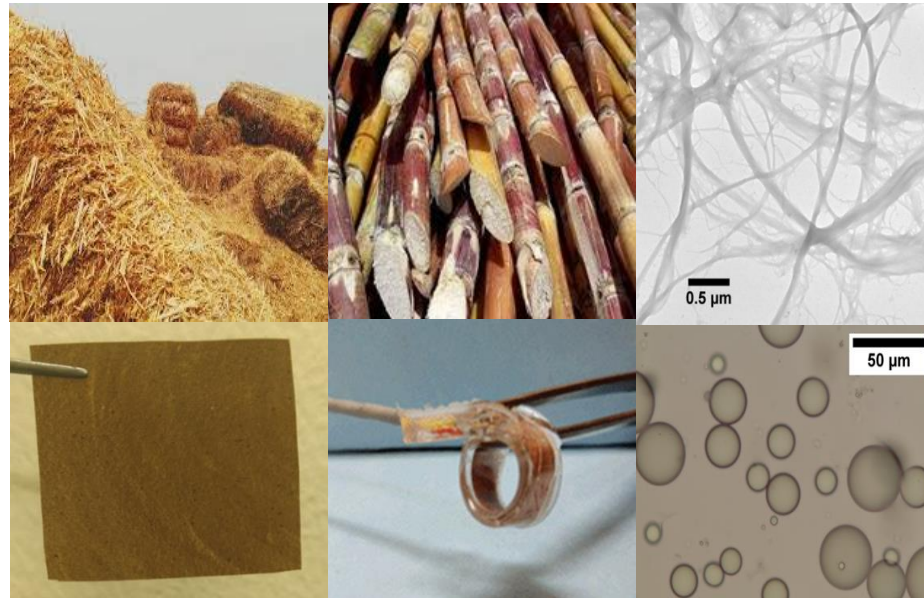


# Conversion of Cellulosic Biomass to Valuable Materials



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# Cellulose

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**Cellulose - the most ubiquitous renewable polymer resource in the nature**

**Estimated annual production of  $7.5 \times 10^{10}$  tons**

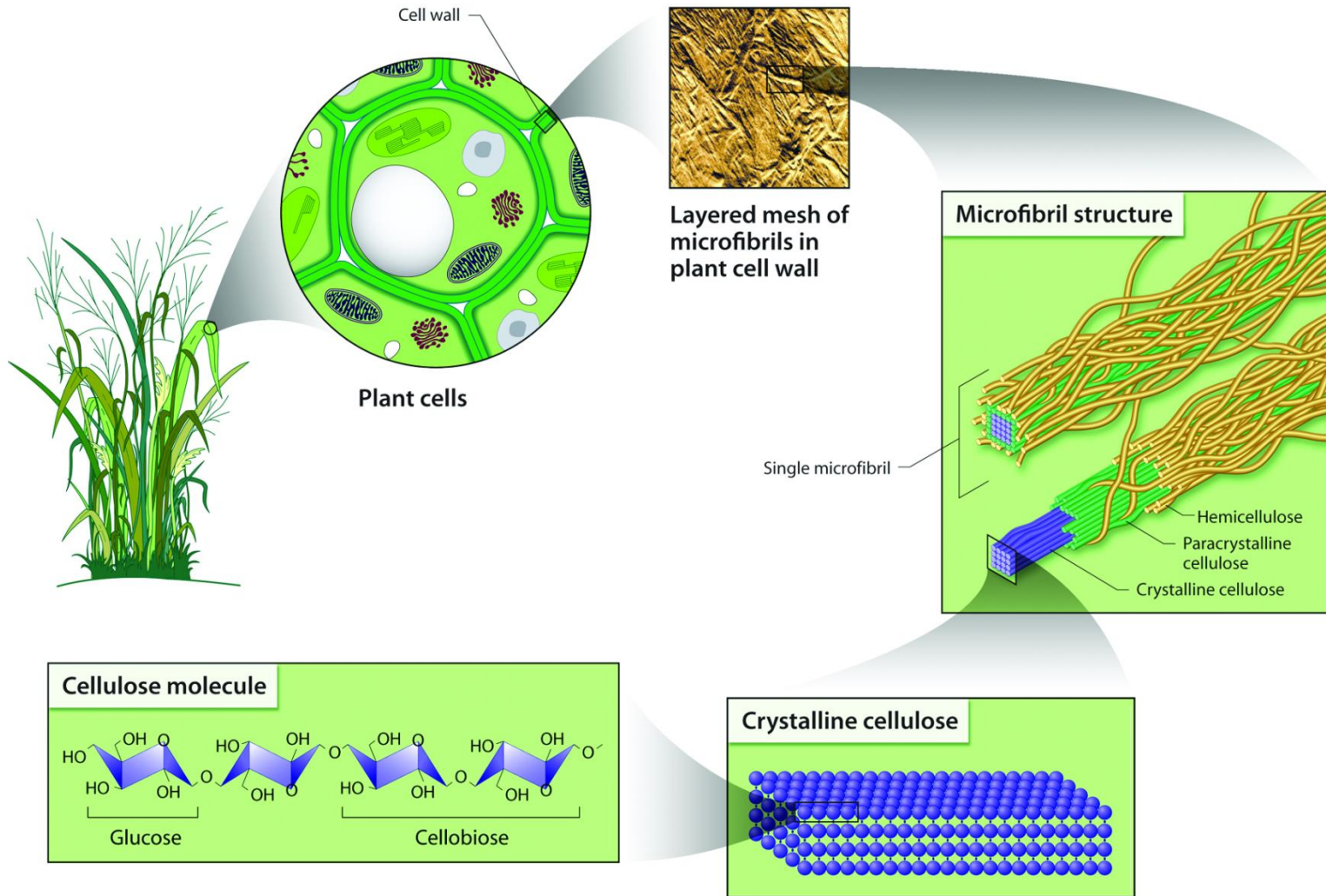
**Lignocellulosic matter - basic building block of plant matter and trees**

**Traditionally used as combustible and load-bearing materials in construction**

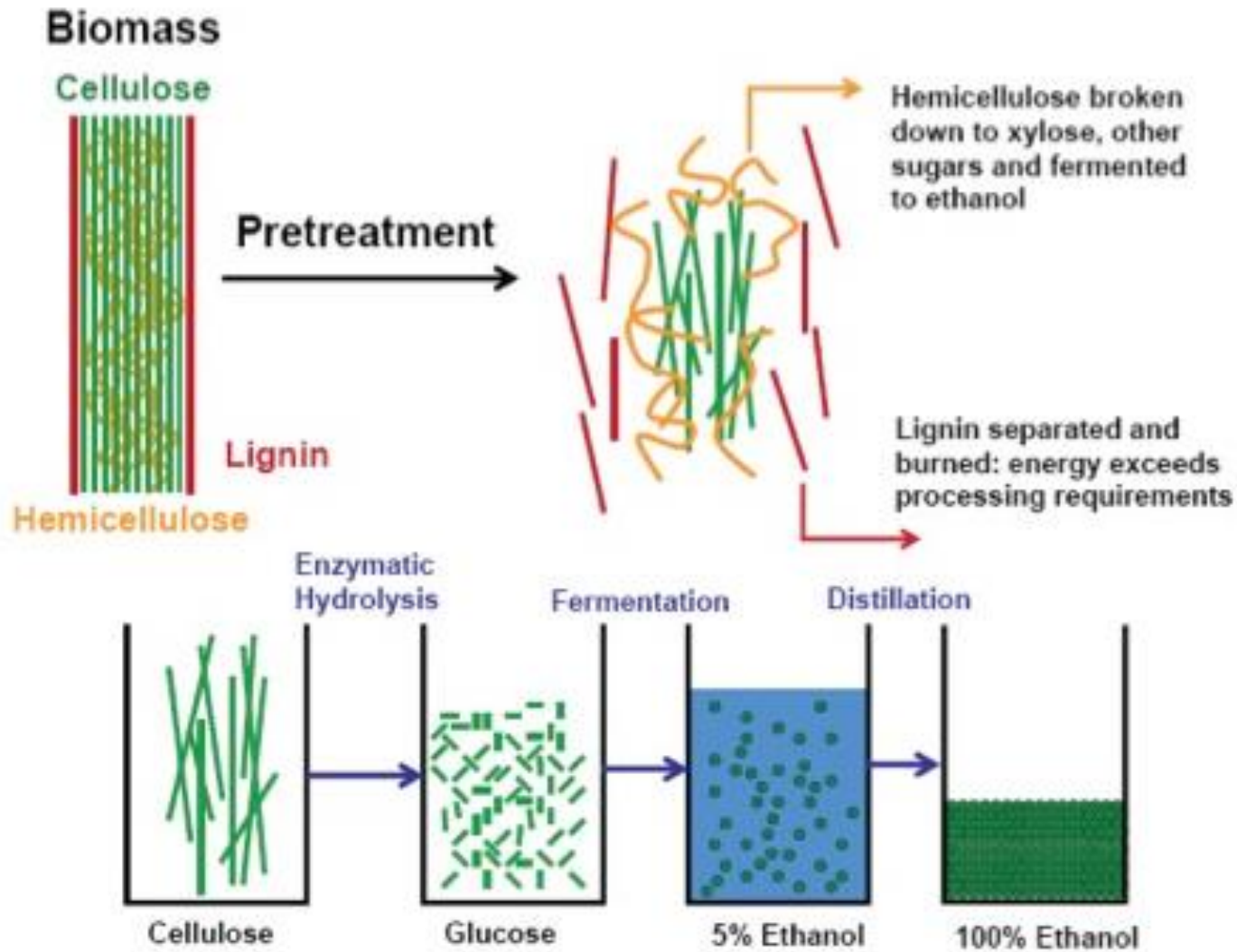
**Paper, cellophane films, explosives, textiles, dietary fibers**



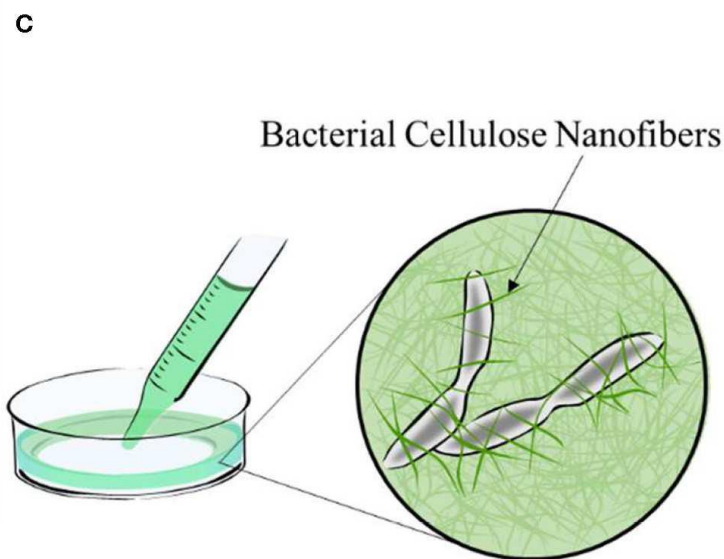
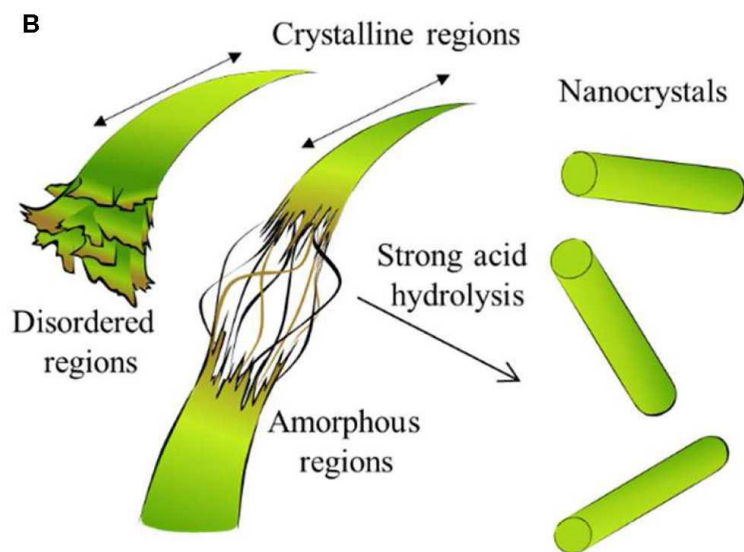
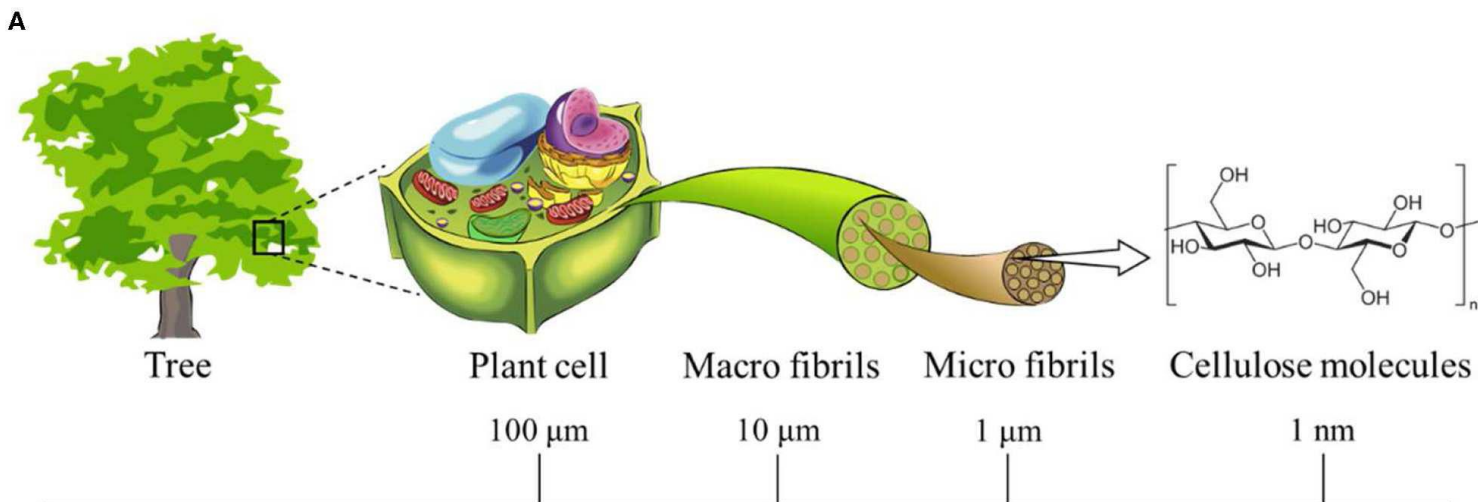
# Cellulose



# Cellulose to Ethanol



# Structure of Cellulose Fiber



# Sources for the Production of Cellulose Fibers

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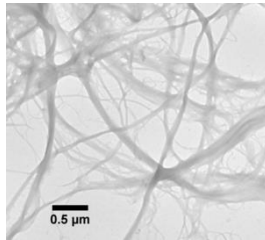
Source group	Sources
Hardwood	Eucalyptus, Aspen, Balsa, Oak, Elm, Maple, Birch
Softwood	Pine, Juniper, Spruce, Hemlock, Yew, Larch, Cedar
Annual plants/Agricultural residues	Oil palm, Hemp, Jute, Agave, Sisal, triticale straw, soybean straw, Alfa, Kenaf, Coconut husk, Begasse, Corn leaf, Sunflower, Bamboo Canola, Wheat, Rice, pineapple leaf and coir, Peanut shells, Potato peel, Tomato peel, Garlic straw residues, Mulberry fiber, Mengkuang leaves
Animal	Tunicates, <i>Chordata</i> , <i>Styela clava</i> , <i>Halocynthia roretzi</i> , <i>Drasche</i>
Bacteria	<i>Gluconacetobacter</i> , <i>Salmonella</i> , <i>Acetobacter</i> , <i>Azotobacter</i> , <i>Agrobacterium</i> , <i>Rhizobium</i> , <i>Alkaligenes</i> , <i>Aerobacter</i> , <i>Sarcina</i> , <i>Pseudomonas</i> , <i>Rhodobacter</i>
Algae	<i>Cladophora</i> , <i>Cystoseria myrica</i> , <i>Posidonia oceanica</i>

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# Nanocellulose

## Nanocellulose

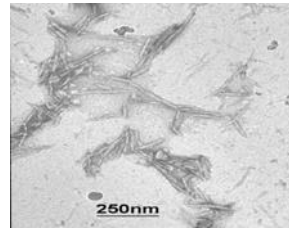
**Cellulose nanofibres or microfibrillated cellulose**



Produced by mechanical treatment of cellulose pulp

Adv: High production rate, no chemical waste, thermal stability  
Disadv: Energy intensive, crystallinity 40-78%

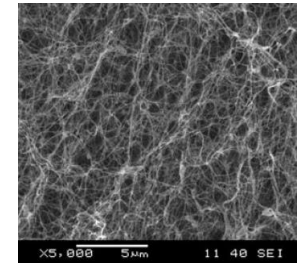
**Cellulose nanocrystals or nanocrystalline cellulose**



Produced by acid hydrolysis

Adv: High crystallinity 60-90%  
Better dispersibility in polymers  
Disadv: Low production rate, more chemical waste, low thermal stability

**Bacterial nanocellulose**



Synthesized by bacteria

Adv: Purified form of cellulose, High crystallinity 80-90%  
Disadv: Low production rate,

# Properties and Applications

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## Sources for CNC and CNF extraction

Wood, cotton,  
hemp, flax, wheat  
straw, sugar beet,  
potato tuber,  
mulberry  
bark, ramie, algae,  
and tunicin

## Lignocellulosic biomass contains

30–50 wt % cellulose,  
19–45 wt % hemicellulose  
15–35 wt % lignin.

## Properties

- Natural abundance
- Biodegradable
- Non-toxic
- Biocompatible
- Exceptional strength characteristics at par with Kevlar
- Light weight
- Functionalizable surface

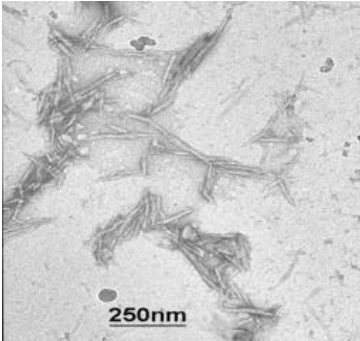
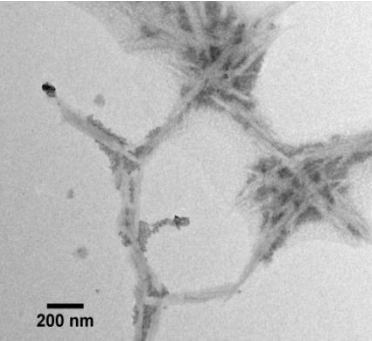
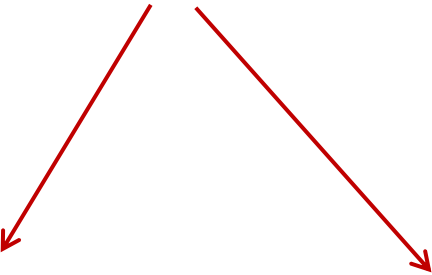
## Applications

- Composites and foams for automotive, aerospace, and building construction, viscosity modifiers for cosmetics and oil drilling fluids,
- High performance fillers for paper, packaging, paints, plastics, and cement.
- Supercapacitors
- Battery separators
- Membranes
- Packaging
- Biomedical: Scaffolds, drug excipients and drug delivery, wound healing

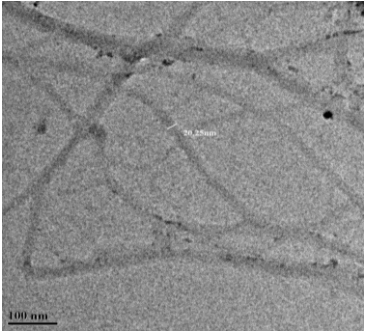
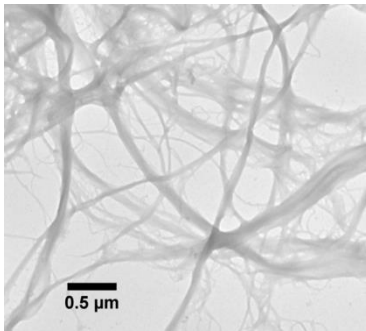
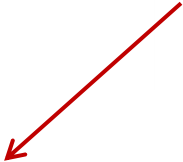


# Cellulose Nanocrystals and Nanofibres

## Acid hydrolysis



## Mechanical treatment



# Acid Hydrolysis

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In acid hydrolysis, the hydronium ions penetrate the amorphous regions of cellulose chains and hydrolytically cleave glycosidic bonds, to release individual crystalline cellulose nanoparticles.

Sulfuric acid, highly concentrated (~64%), is the most common reagent reported for acid hydrolysis

Results in partial functionalization of the surface hydroxyl groups with sulfate half-esters, which confer surface charges

Provides aqueous suspendability to the resulting CNCs

## **Other acids**

Hydrochloric acid

Phosphoric acid

Hydrobromic acid

Nitric acid

Result in fewer or no charge incorporation to the surface.

# Morphology of Nanocellulose

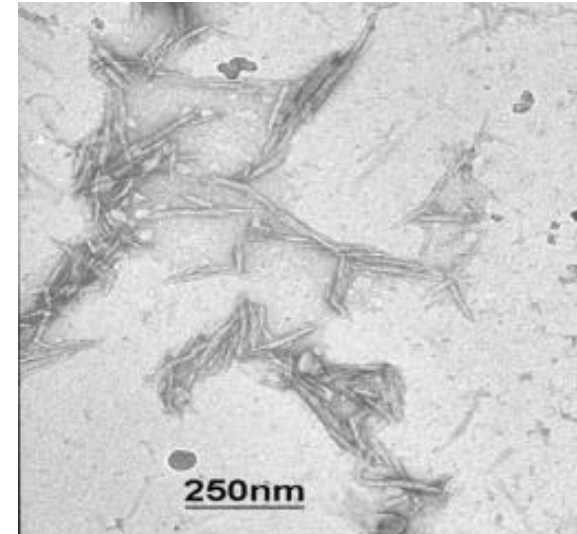
Source	Length	Cross section	Aspect ratio
Tunicate	100 nm – microns	10-20 nm	5 to > 100 (high)
Algal (Valonia)	> 1000 nm	10 to 20 nm	50 to > 10 nm (high)
Bacterial	100 nm – microns	5-10 x 30-50 nm	2 to > 100 (medium)
Cotton	200-350 nm	5 nm	20 to 70 (low)
Wood	100–300 nm	3 – 5 nm	20 to 50 (low)

# Acid Hydrolysis

CNCs are rods or whiskers

Typically ranging from 3 to 50 nm in width and 50–500 nm in length.

- High axial stiffness (105– 168 GPa)
- High Young's modulus (20–50 GPa)
- High tensile strength ( $\sim 9$  GPa),
- Low coefficient of thermal expansion ( $\sim 0.1$  ppm/K),
- High thermal stability ( $\sim 260^\circ\text{C}$ ),
- High aspect ratio ( $\sim 10$ – $70$ ),
- Low density (1.5–1.6 g/cm<sup>3</sup>),
- Lyotropic liquid crystalline behavior, and
- Shear thinning rheology



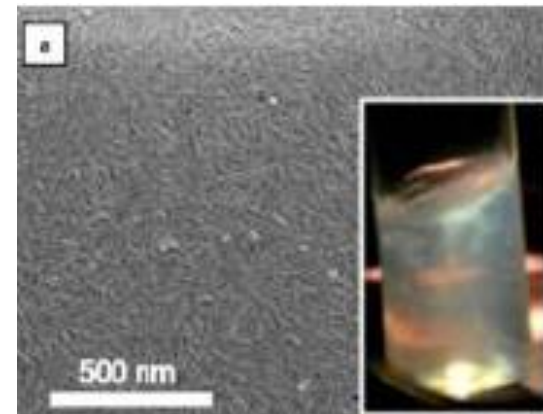
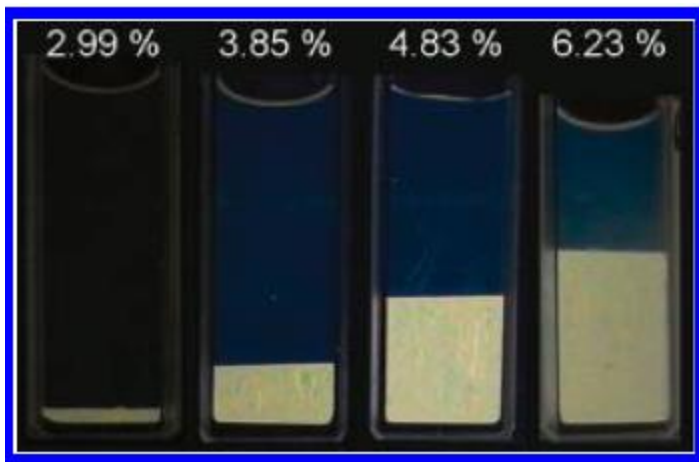
# Acid Hydrolysis

The phase behavior of lyotropic CNC suspensions of sulfonated CNCs produced from cotton.

Between 3.07 and 10.4 vol %,- phase separation into liquid crystalline and isotropic

~ 12.1 vol %, the isotropic phase disappeared, giving a fingerprint texture which is characteristic of a cholesteric liquid crystal.

At even higher concentrations, the fingerprint texture of the liquid crystal phase disappears and the suspension behaves as a rheological gel.



# Acid Hydrolysis

source	type	method of isolation	dimensions of isolated CNC/CNF		application
			( <i>l</i> )	( <i>d</i> )	
sisal fibers	CNF	acetic acid hydrolysis	658 ± 290 nm	27 ± 13 nm	translucent CNF film
<i>Amorpha fruticosa</i> Linn.	CNF	acetic acid hydrolysis	~10 μm	~10 nm	transparent nanopaper
flax plant	CNC	sulfuric acid hydrolysis	20 nm	300 nm	reinforcing agents
garlic straw residues	CNC	sulfuric acid hydrolysis	~480 nm	~6 nm	reinforcing agents
rice straw, wheat straw, barley straw	CNC	sulfuric acid hydrolysis	~700 nm	~20 nm	reinforcing agents
bamboo	CNF	microwave liquefaction		2–30 nm	reinforcing agents
pine cones	CNF	mechanical grinding		~15 nm	reinforcing agents
waste pulp residues	CNF	mechanical disintegration		10–100 nm	permeable membranes
<i>Gelidium elegans</i> red algae	CNC	sulfuric acid hydrolysis	~547 nm	~21.8 nm	reinforcing agents
corn cob residue	CNC	sulfuric acid hydrolysis	~198 nm	~5.5 nm	further study required to determine end-user applications
	CNF	TEMPO oxidation; pulp refining	~438 nm μm	~2.1 nm	
				~43.1 nm	
sunflower stalks	CNC	sulfuric acid hydrolysis	~175 nm	5–10 nm	reinforcing agents
	CNF	steam explosion		5–10 nm	
cotton stalks	CNF	1. sulfuric acid hydrolysis	100–500 nm	10–50 nm	industrial applications
		2. TEMPO oxidation	10–100 nm	3–15 nm	

# Acid Hydrolysis

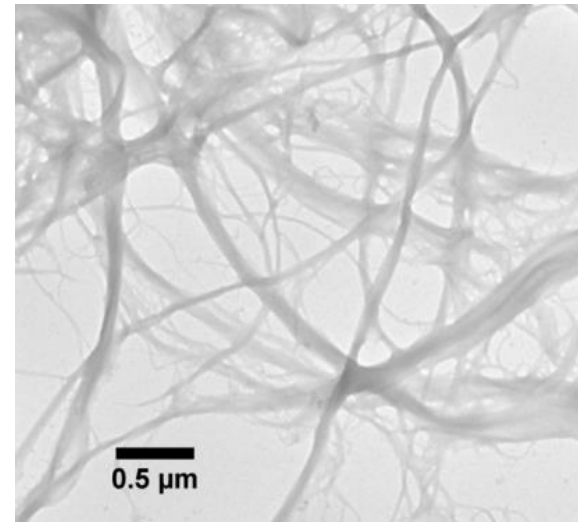
source	type	method of isolation	dimensions of isolated CNC/CNF		application
			(l)	(d)	
tomato peels	CNC	sulfuric acid hydrolysis	~135 nm	~7.2 nm	biocomposites
waste sackcloth	CNF	H <sub>2</sub> O <sub>2</sub> /HNO <sub>3</sub> hydrolysis medium	hundreds of nm	20–50 nm	
jute fibers	CNF	steam explosion		~50 nm	reinforcing agents
<i>Agave tequilana</i> bagasse, barley husks	CNC	sulfuric acid hydrolysis	~322 nm	~11 nm	reinforcing agents
banana peels	CNF	sulfuric acid hydrolysis	~329 nm	~10 nm	reinforcing agents
		enzymatic treatment: xylanase	455 nm	~10.9 nm	
<i>Helicteres isora</i>	CNF	steam explosion		~60 nm	reinforcing agents
maize straw	CNW <sup>r</sup>	sulfuric acid hydrolysis	~388 nm	15–25 nm	nanofillers in polymer matrixes
sawdust wastes	CNC	hydrothermal processing	101–107 nm	18–35 nm	biomedical applications
coir fiber	CNF	steam explosion		~37.8 nm	industrial, biomedical
dry softwood pulp	CNF	high shear homogenization		16–28 nm	optical applications
sugarcane bagasse	CNC	high pressure homogenization		10–20 nm	
eucalyptus kraft pulp	CNF	sulfuric acid hydrolysis	100–150 nm	10–20 nm	polymer composite applications

The current limitations with acid hydrolysis - corrosive nature of the acids and the production of large amounts of chemical waste

Although recycling strategies have been devised at the industrial scale.

# Mechanical Treatment to make Cellulose Nanofibers

- High pressure homogenization
- High shear homogenization
- Cryocrushing
- Microfluidization
- Grinding
- High intensity ultrasonication
- Milling
- Steam explosion



Energy consumption and production costs are high when mechanical treatment alone is used to delaminate the fibers

A pretreatment can reduce the energy consumed by mechanical processing from between 20,000 and 30,000 kWh/ton to 1000 kWh/ton



# Pre-treatment to make Cellulose Nanofibers

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- Alkaline treatment - removal of the lignin and degradation of hemicelluloses, some hemicellulose might remain.
- Reaction conditions should be controlled, to prevent cellulose degradation.
- The obtained pulp is then washed with deionized water until neutralized.
- The cycle may be repeated two to three times depending on the lignin content of the source material.
- Bleaching treatment with peroxide or hypochlorite removes more lignin to yield a white pulp
- The hemicellulosic content that remains after alkali treatment is usually removed via hydrolysis.

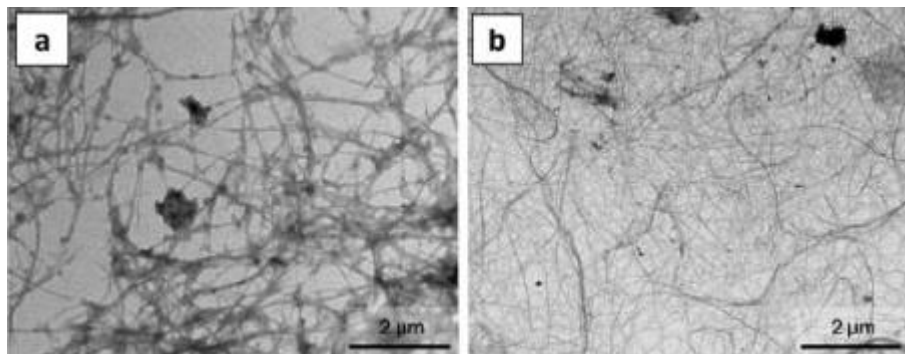
# Carboxylated Cellulose Nanocrystals

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- Cellulose may be oxidized with TEMPO radicals prior to a mechanical treatment.
- TEMPO-mediated oxidation facilitated CNC isolation under mild aqueous conditions, with surface hydroxyl groups being converted to carboxylic acid.
- Ammonium persulfate has also been used to afford similar materials.
- Hydrogen peroxide in ethanol allowed going directly from biomass to oxidized CNCs.
- The aqueous suspension, which is then Soxhlet extracted, air-, freeze-, or spray-dried
- Spray drying being the method of choice for large-scale production.

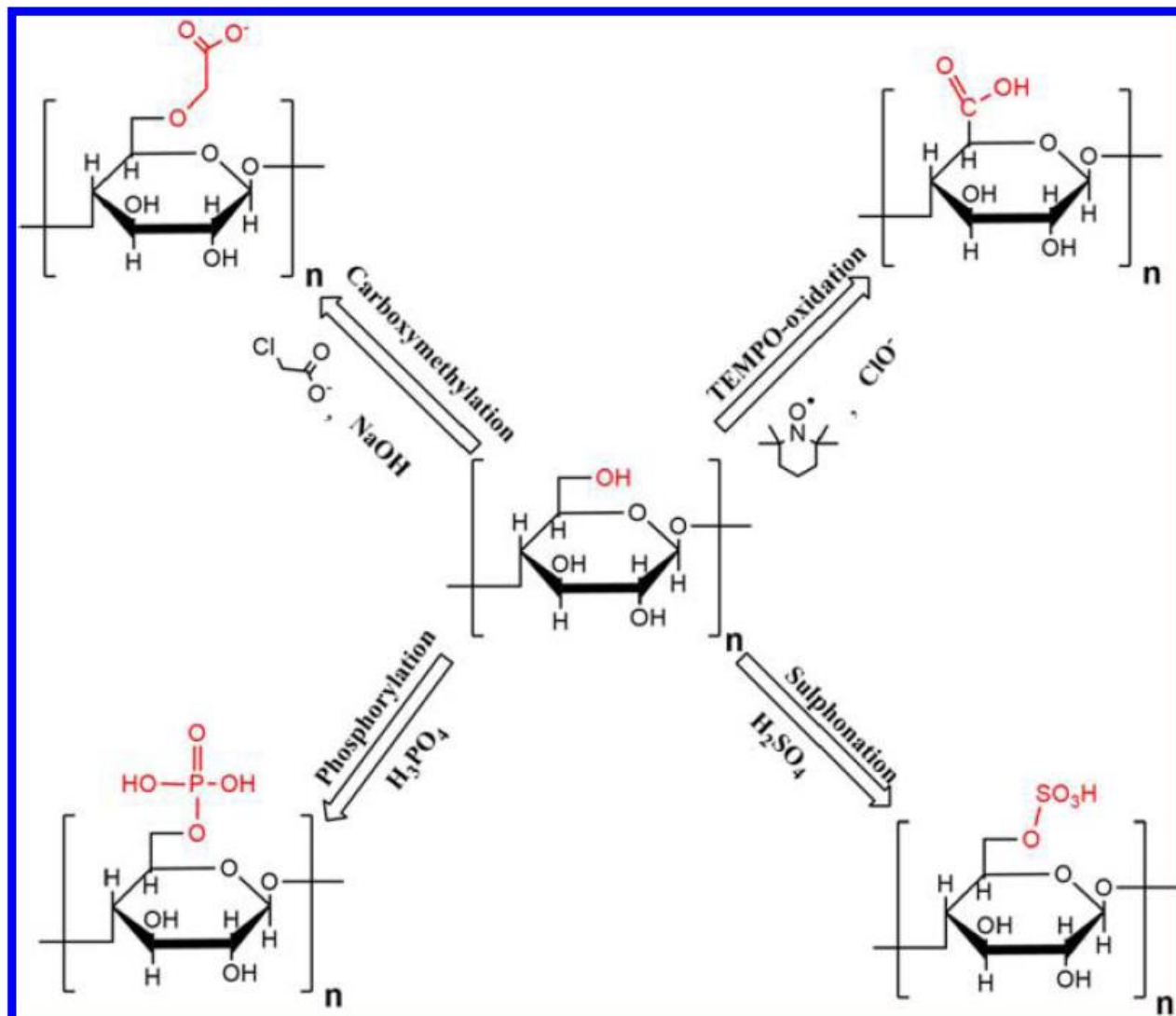
# Enzymatic Hydrolysis

- Enzymatic hydrolysis is considered to be environmentally friendly.
- Enzymes modify or degrade the lignin and hemicellulose, restricting the degree of hydrolysis or selectively hydrolyzing specified components in the cellulosic fibers.
- Xylanases are hydrolytic enzymes that modify the hemicelluloses.
- Production of materials and fine chemicals.
- Co-production of nanocellulose and biofuels using multifunctional cellulolytic enzymes using *Caldicellulosiruptor bescii*.
- Yield low
- Can be tuned to meet societal demands on clean chemical processes for the production of materials and fine chemicals.

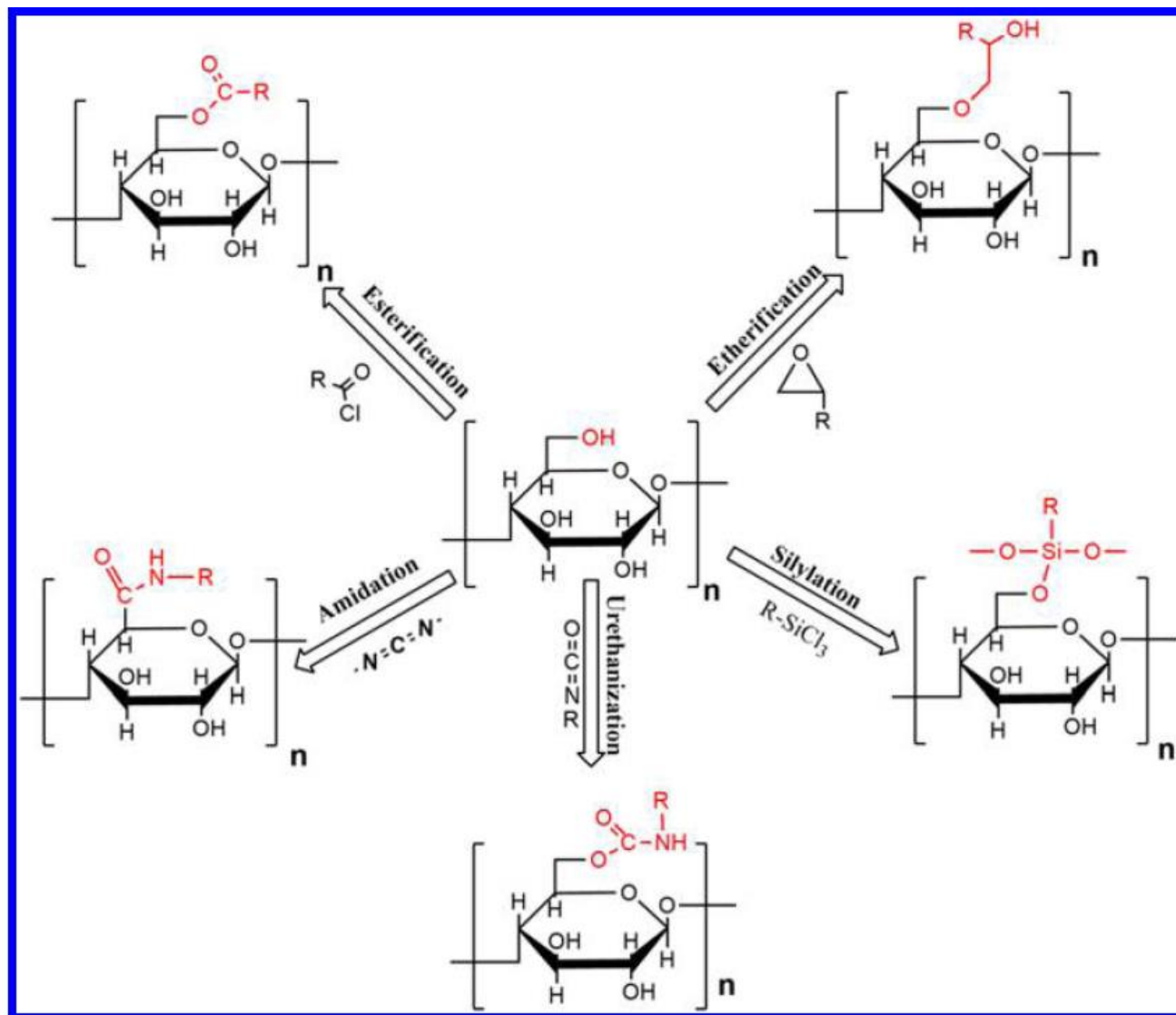


TEM images of the cellulose nanofibers obtained by (a) chemical treatment and (b) enzymatic treatment.

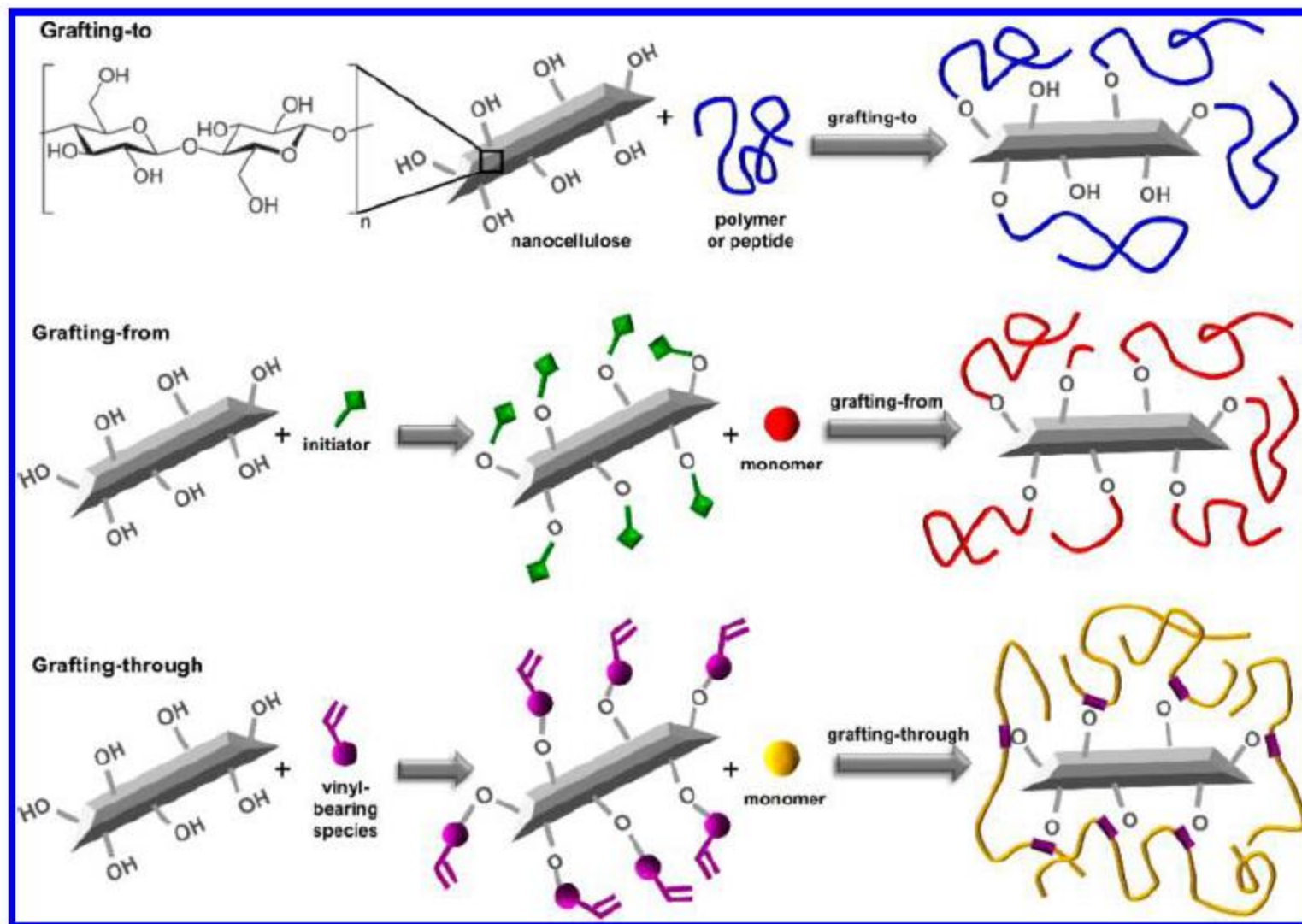
# Chemical Modification of CNC



# Chemical modification of CNC



# Chemical modification of CNC



# Applications

# Applications of Nanocellulose

High Volume Applications	Low Volume Applications	Novel and Emerging Applications
Cement	Wallboard facing	Sensors – medical, environmental, industrial
Automotive body	Insulation	Reinforcement fiber – construction
Automotive interior	Aerospace structure	Water filtration
Packaging coatings	Aerospace interiors	Air filtration
Paper coatings	Aerogels for the oil and gas industry	Viscosity modifiers
Paper filler	Paint – architectural	Purification
Packaging filler	Paint – special purpose	Cosmetics
Replacement – plastic packaging	Paint – OEM applications	Excipients
Plastic film replacement		Organic LED
Hygiene and absorbent products		Flexible electronics
Textiles for clothing		Photovoltaics
		Recyclable electronics
		3D printing
		Photonic films



# Nanocellulose Applications in Paper Industry

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Paper manufacturers typically add fillers in paper to reduce cost and enhance properties

Paper with CNF is less porous, the printing quality is higher, and it is less translucent.

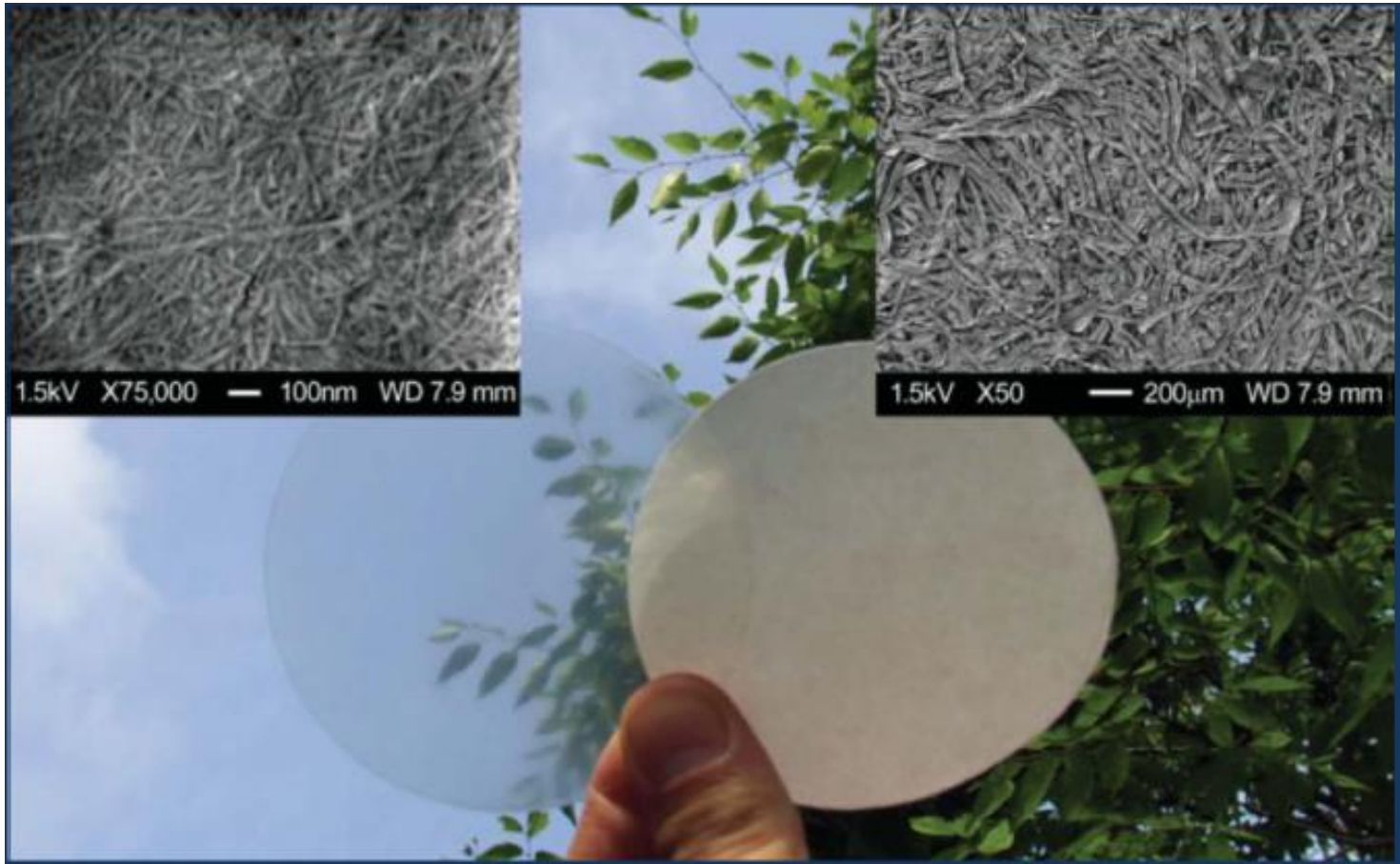
In addition, it takes less energy to dry the paper because much less cellulose is needed through the thickness.

This application reduces material inputs and energy in the production stage

**3 g/m<sup>2</sup> coating of CNF will permit less use of nano-clays, resulting in a reduction in weight of the paper by as much as 12.5 g/m<sup>2</sup> while maintaining the paper's strength.**

UPM-Kymmene Corporation, pat. WO 2013072550 A3, 2013.

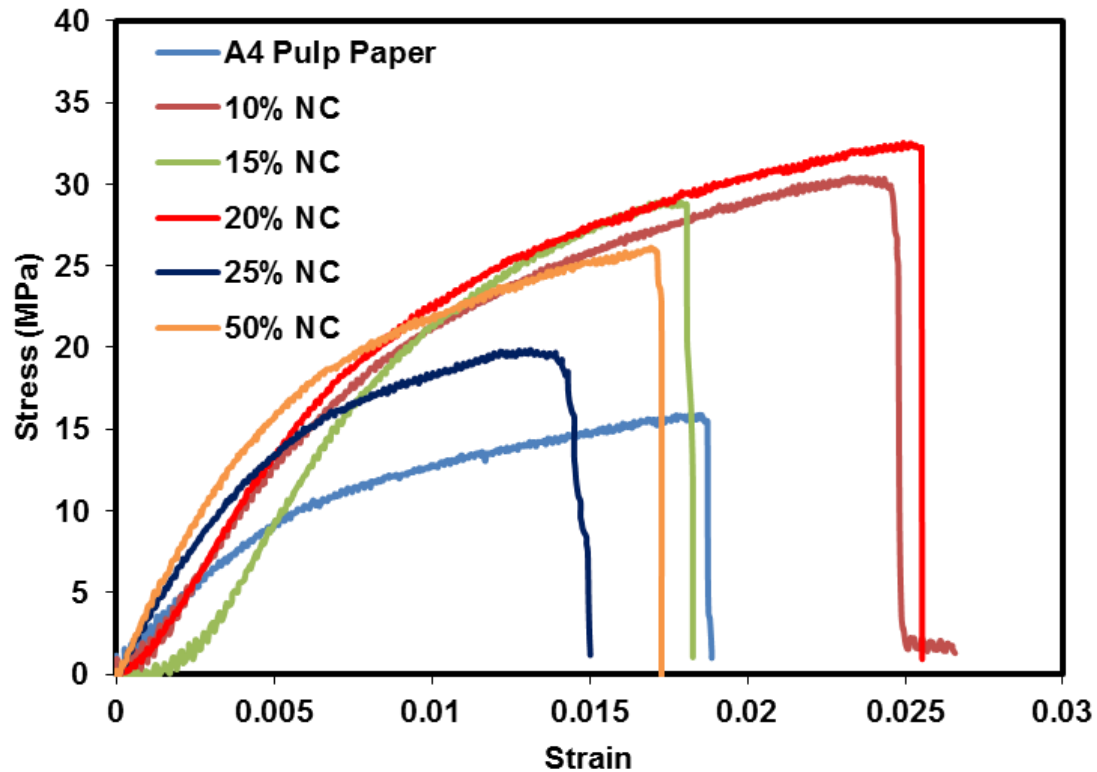
# Transparent Paper



Nogi, et al. Adv. Mater. 2009, 20, 1–4

# Enhancing Strength of Paper

By adding fibrillated cellulose nanomaterials during the production process, tear strength of paper can be increased



# Barrier Properties and Packaging

Packaging industry mostly uses non-degradable petrochemical-based polymers, creating considerable environmental impact.

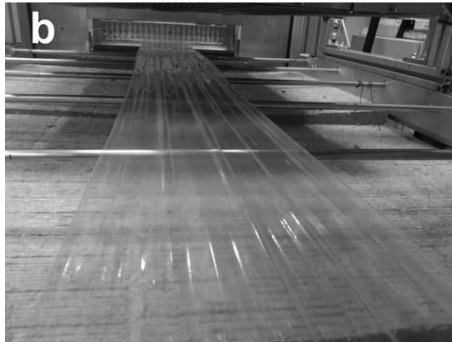
The ability of nanocellulose to form a dense percolating network due to hydrogen bonds results in lower permeability- desirable for filtration and packaging, especially food packaging

Cellulose nanocrystal coatings on plastic films reduce friction in flexible packaging while retaining the optical properties of the coating

Polyethylenimine (PEI) functionalized NFC and PEI/carboxymethyl cellulose have oxygen permeabilities of 0.34 and 0.71  $\text{cm}^3 \cdot \mu\text{m} / \text{m}^2 \cdot \text{day} \cdot \text{kPa}$  at 23 °C and 50% relative humidity, close to poly(vinyl alcohol) and ethylene vinyl alcohol deposited on PLA.



# HDPE with CNF Coating



Pilot facilities used to produce the biobased multilayer films with casting of the bio-HDPE (high density polyethylene) (a), coating with the CNF (b), and finally extrusion coating with the bio-LDPE resin (c).

# Hydrogels of Nanocellulose

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Hydrogels are highly hydrated (> 90% water uptake) chemically or physically cross-linked networks

Can be produced from nanocellulose alone, or with additional polymers such as PVA

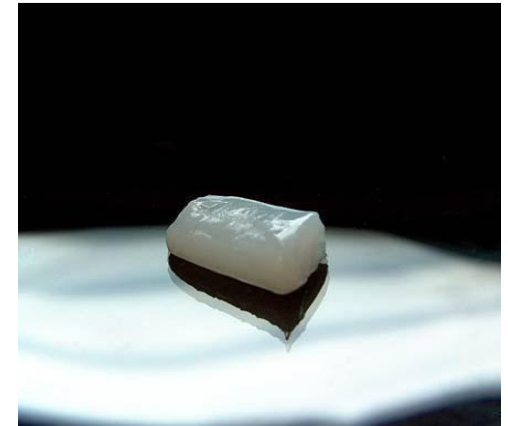
CNCs gel in water above a concentration of 10 wt %. pH can influence CNC gelation behavior, as CNC is itself a charged species

CNFs, as longer and more flexible forms of nanocellulose, create more elastic gels than CNCs.

CNFs will afford such structures at concentration <6 wt %.

Hydrogels of CNF have been used as starting materials to spin fibers with excellent strength

The mechanical properties of CNCs allow the formation of aerogels with much improved mechanical resistance compared to inorganic oxide based systems.



# Nanocarbons and Nanocellulose

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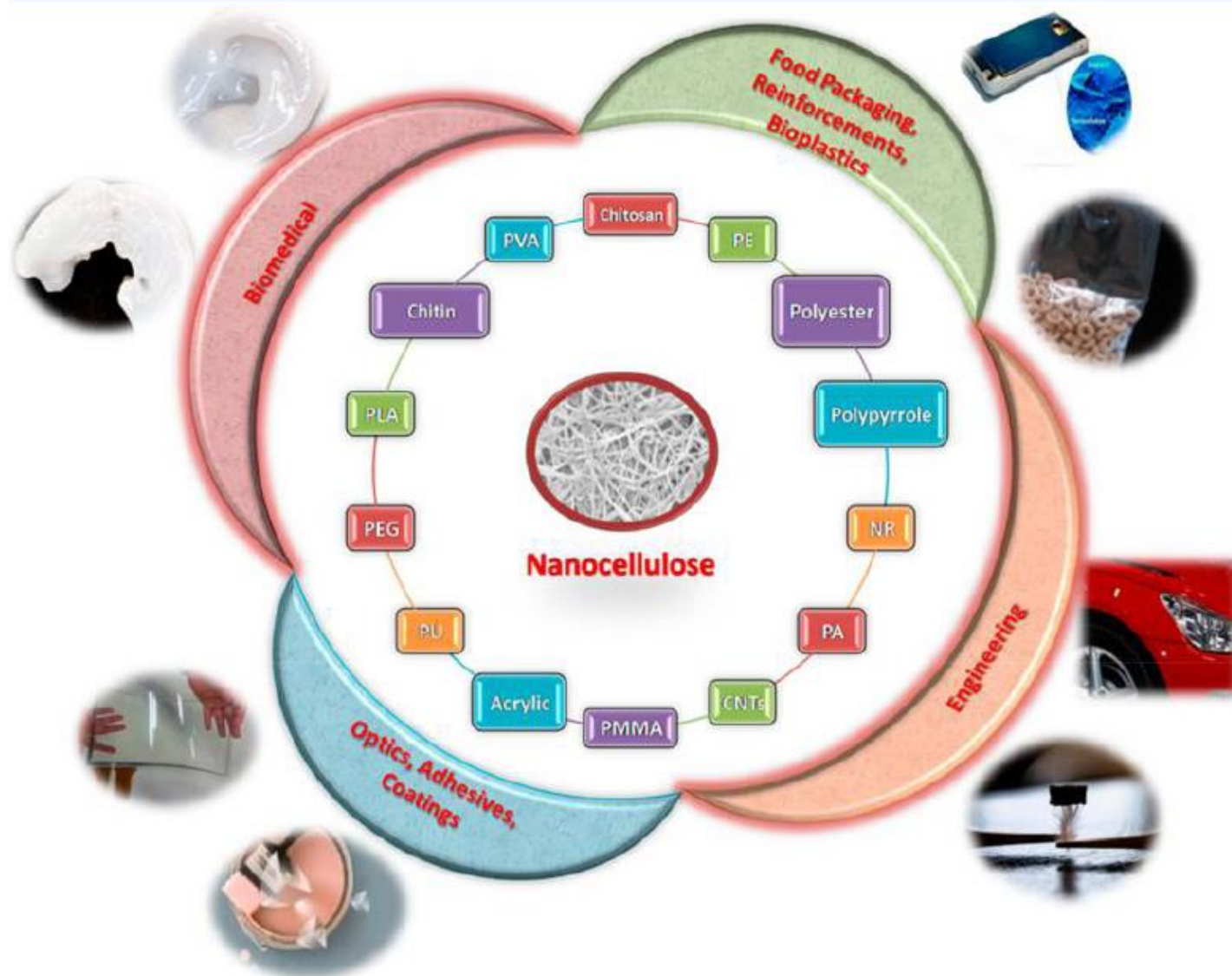
**The favorable interactions between the nanocarbon and the cellulose interrupt the tendency for both cellulose and nanocarbons to autoaggregate.**

**Carbon nanotube–cellulose composites have been predominantly investigated as conductive papers and conductive fibers for wearable electronics**

**Graphene oxide–cellulose composites : sensitive and selective solvent sensors. The adsorption of ethanol, acetone, toluene, chloroform, and n-hexane could all be distinguished from one another based on the relative capacitance change.**

**The role of the cellulose is to provide a strong, flexible scaffold for the nanocarbon, allowing the desirable properties of the nanocarbon to be integrated into a nontoxic, environmentally friendly device.**

# Nanocellulose- Polymer Composites





# Nanocellulose–Polymer Composites

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- Nanocellulose has been used to reinforce a wide range of polymer matrixes, such as poly(styrene-co-butyl acrylate), poly(vinyl acetate), poly-(ethylene oxide-co-epichlorohydrin), poly(styrene-co-butadiene), polyurethane, and epoxy resins
- A number of methods such as compression molding freeze-drying, hot pressing, and solution impregnation are employed for the preparation of these organic composites
- Nanocellulose fibers are added to cement to decrease shrinkage during drying, to increase sound absorption, and to produce a more environmentally friendly, less hazardous material.
- Such composites are an alternative to asbestos.
- Hydrophilicity of the cellulose component could affect long term performance

# Medical Applications

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Nanocellulose is interesting for biomedical materials : mechanical properties, its nanofibrous network, and its natural source.

**Poly(vinyl alcohol)-based hydrogels containing nanocellulose good for ophthalmic applications: soft and flexible, yet mechanically strong. They can also be transparent and can have a water content of up to 90%.**

Soft Matter 2017, 13, 3936–3945.

**Nanofibrillated cellulose cross-linked with calcium ions to form a hydrogel for wound-healing dressings The hydrogel is nontoxic and non-inflammatory. It retained a desirably moist environment to promote healing.**

Carbohydr. Polym. 2017, 174, 299–308.

**A double membrane hydrogel composed of alginate and CNC shows great promise for the targeted released of antibiotic drugs via controlled swelling mechanisms**

ACS Appl. Mater. Interfaces 2016, 8, 6880–6889.

**CNC–chitosan hydrogels produced via a solvent-free process - for stomach specific drug delivery due to their mechanical properties and pH sensitive drug delivery characteristics**

Polymers 2017, 9, 64.

# Toxicity of Nanocellulose

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Nanocellulose has been found to be non-cytotoxic and has been explored as a tissue culture medium to support cell proliferation.

## Conflicting observations

- Hydrosoluble phosphorous acid functionalized cellulose was evaluated for cytotoxicity and for use as a tissue scaffold material.
- The obtained water-soluble films were subjected to cell compatibility studies and found to exhibit good cytocompatibility due to their nontoxic nature.
- However, a more recent report has found that cellulose nanocrystals induced an inflammatory response and were capable of entering cells, where nanofibrillated cellulose was relatively toxic
- Thus, the size and shape seem to have a large influence on the cytotoxicity and inflammatory response to nanocellulose. The surface chemistry has also been shown to have a large effect on inflammatory response.

# Electronic and Engineering Applications

## Lightweight, flexible supercapacitors

Nanocellulose provides the needed mechanical support for free-standing and flexible materials

A conductive material such as polypyrrole, polyaniline, and poly(ethylenedioxythiophene) is coated to provide high volumetric capacitance

ACS Nano 2015, 9, 7563–

## Biosensors

TEMPO-oxidized nanofibrillated cellulose used as a platform for immobilizing C-phycocyanin, as an effective biosensor for copper ion detection

Soy protein could be cross-linked to CNC to afford robust films with flexible electromechanical properties for applications in sensing

ACS Sustainable Chem. Eng. 2017, 5, 7063–7070. Adv. Funct. Mater. 2017, 27, 1604291.

CNC and silver have been 3D printed with high resolution into conductive tracks, reducing the quantity of silver needed

RSC Adv. 2017, 7, 15372–15381.

## Field effect transistors

CNCs have been reported in composite electronics with tin oxide layers for flexible organic field effect transistors

Mater. Lett. 2014, 126, 55–58.

# Adsorption, Separation, Decontamination, and Filtration

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Nanocellulose is valued in adsorption and separation due to its high hydrophilicity as well as its morphology and mechanical properties to form supports and membranes

## Nanocellulose composites

- Water and air purification
- Catalytic degradation of toxic organic compounds,
- Adsorbents for oil contamination,
- Sensors for waterborne pathogens

Nanocellulose based systems have been used in chromatographic columns for the separation of chiral enantiomers, necessary to pharmaceutical, clinical, food, and environmental science

Enzymatically phosphorylated nanocellulose adsorbents removed metal ions ( $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$ ) from an aqueous model of industrial effluents

Phosphorylated nanocellulose was able to remove above 99% of the  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ .

# Subjects of Patents

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- FPI+UBC+McGill - manufacture of CNC, dispersion of dried CNC, CNC as base for thermoplastic composites and scaffolds, hydrogels, barrier coatings, semiconductor, chiral surfaces, binding drugs, adhesive, controlled color/iridescence, wood coatings, fire retardant coating
- Rhone Poulenc/Rhodia/Danisco - CNC in oil drilling fluid
- AITF - CNC in de-icing fluid/rheology control
- Intelligent Nano - magnetic means of entering cells
- UPM - base for cell culture
- Kruger – coating for fabrics and textiles
- Chalmers – CNC as base for tissue scaffolds
- U of T – transparent conductive coatings
- Shingua – rubber reinforcement

# Commercial Interest

Commercial interest in nanocellulose is growing at a phenomenal rate following predictions of a possible 35 million tonnes per year market by the 2020s



Bio Vision (Canada), CelluForce (Canada)  
US Forest Service Forest Products Laboratory  
(USA);  
Centre Technique du Papier (France),  
Stora Enso (Finland),  
UPM Fibril cellulose (Finland),  
Borregaard Chemcell (Norway), etc



In 2011, Innventia opened the world's first pilot plant for the production of nanocellulose, which has a capacity of 100 kg/day.

Innventia AB  
Drottning Kristinas väg 61  
Stockholm, Sweden  
Phone +46 (0)8-676 70 00



## The Process Development Center

### Nanocellulose Facility - Nanocellulose Requests

The UMaine Process Development Center is pleased to supply nanocellulose samples to the research and business communities. Currently, we are producing cellulose nanofibrils (CNF) as slurries of approximately 2.8% solids, as well as CNF in a spray-dried form. UMaine is also distributing [Cellulose Nanocrystals](#) (CNC) manufactured at the [U.S. Forest Products Laboratory \(FPL\)](#). The FPL nanocrystals are available as a 11.8% slurry, and also in both freeze-dried and spray-dried form. In the near future we will carry a number of other types of nanocellulose, in both slurry and dry forms. If you would like to request a sample, please fill in the [Nanocellulose Request Form](#) and e-mail it to us at [umaine.pdc@maine.edu](mailto:umaine.pdc@maine.edu) or fax it to us at 207-581-4174.

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## ICAR-CIRCOT NANOCELLULOSE PILOT PLANT

inaugurated On August 21, 2015

by

**Padma Vibhushan Dr. R.A.  
Mashelkar**

National Research Professor, CSIR-NCL, Pune  
President, Global Research Alliance & Former  
DG, CSIR, New Delhi

[IMAGE GALLERY](#)

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# Challenges

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- 1. Moisture sensitivity of nanocellulose**
- 2. High aspect ratio of cellulose nanofibrils leads to a gel at low concentrations**
- 3. Manufacturing dry nanocellulose**
- 4. Economically efficient productions of films, aerogels and filaments are lacking**
- 5. Most nanocellulose product development -TRL 2 to 4**

