JULY 24–27, 2018

ISBBB 2018 Circular Economy for Bioproducts Innovation

15th International Symposium on Bioplastics, Biocomposites and Biorefining

Guelph, Canada

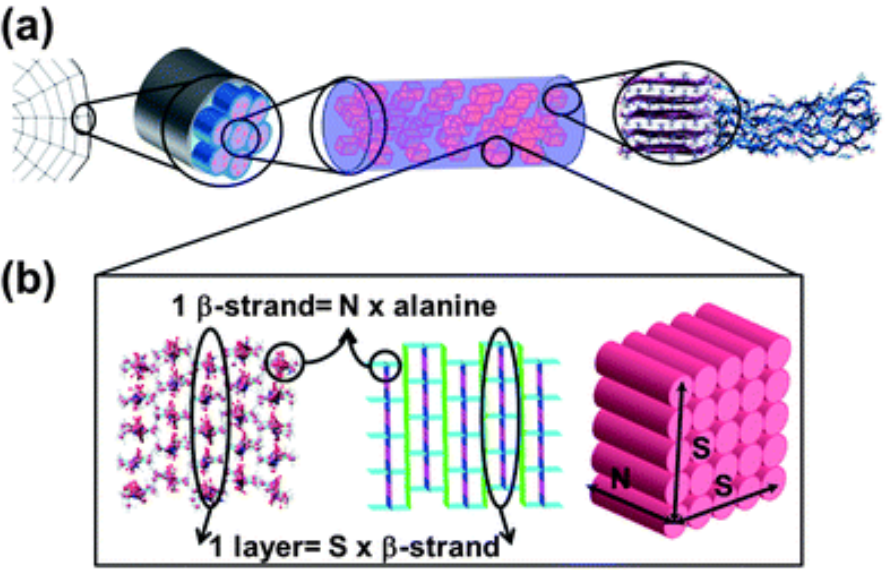
Hierarchical Structures Assembled from Cellulose Nanofibrils for Advanced Applications

Feng Jiang
Assistant Professor
Department of Wood Science
University of British Columbia

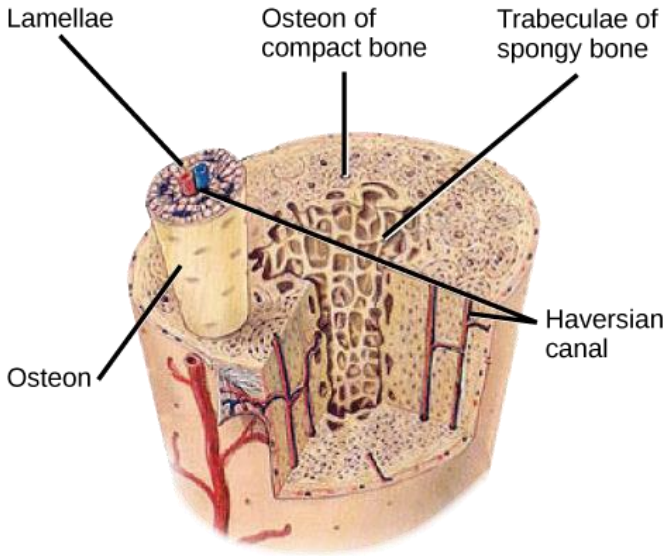
July 27, 2018,
Guelph, Ontario, Canada



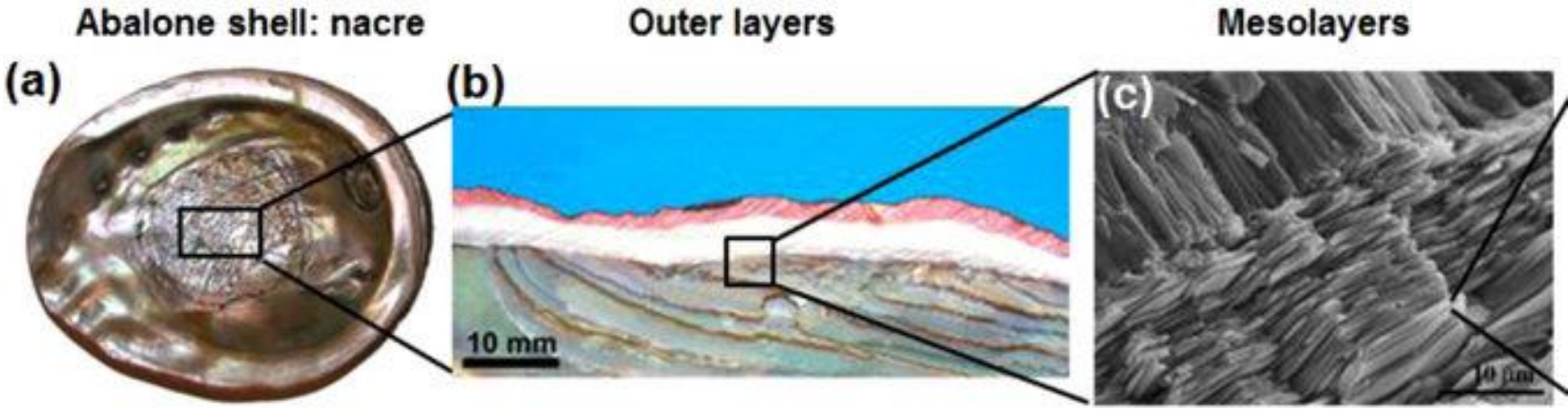
Hierarchical structure in nature



Soft matter, 7, 8142-8148 (2011)

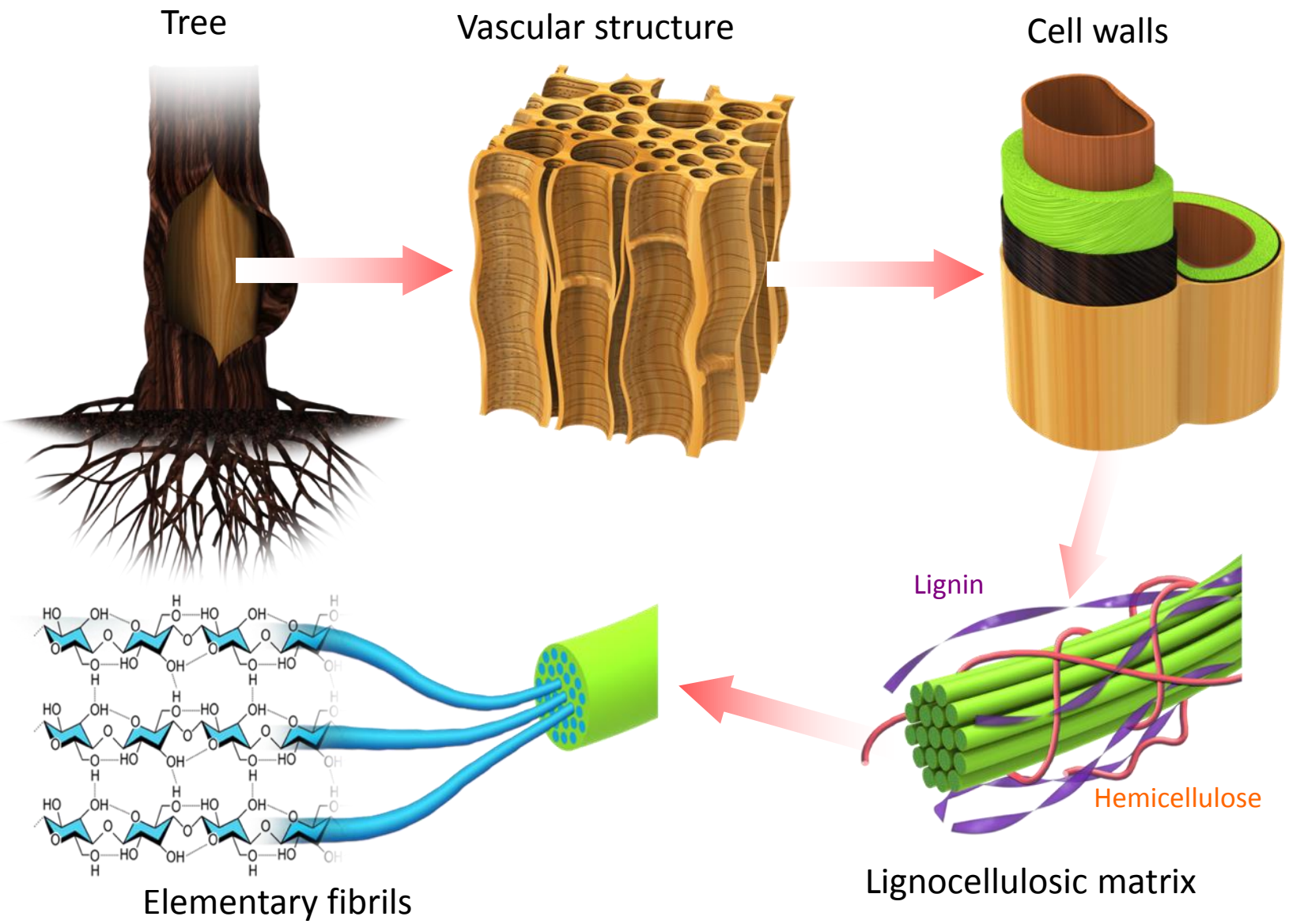


https://commons.wikimedia.org/wiki/File:Figure_38_02_04.png



J. Mech. Behav. Biomed. Mater. 53, 200-209 (2016)

Hierarchical structure in trees



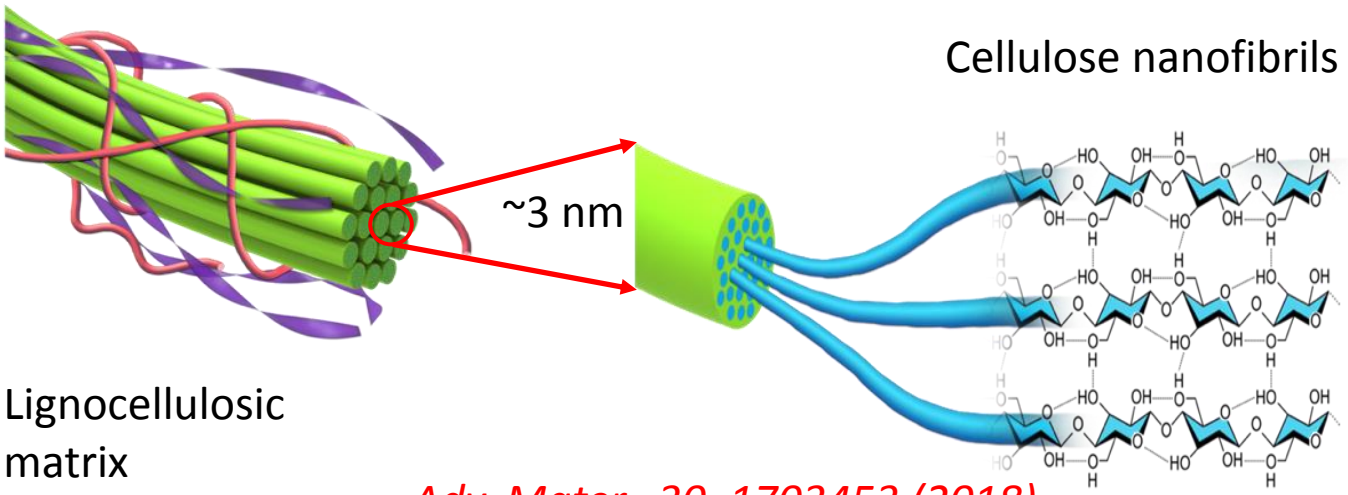
Adv. Mater., 30, 1703453 (2018)

Outline

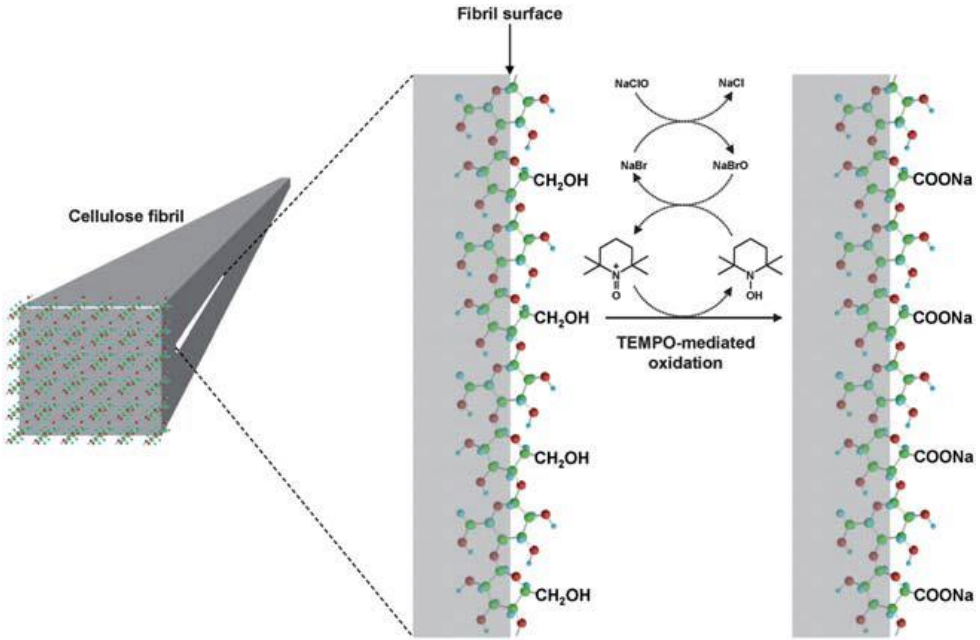
- Cellulose nanofibrils
- Self-assembly
  - Sub-micron and nano fibres
  - Aerogels
- Applications
  - Environmental remediation
  - Energy storage devices



Cellulose nanofibrils



Adv. Mater., 30, 1703453 (2018)



Why cellulose nanofibrils:

- High crystallinity;
- Excellent mechanical properties;
- Low thermal expansion coefficient;
- Nanoscale dimension;
- High specific surface area;
- Abundant surface functional groups;
- High aspect ratio.

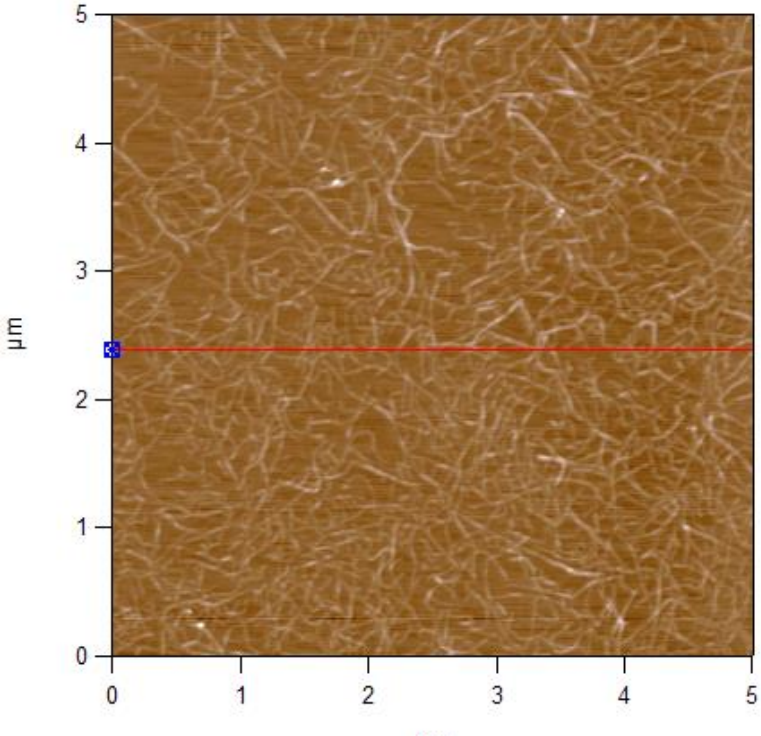
Biomacromolecules, 2010, 11, 1696-1700

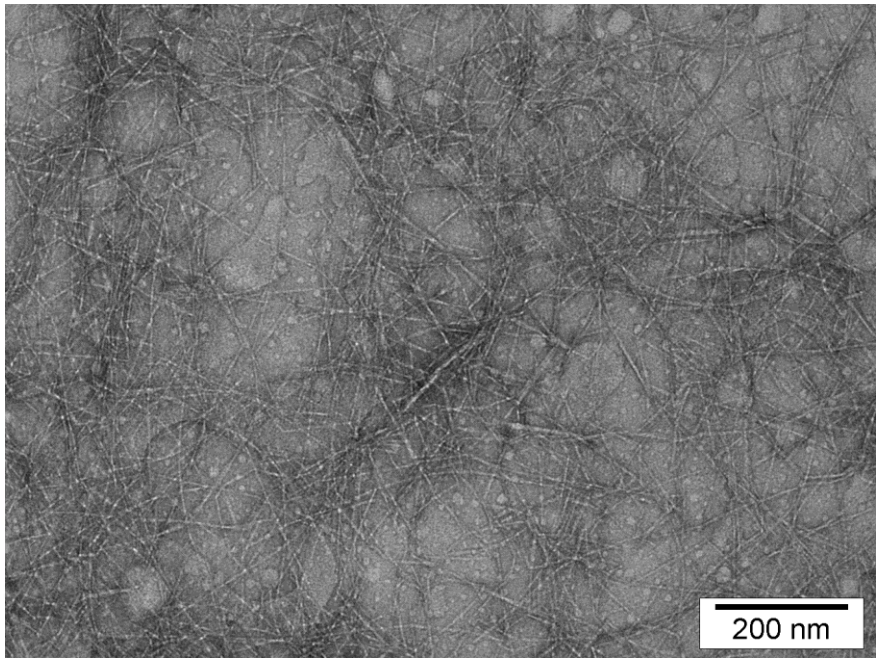
Cellulose nanofibrils – characteristics



Characteristics:

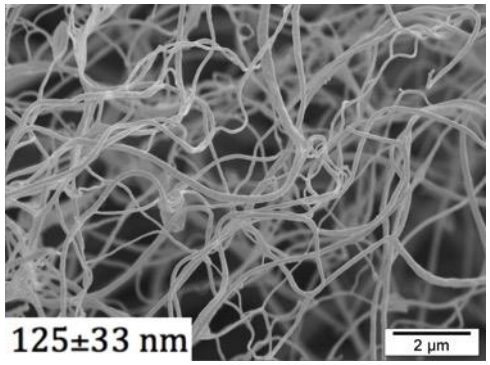
- Long, flexible
- D: < 2 nm, L: up to 1 µm
- Aspect ratio: 500-1000
- Surface charge: 1.29 mmol/g
- Yield: 96%
- Crystallinity: 50-70 %



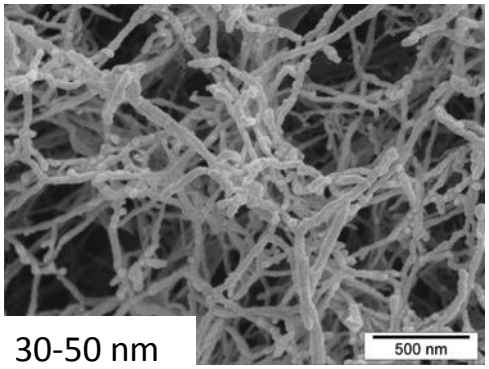


Self-assembled hierarchical structures

Sub-micron fibers

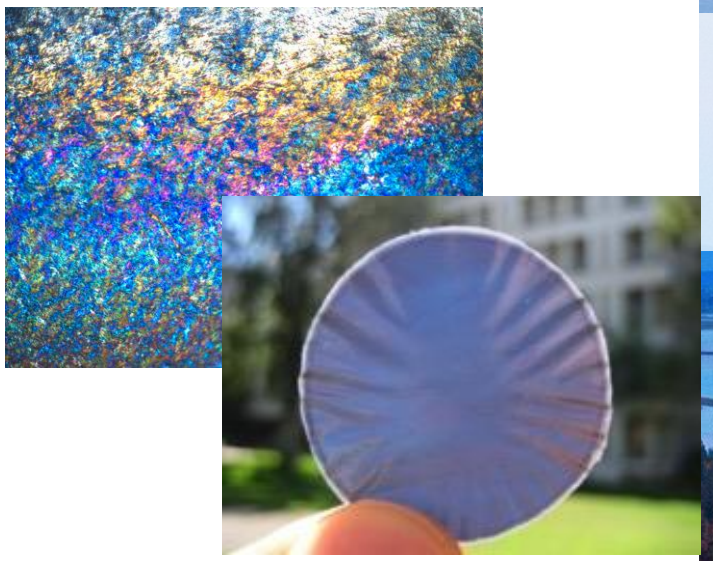


Nano-fibers



ACS Appl. Mater. Interfaces. 2014;
ACS Sustainable Chem. Eng. 2016;

Film



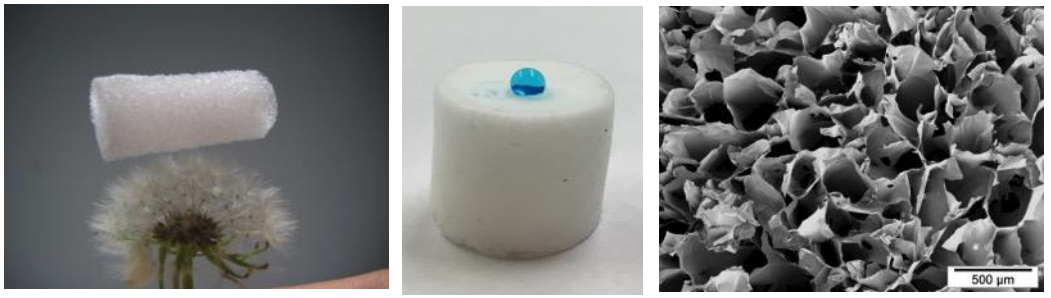
Biomacromolecules, 2015

Hydrogels



ACS Appl. Mater. Interfaces 9, 2825 (2017)

Aerogels



J. Mater. Chem. A. 2, 350 (2014);
J. Mater. Chem. A. 2, 6337 (2014);
ACS Omega 3, 3530-3539 (2018)

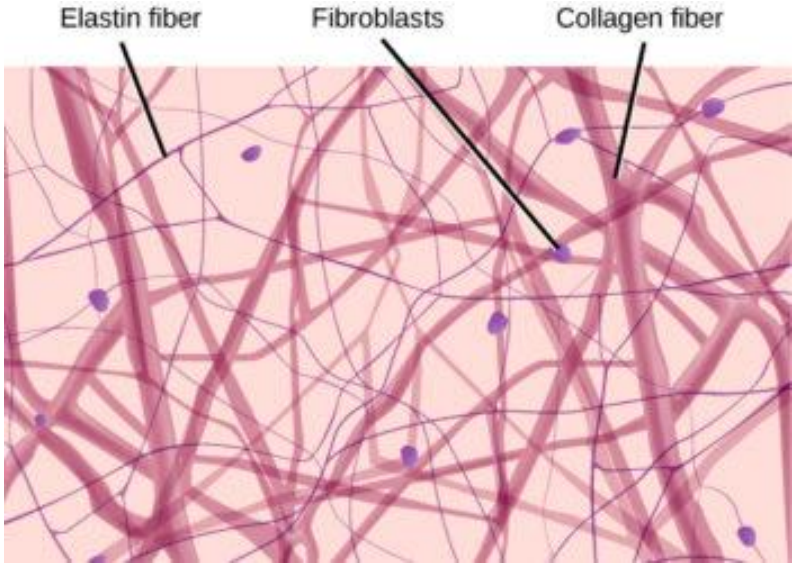
Fibrous materials



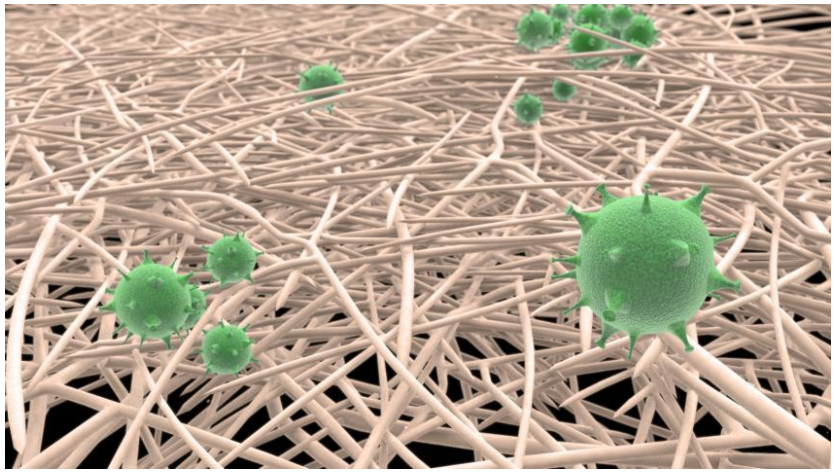
Ceramic fibre insulation materials



Carbon fibre reinforced polymer

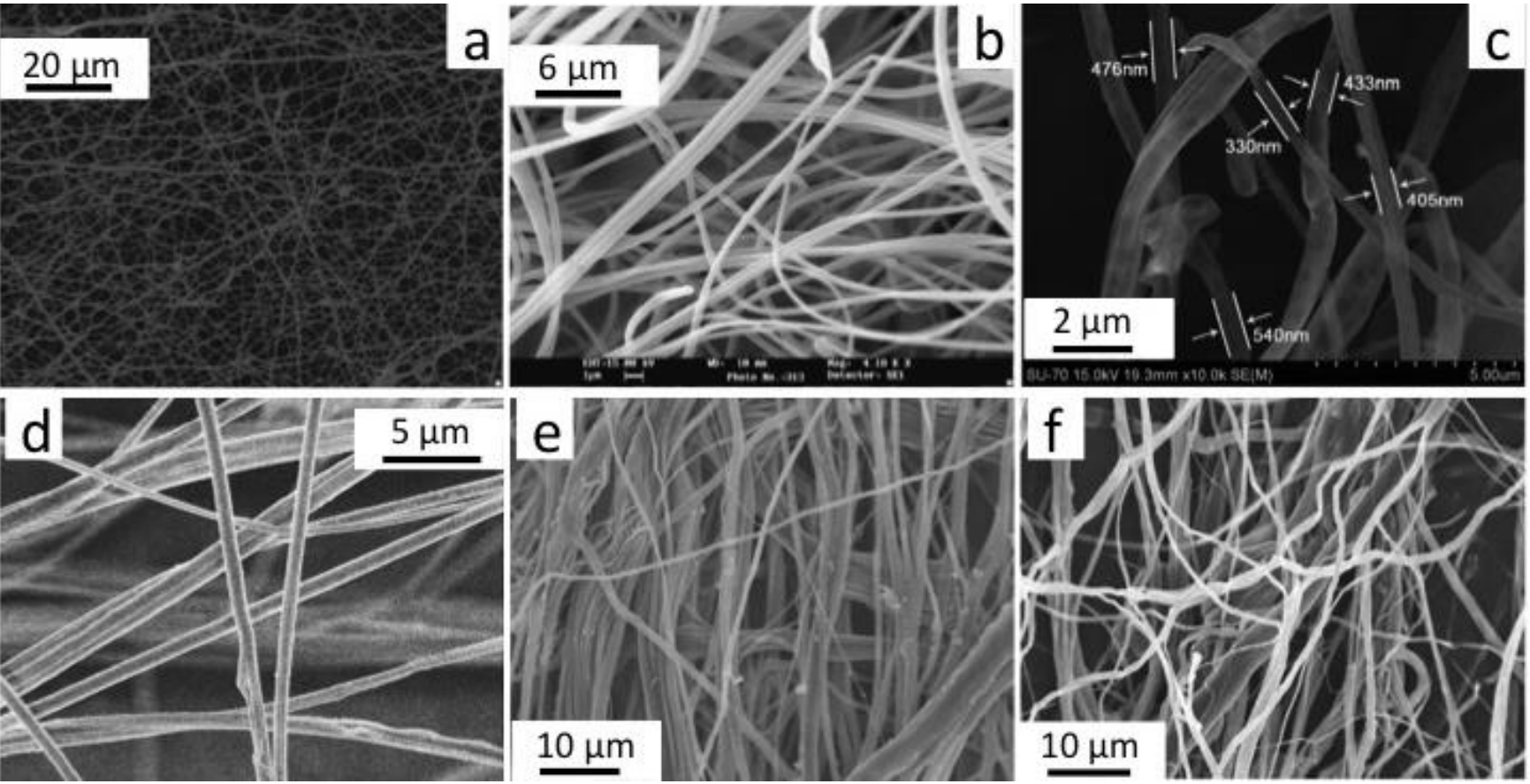


https://courses.lumenlearning.com/wm-biology2/chapter/connective-tissues/



https://phys.org/news/2014-03-nano-paper-filter-viruses.html

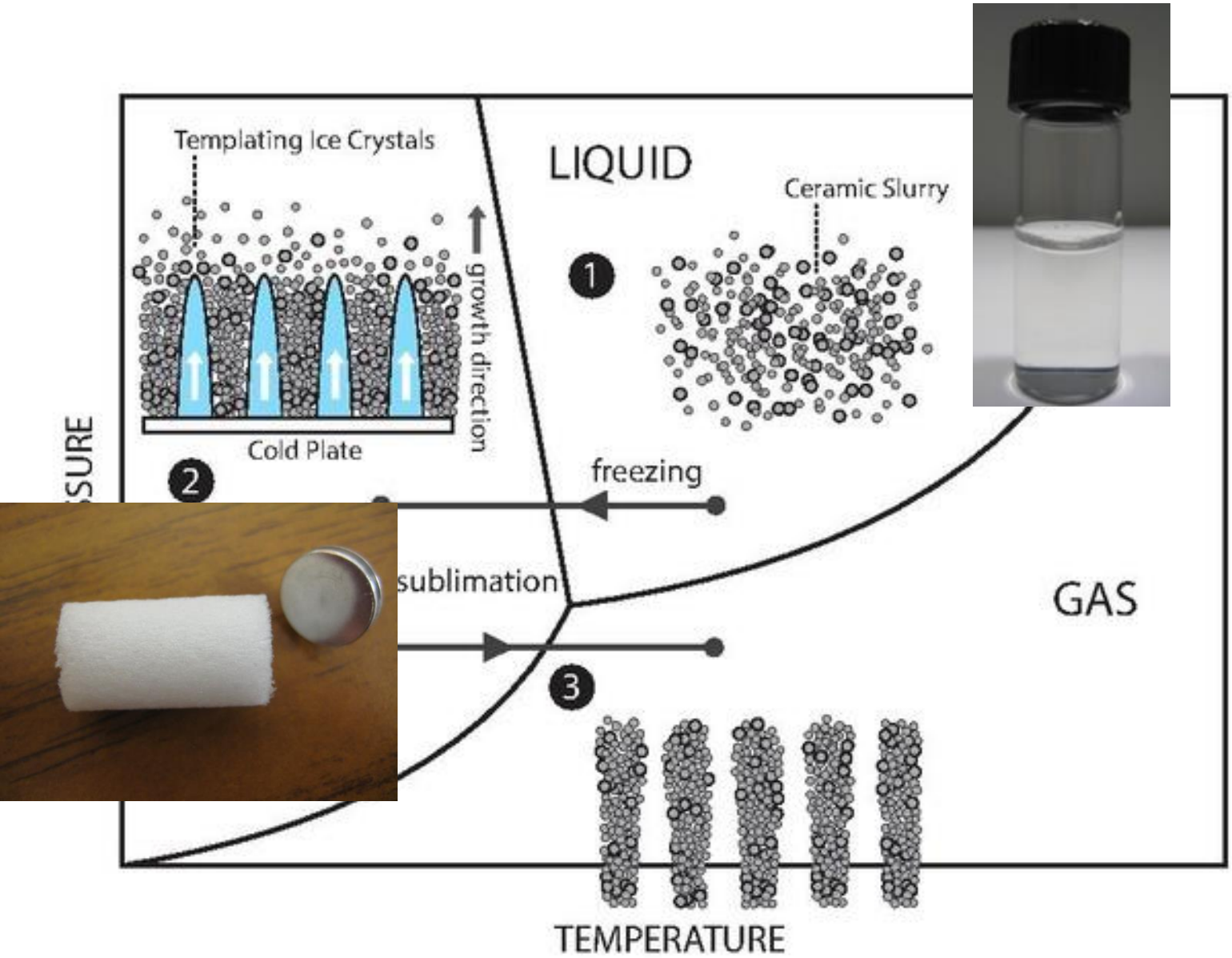
Formation of sub-micron fibres - electrospinning



a. Cellulose/8% LiCl/DMAc
b. Cellulose/NMMO/H_2O
c. Cellulose in [C_2mim][CH_3CO_2] ionic liquid
d. Cellulose in AMMIMCl/DMSO
e. Cellulose in [C_2min][OAC]/DMF
f. Cellulose in [C_2min][OAC]/DMAc

Handbook of Fibrous Materials, Wiley, 2019

Formation of sub-micron fibres – ice crystal templating



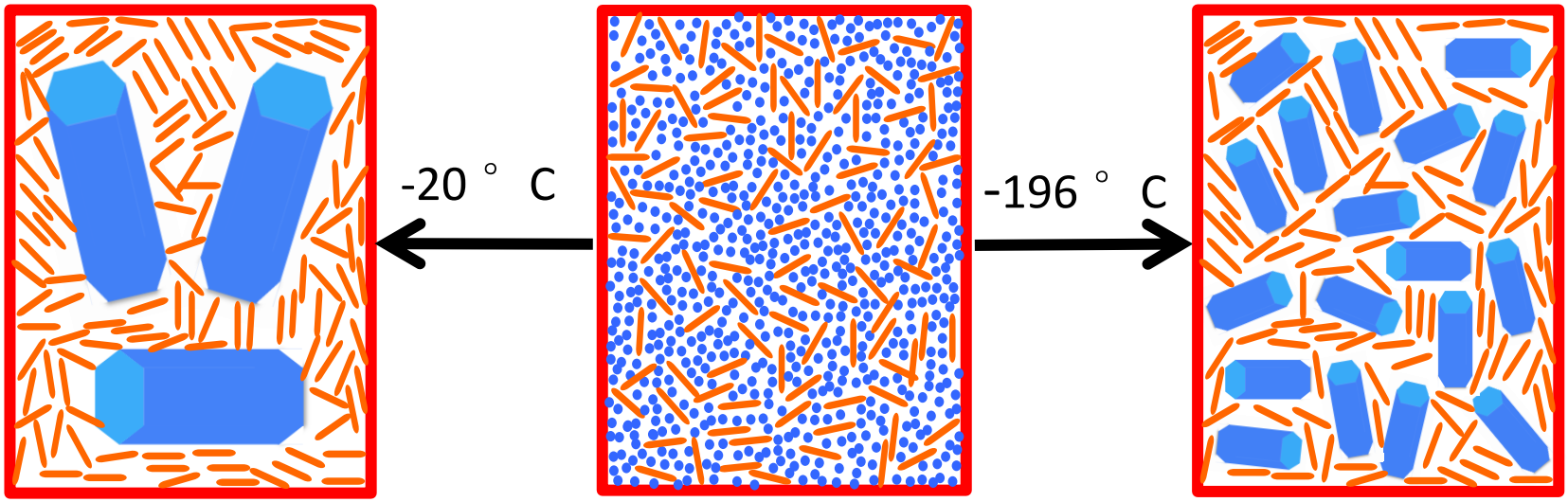
Assembly into sub-micron fibres

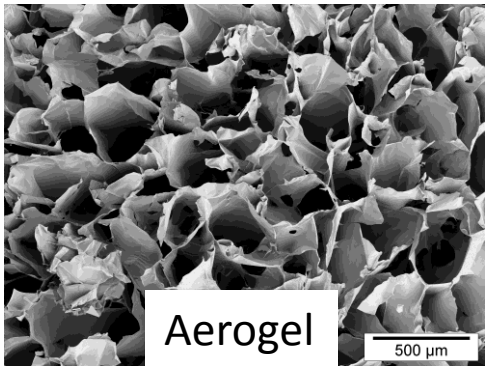
-20 °C

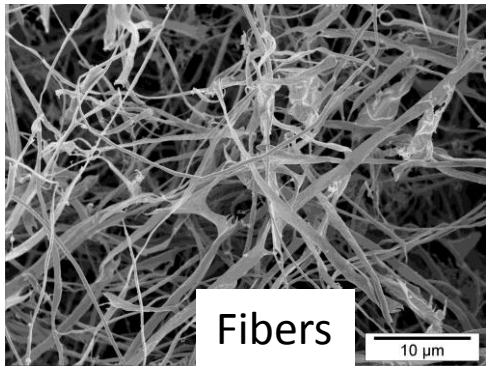
- Slower ice nucleation rate;
- Large ice crystals.

-196 °C

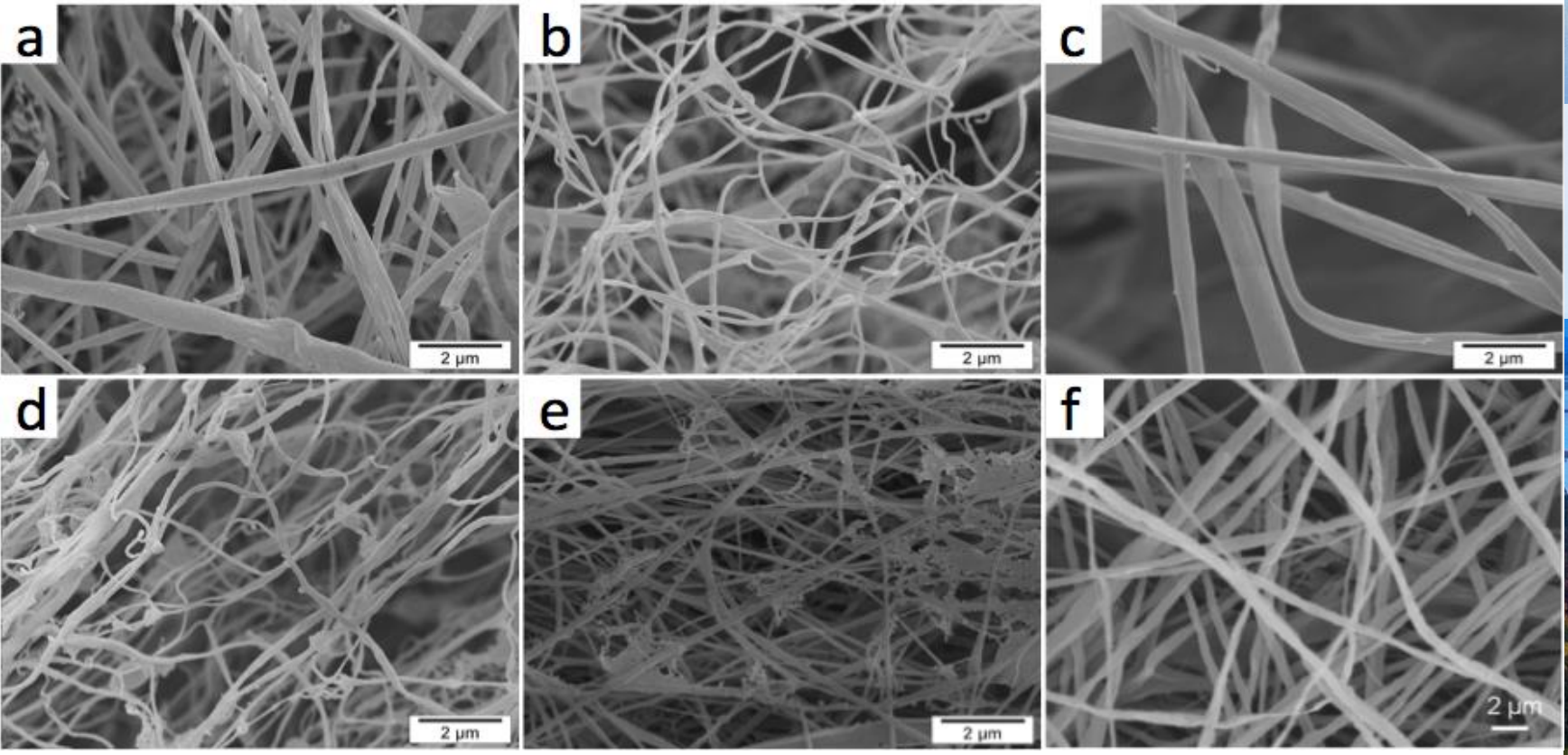
- Fast ice nucleation rate;
- Small ice crystals.







Formation of sub-micron fibres – ice crystal templating



a. Cellulose nanocrystals
b. TEMPO oxidized cellulose nanofibrils
c. TEMPO oxidized cellulose nanofibrils
d. Blending cellulose nanofibrils
e. Cellulose nanofibrils from ACC
f. Ultrasonication cellulose nanofibrils

Advantages:

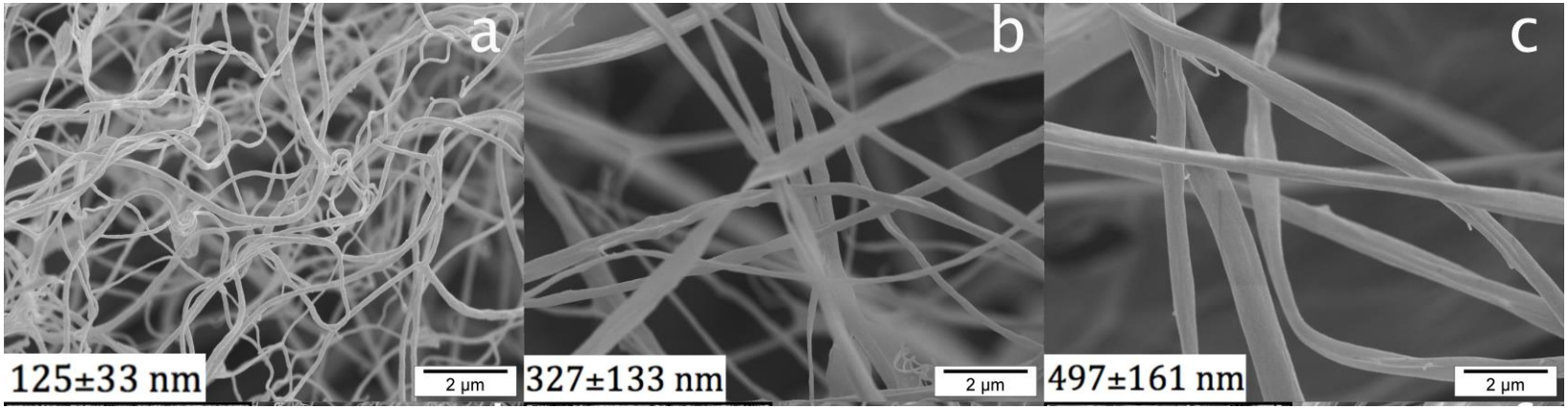
- Preservation of natural Cellulose I crystal structure
- No solvent to dissolve cellulose
- Controllable diameters and surface areas

Handbook of Fibrous Materials, Wiley, 2019

Effects of surface charge

mmol/g NaClO/cellulose:

1.5 mmol/g	3 mmol/g	5 mmol/g
CNF Yield: 60.3%	**84.5%**	**96.8%**
D: 2-10 nm **L: several micrometers**	**D: 2-8 nm** **L: 1-2 µm**	**D: <2 nm** **L: up to 1 µm**
Surface C6 OH-to-COOH:		
32.2%	**50.3%**	**70.6%**

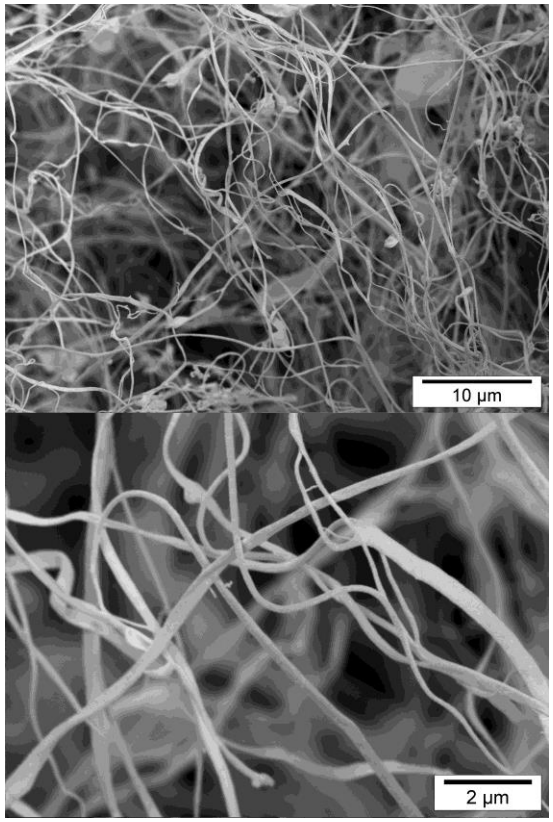


CrI:	**70.8%**	**71.5%**	**64.3%**
ζ Potential (mV):			
	-69.3±0.3	**-86.3±1.6**	**-97.6±1.5**

RSC Advances. 2013, 3, 12366-12375

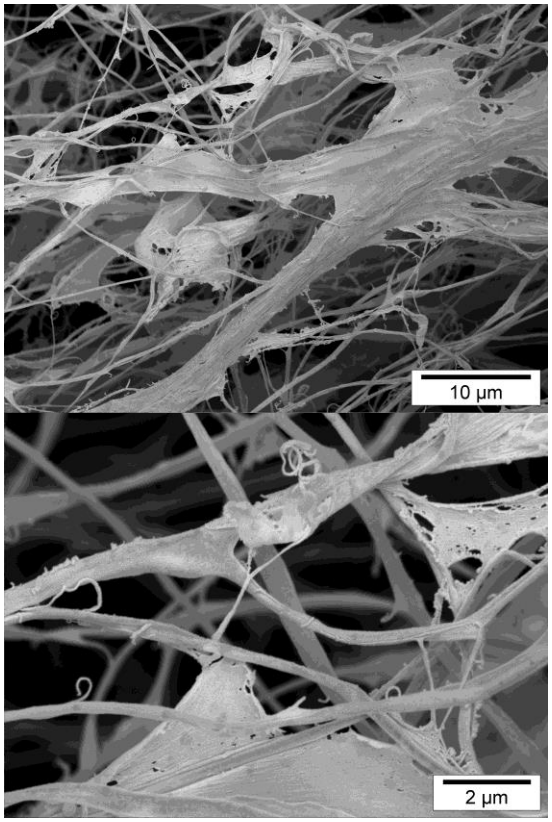
Effects of CNF concentration

0.01%



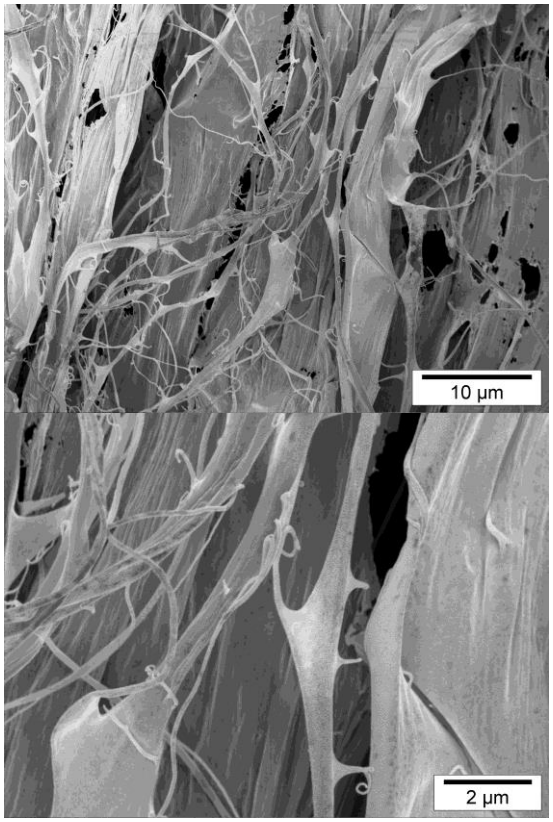
Fibers
D: 236 ± 95 nm

0.05%



Fibers and films
D: 375 ± 105 nm

0.1%



Fibers and films
D: 393 ± 144 nm

ACS Applied Materials and Interfaces. 2014, 6, 20075-20084

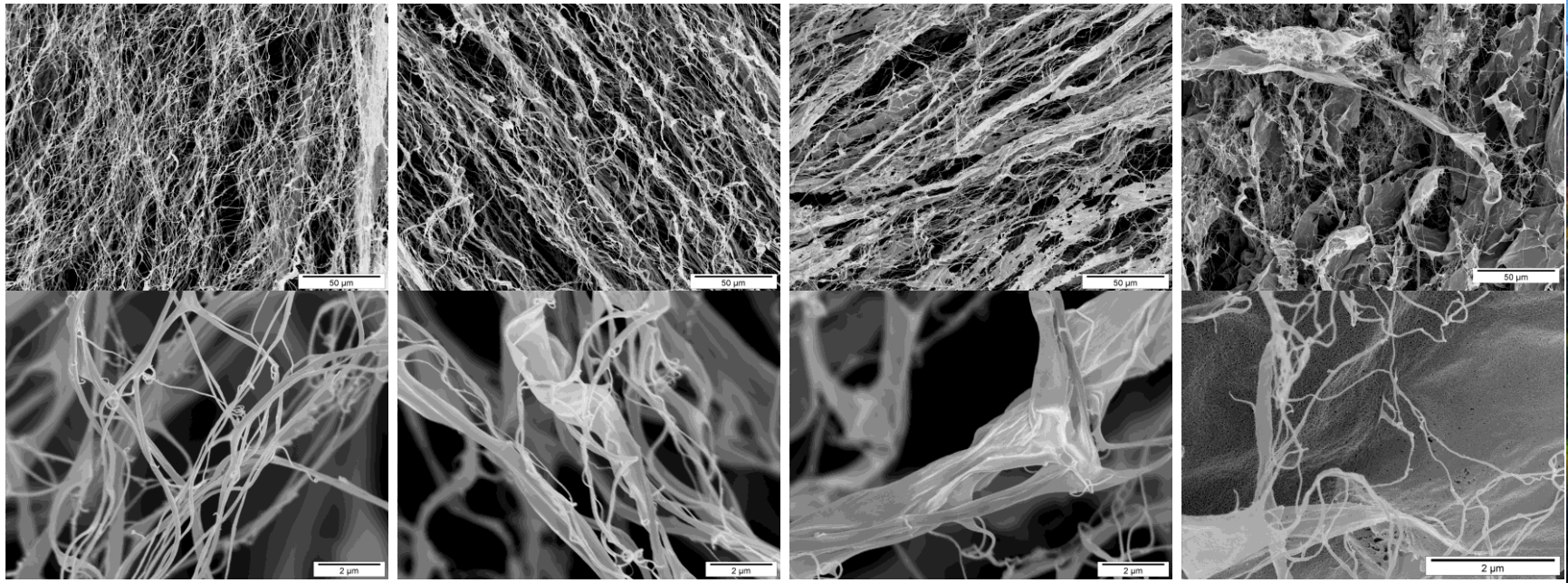
Effects of CNF surface charge protonation

COOH content (mmol/g):

0.12	0.28	0.72	1.16

COONa content (mmol/g):

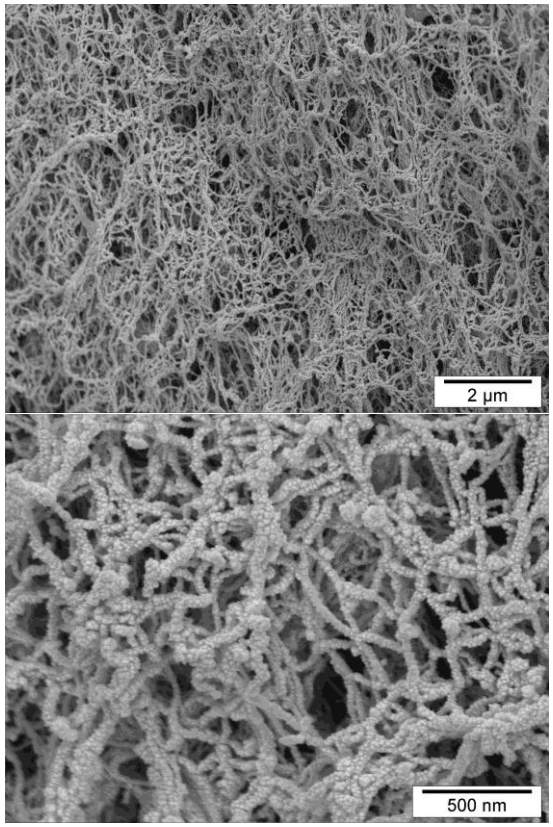
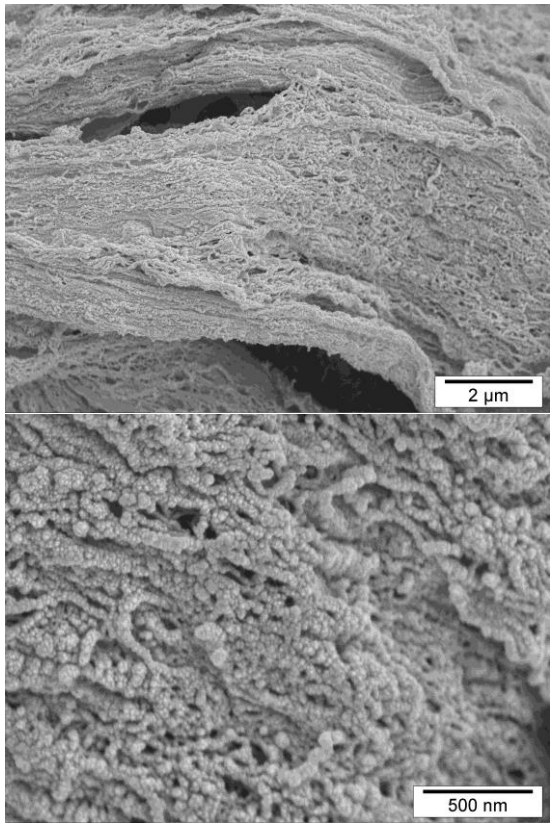
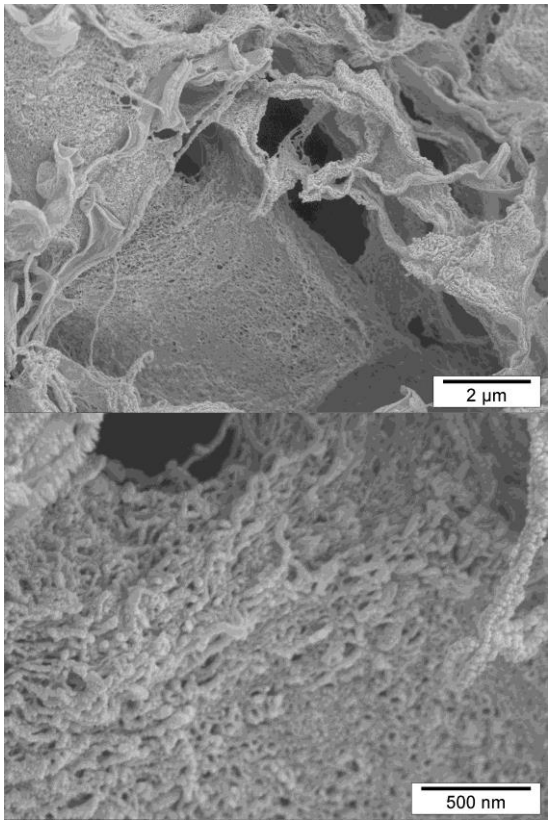
1.02	0.88	0.44	0



ACS Sustainable Chemistry & Engineering. 2016, 4, 1041-1049

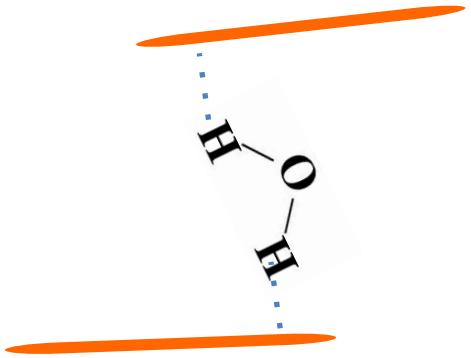
Effects of tert-butanol

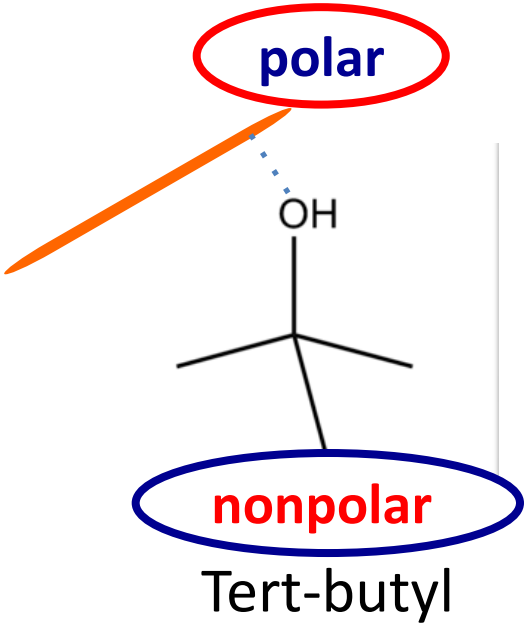
CNC Concentrations:

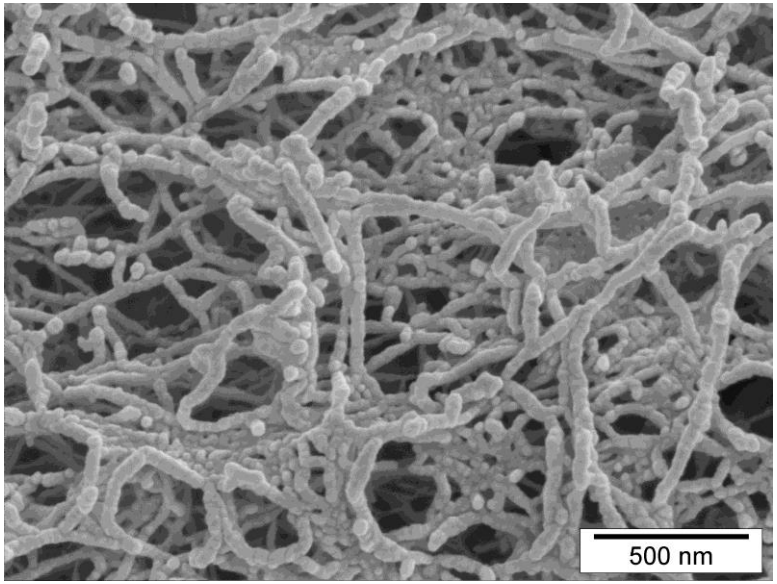
0.01%	0.05%	0.1%
		
Nanofibers **D: 33 ± 7.1 nm**	**Nanofibers and films** **D: 46 ± 8.9 nm**	**Nanofibers and film** **D: 42 ± 6.8 nm**

ACS Applied Materials and Interfaces. 2014, 6, 20075-20084

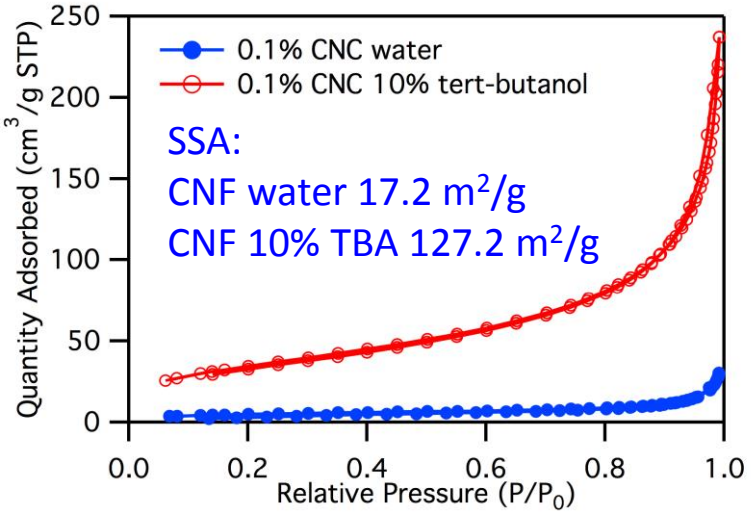
Effects of tert-butanol





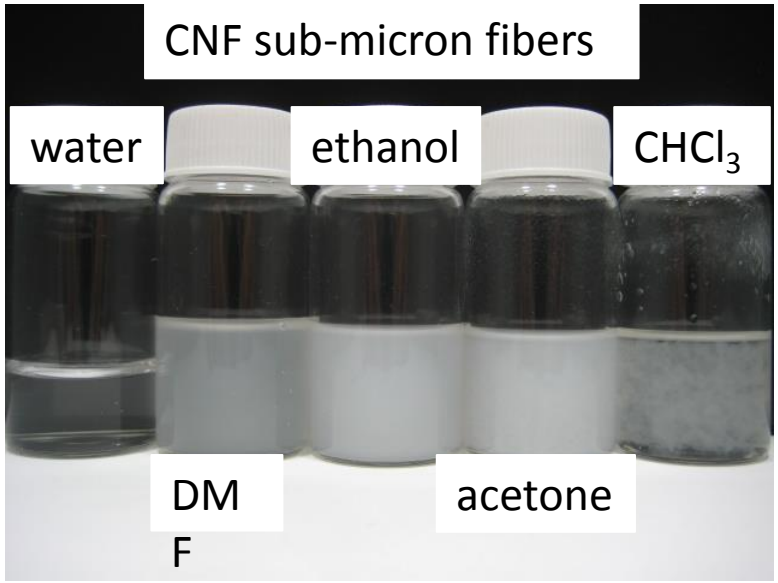


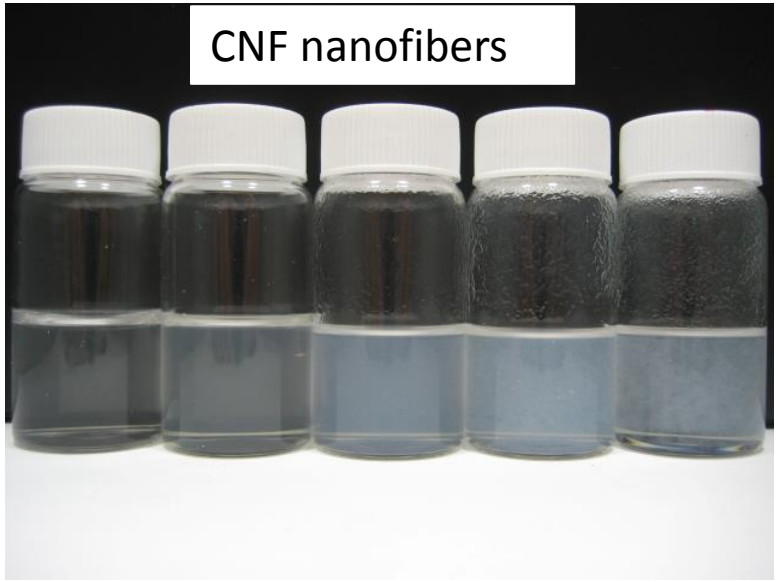
D: 34.3 ± 7.2 nm

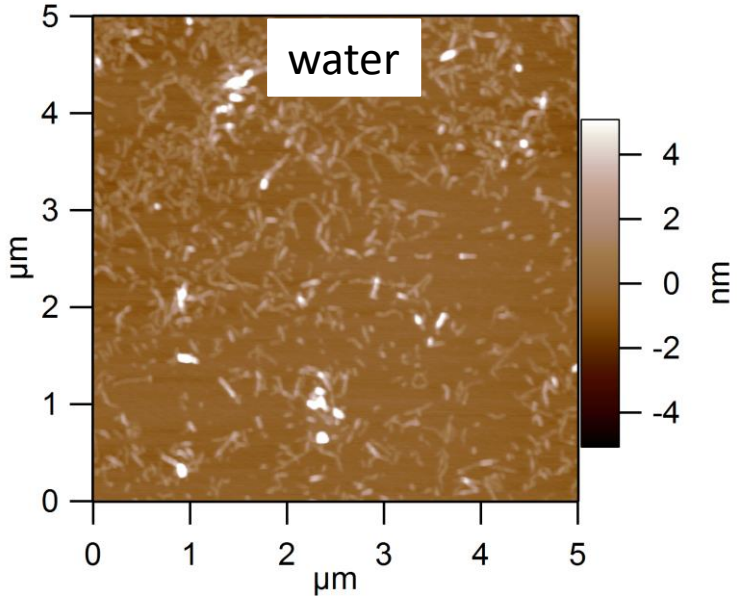


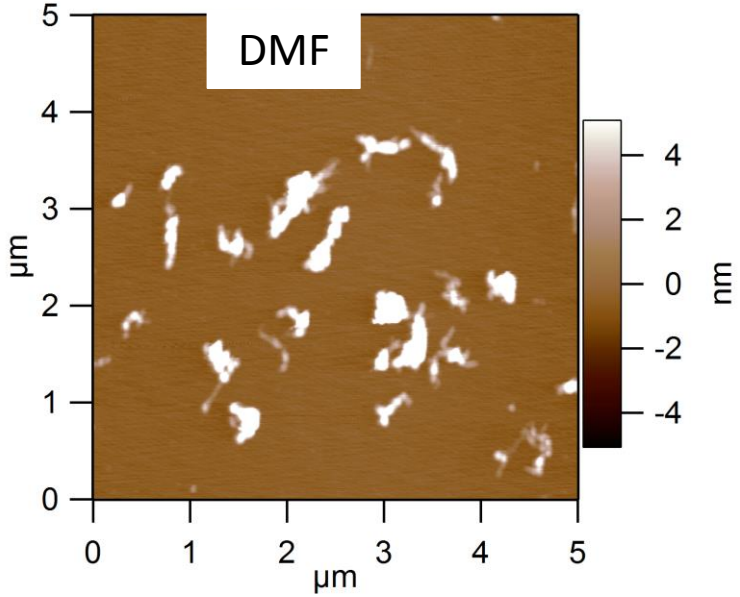
ACS Applied Materials and Interfaces. 2014, 6, 20075-20084

Re-dispersibility





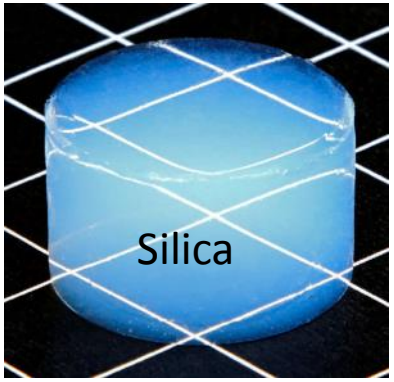




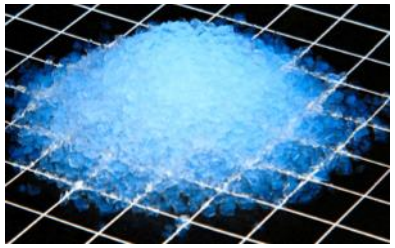
ACS Applied Materials and Interfaces. 2014, 6, 20075-20084

Aerogel

Inorganic



Brittleness



Polymeric



Non-degradable



Aerogel:

- Light
- Porous
- 3D network
- Filled with air

www.buyaerogel.com

http://inhabitat.com

Carbonaceous



Graphene

Expensive



https://www.extremetech.com/

Biobased



- Biodegradable;
- Abundant;
- Low cost;
- Easy to process;

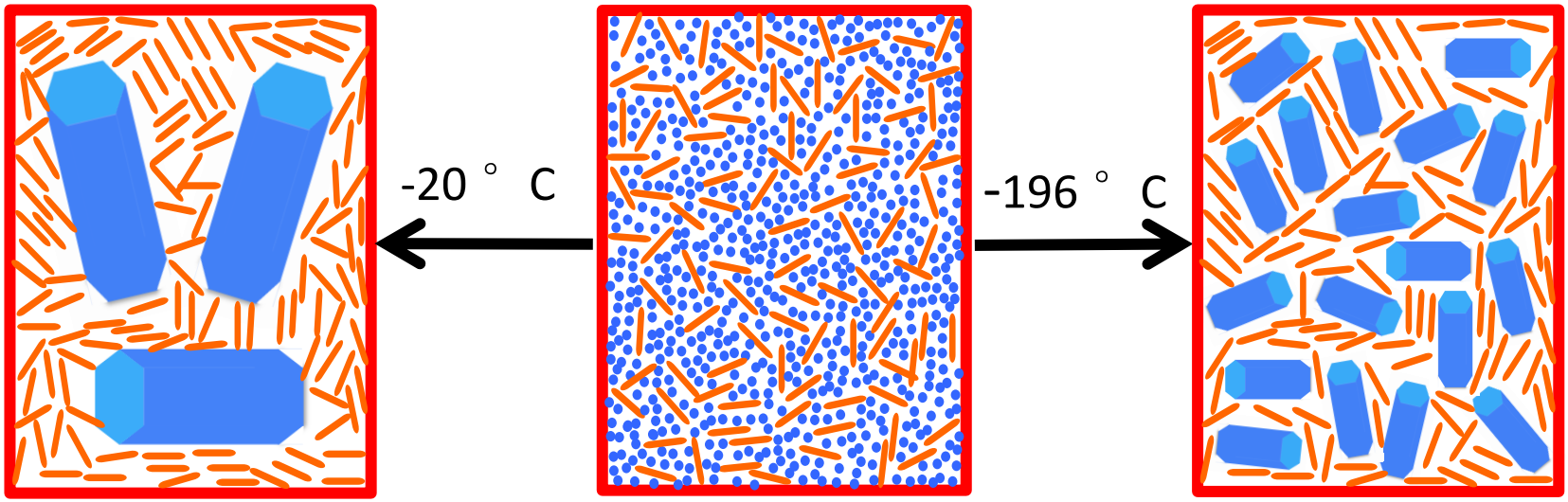
Assembly in to aerogels

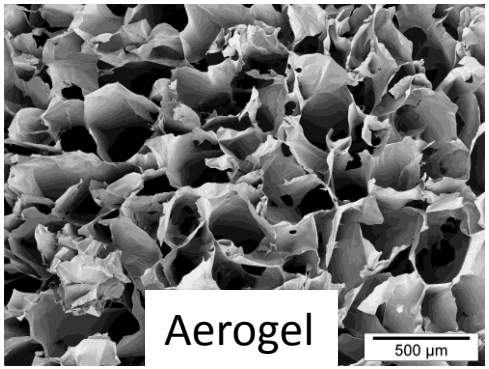
-20 °C

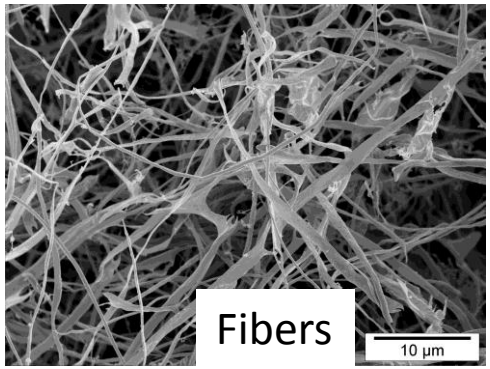
- Slower ice nucleation rate;
- Large ice crystals.

-196 °C

- Fast ice nucleation rate;
- Small ice crystals.

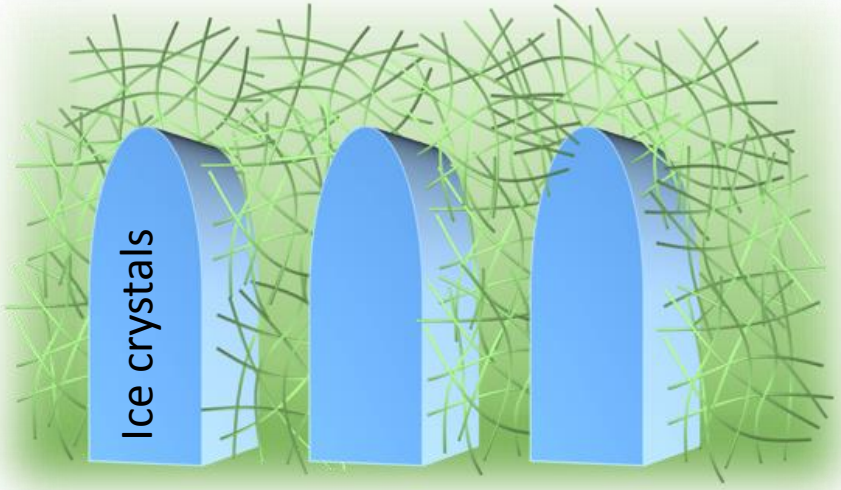




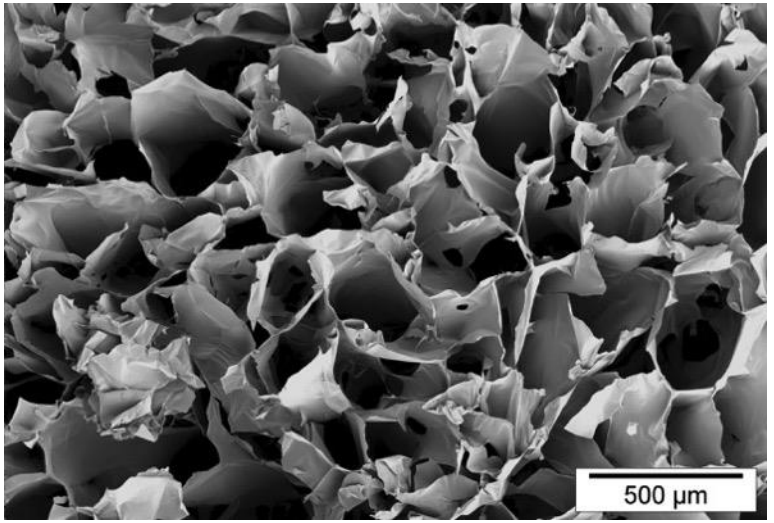


Cellulose nanofibrils aerogels

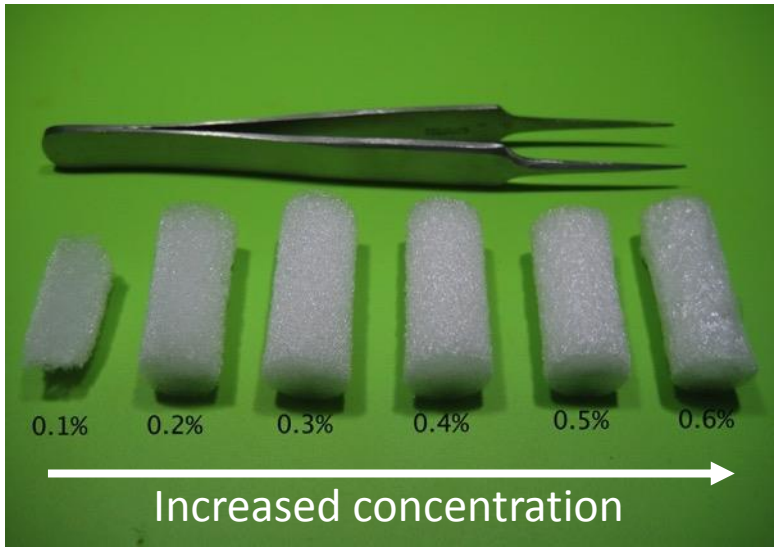
Cellulose nanofibrils



Vertically aligned macropores

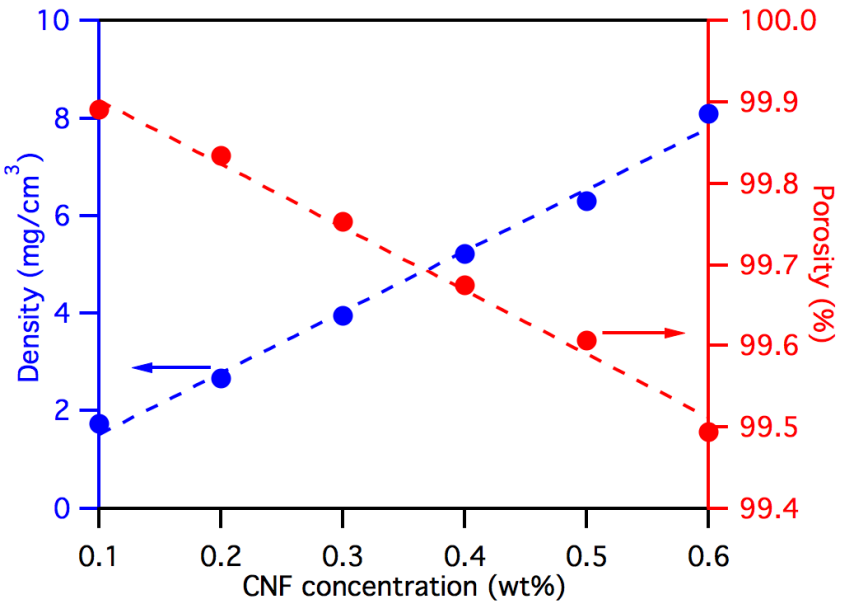






J. Mater. Chem. A. 2014, 2, 6337-6342; J. Mater. Chem. A. 2014, 2, 350-359

Cellulose nanofibrils aerogels - lightweightness

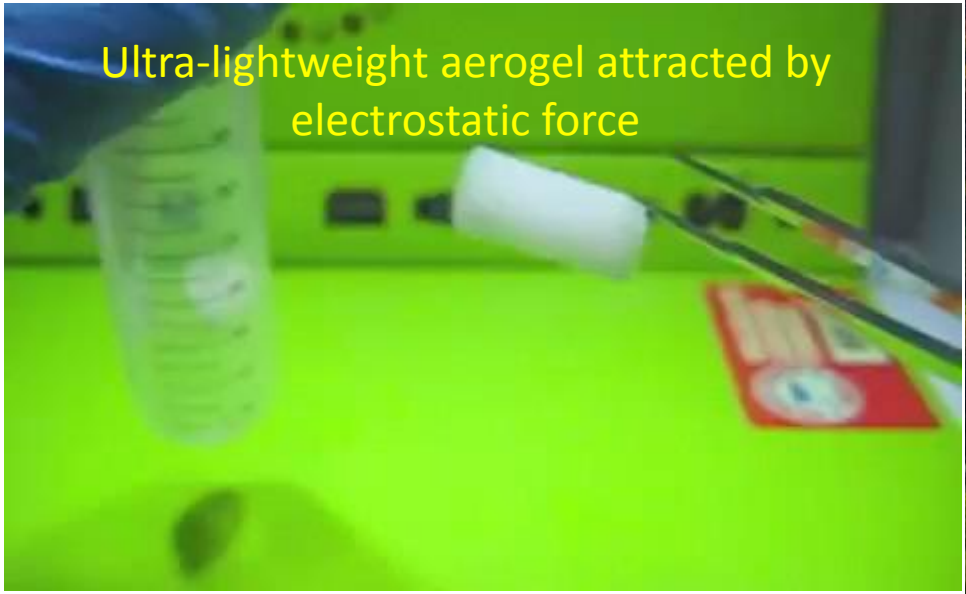


Density: 1.74-8.09 mg/cm^3

Porosity: 99.6-99.9%

Potential applications:

- Insulation
- Packaging
- Aerospace

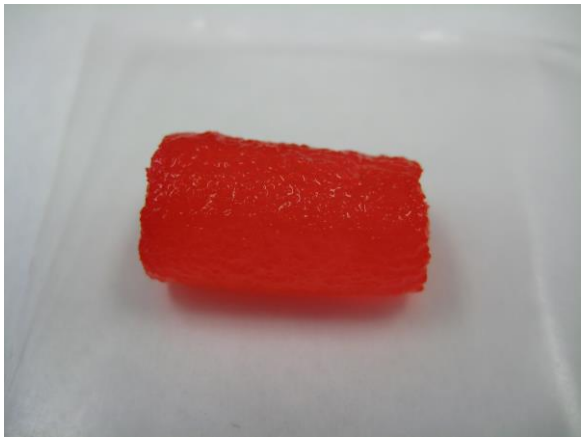


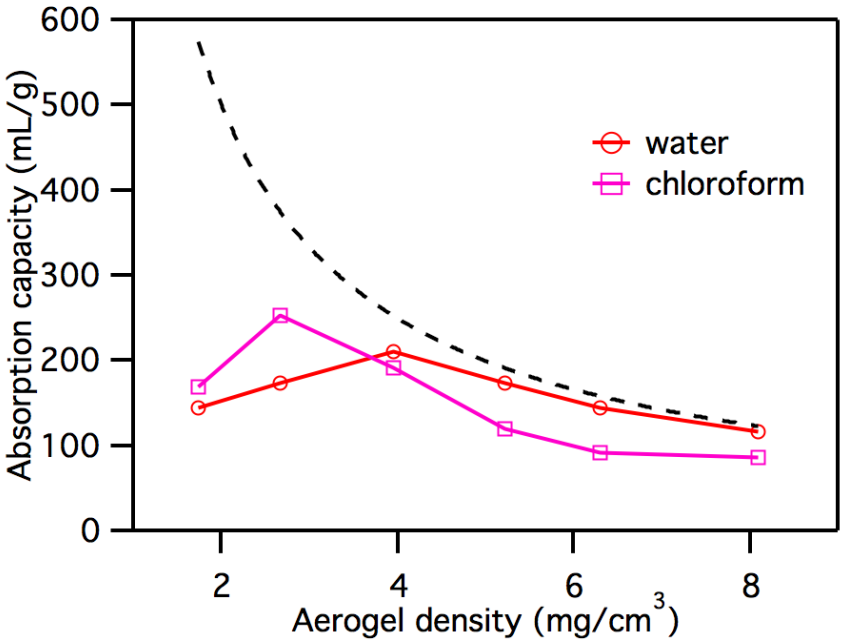
J. Mater. Chem. A. 2014, 2, 350-359

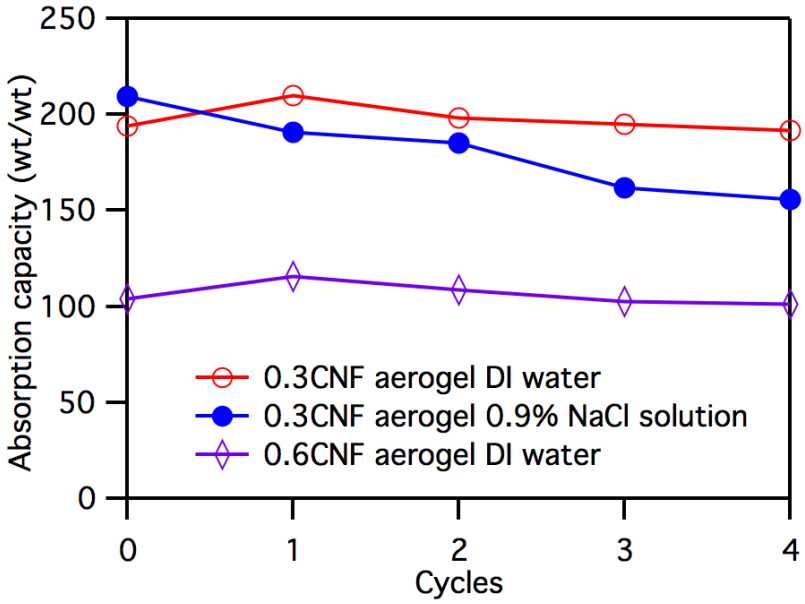
Cellulose nanofibrils aerogels - superabsorbency



Water absorption

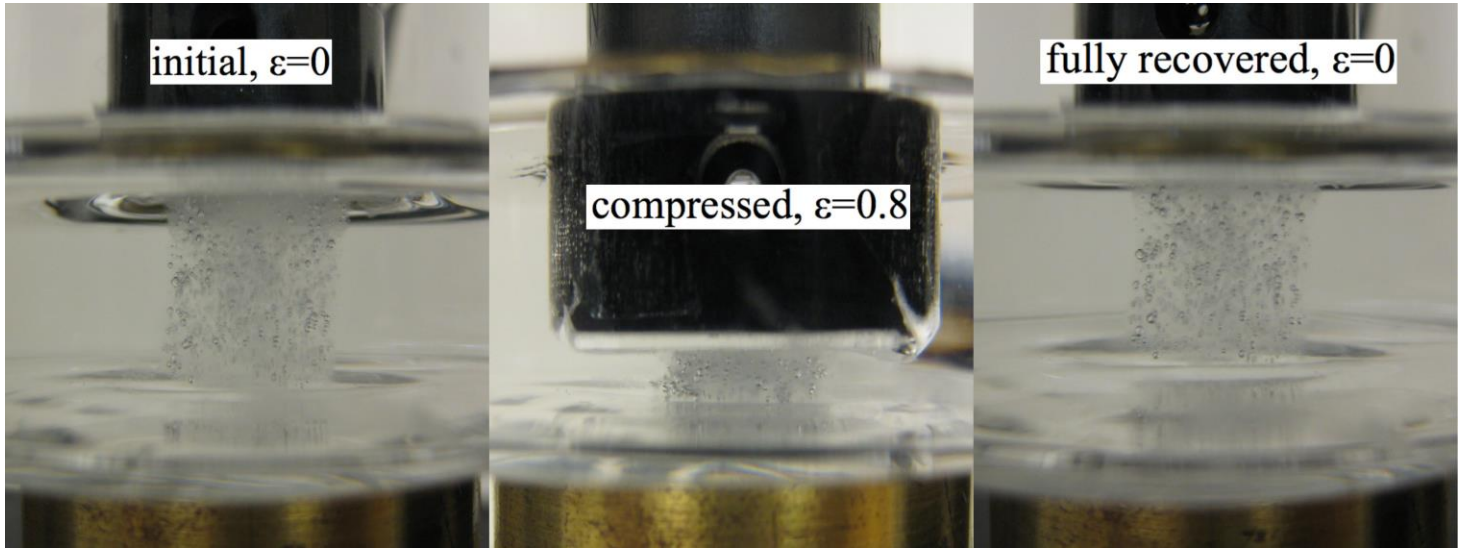


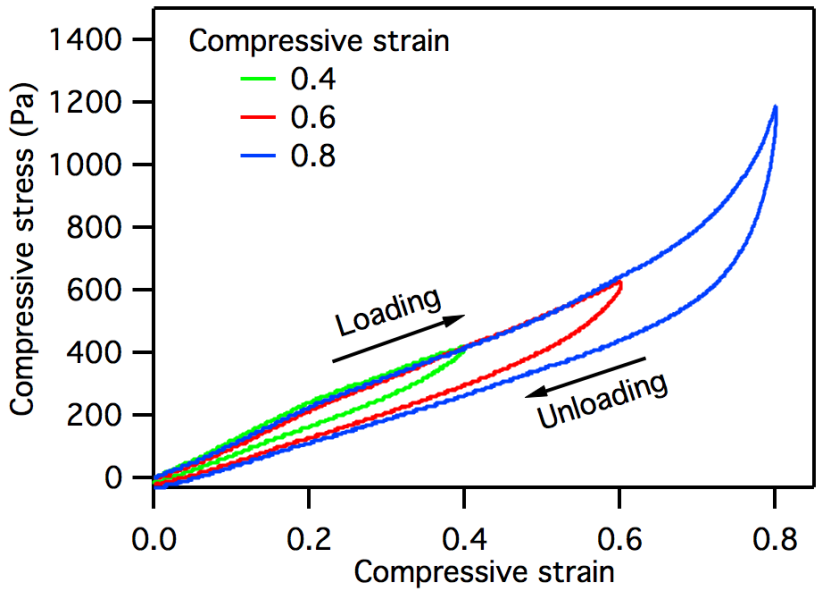


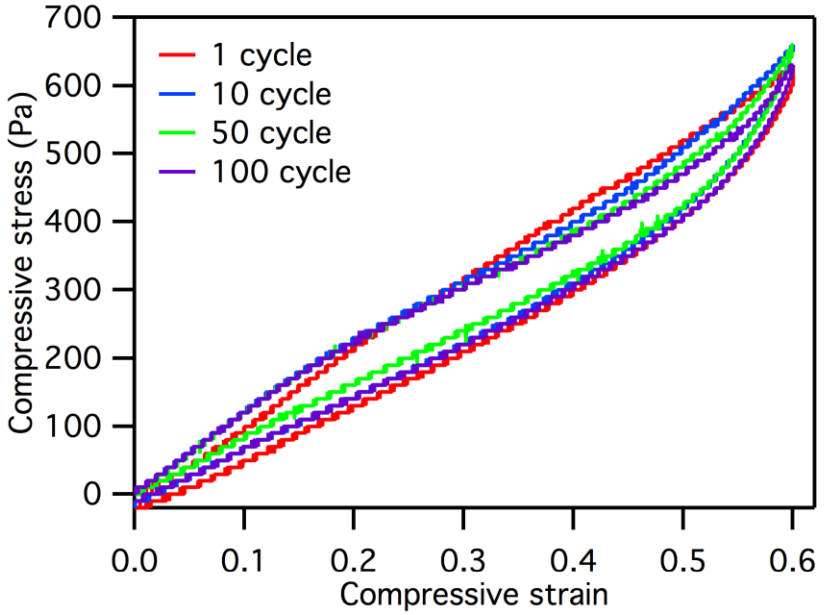


J. Mater. Chem. A. 2014, 2, 350-359

Cellulose nanofibrils aerogels – wet strength

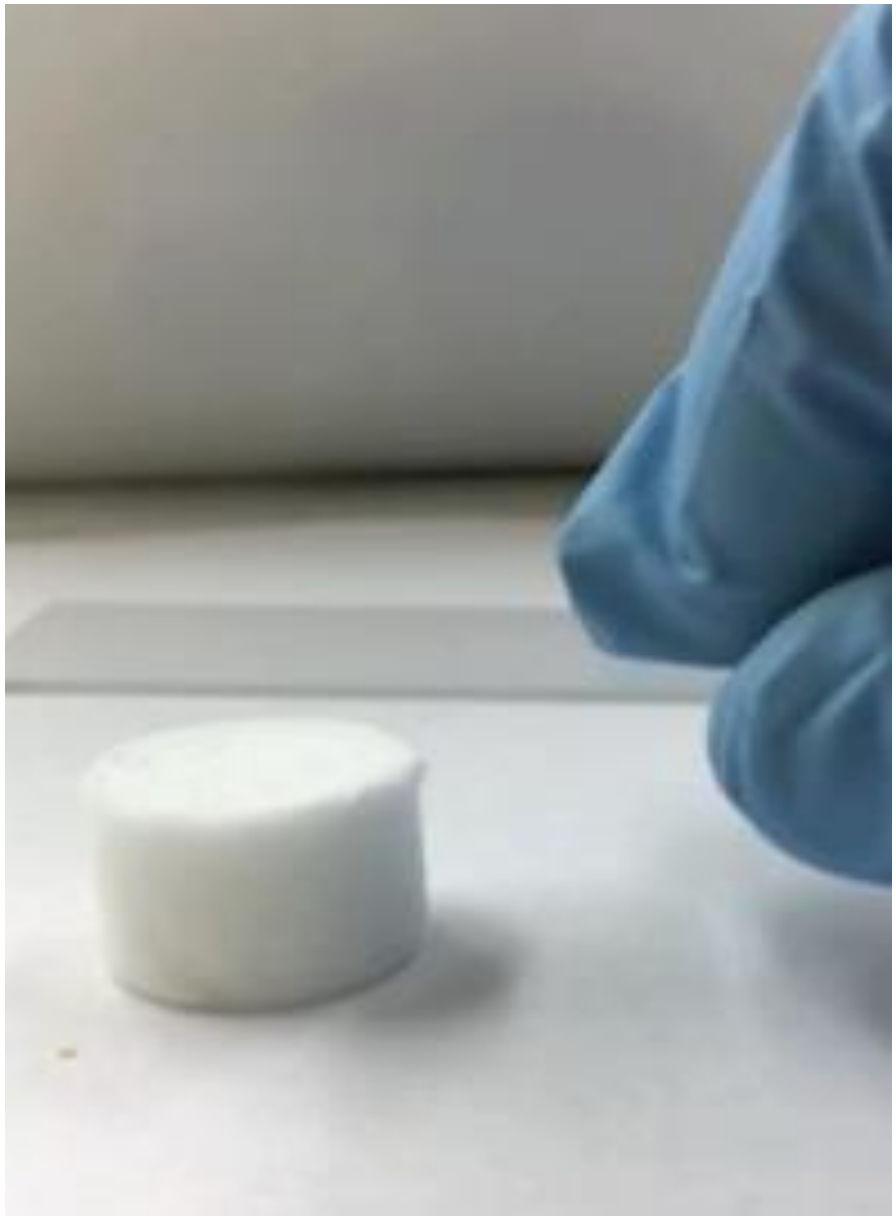






J. Mater. Chem. A. 2014, 2, 350-359

Cellulose nanofibrils aerogels – dry resiliency





- Excellent dry resiliency
- Fast shape recovery Much Stronger than silica aerogel
- Useful for packaging, buffering, insulation

Cellulose nanofibrils aerogels – tunable properties

Surface Chemistry

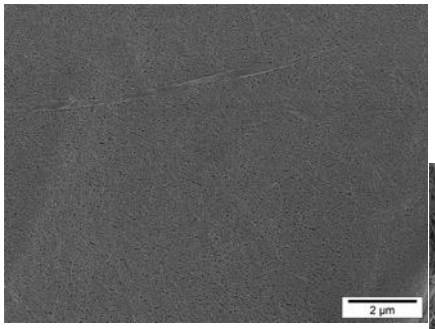


Hydrophilic

Hydrophobic

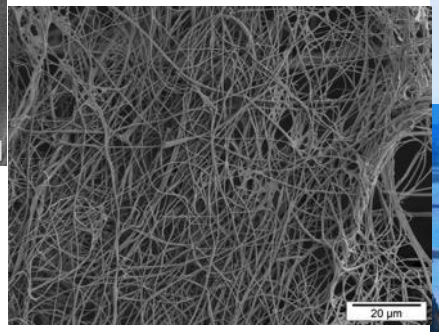


Morphology

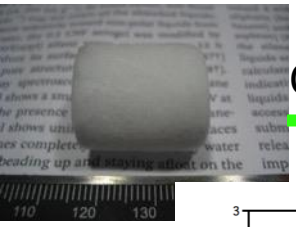


Films

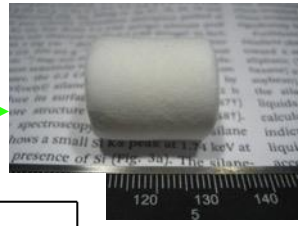
Fibers

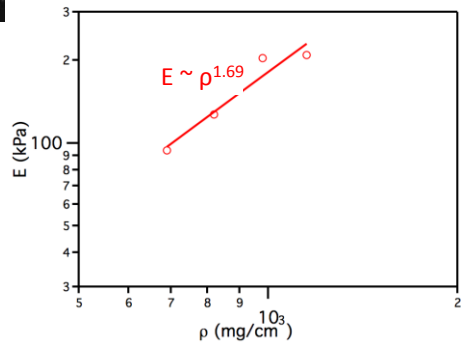


Mechanical



Crosslinking





Light yet Strong

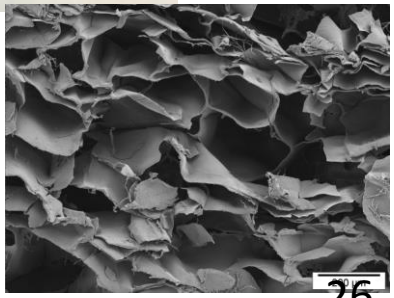
Air-drying



Air-Drying

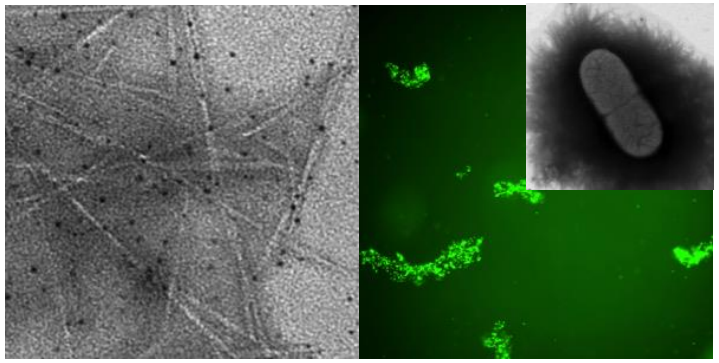


Scalable air-drying



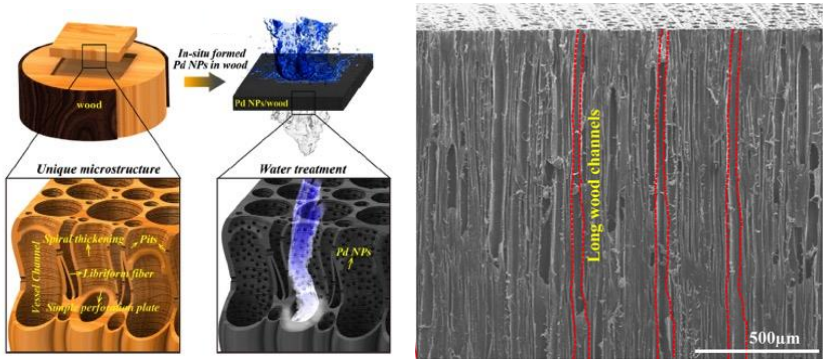
Environmental application – organic/inorganic

Antibacterials



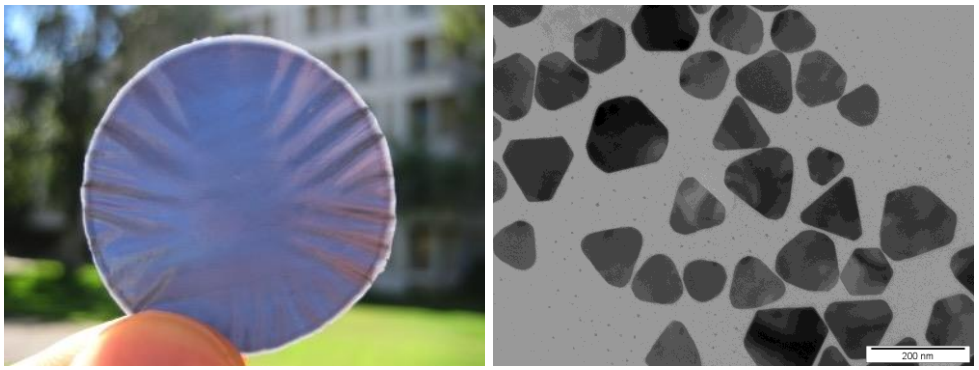
J. Mater. Chem. B. 2, 6226 (2014);

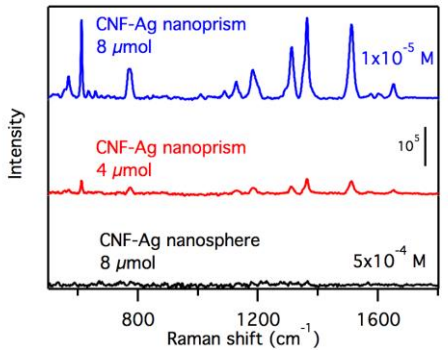
Catalysts



ACS Nano. 11, 4275-4282 (2017);

Chemical sensors – surface enhanced Raman scattering

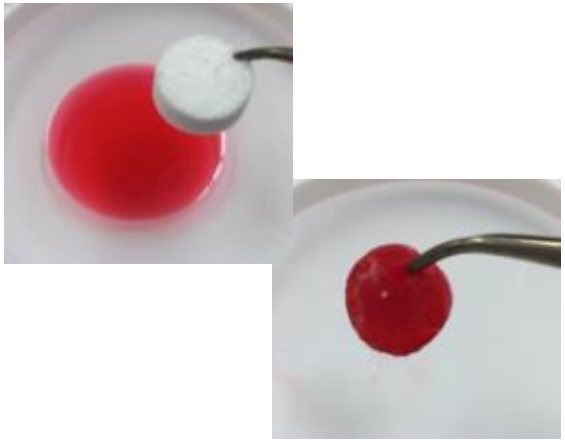




Biomacromolecules. 15, 3608 (2014);

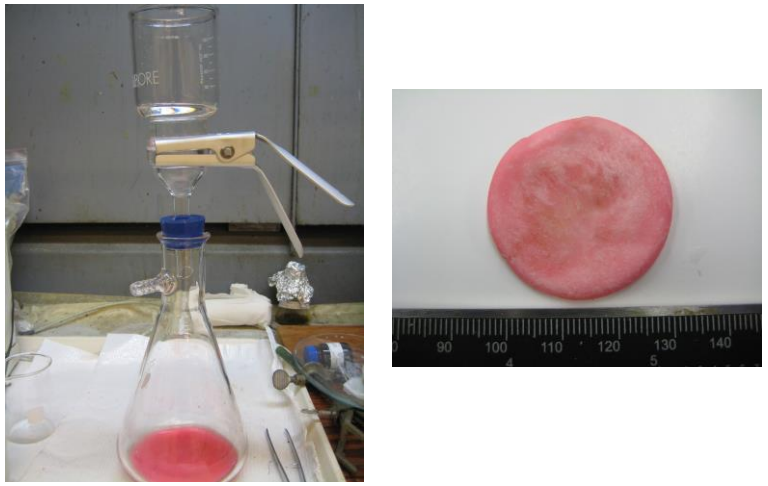
Environmental application – water treatment

Oil/water separation



J. Mater. Chem. A. 2, 6337 (2014)

Water filtration



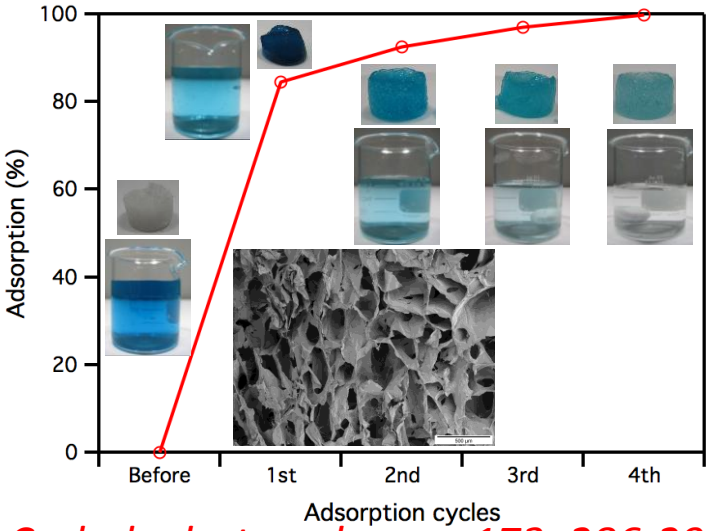
ACS Appl. Mater. Interfaces 9, 2825 (2017)

Solar steam generation



ACS Appl. Mater. Interfaces 10, 1104 (2018)

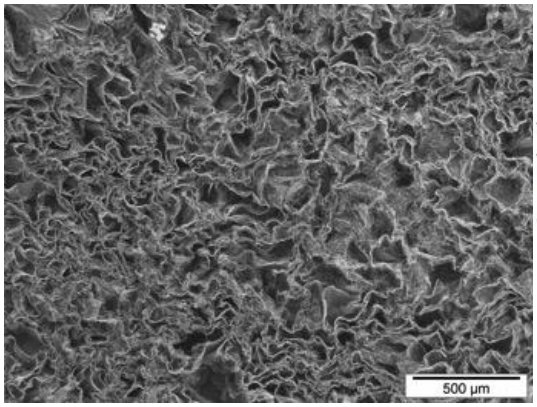
Dye removal

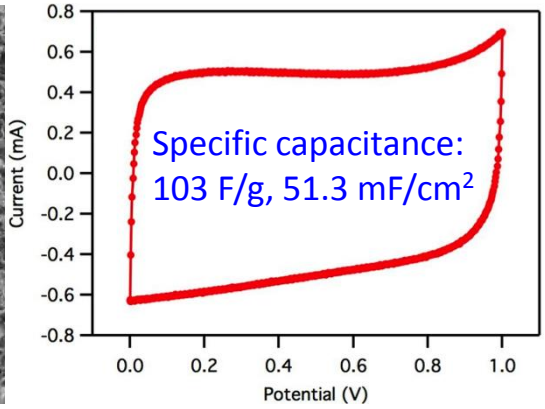


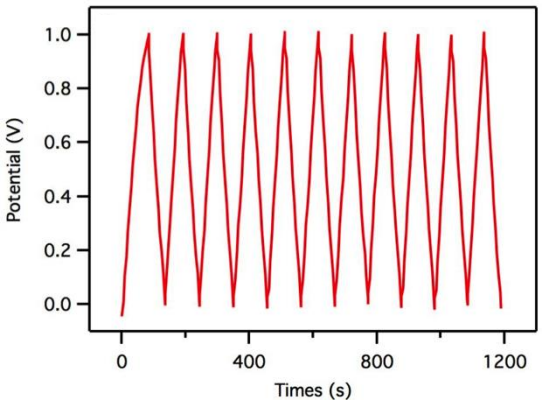
Carbohydrate polymers 173, 286-294

Energy storage application

Supercapacitor

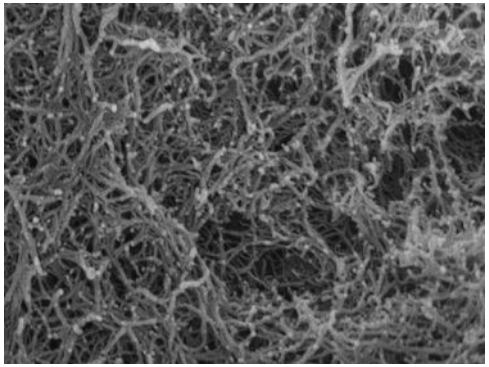


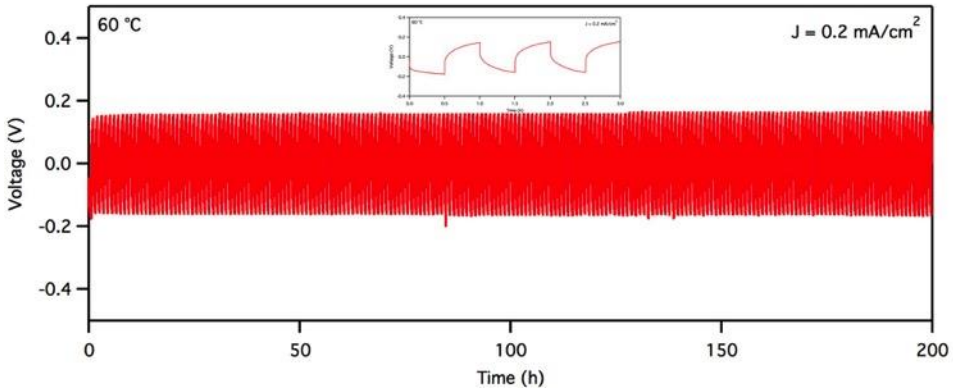




ACS Omega 3, 3530-3539 (2018)

Solid state electrolytes





Acknowledgement

Chaires de recherche du Canada
Canada Research Chairs

forestry
university of british columbia

Canada

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