Manufacturing of Nanomaterials from Agrobio-Wastes and Production of Eco-Friendly Bionanocomposites

Sabu Thomas

International and Inter University Centre for Nanoscience and Nanotechnology

Mahatma Gandhi University, Kottayam, Kerala, India

Global Scenario:

Solid Urban Waste(SUW)

Where are we now standing? !!!

- 1.3 billion tones of solid urban waste annually
- 1.2 Kg per person

Situation 10 years ago!!

0.68 billion tones produced 10 years ago

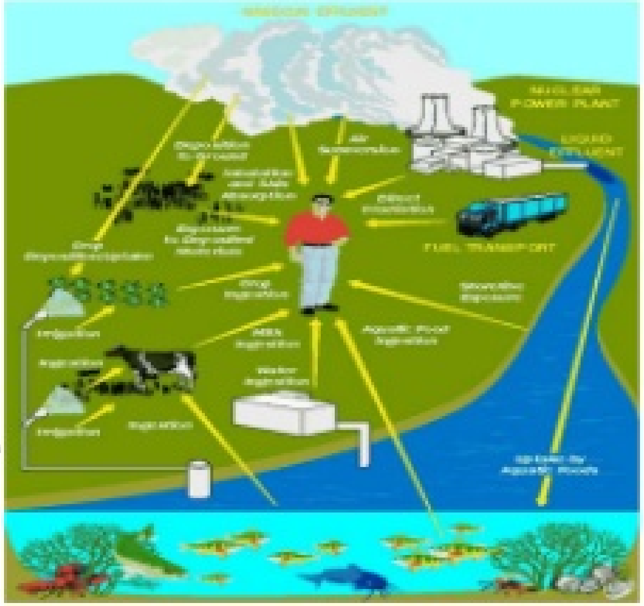
Indian Scenario:
Solid Urban Waste(SUW)

About 0.1 million tonnes of municipal solid waste is generated in India every day. That is approximately 36.5 million tonnes annually.

Per capita waste generation in major Indian cities ranges from 0.2 Kg to 0.6 Kg.

EFFECTS OF WASTE IF NOT MANAGED

- Affects on human health
- Affects on animals health
- Affects our climate
- Rise in global temperature
- Rise in sea levels
- Affects our coastal and marine environment



- Nanomaterials demonste superior performance in numerous applications, including **medicine, energy, environment, and advanced manufacturing.**
- However, many of the materials and processes currently used are not only dependent on **non-renewable resources but also create hazardous wastes.**
- Green nanotechnology, the **combination of nanotechnology and the principles and practices of green chemistry, may hold the key to building an environmentally sustainable society in the twenty-first century.**

-CONVERT AGRO WASTE INTO BIONANOMATERIALS-

1.6 billion tonnes of agro waste is being accumulated every year around the globe.

Agrowastes….

- sugarcane bagasse
- wheat bran, rice bran
- corn cob, wood flower
- wheat and rice straw
- jute, coir, pineapple, hemp, banana, bamboo
- fish industry waste (crab shells, prawn shells..)
- waste starch form agri fields..(potato, cassava)

Commercially important plant based resources

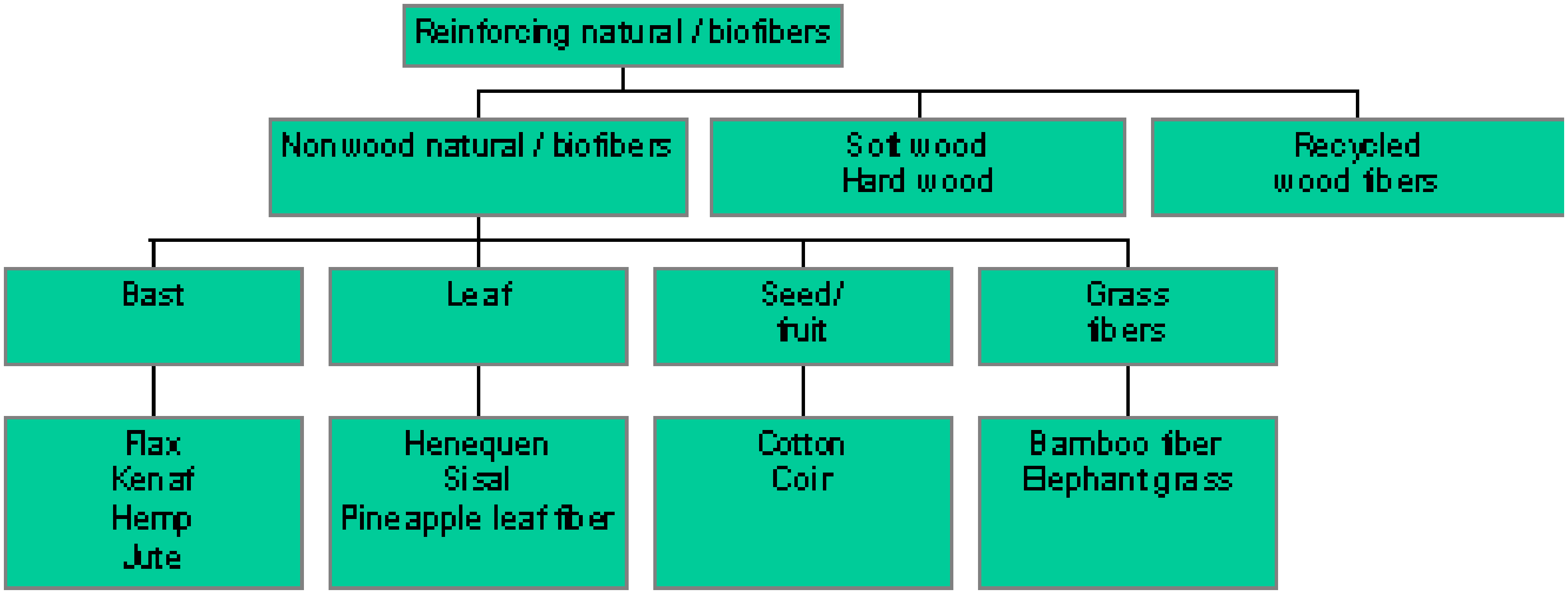
Fibre source	Species	World production (10^3 tonnes)	Origin
Wood	(>10,000 species)	1,750,000	Stem
Bamboo	(>1250 species)	10,000	Stem
Cotton lint	*Gossypium* sp.	18,450	Fruit
Jute	*Corchorus* sp.	2,300	Stem
Kenaf	*Hibiscus cannabinus*	970	Stem
Flax	*Linum usitatissimum*	830	Stem
Sisal	*Agave sisilana*	378	Leaf
Roselle	*Hibiscus sabdariffa*	250	Stem
Hemp	*Cannabis sativa*	214	Stem
Coir	*Cocos nucifera*	100	Fruit
Ramie	*Boehmeria nivea*	100	Stem
Abaca	*Musa textiles*	70	Leaf
Sunn hemp	*Crorolaria juncea*	70	Stem

Plant Fibres

- Environmentally benign
- Cost effective
- Abundantly available
- Non-abrasive
- Acoustic and thermal insulators
- High specific properties
- Sustainable raw resource.
- Under utilized
- Societal need

Thomas et al. Carbohydrate Polymers, 71 (3) (2008) 343

Classification of plant fibres based on origin



Source: Mohanty, Misra, Drzal: Natural fibers. Biopolymers and Biocomposites, 2005

Important plant fibres

Banana plant

Oil palm fibre

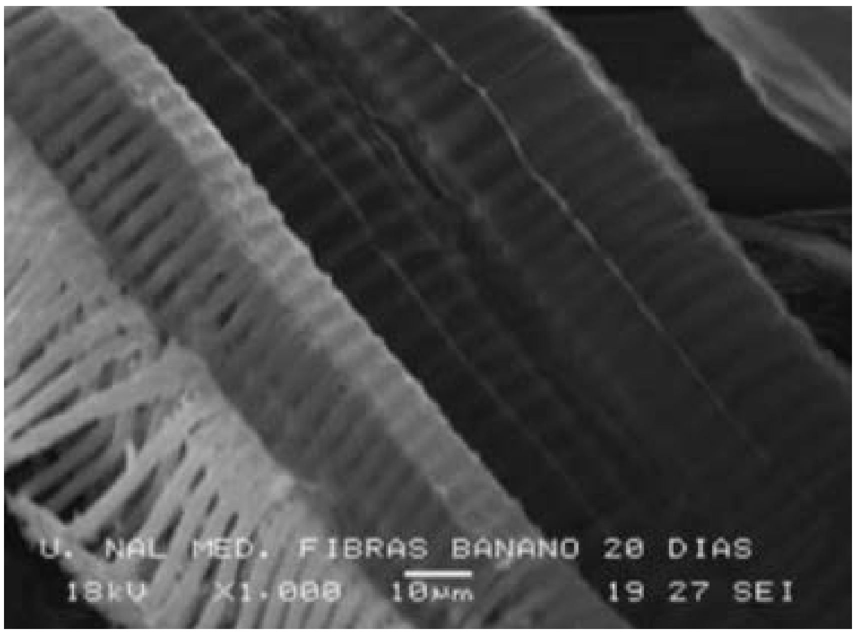
Pineapple leaf

Coir fiber

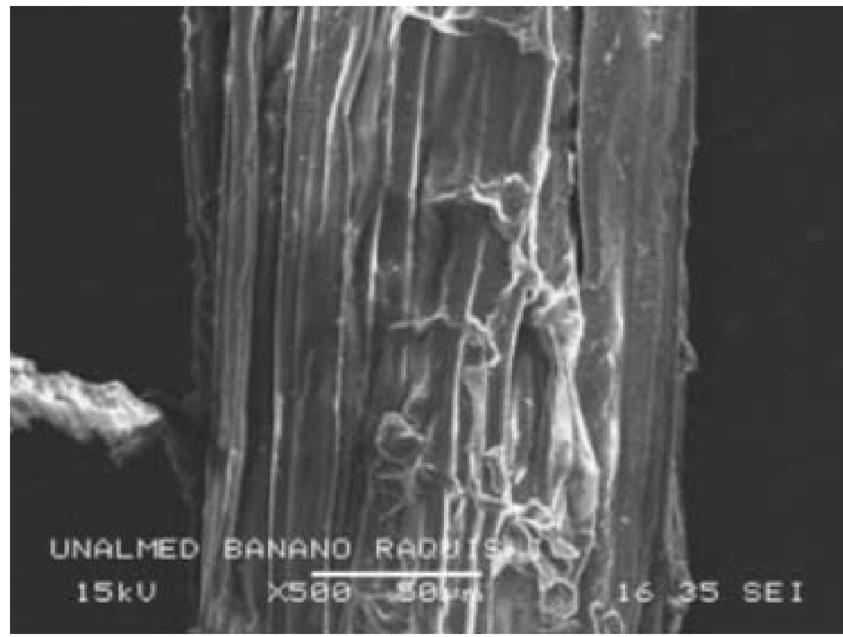
Coconut tree

Coconut fibre

Extraction Methods - Comparison,



Fibre extracted by biological retting (20days)



Fibre extracted by mechanical process

Thomas et al *Waste and Biomass Valorization, 1 (1) (2010) 121-134, DOI: 10.1007/s12649-010-9009-7*

Socio-economical and Environmental Advantages

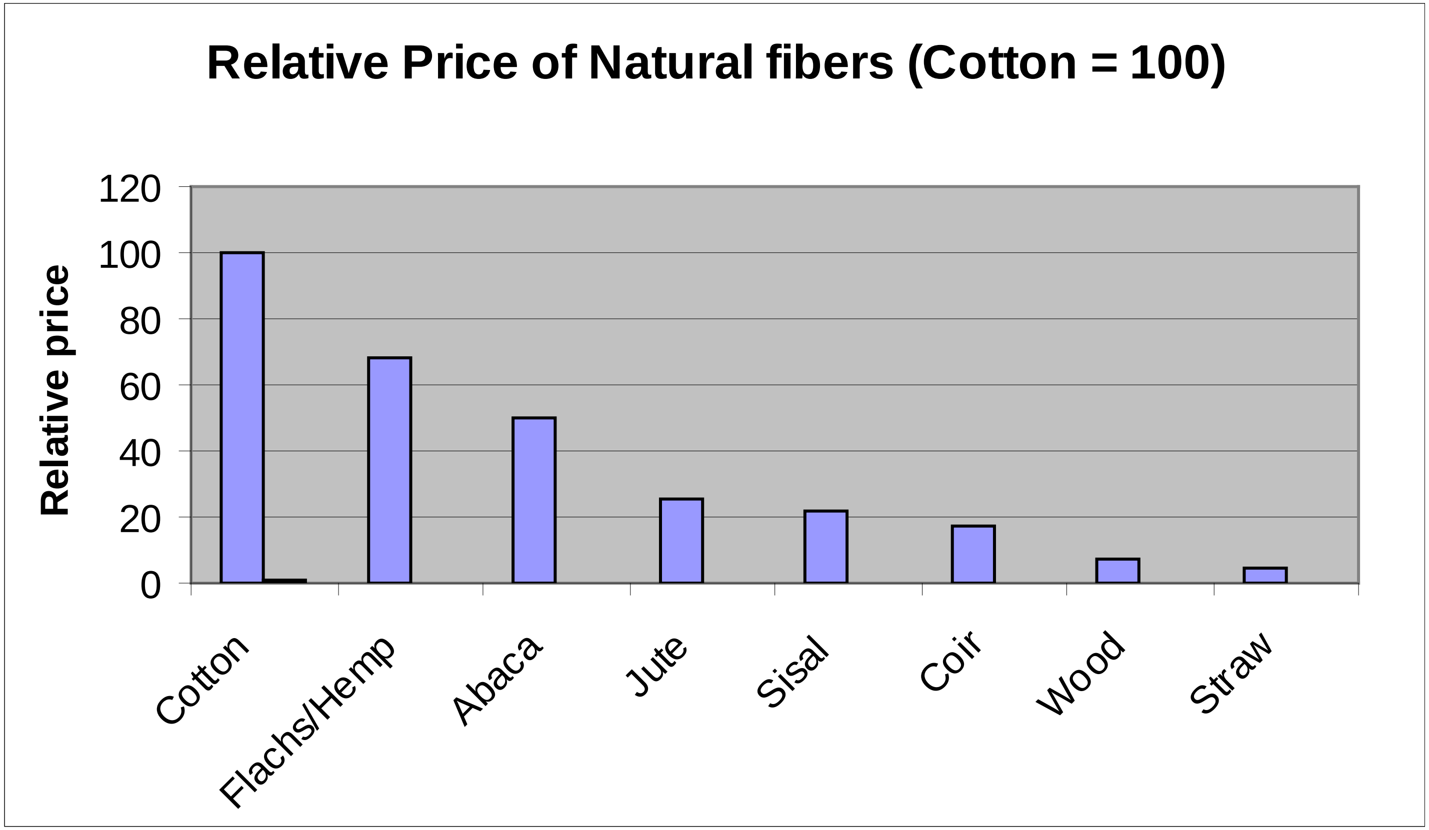
Thomas et al. Waste and Biomass Valorization, 1 (1) (2010) 121-134, DOI: 10.1007/s12649-010-9009-7

- Creates rural jobs
- Renewable resources used
- Possible bio-degradable with bio-plastics
- Wide variety of fibres available throughout the world
- Non-food agricultural/farm based economy
- Low cost

Costs of waste management options in Germany, Belgium and The Netherlands (in US$ per ton)

Option	Germany	Belgium	The Netherland
Composting	151	80	60
Incineration	486	110	135
Landfilling	402	75	105

Relative prices of AGRO fibers



Cotton is used for textiles while wood and straw is often applied for paper industry

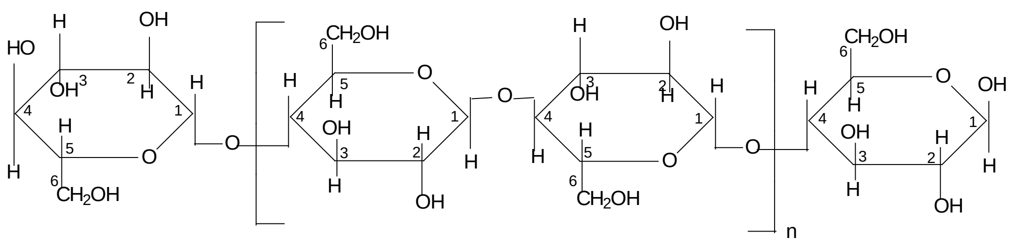
Introduction

Physico-mechanical properties of natural fibers.

Fiber	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Density [g/cm^3]
Abaca	400	12	3–10	1.5
Bagasse	290	17	–	1.25
Bamboo	140–230	11–17	–	0.6–1.1
Flax	345–1035	27.6	2.7–3.2	1.5
Hemp	690	70	1.6	1.48
Jute	393–773	26.5	1.5–1.8	1.3
Kenaf	930	53	1.6	–
Sisal	511–635	9.4–22	2.0–2.5	1.5
Ramie	560	24.5	2.5	1.5
Oil palm	248	3.2	25	0.7–1.55
Pineapple	400–627	1.44	14.5	0.8–1.6
Coir	175	4–6	30	1.2
Curaua	500–1150	11.8	3.7–4.3	1.4

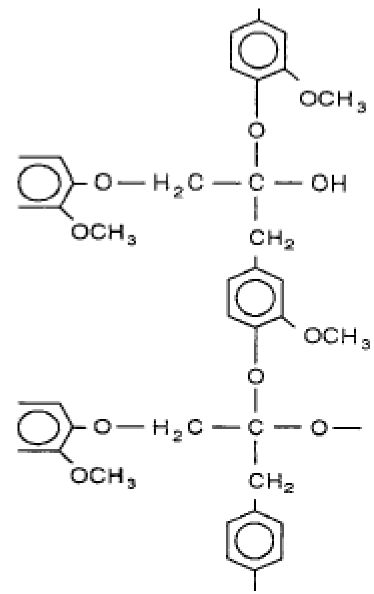
Mechanical properties of natural fibers can be influenced by many factors. Such as either fiber bundles or ultimate fiber is being tested.

Haworth projection formula of cellulose

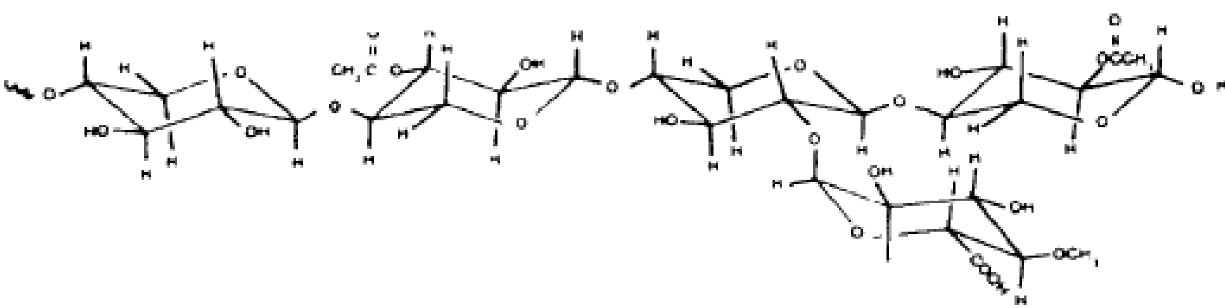


Macromolecules of Cellulose

linear condensation polymer consisting of d-anhydroglucopyranose units joined together by β-1,4-glycosidic bonds



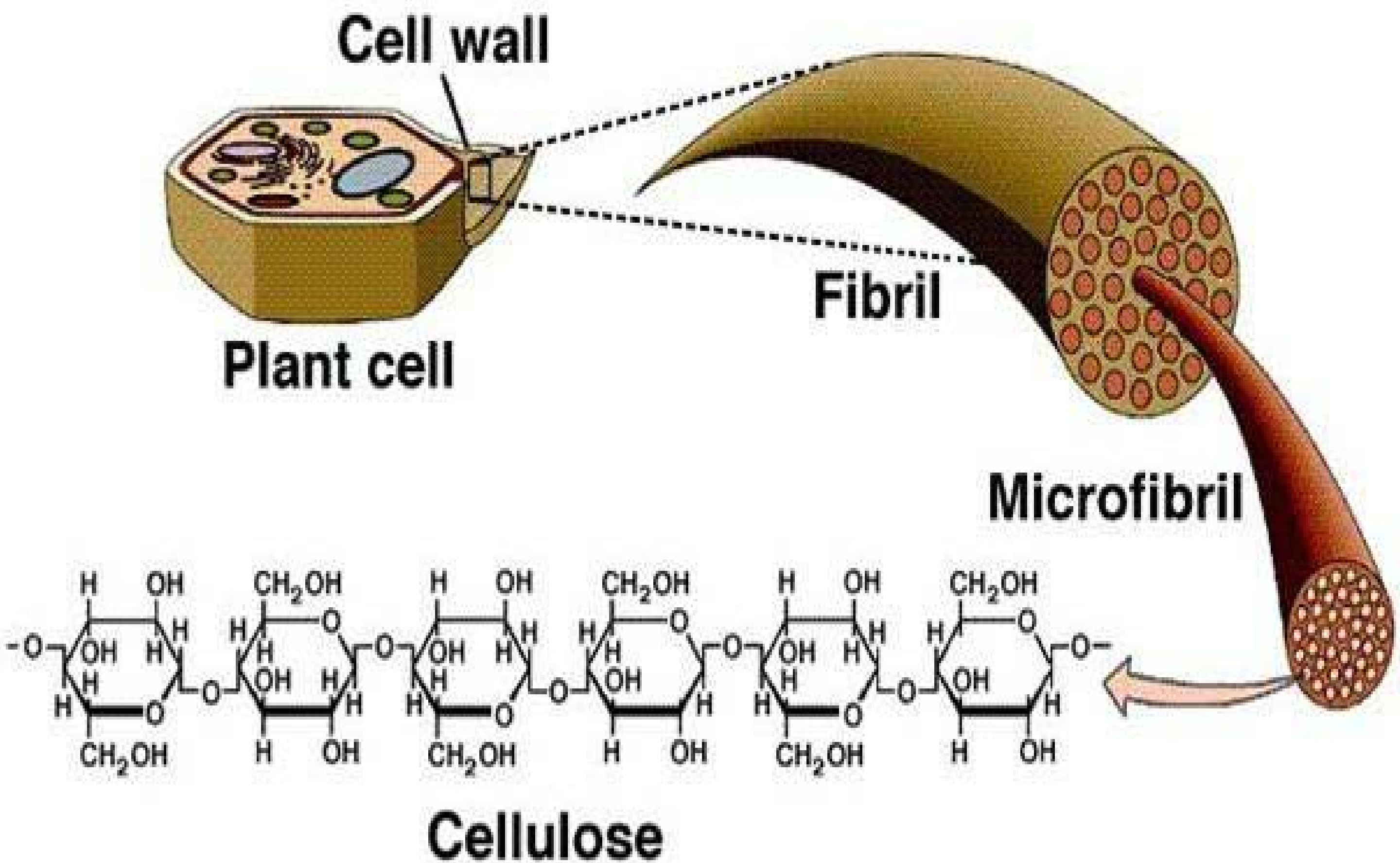
Structure of hemicellulose



Structure of Lignin

complex hydrocarbon polymer with both aliphatic and aromatic constituents

Plant Fibre - Structure

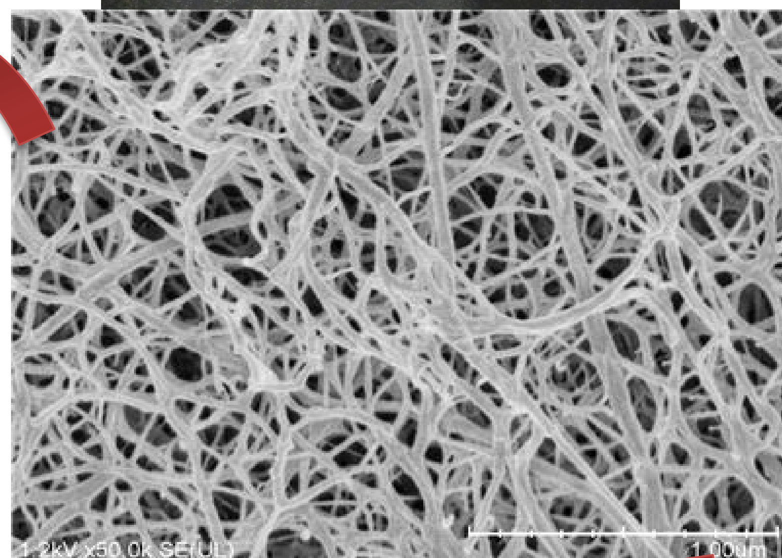


Why Nanocellulose?

- Higher water holding capacity.
- Higher crystallinity.
- High tensile strength.
- Low density.
- High specific strength & modulus.
- High aspect ratio & reactive surface.
- In a combination with suitable matrix polymer Nano cellulose shows an effective reinforcement for speciality application of bio Nano composites.

Strategic platform for sustainable development

NANOCELLULOSE EXTRACTION TECHNIQUES



1) HIGH PRESSURE HOMOGENIZATION

2) GRINDING

3) CRYOCRUSHING

4) HIGH INTENSITY ULTRASONICATION

5) STEAM EXPLOSION

6) ACID HYDROLYSIS

1) High Pressure Homogenization

- High pressure homogenization (HPH) process includes passing the cellulose slurry at high pressure into a vessel through very small nozzle.

- High velocity and pressure as well as impact and shear forces on fluid generate shear rates in the stream and decrease the size of fibers to nanoscale.

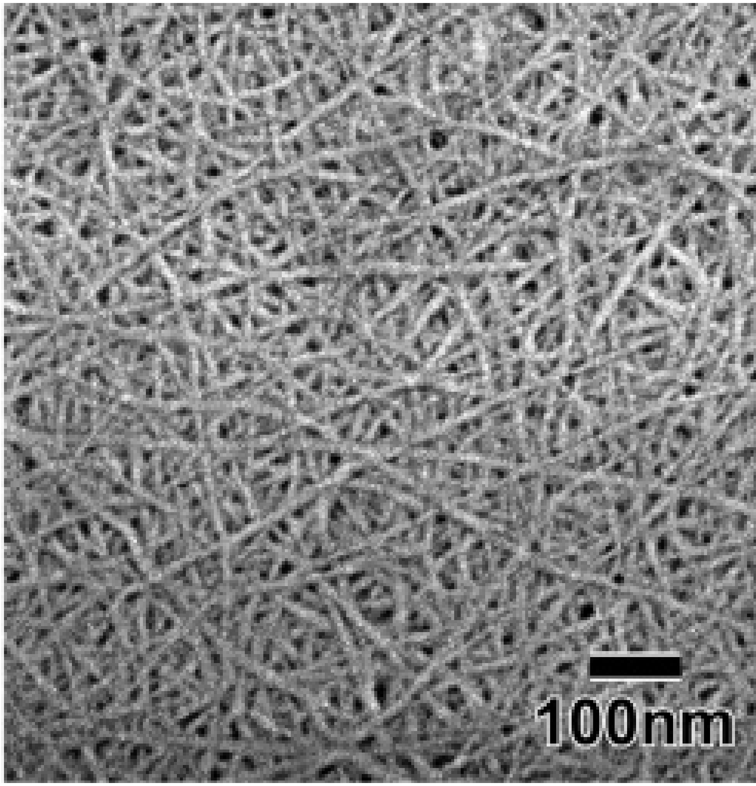
- HPH can be considered as an efficient method for refining of cellulosic fbers, because of high its efficiency, simplicity and no need for organic solvents.

- The first application of HPH to produce NFC from wood pulp was introduced at 1983 (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983).

(Frone, Panaitescu, & Donescu, 2011).

2) Super Grinding

- Another strategy to break up cellulose into nanosize fibers is grinding.
- In grinding equipment, there is static and rotating grind stone and pulp slurry passes between these two stones.
- The mechanism of fibrillation in grinder is to break down of hydrogen bond and cell wall structure by shear forces and individualization of pulp to nanoscale fibers.
- Abe et al. (2007) obtained cellulose nanofibers with a uniform width of 15 nm from wood via grinding.

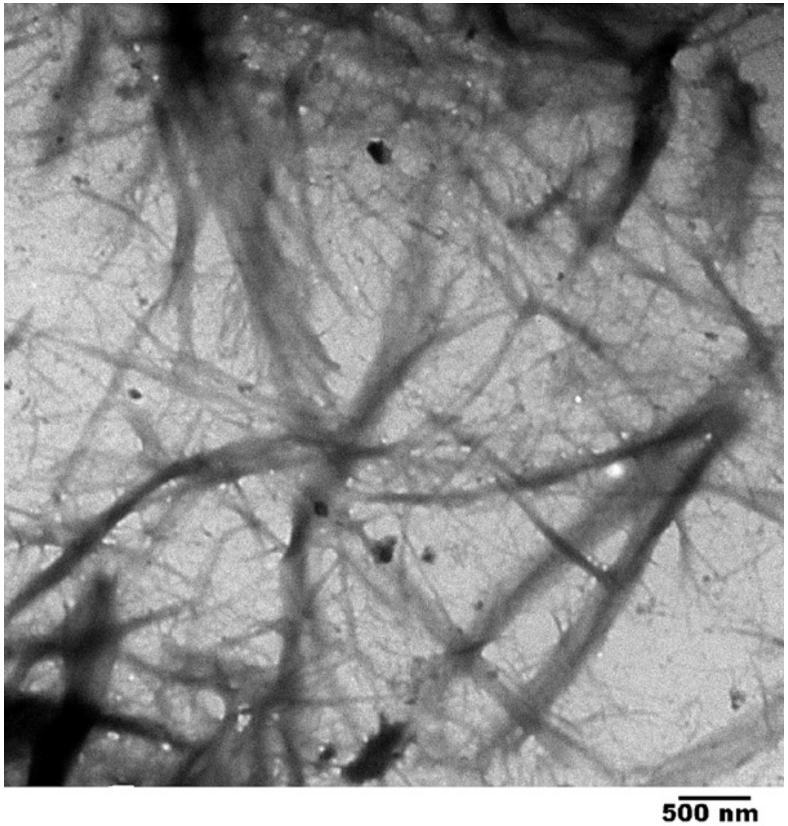


FESEM image of cellulose nanofibers with a uniform width of 15 nm from wood via grinding treatment

Kentaro Abe, Shinichiro Iwamoto, Biomacromolecules, Vol. 8, No. 10, 2007*

3) Cryocrushing

- Cryocrushing is another method for mechanical fibrillation of cellulose. In this process, water swollen cellulosic fibers immerse in liquid nitrogen and subsequently crush by mortar and pestle.
- Application of high impact forces to the frozen cellulosic fibers leads to rupture of cell wall due to exert pressure by ice crystals and thus, liberating nanofibers.
- Alemdar et al. (2008) found that the cryocrushing of the soy hull fibers resulted in defibrillation of nanofibers from the cell walls and these TEM pictures of the cellulose fibers show the separation of the nanofibers from the micro-sized fibers.



Transmission electron micrograph of the soy hulls nanofibers prepared via cryocrushing

A. Alemdar, M. Sain / Bioresource Technology 99 (2008) 1664–1671

4) High Intensity Ultrasonication (HIUS)

- High intensity ultrasonication (HIUS) is a mechanical process in which oscillating power is used to isolate cellulose fibrils by hydrodynamic forces of ultrasound.

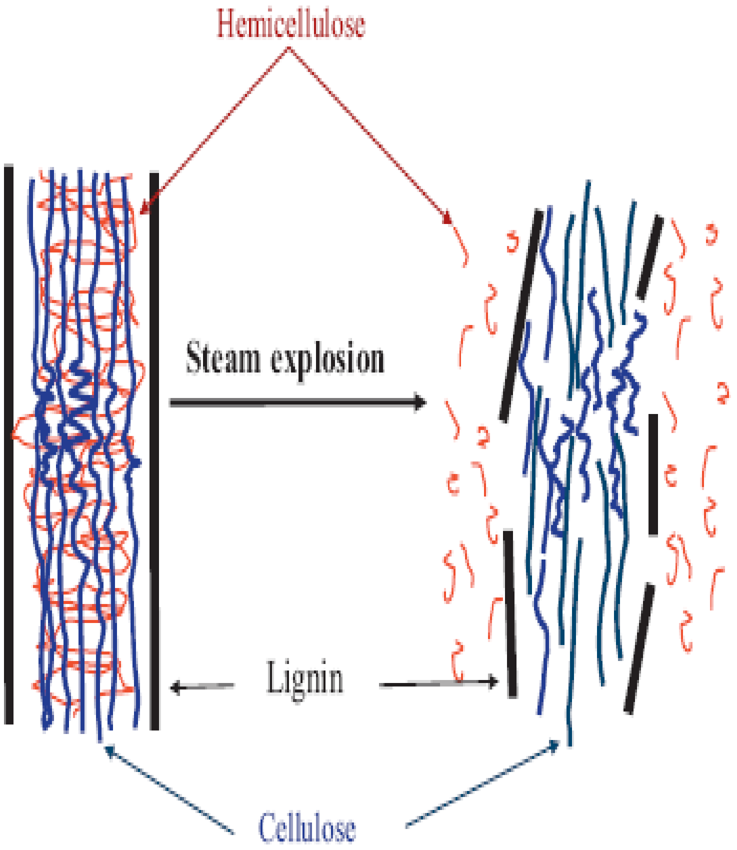
- During the process, cavitation leads to a powerful mechanical oscillating power and therefore, high intensive waves, which consists of formation, expansion, and implosion of microscopic gas bubbles when molecules absorb ultrasonic energy.

(Cheng, Wang, & Rials, 2009).

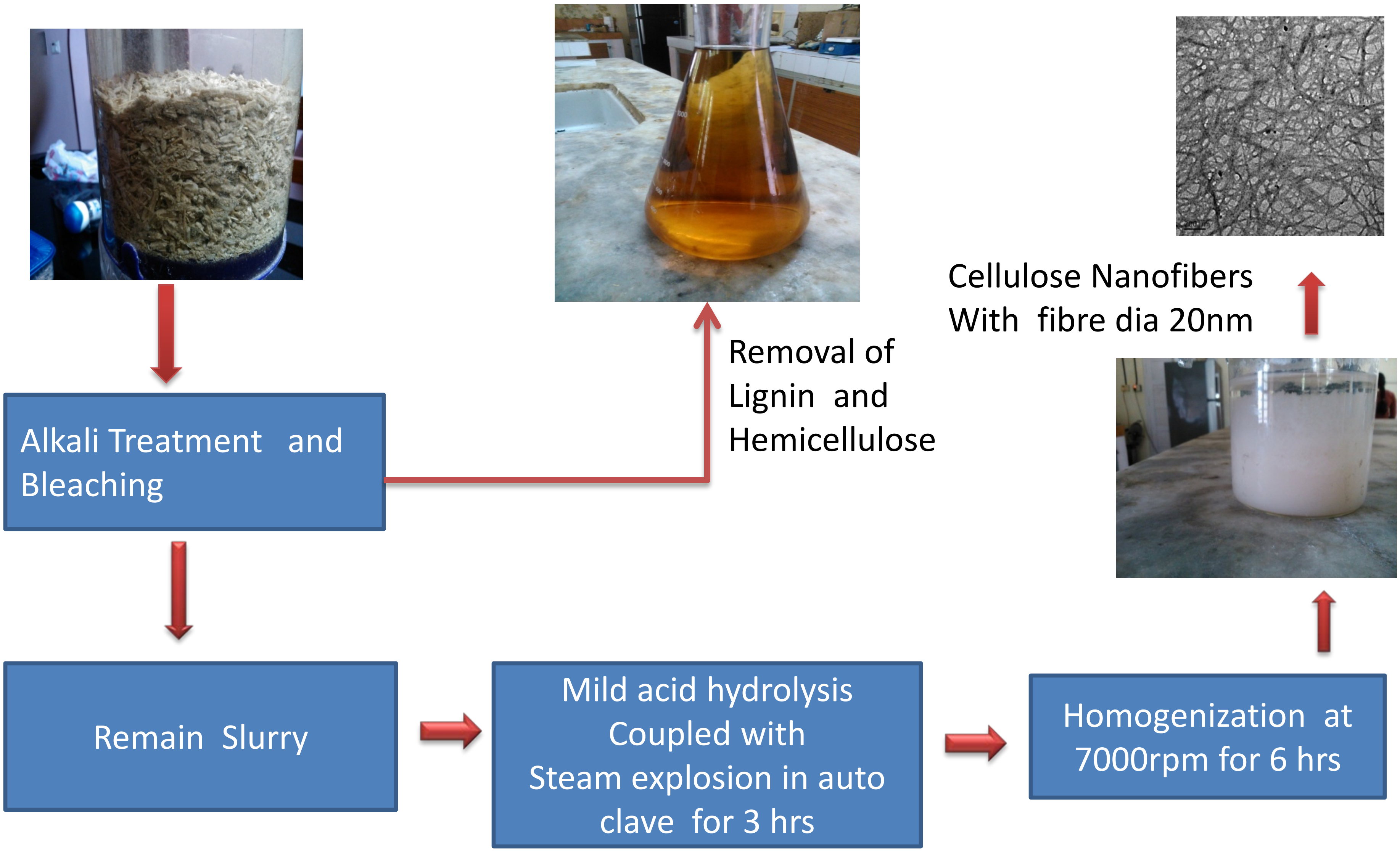
5) Steam explosion

- A laboratory autoclave which can work with 137 Pa pressure will be used for steam treatment.

- Steam explosion technique will be applied on the alkali treated fiber for one hour and steam pre treatment will be performed by loading the lingo cellulosic material directly into the steam gun and treating it with high pressure steam at temperature within 100 to 150ºC followed by sudden release of pressure.

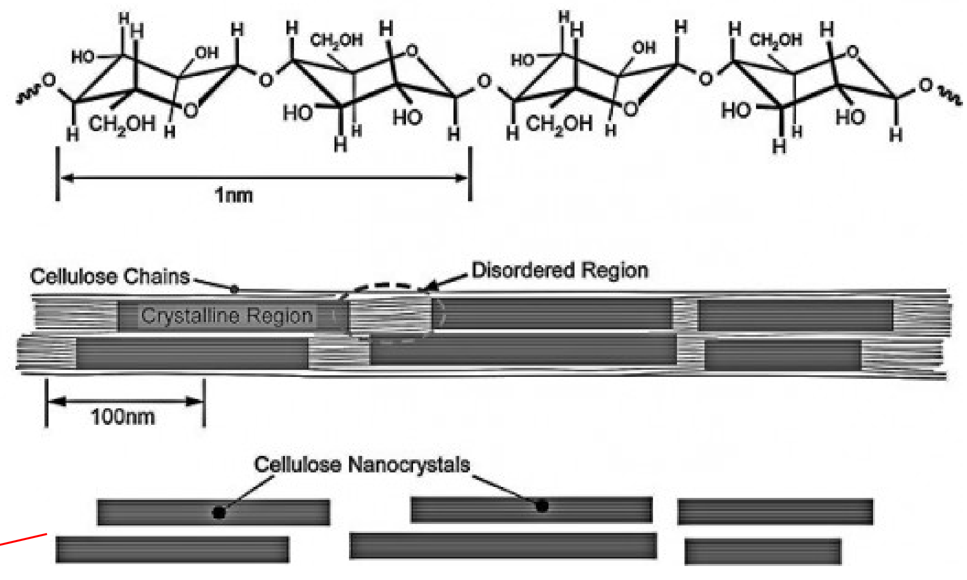


Cordeiro & Abraham et.al (2013)


Alkali Treatment and Bleaching
Removal of Lignin and Hemicellulose
Remain Slurry
Mild acid hydrolysis Coupled with Steam explosion in auto clave for 3 hrs
Homogenization at 7000rpm for 6 hrs
Cellulose Nanofibers With fibre dia 20nm

Common techniques used for preparation of Nano cellulose is acid hydrolysis & steam explosion.

Nanofiber containing both amorph
And crystalline cellulose.



Cellulose Nano crystals after the
removing of amorphous cellulose
by Acid hydrolysis.

(Zhou et.al)

Whiskers

Native Cellulose

↓ Chemical treatment
Mechanical treatment

Cellulose Microfibrills

↓ Acid hydrolysis

Cellulose whiskers

↓ Dialysis

Cellulose whiskers

↓ Homogenization

Cellulose whisker suspension

- Low cost
- Regular shape
- High axis ratio
- Monocrystalline nature
- Modulus as cellulose crystal

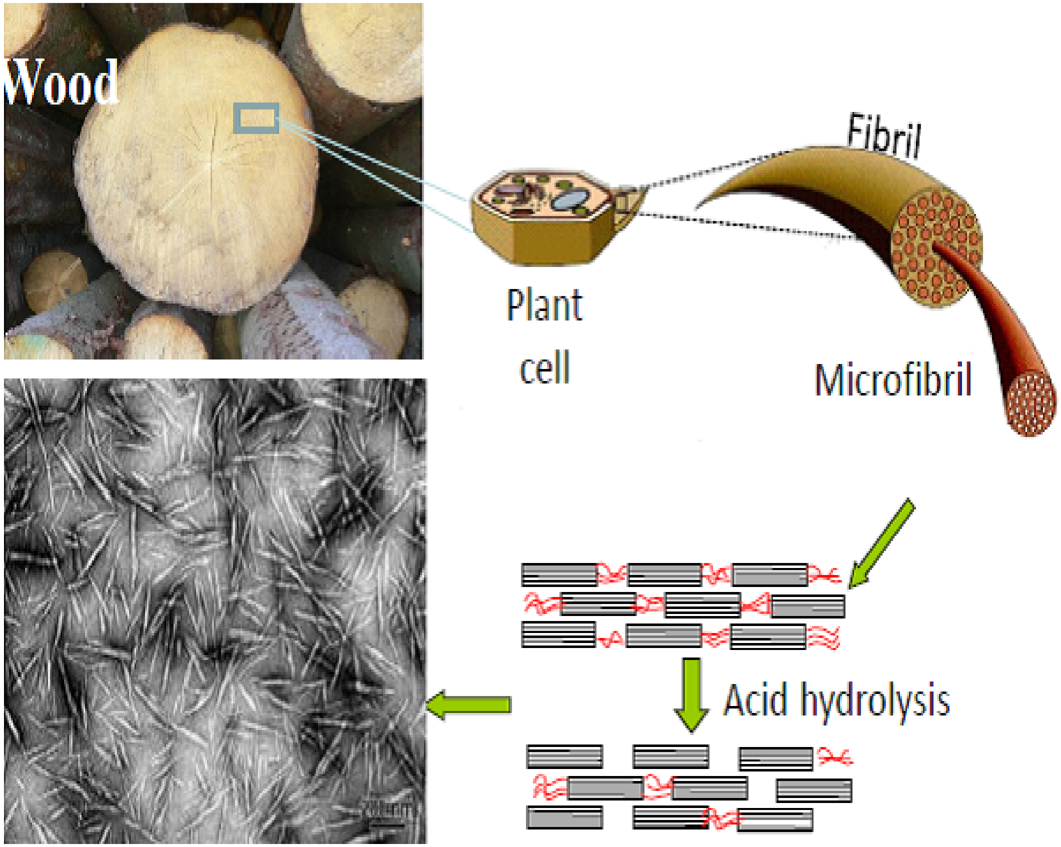
↓

E = 130 GPa

σ = 10 GPa

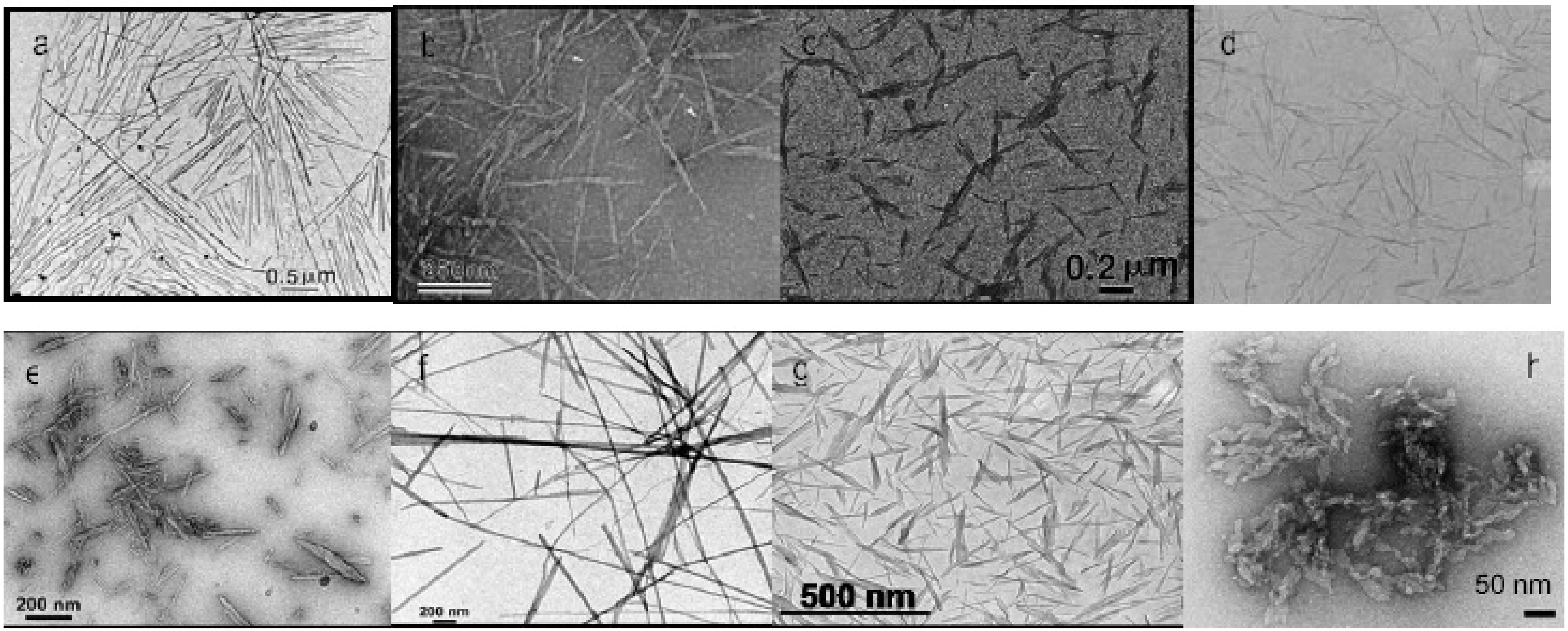
Preparation of Cellulose nanocrystals by Acid hydrolysis

The prepared cellulose was added to 65wt% sulphuric acid solution at 45 °C.



Mohammed et al./ *RSC Adv, 2015,5, 29842*

Surface morphology by TEM analysis

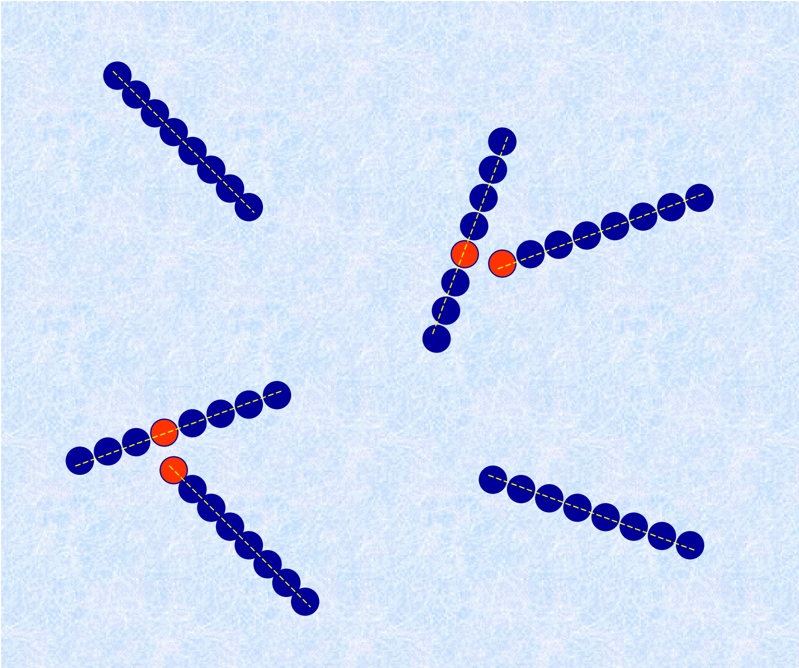


Transmission electron micrographs from a dilute suspension of hydrolyzed (a) tunicin, (b) wheat straw, (c) cotton, (d) sugar-beet pulp, (e) squid pen, (f) *Riftia* tubes, (g) crab shell, and (h) waxy maize.

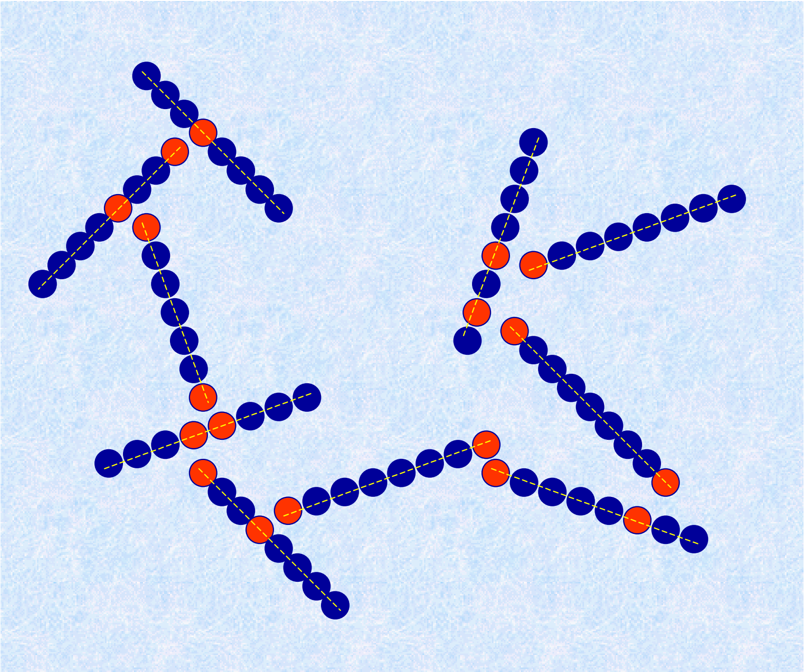
Courtesy: Alain Dufresne, ICBC , M.G University, Kottayam

Connectedness Percolation: What ?

Percolation: The formation of infinite, spanning clusters of “connected” (defined by spatial proximity) particles.



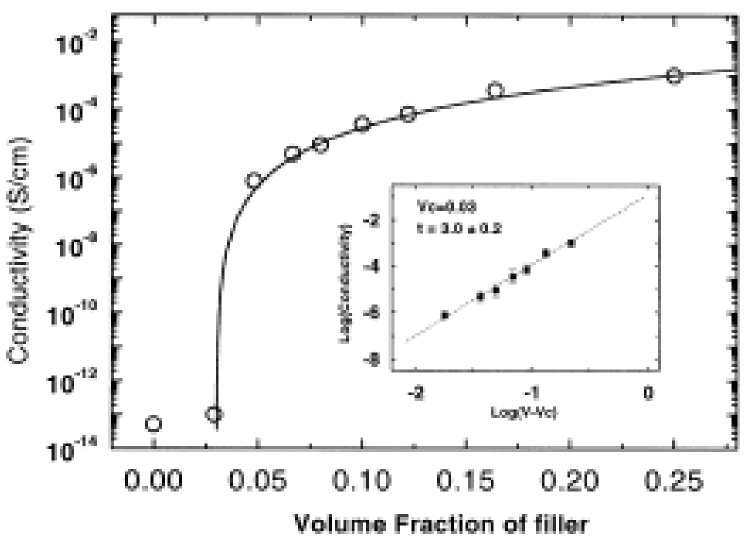
Non-percolated system

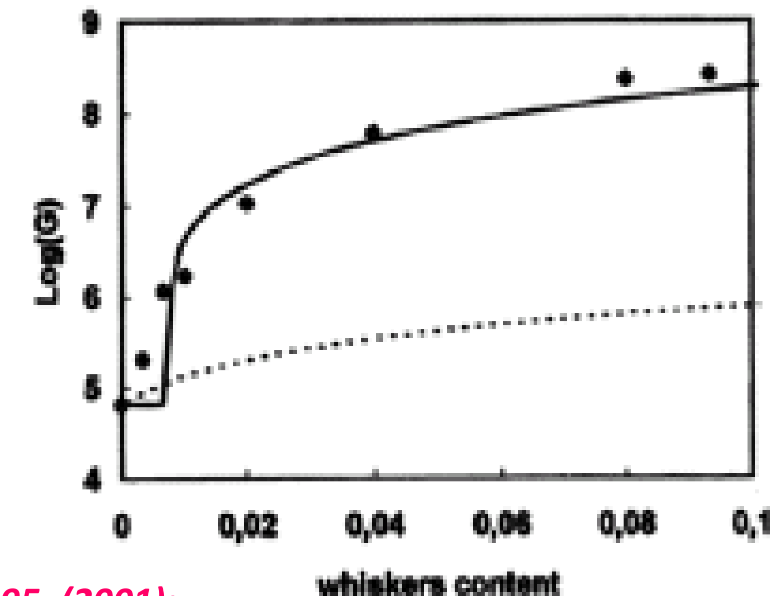


Percolated system

Percolation and Cellulose-based Nanocomposites:

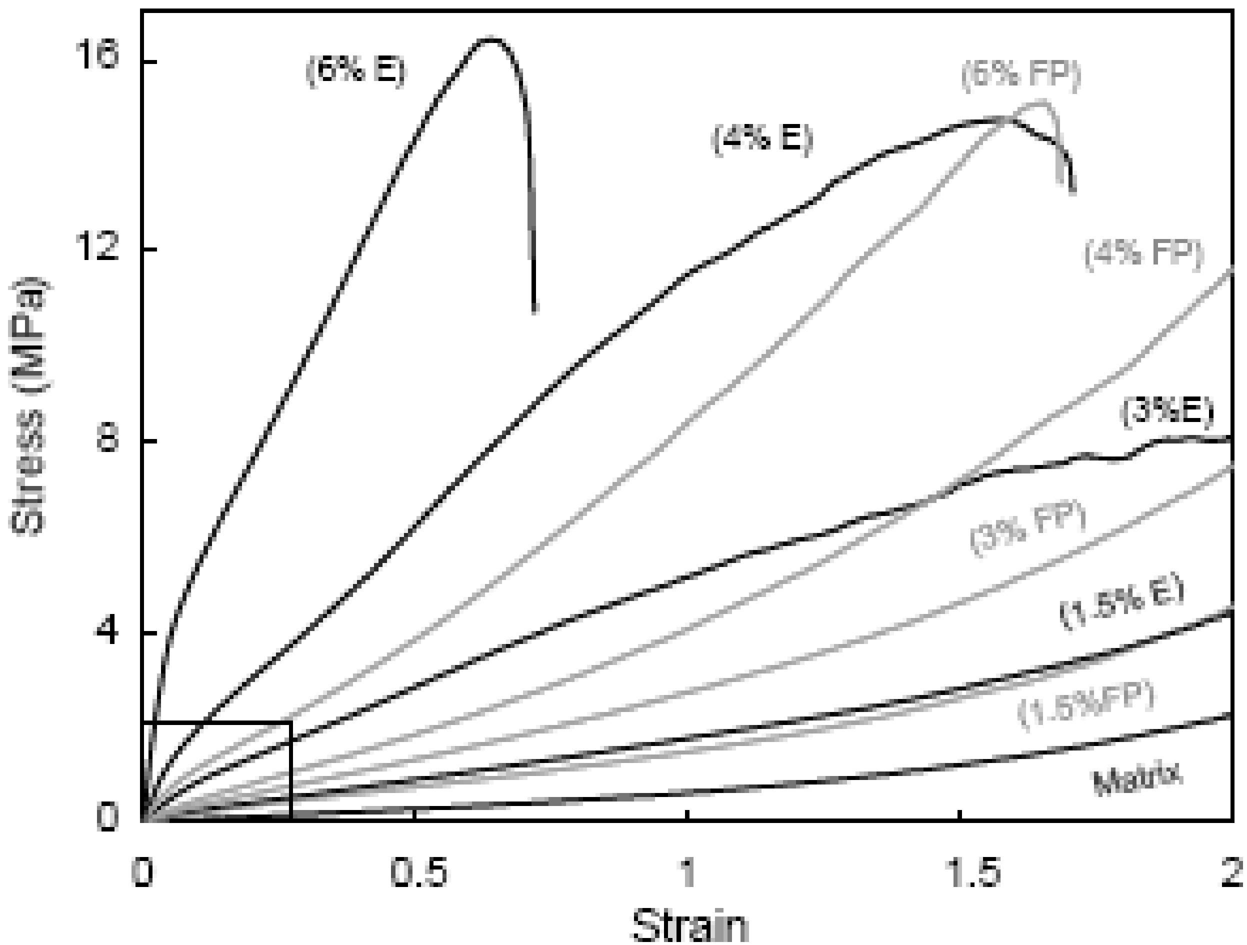
- Polypyrrole-coated cellulose whiskers investigated as filler particles providing (i) electrical conductivity and (ii) mechanical reinforcement/shear modulus enhancement: The matrix was a styrene-butyl acrylate copolymer; Particle aspect ratio ~ 100).



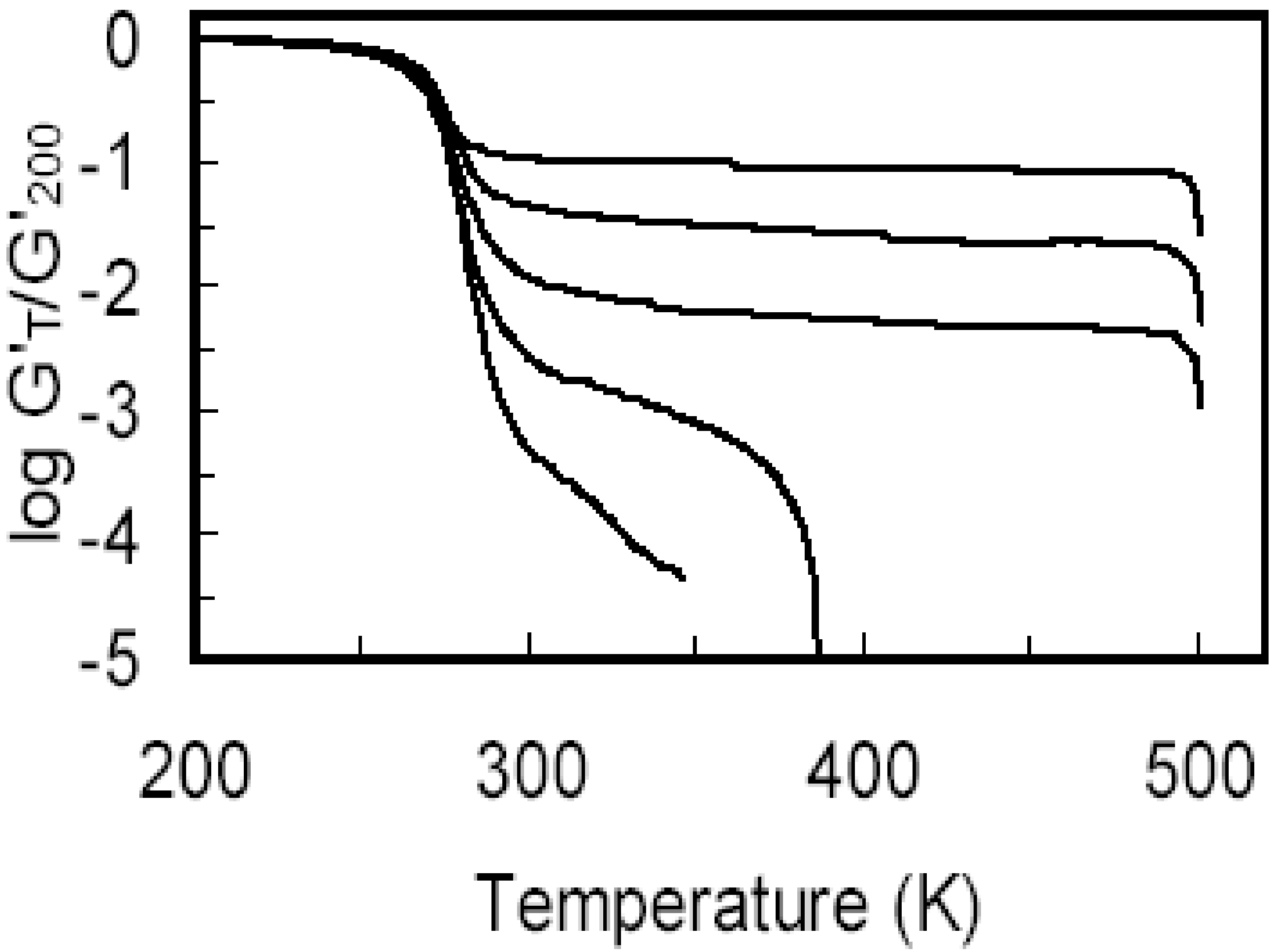


(J.Y. Cavaille, et. al., Compos. Sci. Technol., 61, 895, (2001);

Tensile tests performed at room temperature on pure P(S-BuA) matrix and related cellulose filled composites (Cavaille et al.)



Logarithm of the normalized storage shear modulus (log G'T/G'200, where G'200 corresponds to the experimental value measured at 200 K) vs. temperature at 1 Hz for tunicin whiskers reinforced poly(S-co-BuA) nanocomposite films (Cavaille et al)

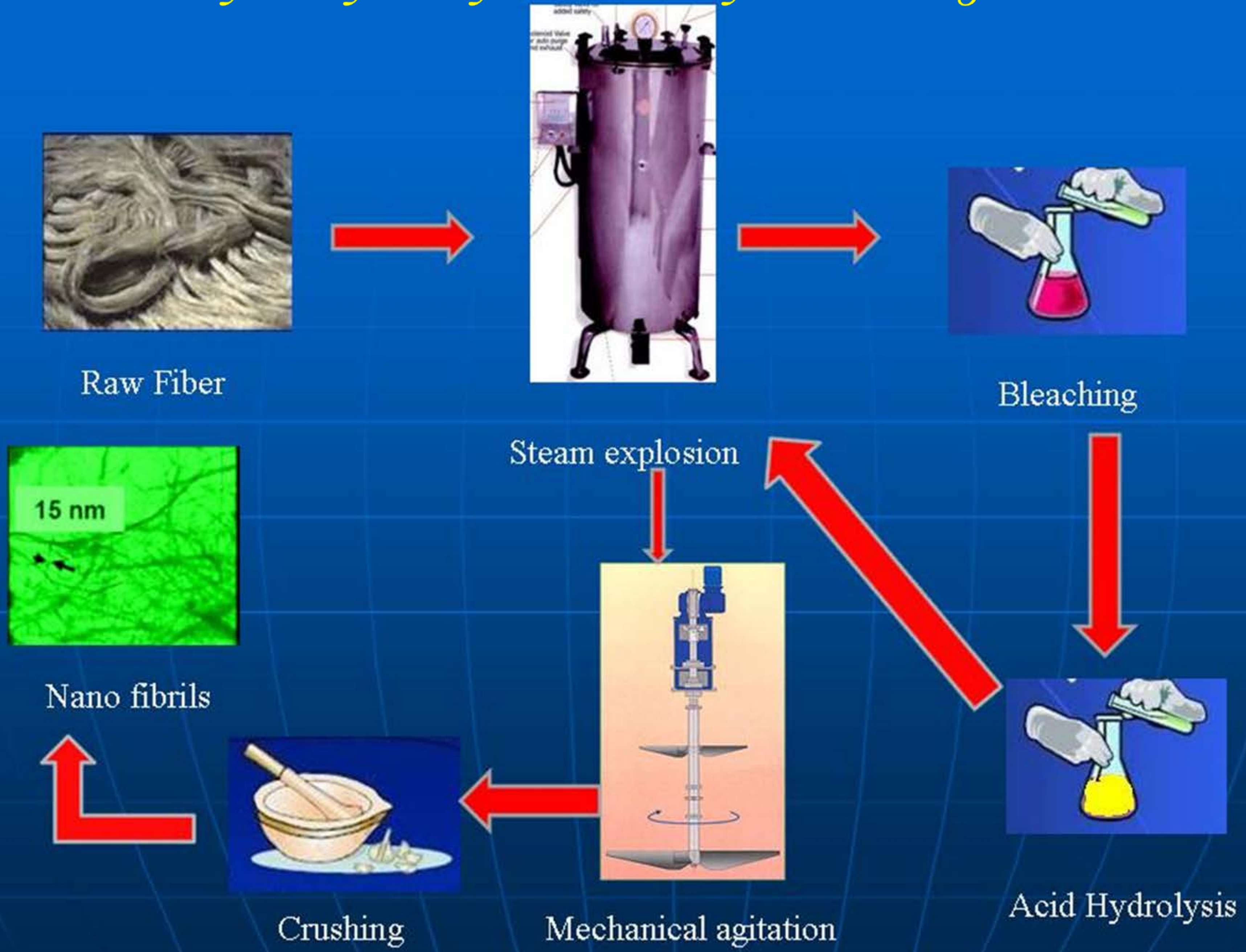


Process at MGU India

- Steam explosion of raw banana fibres in alkaline medium
- Bleaching of the steam exploded mass
- Bleached material subjected to acid hydrolysis followed by steam explosion

Thomas et al.Carbohydrate Polymers, 86, 2011, 1790-1798

Isolation of nanofibrils from narural fibres: At a glance



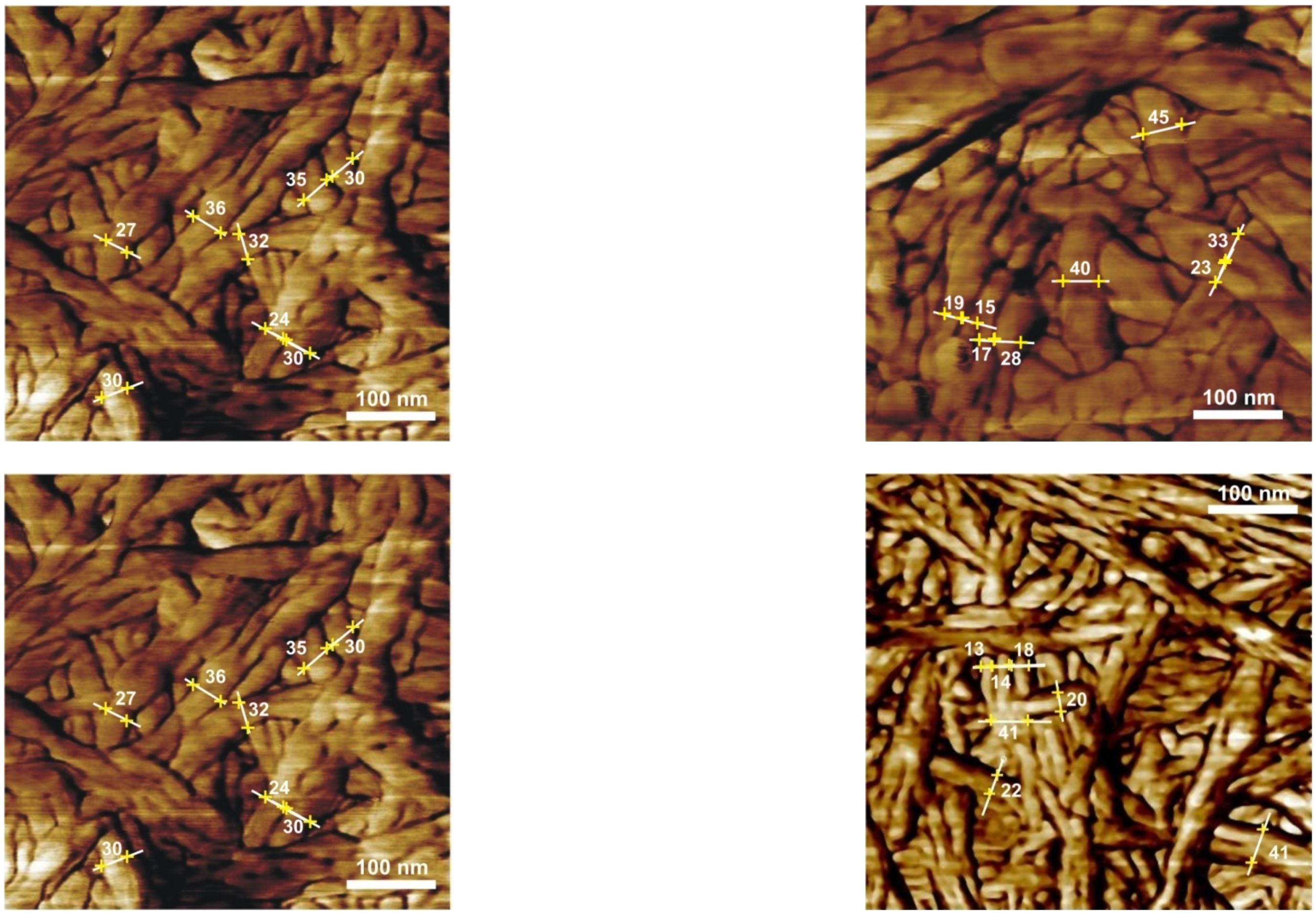
Change in Chemical Composition during the process

Material	% of α-Cellulose	% of Hemi-Cellulose	% of Lignin
Raw Fibre	64.04%	18.6%	4.9%
Steam Exploded Fibre	82.37%	13.97%	3.64%
Bleached Fibre	95.86%	3.00%	1.86%

Chemical estimation, also supported by FTIR

Moisture and Volatile components not considered, ***thomas et al Carbohydrate Polymers, 81 (3) (2010) 720***

Nano from Banana stalk wastes

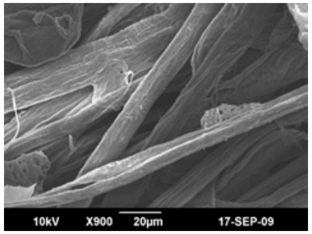


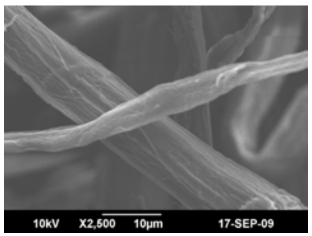
Phase SPMs by Multimode SPM with a Nanoscope IV controller in tapping mode , ***Thomas et al. Biomacromolecules***

Characterizations nanowhiskers (nano from wood flower)

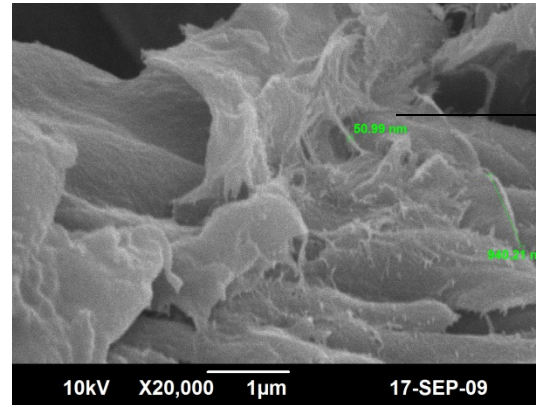
I. Cellulose

SEM



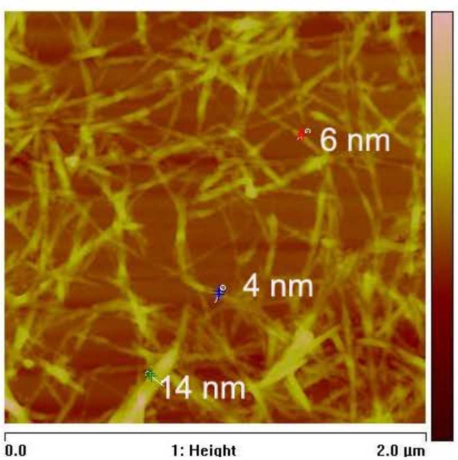


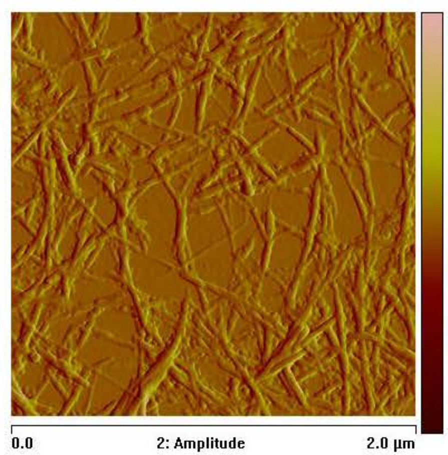
Macro to Nano

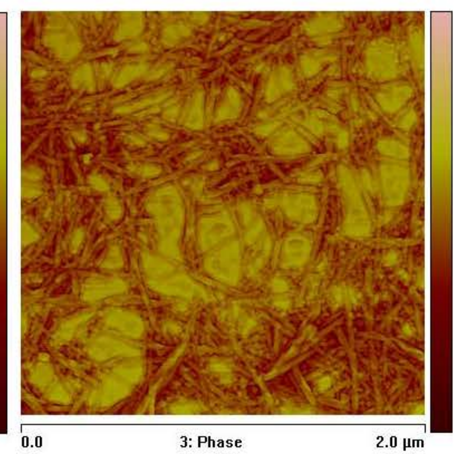


50 nr

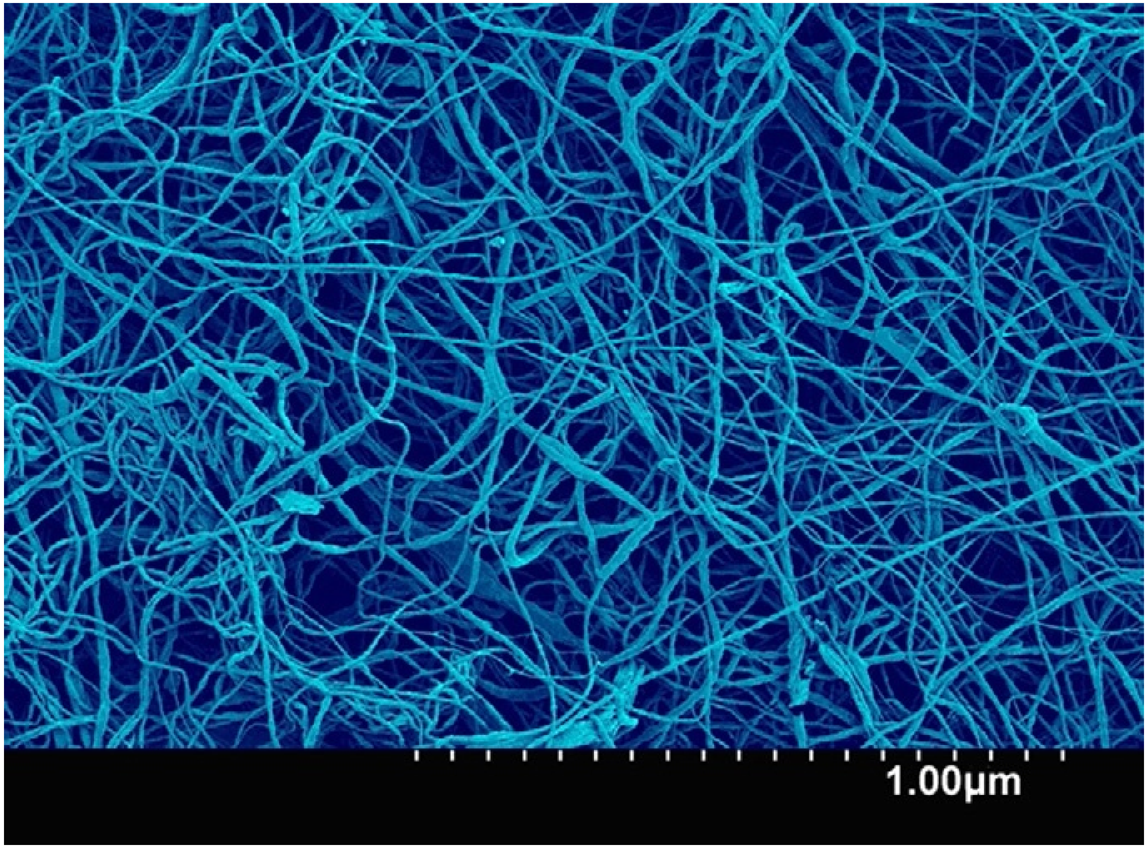
AFM







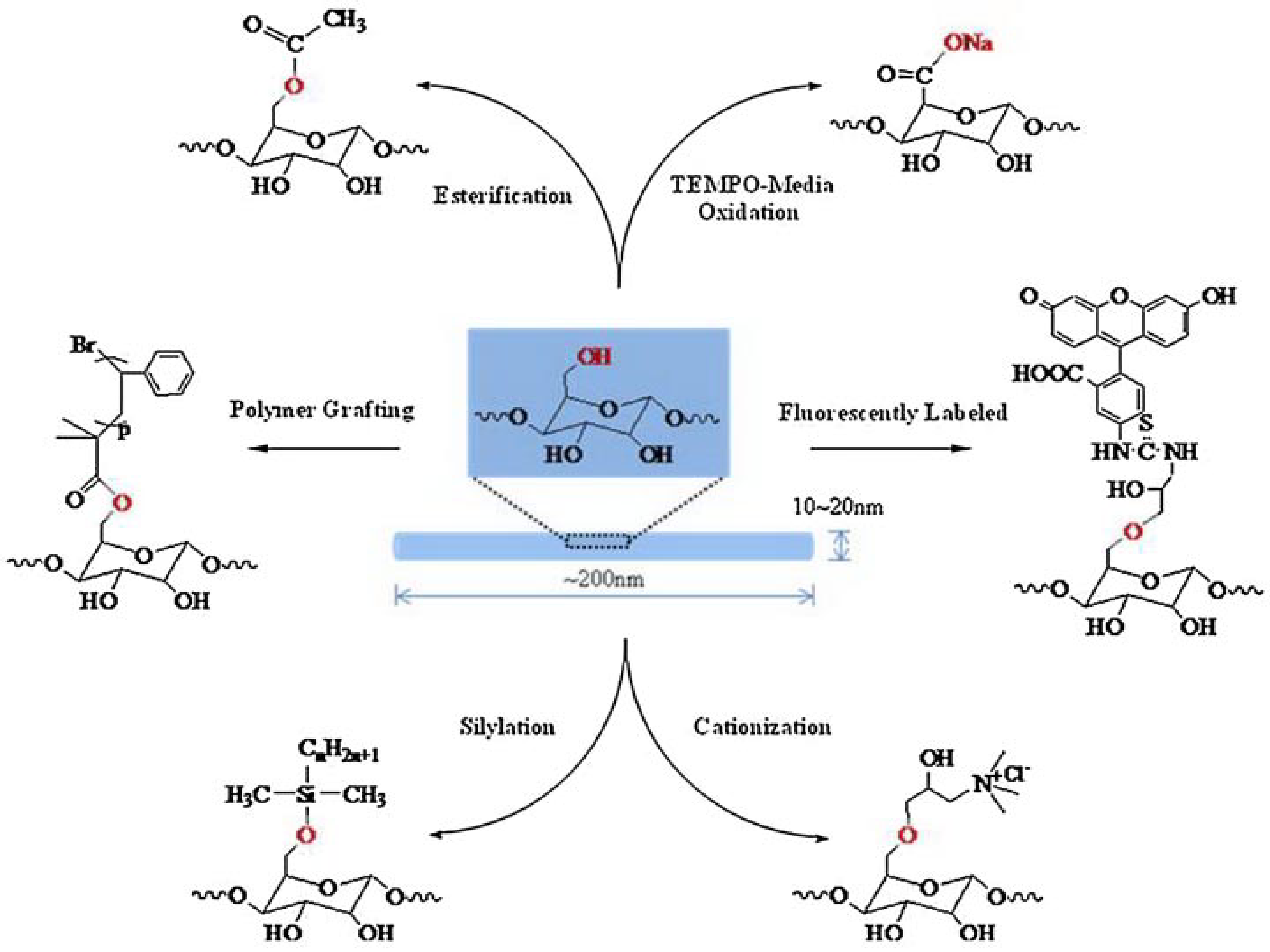
Nano from Pine Apple Fiber



ESEM image of acid treated PALF fibre
Carbohydrate Polymers **86, no. 4 (2011): 1790-1798**.

(Chemical modification of cellulose Nano particles)

- One of the drawback of Nano cellulose with polar surfaces is poor dispersiblity/compatibility with non polar solvents or resins.
- Applications largely limited to aqueous or polar systems.
- To overcome this problem it is necessary to reduce the entanglement of the fibrils to improve their dispersion in matrix by chemical or surface modification.

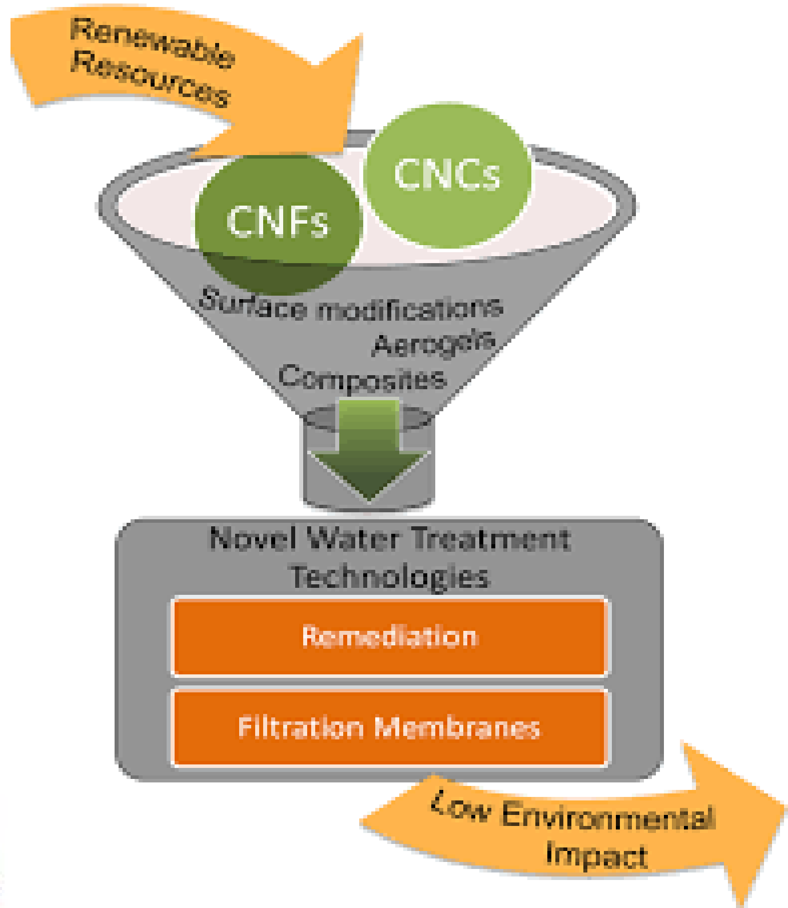


Esterification
TEMPO-Media Oxidation
Polymer Grafting
Fluorescently Labeled
Silylation
Cationization
10~20nm
~200nm

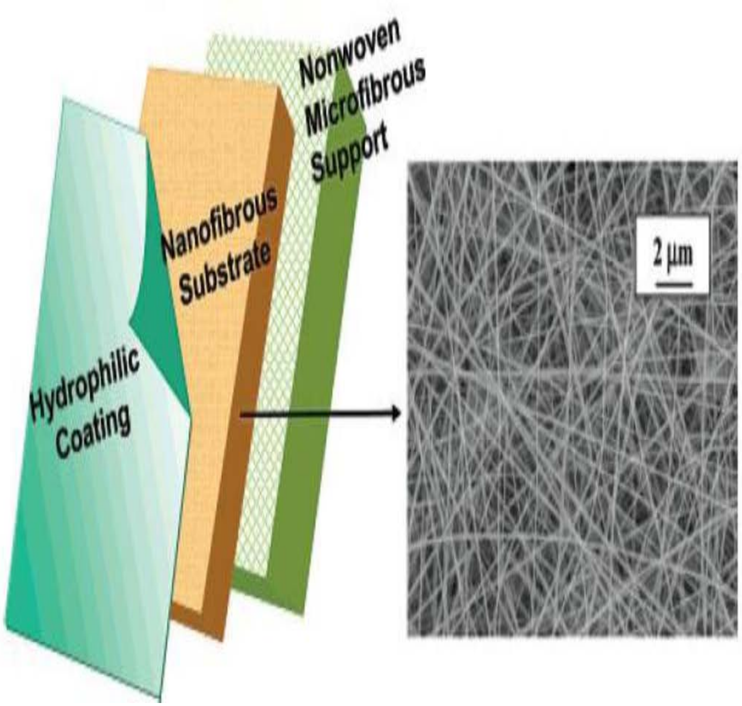

Wound Healing
Water Purification
Nanocelluloses
EMI shielding
(b)
Sensors

Cellulose nanomaterials in membranes for water filtration

Duke SRP researchers describe the potential benefits of advancing the use of cellulose nanomaterials in water filtration and environmental remediation technologies. (Image by Charles de Lannoy)



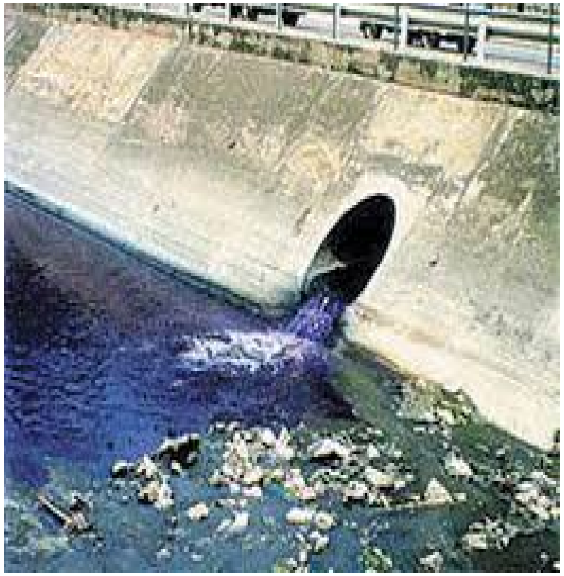
- Nanocellulose has been incorporated into a multitude of polymer matrices including cellulose triactetate, polyether sulphone (PES), poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), Poly (acrylonitrile) (PAN) and poly(3-hydroxybutyrate) (PHB).
- The membrane showed greater hydrophilicity, permeability, greater selectivity and greater resistance to bio-fouling.



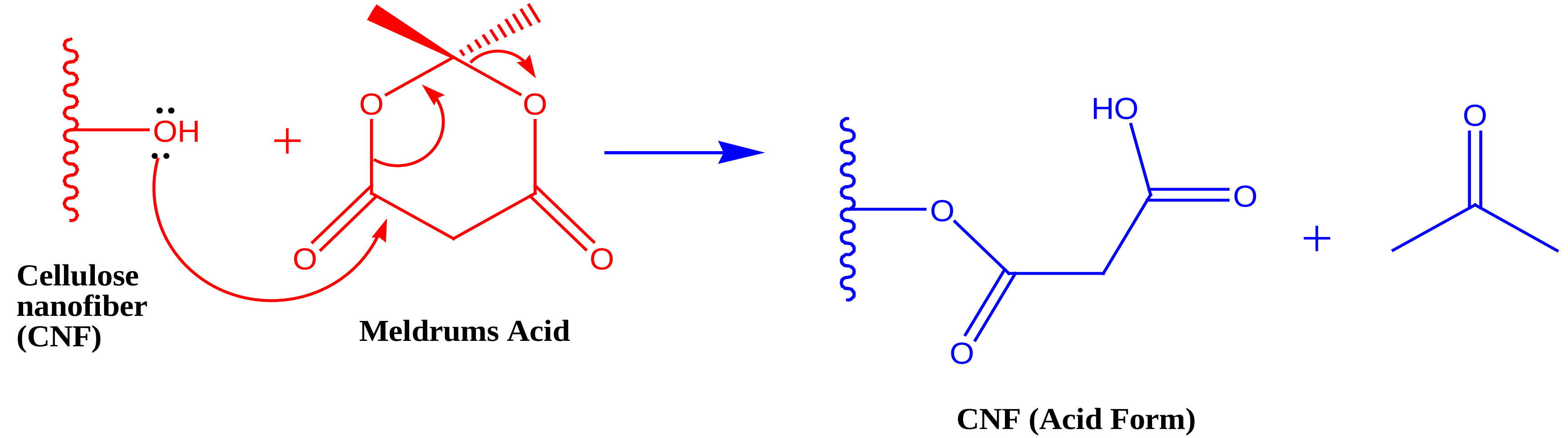
Removal of Dyes, Nanoparticles, Heavy Metals, Oils, Bacteria/Virus,

Nanocellulose based Microfiltration Membranes for Dye removal

- Thomas et al. removed crystal violet (CV) dye from the water using cellulose nanofiber based PVDF nanofibrous microfiltration membrane.
- The surface of the cellulose nanofibers (CNFs) was modified via esterification reaction by using meldrum acid (Meldrum's acid or 2,2-dimethyl-1,3-dioxane-4,6-dione is an organic compound).



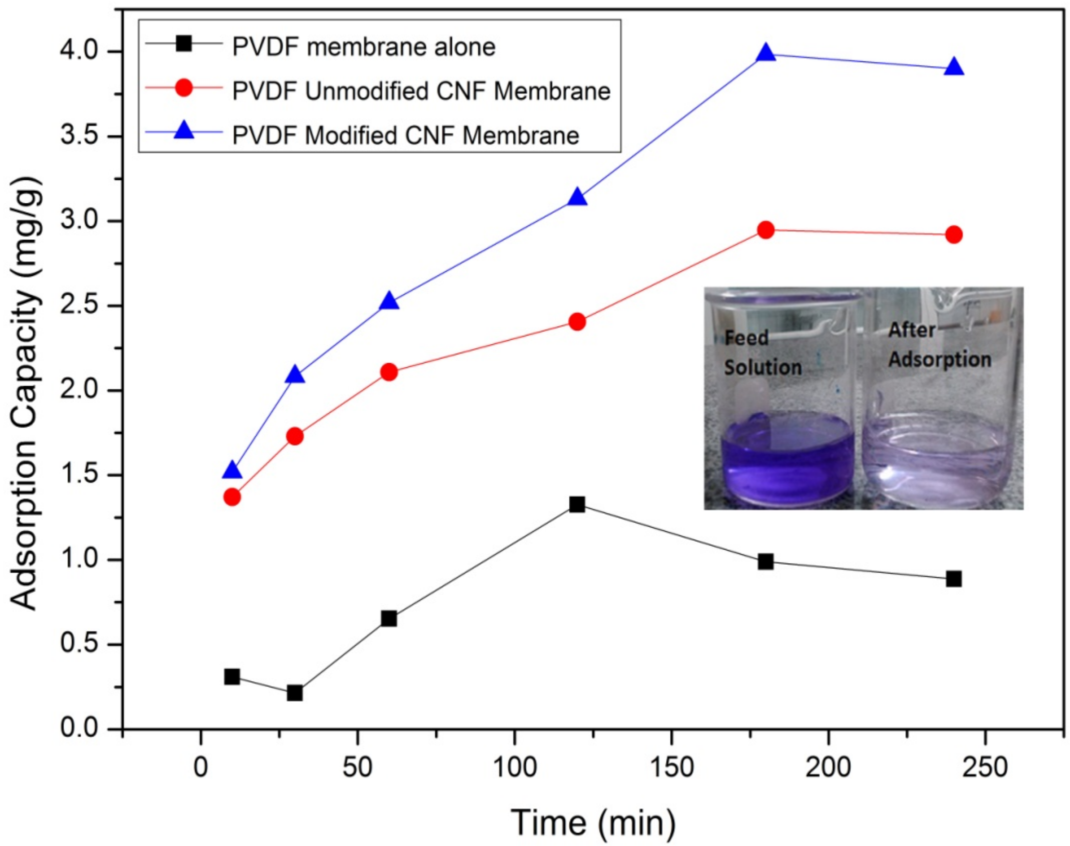
Gopakumar, Pasiquini and Thomas, Sustainable Chem. Eng. ACS, Submitted



Scheme illustrating the synthesis path used to prepare carboxylate –functionalized cellulose nanofibers using meldrums acid.

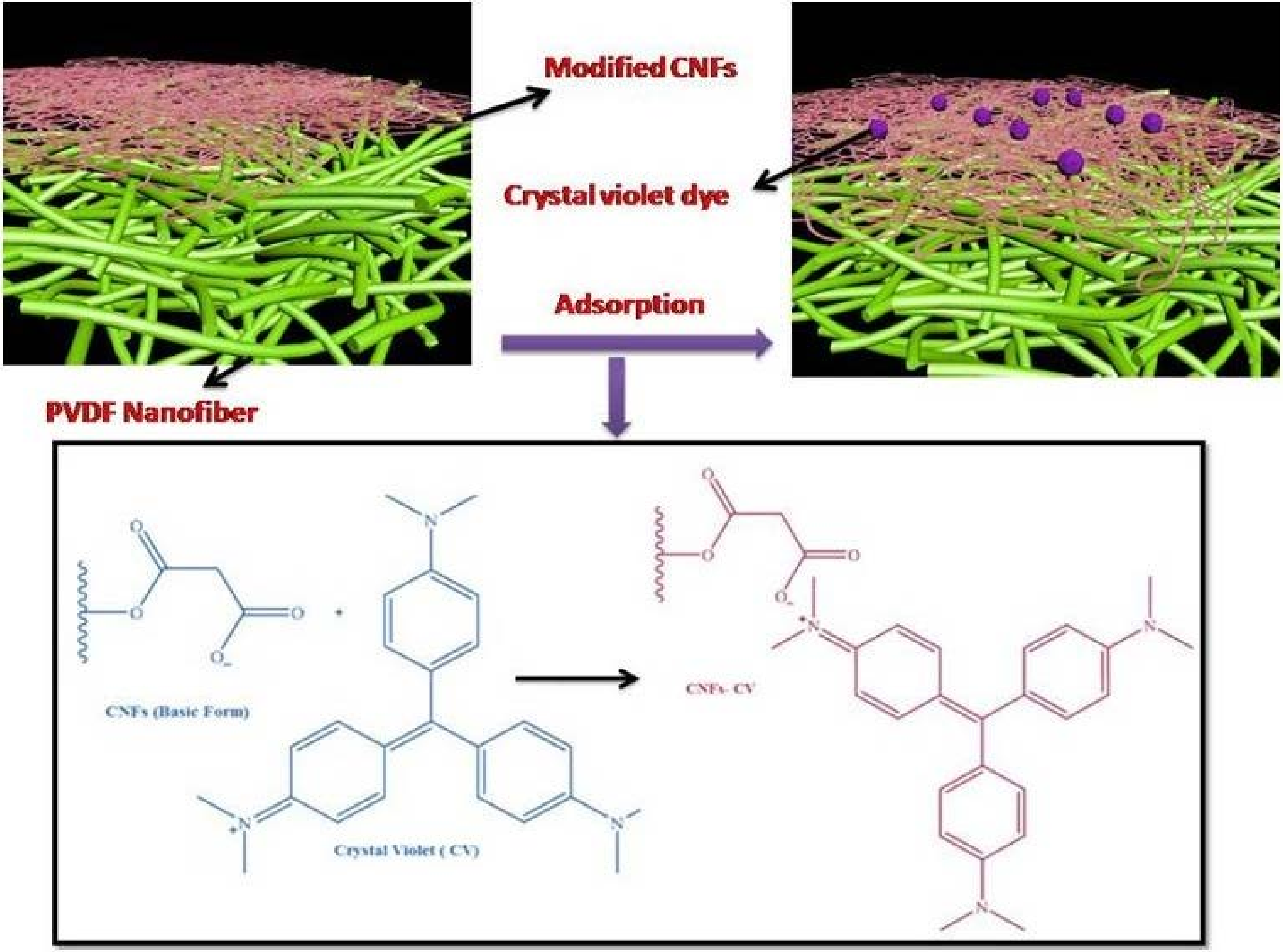
- **It was found with the 10mg/L of Crystal violet (CV) aqueous solution, CV adsorption of PVDF electrospun membrane and unmodified CNFs based PVDF membrane was around 1.368 and 2.948 mg/g of the membrane, where as it was 3.984 mg/g of the membrane by the meldrum's acid CNFs based PVDF membrane.**

Gopakumar, Pasiquini and Thomas, Sustainable Chem. Eng. ACS, Submitted

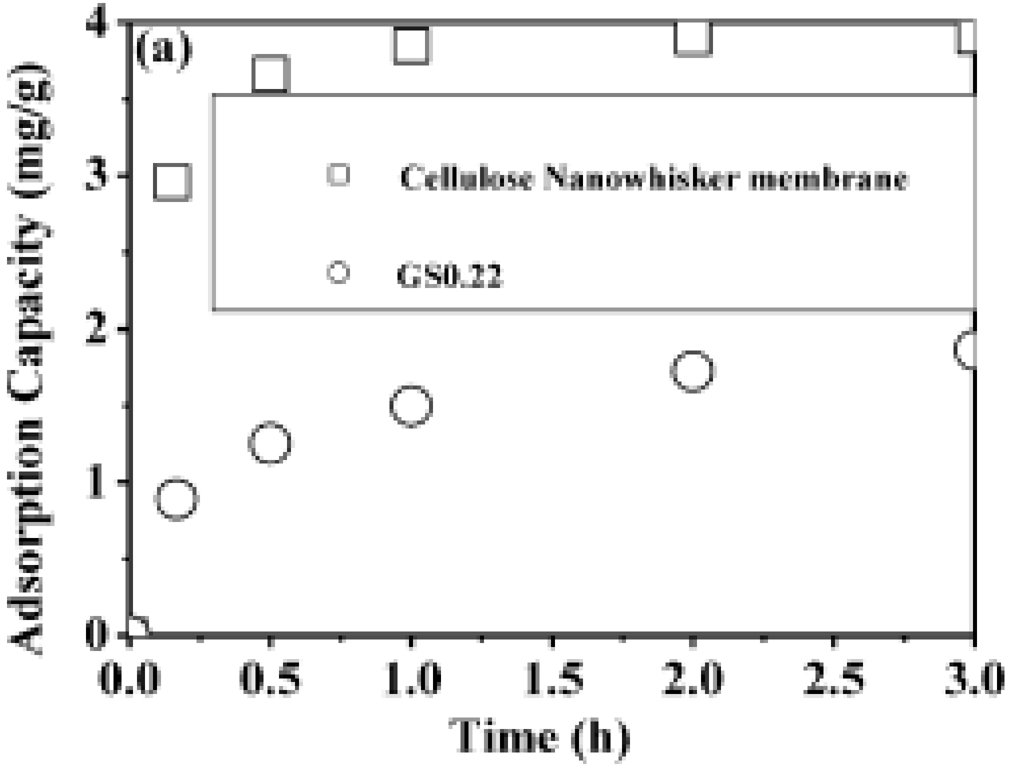


The **enhancement in the dye adsorption of the meldrum's modified CNFs based PVDF membrane can be justified by the strong electrostatic attraction between the negatively charged carboxylate groups on the meldrum's acid modified CNFs surface and Protonated CV molecules.**

Gopakumar, Pasiquini and Thomas, Sustainable Chem. Eng. ACS, Submitted



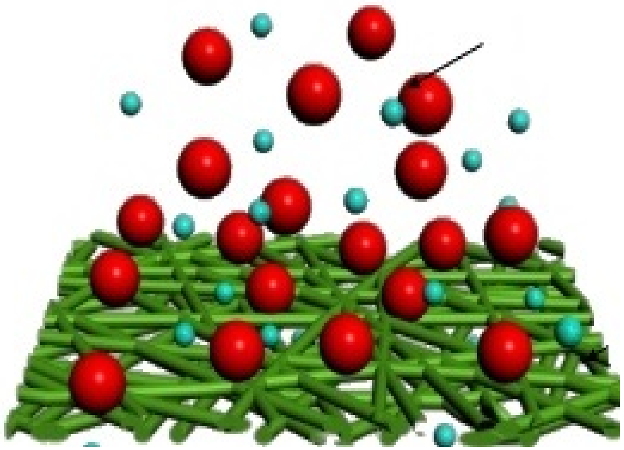
Gopakumar, Pasiquini and Thomas, Sustainable Chem. Eng. ACS, Submitted



Adsorption capacity of cellulose nanowhisker-based nanofibrous MF membrane and GS0.22 for CV dyes against time.

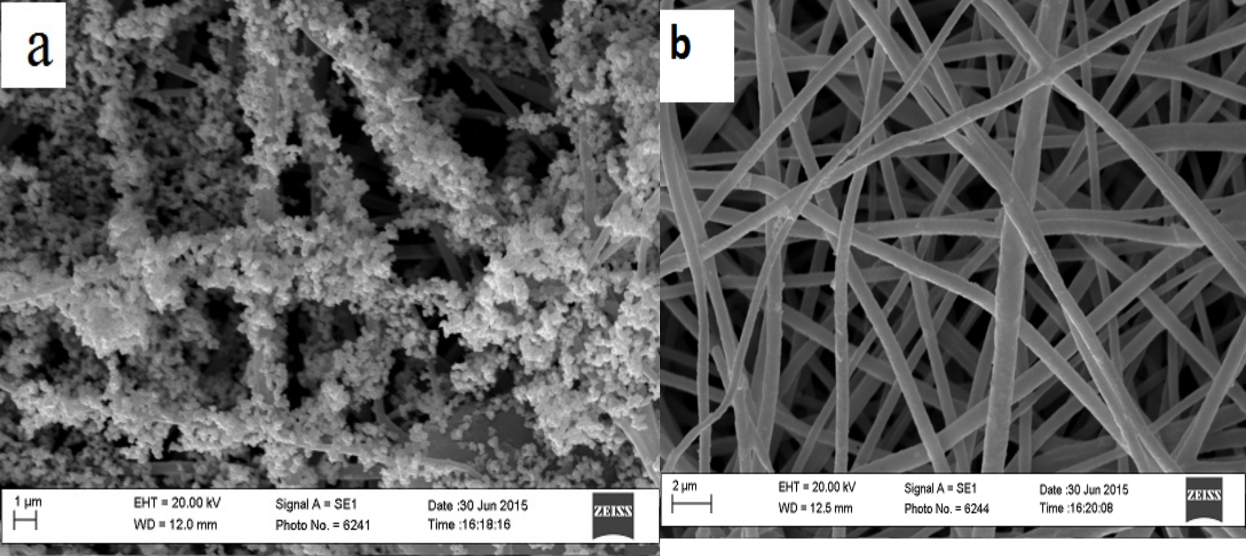
Ma et al. (2011) *Biomacromolecules* 13, no. 1 (2011): 180-186.

Nanocellulose based Microfiltration Membranes for Nanoparticles removal

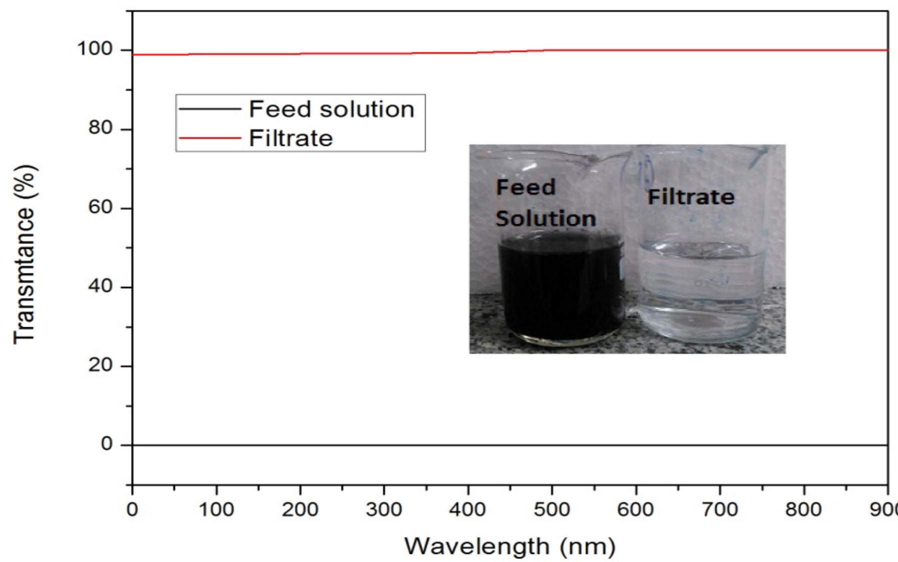


- Thomas et al. removed $Fe_2 0_3$ nanoparticles (50-100 nm) from the water using cellulose nanofiber based PVDF nanofibrous microfiltration membrane.
- From BET measurements it was confirmed that average pore diameter of PVDF membrane alone and Meldrum modified CNF based PVDF membrane was 8.673 to 6.395 nm respectively.

Gopakumar, Pasiquini and Thomas, Sustainable Chem. Eng. ACS, Submitted



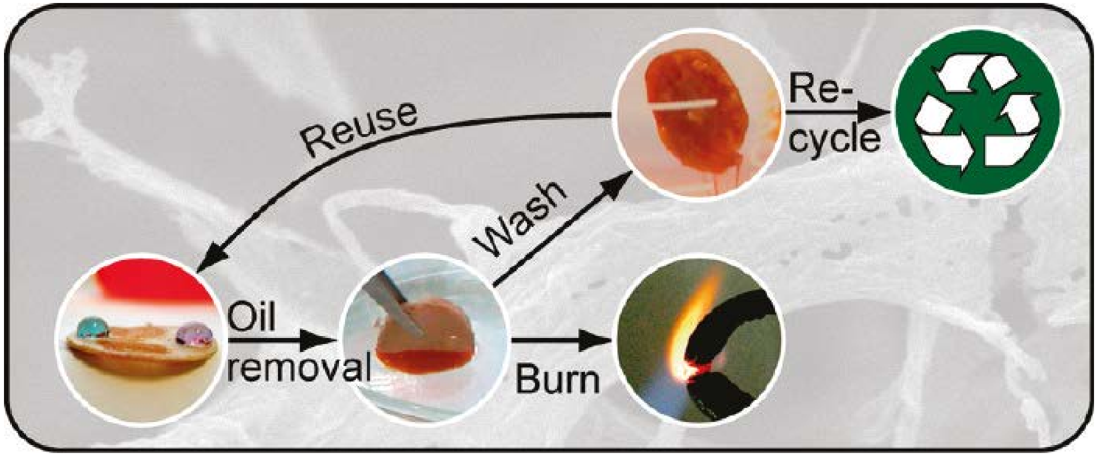
SEM images of Meldrum's acid modified CNFs based PVDF nanofibrous MF membrane after filtration of $Fe_2 0_3$ nanoparticles, top surface (a) and bottom surface (b).



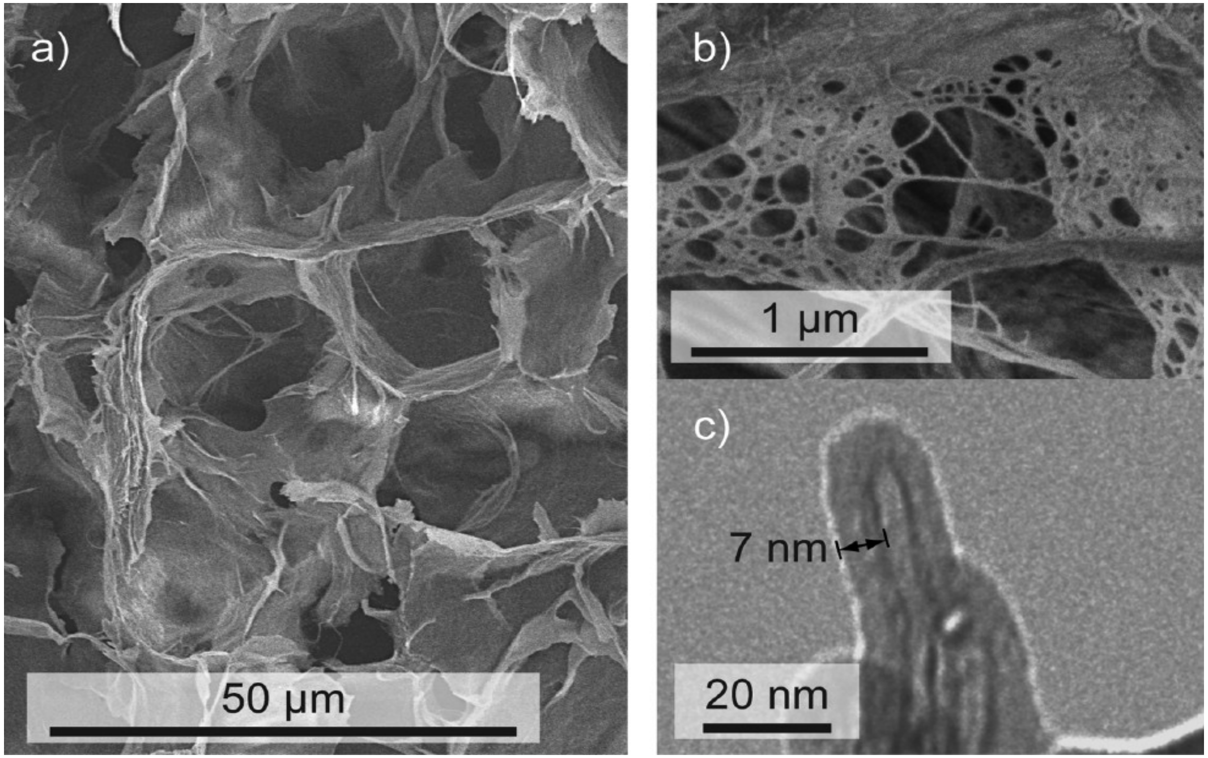
Gopakumar, Pasiquini and Thomas, Sustainable Chem. Eng. ACS, Submitted

Nanocellulose For Oil Adsorption

- **Korhonen et al**. demonstrated that hydrophobized nanocellulose aerogels achieved by coating the native cellulose nanofibrils with TiO2 show highly selective absorption of oils.
- The absorption was close to the overall volume of the aerogel (80-90% vol/vol) and the mass-based absorption capacity varies from 20 to 40 (wt/wt) depending on the density of the liquid.
- Organic liquids were readily removed by drying and oils could be washed out with a proper solvent, such as ethanol.



Korhonen et al. / *ACS Appl. Mater.Interfaces* 2011, 3, 1813-1816



Microscopic structure of the native nanocellulose aerogels. SEM micrographs of
(a) freeze-dried nanocellulose aerogels with fibrils packed into sheets, which are connected to form an open, porous aerogel structure, and
(b) a magnification of a sheet, which is composed of fibrils making the structure also nanoporous.
(c) TEM micrograph of a nanocellulose fibril with a uniform 7 nm TiO_2 coating.

Korhonen et al. / *ACS Appl. Mater.Interfaces* 2011, 3, 1813-1816

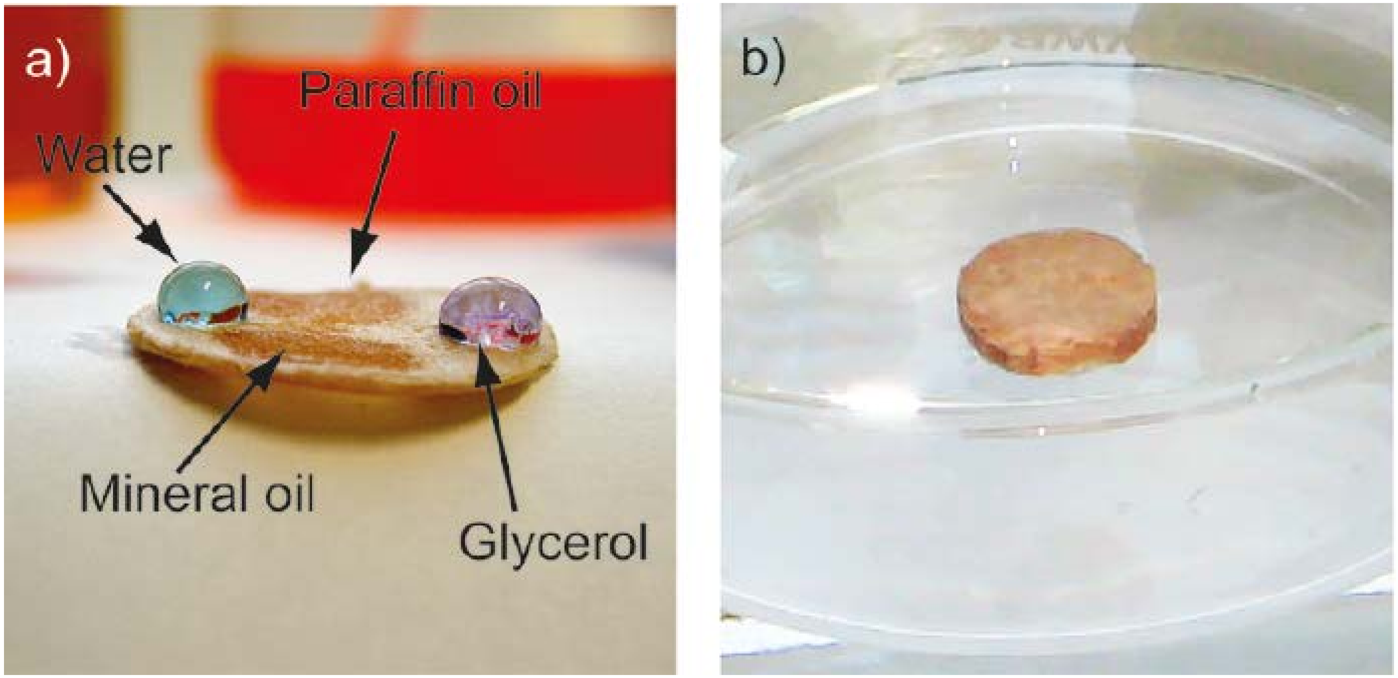


Figure (a) TiO2-coated aerogels are hydrophobic and oleophilic: the water and glycerol stay as droplets (colored with Reactive Blue dye for clarity), whereas paraffin oil andmineral oil are readily absorbed.
(b) Coated aerogel floating on water

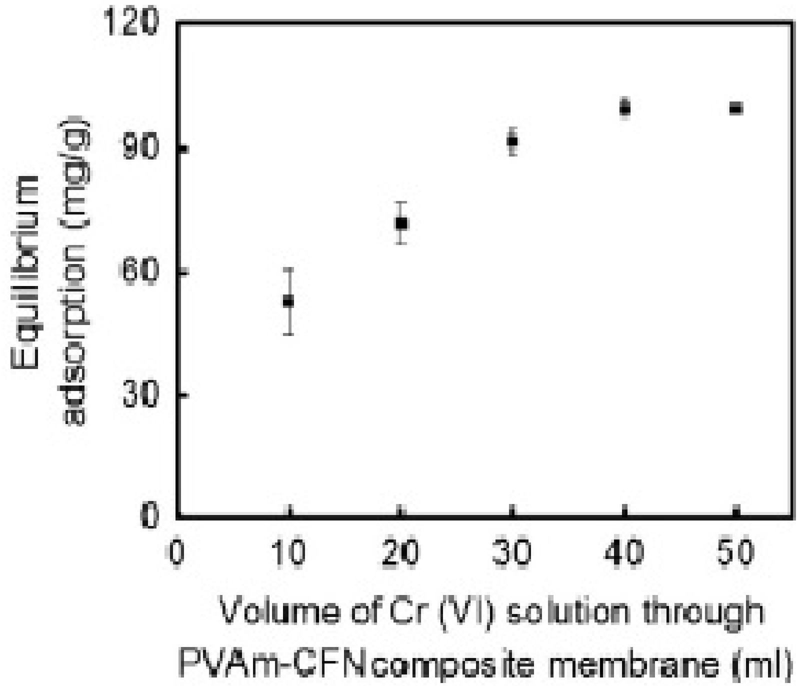
➢The aerogel absorbs a large amount of oil within the interior pores from the surface of water.

Korhonen et al. / *ACS Appl. Mater.Interfaces* 2011, 3, 1813-1816

Nanocellulose for Heavy metal adsorption

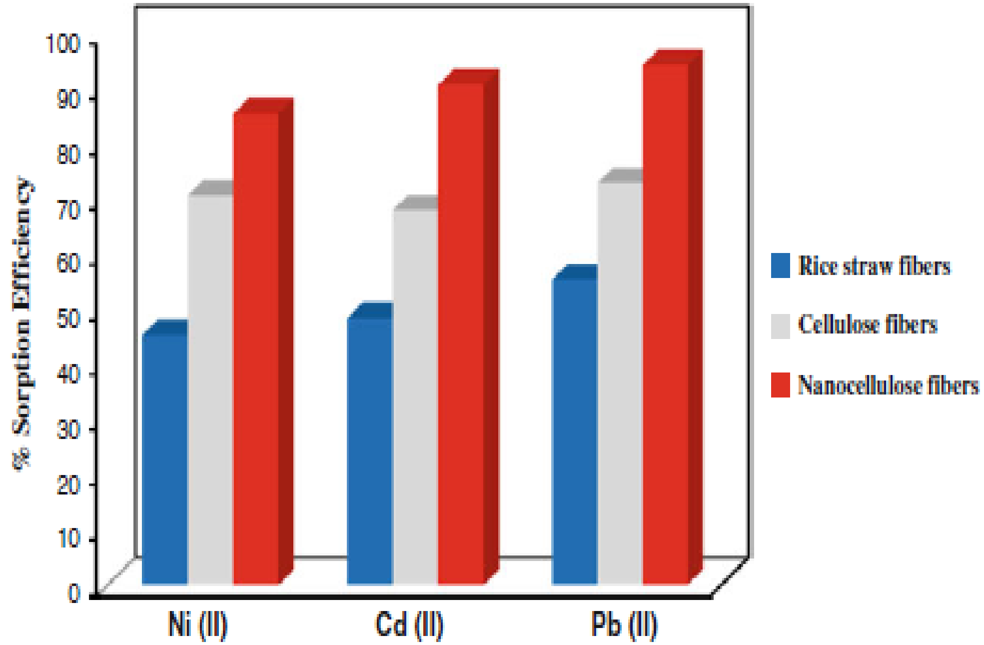
A novel class of microfiltration membrane, based on a two layered nanoscale PAN , microscale PET fibrous scaffold containing infused ultra-fine functional cellulose nanofibers (diameter about 5nm) was demonstrated by Wang et al. (2013).

- They have done amidation of ultra cellulose nanofibers using PVAm (polyvinyl Amine) which resulted the introduction of massive amount of amine groups on cellulose nanofibers (PVAm-CNF).
- The introduction of amine groups on PVAm-CNF resulted in a substantial increase of positive charge density on the nanofiber surface and which led to the efficient adsorption of negatively charged Cr (chromium) ions from the aqueous solution.
- For the total 50 ml of 50 ppm Cr (VI) solution, the maximum adsorption efficiency of Cr (VI) on PVAm-CNF was 100 mg/g of the membrane.



Dynamic adsorption of Cr (VI) on PVAm-CNF membrane

Wang et al. / *Journal of Membrane Science 446 (2013) 376-382*



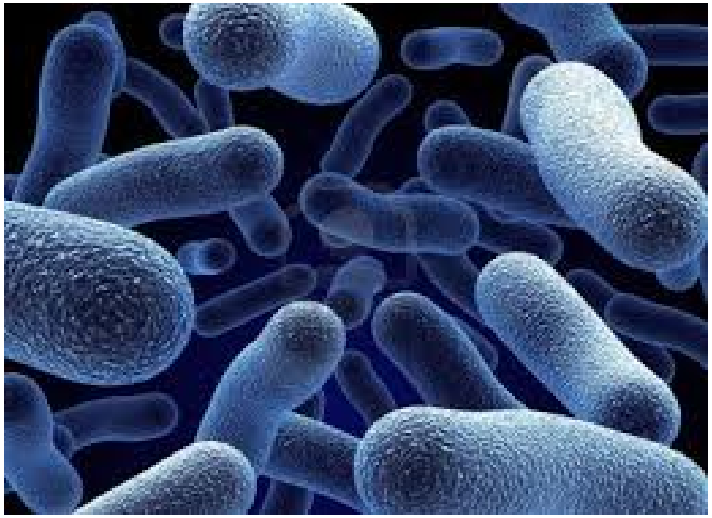
➢Cellulose nanofibers shows maximum removal efficiency comapared to the cellulose and native rice straw at minimum dose (0.5g) due to the removal of the non cellulosic amorphous constituents promoting the availability o f large number of –OH groups on the nanocellulose chains.

➢Acid hydrolysis of the cellulose fibers also increases the negative charge on the surface of the cellulose nanofibers , thus enabling the electrostatic interaction with the divalent cationic metal species.

Kardam et al. / ***Clean Tech Environ Policy (2014) 16: 385-393***

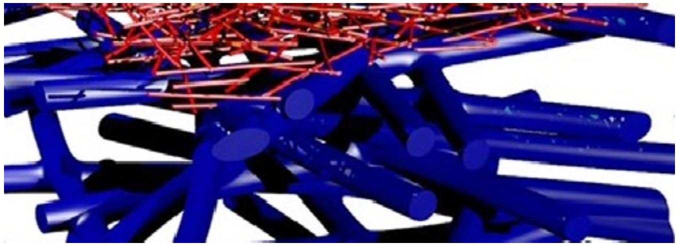
Problem with Bacteria and Virus

- Bacteria can be found in large numbers in raw sewage, effluents, and in natural waters. Some well-known diseases caused by pathogenic bacteria include:
cholera, dysentery, shigellosis, and typhoid fever
- Many viruses can survive for extended periods of time in natural waters and can occasionally withstand the treatment process, they pose a public health concern.



Microorganism	Some Symptoms and Illness
Bacteria	Gastroenteritis (includes diarrhea and abdominal pain), salmonellosis, and cholera.
Viruses	Fever, common cold, gastroenteritis, diarrhea, respiratory infections, and hepatitis.

Nanocellulose based Microfiltration Membranes for Bacteria and Virus removal



- Wang et al. demonstrated a microfiltration membrane , based on a two layered nanoscale PAN , microscale PET fibrous scaffold containing infused ultra-fine functional cellulose nanofibers (diameter about 5nm) capable to remove both bacteria (*Escherichia coli*) by size extrusion and MS2 virus by adsorption.
- They have done amidation of ultra cellulose nanofibers using PVAm (polyvinyl Amine) which resulted the introduction of massive amount of amine groups on cellulose nanofibers (PVAm-CNF).
- The bacterial removal test indicated the complete removal of E.coli, and LRV (log reduction value) was achieved for both PVAm modified and unmodified membranes. This was due to the bacteria cell size (2 µm x 1 µm) was much larger than their maximum pore sizes.

PET/PAN layer thickness (µm)	Max.pore size (µm)	LRV for E.coli	LRV for MS2
100+ 40	0.78 ± 0.03	˜ 6	0
100+40*+2	0.73 ± 0.01	˜ 6	˜ 0
100+40**+2	0.78 ± 0.01	˜ 6	>4

Retention of MS2 of composite membranes

*Cellulose nanofibers without PVAm grafting

** Cellulose nanofibers with PVAm grafting

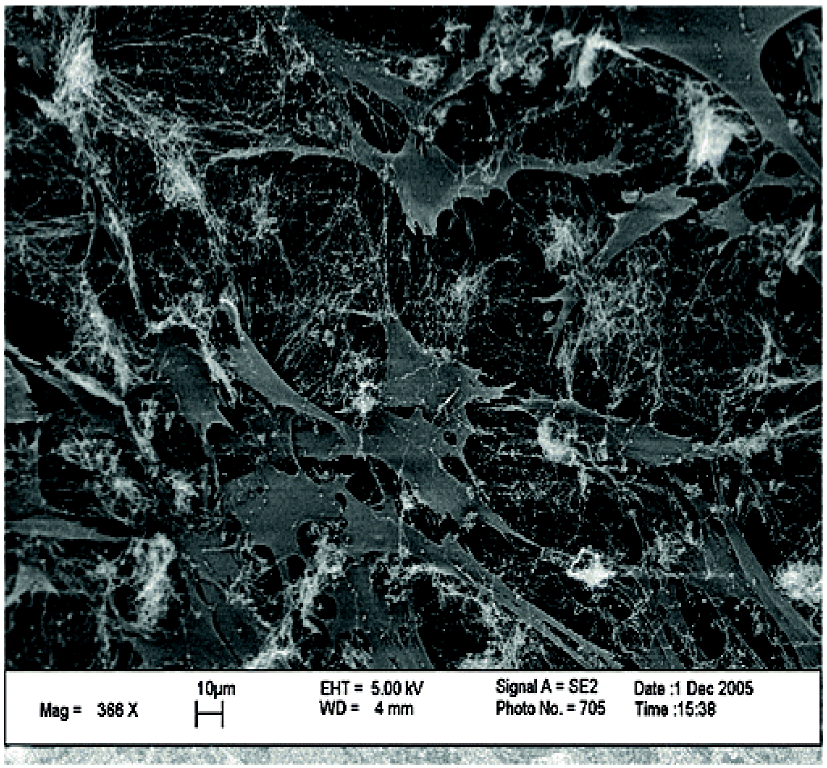
PVAm grafted CNF possessed a large amount of amine groups, resulting in positive charges in the solution of pH=7. So the electrostatic interactions between the positively charged nanofiber surface and the negatively charged virus MS2 became favorable and the adsorption took place. This is because most viruses including MS2 have an isoelectric point of less than 7, leading to a negatively charged surface in neutral solution.

Note: 6 log reduction means the number of germs is 1,000,000 times smaller number of microorganisms

Wang et al. / *Journal of Membrane Science 446 (2013) 376-382*

Biomedical applications-as scaffolds,

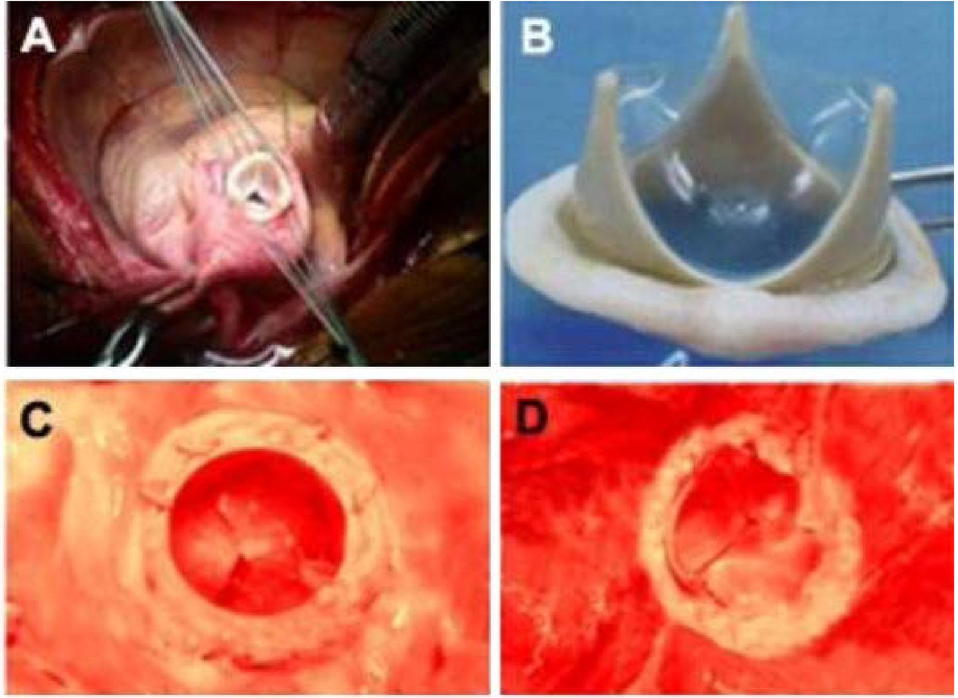
- *Biomacromolecules*, **2007**, *8* (1), pp 1–12
-



Mechanical properties of pure polyurethane and cellulose embedded composites.

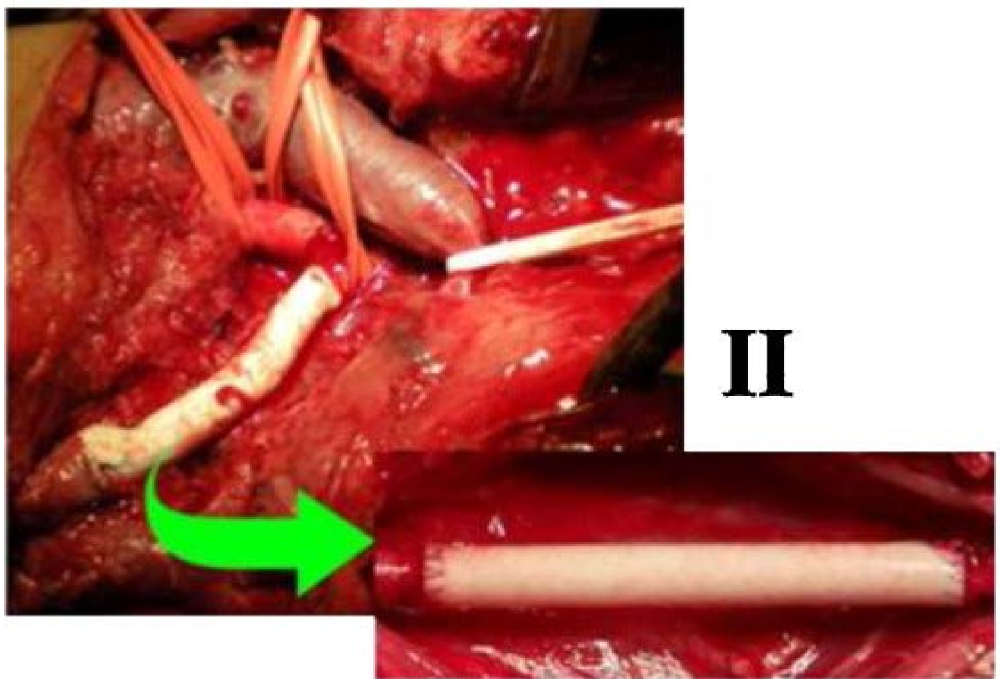
Sample	Tensile strength (MPa)	E-modulus (MPa)
PU	17,5 ± 0,4	37,5 ± 0,5
PU–NC(2%)	28,2 ± 1,2	94 ± 1,6
PU–NC(5%)	52,6 ± 0,7	992,4 ± 1,9
PU–NC(10%)	51,3 ± 0,1	786,8 ± 1,4

I



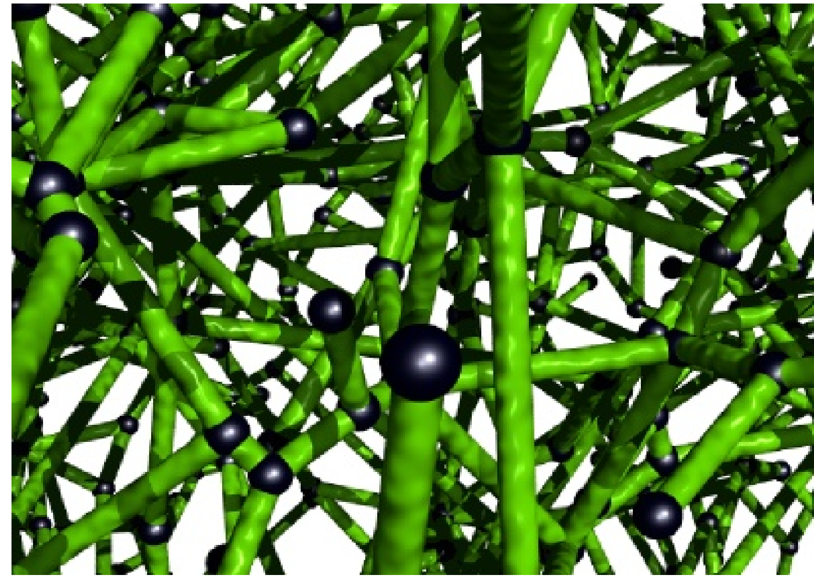
I) Nanocellulose–polyurethane prosthetic heart valve: (A) valve implant, (B) heart valve, (C) viewed in situ immediately prior to explant (inflow surface), (D) viewed in situ immediately prior to explant (outflow surface). Thomas et al. ***Carbohydrate Polymers*** **86, no. 4 (2011): 1790-1798**

II



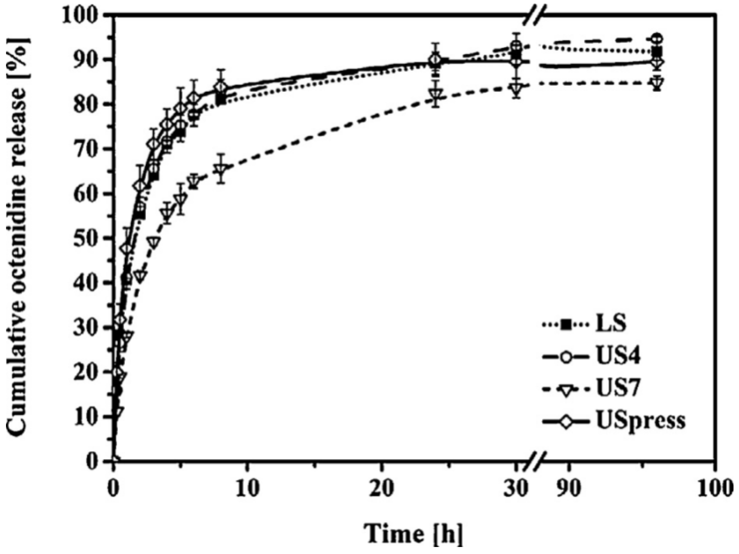
((II) Vascular prostheses made of nanocellulose-polyurethane placed between the brachiocephalic trunk and the right common carotid artery in a 26-year-old male patient with multiple endocrine neoplasia 2B (MEN 2B).
Thomas et al. Carbohydrate Polymers **86, no. 4 (2011): 1790-1798**

Nanocellulose for Wound healing applications



Nanocellulose for wound healing applications

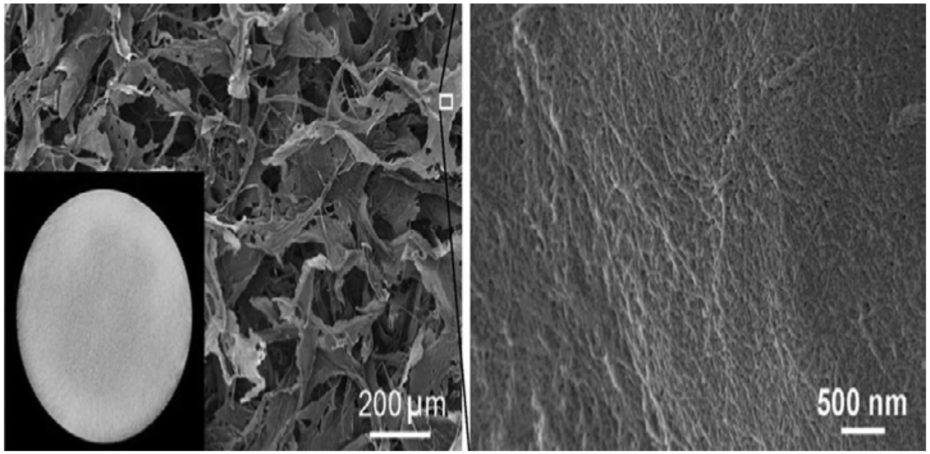
- **Sebastian Moritz et al,** prepared active wound dressings based on bacterial nanocellulose (BNC) as drug delivery system for octenidine.
- Octenidine loaded BNC presents a ready-to-use wound dressing for the treatment of infected wounds that can be stored over 6 months without losing its antibacterial activity.
- Octenidine loaded BNC demonstrated release profiles that were comparable to already marketed products.
- This portrays the tremendous potential as wound dressing with controlled drug delivery



Sebastian Moritz et al,

International Journal of Pharmaceutics, 471 (2014) 45–55.

Nanocellulose composite aerogels for wound healing applications



- *The aerogels also exhibited good biocompatibility as well as high level of cell activity and proliferation, which may be suitable for biological wound dressings and tissue engineering scaffolds.*

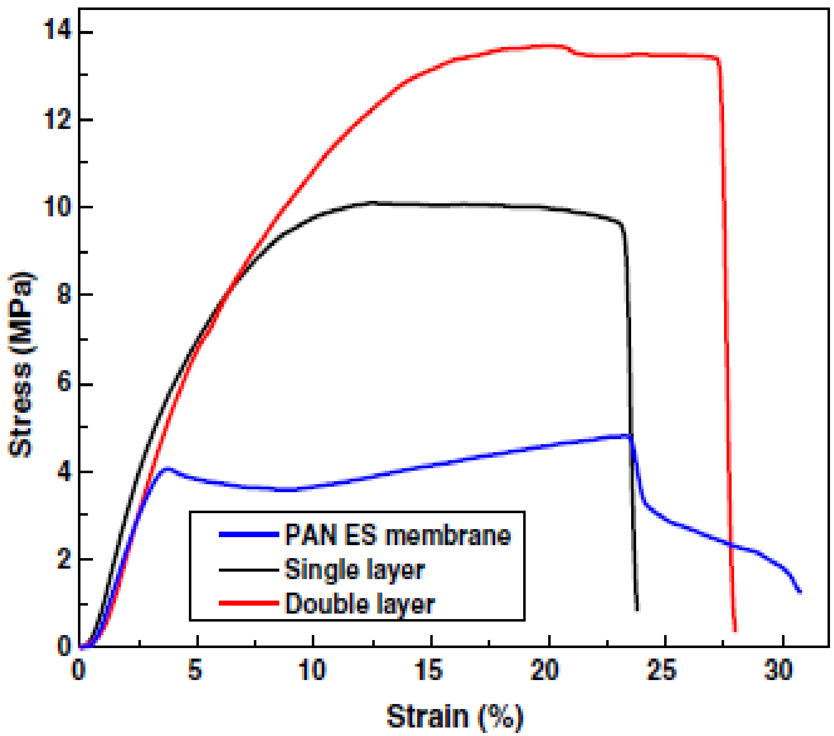
- ***Tianhong Lu et al***, isolated Nanocellulose fibers (NCFs) from wood powder, and were then oxidized into dialdehyde NCFs by sodium periodate, which offers active sites for introducing collagen.
- NCF/collagen composite aerogels, exhibited low-densities between 0.02 and 0.03 g cm3, high-porosities ranged from 90% to 95%, and strong water absorption up to 4000%.

Tianhong Lu et al, Composites Science and Technology, 94 (2014) 132–138

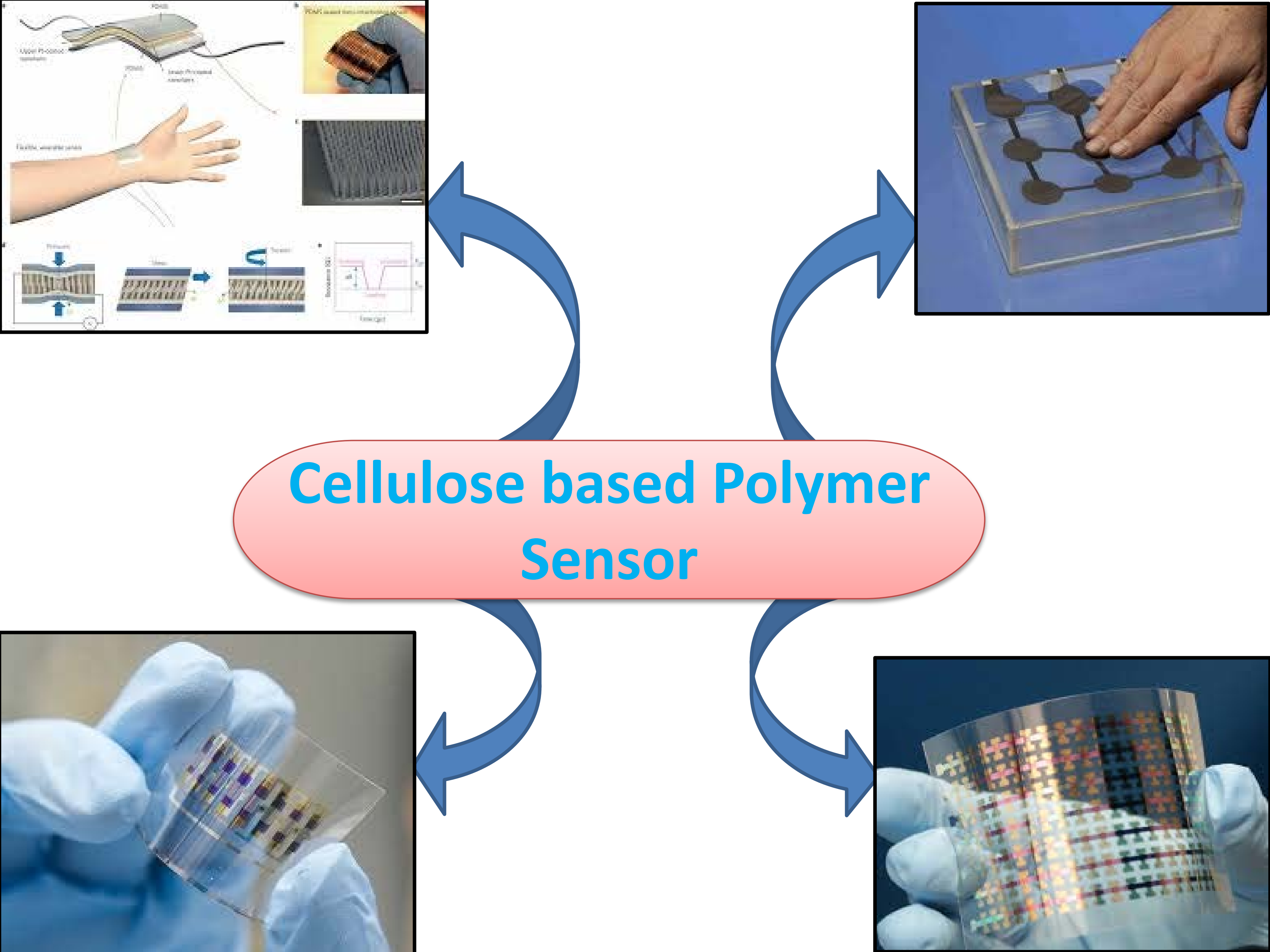
Nanocellulose for mechanical property enhancement for membranes

- Mechanical properties are one of the most important factors for filtration materials.
- Cao et al. showed high mechanical property for PAN electrospun membrane reinforced with jute cellulose nanowhiskers (CNWs) compared to PAN electrospun alone.
- They compared mechanical properties of PAN electrospun membrane alone , PAN electospun membrane with one CNWs coating and double CNWs coating.

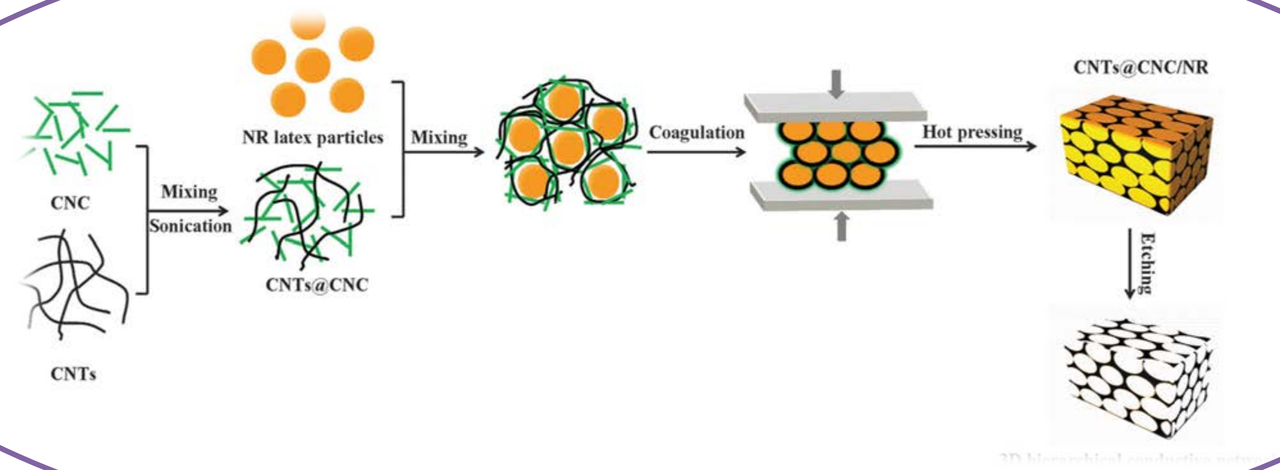
- PAN ES membrane had poor mechanical property with a tensile strength of 4 MPa.
- The introduction of jute cellulose nanowhiskers (CNWs) into composite membrane have improved the mechanical properties such as tensile strength increased to 10 MPa for single layer of CNWs coating and 14 MPa for double layer of CNWs coating.
- This can be interpreted by the strong hydrogen bonding of CNWs network formed on the surface of PAN nanofibers.



X. Cao et al. / Desalination 316 (2013) 120–126


Cellulose based Polymer Sensor

CNT@CNC/NR Strain sensor

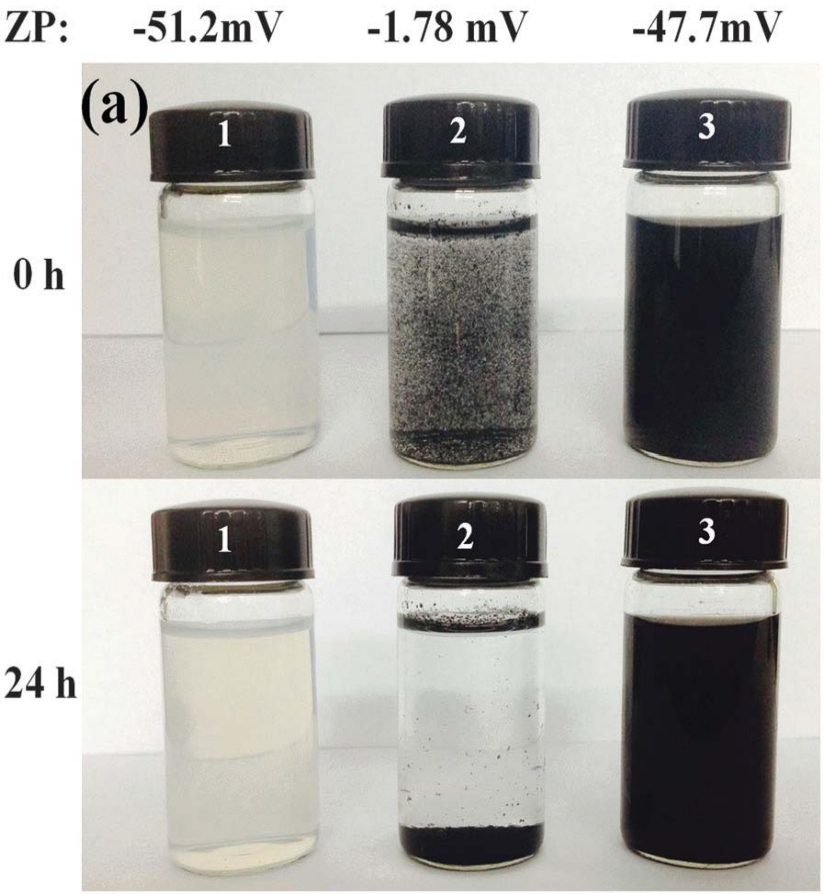


- **CNT@CNC (1/1 wt%) nanohybrid suspension.**
- **1.2, 2.0, 2.8, 3.5 and 4.2**

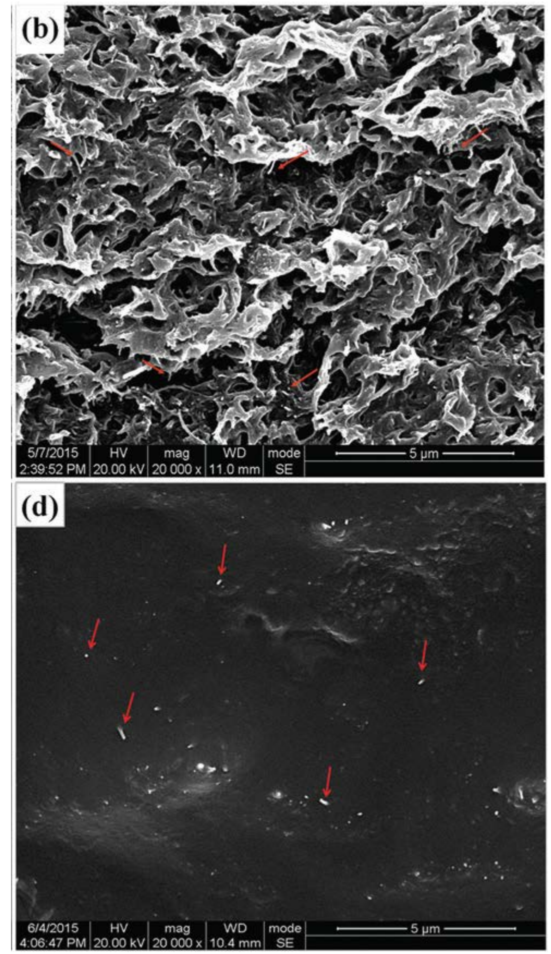
S. Wang et.al *Soft Matter,* 2016, 12, 845--852

Z-Potential

SEM



CNC | CNT | CNT/CNC

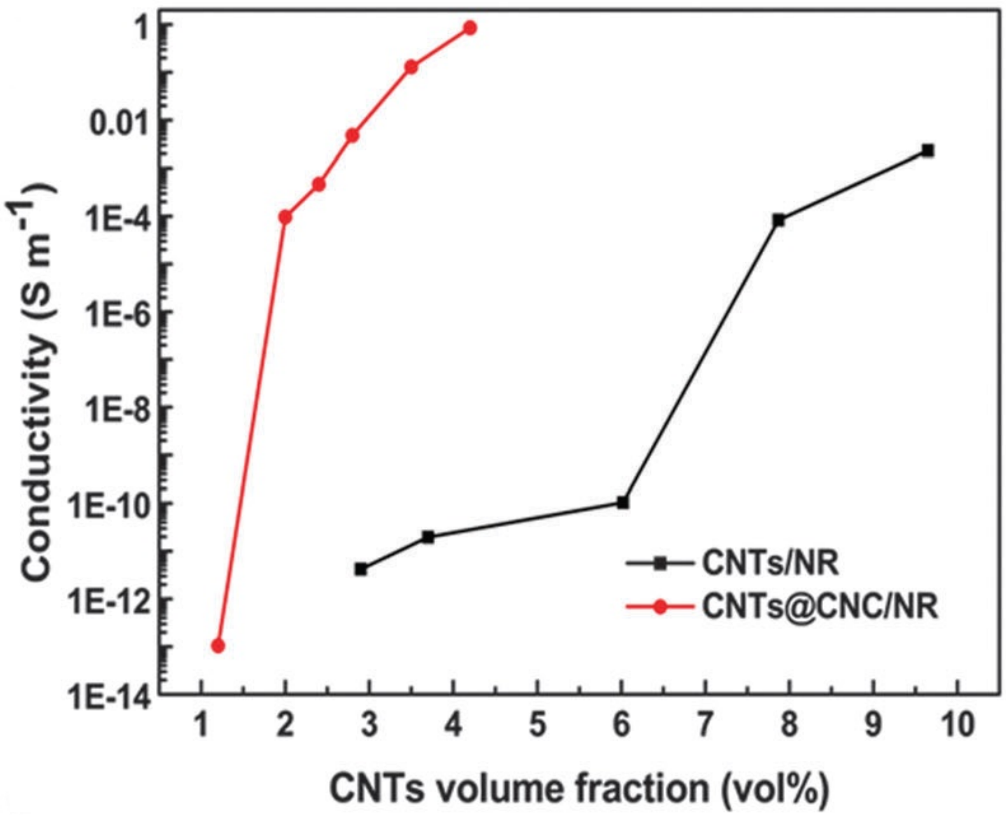


CNT/CNC-NR

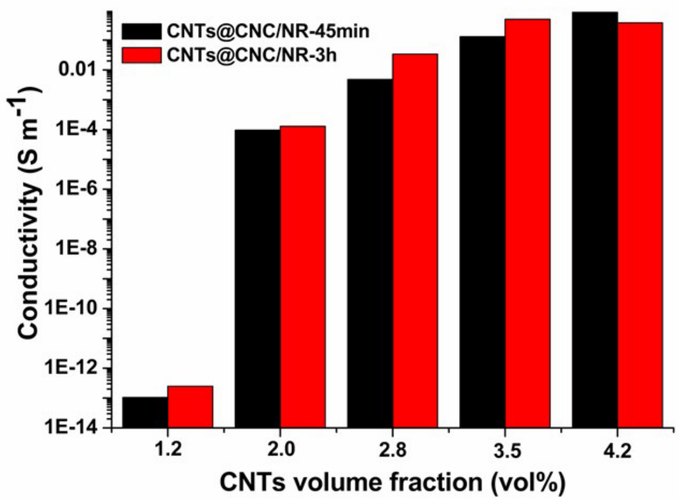
CNT-NR

S. Wang et.al *Soft Matter,* 2016, 12, 845--852

Electrical conductivity



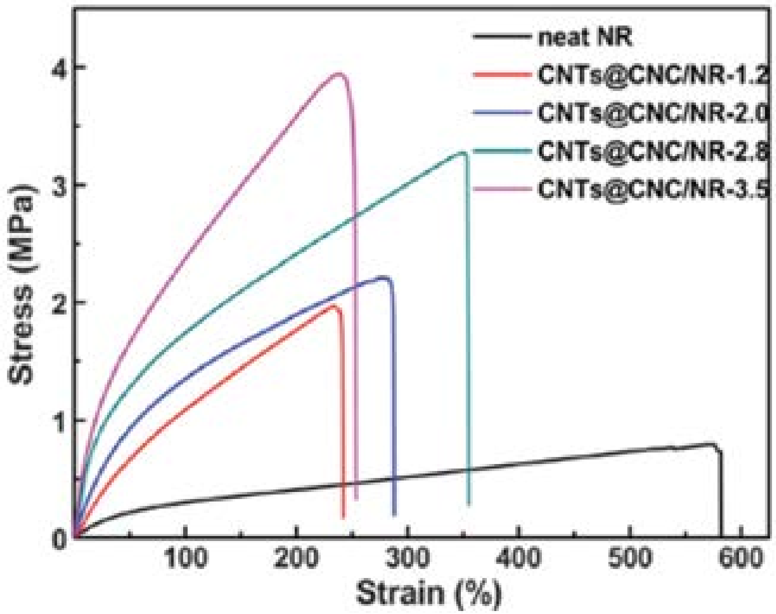
- CNT@CNC/NR percolation threshold (1.6 vol%)
- 4-fold lower than that of the CNT/NR (7vol%)
- CNT@CNC/NR-2.8 is 9 orders magnitude of CNT/NR

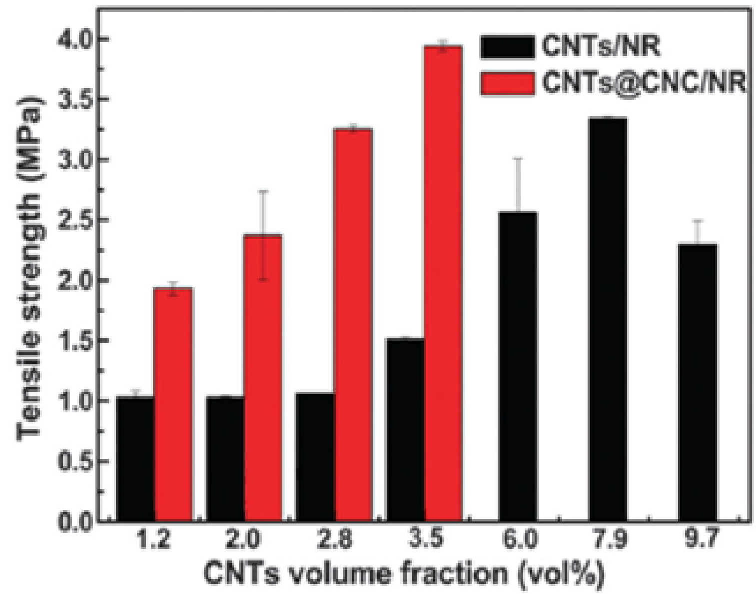


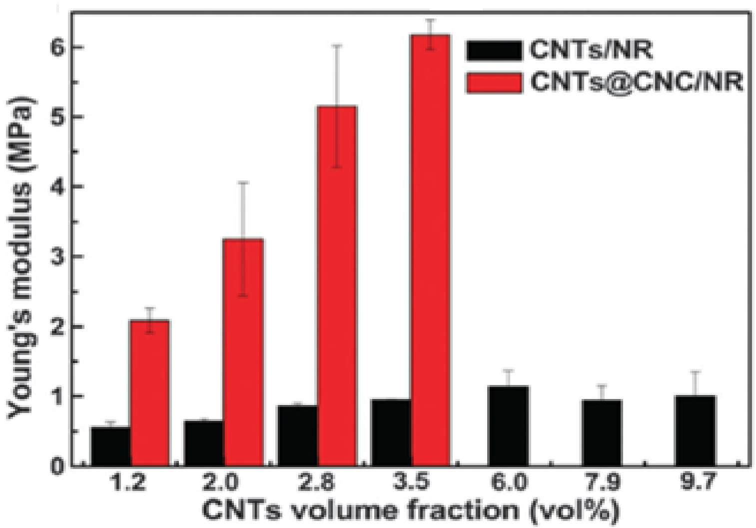
No significant effect on aspect ratio of CNC

S. Wang et.al *Soft Matter,* 2016, 12, 845--852

Tensile Properties



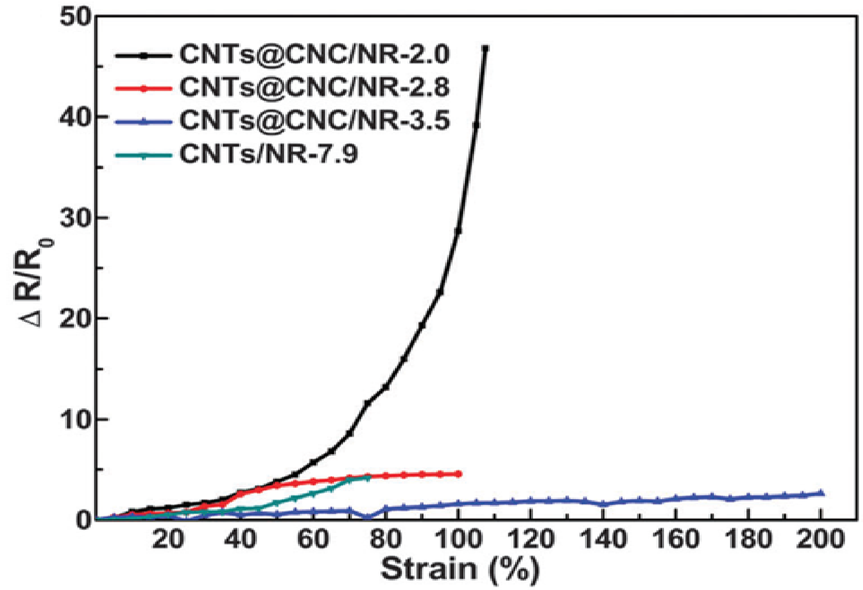


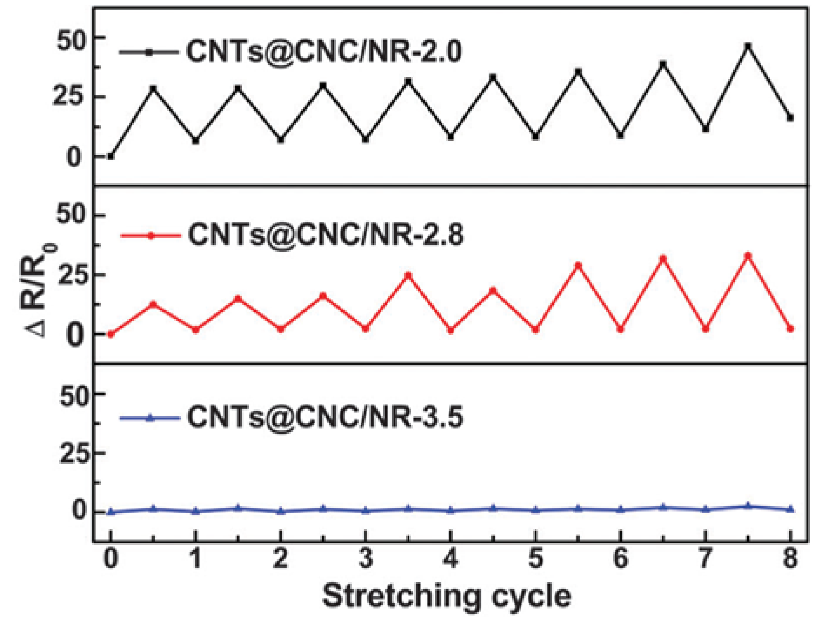


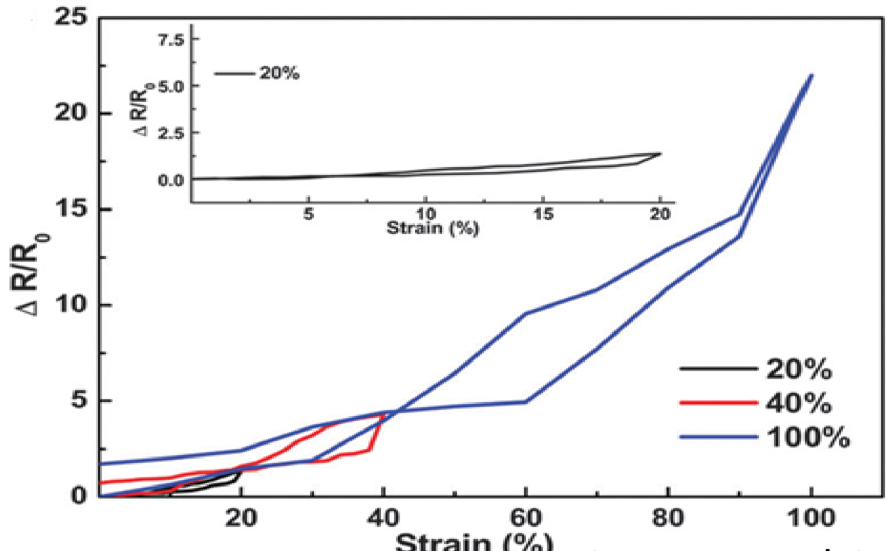
- The CNT@CNC/NR samples higher tensile strength and Young's modulus.
- CNC role in reducing the percolation threshold and enhancing mechanical property

S. Wang et.al *Soft Matter,* 2016, 12, 845--852

Strain sensing



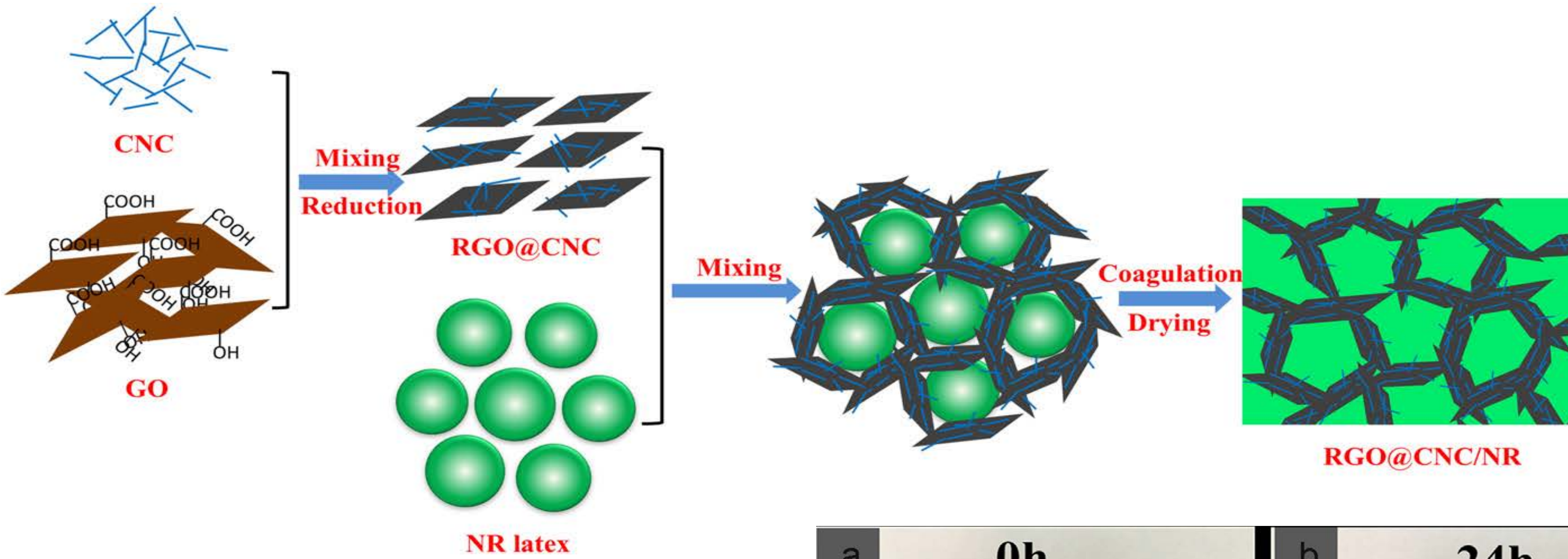


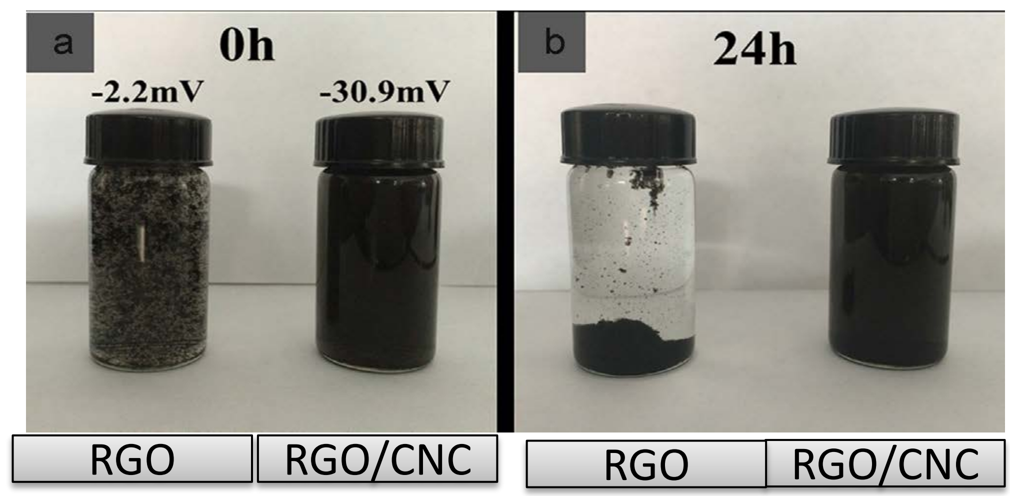


- GF-43.5 @100 %
- Just above the percolation show high sensitivity.
- CNTs@CNC/NR-2.0
- below 20% strain exhibits highly reversible in resistance

S. Wang et.al *Soft Matter,* 2016, 12, 845--852

RGO@CNC/NR Chemical sensor

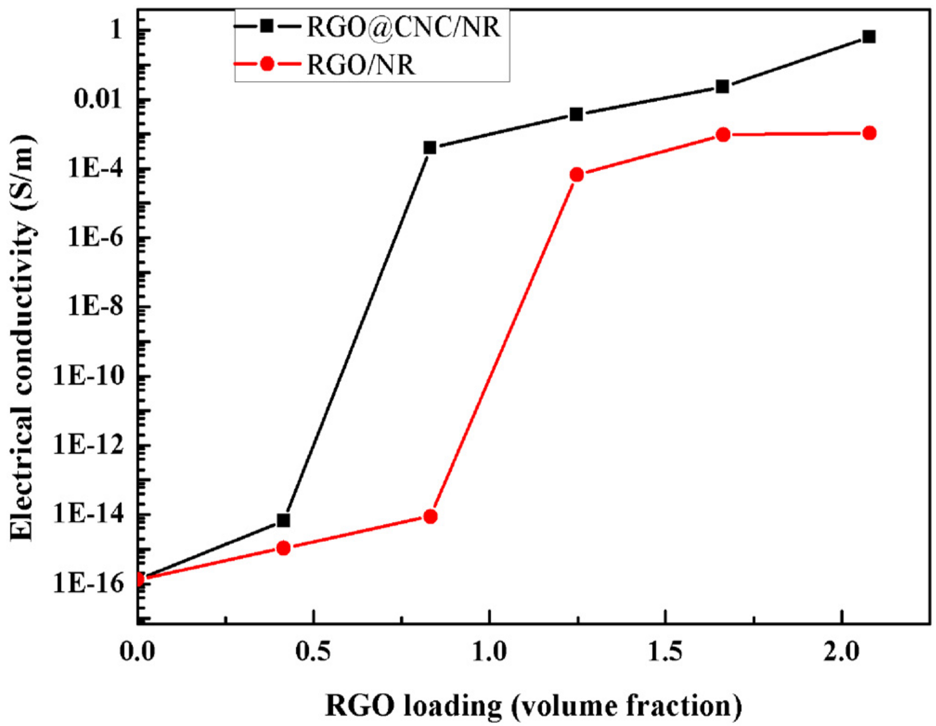




- **1, 2, 3, 4 and 5 phr of RGO**

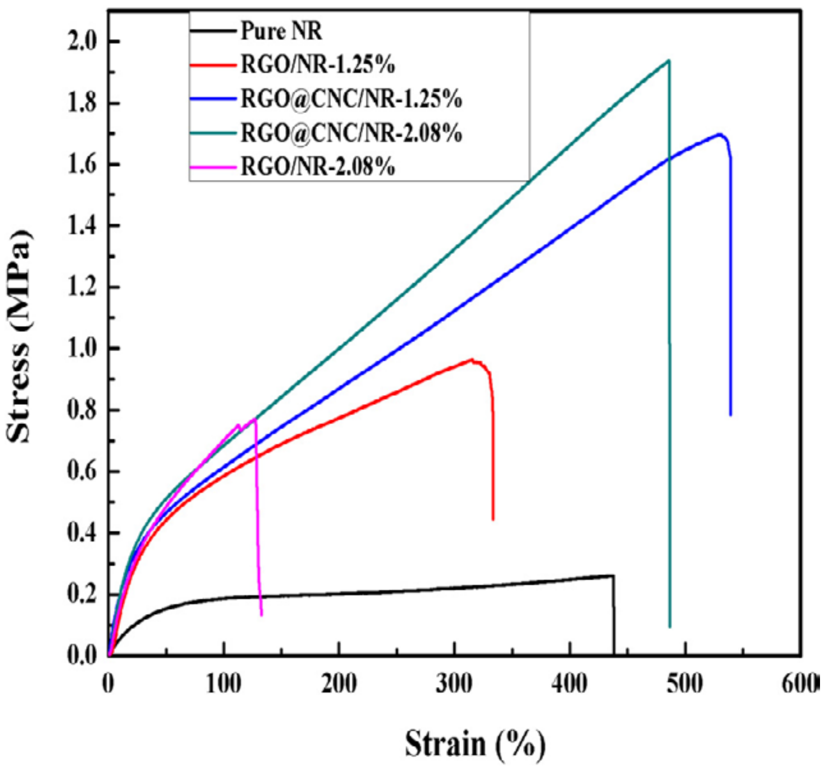
J. Cao et al. Carbohydrate Polymers 140 (2016) 88–95

Electrical conductivity



- RGO@CNC/NR nanocomposites is only 0.66 vol %
- RGO /NR 1.7 vol%

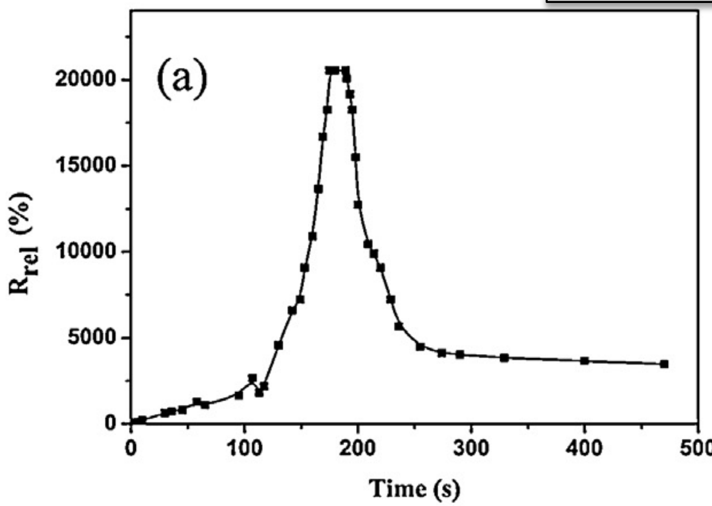
Tensile Properties

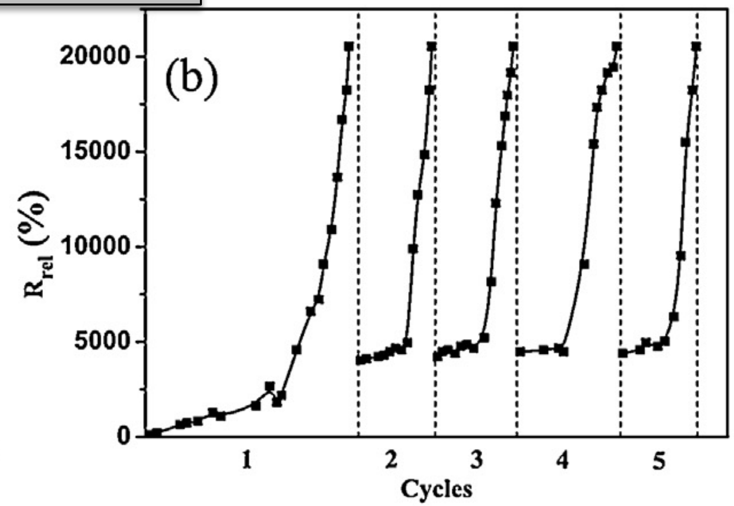


J. Cao et al. Carbohydrate Polymers 140 (2016) 88–95

Responsivity–Time relationship

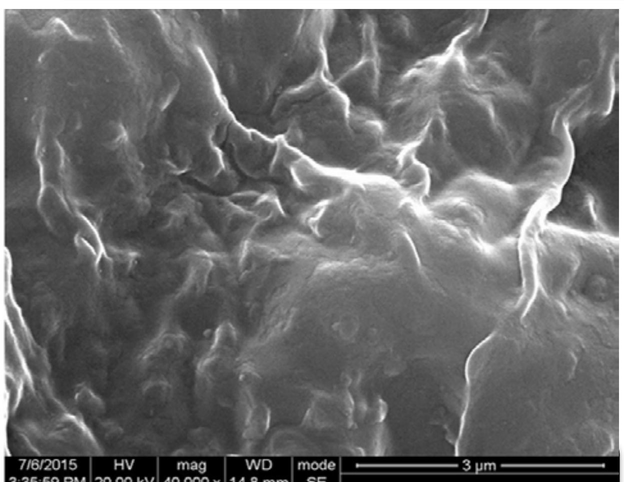
RGO@CNC/NR2.08



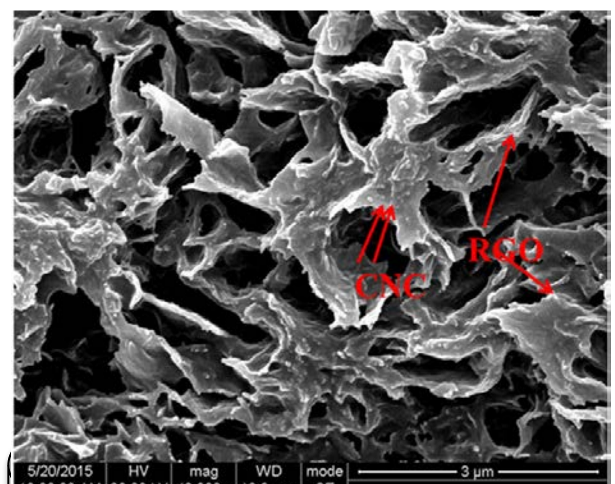


Exposed to toluene

During five immersion drying runs



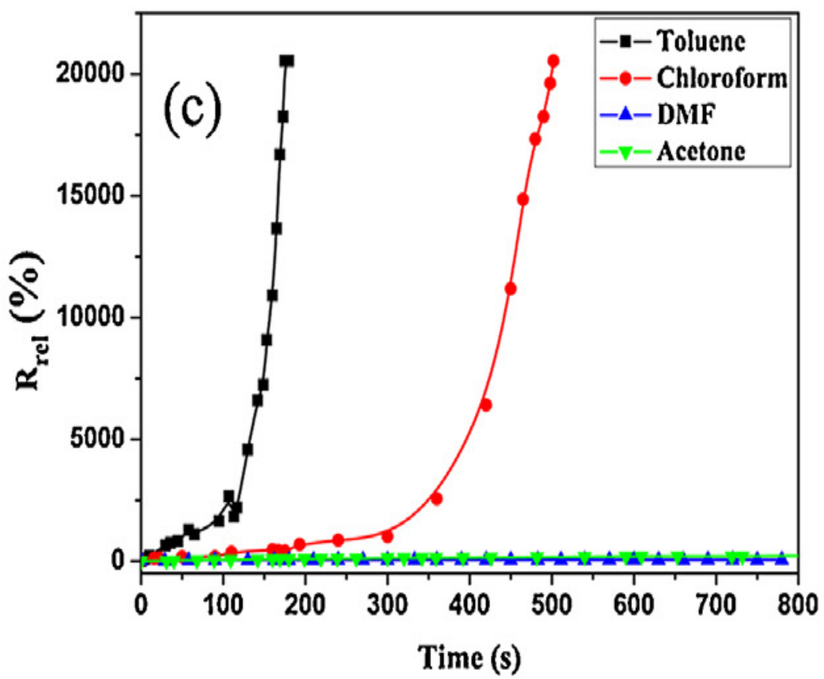
RGO/NR



RGO@CNC/NR

J. Cao et al. Carbohydrate Polymers 140 (2016) 88–95

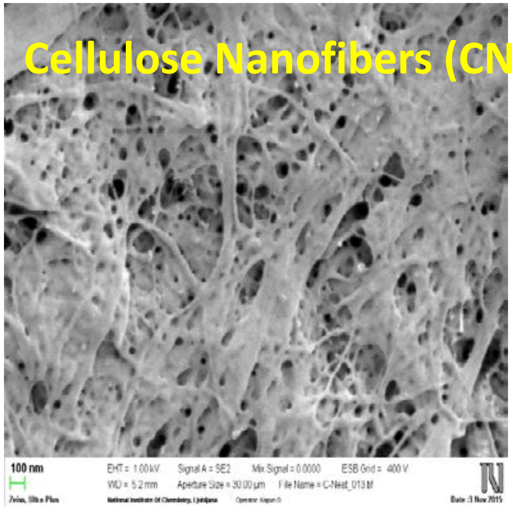
Responsivity–time relationship RGO@CNC/NR 2.08- Different solvents

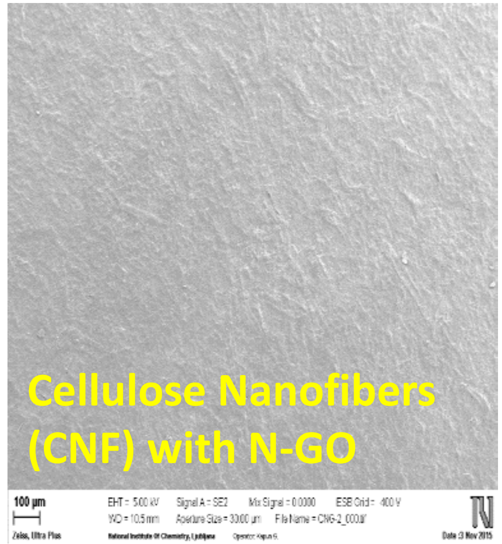


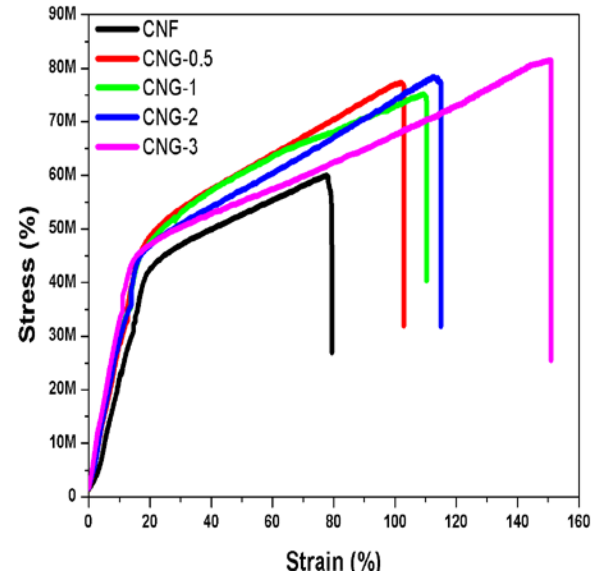
- **RGO@CNC/NR nanocomposites have remarkable liquid response sensitivity for toluene and chloroform.**
- **The resistivity changes are attributed to the different solubility parameter between the NR and the used organic solvents.**
- **The solubility parameter of NR, toluene, chloroform, dimethyl formamide and acetone are 8.5, 8.9, 9.6, 9.9 and 12.1**

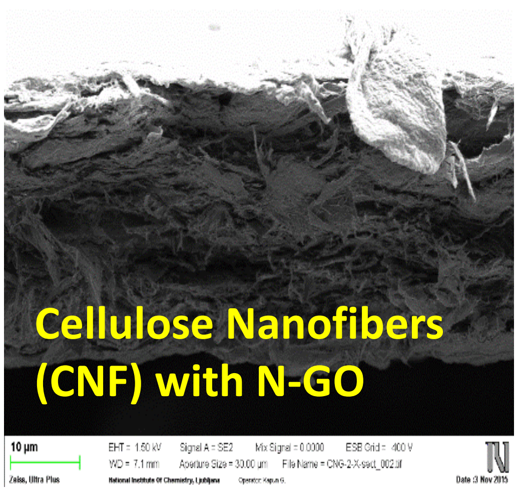
J. Cao et al. Carbohydrate Polymers 140 (2016) 88–95

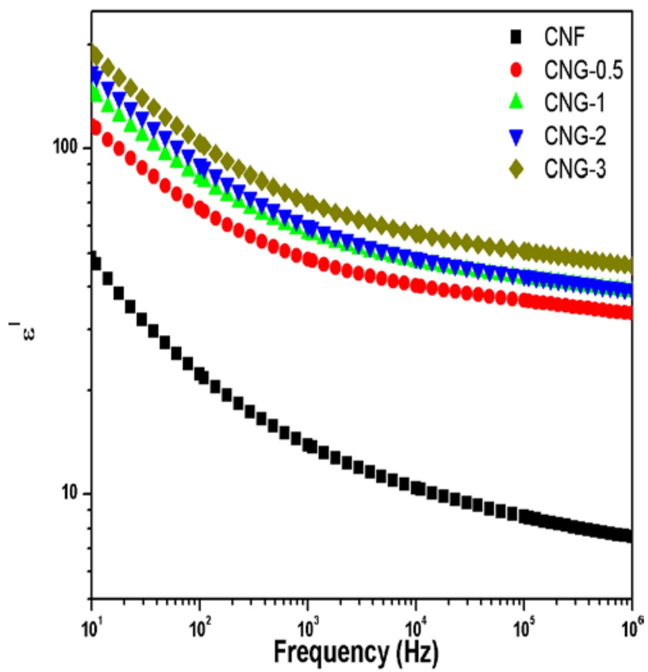
Cellulose Nanofibers (CNF) – Nitrogen doped Graphene oxide composite





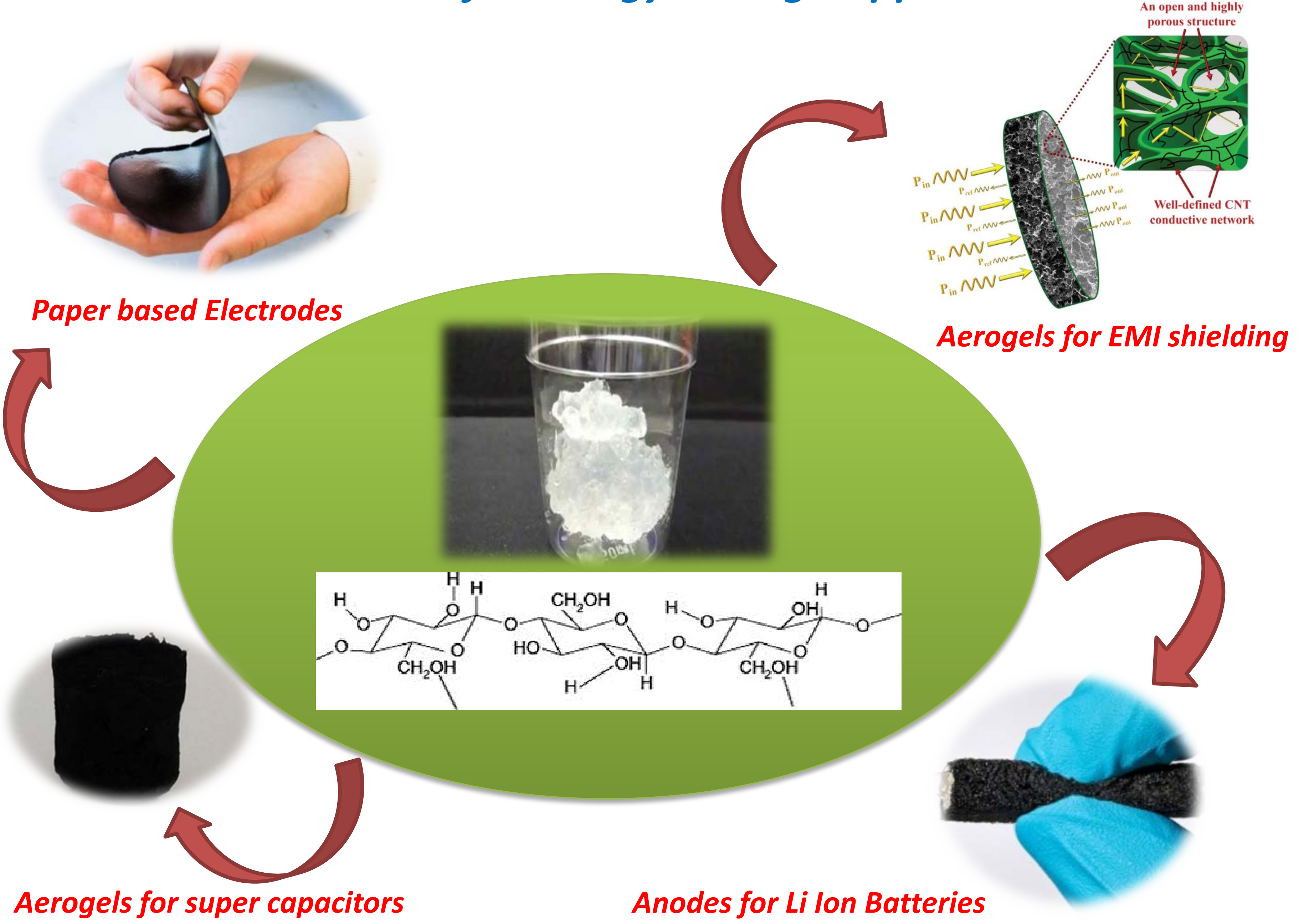






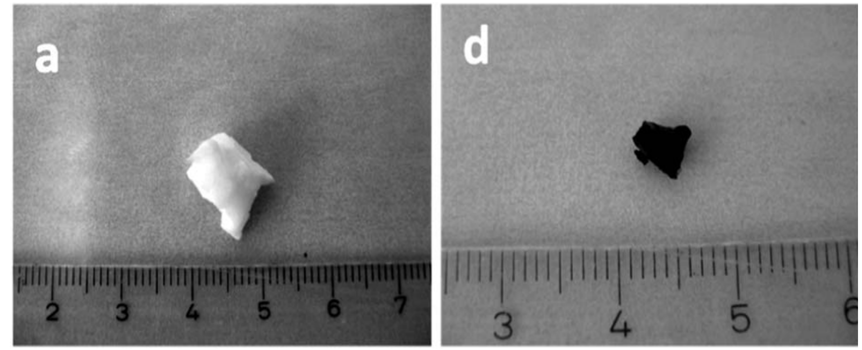
Thomas et al. RSC Advances (2016). **6**, 49138-49149

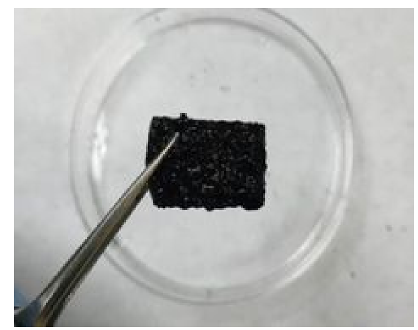
Nanocellulose for Energy Storage Applications

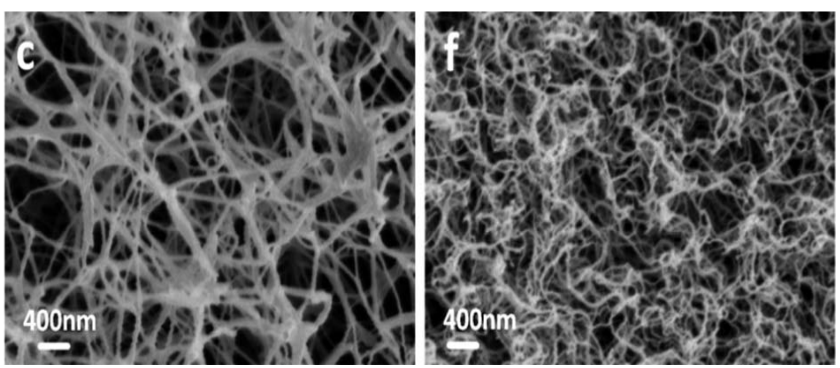


Nanocellulose Aerogels for Energy Storage Applications

- ***Liping Wang et al,*** synthesized carbon aerogels by pyrolysis of bacterial nanocellulose aerogels at 900°C. (Fig a, d)**.**
- Carbon aerogel hence prepared were used as anode materials for Li Ion batteries.
- SEM images (Fig c, f) confirms the high porous nature of the carbon aerogels.
- The high surface area and open pore structure offer a large electrode/electrolyte contact area, favorable for charge-transfer reaction

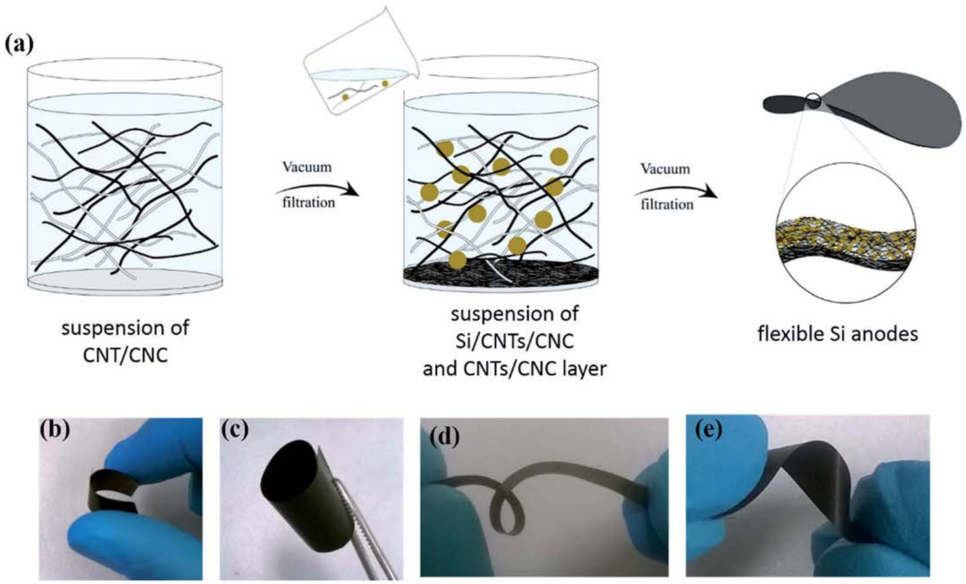






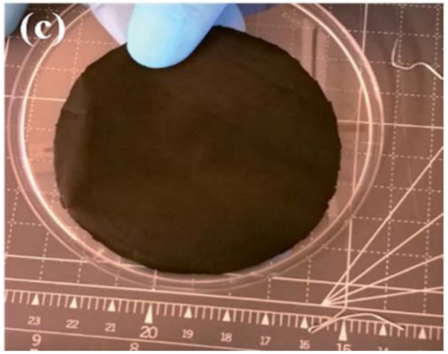
Liping Wang et al, RSC Adv., 2014, 4, 17549

Nanocellulose Paper for Energy Storage Applications



- ***Zhaohui Wang et al***, prepared a free standing, flexible & lightweight Si paper using *Cladophora* Nanocellulose and CNTs.
- Suspension of CNT & *Cladophora* Nanocellulose fibers (CNC) was first sonicated and vacuum filtered on a membrane.
- Si NPs, CNC & CNT was then vacuum filtered onto the first layer to make a silicon containing layer on the top of the supporting layer.

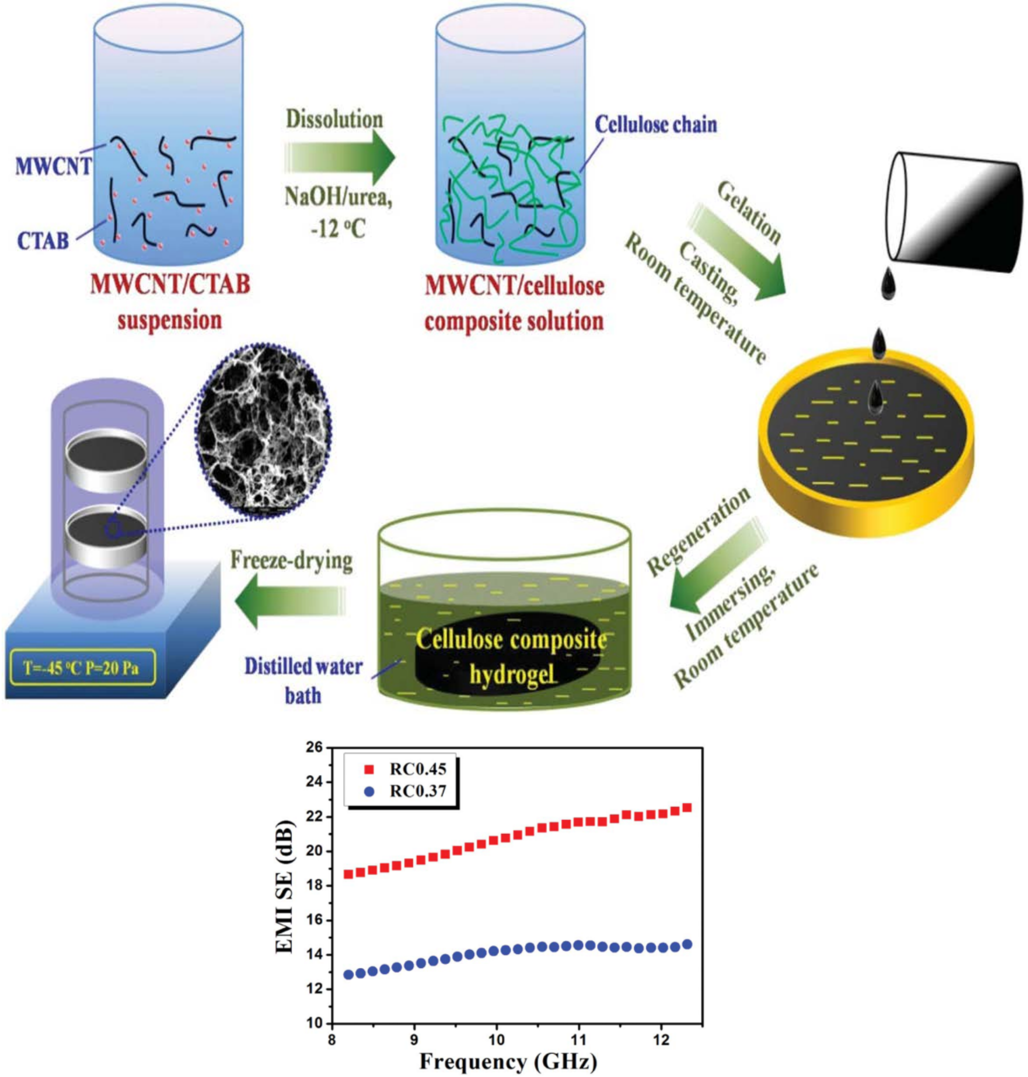
- The paper was ~30µ thick and can be used as electrodes for Li Ion batteries.
- The Si-based anodes thus demonstrated excellent mechanical flexibility and could be bent, rolled and twisted without any resulting loss of performance

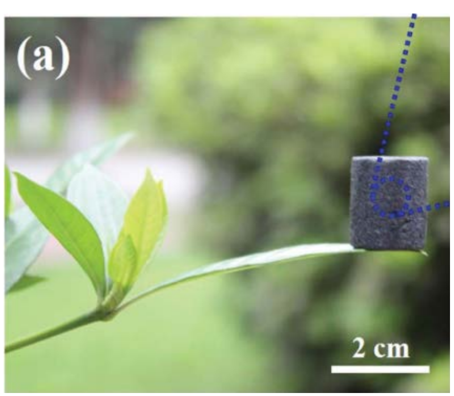


Zhaohui Wang et al , J. Mater. Chem. A, 2015,3,14109

Nanocellulose Aerogels for EMI Shielding Applications

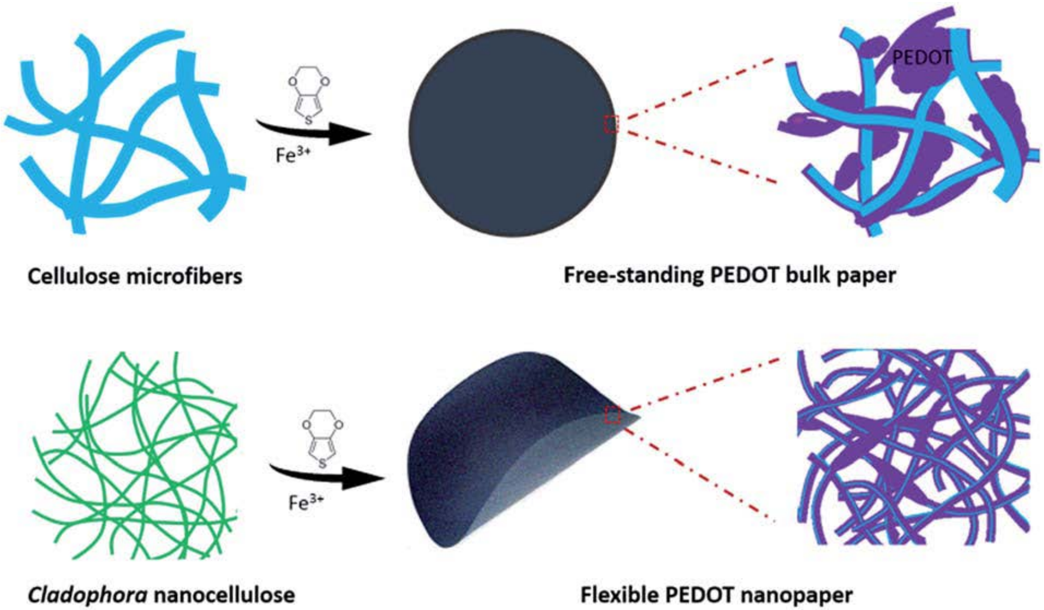
- ***Hua-Dong Huang et al***, first reported the use of nanocellulose-MWCNTs based conductive aerogels for EMI shielding applications.
- EMI shielding effectiveness of ~ 20 dB was achieved in X Band.
- Conductive CNT/cellulose aerogels exhibits low densities (0.095 g/cm3) and high porosities reaching 93.9%.

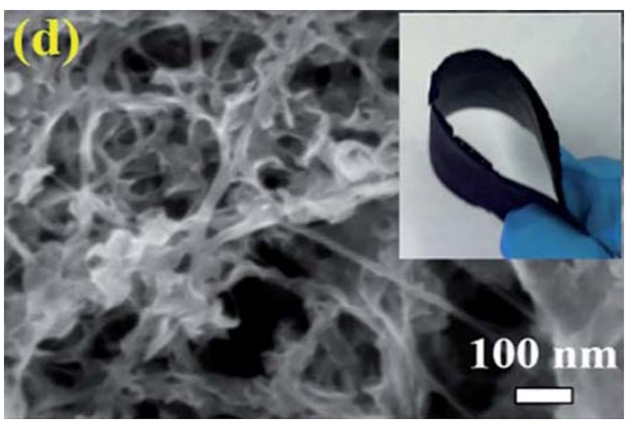




Hua-Dong Huang et al, J. Mater. Chem. A, 2015, 3, 4983

Nanocellulose paper as electrodes for supercapcitors



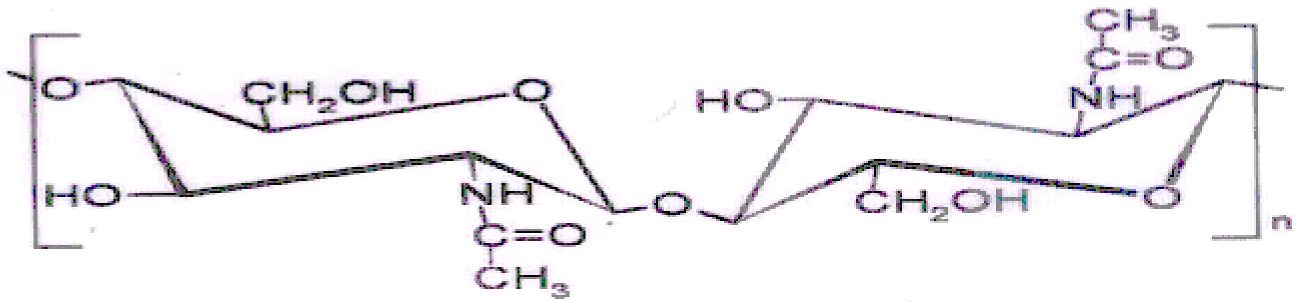


- ***Zhaohui Wang et al,*** prepared in-situ polymerized PEDOT-*Cladophora* nanocellulose paper by solution technique.
- The nanopaper exhibits large surface area (137 m^2 g^{-1}).
- Excellent cycling stability (93% capacity retention after 15,000 cycles)
- Has great potential for developing flexible energy storage devices.

Zhaohui Wang et al , J. Mater. Chem. A, 2016, 4, 1714

CHITIN NANO FIBERS AND WHISKERS

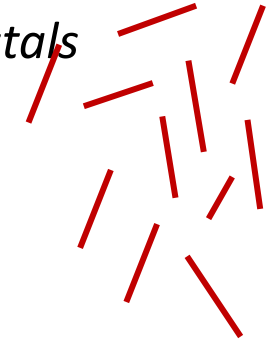
CHITIN STRUCTURAL POLYMER



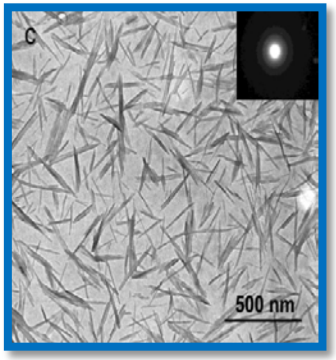
- High MW linear polymer of N-acetyl-D-glucosamine units linked by β-D(1-4) bonds
- Constitutes the structure of the external skeleton in shell fish and insects
- 10^{10}-10^{11} tons synthesized each year
- Main source: Shellfish canning industry waste (shrimp of crab shell contains = 8.33%)
- Native Chitin : Highly crystalline
- Forms microfibrillar arrangements embedded in a protein matrix (2.5 – 25nm)

Nanoforms of chitin

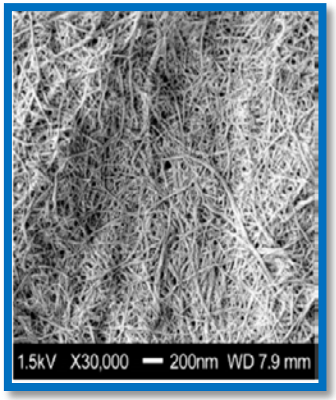
- *Mainly 3 types*
  - *Whiskers or Crystals*
  - *Fibers*



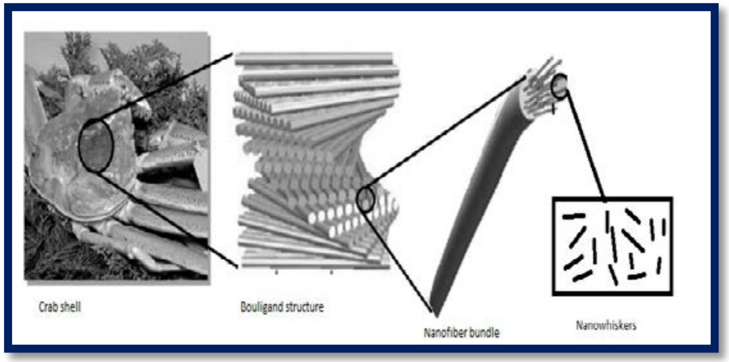
It has desired shape and size



Long length, no particular shape, nonwoven type



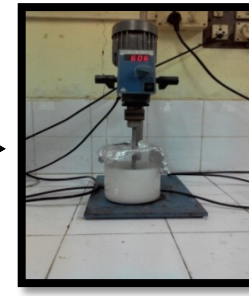
Extraction of nanochitin whiskers



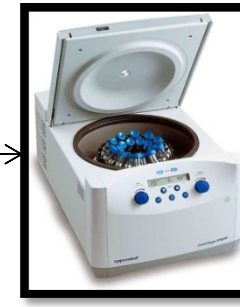
Nano whiskers and crystals of chitin obtained by strong acid hydrolysis.

Heated for 2Hr with Sodium hypochlorite in 1L water. Kept in 5%KOH solution for 72Hr

Bleached chitin



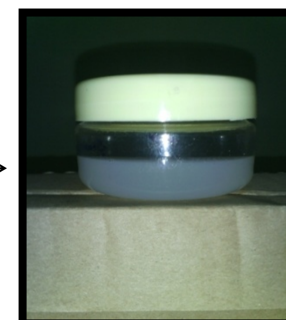
Hydrolyzed by Hydrochloric acid (2Hr under 80^0C and Stirring)



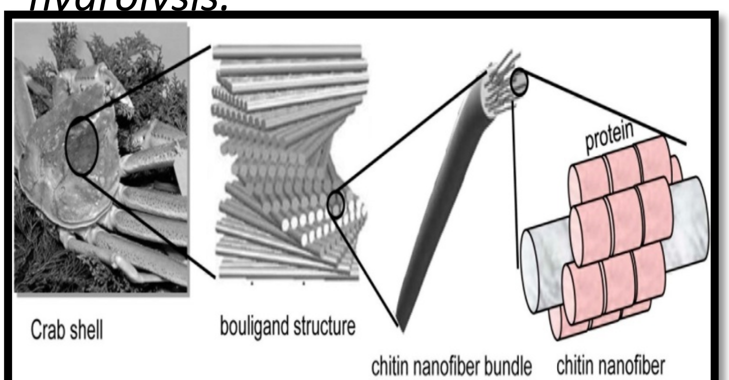
Centrifuged

Chitin dispersion

Dialyzed for 24Hr



Chitin whisker in solution



Nanofibers obtained by a series of chemical and mechanical treatment

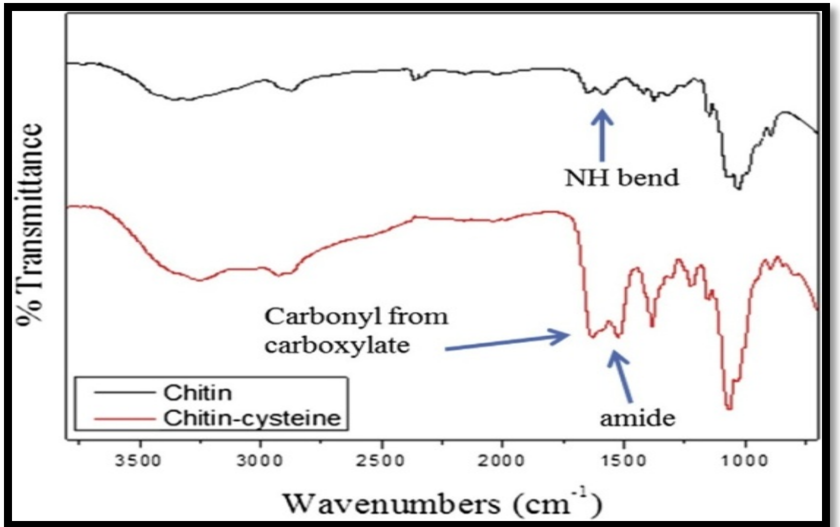
Application. Water purification

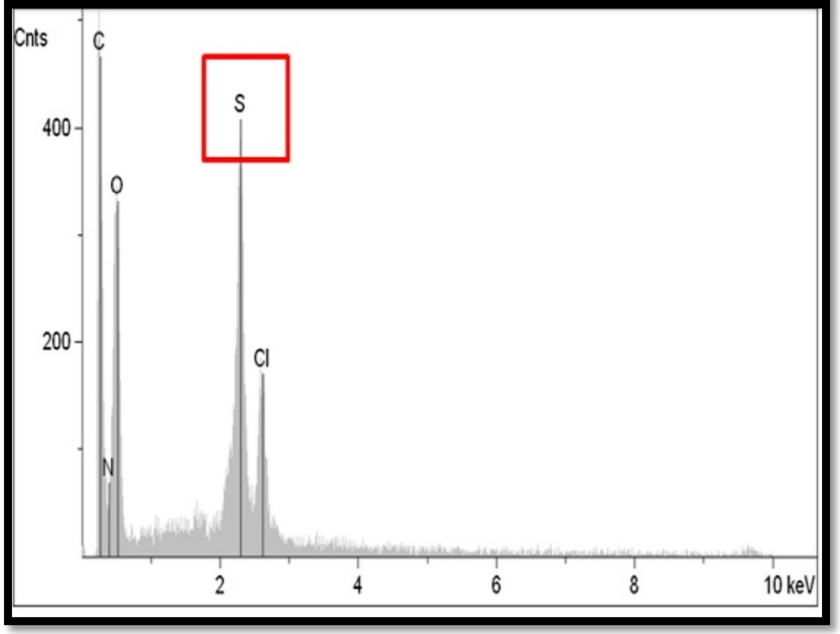
Thiol-functionalized chitin nanofibers for As (III) adsorption

- *Natural polysaccharide chitin nanofibers, prepared with a series of chemical and mechanical treatments,were used as an absorbent material for arsenic (As(III)) removal.*
- *In this study, grafting of cysteine was carried out to create adsorption sites for arsenic metal ion (AsO2) removal*

Characterization for thiol-functionalized chitin nanofibers

- *Fourier transform infrared (FT-IR) spectroscopy*
- *Energy dispersive spectroscopy (EDS).*





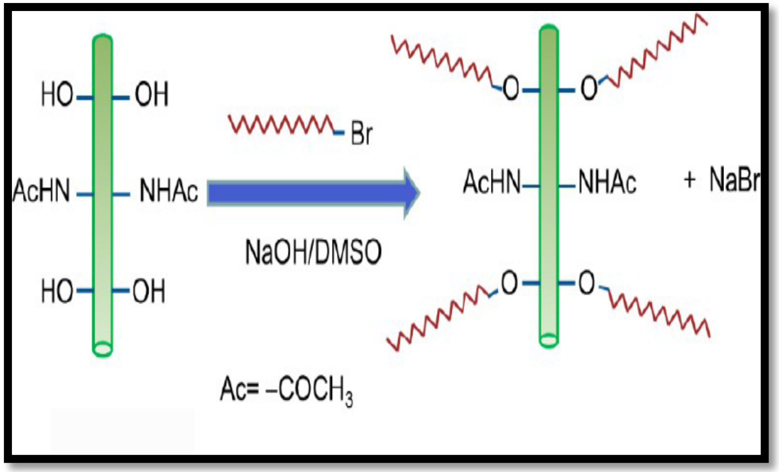
Rui Yang et. Al, Polymer, 60 (2015) 9 - 17

Hydrophobic Modification of Chitin Whisker and Its Potential Application in Structuring Oil

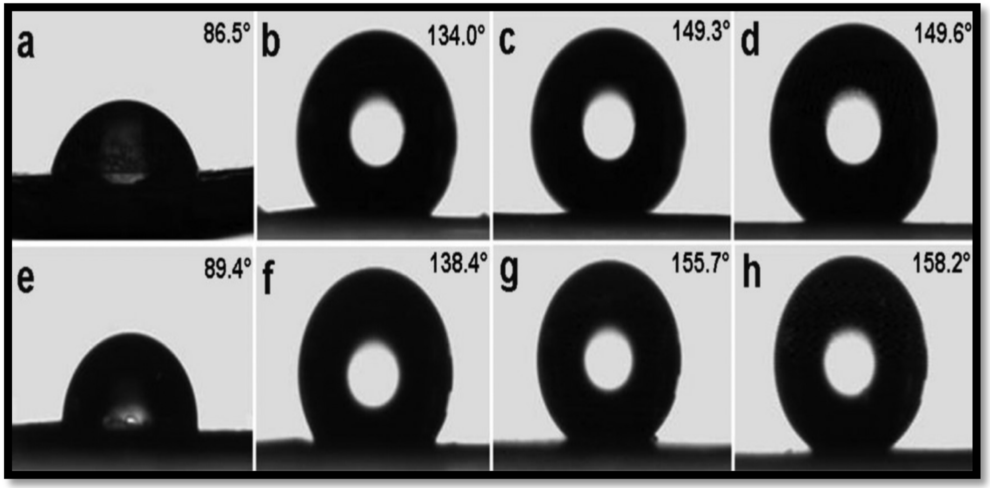
- *Recently, the demand for reducing the saturated or trans fatty acids in foodstuff has grown extensively, for health and nutritional considerations*
- *Natural polymers in the nanofibrils or nanocrystal form have attracted great interest due to their excellent biocompatibility, biodegradability, and mechanical reinforcement*
- *In this work, attempted to study the physical properties of hydrophobically modified chitin whiskers and evaluate their performance in oil thickening.*

Note: By changing the molar ratio of bromohexadecane to anhydroglucose unit (AGU) of chitin from 3:1, 6:1, and 12:1, corresponding samples were obtained, denoted as D3, D6, and D12, respectively.

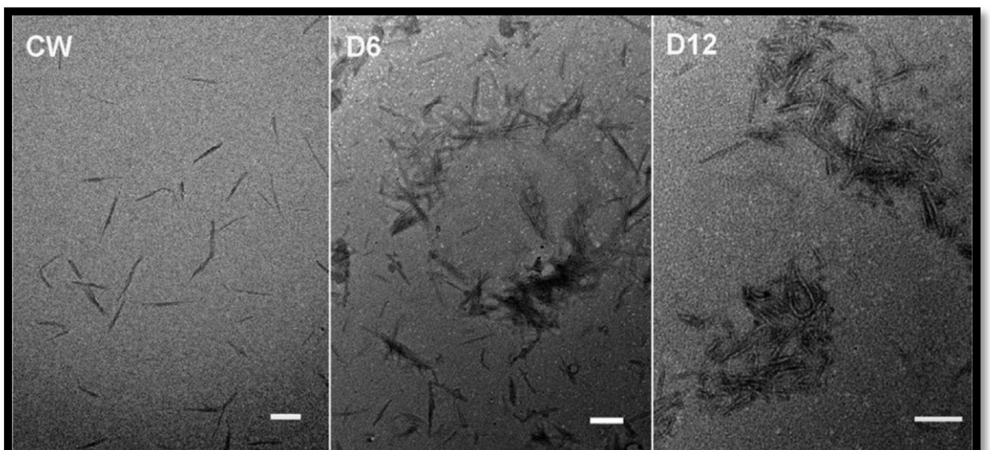
- *chitin whiskers were modified with long chain alkyl group reacting with bromohexadecane*



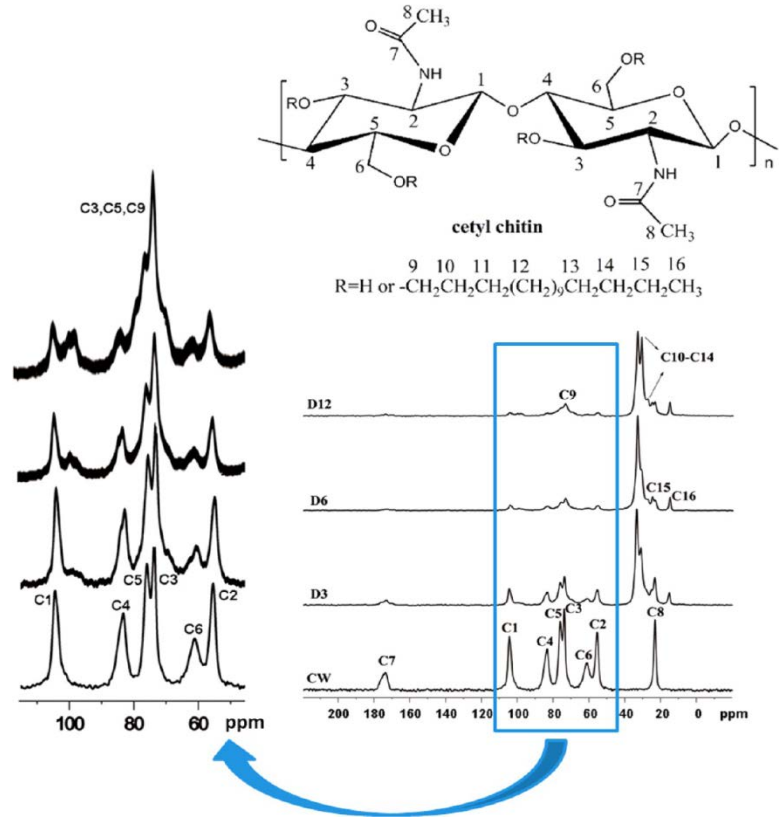
Huang et. al, Langmuir 2015, 31, 1641−1648



Compared to chitin whisker, the water contact angles of the modified whiskers were greatly increased



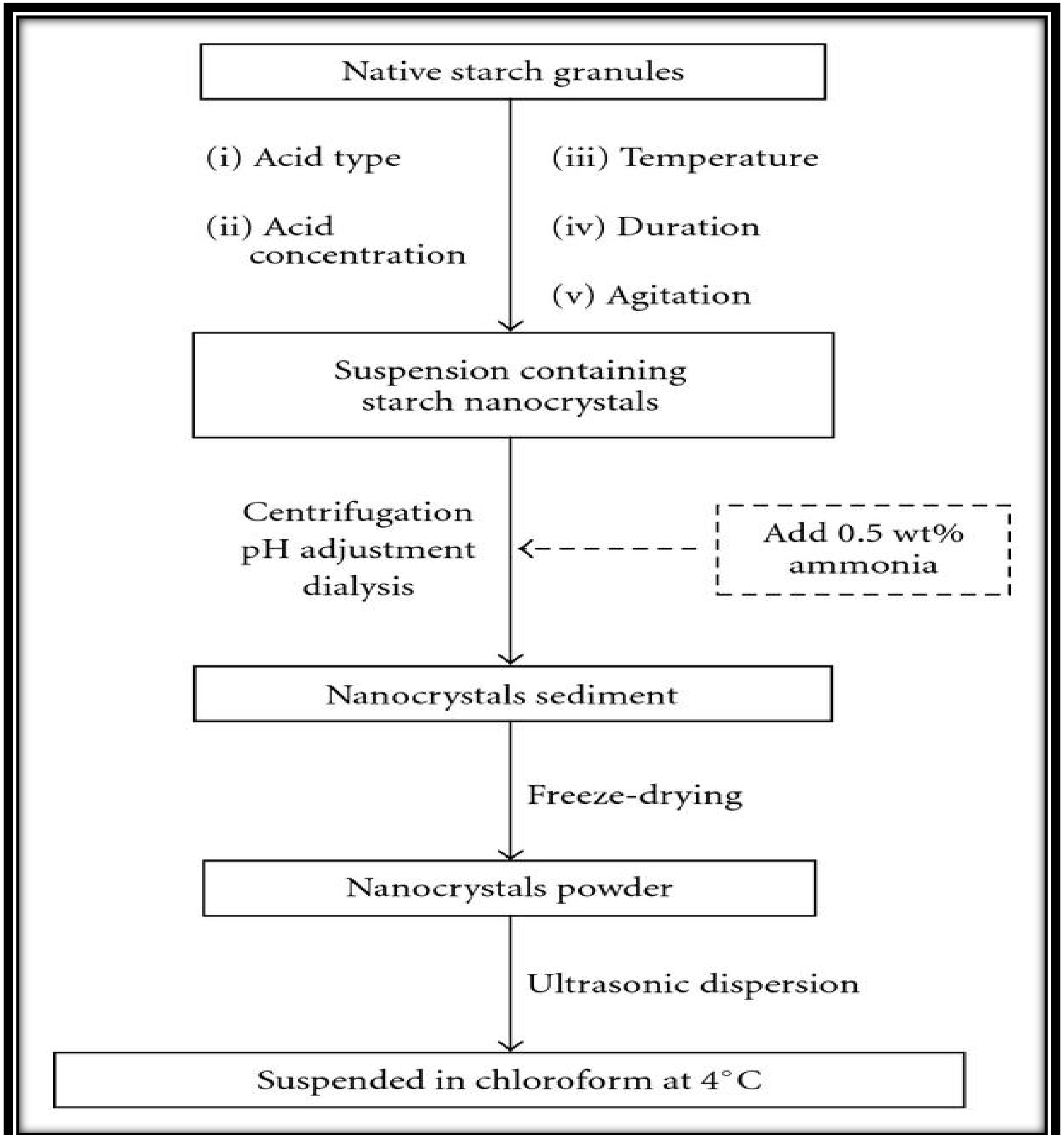
TEM images of chitin whisker (CW) and modified chitin whisker (D6 and D12) in water. Scale bars are 200 nm



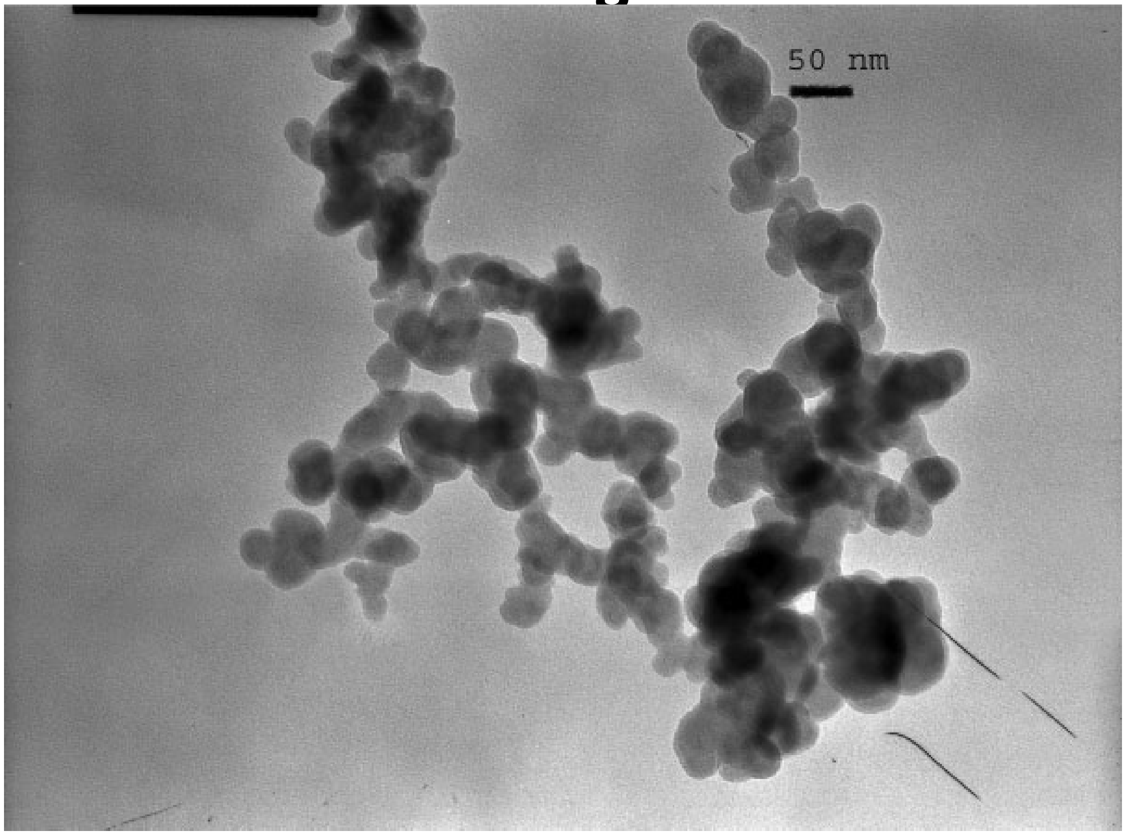
^{13}C NMR CP/MAS solid-state NMR spectra of chitin whisker (CW) and modified chitin whisker (D3, D6, and D12).

Sources of starch

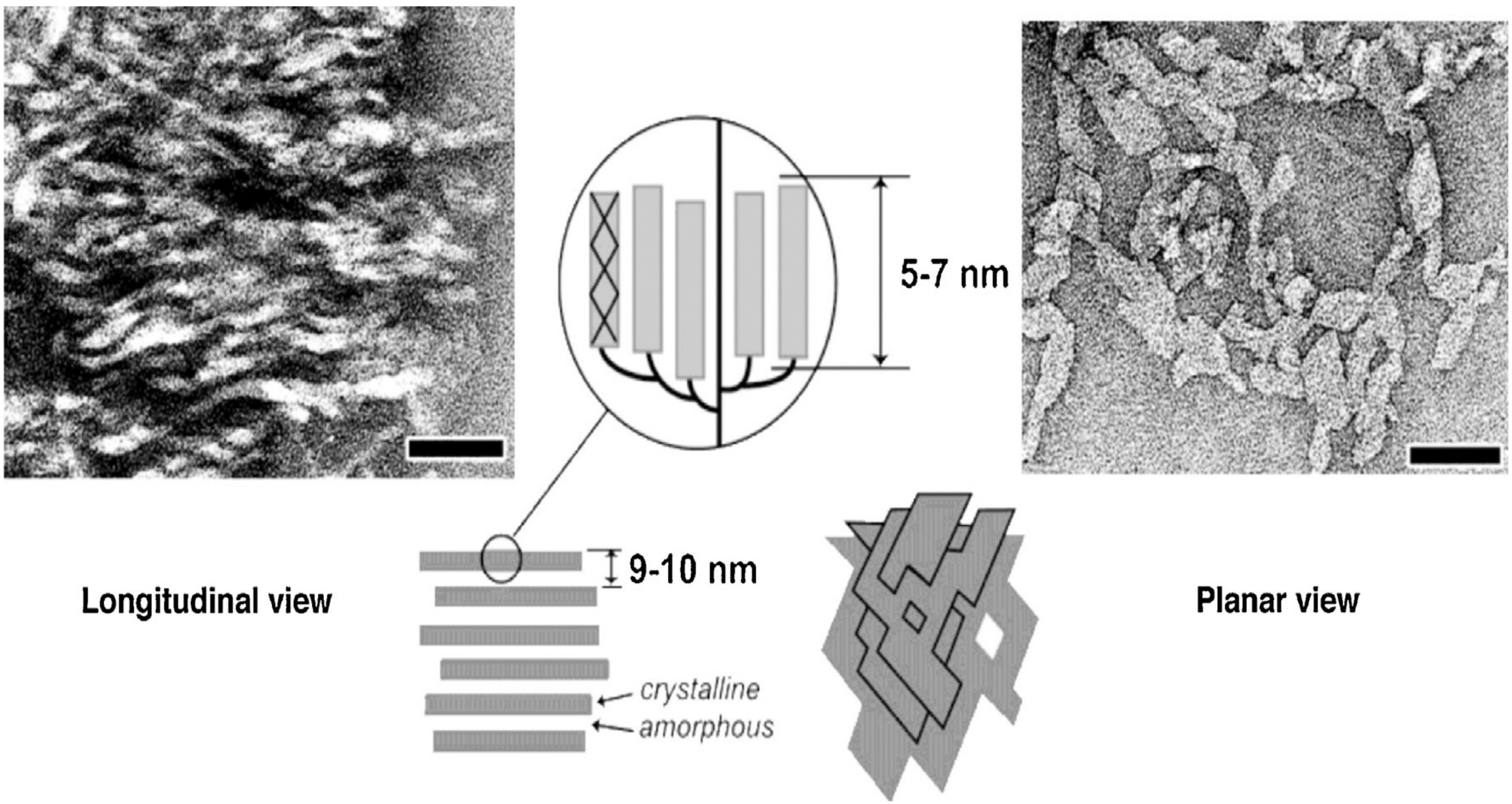
Cassava


Native starch granules
(i) Acid type
(ii) Acid concentration
(iii) Temperature
(iv) Duration
(v) Agitation
Suspension containing starch nanocrystals
Centrifugation
pH adjustment
dialysis
Add 0.5 wt% ammonia
Nanocrystals sediment
Freeze-drying
Nanocrystals powder
Ultrasonic dispersion
Suspended in chloroform at 4°C

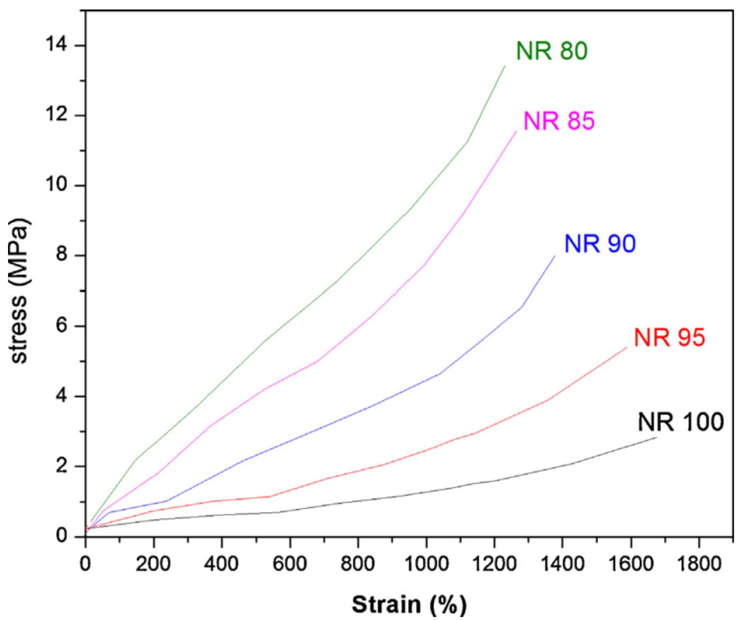
Starch nanoparticles from starch waste from agro farms

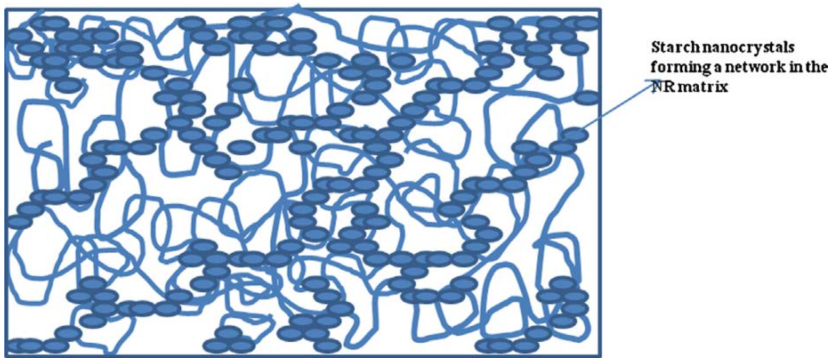


TEM of waxy maize-starch nanocrystals (Dufresne et al.)



Putaux JL, Molina-Boisseau S, Momaur T, Dufresne A. Platelet nanocrystals resulting from the disruption of waxy maizestarch granules by acid hydrolysis. Biomacromolecules 2003;4:





Potato starch nanocrystals appeared to be an effective reinforcing agent for natural rubber.

Preparation and characterization of potato starch nanocrystal reinforced natural rubber nanocomposites, International Journal of Biological Macromolecules 67 (2014) 147–153 K.R. Rajishaa, H.J. Mariab, L.A. Pothanc, Zakiah Ahmadd, S. Thomas

Conclusions

Agrowaste could be transformed into advanced functional green nanomaterials.

- **Agrowaste: Cellulose nanofibers and whiskers.**

  Areas of application: reinforcing nano filler, water purification, wound healing, energy storage, EMI Shielding.

- **Sea food waste: Chitin nanofibers and whiskers.**

  Areas of application: reinforcing filler, water purification, tissue engineering, heavy metal removal.

- **Starch waste: Starch nanofibers and crystals.**

  Areas of application: reinforcing filler, packaging

Thank you for your Attention

ZeroWaste
Making it Happen

Acknowledgements

Co-workers: Laly, Visak, Bibin,Eldhow, Deepu, Srerag, Rajisha

Government Funding

DST, Nanomission (Prof. CNR Rao)

ISRO, CSIR, DBT, AICTE, UGC, DRDO, DIT, TWAS,BRNS

Industrial Funding

Surface treat, Czech

MRF Tires, Apollo Tires, India

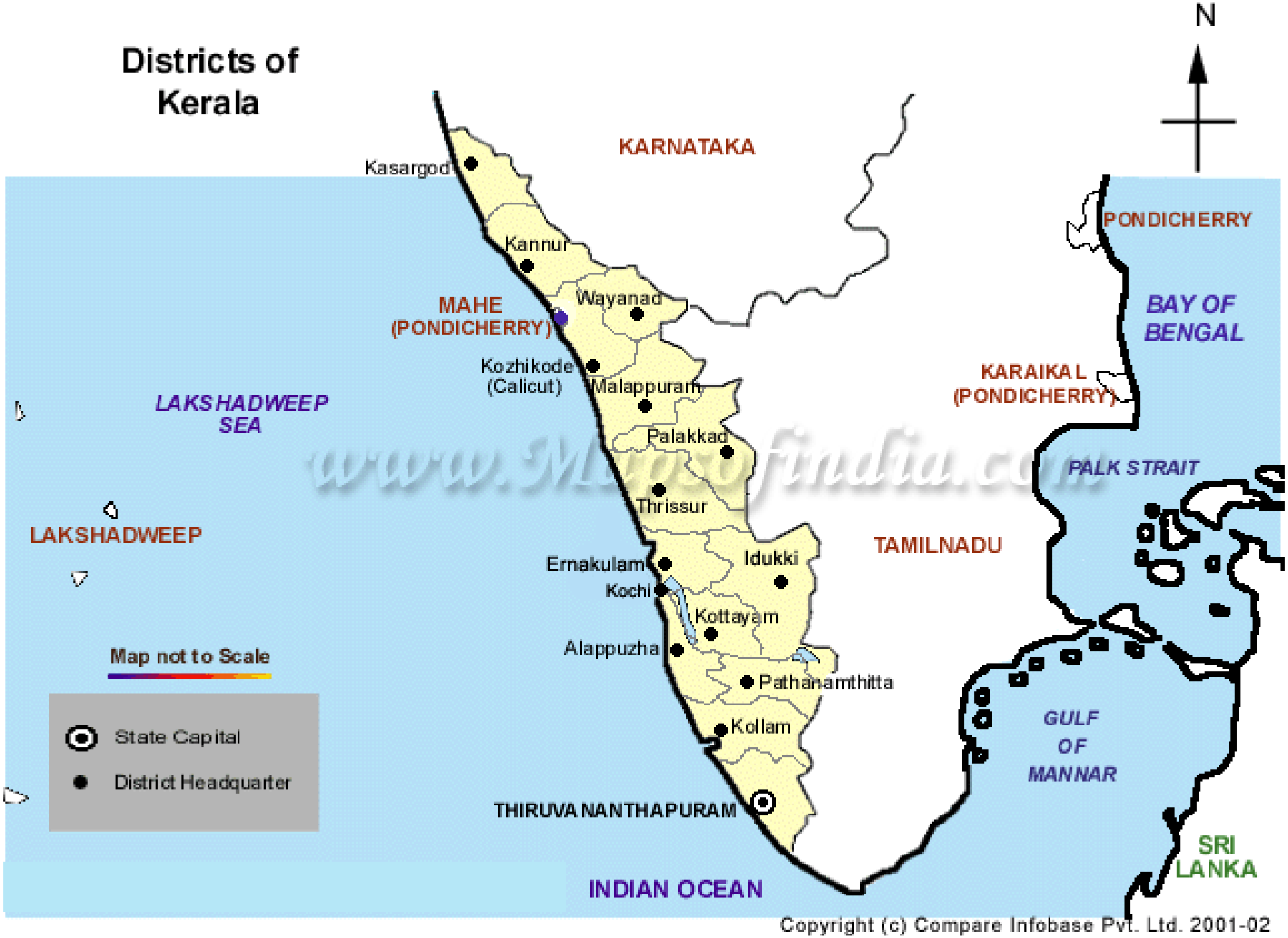
Collaborators

- Prof. Plasquini, Brazil
- Prof. A. Mathew, Sweden,
- Prof. Yves Grohens, Uni of South Brittany, France
- Prof. Jose M Kenny, Uni of Perugia, Italy
- Prof.Ange Nzihou, Albi School of Mines, France

Thank you for Your Attention

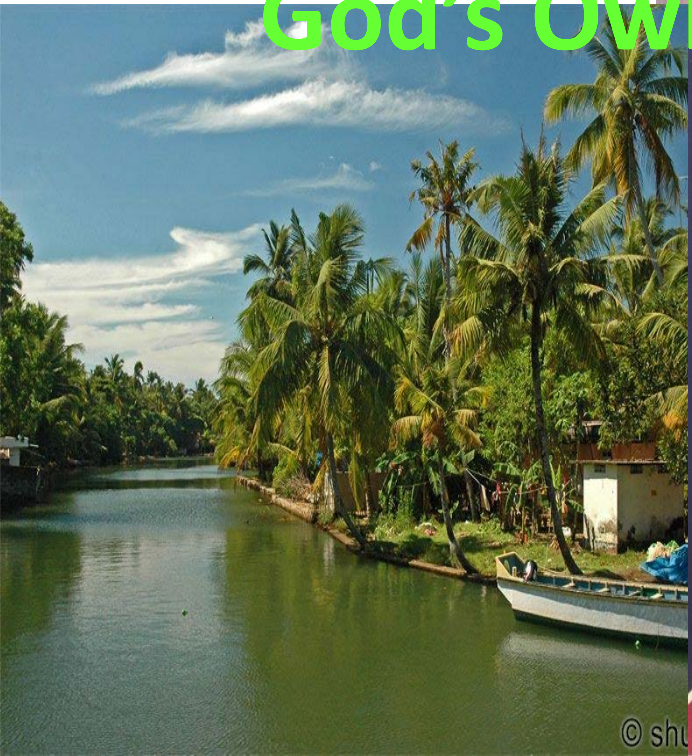
Nano Group

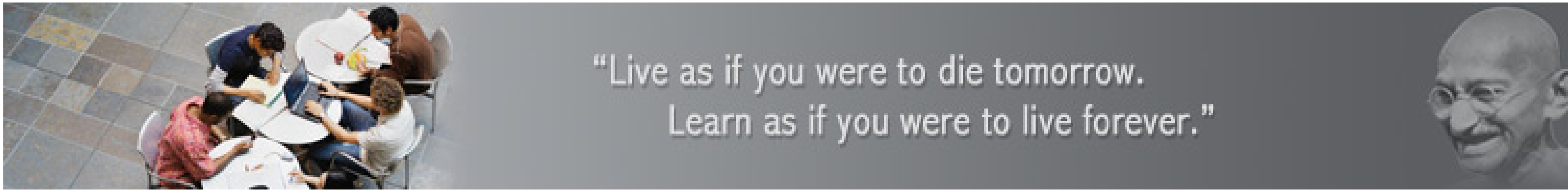

LOCATION OF KERALA
IN INDIA
N
CHINA
PAKISTAN
JAMMU & KASHMIR
UTTARANCHAL
DELHI
NEPAL
BHUTAN
Patna
JHARKHAND
Calcutta
CHHATTISGARH
Mumbai
(Bombay)
ARABIAN SEA
BAY OF BENGAL
KARNATAKA
KERALA
Thiruvananthapuram
Map not to Scale
Copyright (c) Compare Infobase Pvt. Ltd. 2001-02



Districts of Kerala
N
KARNATAKA
Kasargod
Kannur
Wayanad
MAHE (PONDICHERRY)
Kozhikode (Calicut)
Malappuram
Palakkad
Thrissur
Ernakulam
Kochi
Idukki
Kottayam
Alappuzha
Pathanamthitta
Kollam
THIRUVANANTHAPURAM
PONDICHERRY
BAY OF BENGAL
KARAIKAL (PONDICHERRY)
PALK STRAIT
TAMILNADU
GULF OF MANNAR
SRI LANKA
INDIAN OCEAN
LAKSHADWEEP SEA
LAKSHADWEEP
Map not to Scale
State Capital
District Headquarter
www.Mapsofindia.com
Copyright (c) Compare Infobase Pvt. Ltd. 2001-02

God’s Own Country Kerala





MAHATMA GANDHI UNIVERSITY
KOTTAYAM, KERALA, INDIA

-Polymer , Organic, Inorganic, Physical and Technology


Welcome to
INTERNATIONAL CONFERENCE ON POLYMER PROCESSING AND CHARACTERISATION
Venue :MAHATMA GANDHI UNIVRSITY CAMPUS. Kottayam, KERALA,INDIA
Date: December 9-11, 2016
Website: www.polymerprocessing@macromol.in