Electronic Supplementary Information for

Organic solvent-free and efficient manufacture of functionalized cellulose nanocrystals via one-pot tandem reactions

Lirong Tang, Biao Huang*, Nating Yang, Tao Li, Qilin Lu, Wenyi Lin, Xuerong Chen

Fujian Agriculture and Forestry University, Fuzhou 350002, China
Phone: (+86)-18950293837; fax: (+86)-591-83715175
e-mail: fjhuangbiao@hotmail.com

Experimental

The cellulose substrates were pure wood pulp filter paper, kindly supplied by Hangzhou Fuyang Special Paper Industry Co., Ltd. (Hangzhou, Zhejiang, China). Maleic anhydride (MA) and sulfuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China). All chemicals were of analytical reagent grade.

The cellulose pulp (CP) was obtained from the filter paper as described in our previous work.[1] Briefly, the filter paper was disintegrated with a Fiber Standard Dissociation device (GBT-A, Changchun Yueming Small Testing Machine Co., Ltd.) for 20 min at 3000 rpm, and then lyophilized at -54 °C for 24 h. Mechanochemical pretreatment of cellulose pulp was performed within the planetary ball mill (BXQM-0.4L, Special Round of the New Instrument Co., Ltd. Nanjing) equipped with four agate jars, each of which was 100 cm^3 in volume and loaded with 25 agate balls. For each experiment, a mixture of 1 g of CP, 5 g maleic anhydride and 11.4 g 20 % (w/w) H_2SO_4 was added into the jar and milled at a rotational speed of 500 rpm for 0.5, 1, 1.5, 2 h, which were labeled as BM-0.5 h, BM-1 h, BM-1.5 h and BM-2 h, respectively. The difference in speeds between balls and grinding jars produces an interaction between frictional and impact forces, which release high dynamic energies and can effectively reduce the size of samples. After milling, the balls were removed and cleaned. The samples were introduced into a 150 mL three-necked round-bottom flask equipped with a condenser and kept at 90 °C in an oil bath for 1 h, followed by treatment in an ultrasonic reactor KQ-250DB (Kun Shan Ultrasonic Instruments Co., Ltd., China) at 40 kHz under continuous stirring at 300 rpm with a poly(tetrafluoroethylene) (PTFE)-coated stirring device for 5 to 8 h at 70 to 78 °C. After the reaction, the mixture was washed several times with deionized water by repetitive centrifugations at 12000×g for 10 min until the supernatant liquid presents neutral tested by pH test papers, and finally lyophilized.

The yield (g/g) of MA-CNCs was calculated by the equation as follows:

$Y_{\text{MA-CNCs}}$(g/g) = dry weight of MA-CNCs (g)/dry weight of CP (g)

FTIR spectra were recorded on a Nicolet 380 FTIR Spectrometer (Thermo electron Instruments Co., Ltd., USA). The solid-state CP/MAS (cross-polarization-magic angle spinning) ^{13}C NMR spectra were collected at room temperature with a Bruker Avance III 500 spectrometer (Bruker Biospin AG, Fallanden, Switzerland) at a magic angle spinning (MAS) rate of 5 kHz, a contact time of 2 ms, and at a frequency of 125.73 MHz for ^{13}C NMR. All the spectra were collected over 1.5 h (1024 scans). SEM images were collected with a FEI XL30 ESEM-FEG at an operating voltage of 20 kV. Elemental analysis was conducted on an Elementar vario MICRO analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). Structure and phase analysis of the samples were performed using an X-ray diffraction (XRD, X'Pert Pro MPD, Philips, Netherland) with Cu Kα radiation ($\lambda = 0.154$ nm).

References

1 L. Tang, B. Huang, Q. Lu, S. Wang, W. Ou, W. Lin and X. Chen, *Bioresour. Technol.*, 2013, **127**, 100-105.

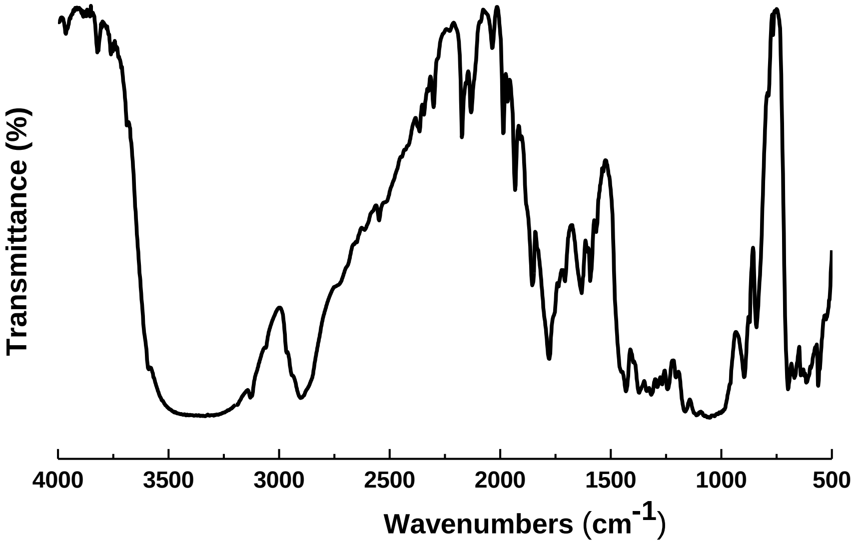

Fig. S1 FTIR spectrum of mixture of CP and maleic anhydride.

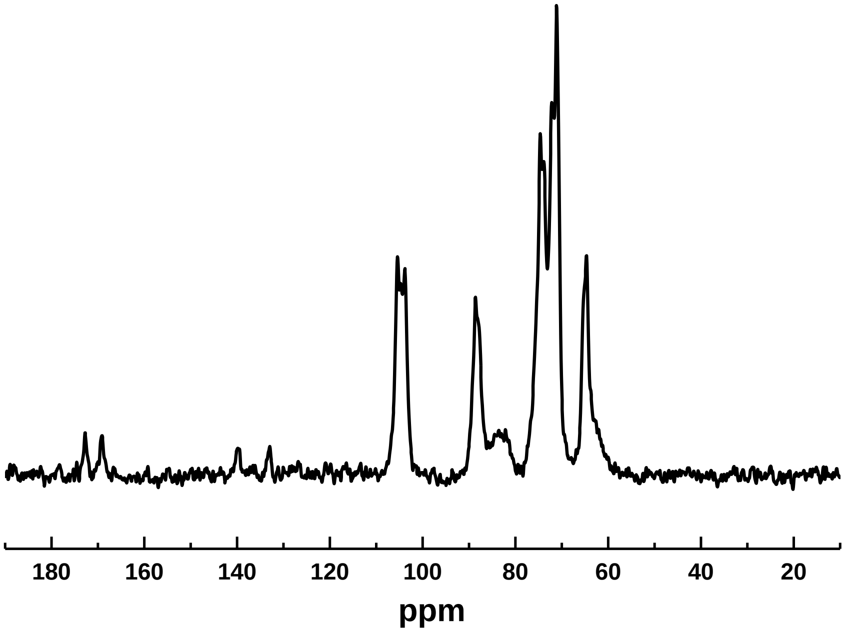

Fig. S2 Solid-state CP/MAS ^{13}C NMR spectrum of mixture of CP and maleic anhydride.