



Hairy Cellulose Nanocrystals: Fundamentals and Emerging Applications

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Assistant Professor

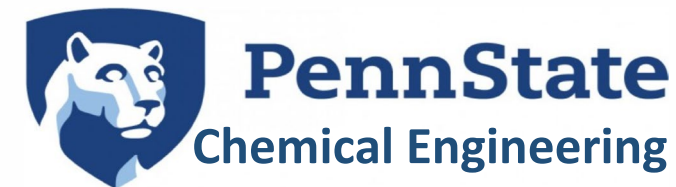
Department of Chemical Engineering

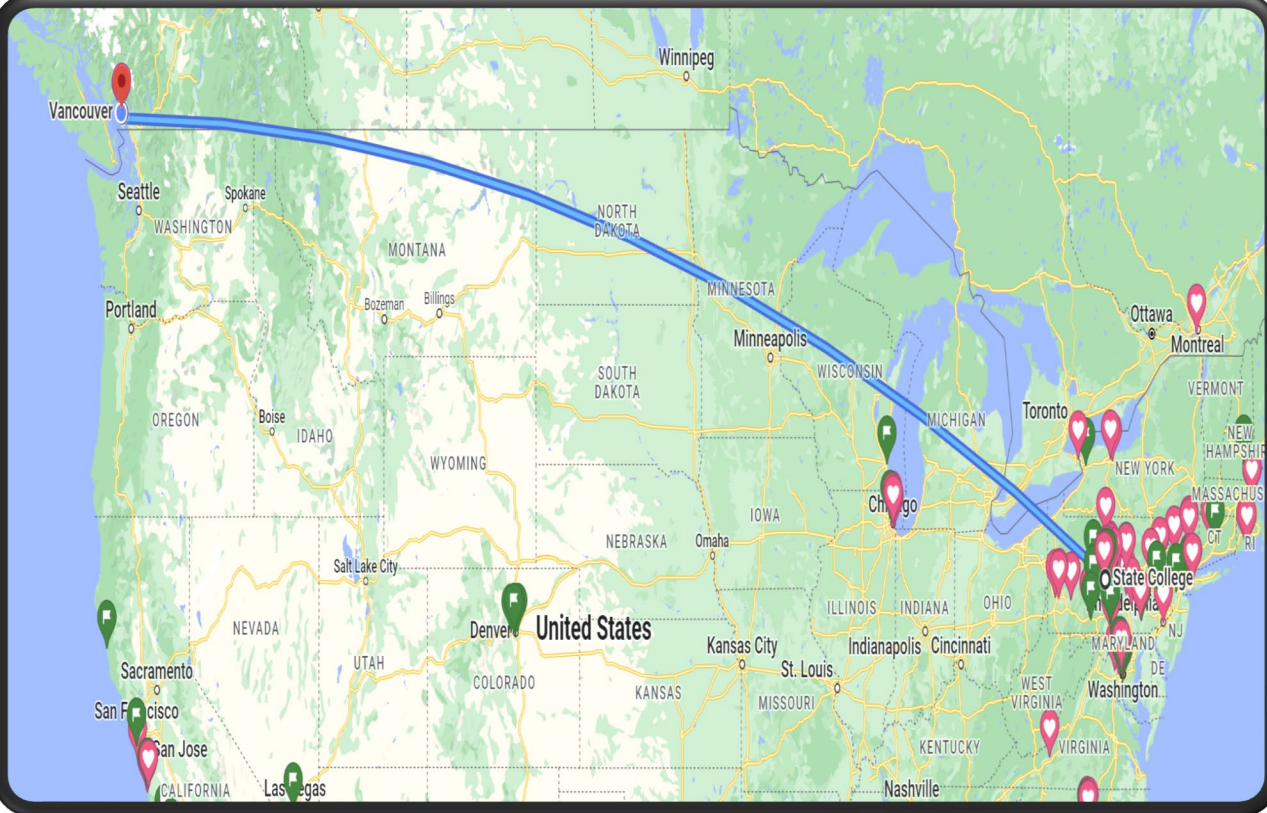
Department of Biomedical Engineering (Courtesy)

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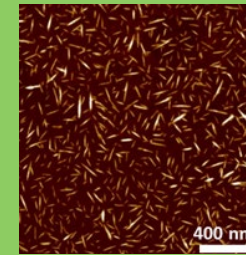


Outline

**Part I:
Hairy cellulose
nanocrystals (HCNC)
synthesis**



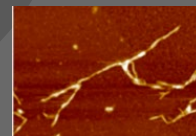
**Part II: HCNC
properties**



**Part IV:
Unique applications of
HCNCs**

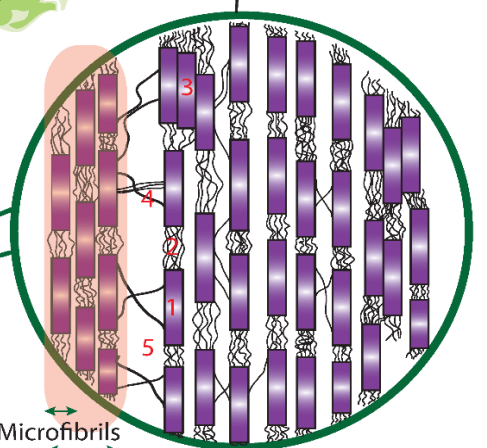
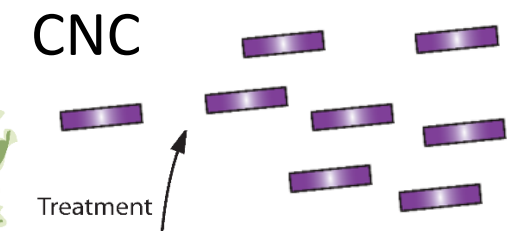
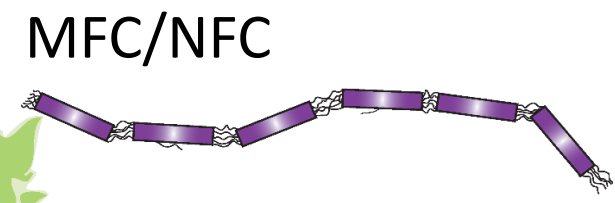
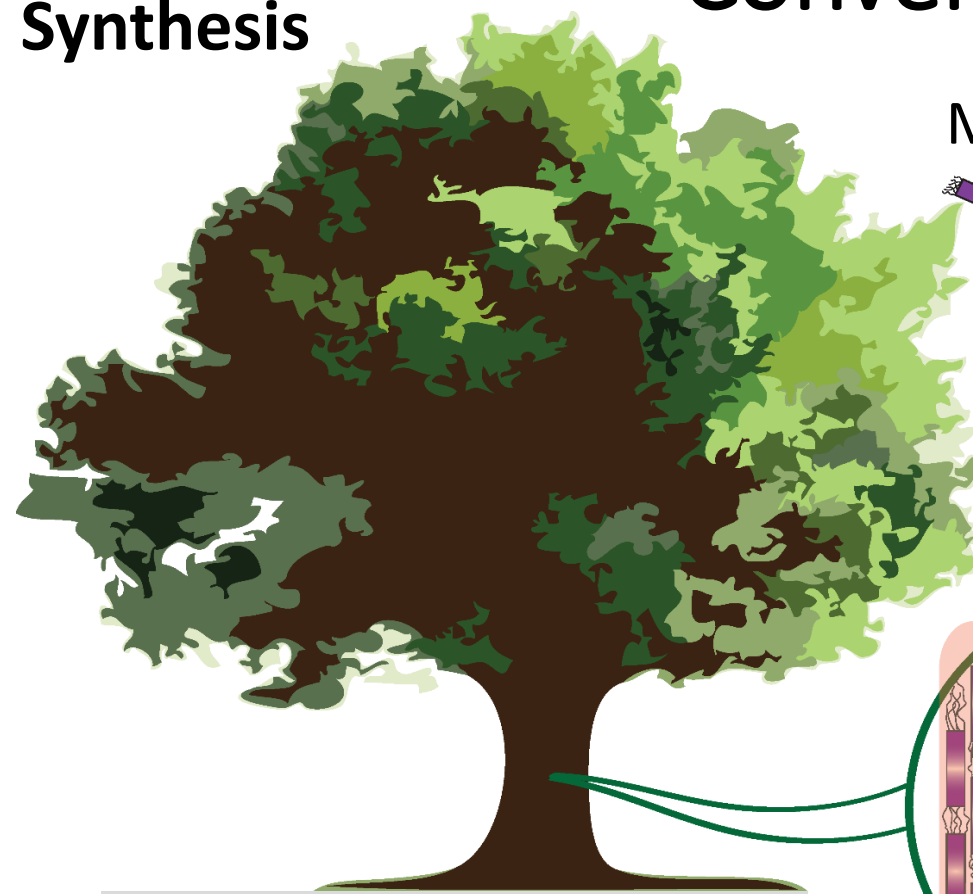


**Part III:
Evidence of
protruding chains**

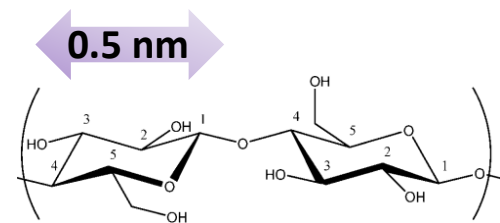
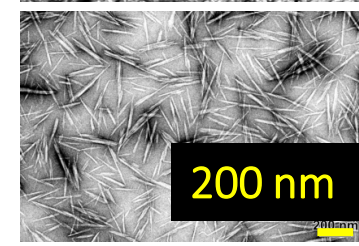
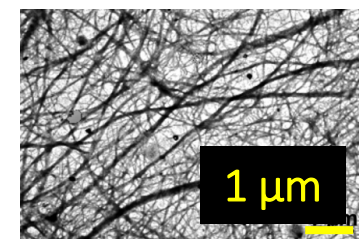


Part I: Synthesis

Conventional nanocelluloses



(1) Crystallites, (2) Amorphous region, (3) Cluster, (4) Inter-fibrillar molecular tie, (5) Void

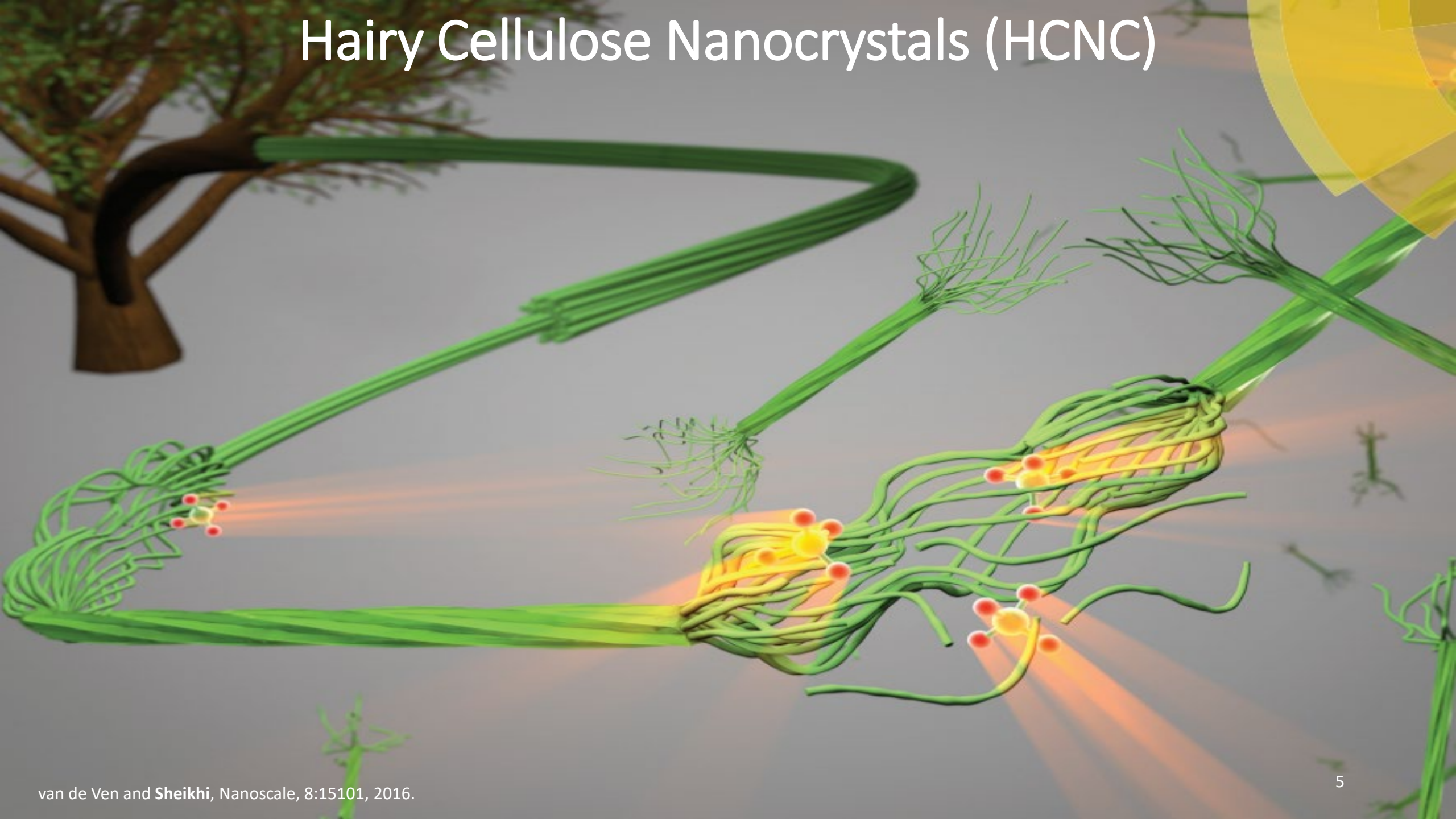


Maximum theoretical charge content ~ 1.4 mmol/g.

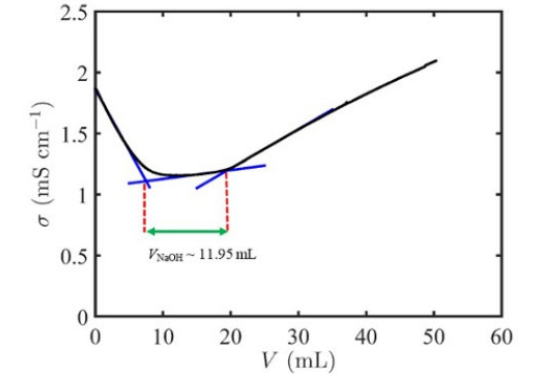
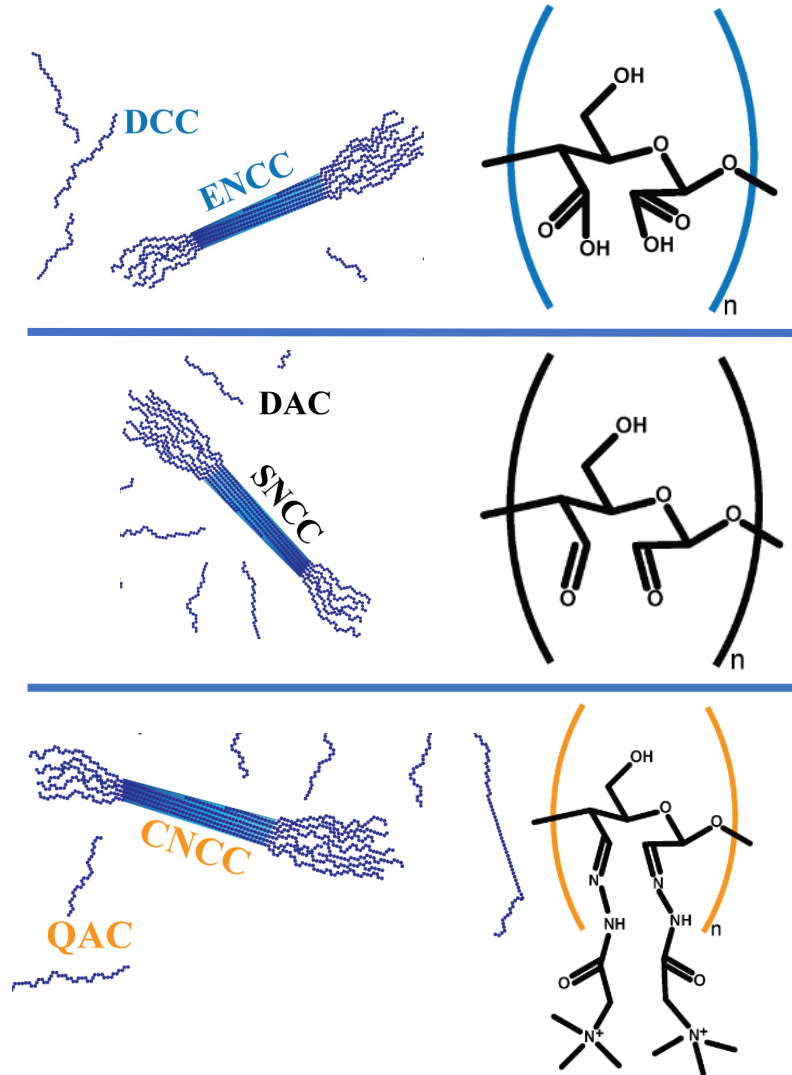
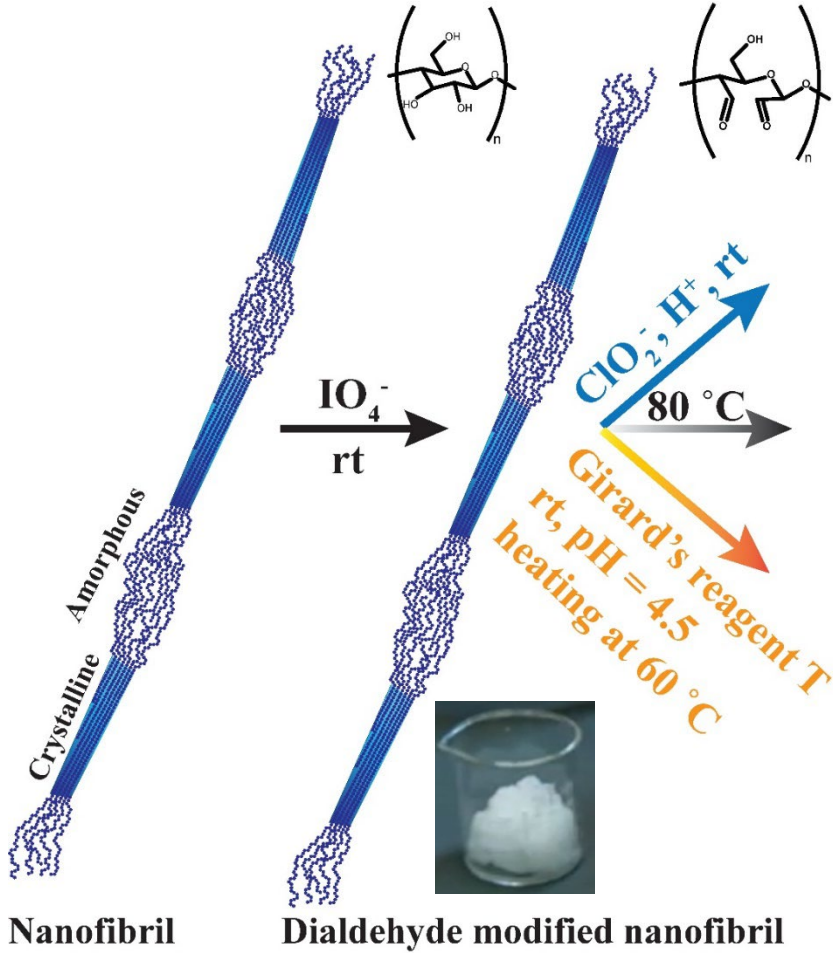
- ✓ Biorenewable
- ✓ Biodegradable
- ✓ Cost effective
- ✓ Environmentally friendly
- ✓ Large surface area (>100 m²/g)

Kontturi et al., *Advanced Materials*, 30:1703779, 2018.
 Dufresene, *Materials Today*, 16:220, 2017.
 Habibi et al., *Journal of Materials Chemistry*, 18:5002, 2008.
 Malainine et al., *Carbohydrate Polymers*, 51:77, 2003.
 Yang et al., *Cellulose*, 20:1865, 2013.

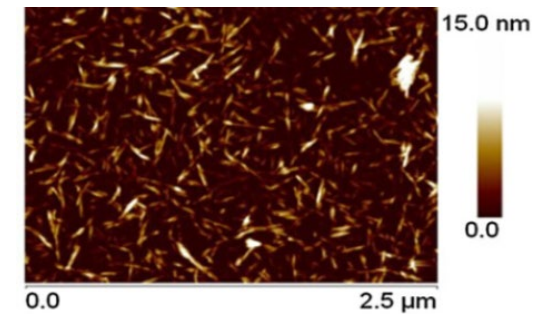
Hairy Cellulose Nanocrystals (HCNC)



HCNC synthesis



COOH concentration =
 $0.01195 (V_{\text{NaOH}}) \times 10 \text{ mM}$
 (NaOH concentration) / 0.02 g
 (initial ENCC) $\sim 5.98 \text{ mmol/g}$



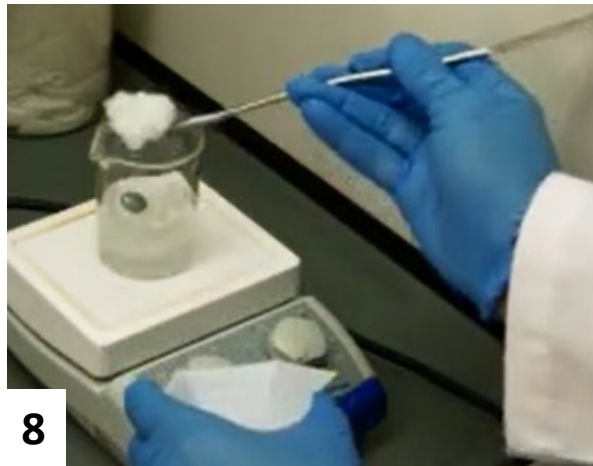
Yang et al., Langmuir, 28:7834, 2012.

Sheikhi and van de Ven, Current Opinion in Colloid & Interface Science, 29:21, 2017.

Sheikhi et al., Journal of Visualized Experiments: JoVE, 113 e54133, 2016.

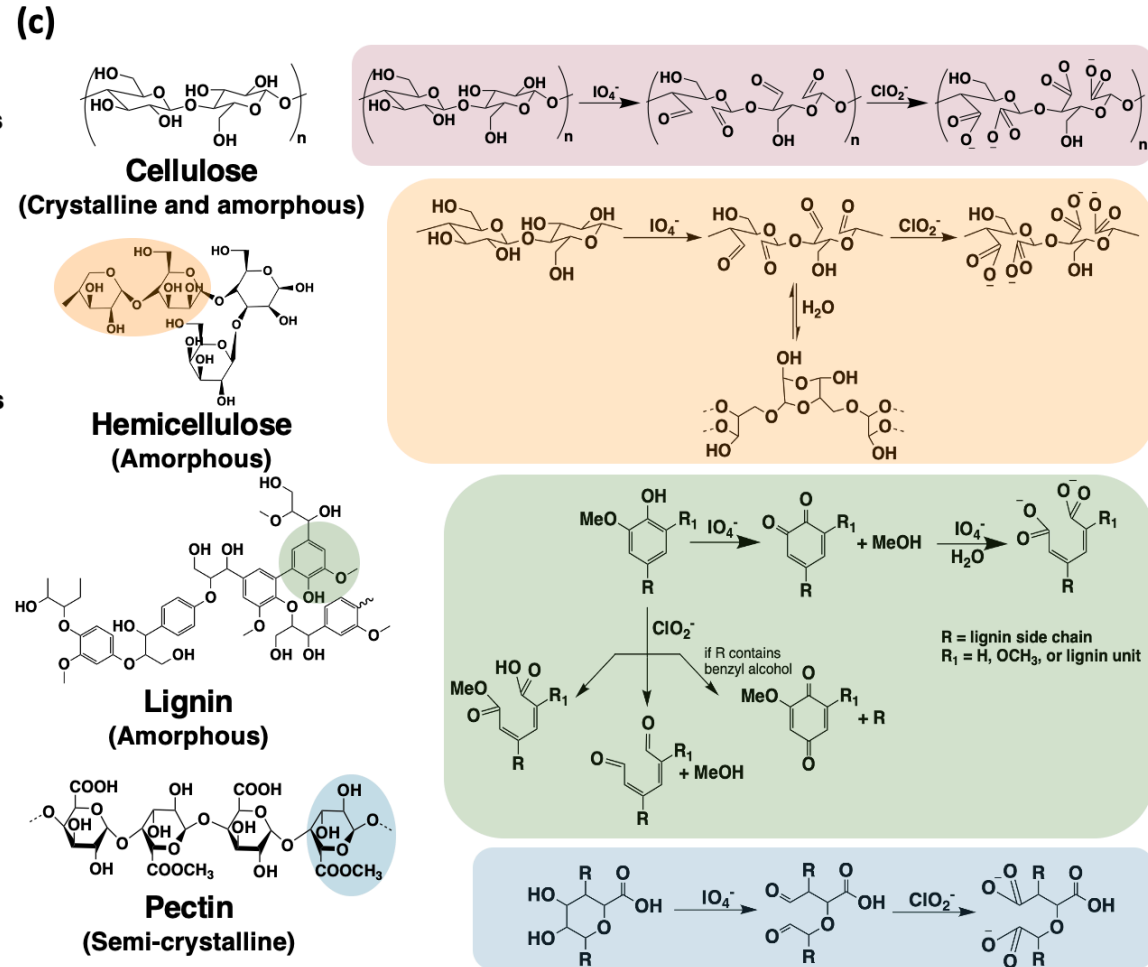
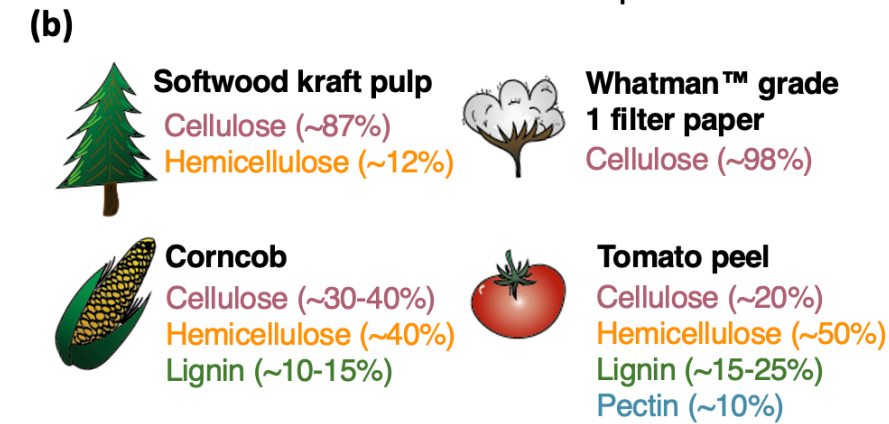
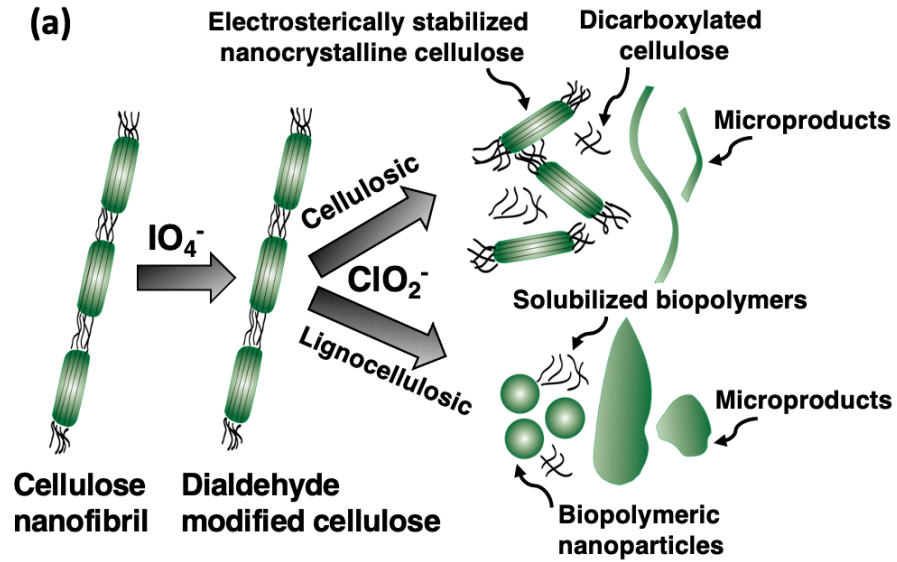
HCNC synthesis

Preparing partially oxidized fibers



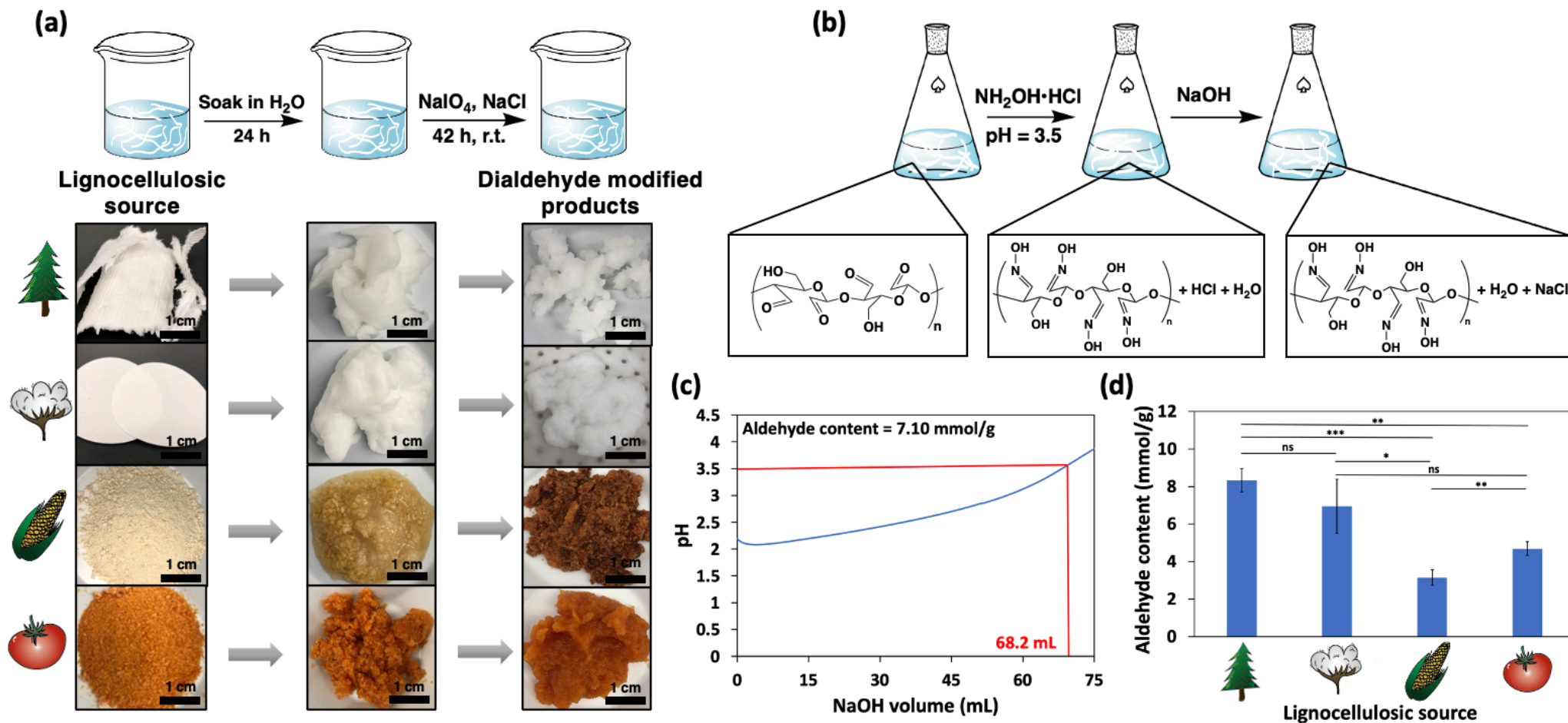
Preparing electrosterically stabilized nanocrystalline celluloses (ENCC)

Universality of HCNC synthesis



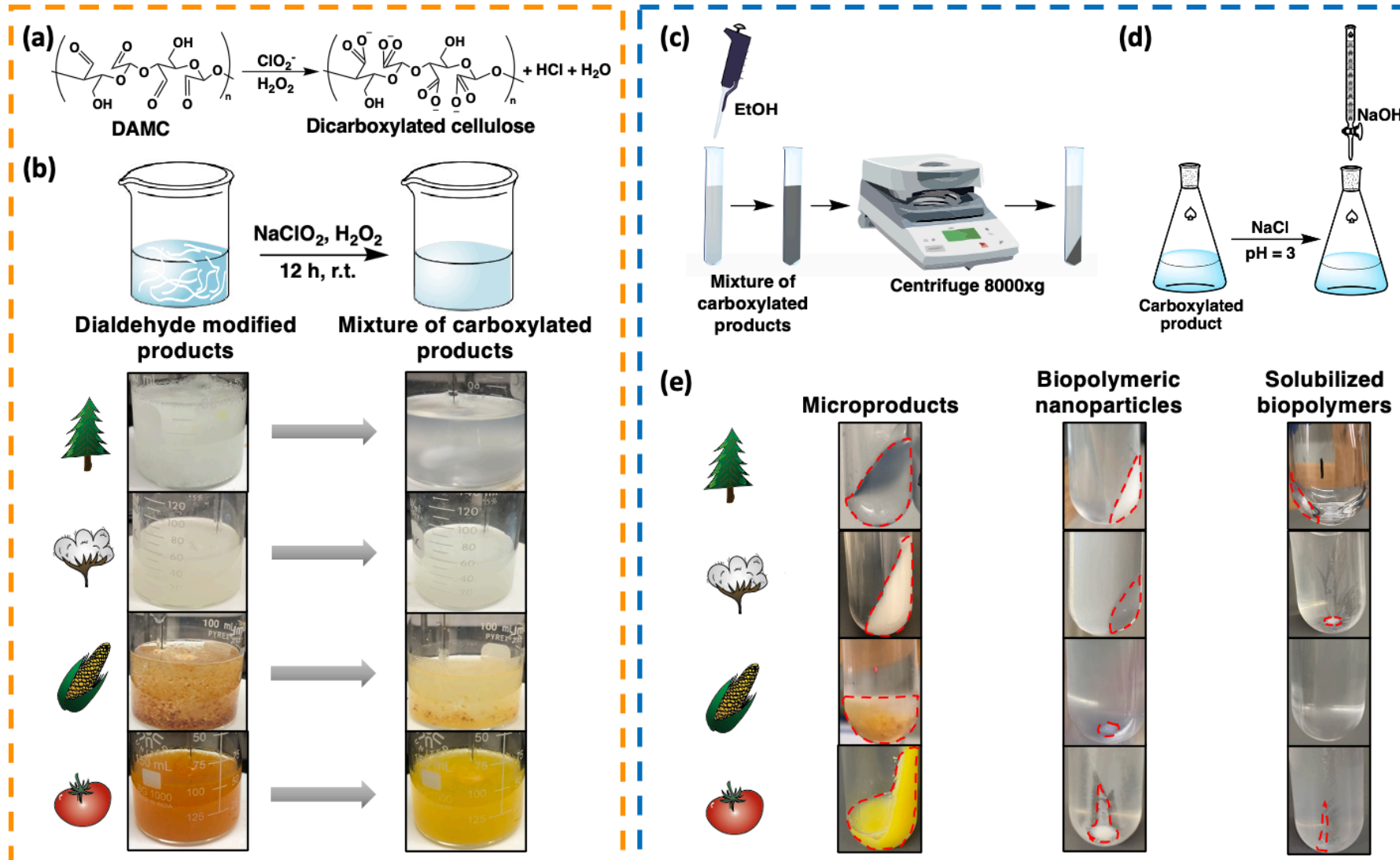
Pitcher and Sheikhi et al., Chemical Engineering Journal, 447:137418, 2022.
Provisional Patent Application filed.

Universality of HCNC synthesis: Periodate reaction



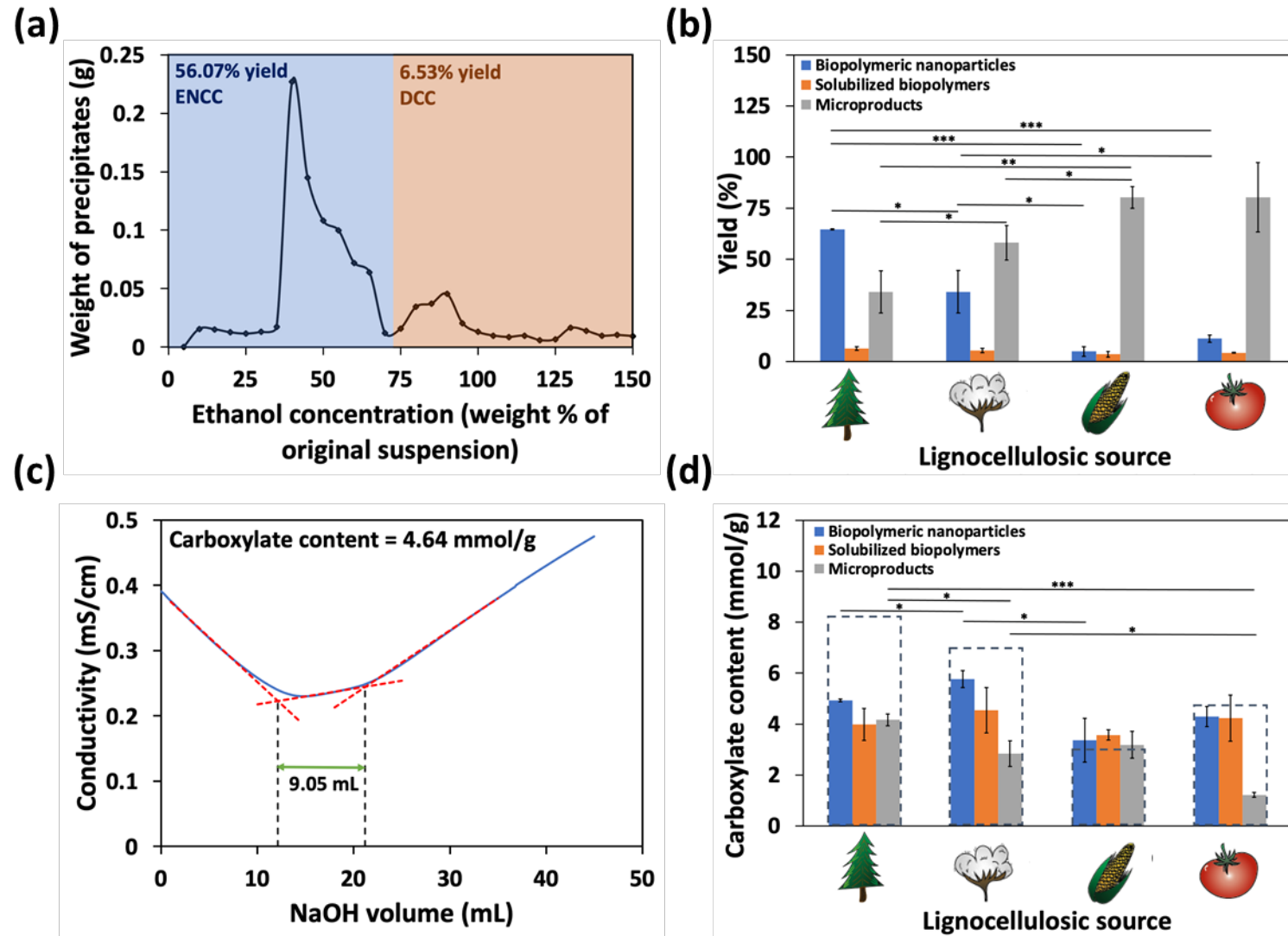
Pitcher and **Sheikhi** et al., Chemical Engineering Journal, 447:137418 (2022).
Provisional Patent Application filed.

Universality of HCNC synthesis: Chlorite reaction



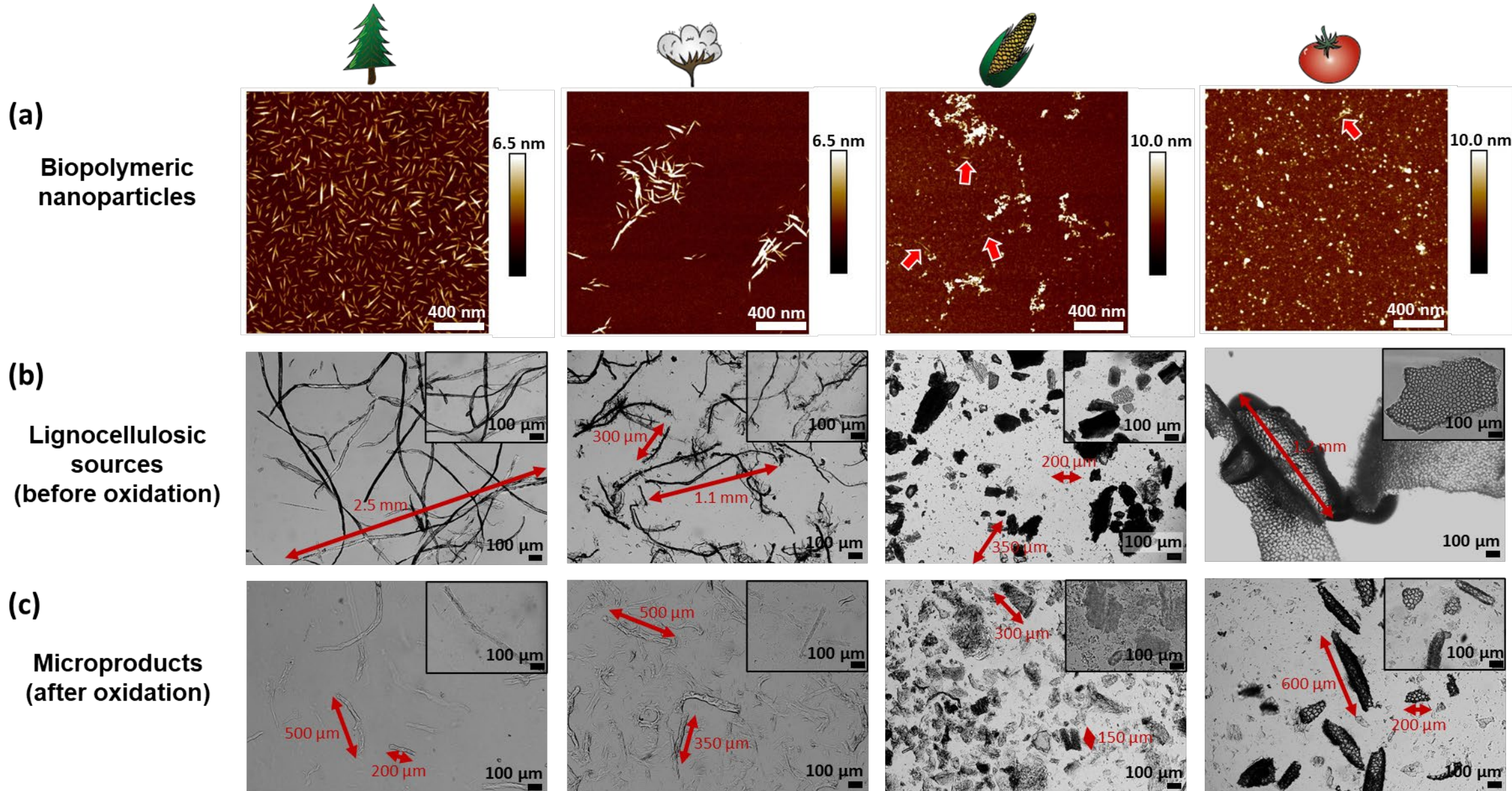
Pitcher and **Sheikhi** et al., Chemical Engineering Journal, 447:137418, 2022.
Provisional Patent Application filed.

Universality of HCNC synthesis: Characterization



Pitcher and Sheikhi et al., Chemical Engineering Journal, 447:137418, 2022.
Provisional Patent Application filed.

Universality of HCNC synthesis: Characterization



Part II: Properties

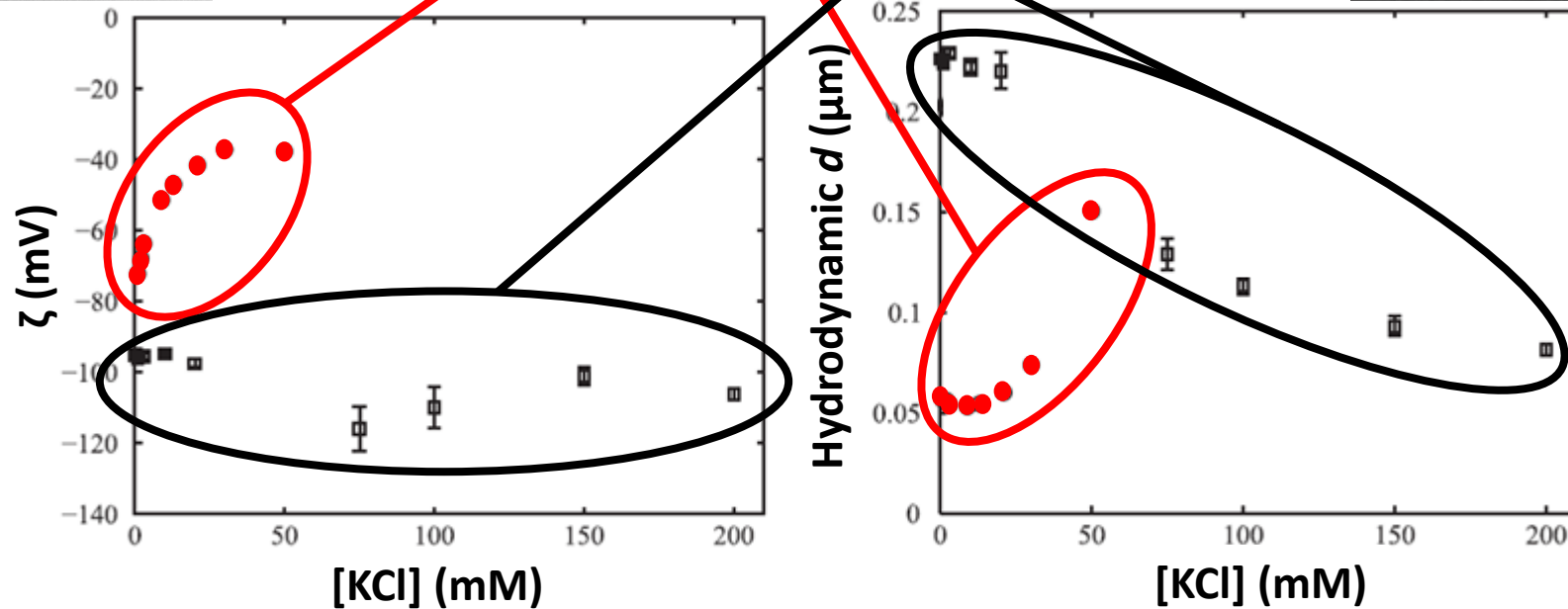
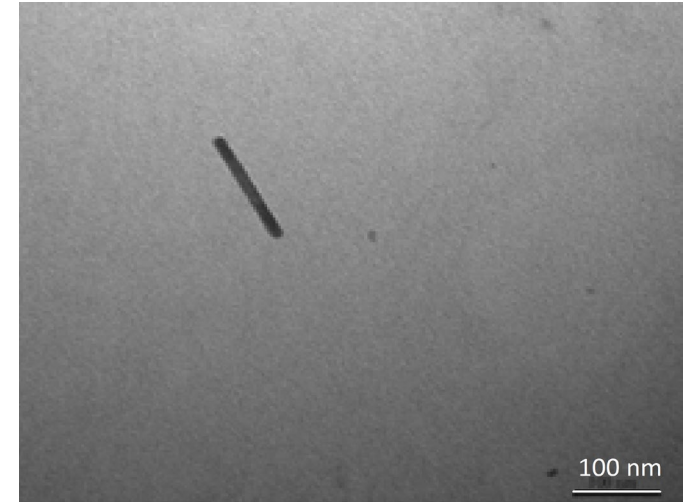
CNC versus HCNC



**Anionic
CNC**

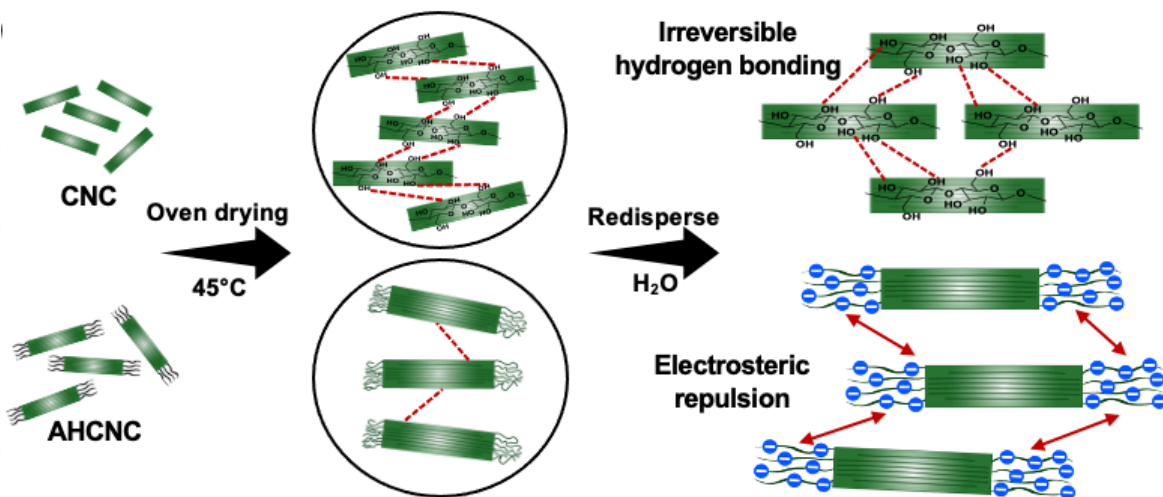
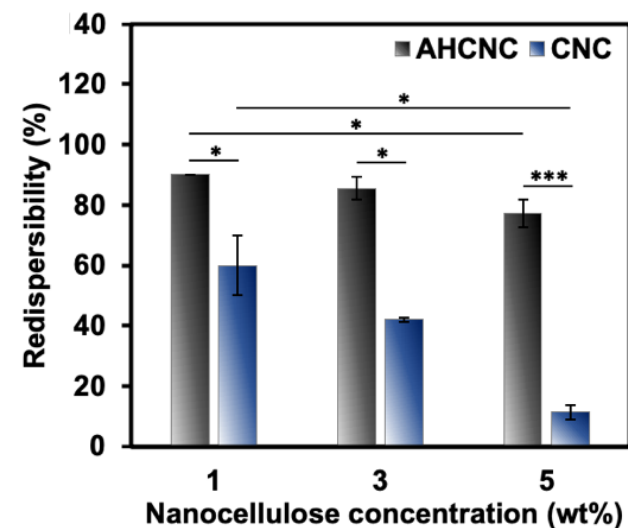
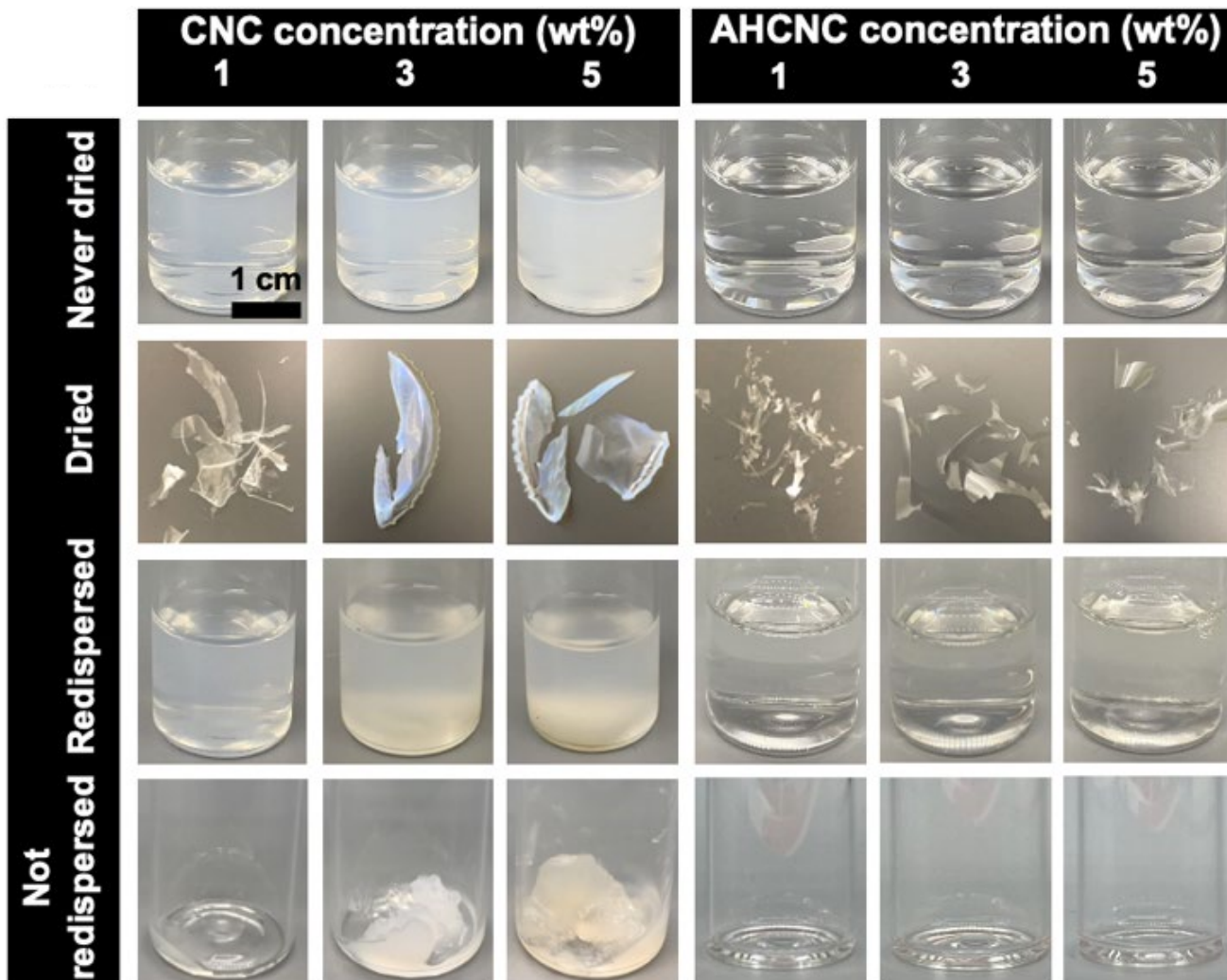


**Anionic
HCNC**



Part II: Properties

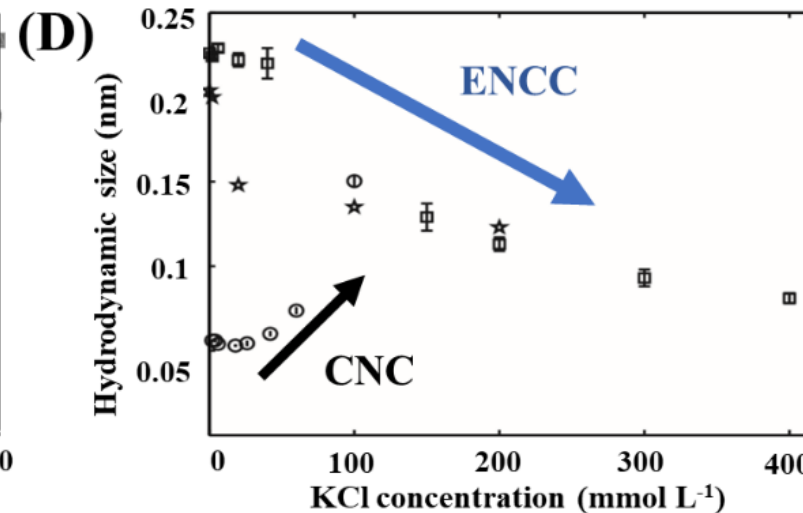
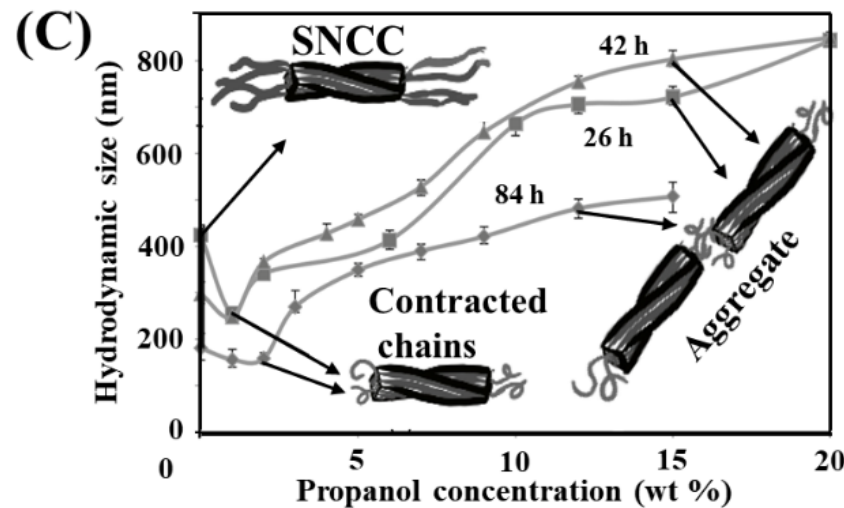
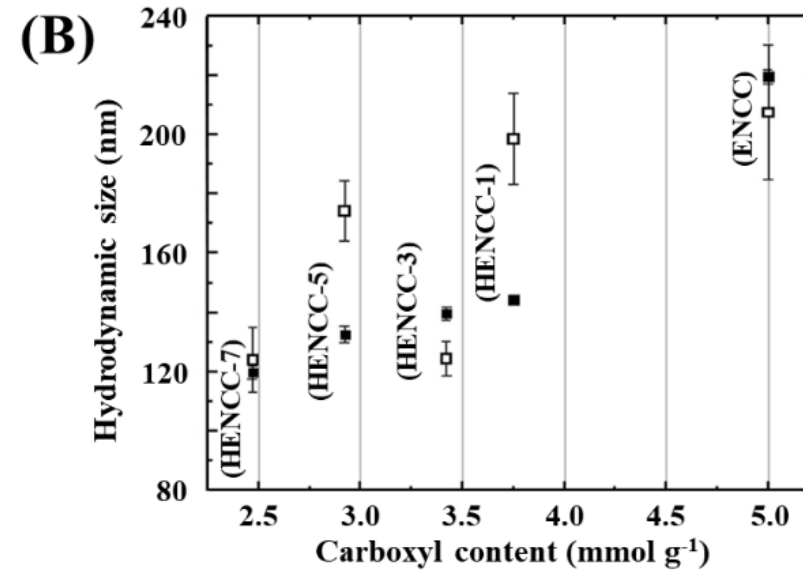
Redispersibility



Part III: Evidence of protruding chains

(A)

Hydrolysis time (h)	Hairy nanocelluloses	Carboxyl content
0	(ENCC)	5.0 mmol g ⁻¹
1	(HENCC-1)	3.8 mmol g ⁻¹
3	(HENCC-3)	3.4 mmol g ⁻¹
5	(HENCC-5)	2.9 mmol g ⁻¹
7	(HENCC-7)	2.5 mmol g ⁻¹

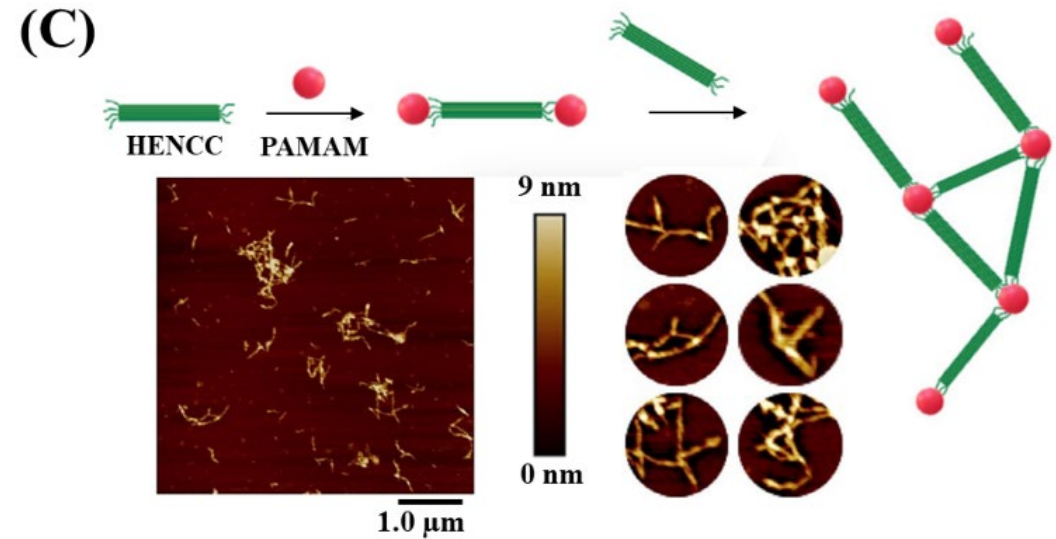
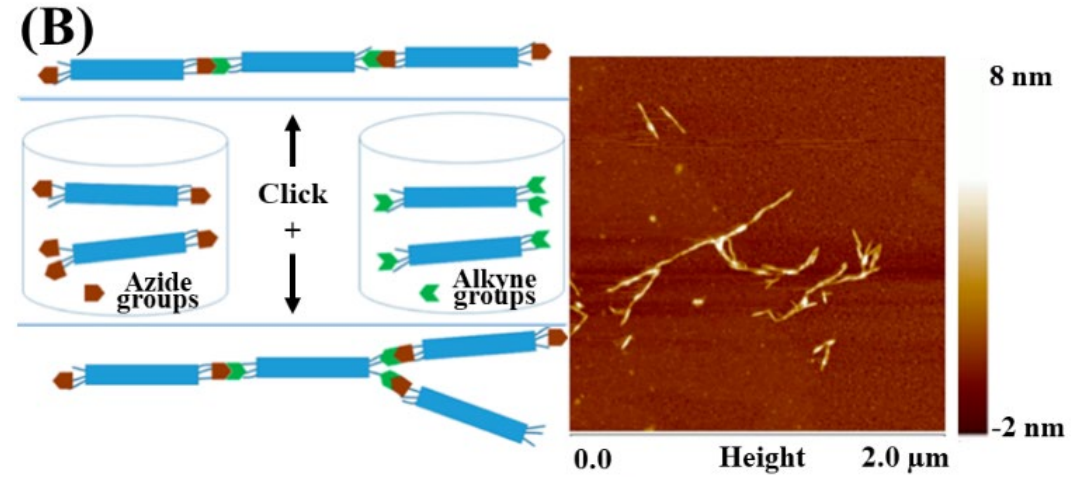
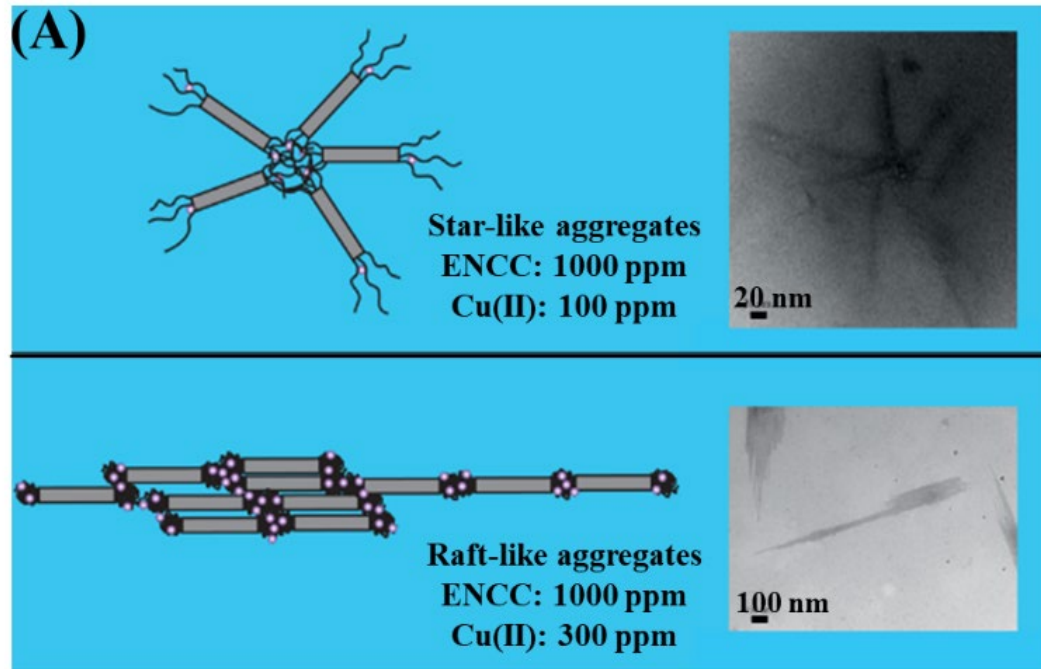


Koshani and van de Ven, Journal of Colloid and Interface Science, 563:252, 2020.

Chen and van de Ven, Cellulose, 23:1051, 2016.

Sheikhi et al., Journal of Colloid and Interface Science, 432:151, 2014.

Part III: Evidence of protruding chains



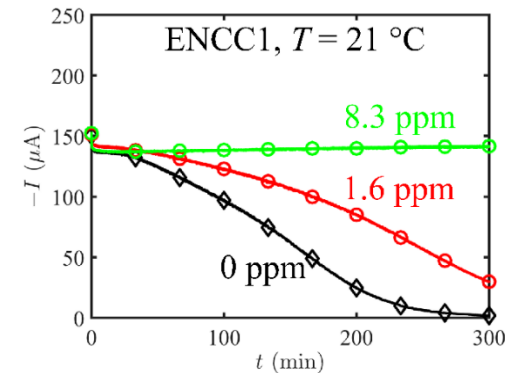
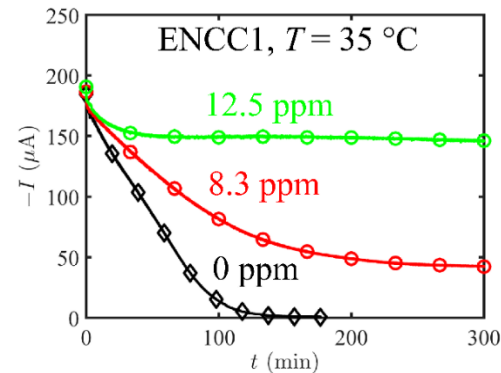
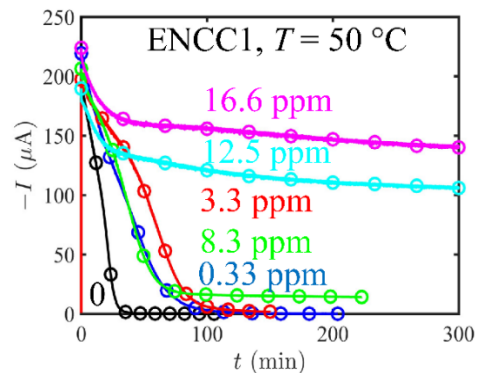
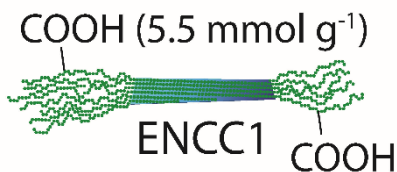
Sheikhi et al., ACS Applied Materials & Interfaces, 7:11301, 2015.

Yang et al., Biomacromolecules, 17:2240, 2016.

Tavakolian et al., Journal of Colloid and Interface Science, 541:444, 2019.

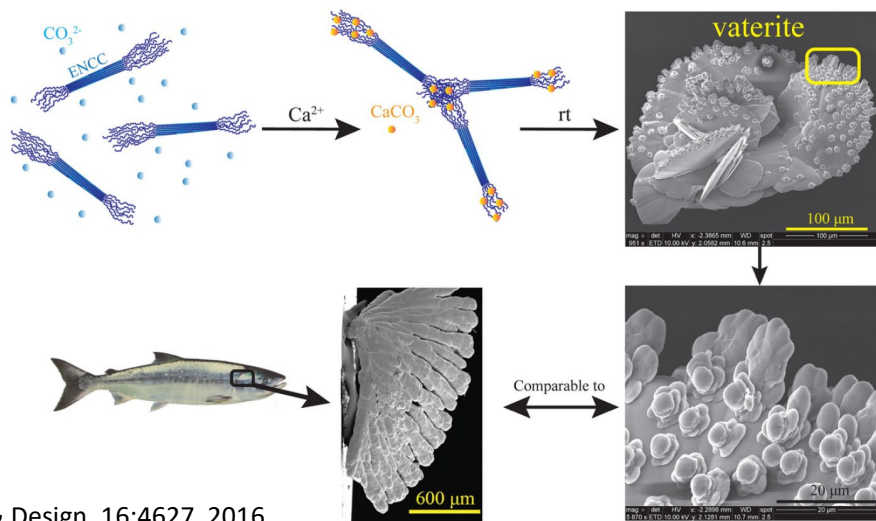
Part V: Unique applications

➤ Scale inhibition



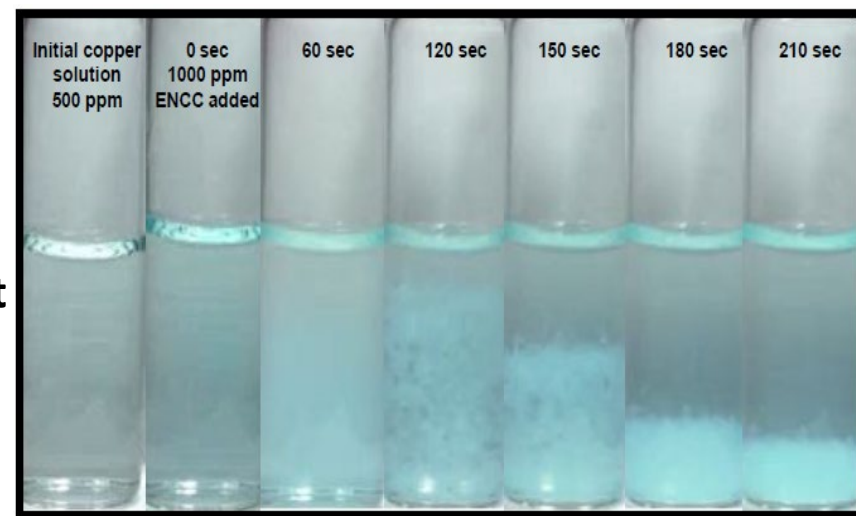
Sheikhi et al., Materials Horizons, 5:248, 2018.

➤ Biomimetic mineralization



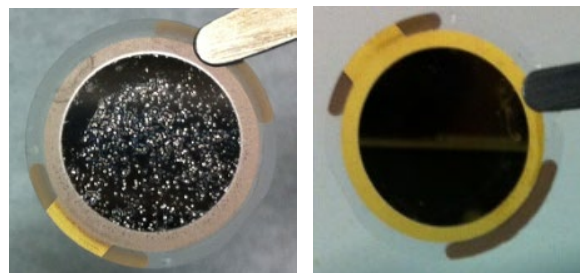
Sheikhi et al., Crystal Growth & Design, 16:4627, 2016.

➤ Water treatment



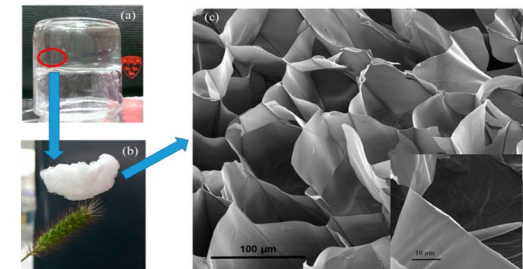
Sheikhi et al., ACS Applied Materials & Interfaces, 7:11301, 2015.

➤ Anti-scaling surfaces



Sheikhi et al., ACS Applied Materials & Interfaces, 10:34553, 2018.

➤ Lightweight materials



Yang and Sheikhi et al., Langmuir, 32:11771, 2016.

brain fog, or "chemo brain"

Foggy thinking and memory problems are often referred to as having "chemo brain." This side effect can cause further anxiety and stress during your recovery.

anxiety and depression

Chemotherapy and its side effects add to the stresses of everyday life and can become overwhelming, leading to anxiety or depression.

hot flashes and menopause

Chemotherapy can affect the menstrual cycle, cause hot flashes, and trigger early menopause.

weak heart

Chemotherapy can weaken the heart muscle, especially if you have a preexisting heart condition.

nausea and vomiting

Nausea is one of the most common symptoms of chemotherapy.

discolored and cracked nails

During chemo treatments, you might develop brown, cracked fingernails and toenails.

loss of appetite

Chemotherapy can disturb the entire digestive system, causing a wide variety of unpleasant symptoms that disturb appetite.

sexual dysfunction

A low libido is common after going through chemo. If symptoms are severe, it might be hard to "get in the mood," but it's usually a temporary issue.

skin sensitivity

Chemotherapy can cause dry, irritated skin. Your skin may also develop sensitivity to sunlight.

hair loss

Chemo can damage hair follicles and cause them to temporarily stop producing new hairs. Hair loss can be disheartening, but remember that this side effect is only temporary.

mouth sores

The gums, insides of the cheeks, tongue, and throat are prone to sores. Early treatment can help prevent infections.

lower blood cell count

Chemotherapy can interfere with the body's ability to produce healthy blood platelets as well as red and white blood cells. Low blood counts can lead to a variety of serious side effects.

digestive distress

Chemotherapy can cause constipation, diarrhea, and other forms of digestive distress. As a result of this, you may also experience weight loss and weakness.

decreased urination

Decreased urination may be a sign that chemotherapy is harming the kidneys.

red urine

Your urine may be red due to certain chemotherapy drugs working their way out of your system.

bone loss

Osteoporosis, or loss of bone density, can be a long-term side effect. Women are especially susceptible to bone loss. Chemotherapy could worsen these effects as you age.

poor coordination and tired muscles

Tired, achy muscles can interfere with balance, coordination, and motor skills.

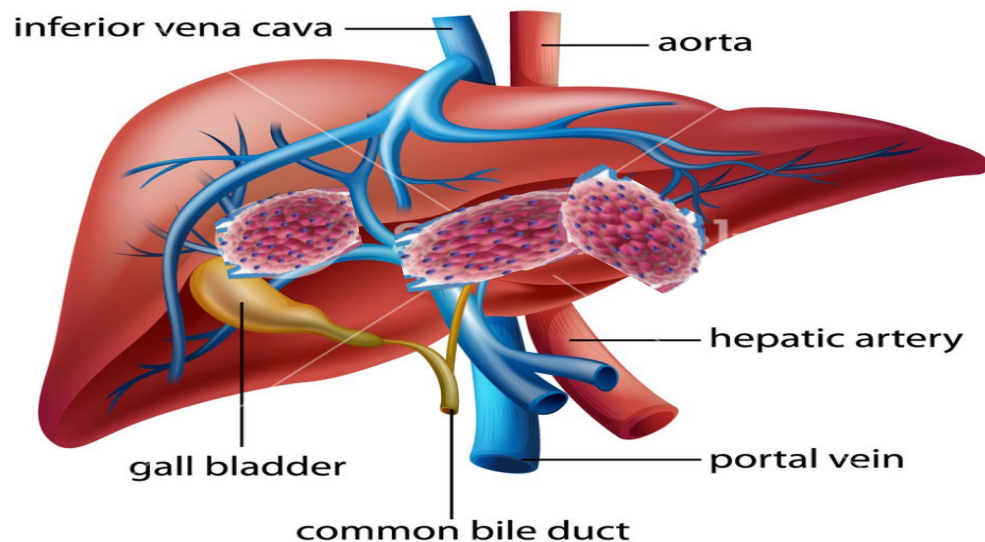
swollen hands and feet

Swollen hands and feet may be a sign that your kidneys are working overtime.

Drug capture



Human Liver Anatomy

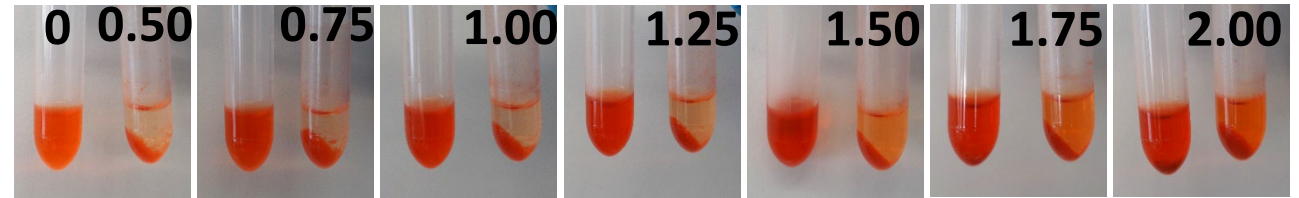


HCNC for capturing off-target drugs

Magnetic device
 $25 \mu\text{g mL}^{-1} \rightarrow 5 \mu\text{g mL}^{-1}$

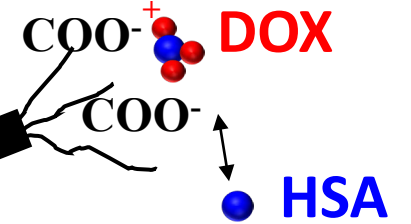


Blumenfeld et al., Nature Communication (2018) (Grubbs @ Caltech)

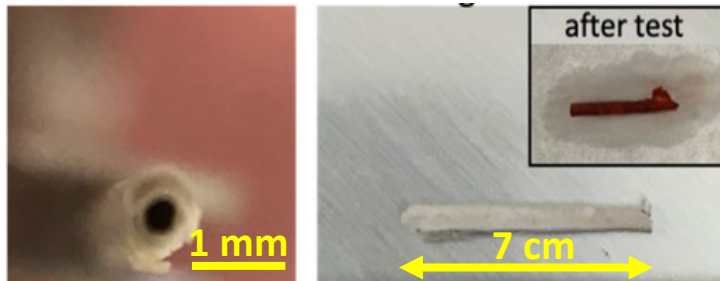


ENCC/DOX

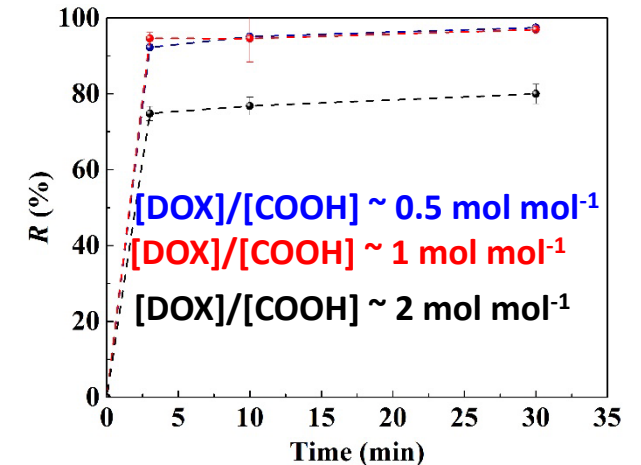
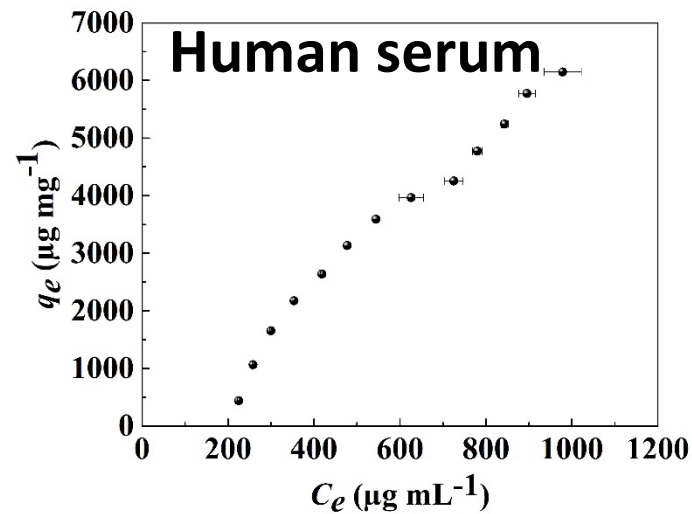
$6000 \mu\text{g mg}^{-1}$



ENCC device
 $100 \mu\text{g mL}^{-1} \rightarrow 10 \mu\text{g mL}^{-1}$

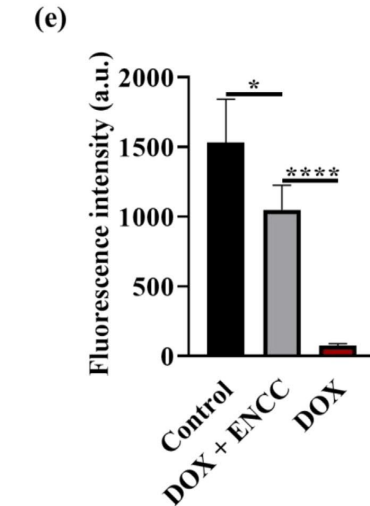
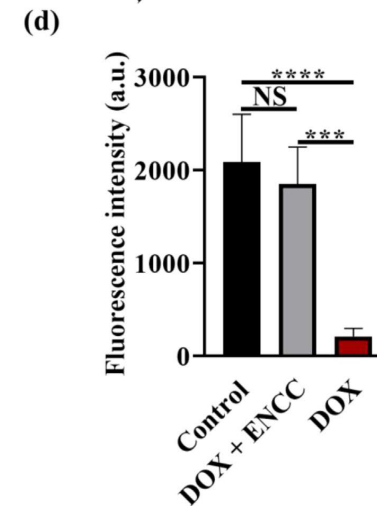
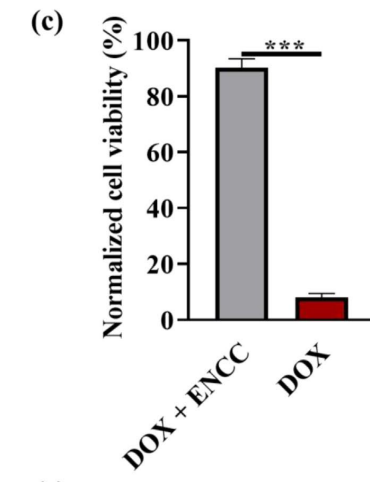
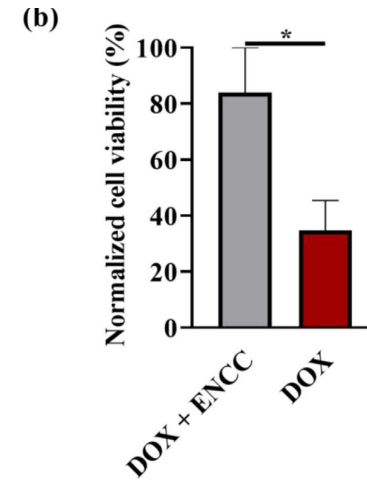
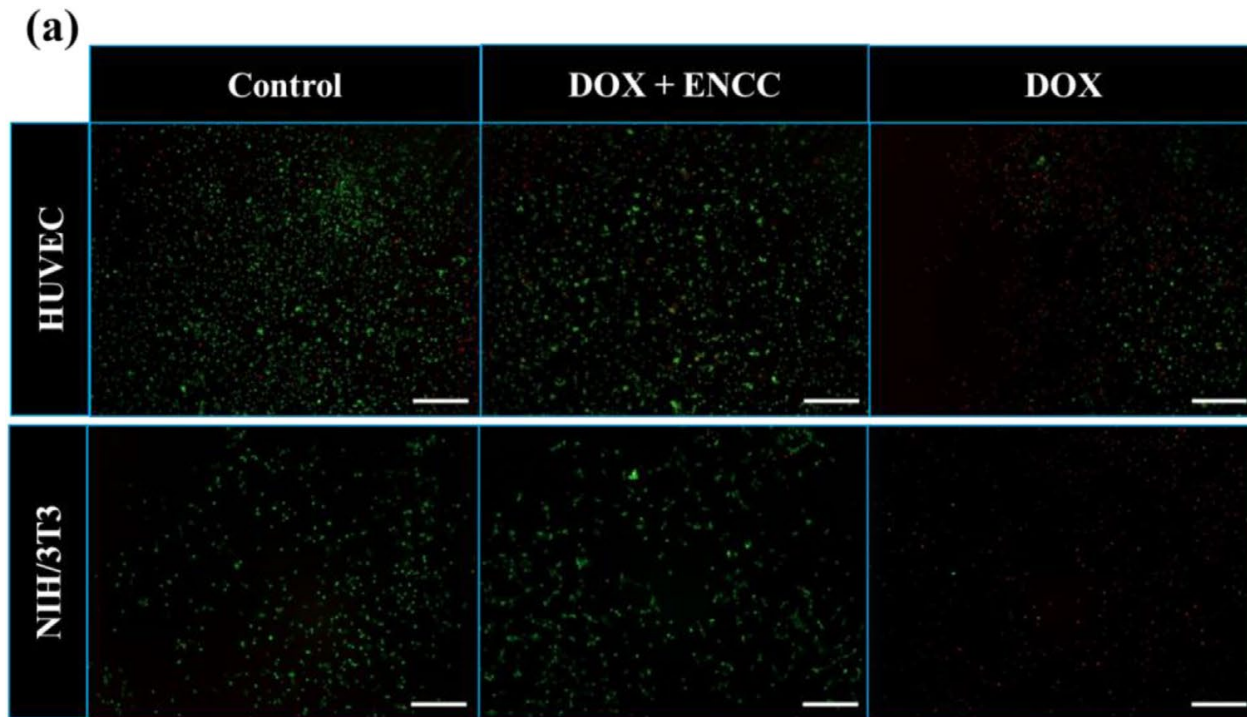


$V = 100 \times 5 \sim 500$ time smaller



Young and Sheikhi et al., Materials Today Chemistry, 23:100711, 2022.
 Provisional Pending Application filed.

HCNC for capturing off-target drugs



Young and **Sheikhi** et al., Materials Today Chemistry, 23:100711, 2022.
Provisional Pending Application filed.

HCNC for the selective removal of rare earth elements (REEs)

Neodymium — An Element for a Modern World

ACS Green Chemistry Institute
Chemistry for Life®
AMERICAN CHEMICAL SOCIETY

THE PERIODIC TABLE'S ENDANGERED ELEMENTS

■ Limited availability, future risk to supply
■ Rising threat from increased use
■ Serious threat in the next 100 years

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	* 57-71 La-Lu	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	** 89-103 Ac-Lr	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson
*Lanthanide series		57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium	
**Actinide series		89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium	

60
Nd
Neodymium

Source: Chemistry Innovation Knowledge Transfer Network



MAGNETS 37%
Optical drives, speakers, smartphones, wind turbines, electric /hybrid vehicles



PHOSPHORS & LUMINESCENCE 32%
Displays, LEDs, lamps



METAL ALLOYS & BATTERIES 14%
NiMH batteries, fuel cells



GLASS POLISHING & CERAMICS 9%
Coloring and decoloring agents in glass

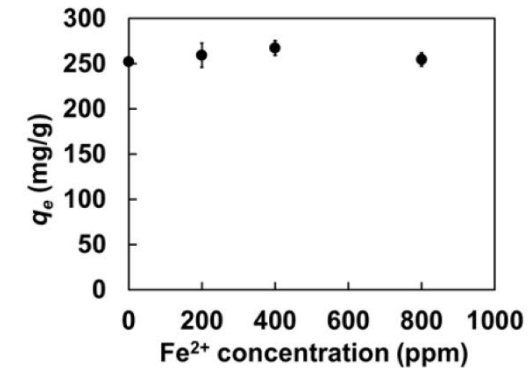
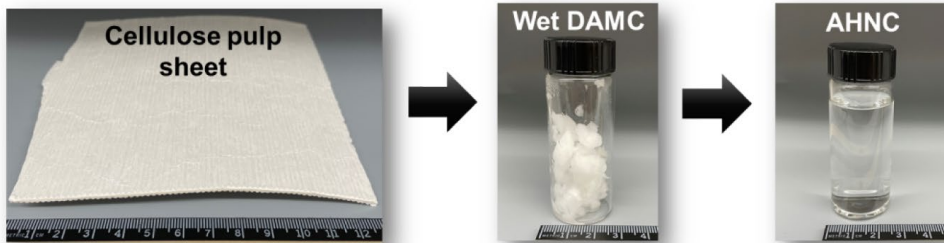
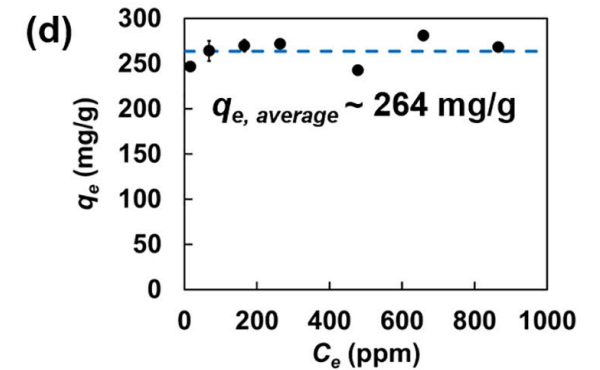
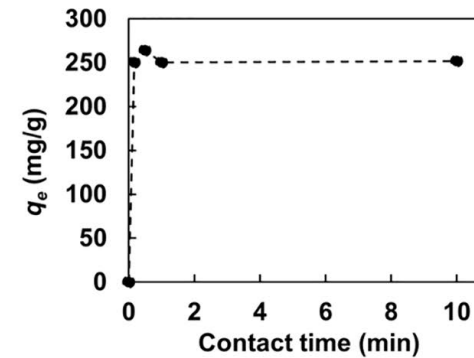
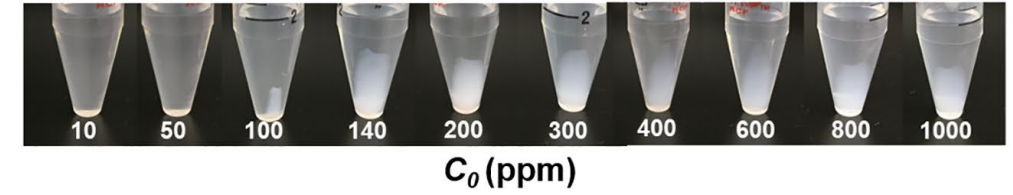
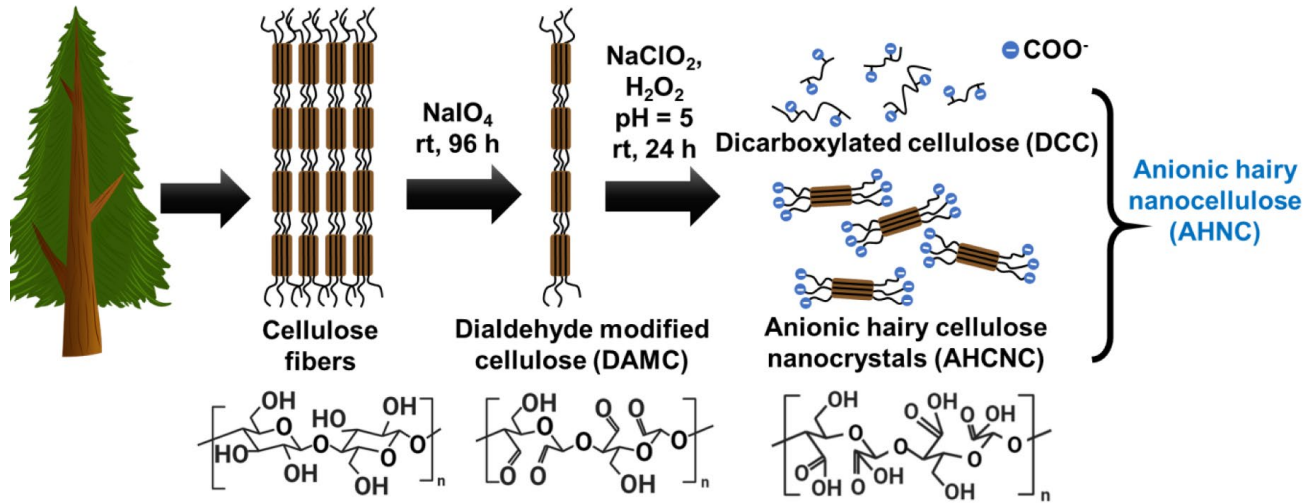


CATALYSTS 5%
Automotive & chemical processes



Creating a sustainable, circular economy for neodymium will empower us to meet U.N. Sustainable Development Goal #11: Sustainable Cities and Communities.

HCNC for the selective removal of rare earth elements (REEs)



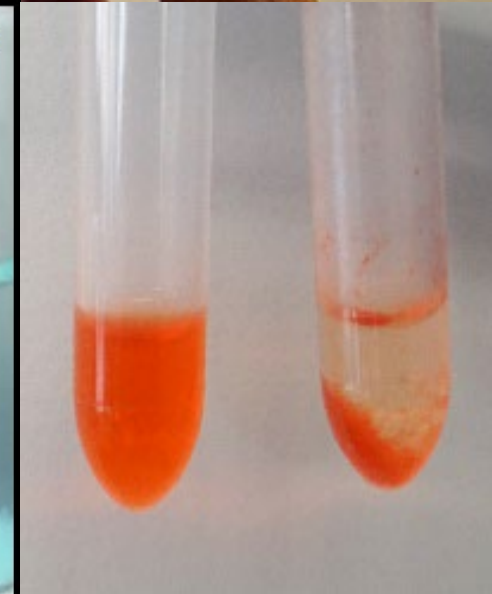
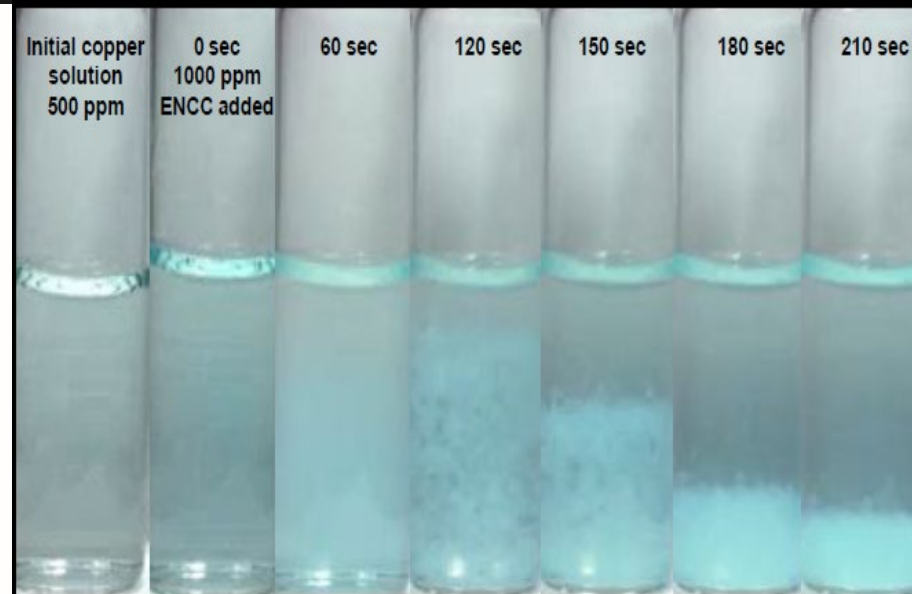
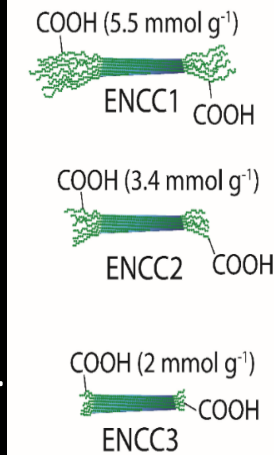
Wamea and **Sheikhi** et al., Chemical Engineering Journal, 428:131086, 2022.
Provisional Patent Application filed (2022).

Future directions

- 1) Pathological crystal inhibitors
- 2) Pickering emulsions
- 3) Food additives
- 4) Water treatment
- 5) Blood purification
- 6) Bioadsorption
- 7) Sensors
- 8) Additive manufacturing
- 9) Inorganic nanoparticle synthesis
- 10) Antifouling coatings



Hairy nanocelluloses

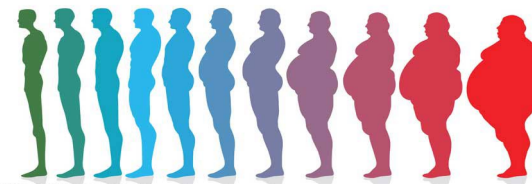


Conclusions

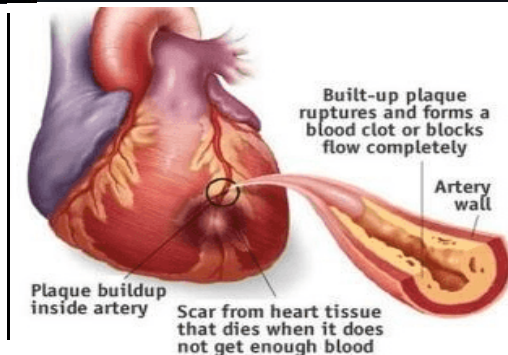
- 1) HCNC has unique colloidal properties.
- 2) HCNC is an emerging sustainable nanomaterial for environmental and healthcare applications.
- 3) Scale up of HCNC could be the next step in democratizing its use.



OBESITY IS NOW A GLOBAL EPIDEMIC!

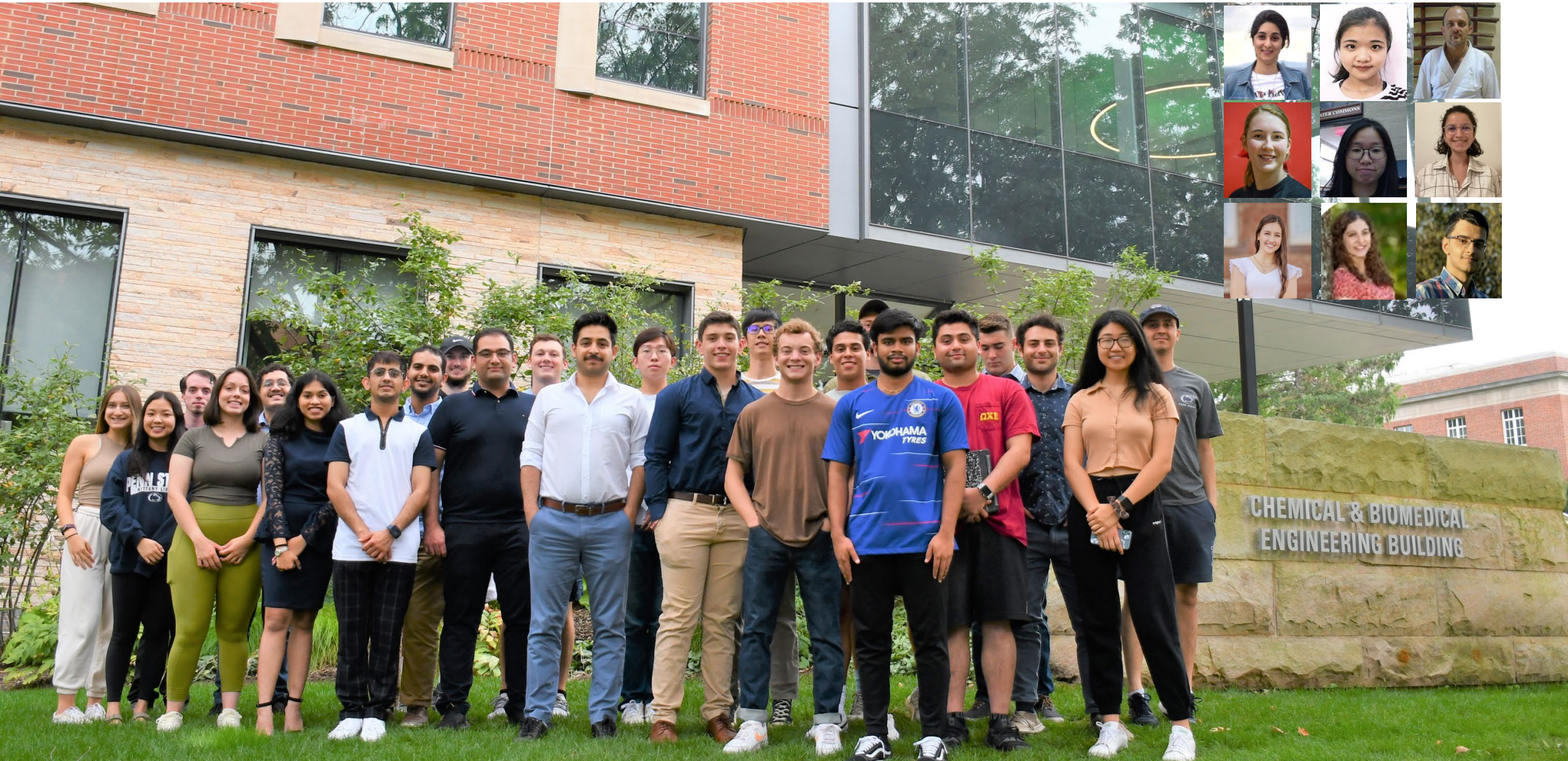


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Acknowledgments

Sheikhi lab members:



From Left to Right: Jules, Rhea, Kyler, Mica, Aneesh, Shambhavi, Sam, Nawaf, Sean, Arian, Carter, Amir, Zeming, William, Shang-Lin, Colin, Gerald, Luke, Naveen, Daksh, Christian, Alex, Jenna, Zaman
From Top to Bottom: Roya, Hai, Angelo, Marisa, Shufang, Catherine, Caitlyn, Mitchel, Sina

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