Tunable Pickering Emulsions Based on Cellulose Nanomaterials and Cellulose Derivatives

Francesco **D'ACIERNO***, Isabelle **CAPRON**

INRAE – BIA Unit – NANO Team

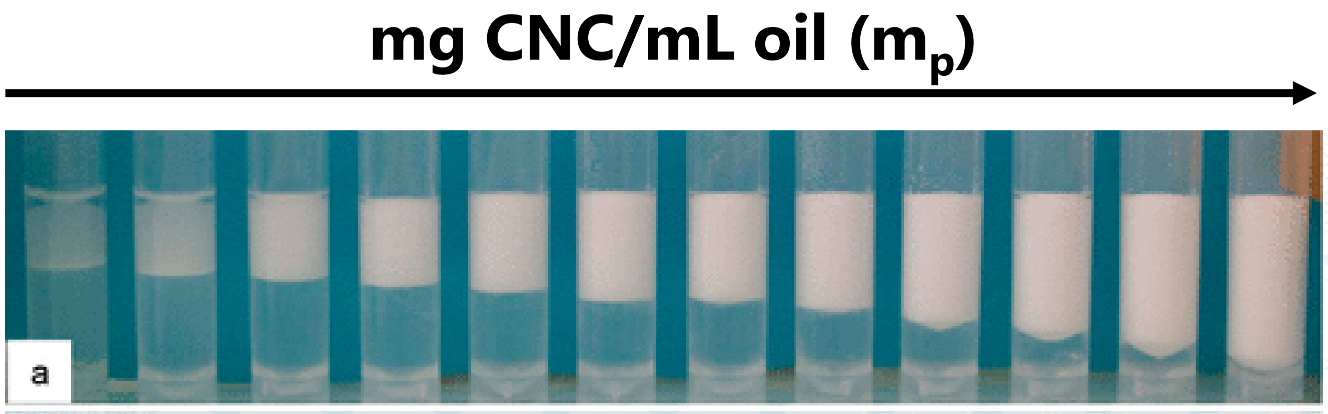
TAPPI Nano Conference 2023

13/06/2023

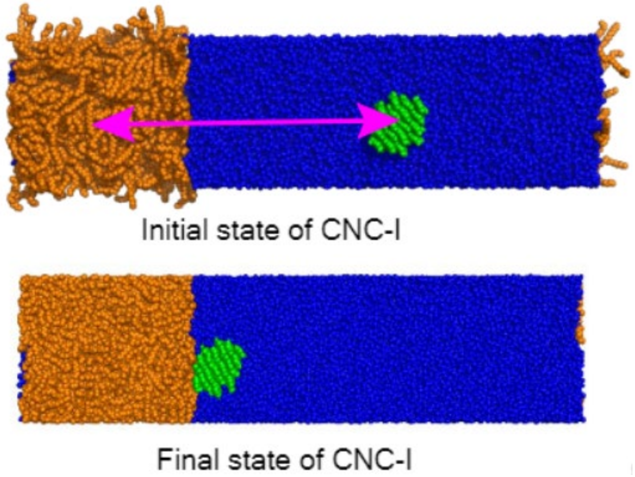
la science pour la vie, l'humain, la terre

Pickering Emulsions Stabilized by CNCs

- **Emulsions** are widely used to easily **encapsulate** and **carry** various liquids.
- CNCs can be used to stabilize oil-in-water (O/W) **Pickering emulsions**.
- CNCs **irreversibly adsorb** on the surface of oil droplets, forming a protecting shell that can resist over time to **mechanical and chemical stress**.



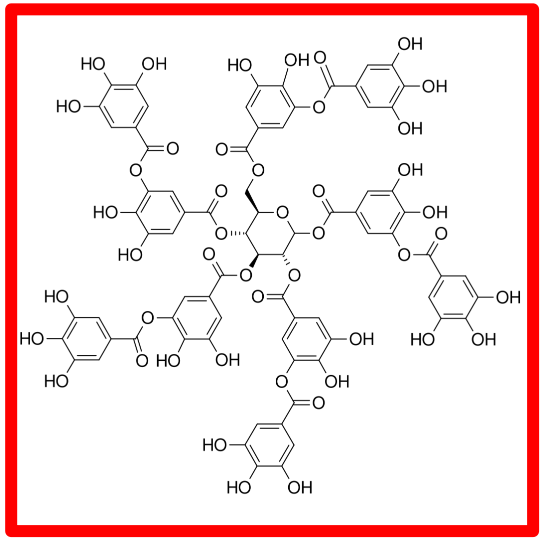
Langmuir **2011**, *27*, 7471-7479.

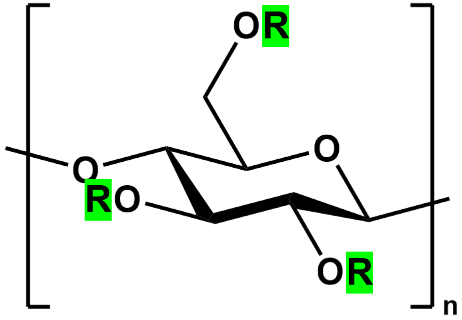


Biomacromolecules **2022**, 23, 3517–3524.

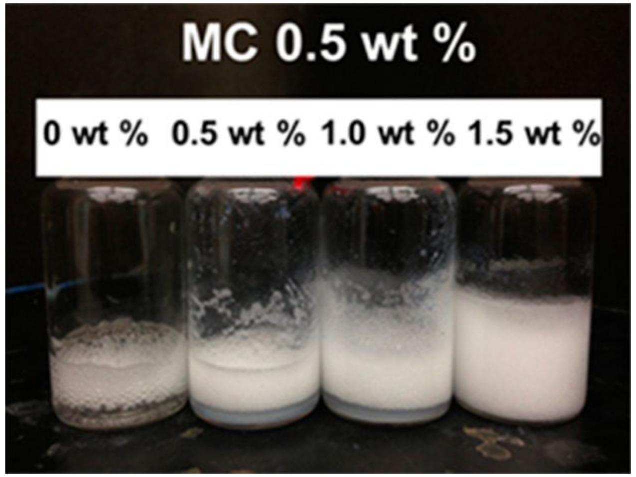
Surface Adsorption of Tannic Acid (TA) and Alkyl (Ether) Cellulose Derivatives (ACDs)

- **Commercially** important bio-compounds, <u>**not toxic**</u>.
- **Tannic acid** (**TA**): paint, food additive, burn medication.
- **Methyl cellulose** (**MC**): thickener, food emulsifier, binder in medications.
- **Ethyl cellulose** (**EC**): ingredient in adhesives, food additive, microencapsulant.
- Literature on CNC@MC and CNC@EC: emulsions, foams and composites (**high ACD fraction, >90 wt%**).





R = $(CH_2)_nCH_3$

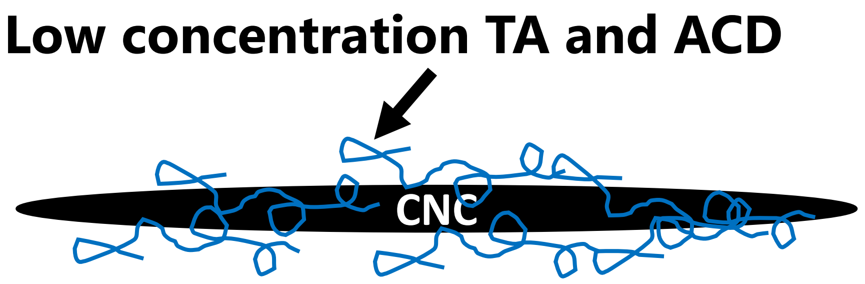


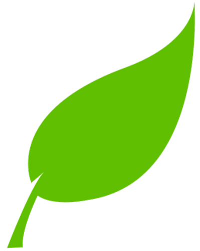
CNC

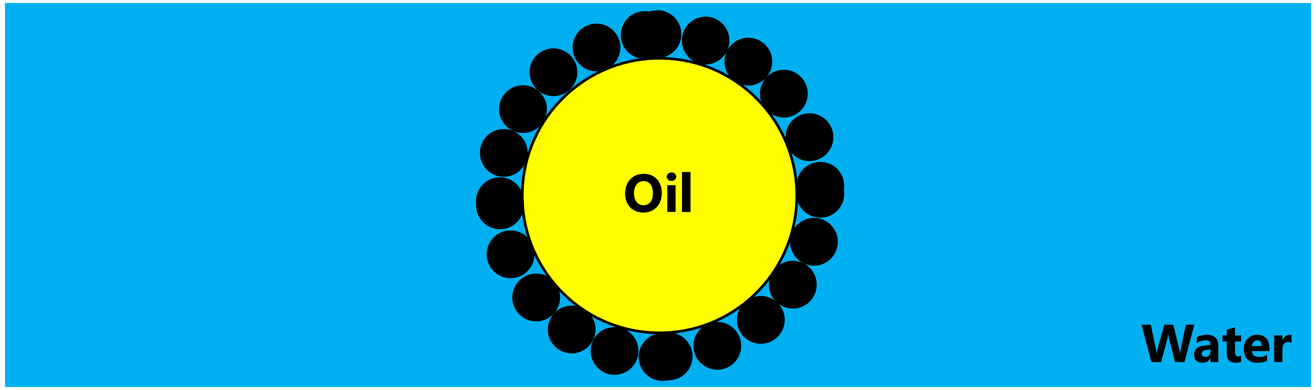
Biomacromolecules **2016**, *17*, 4095–4099

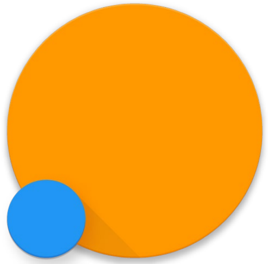
Objectives

- Prepare **sustainable** CNCs **coated** with TA or ACDs (lower TA or ACD fraction) to control their emulsification properties.
- Prepare **novel Pickering emulsions** with increasing **stability** and various **droplet sizes and morphology** to tailor properties and performance to specific applications (controlled release, mouthfeel, bioavailability, etc).







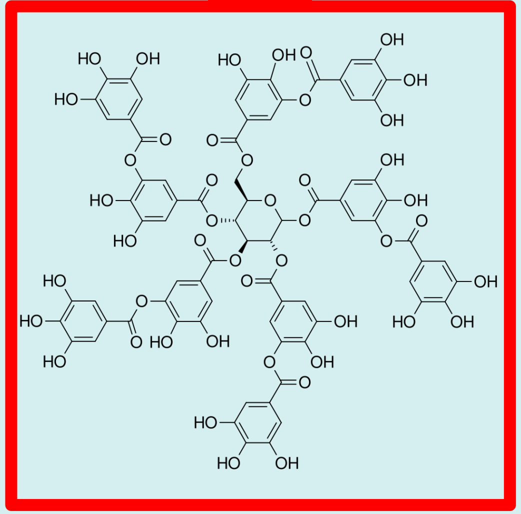


Preparation of CNC@TA Emulsions

CNC

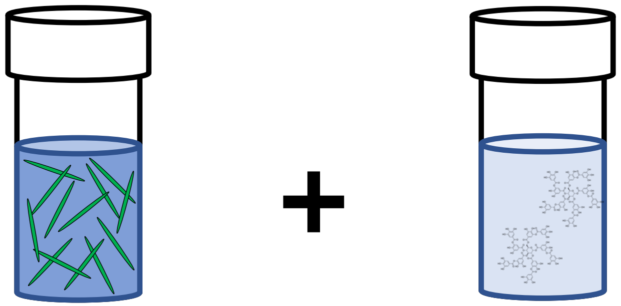
M_w=40000 g/mol

TA



$C_{76}H_{52}O_{46}$

M_w=1701.19 g/mol



20 g/L CNC in H_2O

1 g/L TA in H_2O

mixing

pH 8

dialysis

dilution

Colloidally stable 5 g/L suspensions

Aqueous phase percentage: 70%

0.5, 1.0, 2.0, 3.0, 4.0 g/L CNC@TA in H_2O

+

hexadecane

Oleic phase percentage: 30%

sonication

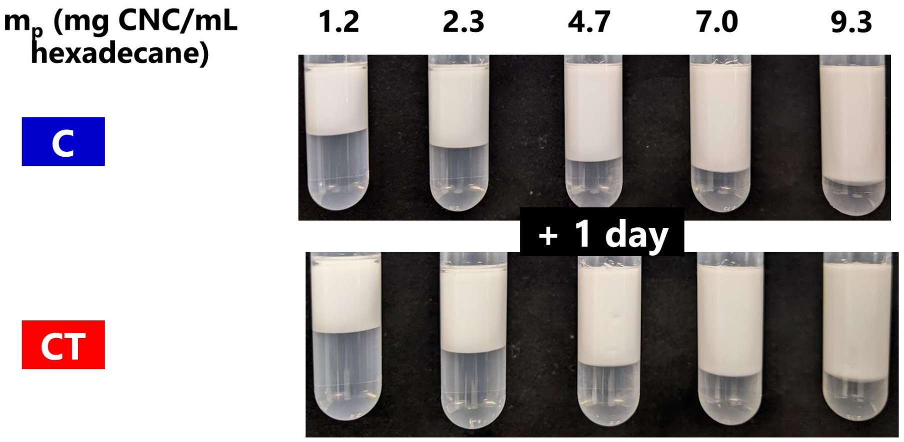
Pickering emulsions

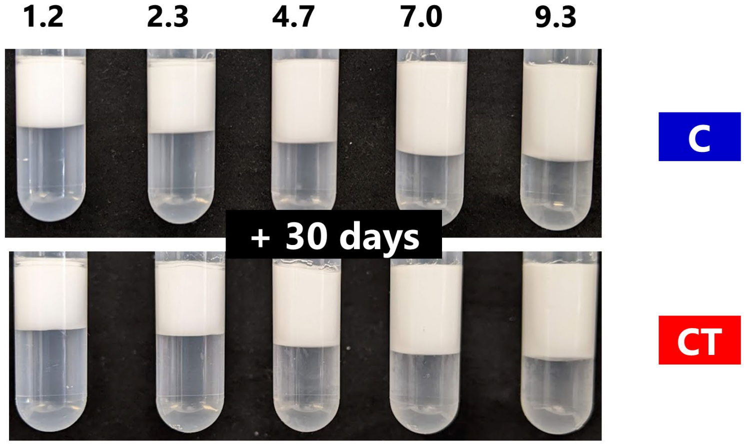
m_p=1.2, 2.3, 4.7, 7.0, 9.3

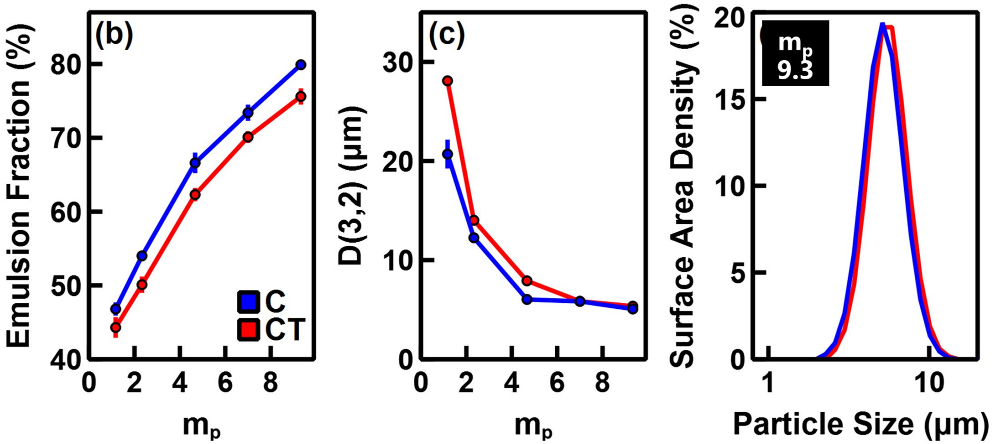
CNC vs CNC@TA Emulsions

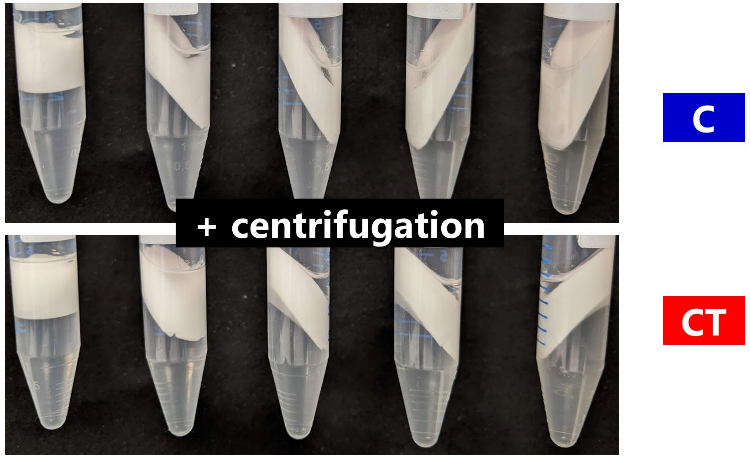
Camera
Granulometry

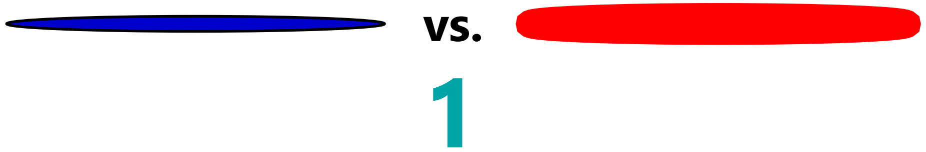
- CNC and CT: **shelf stability** over time, **fair** resistance to mechanical stress.
- CT emulsion **volume** is **lower**, and **droplet size** is **larger**.
  1. Thick TA coating, large interfacial gaps.
  2. Altered interfacial properties.

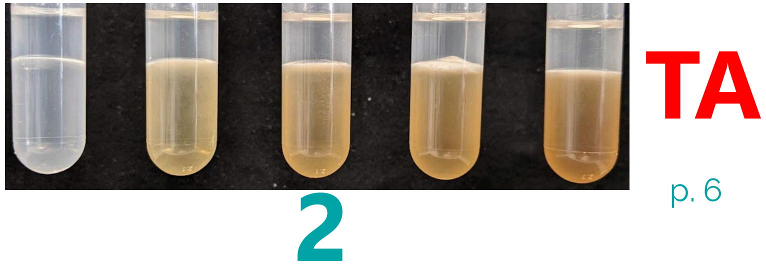






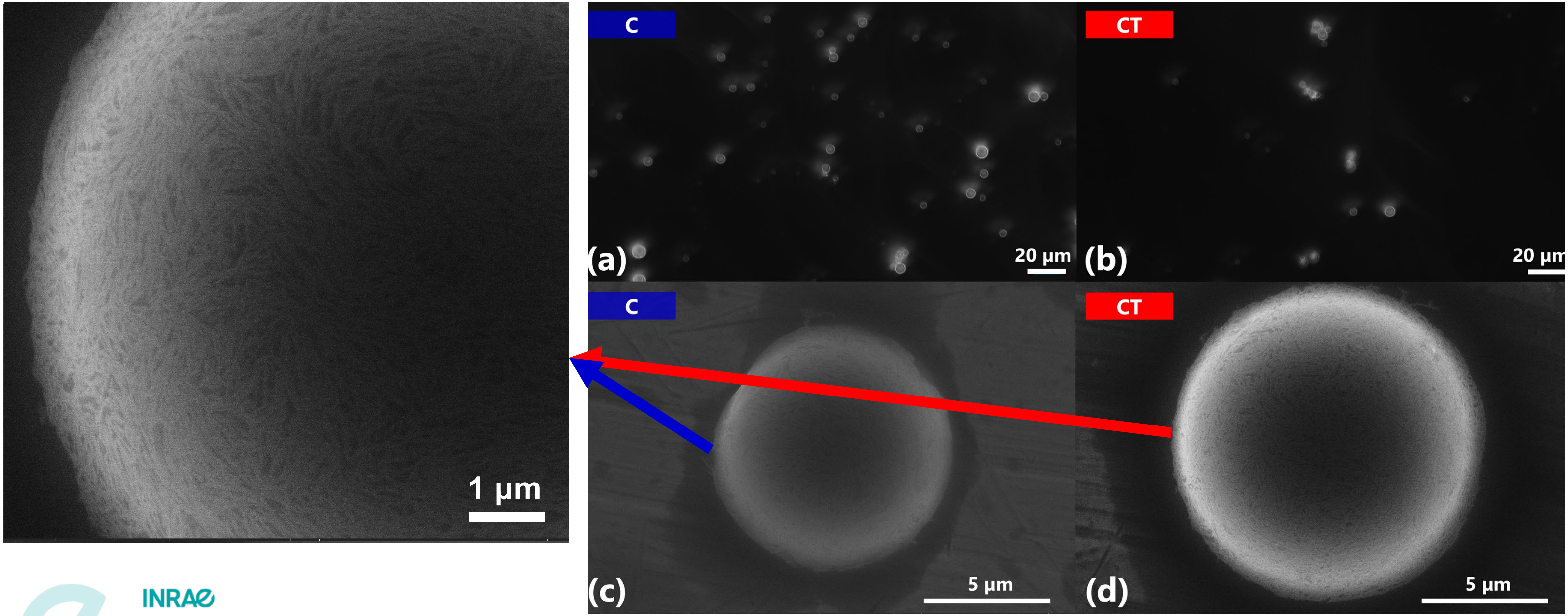




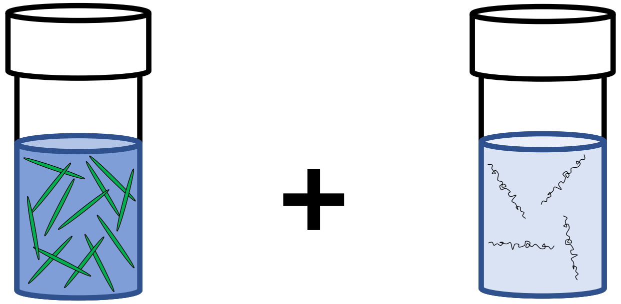


CNC vs CNC@TA Emulsions

- CNC and CNC@TA: monomodal distribution, **no visible sign of aggregation**.
- CNC@TA droplet: presence of **interfacial gaps**.



Preparation of CNC@MC Emulsions

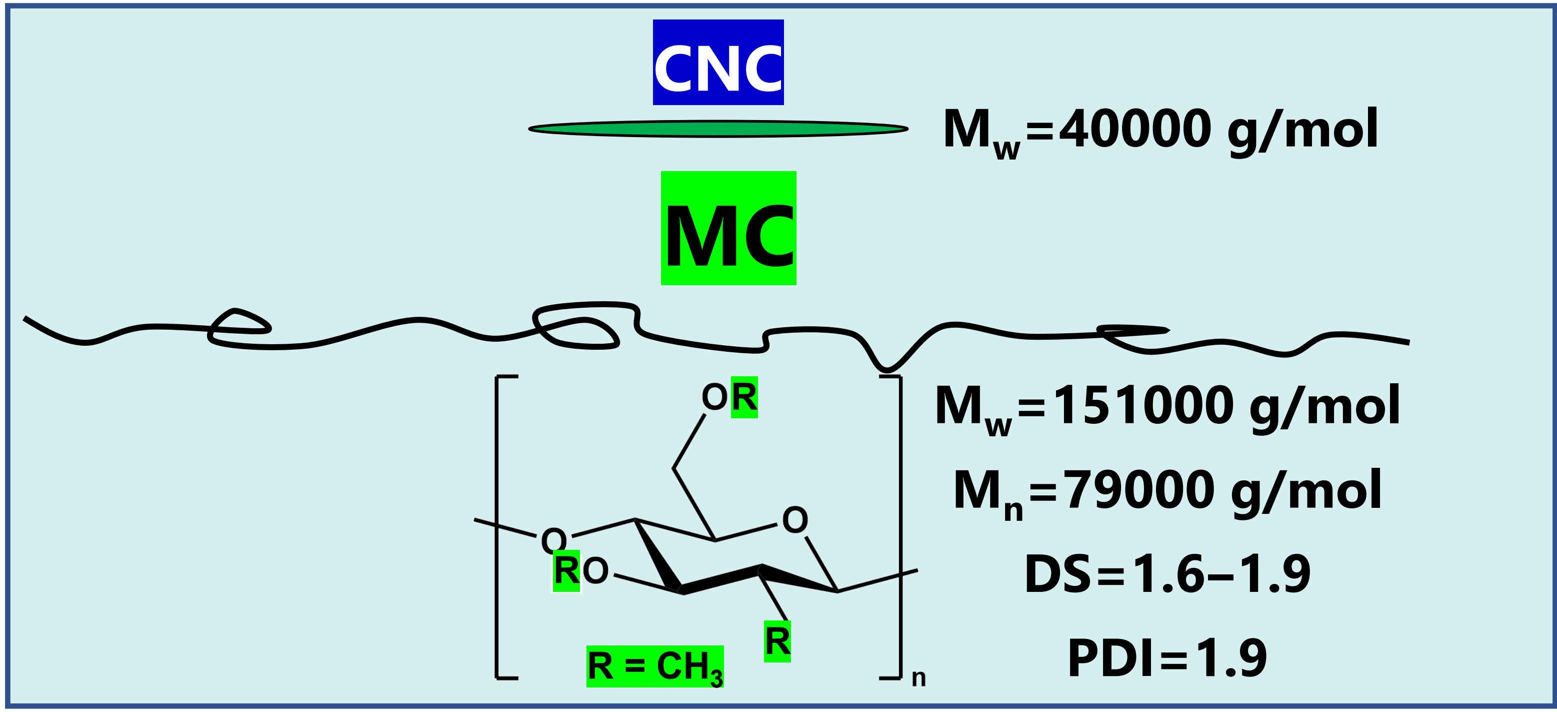


5 g/L CNC in H_2O + 1 g/L MC in H_2O

Various MC weight fractions
→ **5%, 20%, 40%** (w/w)

mixing

H_2O evaporation through rotovapor



Colloidally stable 5 g/L suspensions

Aqueous phase percentage: 70%

0.5, 1.0, 2.0, 3.0, 4.0 g/L CNC@MC in H_2O

+

hexadecane

Oleic phase percentage: 30%

sonication →

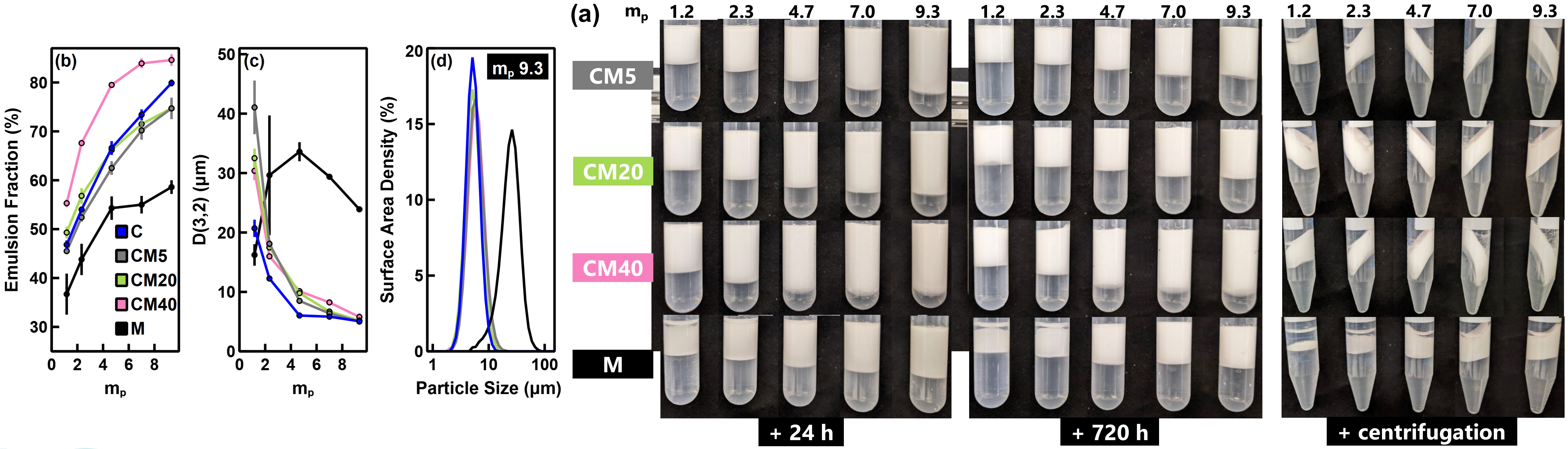
Pickering emulsions

m_p=1.2, 2.3, 4.7, 7.0, 9.3

Camera
Granulometry

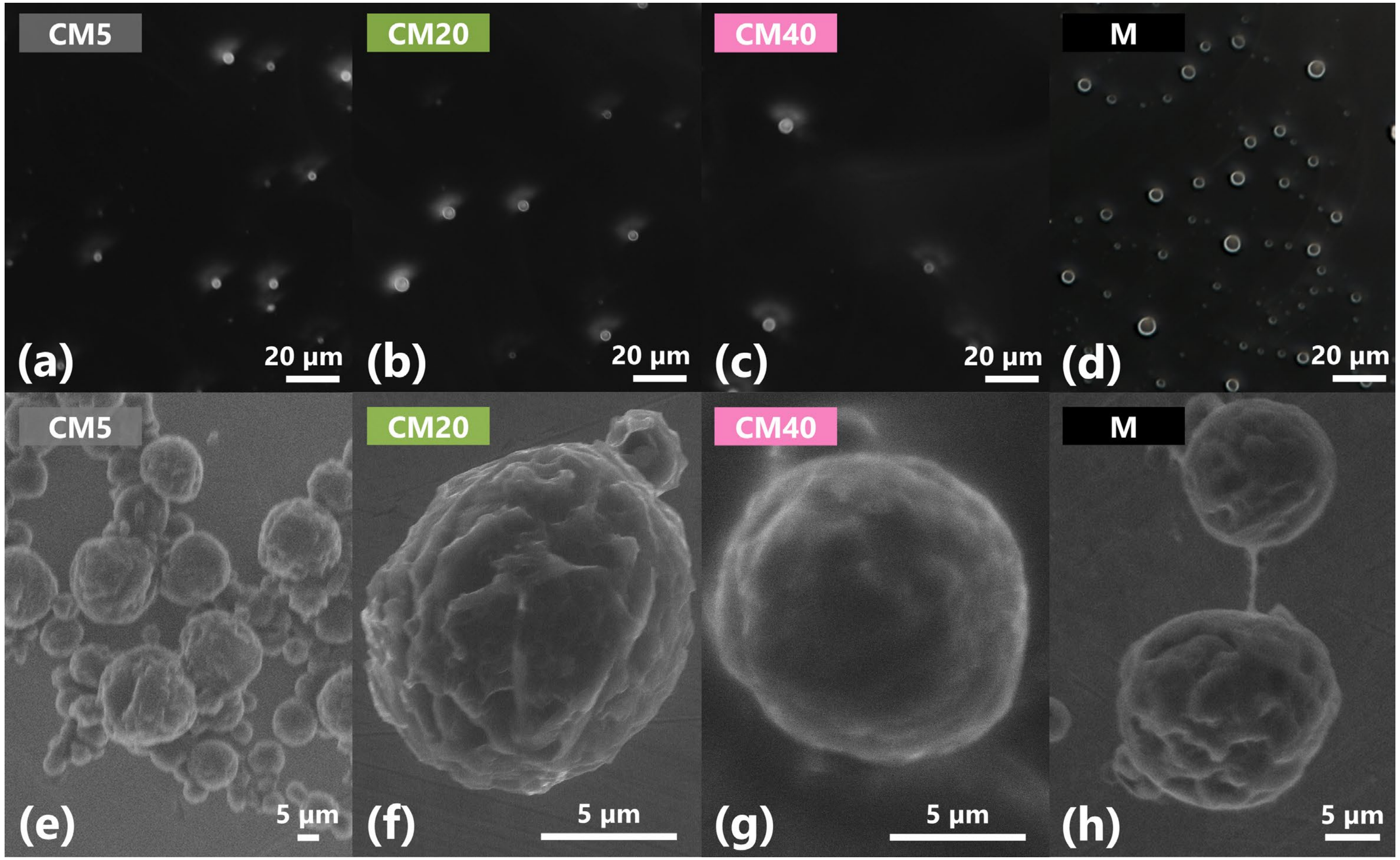
CNC vs CNC@MC Emulsions

- CM: excellent **shelf stability** and resistance upon centrifugation, better than CNC → ↑ particle coverage, steric hindrance, gel network formation, rheological properties.
- CM40 **volume** is significantly **larger**, and **droplet size** upon MC addition is always bigger than CNC → reduced adsorption at oil interface with ↑ hydrophilic MC.

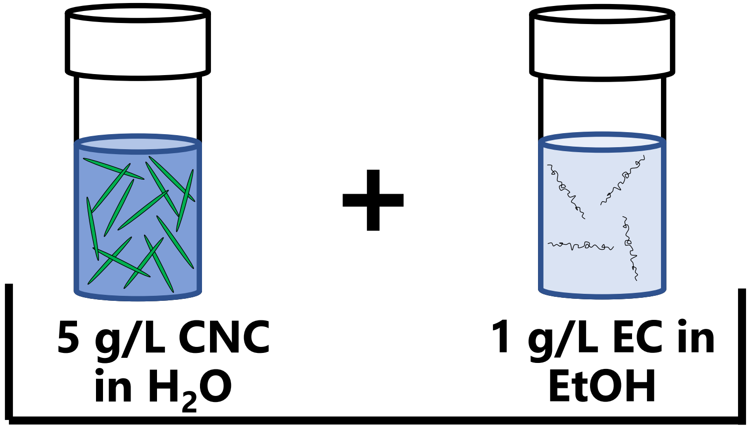


CNC vs CNC@MC Emulsions

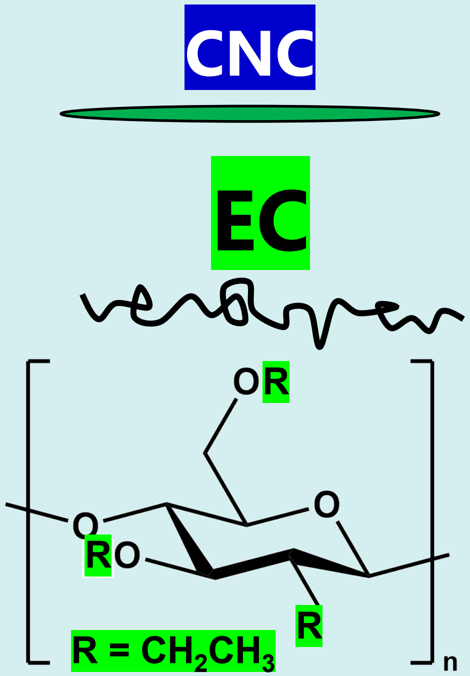
- CM and MC: **no apparent sign of aggregation**.
- CM droplet: quasi spherical, rough surface, partially aggregated → MC interaction.



Preparation of CNC@EC Emulsions



Various EC weight fractions
→ **5%, 20%, 40%** (w/w)



M_w=40000 g/mol

M_w=33700 g/mol
M_n=9800 g/mol
DS=1.44
PDI=3.4

mixing

EtOH evaporation through rotovapor

Colloidally stable 5 g/L suspensions

Aqueous phase percentage: 70%

0.5, 1.0, 2.0, 3.0, 4.0 g/L CNC@EC in H_2O

+

hexadecane

Oleic phase percentage: 30%

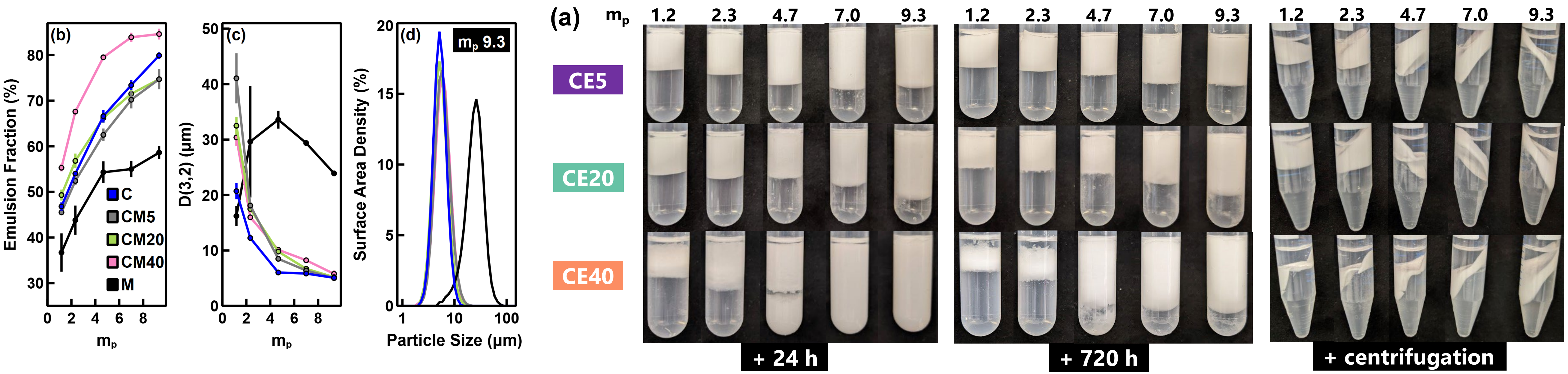
sonication →

Pickering emulsions

m_p=1.2, 2.3, 4.7, 7.0, 9.3

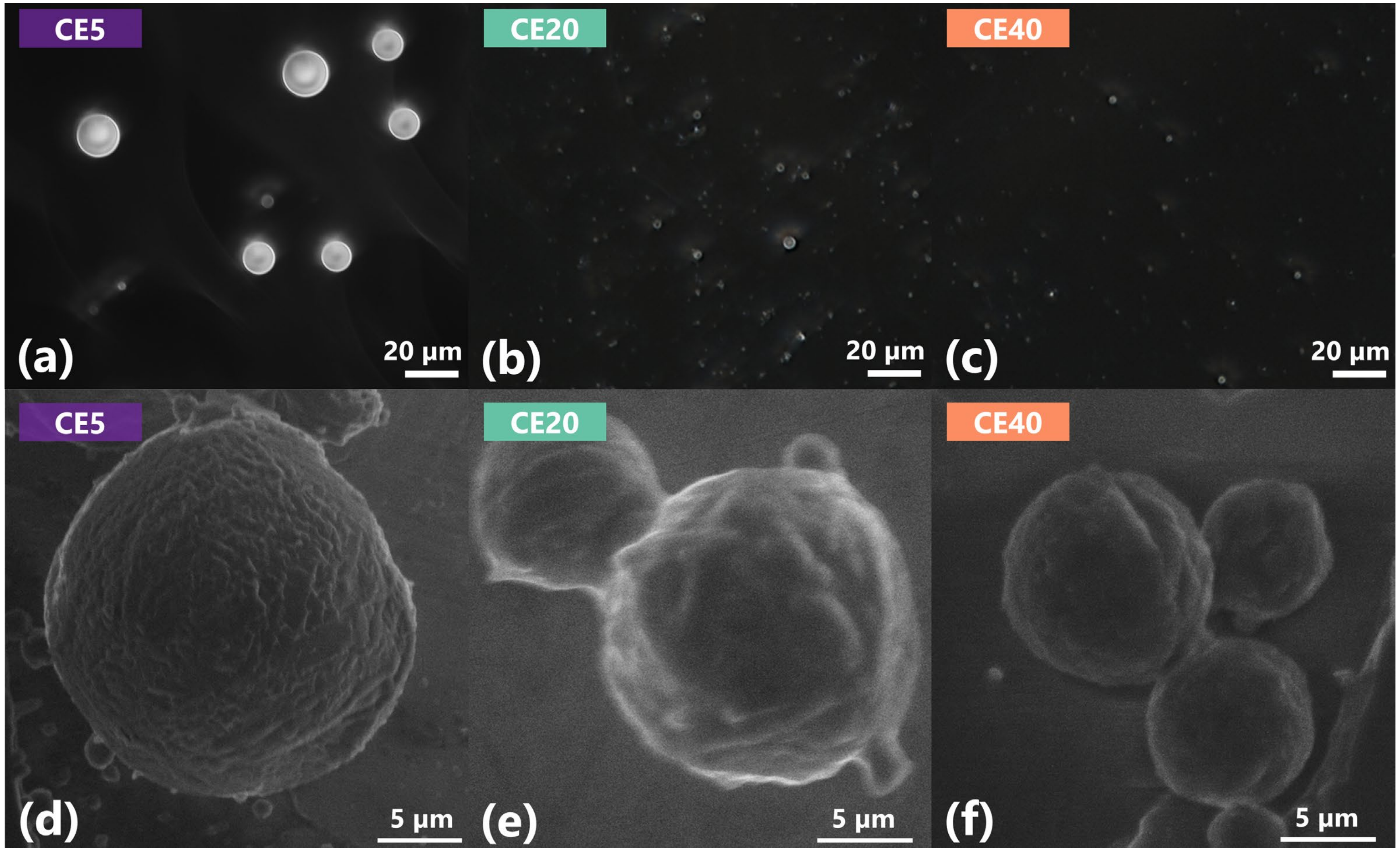
CNC vs CNC@EC Emulsions

- CE: **poor shelf stability** and resistance upon centrifugation → hydrophobic EC.
- CE40 **volume** is significantly **larger**, while CE5 and CE20 are **lower**. **Droplet size** upon large EC additions is smaller → higher viscosity impedes droplet movement and coalescence.



CNC vs CNC@EC Emulsions

- CNC@EC: **no visible sign of aggregation**.
- CNC@EC droplet: quasi spherical, smoother surface than CM, coalesced in CE5.



Conclusions

- **Sustainable colloidally stable** suspensions can be made by mixing **CNC** suspensions and tannic acid (**TA**) or alkyl cellulose derivative (**ACD**) solutions.
- More stable oil-in-water **Pickering emulsions** can be made from modified CNCs, especially with **methyl cellulose**.
- **Droplet size** can vary between a minimum of **2 µm** to a maximum of **55 µm**.
- The **interfacial behavior** and **weight fraction** of the additive determine several emulsion properties.

	Stability	Volume	Droplet size	Distribution
C	-	-	-	Mono
CT	=	↓	↑	Mono
CM5	↑	↓	↑	Mono
CM20	↑	↓	↑	Mono
CM40	↑	↑	↑	Mono
M	↓	↓	↑	Mono
CE5	↓	↓	↑	Mono
CE20	↓	↓	↓	Mono
CE40	↓	↑	↓	Mono

Thank you.

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INRAE
la science pour la vie, l'humain, la terre

TAPPI NANO DIVISION

Appendix

Francesco **D'ACIERNO***, Isabelle **CAPRON**
INRAE – BIA Unit – NANO Team
TAPPI Nano Conference 2023
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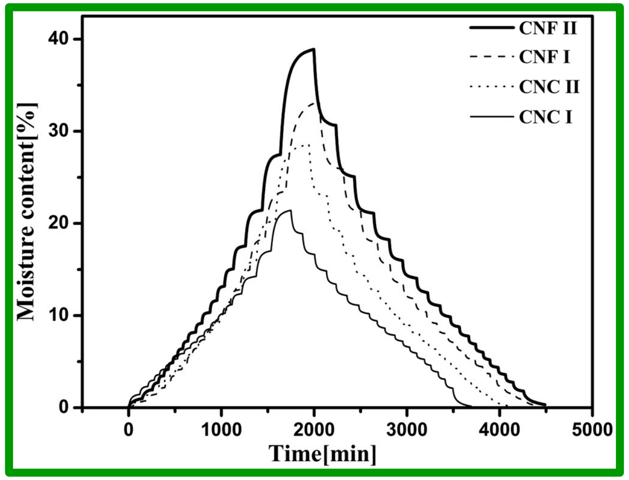
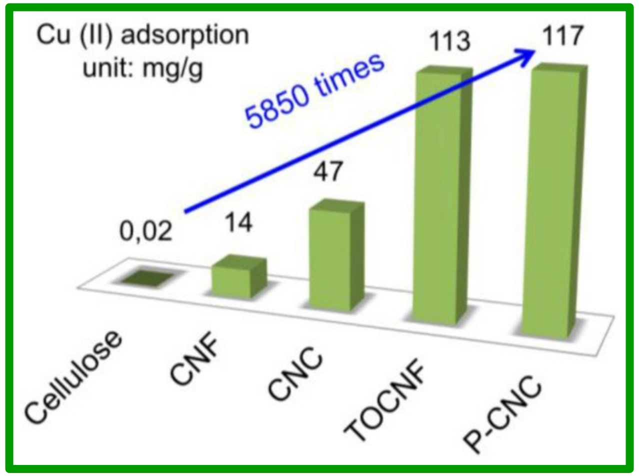
la science pour la vie, l'humain, la terre

Advantages and Drawbacks of CNC Hydrophilicity

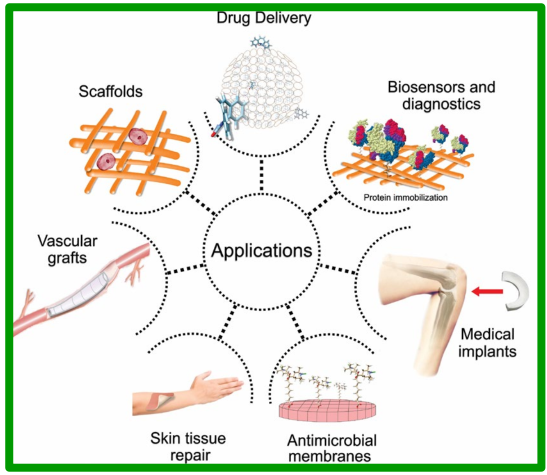
- ✓ Water **sorption**
- ✓ Water **purification**
- ✓ **Biomedical** applications



Sci. Rep. **2017,** *7*, 14207.

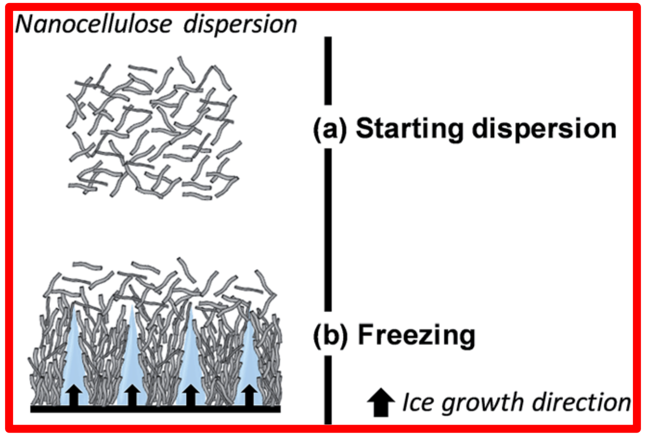


Nanomaterials **2017**, *7*, 57.

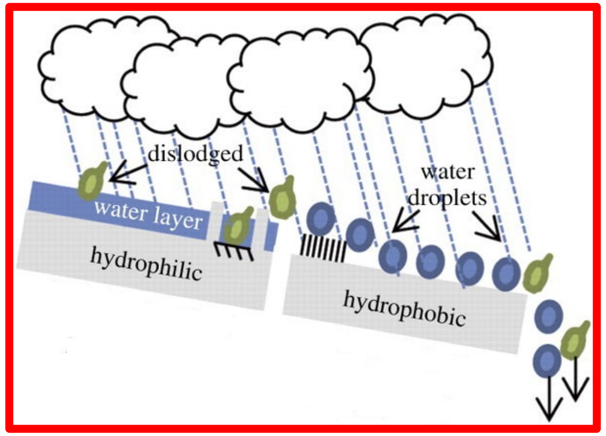


Cellulose-fundamental aspects and current trends, 193-228 (2015).

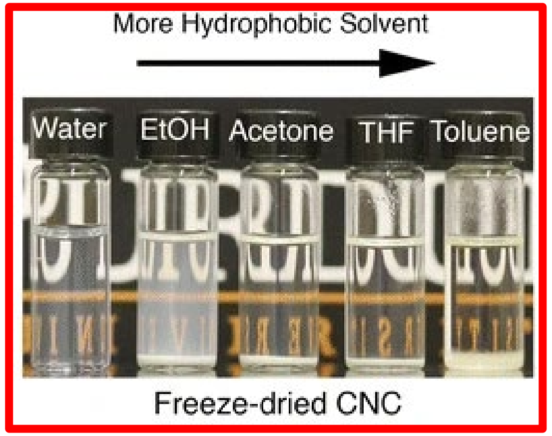
- χ **Ice** formation
- χ **Biofouling**
- χ Incompatibility with common **organic solvents** and **polymer** matrices



J. Mater. Chem. A **2017**, *5*, 16105-16117.

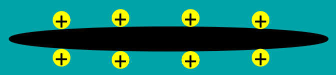
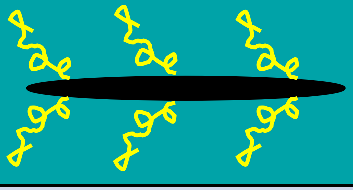
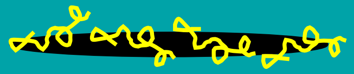


Phil. Trans. Royal Soc. A **2012**, *370*, 2381-2417.



Cellulose **2016**, *3*, 1825–1846.

Surface Modifications of CNCs

	Electrostatic interaction 	Covalent grafting 	Surface adsorption 
One-pot reaction	✓	✗	✓
Chemical stability	✓	✓	✓
Compatible solvents	✓	✗	✓
Sustainable reagents	✓	✗	✓
Controlled polymerization	✗	✓	✗
High yield	✓	✗	✓
Wide range of additives	✗	✓	✓
Change in wettability	✓	✓	✓

Manipulating Wettability through Surface Adsorption

- **Hydrophilization**

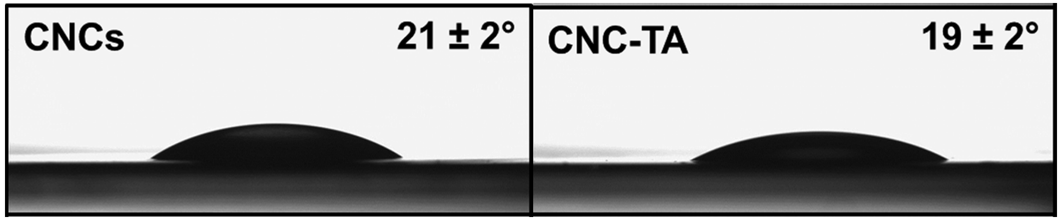
Plant polyphenols: tannic acid (TA) → 19°

- **Hydrophobization**

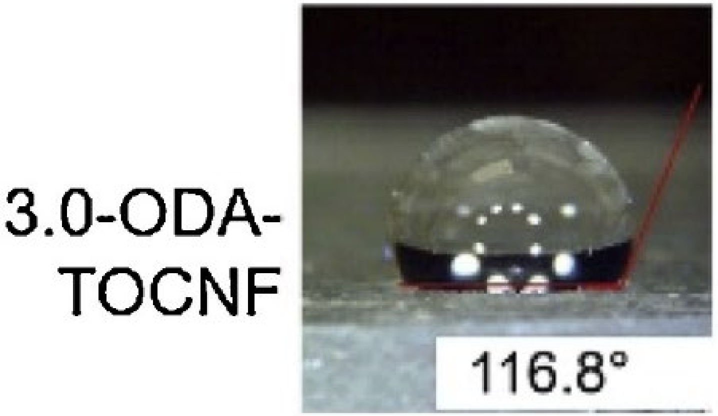
Surfactants: octadecylamine → 117°

- **Superhydrophobization**

Other additives: nanosilica and methyltrimethylsilane → 159°



ACS Sustain. Chem. Eng. **2017**, 5, 5018–5026.



Carbohydr. Polym. **2021**, *256*, 117536.

Carbohydr. Res. **2022**, *511*, 108488.

Current Issues & Possible Solutions

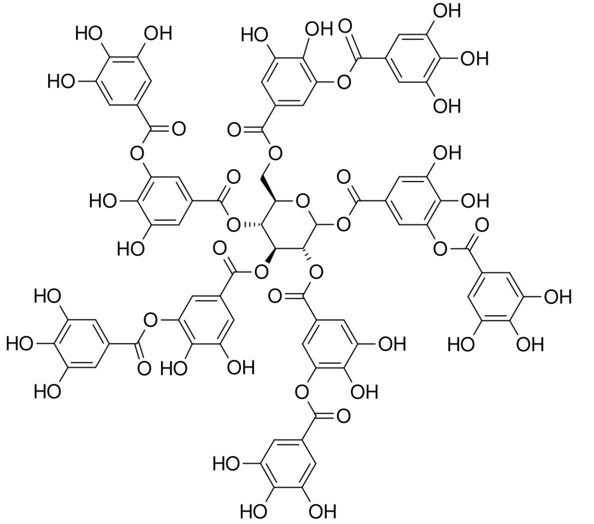
Issue	Possible solution
Some adsorbates are nonsustainable	**Sustainable** adsorbates can be used
Achieved wettability ranges are limited	Adsorbate **substituent** and **concentration** can be varied
Most cases involve CNC hydrophobization	Hydrophilizing adsorbate can be used to attain **superhydrophilicity**
Resource availability can be scarce	**Cellulose derivatives** can be used

Preparation of CNC@TA Suspensions

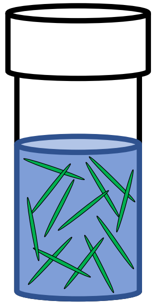
CNC

M_w=40000 g/mol

TA



M_w=1701.2 g/mol



20 g/L CNC in H_2O at pH 8

+

0.1 g TA powder

mixing & dialysis →

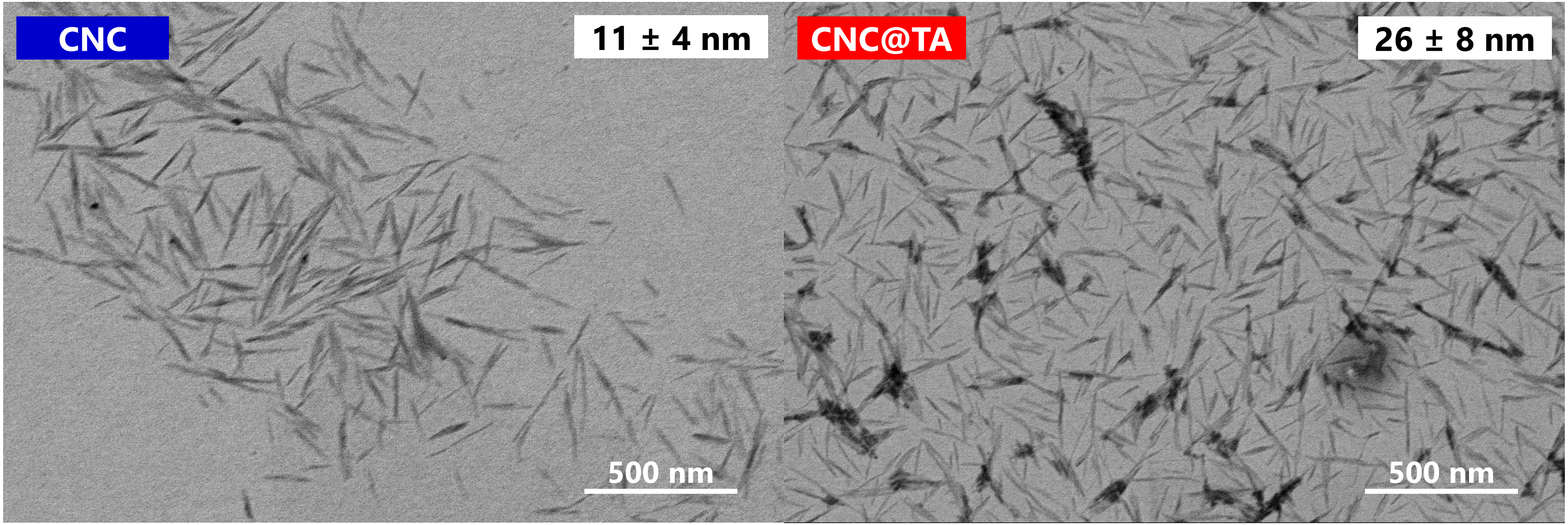
Colloidally stable CNC@TA suspensions

ACS Sustain. Chem. Eng. **2017**, *5*, 5018–5026.

The presence of TA precoating may favor more interactions with ACDs.

STEM

Morphology of CNC vs CNC@TA Nanoparticles



CNC width increase

Preparation of CNC(@TA)@MC Suspensions

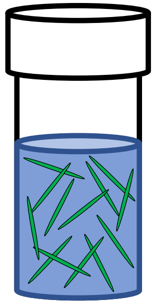
CNC

M_w=40000 g/mol

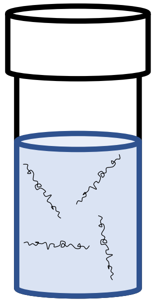
OR

CNC@TA

M_w=40000 g/mol



\+

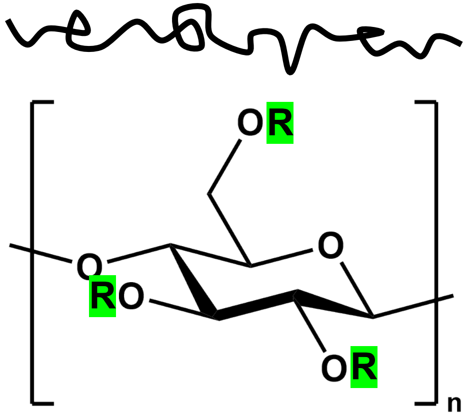


5 g/L CNC(@TA) in H_2O

1 g/L MC in H_2O

Various MC weight fractions
→ from <u>3%</u> to <u>64%</u> (w/w)

MC



R = CH_3

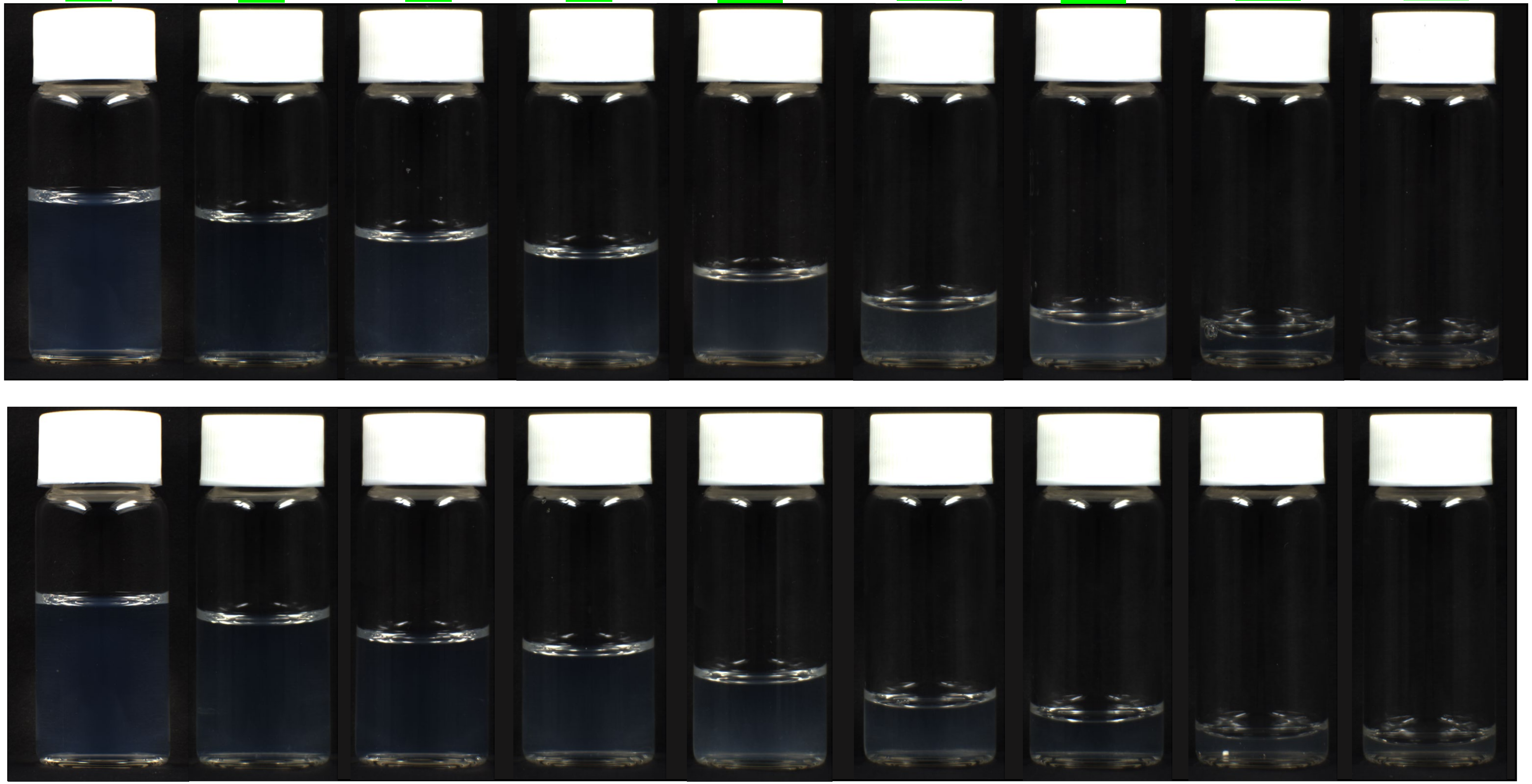
M_w=?
M_n=40000 g/mol
DS=1.6–1.9
PDI=?

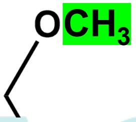
mixing

H_2O evaporation
through rotovapor

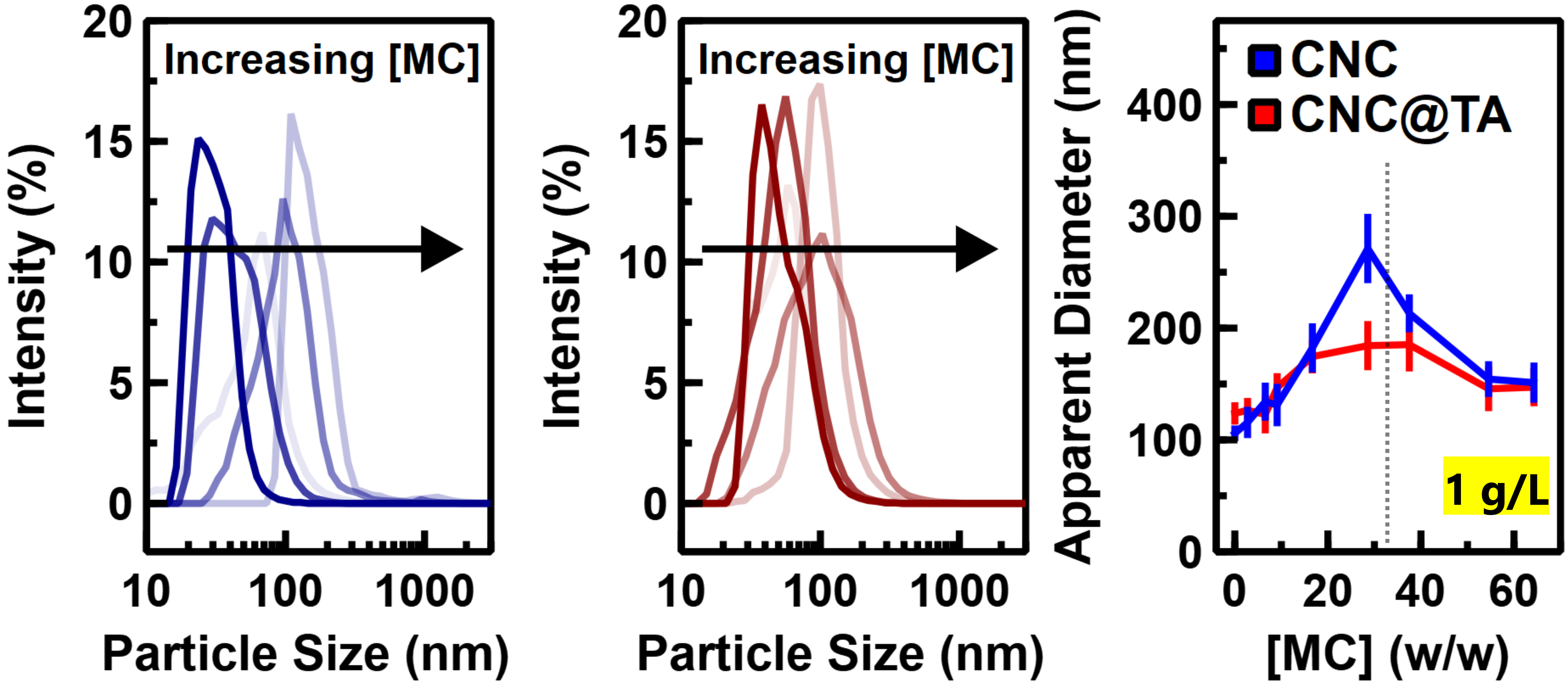
Colloidally stable
5 g/L suspensions

CNC(@TA)@MC Suspensions

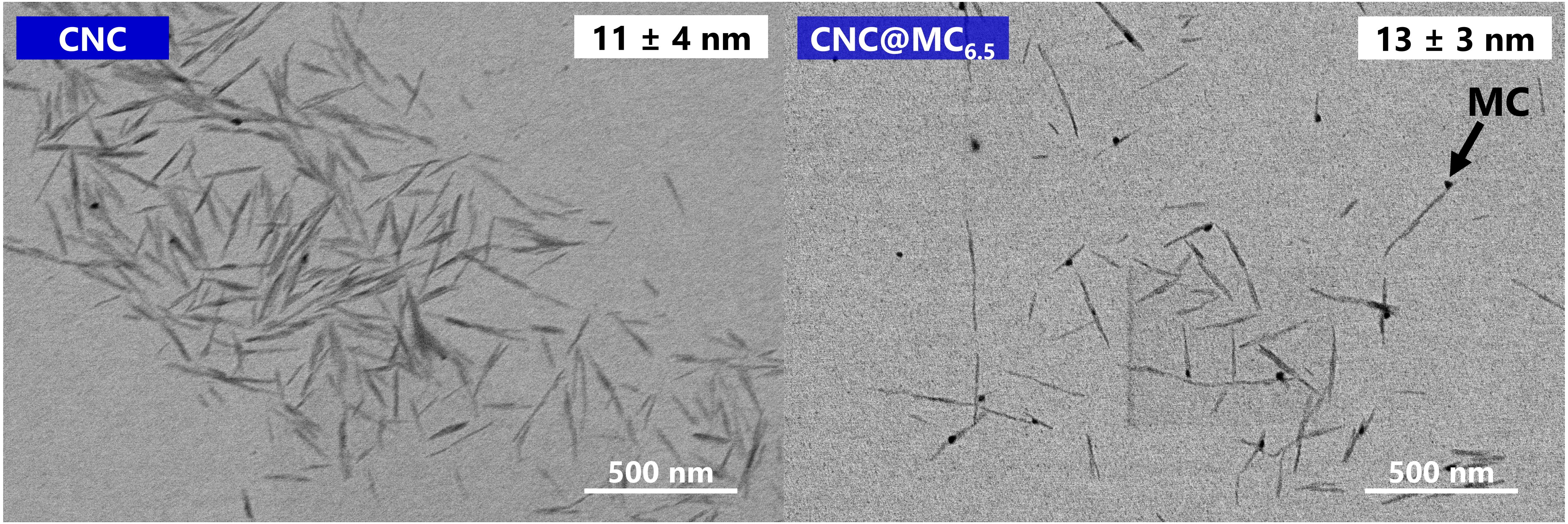




Apparent Diameter of CNC(@TA)@MC Suspensions

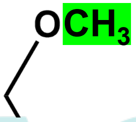


Morphology of CNC vs CNC@MC Nanoparticles

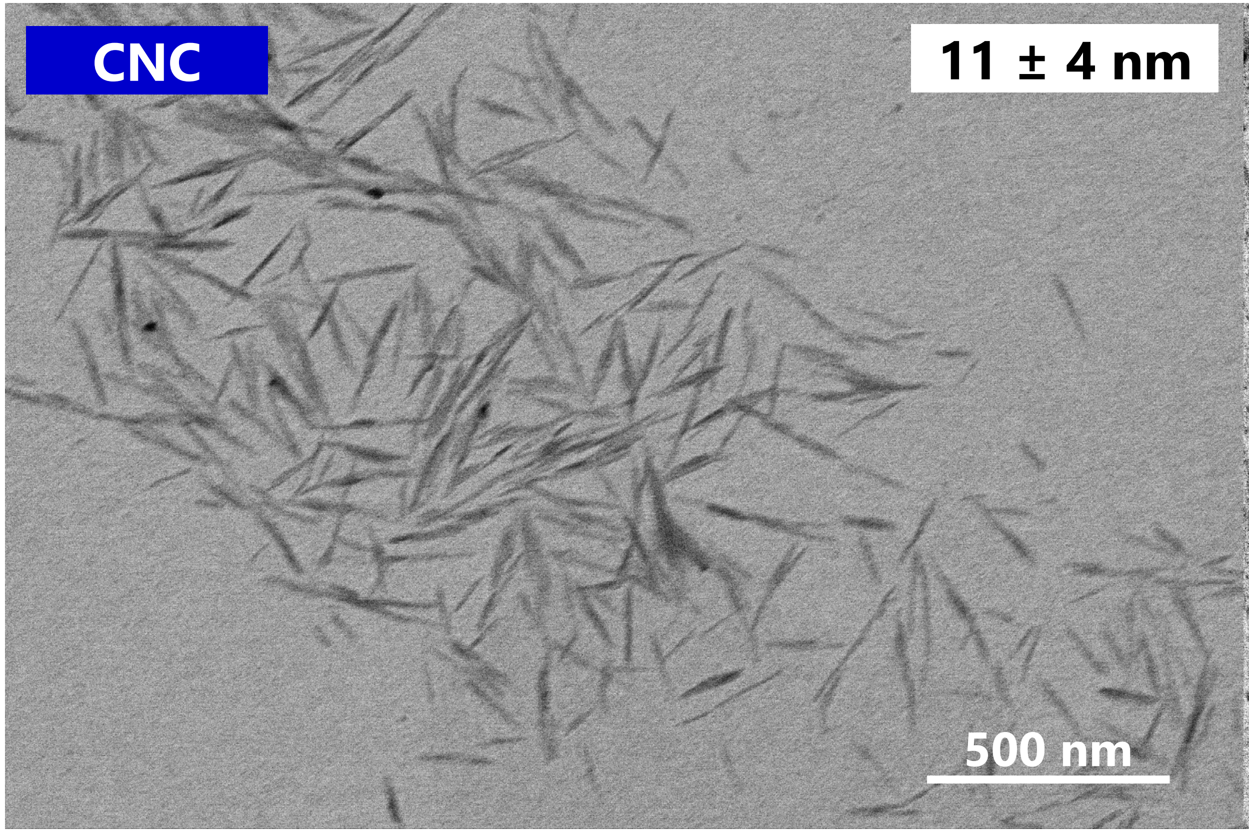


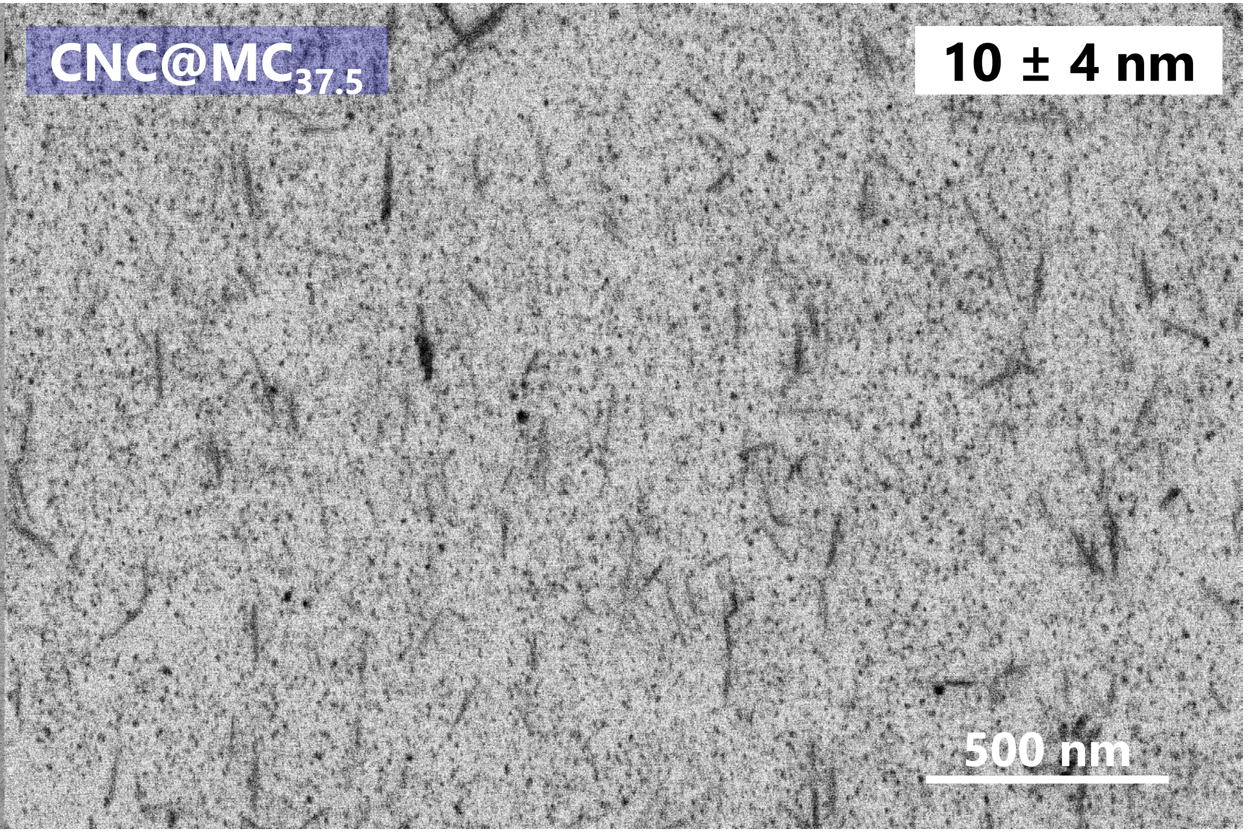
Low [MC] regime

CNC width increase:
MC coiling on surface



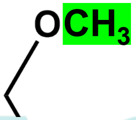
Morphology of CNC vs CNC@MC Nanoparticles





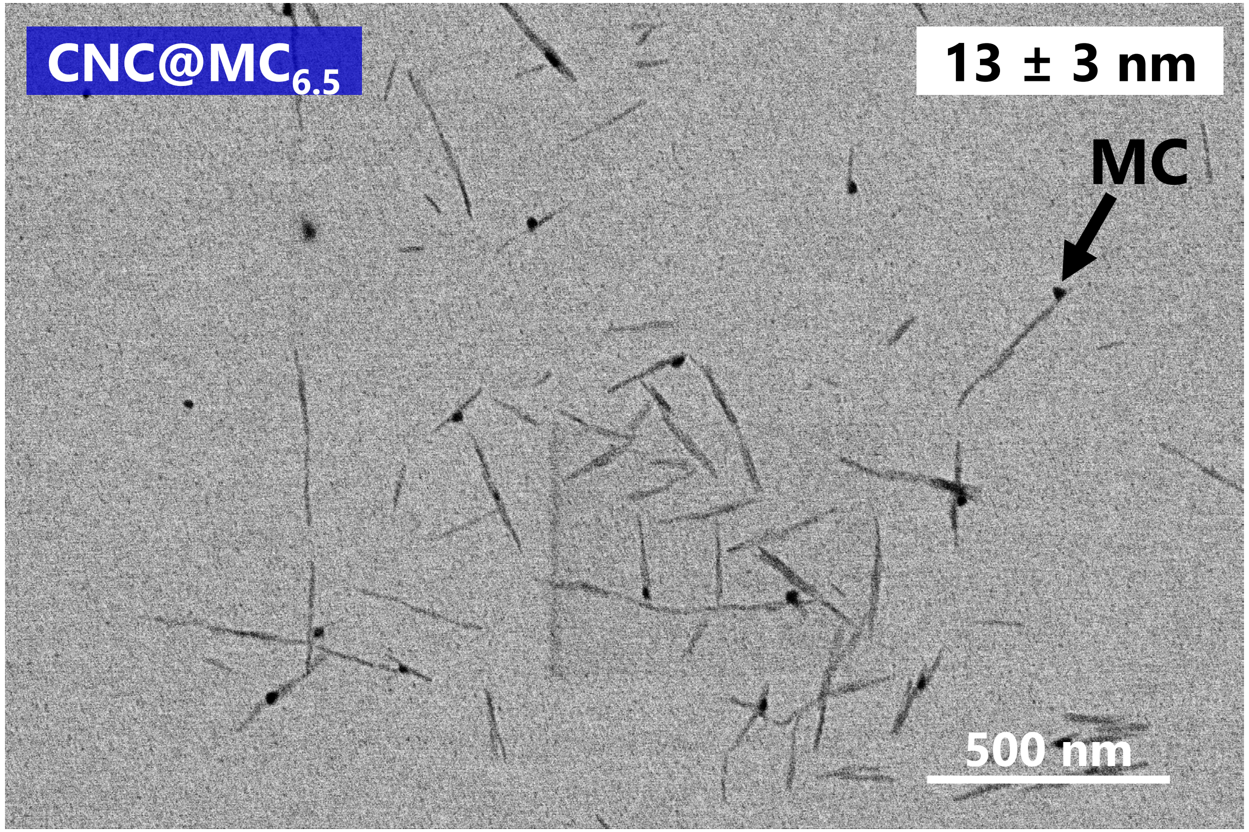
High [MC] regime

CNCs frozen in a matrix



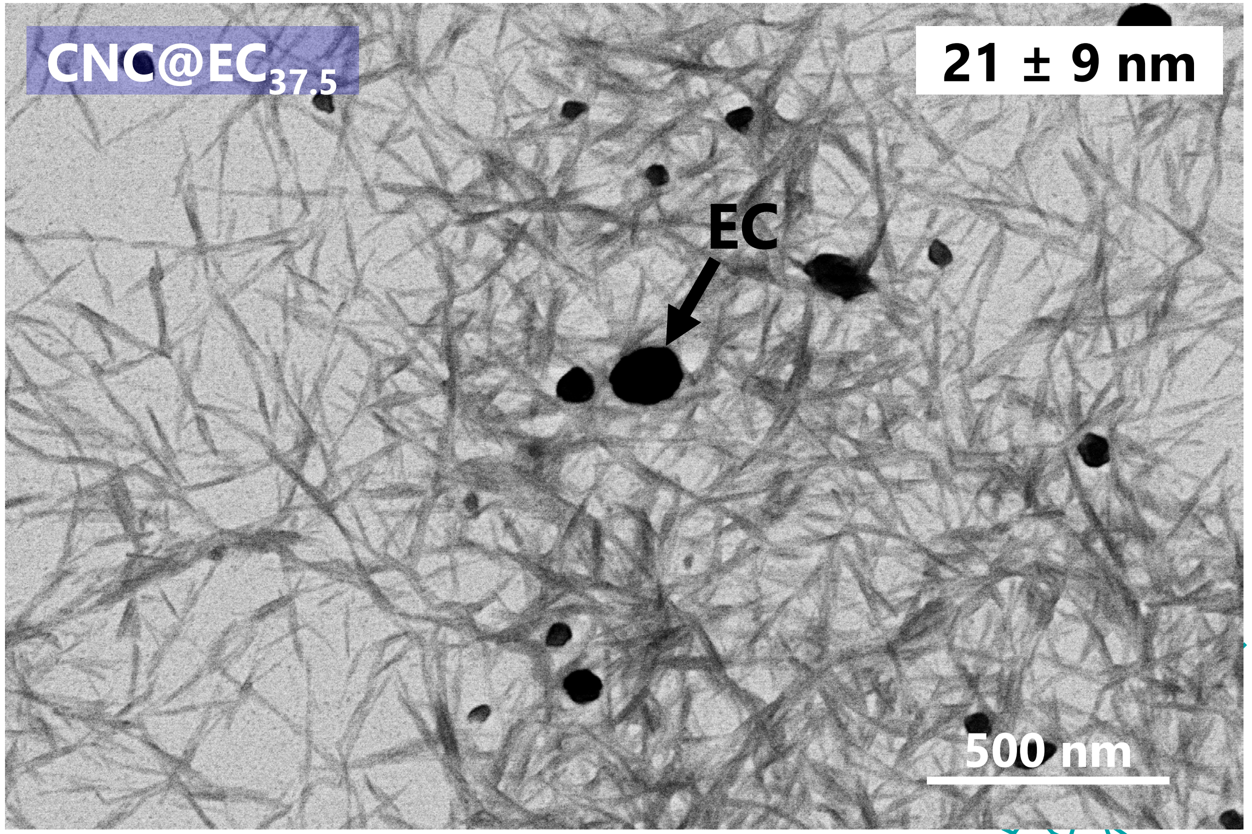
Simplified Model of CNC-ACD Interactions

Low [ACD] regime: coiling and/or coating



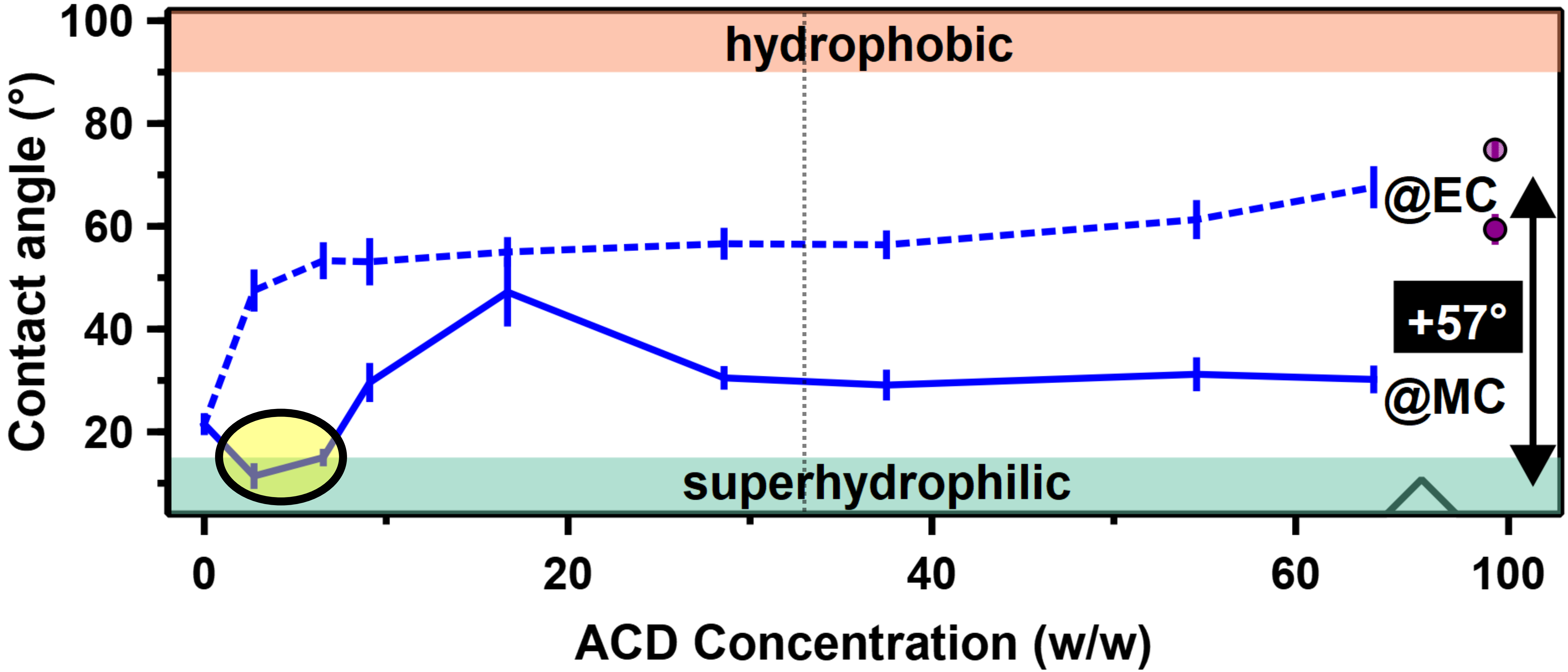
Hydrophobic effect

High [ACD] regime: composite



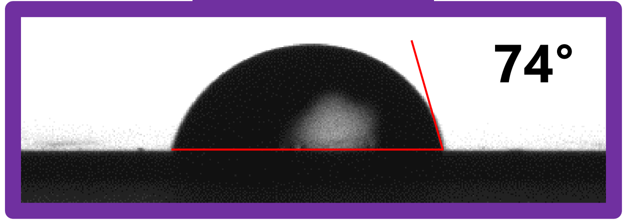
Critical point → CNC:ACD 2:1

Wettability of CNC@ACD Solid Surface

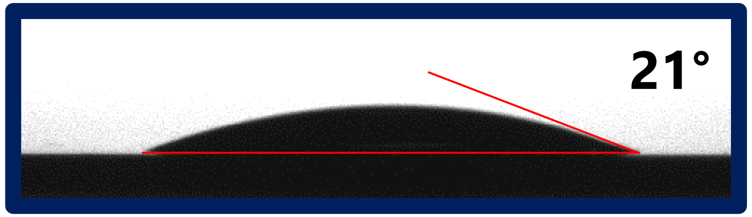


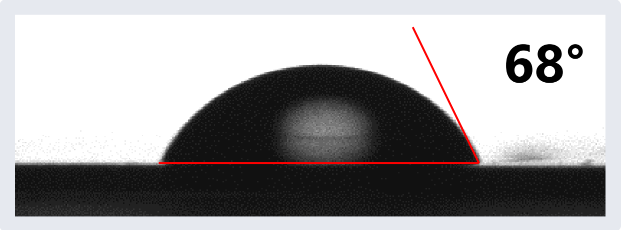
Water in Air Contact Angle Pictures

EC



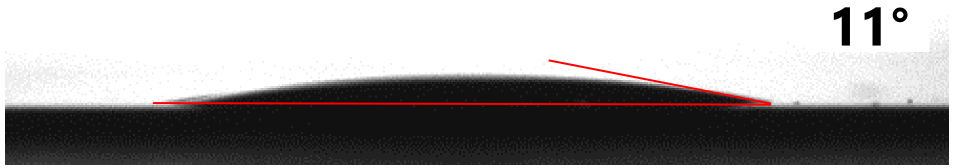
CNC





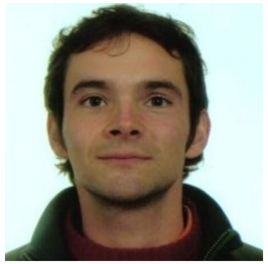
[EC] (w/w)

CNC@MC (2.7% w/w)



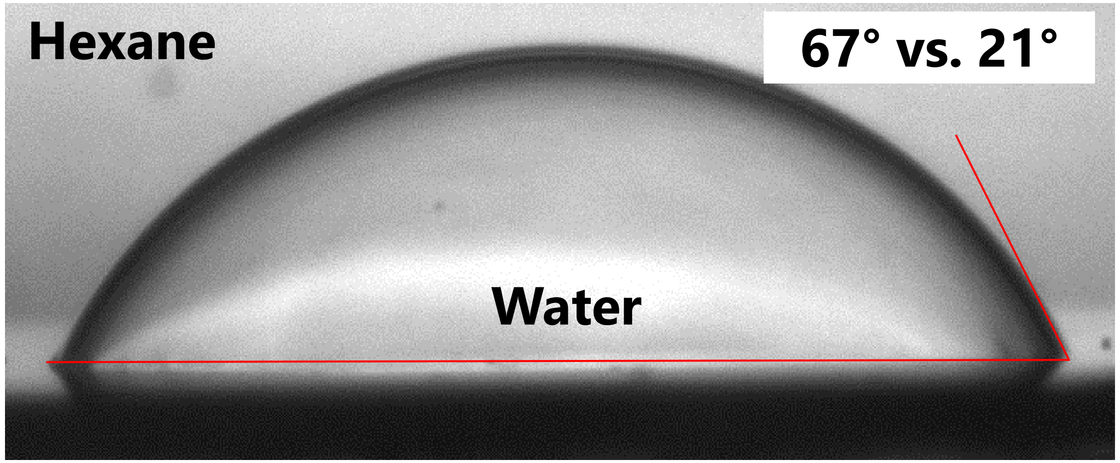
Superhydrophilic

Water in Hexane Contact Angle Pictures



Benoit Duchemin

CNC



CNC@$MC_{2.7}$

25° vs. 11°

Some sites are occupied by alkane molecules

Conclusions

- **Sustainable colloidally stable** suspensions can be made by mixing **CNC** and **CNC@TA** suspensions and alkyl cellulose derivative (**ACD**) solutions.
- Depending on [ACD], **uniform coating** (low ACD weight) or **heterogeneous composite** (high ACD weight) is formed.
- The **critical** transition is around CNC:ACD **2:1** ([ACD]=**33% (w/w)**).
- Wettability ranges **from 11° to 68°**.
- Wettability can be finely **tuned** by **adjusting [ACD]**.
- **Superhydrophilicity** can be attained, not hydrophobicity yet.

Acknowledgments

Isabelle Capron

Bruno Novales

AGENCE NATIONALE DE LA RECHERCHE ANR

ANR-20-CE43-0011

INRAE

science for people, life & earth

Preparation of CNC(@TA)@EC Suspensions

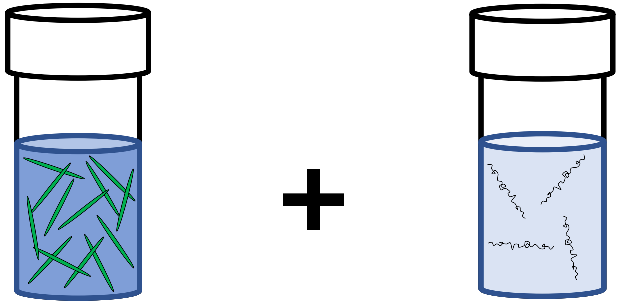
CNC

M_w=40000 g/mol

OR

CNC@TA

M_w=40000 g/mol

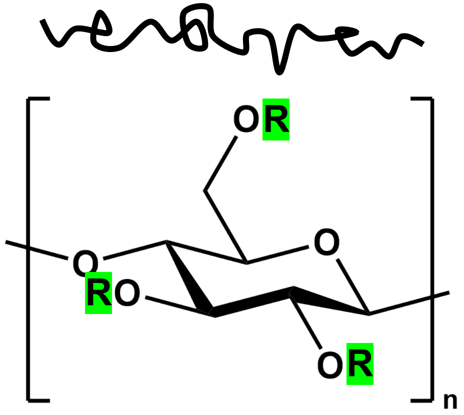


5 g/L CNC(@TA) in H_2O

1 g/L EC in EtOH

Various MC weight fractions
→ from 3% to 64% (w/w)

EC



R = CH_2CH_3

M_w=33700 g/mol

M_n=9800 g/mol

DS=1.44

PDI=3.4

mixing

EtOH evaporation

through rotovapor

Colloidally stable
5 g/L suspensions

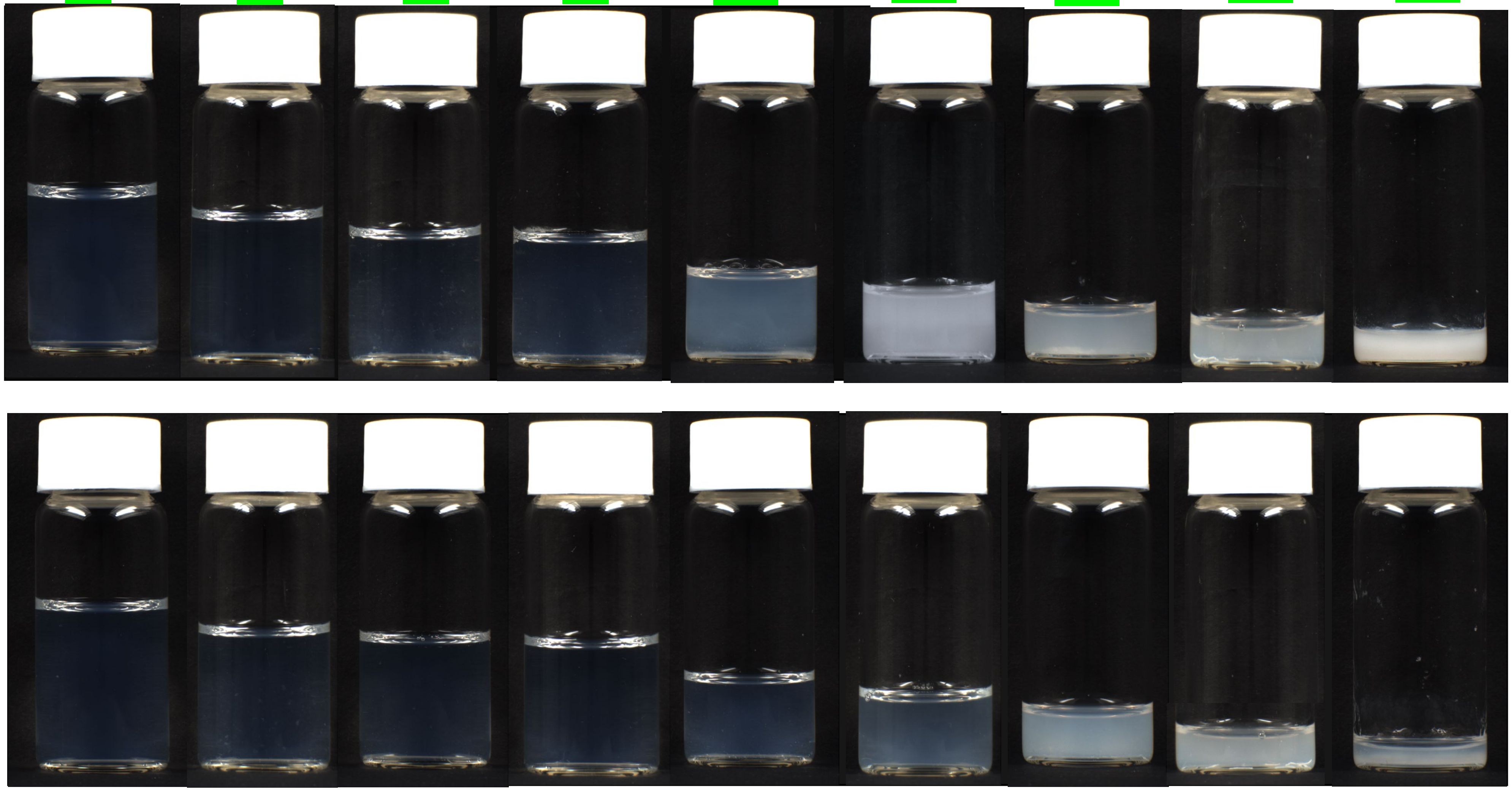
Camera

CNC(@TA)@EC Suspensions

[EC] (w/w) 0.0 2.7 6.5 9.1 16.7 28.6 37.5 54.5 64.3

CNC

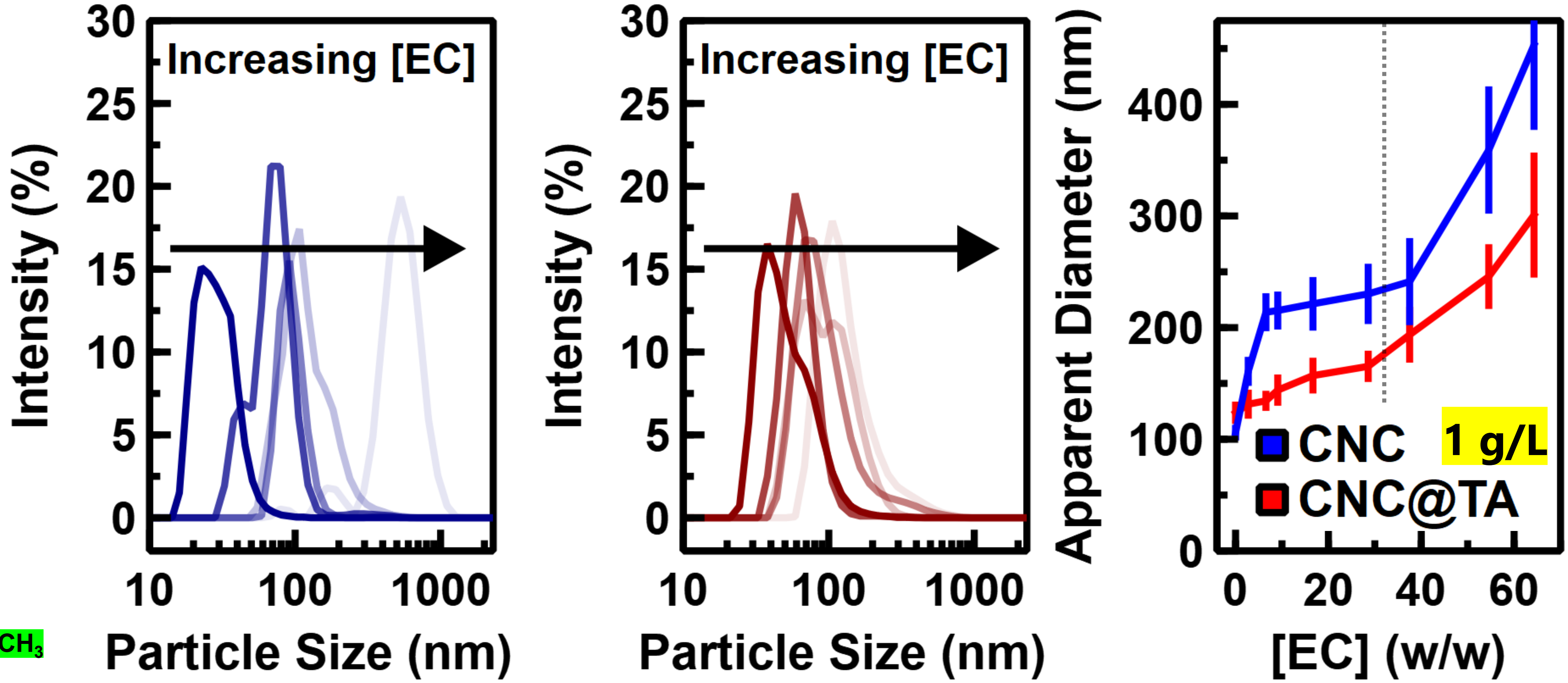
CNC@TA

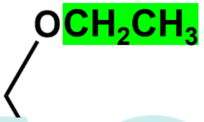


OCH_2CH_3

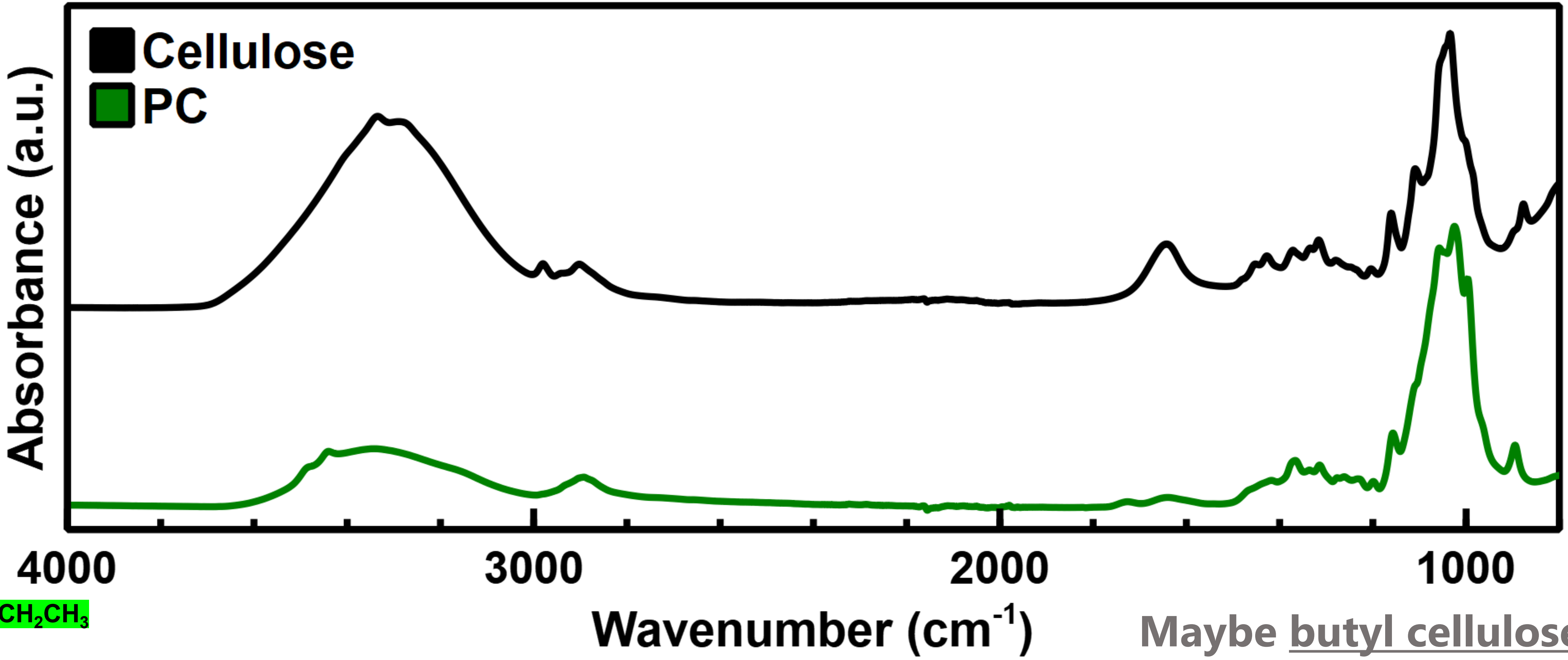
[EC] (w/w)

Apparent Diameter of CNC(@TA)@EC Suspensions





Molecular Analysis of Cellulose vs Propyl Cellulose



O$CH_2CH_2CH_3$

Maybe **butyl cellulose** is next?

O$CH_2CH_2CH_2CH_3$

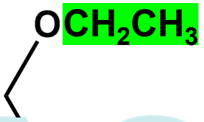
Ethyl Cellulose (EC) Solubility

Solubility Parameter Ranges for Ethylcellulose

DS	Ethoxyl content %w/w	Solubility parameter range $MPa^{1/2}$ Poorly	Moderately hydrogen-bonded solvents	Strongly
2.28-2.38	45.5-46.8	0	17.4-22.1	19.4-23.3
2.42-2.53	47.5-49.0	16.6-22.7	15.1-22.1	19.4-29.7
>2.53	>50.0	17.4-19.4	16.0-20.1	19.4-23.3

Rekhi, G. S., & Jambhekar, S. S. (1995). Ethylcellulose-a polymer review. *Drug development and industrial pharmacy*, *21*(1), 61-77.

- EC is soluble in **esters**, aromatic **hydrocarbons**, **alcohols**, **ketones**, and **chlorinated** solvents.
- The solubility depends on the **degree of substitution** (DS).



EC Viscosity in Various Solvents

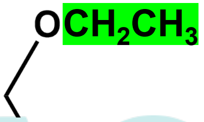
Viscosity and Film Properties of Ethylcellulose

(15 g Resin in 100 cc Solvent)

Solvent	Solution Properties @ 25°C		Film Properties	
	Viscosity cps	Specific Gravity	Yield Pt. Kg/cm^2	Elongation %
n-Butanol	1900	0.848	425	6
Butyl acetate 90%	590	0.901	430	7
Ethanol, Formula 30	560	0.850	—[1]	—[1]
Ethyl Acetate, 99%	360	0.924	440	9
Ethylene dichloride	470	1.238	420	5
Methyl ethyl ketone	320	0.845	428[2]	7[2]
Toluene	1930	0.890	440	12
80-20 Toluene-ethanol	260	0.887	440	7

[1] Too brittle to test properly

[2] Films show "orange peel"



Rekhi, G. S., & Jambhekar, S. S. (1995). Ethylcellulose-a polymer review. *Drug development and industrial pharmacy*, *21*(1), 61-77.

- **Ethanol** and **methanol** yield **less viscous** EC solutions and they are easier to work with
- However, the **higher** the **DS** of EC, the **lower** the **solubility in ethanol** (toluene fraction required to make them less viscous).

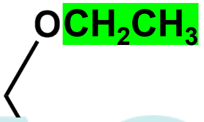
Minimum Solution Viscosity of EC Solutions

Solvent Compositions for Minimum Solution Viscosity for Ethylcellulose

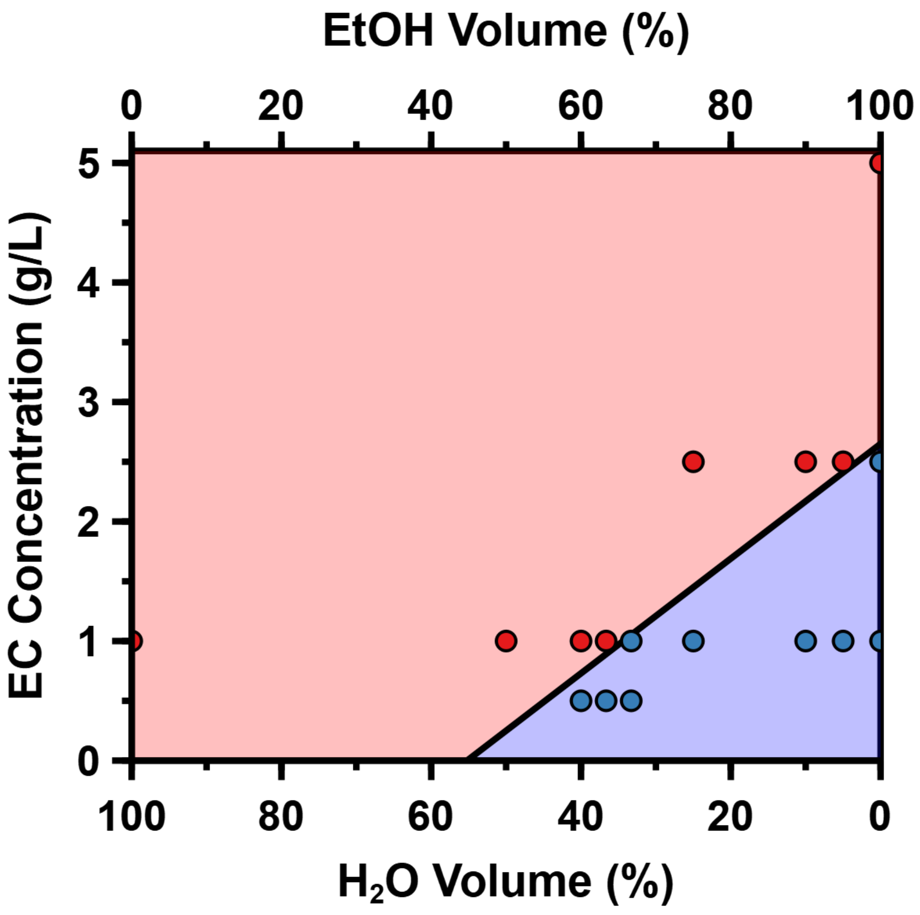
Solvent Mixture	Solvent Composition
Aromatic/ethanol	20% ethanol
Aromatic/ester	No change by varying ester
Esters/ethanol	20% ethanol
Ketones/ethanol	20% ethanol
Aromatic naphthas/ethanol	30% ethanol
Aliphatic naphthas/ethanol	30 % ethanol

Rekhi, G. S., & Jambhekar, S. S. (1995). Ethylcellulose-a polymer review. *Drug development and industrial pharmacy*, *21*(1), 61-77.

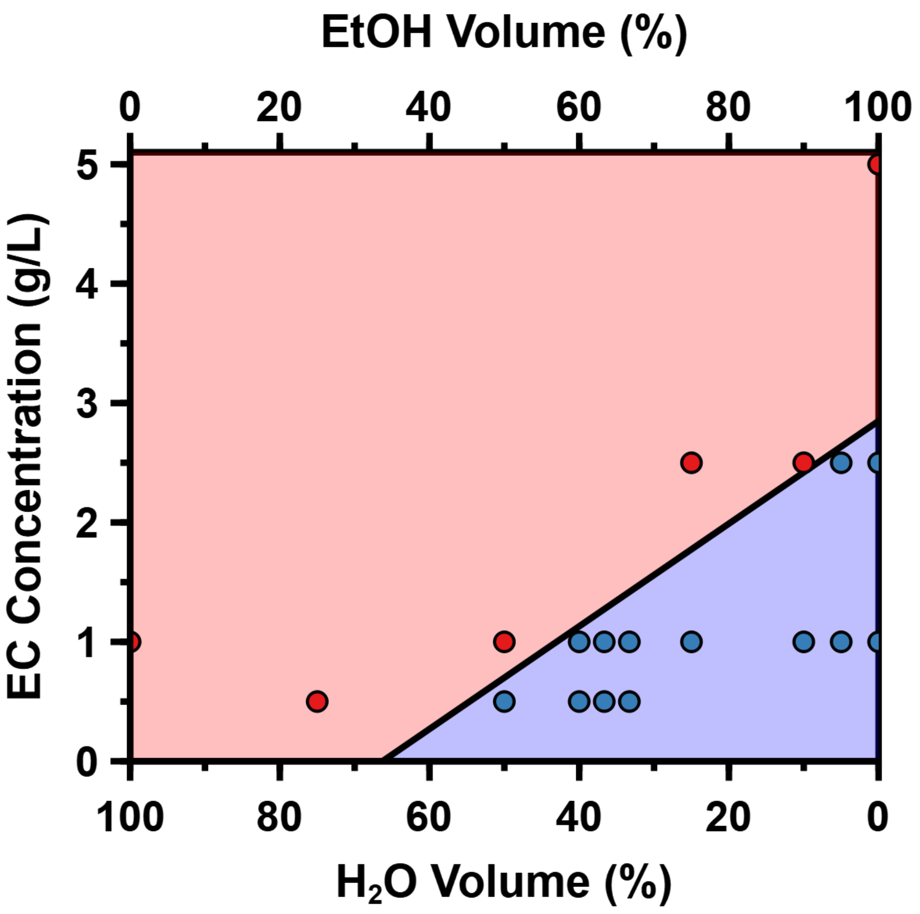
- Aliphatic **esters** and **ketones** → low viscosity due to **low M_w**
- In these cases, adding a bit of **alcohol** will make the solutions less viscous.



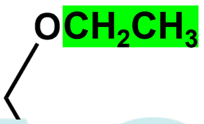
Solubility phase diagram of ethylcellulose (EC) in H_2O/EtOH



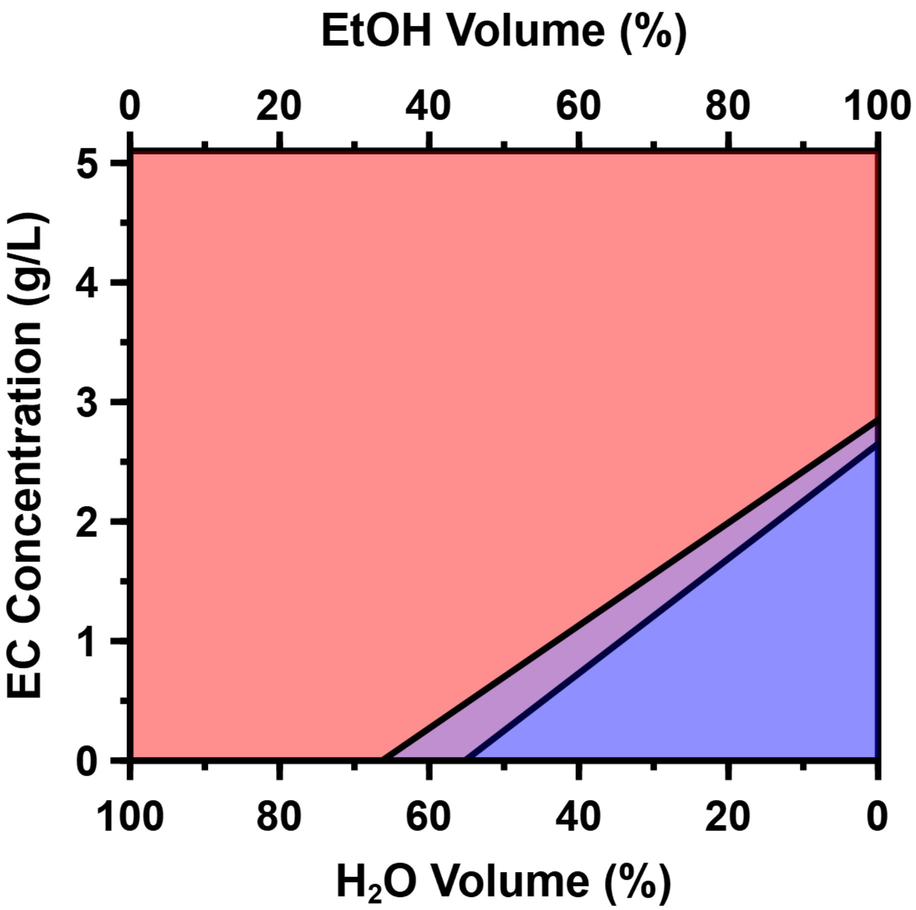
Approach #1

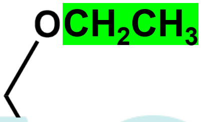


Approach #2: Solvent #1 is EtOH

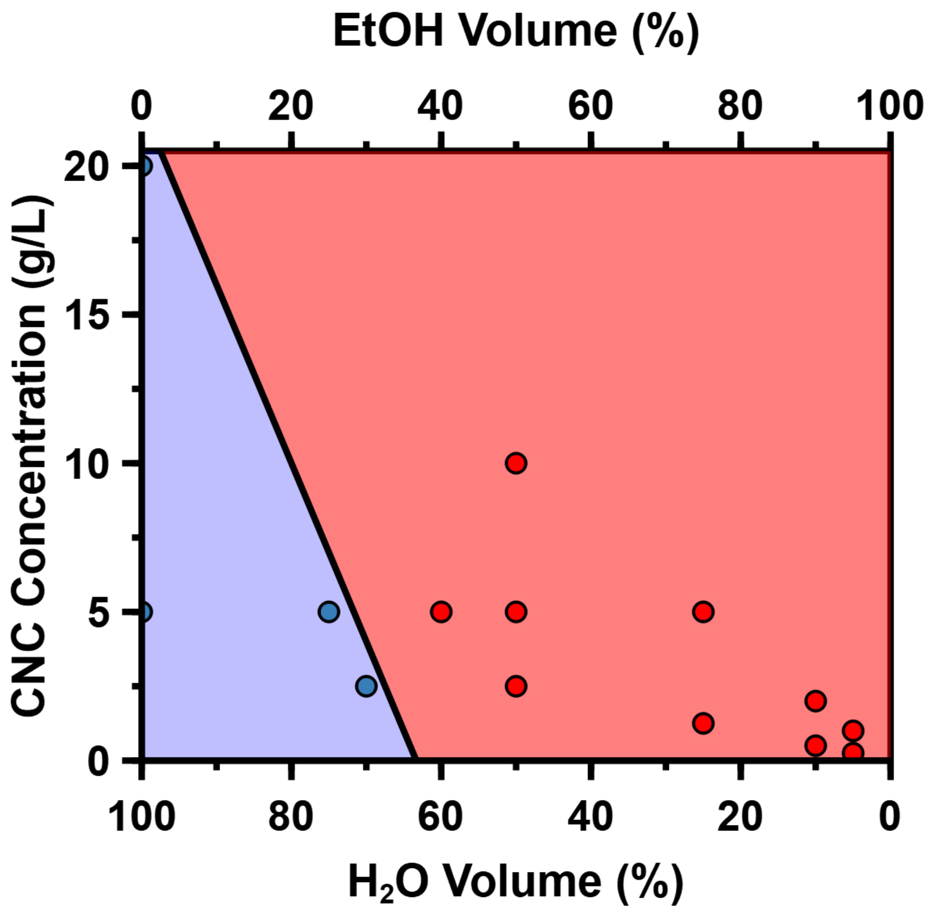


Solubility enhancement of ethylcellulose (EC) in H_2O/EtOH

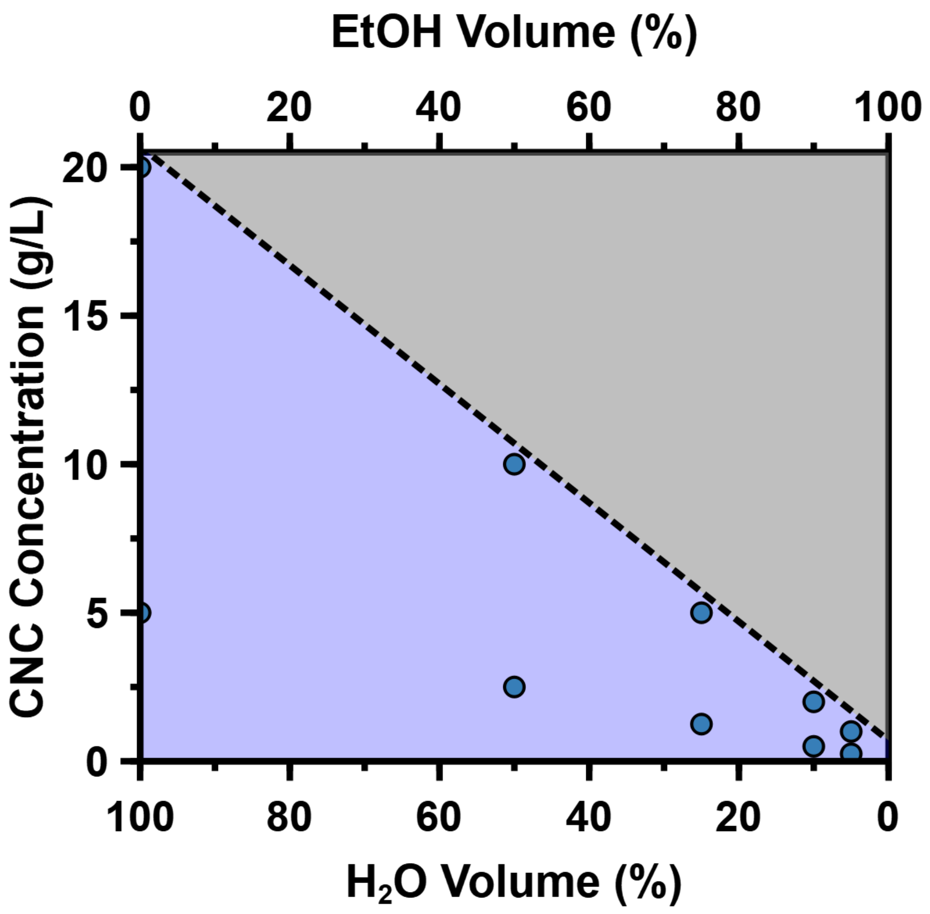




› Dispersibility phase diagram of cellulose nanocrystals (CNCs) in H_2O/EtOH

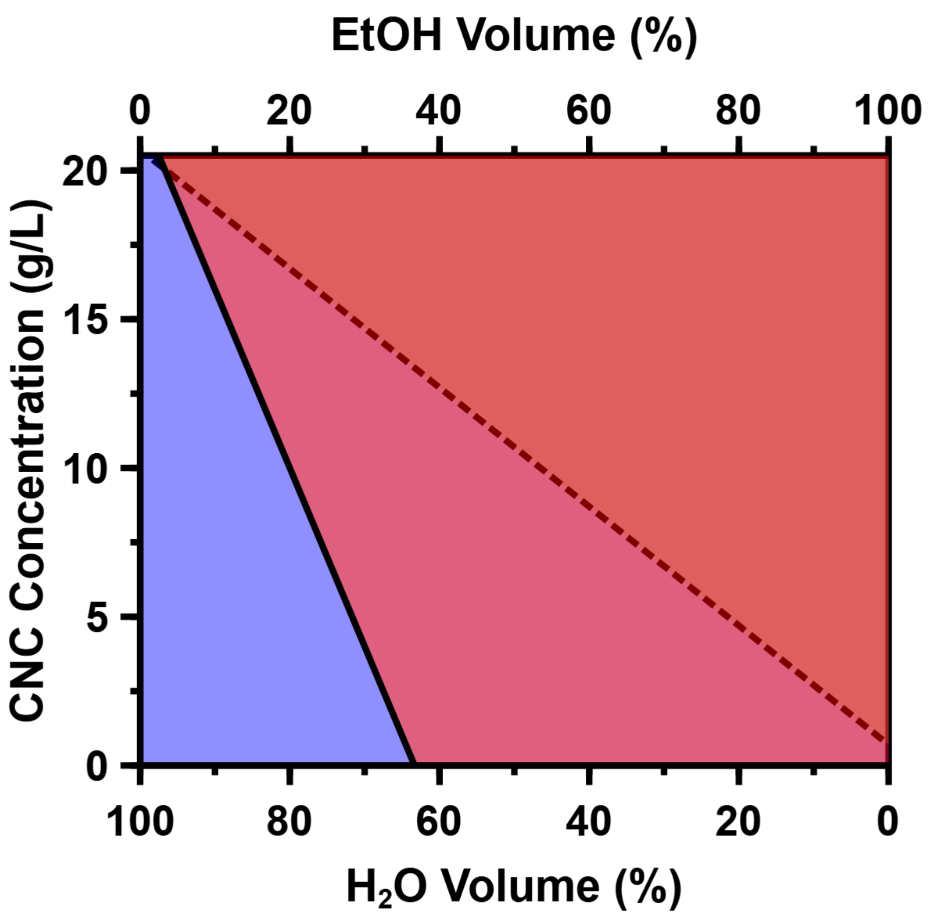


Approach #1



Approach #2: Solvent #1 is H_2O

Dispersibility enhancement of cellulose nanocrystals (CNCs) in H_2O/EtOH



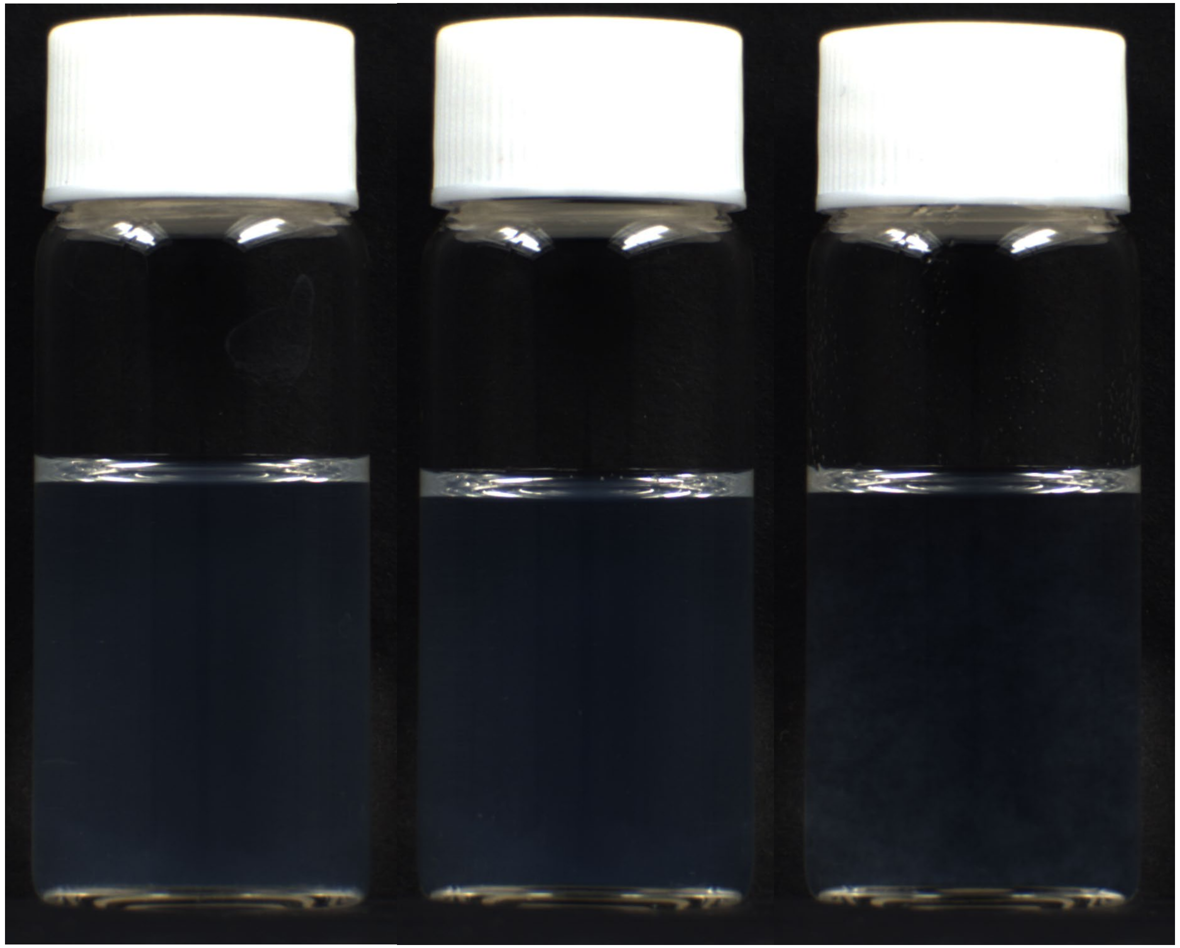
Approach #2 (subsequent addition of co-solvent) is effective to enhance solubility and dispersibility

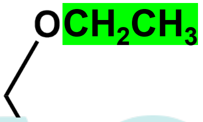
CNC(@TA)@EC Suspensions before EtOH evaporation

[EC] (w/w)

6.5 16.7 64.3

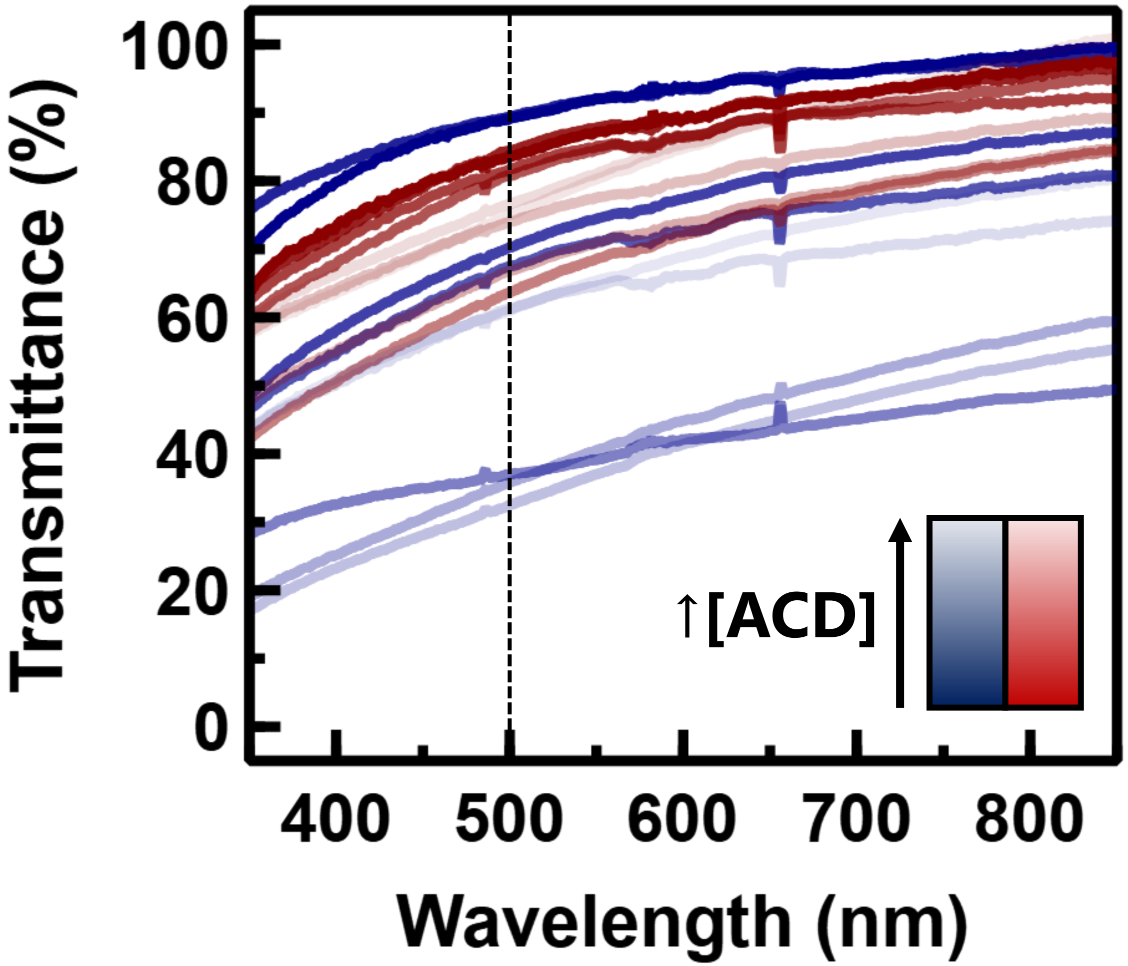
CNC

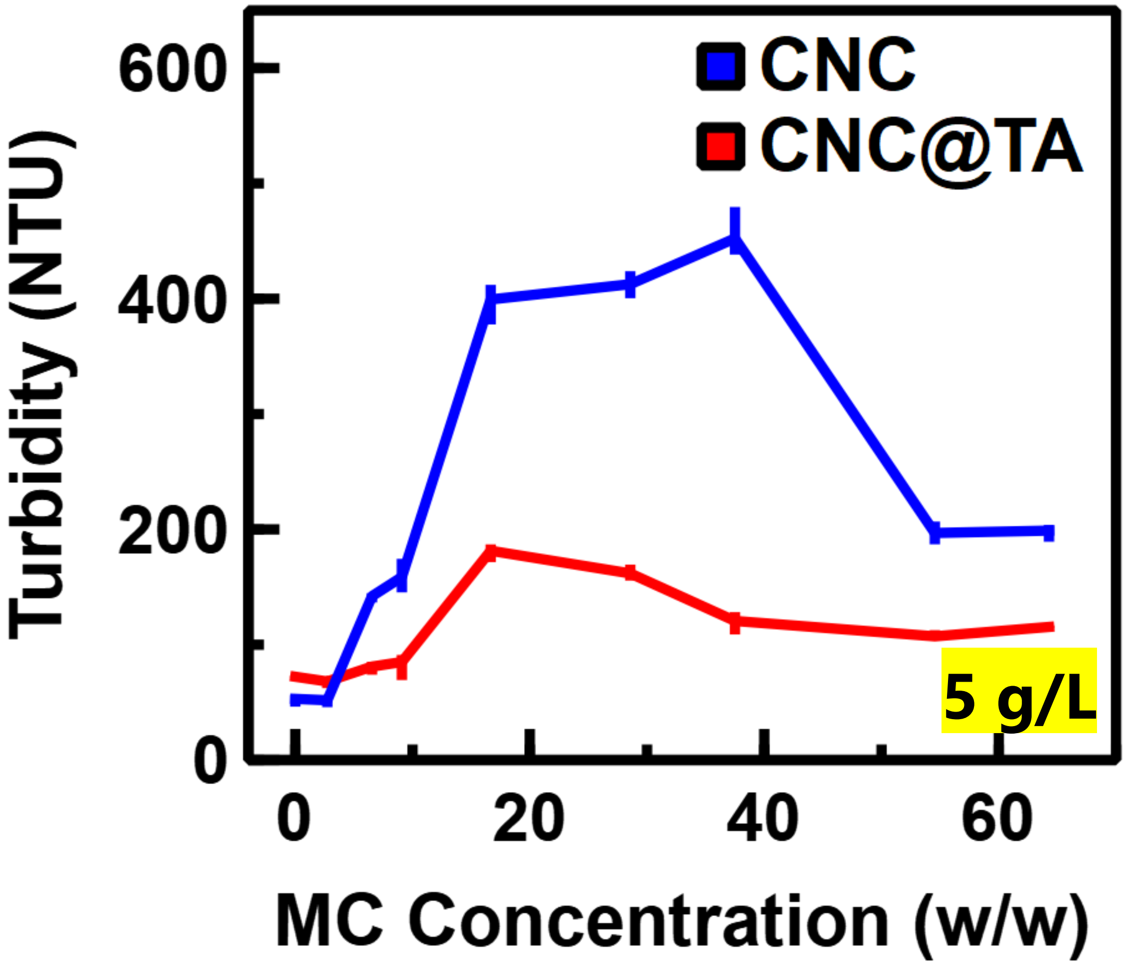




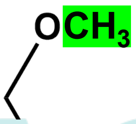
[EC] (w/w)

Turbidity of CNC(@TA)@MC Suspensions

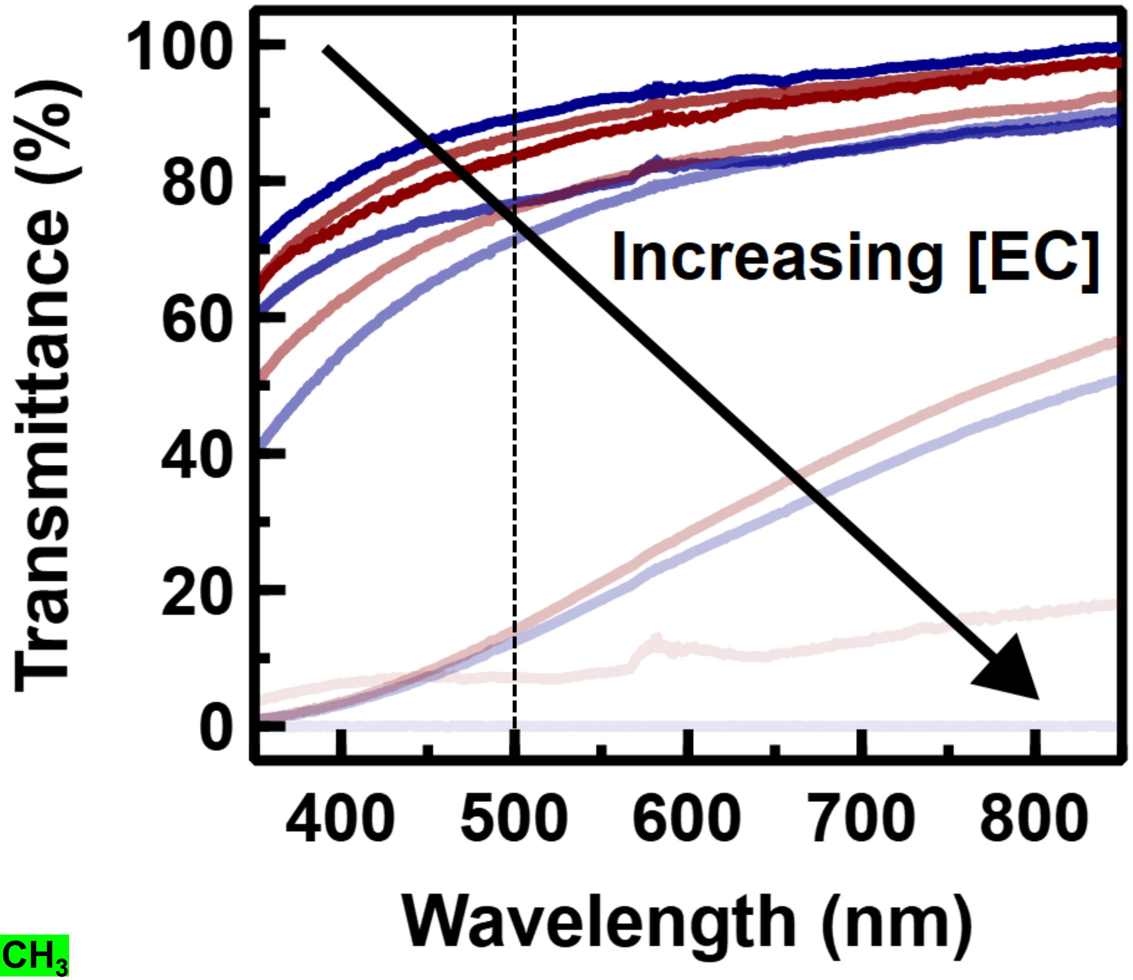


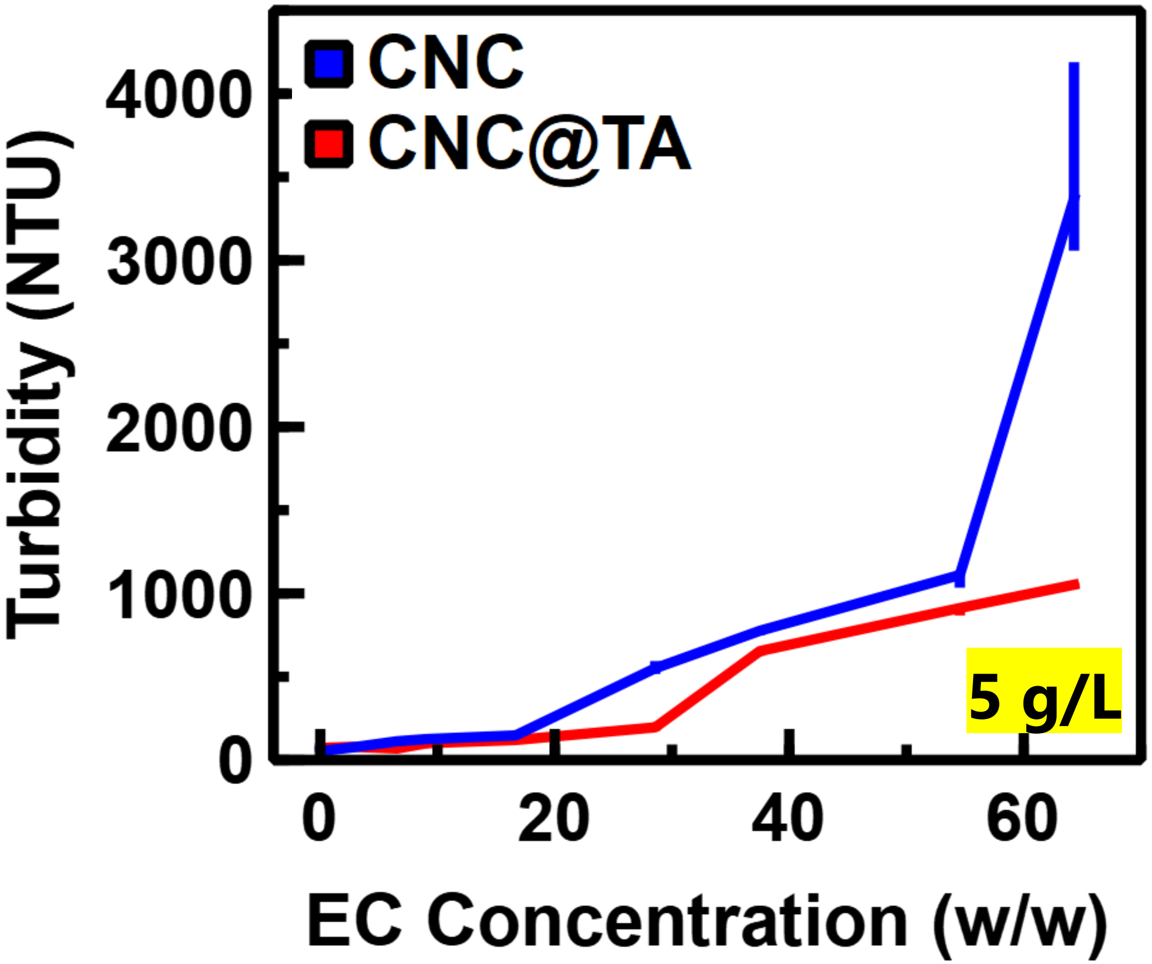


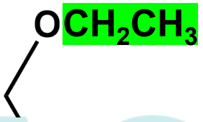
$NTU = 0.191+926.1942*A_{500}$



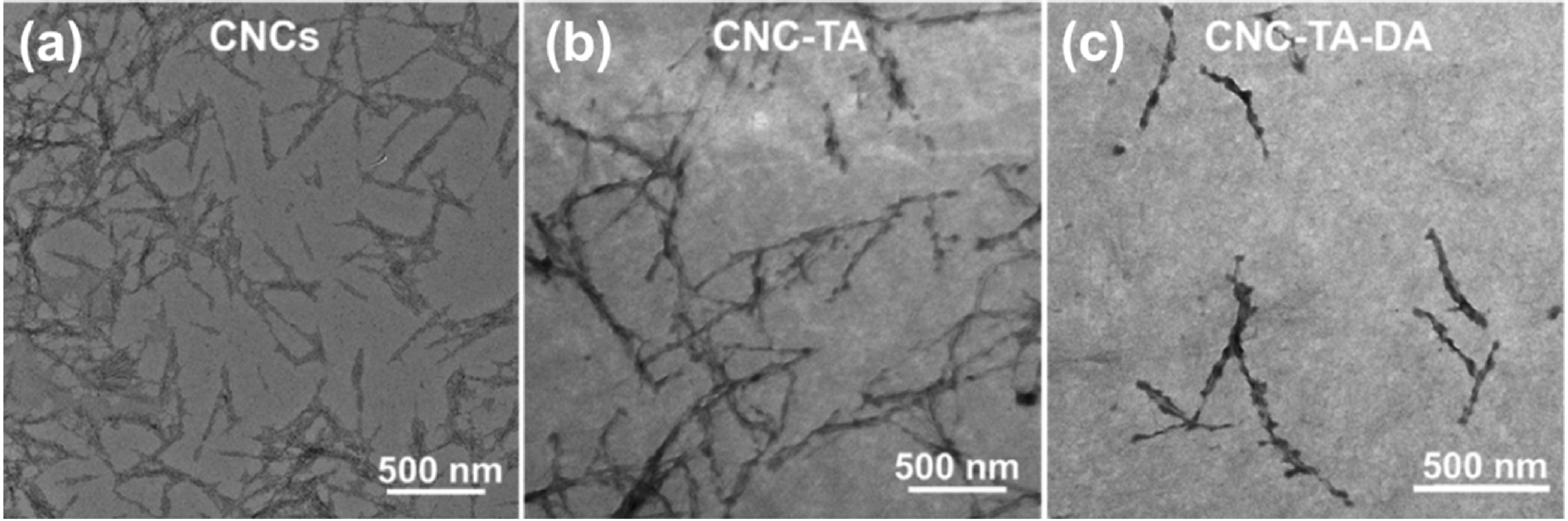
Turbidity of CNC(@TA)@EC Suspensions





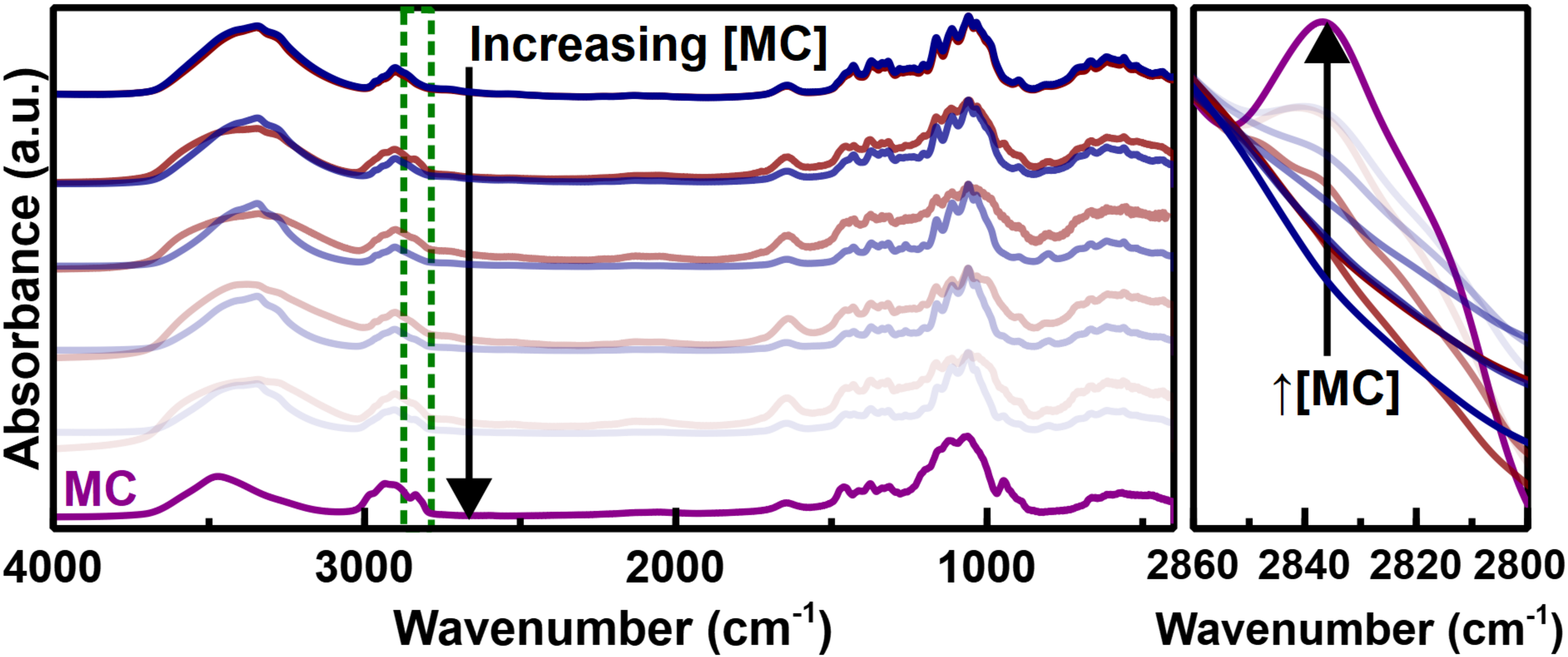


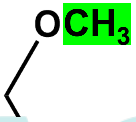
Example of Microscopic Imaging of CNC Adsorption in Literature



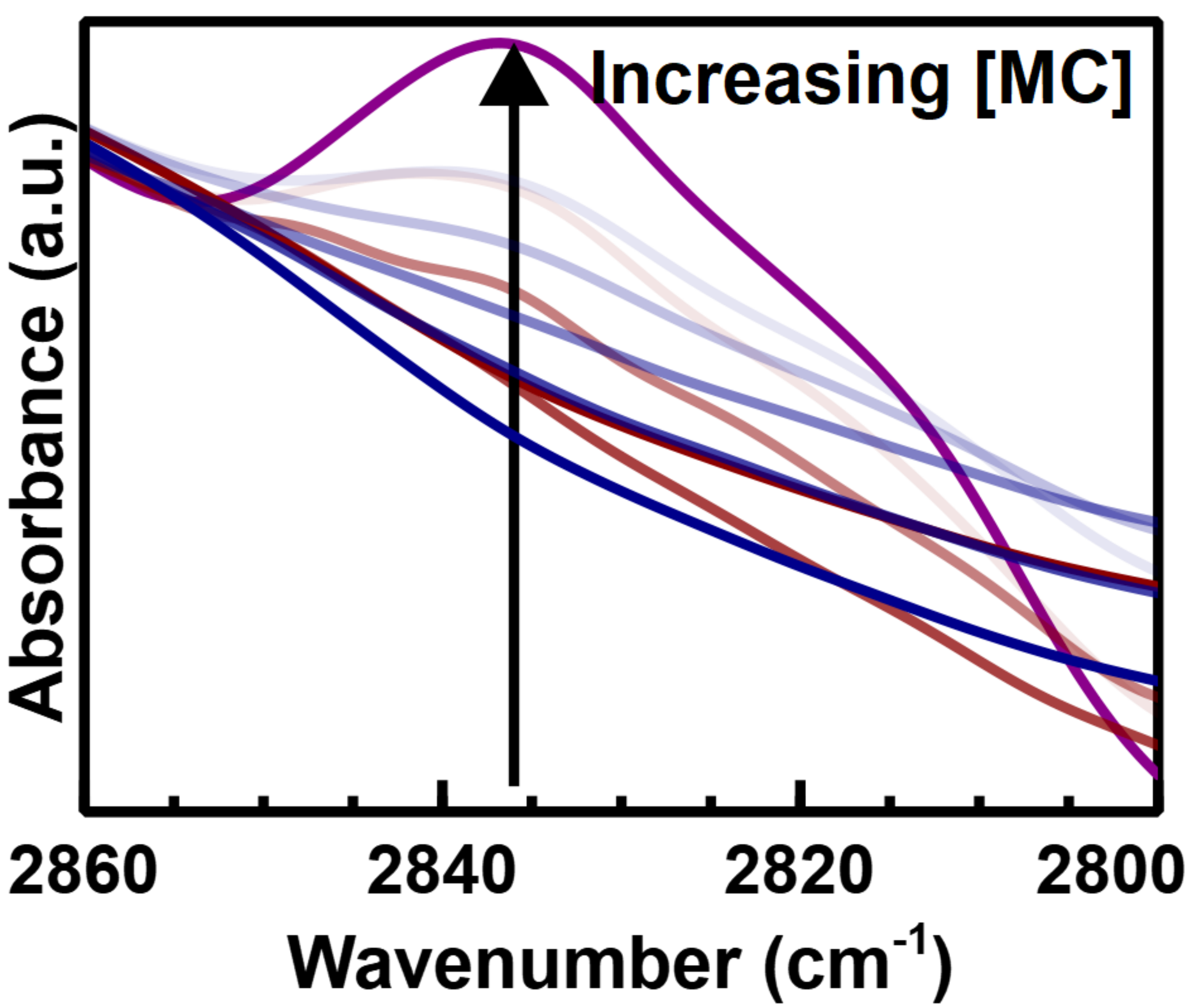
ACS Sustain. Chem. Eng. **2017**, 5, 5018–5026.

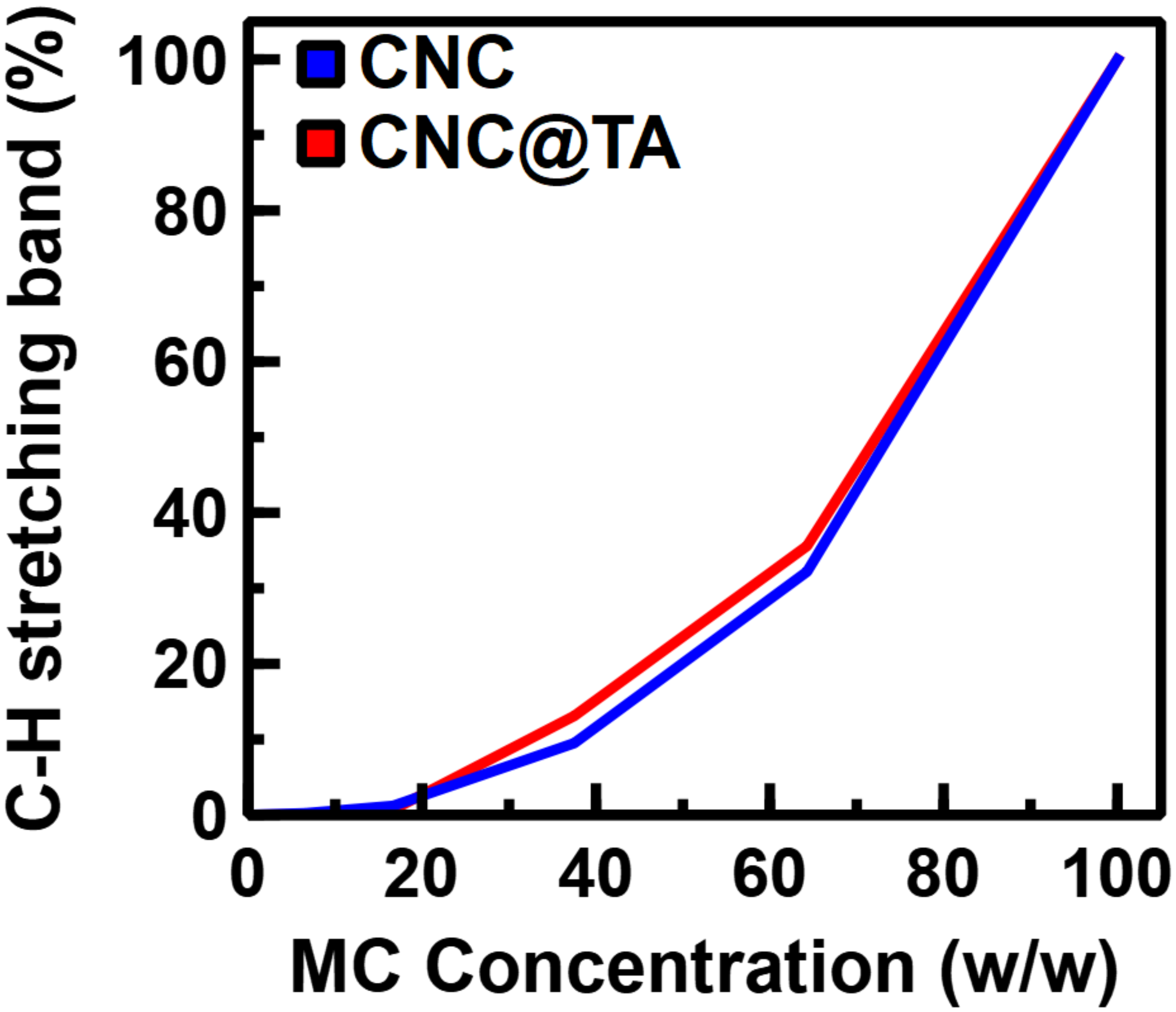
Molecular Analysis of CNC(@TA)@MC Aerogels

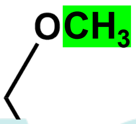




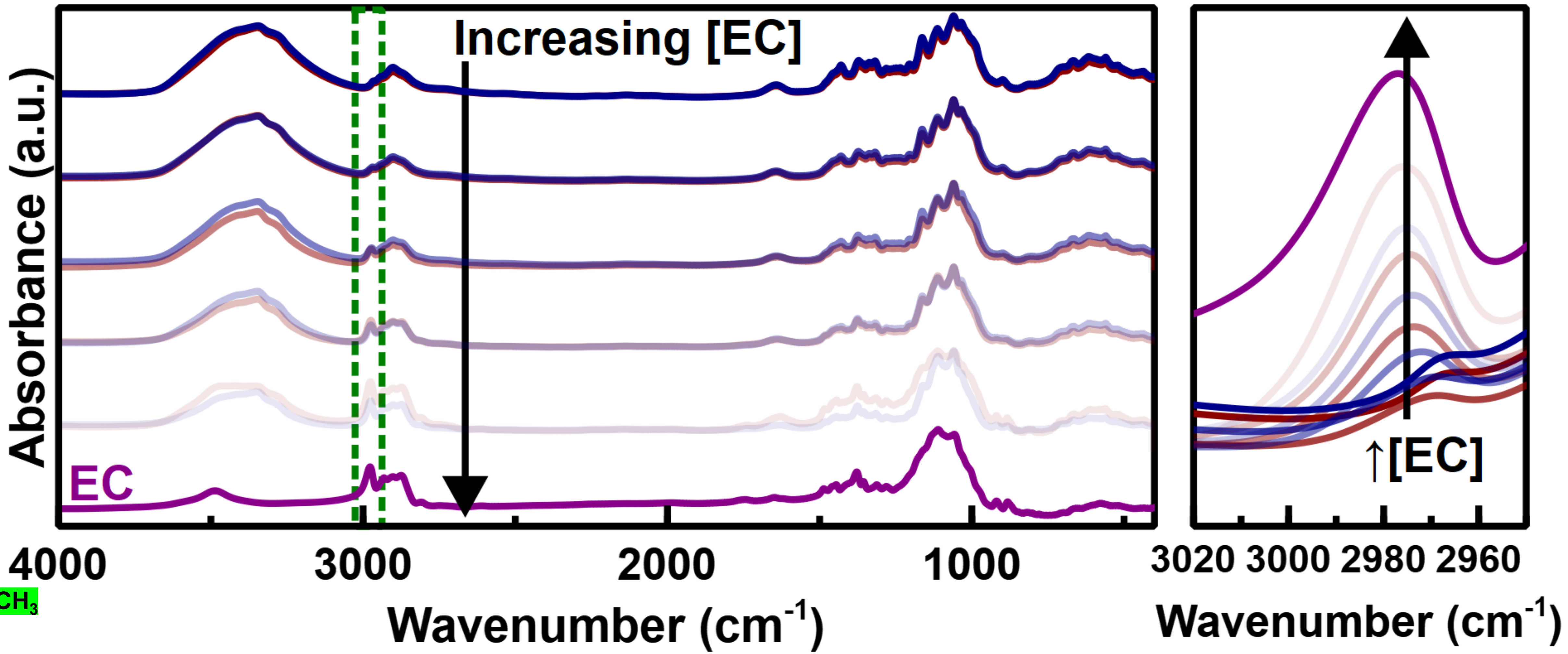
Molecular Analysis of CNC(@TA)@MC Aerogels

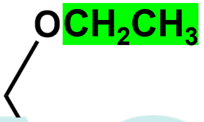




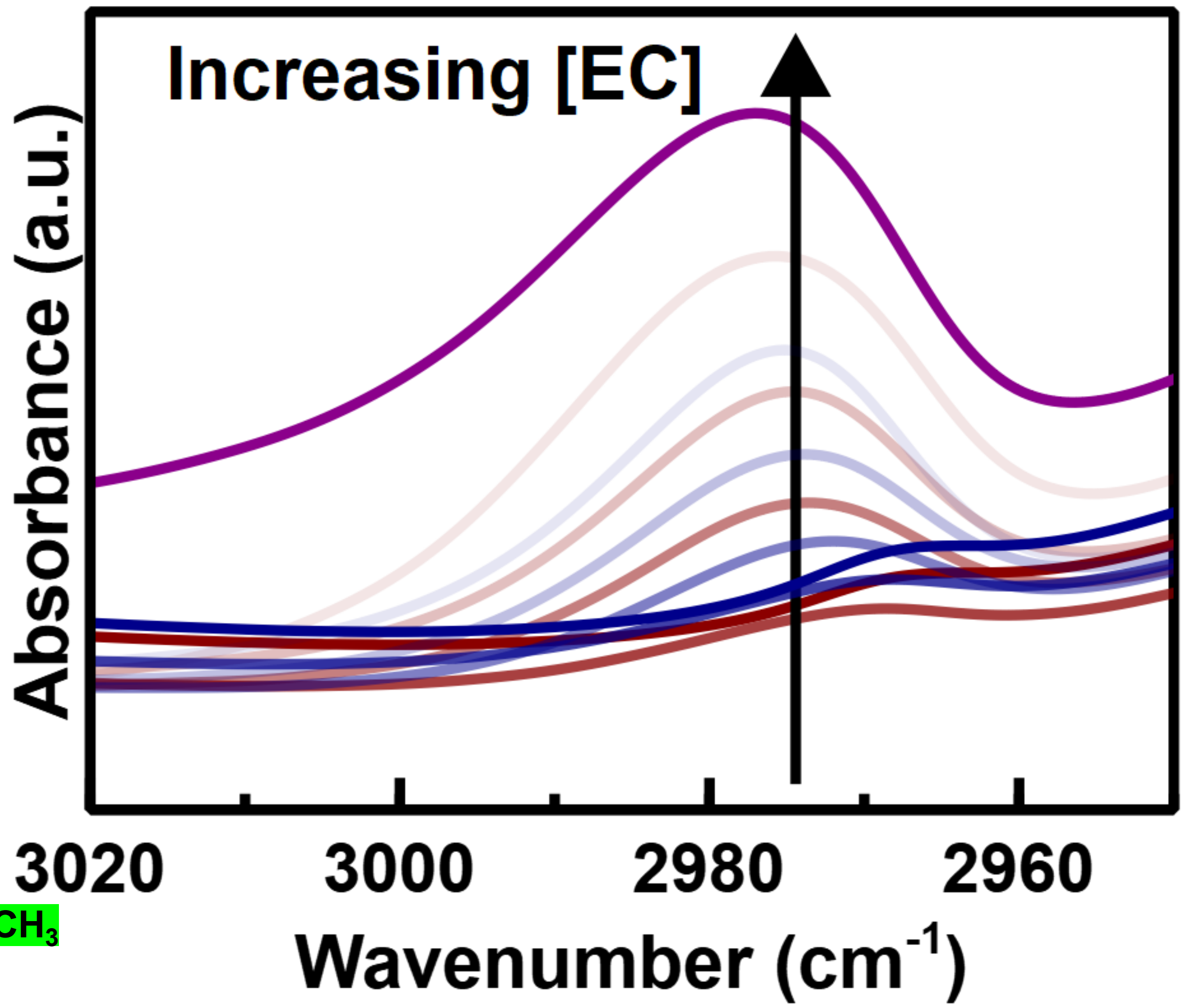


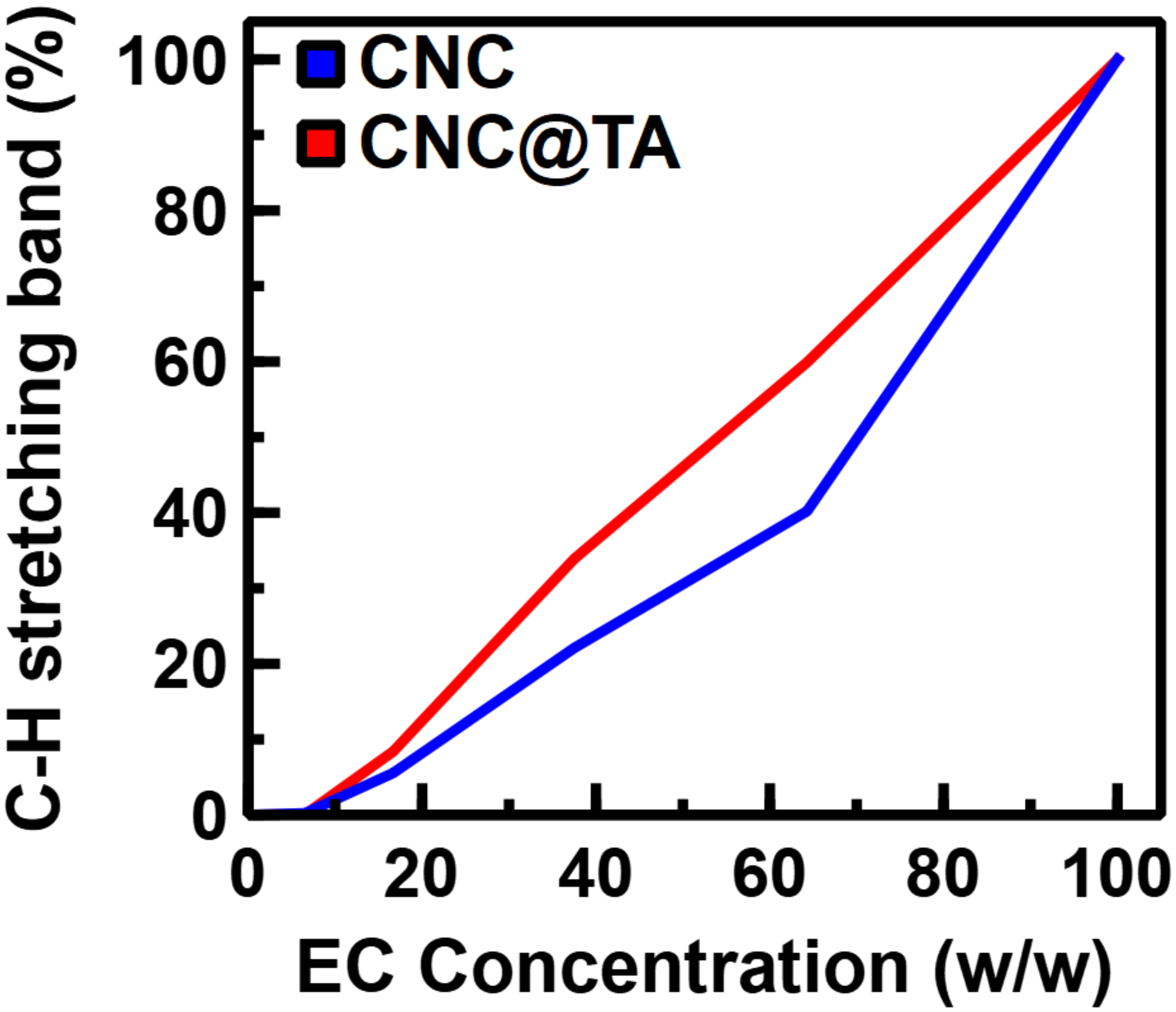
Molecular Analysis of CNC(@TA)@EC Aerogels

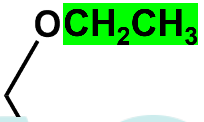




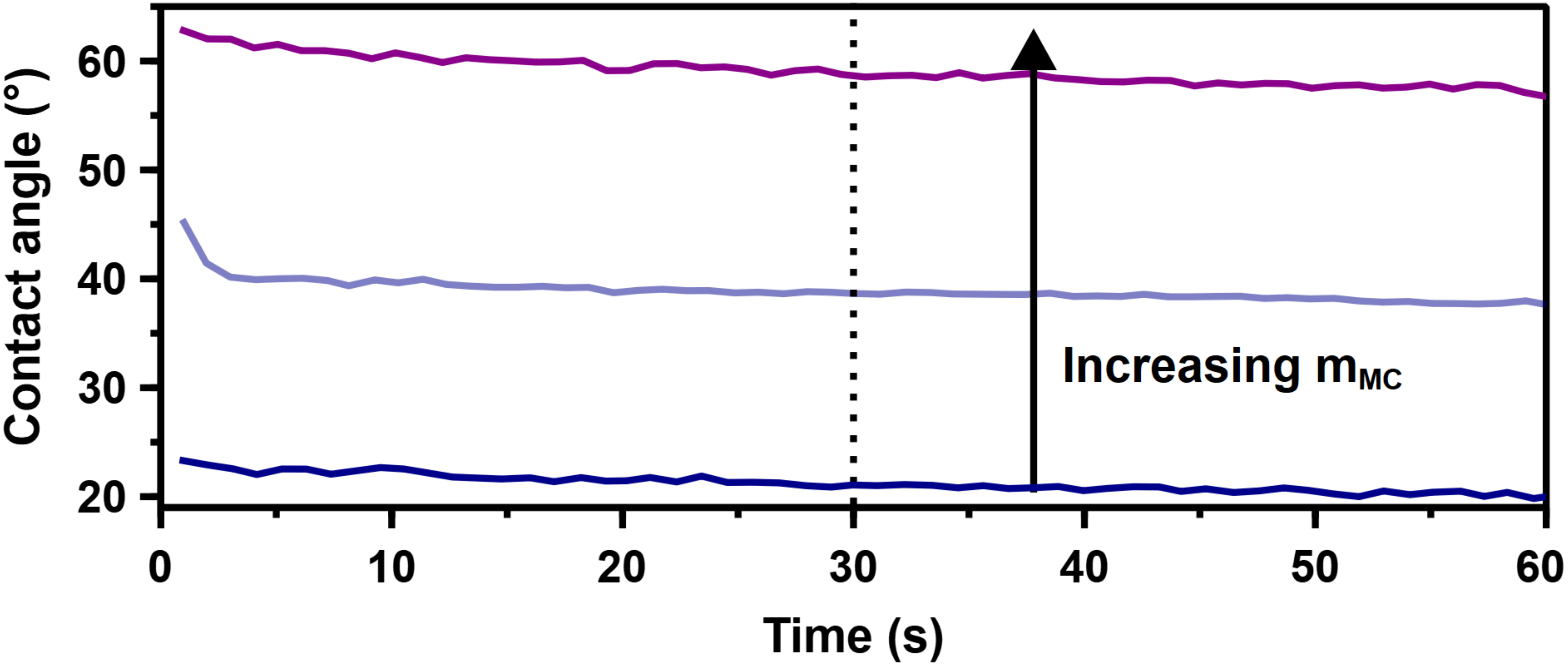
Molecular Analysis of CNC(@TA)@EC Aerogels

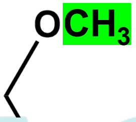




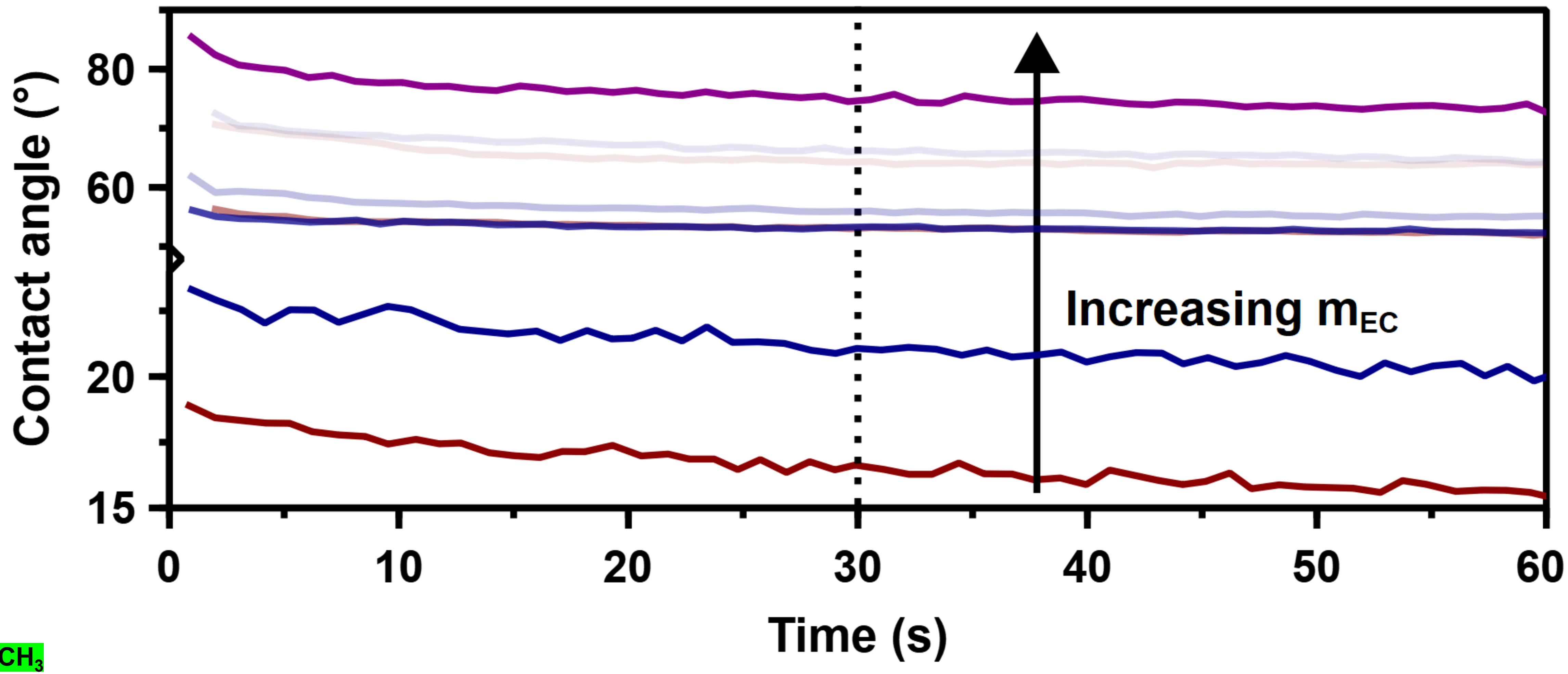


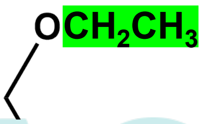
Water droplet dynamics on CNC(@TA)@MC solid interface





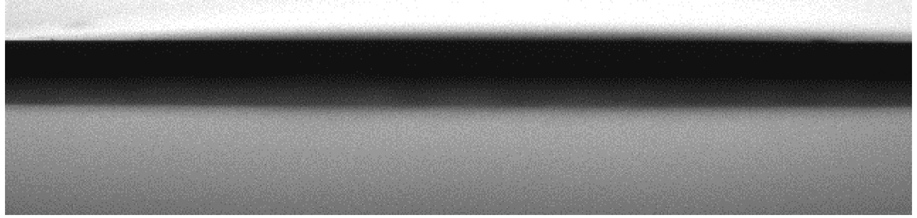
Water droplet dynamics on CNC(@TA)@EC solid interface



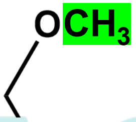


Hexadecane Contact Angle Pictures

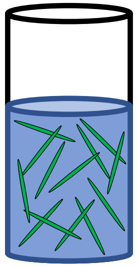
CNC@MC (2.7% w/w)



Superlipophilic

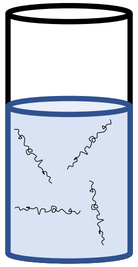


Sedimentation of CNC(@TA)@ACD Suspensions



5 g/L CNC(@TA) in H_2O

+



1 g/L ACD in H_2O or EtOH

Various ratios → from 250:7 to 5:9

+ Mixing + H_2O or EtOH evaporation through rotovapor + AcO addition

+ AcO evaporation on hotplate (slow)

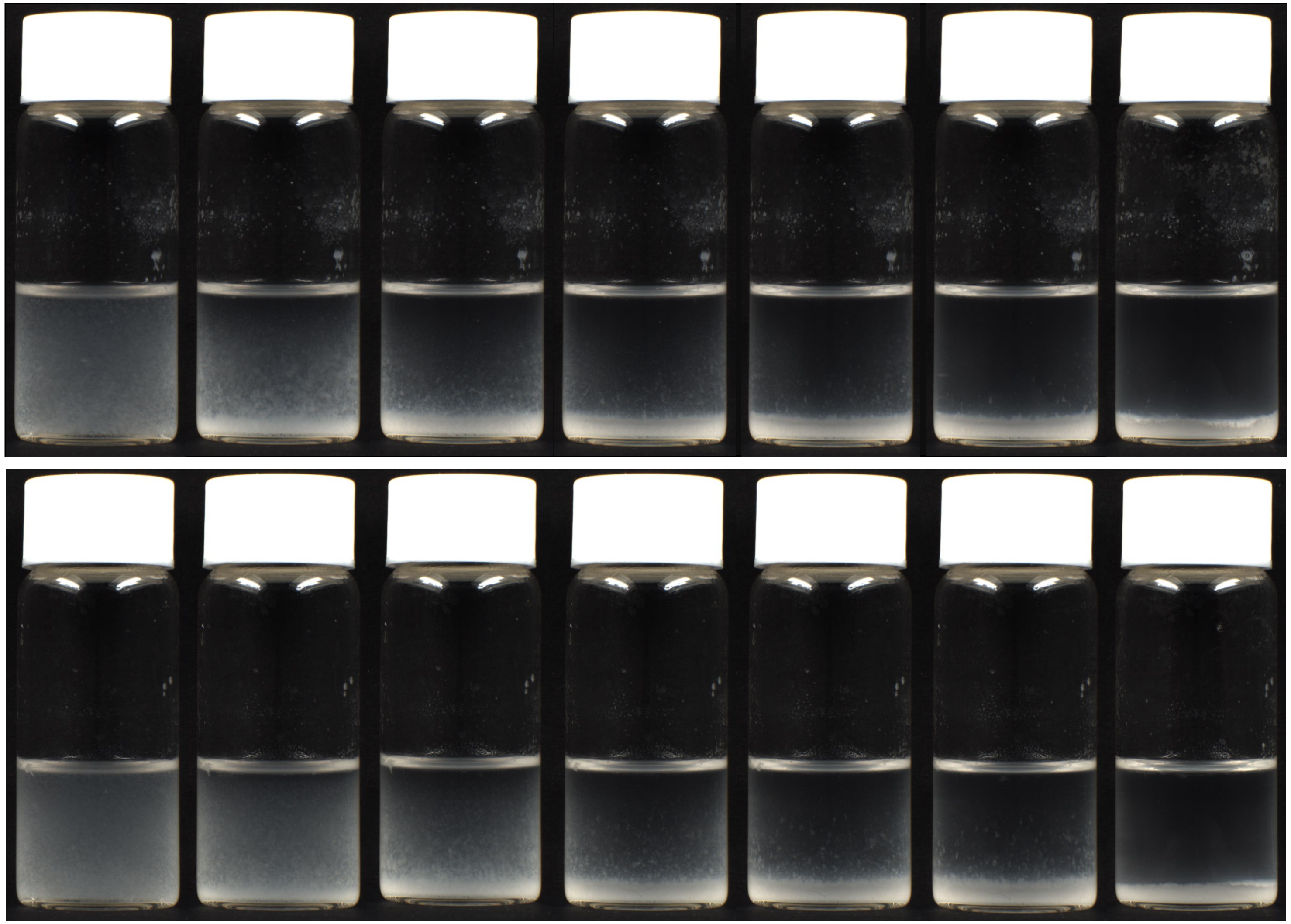
= **Unstable colloidal suspensions / sedimentation**

Sedimentation of CNC@EC and CNC@TA@EC Suspensions (64.3 wt%)

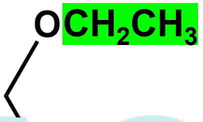
minutes 0 0.5 1 2 4 8 10080

CNC@TA

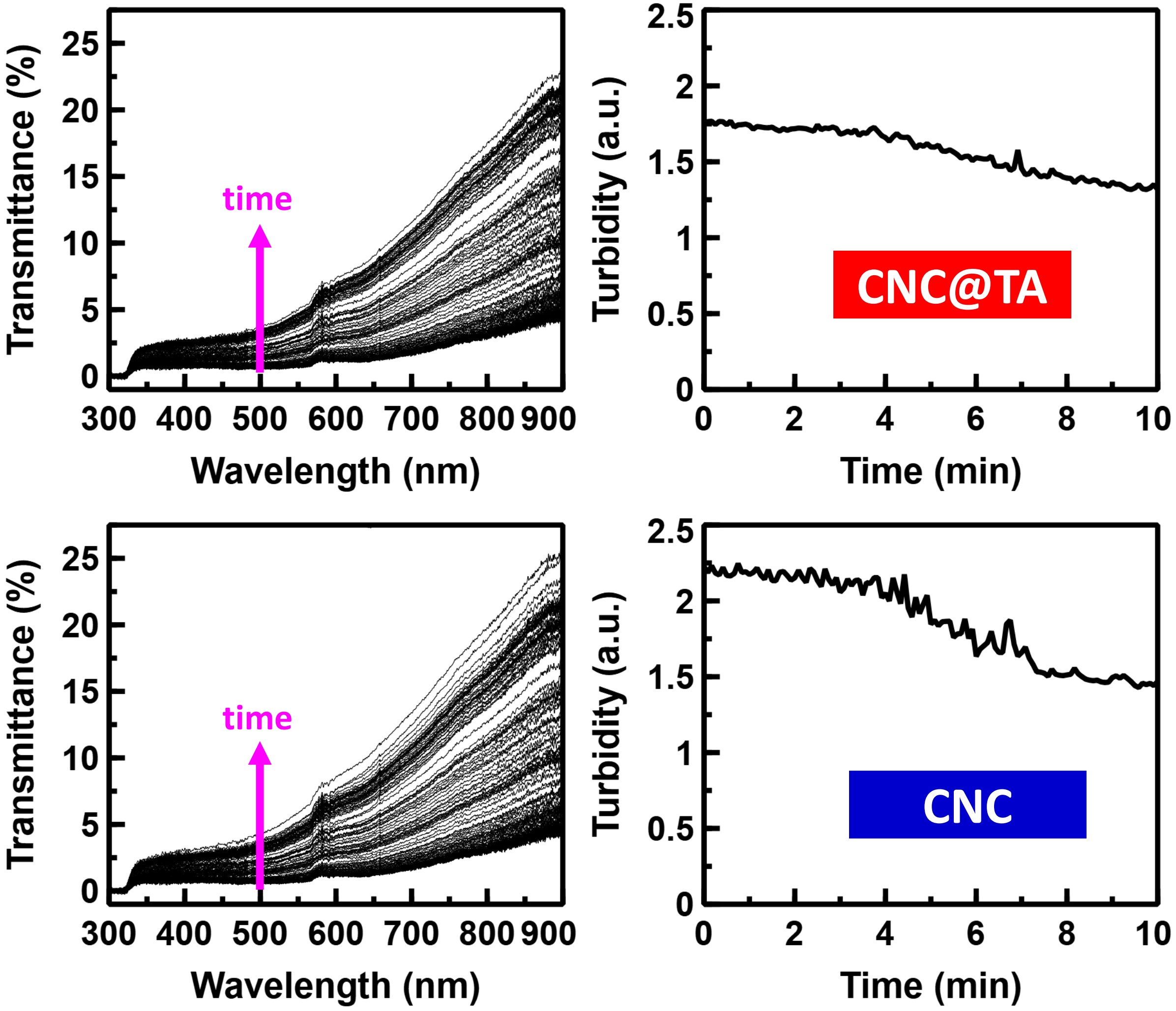
CNC

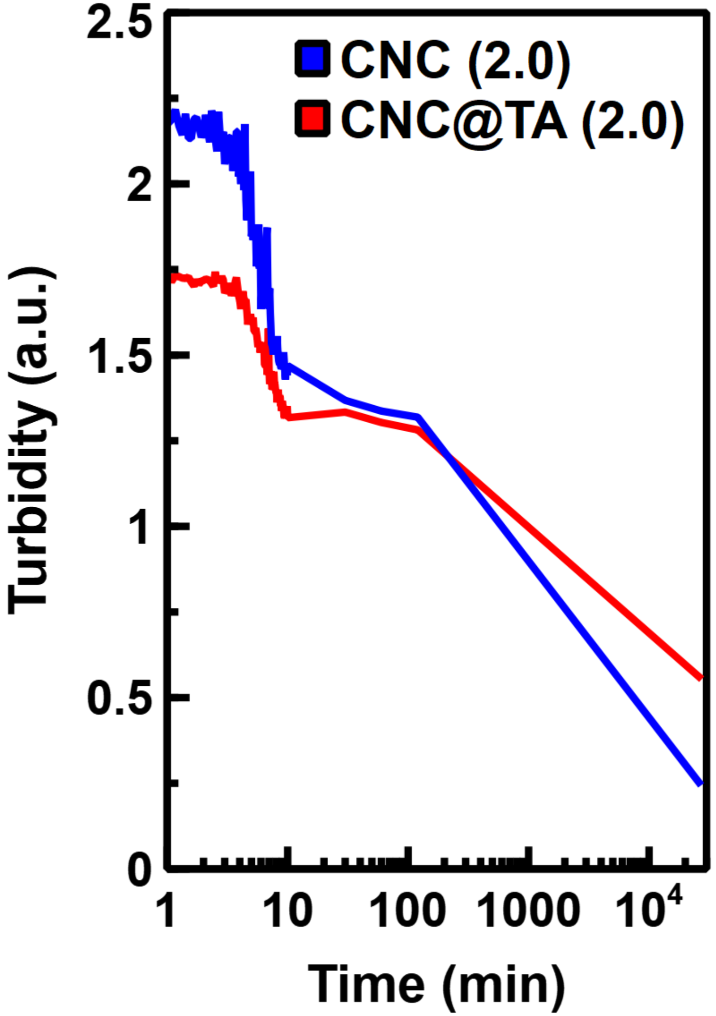


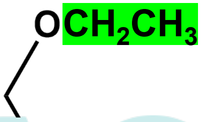
time



Sedimentation of CNC@EC and CNC@TA@EC suspensions





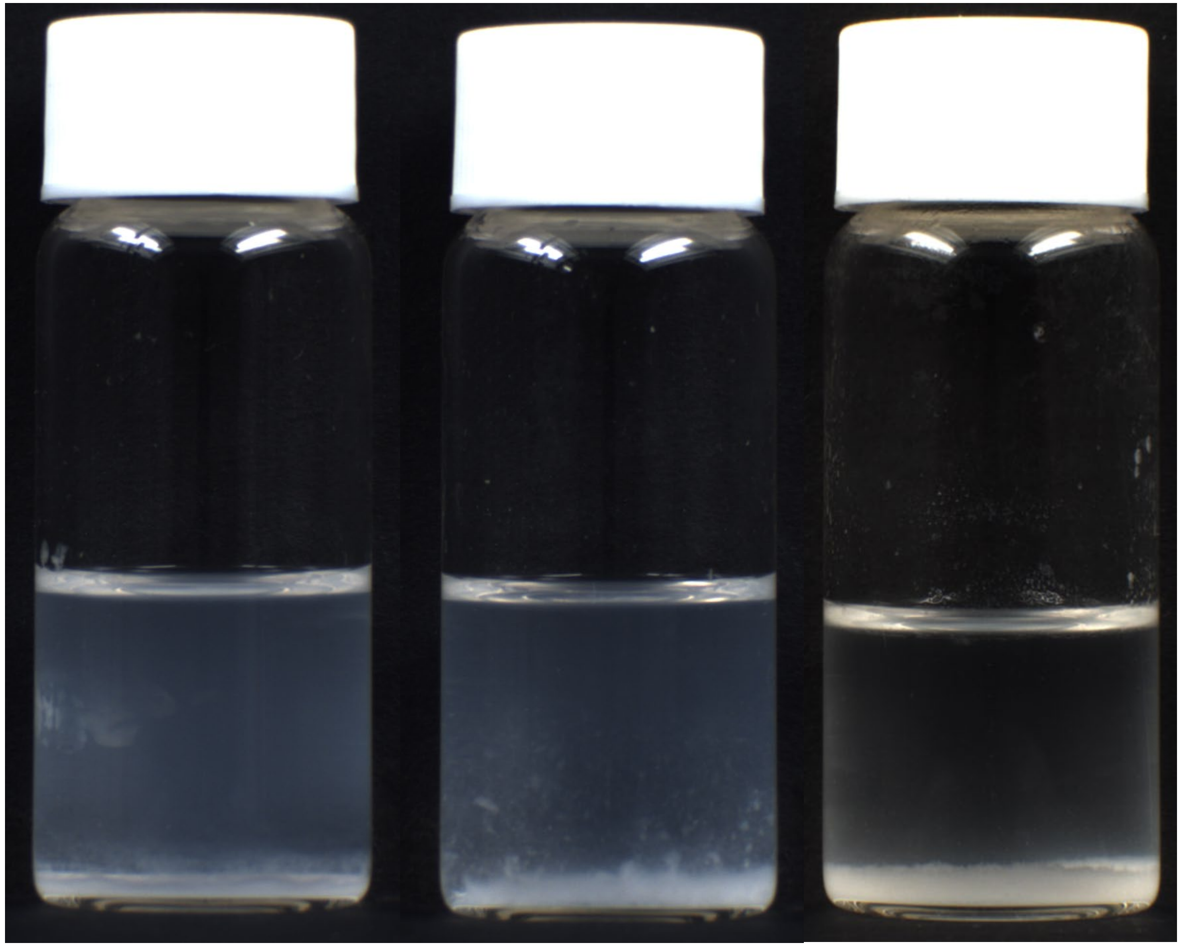


CNC(@TA)@EC Sedimentation Depending on EC mass

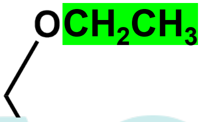
[EC] (w/w)

6.5 | 16.7 | 64.3

CNC

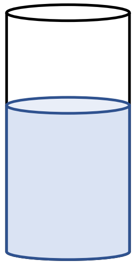


t = 10080 min



[EC] (w/w)

Redispersibility of CNC(@TA)@EC aerogels



1 mL
solvent

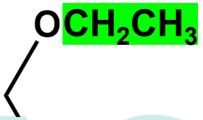
in

+

1 mg aerogel

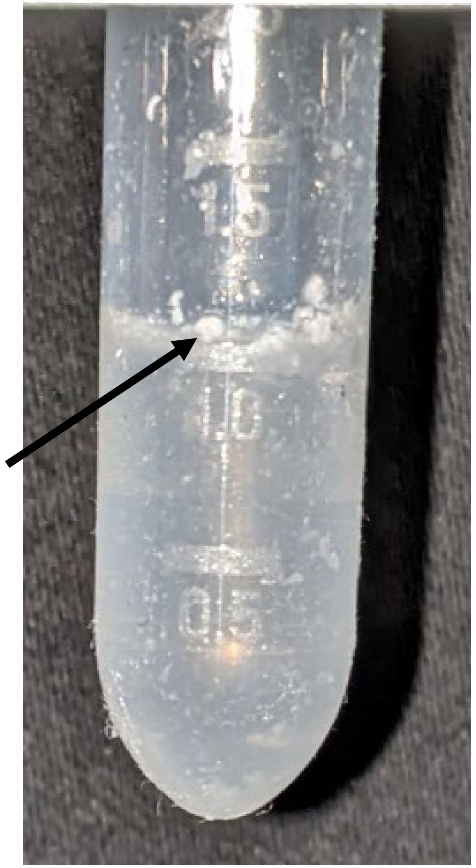
+

Vortex mixing (10 sec)



Redispersibility of CNC(@TA)@EC Aerogels (1 mg/1 mL)

CNC@TA@EC (64.3) in water

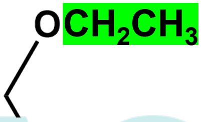


pieces of aerogel

CNC@TA@EC (64.3) in hexadecane

organogel

EC in hexadecane

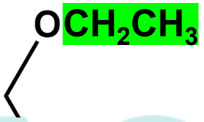


All redispersible in water and not hexadecane **APART FROM CNC@TA@EC (64.3% w/w)** which is not redispersible in water and form an **organogel** in hexadecane

Redispersibility of CNC(@TA)@EC Aerogels (1 mg/1 mL)

[EC]	Water		Hexadecane		Ethanol		Toluene		Acetone	
0.0	CNC	CNC@TA	CNC	CNC@TA	CNC	CNC@TA	CNC	CNC @TA	CNC	CNC @TA
6.5										
16.7										
37.5										
64.3										
100.0										

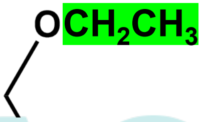
Green = redispersible; Blue = swelling/gel; Red = not redispersible; Grey = N/A.



Redispersibility of Sedimented CNC(@TA)@EC Aerogels (1 mg/1 mL)

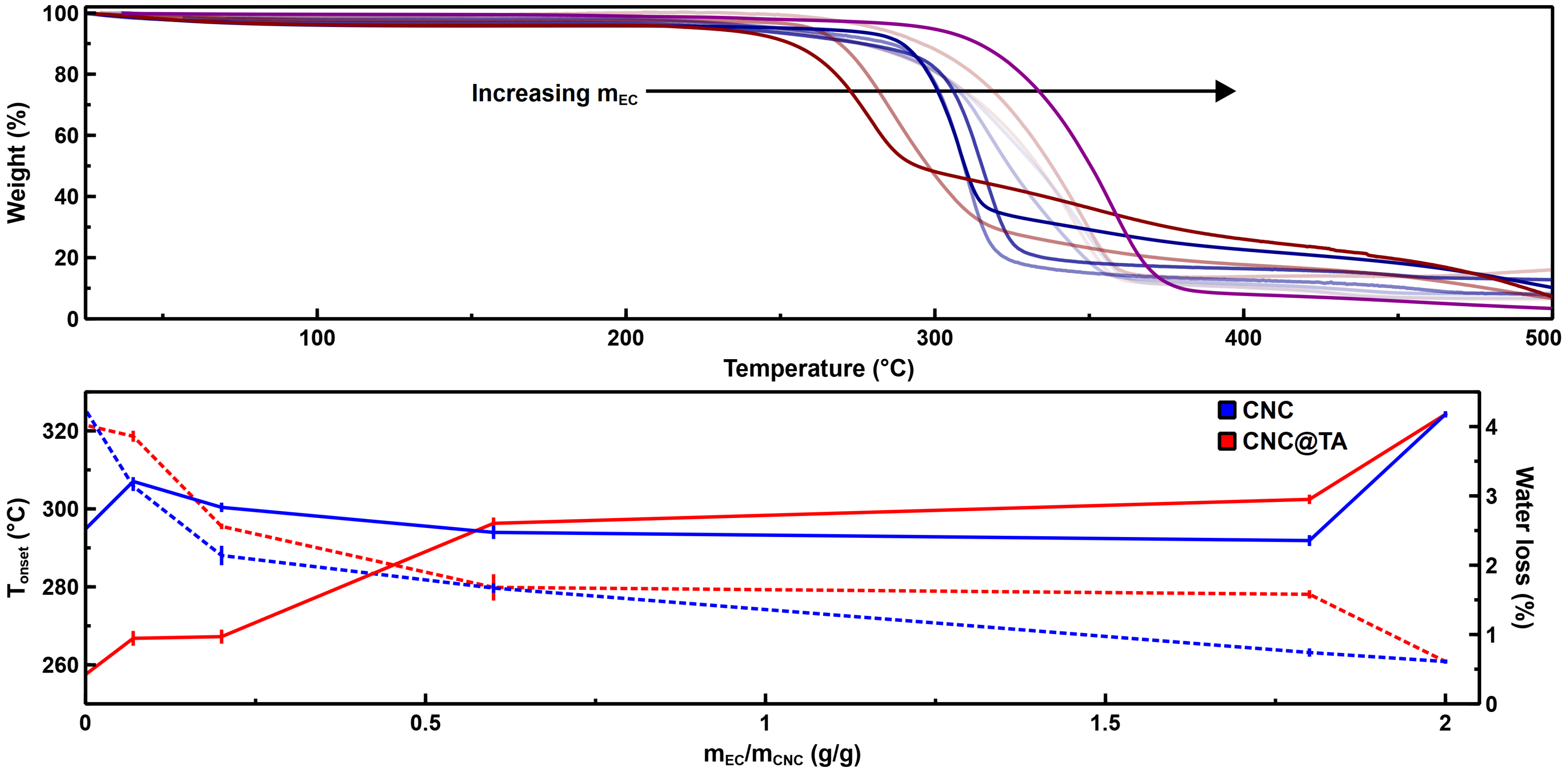
[EC]	Water		Hexadecane		Ethanol		Toluene		Acetone	
0.0	CNC	CNC@TA	CNC	CNC@TA	CNC	CNC@TA	CNC	CNC @TA	CNC	CNC @TA
6.5										
16.7										
37.5										
64.3										
100.0										

Green = redispersible; Blue = swelling/gel; Red = not redispersible; Grey = N/A.



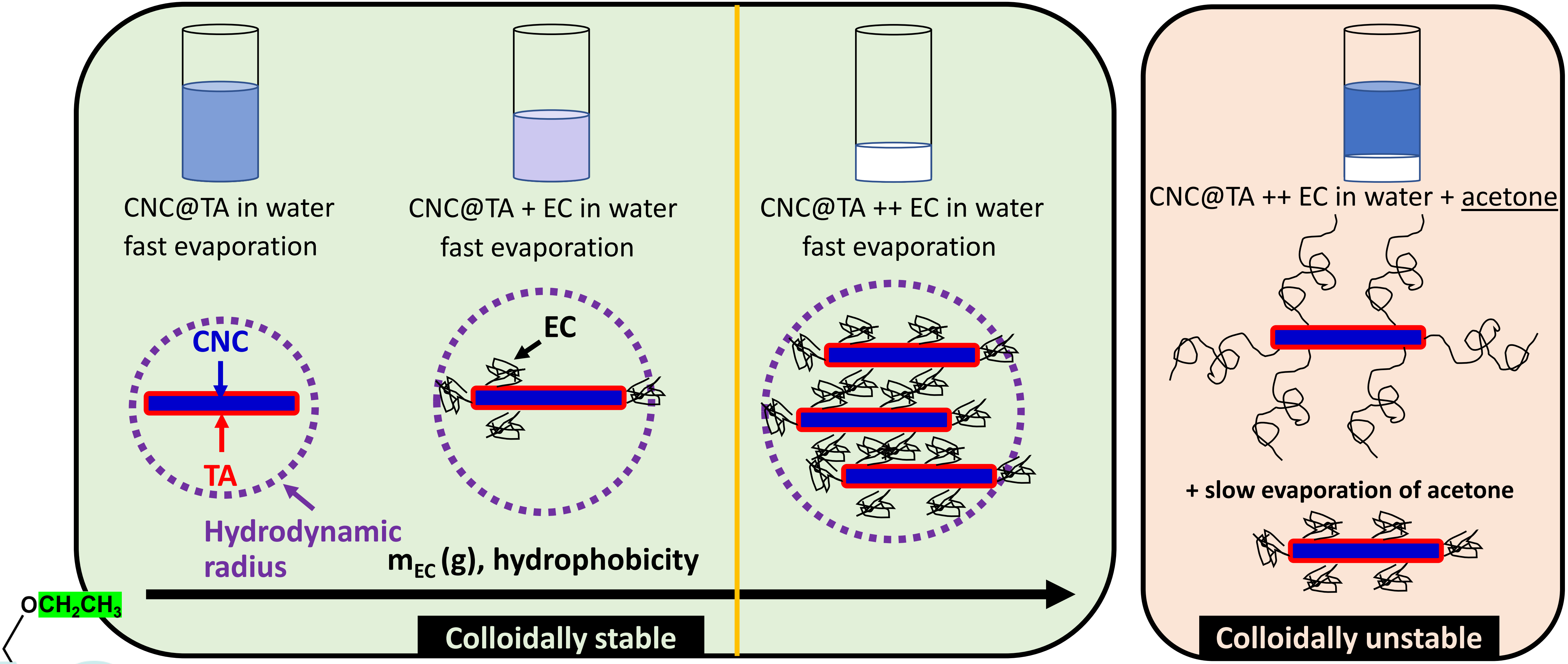
INRAE

Thermal Stability of CNC(@TA)@EC Aerogels



OCH_2CH_3

Model of CNC@TA@EC Nanoparticles



Phase transition from CNC coating to CNCs in EC matrix

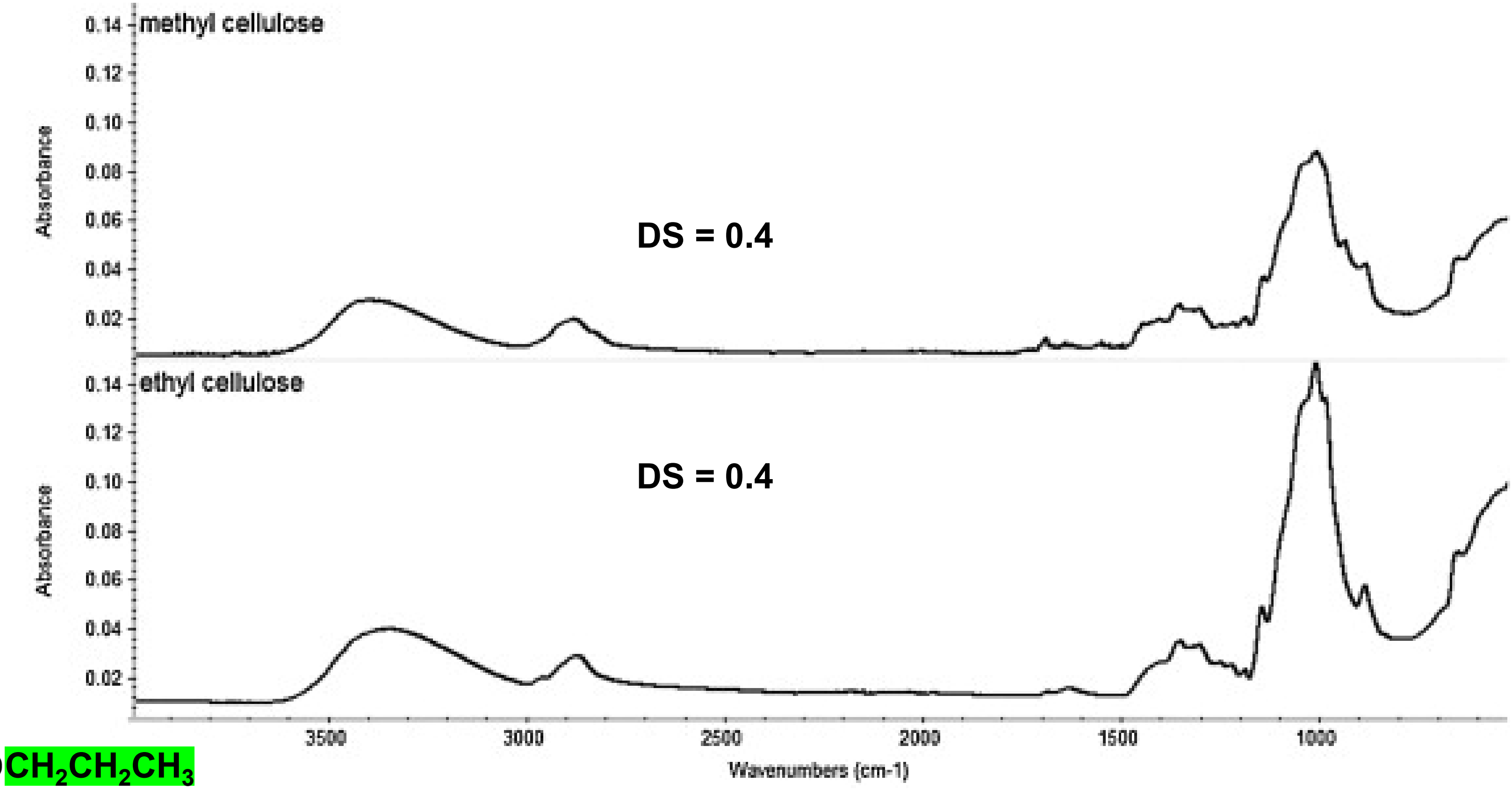
Properties of Propyl Cellulose

Carbohydrate Polymers
Volume 94, Issue 1, 15 April 2013, Pages 120-123

Short communication

Microwave-assisted synthesis of alkyl cellulose in aqueous medium ☆

Atanu Biswas [a], S. Kim [a], G.W. Selling [a], H.N. Cheng [b]



$OCH_2CH_2CH_3$

Probable DS of our PC = 0.4
Unknown molecular weight