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ORIGINAL RESEARCH

Cellulose nanofiber extraction from unbleached kraft pulp for paper strengthening

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Abstract CNF-based materials have developed into the current global research and development hotspot, while the high cost of preparation and the difficulty of industrialization restrict their large-scale application. Therefore, how to efficiently and greenly prepare CNFs is still the key challenge to promote the development of CNF-based materials. In this work, we propose a few-chemical, low-energy process for the direct extraction of cellulose nanofibers (CNFs) from unbleached kraft pulp (UBKP), which simultaneously realize delignification and defibrillation by potassium permanganate oxidation. It is worth mentioning that the residual lignin and hemicellulose in the pulp also have been converted into active components during the oxidation process, which can promote defibrillation (nanofibrillation efficiently achieved in 0.3–1 h). Meanwhile, the activated residual lignin significantly improved the UBCNF properties, especially tensile strength (stress reached 151 MPa, elastic modulus was 4.1 GPa) of the UBCNF films. Finally, the UBCNFs were used as an eco-friendly paper strengthening agent and prominent enhancement was achieved with only 3% addition of UBCNFs (17.37%, 17.36%, and 16.20% increase in tensile strength, breaking strength, and tear strength, respectively, and the brightness improved from 72.34 to 74.89%).

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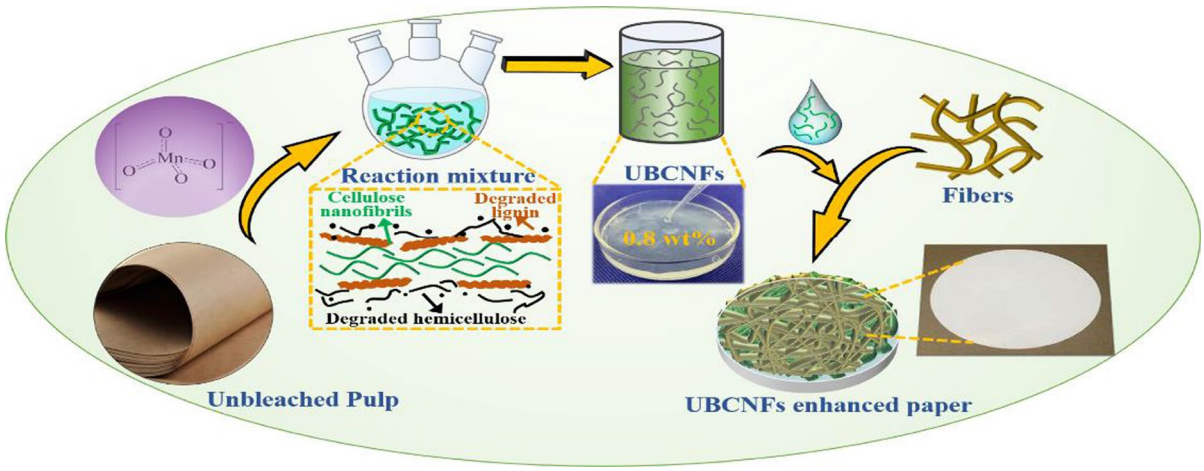
Graphical Abstract



Keywords Unbleached kraft pulp · Oxidative defibrillation · Cellulose nanofibers · Residual lignin · Paper strengthening

Introduction

Cellulose nanofibrils (CNFs) extracted from renewable wood resources with functional properties such as mechanical, optical, thermal and fluidic properties endows this nanomaterial with unique technological attractiveness in reinforcing materials, flexible materials, pharmaceuticals and coatings industries and broad application prospects (Govil et al. 2020; Heise et al. 2021; Li et al. 2021b).

The preparation cost as well as performance of CNFs are largely dependent on the cellulose source and extraction method (Liu et al. 2021a; Rol et al. 2019). Normally, lignin-free bleached pulp generally is used as the main raw material for CNF preparation. However, the delignification and bleaching process used to produce bleached pulp consumes more chemicals and energy and is largely harmful to the environment (Hong et al. 2020; Oliaei et al. 2019; Visanko et al. 2017). Accordingly, some researchers have used lignin-containing unbleached pulp to extract CNFs directly, and explored the influence of lignin and other non-fibrous components on the defibrillation process (Liao et al. 2021). These works show that CNFs can be isolated from unbleached softwood (Oliaei et al. 2019) or hardwood pulp (Nie et al. 2018; Serra-Parareda et al. 2021), as well as from non-wood pulp (Liu et al. 2019; Luo et al. 2021a; Yu et al. 2020). Meanwhile these CNF preparations have many advantages, including higher yields, lower production costs, and a reduced environmental burden, except for the color of nanocellulose is brown (Yu et al. 2021). It indicated that the small amount of lignin remaining in unbleached chemical pulp does not hinder CNF preparation. Furthermore, some studies even hold that lignin plays a unique role in promoting pulp defibrillation, resulting in finer lignin-containing cellulose nanofibrils (LCNFs) (Jiang et al. 2020; Liu et al. 2021a). This promotion phenomenon was deduced to be due to the degradation of residual lignin macromolecules, which result in the formation of debonding agent of polycarboxylic acids (Lin et al. 2021; Robles et al. 2020; Wang et al. 2019) for pulp swelling and defibrillation.

In our previous work, bleached softwood pulp (BKP) was used as a raw material to efficiently obtain CNFs through potassium permanganate ($KMnO_4$) oxidative defibrillation, which has the advantages of short reaction time, low mechanical energy consumption, and good product performance, which is enough to show that this method coincides with the concept of green chemistry (Liu et al. 2021b). Additionally, the washing filtrate (containing Mn^{2+}) can be recycled as an oxidation reaction solvent and reduce the

amount of subsequent addition of $KMnO_4$. Based on this, in this work we aim to achieve three goals: (1) seek more universality of potassium permanganate oxidative defibrillation, (2) attempt to explore the influence of existing lignin on the defibrillation process and the properties of as-prepared CNF, and (3) harvest a green, efficient paper strengthening agent. For these purposes, the potassium permanganate oxidation method was used to treat UBKP for simultaneously realizing delignification and defibrillation for harvesting UBCNFs with superior mechanical properties for use as a clean and efficient paper strengthening agent. Hypothetically, lignin-contained UBKP, when treated with potassium permanganate oxidation, will result in more efficient defibrillation and UBCNFs with improved properties. This hypothesis was tested by comparing the defibrillation results of UBKP and BKP, under the same conditions, and the performance of the resulting CNFs in response. Overall, we have developed a simplified, clean, and economical production strategy to harvest CNFs with excellent mechanical properties can be used as a green and efficient paper reinforcement additive.

Material and methods

Materials

Unbleached kraft pulp (UBKP, DP 1192), containing 65.51 wt% of holocellulose, 16.74 wt% of hemicelluloses, 10.05 wt% of acid-insoluble and 0.31 wt% of acid-soluble lignin, was provided from Tianjin Zhongchao Paper Co., Ltd. (Tianjin, China) (Reference standard: GB/T 2677.10-1995, GB/T 2677.8-1994, GB/T 10337-2008). Potassium permanganate ($KMnO_4$), and sulfuric acid (H_2SO_4, 98%), all the reagents and solvents were obtained from commercial sources in A.R. grades and used directly without further purification.

Isolation of UBCNFs

40 mL of 8 wt% H_2SO_4 was added into a three-necked flask, then potassium permanganate and UBKP were added in a mass ratio of 1.4:1 while stirring, and the reaction was carried out at 50 °C for 0.3–2 h. After the reaction was over, the mixture was washed to neutrality with distilled water, then diluted with water to obtain a dispersion of 1 wt%, which was subjected to homogenization (AH-100D, ATS, Canada) for 3 times at 300 bar pressure. The resulting UBCNF system was stored at 4 °C until use.

Preparation of UBCNF films

A specified amount of UBCNFs suspension was diluted with water, and sonicated for 10 min to ensure a uniform UBCNF dispersion, and then vacuum filtered to form a film. Vacuum-drying at 60 °C to obtain transparent UBCNF films.

Enhancement effect of the UBCNFs on paper

The BKP was beaten by a Valley beater (CH-1023, China) with a beating consistency of 2% (the specific conditions refer to GB/T 3702-1999) and to a final beating degree of 40° SR (the determination method refers to GB/T 3332-1982). The required pulp was placed in a fiber standard dissociator (AT-XW-1, GBJ-A, China), to which a certain amount of UBCNFs were added, and then a Kaiser rapid sheet former (RK3AKWT, Austria) was used to make paper sheets, where the grammage of the sheets was 80 g/m^2.

UBKP morphology and chemical composition

The morphology of the UBKP was observed by using a scanning electron microscope (SEM) (Tescan, Vega 3 SBH, Czech Republic). The total cellulose content of the UBKP was determined using $NaClO_2$ for the delignification of the residue (GB/T 2677.10-1995), where the hemicellulose content was measured in accordance with the polypentose content (GB/T 745-2003). The content of insoluble acid lignin was determined gravimetrically depending on the GB/T 2677.8-1994, and the soluble acid lignin was measured by a UV–Vis spectrophotometer (Varian, model Cary 100) with an absorbance of 240 nm according to the GB/T 10337-2008 standard method (He et al. 2018; Marinho et al. 2020). The fiber properties of the raw UBKP were determined by a Fiber Quality Analyzer (FQA) (Techpap, MorFi Compac, France), and according to the FQA test, fines were considered to be cell wall elements between 0.05 and 0.20 mm in length.

Yield of UBCNFs

The yield and dispersion concentration of CNFs were determined according to existing methods (Wang et al. 2021b). A certain amount of UBCNF suspension was dried to constant weight at 105 °C. The yield was calculated according to Eq. (1):

$$Yield\ (\%) = \frac{M_1 \times V_0}{M_0 \times V_1} \times 100\% \quad (1)$$

where M_0 is the total mass of the UBKP; M_1 is the mass of the UBCNF suspension taken to dry to constant weight at 105 °C; V_1 is the volume of the UBCNF suspension taken; V_0 is the total volume of the UBCNF suspension.

Surface morphological analysis of UBCNFs

The morphology of UBCNFs was characterized by scanning electron microscopy (SEM) (HITACHI, SU8100, Japan) in film form at low acceleration voltages (5–15 kV). Prior to SEM observation, samples were coated with platinum using a vacuum sputter coater. More precise observation and statistical analysis of the nanometer size of UBCNFs through transmission electron microscopy (TEM) (JEOL, JEM-1200EX, Japan) using Nano Measure 1.2.5 software (Fu Dan University, China). Test samples were prepared as follows: a drop of diluted UBCNF suspension was deposited on a carbon-coated electron microscope grid, followed by negative staining in a 1 wt% solution of phosphotungstic acid to enhance image contrast.

Characterization of physical and chemical properties of UBCNFs

The degree of polymerization (DP) of UBCNFs and UBKP were estimated from the intrinsic viscosity ([η], mL/g) of micro and nanofibers dissolved in copper (II) ethylenediamine at 25 °C, and [η] was measured using a cellulose viscometer (Ubbelohde Viscometers, SI Analytics, Germany) according to the GB/T1548-2016. The DP was calculated according to the Mark–Houwink–Sakurada equation, and all experiments were repeated (Serra-Parareda et al. 2021). The intrinsic viscosity [η] of the solution and the average DP satisfied Eq. (2).

$$Dp^{0.905} = 0.75\,[\eta] \quad (2)$$

The crystal structure of the samples in film form were characterized using an X-ray diffractometer (XRD) (Bruker, D8 Advance, Germany) at room temperature with a monochromatic Cu-Kα radiation source in step-scan mode over a 2θ range of 10° to 40°, where the step interval was 0.02° and the scan rate was 5° min^{-1}, and a blank run be recorded and subtracted from the sample XRD data before crystallinity analysis. The crystallinity index (CrI) was calculated as follows Eq. (3) (Segal et al. 1959).

$$CrI\ (\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \quad (3)$$

where I_{200} is the maximum diffraction intensity of crystalline from plane (200) (at 22.7° of 2θ for cellulose I); I_{am} is the minimum diffraction intensity between planes (200) and (110) (2θ ≈ 18.5°).

The tensile strength of the UBKP and UBCNF films (grammage of ~80 g/m^2) were assessed by a universal testing machine (Goodtechwill, AI-7000-NGD, Dongguan, China), with a 10 mm gauge length (dimensions 10 mm × 30 mm) at a stretching velocity of 1 mm min^{-1} of a load cell of 500 kg. The light transmittance of UBCNF films was measured by UV/Vis/NIR spectrophotometer (PerkinElmer, Lambda 35) at wavelengths from 400 to 800 nm.

The fourier transform infrared spectroscopy (FT-IR) spectra (Shimadzu, IRAffinty-1, Germany) data of the samples in film form were collected in KBr tableting mode at room temperature from 4000 to 400 cm^{-1} with 50 scans.

The carboxyl groups' content ([COOH]) was determined using the calcium-acetate method. Freeze-dried sample powder (0.5 g) was treated with 0.01 M HCl for 1 h to achieve replacement of their cations with hydrogen ions to obtain the acid form of cellulose, which was then washed with distilled water. Next, 50 mL of distilled water and 30 mL of 0.25 M calcium acetate solution were added to the sample, shaken for 2 h to facilitate the completion of the exchange, and finally 30 ml of the liquid was titrated with 0.01 M sodium hydroxide, with phenolphthalein as the indicator. The *[COOH]* was calculated on Eq. (4) (Knežević et al. 2020):

$$[\mathrm{COOH}] = \frac{\frac{80}{30} \times 0.01\mathrm{M} \times V(\mathrm{NaOH})}{m \times \left(1 - \frac{w}{100}\right)} \quad (4)$$

where 0.01 M is the concentration of NaOH; V (NaOH) is the volume of NaOH solution used for titration (mL); m is the weight of treated fibers (g); and w is moisture content (%).

The zeta potential can evaluate the stability of UBCNF suspension, and can also reflect the level of carboxyl group content of the sample (Xu et al. 2021). The zeta potentials are of the UBCNF suspensions were analyzed using a Zetasizer Nano ZS90 (Malvern, Instruments, UK) and then calculated with the Smoluchowski equation. Before detection, the samples were diluted to a suspension with deionized water (0.1% by mass), and then the scanning temperature and time were set at 25 °C and 30 s, respectively.

X-ray photoelectron spectroscopy (XPS, Kratos, AXIS Ultra^{DLD}, Japan) has shown to be one of the most effective surface analytical techniques for determining fiber surface chemical composition, especially surface lignin concentrations (Fardim et al. 2006; Kesari et al. 2020; Luo et al. 2021b).

Paper morphology characterization and physical property testing

According to the criteria described in Table 1, the physical and mechanical properties of cellulose paper reinforced with UBCNF nanofibers were determined. The surface fiber morphology of the paper was characterized by scanning electron microscope (SEM) (TESCAN VEGA 3 SBH, Czech) and (HITACHI, SU8100, Japan).

Description of test methods and data processing

All of the above characterizations were performed on three parallel samples, and the data obtained were averaged to report the results. The data obtained in this paper were handled through Origin 9.0.

Results and discussion

Chemical composition and fiber morphology analysis of UBKP and UBCNFs

Through standard testing methods, the main chemical composition and fiber properties of the UBKP were determined. As shown in Table 2, the cellulose, hemicellulose, and lignin content values were 65.51%, 10.36%, and 16.74%, respectively. By

Table 1 Standard for physical–mechanical characterization of the paper sheets

Physical–mechanical test	Standard	Test instruments
Standard atmosphere for sample handling and testing	GB/T10739-89	–
Grammage	GB/T451.1-89	(BSA224S, Sartorius, Germany)
Brightness	GB/T7974-87	(ColorTouch PC, Technidyne, USA)
Tensile strength	GB/T453-89	(CE062, L&W, Sweden)
Tearing strength	GB/T455.1-89	(009, L&W, Sweden)

At least 10 parallel samples were taken for each test

Table 2 Chemical compositions and fiber characteristics of pulp and UBCNFs

Sample	Cellulose (%)	Hemicellulose (%)	Lignin[a] (%)	Mean length (mm)	Mean width (μm)	Fines (%)
UBKP	70.21	16.74	10.36	1.9	31.4	16.9
0.3 h UBCNFs	82.86	10.88	5.43	–	–	–
1 h UBCNFs	90.13	6.11	2.85	–	–	–
2 h UBCNFs	93.35	4.46	1.62	–	–	–

[a]Including acid-insoluble and acid-soluble lignin

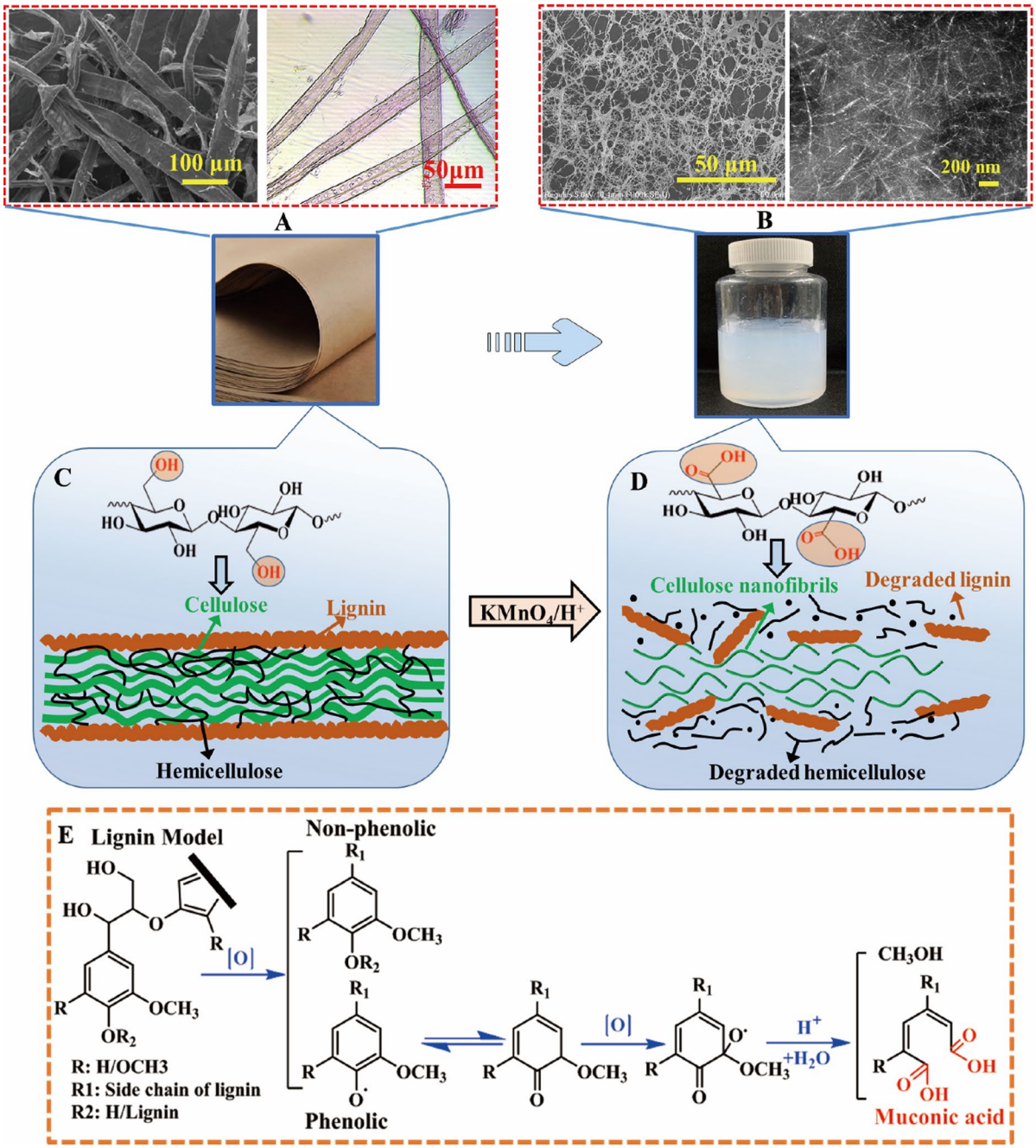


Fig. 1 The morphology of UBKP (**A**) and UBCNFs (**B**), scheme of oxidative delignification and defibrillation process (**C**, **D**), and possible mechanism about oxidative degradation of phenolic/non-phenolic lignin during the defibrillation process (**E**)

analyzing the fiber quality data, the UBKP was found to be nearly 2 mm in length and over 30 μm in diameter, and 16.9% fine content was also observed. The fiber quality of UBCNFs will be analyzed later by TEM data. With the oxidative treatment, the lignin and hemicellulose contents in the pulp were greatly reduced, and the cellulose content of the pulp was increased. The effect of residual small amounts of lignin and hemicellulose in UBCNFs on their properties has been discussed in the following sections.

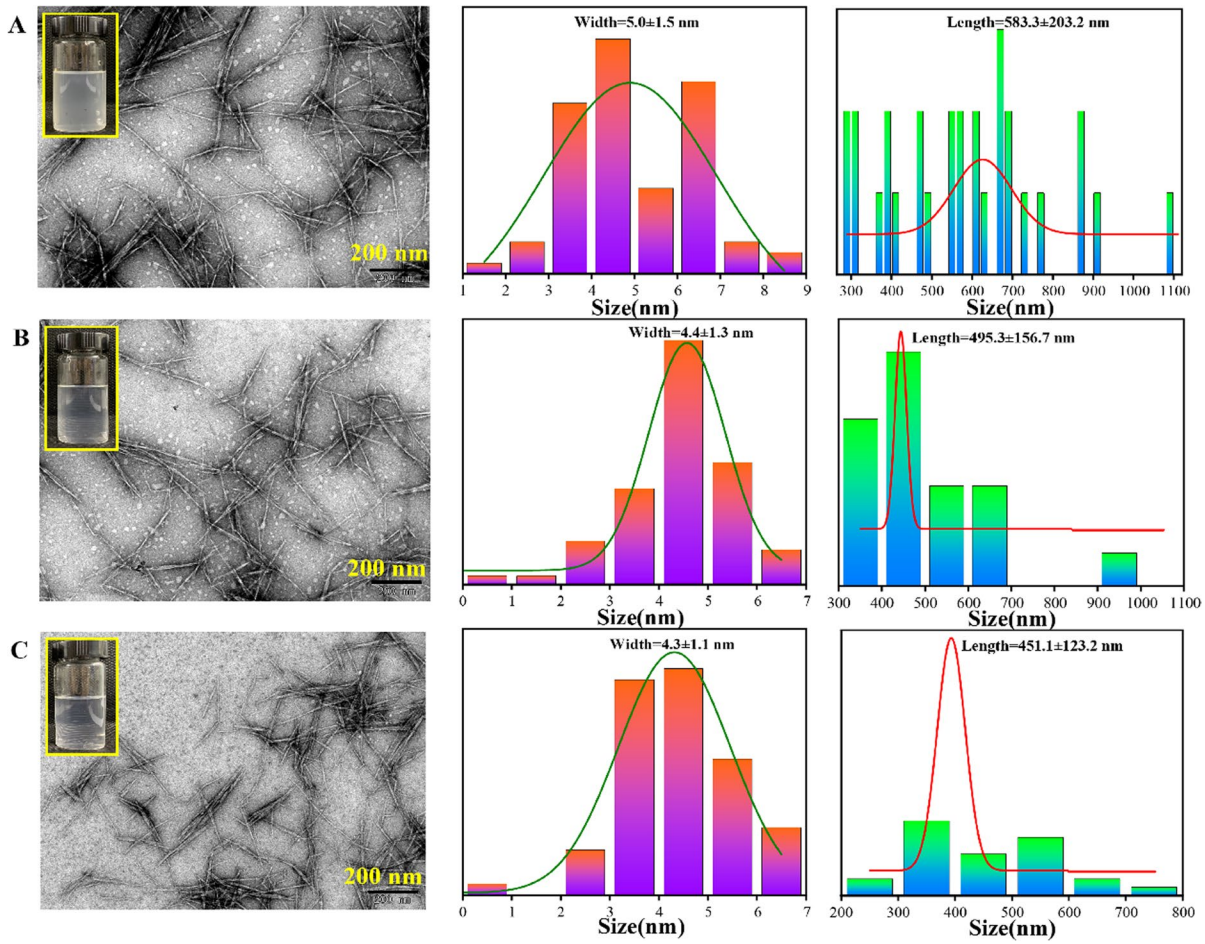


Fig. 2 TEM image and size statistics of UBCNFs (**A**–**C** was the products of reaction 0.3 h, 1 h and 2 h, respectively, from left to right were the TEM images, diameter and length of UBCNFs obtained at different reaction times)

Morphology of UBKP and UBCNFs and the possible reaction mechanism

To study the physicochemical properties of the pulp and UBCNFs, the macroscopic and microscopic morphologies were first observed (Fig. 1). As shown in the SEM morphology, the pulp fibers were 30–40 μm in diameter, which was also consistent with the FQA analysis results (Fig. 1A). After mechanical separation by oxidative defibrillation, the diameters of the UBCNFs were determined to be nanoscale (Fig. 1B).

The particle size distribution of the UBCNFs was obtained from the statistics of at least 100 fibers in TEM images (Fig. 2). The physical size of UBKP original fibers decreased dramatically from hundreds of microns to the cellular scale, with a length of 0.3–1.1 μm, diameters ranging from 2 to 8 nm. The average BCNF length and diameter sizes of our previous obtained BCNF was 0.7–2.1 μm and 4–12 nm, respectively (Liu et al. 2021b). It shows that the UBCNF sizes were smaller than that of the BCNFs, while the size distribution was narrower.

These size features attributed to the presence of residual lignin and hemicellulose during the oxidation process, which also decreased from 10.36 and 16.74% to 1.85% and 4.3%, respectively (Table 2). The reason for this phenomenon is that they might experience some degree of beta elimination and depolymerization, ultimately leading to their degradation. A schematic diagram depicting the mechanism of this process is shown in Fig. 1C, D. In addition to crystalline regions of cellulose molecules, residual hemicellulose

contributes to efficient fibrillation and dispersion stability of CNFs through electrical and/or steric mechanisms (Carvalho et al. 2019; Kumagai and Endo 2020). Therefore, the defibrillation effect was better. In view of the complex role of lignin, we will discuss it in the following mechanism explanation part.

It was evident from the images and statistical data in Fig. 2 that the diameters and lengths of the obtained CNFs significantly decreased as the reaction proceeded. The UBCNFs harvested from 1 h reaction (Fig. 2B) had the highest aspect ratio (435) and a more uniform nanometer size distribution.

Based on the previous literatures (Ma et al. 2015; Wang et al. 2019), the possible mechanism about possible oxidative degradation of phenolic/non-phenolic lignin by potassium permanganate oxidation during the defibrillation stages of UBKP was presented in Fig. 1E. Studies found that phenolic lignin molecule was first cleaved into aromatic monomers during potassium permanganate oxidation, and aromatic ring opening is a favorable pathway, leading to the formation of activated components such as dicarboxylic acids and their derivatives. According to researches, dicarboxylic acids could promote the hydrolysis and defibrillation (Lin et al. 2021; Robles et al. 2020) to obtain UBCNFs with finer nanometer sizes. Simultaneously, the increased carboxylic groups (showed in Table 3) in UBCNFs were mainly assigned to the ring-opening and further oxidation of lignin aromatic rings. Although potassium permanganate has been used as a green bleaching agent for a long time, there are few reports on its bleaching mechanism (Garves 1997; Chai et al. 2000). In this paper, this possible mechanism of potassium permanganate delignification bleaching was proposed. Different from H_2O_2 and O_3 bleaching processes, which mainly destroy the chromophore structure in lignin for bleaching purposes (Cequier et al. 2019; Hage and Lienke 2005), potassium permanganate bleaching is similar to ClO_2 bleaching (Wang et al. 2019), while more environmentally friendly and efficiently. Actually, it is still necessary to explore more convincing evidence to support the mechanism of potassium permanganate to simultaneous achieve defibrillation and delignification.

Table 3 Summary of physical property statistics (yields, average dimensions, DP, aspect ratios, tensile strength and light transmittance) and chemical properties (carboxyl contents, zeta potential and CrI) of UBKP and UBCNFs (the relative properties of the control group BCNFs were presented)

Samples	Yield (%)	Size		DP	Aspect ratio	[COOH] (mmol/g)	Zeta potential (mV)	CrI (%)	Stress (MPa)	Strain (%)	Mulder (GPa)	$T^a_{at\ 550\ nm}$ (%)
		Diameter (nm)	Length (μm)									
UBKP	–	3.14×10^4	1.94×10^3	1245	~38	0.643	–15.3	51.13	23.30	4.80	1.32	22.78
0.3 h UBCNFs	88.2	5.1–8.9	0.31–1.10	230	~216	0.892	–26.8	81.79	121.94	4.84	3.53	78.87
1 h UBCNFs	85.4	2.3–7.7	0.32–1.00	221	~435	1.254	–29.3	90.30	150.80	5.26	4.03	89.92
2 h UBCNFs	82.5	2.3–6.9	0.32–0.72	204	~313	1.380	–37.2	62.46	108.05	3.43	5.02	93.82
BCNFs	95.9	4.0–6.9	0.70–2.10	235	~525	1.288	–27.7	82.88	75.00	5.70	2.40	84.03(Liu et al. 2021b)

[a]The light transmittance of CNF films at 550 nm wavelength

Physical and chemical properties of UBCNFs

The physicochemical properties of the UBKP and UBCNFs are summarized in Table 3. UBCNFs were obtained in 94.5%, 92.9% and 86.5% yields after 0.3, 1 and 2 h of treatment, respectively. It was apparently that the yield showed a downward trend decreases with the extension of processing time.

The DP data also confirmed these results, which decreased from 1245 to 200. The aspect ratio, as calculated by the TEM image size statistics of the UBCNFs, was between 216 and 313, which was much higher than the original UBKP (~38). We found that the carboxyl group content of UBKP (0.634) was higher than BKP (0.552), and the corresponding UBCNFs had higher carboxyl group content than BCNFs (1 h UBCNFs 1.254 and 1 h BCNFs 1.227, 2 h UBCNFs 1.380 and 2 h BCNFs 1.288) (Liu et al. 2021b), which was also verified by the zeta potential. This was probably because the lignin structures that formed during the oxidation process contained both carboxyl and active hydroxyl groups. The active hydroxyl groups were easily oxidized to carboxyl groups, forming lignin containing dicarboxylic acid structures, resulting in the increase of carboxyl group content (Wang et al. 2019).

According to the XRD spectrum of the UBKP and UBCNFs (Fig. 3A), the characteristic signals of cellulose I appearing at 16° 2θ is attributed to the overlap of adjacent peaks of (110) and (1–10)

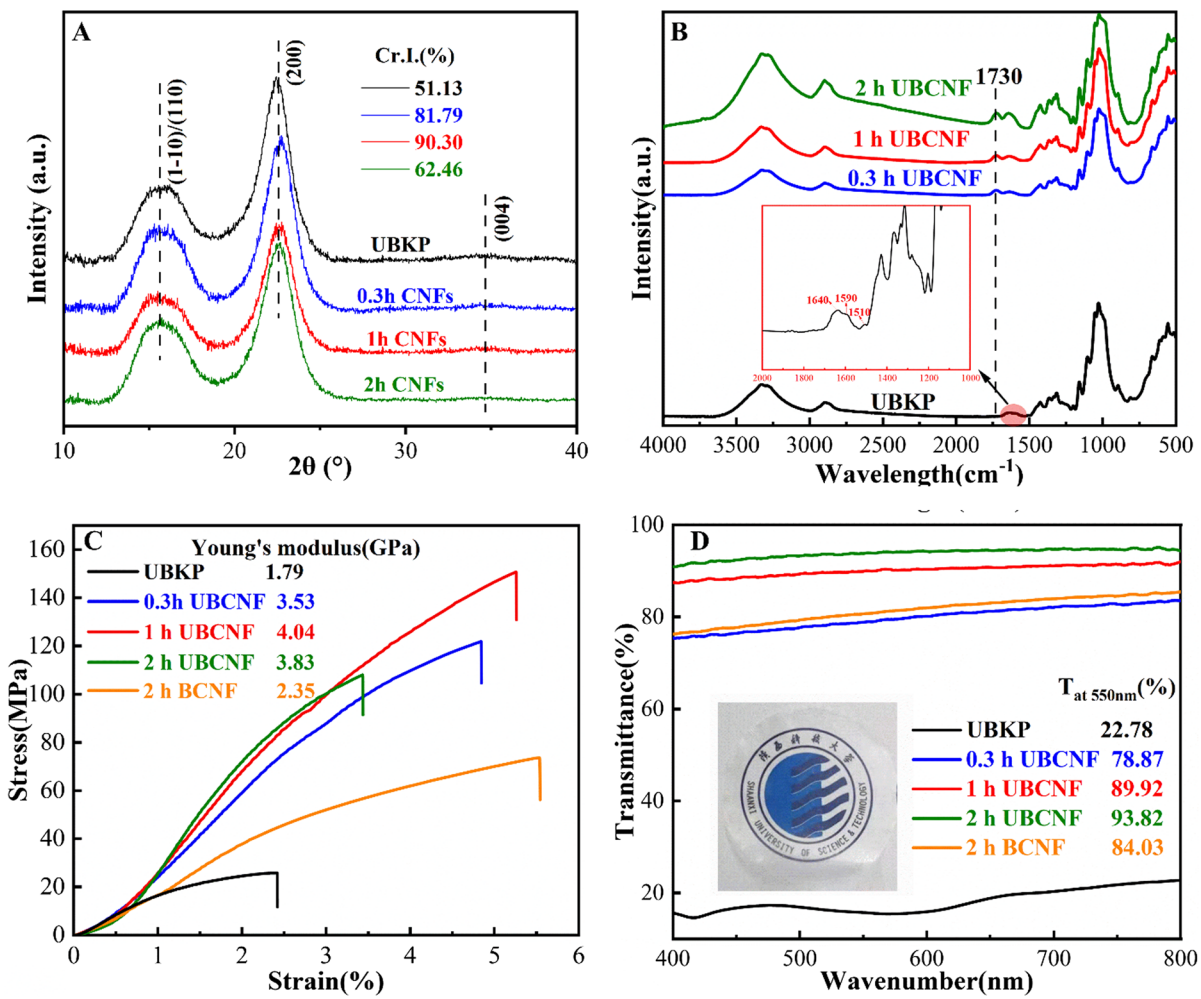


Fig. 3 The XRD (**A**) and FT-IR spectrum (**B**) of UBKP and UBCNFs, tensile strength (**C**), and optical properties (**D**) of UBKP and UBCNF films

(French 2020), and 2θ angles of 22° and 34° are associated with (200) and (004) diffraction surface, respectively (Cheng et al. 2020). These results indicated that the simultaneous oxidative delignification and defibrillation treatments had little effect on the aggregated structure of UBKP cellulose. Conversely, CrI of as-prepared UBCNFs was significantly higher than their parental counterparts (51.2%), and with the highest values of 90.3%. This increase was possibly related to the degradation of the amorphous portion of UBKP cellulose into solution (Wu et al. 2021). In addition, the oxidizing agent was also conducive to the removal hemicellulose and lignin, which are more abundant in UBKP, accordingly, the increase of CrI is more pronounced. Whereas, with the prolongation of the processing time, the crystalline region would also undergo a certain degree of oxidative degradation, resulting in a decrease in CrI, which will adversely affect the mechanical strength of CNFs (Liu et al. 2021b). Hence, the control of the reaction time is very necessary.

The FT-IR spectrum of the UBCNFs obtained with different times of treatment (0.3 h, 1 h, 2 h) are presented in Fig. 3B. We found that in addition to maintaining the basic chemical structure of cellulose, all spectra of UBCNFs have strong absorption at 3400 and 2900 cm^{-1}, which represent O–H stretching and C–H stretching vibrations, respectively, 1640 cm^{-1} is related to the abundant hydrophilic –OH in cellulose, 1167 and 897 cm^{-1} are assigned to C–O–C bending and symmetric stretching of the β-(1-4) glycosidic bond, and 1060 and 1113 cm^{-1} are corresponding to pyranose and glucose ring-skeletal vibrations, respectively (Liu et al. 2021b). While several notable changes were presented in the resulting UBCNFs, including a gradual increase in absorbance at 1728 cm^{-1} due to carbonyl stretching of the newly formed carboxyl groups (Liu et al. 2020), as well as disappearance of skeleton vibrations of the benzene ring in the lignin structure at 1595–1641 cm^{-1} (Watkins et al. 2015) appearing in UBKP. These changes demonstrated that the hydroxyl groups in the cellulose molecules of the UBKP were oxidized to carboxyl groups by potassium permanganate, meanwhile, the aromatic rings of the residual lignin components were also oxidized to open rings and additional carboxyl groups were formed. These results strongly confirmed the oxidative degradation of potassium permanganate-lignin on the fiber surface of UBKP, moreover, verified that the oxidation method could simultaneously achieve delignification and defibrillation.

It can be clearly observed from Fig. 3C that with the progress of the reaction, the tensile strength of the obtained UBCNF film increases significantly and can reach up to 151 MPa. Compared with the raw UBKP film (about 20 MPa), the tensile strength of the 1 h UBCNF film was increased by nearly six times, and it is two times higher than that of the BCNF film (75 MPa) prepared from BKP in our previous work (Liu et al. 2021b). The flexibility of the film (strain 5.3%) was also slightly higher. In addition to the contribution of aspect ratio and the role of strong hydrogen bonds caused by carboxyl groups, the activated residual lignin and hemicellulose obtained during oxidation as reinforcement endows nanofiber films with excellent mechanical strength (Govil et al. 2020; Jiang et al. 2020; Wang et al. 2021a).

Light transmittance is often considered a fundamental performance requirement for many optical or electronic devices (Jacucci et al. 2021). In this study, the light transmittance is directly related to the nanoscale size of the UBCNF film. The optical properties of the UBCNF film are shown in Fig. 3D, and the picture letters under the film are clearly identifiable by the naked eye, which is an intuitive reflection of the excellent transmittance of the film. By analyzing the optical transmittance data, which was compared to the control group UBKP film, the light

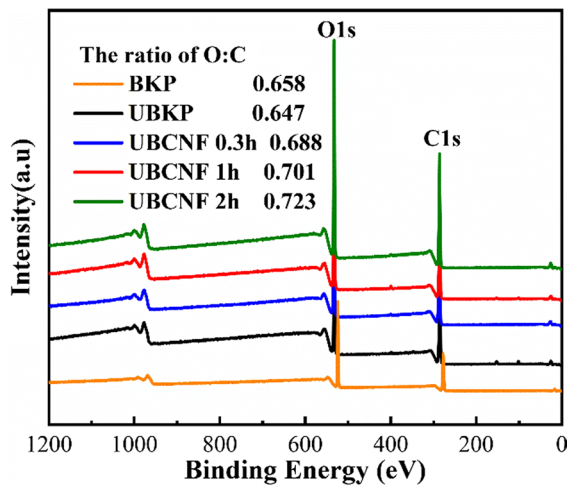


Fig. 4 XPS spectra of the UBKP and as-prepared UBCNFs

transmittance of the obtained UBCNF films increased significantly with oxidation treatment, from 22.78% to more than 78.87%, and up to 94%. These values were also higher than the BCNF film in the literature (80.69%), and this was also related to the superior nanoscale effect of the UBCNFs. Accordingly, UBCNF films can be expected to have great application potential in flexible transparent optoelectronic materials (Pakharenko et al. 2021; Zhang et al. 2022).

XPS is considered an effective surface element analysis method and has been extensively used in the study of fiber surface lignin concentrations for studying fiber materials. Correlation qualitative analysis was based on the theoretical O/C values of cellulose, lignin, and extractives, which were 0.83, 0.33, and 0.11, respectively (Johansson and Campbell 2004). The UBKP, with the CNFs obtained at different oxidation times and BKP as the control, was subjected to broad-spectrum scanning, and the spectrum was presented in Fig. 4. Obviously, the O/C ratio (0.647) of the UBKP was lower than the BKP (0.658), due to the high content of lignin (16.74%), as shown in Table 2. As the oxidation reaction proceeded, the O/C ratio of the obtained CNFs increased significantly, which was attributed to two effects, namely, the decrease in lignin content and the increase in the carboxyl group content obtained by oxidation (Khiari et al.

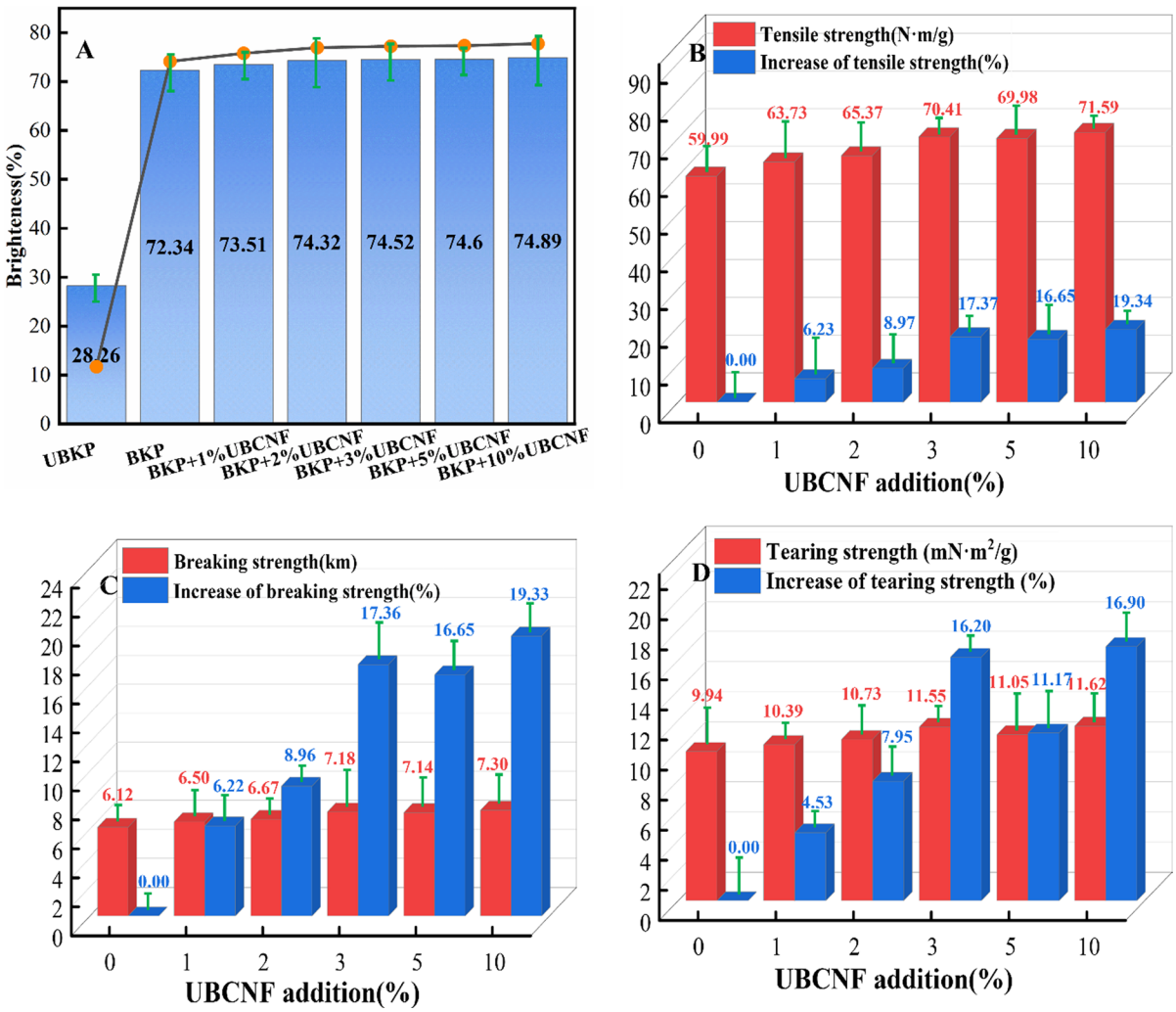


Fig. 5 Brightness (**A**), tensile strength and their increase (**B**) breaking strength and their increase (**C**) tearing strength and their increase (**D**) with the addition of different amounts of UBCNFs

Table 4 The effect of UBCNFs on paper strengthening

UBCNFs dosage (wt%)	Brightness (%)	Tensile strength (N·m/g)	Increase of tensile strength (%)	Breaking strength (m)	Increase of breaking strength (%)	Tearing strength ($mN·m^2/g$)	Increase of tearing strength (%)
0	72.34	59.99	–	6121.73	–	9.94	–
1	73.51	63.73	6.23	6502.71	6.22	10.39	4.53
2	74.32	65.37	8.97	6670.31	8.96	10.73	7.95
3	74.52	70.41	17.37	7184.47	17.36	11.55	16.20
5	74.60	69.98	16.65	7140.96	16.65	11.05	11.17
10	74.89	71.59	19.34	7304.78	19.33	11.62	16.90

2019). Therefore, the O/C (up to 0.723) ratio of the UBCNFs obtained in this system was higher than the BCNFs from the bleached pulp (up to 0.695).

The effect of UBCNFs on paper strengthening

The obtained UBCNFs were added to the paper stock alone as an auxiliary additive. Then, the paper surface morphology and physical properties were measured, and the strengthening effect on the paper was investigated, and the effects are shown in Fig. 5 and Table 4. Compared with the raw UBKP paper with darker color and low brightness (28.26%), the obtained UBCNFs can increase the brightness of the paper from 72.34 to 74.89% (Fig. 5A), which indicates that the bleaching effect of potassium permanganate oxidation is also ideal. The use of potassium permanganate for chlorine-free bleaching of pulp has also been demonstrated (Fahmy et al. 2008; Knežević et al. 2020). By analyzing Fig. 5B–D, we found that the tensile, tearing, and bursting strengths of the paper sheets with added UBCNFs significantly improved. Compared with blank BKP paper sheets, the strength improvement of BKP paper sheets with 1.0 wt% or 2.0 wt% UBCNF addition was not obvious. A plausible explanation is that the retention rate of CNFs is lower because they mostly flow away with water during paper forming (Zeng et al. 2021). While the enhancement effect was prominent when the addition amount of UBCNFs was 3 wt%. With increasing addition amount, the enhancement effect slightly improved, but considering the cost and water filtration performance, we concluded that 3 wt% UBCNF addition was the optimal dosage. Therefore, the CNFs could be preferentially used as an eco-friendly alternative to synthetic reinforcing agents widely used in the paper industry, to improve the mechanical strength and durability of paper.

It is generally considered that the strength of paper depends mainly on the strength of the fibers themselves, aspect ratio of fibers, fiber orientation distribution, contact area between fibers, and the strength and number of hydrogen bonds in the matrix (Li et al. 2021a). The introduction of CNF is generally achieved by increasing the bonding area of the sheet to enhance the strength of the paper (Zeng et al. 2021). By comparing the SEM images in Fig. 6A–F, we found that the UBCNFs were distributed between the fibers, being well retained in the wet web, filled in the holes in the paper structure, and strengthened the bonds between the inter fibers (Serra-Parareda et al. 2022). In addition, the surface of the paper was tighter and smoother. Accordingly, we propose that the enhanced mechanism of COOH-CNFs prepared in this study on paper strength may be that its surface is rich in free hydroxyl groups and active carboxyl groups. When added to the pulp, it is distributed between the fibers or on the surface of the fibers, and is closely combined with the pulp fibers, enhancing the adhesion between the fibers, being well retained in the wet web, filling the gaps in the paper, and improving the strength of the paper, schematic diagram as shown in Fig. 6G.

The comparison of publications related to application of CNFs manufactured by various methods as a bulk additive into papermaking

A large number of studies have used renewable and environmentally friendly nanocellulose to replace traditional petroleum-based as a "green" nano-additive to enhance and functionalize paper and paper-based

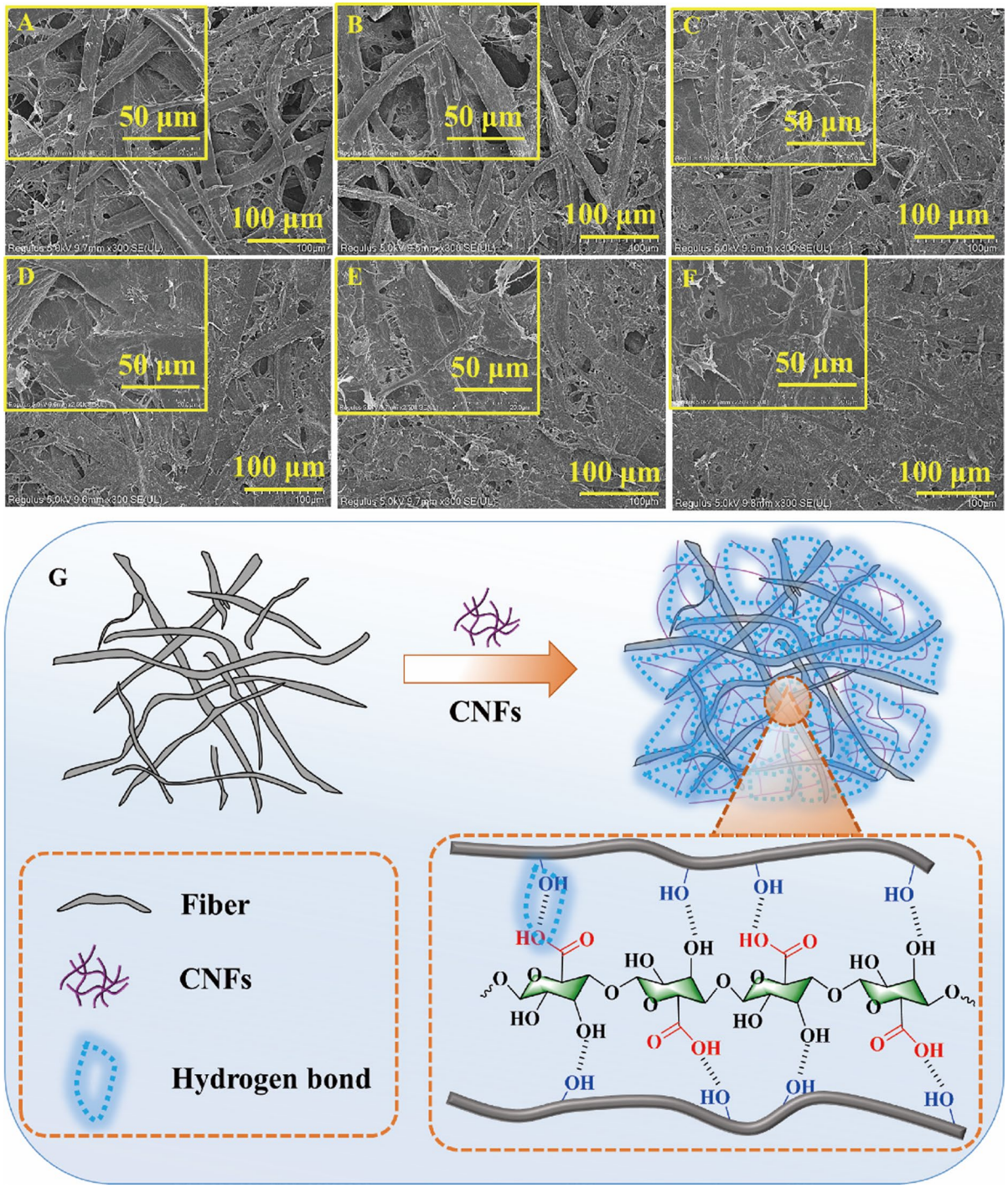


Fig. 6 Typical SEM micrographs obtained for cellulose paper sheets surface with the addition of UBCNFs (**A**–**F** correspond to CNF additions of 0%, 1%, 2%, 3%, 5% and 10%, respectively) and the schematic illustration of the combined effect of fiber entanglement and CNF reinforcement in the paper (**G**)

Table 5 The comparison of publications related to application of CNFs as a bulk additive into papermaking

Series	Type of CNFs*	Pulp for paper-sheets	CNF dosage (wt%)	Additives added	Tensile index increment (%)	References
1	Mechanical (grinding)	Unbeaten thermo mechanical pulp	9.6	None	13.6	Mörseburg and Chinga-Carrasco (2009)
2	Mechanical (grinding)	Beaten thermo mechanical pulp	4	None	21	Øyvind Eriksen and Gregersen (2008)
3	Mechanical refining	Beaten bleached eucalyptus kraft pulp	3	CS and alkenyl succinic anhydride (ASA)	38	Lourenço et al. (2020)
4	Enzymatic hydrolysis	Beaten bleached eucalyptus kraft pulp	3	CS and ASA	23	Lourenço et al. (2020)
5	TEMPO-mediated oxidation	Beaten bleached eucalyptus kraft pulp	3	None	15	Lourenço et al. (2020)
6	Carboxymethylation	Beaten bleached eucalyptus kraft pulp	3	None	10	Lourenço et al. (2020)
7	This work	Beaten bleached softwood kraft pulp	3	None	18	–

*All the different type of CNFs listed in the table were homogenized after pretreatment

products to achieve sustainable economic development (Li et al. 2021b). As mentioned above, there are many factors that affect the mechanical strength of paper, therefore, the enhancement effects of different CNFs on paper sheet were compared and evaluated in Table 5 from multiple perspectives.

Comparing the research of 1 and 2, the results show that, compared with the unbeaten pulp, after CNFs are introduced into the beaten system, more fine fibers are more conducive to better bonding between CNFs and fibers, which greatly improves the strength of the paper. Series 3–6 compared the enhancement effect of CNFs prepared by different methods and additional additives on paper. It was found that the presence of additives has a significant enhancement effect for the CNFs (series 2 and 3) obtained by the physical method, while the functionalized CNFs (series 4 and 5) obtained by the chemical method can improve the tensile strength in the absence of additives. This may be because the highly negative CNFs bind to cationic additives rather than to fibers, as previously reported (Lourenço et al. 2020). In this study, the UBCNFs extracted from UBKP was used as a paper strengthening agent. Our method is more advantageous by comparison with published studies. On the one hand, the preparation of CNFs was greener and more efficient than other methods. On the other hand, under the same conditions, the mechanical strength of paper sheets improved more significantly by the obtained UBCNFs with no other chemical additives. From the perspective of green chemistry, this is of strategic significance for the sustainable development of the paper industry our environment.

Conclusion

This work developed an efficient approach simultaneously realizing delignification and defibrillation of UBKP (achievable in 0.3–1 h) in a streamlined, cost-effective, and green way to directly harvest UBCNFs with improved properties, especially its films exhibit excellent tensile strength (stress reached 151 MPa, elastic modulus was 4.1 GPa) and superior transmittance (up to 94%). This is attributed to the oxidative degradation products or intermediates of residual lignin and hemicellulose in unbleached pulp, which would have positive lay a positive effects on defibrillation. Finally, the UBCNFs were used as an eco-friendly paper strengthening agent and prominent enhancement was achieved with 3% addition of UBCNFs (17.37% preparation of CNFs to their enhanced application, 17.36%, and 16.20% increase in tensile strength, breaking strength, and tear strength, respectively, and the brightness improved from 72.34 to 74.89%).

Comparing with published representative studies, our method is more advantageous from the preparation of CNFs to its enhanced application to paper. From the perspective of green chemistry, this has strategic significance for the sustainable development of nanocellulose preparation and papermaking industry.

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Availability of data and materials Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

Declarations

Competing interests The authors declare no competing interests.

Consent for publication All authors approved the final manuscript and the submission to this journal.

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