

Transparent Nanopaper from Nanofibrillated Bamboo Pulp

Xuran Liu,^{a,1} Xilong Dong,^{b,1} Hongkun Wang,^b Min Wu,^{b,*} and Yong Huang^b

Bamboo pulp was used to produce modified cellulose nanofiber (M-CNF) with 3,4-dichlorophenyl isocyanate through a one-step mechano-chemical method by ball milling. The structural variations of bamboo cellulose with different degrees of substitution (DS) for hydroxyl groups were studied by FTIR, XRD, TEM, AFM, and elemental analysis. The DS was as high as 0.88 after just 2 h of ball milling, and the diameter of M-CNF was 2 to 3 nm after just 1 h of ball milling. The modified nanocellulose was hydrophobic, with a water contact angle as high as 87°. The nanopaper made from the nanocellulose by vacuum filtration was transparent, with an optical transmittance up to 88.8% at 550 nm. However, the transmittance of the modified nanopaper decreased to nearly 0 over the wavelength range of 200 to 300 nm. This nanopaper can be used as flexible optoelectronic material, packing material, or ultraviolet shielding material.

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Contact information: a: College of Materials Engineering, North China Institute of Aerospace Engineering, Hebei, Langfang, 065000, People's Republic of China; b: Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190; 1: Authors are equal contributors;

*Corresponding author: 2895149488@qq.com

INTRODUCTION

Many methods have been developed to produce cellulose nanofibers from different cellulosic materials. These include cryocrushing, acid or enzymatic hydrolysis, TEMPO-mediated oxidation, and grinding. One obstacle in nanocellulose preparation is aggregation arising from H-bonding and van der Waals interactions. Several methods have been proposed to make the cellulose hydrophobic, including physical and chemical modification (Habibi *et al.* 2010; Eyley and Thielemans 2014). For example, Zhao *et al.* (2016) reported nanocoating of polytetrafluoroethylene on cellulose particles to give a water contact angle of 110 to 121°. Shang *et al.* (2018) used thiol-containing castor oil to modify cellulose nanocrystals (CNC) to produce a contact angle of 95.6°. Zhang *et al.* (2016) grafted n-octadecyl isocyanate onto microcrystalline cellulose, giving a contact angle 67.8°.

An important product of nanocellulose is nanopaper with high transparency and water resistance (Kasuga *et al.* 2018). Zhu *et al.* (2013) prepared nanopapers with different fiber diameters, finding that the transparency strongly depends on the nanofiber diameter and their packing density. Introducing hydrophobicity to well-dispersed nanofiber is an important requirement for nanopaper preparation. In the present work, a hydrophobic nanocellulose was prepared by modification with 3,4-dichlorophenyl isocyanate. The nanopaper from the product is highly transparent and water-resistant.

As a rich biomass resource, cellulose has the characteristics of environmental compatibility, green and renewable nature, and it is commonly used in the preparation of paper and cellulose film. Paper used in daily life is formed by fibers intertwined with each other, while the hydroxyl groups of the fibers themselves and the capillary action between fibers make the paper hydrophilic, limiting the application of paper products in hydrophobic materials. Therefore, surface modification or fiber hydrophobization modification of hydrophilic paper is required for some applications.

Cellulose nanopaper is highly transparent, flexible, and thermally resistant, which makes it very suitable for use as a substrate material for optoelectronic materials. Cellulose not only undergoes irreversible agglomeration on drying, but also hydrogen bonding is significantly weakened in the wet state, which causes a significant reduction in its mechanical properties. However, the cellulose surface is rich in hydroxyl groups, leading to a high hydrophilicity of cellulose, which affects the further development of cellulose-based materials. In addition, water also softens the cellulose, which has a serious effect on the local stress transfer. In order to overcome the above disadvantages, many authors have proposed to improve the hydrophobicity of cellulose.

In this paper, the modification of bamboo pulp cellulose was brought about using 3,4-dichlorophenyl isocyanate, and the modified nanocellulose was prepared by a simple and efficient mechanochemical method in one step. The prepared modified cellulose had a very fine diameter and high hydrophobicity. In addition, the cellulose nanopaper made from the modified nanocellulose had a high transparency.

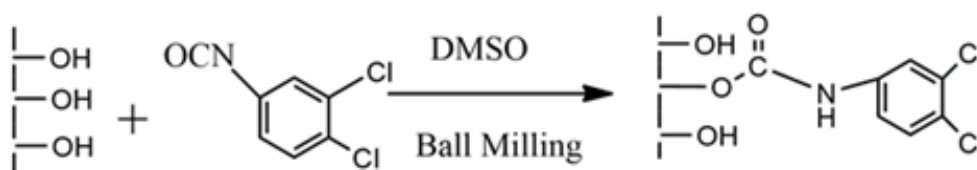


Fig. 1. Scheme of modification of CNF by 3, 4-dichlorophenyl isocyanate

EXPERIMENTAL

Bamboo cellulose was kindly provided by Sichuan Fengsheng Zhiye Group, Sichuan. The degree of polymerization of cellulose was determined as 819 by viscometry for copper-ethylenediamine. The 3,4-dichlorophenyl isocyanate (DCPI) and dimethyl sulfoxide (DMSO) were provided by Bailingwei Chemical Reagent company. The DMSO was dewatered by Molecular Sieve 4 A. The N,N-Dimethylformamide (DMF) and t-butyl alcohol were provided by Beijing Chemical Reagent without further treatment. All reagents were of analytical grade.

Preparation of CNF

First, 0.5 g of oven-dry bamboo pulp, 20 mL of DMSO, and varied amount of DCPI were added to a zirconia pot (45 mL volume) with seven zirconia balls (10 mm diameter). Ball milling was done using a Fritsch P7 at 200 rpm under programmed punctuated operation (2 min pause and 20 min working time). The milled sample was washed with DMSO by centrifugation for 5 min at 20000 rpm four times to remove unreacted DCPI. The sample was solvent-exchanged from DMSO to t-butyl alcohol by centrifugation and

freeze dried. The samples were denoted as M***-CNF***, where M means “modified”, M*** indicates the molar ratio of DCPI to OH groups of cellulose, and CNF*** indicates the milling time. The sample milled without DCPI was denoted as Um-CNF. Table 1 shows the sample nomenclature and reaction conditions.

Preparation of Nanopaper

The CNF sample was dispersed in DMF to 0.1 wt.% and sonicated for homogeneous dispersion (Tip-type sonicator JY99-IIDN, Ningbo Scientz Biotechnology, China). The suspension was vacuum filtered on a nylon membrane filter (0.22 μm). The wet cellulose film was carefully peeled off and dried in a 60 °C oven overnight. The thickness of the film was 0.030 ± 0.002 mm adjusted by the amount of suspension used.

Characterization

The cellulose sample was pelleted with KBr for FTIR spectroscopy (Varian 3100). Nitrogen content of DCPI-modified CNF was determined by a Vario ELIII elemental analyzer. The degree of substitution (DS) was calculated from nitrogen content according to Eq. 1:

$$DS = \frac{162 \times \%N}{1400 - 188 \times \%N} \quad (1)$$

The crystal structure of the samples was studied by X-ray diffraction (Bruker AXS GmbH), using Cu radiation ($\lambda=0.154184$ nm) from $2\theta=5^\circ$ to 70° with 0.02° increment and scan speed of 0.1 s/step. The crystallinity index was calculated by Eq. 2. I_1 is the intensity of amorphous scattering at $2\theta=18.6^\circ$ and I_2 is the intensity of 200 crystalline peak at $2\theta=22.7^\circ$.

$$I_c = \frac{I_2 - I_1}{I_2} \quad (2)$$

The hydrophilicity/hydrophobicity of the sample was examined by water contact angle on pelleted samples using a Data-Physics OCA-20 by static sessile drop mode. The morphology of samples was observed by transmission electron microscopy (JEOL E-2100) with acceleration voltage of 200 KV. A 2 μL drop of diluted suspension of CNF was deposited onto a carbon film-coated grid. AFM was done by a Bruker Multimode 8 in Scanasyt mode. A 2 μL drop of CNF suspension was deposited onto mica surface.

Light transmittance of CNF dispersion and 3, 4-dichlorophenyl isocyanate solution were analysed from 200 to 800 nm with a spectrometer (Varian Cary 5000) in UV-VIS-NIR regions. Light transmittance of CNF nanopapers were analysed from 200 to 800 nm in a spectrometer (Varian Cary 7000) in UV-VIS-NIR regions containing an integrating sphere.

RESULTS AND DISCUSSION

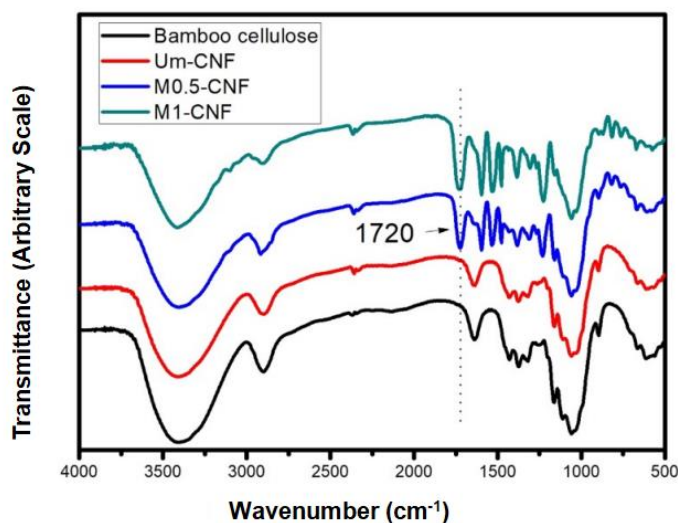
Table 1 gives the sample preparation conditions and analytic results. The DS of M1-CNF increased fast during the first 80 min, then it grew slowly and reached the maximum value of 0.65 after 100 min ball milling (Table 1). The DS also increased with the increase of the amount of 3,4-dichlorophenyl isocyanate, and it reached the value of 0.88, which is a very high substitution, when the molar amount of 3,4-dichlorophenyl isocyanate was 2 times of the hydroxyl groups of bamboo cellulose.

Table 1. Elemental Composition of CNFs and Calculated Degree of Substitution for Hydroxyl Groups of Modified CNFs

Sample	DCPI/OH Ratio	Milling Time (min)	Nitrogen Content (%)	Degree of Substitution
M0-CNF0	0.0	120	(0.052)*	(0.007)*
M0.5-CNF120	0.5	120	1.45	0.21
M1-CNF120	1.0	120	3.109	0.61
M1.5-CNF120	1.5	120	3.464	0.75
M2-CNF120	2.0	120	3.763	0.88
M1-CNF20	1.0	20	2.287	0.38
M1-CNF40	1.0	40	2.621	0.47
M1-CNF60	1.0	60	2.65	0.48
M1-CNF80	1.0	80	2.994	0.58
M1-CNF100	1.0	100	3.209	0.65
M1-CNF120	1.0	120	3.109	0.61

* () shows the level of instrumental error.

The defibrillation and modification procedure occur simultaneously (Fig. 1), as confirmed by the FTIR spectra (Fig. 2). Both the Um-CNF and M-CNF have the bands of cellulose. The OH stretching is in the range 4000 to 2995 cm^{-1} , and the C-H stretching is at 2900 cm^{-1} . The C-O-C, C-C-O, and C-C-H deformation and stretching vibration is at 900 cm^{-1} . The C-O-H out-of-plane bending vibration is at 668 cm^{-1} (Tursi *et al.* 2018). For M-CNF, there is a new peak at 1720 cm^{-1} that belongs to the C=O vibration due to the reaction of -NCO and -OH, which forms the carbamate ester (Karmarkar *et al.* 2007). The violent vibration at 1500 to 1750 cm^{-1} belongs to the urethane groups, suggesting that the cellulose was successfully modified with 3,4-dichlorophenyl isocyanate (Girouard *et al.* 2016).

**Fig. 2.** FTIR of bamboo cellulose, Um-CNF, and M-CNF

X-Ray Diffraction Analysis

The crystallinity index of Um-CNF and M-CNF was measured by X-ray scattering (Fig. 3). The crystallinity index was determined according to Eq. 1. The crystallinity index of Um-CNF was 56.9%, but the crystallinity index of M2-CNF declined to 35.6% (Table 2). Similar results were reported by Zheng *et al.* (2018). The crystallinity index of

microcrystalline cellulose (MCC) decreased from 56.34% to 25.15% with increasing grinding time; this was attributed to disrupting the crystalline structure and increasing of the content of amorphous structure. Silva *et al.* (2012) also reported that ball milling damaged the cellulose crystalline structure because of the reduction of crystallites thickness and the shortening of crystallites. The decrease of crystallinity index of M-CNF may also be explained by the surface grafting of cellulose, which may lead to peeling (Espino-Pérez *et al.* 2013).

Table 2. Crystallinity Index of Bamboo Cellulose, Um-CNF, and M-CNF

Sample	Bamboo Cellulose	Um-CNF	M0.5-CNF	M1-CNF	M1.5-CNF	M2-CNF
Crystallinity index (%)	66.8	56.9	47.8	39.3	38.1	35.6

Note: The milling time of all samples measured was 120 min.

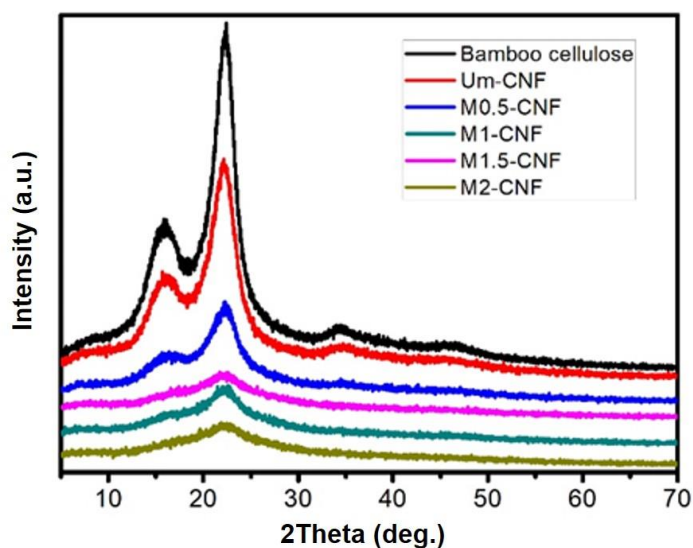


Fig. 3. XRD spectra of bamboo cellulose, Um-CNF, and M-CNF

Contact Angle of CNF

The contact angle of bamboo cellulose modified by different amounts of 3,4-dichlorophenyl isocyanate is shown in Fig. 4. The contact angle of Um-CNF was 41°. With the 3,4-dichlorophenyl isocyanate content increase, the contact angle increased. For M2-CNF, the contact angle reached the maximum of 87°. The significant increase of water contact angle of the M-CNF was ascribed to the grafted 3,4-dichlorophenyl isocyanate on the CNF surface. There are many hydroxyl on the surface of unmodified bamboo cellulose so that the water could be quickly absorbed. Isocyanate could easily react with the hydroxyl groups of bamboo cellulose, so the hydrophobicity of modified cellulose was enhanced (Ye *et al.* 2017).



Fig. 4. Water contact angle of Um-CNF and M-CNF

Morphology of CNF

The diameters of Um-CNFs were several nm to 20 nm (Fig. 5 d). The diameters of M0.5-CNF120 and M1-CNF120 were a few nm to 10 nm (Fig. 5 e and f). The M-CNFs become thinner as the modify time increased (Fig. 5 a, b, and c). The esterifying agents could promote nanofiber dispersion in the cellulose-organic solvent system and thus promote the defibrillation of the cellulose (Chao *et al.* 2017). A more accurate estimation of the fibril width was possible by AFM (Fig. 6). For the M1-CNF20 (Fig. 6a), the heights of some nanocellulose pieces were about 20 nm and a large proportion of nanocellulose objects (*i.e.* nanofibrils) were about 2 to 4 nm. As ball milling time increased, the height of cellulose became more uniform. For the M1-CNF40 (Fig. 6b), the height of some cellulose pieces were about 4 nm and some CNFs were as thin as 1 nm. After 60 min ball milling (Fig. 6c), the height of cellulose became very uniform, such that most objects were about 2 to 3 nm. The heights of M0.5-CNF120 (Fig. 6e) and M1-CNF120 (Fig. 6f) were also in the range about 2 to 3 nm. As the TEM graphs show, the length of fibrils became shorter as the ball milling time and modify reagent increased, which was in accordance with the results of the AFM.

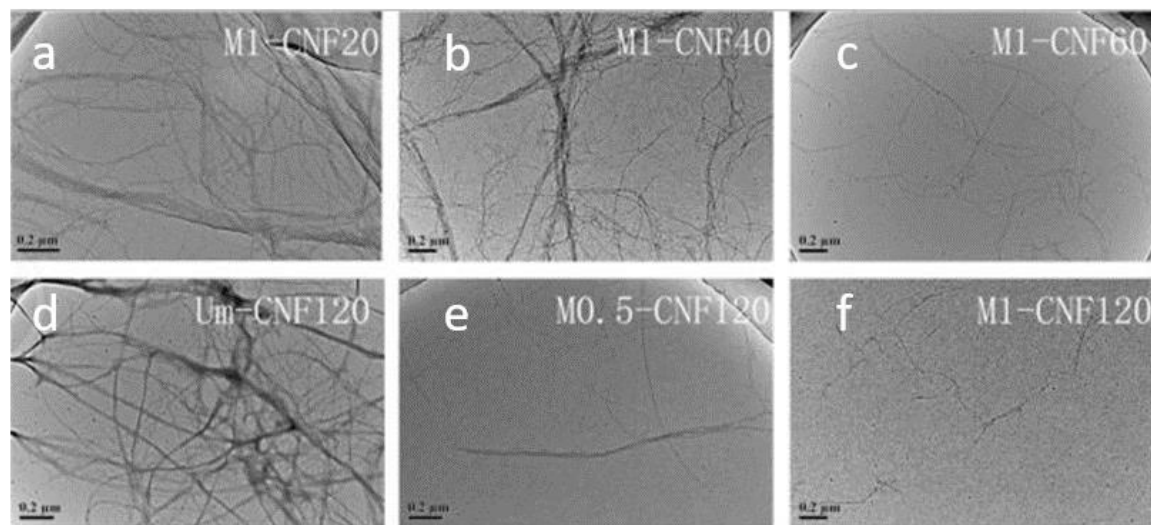


Fig. 5. TEM of Um-CNF and M-CNF

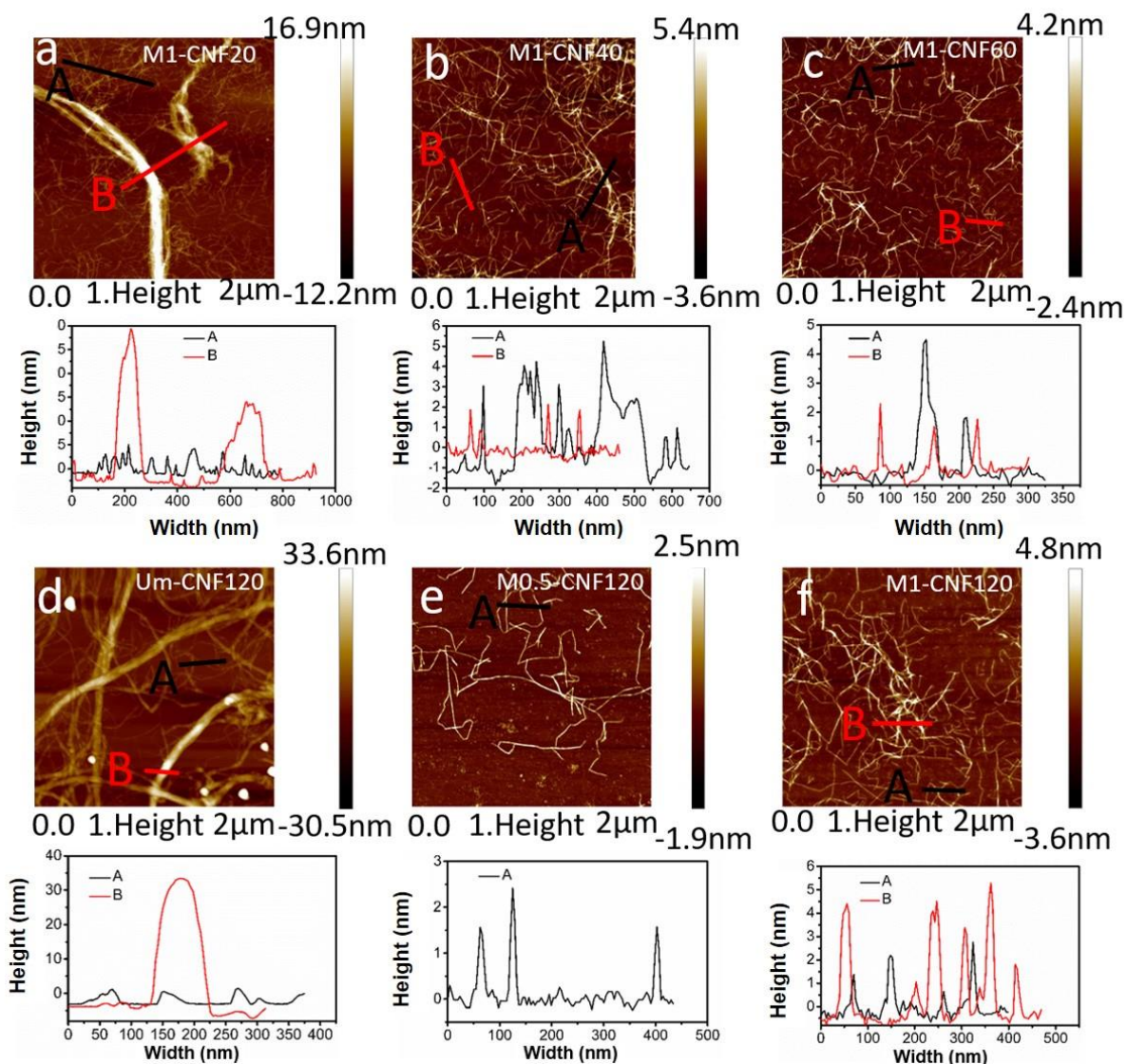


Fig. 6. AFM images of Um-CNF and M-CNF

Optical Property of CNF and Nanopapers

The nanopaper made from the M-CNF (except for the first one) was more transparent than that made from Um-CNF (the first one) (Fig. 7e). The nanopaper made from the Um-CNF showed a transmittance of 74.9% while the nanopaper made from the M2-CNF showed a transmittance up to 88.8% (Fig. 7d). The capacity of the films to scatter the visible light can be used to assess the fibrillation degree of cellulose, and the light scattering will reduce the transparency. Also, the increased fibrillation degree of cellulose makes the surface of the film smoother and the light reflection due to the rough surface will also be reduced. This leads to a transparency increase from Um-CNF to M2-CNF (Rajinipriya *et al.* 2018). The transparency of film of M2-CNF was increased by 19% relative to the film of Um-CNF. The wavelength of sunlight in the range of 200 to 400 nm is the ultraviolet area, which is further subdivided into the UV-C (200-280 nm) area, the UV-B (280-315 nm) area, and the UV-A (315-400 nm) area (Hou and Sun 2013). The transmittance of the nanopaper made by the modified nanocellulose falls to below 1.00% between 200 nm-300 nm, which is due to the strong absorption of the 3,4-dichlorophenyl

isocyanate between 200 and 300 nm. The transmittance of solution of 3,4-dichlorophenyl isocyanate falls to 0.057% when the concentration is more than 0.04 wt% at the wavelength of 300 nm (Fig. 7a). The transmittance of the dispersion of Um-CNF (Fig. 7b) with a content of 0.07 wt% is 25.0% at wavelength of 300 nm, while that of the M-CNF (Fig. 7c) falls to 0.704%.

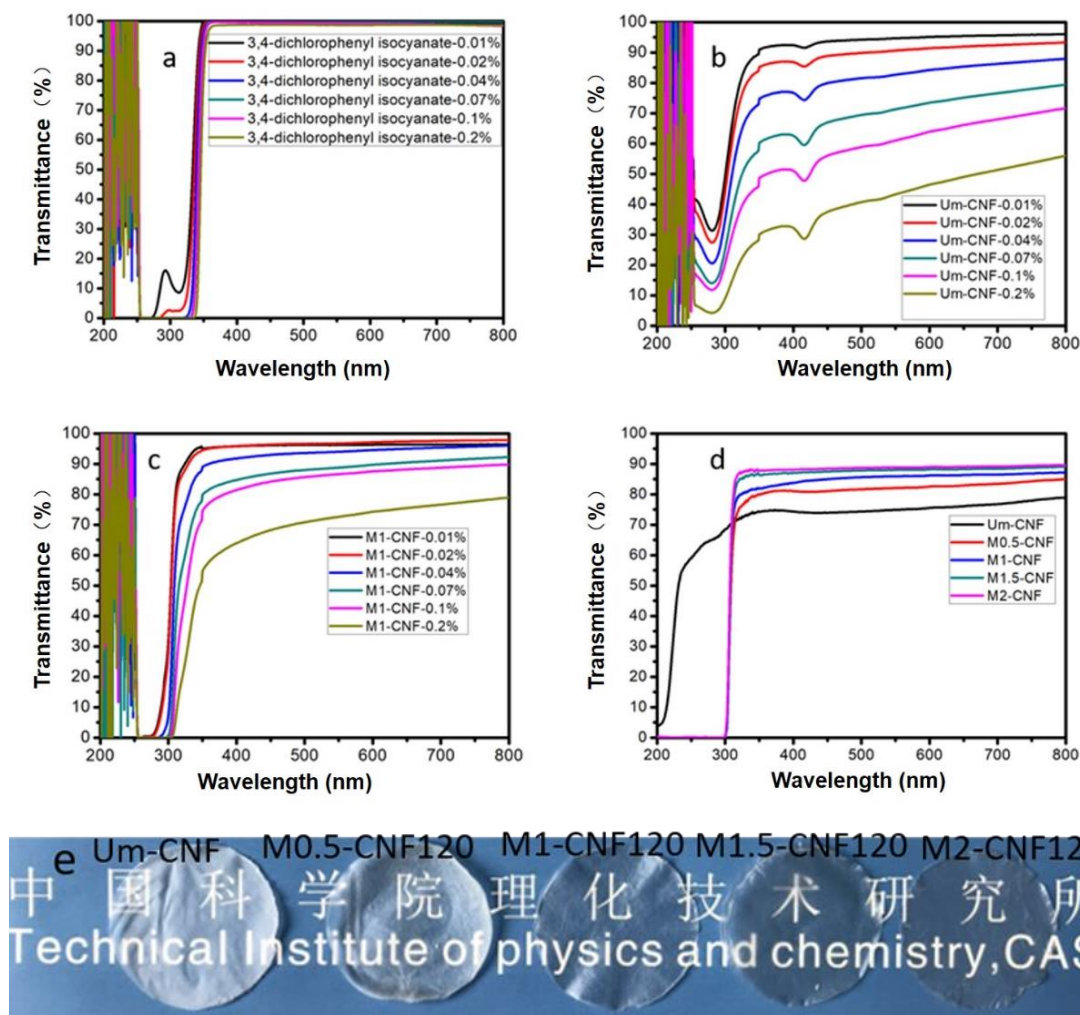


Fig. 7. (a). Light transmittance of 3,4-dichlorophenyl isocyanate. (b). Um-CNF (c). M-CNF (d). Um-CNF nanpapers and M-CNF nanpapers. (e). Photographs of Um-CNF and M-CNF nanpapers (% indicates the concentration of the sample, and the milling time of all samples measured was 120 min.)

Deng *et al.* observed that the UV-spectrum of alkali lignin solution in THF exhibits absorption peaks at 237 nm and 280 nm caused by K and B bands of the π - π^* transitions of the aromatic groups in the alkali lignin (Deng *et al.* 2011). The molecular orbital theory suggests that lone electrons on p orbitals of the substituted groups on benzene rings could conjugate with electrons on π orbital of the benzene ring, which is called the p- π conjugation effect. Because of this p- π conjugation effect, the π - π^* transition energy will be distinctly decreased (Zhou *et al.* 2016). There are two chlorine atoms linked to the benzene ring of the 3,4-dichlorophenyl isocyanate modified cellulose, and the ester groups are connected to the benzene ring by the nitrogen. The Density Functional Theory level

suggests that the lone pair of the nitrogen atoms could take part in extended conjugation; thus, the electron density increases distinctly, and the electron density could be further enhanced if there is an ester group (Bansal *et al.* 2018). All these factors may contribute to the low transmittance over the wavelength range of 200 to 300 nm of the nanopapers made by the modified cellulose. Therefore, nanopapers may be used for ultraviolet light protective materials.

CONCLUSIONS

1. Modified bamboo nanocellulose was prepared by a one-step method by ball-milling with the addition of 3,4-dichlorophenyl isocyanate, and the transparent nanopapers were made by both modified nanocellulose and unmodified nanocellulose.
2. The modified bamboo cellulose was much thinner and more hydrophobic than the unmodified one.
3. The nanopaper made by the modified nanocellulose was more transparent than the unmodified nanocellulose.
4. The nanopaper made by the modified cellulose exhibited high ultraviolet light blocking ability.

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