Isolation of nanocellulose from biomass *via* nontraditional routes

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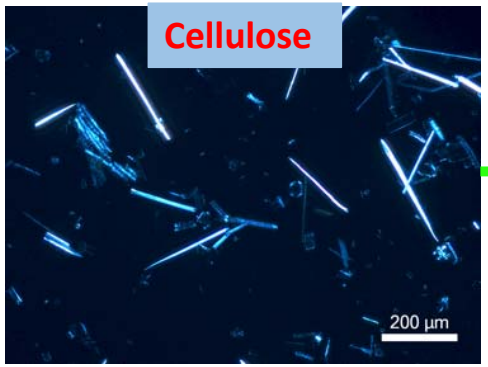
TAPPI

Outline

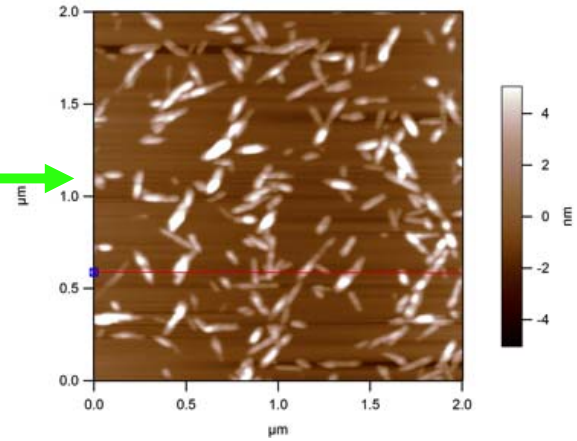
- Motivation
- Nanocellulose isolation
  - Solid-state Bronsted acid hydrolysis
  - Aqueous counter collision with low energy consumption
  - Holocellulose as source materials
- Conclusion and perspectives

MOTIVATION – LIMITATIONS ON ACID HYDROLYSIS

Nanocellulose could be isolated via some traditional isolation methods, such as sulfuric acid hydrolysis and TEMPO oxidation, but each is restricted with some fundamental limitations.



Acid hydrolysis



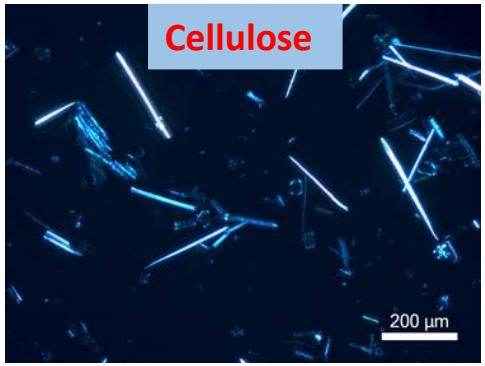
D: 4.7±1.3 nm
L: 143±31 nm
Yield: 4.9-16.9 %

Limitations:

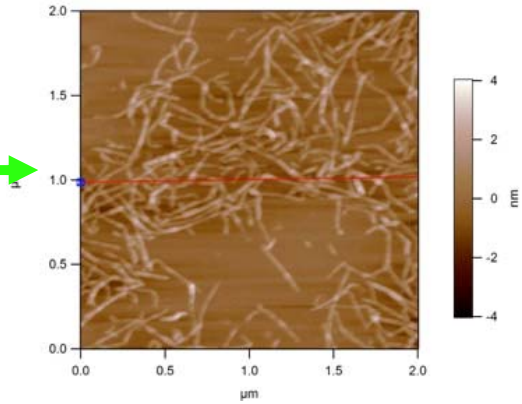
- Low yield due to strong acid hydrolysis to remove amorphous pats;
- Caustic conditions;
- Acid waste.

Carbohydrate Polymers. 2013, 95, 32-40

MOTIVATION – LIMITATIONS ON TEMPO OXIDATION



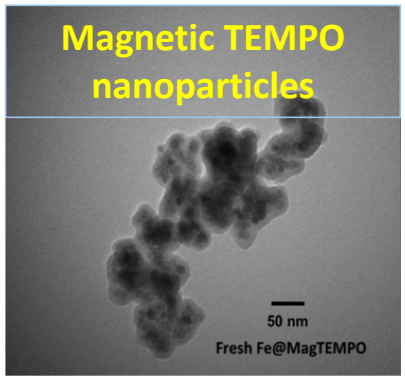
TEMPO oxidation

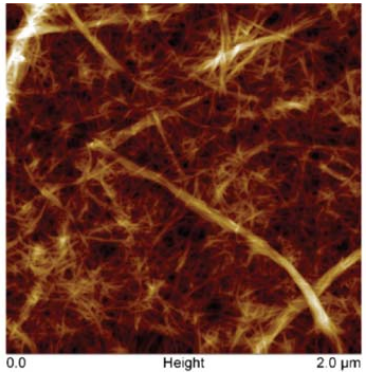


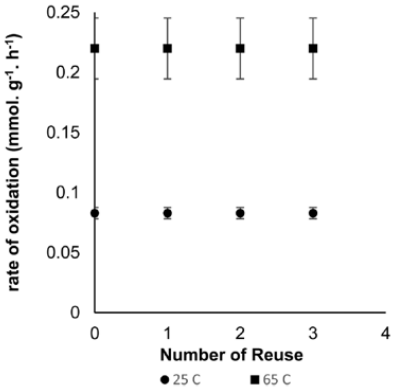
D: <2 nm
L: up to 1 µm
Yield: 96.8 %

Limitations:

- Chemical toxicity;
- Environmental concern;







Green Chemistry. 2017, 19, 4792
RSC Advances. 2013, 3, 12366-12375

MOTIVATION – LIMITATIONS ON THE SOURCES MATERIALS

Source materials:

- Cotton;
- Bleached pulp (Kraft or Dissolving pulp);
- Bacterial cellulose;
- Microcrystalline cellulose;
- Tunicate cellulose;
- Purified cellulose from agricultural residues.

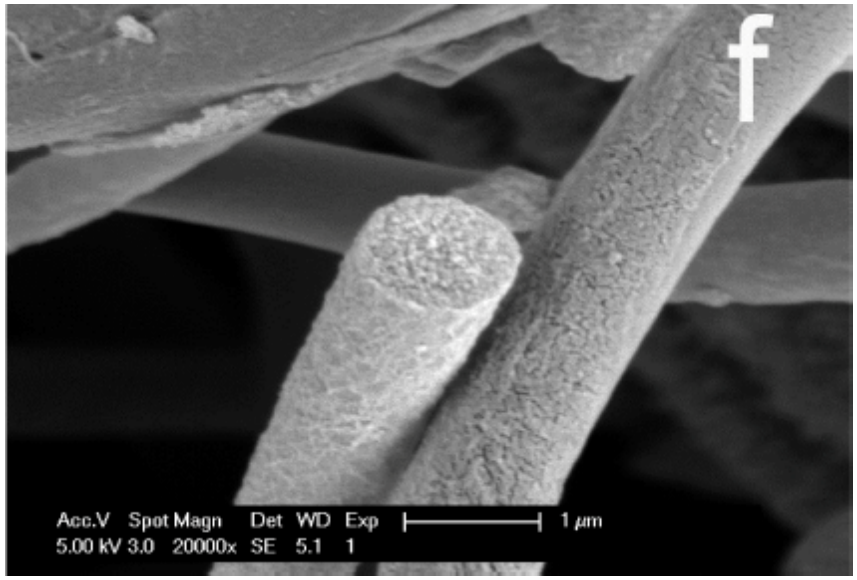
It is advantageous to use chemically impure cellulose as raw materials for producing nanocellulose, including:

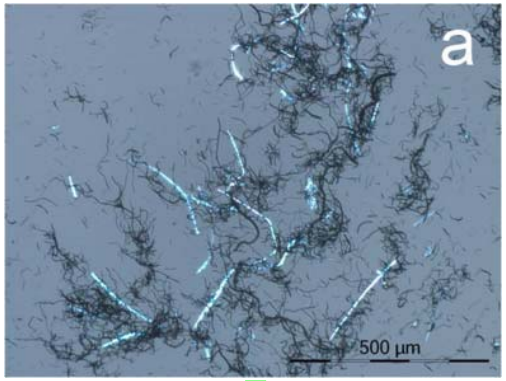
- Reduced cost;
- Increased yield;
- In-situ modification of nanocellulose with hydrophobic lignin;

NANOCELLULOSE ISOLATION – SOLID STATE ACID HYDROLYSIS

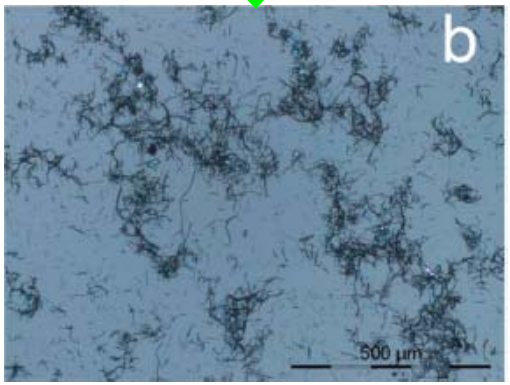
Over 80 % of cellulose was lost in sulfuric acid hydrolysis, how to resolve this loss and achieve total conversion to valuable products?

Sulfonated activated carbon fibers from lignin
Total acid density: 0.88 mmol/g



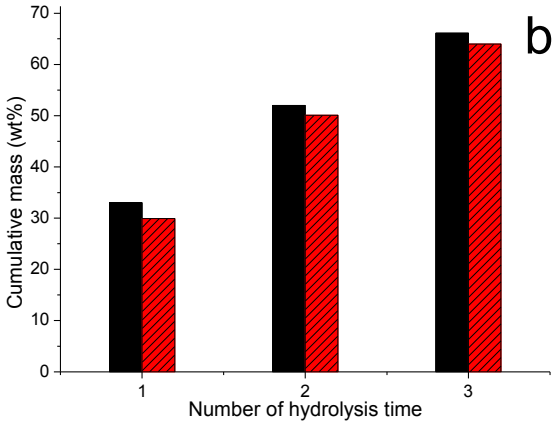


4:1 catalyst : cellulose
150 ℃ for 24 h
Hydrothermal condition



ACS Sustainable Chemistry & Engineering. 2015, 3, 2566-2574

NANOCELLULOSE ISOLATION – SOLID STATE ACID HYDROLYSIS



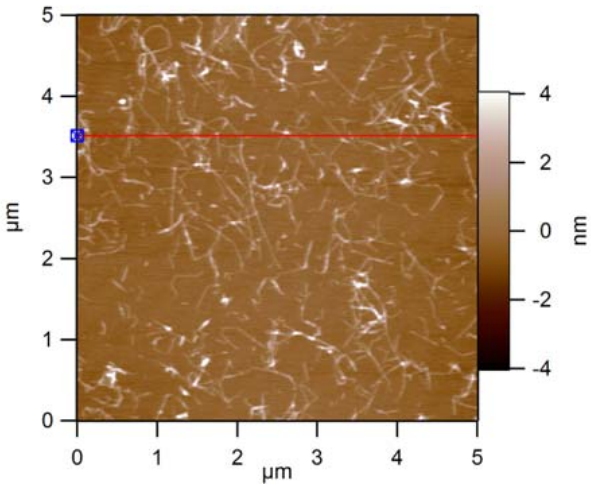
Yield of glucose :

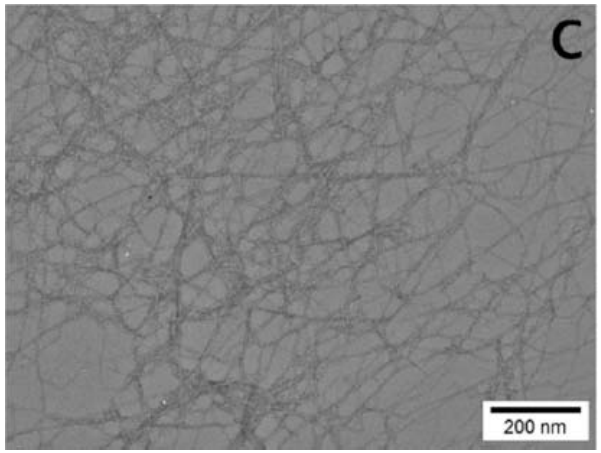
1st hydrolysis: 29.9%

2nd hydrolysis: 50.1%

3rd hydrolysis: 64%

Yield of Nanocellulose : 8.1 %





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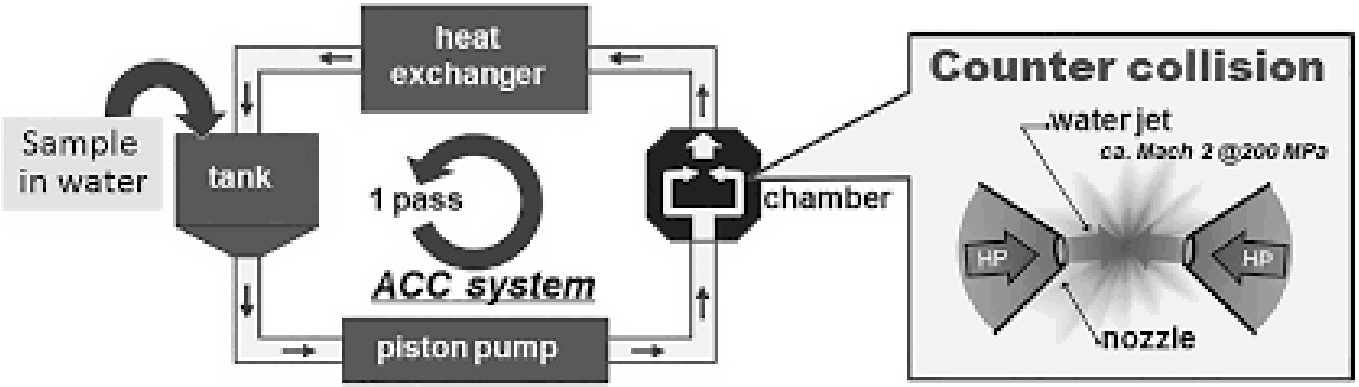
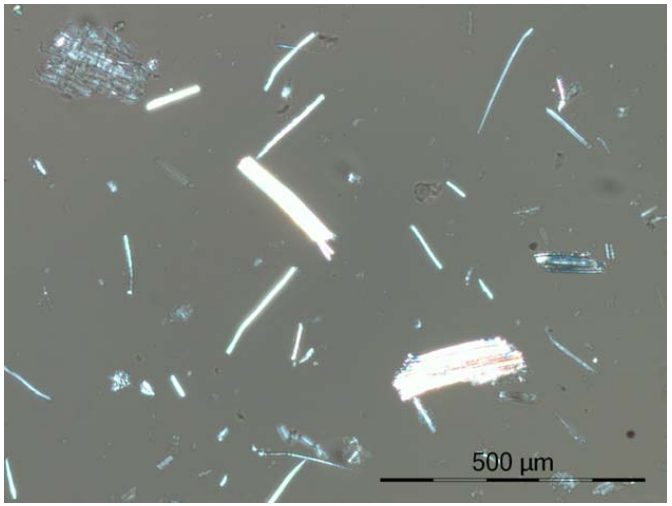
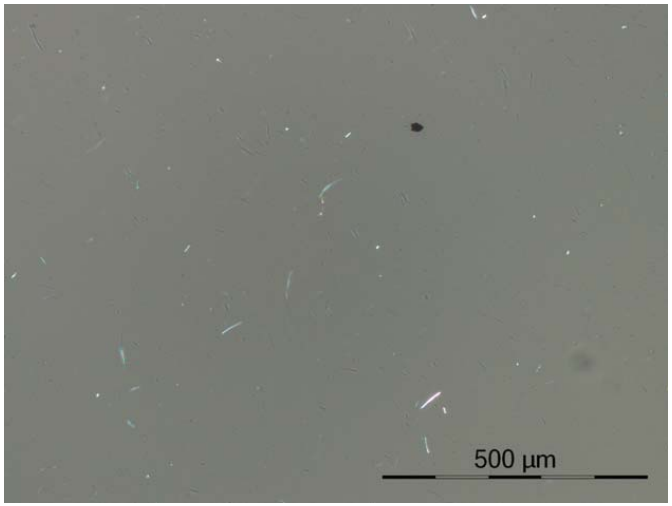
NANOCELLULOSE ISOLATION – ACQUEOUS COUNTER COLLISION





ACC
180 MPa
30 passes

15 kWh/kg



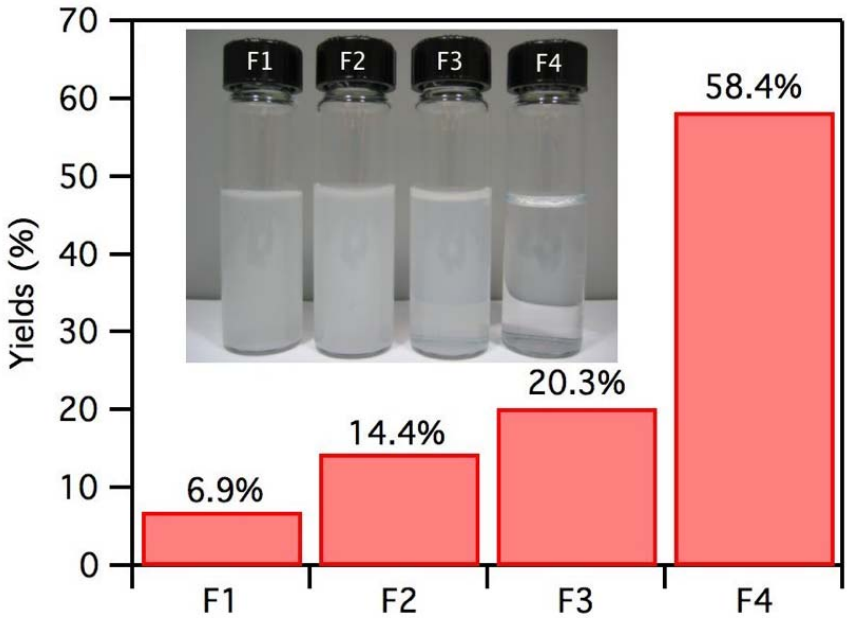
α-cellulose

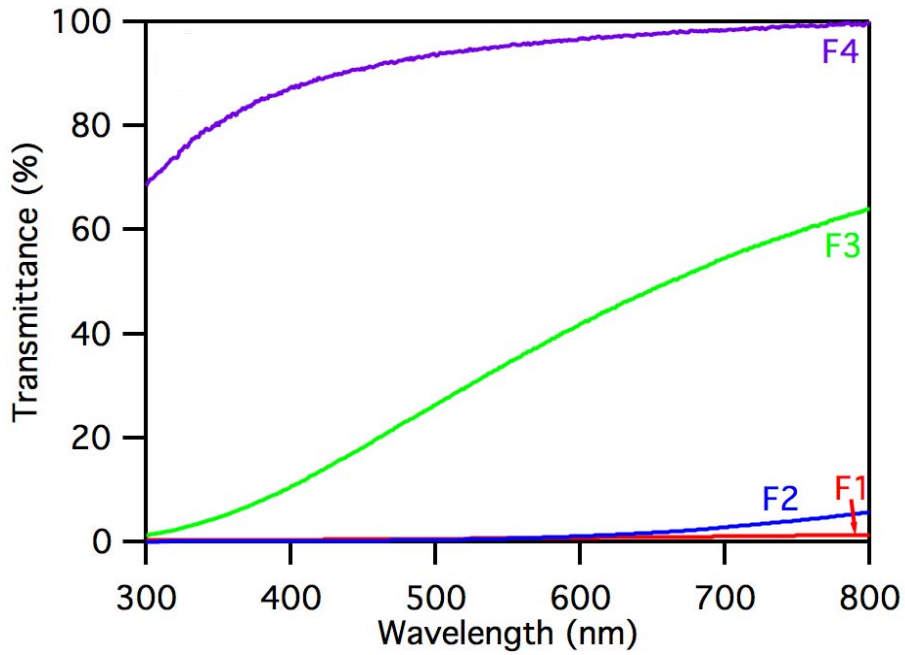
ACC treated α-cellulose

ACS Sustainable Chem. Eng. 2016, 4, 1697−1706

FRACTIONATION OF ACC TREATED CELLULOSE

- F1: Precipitate at 1500 rpm;
- F2: Supernatant at 1500 rpm, and precipitate at 5000 rpm
- F3:Supernatant at 5000 rpm, and precipitate at 14000 rpm
- F4:Supernatant at 14000 rpm





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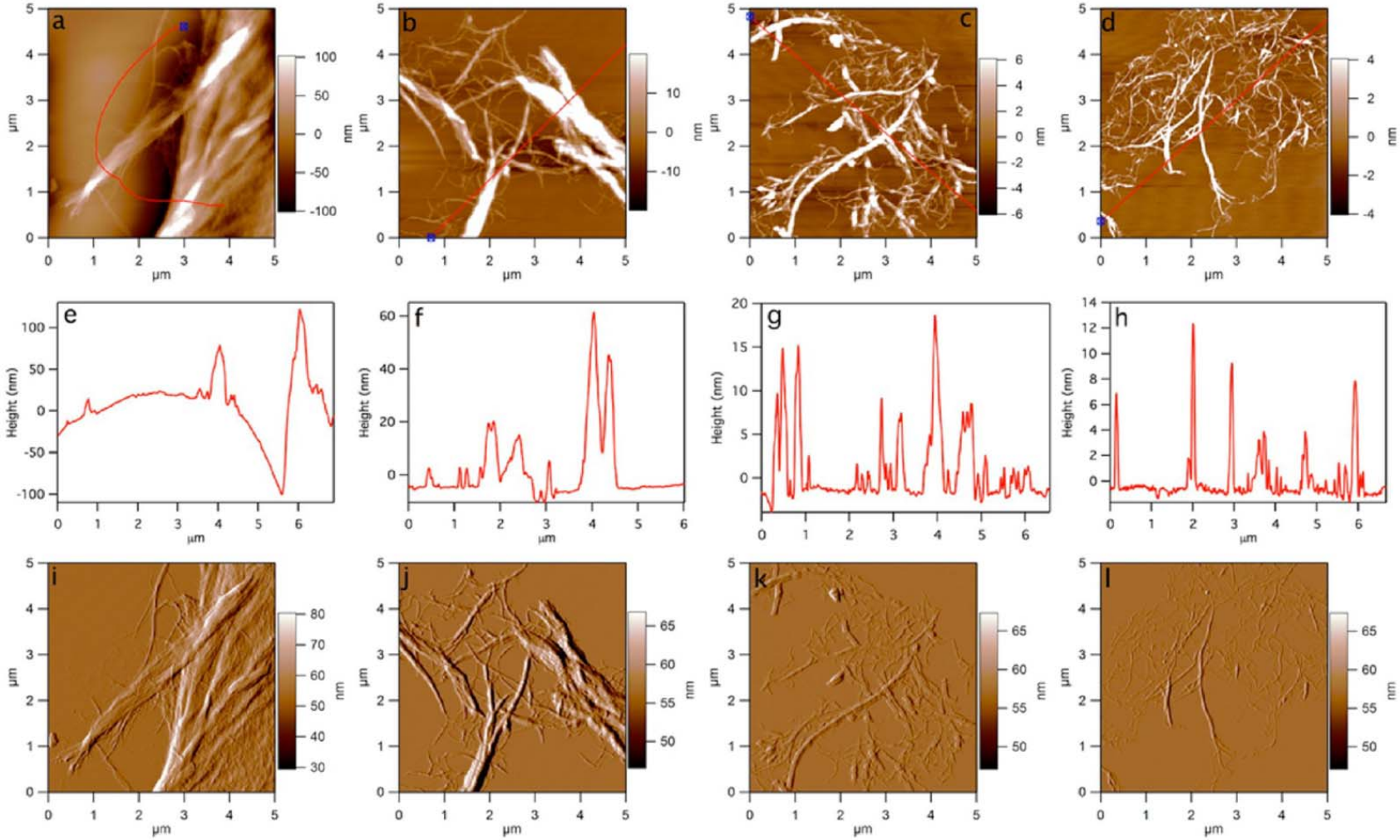
MORPHOLOGIES OF THE FRACTIONATED ACC NANOCELLULOSE



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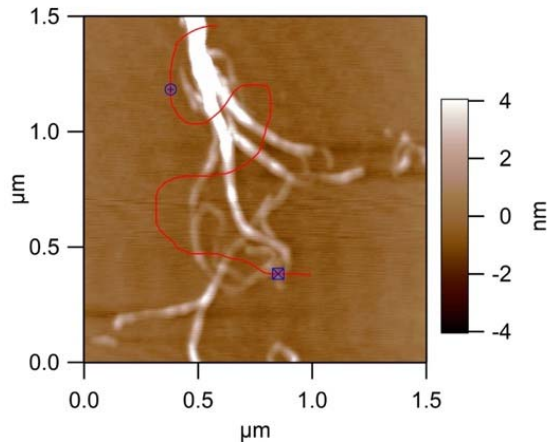

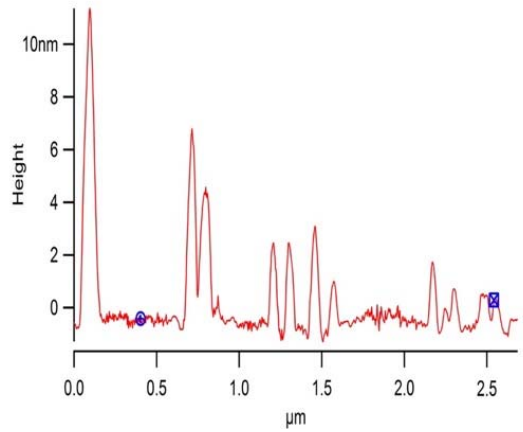

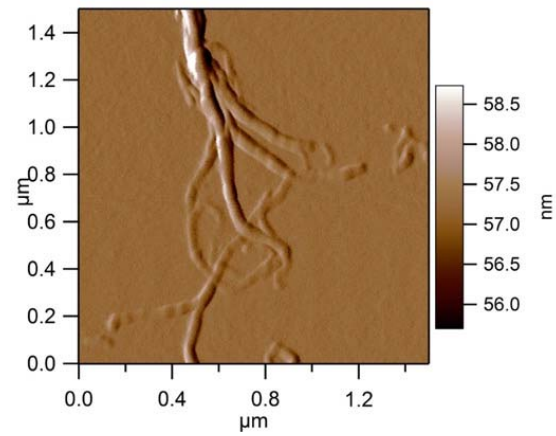

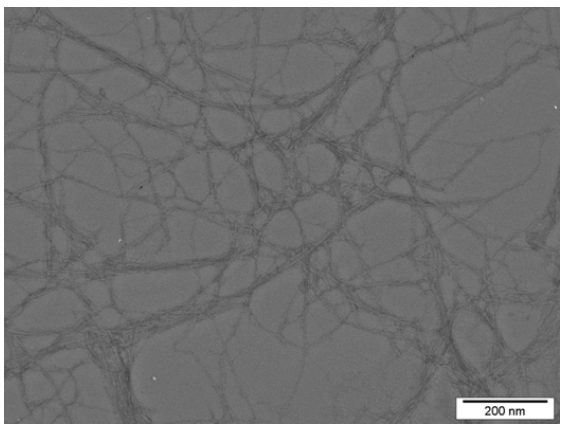

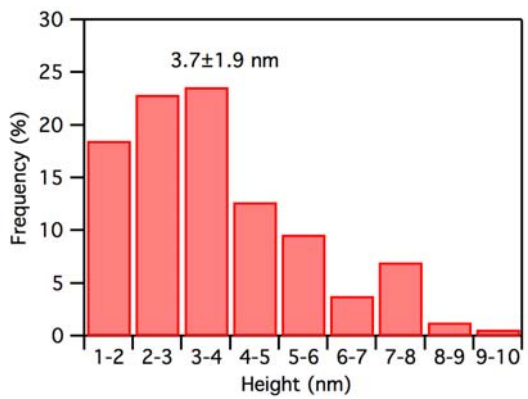

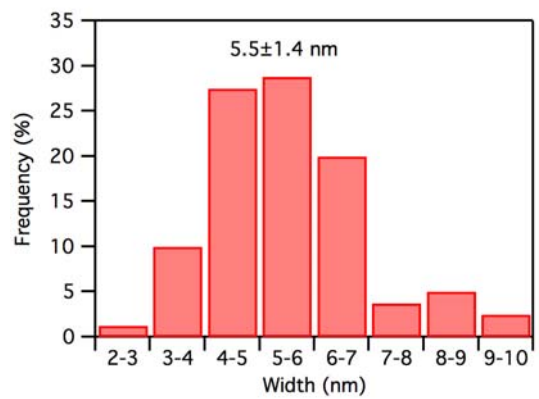

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HOLOCELLULOSE AS SOURCE MATERIALS

Rice straw (RS)

↓ Washing and ground to pass through 60 mesh sieves

RS powder (30 g)

↓ Extract with toluene and ethanol (2:1, v/w) for 20 h

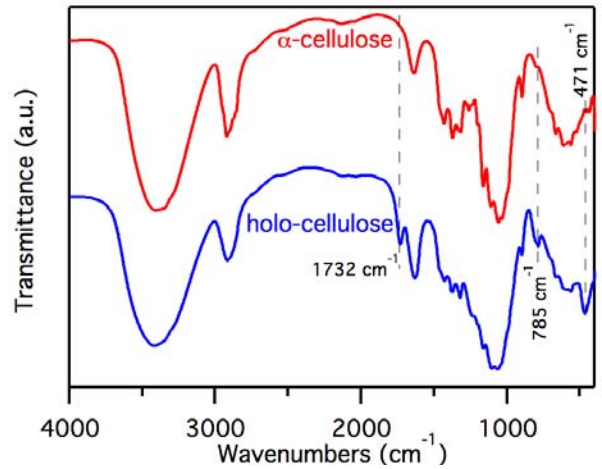
Dewaxed RS

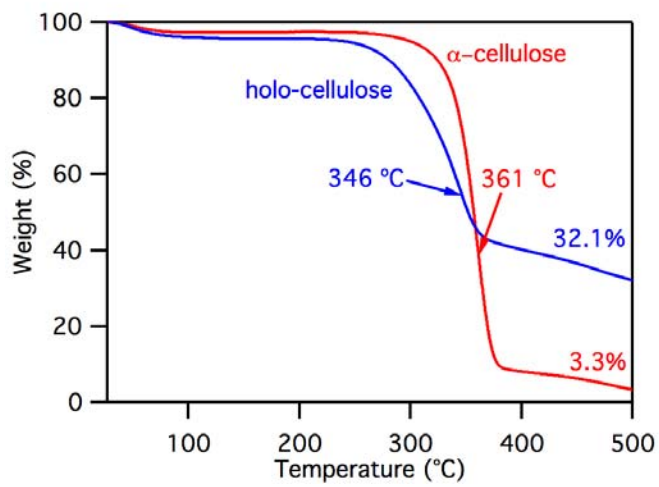
↓ 1000 mL 1.4% $NaClO_2$, adjust pH 3-4 with acetic acid, 70 °C, 5h

Holo-cellulose Yield: 75.4%

↓ 600 mL 5% KOH, RT 24h, and 90°C for 2h

α-cellulose Yield:36.4%





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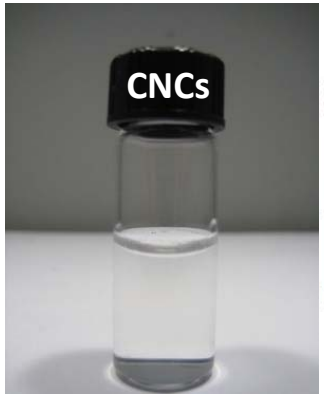
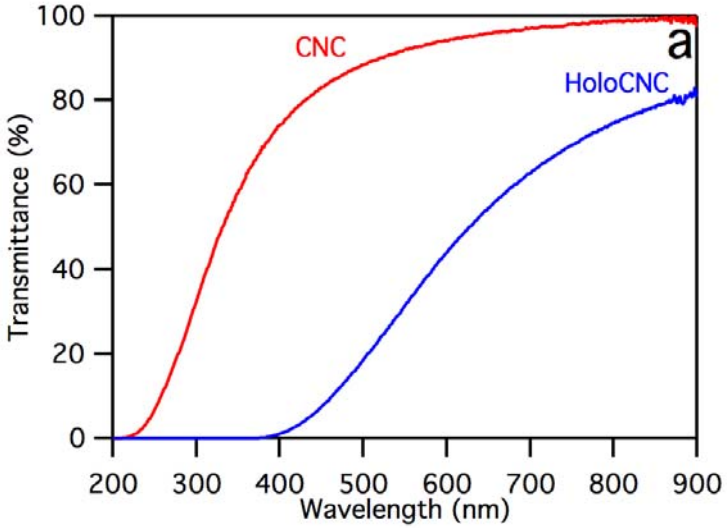
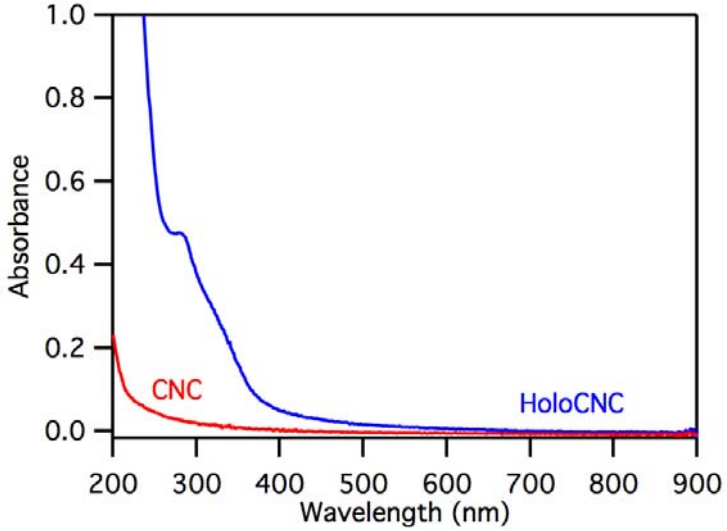
ISOLATION OF CNC AND HOLOCNCS

- Sulfuric acid hydrolysis:
  - 64% H_2SO_4
  - 8.75:1 mL/g liquid to solid
  - 45 °C
  - 45 min

- Yields:
  - 6.8% CNCs
  - 11.6 % HoloCNCs







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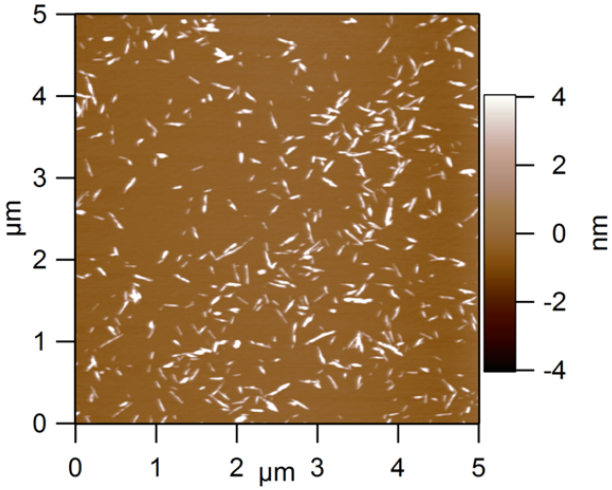
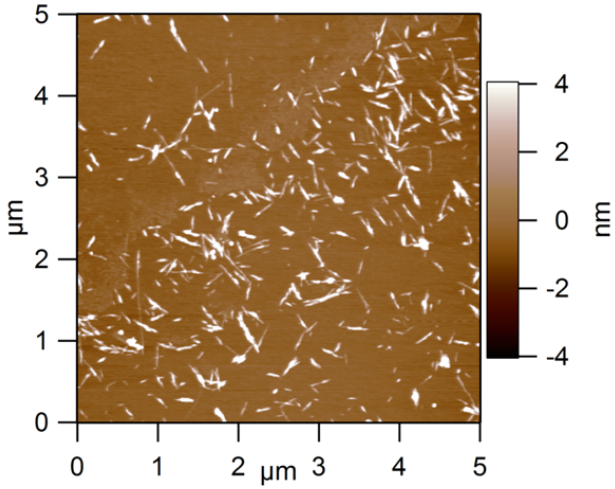
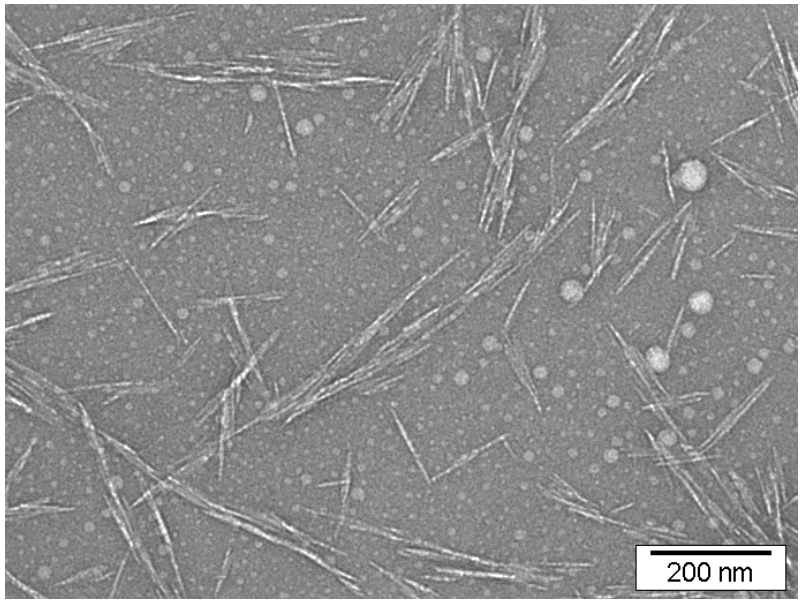
MORPHOLOGIES OF CNC AND HOLOCNC

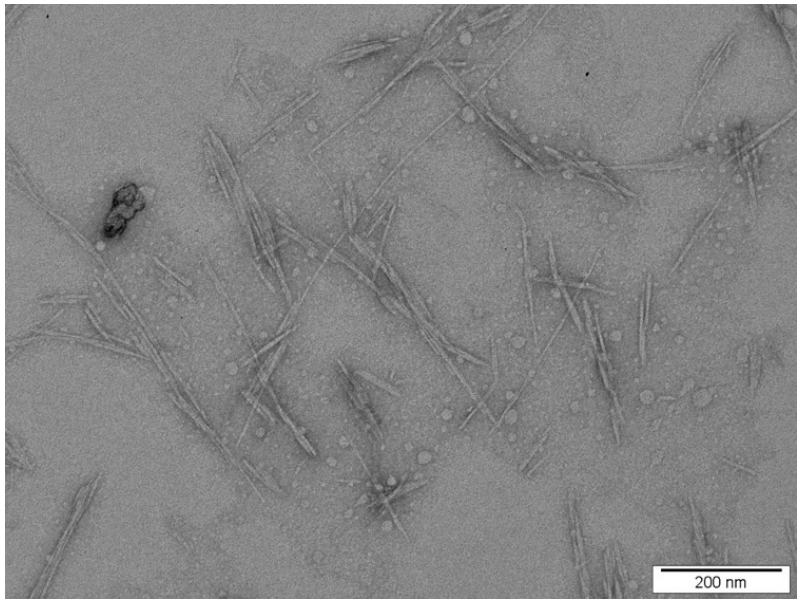


T: 4.7±1.3 nm
W: 6.4±1.2 nm
L: 143±31 nm

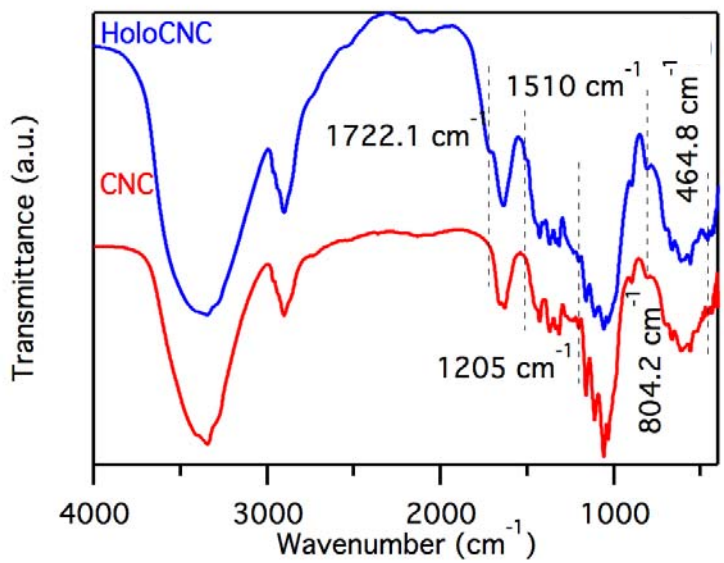


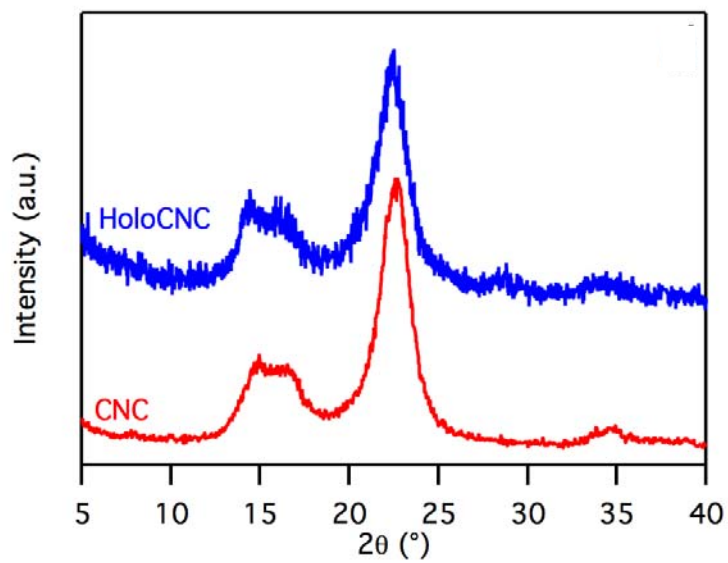
T: 4.1±1.6 nm
W: 6.4±1.8 nm
L: 113 ± 70 nm





FTIR AND XRD





CrI: 90.7% CNCs
84.4% HoloCNCs

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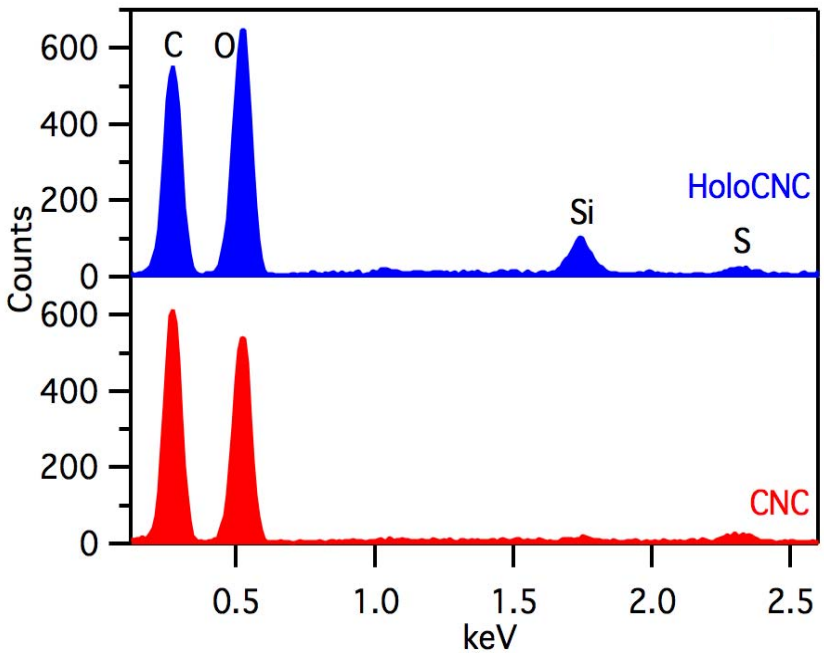
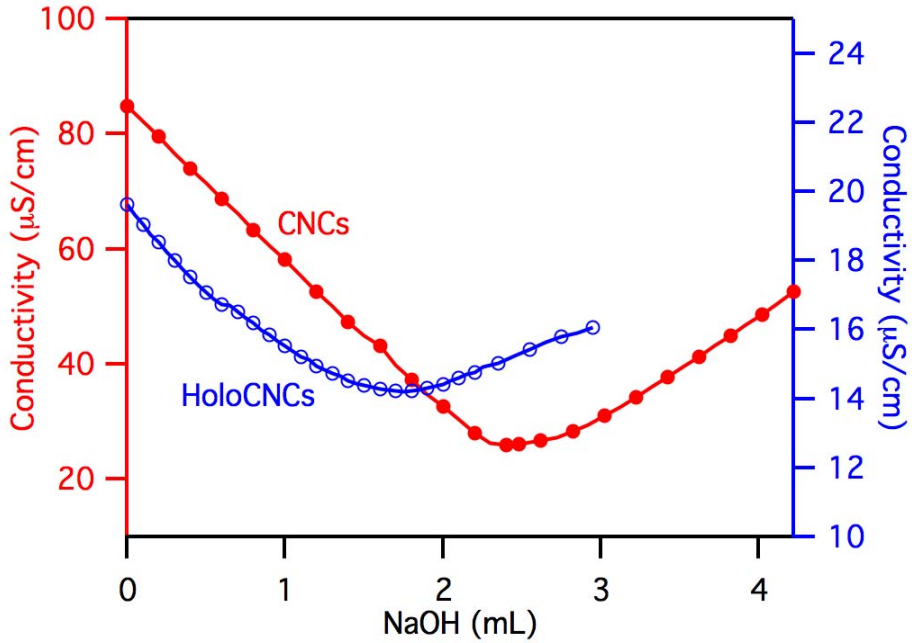
EDS AND SURFACE CHARGE DENSITY





Samples	Atomic concentrations (at%)				Surface charge density (mmol/g)
	C	O	Si	S	
CNC	60.4	38.9	N/A	0.7	0.237
HoloCNCs	55.8	41.2	2.5	0.6	0.128

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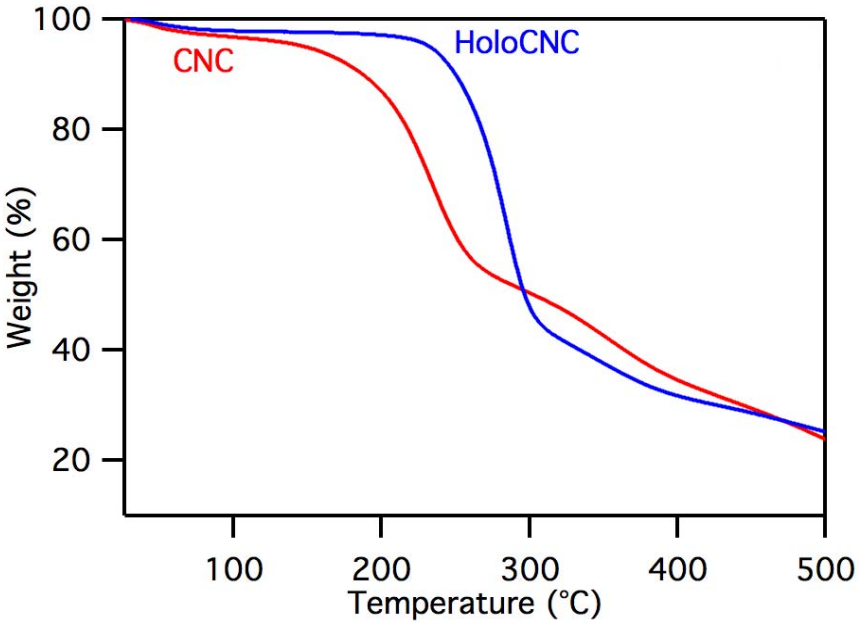
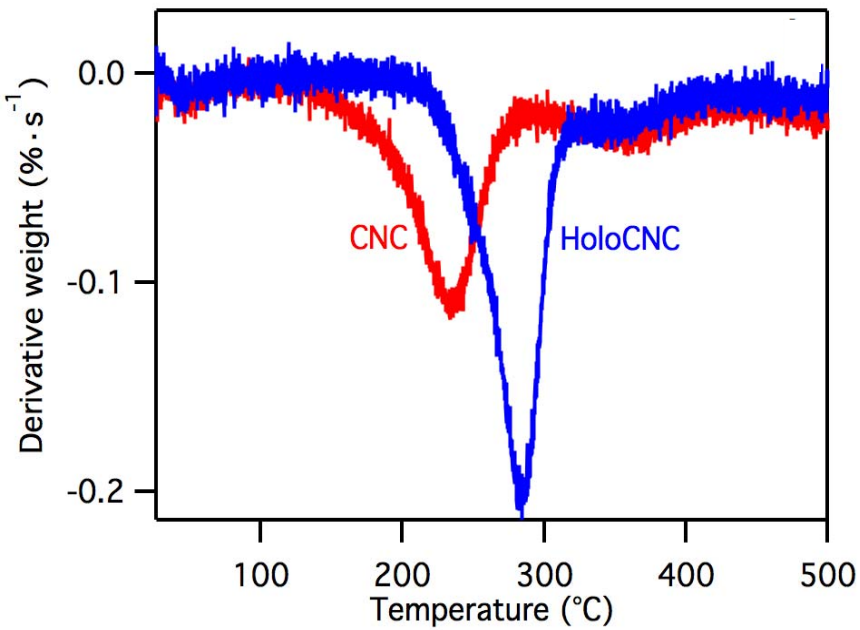
THERMAL STABILITY





Sample	T_{max} (°C)	% Char residual at 500 °C
CNC	234	23.9
HoloCNC	285	25.3

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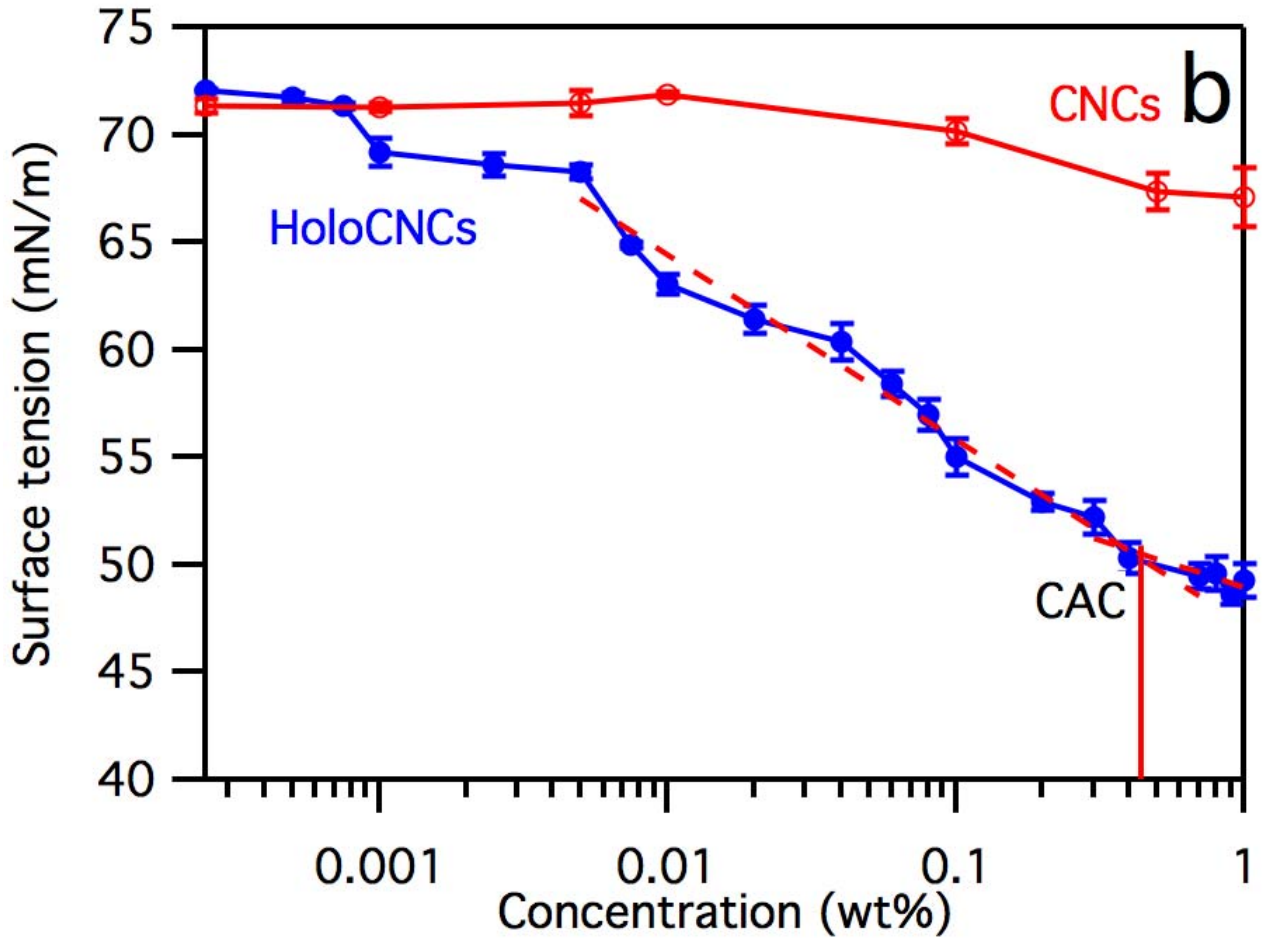
SURFACE TENSION OF CNCS AND HOLOCNCS



Critical aggregation concentration = 0.46%

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PICKERING EMULSION

- 30:70 hexadecane/aq. CNC (450 µL:1050 µL)
- CNCs at 0.01%, 0.05%, 0.1%, 0.2%, 0.3%
- 30 min Water bath sonication

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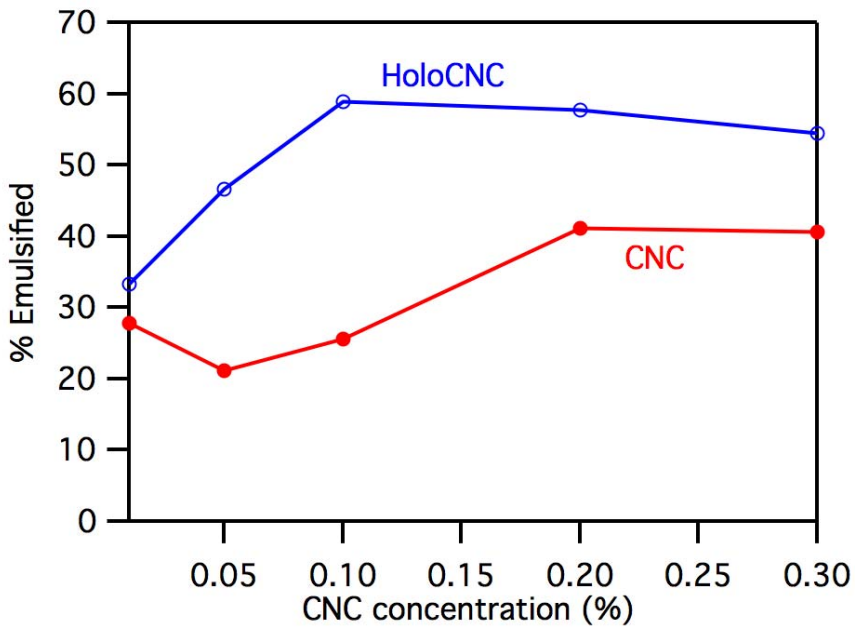
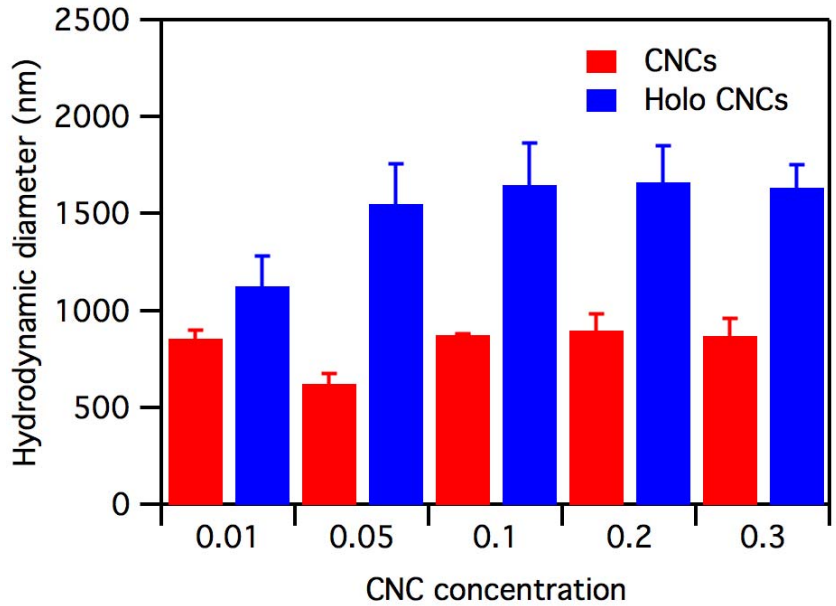
% EMULSIFIED AND HYDRODYNAMIC DIAMETERS





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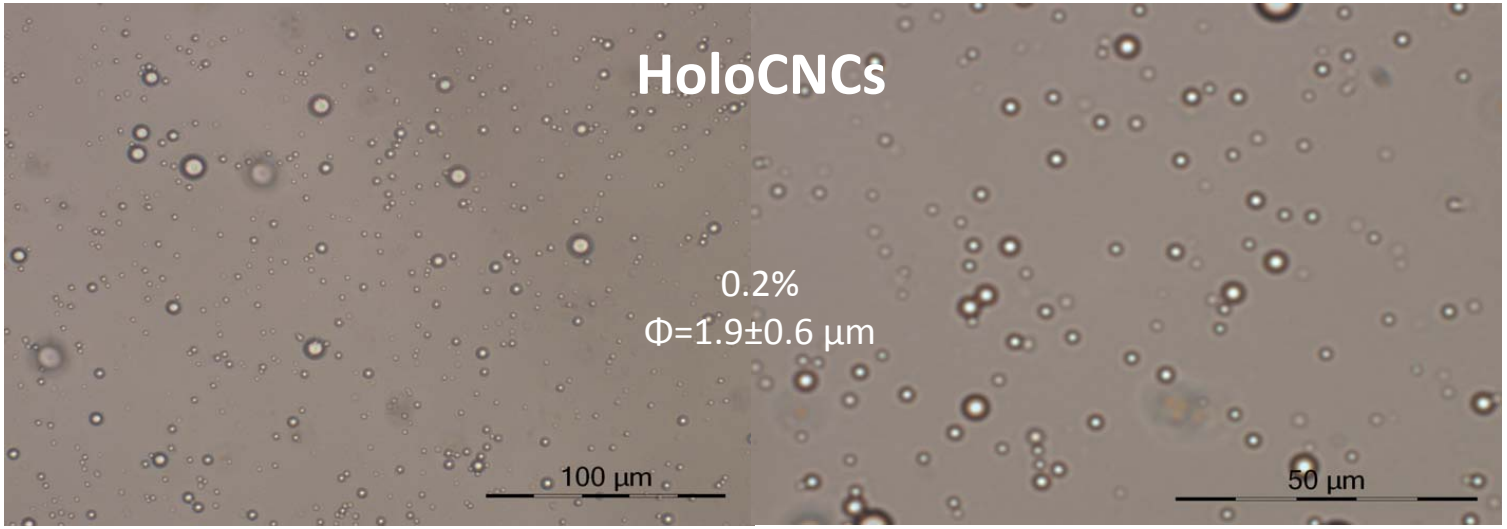
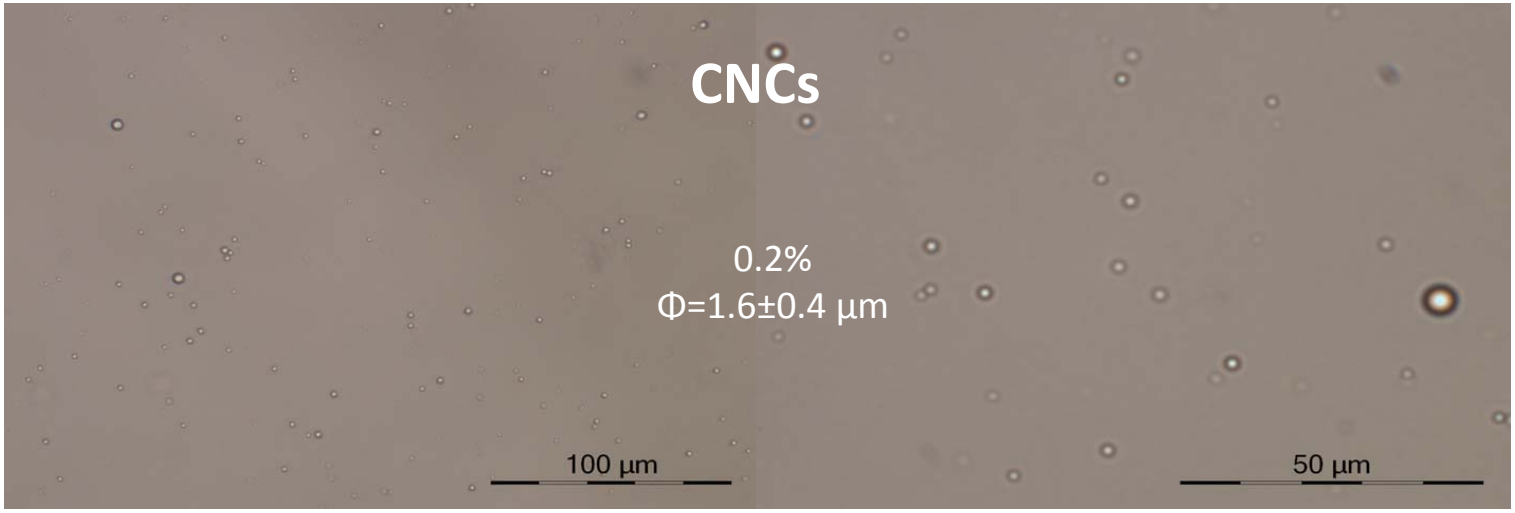
PICKERING EMULSION





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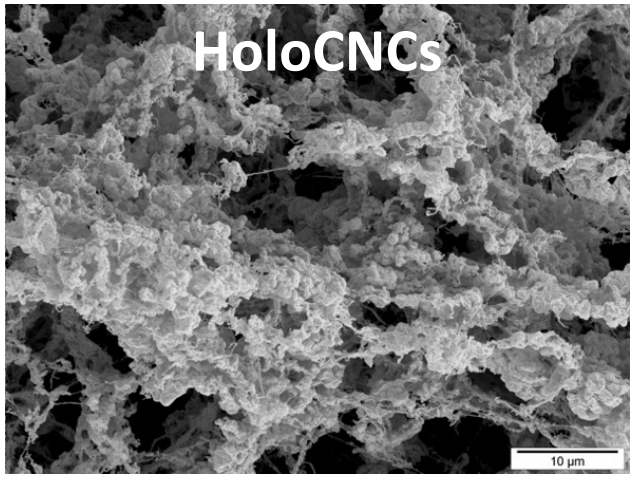
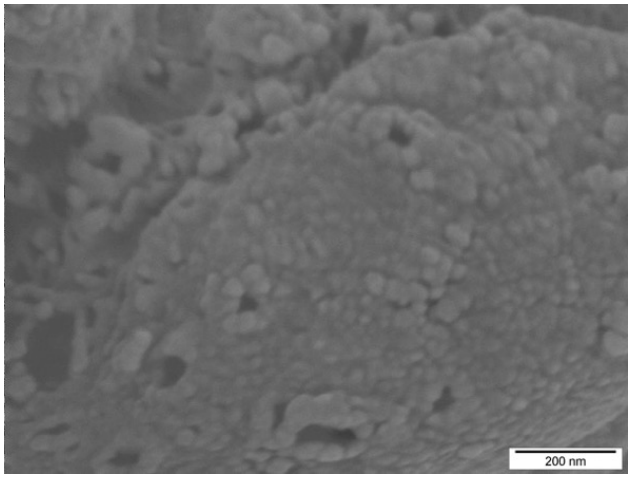
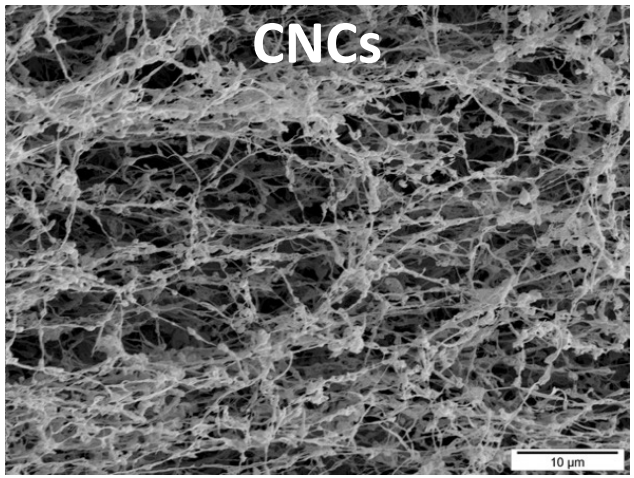
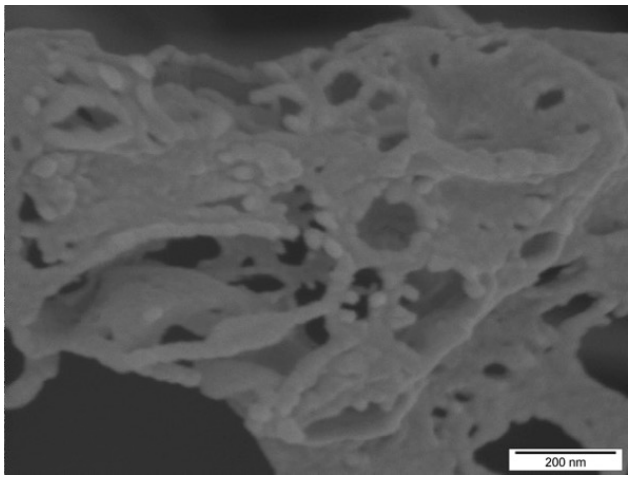
ASSEMBLED STRUCTURE

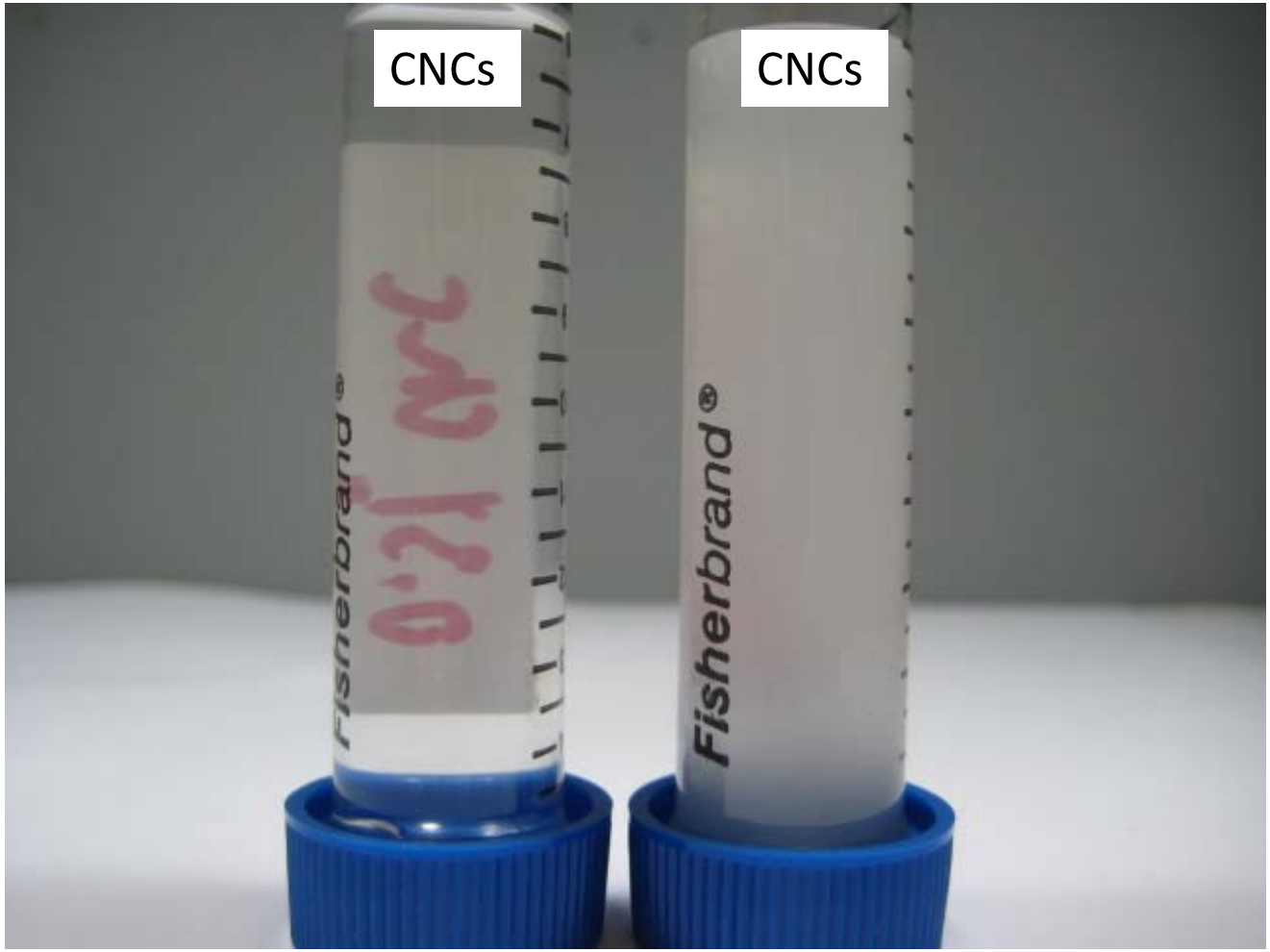








PICKERING EMULSION STABILITY AFTER 4 DAYS



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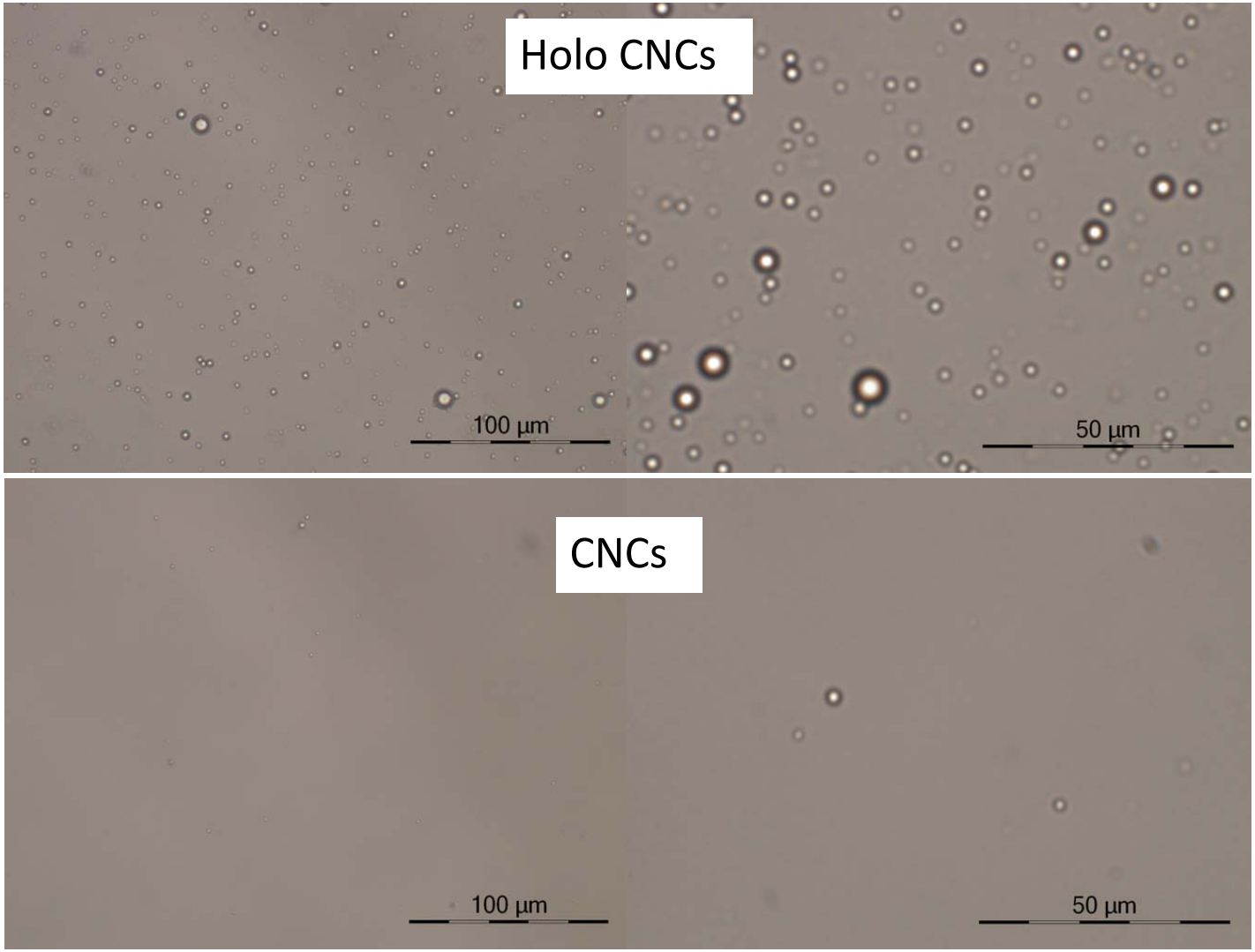

CONCLUSION AND PERSPECTIVES

- Co-production of glucose and nanocellulose could be achieved by using lignin based solid state acid catalysts;
- Aqueous counter collision can isolated nanocellulose at relative low energy consumption, and the isolated nanocellulose could be fractionated based on the dimension by centrifugal forces;
- By using chemically impure source materials, lignin containing holoCNCs could be obtained showing many advantages compared to the pure CNCs, including, higher yield, better thermal stability, improved amphiphilic properties, etc.
- Research on nanocellulose isolation should be focused on the following perspectives: reduced energy consumption, recyclable chemicals/solvents, lignin containing biomass source, minimum pretreatment required.

Thank you

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