Im Kleinen liegt Großes
–
Nanostrukturierte funktionelle Materialien aus Holzkomponenten

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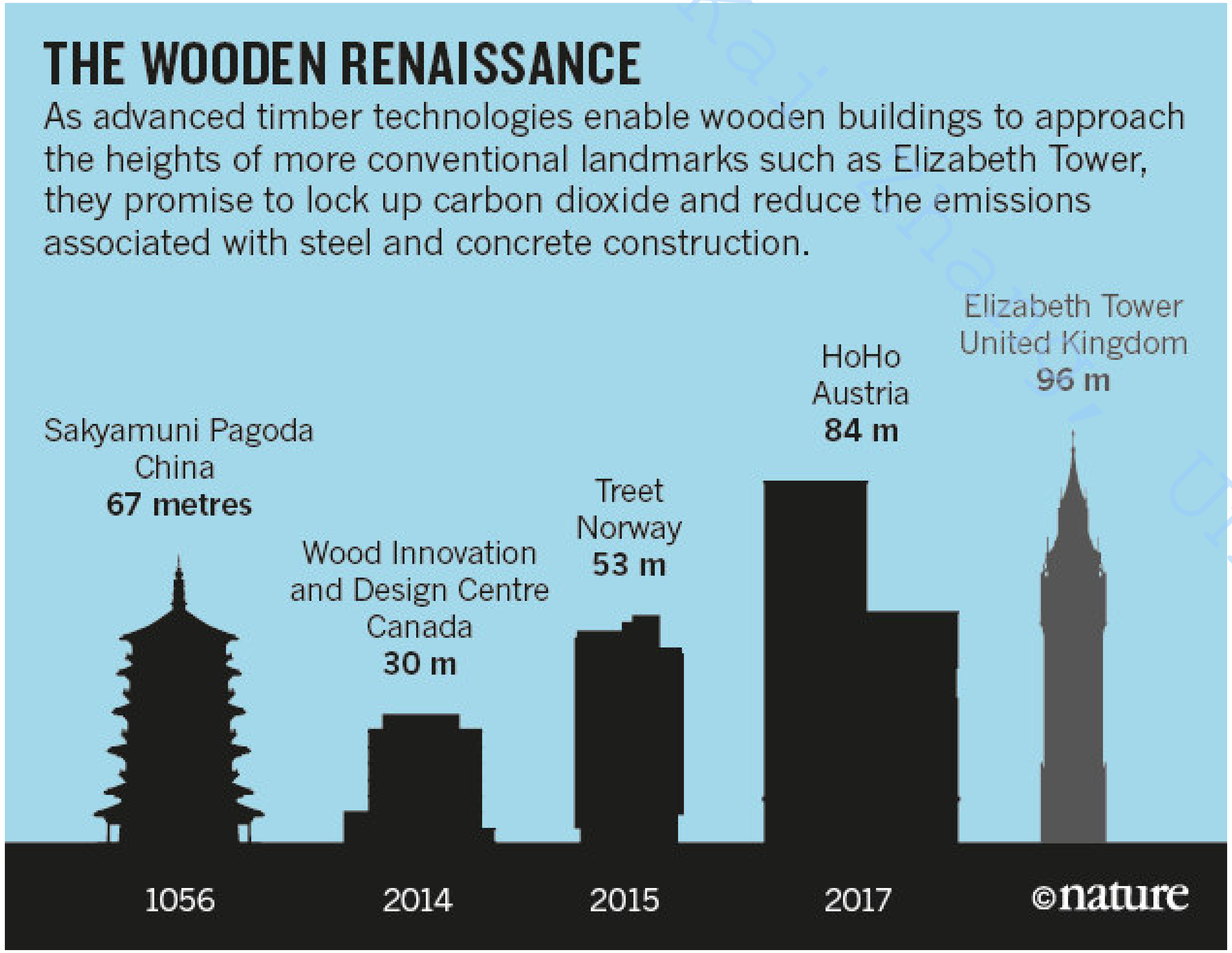
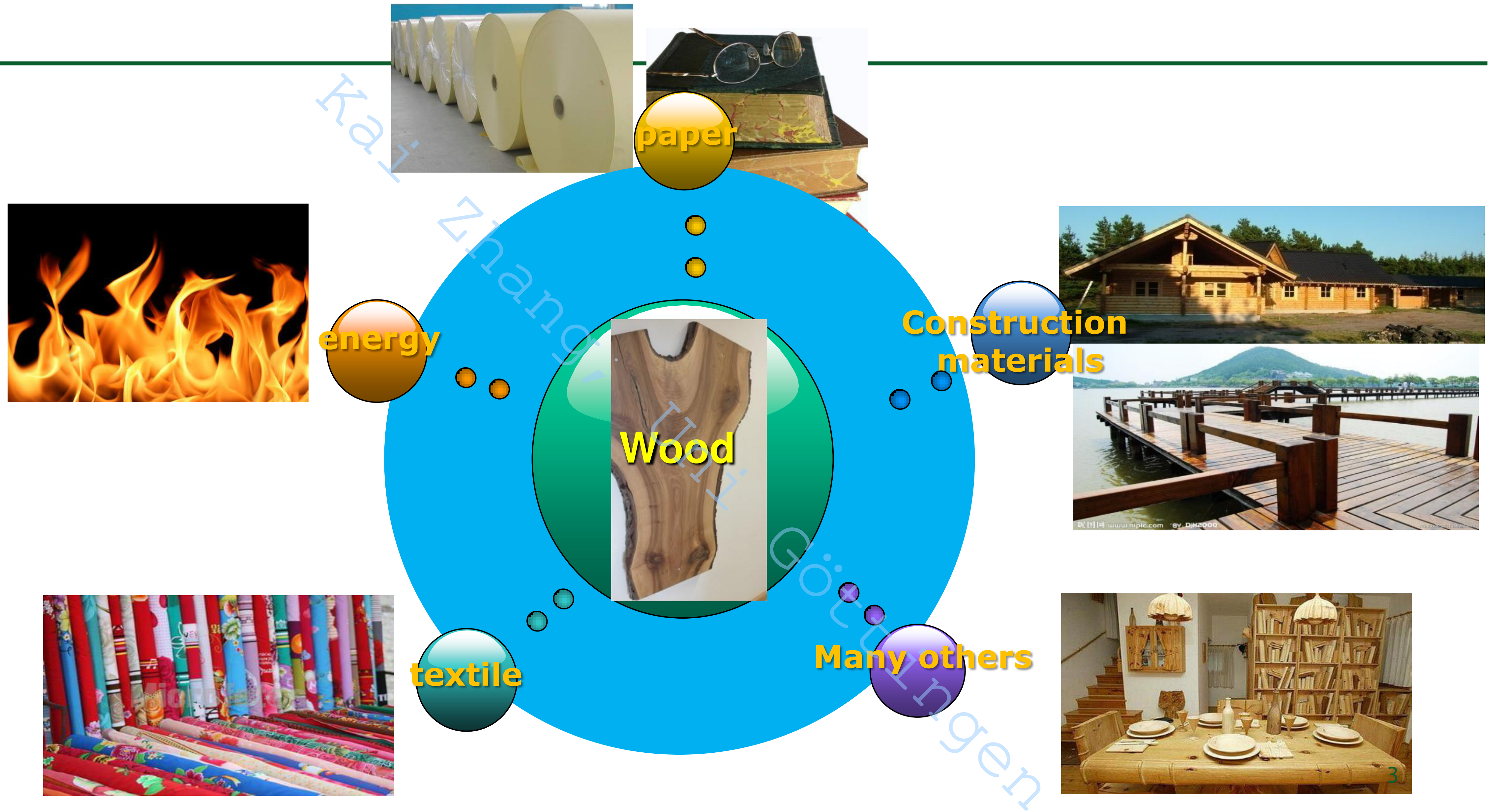
JP Holztechnologie & Holzchemie
Georg-August-Universität Göttingen

NHN Tagung, Jun. 2017

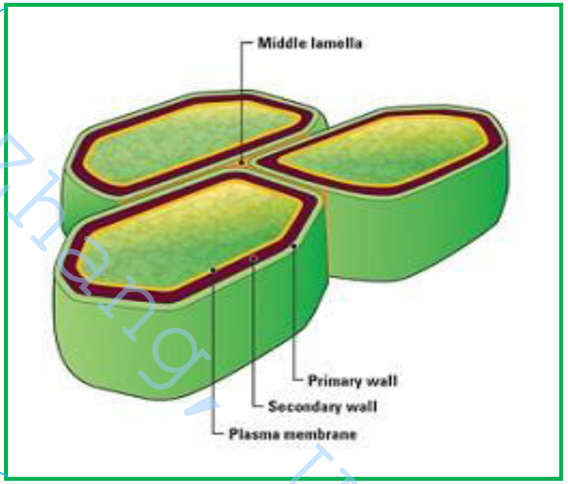


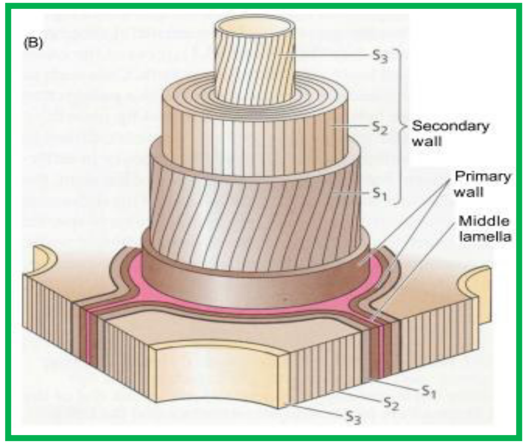
53-metre dormitory at the University of British Columbia in Vancouver

http://www.nature.com/news/the-wooden-skyscrapers-that-could-help-to-cool-the-planet-1.21992

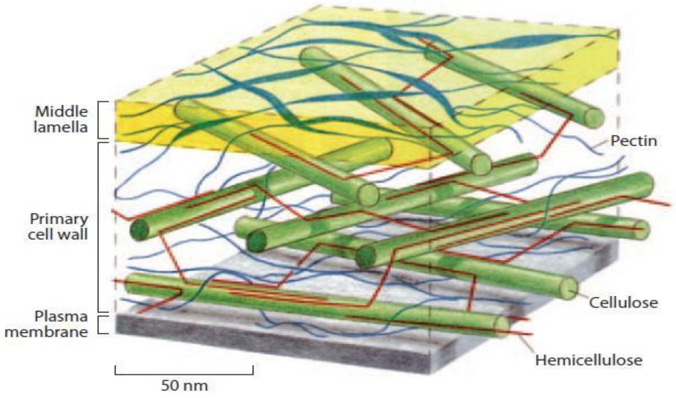

paper
energy
Construction materials
Wood
textile
Many others

Hierarchical structure in plant cell wall

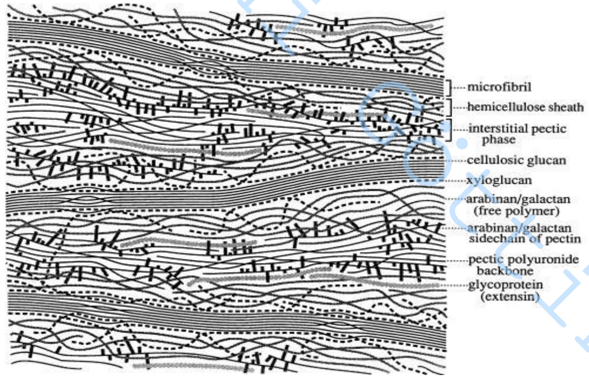




Taiz and Ziegler 1993

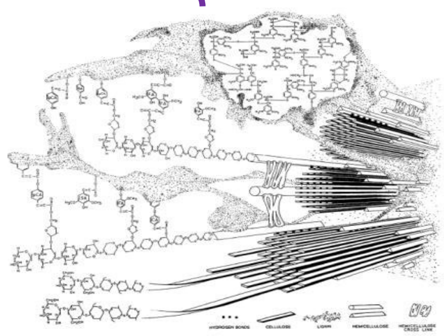


Scheller 2010 Annu Rec Plant Biol



Pea primary cell wall

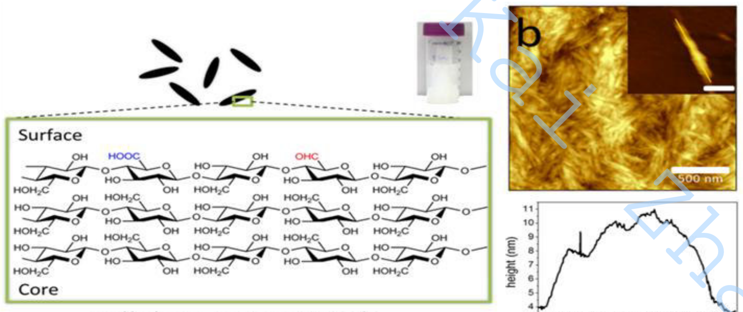
Talbott and Ray, 1992 Plant Physioll



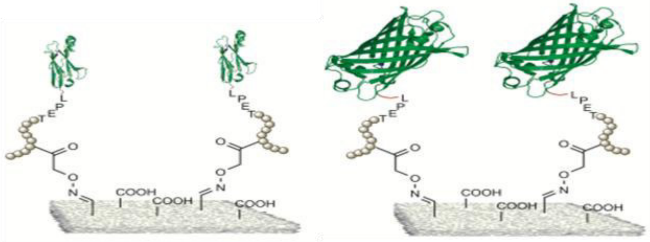
Secondary cell wall

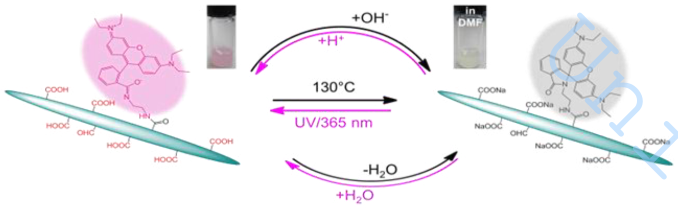
Bidlack et al., 1992 Proc Okla Acad Sci

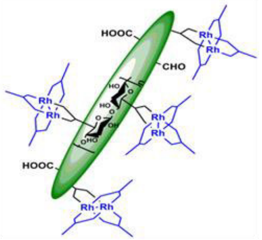
Nanocellulose

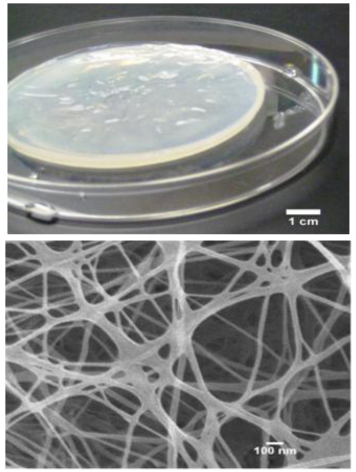


Cellulose nanocrystals

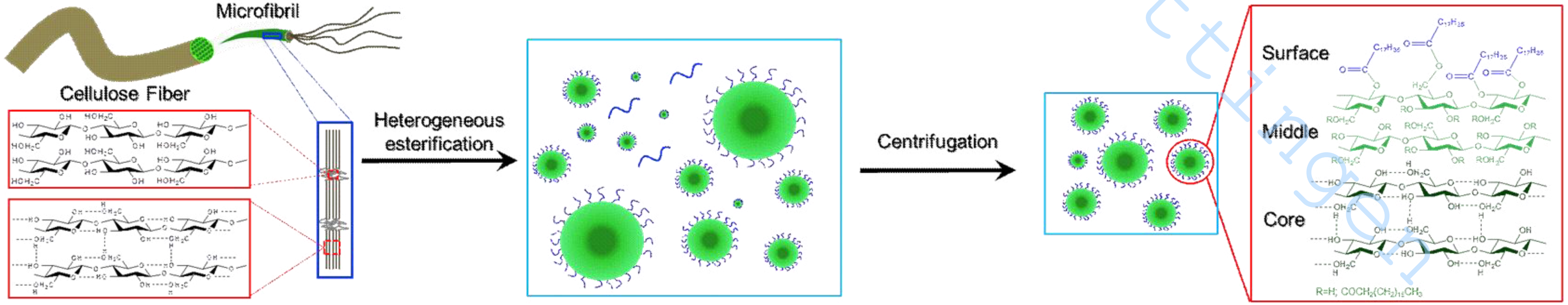








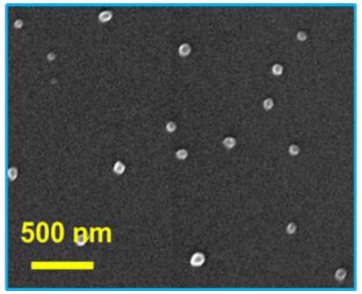
bacterial cellulose



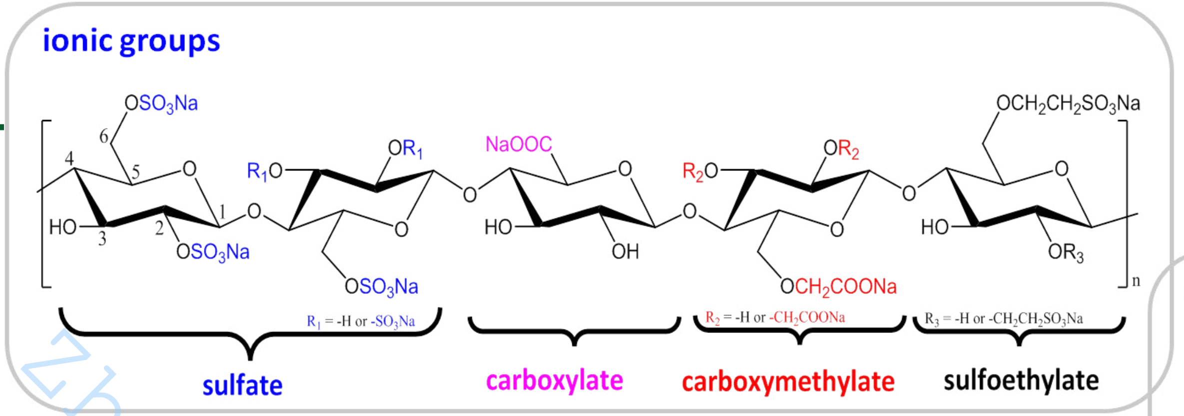
Cellulose

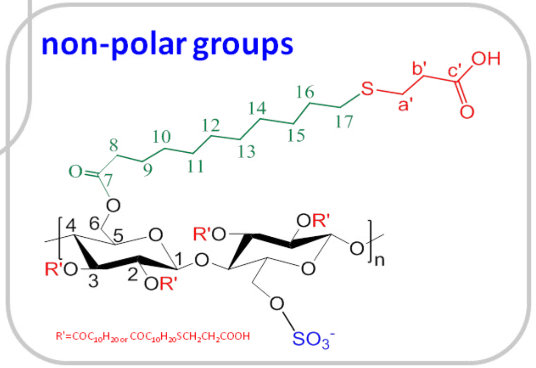
Crude product

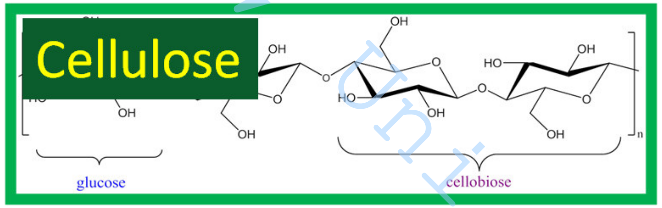
Surface-Stearoylated Cellulose Nanoparticles (SS-CNPs)



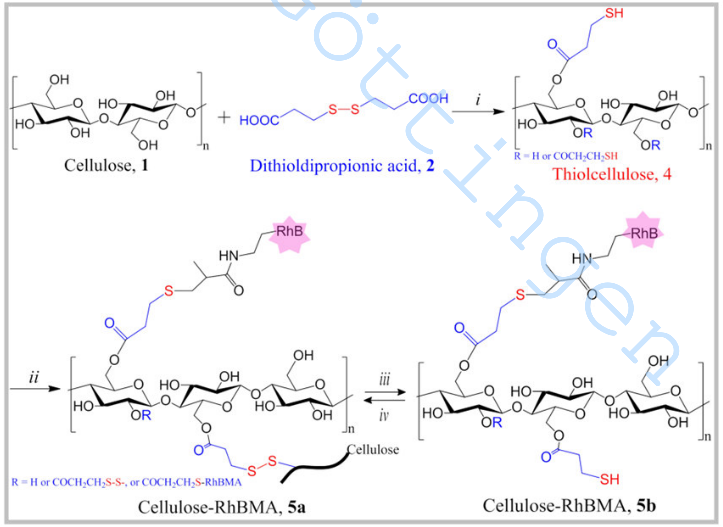
Holzchemie und Cellulosechemie

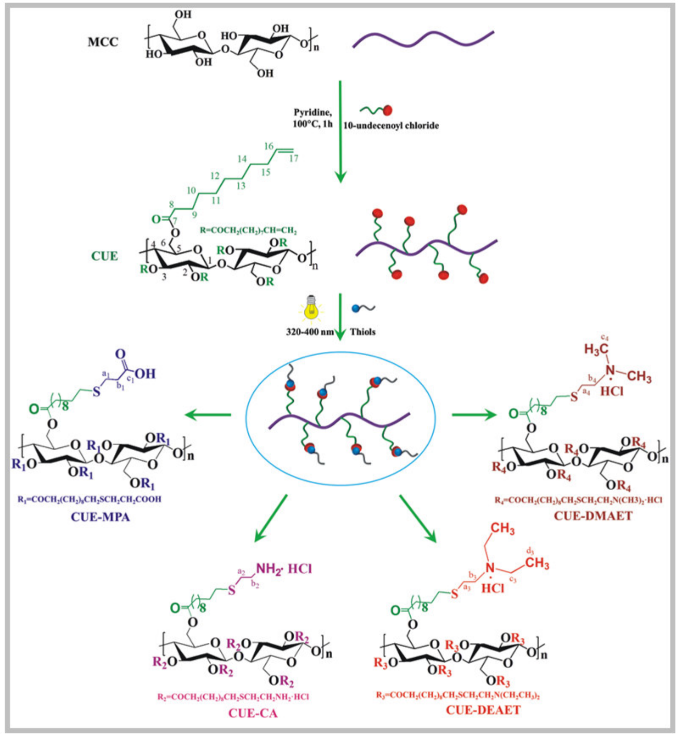






& more





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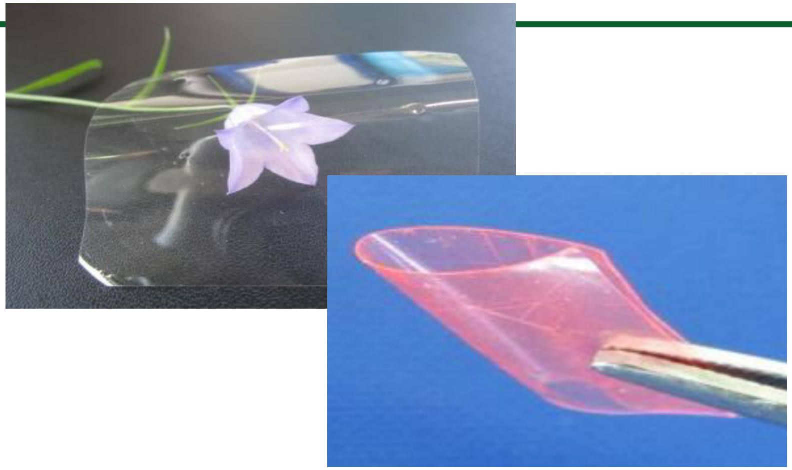
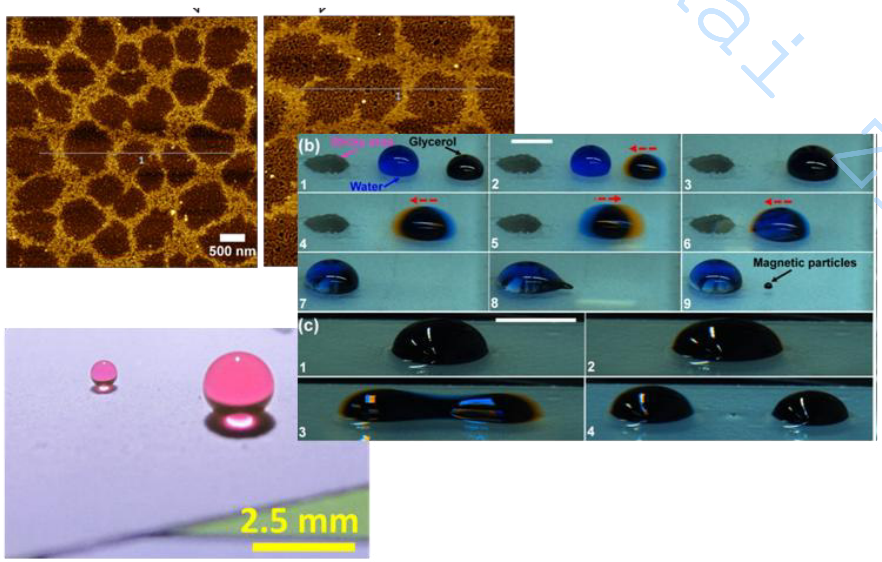
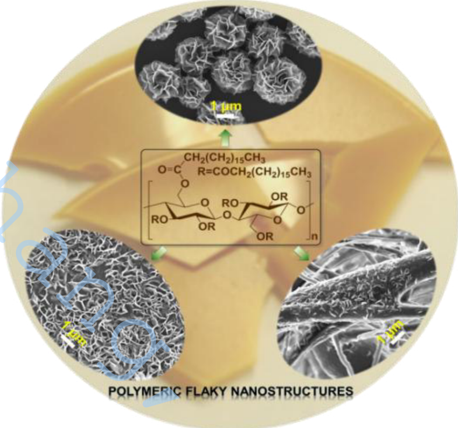
Funktionelle Materialien

Responsive, self-standing films

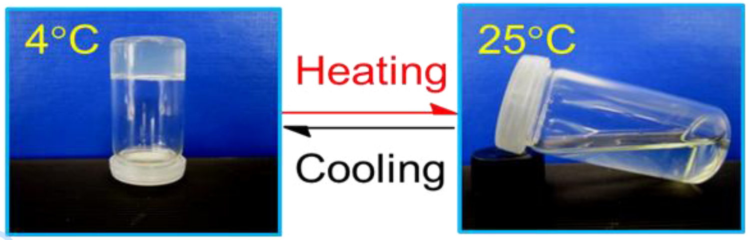


Surface coating (e.g. super/hydrophobization)

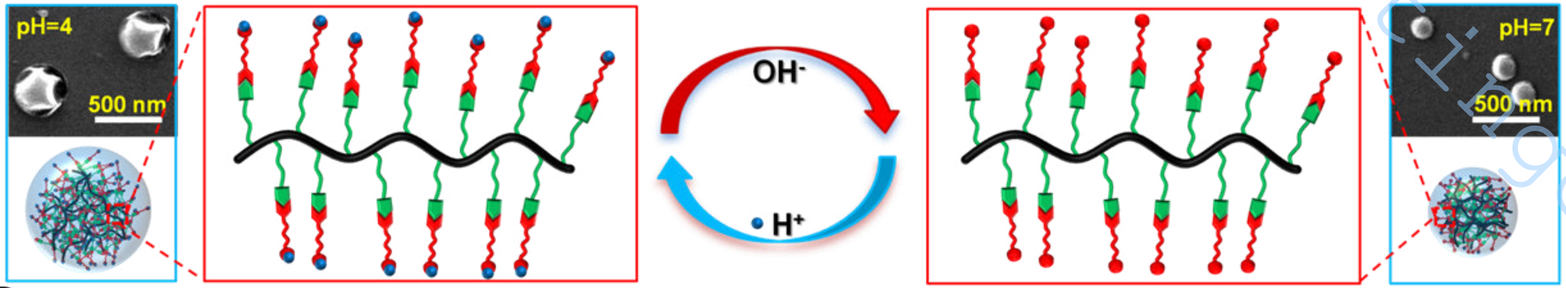


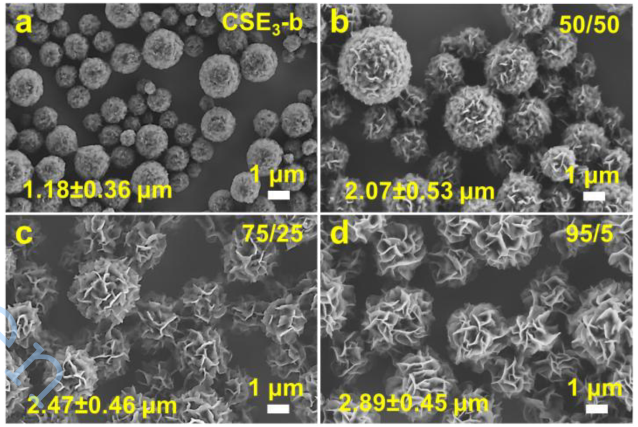


gels



nanoparticles / microparticles





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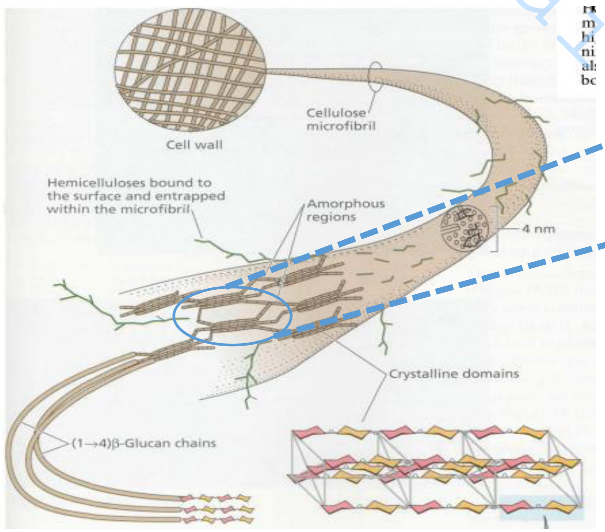
(1) *The Journal of Physical Chemistry C* 2014, *118*, 2408-2417. (2) Angewandte Chemie Int Edition, 2014, 12618-12623. (3) Chemistry – A European Journal 2015, 21, 1-8 (4) *Physical Chemistry Chemical Physics,* 2014, 26322-26329. (5) Advanced Functional Materials, *2015,* , 25, 1434-1441. (6) Nanoscale, 2016, 8, 648.

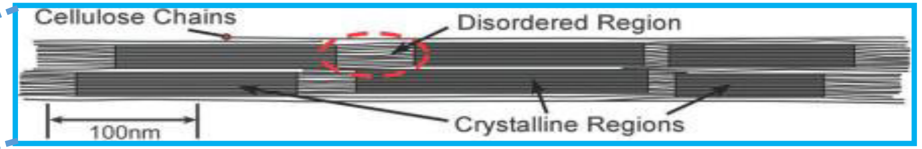
Synthesis of crystalline nanocellulose

Native Cellulose



Taiz and Ziegler 1993

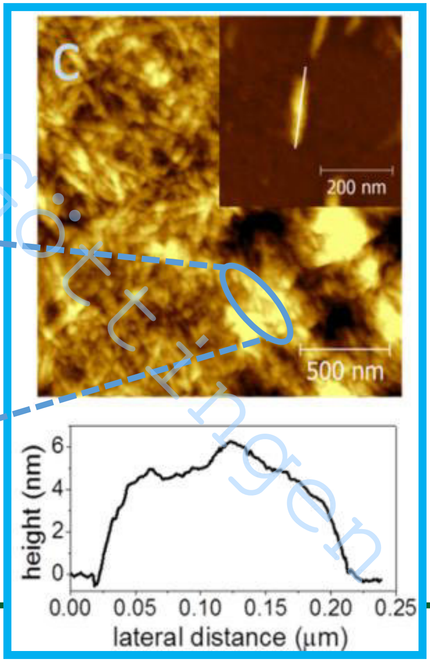
Cellulose at nanoscale and molecular level



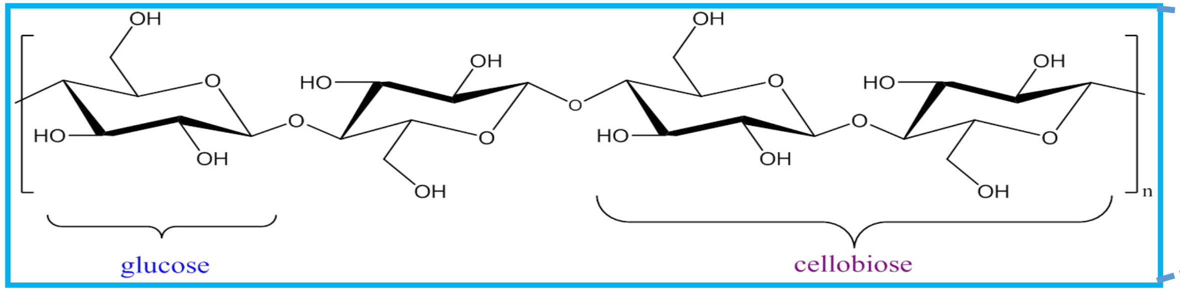
Moon et al., 2011 Chem Soc Rev

chemically / mechanically

Microfluidizer (microfluidics incorp.)

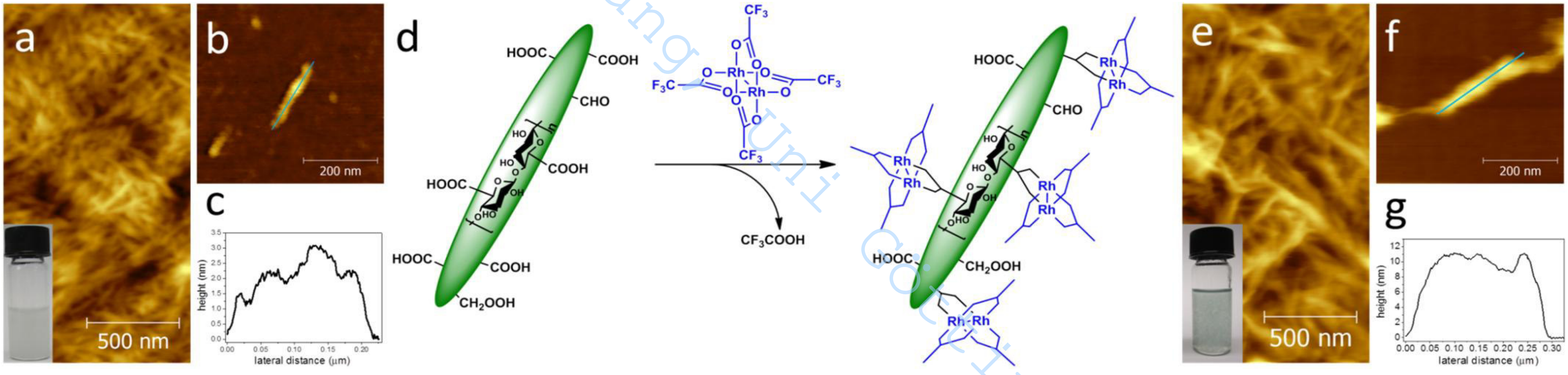


Nano/Microfibrillated cellulose (NFC)
Cellulose nanocrystals (CNC)
Cellulose nanowhiskers (CNW)
etc.



Heterogeneous catalysis: Dirhodium (II) complex on CNC

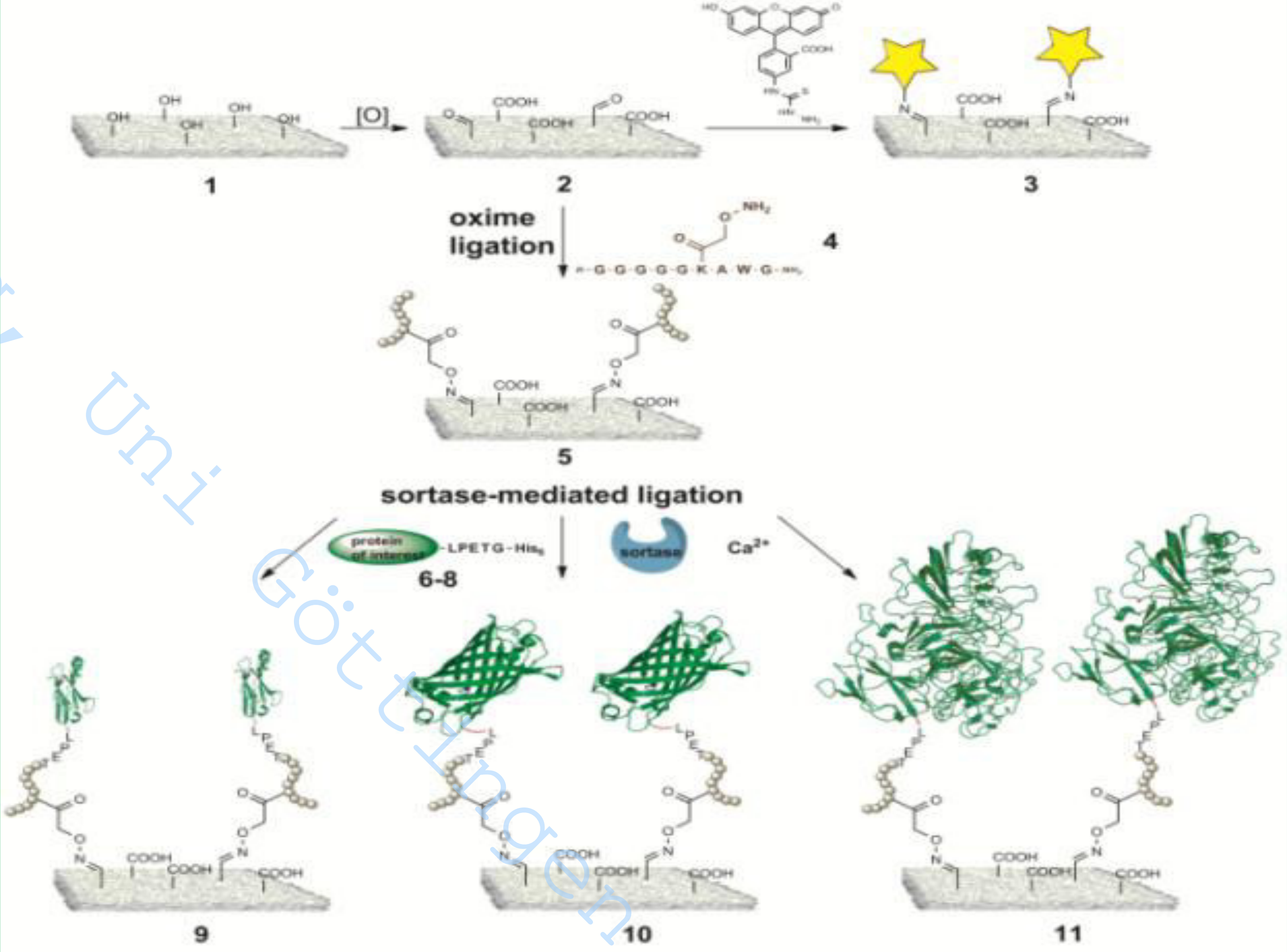
- Synthesis: immbolization of dirhodium complex onto CNC surface



Liu , Plog, Groszewicz, Zhao, Xu, Breitzke, Stark, Hoffmann, Gutmann,* **Zhang,*** Buntkowsky.* Chemistry – A European Journal 2015, 21, 1-8

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

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



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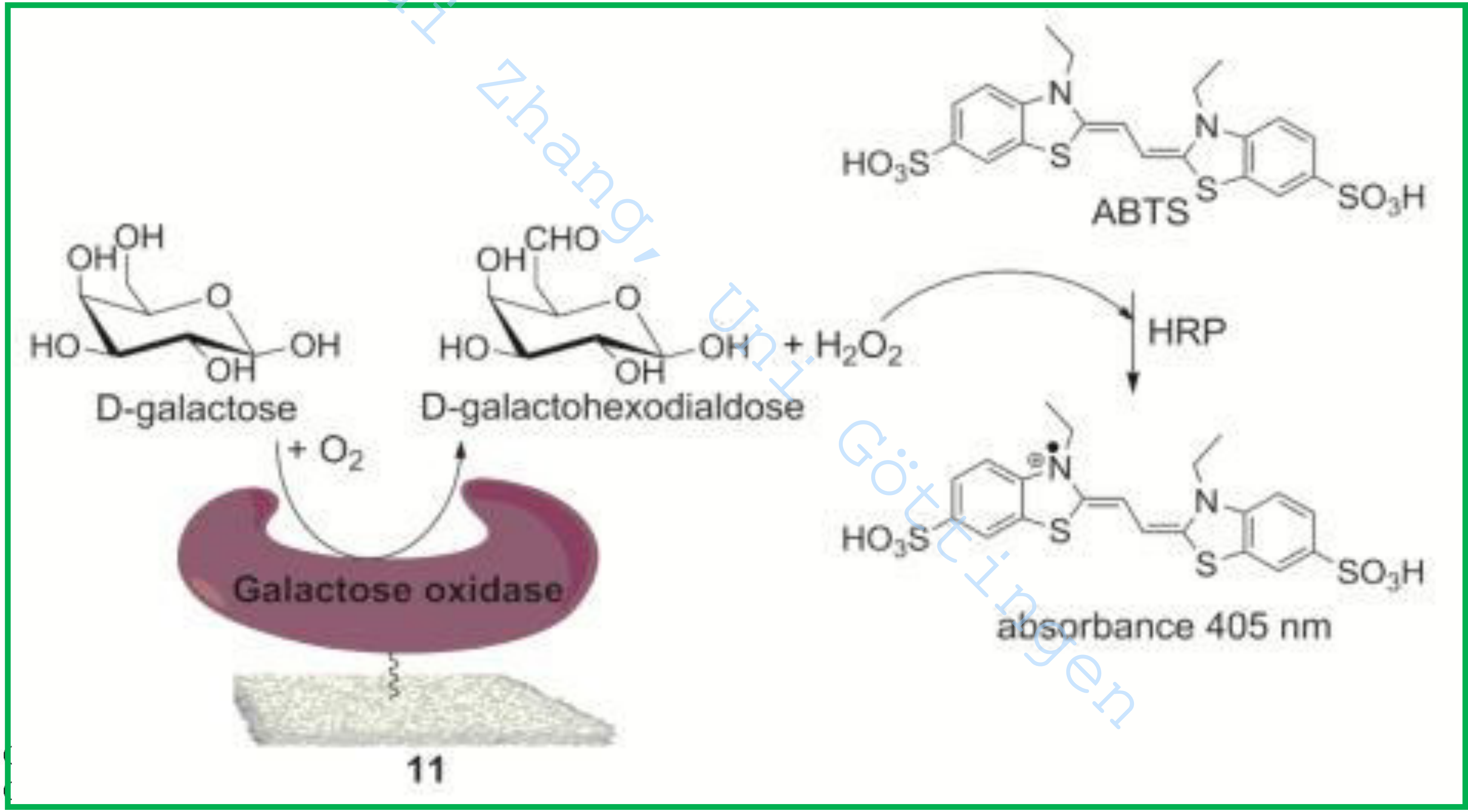
Christina Uth, Stefan Zielonka, Sebastian Hörner, Nicolas Rasche, Andreas Plog, Hannes Orelma, Olga Avrutina, **Kai Zhang,*** and Harald Kolmar*
Angewandte Chemie Int Edition, 2014, 12618-12623.

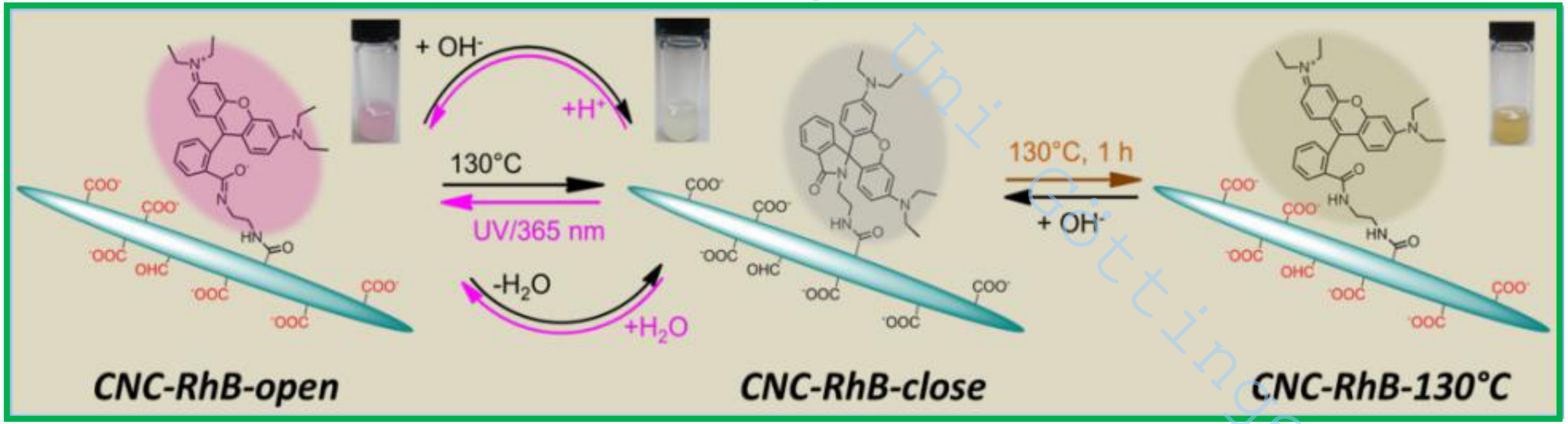
Example: CNC with immobilized galactose oxidase with maintained activity

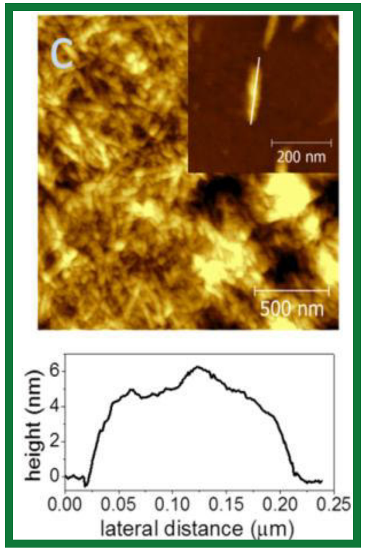


Functional materials based on crystalline nanocellulose

- Responsive CNC via surface-immobilization of stimuli-responsive groups
  - e.g. with stimuli-responsive **rhodamine spiroamide**

- Potentially for biomedical imaging and detection

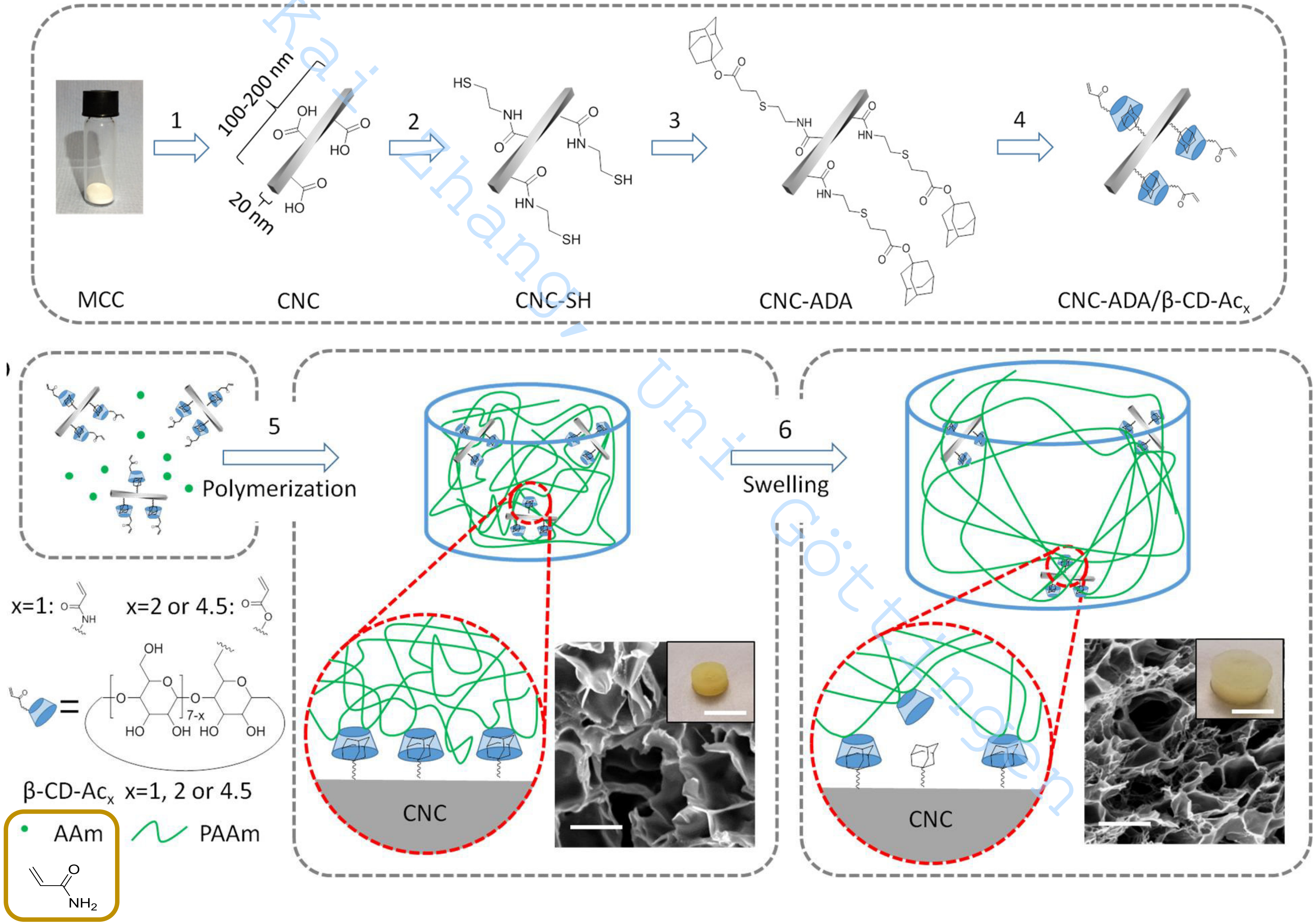




Low amount of RhB spiroamide: 0.2±0.01 mmol/g

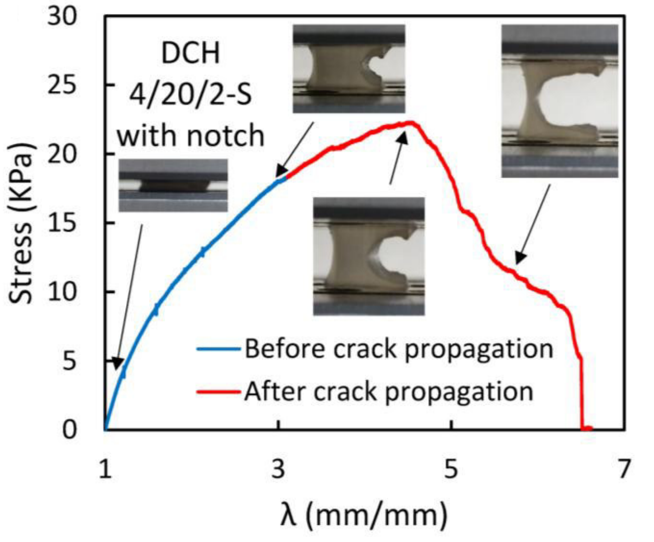
L. Zhao, W. Li, A. Plog, Y. Xu, G. Buntkowsky, T. Gutmann,* **K. Zhang*** *Physical Chemistry Chemical Physics,* 2014, 26322-26329.

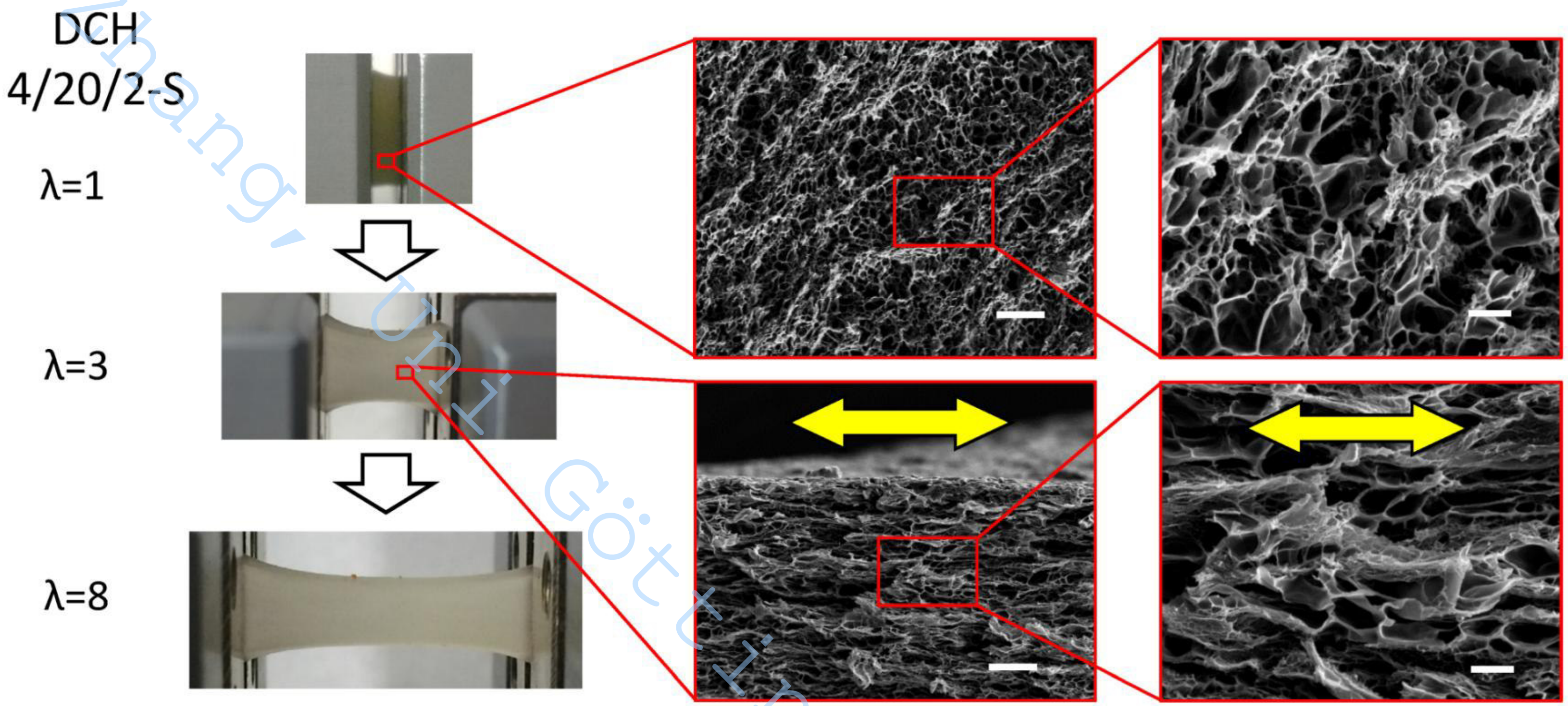
Pre-organized cellulose nanocrystal crosslinker for robust hydrogel



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

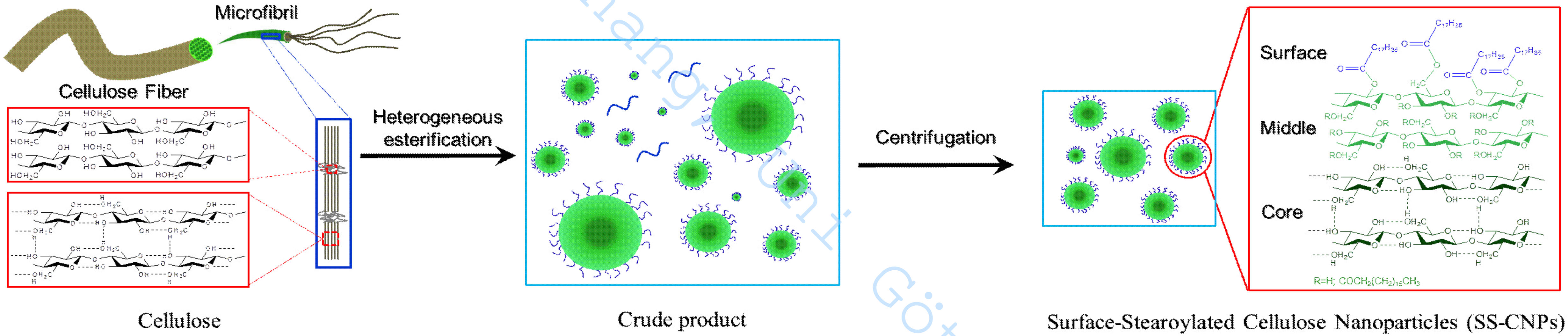
1% CNC as prepared, tensile trial



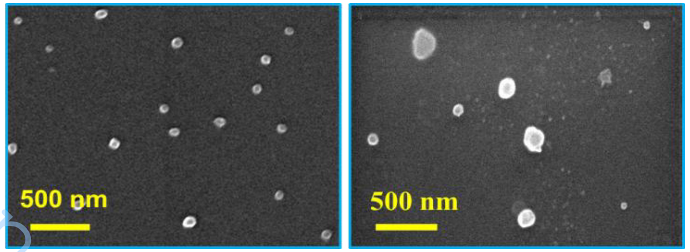


Spheric crystalline cellulose nanoparticles

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



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



Y. Wang, L. Heim, Y. Xu, G. Buntkowsky, **K. Zhang* Advanced Functional Materials, *2015*,** , 25, 1434-1441.

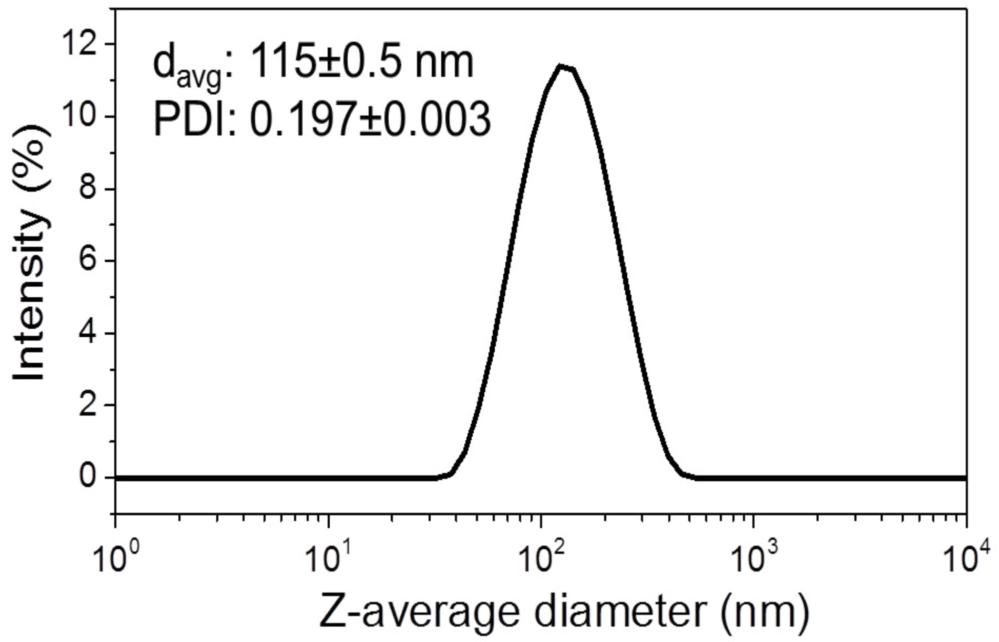
Properties

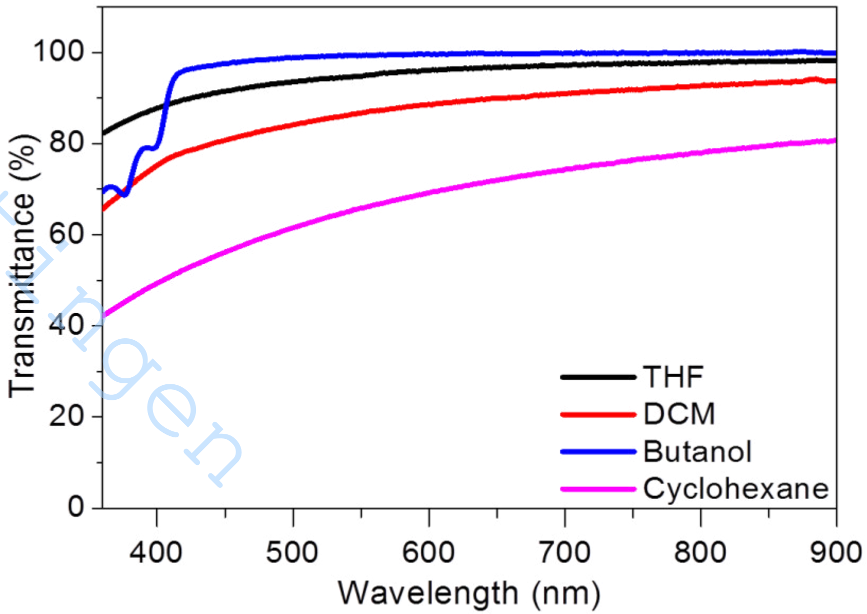
The suspensions of SS-CNPs in organic solvents
→ Stable and (semi)transparent
→ Re-suspendable after drying!

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

5 mg/ml

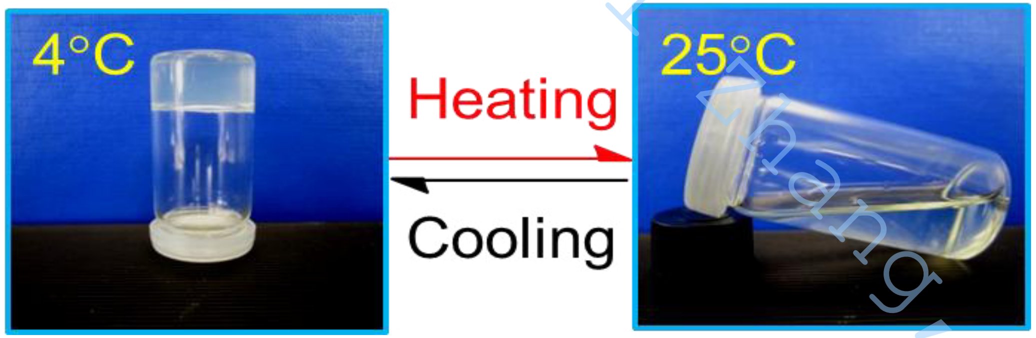
Dynamic light scattering → particle size





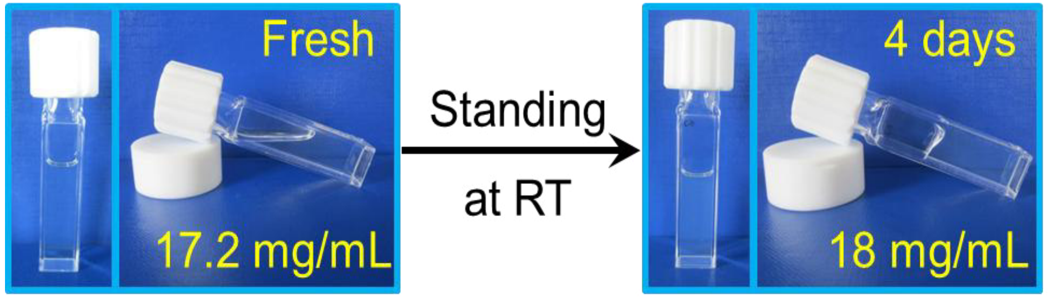
Gelation behaviour of suspensions

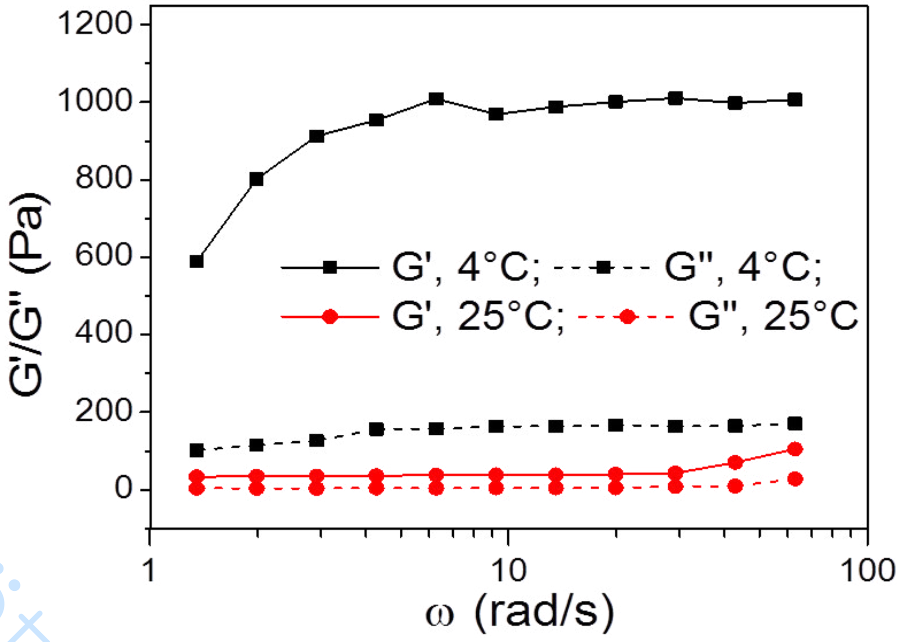
→ Changing temperature: thermo-reversible gelation



5 mg/ml in THF

→ Changing concentration: gelation at RT

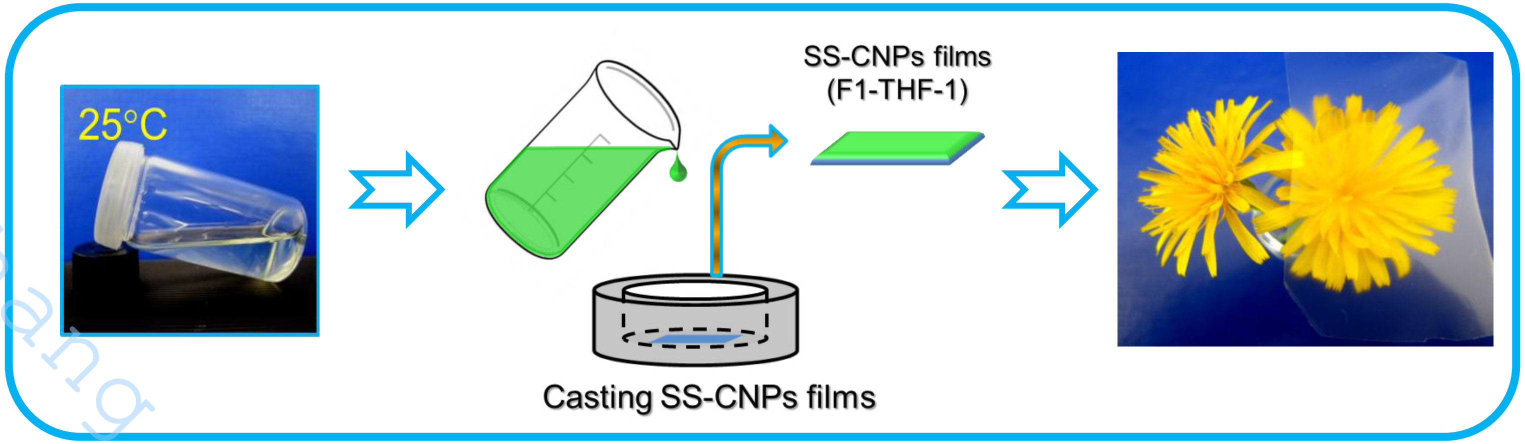




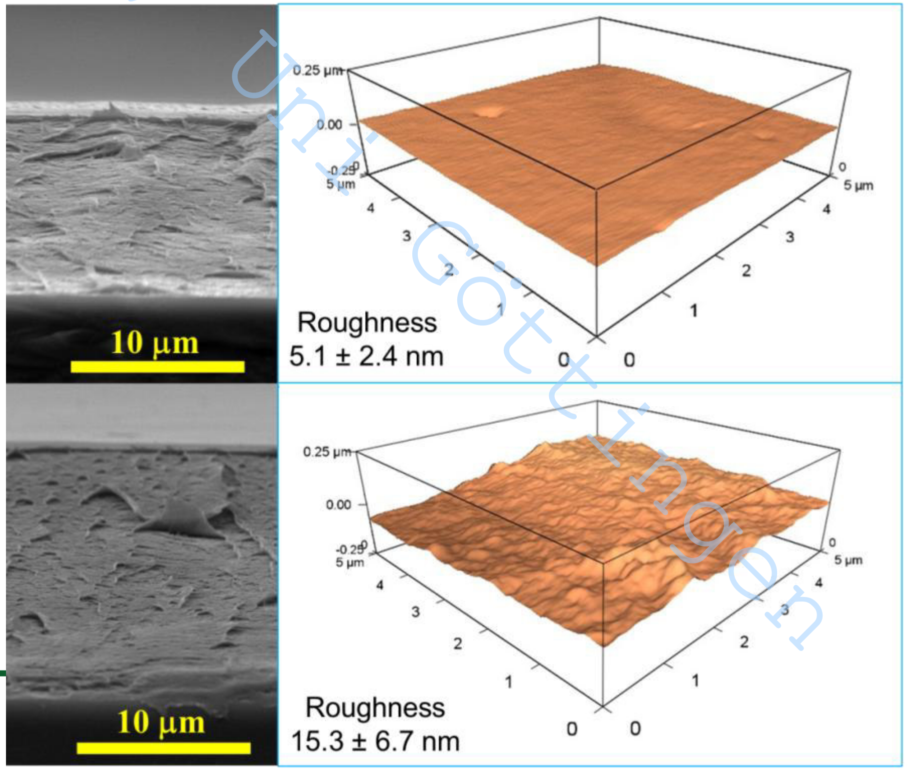
Elastic (G′) and viscous (G″) modulus as a function of oscillatory shear frequency

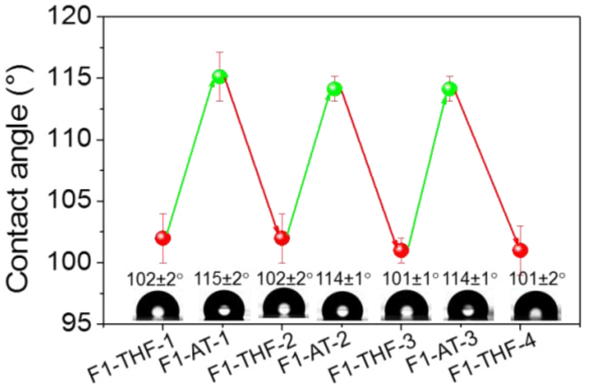
Application of crystalline cellulose nanoparticles: Self-standing films

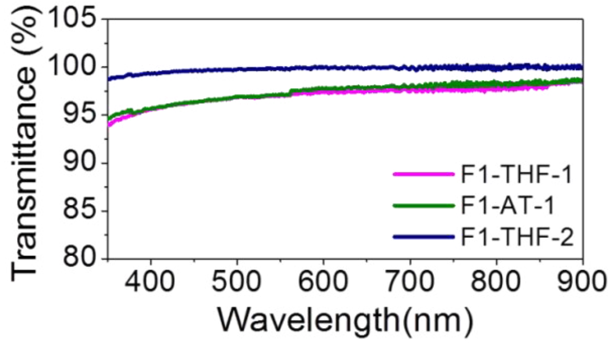
- Solvent casting → Self-standing, flexible, transparent film



- Solvent-switchable surface wettability of SS-CNPs film

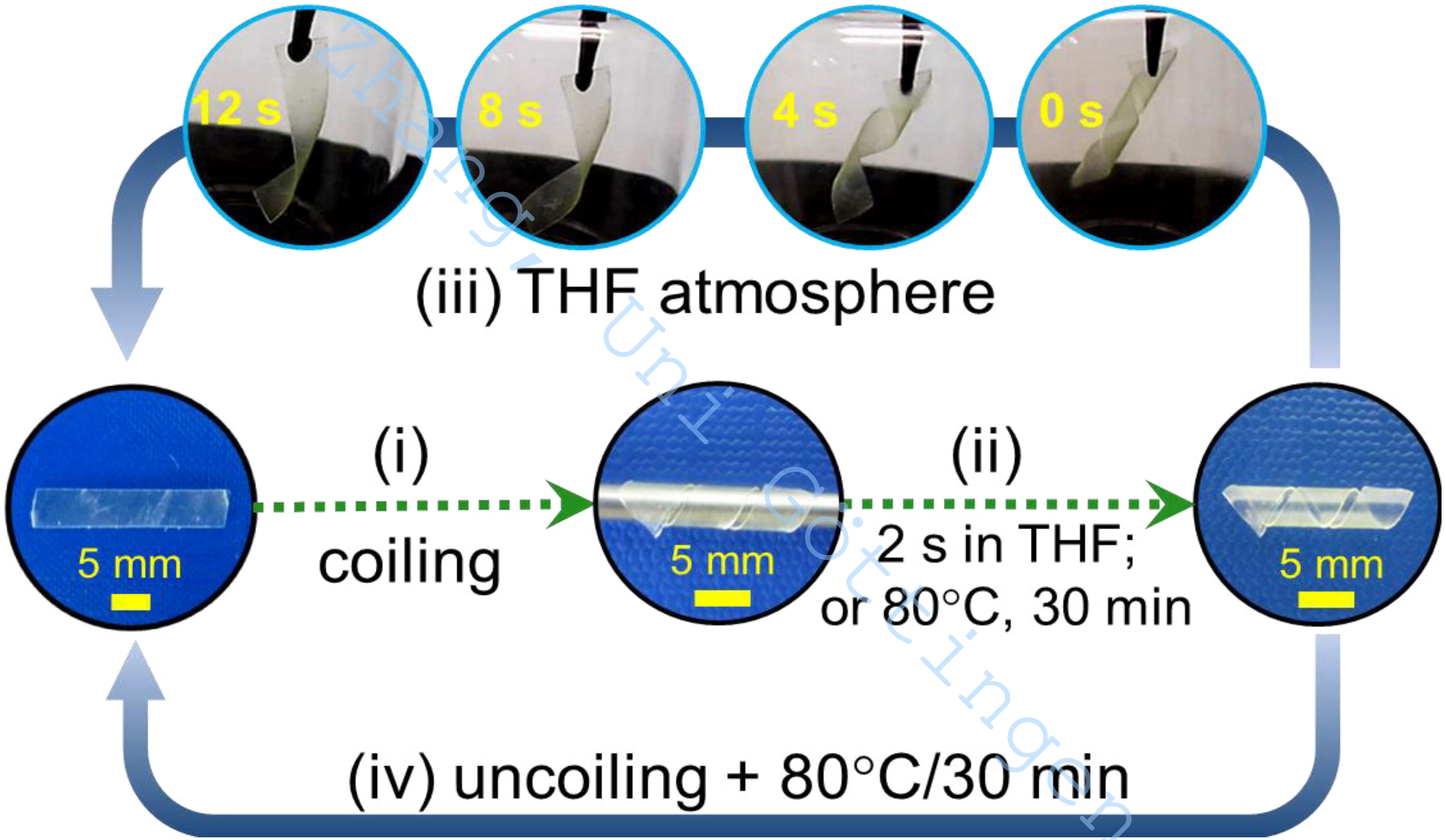




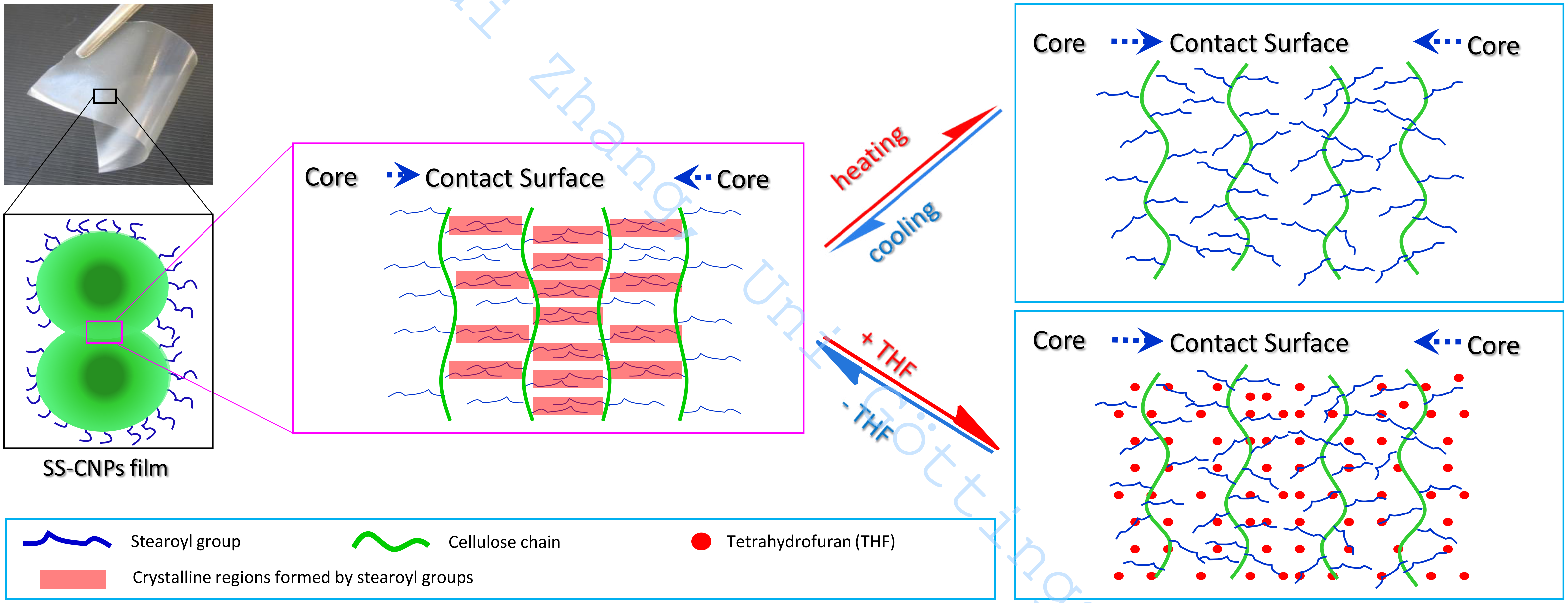


Solvent-responsive shape memory

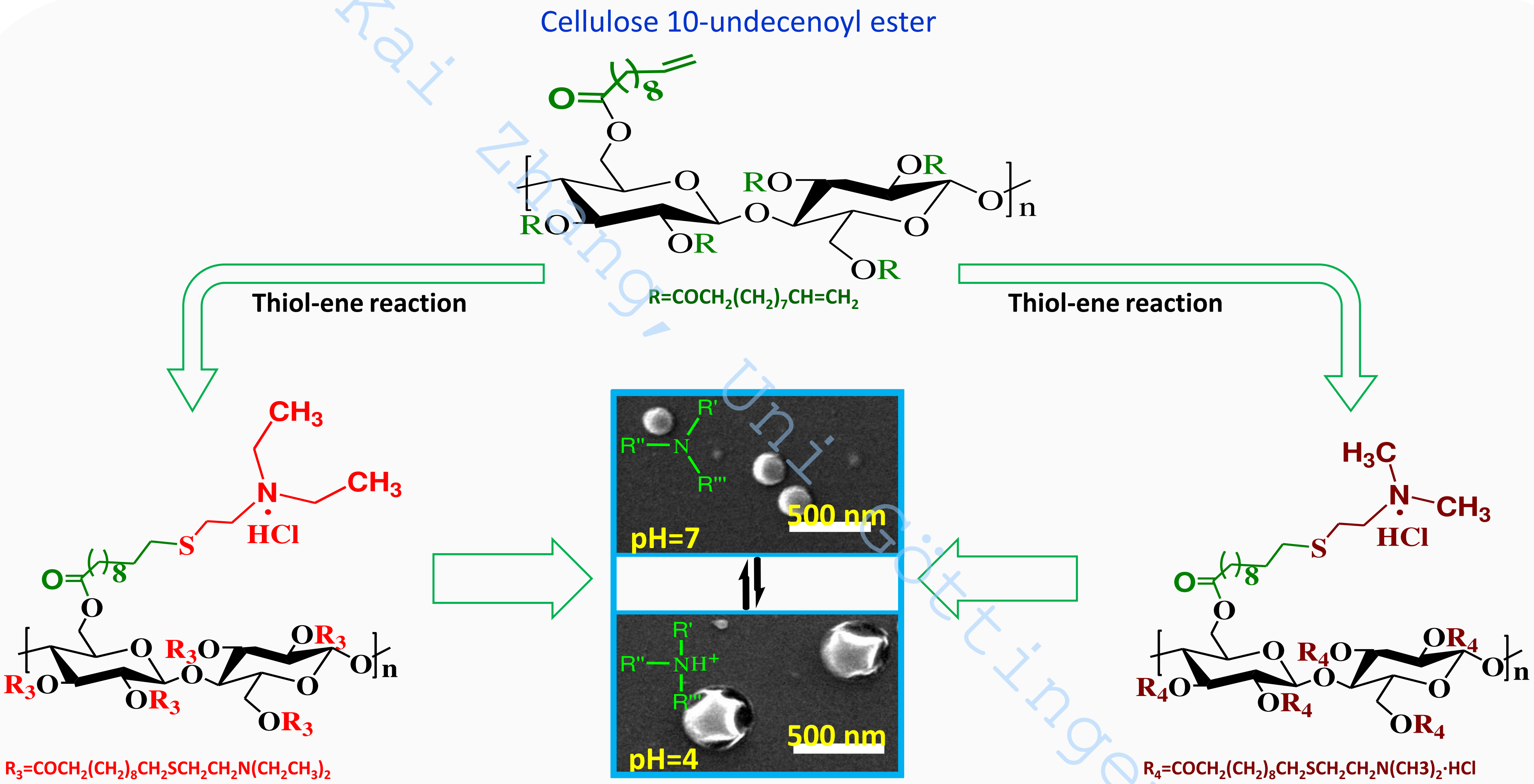
- Good shape fixation by heating or solvent treatment;
- One-way solvent responsive shape-memory behavior;



Proposed mechanism

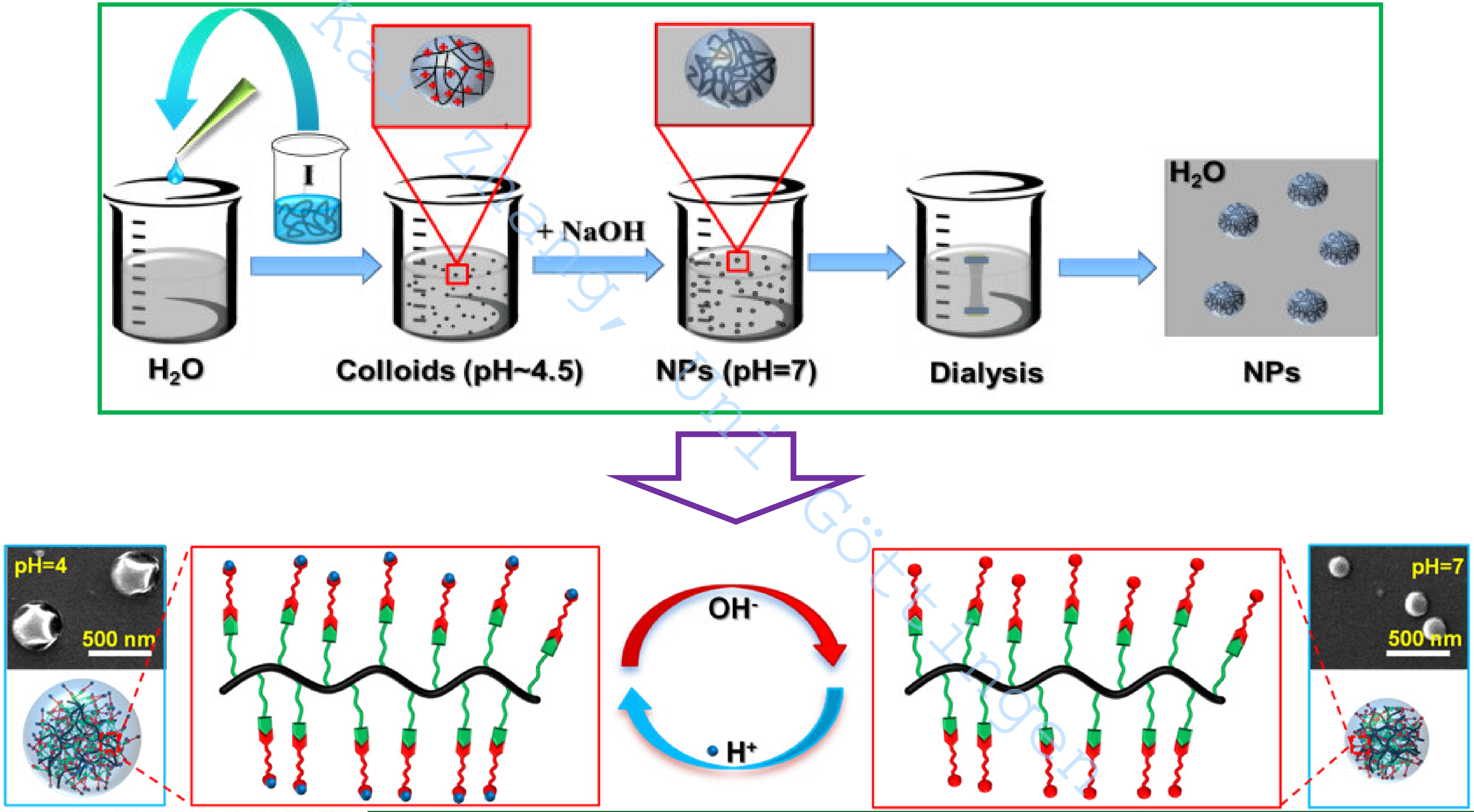


pH responsive NPs

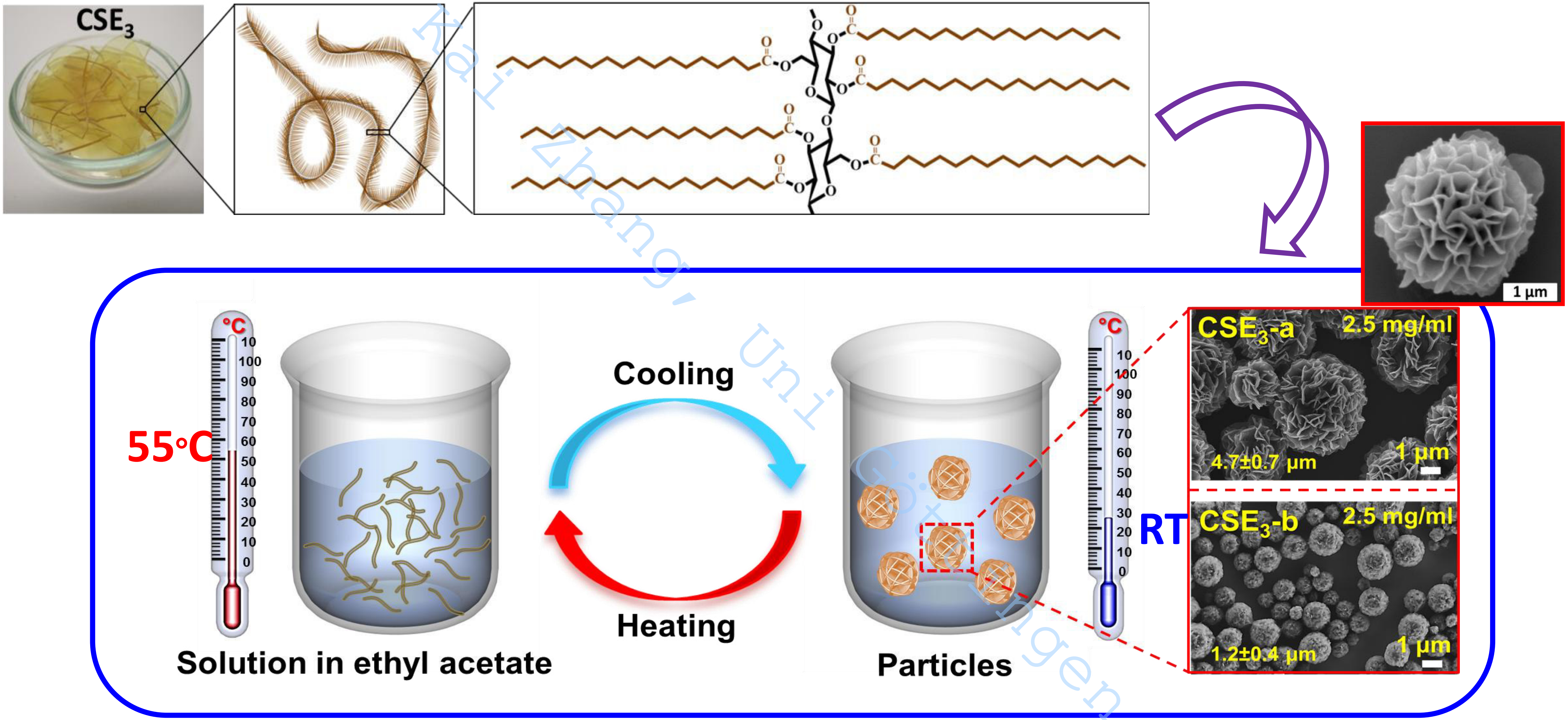


Nanoscale, 2016, 8, 648

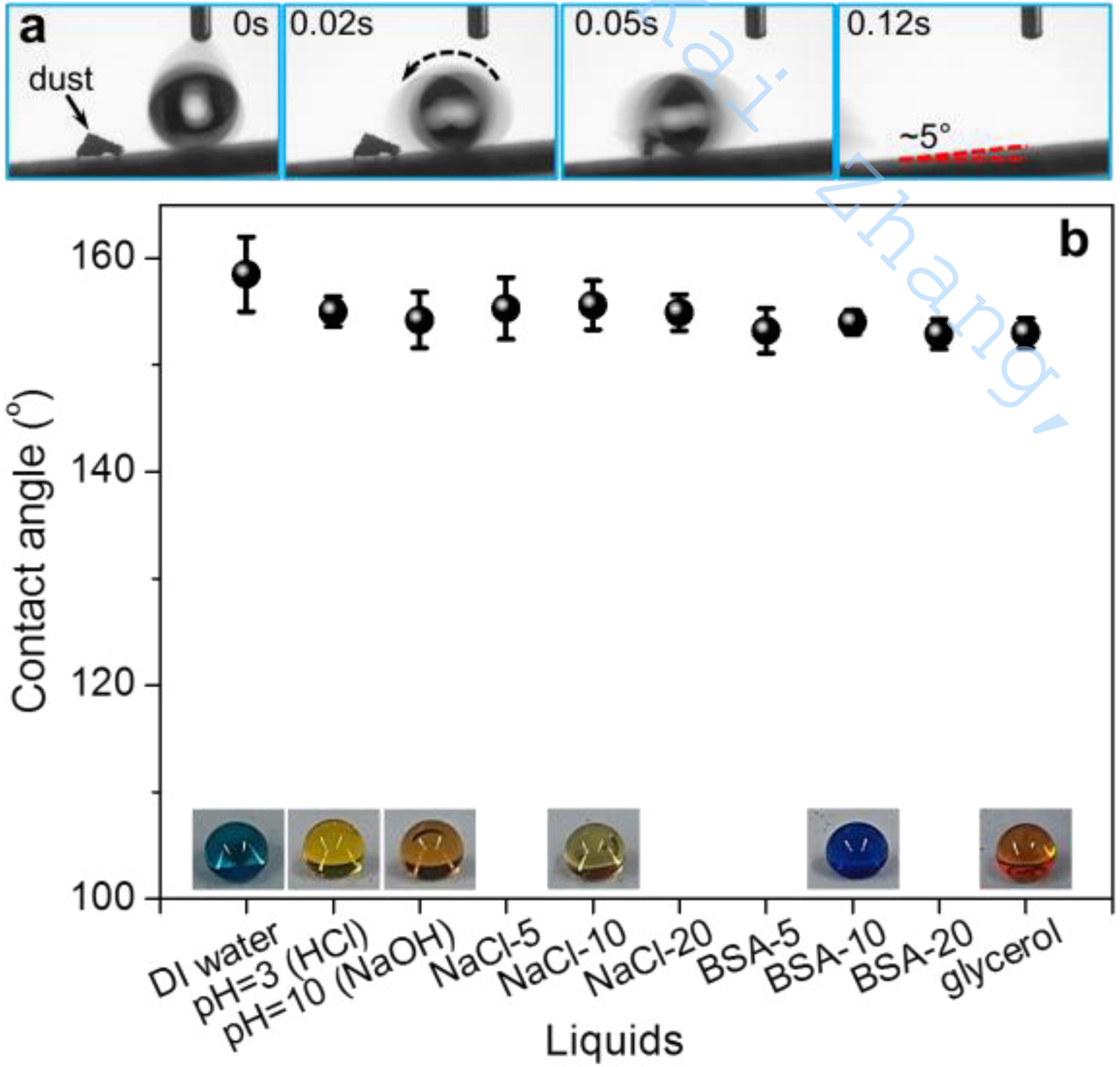
Nanoprecipitation

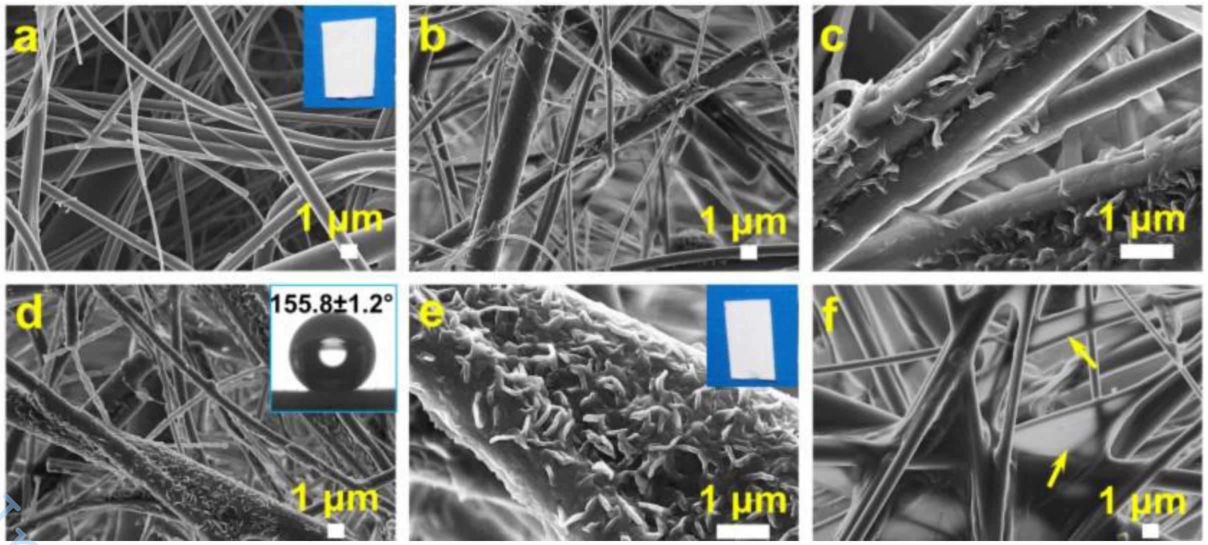


Flower-like Particles via crystallization of cellulose stearoyl esters



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: ~0.01 Pa·s, Glycerol: 0.934 Pa·s, 25°C)

Thank you for your attention!