Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Potassium permanganate oxidation as a carboxylation and defibrillation method for extracting cellulose nanofibrils further fabricate films with high transmittance and haze

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The document consists of **5 pages**, **8 sections** Supporting Information (**S1-S8**).and **4 references**.

S1 Analysis and characterization of polymerization degree.

The degree of polymerization (DP) was measured according to the ISO 5351/2010 standard method. Measure the intrinsic viscosity (*[η]*) of the cellulose dissolved by copper(II) ethylene diamine, then DP were calculated according to the Mark-Houwink-Sakurada equation,[1] all experiments were repeated. The intrinsic viscosity *[η]* of the solution and the average Dp satisfy the Eq. (1).

$$[\eta] = KDp^{a} \quad (1)$$

The test environment temperature is 25 °C, K=1.7 g/mL, a=0.8.

S2 The calculation of crystallinity (Cr) and crystallinity index (CrI).

The crystallinity (Cr) and crystallinity index (CrI) were calculated according to Eq. (2) and Eq. (3), respectively.[2]

$$Cr = \frac{A_{cr}}{A_{cr} + A_{am}} \times 100 \quad (2)$$

Where Acr and Aam are the integrated area of the crystalline and amorphous phases, respectively.

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (3)$$

Where CrI is the degree of crystallinity, I_{002} is the maximum intensity of the (002) lattice diffraction and I_{am} is the intensity diffraction at 18 2θ degrees.

S3 The degree of oxidation (DOFT-IR) was measured by ATR-FTIR spectroscopy.

The DO $_{FT-IR}$ was calculated based on Eq. (4).[2]

$$DO_{FTIR} = 0.01 + 0.7\,(\frac{I_{1730}}{I_{1060}}) \quad (4)$$

S4 The carboxyl group content titration method.

The carboxyl group of cellulose reacts with weak acid salts such as calcium acetate to form cellulose salts and release the same amount of weak acid. Based on this, the following method was used to determine the carboxyl content. A 0.5 g sample was treated with 0.01 M HCl for 1 h, and then washed thoroughly with water. In the next step, add 50 mL distilled water and 30 mL 0.25 M calcium acetate solution to the sample，and then sonicated for 2 h to facilitate the completion of the exchange. After 2 h treatment, use phenolphthalein indicator to titrate 30 mL of liquid with 0.1 M sodium hydroxide. The carboxyl content was calculated based on Eq. (5).[3]

$$[COOH] = \frac{\frac{80}{30} \times 0.01M \times V(NaOH)}{m \times (1 - \frac{w}{100})} \quad (5)$$

At the same time, substitution degree (DS) of carboxyl groups was calculated by Eq. (6).[4]

$$DS = \frac{162 \times [COOH]}{M_{(COOH)} \times 100 - [M_{(COOH)} - 1 \times [COOH]} \quad (6)$$

Where 162 is the molecular weight of the anhydrous glucose units.

Figure S5. The TEM and AFM images.

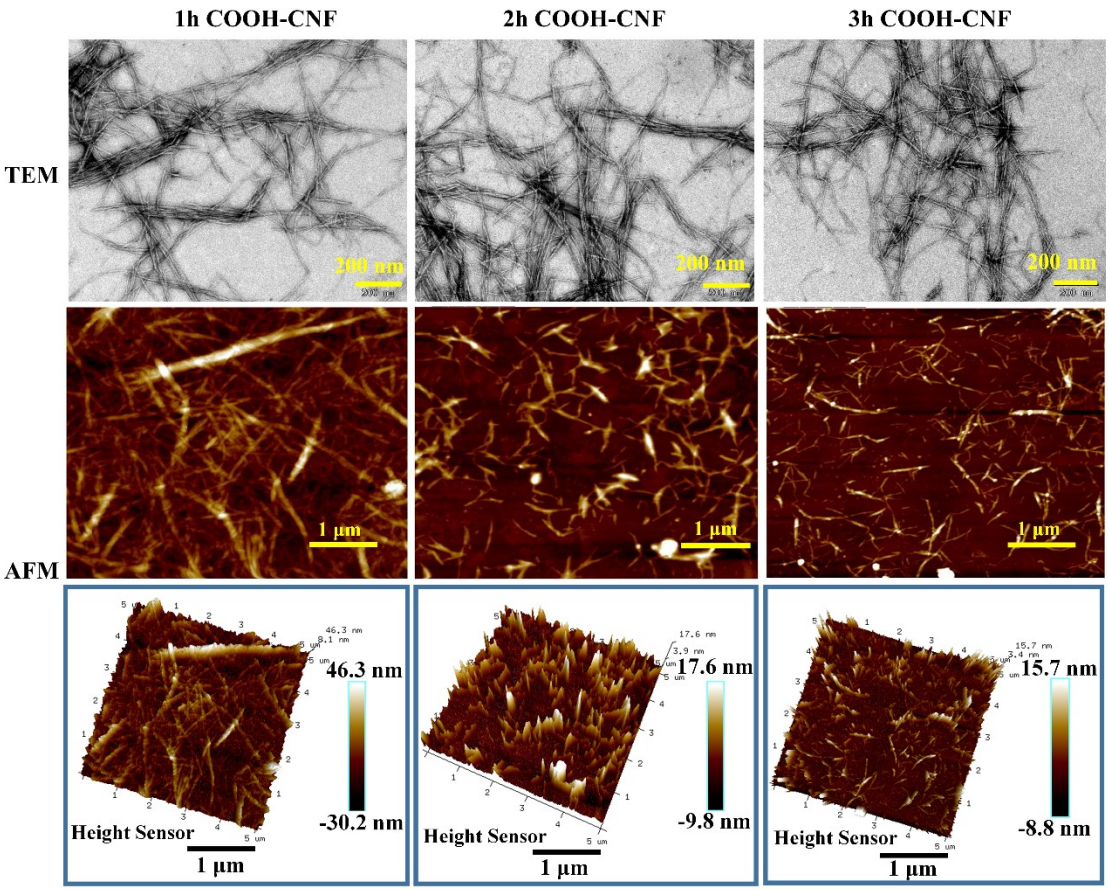

Figure S5. The micro morphology of COOH-CNFs TEM and AFM images.

Video S6. The light scattering phenomenon of COOH-CNFs film.

(See attached video)

Video S7. The quenching phenomenon with hydrogen peroxide. (See attached video)

Figure S8. BET-BJH pore distribution of COOH-CNF film

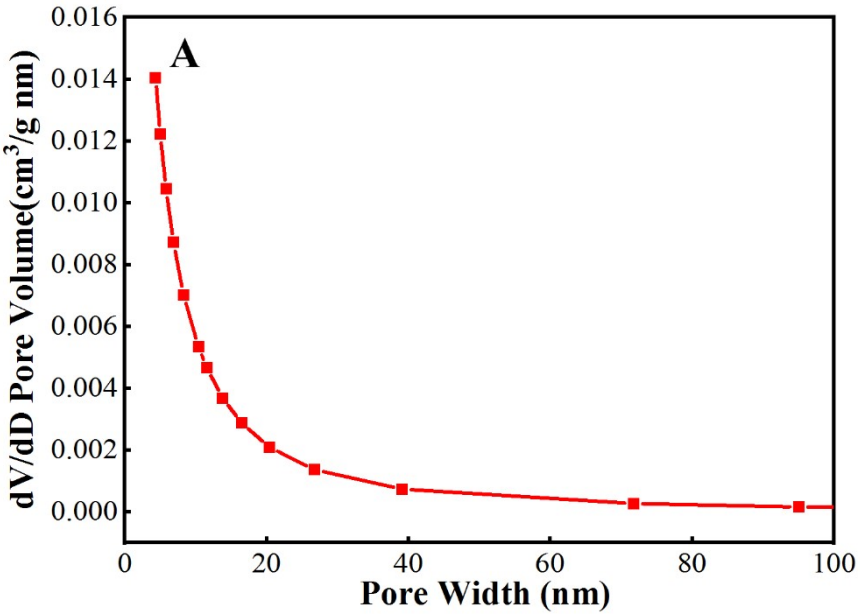

Figure S8. BET-BJH pore distribution of COOH-CNF film.

References

1. R. Khiari, F. Rol, M.-C. Brochier Salon, J. Bras and M. N. Belgacem, *ACS Sustainable Chem. Eng.*, 2019, **7**, 8155-8167.
2. A. Saini, C. Yadav, B.-L. Xue, N. Wang, L. Dai and X. Li, *ACS Appl. Polym. Mater.*, 2019, **2**, 548-562.
3. M. Knežević, A. Kramar, T. Hajnrih, M. Korica, T. Nikolić, A. Žekić and M. Kostić, *J. Nat. Fibers.*, 2020, DOI: 10.1080/15440478.2020.1745120, 1-13.
4. H. Du, C. Liu, Y. Zhang, G. Yu, C. Si and B. Li, *Ind. Crops. Prod.*, 2016, **94**, 736-745.