Structure and functionalities of Cellulose nanofiber nonwoven sheet

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ASAHI KASEI CORPORATION

Contents

- Introduction of **CNF-*nw*** of Asahi Kasei
- Example of membrane application of **CNF-*nw***
- Example of FRP application of **CNF-*nw***
- Conclusion

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ASAHI KASEI CORPORATION

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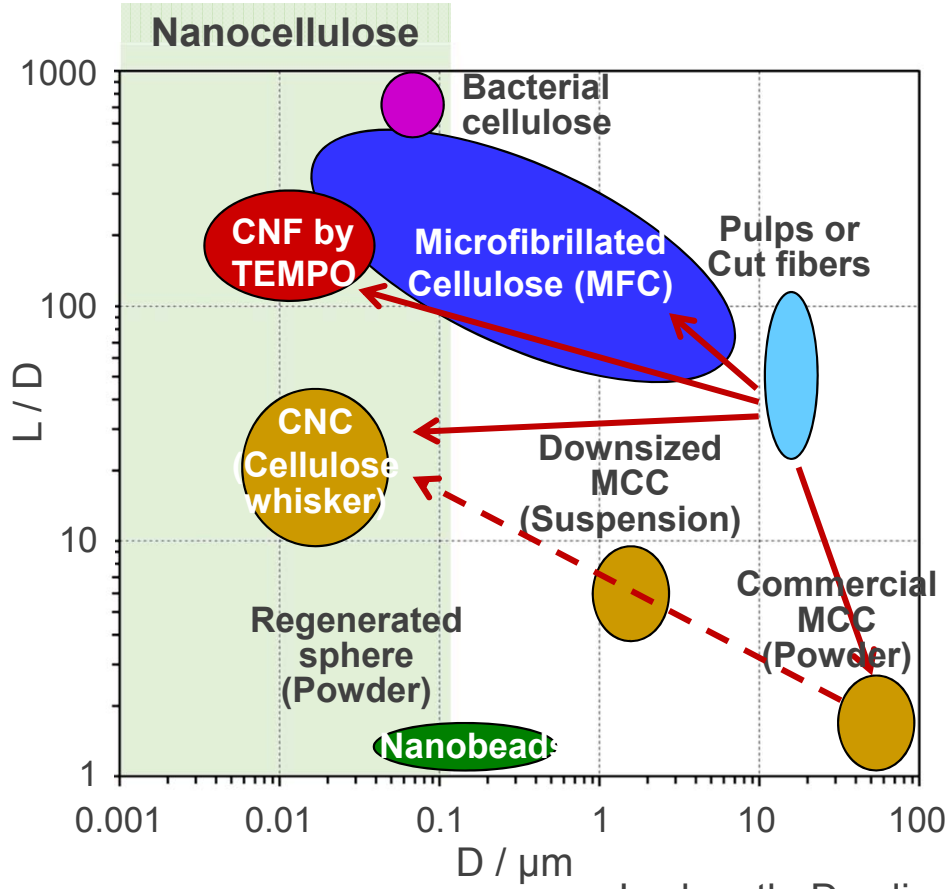
Classification of Nanocellulose

Nanocellulose : fiber diameter is on the nano scale

■ Manufacturing process

- Mechanical downsizing
- Chemical downsizing
- Cultivation
- Acid hydrolysis
- Phase separation

Size of nanocellulose depends on the process



L : length, D : diameter

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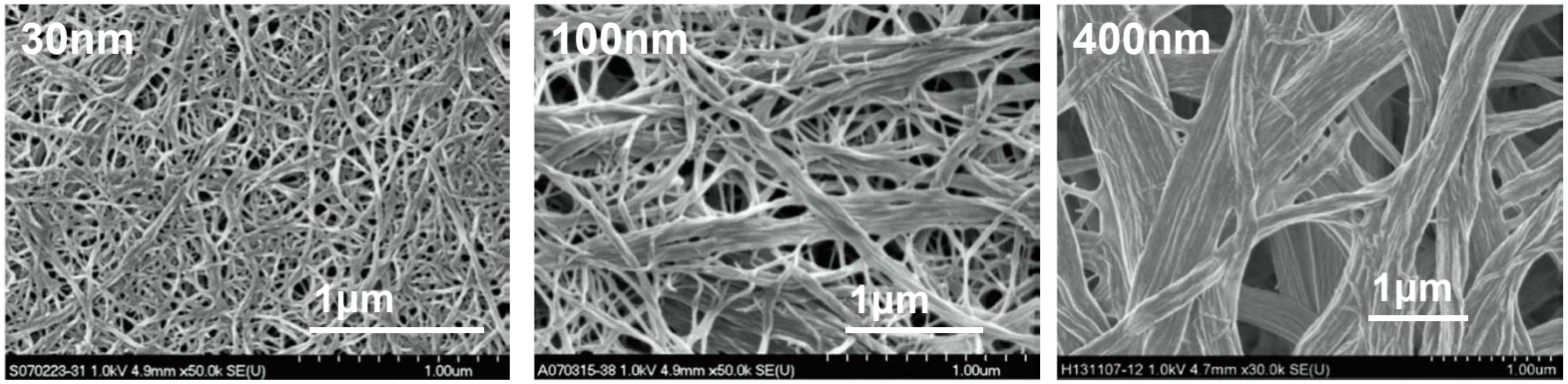
NanoLeaf® (developing stage) of Asahi Kasei

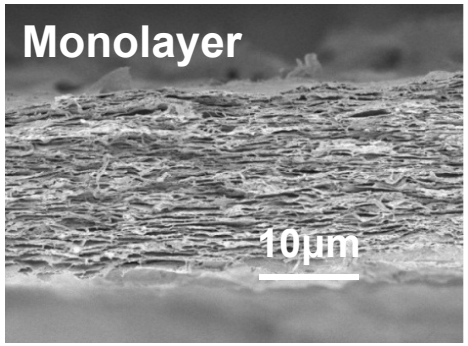
Sheet material including the porous CNF nonwoven layer

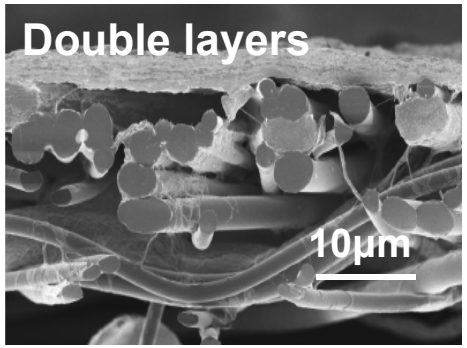
- Various fiber diameters



Small ⟷ *pore size* ⟷ *Large*

- Monolayer / Double layers





CNF layer

Substrate layer

- Paper, nonwovens
- Cellulose, Nylon, PET etc.

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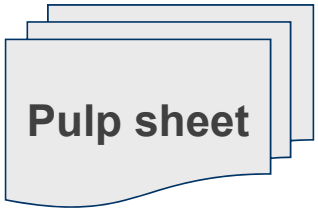
Manufacturing process of CNF-*nw*

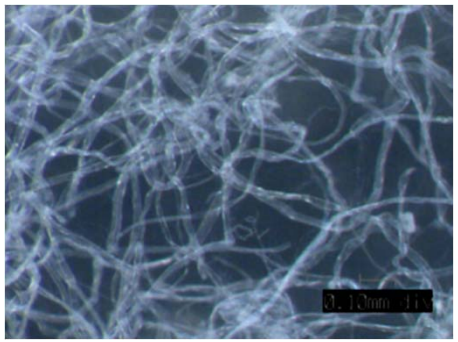


Downsizing to nanofiber

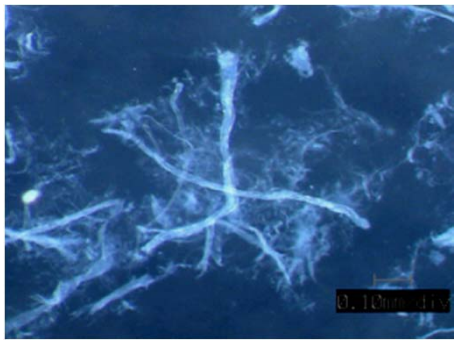
Sheet Making

CNF-*nw*

Downsizing process



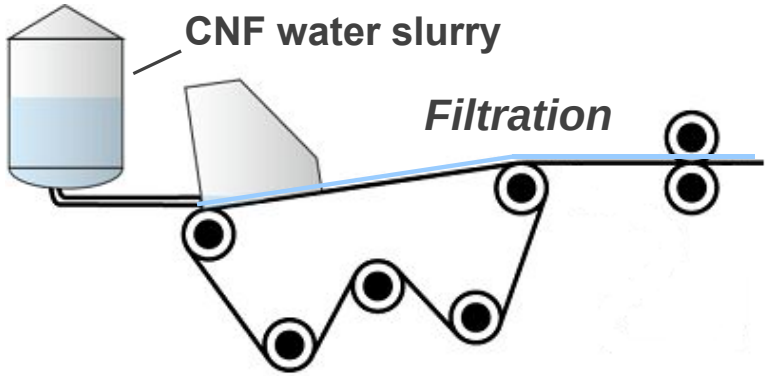
Pulp fiber



Fibrillated fiber

Nanofiber

Sheet making process



Drying process

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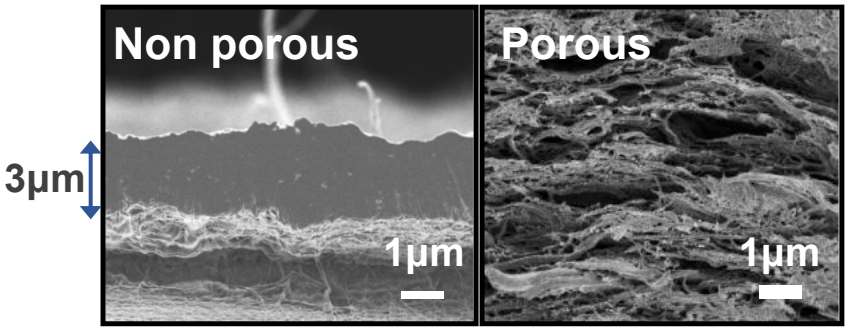
Four characteristic features of CNF-*nw*

1. Thickness range

- CNF layer thickness : 3 ~ 80 μm
- Basis weight : 2 ~ 20 g/m^2



2. Pore size control

- Porosity : 30 ~ 85%
- Surface area : ~ 100 m^2/g

3. Surface modification

- High wet strength sheet
- Hydrophobic sheet

4. High thermal stability

- Low CTE : 5 ~ 10 ppm/℃
- Keeping the thermal mechanical properties up to high temperature (~ 200 ℃)

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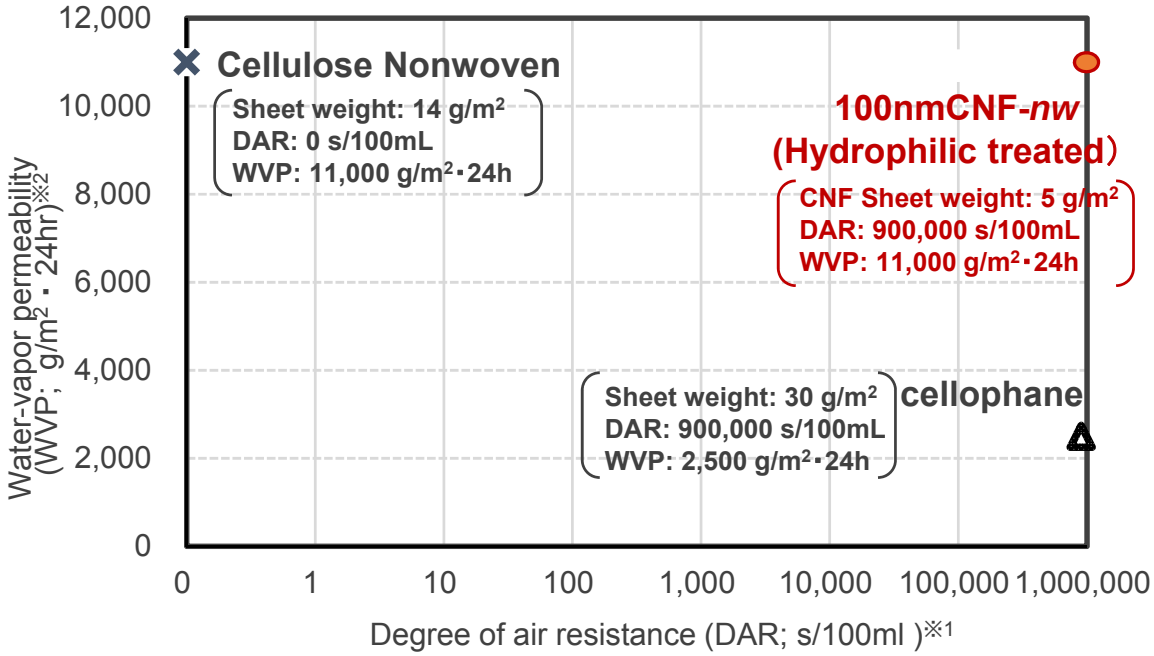
Example of membrane application

Ultra high water vapor permeable membrane



※1 Estimated by JIS P 8117 method
※2 Estimated by JIS L 1099 (A-1) method at 40℃, 90%RH

Possible to design ultra high water vapor permeble membrane within a higher air resistance

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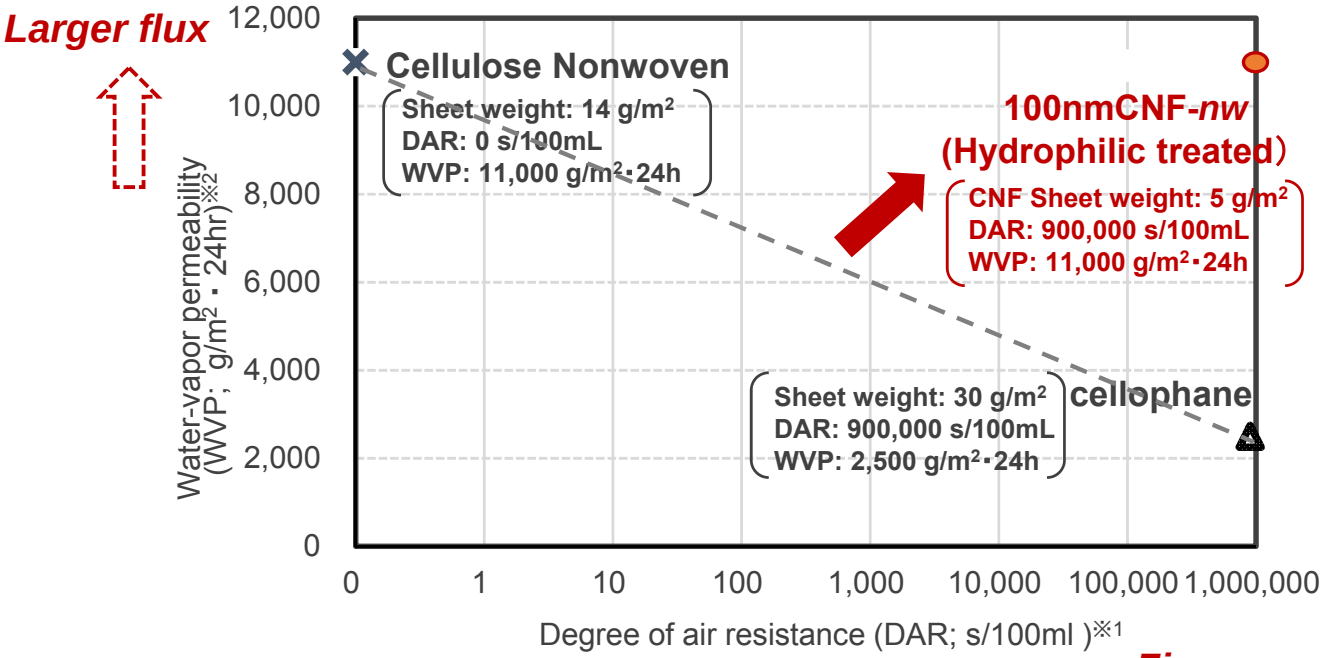
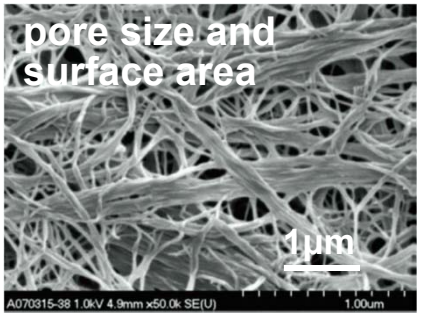
Example of membrane application

Ultra high water vapor permeable membrane





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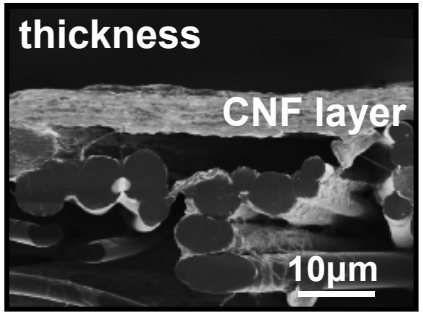

Finer separation with smaller pore size

Properties as a membrane are designable by pore size, surface area, and thickness of CNF-*nw*

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Control of structural factor

1. Thickness range

- CNF layer thickness : 3 ~ 80 μm
- Basis weight : 2 ~ 20 g/m^2

2. Pore size control

- Porosity : 30 ~ 85%
- Surface area : ~ 100 m^2/g

3. Surface modification

- High wet strength sheet
- Hydrophobic sheet

Merits

- Down to the extreme thinness for the lower pressure resistance
- Use as a membrane with wide separation range
- Addition of functionality such as water resistant property

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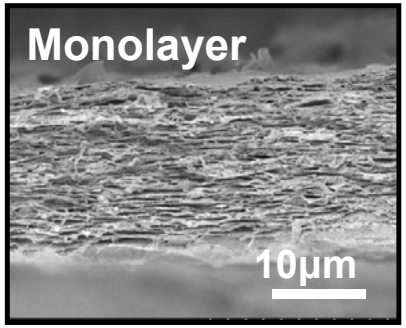
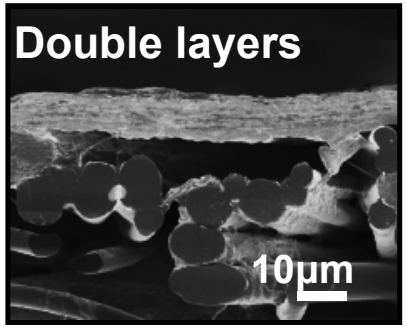
Control of thickness

”CNF layer” can be as thin as possible





CNF layer
(down to extreme thinness)

Substrate
- Paper, nonwovens
- Cellulose, Nylon, PET etc.

Thickness of CNF layer: 10 μm~ ----> 3 μm~

Substrate reinforces the total sheet strength

The merits of a thin CNF nonwoven :

- Lower pressure resistance of a filter when it is used as a membrane
- Lower electric resistance of a battery when it is used as a separator

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Control of pore size

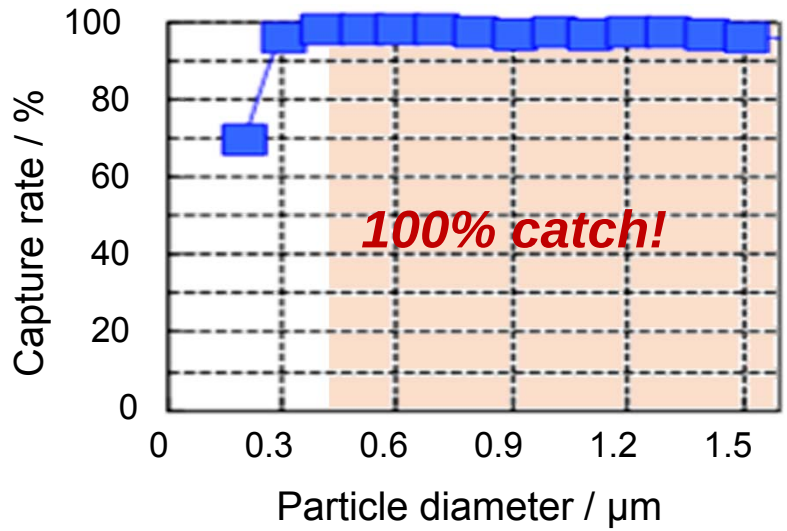
Pore diameter can be controlled by fiber diameter

Fiber diameter vs. Pore diameter

Ave. fiber diameter	Ave. pore diameter**	Max. pore diameter**
30 nm	0.06 μm	0.09 μm
100 nm	0.15 μm	0.33 μm
400 nm	0.70 μm	1.90 μm

* Basis weight : 10g/m^2
** Measured by permporometry testing

PSt particles capture test of 100nmCNF-*nw* (10g/m^2)



100nmCNF-*nw* can catch 100% PSt particles with a diameter over 0.4μm

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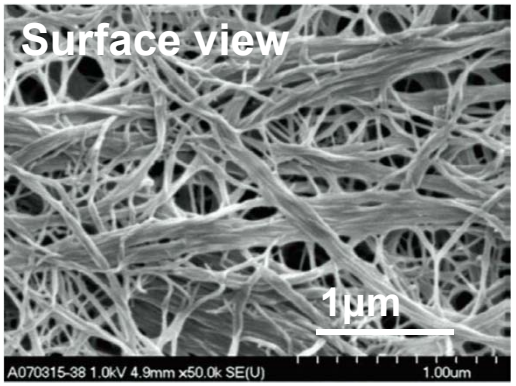
Control of pore size

Basis weight controls average pore diameter and the distribution

Basis weight (g/m^2)	Ave. diameter	Max. diameter	Distribution (S.D.)
5	0.24 μm	0.61 μm	0.0257
10	0.15 μm	0.33 μm	0.0034
20	0.11 μm	0.25 μm	0.0022

SEM images of 100nm CNF-*nw* ($10g/m^2$)



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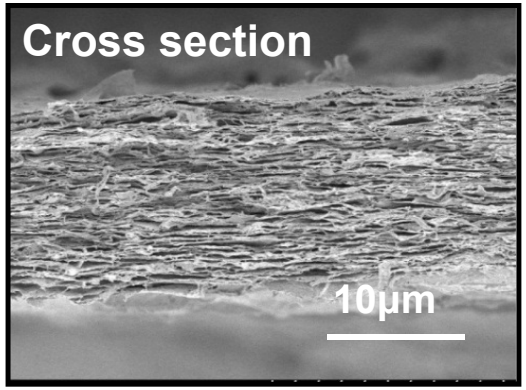

Decrease of pore diameter and distribution (averaging)

Ununiformed pore size

Stacking of hudreds of CNF network layers

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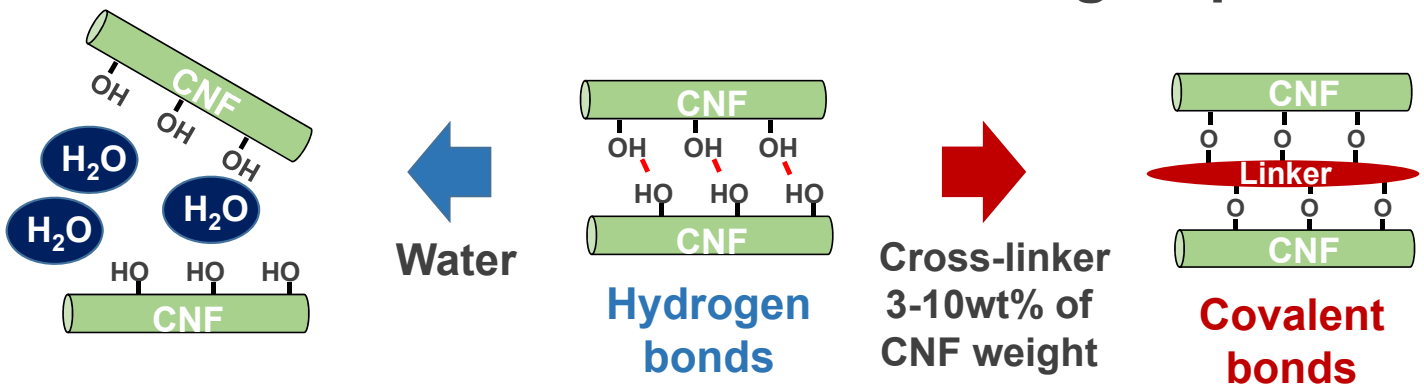
Addition of water resistance property

Various functions based on the surface OH group modification

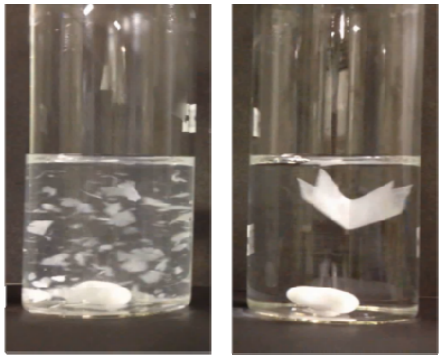


High tensile strength even in water

Water resistance treatment

	Tensile strength (kg/15mm)	
	Dry	Wet
Before	0.9	0.0
After	1.3	1.0

Before After



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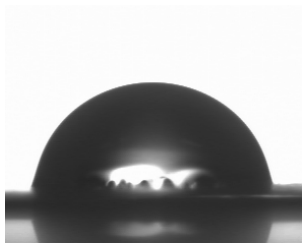
Addition of surface active property

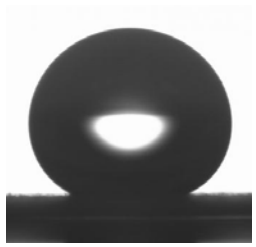
Various functions based on the surface OH group modification

Hydrophobic CNF-*nw*

Low contact angle **High contact angle**

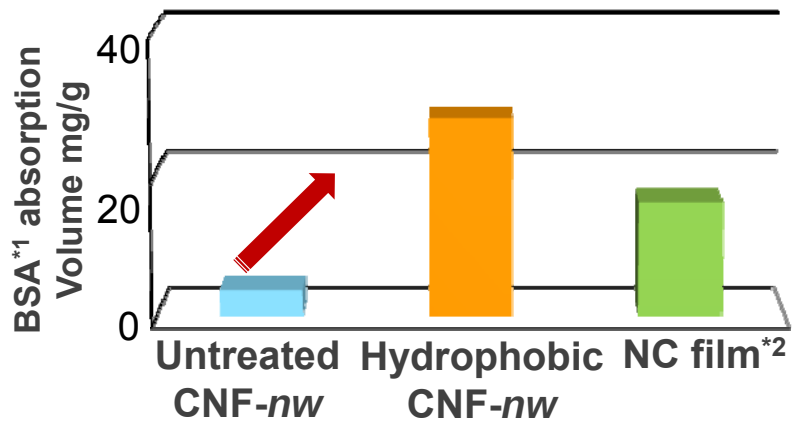


Before



After

Protein absorption of hydrophobic CNF-*nw*



*1 BSA: Bovine Serum Albumin
*2 Nitrocellulose film

Surface modification will further open new applications

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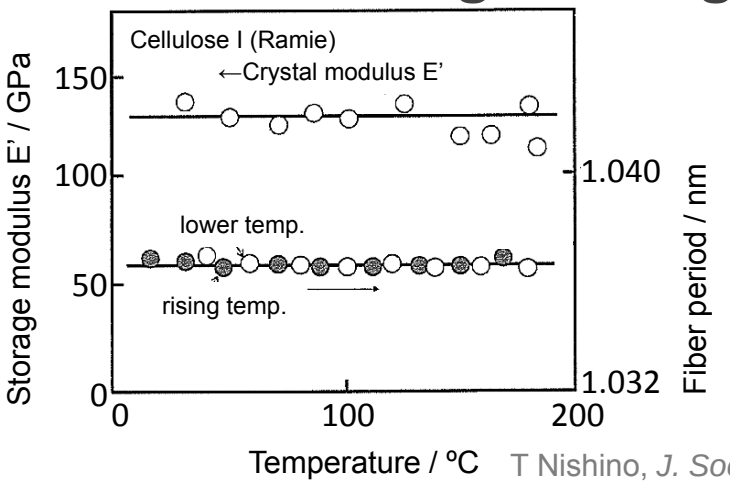
Principle of high thermal stability

Retention of high storage modulus and low CTE up to 200℃



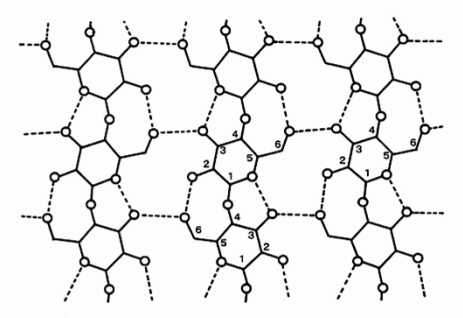
T Nishino, *J. Soc. Mater. Sci.*, 2008, 57, 97

Keeping high modulus and the value of fiber period up to 200℃

⬇

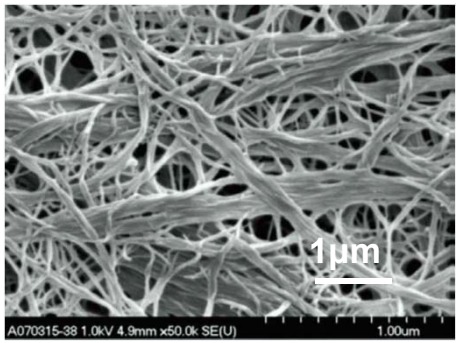
Cellulose crystal has high thermal stability

Hydrogen bonds of intra- and inter-molecular chains



Crystallinity

Hydrogen bonds formed between interface of cellulose fibers



Fiber diameter

or

Nano networks size

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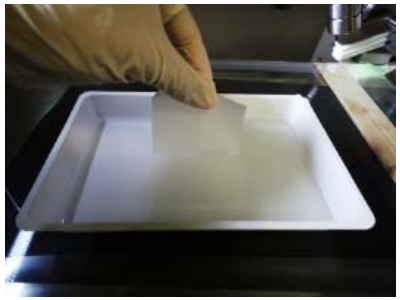
Preparation of FRP film by using CNF-*nw*

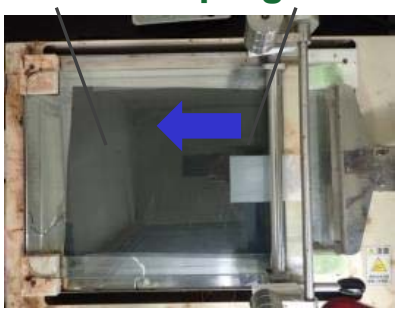
・**FRP film with a core material** (CNF-*nw*, cellulose nonwoven, glass cloth)

Impregnation → *Drying* → Prepreg → *Thermal cure* → FRP film

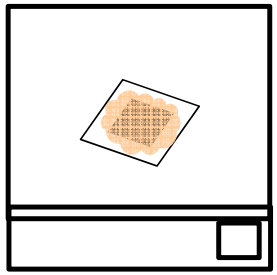
Release sheet Impregnated CNF-*nw*



Impregnation of epoxy resin into sheet



Squeezing out excess resin by bar-coater



Drying

Thermal vacuum press

Pealing off the FRP film

・**Composite film with a filler** (CNF, silica particles)

Mixing → *Forming* → composite film

Filler in suspension and epoxy resin

Film shape

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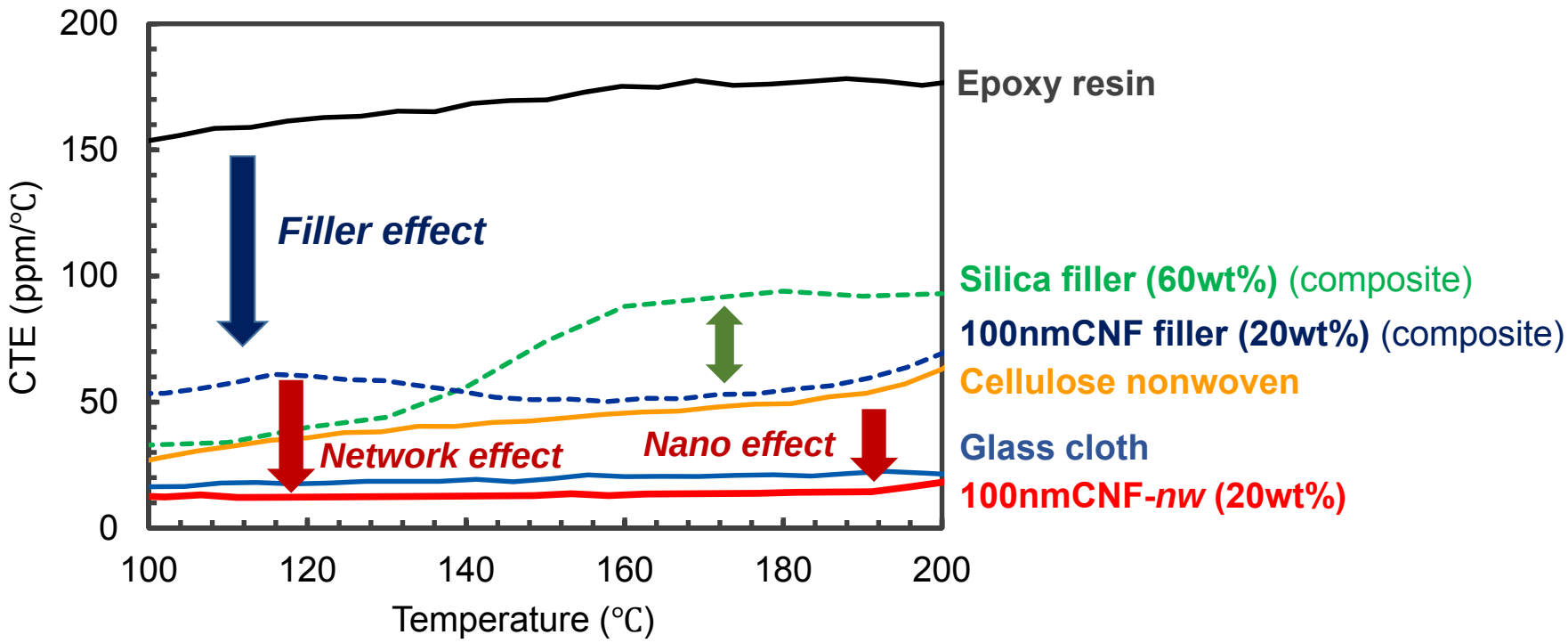
Low CTE of FRP film by using CNF-*nw*

Coefficient of Thermal Expansion (CTE) of FRP or composite films



"Cellulose + Nano + Network" are key points for low CTE

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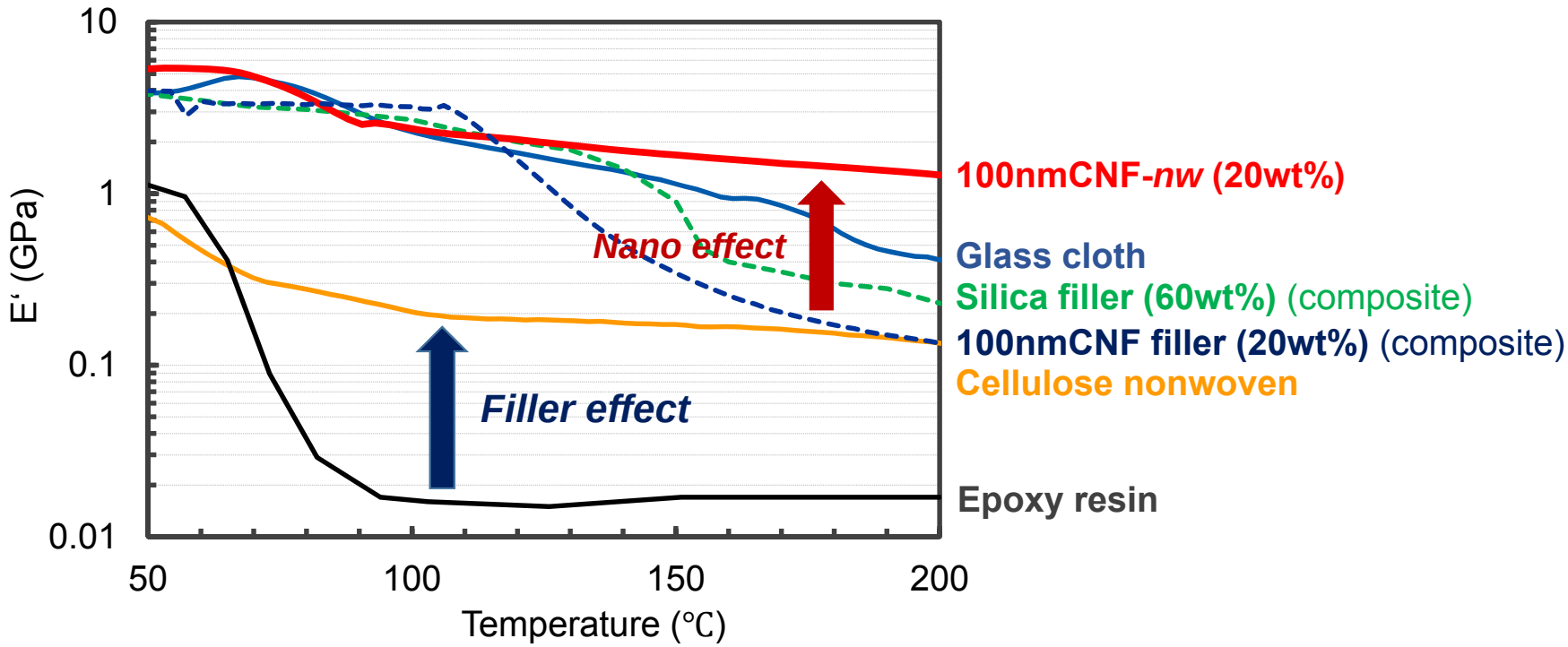
High E' (storage modulus) FRP film by using CNF-*nw*

Storage modulus E' of FRP or composite films



"Cellulose + Nano + Network" are key points for high E'

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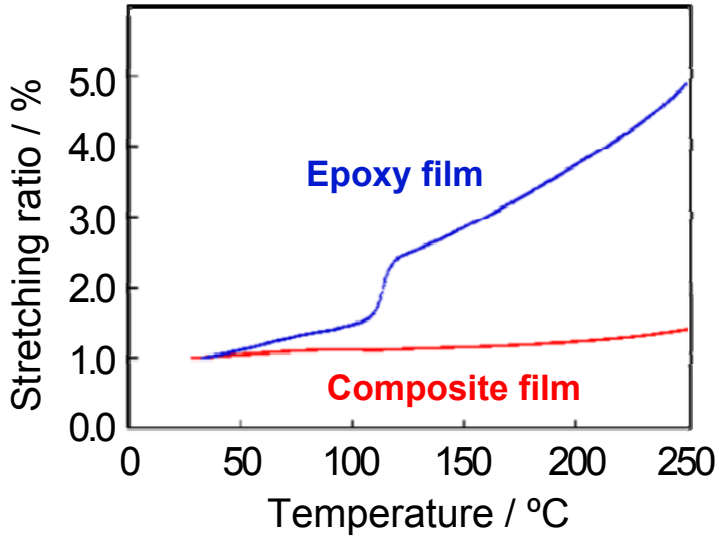
Transparent FRP film by using 30nm-CNF-*nw*

Preparation of transparent composite films with low CTE

30nmCNF-*nw* &epoxy composite film
(CNF/epoxy=20wt%/80wt%)

- **Smooth impregnation of resin solution**
- **High transparency (90%)**

Thermal mechanical analysis



	Transmittance	CTE (ppm/ºC)	
	% (590nm)	50-150℃	50-200℃
30nmCNF–*nw* & epoxy film	90	12.0	13.0
Epoxy film	94	159.0	165.0
30nmCNF-*nw*	2	2.6	8.8

less than 1/10 !

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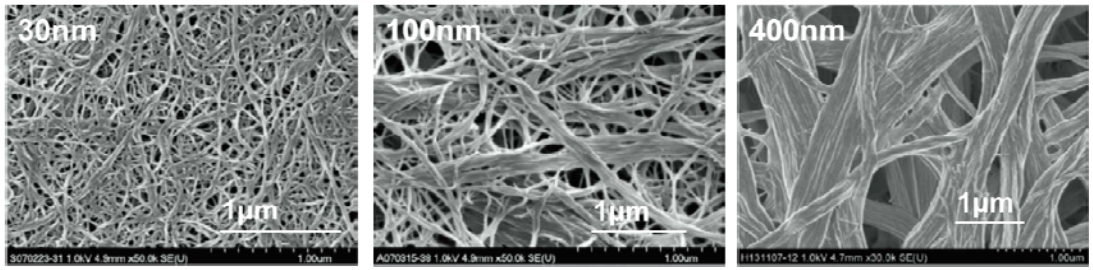
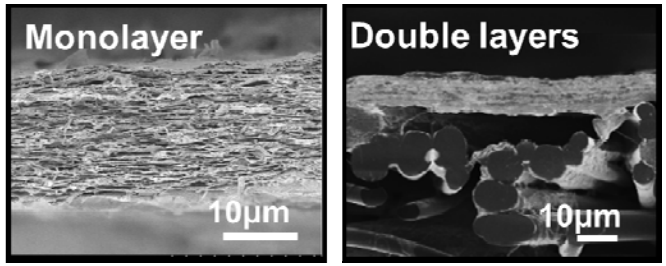
Conclusion

Fiber diameter



Monolayer or double layers



Characteristic features

- Extreme thinness
- Pore size control
- Surface modification
- High thermal stability

- **Membrane**
  - Finer separation
  - Larger flux

  ⇒*ex*) Water permeable membrane

- **Core materials for FRP**
  - Low CTE
  - High modulus
  - Thin
  - Transparent

  ⇒*ex*) Electric material, optical film

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Thank you

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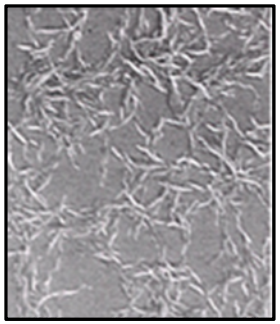
Cellulose products of Asahi Kasei

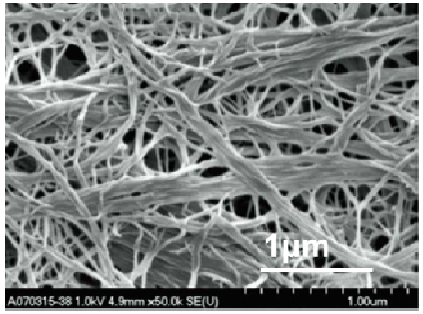
Ceolus®



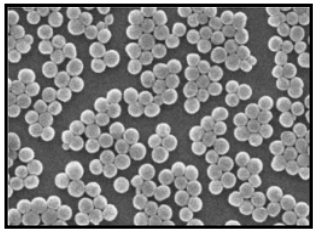
- Low L/D cellulose
- Hydrolysis of pulps
- Additives for foods and pharmaceutics

CNF-*nw* (NanoLeaf®)

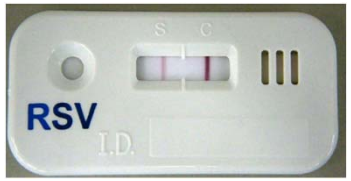
- **High L/D** nanocellulose
- Mechanical downsizing
- **Sheets** for FRP films and filters

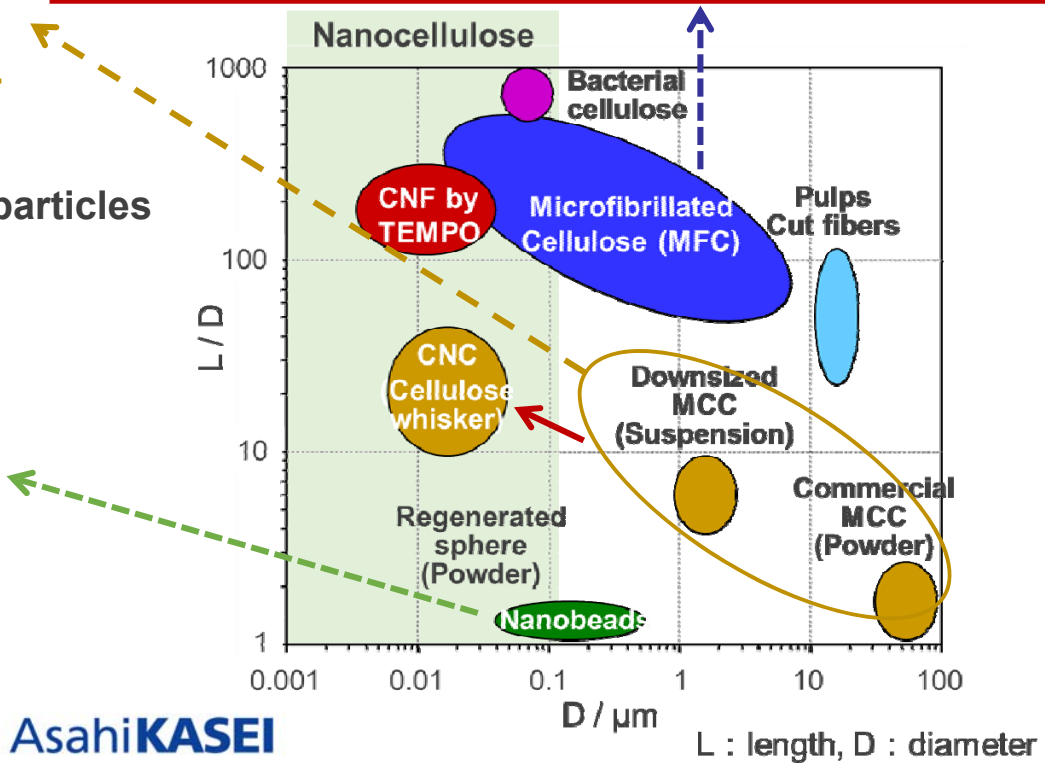


NanoAct™



- Monodispersed nanoparticles (40, 70, 270 & 400nm)
- Phase separation of cellulosic solution
- Diagnostic kits for the flu





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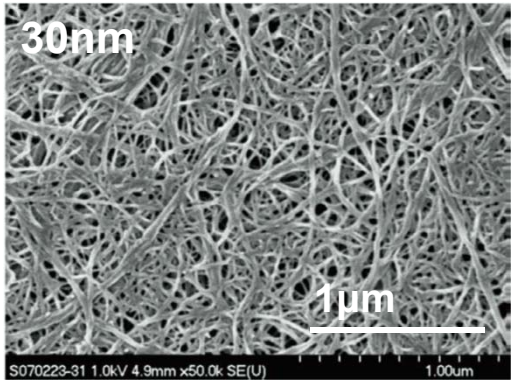
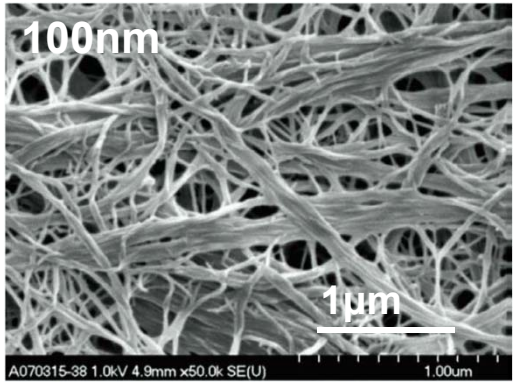
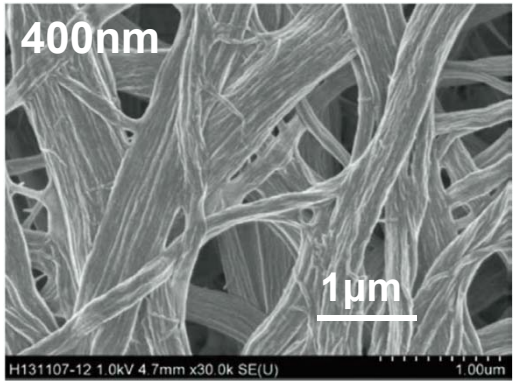
Control of pore size

Pore diameter can be controlled by fiber diameter







Pore diameter and fiber diameter increase

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Features of CNF-*nw* : Surface modification

Water resistance

Untreated CNF-*nw*

Treated CNF-*nw*

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