

Organic solvent-free and efficient manufacture of functionalized cellulose nanocrystals *via* one-pot tandem reaction†

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An environmentally benign approach for the manufacture of maleic anhydride functionalized cellulose nanocrystals (MA-CNCs) *via* one-pot tandem reactions with H₂SO₄ as a catalyst under organic solvent-free conditions was put forward. The effects of ball milling time, ultrasonication temperature and time on the yield and degree of substitution (DS) have been explored.

Cellulose nanocrystals (CNCs), extracted from natural cellulose based materials (wood, hemp, cotton, linen, *etc.*), enjoy the following advantages: similarity to the dimensions of carbon nanotubes, single digit nanometer in width dimension as well as hundreds to thousands of nanometers in length.¹ Many researchers have devoted their attention to isolating cellulose nanocrystals by using enzymes, inorganic acids (*e.g.* H₂SO₄, HCl, H₃PO₄) and high pressure homogenization in recent years, but their methods have drawbacks such as slow reaction rate, corrosion hazards, harsh conditions and low crystallinity.² Meanwhile, as for any nanoparticle, the main challenge is related to their homogeneous dispersion within a polymeric matrix, dispersion of highly polar cellulose nanocrystals in apolar solvents, or difficulty in incorporating them into the most common apolar polymers.^{3,4} The modification of cellulose nanocrystals usually involves complex and time-consuming multi-step synthetic protocols, such as degradation of cellulose, low yield, a lengthy separation process and purification of the intermediates. On the other hand, it is difficult to re-disperse the lyophilized intermediates in solvents, which hinders hinder the sequential modification reactions. Attempts to overcome these limitations cover the utilization of a sequential one-pot route under organic solvent-free reaction conditions and the application of non-classical energy sources including ball milling, microwave heating, ultrasonication or mechanochemical techniques.⁵

Mechanochemistry is the coupling of mechanical and chemical phenomena on a molecular scale and involves phase transition, size reduction, polymer degradation under shear, cavitation-related phenomena, shock wave chemistry and physics, and even the promising field of molecular machines.^{6,7} The size reduction of the solid and accretion of its specific surface area during mechanical milling are accompanied by chemical bonds distorting and bond length extending due to the imposed stress. When the imposed stress is beyond the chemical bonding energy, bond rupture occurs. This produces radicals and activates functional groups which may react with other reagents.⁸ Jeon *et al.*⁹ have achieved a high yield of edge-selectively carboxylated graphite (ECG) by a simple ball milling of pristine graphite in the presence of dry ice. Zhang *et al.*⁶ also found that an esterification reaction took place when cellulose was ball-milled with maleated polyethylene. Therefore, this technique would be a potential method to prepare surface-modified cellulose fillers under mild conditions.

Herein, we wish to gain deeper insight into the efficiency of nanocrystallization and maleation of cellulose. In particular, we disclose a simple, versatile method to manufacture functionalized CNCs in conjunction with ball milling and ultrasonication in tandem mode, in which the nanocrystallization and maleation of cellulose take place simultaneously under organic solvent-free conditions. A schematic representation of the synthesis of the MA-CNCs is shown in Fig. 1.

The cellulose pulp (CP) was obtained from the filter paper as described in our previous work (see ESI†).¹⁰ Mechanochemical pretreatment of cellulose pulp was performed within the planetary ball mill (BM) equipped with four agate jars, each of which was 100 cm³ in volume and was 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) H₂SO₄ with 8.2 g H₂O 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 speed between balls and grinding jars produces an interaction between the frictional and impact forces, which releases high

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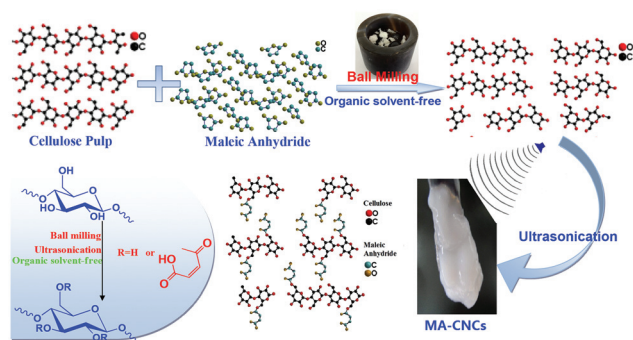


Fig. 1 Schematic model of the mechanochemical assisted manufacture of maleated cellulose nanocrystals (MA-CNCs).

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 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 12 000g for 10 min and lyophilized. This process could effectively improve the efficiency of chemical reaction and avoid a lengthy separation process and purification of the intermediate chemical compounds, which would save time and increase the yield of products. In this work, by applying a small volume of H_2SO_4 as the catalyst and solvent instead of an organic solvent, the benefits of being an organic solvent-free, environmentally-friendly and extraction-time saving process were achieved.

In order to investigate the mechanochemical effects induced by ball milling and ultrasonication on the yield and degree of substitution (DS), organic solvent-free ball-milling was initially chosen as the test reaction. The reaction time of ball milling treatment was 0 to 2 h. As Fig. 2A demonstrates, the sample obtained without ball milling had the lowest yield of 16.3%. To our delight, a high efficiency was achieved when ball milling was treated for 0.5–1 h, which amounted to 56.1–61.1% yield. This may be due to the breakage of intermolecular and intramolecular hydrogen bonds in the main chains of cellulose under the intensive impact of ball milling, which increases the content of free hydroxyl group, and intermolecular hydrogen bonds are re-formed by part of the free hydroxyl groups.¹¹ Also, the efficient mixing of cellulose pulp and maleic anhydride and the continuous particle refinement result from ball milling, which enhances the reactivity of the reagents and promotes sequential reactions.¹² Extending the ball milling time from 1 to 2 h resulted in a decrease from 61.1 to 54.7%, which might be attributed to the excessive destruction of the cellulose crystalline structure during ball milling. In this study, the degree of substitution (DS) of MA-CNCs was estimated by using elemental analysis as described previously.¹³ The graph shows that DS values

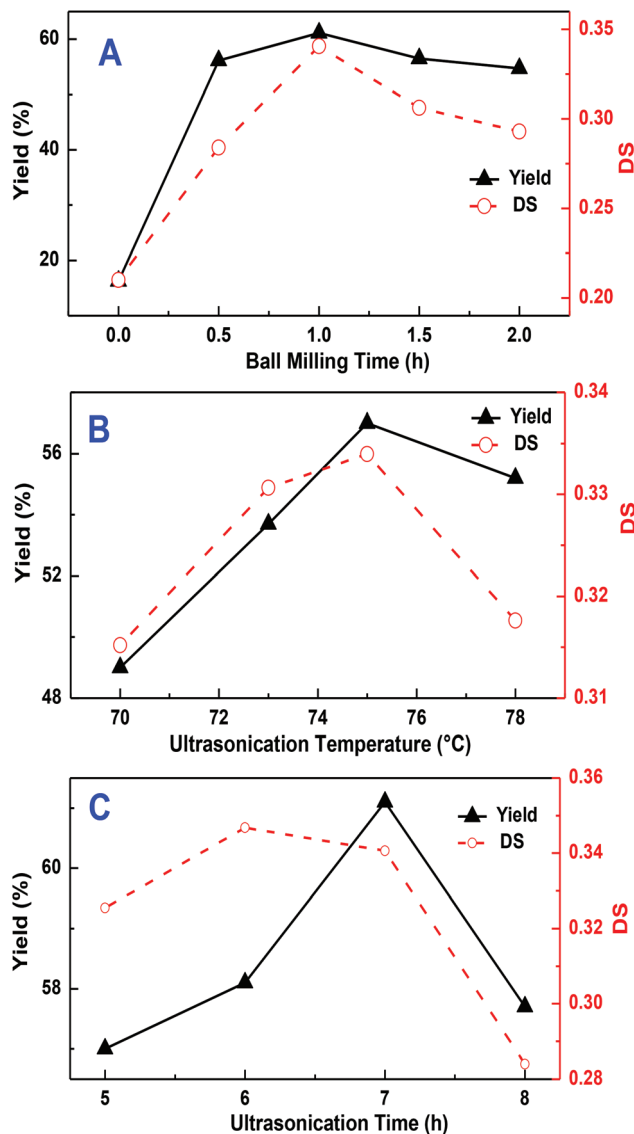


Fig. 2 Effect of ball milling time (A), ultrasonication temperature (B) and ultrasonication time (C) on the yield and degree of substitution (DS) of MA-CNCs.

increased as the ball milling time was extended from 0 to 1 h, and then dropped to 0.29 as the ball milling was prolonged to 2 h. The result can be explained by the initial maleation of the disordered accessible regions of the cellulose followed by esterification at interior regions of the cellulose crystals. As more hydroxyl groups are exposed, only part of them could be maleated under the experimental conditions.

Ultrasonication treatment plays an important role in the degradation of cellulose and esterification. Fig. 2B shows the effect of ultrasonication temperature on the yield and DS values. At a ball milling time of 1 h and an ultrasonication time of 5 h, the yields of the MA-CNCs prepared at 70 and 73 °C were 49 and 53.7%, respectively. The yield and DS values increased slightly with the ultrasonication temperature rising to 75 °C, and the yield and DS values of MA-CNCs amounted to a maximum of 57% and 0.33, respectively.

As can be seen from Fig. 2C, at a ball milling time of 1 h and an ultrasonication temperature of 75 °C, the yield and DS value obtained at an ultrasonication time of 7 h amounted to 61.1% and 0.34, respectively, while the sample obtained at an ultrasonication time of 5 h had the lowest yield and DS value of 57% and 0.33, respectively. The effect of ultrasonication may be explained by the formation, growth, and collapse of cavities in aqueous solution.¹⁴ The energy provided by cavitation is approximately 10–100 kJ mol⁻¹, which is within the hydrogen bond energy scale.¹⁵ Thus the ultrasonic impact can effectively disintegrate the amorphous region of cellulose and is beneficial for the reagent to enter the interior of cellulose fibers. Extending the ultrasonication time from 7 to 8 h resulted in an obvious decrease from 61.1 to 57.7%, which was possibly due to the excessive degradation of cellulose.

FTIR analysis has been proved to be a very useful method to monitor structural changes of cellulose during the reactions. The FTIR spectra of samples are shown in Fig. 3. The absorbances at 3350, 2900, 1430, 1373, 1164, 1113, 1060 and 897 cm⁻¹ in all spectra (Fig. 3a–d) are associated with native cellulose. Compared with the FTIR spectrum of cellulose pulp (Fig. 3a), it can be observed that no new absorption peaks appeared in the FTIR spectrum of the ball-milled sample (Fig. 3b), indicating that the ball milling did not induce carboxylation.^{7,9} However, the O–H stretching vibration peak at 3350 cm⁻¹ became stronger as the treatment proceeded. This could be due to the breakage of intermolecular and intramolecular hydrogen bonds in the main chains of cellulose under the intensive impact of ball milling and ultrasonication, increasing the content of free hydroxyl groups.¹⁶ The absorption peaks located at 2900 cm⁻¹ are due to stretching of C–H groups of cellulose. It has been previously noted that there was a significant increase in absorption at 897 cm⁻¹, along with an obvious increase at 1430 cm⁻¹. While the band at 897 cm⁻¹ is assigned the β-glycosidic linkages between glucose units in cellulose,¹⁷ 1430 cm⁻¹ is indicative of a crystalline band from the CH₂ scissor vibration. At 1373 cm⁻¹, there was a C–H

in-plane deformation band, typical of cellulose. The characteristic band at around 1060 cm⁻¹, corresponding to the C–O stretching mode, was also observed.¹⁸

The presence of carboxylic acid groups in maleated cellulose (Fig. 3c) and MA-CNCs (Fig. 1d) is clearly evident from a strong C=O stretching of carbonyl in the ester bonds at 1721 cm⁻¹. Compared with MA-CNCs (Fig. 3d), the maleated sample (Fig. 3c) showed a low intensity of absorbance peaks at 1721 cm⁻¹, which indicates that the sample has a low degree of maleation. And the peak at 1721 cm⁻¹ was not observed in the spectrum of the ball-milling treated sample (Fig. 3b), indicating that the mechanical treatment does not affect the chemical characteristics in this reaction. On the other hand, compared with the mixture of CP and MA (Fig. 3e), MA-CNCs (Fig. 3d) showed an obvious absorbance peak at 1721 cm⁻¹, which indicates that the esterification reaction successfully occurred.

Powder samples are further characterized by using CP-MAS ¹³C-NMR spectroscopy. As can be seen in Fig. 4, the spectra of all the samples displayed typical signals from cellulose that are assigned as follows: C1 (104.9 ppm), C2/C3/C5 (72 and 75 ppm), C4 (88.7 ppm) and C6 (64.7 ppm) peaks belong to carbons of the glucopyranose rings in the crystalline regions, whereas the C4 (83.8 ppm) and C6 (63 ppm) peaks correspond to carbons of the glucopyranose rings within amorphous parts.^{19–21} The spectrum of the ball milled sample (Fig. 4b) showed no obvious change, compared with untreated CP (Fig. 4a). After maleation and ultrasonication (Fig. 4c and d), the characteristic signals of the grafted moieties emerged at 174 and 21 ppm, corresponding to the carbons of the carbonyl (–C=O) and methyl groups (–CH₃), respectively. In contrast with MA-CNCs (Fig. 4d), carbonyl group signals emerged at 170 to 180 ppm, while no obvious signals appeared at 21 ppm of the mixture of CP and MA (Fig. 4e), which means that the esterification reaction did not occur and the carbonyl group signals observed here result from the maleic anhydride. The signal at 174 ppm and the one observed at 1721 cm⁻¹ in the

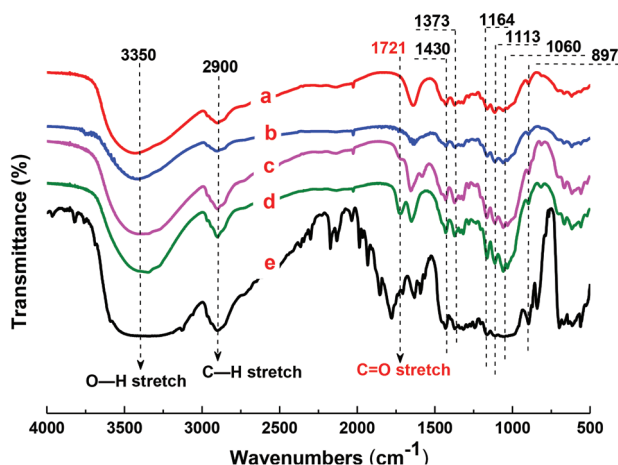


Fig. 3 FTIR spectra: (a) CP, (b) ball milling (1 h), (c) maleation, (d) MA-CNCs and (e) a mixture of CP and maleic anhydride.

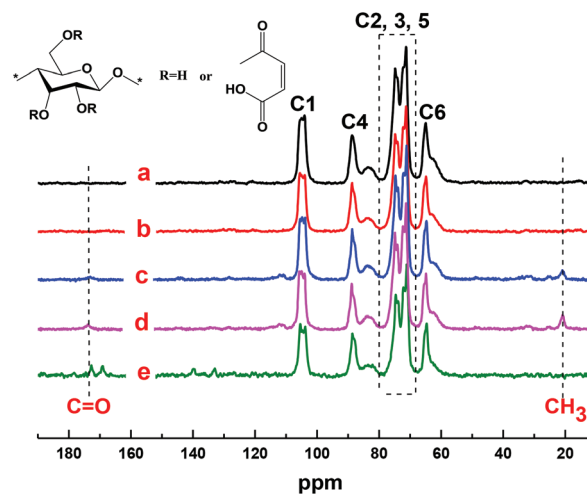


Fig. 4 Solid-state CP/MAS ¹³C NMR spectra: (a) CP, (b) ball milling (1 h), (c) maleation, (d) MA-CNCs and (e) a mixture of CP and maleic anhydride.

FTIR spectrum (Fig. 3) indicate that the reactions of maleic anhydride on cellulose actually occurred under mechanochemical treatment.

The crystal structure of cellulose was also investigated using NMR spectroscopy. The crystallinity can be obtained by evaluating the C4 signal of cellulose.²² As can be seen in Fig. 4, the signals at 86–92 ppm due to the crystalline C4 carbon showed little change, confirming that the crystalline region was not altered.

To gain further insights into the structure changes caused by mechanochemical treatment, X-ray diffraction analysis (XRD) was conducted. XRD patterns of all cellulose samples and the calculated crystallinity index are shown in Fig. 5. The cellulose pulp and mechanochemical treated cellulose pulps all displayed the typical X-ray diffraction pattern of cellulose I, with the main diffraction peaks at around $2\theta = 14.8$, 16.4 and 22.7° , normally assigned to the 101 , $10\bar{1}$ and 002 diffraction planes, respectively.^{23,24} In order to investigate the evolution of the crystal structure of cellulose during the ball milling

process, XRD spectra were measured before and after 0.5, 1, 1.5 and 2 h ball milling and the diffractograms are shown in Fig. 5A. During the ball milling process, the (002) diffraction peak intensity increased, confirming the progressive destruction of the hydrogen bond network in cellulose and cleavage of glycosidic linkages. Compared with CP, the crystallinity of the BM-1 h sample increased from 64.8 to 73.6%. However, extending the ball milling time from 1 h to 2 h resulted in a decrease of crystallinity from 73.6 to 68.5%, possibly due to the excessive destruction of crystalline cellulose. As shown in Fig. 5B, the XRD patterns of mechanochemically treated samples still had the identical peaks of cellulose I, indicating that ball milling, maleation and ultrasonication treatment did not alter the crystal type of cellulose in this study. It is clear that the peak intensity of the (002) plane increased after mechanochemical treatment. Moreover, the calculated crystallinity data show that a significant increase occurred in the crystallinity between CP and mechanochemically treated samples due to the degradation of the amorphous regions of cellulose during the reactions. The crystallinity values of CP, the ball-milled (1 h) sample, the maleated sample and MA-CNCs were 64.8, 73.6, 79.3 and 80.1%, respectively. The result indicates that the mechanochemical treatments effected an improvement in the crystallinity of cellulose samples. On the other hand, the cellulose samples after maleation still had high crystallinity, suggesting that the modification occurred essentially at the surface and probably at the amorphous regions of cellulose.^{25,26} These results are in good agreement with the FTIR results (Fig. 3) as well as the chemical change shown in Fig. 5.

The morphology of CP, ball milled samples and MA-CNCs was observed by using FESEM (Fig. 6). The FESEM micrograph

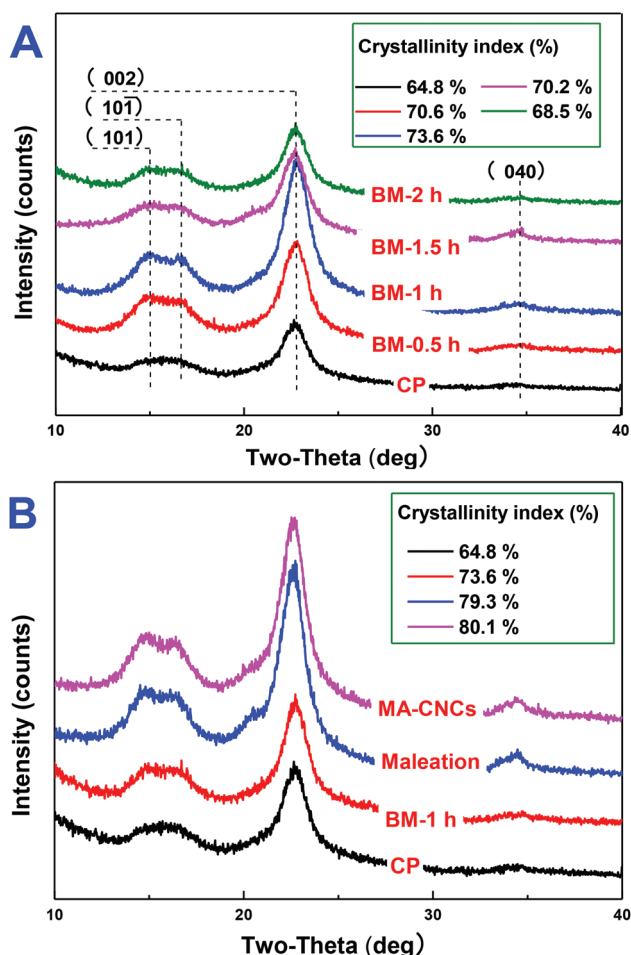


Fig. 5 XRD patterns of untreated and mechanochemical treated cellulose samples. (A) XRD spectra of cellulose pulp (CP) and cellulose samples ball milled for 0.5, 1, 1.5 and 2 h, labeled as BM-0.5 h, BM-1 h, BM-1.5 h and BM-2 h, respectively. (B) XRD spectra of CP and cellulose samples ball milled for 1 h (BM-1 h), maleated and MA-CNCs.

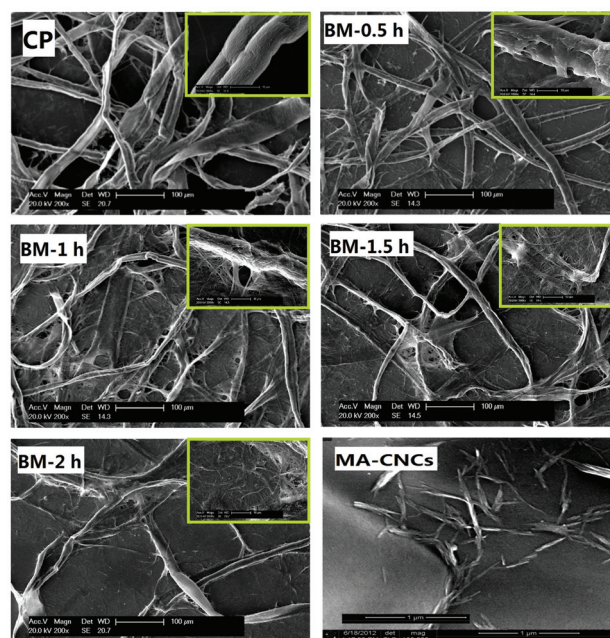


Fig. 6 Field emission scanning electron microscopy (FESEM) images of cellulose pulp, cellulose samples ball milled for 30 min, 60 min, 90 min and 120 min, and MA-CNCs.

of the CP disintegrated from filter paper presented thin and flat bands or ribbons with widths of 12–60 μm and had a rather smooth surface. After a short ball milling time of 0.5 h, there was, apparently, a reduction in the width of (6–24 μm) and the surface of fibers became rougher, indicating that ball milling has affected the structure. In the sample that was ball milled for 1 h (BM-1 h), an apparent open fibrillar network was visualized on the surface of cellulose fibers with a width of 4–24 μm . After 1.5 h, the small-size fibers with a width of about 1.5 μm formed a tight network structure, which may be due to the complete disintegration of fibers during the ball milling. And this effect suggests that the mechanochemical treatment promotes the micronization of fibers into its constituent particles. In addition, destruction of the fiber structure during ball milling might result more readily in isolation of nano-sized cellulose fibers. After maleation and ultrasonication treatment with maleic anhydride as an esterifying agent, sulfuric acid acts as both a catalyst for esterification and a promoter for the hydrolytic cleavage of the glycosidic bonds.¹⁰ It seems that the rod-like shape (shown in Fig. 6) was preserved and its size apparently decreased, with a width in the range of 20–100 nm and a length of 200–960 nm.

Conclusions

In summary, the method developed for manufacturing MA-CNCs *via* one-pot tandem reactions under organic solvent-free conditions could be applied in packing, biomedical and chemical industries. The high yield and crystallinity, organic solvent-free conditions as well as relatively mild conditions make this process a valuable and environmentally-friendly alternative to the currently available methods for the preparation of functionalized cellulose nanocrystals in industry.

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