Cost-Effective and Functional Emulsions Stabilized with Renewable Particles

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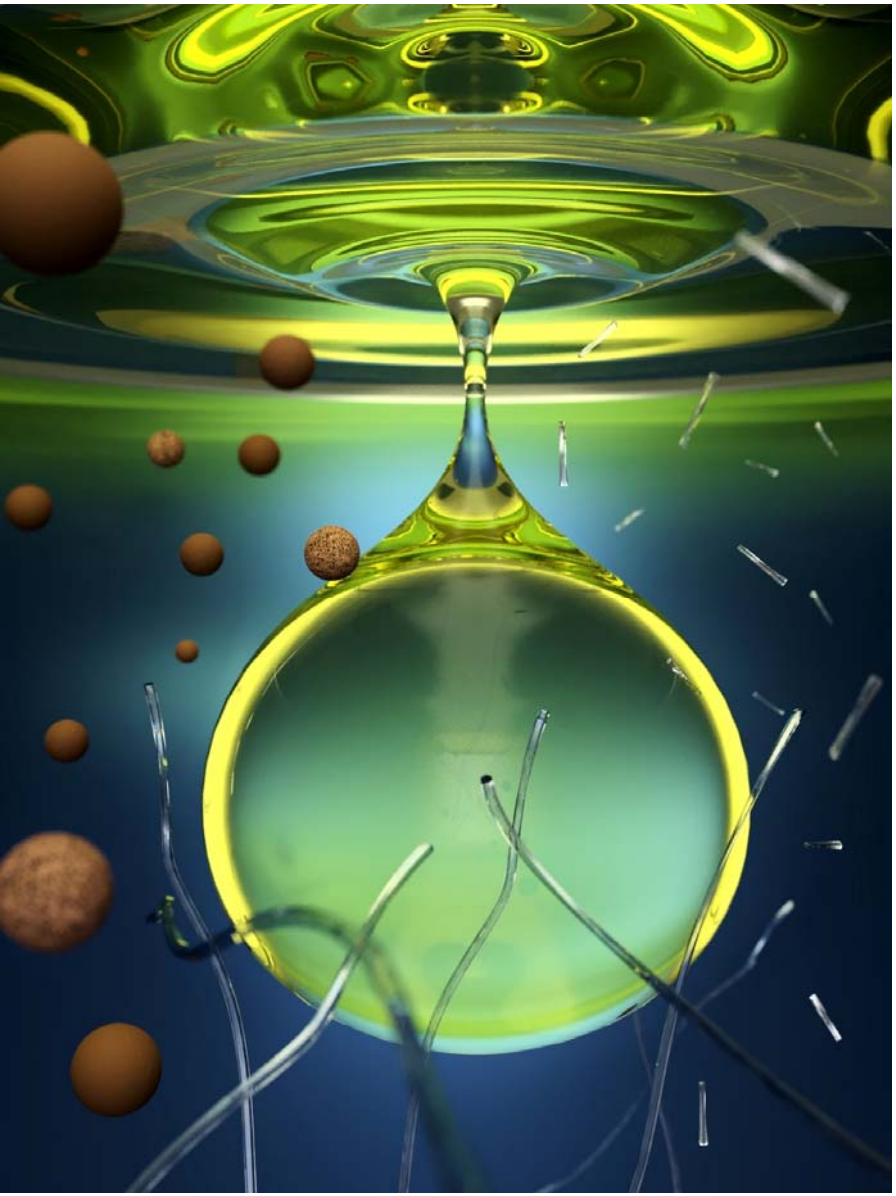
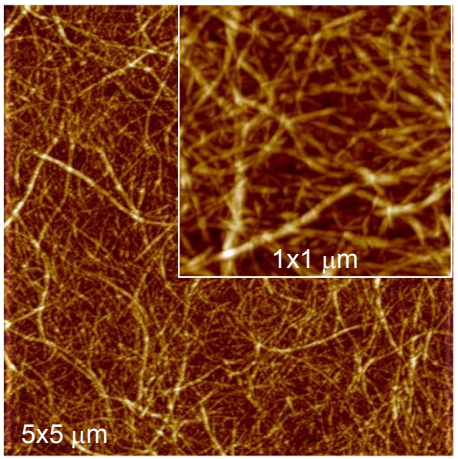


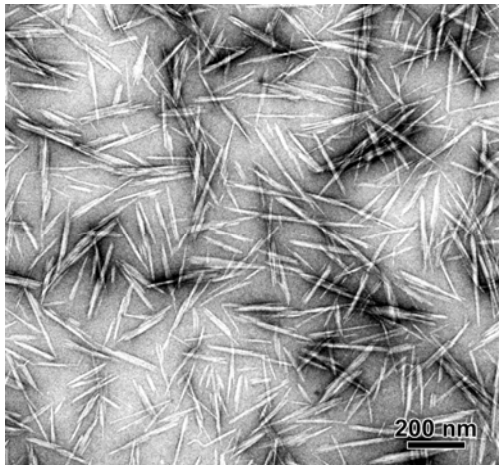
Renewable particles to be considered:

- ***Cellulose Nanocrystals***
- ***Cellulose Nanofibers***
- ***Lignin Particles***
- ***Nanochitin***
- ***…***

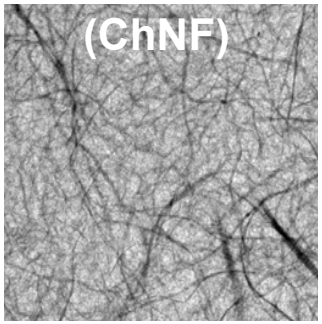
Cellulose Nano/Micro fibrils (CNF or NFC)

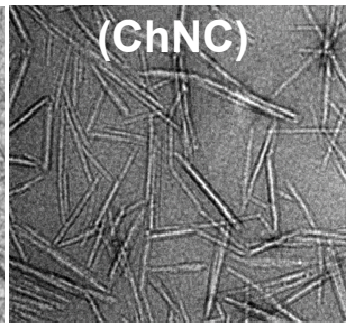


Cellulose nanocrystals (CNC)

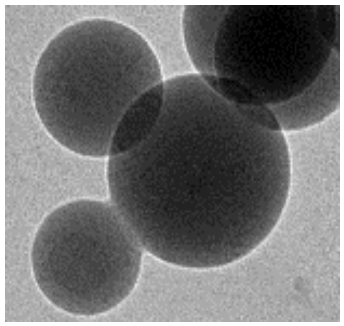


Chitin Nano-crystals/ fibrils (ChNF or ChNc)

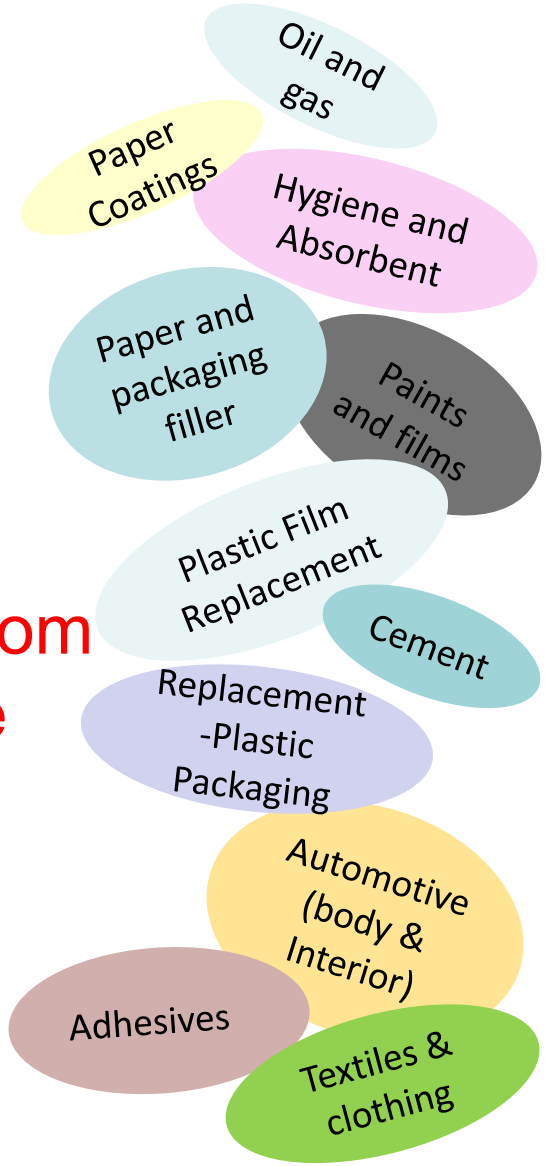




Micro/Nano-lignin particles



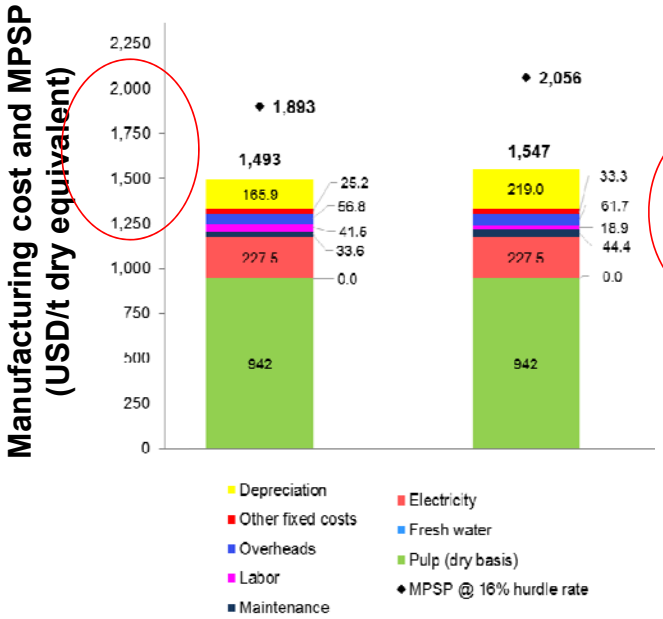
Emulsion properties can benefit greatly from these renewable particles



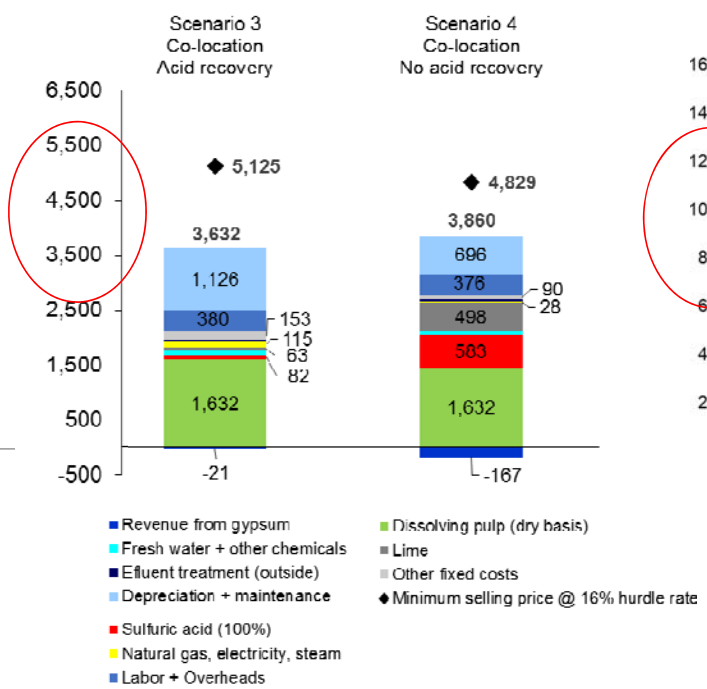
WO/2016/099537 Additive of chemically-modified cellulose nanofibrils or cellulose nanocrystals
WO2016099534 Additive of cellulose nanofibrils or nanocrystals and a second polymer

Manufacturing cost and minimum product selling price (MPSP) of forest-based nanomaterials

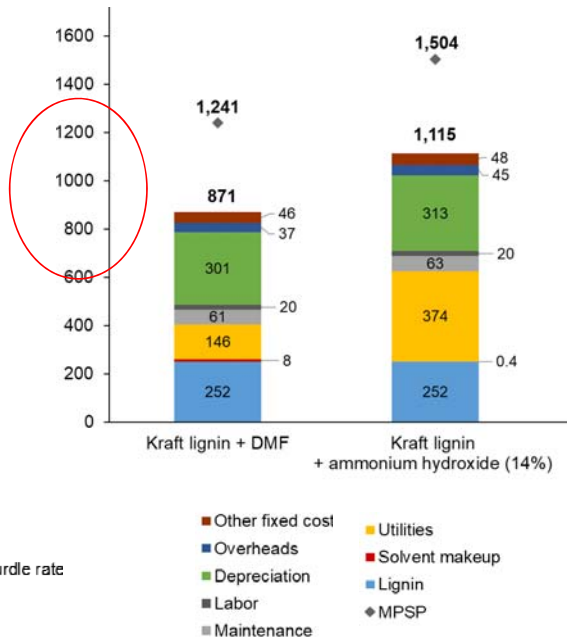
CMNF



CNC



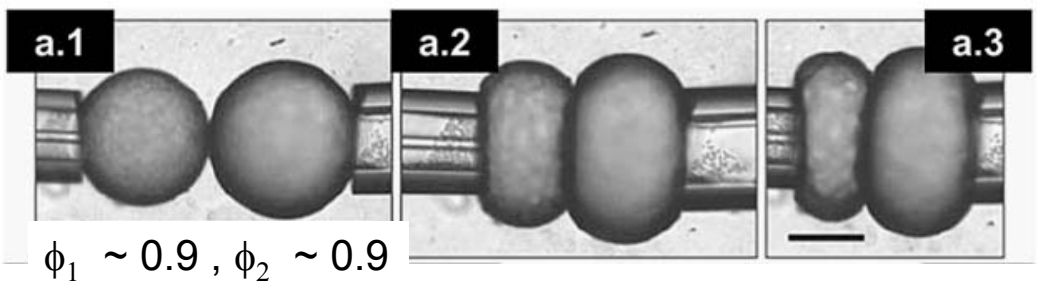
Nanolignin



Biofuels, Bioprod Biorefining, **12**, 251 (2018) *Biofuels, Bioprod Biorefining* **11**, 682 (2017) *ACS Sust Chem & Eng* **6**, 11853 (2018)

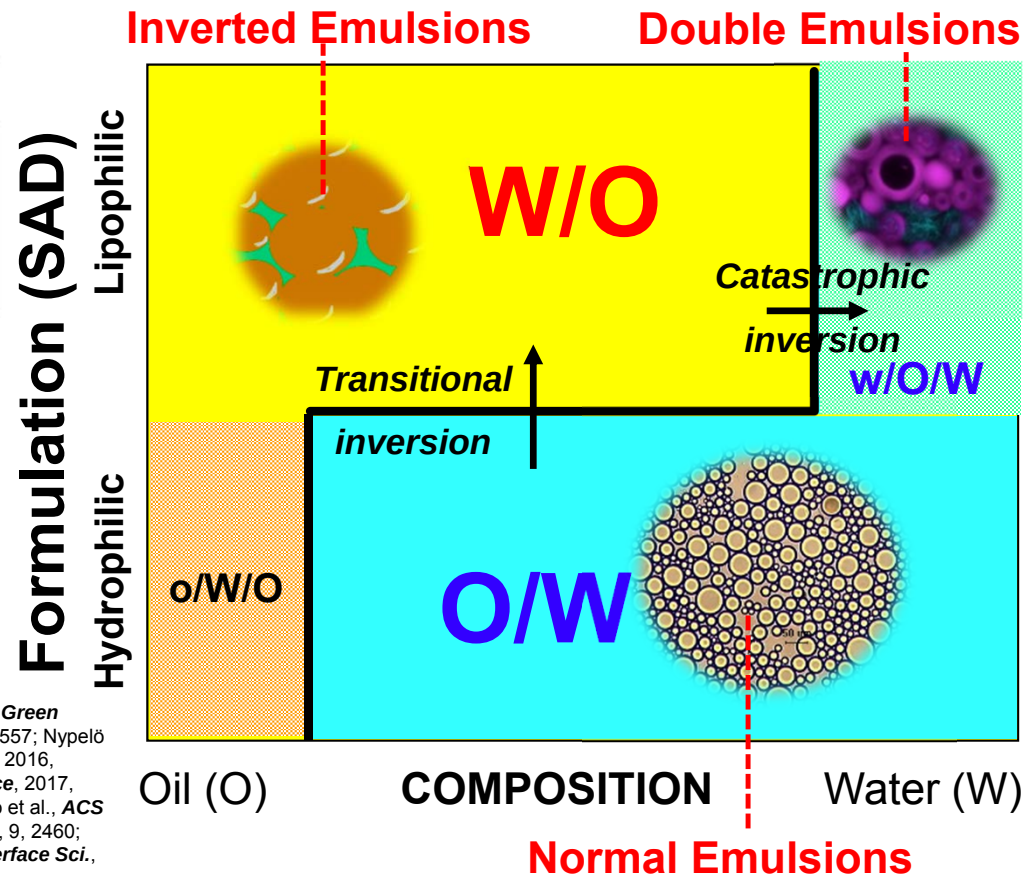
- **Conventional emulsifiers**: diffuse to interfaces and adsorb spontaneously
- **Particle adsorption**: nonspontaneous (energy barrier to adsorb)

Free energy of **desorption**: $\Delta G_d = \pi r^2 \gamma_{OW} (|1 - cos\theta|)^2 \gg kT$



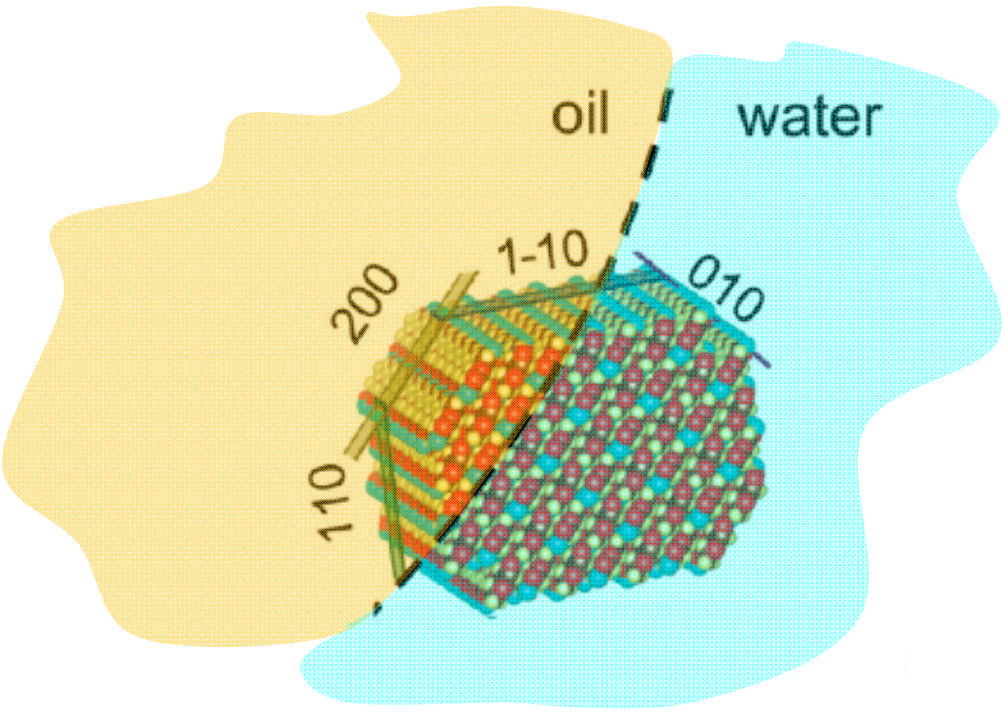
(see Pawar et al. 2011, Soft Matter, 7710)

Arrested coalescence: close-packed surface layer forms a cohesive structure that resists the Laplace pressure gradient



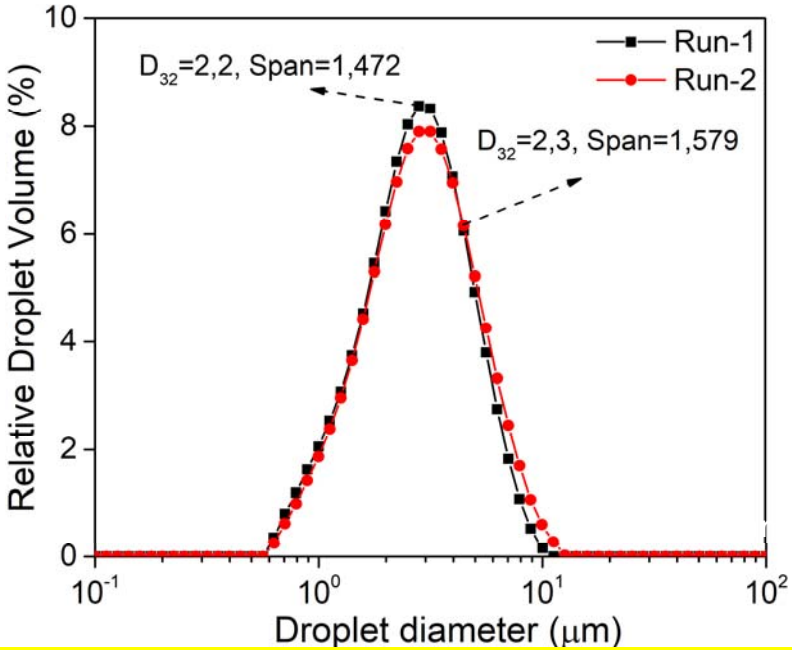
Zoppe et al., ***J. Colloid Interf. Sci.*** 2012, 202; Carrillo et al**.**, ***J Colloids & Interface Sci,*** 2012, 381, 171; Carrillo et al., ***Green Chem***, 2013, 15, 3377; Carrillo et al., ***ACS Applied Mat. & Interfaces*** 2014, 6, 22622; Nypelö et al., ***Cellulose*** 2014, 2557; Nypelö et al., ***ACS Appl. Mater. Interf.*** 2014, 16851; Carrillo et al., ***J. Colloid Interf. Sci.*** 2015, 166; Carrillo et al., ***Soft Matter*** 2016, 2721; Huan et al., ***Biomacromolecules*** 2017, 18, 4393; Capron et al., ***Current Opinion in Colloid & Interface Science***, 2017, 29, 83; Tardy et al. ***Current Opinion in Colloid & Interface Science***, 29, 57–67 (2017); Long et al., ***Green Chem*;** Ago et al., ***ACS Appl. Mater. Interf.*** 2016, 8, 23302; Li et al., ***J Colloid & Interface Sci.*** 2016, 482, 27 ; Li et al., ***ChemSusChem*** 2016, 9, 2460; Nypelö et al., ***Soft Matter***, 2015, 11, 2046 ; Ogunkoya, ***Applied Energy*** 2015, 154, 851 ; Tolosa et al., ***J Colloid & Interface Sci.***, 2006, 294, 182

CNC: interfacial activity - Pickering stabilizer



Kalashnikova et al. ***Biomacromolecules*** 13, 267 (2012)
Adapted with permission from American Chemical Society

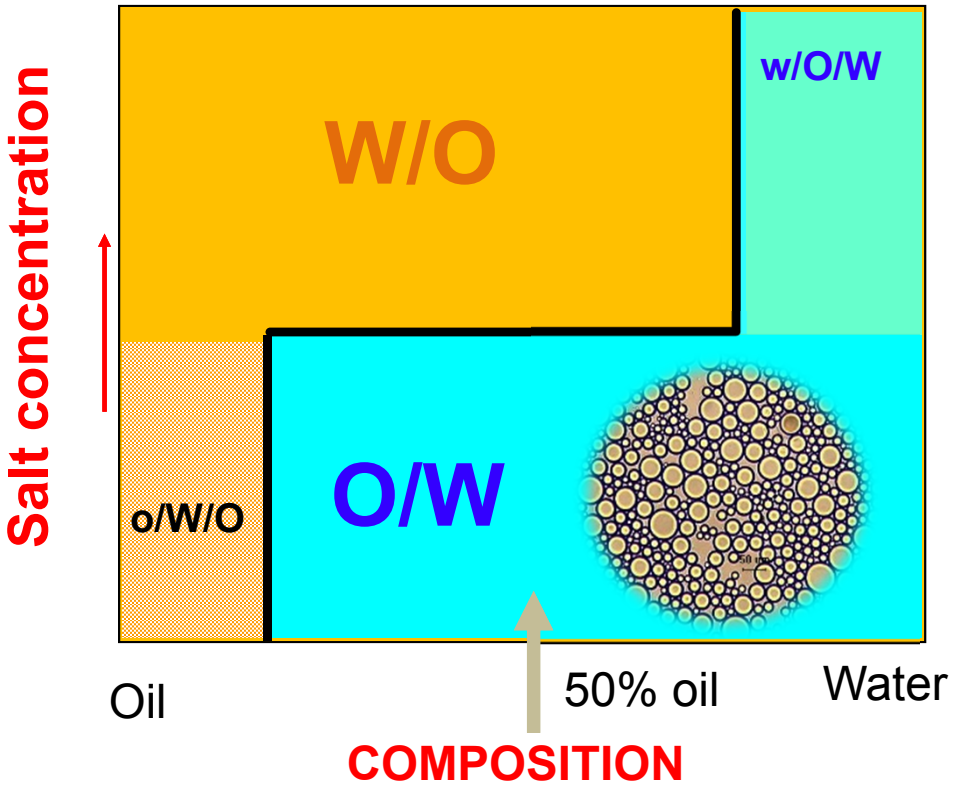
Aqueous phase:
90% water, 0.45% CNC, 0.16% NaCl
Oil phase:
10 wt% sunflower oil

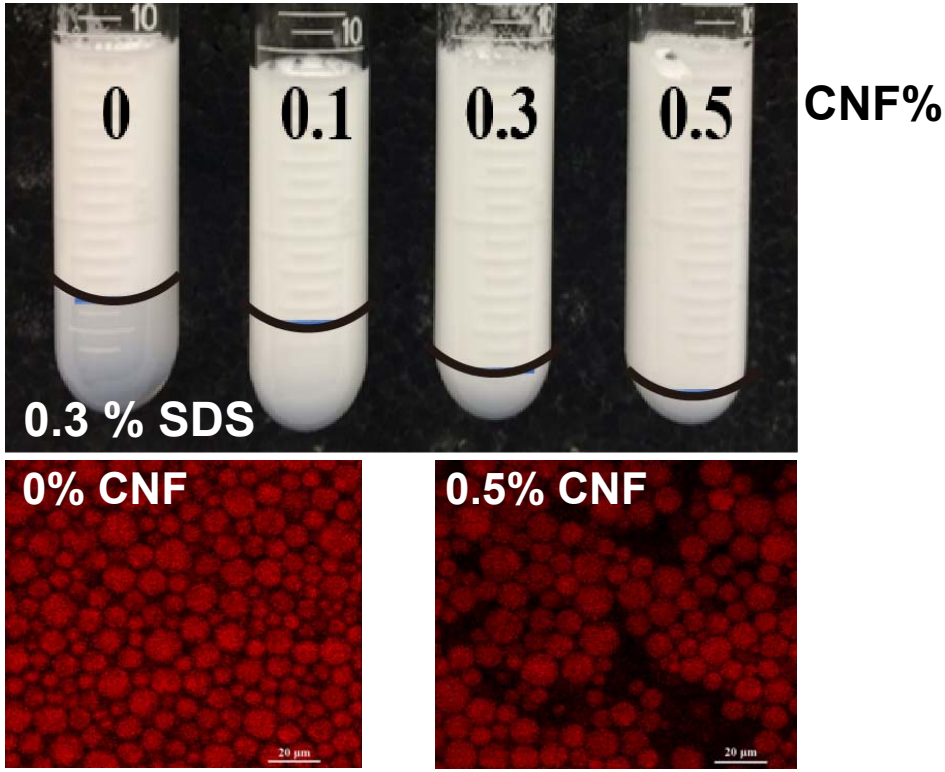


Note: CNF alone fails to stabilize this system stably

CNF: no or little interfacial activity

SDS-assisted emulsions for CNF system

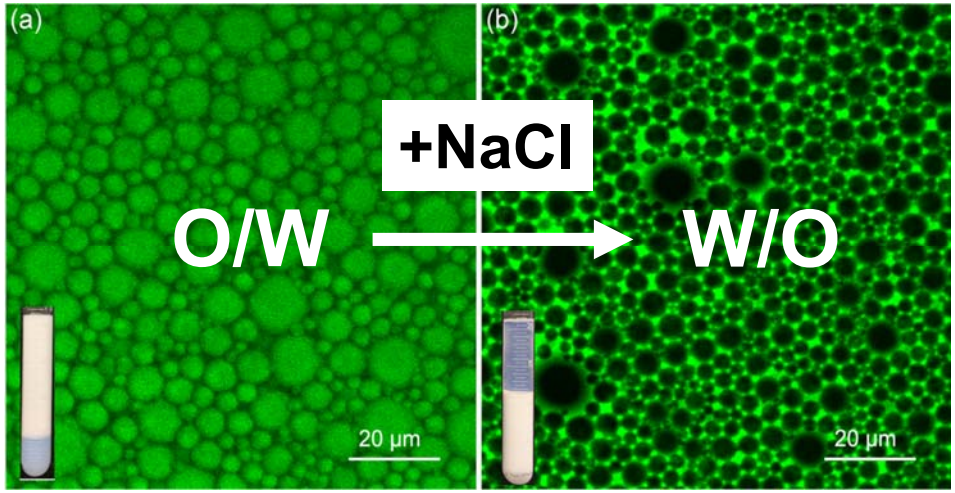




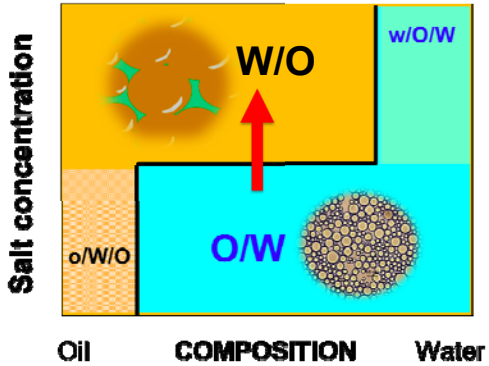
The addition of CNF increases emulsifying capacity with very small amounts of surfactant

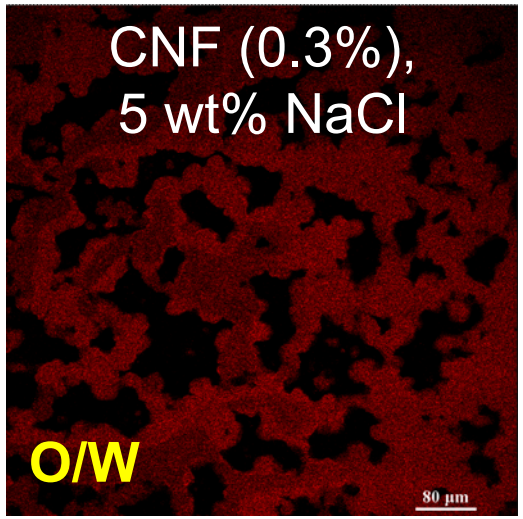
CNF delays or prevents transtional inversion

Possible exception:
Aqueous Counter Collision (ACC) CNF
(less hydrophilic)



Toluene/water (50% oil)
SDS = 1.2%

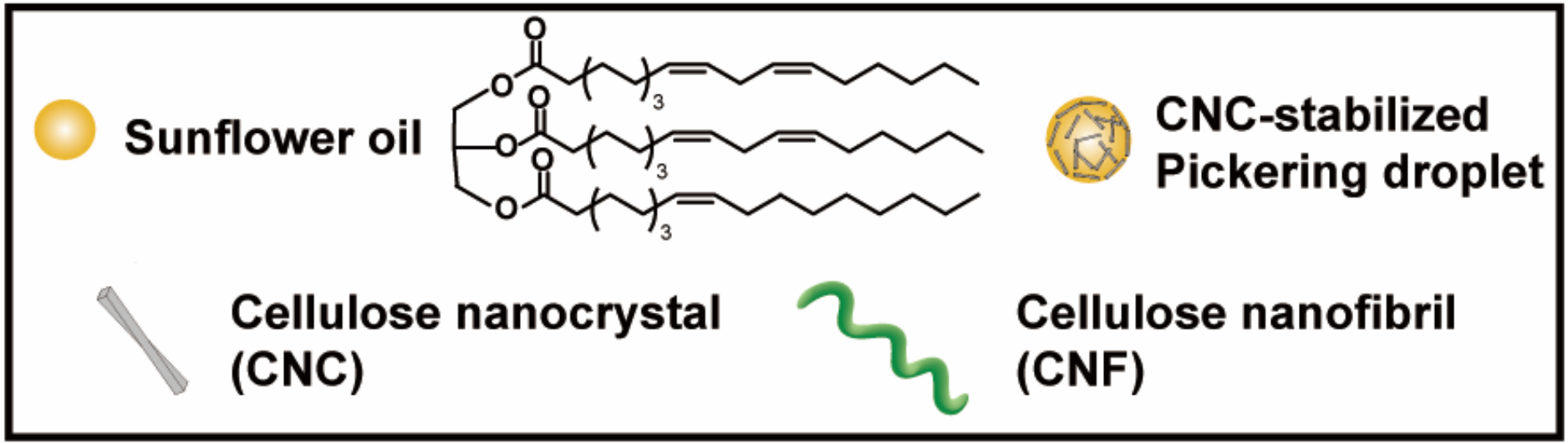




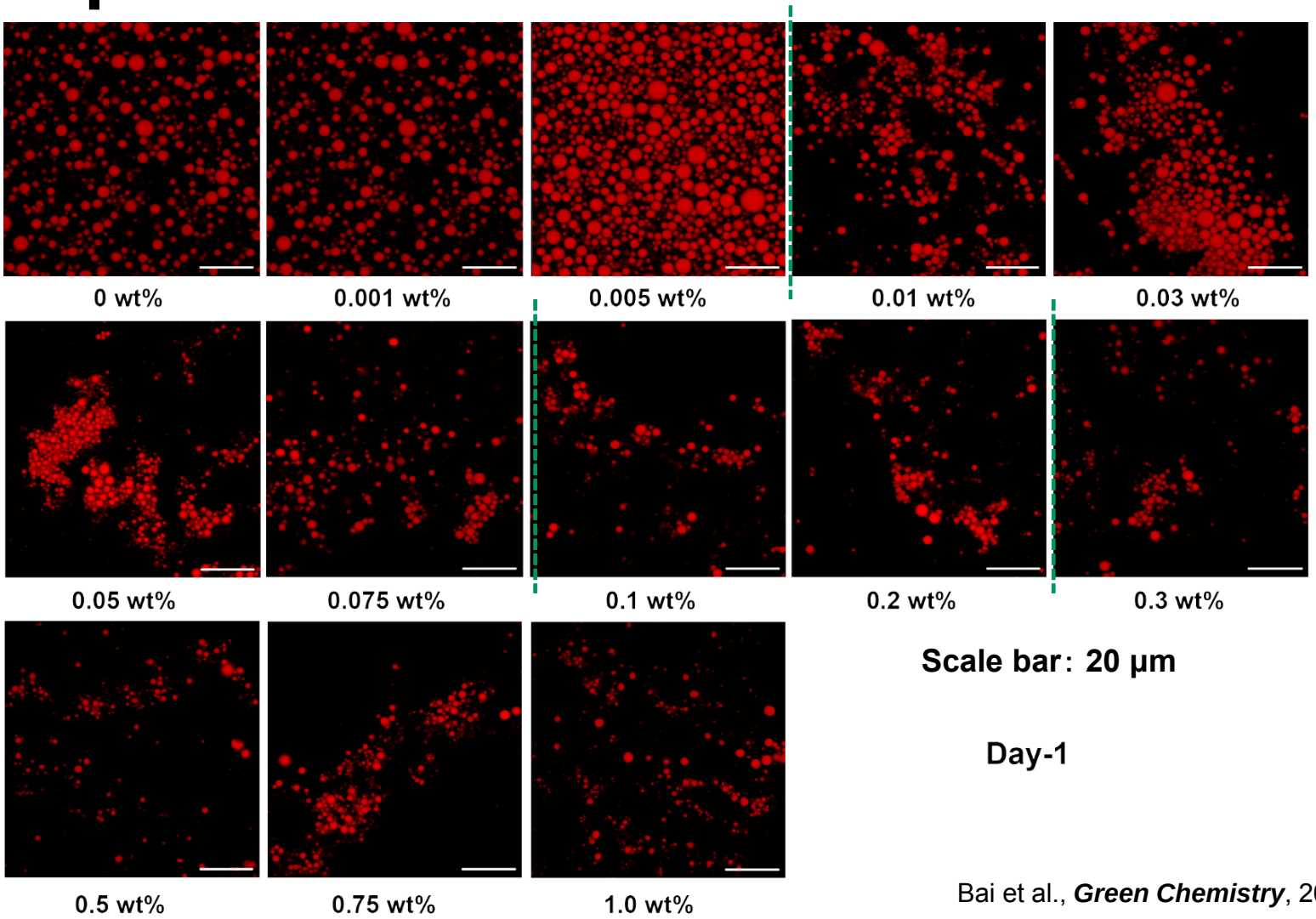
Huan et al., ***Biomacromolecules***, 18, 4393-4404 (2017).

Can different nanocelluloses be combined for synergistic stabilization (surfactant-free emulsions)?

CNC+CNF in emulsion stabilization



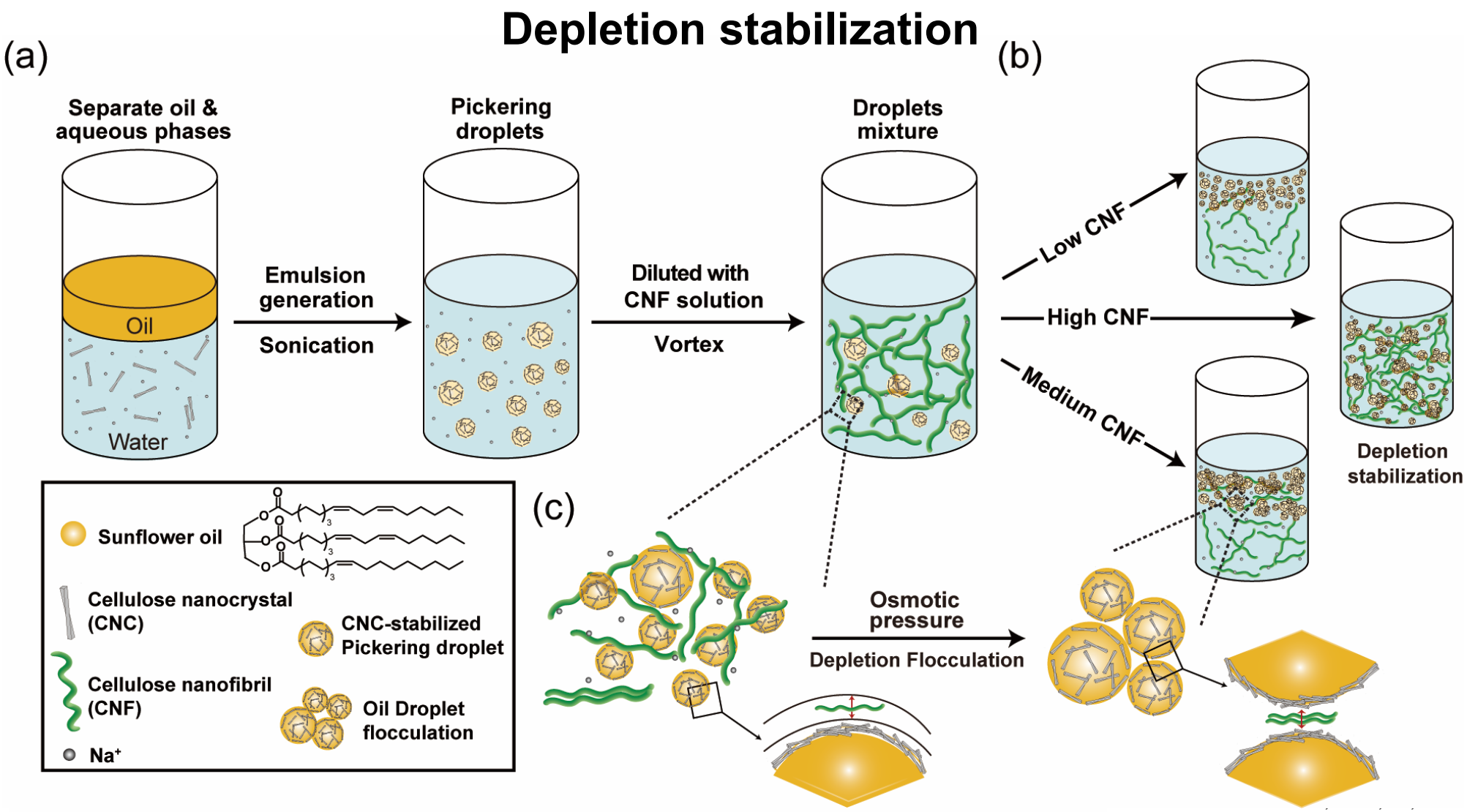
Droplet floc forms at varied CNF loading



Scale bar: 20 μm

Day-1

Bai et al., ***Green Chemistry***, 20, 1571-1582 (2018).


Depletion stabilization
(a)
Separate oil & aqueous phases
Oil
Water
Emulsion generation
Sonication
Pickering droplets
Diluted with CNF solution
Vortex
Droplets mixture
(b)
Low CNF
High CNF
Medium CNF
Depletion stabilization
(c)
Osmotic pressure
Depletion Flocculation
Sunflower oil
Cellulose nanocrystal (CNC)
CNC-stabilized Pickering droplet
Cellulose nanofibril (CNF)
Oil Droplet flocculation
Na+

CNC-stabilized emulsion inhibits lipid digestion

- C
- N
  -
  -
  -
  -
  -
- S
  -
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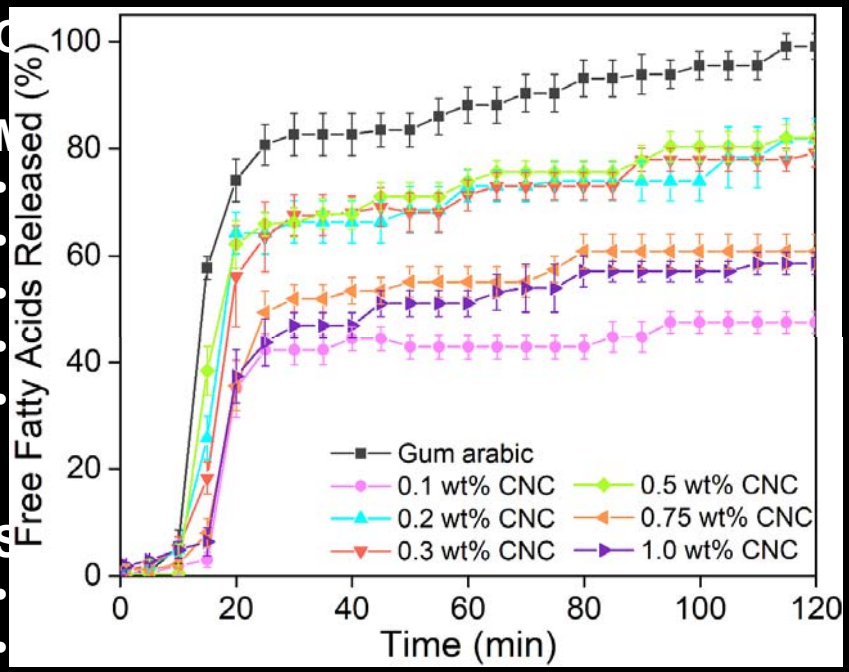
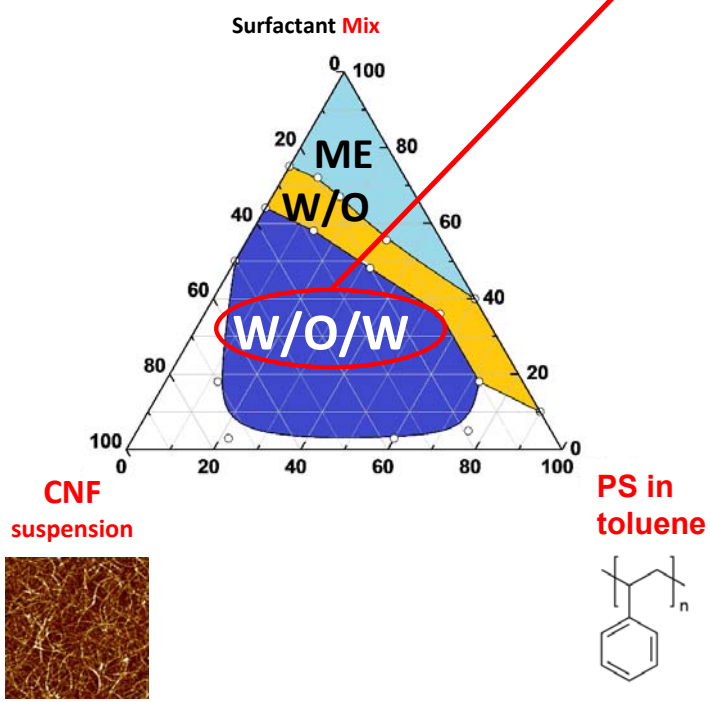


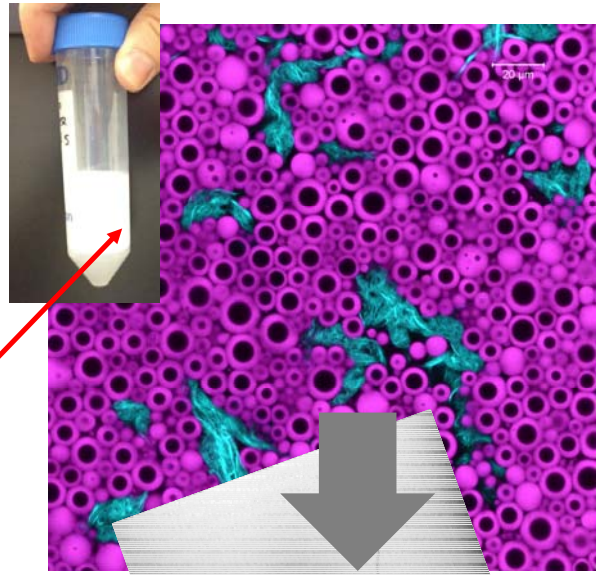
Bai et al., *Food Hydrocolloids,* DOI: https://doi.org/10.1016/j.foodhyd.2019.04.039 (2019)

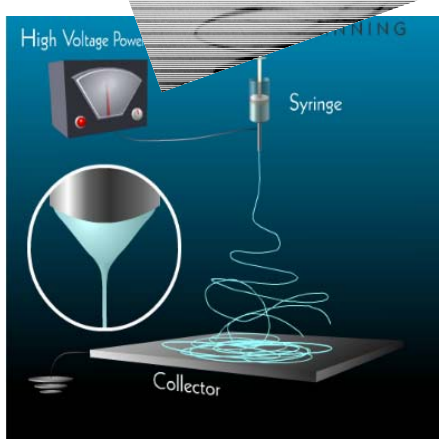
- Enzymes
- Biopolymers
- Agitation
- 30 min - 4 hours

- Enzymes
- Agitation
- 12-24 hours

CNF-based Double emulsions for high-quality electrospun nanofibers





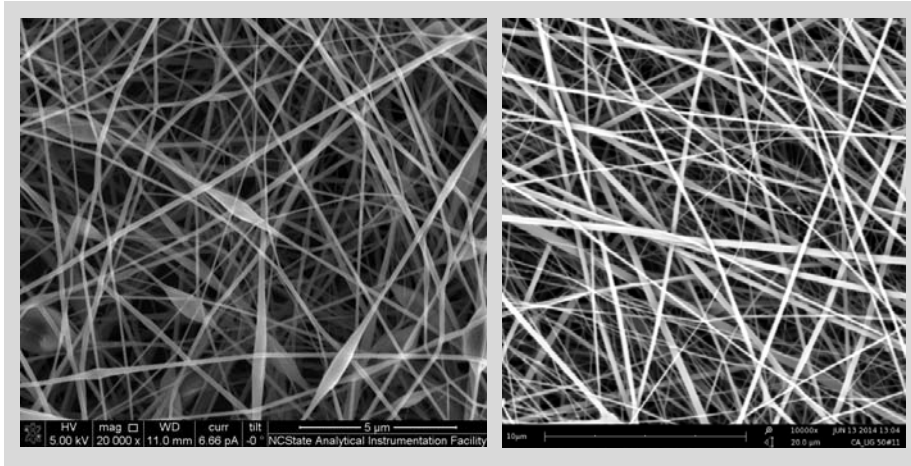


Carrillo et al., ***Soft Matter***, 12, 2721 (2016).

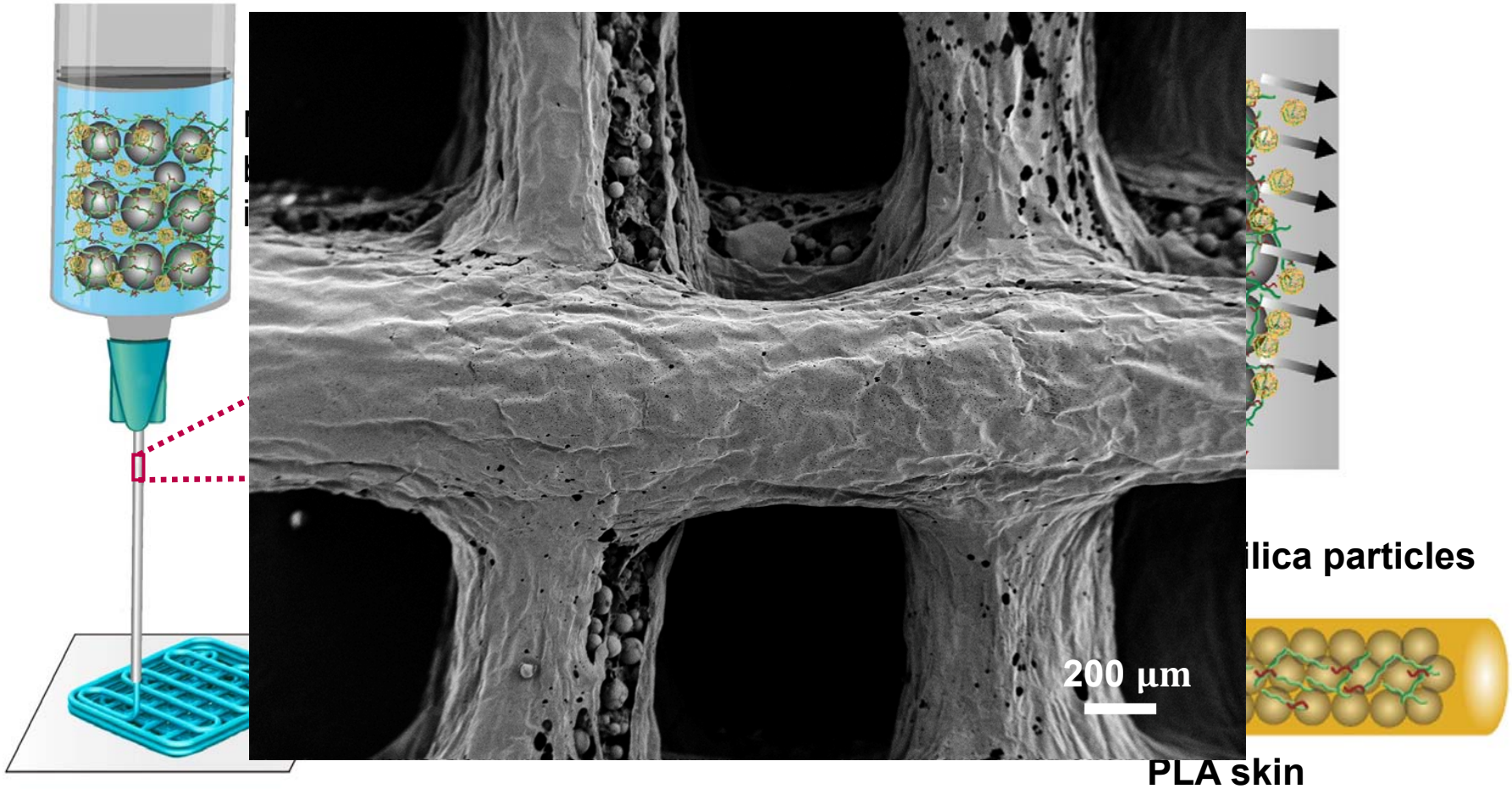
Hydrophobic-hydrophilic compatibility

Allows spinning **hydrophobic fibers** from a system containing CNF and initially up to **76 % water**

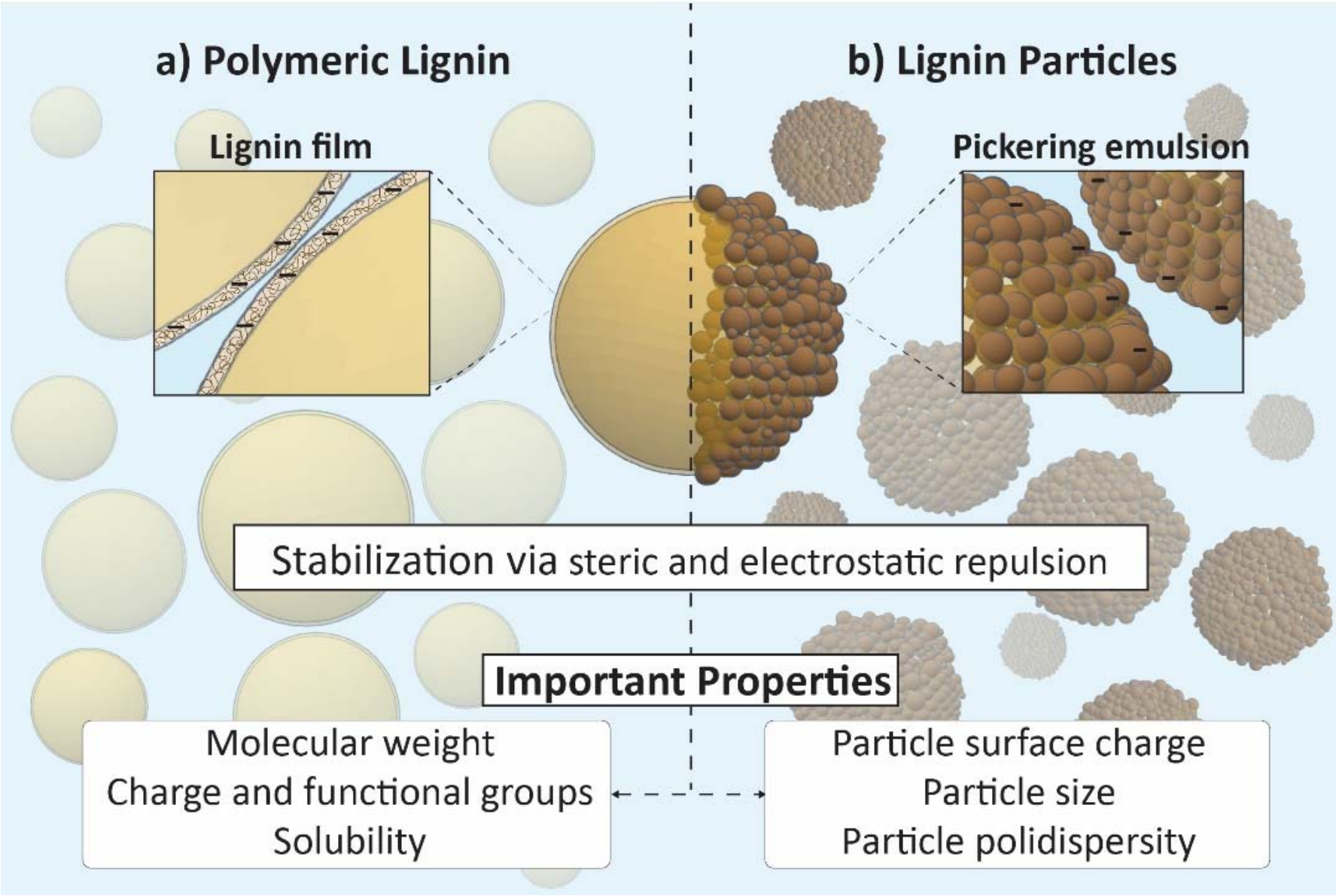
Composite Nanofibers



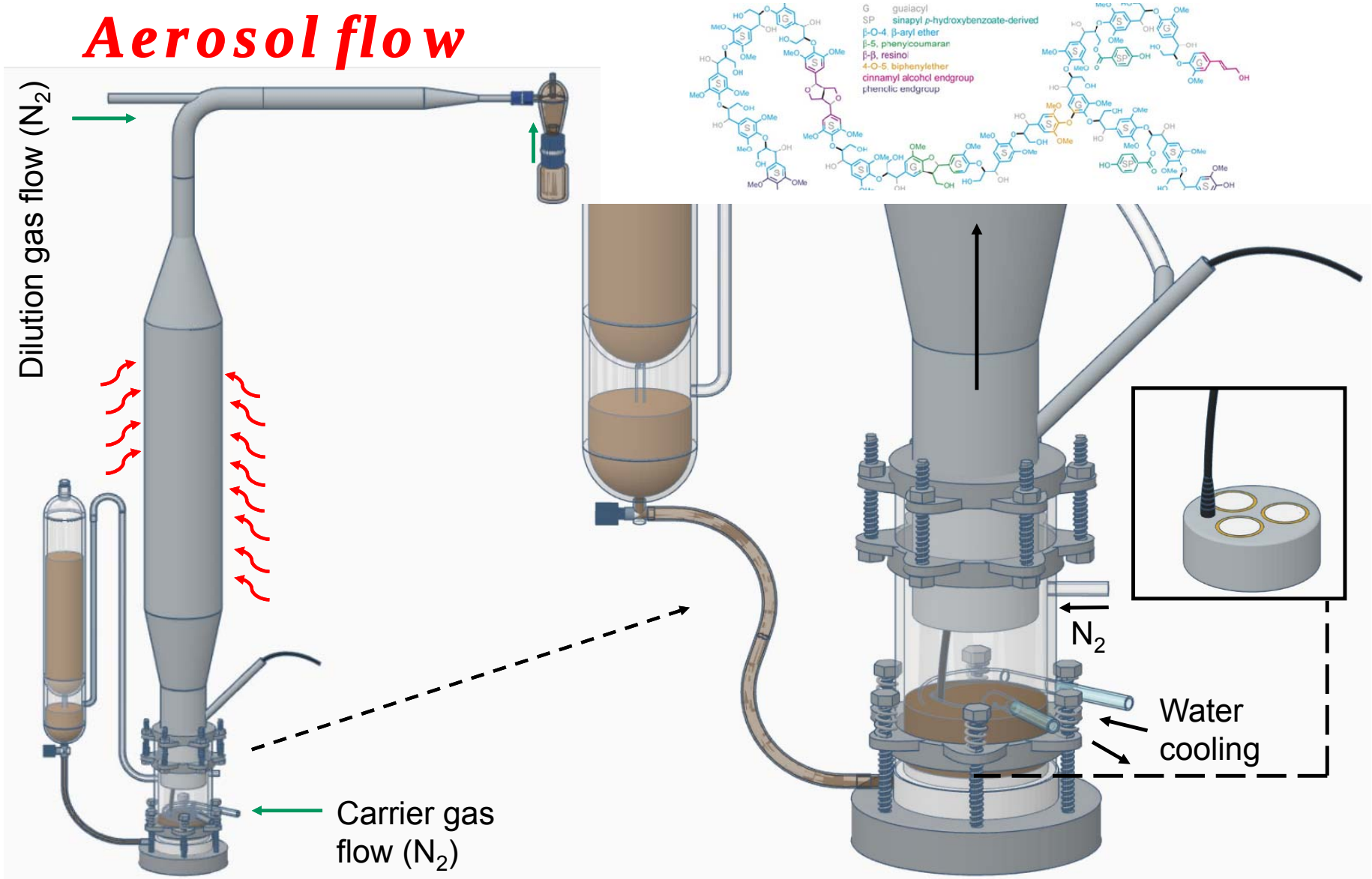
Nanocellulose-stabilized emulsion ink as 3D-printed functional materials

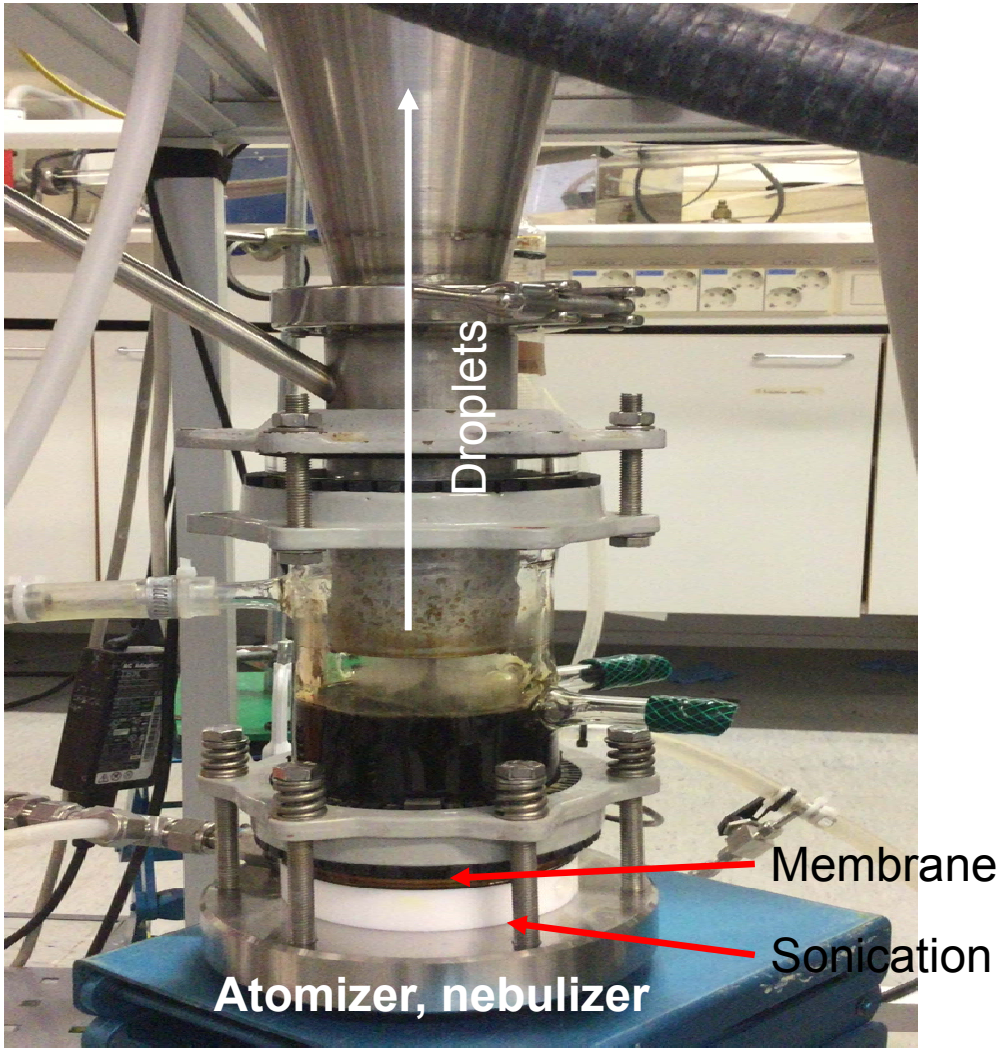


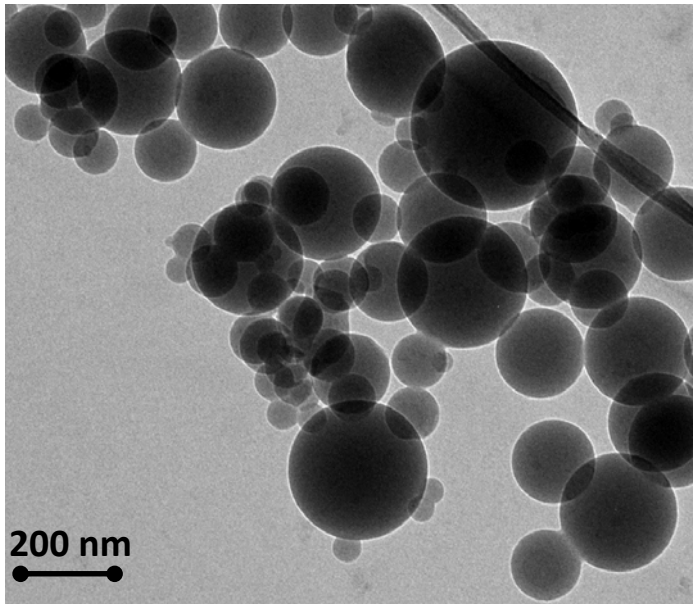
Lignin

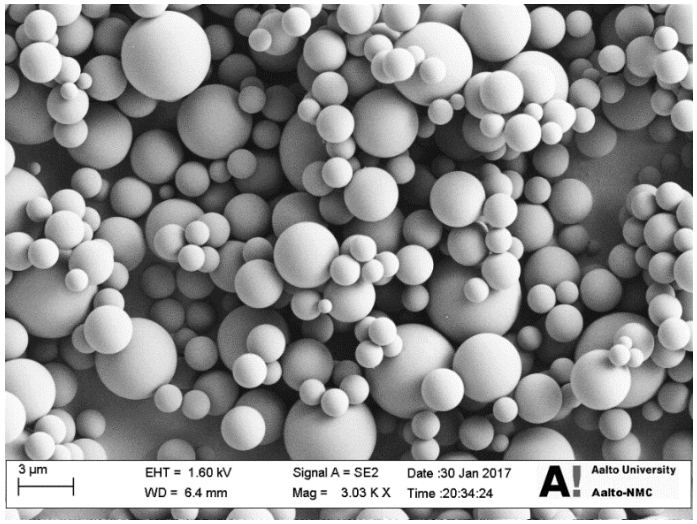

a) Polymeric Lignin
b) Lignin Particles
Lignin film
Pickering emulsion
Stabilization via steric and electrostatic repulsion
Important Properties
Molecular weight
Charge and functional groups
Solubility
Particle surface charge
Particle size
Particle polidispersity

Aerosol flow



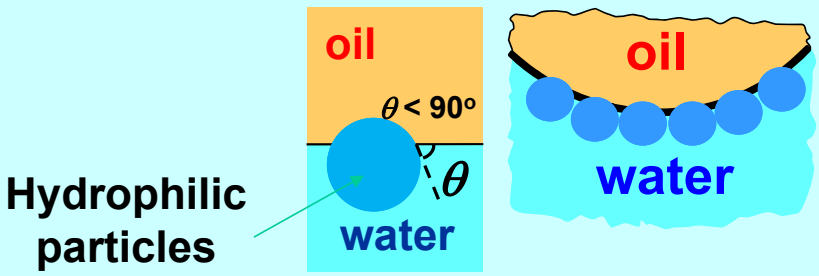


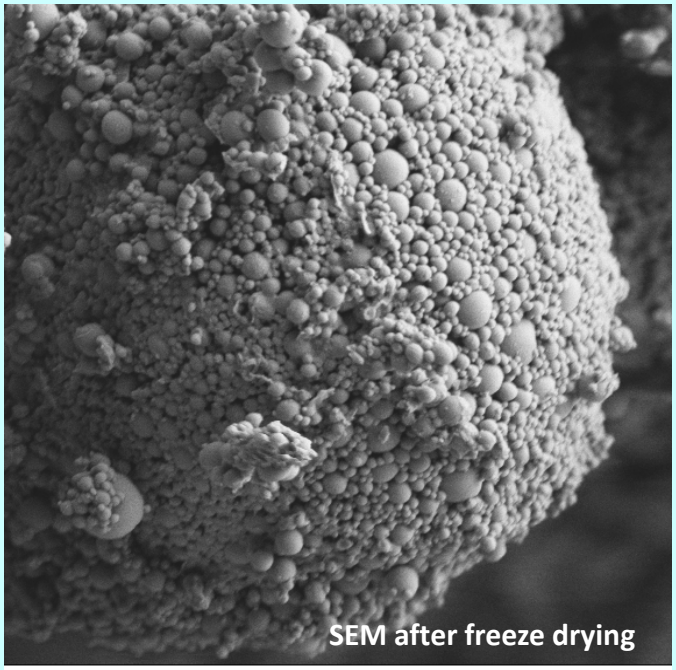




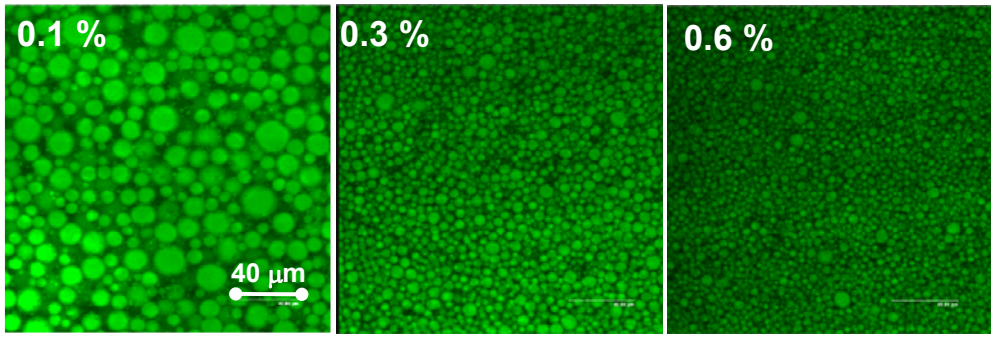
Li et al., ***ACS Sust. Chem. & Eng.*** (2018); Cusola et al., ***Langmuir*** (2018); Tardy et al., ***Green Chem.***, 20, 1335-1344 (2018)

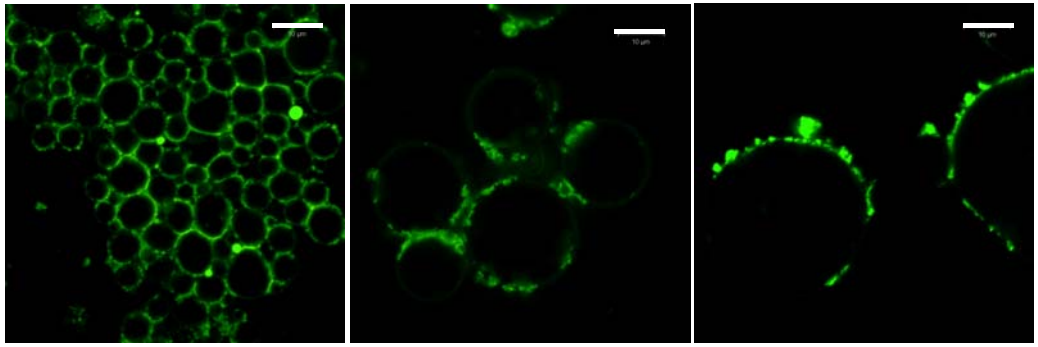
Lignin particles in Pickering stabilization

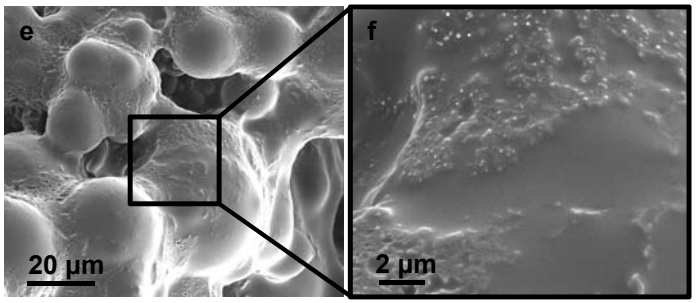




Green = Oil

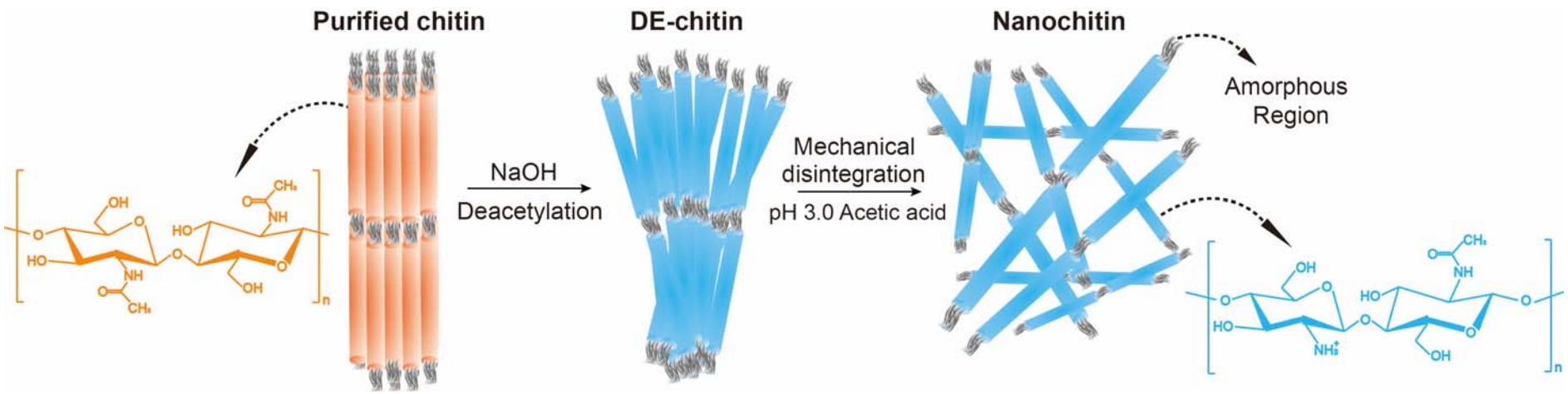






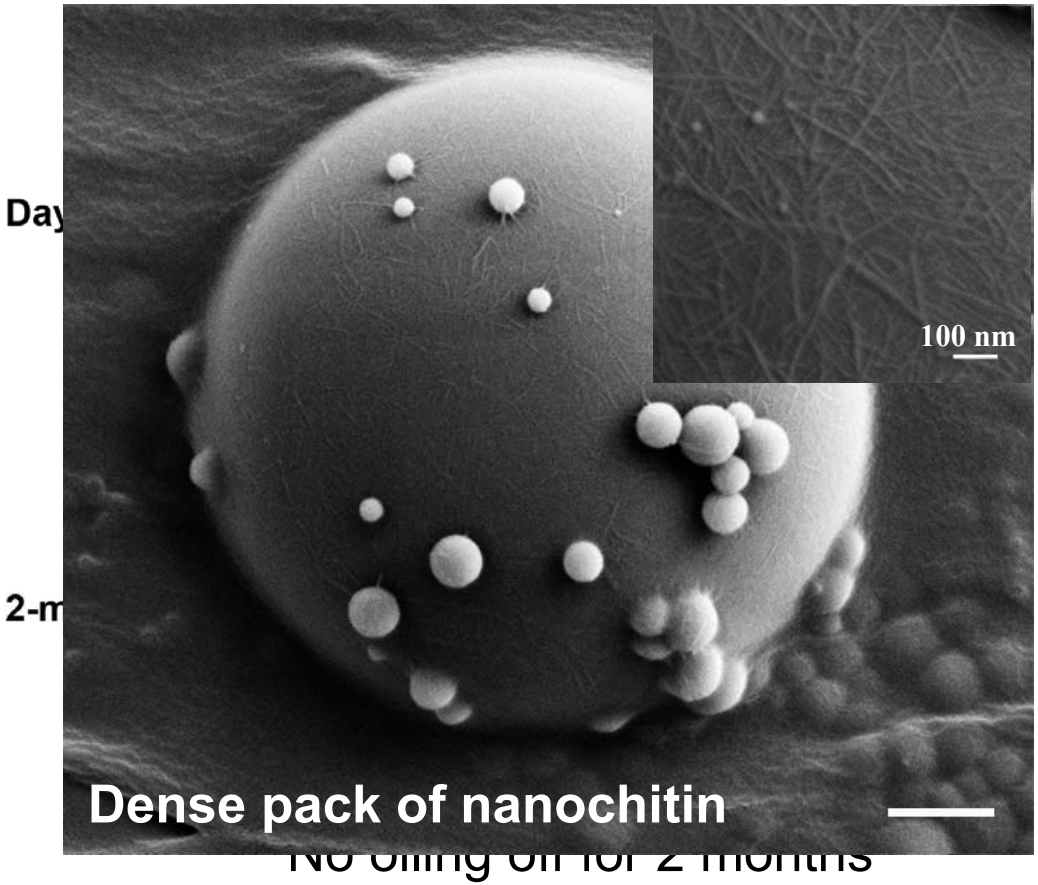
Carrillo et al, ***Soft Matter*** 2046-2054 (2015)
Ago et al., ***ACS Applied Mater. Interf.*** 8, 23302-23310 (2016)
Ago et al., ***MRS Bulletin***, 42, 371-378 (2017).

Nanochitin: a simple stabilizer for super-stable Pickering emulsions

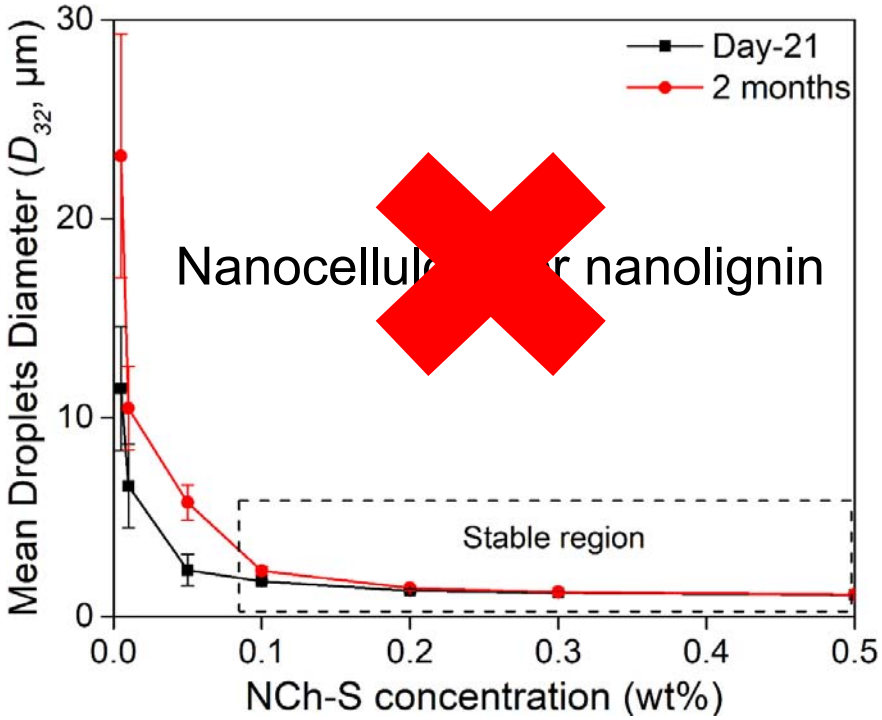


- **Improved interfacial wettability by surface acetyl groups**
- **Less repulsion due to uneven surface charge distribution**

Nanochitin achieves long-term super-stability

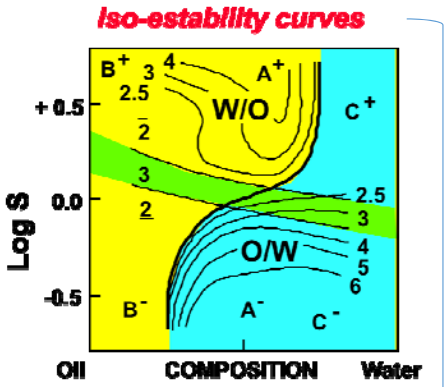


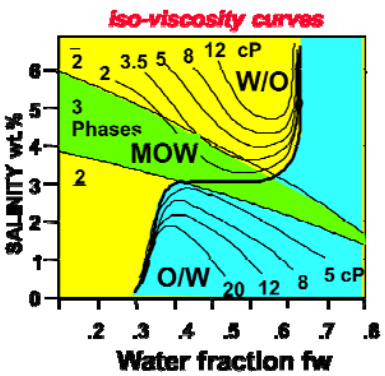
No oiling off for 2 months

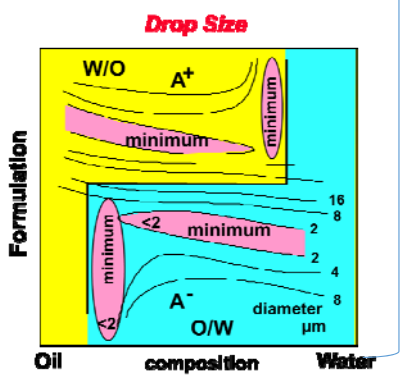


Droplet size was stable over 0.2 wt% nanochitin loading

Bai et al., ***ACS Sust. Chem. & Eng***, 7, 497-6511 (2018)







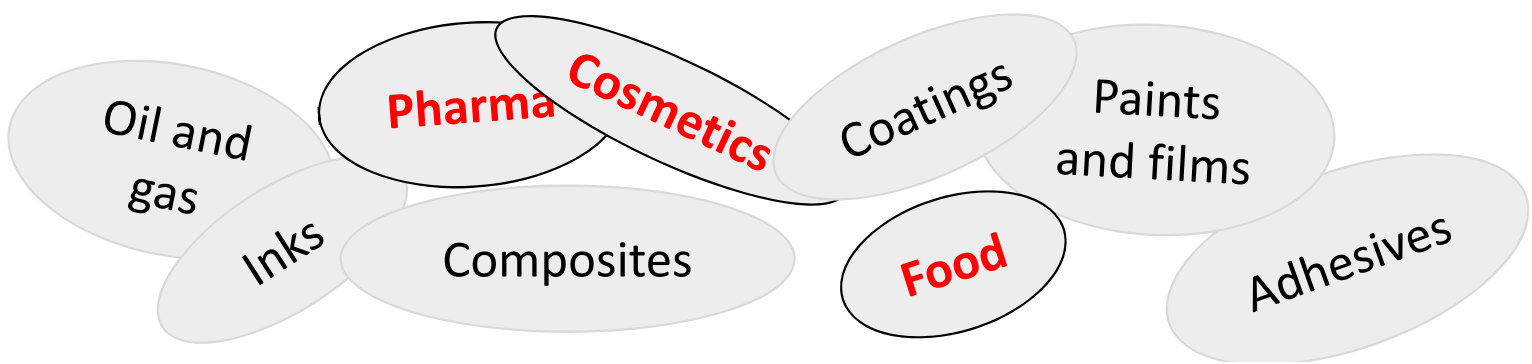
Closing thoughts

1. Nanocellulose, nanolignin and nanochitin:
Keeping them in water → emulsions?

2. Systematic description is possible:

Precise theoretical prediction to guide the preparation and to widen the use

3. Applications (including material development):



Thank you

PRESENTED BY

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BiCMat
Bio-based Colloids & Materials

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