Preparation of Carboxymethyl Nanocellulose Fibers with Tree-like Structure using a Recyclable Etherification Method

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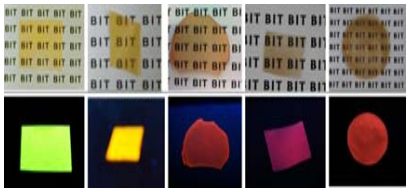
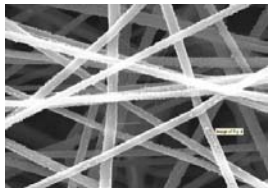
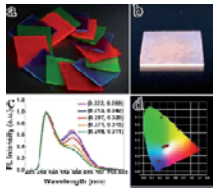
The Beijing Engineering Research Center of Cellulose and Its Derivatives from School of Materials Science and Engineering, Beijing Institute of Technology (BIT) is constitute with an active research team that includes professors, senior engineers, associate professors, lecturers, experimenters, postdoctoral fellows, Ph.D and master students. The center contains more than 30 permanent employees and forms a multi-level team engaged in theoretical, fundamental, and applied sciences. More than 70 papers relates to nanocellulose have been published in ***ACS Appl Mater Interfaces, Chem Eng J, J Mater Chem, Polymer, ACS sustain Chem Eng, Carbohyd Polym, Cellulose, etc.*** and more than 30 patents have been declared for invention in China.

Research Fields includes:

- 1) Green Preparation Process of Nanocellulose;
- 2) Chemical Modification Technology of Nanocellulose (conventional or special);
- 3) Manufacturing Technology of Dry Nanocellulose Powder using non-aqueous approach;
- 4) Preparation Technology of "*Tree-like*" Nanocellulose;
- 5)Application in Supercapacitors, Ultrafiltration Membranes, Electrochromic films, Special polymer composites, Reversible photochromic hydrogels, High dielectric flexibility composite films, Quantum dot enhanced optical conversion films, etc.







Highlight: A production line with a output of 5 tons/year and a capacity of 30 tons/year has been established by our team.

Publications:

ACS sustain Chem Eng. ***2019 (Accepted)***.

Nano Res. **2019**, DOI: 10.1007/s12274-019-2353-4.

Cellulose **2018,** *25* (12), 7143.

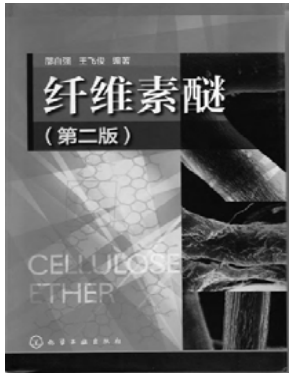
Carbohydr. Polym. **2018,** *193*, 73.

ACS Appl. Mater. Interfaces **2017**, 9 (24), 20885.

Chem. Eng. J. **2017,** *330*, 1166.

Books:

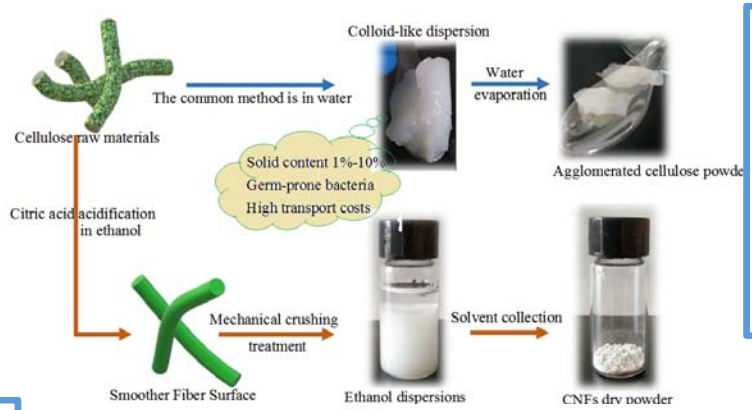
Cellulose Ethers (In Chinese).



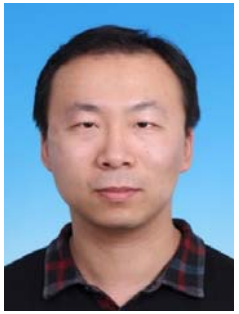
Our research focuses on the scientific research, industrialization and application of nanocellulose. We take into account the physical/chemical modification and application of other natural macromolecule materials such as starch and chitosan. The National Federation of Petroleum and Chemical Industries authorized us the "National Engineering Research Center for Cellulose-based Chemicals in Petroleum and Chemical Industries". The Office of Professional Technical Committee of China Cellulose Industry Association is located in our center.

THE BEIJING ENGINEERING RESEARCH CENTER OF CELLULOSE AND ITS DERIVATIVES

Professor Shao Zi-qiang



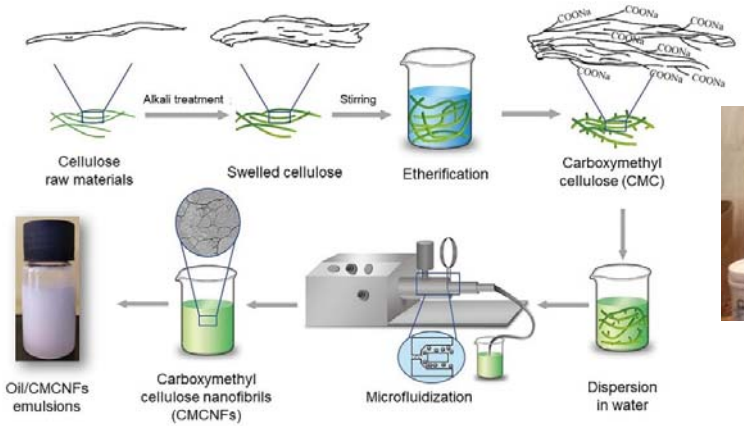
Y. Zhou, J. Wei, Y. Lv, Z. Shao, et al. (2019): Methodology of Redispersible Dry Cellulose Nanofibrils(CNFs) Powder Synthesis Under Waterless Condition, ACS sustain Chem Eng. (Accepted)



Yi Zhou(Doctor)

J. Wei, Y. Zhou, Z. Shao, et al. Carboxymethyl cellulose nanofibrils with tree-like matrix: preparation and behavior of Pickering emulsions stabilization(To be published)

Jie Wei(Doctor)



The team has partnered with professional company to achieve quantified production of nanocellulose : a output of 5 tons/year(2019) and a capacity of 30 tons/year has been achieved in Jiangsu Province, China

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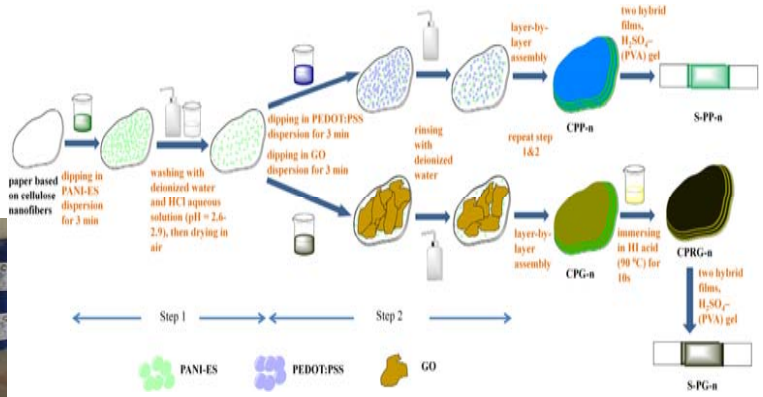
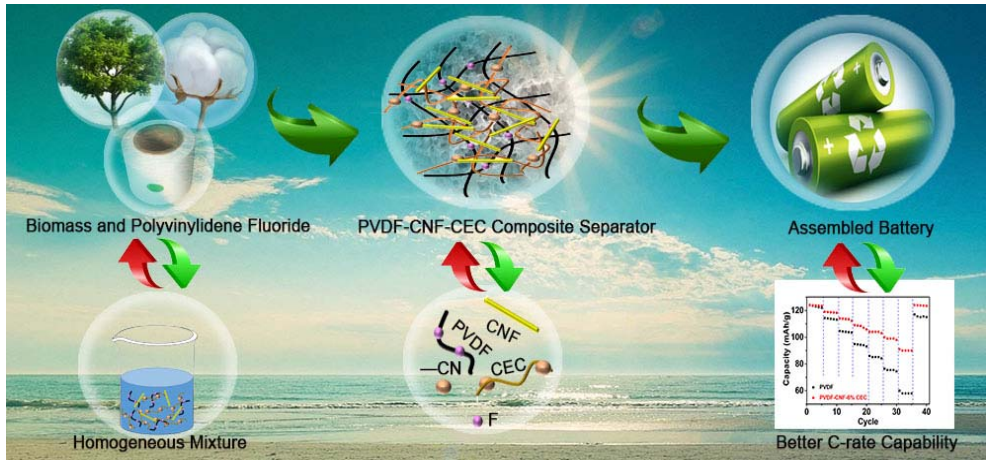


Xi Wang(Master)

Layer-by-Layer assembled hybrid multilayer thin film electrodes based on transparent cellulose nanofibers paper for flexible supercapacitors applications, Journal of Power Sources(2014, 249: 148-155)

Li, L.; Yu, M.; Jia, C.; Liu, J.; Lv, Y.; Liu, Y.; Zhou, Y.; Liu, C.; Shao, Z. Cellulosic Biomass-Reinforced Polyvinylidene Fluoride Separators with Enhanced Dielectric Properties and Thermal Tolerance. ACS Appl. Mater. Interfaces 2017, 9 (24), 20885-20894

Lei Li(Doctor)



Preparation of Carboxymethyl Nanocellulose Fibers with Tree-like Structure Using a Recyclable Etherification

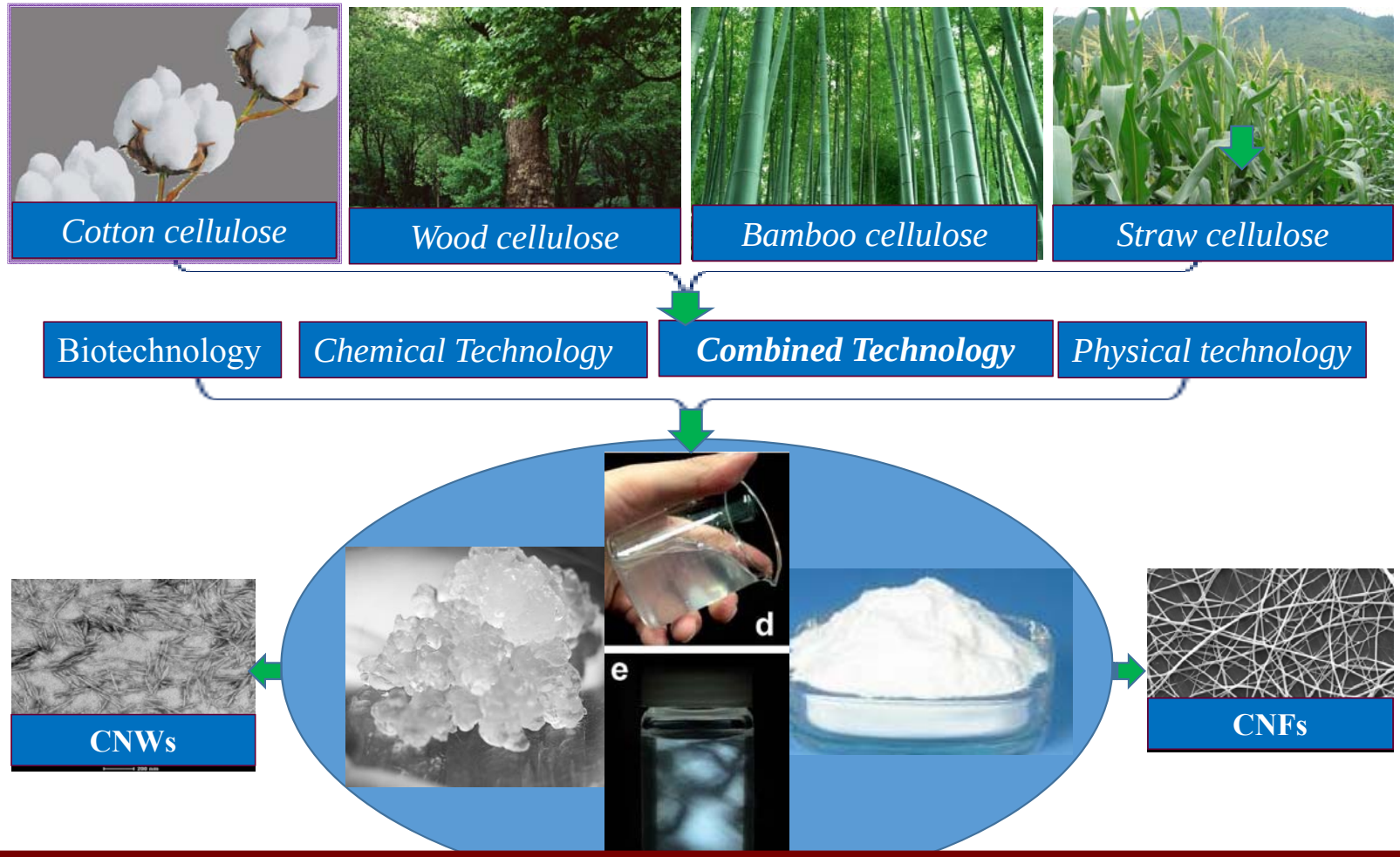
Introduction *Carboxymethyl nanocellulose fibers (CMCNFs) are of great importance in the fields of sustainable chemistry and energy materials, but challenging in productivity and morphology control.*

Objectives *In this work, the aim is to prepare CMCNFs with dendritic matrix by a simple, low-cost and relatively eco-friendly method, which is suitable for quantitative preparation.*

Major findings *Carboxymethyl cellulose (CMC) with low degree of substitution (DS 0.05~0.35) was obtained via alkalization and uniform etherification of cellulose, and then mechanically fibrillated to produce CMCNFs using a microfluidizer. The yield of CMCNFs can be up to 95%.*

Conclusions *As a potential application of the CMCNFs, as a stabilizer, Pickering emulsions were prepared by sunflower oil and CMCNFs with a DS value of 0.227, and nanocellulose fibers (CNFs) was used as a comparison. Detailed studies of zeta potential and size distribution reveal that CMCNFs display much better stabilization role on Pickering emulsions than CNFs.*

1、Introduction



2、 Preparation route

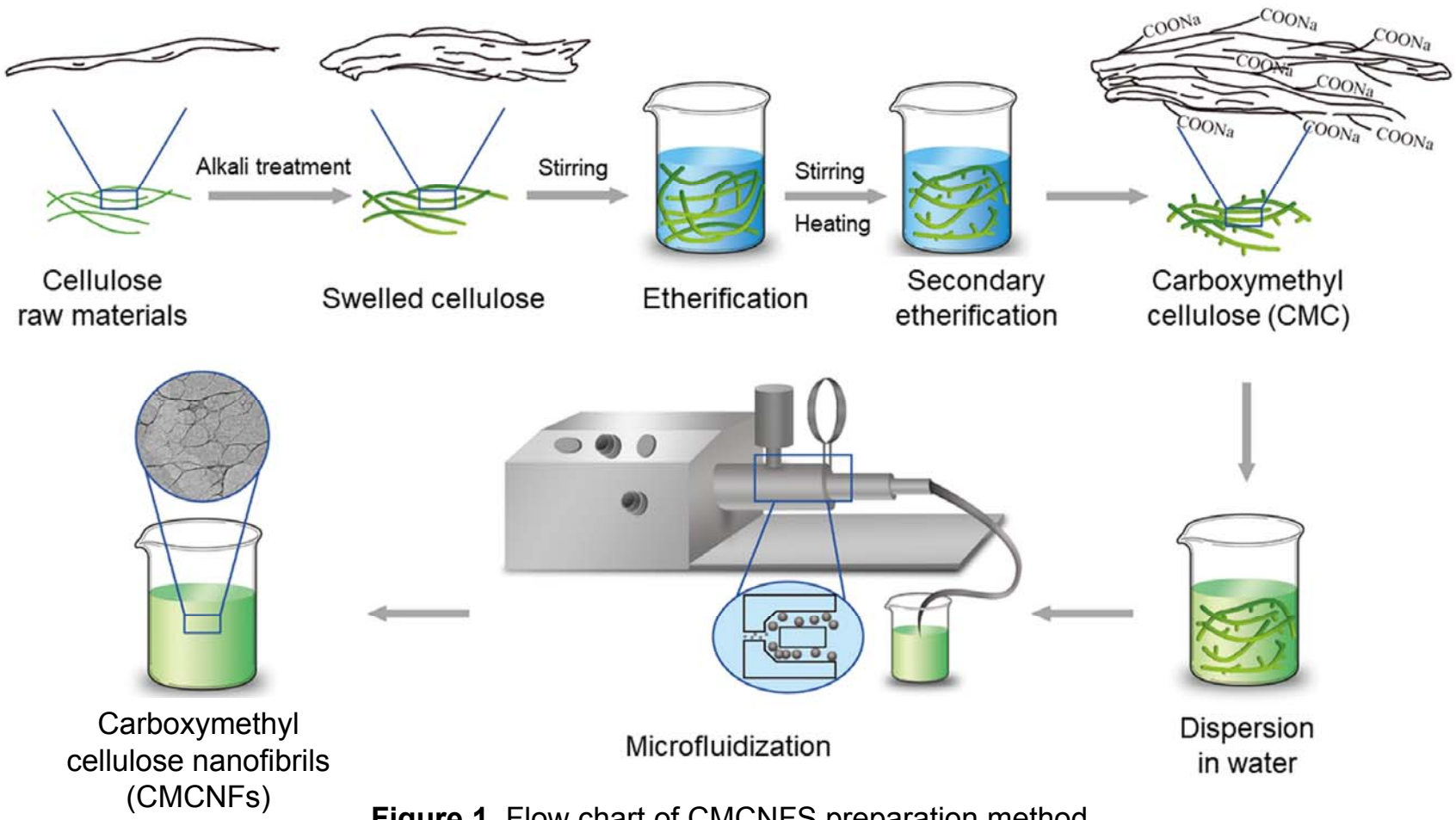
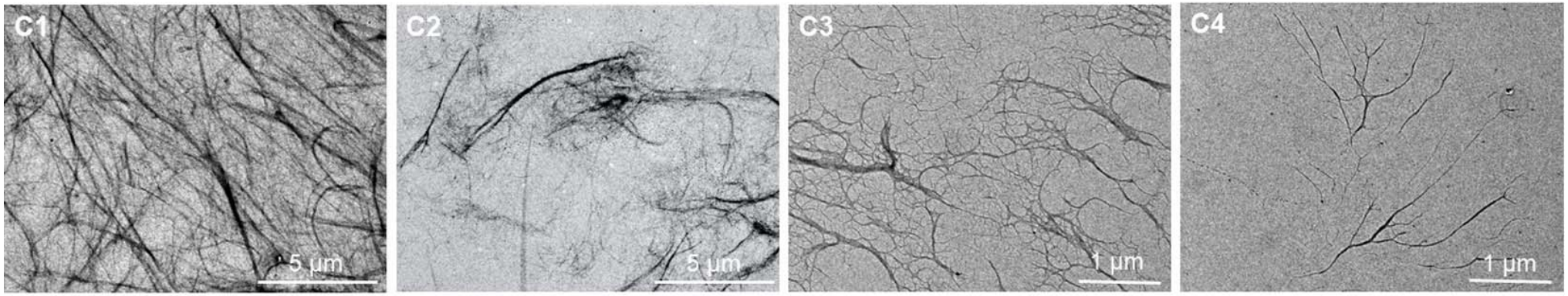


Figure 1. Flow chart of CMCNFS preparation method

3、 Morphology of CMCNFs

(a) The TEM images shown below are CMCNFs made from refined cotton, ‘C’ is short for cotton, 1, 2, 3, and 4 represent samples in DS of 0.05, 0.15, 0.25, and 0.35, respectively.



(b) The TEM images shown below are CMCNFs made from wood pulp powder, ‘W’ is short for wood1, 2, 3, and 4 represent samples in DS of 0.05, 0.15, 0.25, and 0.35, respectively.

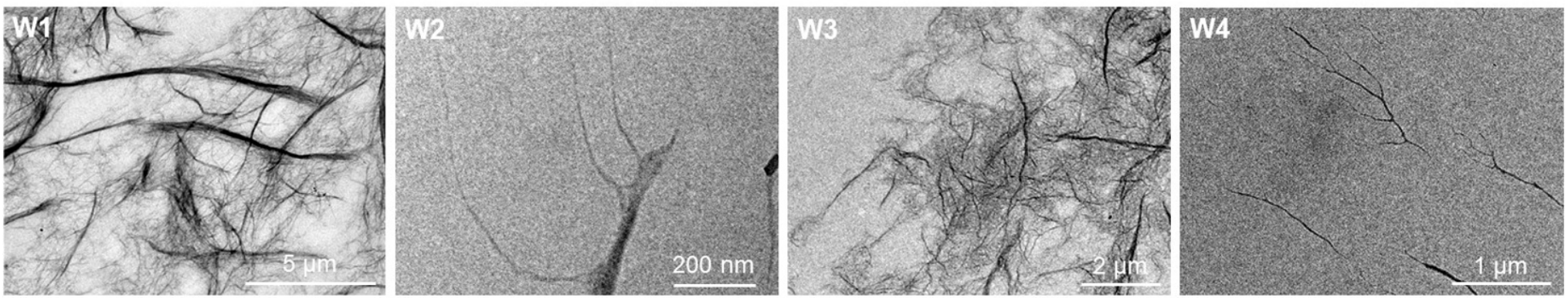


Figure 2. TEM images of CMCNFs made from refined cotton and wood pulp powder.

3、 Morphology of CMCNFs

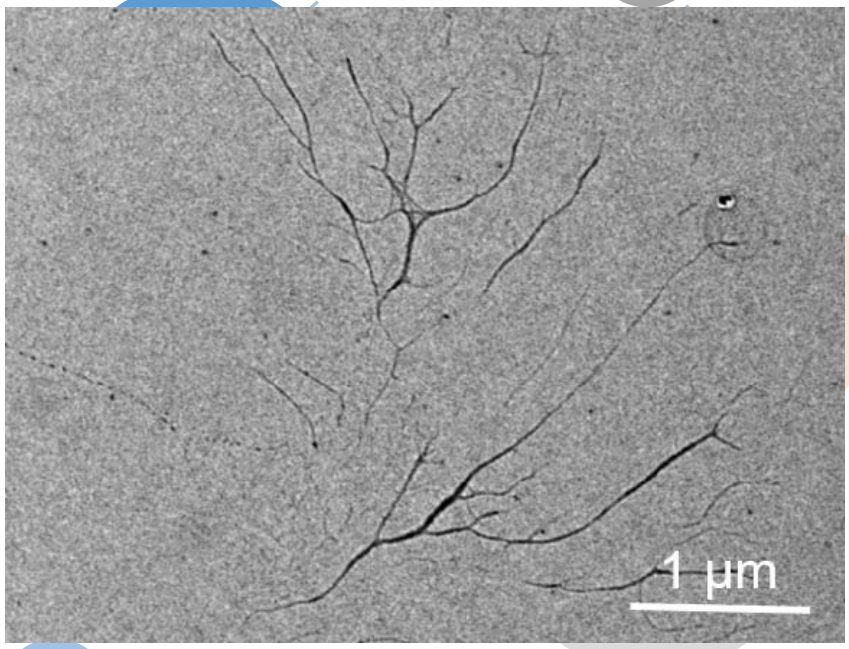


Figure 3. Detailed TEM example of CMCNFs

Performance list of CMCNFs

01 Degree of substitution (DS)

Low DS ranges from 0.05-0.35:
above 0.35, dissolvable; below 0.05, non microfluidization

02 Morphology

Each sample has a central skeleton, just like a trunk of a tree. The length of the central skeleton varies from nanoscale to microscale. Each skeleton comes out of nanoscale fiber filament, just like the branches of a tree.

03 Size

Diameters of CMCNFs distributed from 100 nm to less than 35 nm when DS increases from 0.05 to 0.35.
Length varied from nanometers to micrometers.

04 Raw material influence

Both cotton and wood pulp show similar morphology of CMCNFs

3、 Morphology of CMCNFs

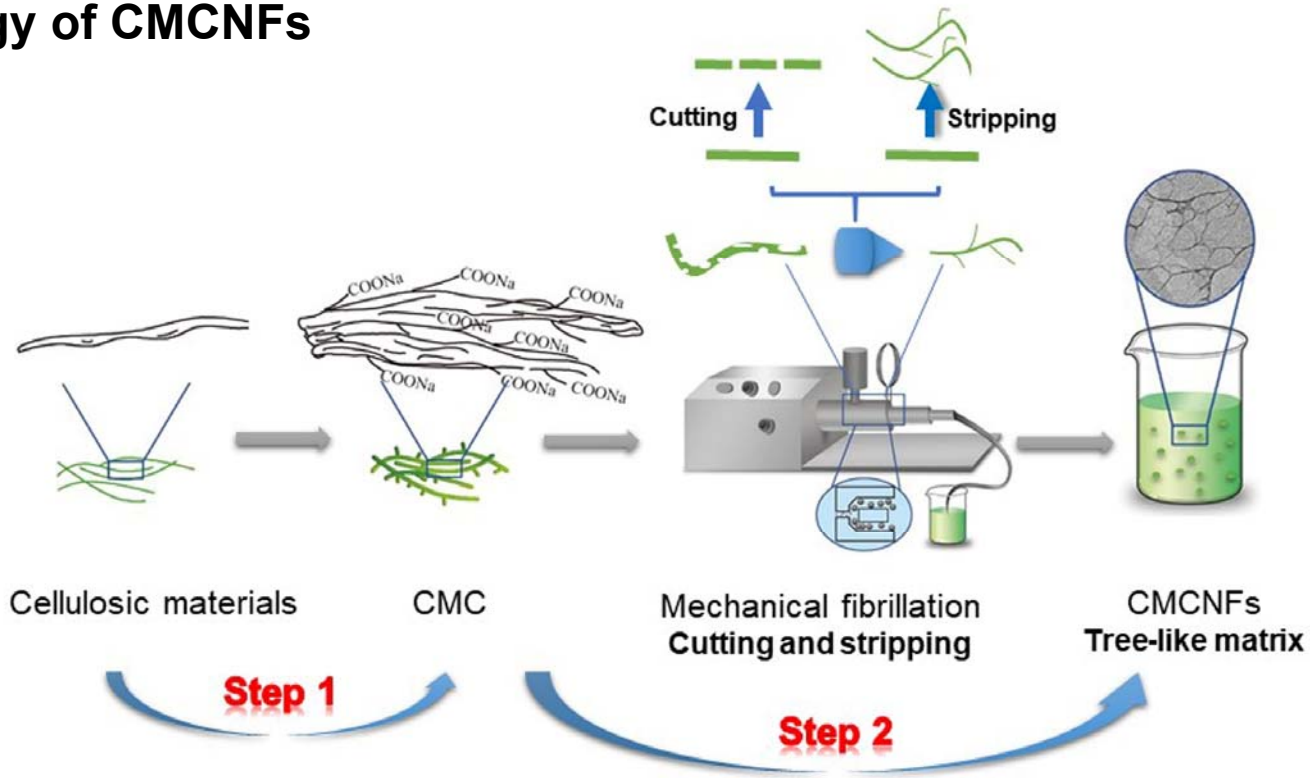
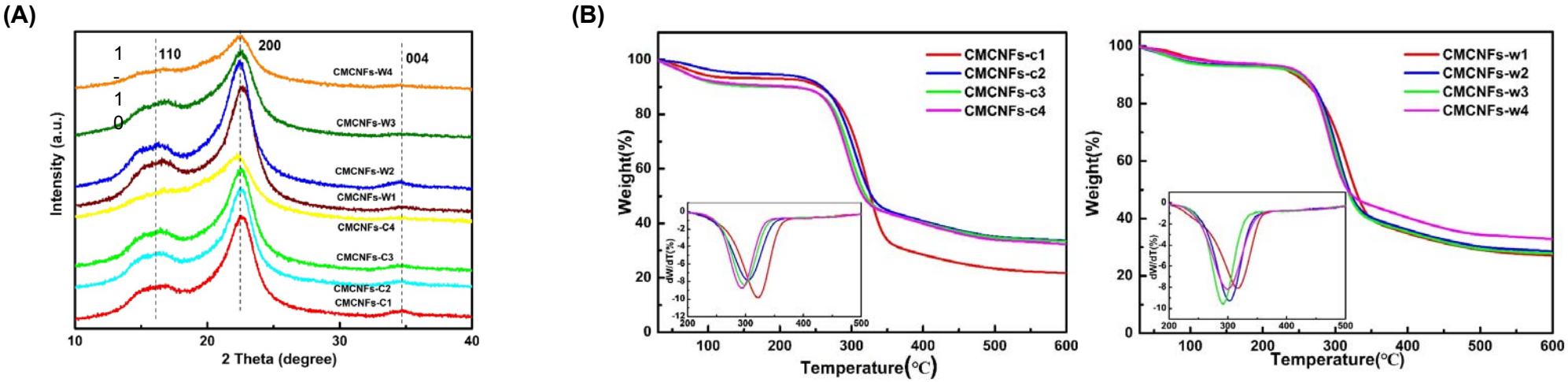


Figure 4. Schematic diagram of CMCNFs preparation.

Cellulose raw materials are modified → Decrease the diameter by surface grafting with hydrophilic groups → Facilitate CMC dispersion in water → Fibers are stretched and fluffy → Microfluidization: cutting and stripping → Formation of Tree-like matrix CMCNFs

4、Additional performances of CMCNFs



(a) (b)

Figure 5. XRD patterns (A), TG/DTG curves (B) of CMCNFs, while 'C' is short for cotton, 'W' is short for wood and 1, 2, 3, and 4 represent DS of 0.05, 0.15, 0.25, and 0.35, respectively.

CMCNFs made from two materials show the same tendency. The crystallinity of samples decreased along with the increase of DS. The crystallinity are all above 55%.

The thermal decomposition temperatures are all above 290℃. Such nanocellulose has a great potential in composite materials which lack high thermal stability.

5、Advantages in Preparation method

Advantages

(1) High yield: ~95%

a. Acidolysis to prepare CNCs: up to 75%, low for the industrialization

b. TEMPO oxidation followed by mechanical operation: around 90%

c. Concentrated oxalic acid hydrolysis and subsequent mechanical fibrillation: CNCs around 5%, CNFs around 90%

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(2) Low cost:
Reaction solvent and washing solvent can be recycled;
Cheap reagents

a. Equipment corrosion, wastewater/salts generation and difficulty of acid recovery

b. TEMPO oxidation is expensive, toxic and corrosive.

c. Insufficient fiber pre-destruction cause risk of microfluidizer clogging rising

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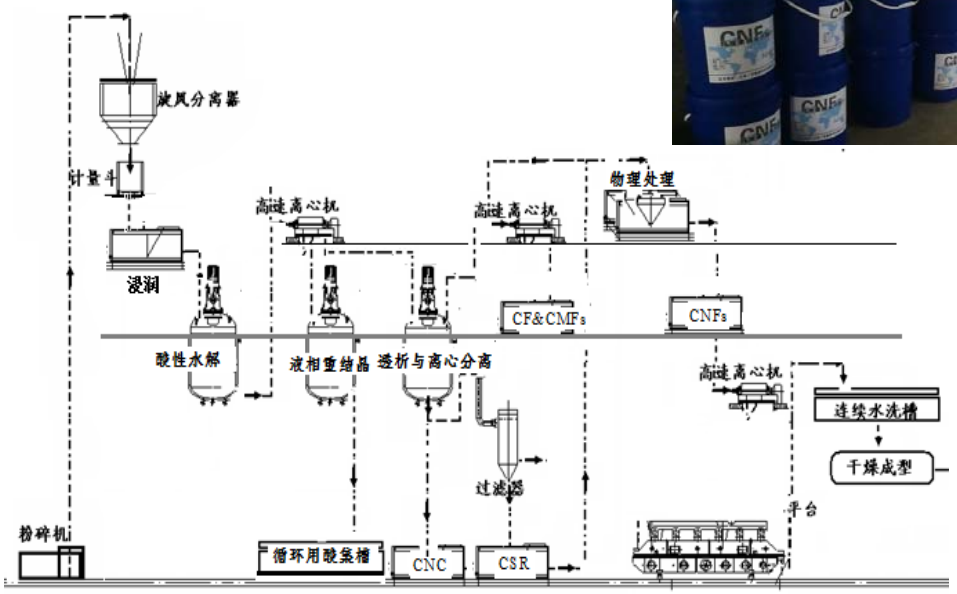
(3) Unique Tree-like matrix: Rod-like, linear, sphere and network

Unsolved problems:

a. Further exploration of tree-like schematic;
b. More accurate control between DS and morphology, detailed experimental scheme;
c. CMCNFs application performances, finding suitable expansion spaces;
d. Industrialization.

6、Large-scale preparation



Highlight: Beijing Institute of Technology and Northern Century (Jiangsu) Cellulose Material Co., Ltd. Realize collaborate and actualize the enlarged and quantified preparation of Nanocellulose. A production line with a output of 5 tons/year and a capacity of 30 tons/year has been successfully established by our team.

Thank you

PRESENTED BY

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