
Im Kleinen liegt Großes
—
Nanostrukturierte funktionelle Materialien aus
Holzkomponenten

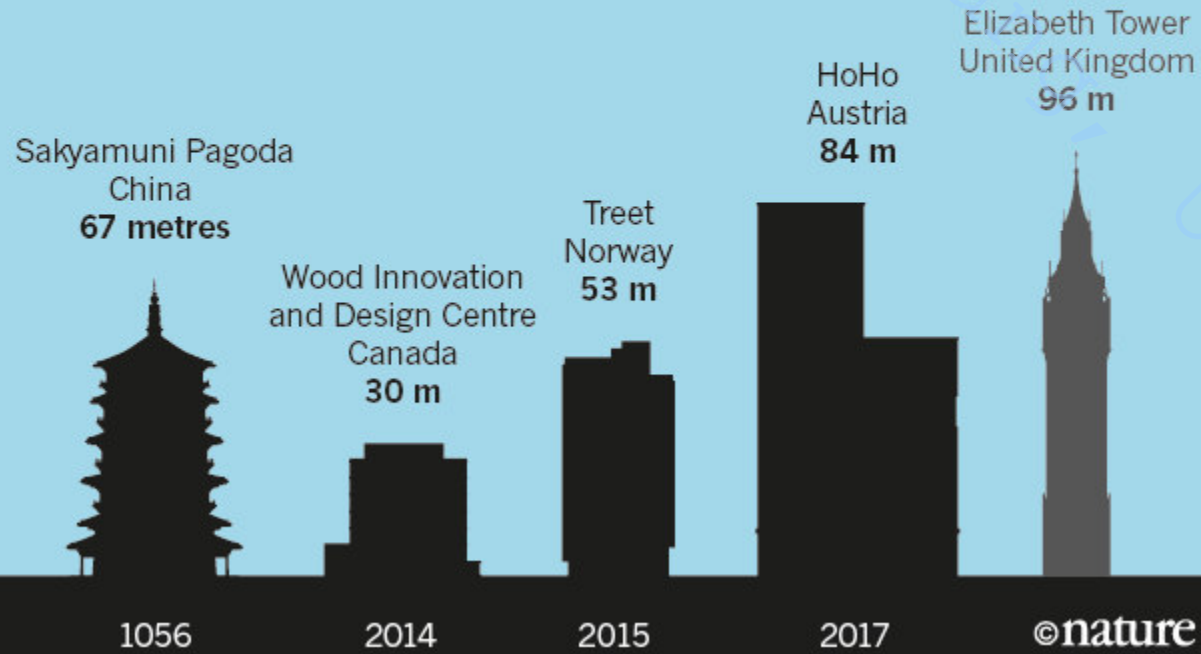
Jr.-Prof. Dr. **Kai Zhang**

*JP Holztechnologie & Holzchemie
Georg-August-Universität Göttingen*

NHN Tagung, Jun. 2017

THE WOODEN RENAISSANCE

As advanced timber technologies enable wooden buildings to approach the heights of more conventional landmarks such as Elizabeth Tower, they promise to lock up carbon dioxide and reduce the emissions associated with steel and concrete construction.



53-metre dormitory at the University of British Columbia in Vancouver



energy



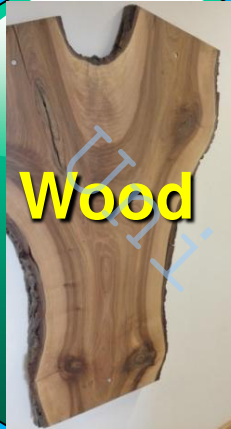
paper



Construction materials



Wood



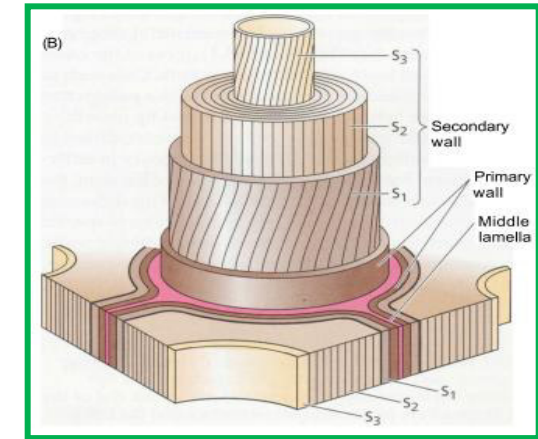
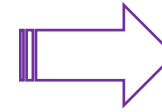
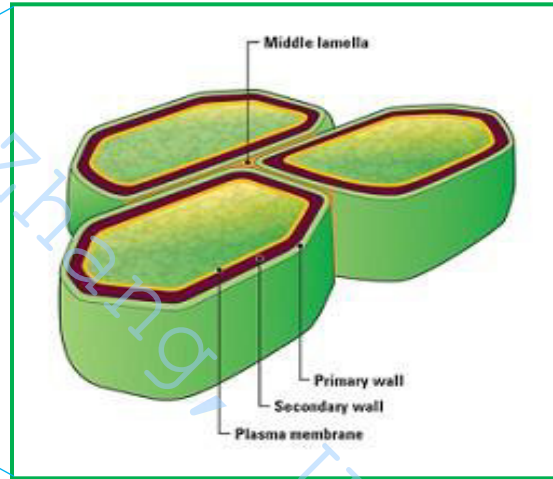
textile



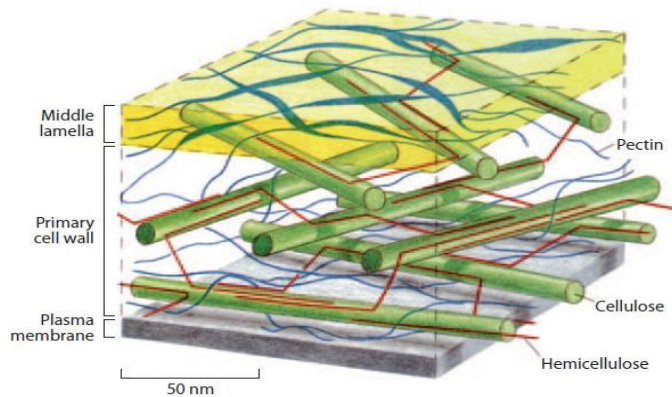
Many others



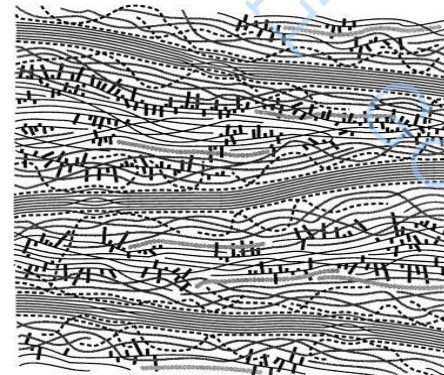
Hierarchical structure in plant cell wall



Taiz and Ziegler 1993

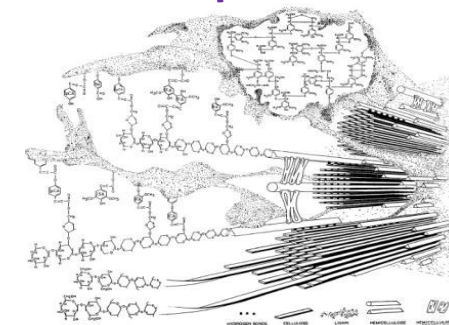


Scheller 2010 Annu Rec Plant Biol



Pea primary cell wall

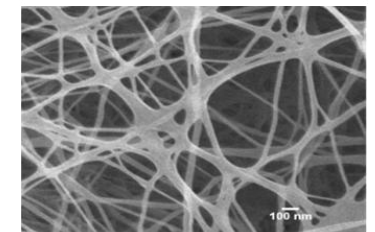
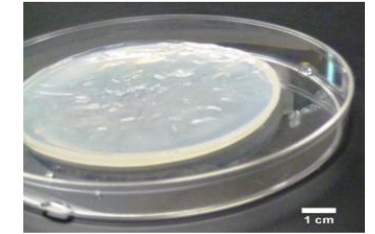
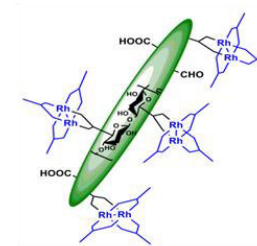
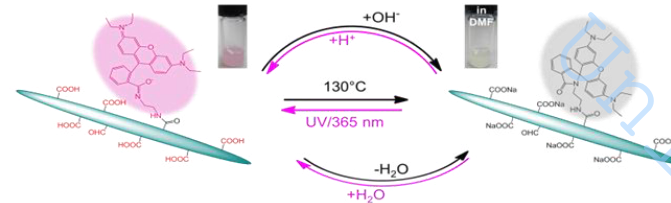
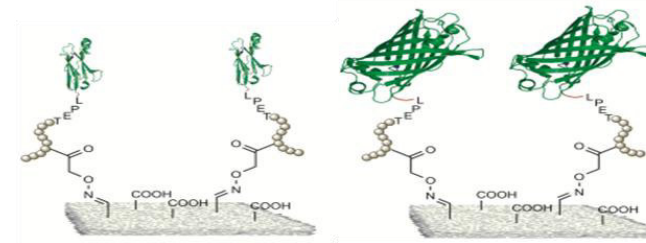
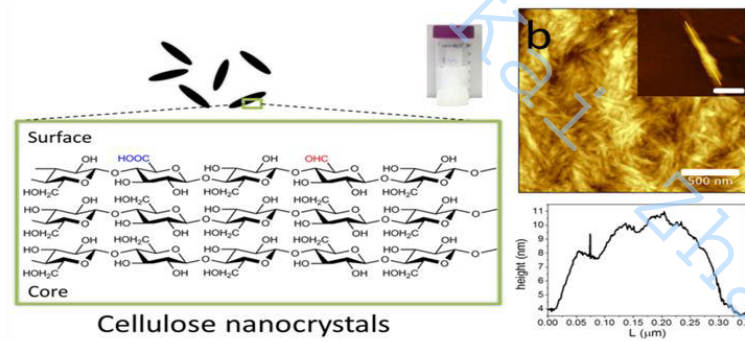
Talbott and Ray, 1992 Plant Physioll



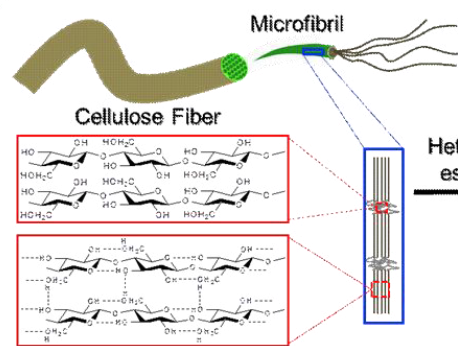
Secondary cell wall

Bidlack et al., 1992 Proc Okla Acad Sci

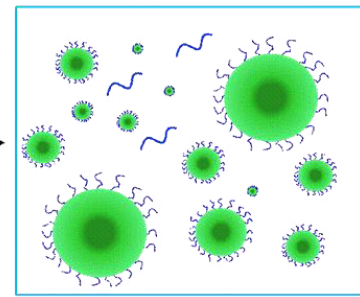
Nanocellulose



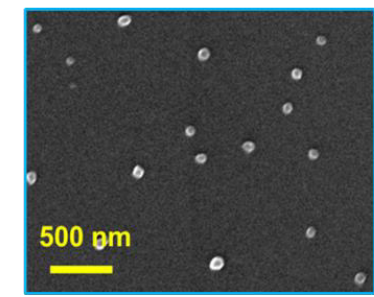
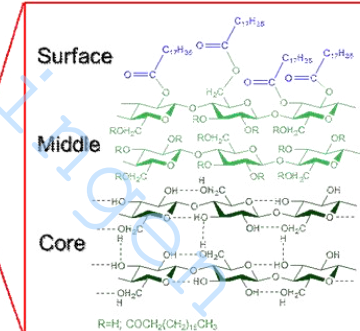
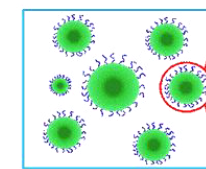
bacterial cellulose



Heterogeneous esterification



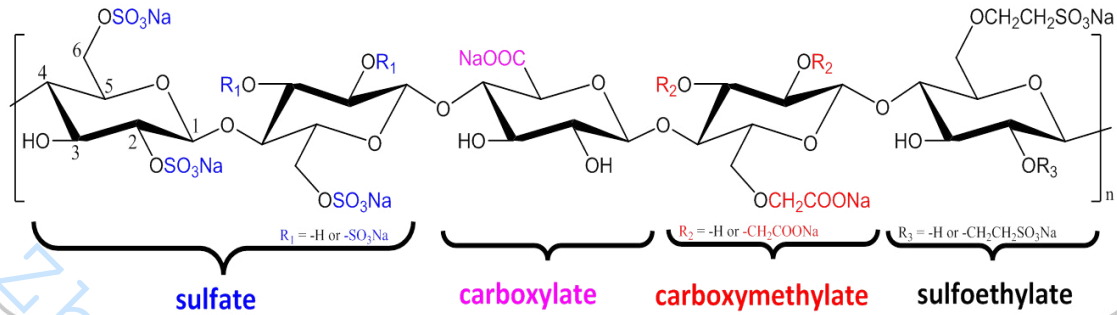
Centrifugation



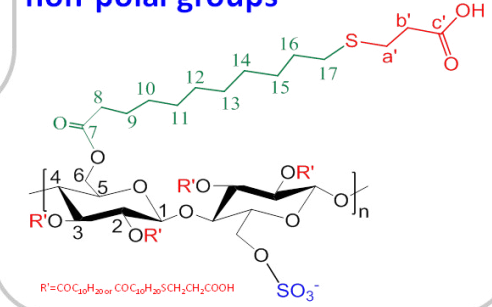
Surface-Stearoylated Cellulose Nanoparticles (SS-CNPs)

Holzchemie und Cellulosechemie

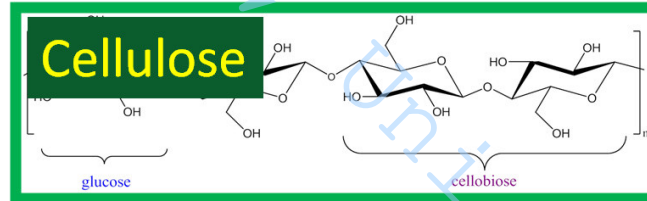
ionic groups



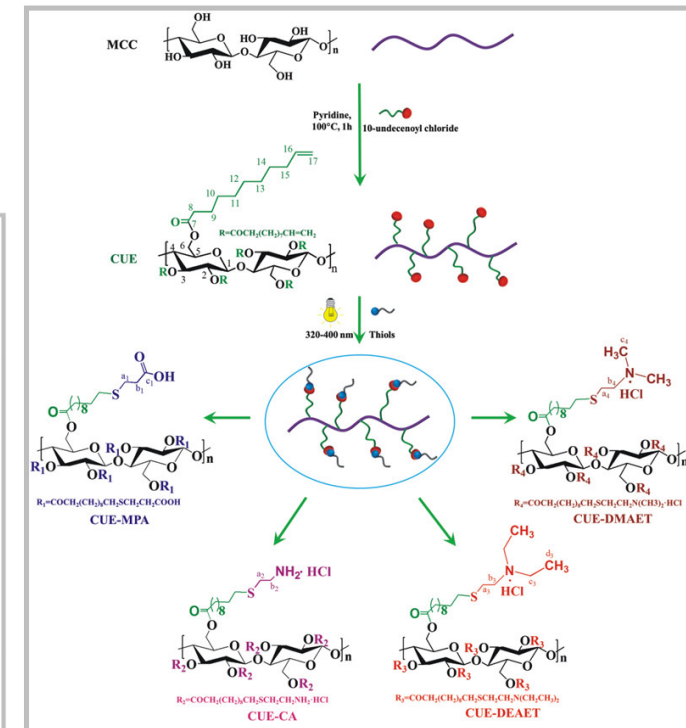
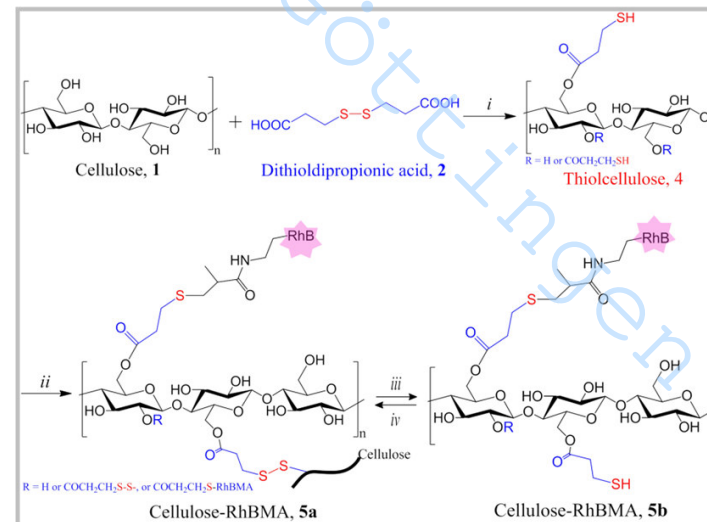
non-polar groups



Cellulose

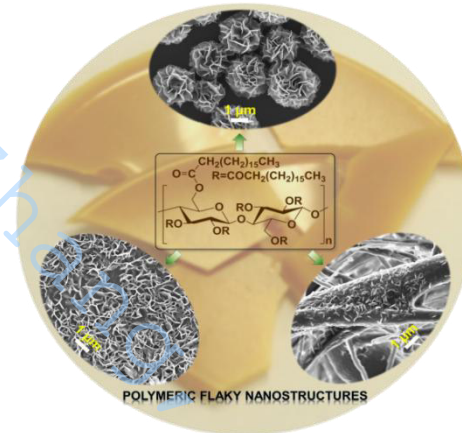
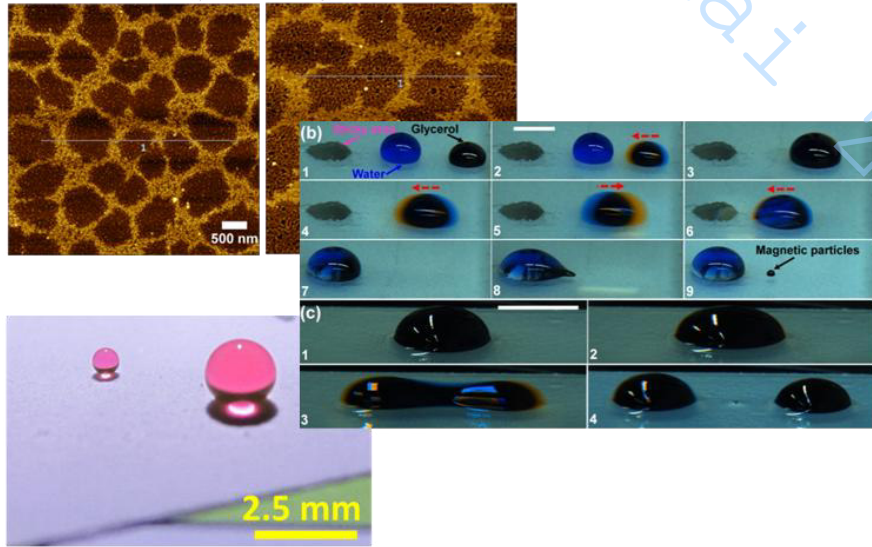


& more

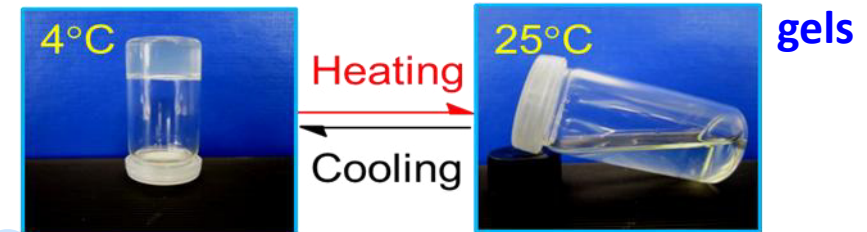


Funktionelle Materialien

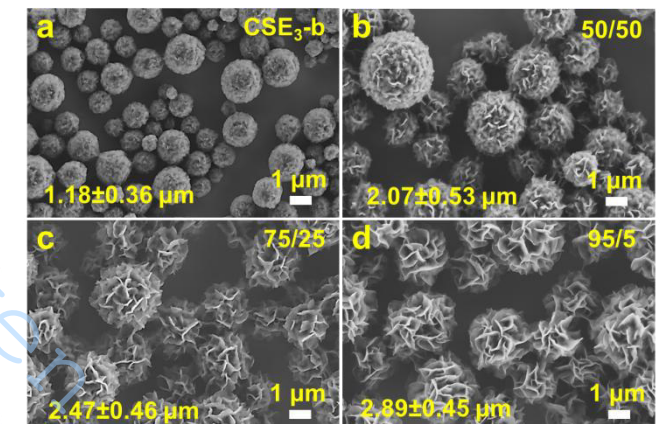
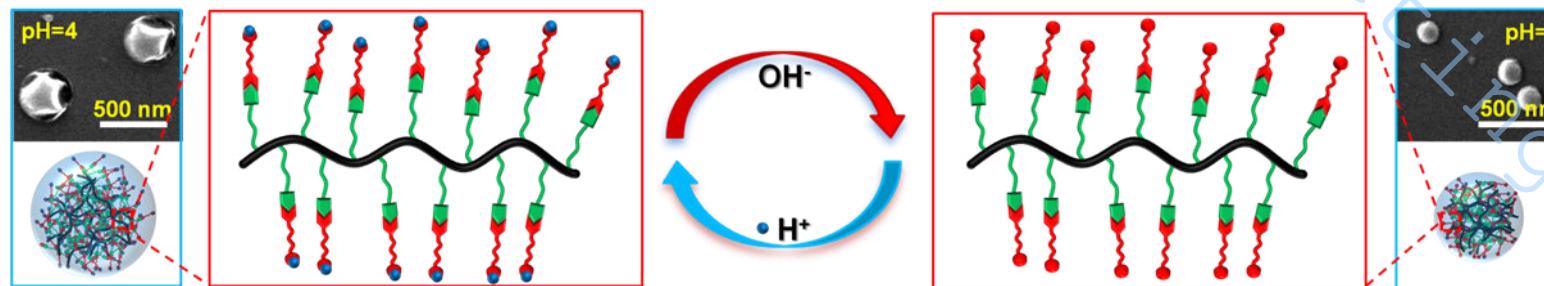
Surface coating (e.g. super/hydrophobization)



Responsive, self-standing films

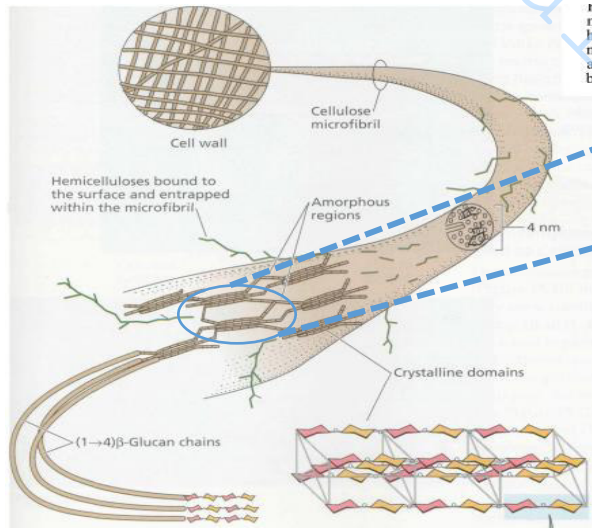


nanoparticles / microparticles



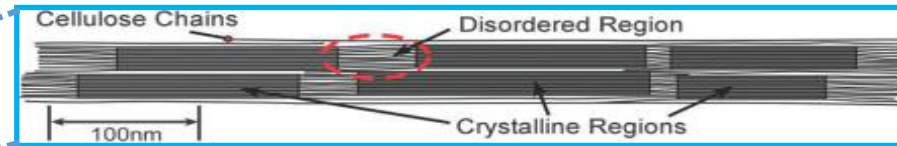
Synthesis of crystalline nanocellulose

Native Cellulose



Taiz and Ziegler 1993

Cellulose at nanoscale and molecular level

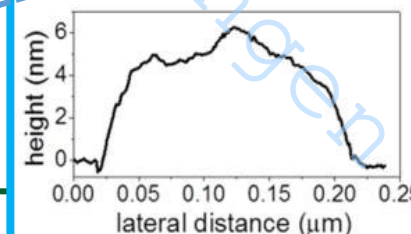
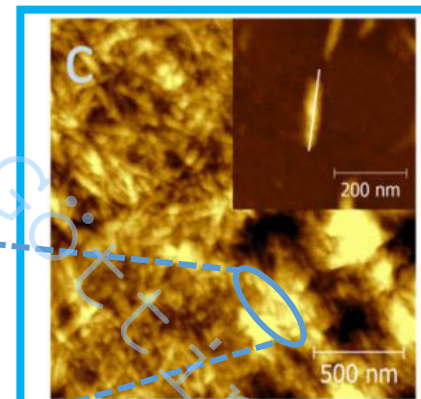


Moon et al., 2011 Chem Soc Rev

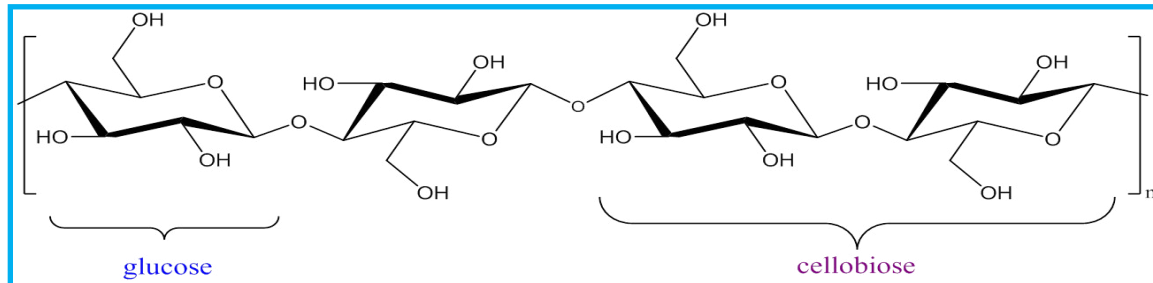
chemically / mechanically



Microfluidizer (microfluidics incorp.)

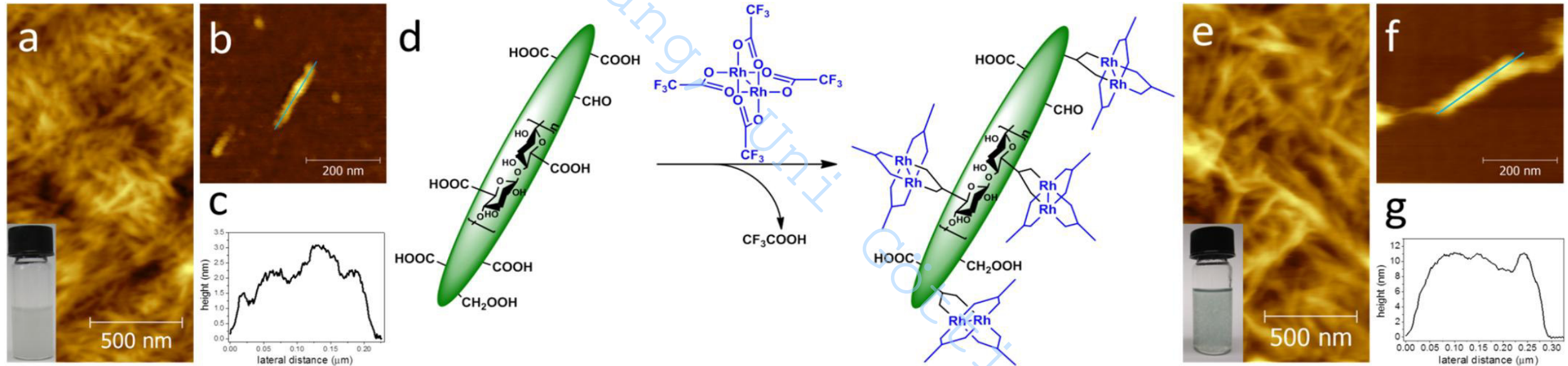


Nano/Microfibrillated cellulose (NFC)
Cellulose nanocrystals (CNC)
Cellulose nanowhiskers (CNW)
etc.



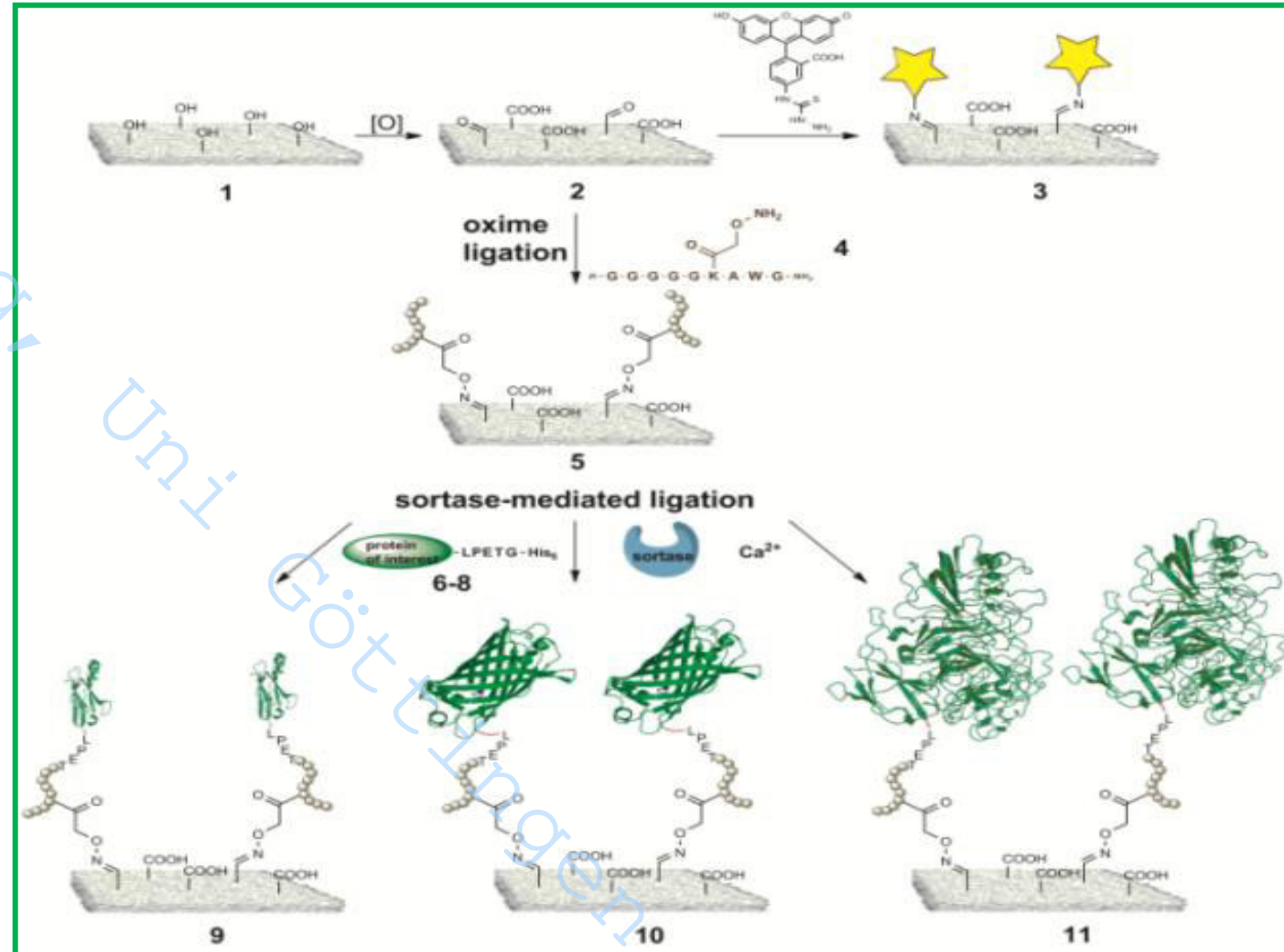
Heterogeneous catalysis: Dirhodium (II) complex on CNC

- Synthesis: immobilization of dirhodium complex onto CNC surface

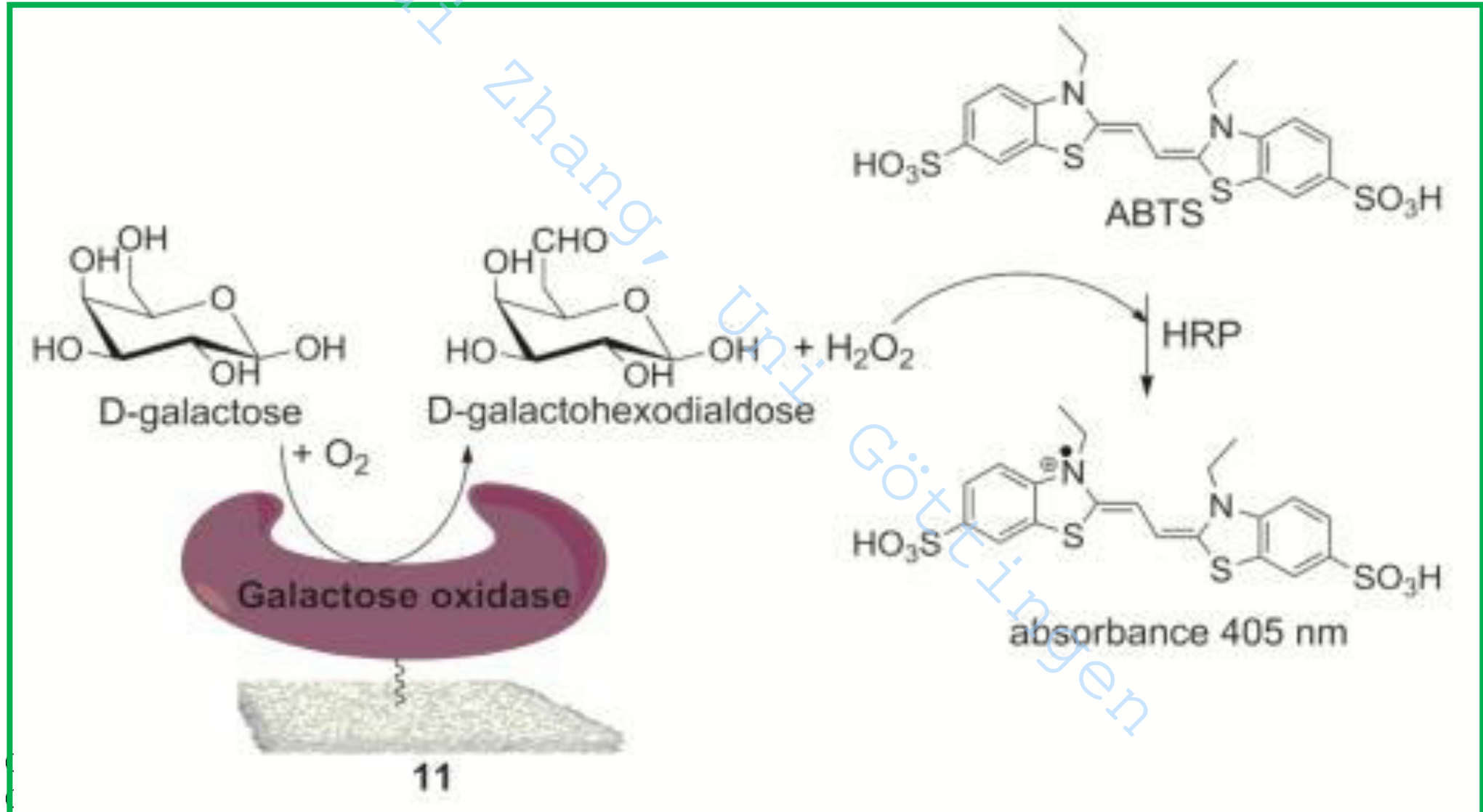


Cellulose nanocrystals (CNC) as substrate for biomacromolecules, e.g enzymes.

- Potential carrier systems
- Accessible surface
- The amount of potential guest compounds at μmol level

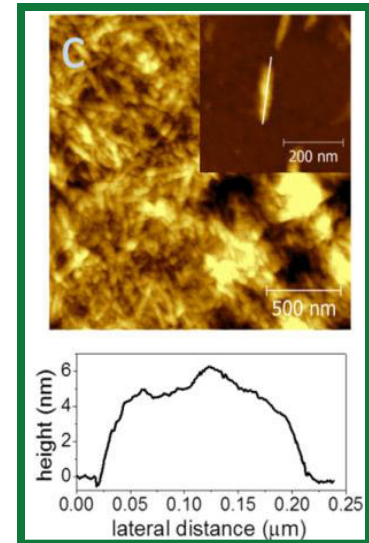
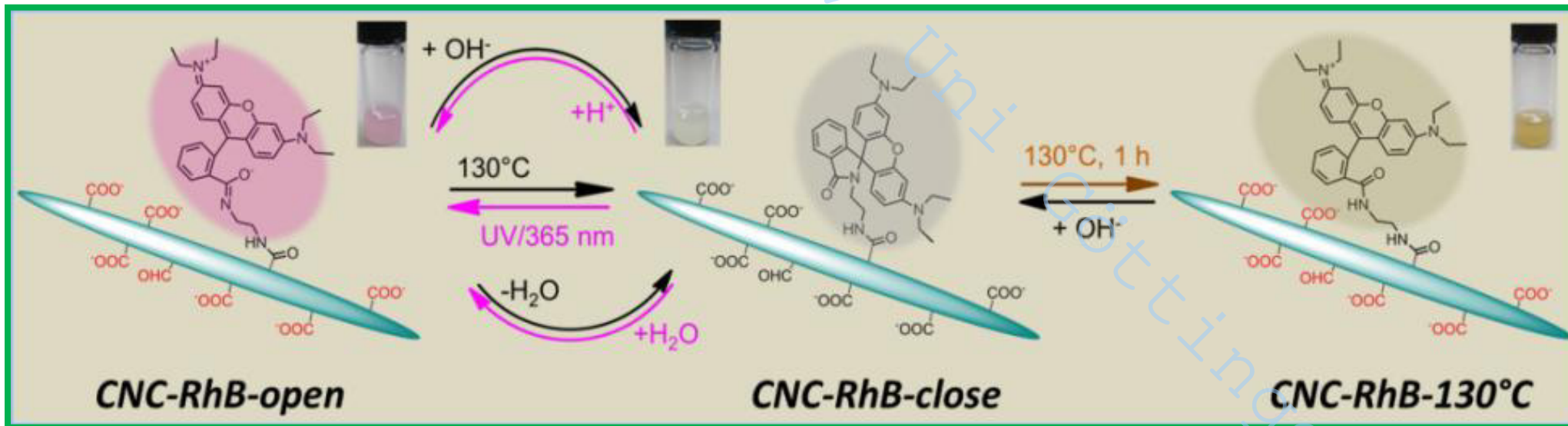


Example: CNC with immobilized galactose oxidase with maintained activity



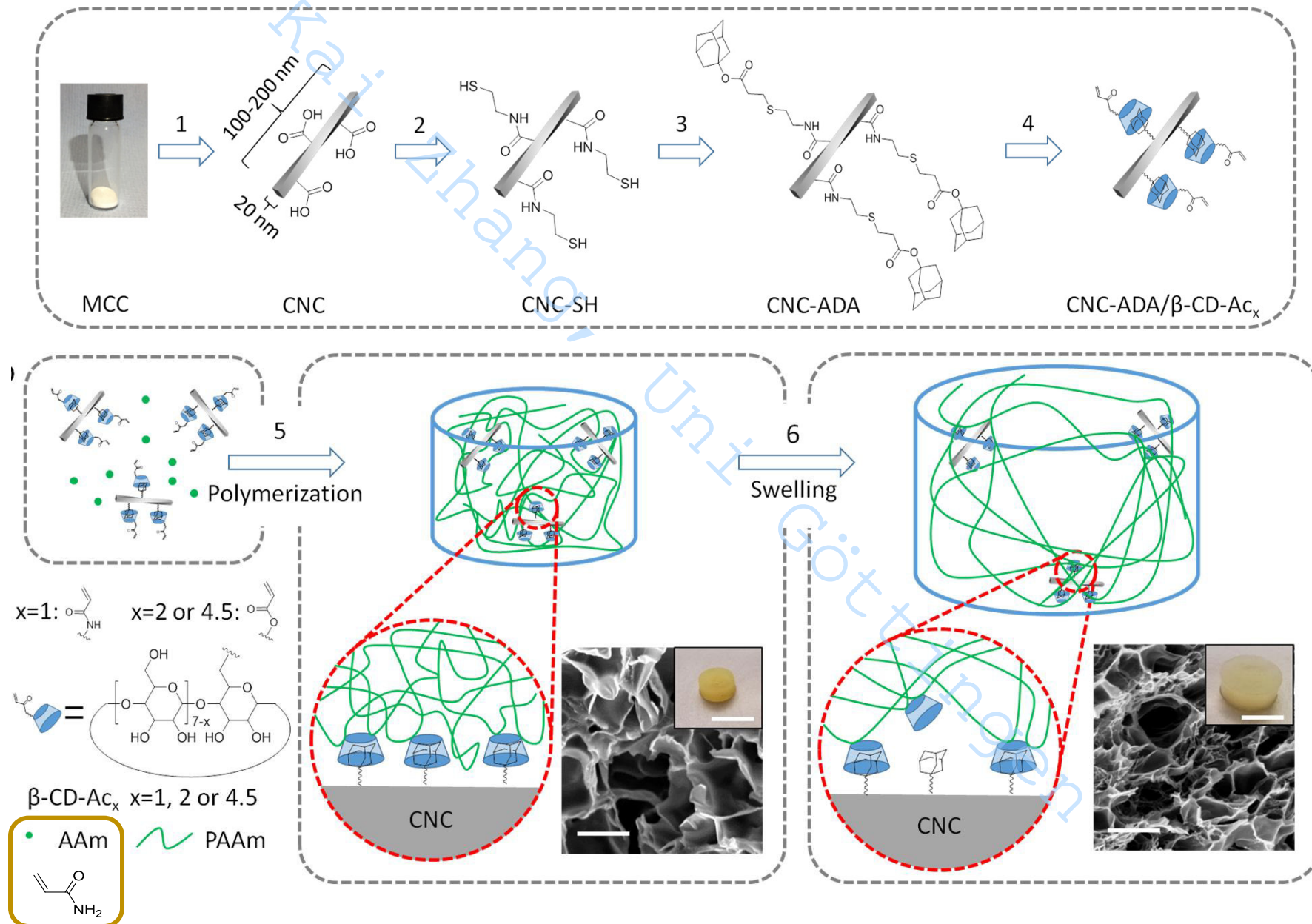
Functional materials based on crystalline nanocellulose

- Responsive CNC via surface-immobilization of stimuli-responsive groups
 - e.g. with stimuli-responsive **rhodamine spiroamide**
- Potentially for biomedical imaging and detection



Low amount of RhB spiroamide: 0.2 ± 0.01 mmol/g

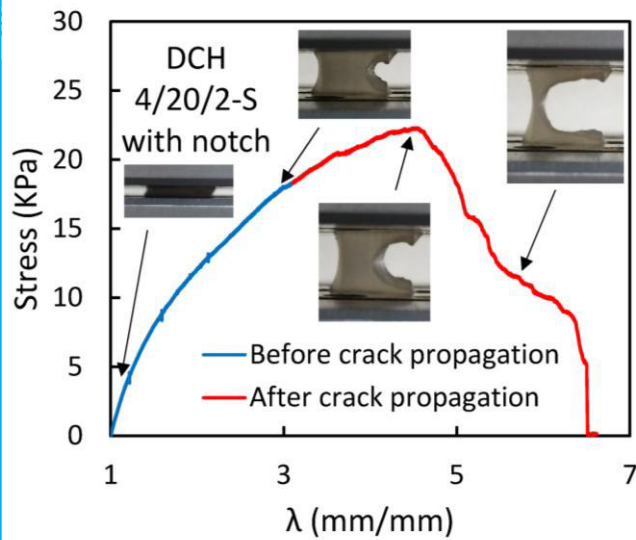
Pre-organized cellulose nanocrystal crosslinker for robust hydrogel



Huang, Wang, Rehfeldt, Zhang. Macromolecular Rapid Communication, 2017, 38, 1600810

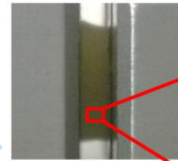


1% CNC as prepared, tensile trial

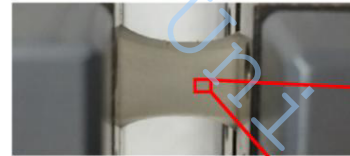


DCH
4/20/2-S

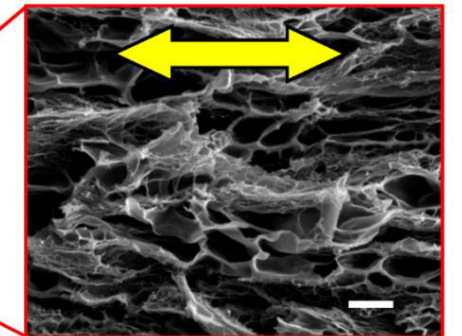
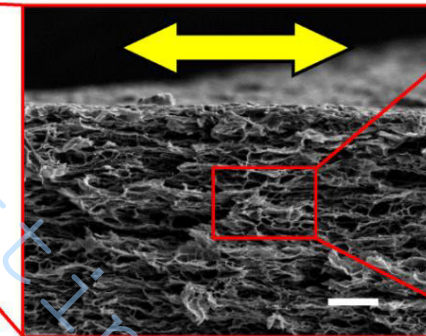
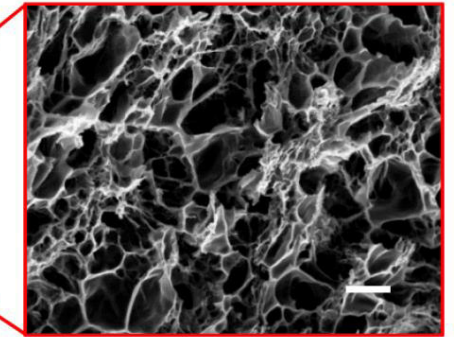
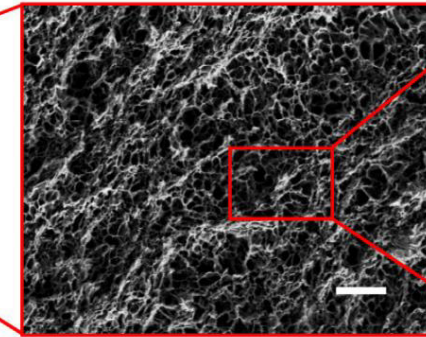
$\lambda=1$



$\lambda=3$

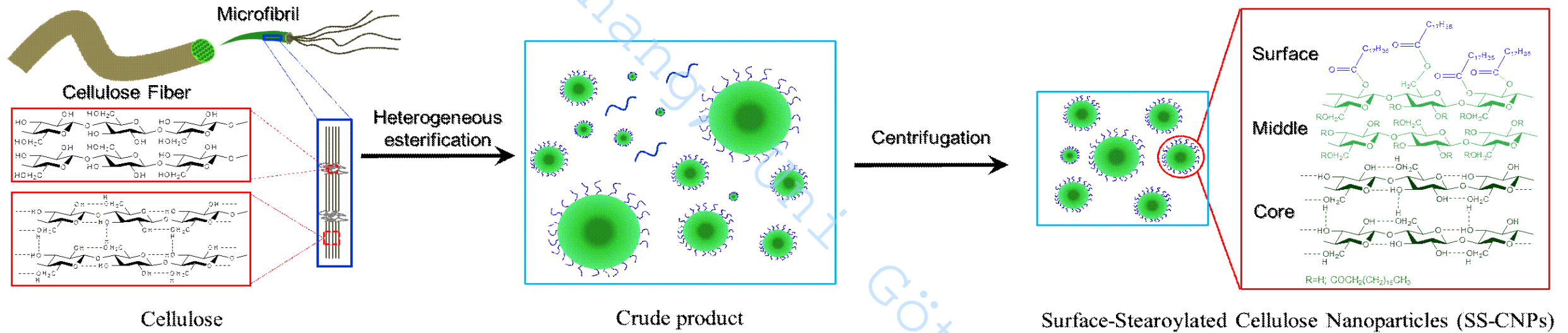


$\lambda=8$

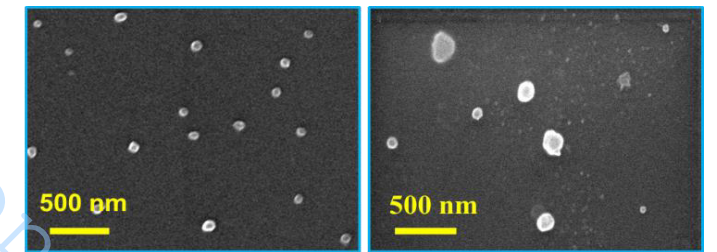


Spheric crystalline cellulose nanoparticles

Heterogeneous esterification using intermediate amount of stearyl chloride
→ Synthesis of surface-stearylated cellulose nanoparticles (SS-CNPs)



- 3 mol stearyl chloride per mol AGU of cellulose
- Removal of soluble product and bigger fragments by centrifugation



Properties

The suspensions of SS-CNPs in organic solvents

→ Stable and (semi)transparent

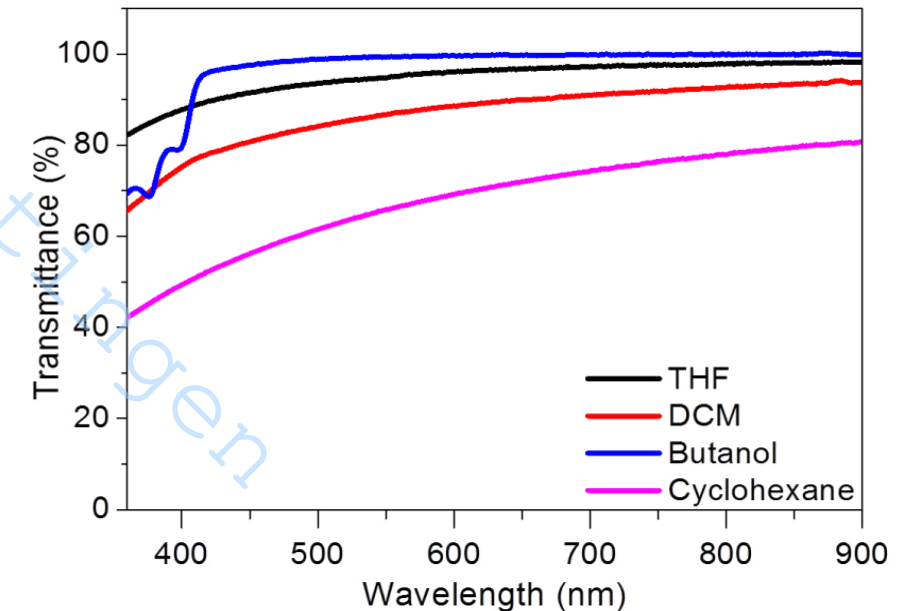
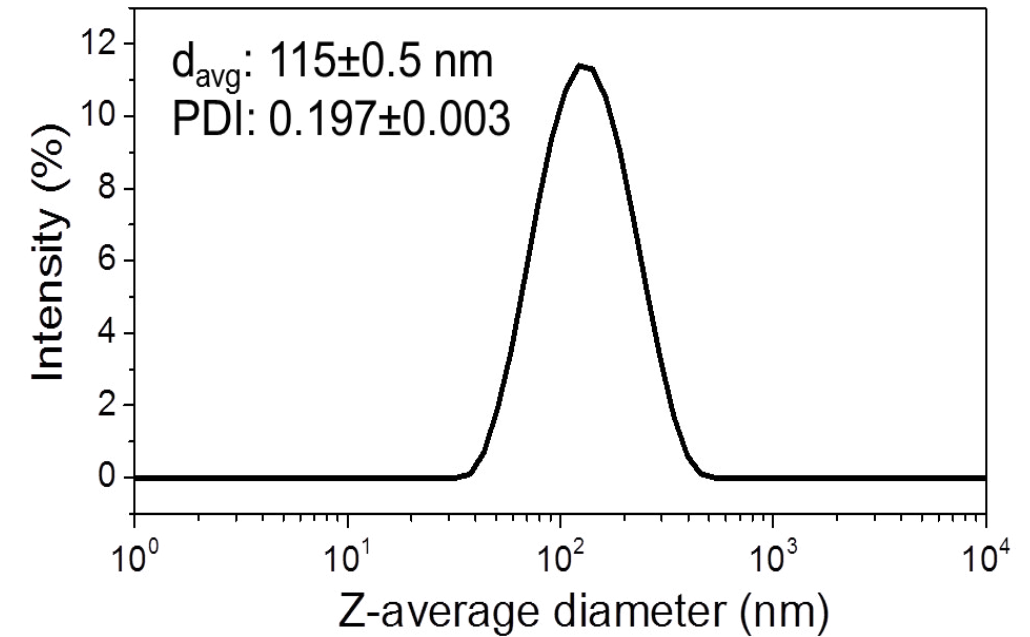
→ Re-suspendable after drying!



i-THF; ii-DCM; iii-cyclohexane; iv-butanol

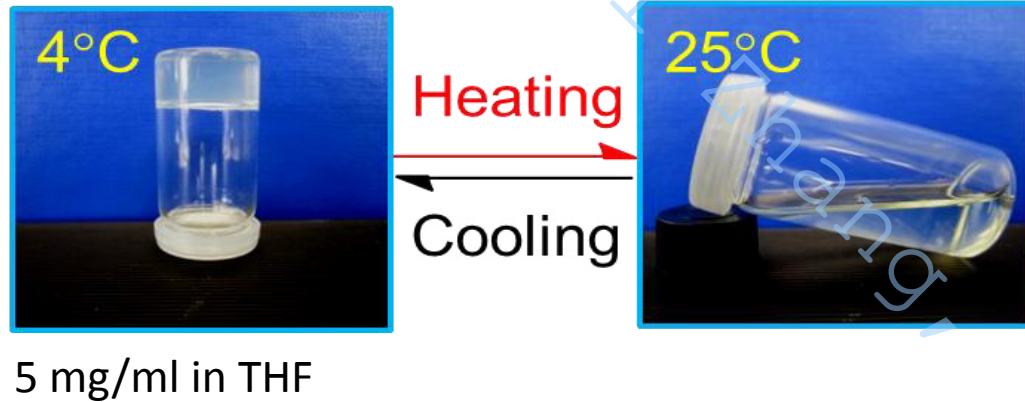
5 mg/ml

Dynamic light scattering → particle size

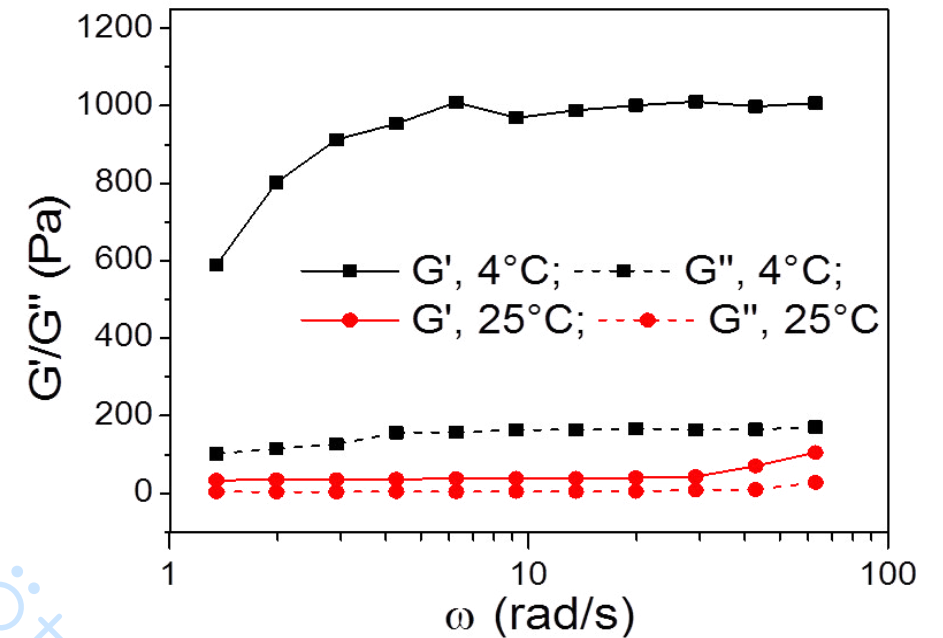
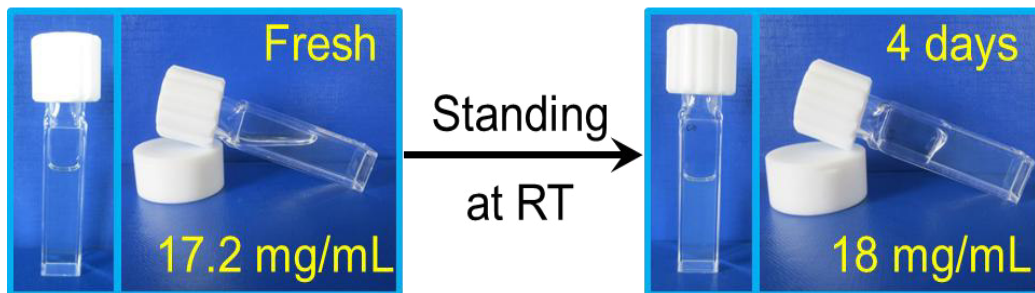


Gelation behaviour of suspensions

→ Changing temperature: thermo-reversible gelation



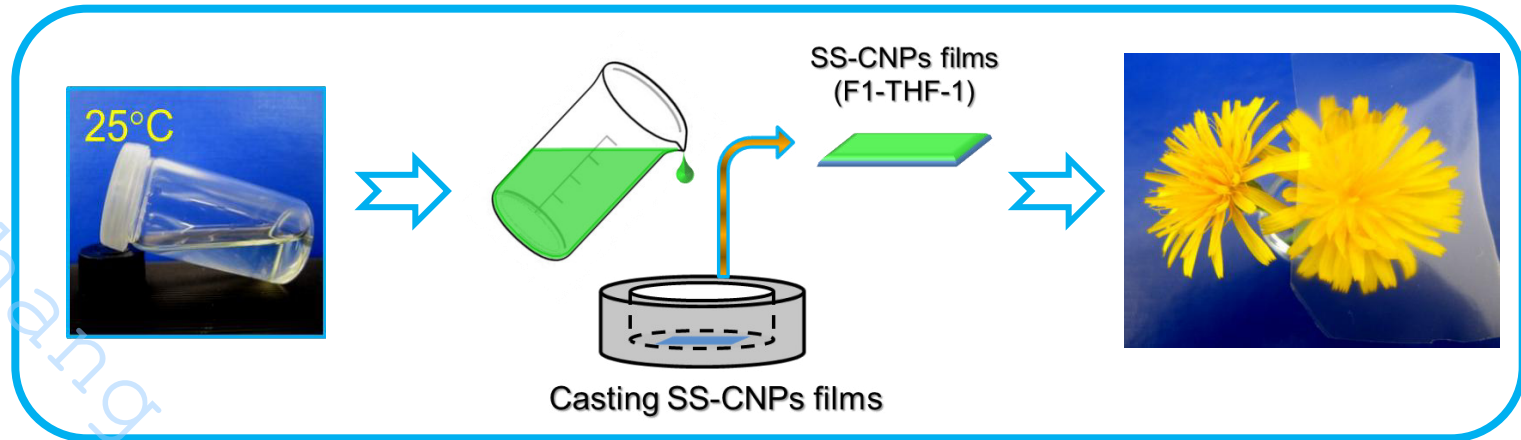
→ Changing concentration: gelation at RT



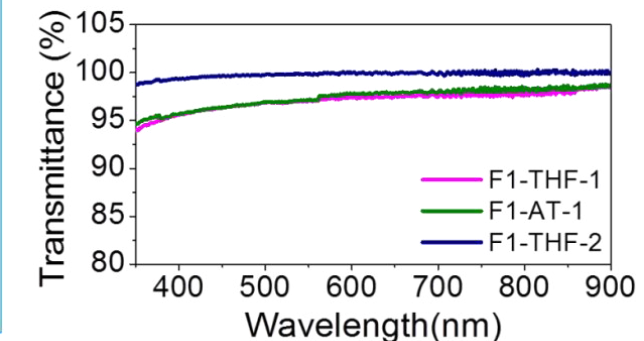
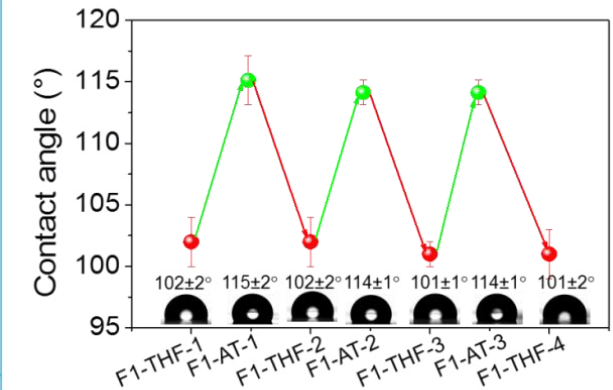
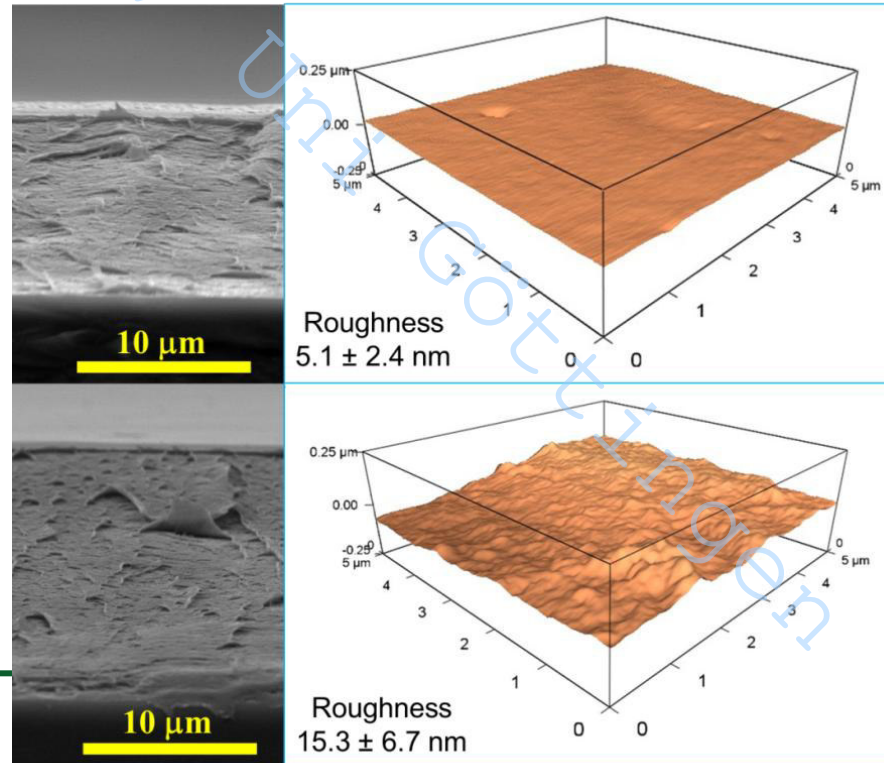
Elastic (G') and viscous (G'') modulus as a function of oscillatory shear frequency

Application of crystalline cellulose nanoparticles: Self-standing films

- Solvent casting → Self-standing, flexible, transparent film

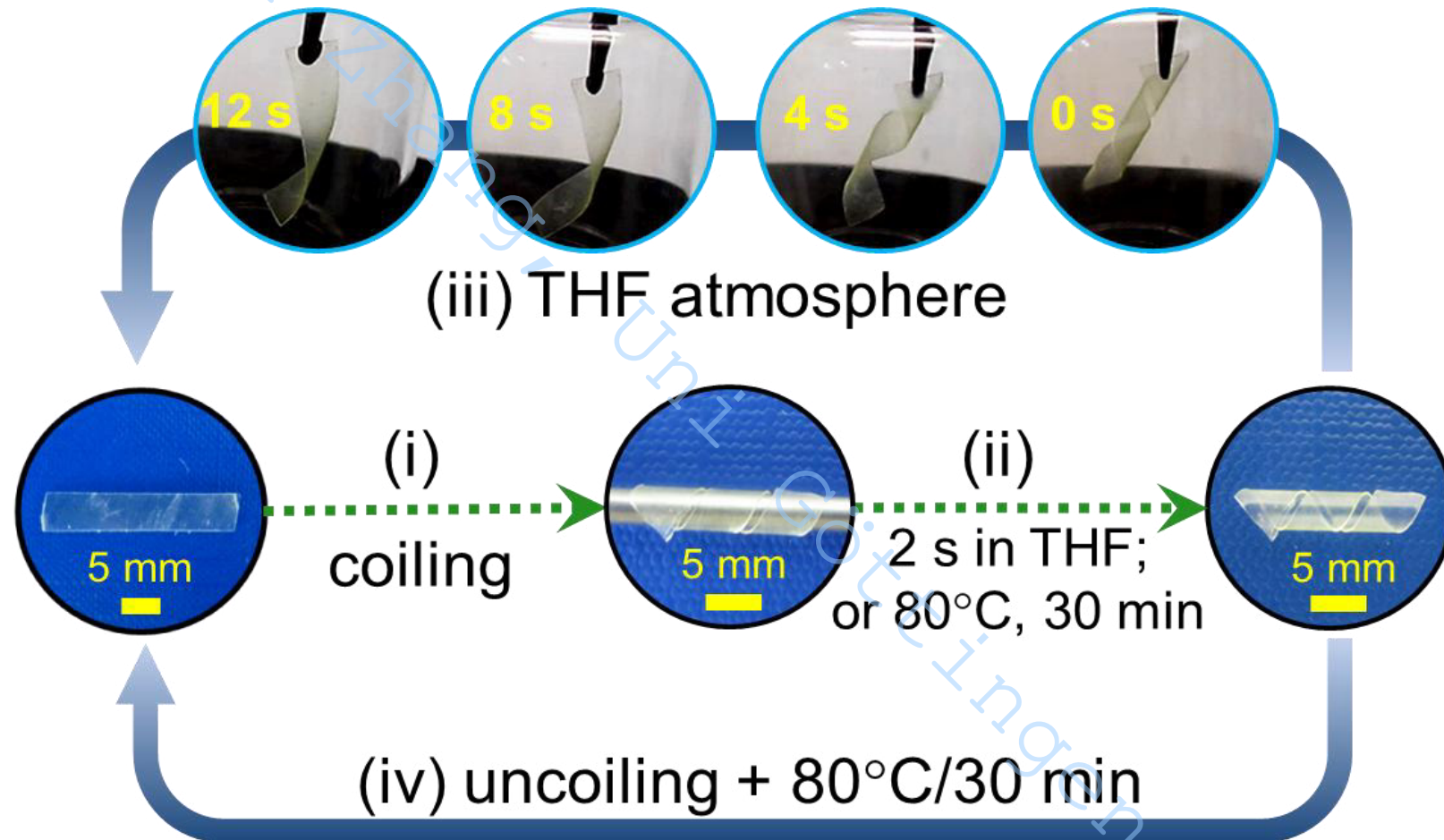


- Solvent-switchable surface wettability of SS-CNPs film

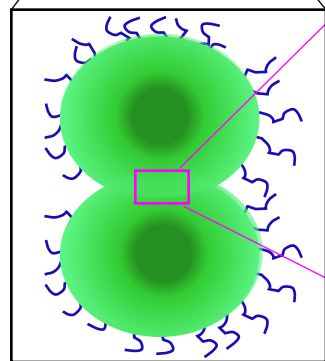
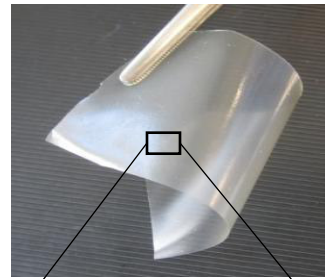


Solvent-responsive shape memory

- Good shape fixation by heating or solvent treatment;
- One-way solvent responsive shape-memory behavior;

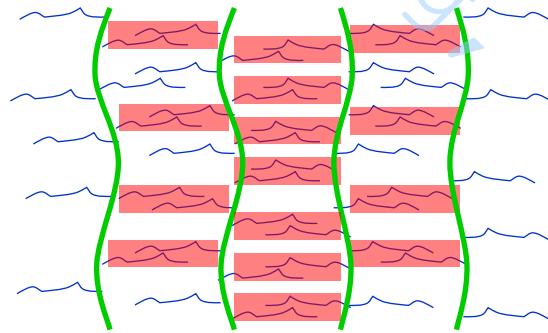


Proposed mechanism



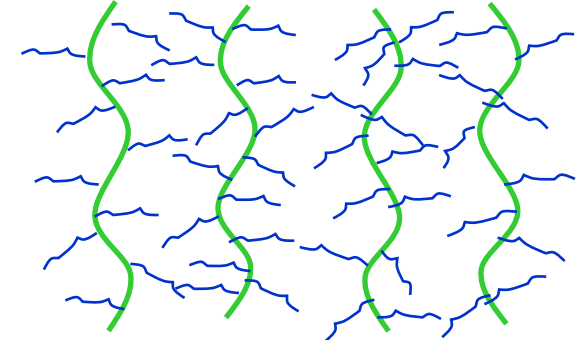
SS-CNPs film

Core → Contact Surface ← Core

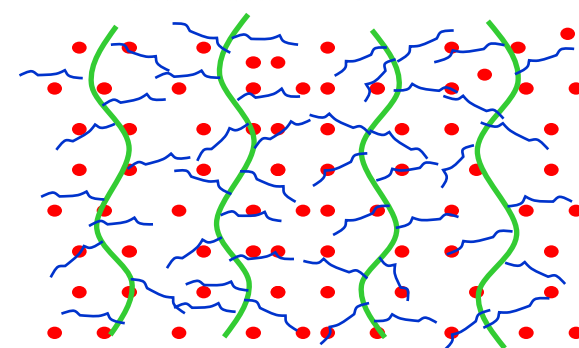


heating
cooling

Core → Contact Surface ← Core



Core → Contact Surface ← Core



Stearoyl group



Cellulose chain

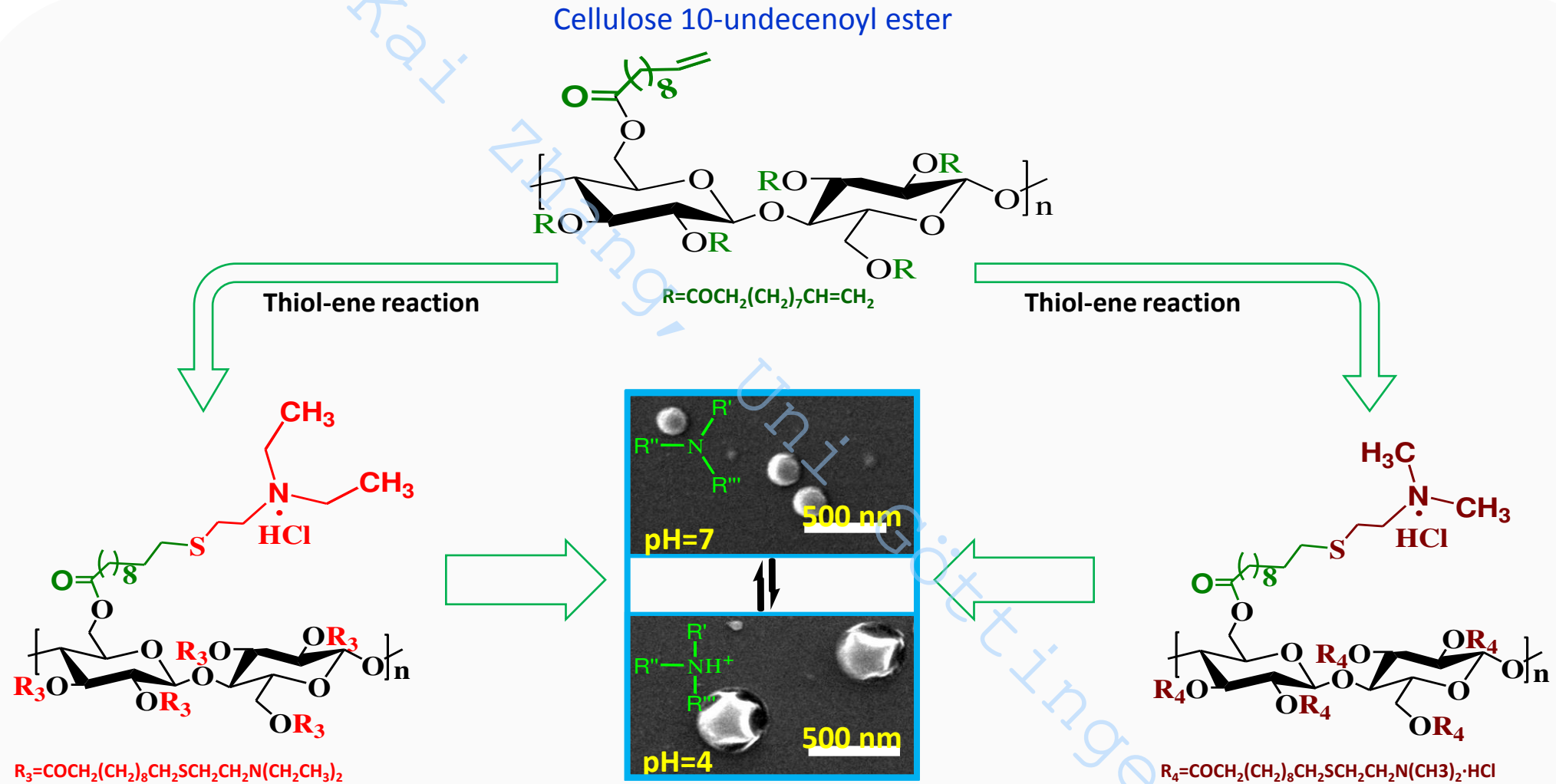


Tetrahydrofuran (THF)

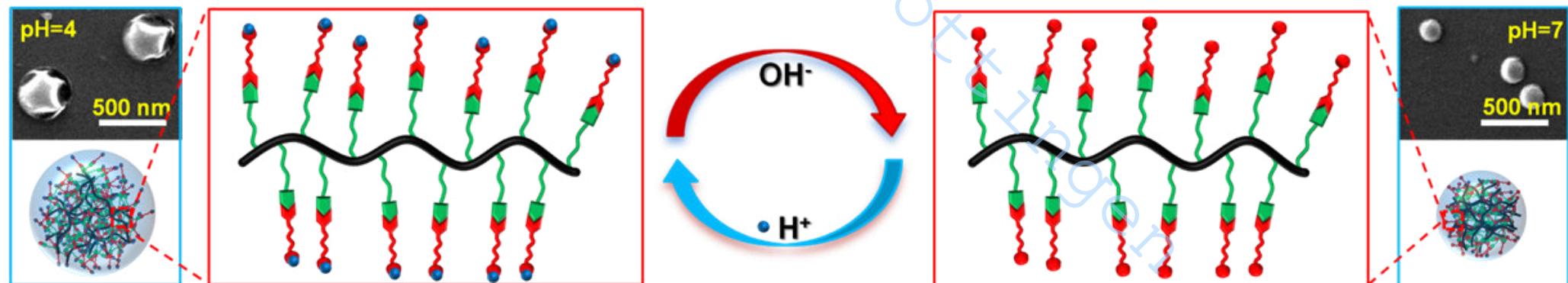
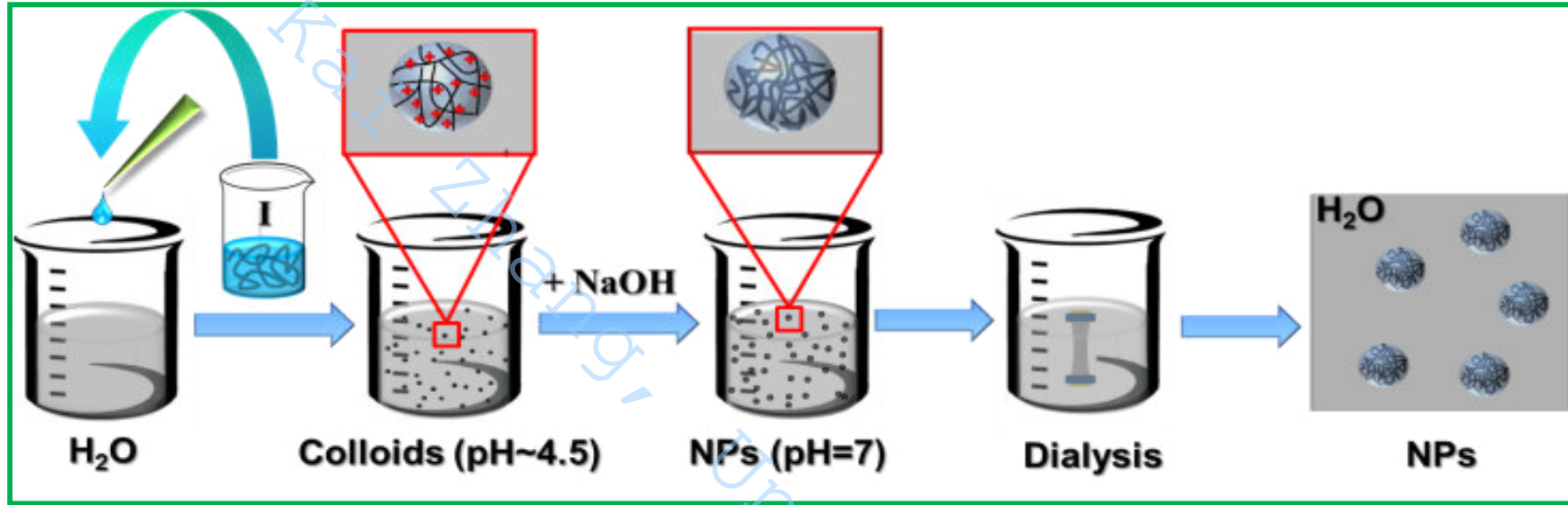


Crystalline regions formed by stearoyl groups

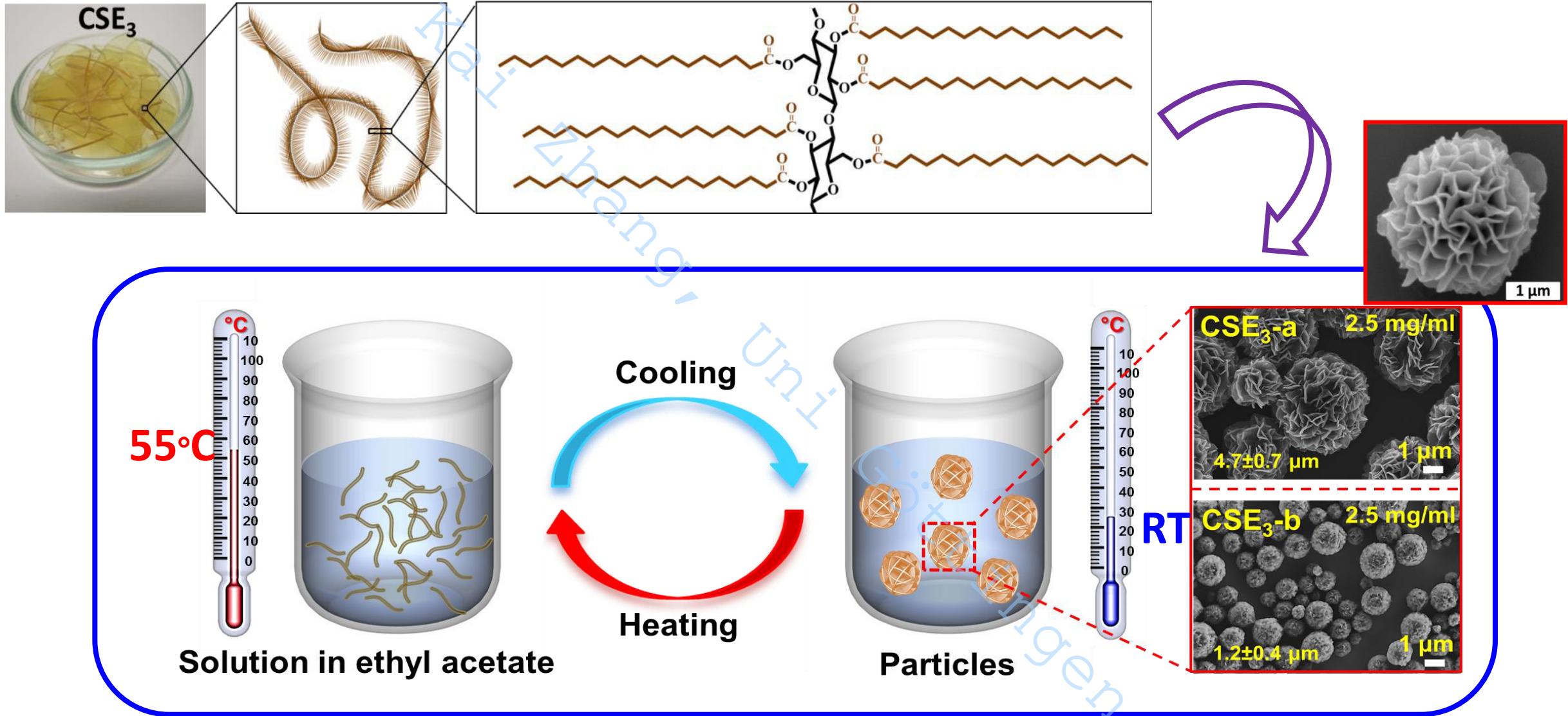
pH responsive NPs



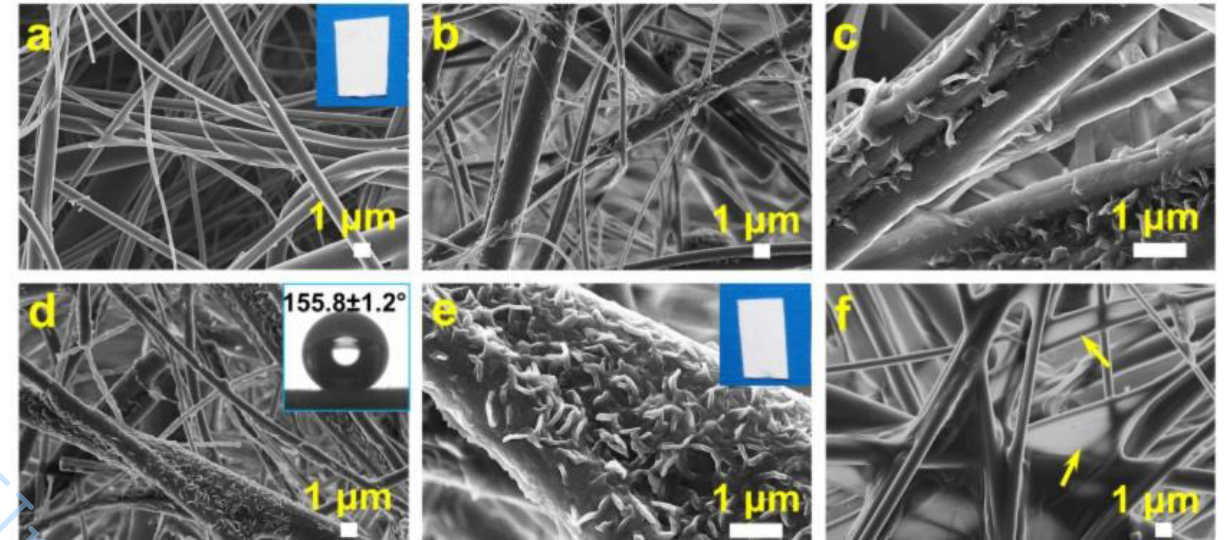
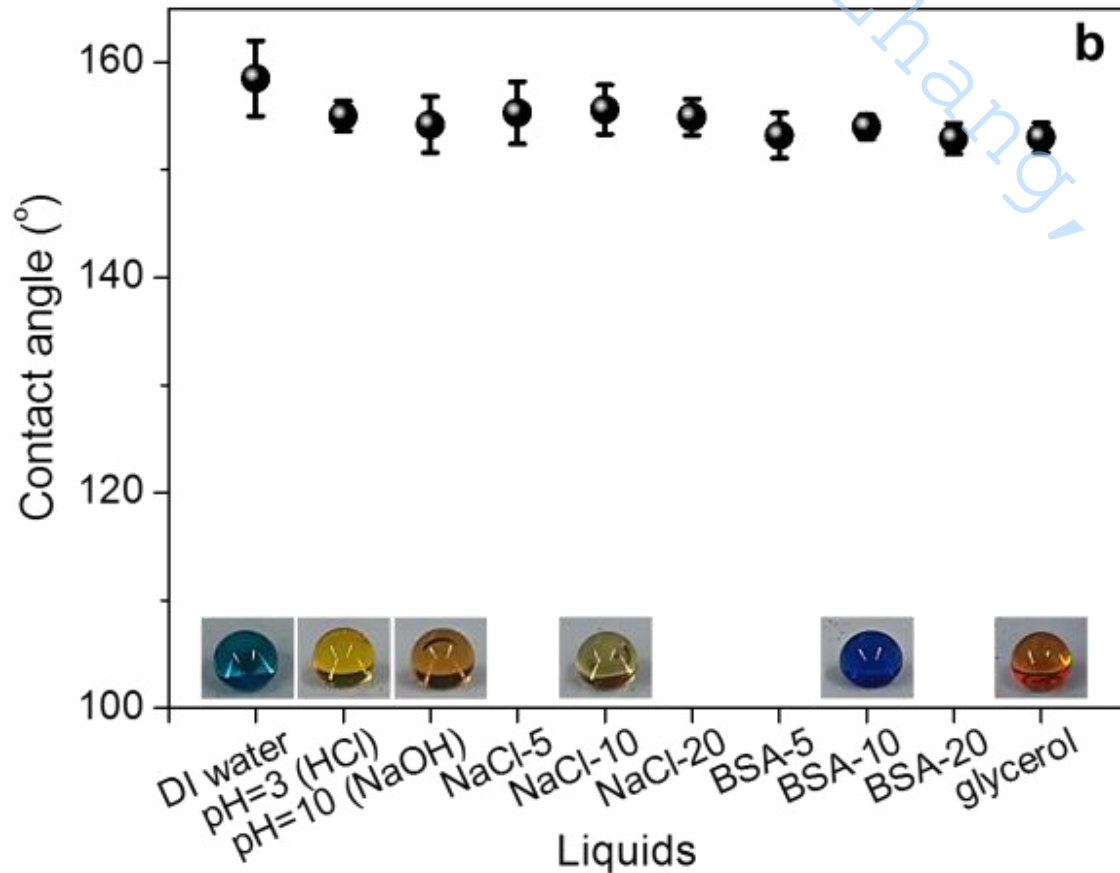
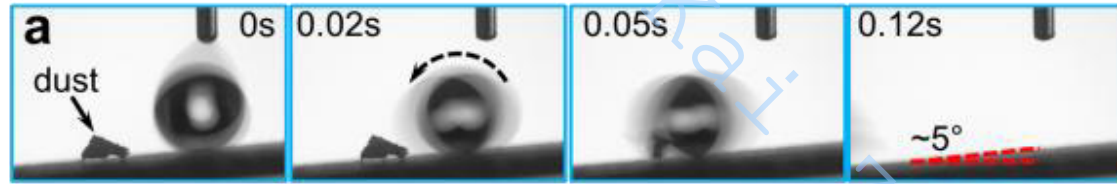
Nanoprecipitation



Flower-like Particles via crystallization of cellulose stearoyl esters



Non-wetting surfaces



Excellent superhydrophobicity against diverse liquids

- Aqueous solutions of salts & different pH values
- Protein solutions, BSA: aqueous bovine serum albumin
- Different viscosities (water: $\sim 0.01 \text{ Pa}\cdot\text{s}$, Glycerol: $0.934 \text{ Pa}\cdot\text{s}$, 25°C)

Thank you for your attention!

