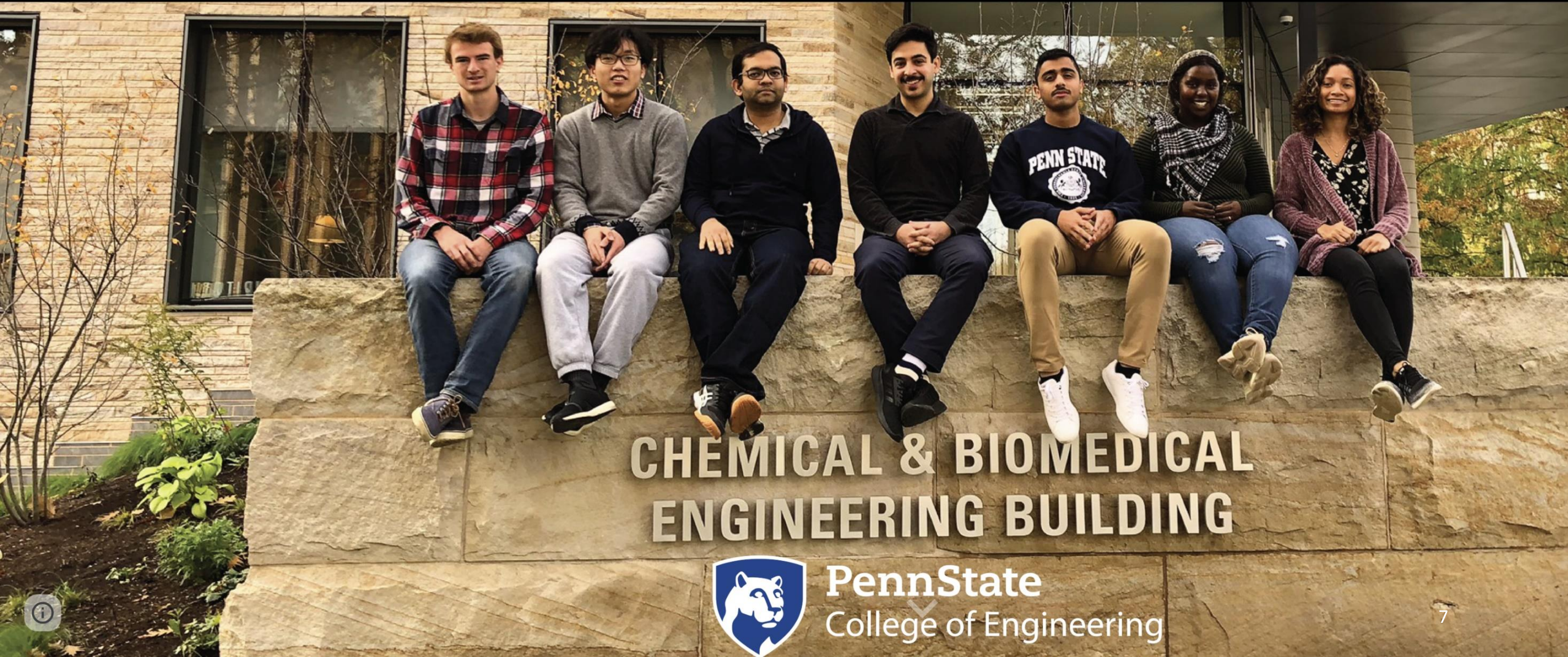
-I was born in **Tehran**, the capital city of Iran.
-When I was a kid, I really wanted to become an **astronaut**! I was kind of addicted to collecting space-related magazines that my parents got worried about me!
-DID YOU KNOW: During the launch phase, an astronaut has to endure a force of up to four times their own body weight. Ill-fitting dental fillings could become loose or fall out → So, I took a good care of my teeth and never had any problem with them…but **never** became an astronaut!!
Many years later, I became a **Chemical Engineering faculty**!!
-Hobbies (Swimming), favorite food (Barberry rice w/ saffron chicken)





BIO-SOFT MATERIALS LABORATORY (B-SMaL)

Shaping the Future of Engineering Soft Materials
for Medicine and the Environment



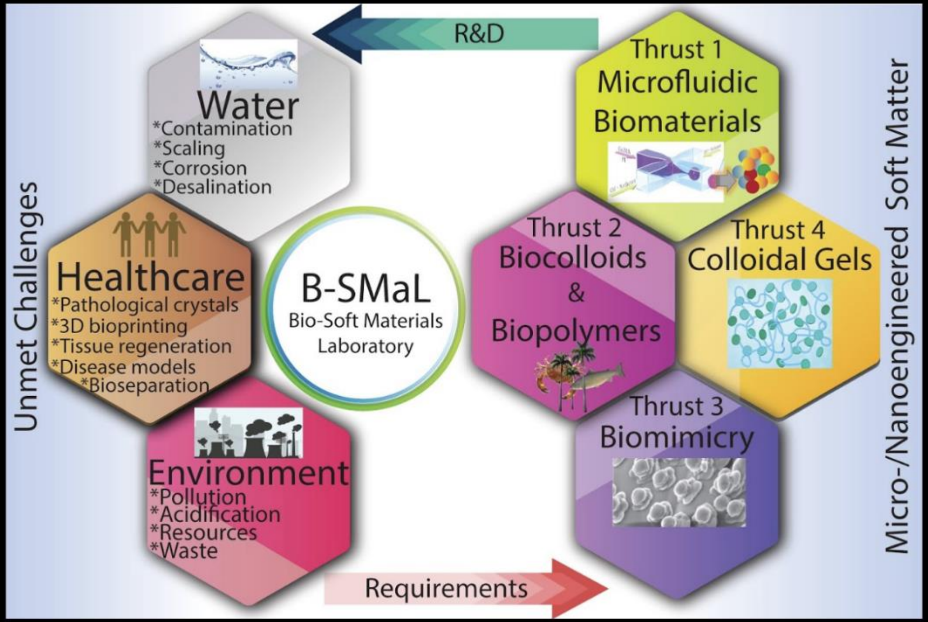
How Can Bio-Based Soft Materials and Biomaterials Impact Society?

Soaring population growth, imbalance supplies and demands, shortage of ready-to-use remedies, and urbanization have introduced unprecedented challenges to satisfying the world's essential needs for water, healthcare, food, and energy. Designing new material platforms inspired by the following questions may take us one step closer to finding solutions to these needs:

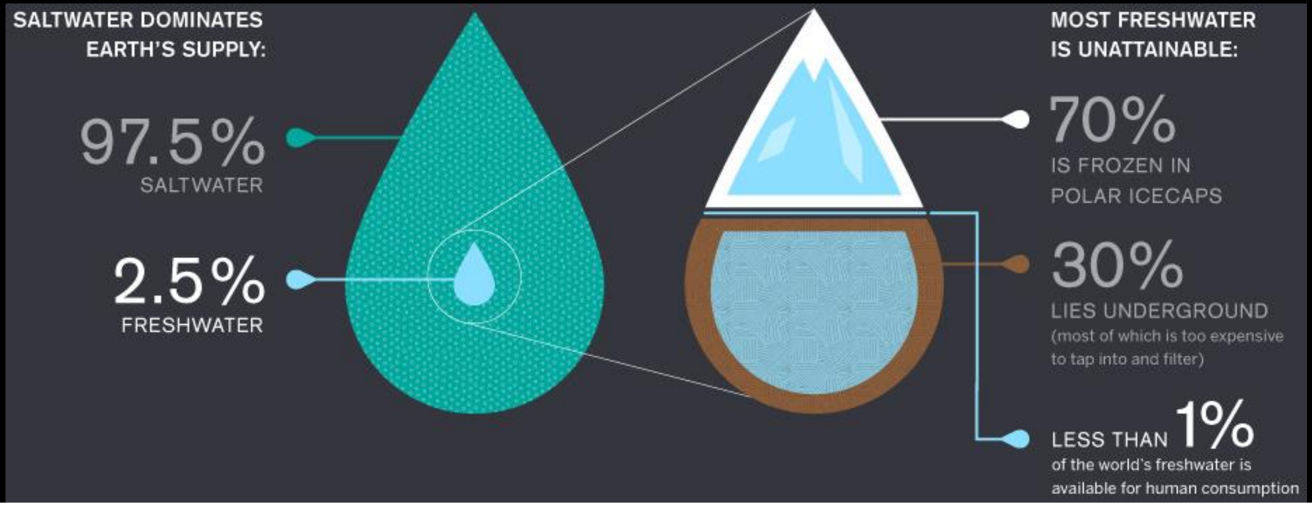
1) How can natural bioproducts be micro-/nanoengineered to overcome the persistent bottlenecks of current synthetic materials?

2) How can the sophisticated structure-property relationships in nature be mimicked to address everyday life challenges?

Our Contributions

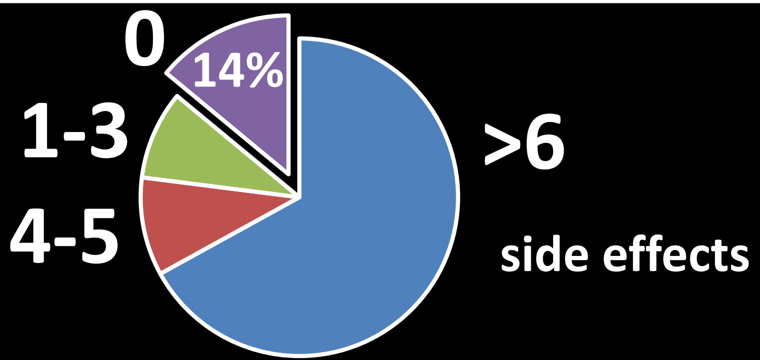


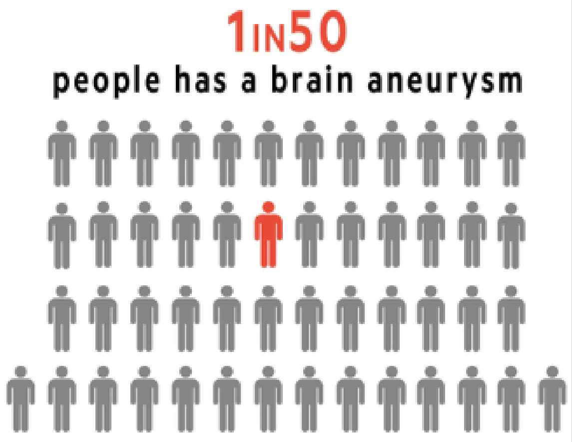
Our team endeavors are geared towards addressing some of the quintessential challenges of the 21st century in biomedicine and the environment by designing novel soft material platforms (e.g., hydrogels and colloidal systems) via micro- and nanoengineering techniques. In 2019, Dr. Amir Sheikhi founded the **Bio**-**S**oft **Ma**terials **L**aboratory (**B-SMaL**) at Penn State Chemical Engineering to develop transformative and/or translational ***bio-derived soft materials*** and ***biomaterials*** that can set the stage for the adoption of affordable, widespread technologies with immediate benefits for humans and ecosystems.

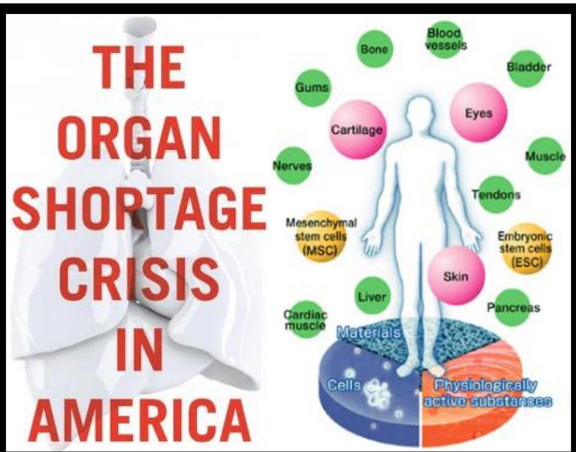


Every **20 seconds, a child dies…**
from not having access to clean water

More than **38% of men and women**
will be diagnosed with **cancer** at some point during their lifetimes
(American Cancer Society, 2013-2015)



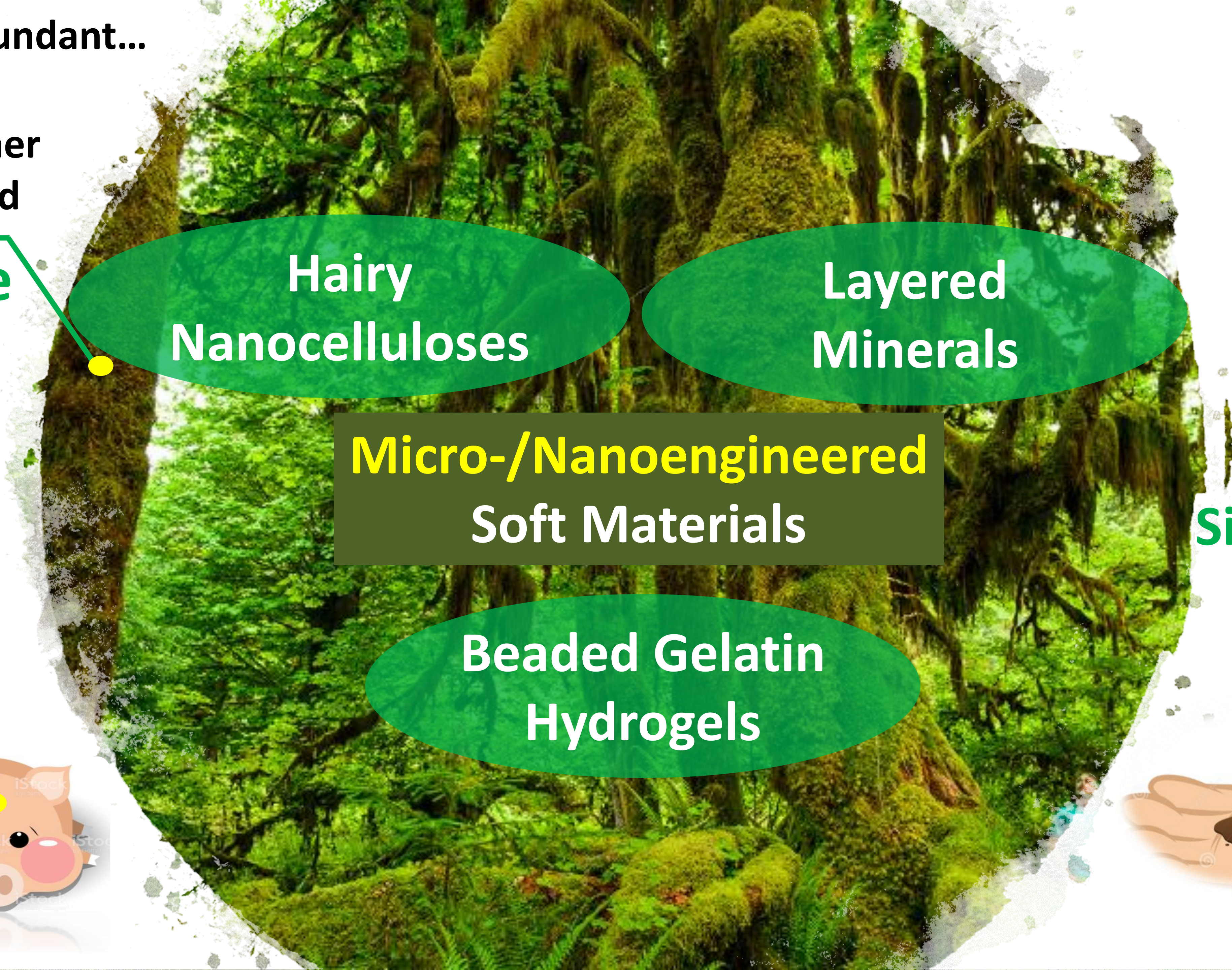




The most abundant…

…biopolymer
in the world

Cellulose



…mineral
in the soil

Silicon (Si)

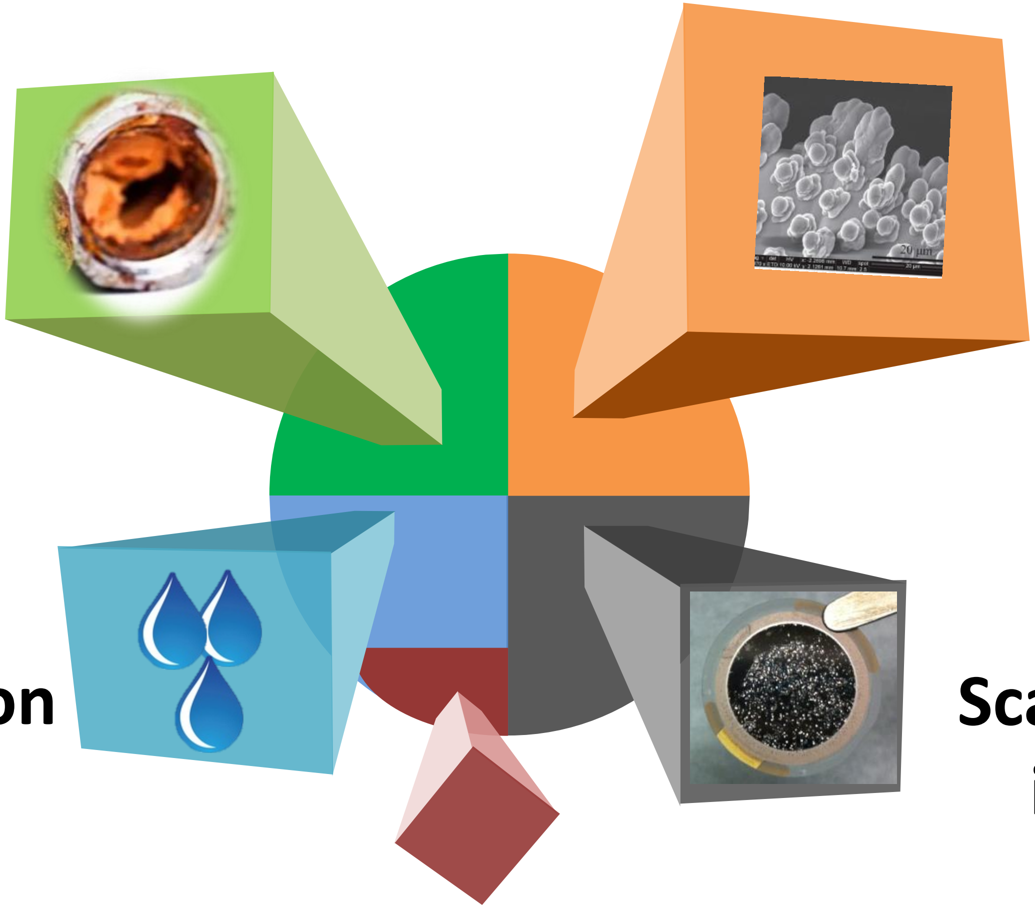
…protein
in the body

Collagen

Outline

Hairy nanocelluloses

Part I:
Scale inhibition



Part II:
Biomimetic mineralization

Part IV:
Water remediation

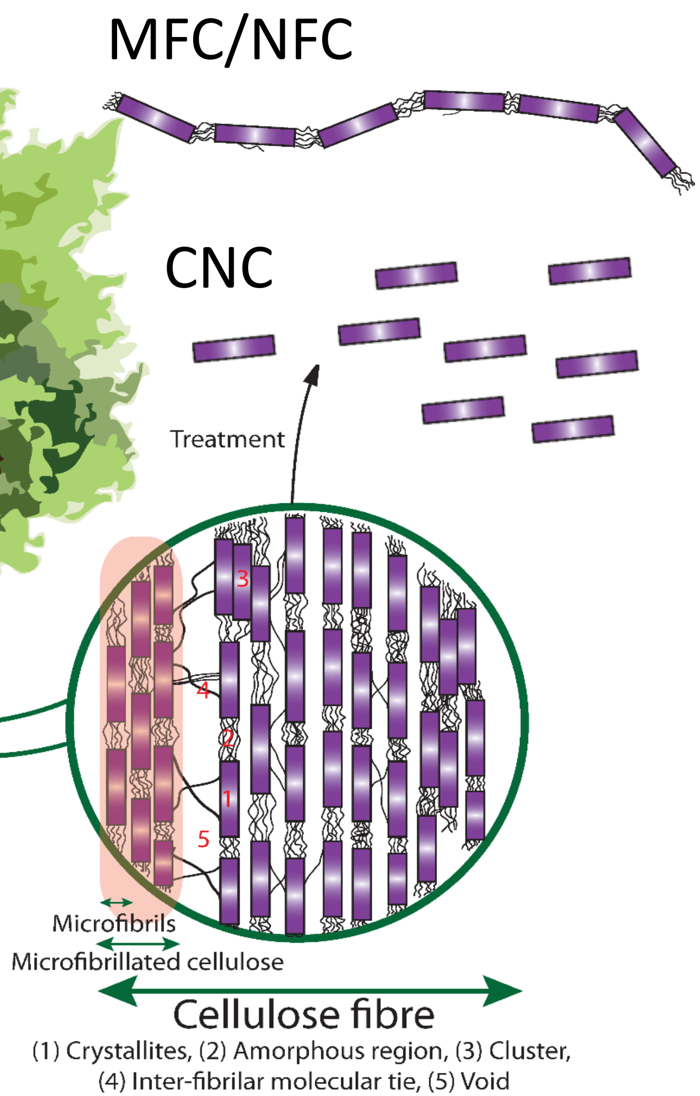
Part III:
Scale-resistant interfaces

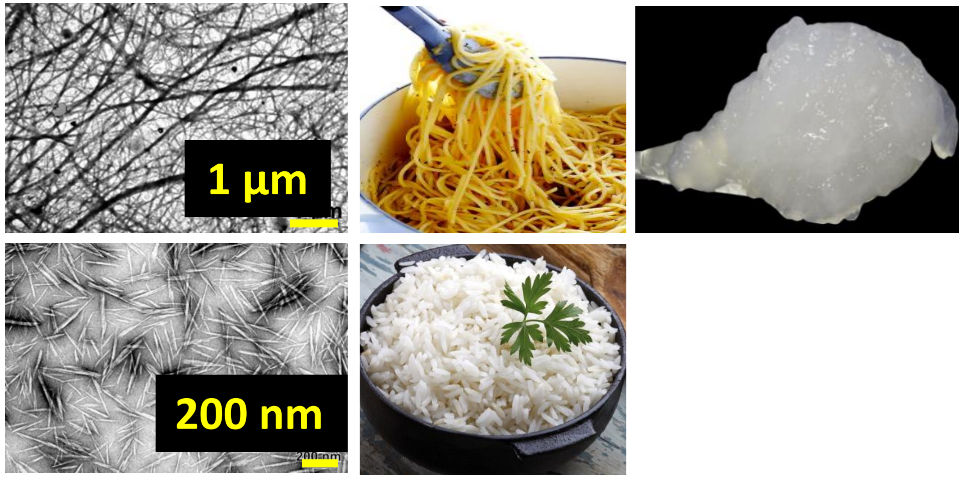
Part V: Other applications

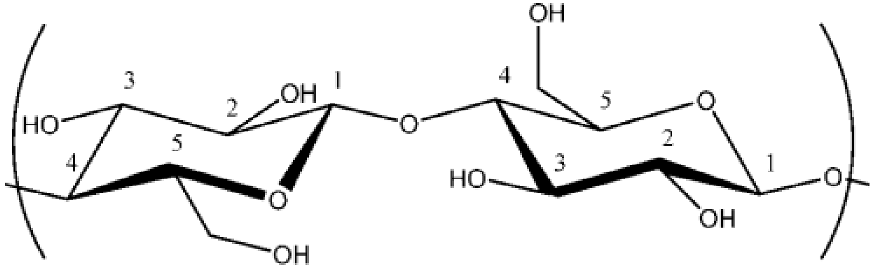
- Nanocomposites
- Bactericides
- Humidity switches
- Rheology modifiers

Conventional nanocelluloses

- ✓ Biorenewable
- ✓ Biodegradable
- ✓ Cost effective
- ✓ Environmentally friendly
- ✓ Large surface area (>100 m^2/g)







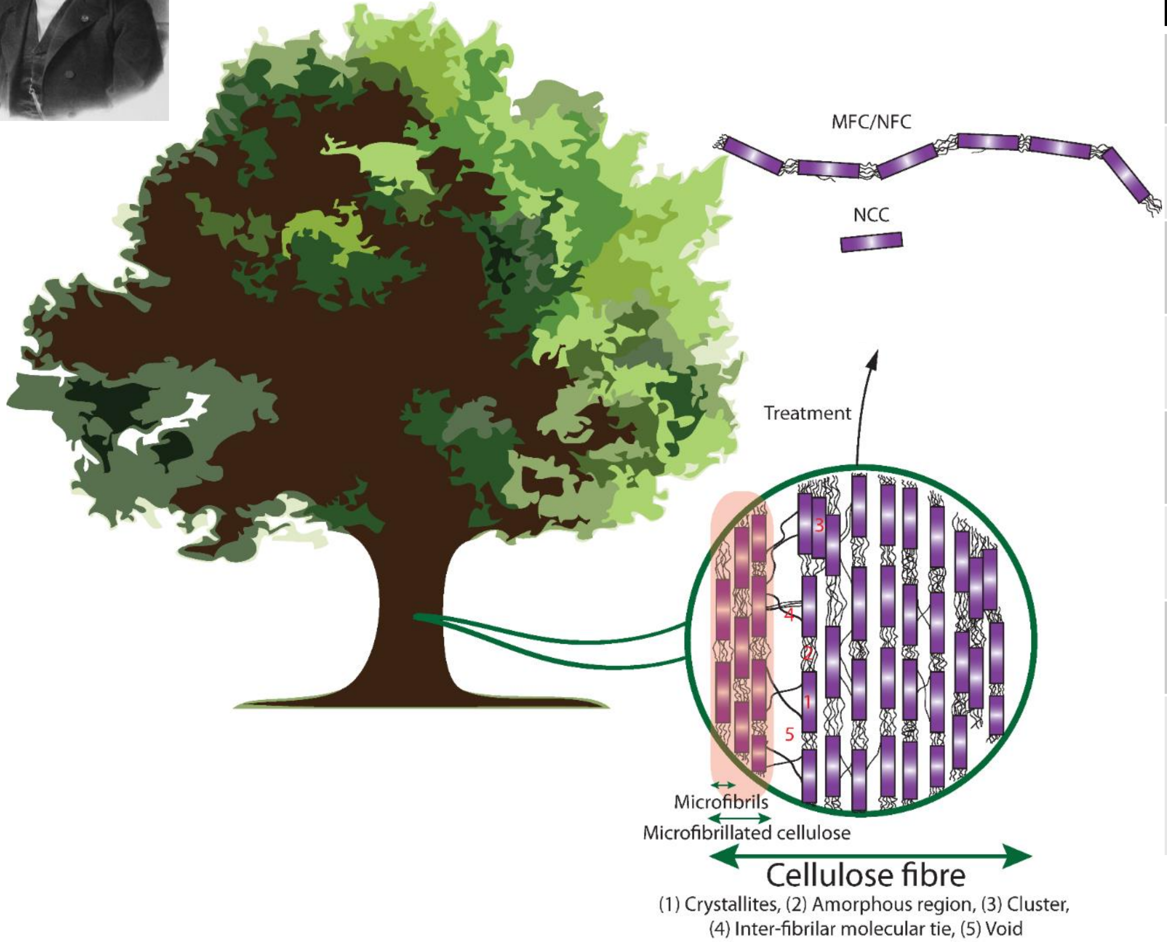
Kontturi et al., Advanced Materials (2018)
Dufresene, Materials Today (2017)
Habibi et al., Journal of Materials Chemistry (2008)
Malainine et al., Carbohydrate Polymers (2003)

Introduction to conventional nanocelluloses

Conventional nanocelluloses

Anselme Payen
1795-1871

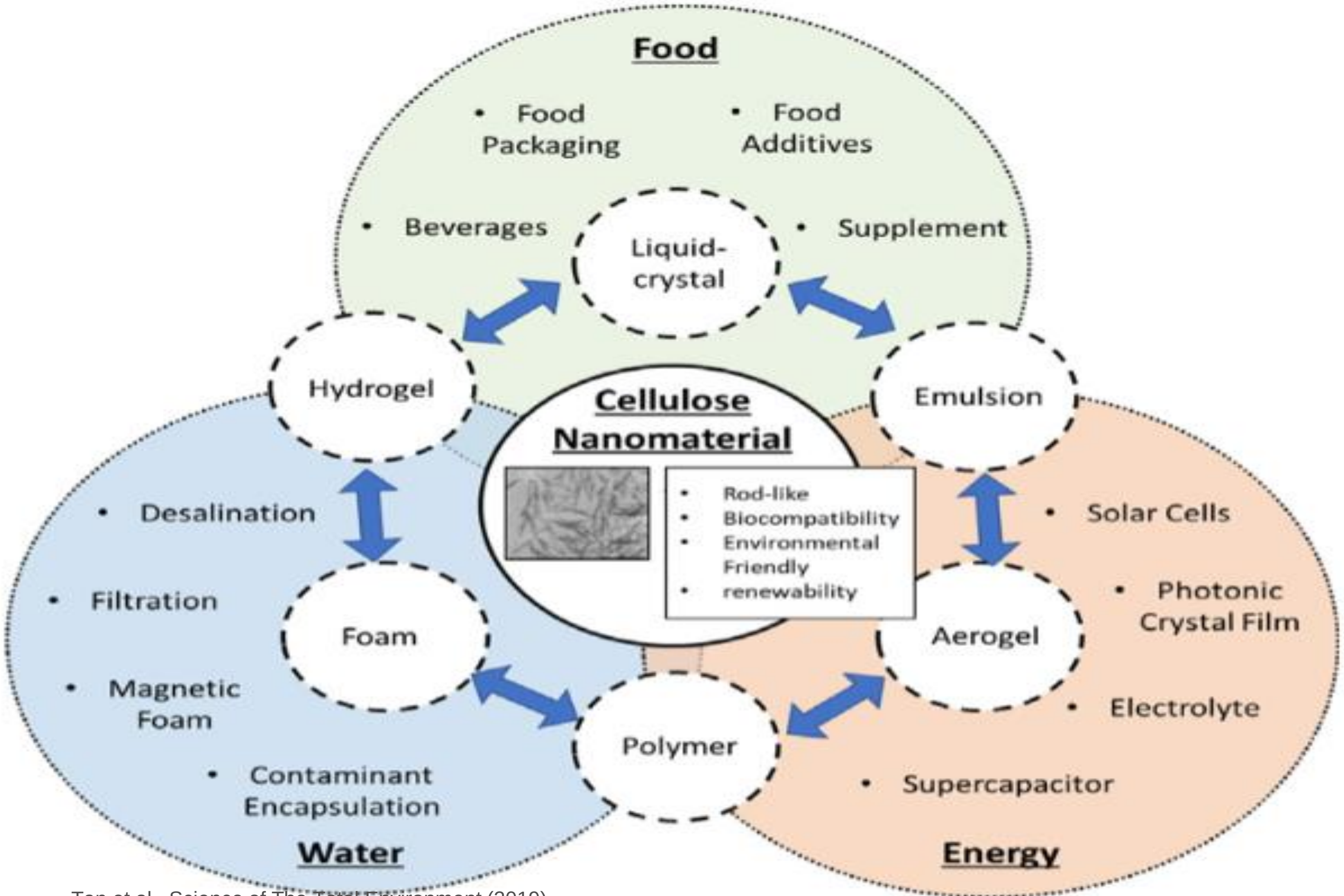
Bengt Rånby
1920-2000



Applications
Nanocomposites (1100 articles)
Films (500)
Hydrogels (240)
Rheology (190)
Coating (160)
Aerogels (145)
Fillers (145)
Optical (140)
Self-assembly (120)

Introduction to conventional nanocelluloses

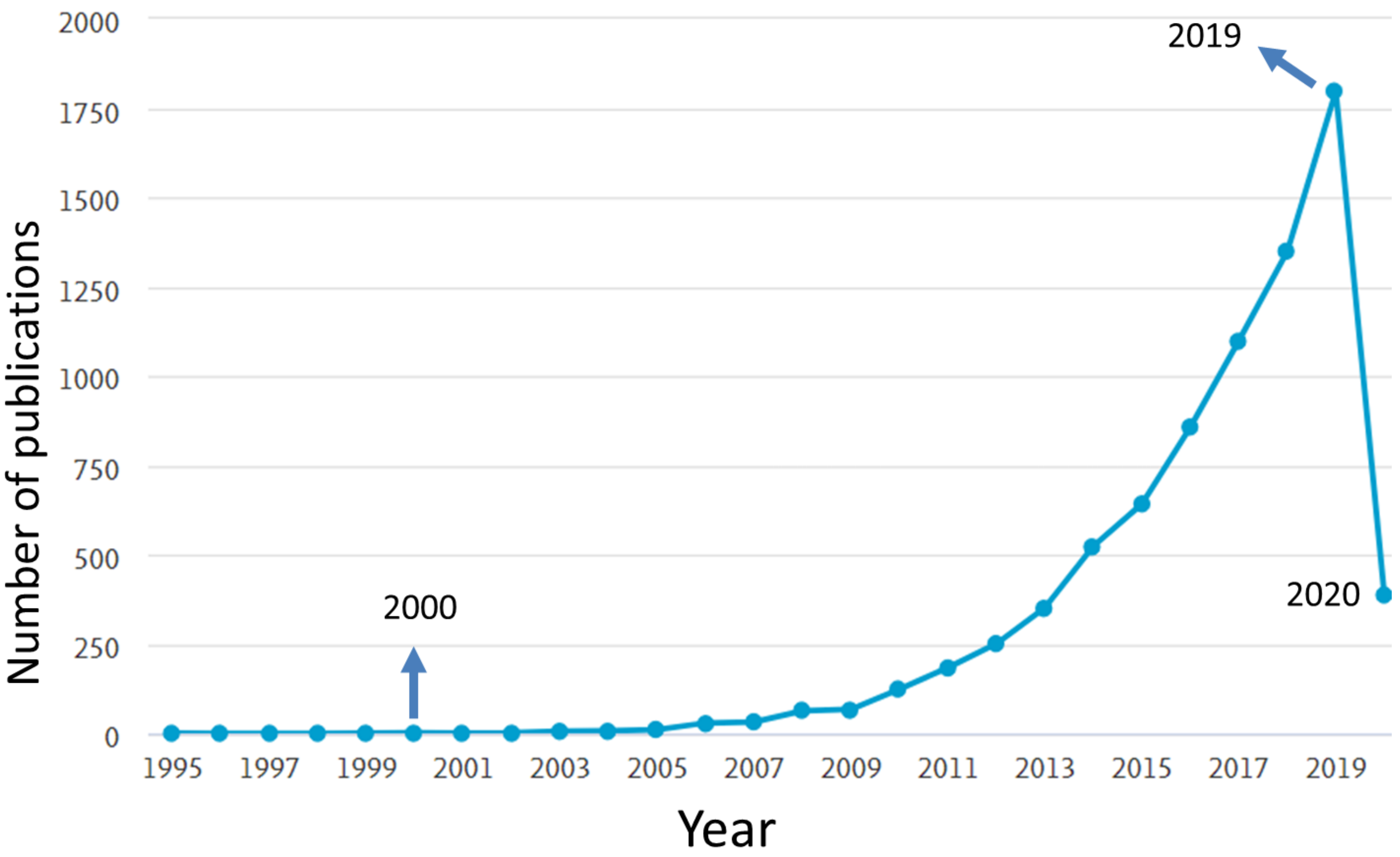
Conventional nanocelluloses | **Applications**



Tan et al., Science of The Total Environment (2019)

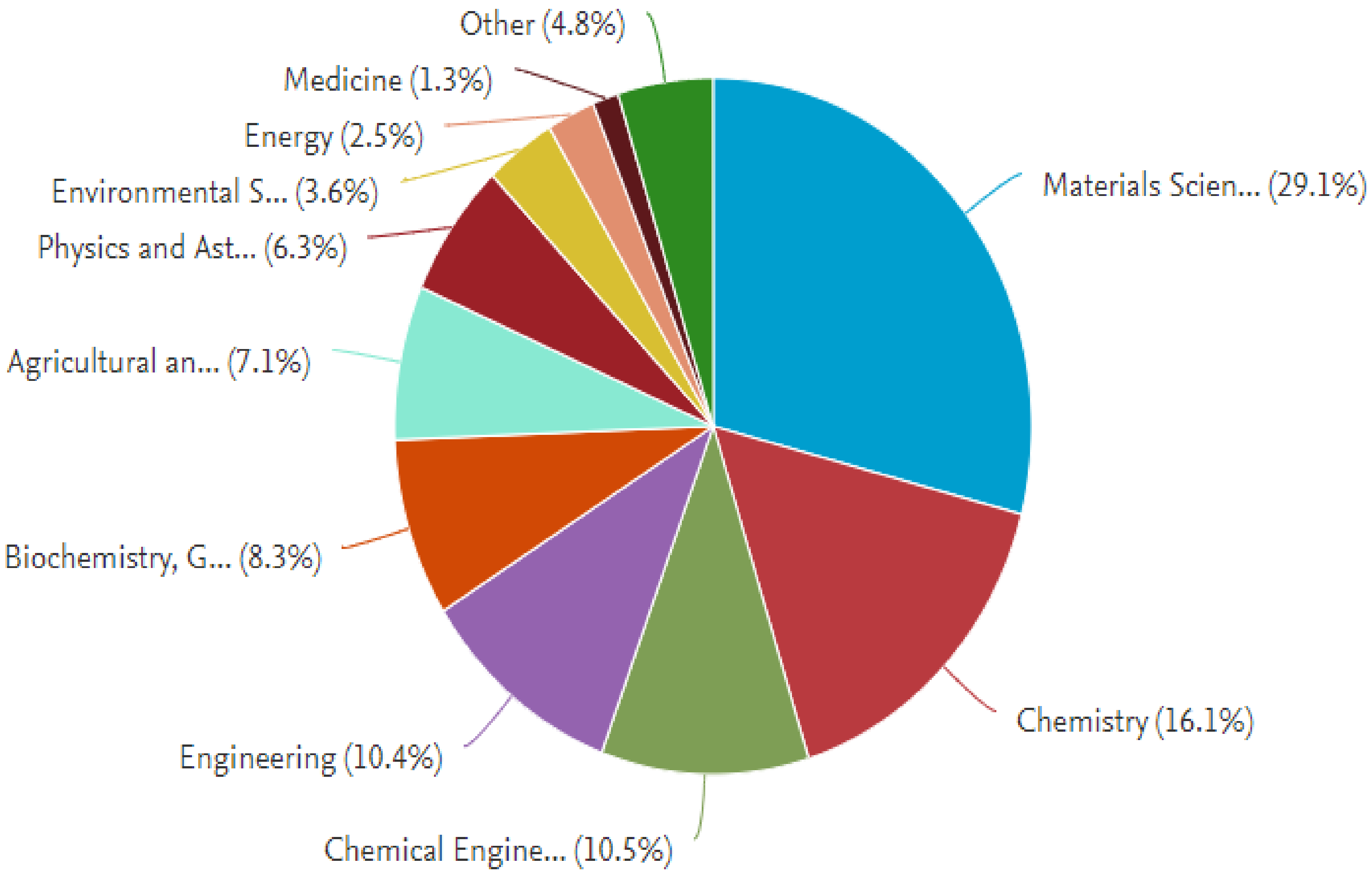
Introduction to conventional nanocelluloses

Conventional nanocelluloses



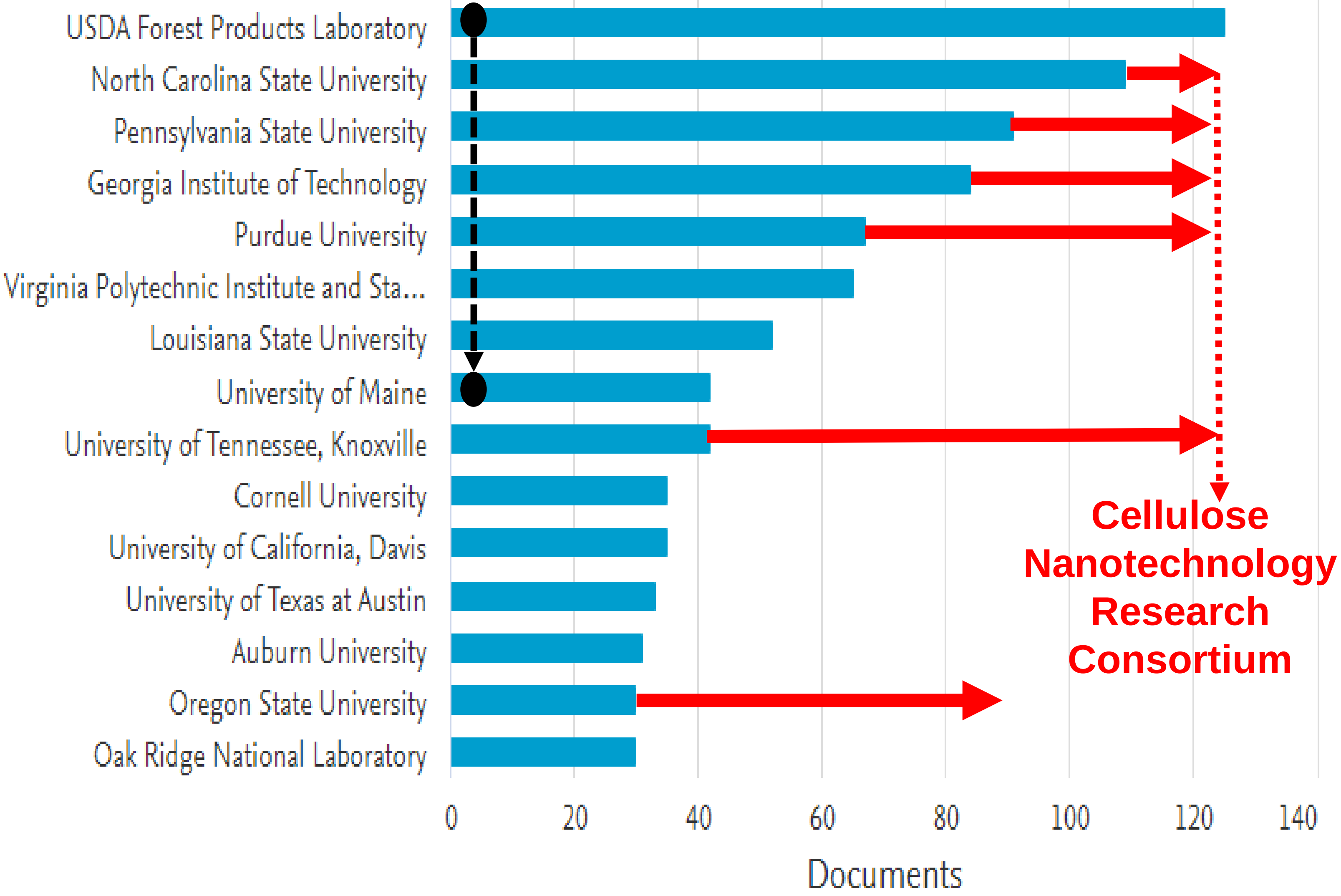
Introduction to conventional nanocelluloses

Conventional nanocelluloses | Applications

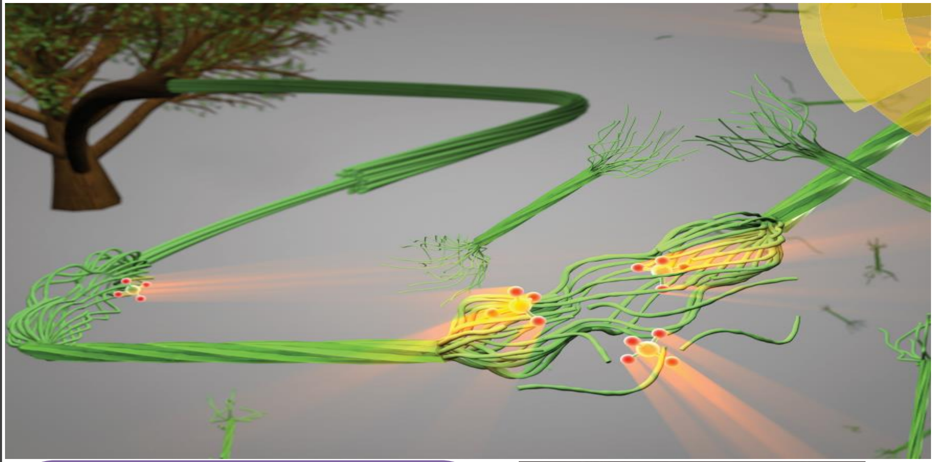


Introduction to Hairy Nanocelluloses

Conventional nanocelluloses



Hairy nanocelluloses

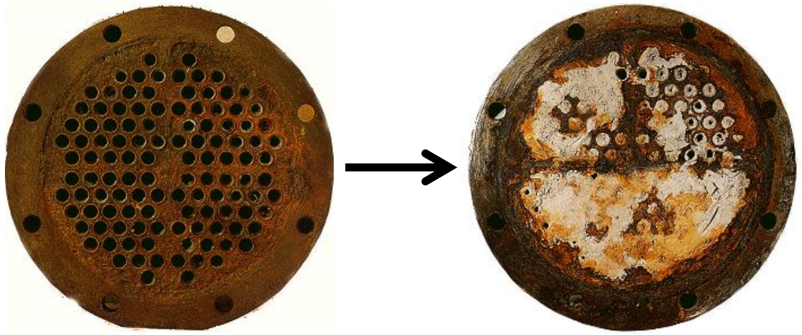


Unique properties

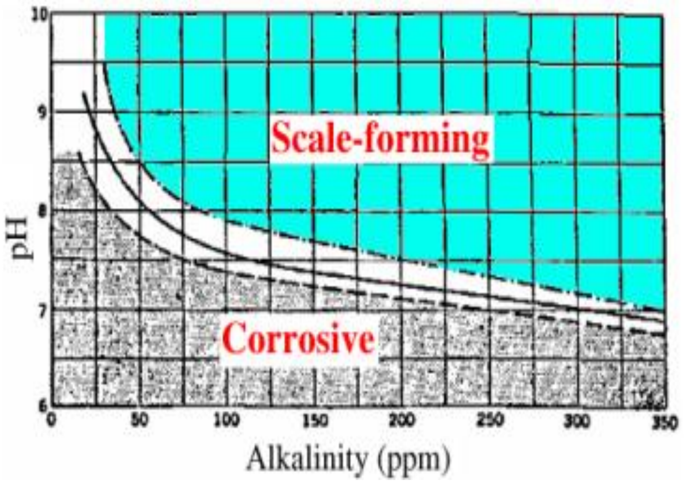
- **Colloidal structure**
- Functional groups
- Charge density
- Colloidal stability
- Facile production
- Biodegradation/ hemocompatibility

Part I: Scale inhibition

- Sparingly soluble salts
  - Anions: CO_3^{2-}, SO_4^{2-}, …
  - Cations: Ca^{2+}, Mg^{2+}, Ba^{2+}, …



- Examples of affected operating units
  - Cooling towers, digesters, evaporators, and heaters
- Problems: Fluid mechanics, heat and mass transfer
- Inhibition methods
  - Acid treatment, ion exchange, macromolecular additives



Drawbacks of current macromolecular antiscalants

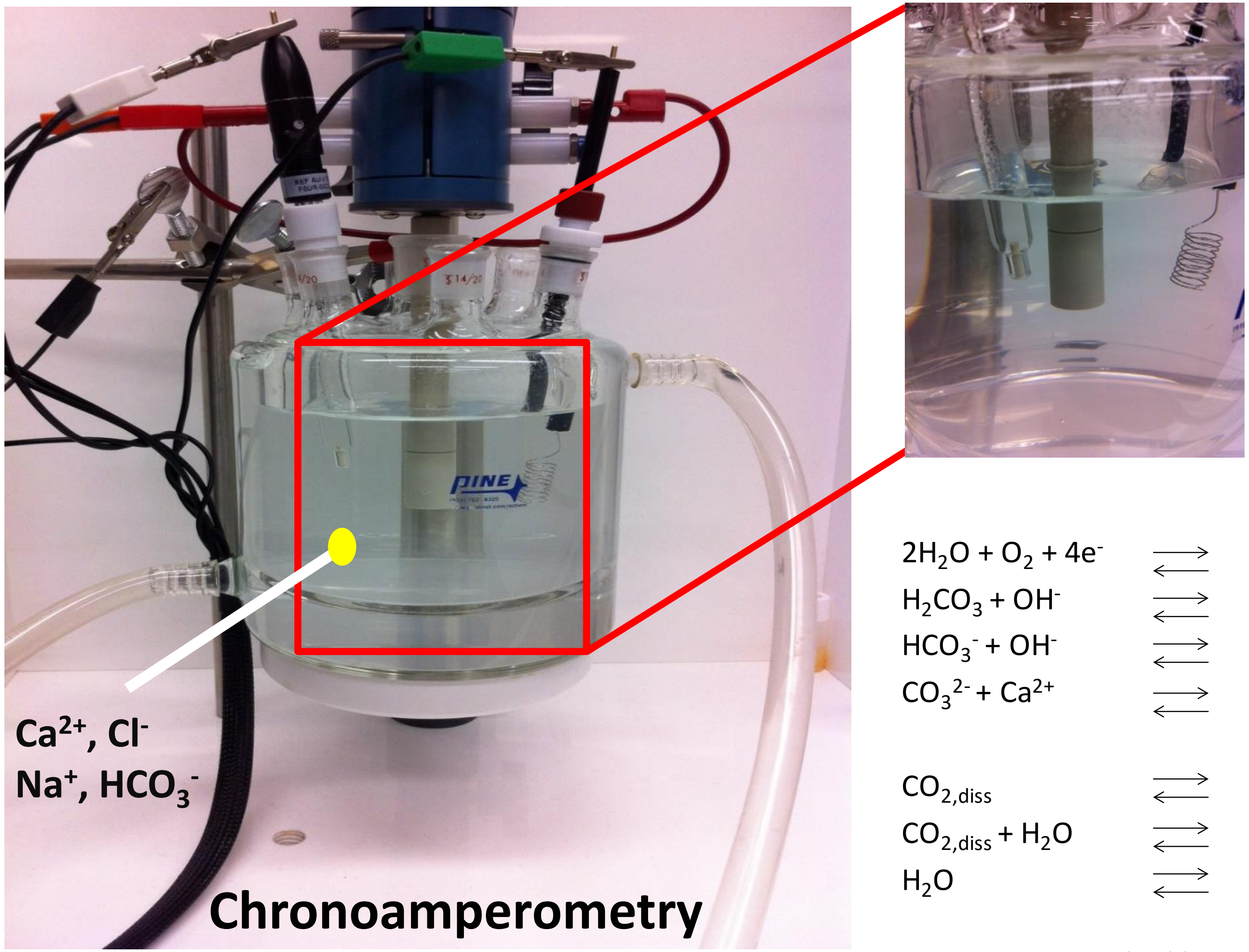
- Most of the antiscalants are not biodegradable
- Their backbone is toxic
- They comprise phosphorus and nitrogen
- Their functional groups result in eutrophication

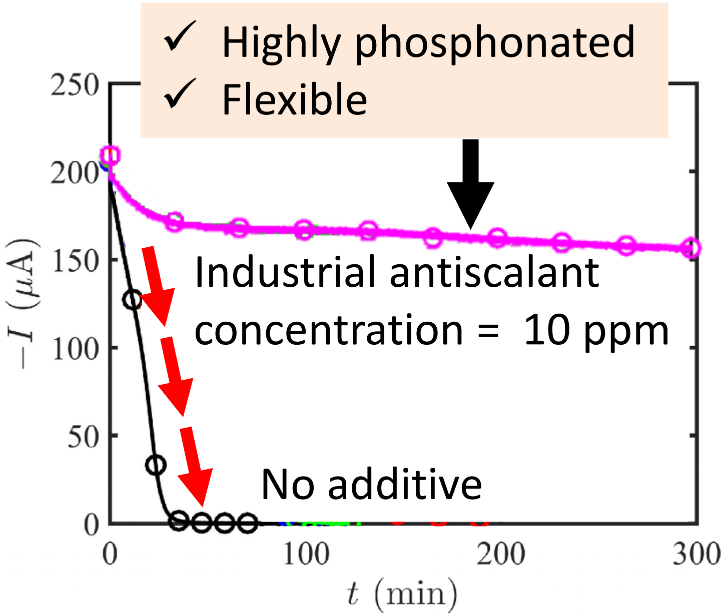
Total phosphorus trigger ranges for Canadian lakes and rivers.

Trophic Status	Canadian Trigger Ranges Total phosphorus ($\mu g \cdot L^{-1}$)
Ultra-oligotrophic	< 4
Oligotrophic	4-10
Mesotrophic	10-20
Meso-eutrophic	20-35
Eutrophic	35-100
Hyper-eutrophic	> 100 = **0.1 ppm**

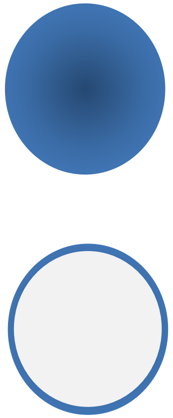
Canadian Water Quality Guidelines for the Protection of Aquatic Life, Canadian Council of Ministers of the Environment, 2004.

Simulated industrial scale formation





Clean electrode

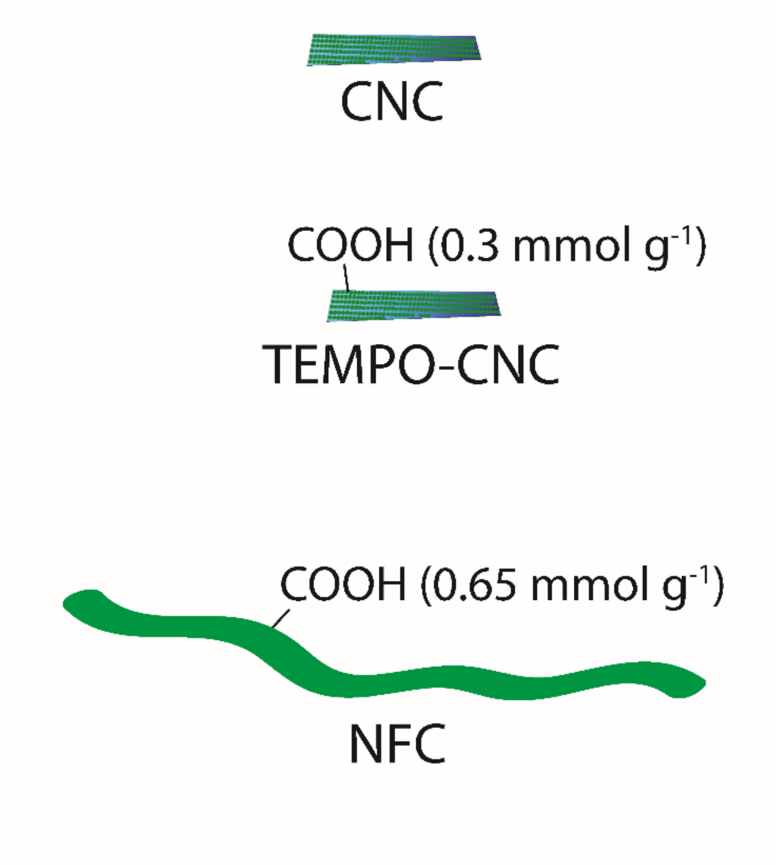


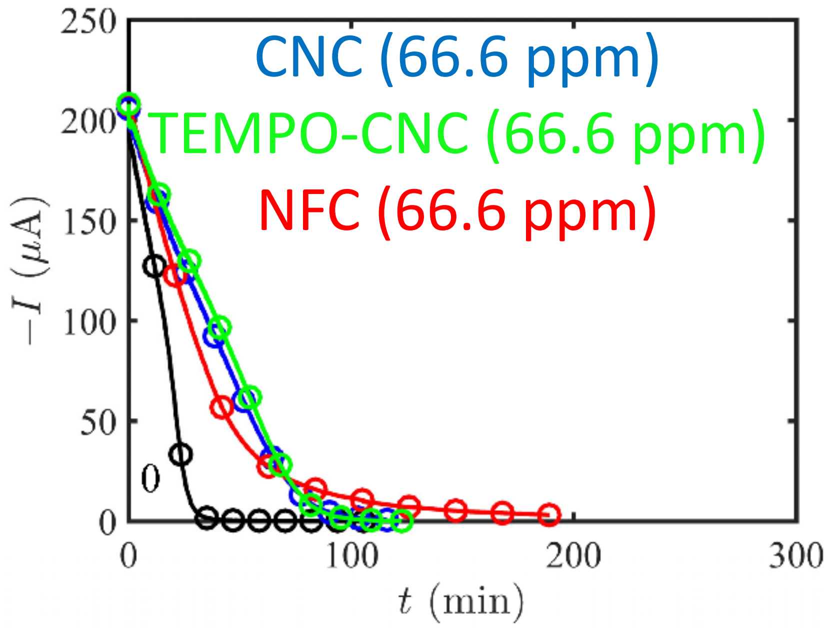
Scaled electrode

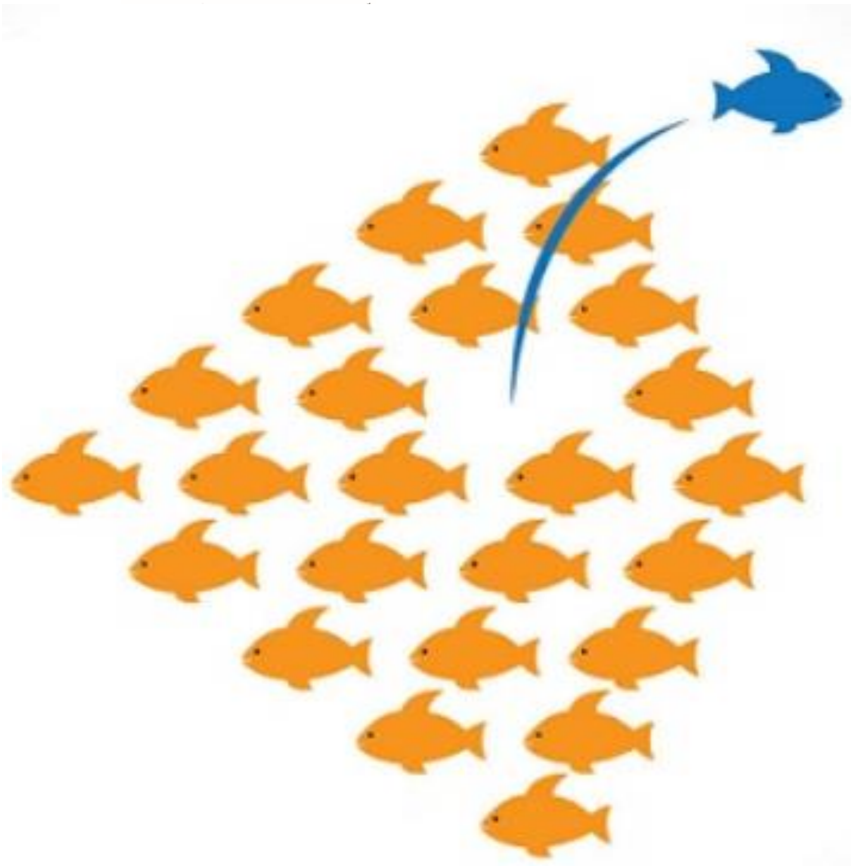
$2H_2O + O_2 + 4e^-$	$\rightleftharpoons$	$4OH^-$	S.R.P. = -1.23 v
$H_2CO_3 + OH^-$	$\rightleftharpoons$	$HCO_3^- + H_2O$	Ka1 ~ 2.5e-4
$HCO_3^- + OH^-$	$\rightleftharpoons$	$CO_3^{2-} + H_2O$	Ka2 ~ 5.6e-11
$CO_3^{2-} + Ca^{2+}$	$\rightleftharpoons$	$CaCO_{3(s)}\downarrow$	Ksp ~ 4e-9
$CO_{2,diss}$	$\rightleftharpoons$	$CO_2(g)$	K_{CO2} = 29.76 atm/mol/L
$CO_{2,diss} + H_2O$	$\rightleftharpoons$	H_2CO_3	Ka ~ 1.7e-3
H_2O	$\rightleftharpoons$	$H^+ + OH^-$	Kw = 1e-14

Sheikhi et al., Environmental Science: Water Research & Technology (2015)

Nanocelluloses as antiscalants







✓ Not enough charge content

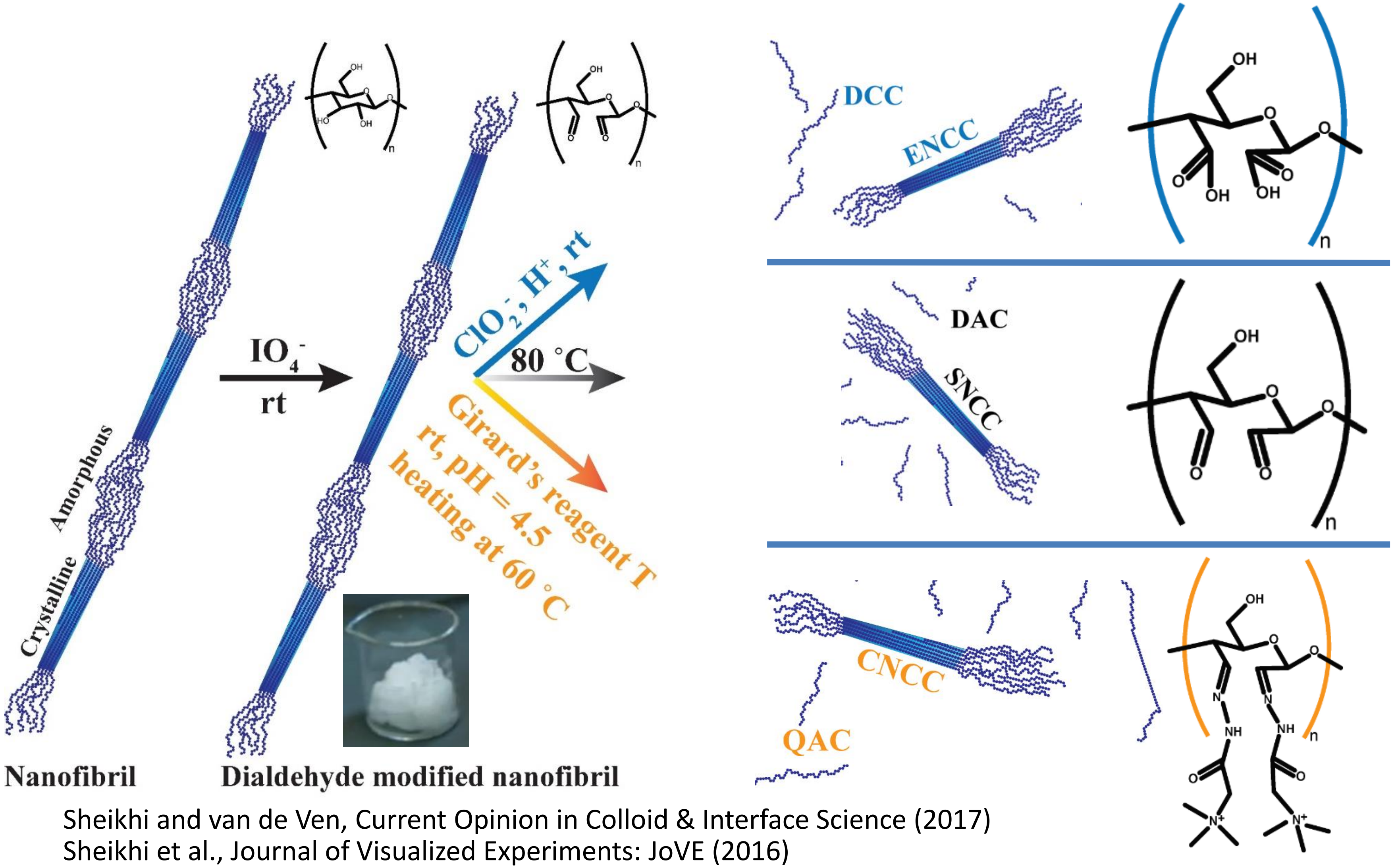
✓ Not enough flexibility

Sheikhi et al., Materials Horizons (2018)

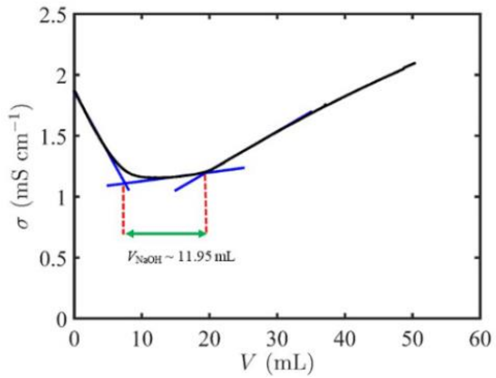
Hairy nanocelluloses

van de Ven and Sheikhi, Nanoscale (2017)

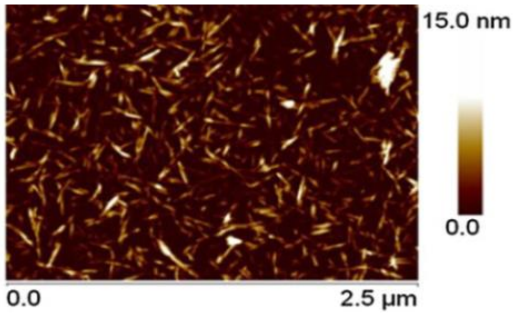
Hairy nanocelluloses



Sheikhi and van de Ven, Current Opinion in Colloid & Interface Science (2017)
Sheikhi et al., Journal of Visualized Experiments: JoVE (2016)



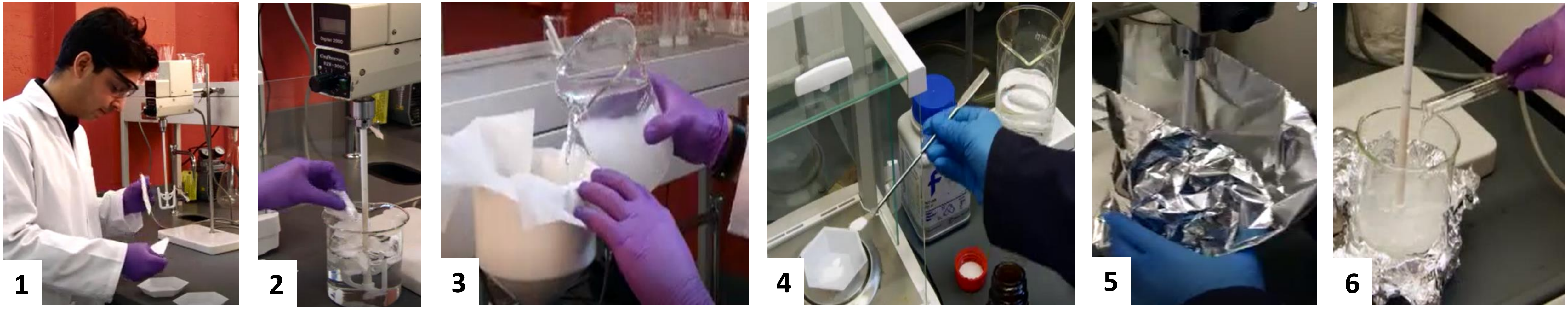
COOH concentration = 0.01195 (V_{NaOH}) × 10 mM (NaOH concentration) / 0.02 g (initial ENCC) ~ 5.98 mmol/g

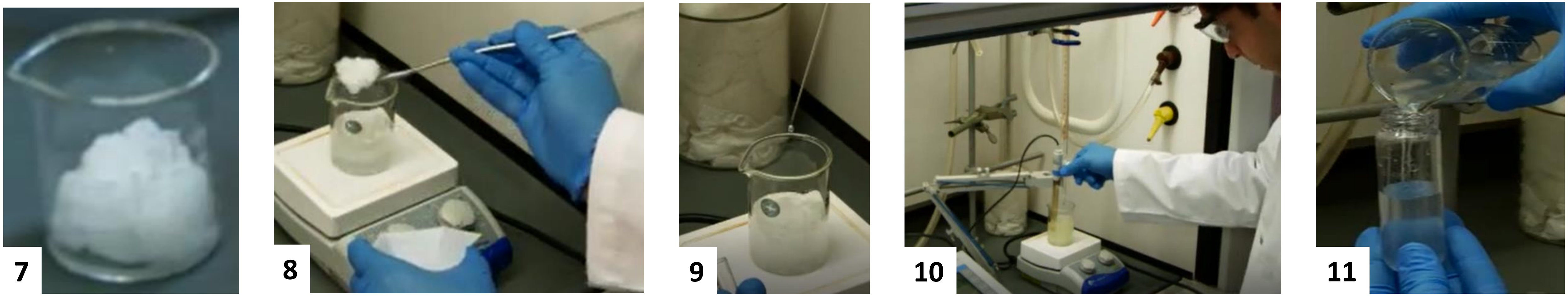


Yang et al., Langmuir (2012)

Hairy nanocellulose synthesis

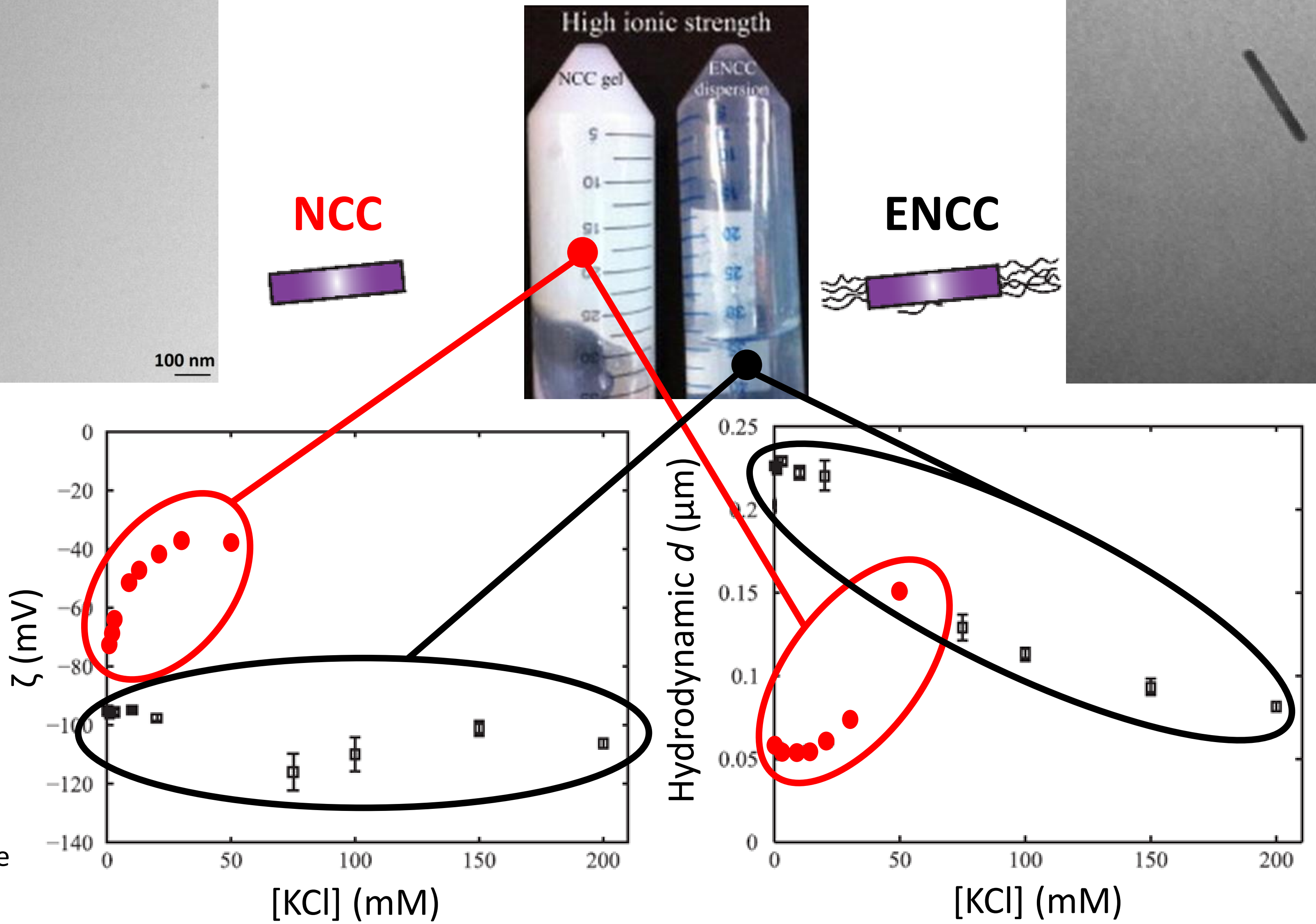
Preparing partially oxidized fibers

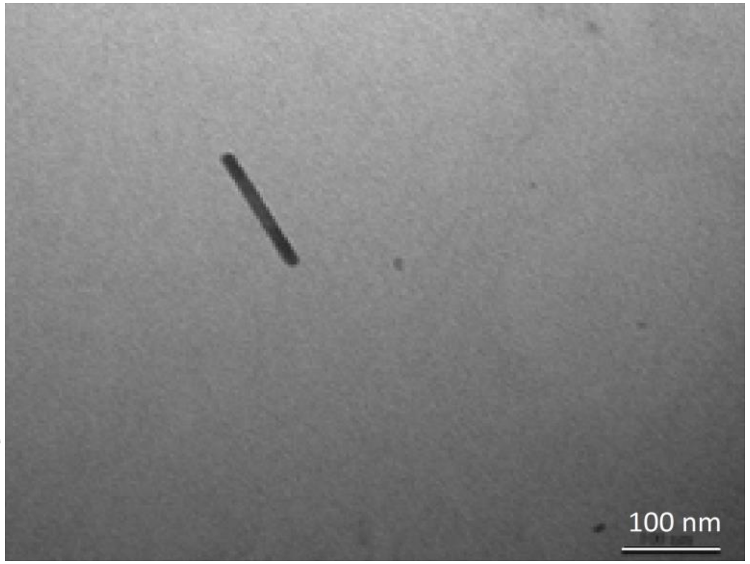




Preparing electrosterically stabilized nanocrystalline celluloses (ENCC)

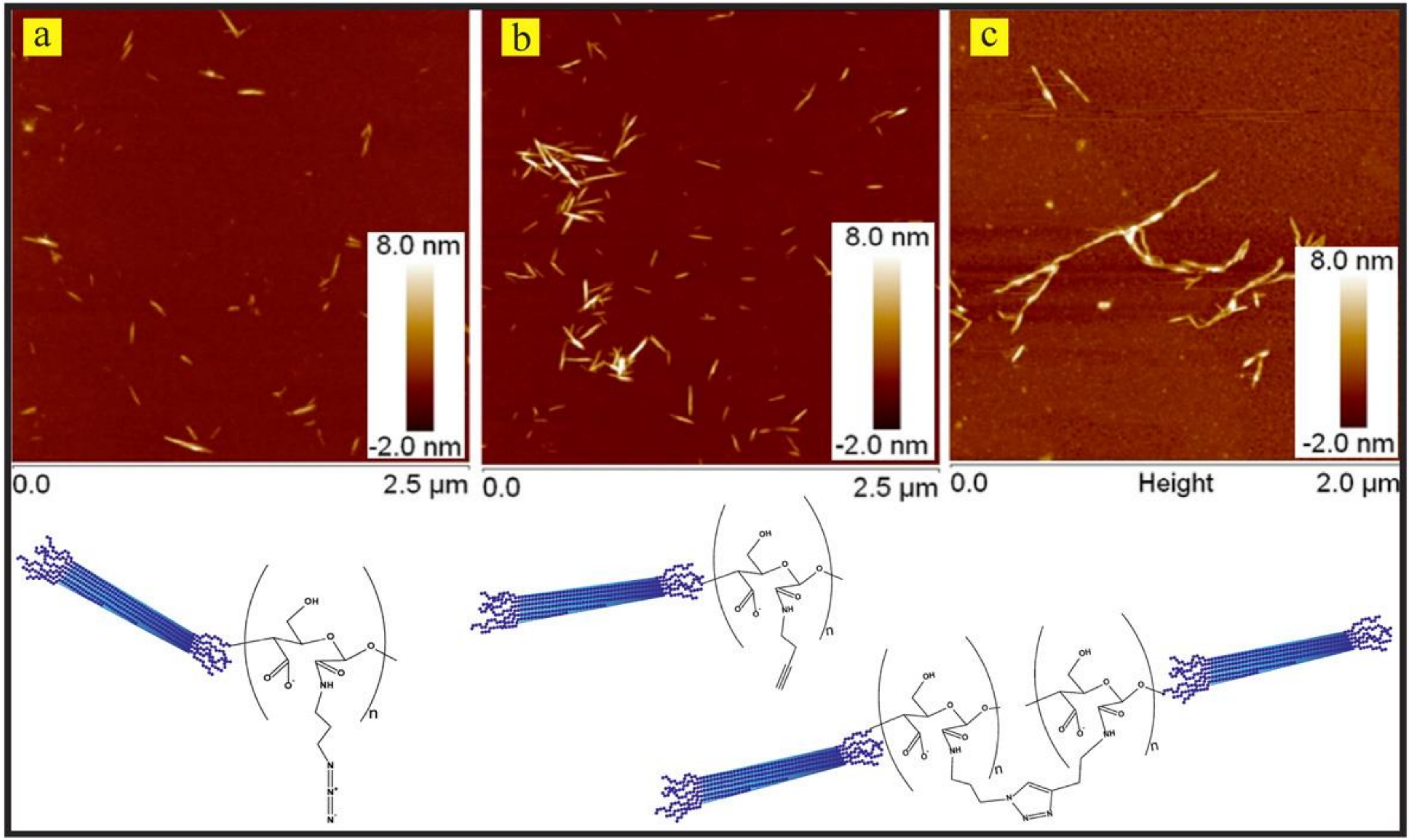
NCC versus ENCC





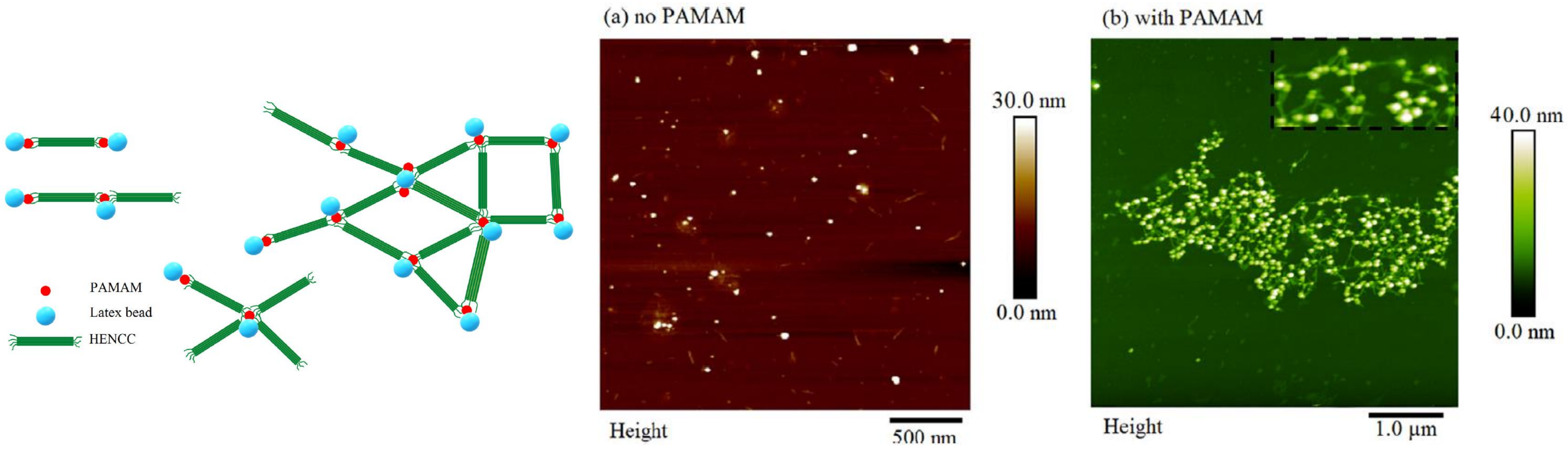
Sheikhi et al., Journal of Colloid and Interface Science (2014)

ENCC assembly



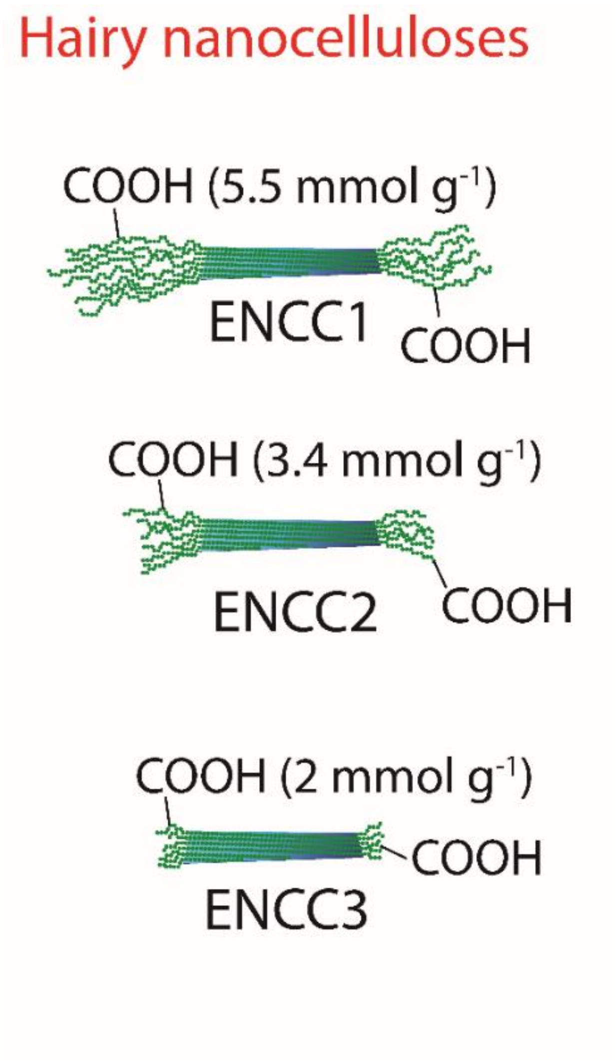
Yang et al., Biomacromolecules (2016)

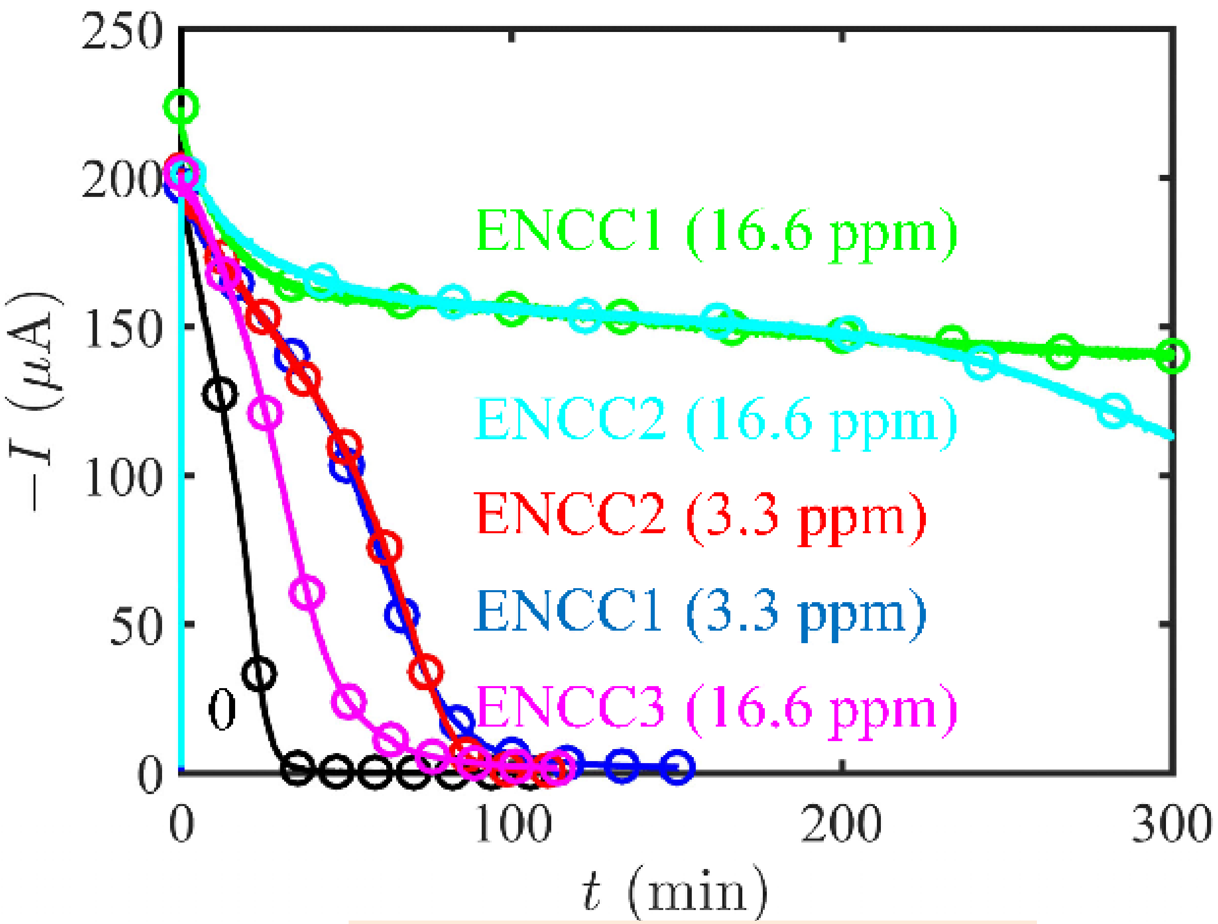
ENCC assembly

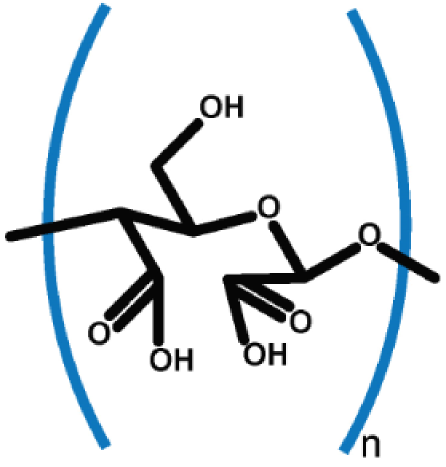


Tavakolian et al., Journal of Colloid and Interface Science (2019)

Hairy nanocelluloses as antiscalants





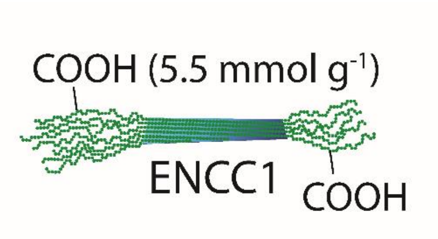


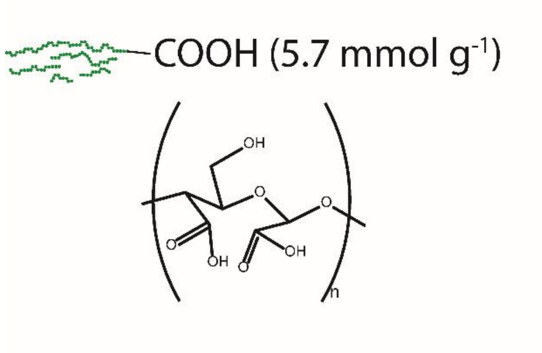
✓ High functional group density

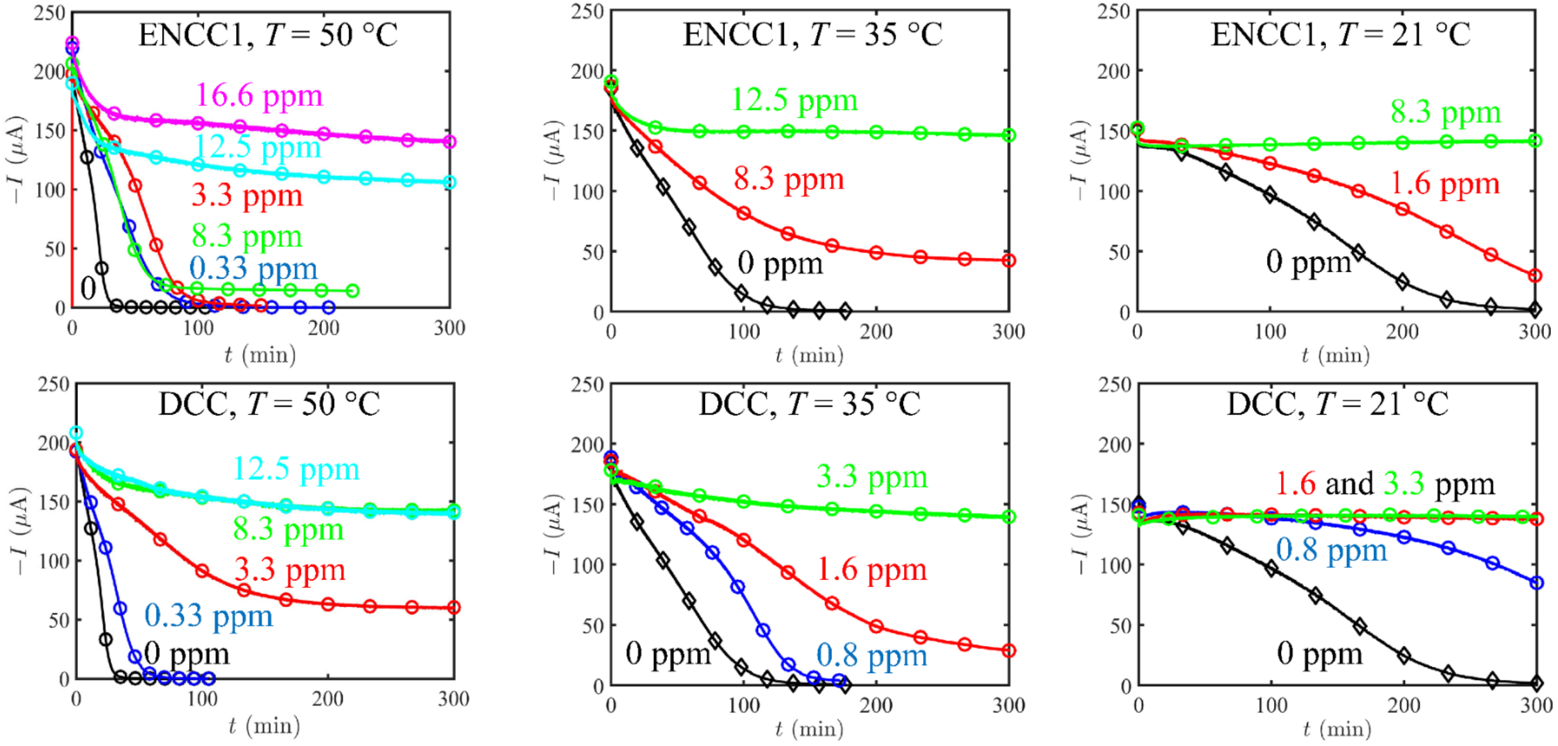
✓ Structural flexibility

Sheikhi et al., Materials Horizons (2018)

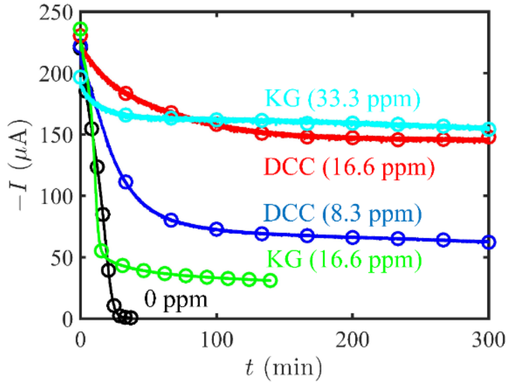
Hairy nanocelluloses as antiscalants

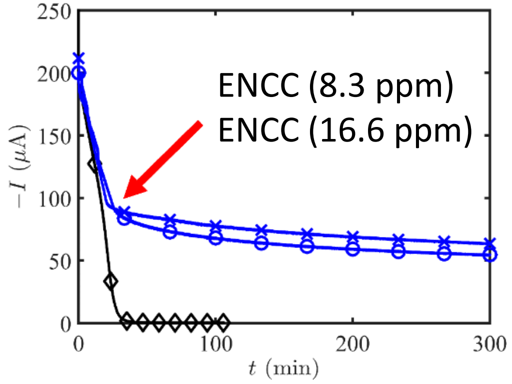






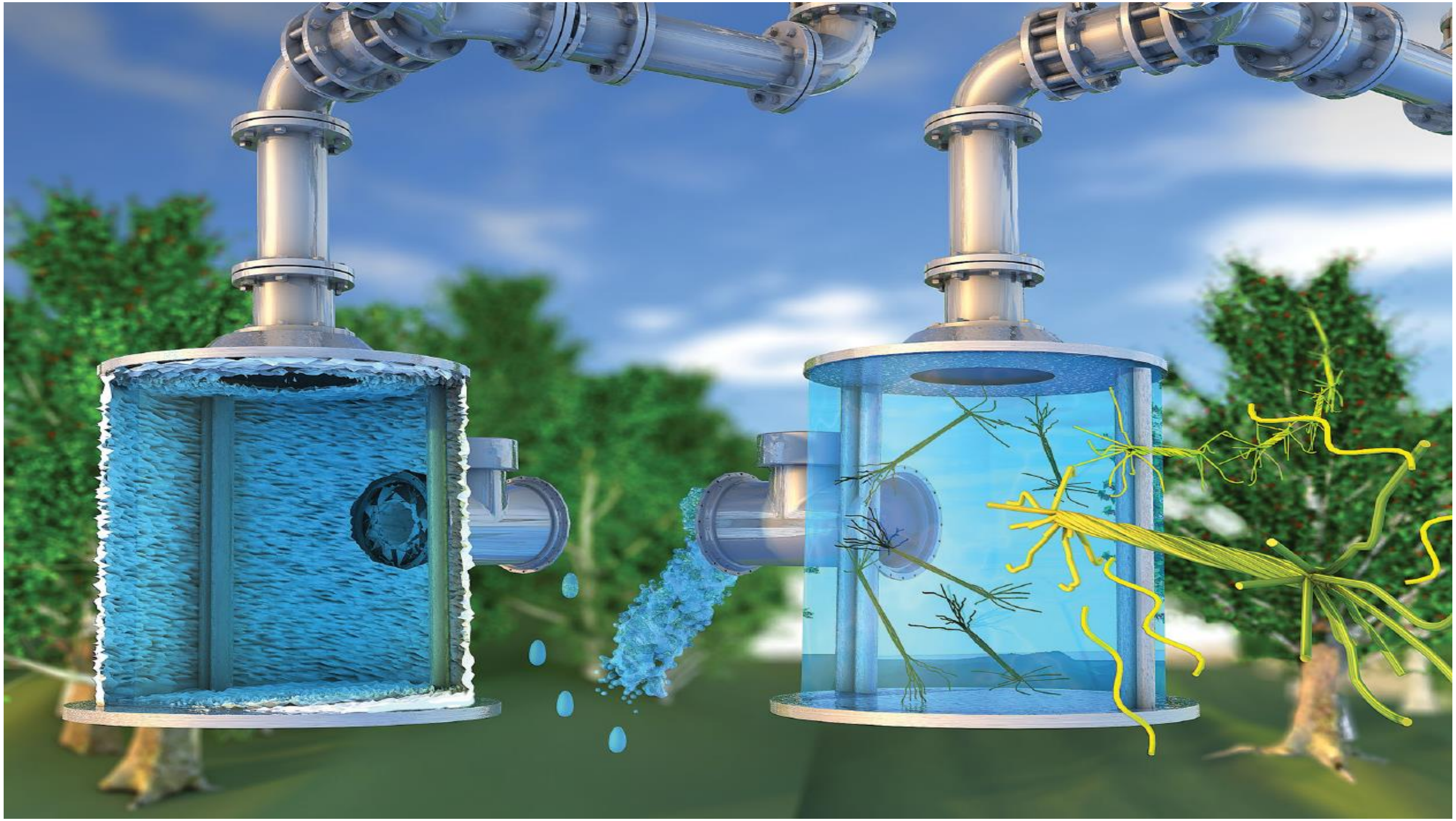
Additive	C (ppm)	COO^-/Ca^{2+} (mol/mol)
ENCC	12.5	0.037
DCC	8.3	0.026





Sheikhi et al.,
Materials Horizons
(2018)

Hairy nanocelluloses as an antiscalant



Sheikhi et al., Materials Horizons (2018)

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PUBLIC RELEASE: 21-NOV-2018

Hairy nanotechnology provides green anti-scaling solution

MCGILL UNIVERSITY

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A new type of cellulose nanoparticle, invented by McGill University researchers, is at the heart of a more effective and less environmentally damaging solution to one of the biggest challenges facing water-based industries: preventing the buildup of scale.

Formed by the accumulation of sparingly soluble minerals, scale can seriously impair the operation of just about any equipment that conducts or stores water - from household appliances to industrial installations. Most of the anti-scaling agents currently in use are high in phosphorus derivatives, environmental pollutants that can have catastrophic consequences for aquatic ecosystems.

In a series of papers published in the Royal Society of Chemistry's *Materials Horizons* and the American Chemical Society's *Applied Materials & Interfaces*, a team of McGill chemists and chemical engineers describe how they have developed a phosphorus-free anti-scaling solution based on a nanotechnology breakthrough with an unusual name: hairy nanocellulose.

An unlikely candidate

PHYS ORG Nanotechnology Physics Earth Astronomy & Space Technology Chemistry

Home » Nanotechnology » Nanomaterials » November 1, 2018

Hairy nanotechnology provides green anti-scaling solution

November 1, 2018, McGill University

Water Technology
Solutions for Industrial Water Management

Treatment Reuse Water Systems Wastewater Industries Solutions

NEWS & INSIGHTS

MCGILL TEAM DEVELOPS ANTI-SCALING SOLUTION; CENTRISYS/CNP

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Science News *from research organizations*

Hairy nanotechnology provides green anti-scaling solution

Date: November 26, 2018
Source: McGill University
Summary: A new type of cellulose nanoparticle is at the heart of a more effective and less environmentally damaging solution to one of the biggest challenges facing water-based industries: preventing the buildup of scale.

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FULL STORY

A new type of cellulose nanoparticle, invented by McGill University researchers, is at the heart of a more effective and less environmentally damaging solution to one of the biggest challenges facing water-based industries: preventing the buildup of

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R&D

Hairy Nanoparticles Make Anti-Scaling Agents More Environmentally Friendly

Mon, 11/26/2018 - 11:25am 1 Comment by Kenny Walter - Digital Reporter - @RandDMagazine

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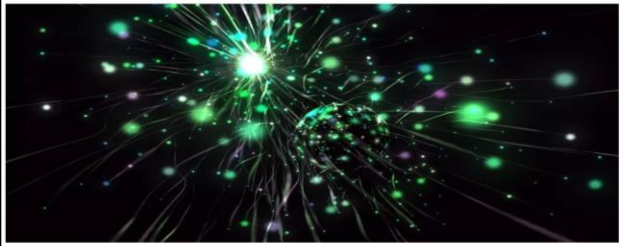
Nanoparticles to be Used as Green Anti-Scaling Solution



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Hairy nanotechnology provides green anti-scaling solution

News

PUBLISHED: 31OCT2018

A new type of cellulose nanoparticle, invented by McGill University researchers, is at the heart of a more effective and less environmentally damaging solution to one of the biggest challenges facing water-based industries: preventing the buildup of scale.

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Part II: Biomimetic mineralization

http://biologyencore.tumblr.com/
Accessed on 12/08/2015

http://www.123rf.com
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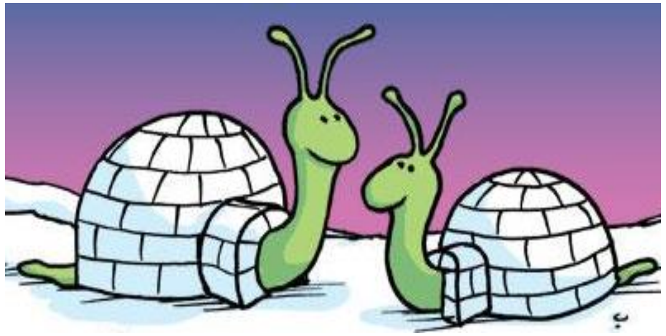

http://www.toonpool.com
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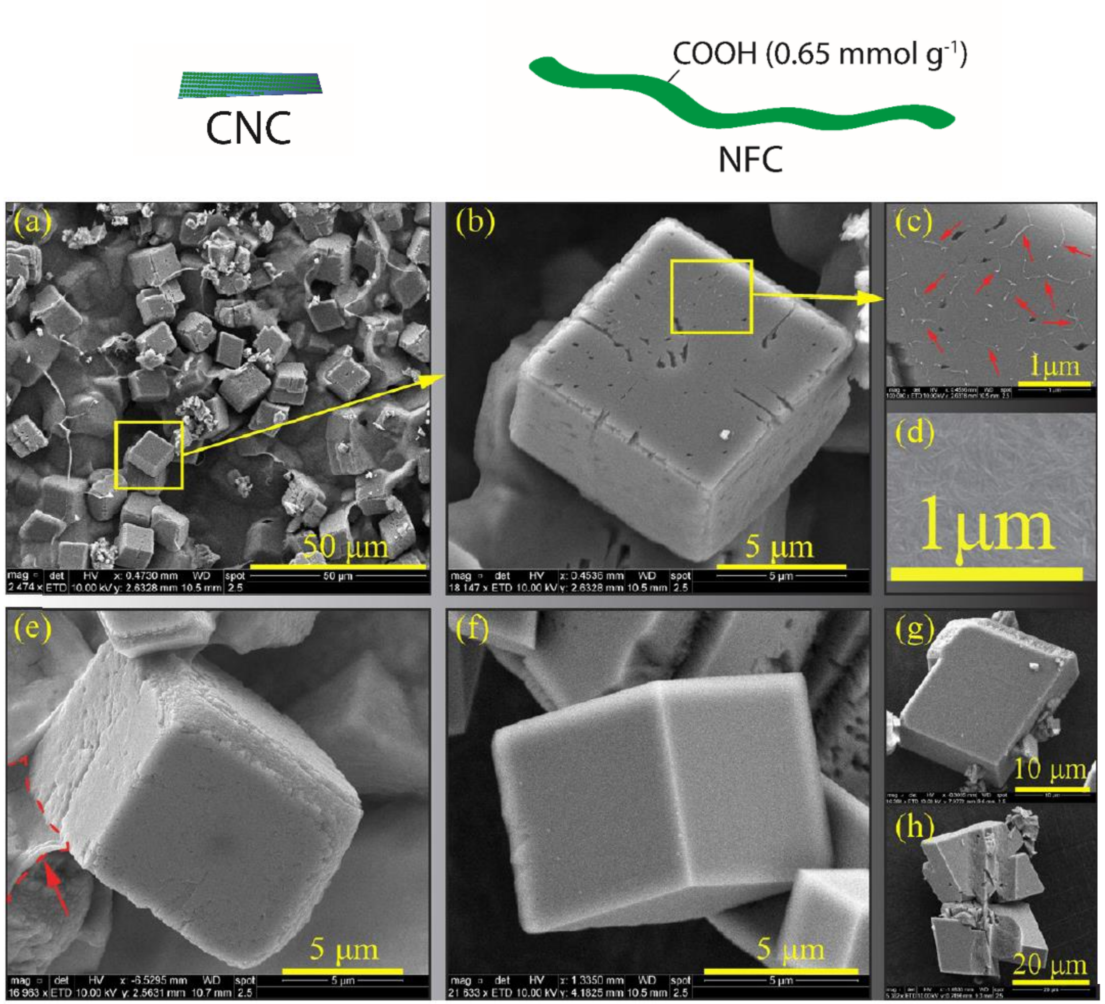
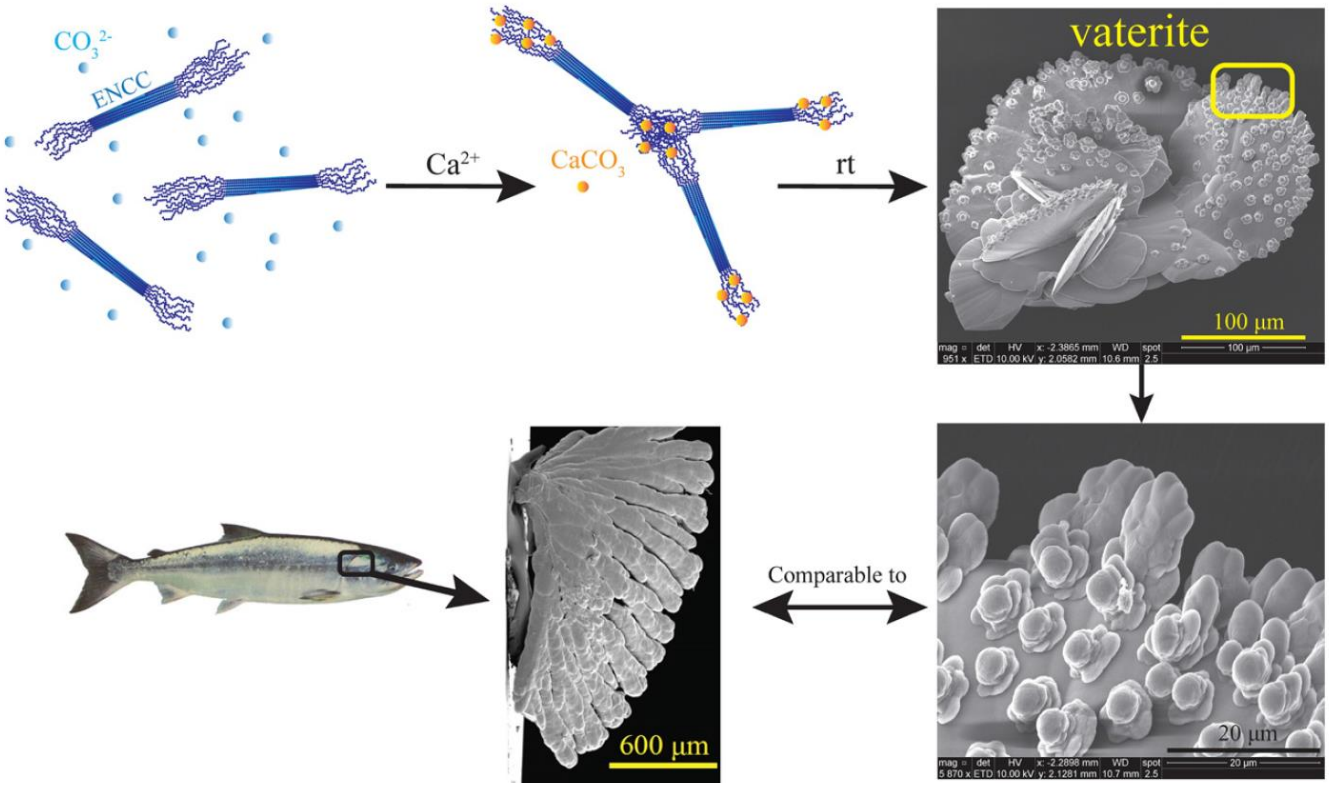
Biomimetic mineralization of $CaCO_3$ using ENCC

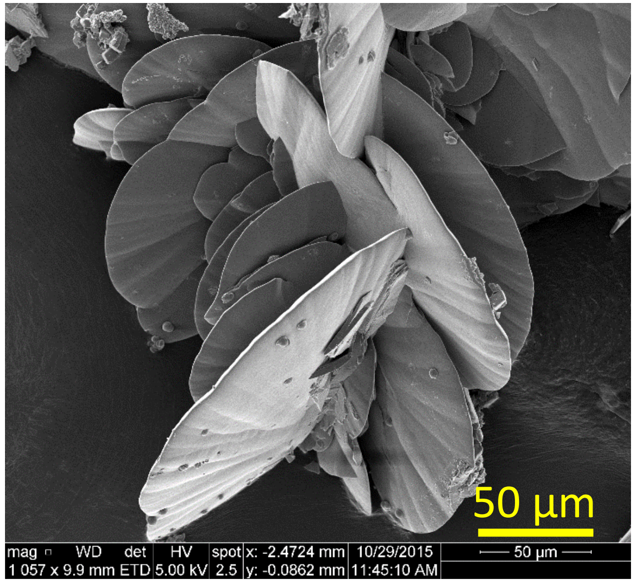


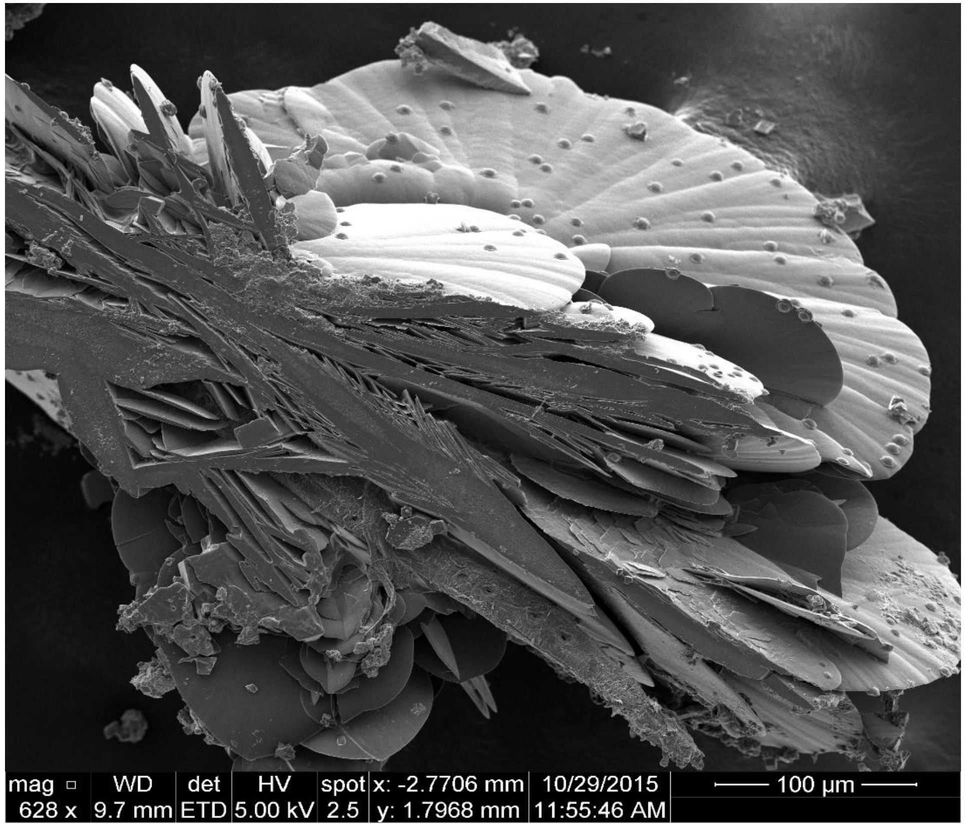
Anionic hairy nanocelluloses (ENCC)

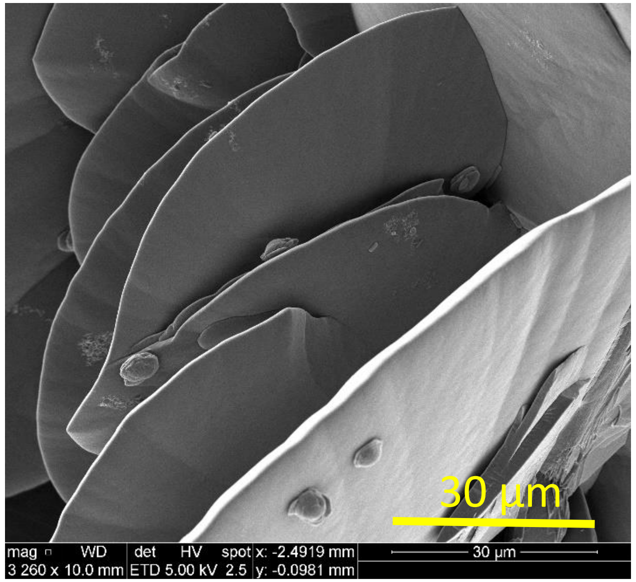


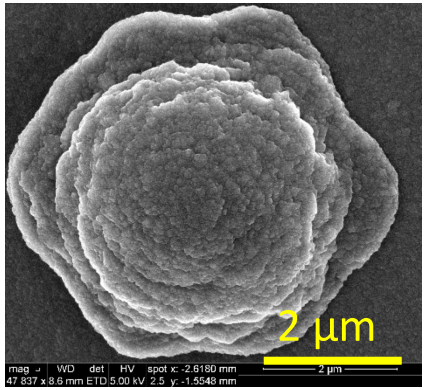
Sheikhi et al., Crystal Growth & Design (2016)

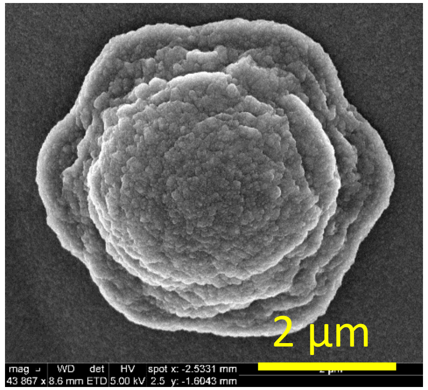
Biomimetic mineralization of $CaCO_3$ using ENCC



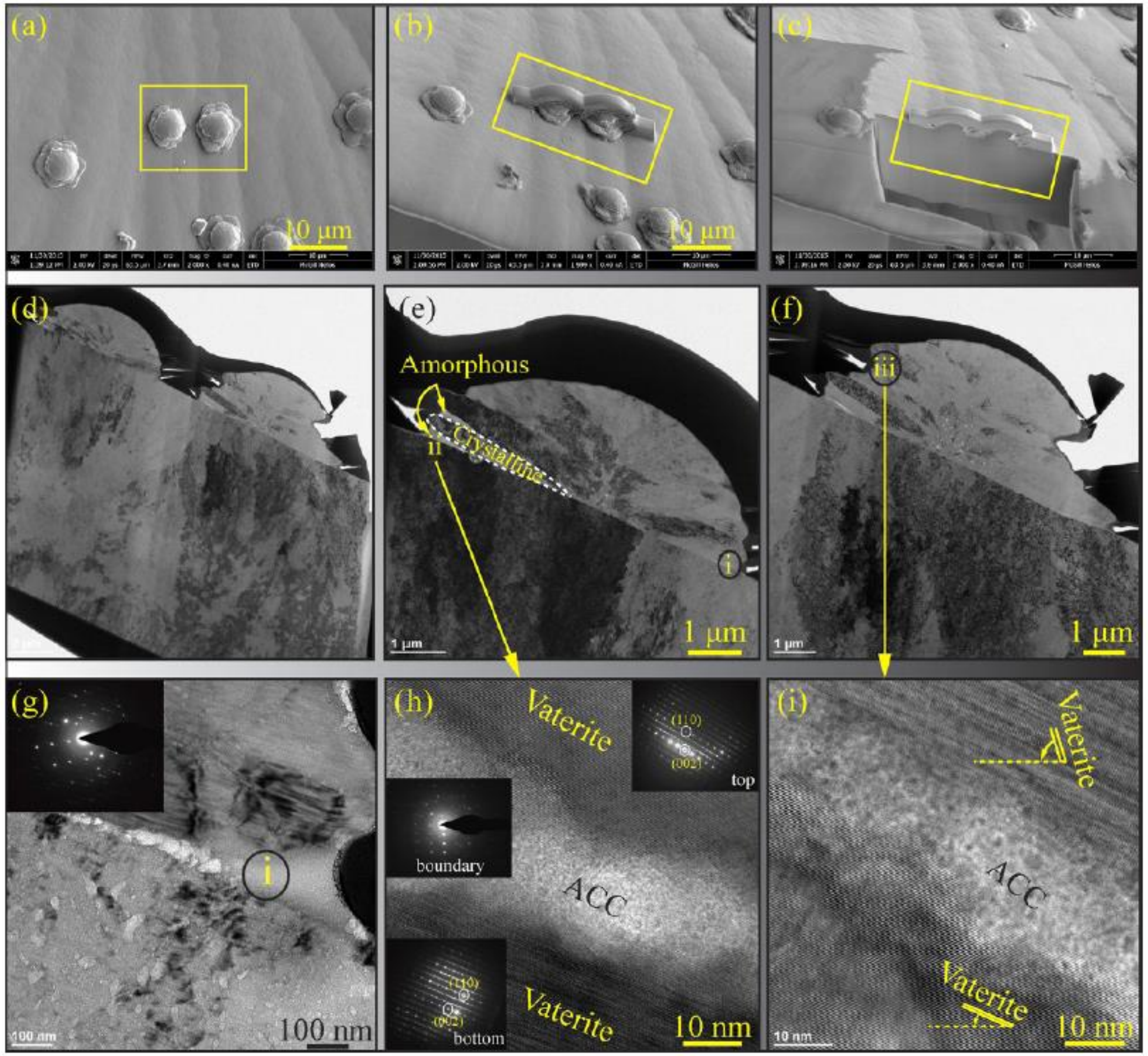


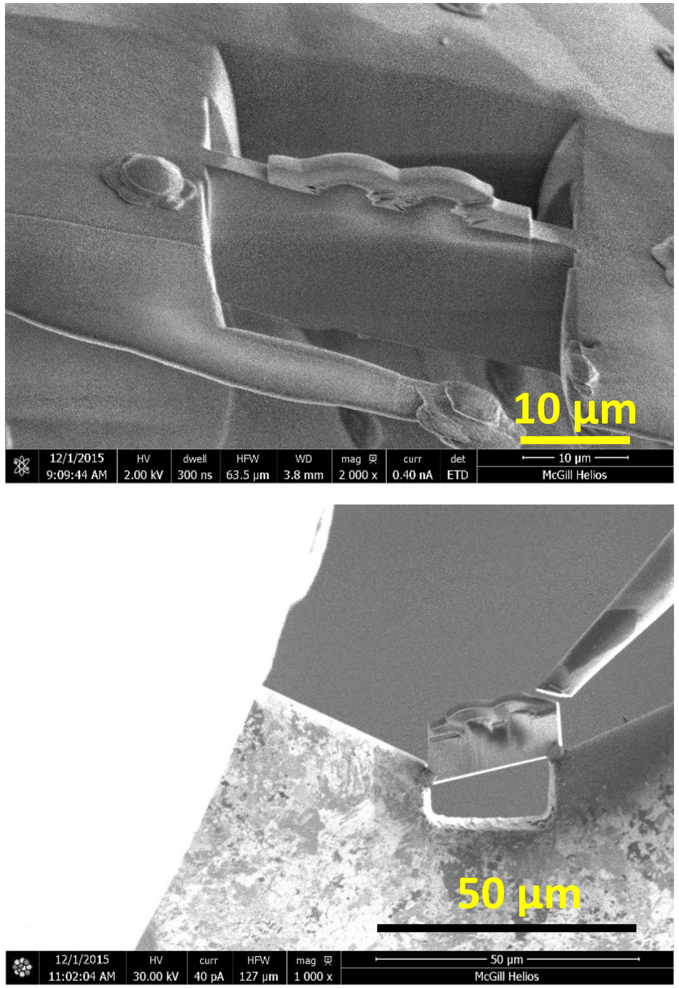






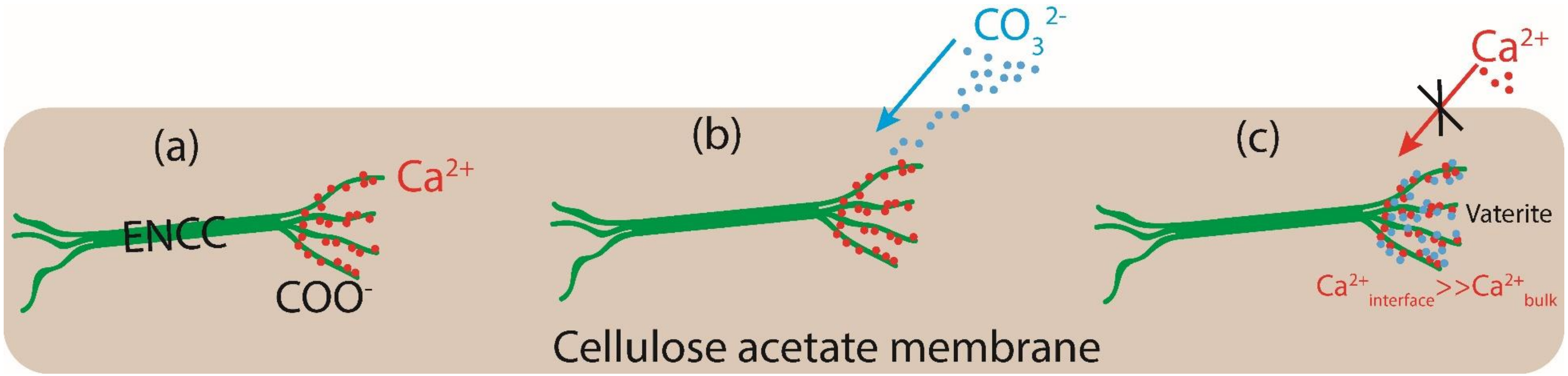
Biomimetic mineralization of $CaCO_3$ using ENCC

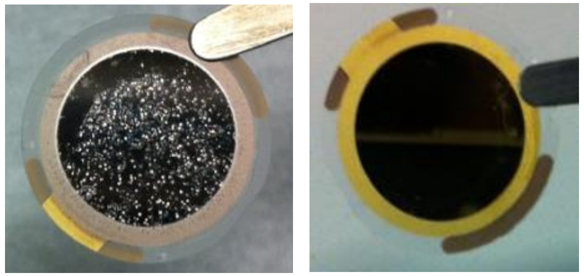




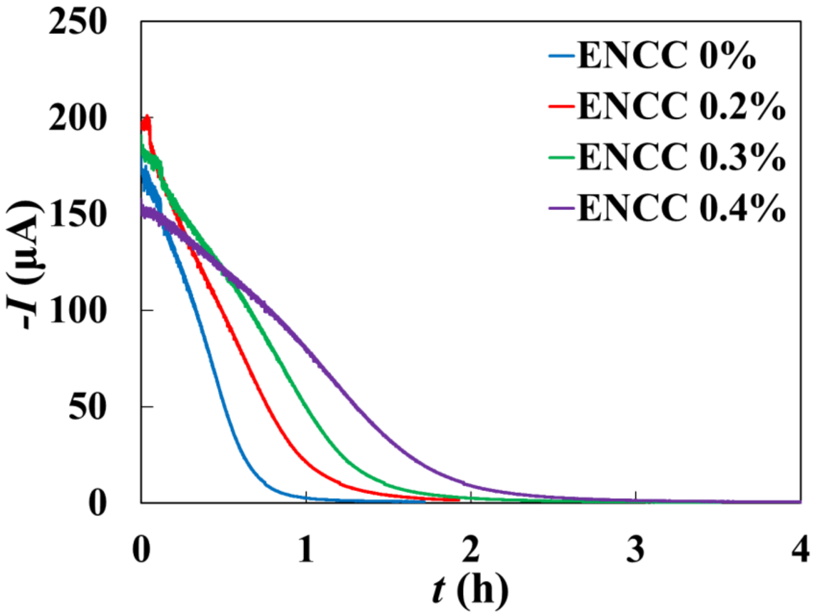
Sheikhi et al., Crystal Growth & Design (2016)

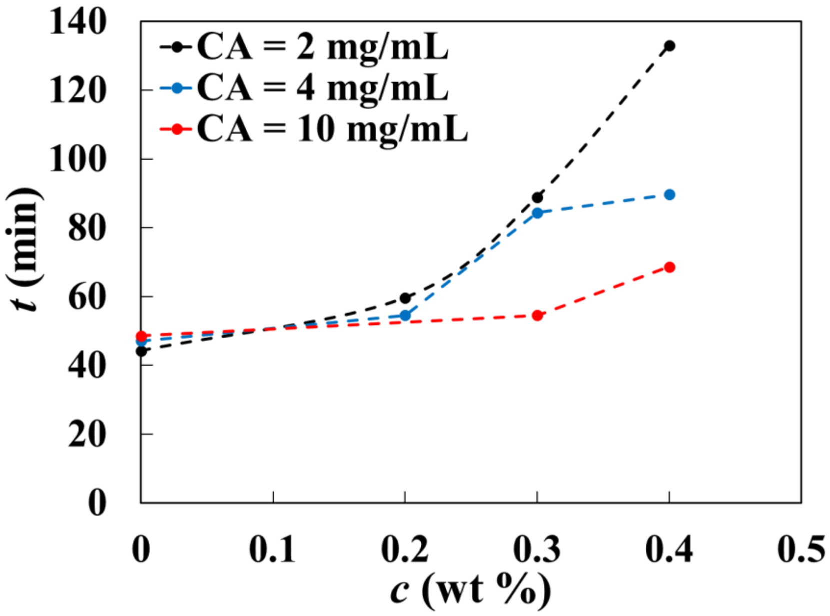
Part III: Scale-resistant interfaces



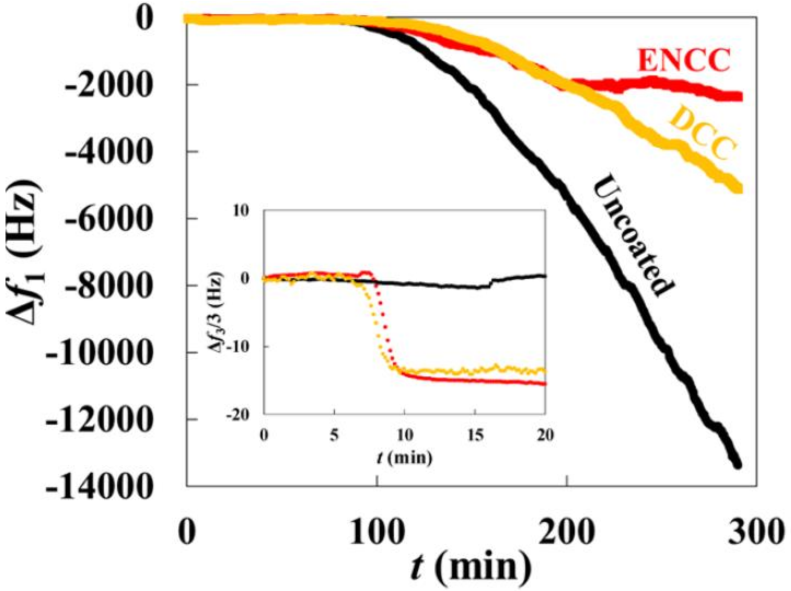


Uncoated ENCC coated



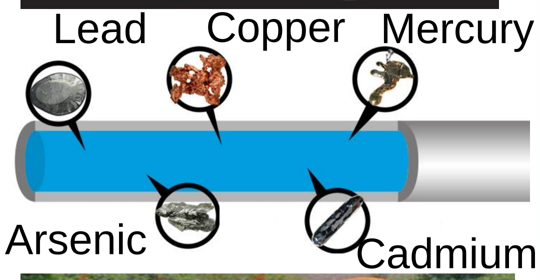


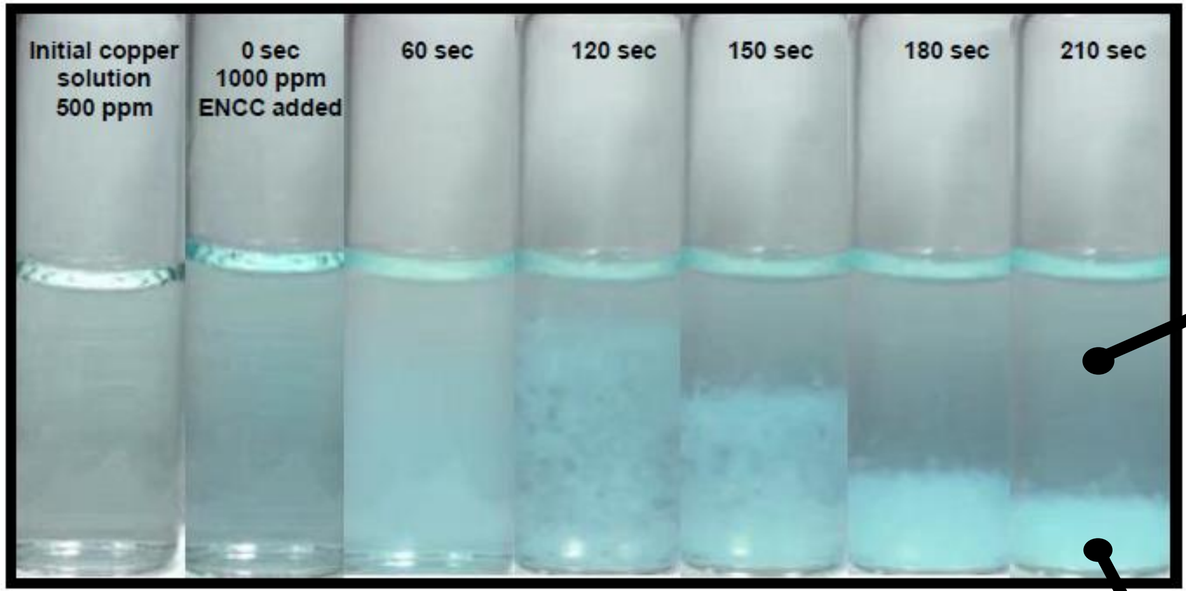
Sheikhi et al., Journal of Materials Chemistry A (2018)

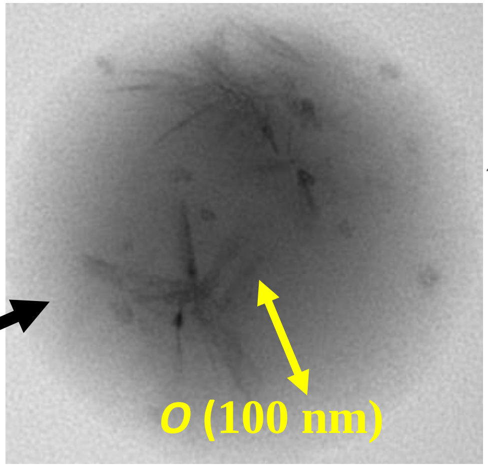


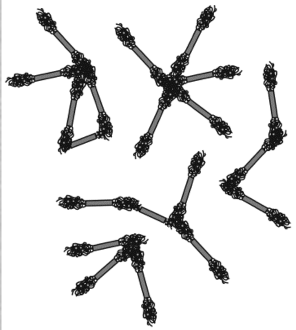
Sheikhi et al., ACS Applied Materials & Interfaces (2018)

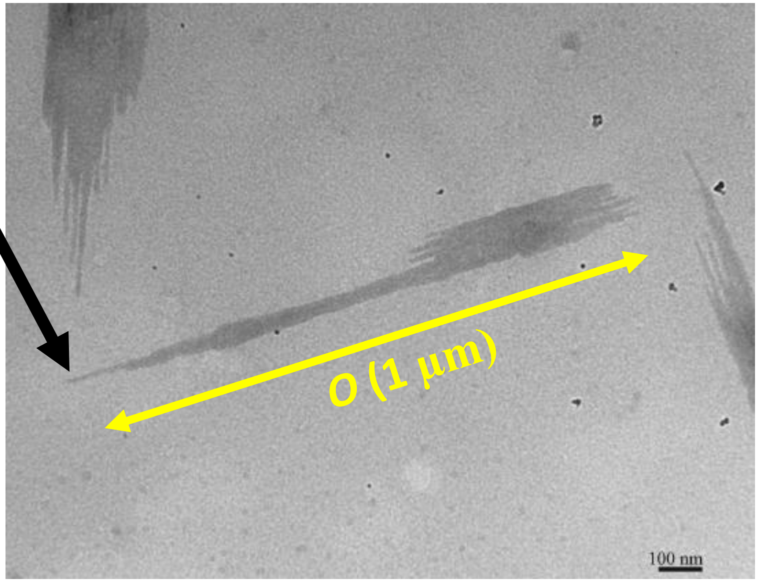
Part IV: Water remediation







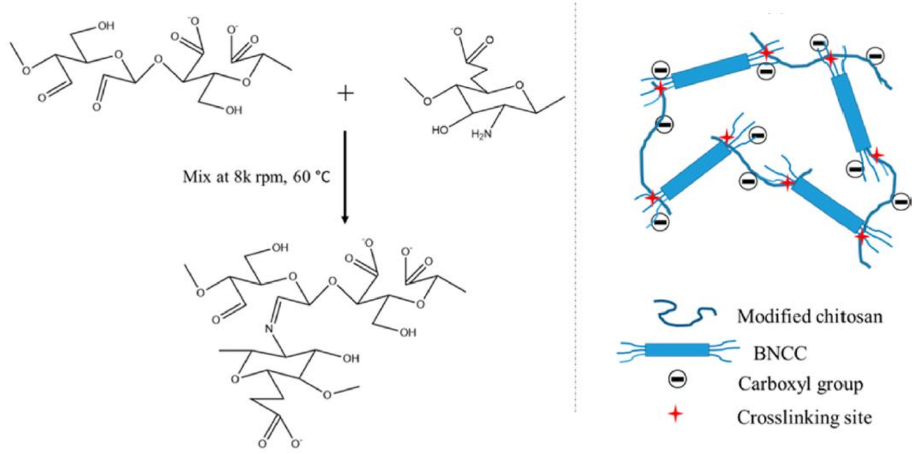


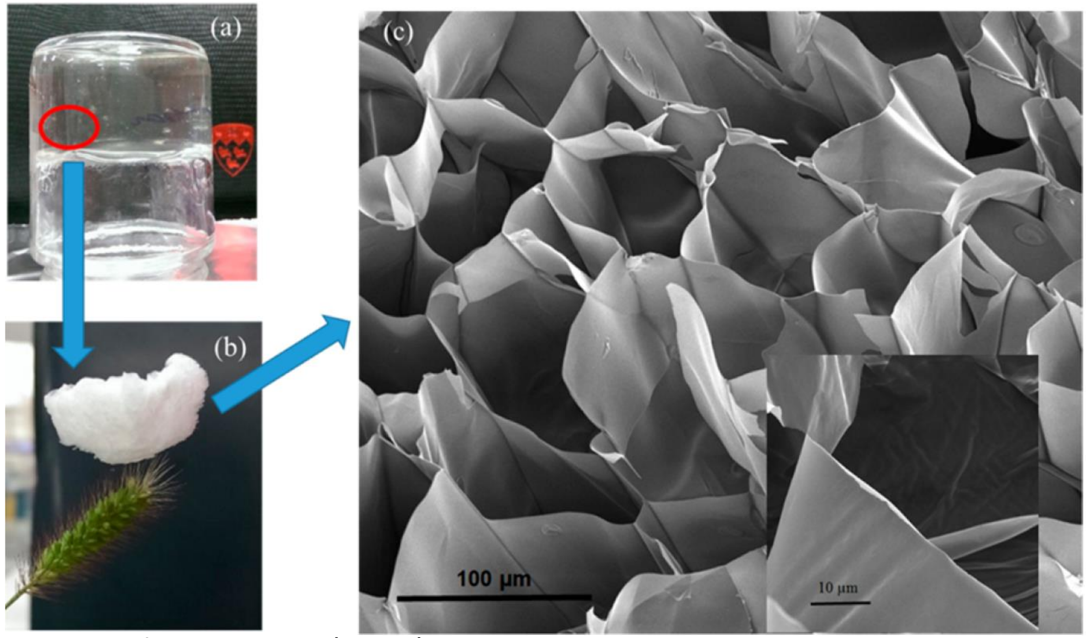


Additive	q_e (mg/g)
ENCC	185
CM-BNCC	9.7
Activated C	4.4

Sheikhi et al., ACS Applied Materials & Interfaces (2015)

Dye removal using hairy nanocellulose-based foams

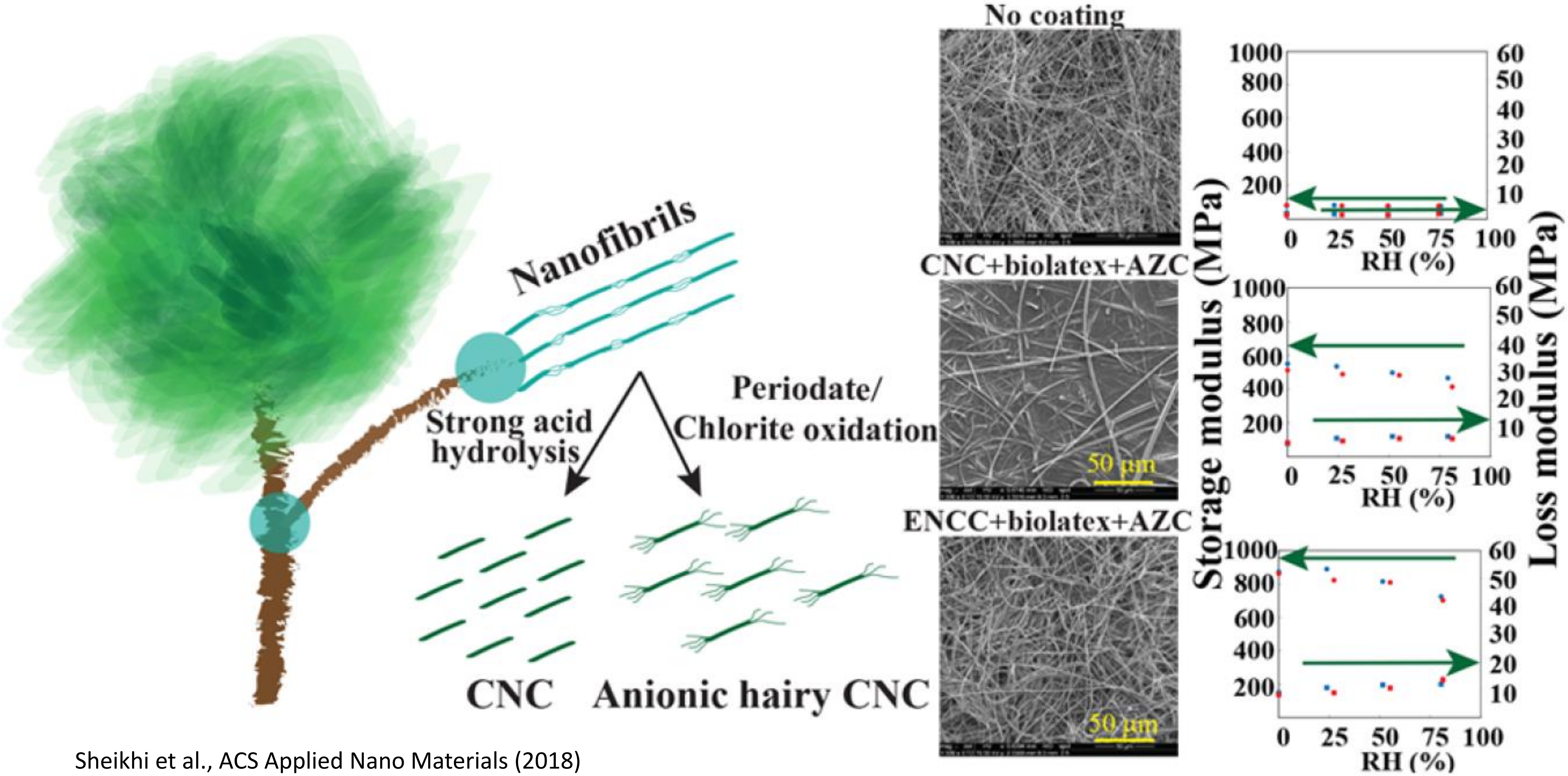




Yang et al., Langmuir (2016)

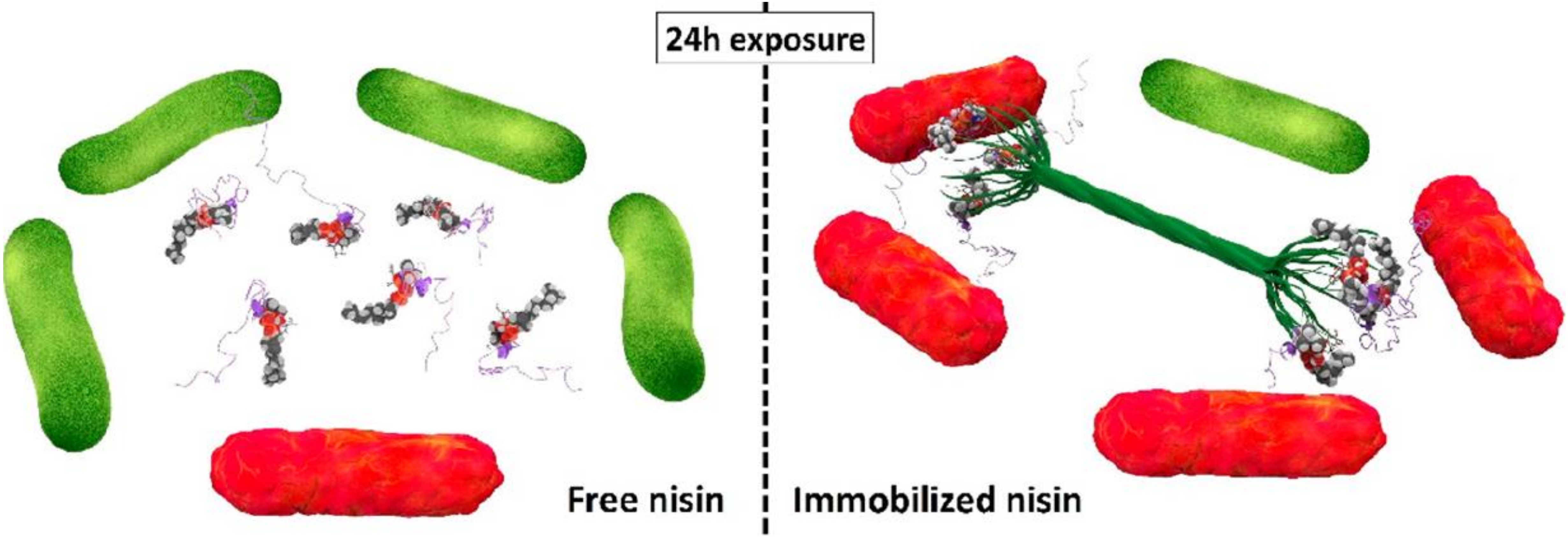
adsorbent	pH	Γ_m (mg g^{-1})
rice husk[5]	7	312.0
sugar cane bagasse[9]	7	99.6
NCC[17]	7.5	101.2
NCC modified by TEMPO reaction[18]	6.5	769.0
commercial activated carbon[45]	7.4	980.3
cellulose nanofibrils[46]	9	122.2
cellulose nanofibrils aerogel[47]		3.70
banana pith carbon[48]	4	233.4
chitosan/bentonite composite[49]	5.1	142.9
BNCC–CMCT aerogel (this work)	7.5	785

Part V: Reinforcing papers



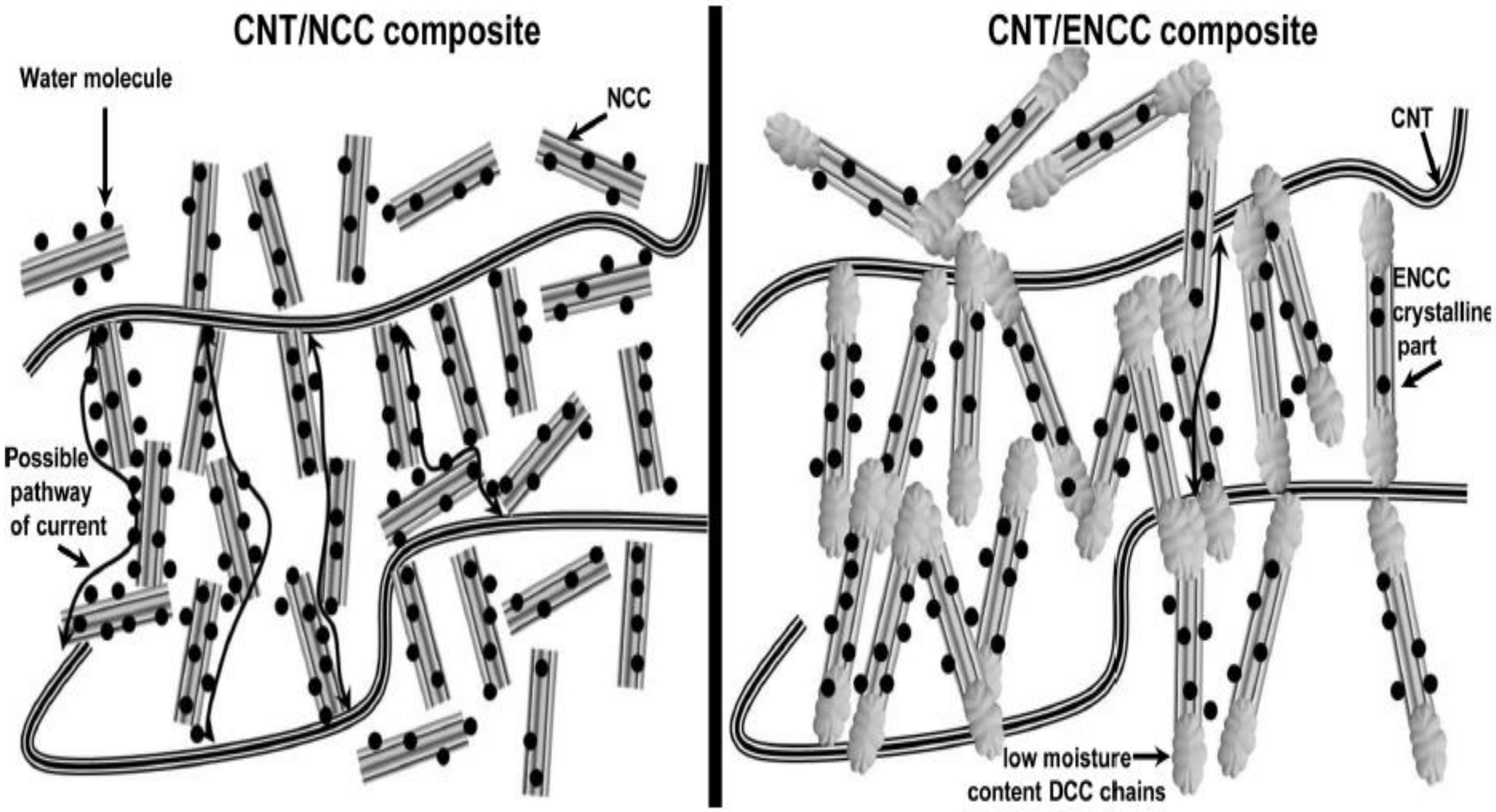
Sheikhi et al., ACS Applied Nano Materials (2018)

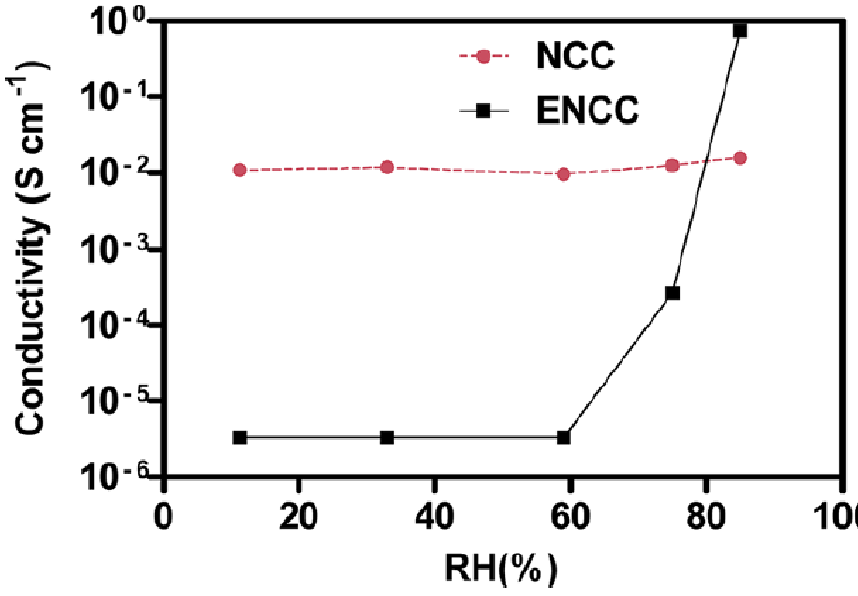
Part V: Antibacterial nanocrystalline cellulose



Tavakolian et al., ACS Applied Materials & Interfaces (2018)

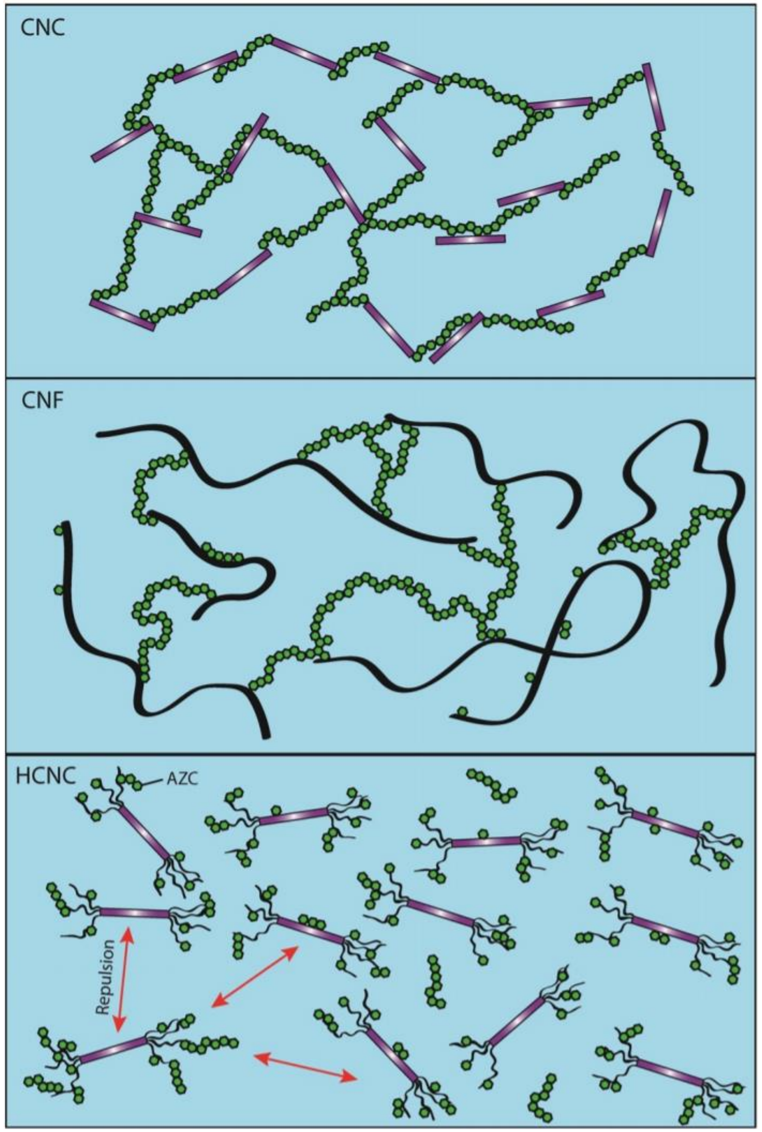
Part V: Nanocellulose-based humidity switch

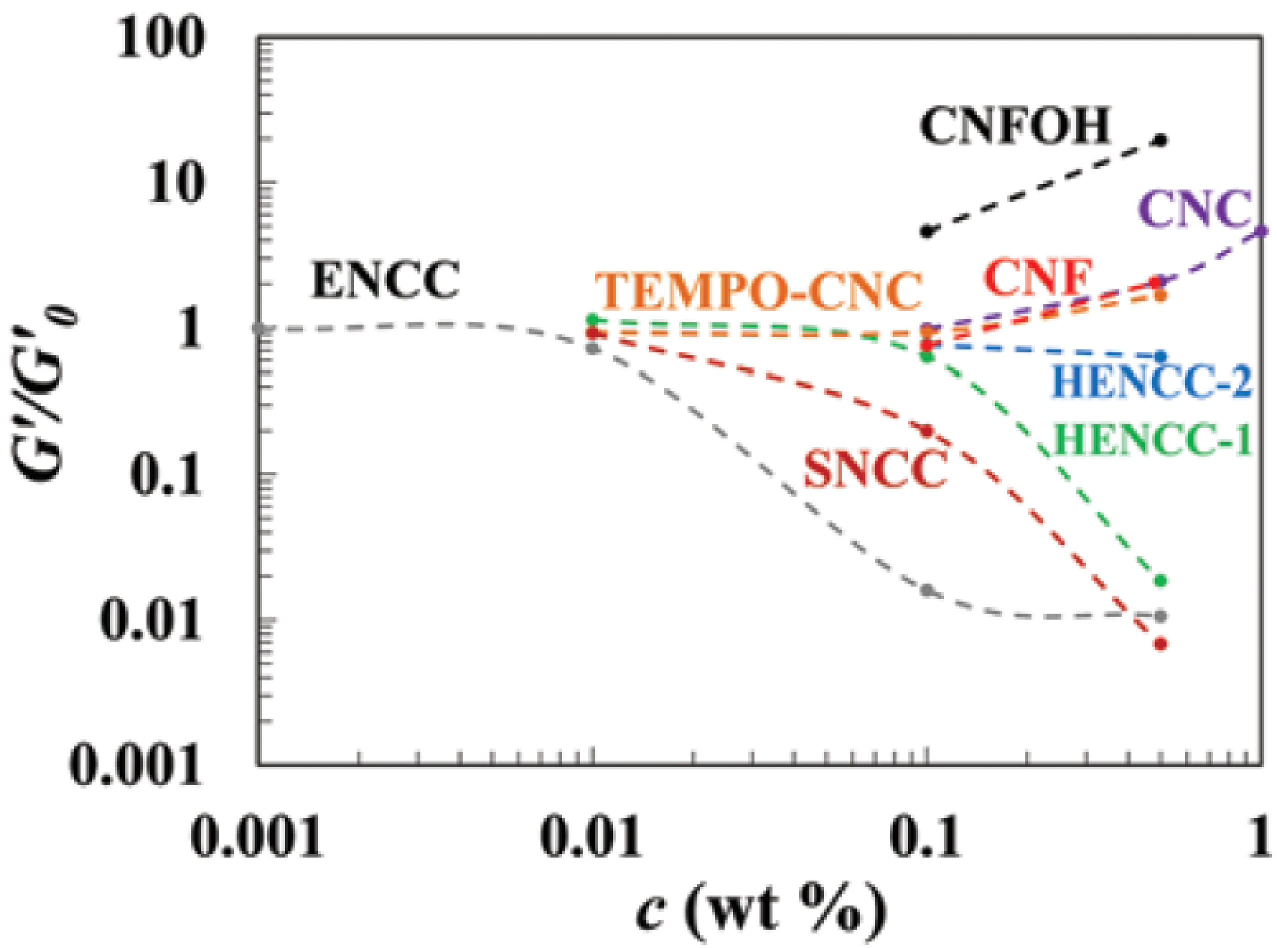




Safari et al., ACS Applied Materials & Interfaces (2016)

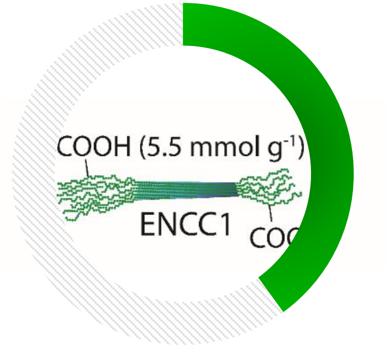
Part V: Colloidal nano-toolbox for molecularly regulated polymerization





Sheikhi et al., Materials Horizons (2017)

Concluding remarks



Hairy nanocelluloses (HNCs)

✓Nanoengineering cellulose fibers via facile chemistry yields HNCs.

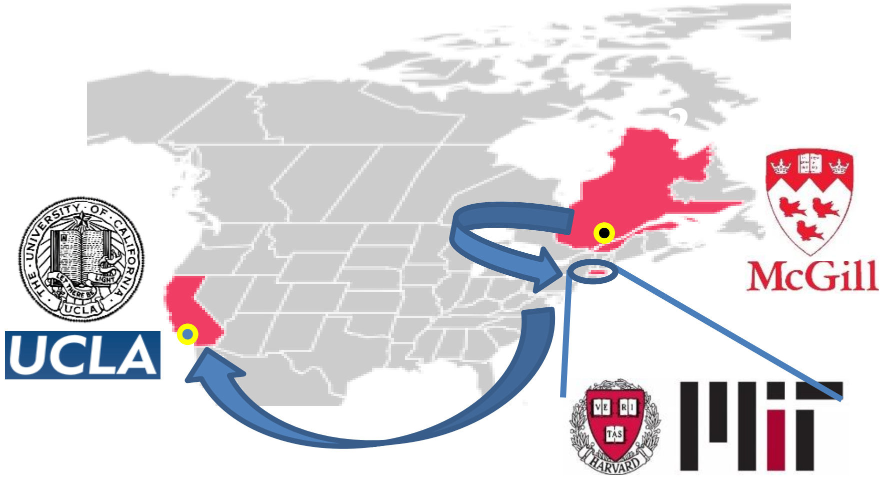
✓HNCs overcome the structural limitations of conventional nanocelluloses.

✓HNCs can provide reliable, green scale inhibitors.

✓Cellulose-based scale-resistant membranes are now feasible.

✓HNCs are promising candidates for water remediation, reinforced nanocomposites, bactericides, humidity switches, and rheology modifiers.

Acknowledgments



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Amir Sheikhi

Assistant Professor

Affiliation(s):

- Chemical Engineering
- Biomedical Engineering

413 Chemical and Biomedical Engineering Building
sheikhi@psu.edu
814-863-7564
Research Website
Google Scholar Profile

Research Areas:

Biotechnology and Synthetic Biology; Energy and Environment; Interfaces and Surfaces; Materials and Nanotechnology; Separations and Transport

Interest Areas:

Micro- and nanoengineered soft materials for medicine and the environment; microfluidic-enabled biomaterials for tissue engineering and regeneration; living materials; next-generation bioadhesives, tissue sealants, and hemostatic agents; hydrogels for minimally invasive medical technologies; self-healing and adaptable soft materials; smart coatings; hairy nanocelluloses as an emerging family of advanced materials

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Luminescent Nanoparticles of Metal Oxides

Yuanbing Mao, PhD

Professor and Chair

Department of Chemistry

Illinois Tech