

Biobased materials – towards technical feasibility

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Centre of Excellence in Molecular Engineering of Biosynthetic Hybrid Materials Research



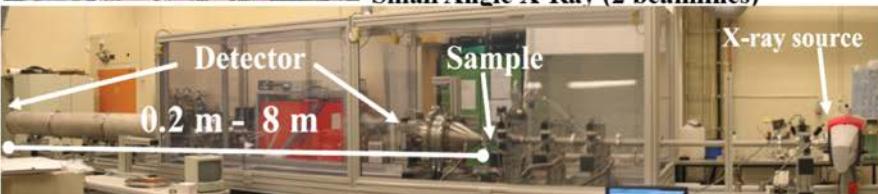
Hierarchical self-assemblies and biomimetics



Nanomicroscopy Center and Nanopolis



Small Angle X-Ray (2 beamlines)



Liq-He cryo-TEM JEOL 3200FSC



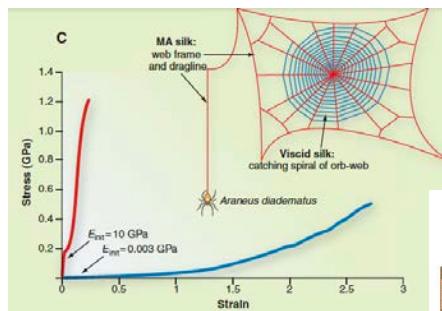
Ruokolainen

Why biological materials start attracting materials scientists

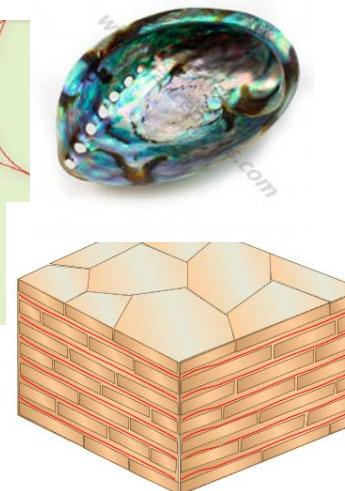
Why biological materials interest

- Sustainability
- Developing/foreseen economics
- Biological processing
- Inspire also to adapt the concepts to biomimetic materials

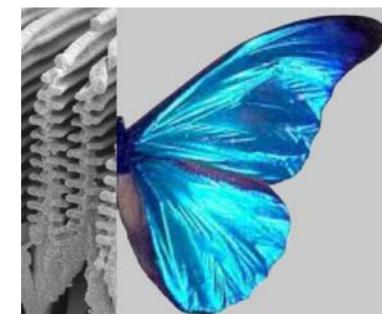
Mechanical properties:
strong and tough



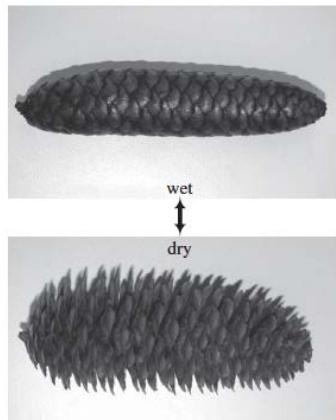
Omenetto, Kaplan,
Science 2010 329 528



Structural
iridescent
colours



Responsive/actuating



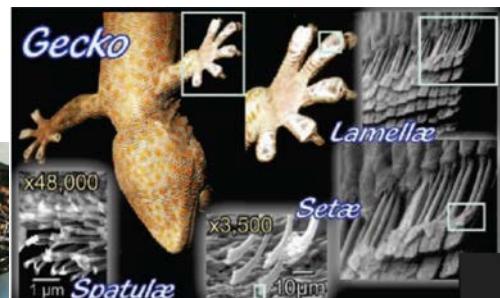
Reyssat, Mahadevan,
J. R. Soc. Interf., 2009, 6, 951

Glues

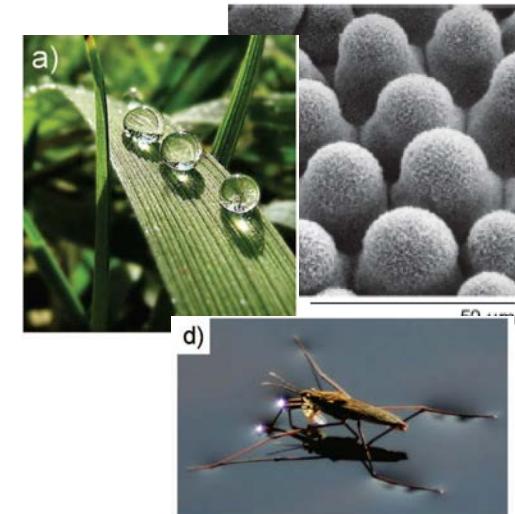


H Waite lab,
Santa Barbara

Sticky

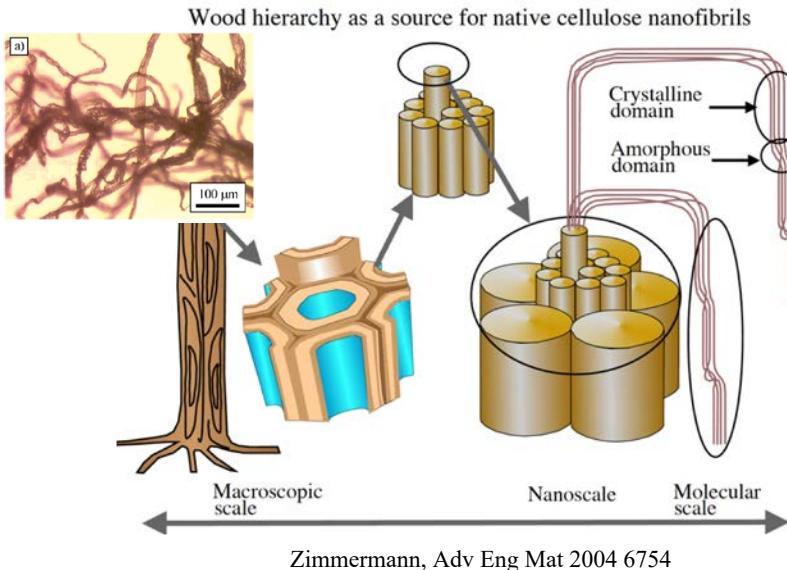


Water repellent

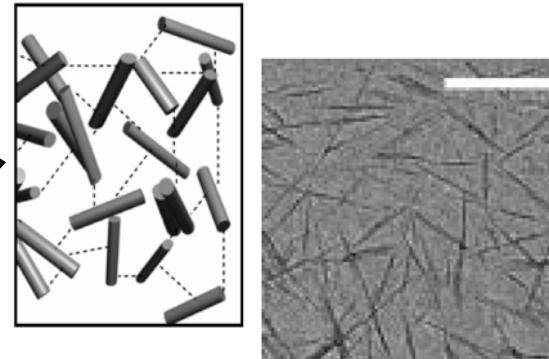


Nanocellulose

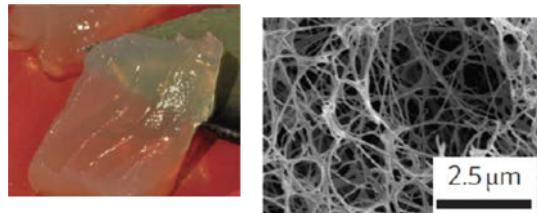
Types of (native) nanocelluloses



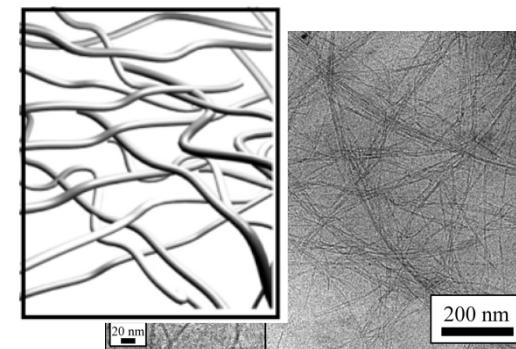
Cellulose nanocrystals (CNC)



Bacterial cellulose



Cellulose nanofibrils (CNF)



Reviews:

Klemm, Kramer, Moritz, Lindström, Ankerfors, Gray, Dorris,
Angew. Chem. Int Ed. 2011, **50**, 5438

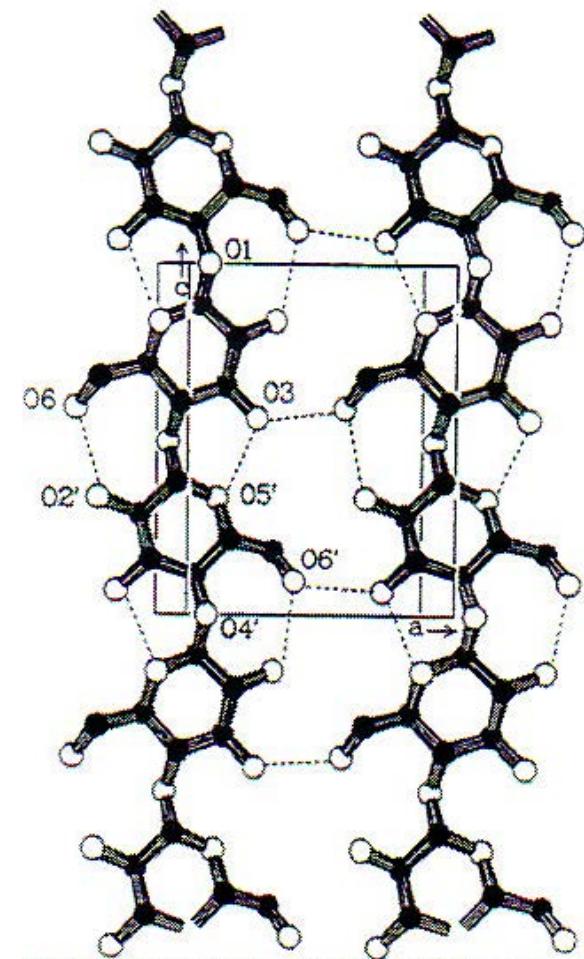
Kontturi, Laaksonen, Linder, Nonappa, Gröschel, Rojas, Ikkala,
Adv Mat. 2018, 1703779

Native nanocelluloses:

- Native cellulose I crystal modification
 - Parallel hydrogen bonded chains
- Modulus up to ca. 130-150 GPa
 - Iwamoto, Kai, Isogai, Iwata,
Biomacromolecules 2009 10 2571
- Strength in the 2-6 GPa range
 - Saito, Kuramae, Wohlert, Berglund, Isogai,
Biomacromolecules 2013, 14, 248
- Very good mechanical properties !

Platform for chemical modification

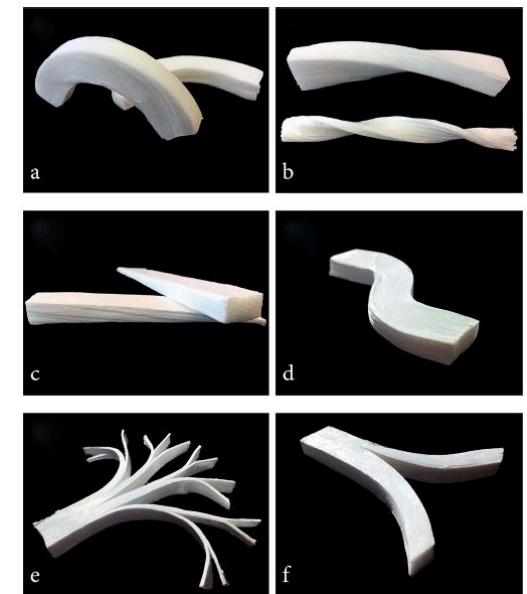
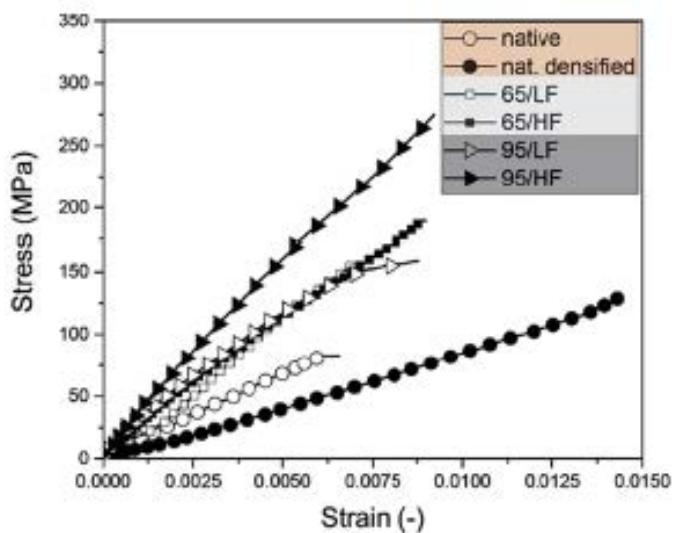
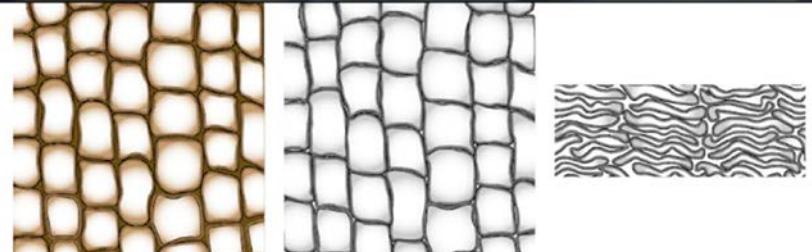
Cellulose I crystal



Preserving wood hierarchies in composites

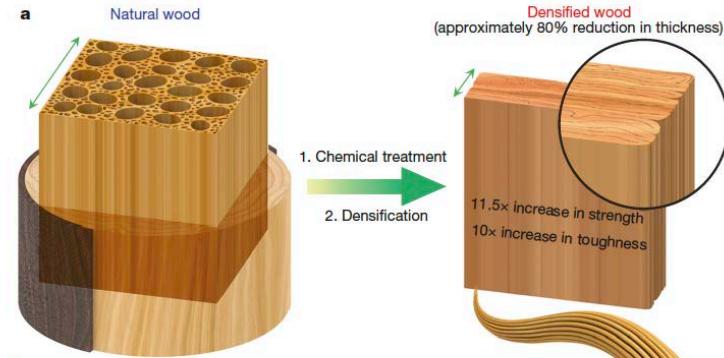
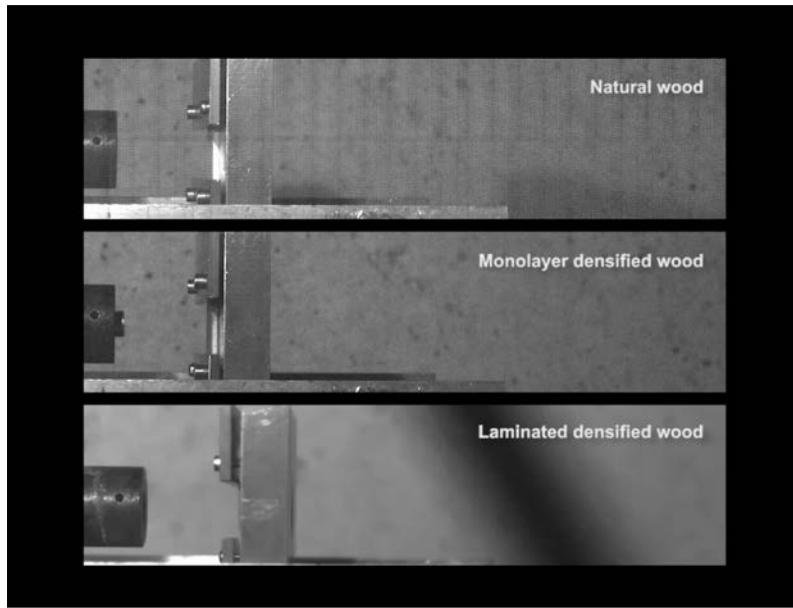
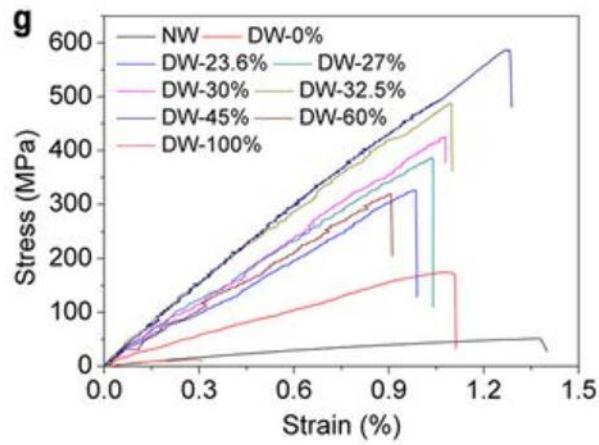
Delignified and densified wood

- Delignification
 - Hydrogen peroxide & acetic acid
- Compression
 - Deformability
- High mechanical properties



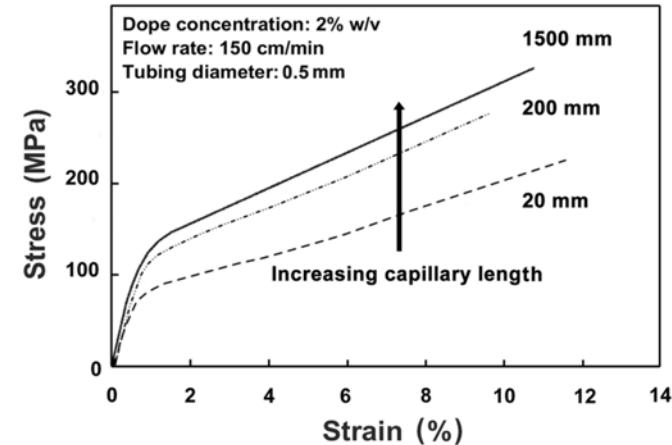
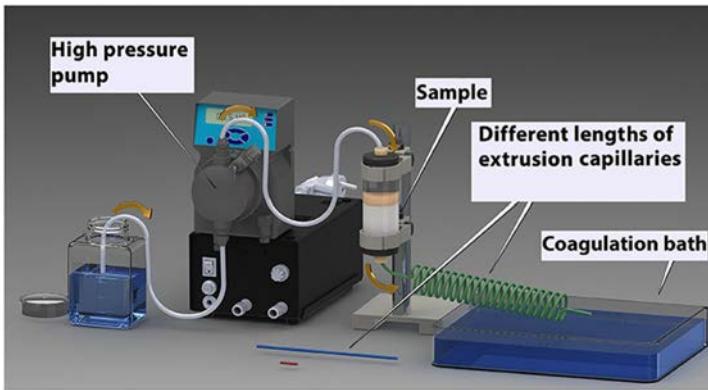
Partial removal of lignin and hemicellulose from wood

- Aqueous mixture of NaOH and Na₂SO₃
- Compression



Nanocellulose fibers

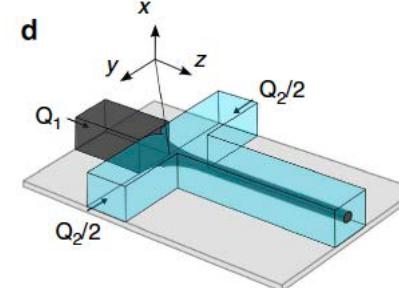
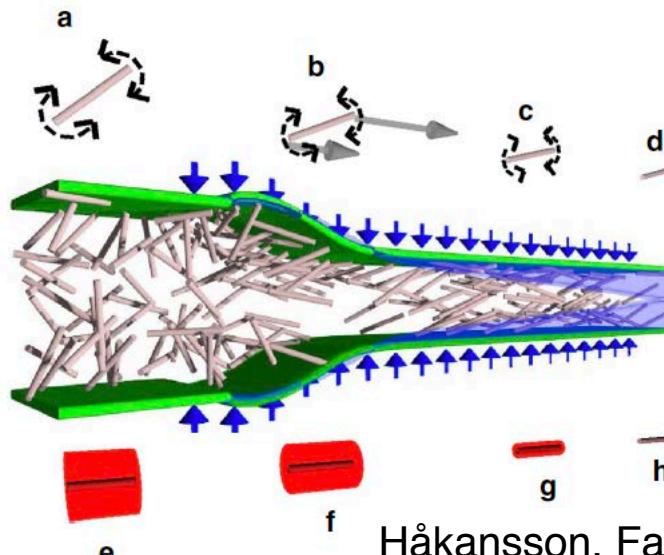
Spinning cellulose nanofibers



Iwamoto, Isogai, Iwata, *Biomacromolecules*, 2011, 12 831

Walther, Timonen, Díez, Laukkanen, Ikkala , *Adv Mat*, 2011, 23, 2924

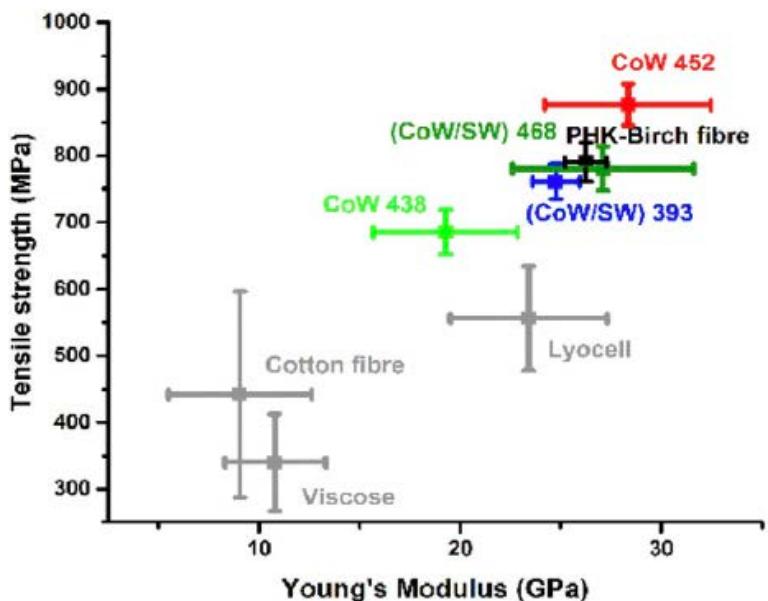
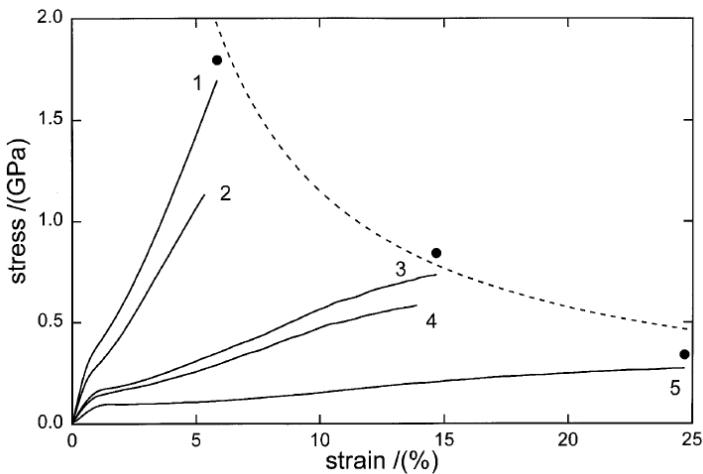
Mohammadi, Toivonen, Ikkala, Wagermaier, Linder, *Sci Rep* 2017 7, 11860



Strength 490 MPa
Modulus 17.6 GPa
Strain 6.4 %

Håkansson, Fall, Lundell, Shun Yu, Krywka, Roth, Santoro, Kvick, Wittberg, Wågberg, Söderberg, *Nat. Comm* 2014 5 4018

But, regenerated cellulose fibers have extraordinary mechanical properties

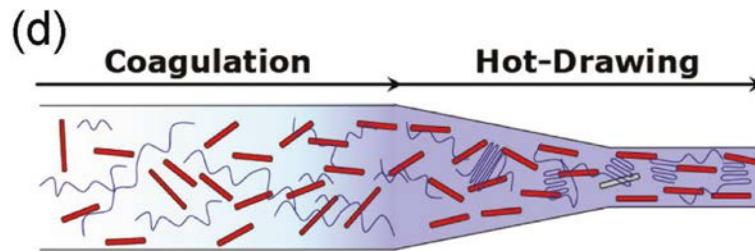


- Compare
 - Polyvinyl alcohol 2 GPa
 - Polybenzoxazoline 5 GPa !

Northolt, Lenzinger Berichte 1985 59 71
Sikkema, Northolt, Pourdeyhimi, MRS Bull 2003 28 579

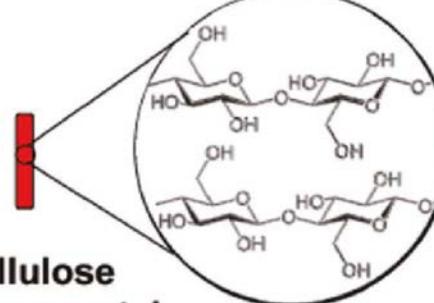
Asaadi, Hummel, Hellsten,
Härkäsalmi, Ma, Michud, Sixta,
ChemSusChem 2016 9 3250

Cellulose nanocrystal composite fibers

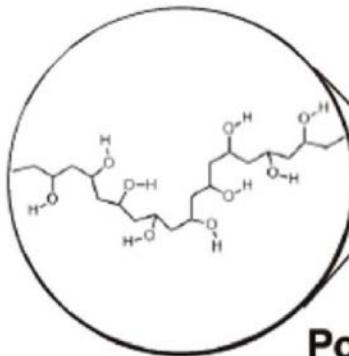


$E = 29.9 \text{ GPa}$

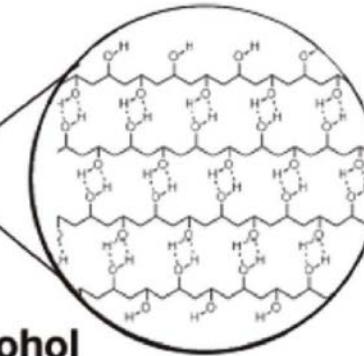
$\sigma = 880 \text{ MPa}$



Cellulose
Nanocrystal

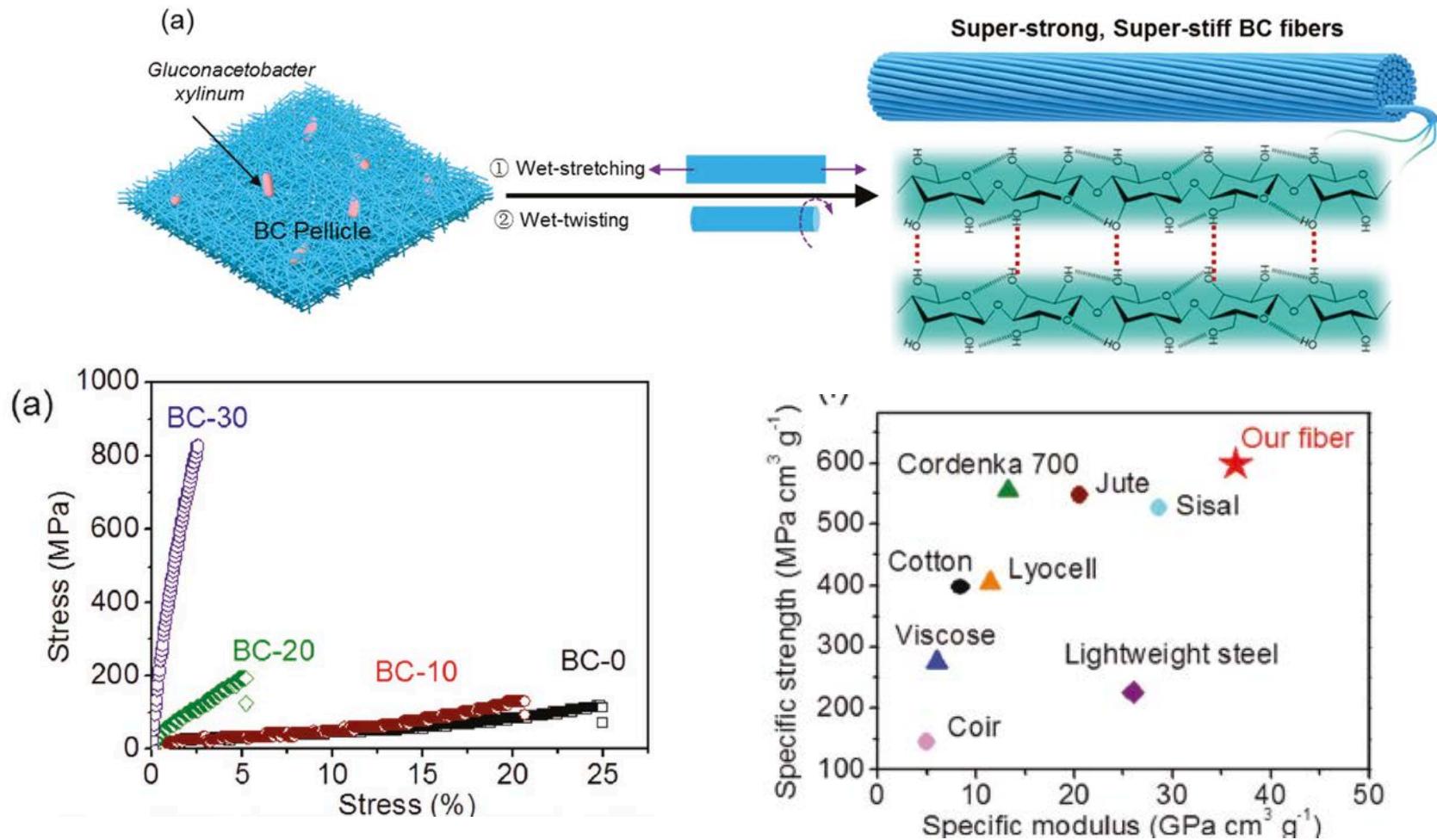


Poly Vinyl Alcohol



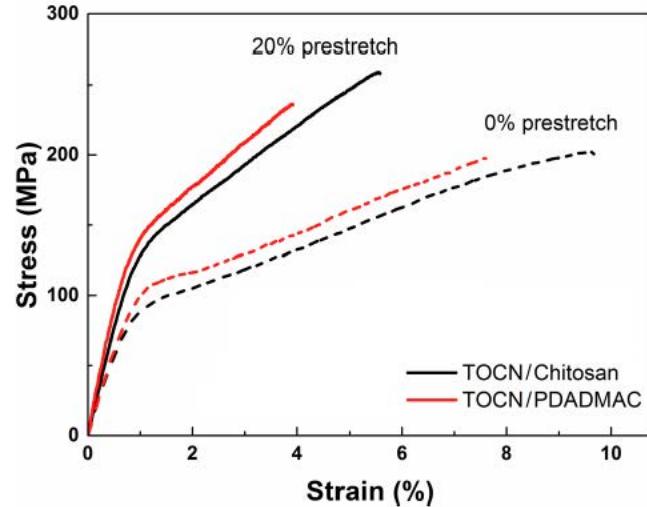
- Probably the best CNC fiber so far
- Still, pure polyvinyl alcohol 2 GPa

Twisted bacterial cellulose fibers

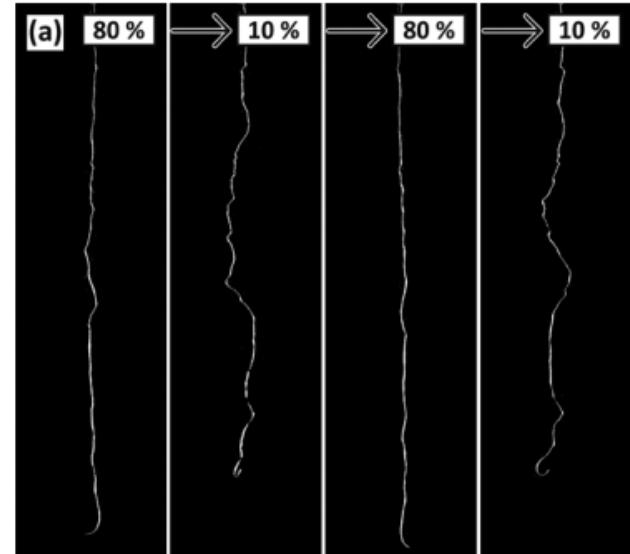


Interfacial polyelectrolyte complex spinning

- TEMPO-CNF
- Poly(diallyldimethylammonium chloride) (PDADMAC)



Crimping

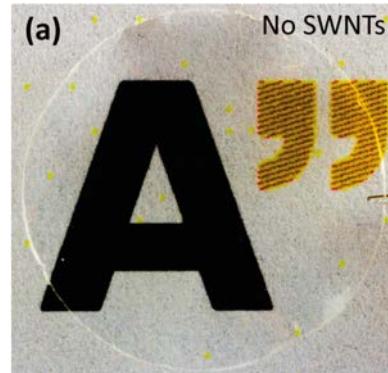
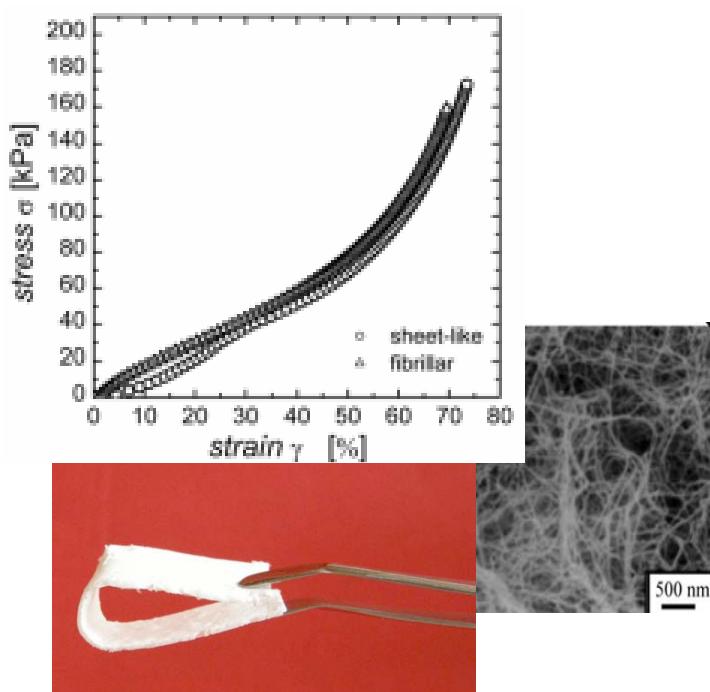


Toivonen, Kurki-Suonio, Wagermaier, Hynninen, Hietala, Ikkala,
Biomacromolecules, 2017 **18** 1293

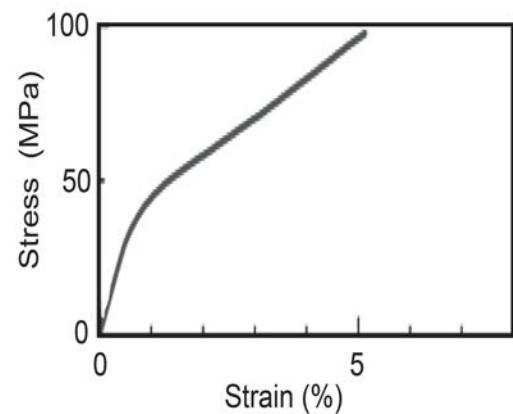
Porous properties

Tunable nanocellulose aerogels and foams

- From low density highly compressible
- To strong in tension, still flexible in bending



Density 0.6 g/cm³
Surface area 208 m²/g
Pores 10-30 nm

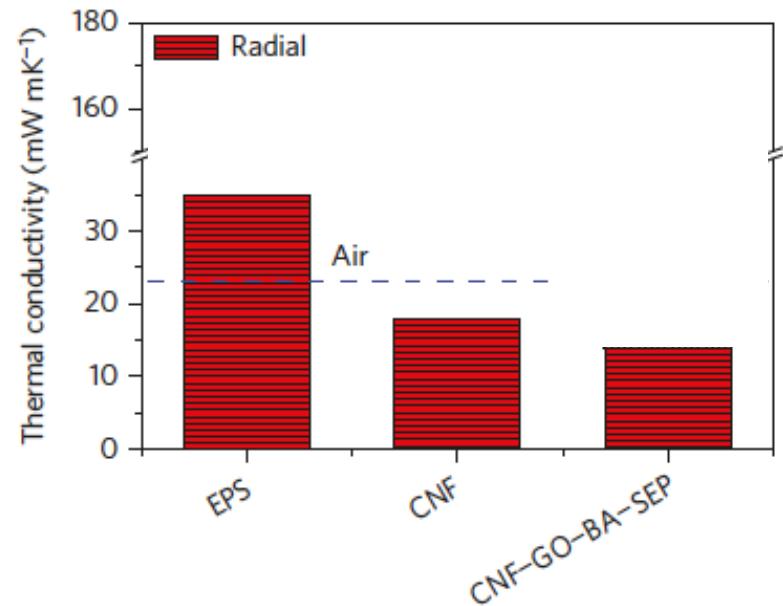
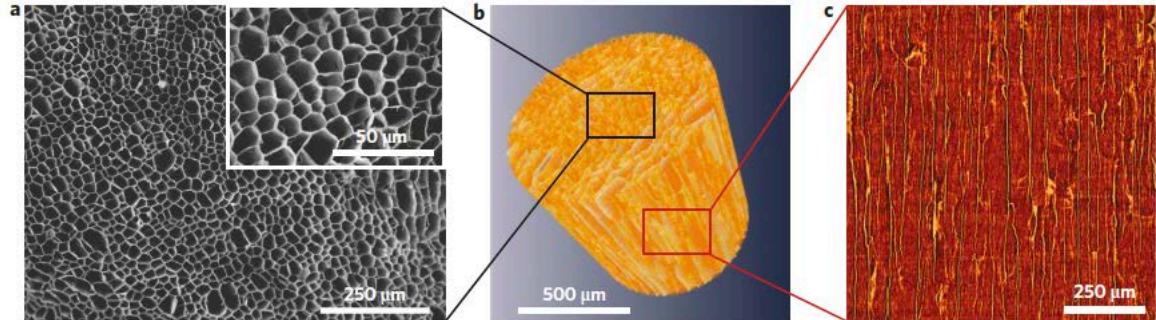


Pääkkö, Silvennoinen, Vapaavuori,
Nykänen, Ankerfors, Kosonen,
Ruokolainen, Lindström, Berglund,
Ikkala, *Soft Matter*, 2008, **4**, 2492

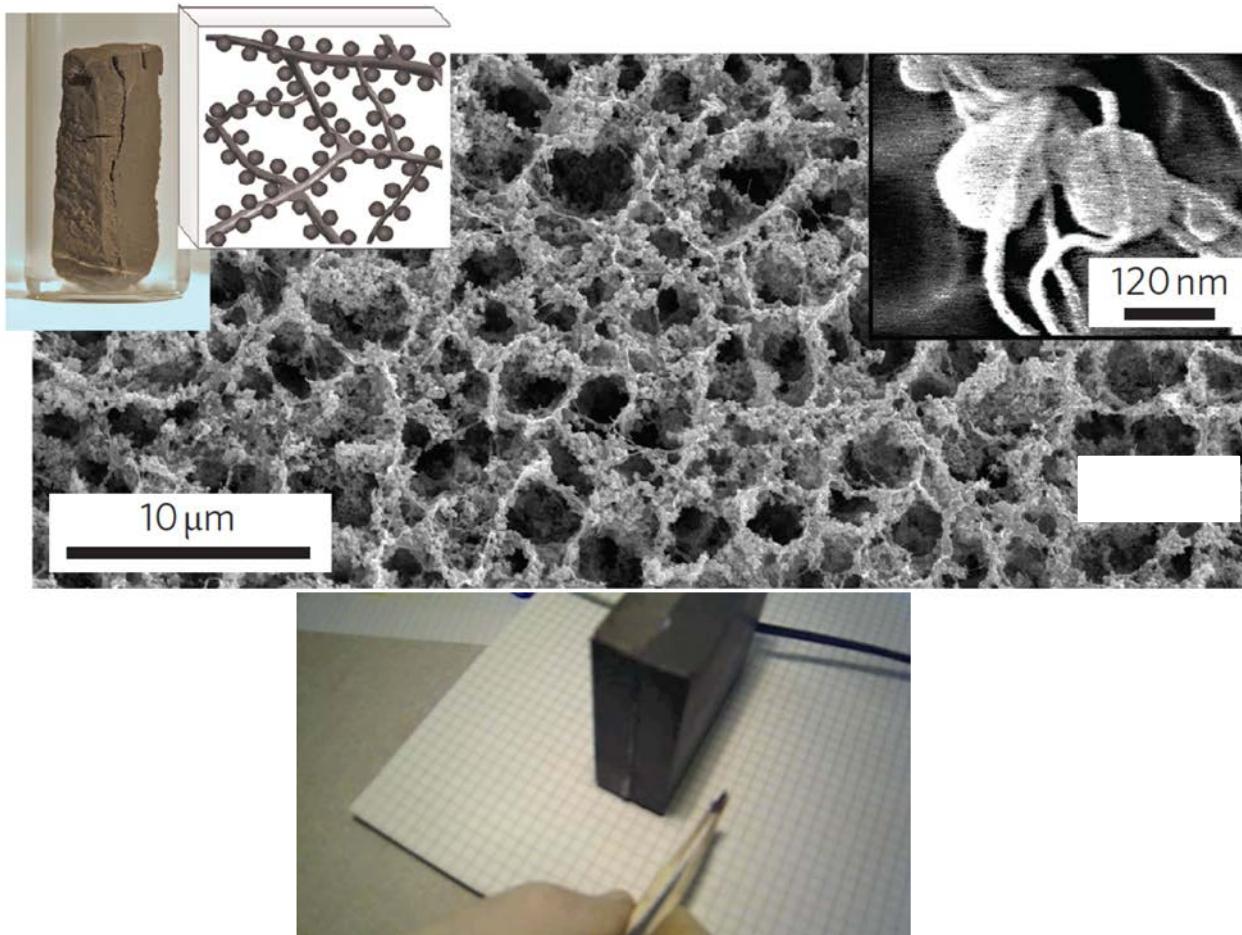
Toivonen, Kaskela, Rojas,
Kauppinen, Ikkala, *Adv Funct Mater*, 2015, **25**, 6618

Thermal insulation

- Composite of cellulose nanofibres, graphene oxide and sepiolite nanorods
- Thermal conductivity $15 \text{ mW m}^{-1} \text{ K}^{-1}$
 - Half that of expanded polystyrene.



Magnetic actuating nanocellulose aerogels

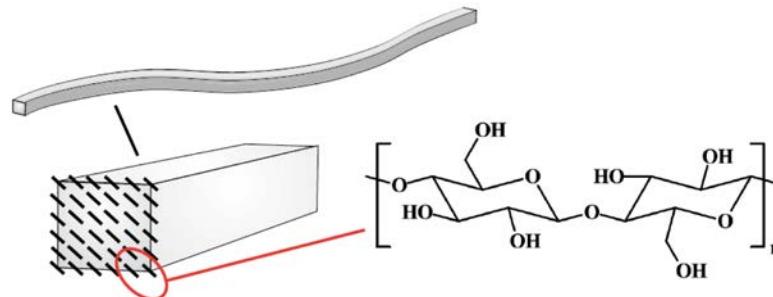


Olsson, Azizi Samir, Salazar-Alvarez, Belova, Ström, Berglund, Ikkala, Nogués, Gedde, *Nature Nanotech*, 5, 584 2010

Electrical properties

Combine the best of two different worlds:

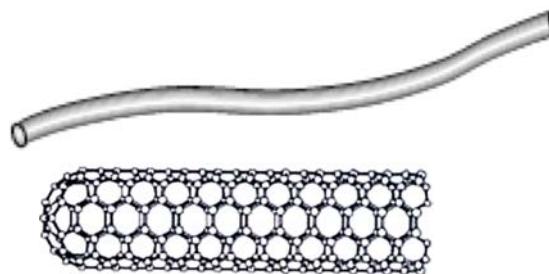
Nanocellulose



Modulus 140 GPa
Strength GPa's
Sustainable

and

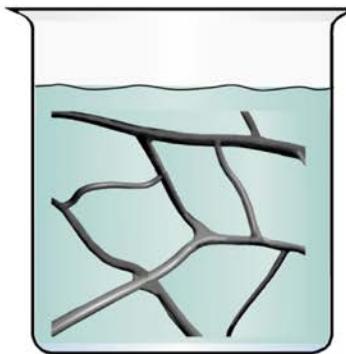
Carbon nanotubes



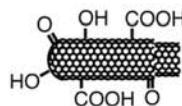
Modulus 1000 GPa
Strength 30-60 GPa
Electrical

Sensing movement

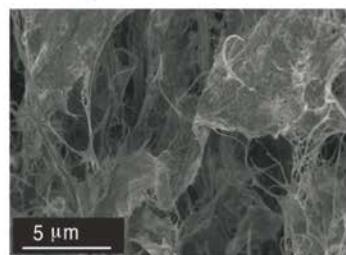
Native nanocellulose hydrogel



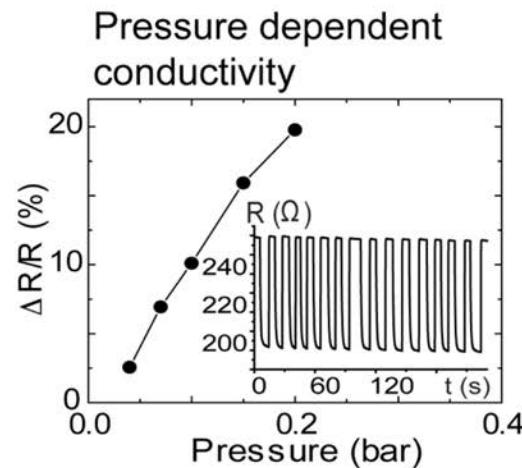
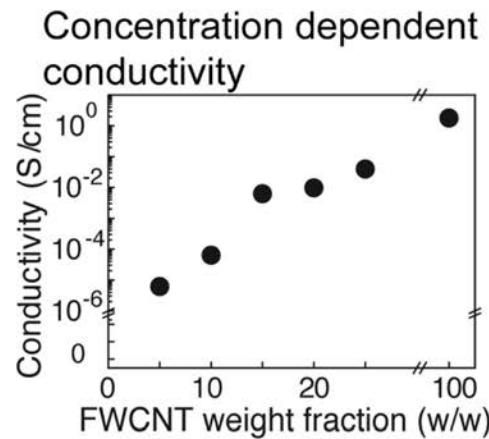
Carbon nanotubes added



Water removal

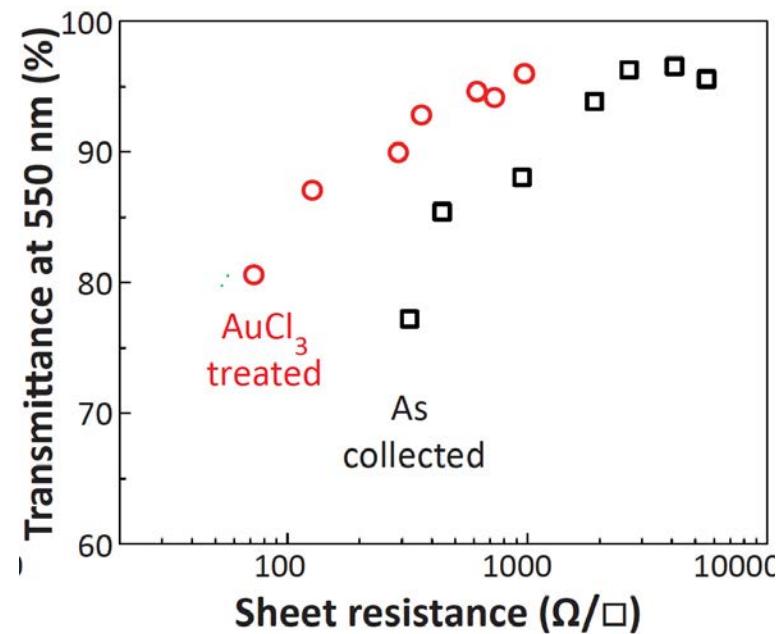
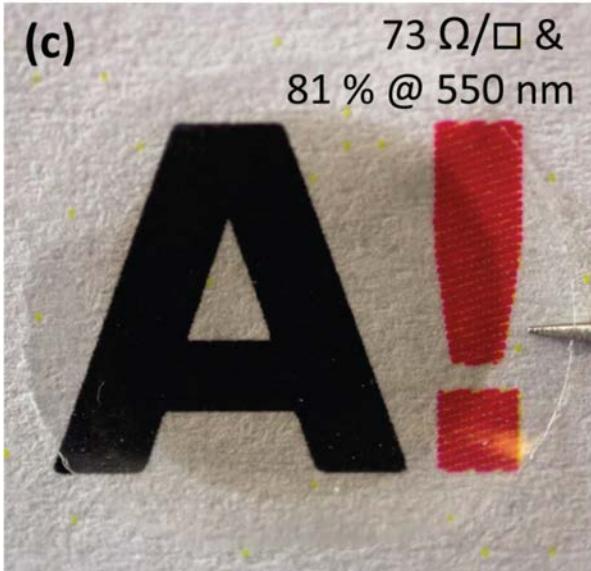


Hybrid aerogel

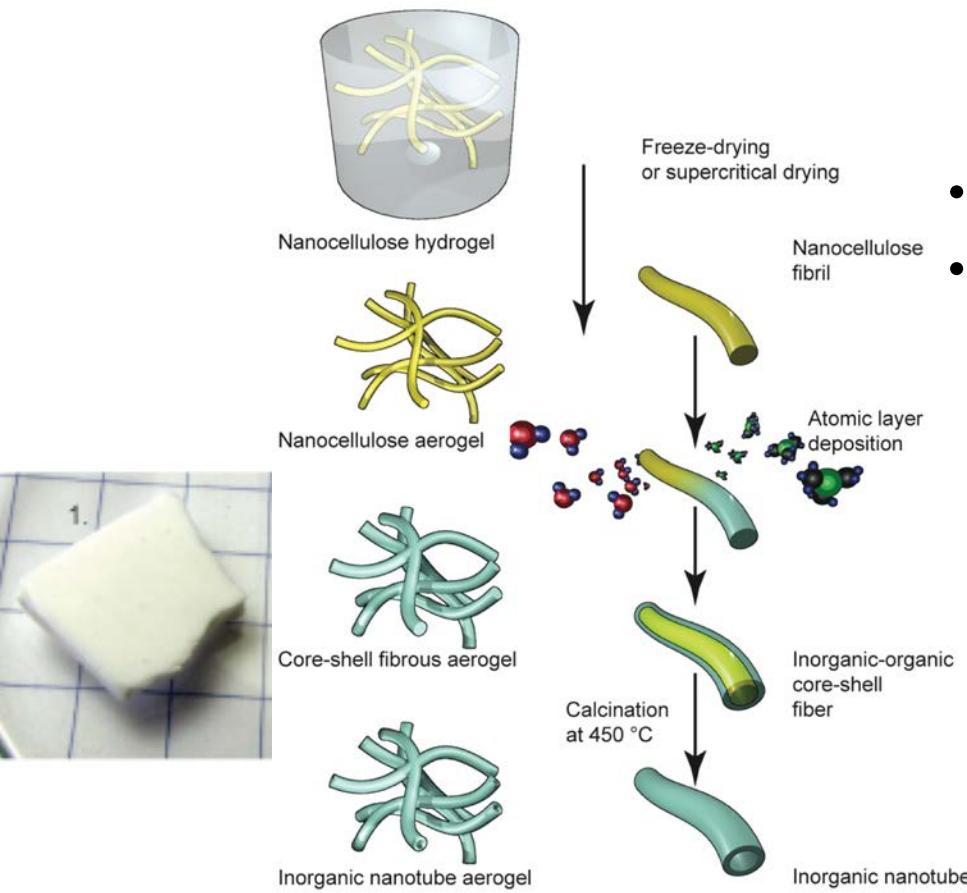


Wang, Anoshkin, Nasibulin, Korhonen, Seitsonen, Pere, Kauppinen, Ras, Ikkala, *Adv Mat* **25** 2428 2013

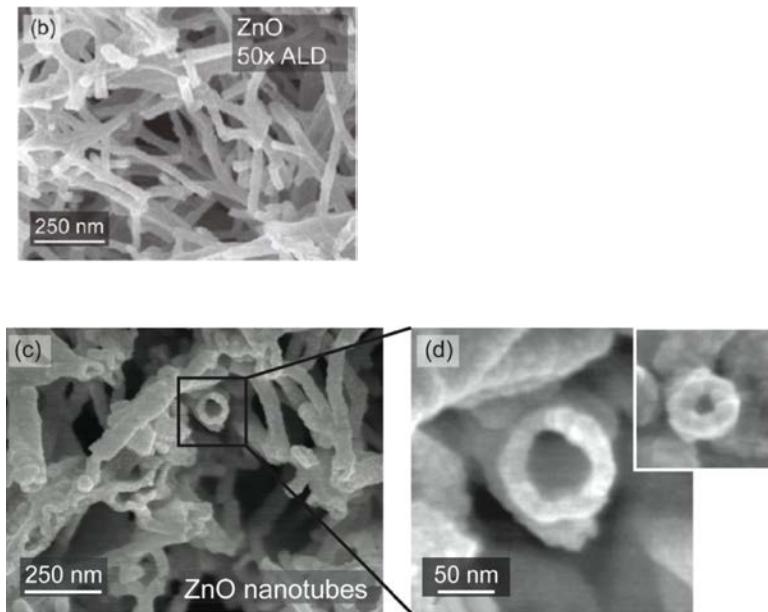
Transparent conducting nanocellulose/carbon nanotube films



Oxide semiconductors on by atomic layer deposition

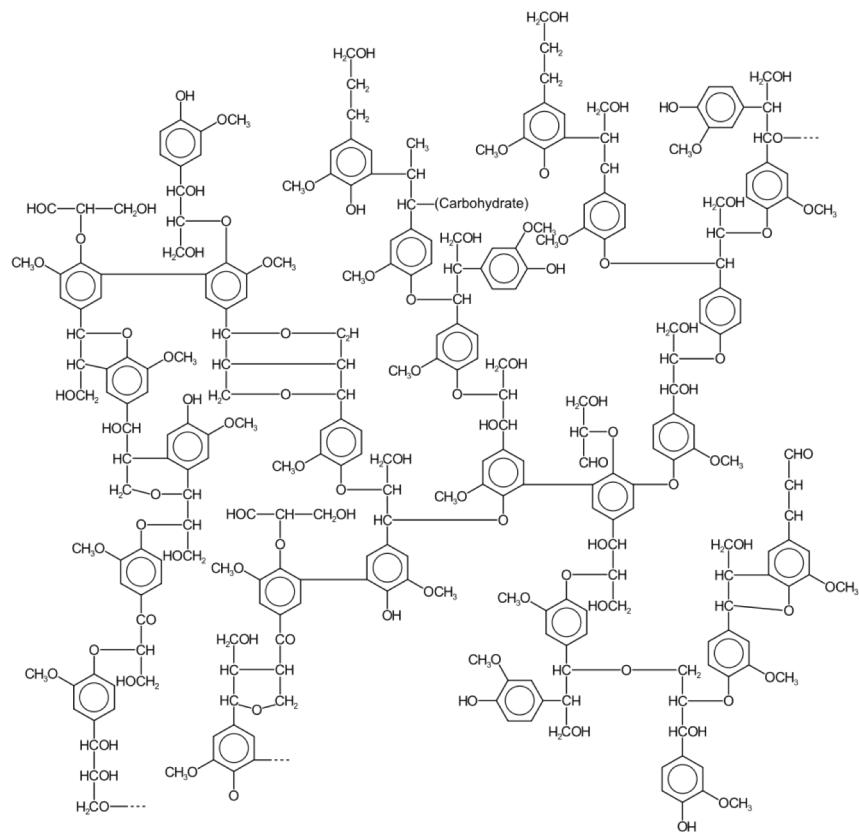


- Prepare ZnO by alternating treatments by
 - diethyl zinc $\text{CH}_3\text{-CH}_2\text{-Zn-CH}_2\text{-CH}_3$
 - Water
- ZnO n-type semiconductor
- Bandgap 3.37 eV



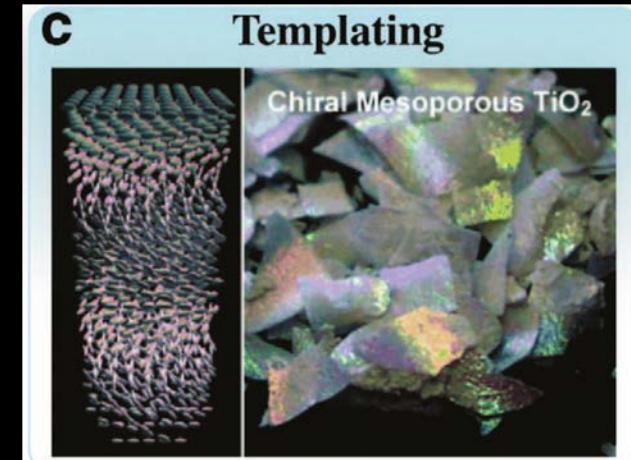
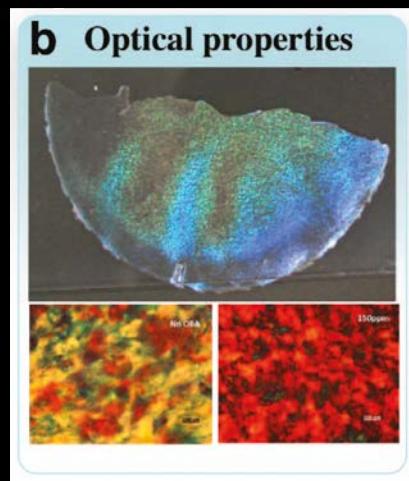
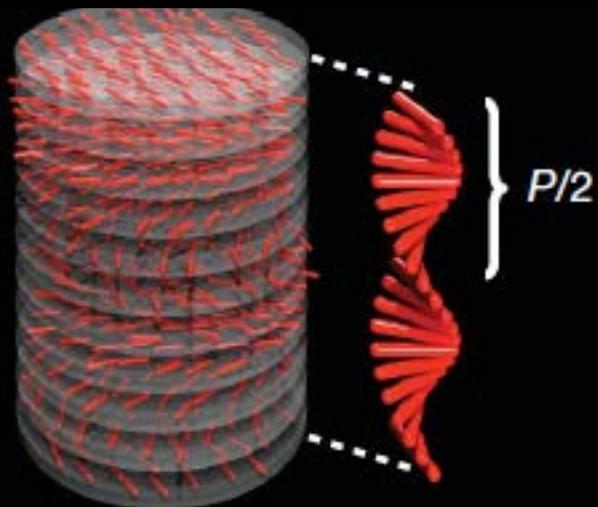
Lignin for electrochemical energy storage

- Lignin redox active
- Electrically insulating
- Compound with electrically conducting polymer
- High charge capacity and capacitance per mass
 - 80 mAh/g



Optical properties

Left-handed CNC liquid crystal

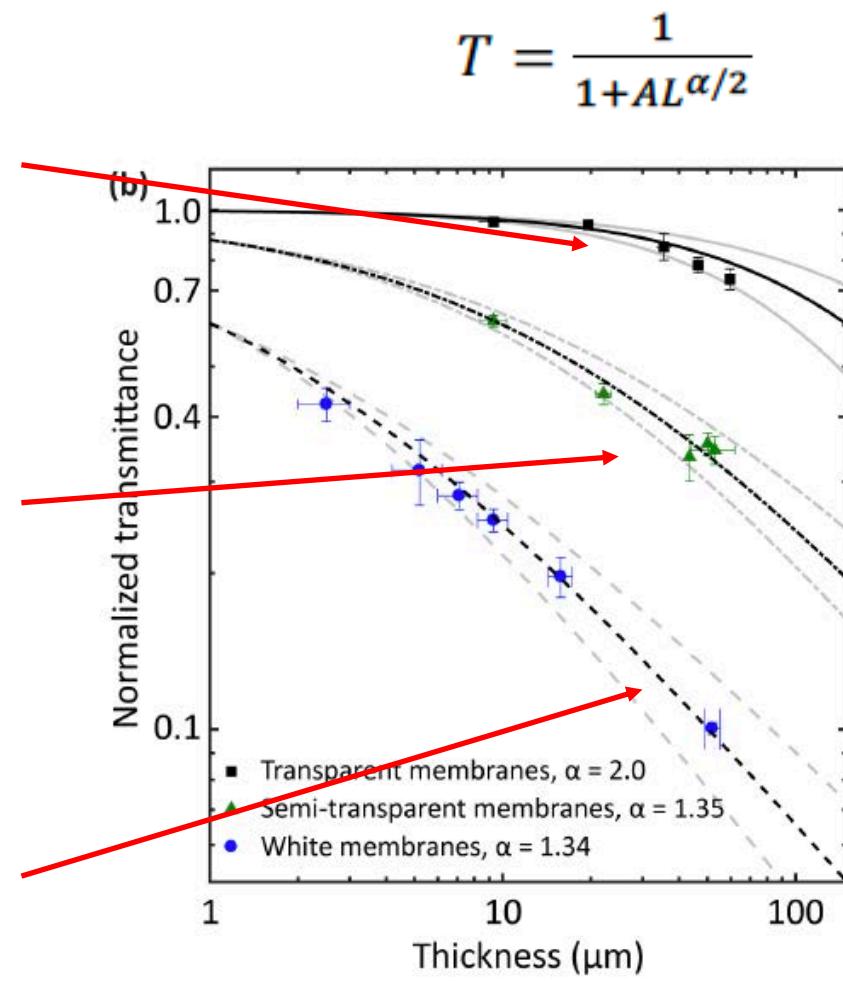
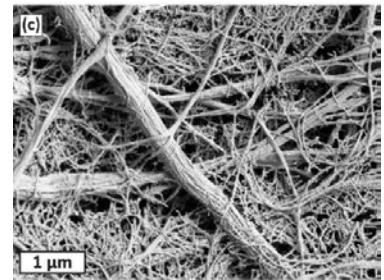
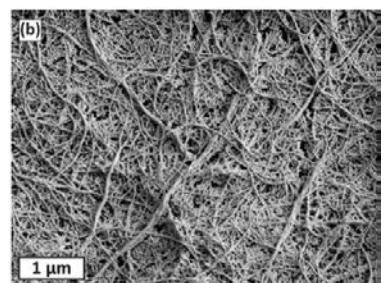
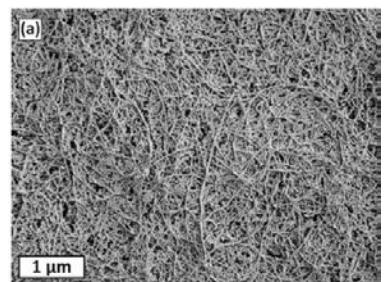


Gray et al
Qi, Shopsowitz, Hamad, MacLachlan, *J. Am. Chem. Soc.* 2011, **133**, 3728

White beetle

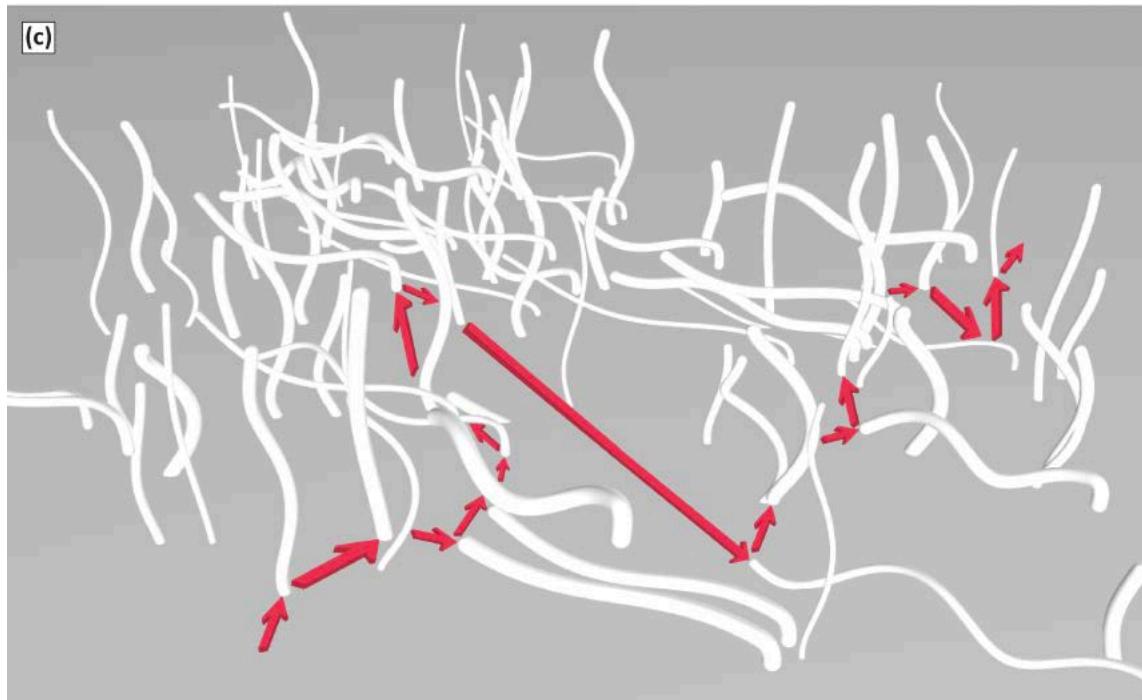


Anomalous Diffusion-Assisted Brightness in White Cellulose Nanofibril Membranes



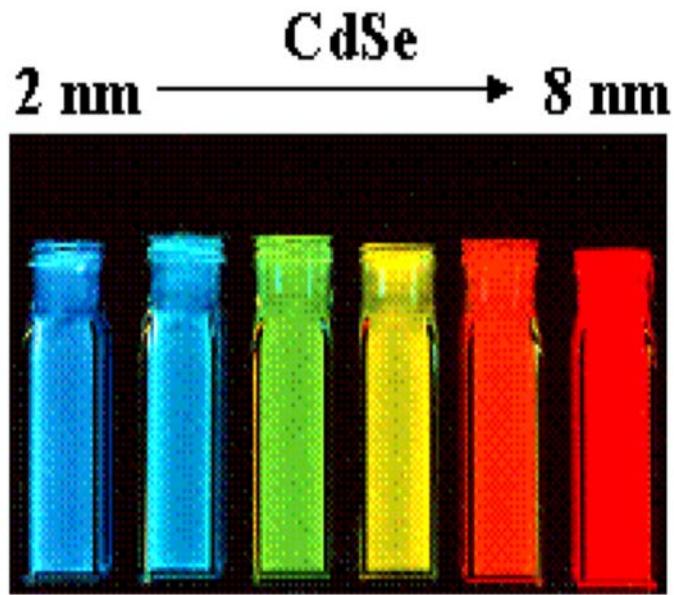
Toivonen, Onelli, Jacucci, Lovikka, Rojas, Ikkala, Vignolini,
Adv. Mat, 2018, 1704050

Anomalous Diffusion-Assisted Brightness in White Cellulose Nanofibril Membranes



Toivonen, Onelli, Jacucci, Lovikka, Rojas, Ikkala, Vignolini,
Adv. Mat, 2018, 1704050

Textile colours due to metallic nanoparticles



More functions...

- Composites
- Fibers
- Foams, aerogels
- Films
- Gels
- Magnetic
- Electrically conducting
- Semiconducting
- Thermally isolating
- Transparent
- Structural colours
- Mechanically strong
- Catalytic, photocatalytic
- Energy storage
- Ionically conducting
- Biological templating
- Analytics
- Membranes, filtration
- Ballistic

**Future:
computational materials science
vs machine learning**

In the future: use of Big Data

- Reduce trial and error approaches
 - Screen larger parameter space
-
- Now used in selected area in materials science: "Materials Genome Project"
 - In the future more for complex biological materials

