ORIGINAL RESEARCH

Preparation of cationic lignocellulose nanofbers from reed straw via mechanochemical method and its application

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Abstract Crop wastes are renewable and abundant lignocellulosic resource, while their efective utilization is limited due to the recalcitrance of plant cell wall. In this study, by using a facile mechanochemical method, reed straw fber was simultaneously cationized and defbrillated to obtain cationic lignocellulose nanofbers (LCNFs) without organic solvent. The obtained cationic LCNFs were 2–4 nm wide and several micrometers long with excellent re-dispersibility in water arising from the high zeta potential of +40 mV. As a paper-reinforcement agent, cationic LCNFs could give coated paper good oil resistance with the maximum Kit rating of 12/12. Meanwhile, the mechanical properties of the coated paper were also remarkably enhanced with the tensile strength and Young's modulus increased by 144% and 124%, respectively. They also gave the paper antibacterial properties because of the presence of quaternary ammonium groups. Overall, this study provides an efficient utilization option for crop wastes as well as a value-added lignocellulosic product.

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Graphical abstract

Keywords Reed straw · Lignocellulose nanofiber · Cationization · Ball-milling · Oil resistance

Introduction

Crop wastes, including various straw, rice husk, corn cob, bagasse, etc., are rich biomass resources, which mainly consist of cellulose, lignin, and hemicellulose. They are potential substitutes for fossil energy because of their renewability, abundance, less pollution and low price (Yan et al. [2020;](#page-13-0) Zhang et al. [2019a](#page-13-1), [b](#page-13-2)). In China, a large amount of crop straw is produced annually, but only a small amount is used efectively because of their recalcitrance. Common reed (*Phragmites australis*), as one kind of crop wastes, is widespread with annual production reaching millions of tons in Chinese wetlands (Ye et al. [2016\)](#page-13-3). In addition to applications for pulp, animal feed, and weaving, reed straw is always burned to generate low-value heat or discarded in nature, which not only causes a waste of resources, but also further aggravates environmental pollution (Zhang et al. [2016\)](#page-13-4). In order to alleviate the energy crisis and reduce environmental pollution, the exploitation and utilization of biomass resources have attracted people's attention. The three main components (cellulose, lignin, and hemicellulose) of biomass are used to prepare target chemicals and fuels by the process of oxidation, hydrogenation, dehydration, pyrolysis, catalytic polymerization, dissolution and biorefning (Cheng et al. [2021;](#page-11-0) Jiang et al. [2021;](#page-11-1) Padilla et al. [2021\)](#page-12-0). Nevertheless, these steps are so complicated and the yields of the product are not always satisfactory (Fahmy et al. [2020;](#page-11-2) McClelland et al. [2017;](#page-12-1) Pourkarimi et al. [2019](#page-12-2); Yang et al. [2019\)](#page-13-5).

In recent years, to achieve innovative valorization of crop wastes, many eforts have been focused on preparing cellulose nanomaterials (CNM) (Priyadarshana et al. [2022](#page-12-3); Rajinipriya et al. [2018](#page-12-4); Ramadhani et al. [2022](#page-12-5); Ventura-Cruz et al. [2021\)](#page-13-6). For instance, the crop wastes of orange bagasse, corn husks, sugarcane straw produced in Brazil, were used to prepare cellulose nanofbers by alkali treatment, bleaching with sodium chlorite and extraction with oxalic acid, followed by sonication. This approach could add new value to crop wastes and might bring great economical valorization to crops production (Marino et al. [2021\)](#page-12-6). Cellulose nanowhiskers were also successfully obtained from agricultural wastes and isolated with a 33% average yield by mild acid treatment (Moreno et al. [2018\)](#page-12-7).

In addition, several studies prepared functional CNM from crop wastes, especially the cationic CNM, such as cationic nanocrystalline cellulose and cellulose nanoparticles (Arnata et al. [2020](#page-11-3); Gu et al. [2020\)](#page-11-4). Cationic CNM have received extensive attention recently and were used as antibacterial agent, biological focculant, adsorbent and emulsion stabilizer for wastewater treatment, papermaking, composite and other felds (Lai et al. [2021](#page-12-8); Zhang et al. [2021](#page-13-7); Morantes et al. [2019](#page-12-9); Sehaqui et al. [2016;](#page-12-10) Silva et al. [2020\)](#page-12-11). The techniques of preparing cationic CNM mainly rely on a two-step method. For one, the raw material was reacted with cationic agent following by mechanically treating to obtain cationic CNFs (Rol et al. [2019;](#page-12-12) Ru et al. [2019](#page-12-13)). For another, the CNM were fabricated frstly, which were then reacted with cationic agent (Wei et al. [2021](#page-13-8)). Aulin et al. ([2010\)](#page-11-5) were the frst to obtained cationic CNFs by reacting with 2,3-epoxypropyl trimethylammonium chloride (EPTAC) in water, isopropanol and sodium hydroxide, following with microfuidization. After that, many diferent preparation processes of cationic CNM were reported and the cationic agents used were 2,3-epoxypropyl trimethylammonium chloride (EPTAC), 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), 3-chloro-2-hydroxy-propyl dodecyl dimethyl ammonium, *N,N*-dimethyl-1-octadecylamine, Girard's reagent T ((2-hydrazinyl-2-oxoethyl) trimethylazanium chloride, GT), cetyltrimethyl ammonium bromide (CTAB), etc. (Arnata et al. [2020;](#page-11-3) Keyvani et al. [2021;](#page-11-6) Lu et al. [2020;](#page-12-14) Rol et al. [2019\)](#page-12-12). Among these, EPTAC has the highest reaction efficiency and is commonly used in industry (Prado et al. [2014;](#page-12-15) Zaman et al. [2012](#page-13-9)).

However, the above method of preparing CNM or cationic CNM always contained delignifcation and bleaching processes and only cellulose was utilized, which caused a waste of other components. Actually, the lignin component can endow CNM with advanced properties, such as hydrophobicity, UV absorption ability and thermal stability (Bai et al. [2021](#page-11-7); Pylypchuk et al. 2021 ; Shao et al. 2021). Therefore, the lignin-containing cellulose nanomaterials (LCNM) obtained from crop wastes were studied and various techniques have been applied to prepare LCNM based on mechanical methods, chemical treatments and their combination (Liu et al. [2021;](#page-12-18) Zhou et al. [2023](#page-13-10)). Among these, commonly used mechanical methods were high pressure homogenization (Tarres et al. [2020;](#page-13-11) Zhang et al. [2019a](#page-13-1), [b](#page-13-2)), ball-milling (Ewulonu et al. [2019\)](#page-11-8) and ultrasonication. For improving the efficiency of mechanical processing, chemical methods were used for pretreatment, such as traditional pulping process, alkali treatment, acid hydrolysis, TEMPO oxidation and enzymatic hydrolysis (Ehman et al. [2016](#page-11-9)). Other treatment was also designed for preparing LCNM such as pretreating thermomechanical pulp and bagasse in deep eutectic solvent (Jiang et al. [2020;](#page-11-10) Zou et al. [2022](#page-13-12)). However, few studies about functional LCNM prepared from crop wastes were reported as far as we know except one report about cationic LCNFs prepared by sugarcane bagasse reacting with glycidyltrimethylammonium chloride and following by high pressure homogenization. There are hardly any researches on one-step preparation of functional LCNM from crop wastes.

Here, we developed a one-pot method for the preparation of cationic LCNFs from reed straw, which was achieved simply by ball milling reed four with EPTAC in mild alkaline condition. During ball milling process, the straw fber was defbrillated and cationized simultaneously. Long nanofbers were obtained only by ball milling for 2 h. The composition, morphology, chemical and crystalline structures of the obtained cationic LCNFs were systematically characterized, and the zeta potential of the cationic LCNF suspension was also tested. Furthermore, the barrier and mechanical properties of paper coated by cationic LCNFs were analyzed.

Experimental

Materials

Reed (*Phragmites australis*) straw was collected at Baiyang Lake in Hebei Province, China. The root of the straw was removed and the stem was dried at 60 °C and cut into approx. 50 mm-long pieces after being rinsed with water. The straw was pulverized by a waring blender and 80-mesh-pass fraction was collected as four (Fig. S1). 2,3-epoxypropyl trimethyl ammonium chloride (EPTAC, 95%) was purchased from Innochem (Yinuokai Technology Co., Beijing, China). Deionized water was used in all experiments while Milli-Q water was used for dialysis.

Preparation of cationic LCNFs

Dried reed four (0.5 g), EPTAC and 10 mL of NaOH solution (3.7 wt%) were added to a 45 mL zirconia pot containing seven zirconia balls $(d = 10 \text{ mm})$ and milled by a planetary ball mill (Pulverisette 7, Fritsch, Germany). Control experiment was also performed

without EPTAC. Ball-milling was carried out with punctuated operation (working time 20 min and interval of 2 min) with a rotation speed of 300 rpm at room temperature. The milling time was varied from 1 to 12 h. The milled mixture was neutralized to $pH = 7$ with dilute HCl (3 wt%) and washed with water several times until no free chloride detected in the supernatant. Finally, the product was purifed by dialyzing against Milli-Q water for 3 days.

a Amount of hydroxyl group was calculated by 3 m/162 (assuming all solid was cellulose).

Redispersion of dried cationic LCNFs

About 0.3 g freeze-dried cationic LCNFs (1-M4) were dispersed in 100 mL of water by sonication for 2, 4, 10 min in an ice bath by intermittent operation (2 s run-2 s pause at the power of 180 W (Scientz-IID, Ningbo Scientz Biotechnology)) and the cationic LCNF dispersion was obtained. The dispersion was centrifuged at 2000 rpm for 5 min. The sediment and the turbid supernatant were separated by pipetting and dried following by weighing. The yield of LCNFs was calculated according to Eq. [\(1](#page-3-0)) as follows:

$$
Yield(\%) = \frac{m_s}{M} \times 100\tag{1}
$$

where m_s is the solid weight of supernatant, and *M* is the total dry weight of redispersed cationic LCNFs.

Compositional analysis

The compositional analysis of raw reed flour and obtained samples were analyzed according to laboratory procedures of Determination of Structural Carbohydrates and Lignin in Biomass by the National Renewable Energy Laboratory (NREL) (Sluiter et al. [2011\)](#page-12-19). Briefy, cellulose and hemicellulose were hydrolyzed into monosaccharides by sulfuric acid, and then the concentration of monosaccharides was detected by external standard method using HPLC to calculated the content of cellulose and hemicellulose. The total content of lignin included acid-soluble lignin and acid-insoluble lignin and the later was calculated by measuring the absorbance of the sample at 320 nm on a UV–visible spectrophotometer.

Morphology analysis

The morphology of the cationic LCNFs was observed by atomic force microscopy (AFM, Bruker Multimode 8, Germany) in ScanAsyst mode to evaluate the extent of defibrillation of the fibers. 5 µL of diluted LCNF suspension (0.01%) was deposited on freshly cleaved mica after sonicating for 2 min, and it was completely dried at room temperature before testing.

The surface morphology of paper coated by cationic LCNFs was observed using Scanning electron microscopy (SEM, Hitachi S-4800, Japan) at 5 kV acceleration voltage. The SEM samples were precoated with gold for 60 s using a vacuum-ion sputtercoater (Hitachi MC1000).

Chemical structure analysis

The cationization of the reed flour was characterized by Fourier transform infrared spectroscopy (Varian 3100) with the KBr disc method (1:100 dilution by KBr) for 400–4000 cm^{-1} with 64 scans in absorption mode.

X-ray photoelectron spectroscopy (XPS) spectra were obtained with an ESCALAB220i-XL Photoelectron Spectrometer (VG Scientifc). A Gaussian curve ftting program was used to analysis the signal of C1s, O1s, N1s and the following binding energies.

Crystalline structures analysis

X-ray difraction (XRD) patterns of the products were recorded using an X'Pert PRO X-ray difractometer with Cu K α radiation (λ =0.154184 nm) in the 2 θ range of 5–50° with increment step of 0.02°. Then, the crystallinity index (CrI) of samples was calculated according to the empirical Eq. ([2\)](#page-3-1) (Segal et al. [1959](#page-12-20)):

$$
CrI(\%) = \frac{(I_{200} - I_{am})}{I_{200}} \times 100
$$
 (2)

where I_{200} is the maximum peak intensity of the crystalline region of cellulose ($2\theta = 22.3^{\circ}$), and I_{am} is the intensity of the amorphous phase $(2\theta = 18.6^{\circ})$.

The content of trimethylammonium chloride groups in cationic LCNFs was measured by elemental analysis of N. Elemental analysis was performed using Vario MACRO cube (Elementar, Germany). The content of quaternary ammonium group in cationic LCNFs was determined by the following Eq. [\(3](#page-4-0)):

$$
N_c(mmol/g) = \frac{x \times 10}{14}
$$
 (3)

where N_c is the content of quaternary ammonium group, and the x is the weight% of N element in the cationic LCNFs (*x* wt%).

Zeta potential

Zeta potential of LCNFs was measured using Zetasizer Nano ZS (Malvern) at the concentration of 0.1 wt%. Each sample was tested three times at 25 °C and the results were averaged.

Application of cationic LCNFs to paper

The cationic LCNF (1-M4) dispersion was coated on the paper (grammage 80 g/m^2) surface by vacuum filtration. The coating level was controlled by changing the concentration of LCNF suspensions.

Grease resistance of coated paper

Grease resistance of the paper coated with cationic LCNFs was tested according to the TAPPI T 559 cm-12 standard. The solution containing diferent ratios of castor oil/heptane/toluene ranging from No. 1 to 12 was dropped on the paper surface and wiped out after 15 s. The results were reported as Kit rating number, where a higher number indicates a better oil resistance performance.

Mechanical properties of coated paper

The mechanical properties of paper with the cationic LCNF coating were measured by an MTS Sintech tensile tester (MTS Sintech, Beijing) with a strain rate of 5 mm/min. Specimen strip was 5 mm wide and 60 mm long with a gauge span of 30 mm. At least fve strips were measured and the results were averaged.

Results and discussion

Cationization and defbrillation of reed four and chemical compositional analysis

Cationic lignocellulose nanofbers (LCNFs) were prepared by a mechanochemical method. During the ball milling process, the lignocellulose fber would be swelled by NaOH solution and defbrillated under the action of mechanical force, exposing more hydroxyl groups. Meanwhile, hydroxyl groups reacted with EPTAC to increase the electrostatic repulsion between fbers, which in turn could further promote defbrillation of fbers (Fig. [1](#page-5-0)). As a result, LCNFs were obtained and the compositional analysis of the reed four and LCNFs was performed (Fig. [2](#page-6-0)). In reed four, the content of cellulose, hemicellulose, and lignin was 42%, 19%, and 26%, respectively. With the ball milling time increasing, the content of hemicellulose and lignin was decreased. The hemicellulose content was reduced by 71.4% after ball milling 12 h, since the hemicellulose could be dissolved and removed during milling. In addition, lignin-hemicellulose ester bonds could also be hydrolyzed by the alkaline treatment, which also resulted in the hemicellulose and lignin dissolution (Liu et al. [2019](#page-12-21); Ru et al. [2019\)](#page-12-13).

Chemical structure of cationic LCNFs

The reaction mechanism of lignocellulose and EPTAC under alkaline condition is that the alkaliactivated hydroxyl groups of lignocellulose react with epoxy groups of EPTAC. Figure [3](#page-6-1)a, b show FT-IR spectra of reed flour and LCNFs. The chemical structure of the LCNFs is similar to that of the reed flour. The absorption peaks at 1600 cm^{-1} , 1508 cm^{-1} and 1238 cm^{-1} are the characteristic peaks of the aromatic structure of lignin, which are the stretching vibration absorption peaks of the aromatic structure skeleton C=O and C=C (McClelland et al. [2017](#page-12-1)). The absorption peak at 1735 cm⁻¹ represents the carbonyl groups, which are attributed to the hemicellulosic acetate and uronate ester groups, or ester groups of lignin/hemicellulose (Yang et al. [2018](#page-13-13)). Additionally, the absorption peak at 1735 cm^{-1} almost disappeared after ball milling, indicating that ester groups were hydrolyzed as well as hemicellulose was lost in alkaline condition evidenced by the hemicellulose

Table 1 Preparation condition of cationic LCNFs

Sample	Ball-milling time/h	EPTAC molar ratio/hydroxyl ^a	N^+ content (mmol/g)
$0-M4$	4	0:1	
$0.5-M4$	4	0.5:1	0.41
$1-M4$	4	1:1	0.68
$1.5-M4$	4	1.5:1	0.89
$2-M4$	4	2:1	0.95
$1-M2$	2	1:1	0.35
$1-M6$	6	1:1	0.96
$1-M8$	8	1:1	0.92
$1-M10$	10	1:1	0.91
$1-M12$	12	1:1	0.93

content reduced during ball milling (Fig. [2\)](#page-6-0). Appearance of new peak at 1489 cm⁻¹ belongs to the stretching of methyl groups on the quaternary ammonium group (Zaman et al. 2012). The peak at 1418 cm^{-1} is ascribed to C–N stretching (Pal et al. [2005](#page-12-22); Song et al. [2010](#page-13-14)). These are evidences of successful cationization of reed four by EPTAC during ball milling.

Additional evidence of the cationization was obtained by X-ray photoelectron spectroscopy (XPS). Results of curve-ftting for the C1*s*, O1*s* and N1*s* region using a Gaussian function are shown in Fig. [4](#page-7-0). Compared with the reed flour, a new peak of N1*s* appeared at 403 eV characteristic for C–N of the substituted ammonium. This further confrms that LCNFs are cationized by EPTAC. The content of quaternary ammonium groups on the fber surface was tested as shown in Table [1.](#page-5-1) The content of quaternary

Fig. 1 Scheme of the cationic LCNFs fabrication from reed straw and application to paper

Source of lignocellulose

Fig. 2 Compositional analysis of the reed four and cationic LCNFs

ammonium groups on the fber surface was increased with increasing milling time and the molar ratio of EPTAC/hydroxyl. However, milling more than 8 h and more EPTAC did not give more quaternary ammonium groups on the fber surface. These could be resulted from the hydrolysis of EPTAC occurred in the reaction system, which would reduce reaction efficiency (Odabas et al. [2016;](#page-12-23) Zaman et al. [2012](#page-13-9)). Furthermore, the cationic LCNFs would also hydrolyze in alkaline condition (Moral et al. [2015\)](#page-12-24).

Crystal morphology and crystallinity of cationic LCNFs

The crystal morphology and crystallinity of cationic LCNFs were characterized by X-ray difraction (XRD) analysis (Fig. [5](#page-8-0)). It shows that the mechanochemical process did not change the crystal form of the cellulose and the cationic LCNFs maintained cellulose I crystallinity. The peak positions of samples before and after cationization were almost the same, appearing at 14.9°, 16.5° and 22.3° 2θ, respectively, which were corresponding to Miller indices $[(1-10),$ (110) and (200)]. However, the degree of crystallinity decreased from 65.3 to 46.3% after 12 h milling at a constant molar ratio (EPTAC/hydroxyl) of 1. The degree of crystallinity was also decreased with increasing the molar ratio of EPTAC/hydroxyl and the molar ratio of 2 gave a lower crystallinity of 44.8%, which was likely to be associated with the increase of chemically modifed cellulose chains on the fbril surfaces.

Morphology of cationic LCNFs

The morphology of prepared samples was examined by AFM (Fig. 6 , Fig. S2). The fiber was partial defibrillated after 4 h ball-milling only under alkaline condition, which was same as our previous work (Liu et al. [2019](#page-12-21)). The addition of EPTAC to the milling system resulted in extensive individualization of

Fig. 3 FT-IR spectra of reed four and LCNFs prepared by milling with various time (**a**) and associated partial spectroscopy (**b**)

Fig. 4 a XPS spectra of reed four and cationic LCNFs, **b**, **c** high-resolution scans of C1*s* and O1*s* of reed four, and **d**, **e** and **f** highresolution scans of C1*s*, O1*s*, and N1*s* of cationic LCNFs

the 2–4 nm-wide elementary fbrils. The diameter of lignocellulose fber decreased with the milling time increasing. In fact, the nanofber with diameter less than 10 nm was obtained only by milling for 2 h with the assistance of EPTAC. Besides, with the molar ratio of EPTAC/hydroxyl increasing, the diameter of lignocellulose fber also decreased and became uniform. Since the content of quaternary ammonium groups on the fber surface increased with the molar ratio of EPTAC/hydroxyl and milling time increasing, it can be concluded that the cationic groups introduced by EPTAC should be efective in separation of fbers by electrostatic mutual repulsion. In the AFM images, the minute particles attaching to LCNFs or distributing in the background were lignin particles (Fig. [6b](#page-9-0), c) because alkali-soluble lignin could be precipitated and agglomerate into particles when neutralized.

Zeta potential of cationic LCNF suspensions

Figure [7](#page-10-0)a and b show the variation of the zeta potential of LCNFs with the milling time and molar ratio of the EPTAC/hydroxyl, respectively. It can be seen that the zeta potential of LCNFs is negative (−16 mV) after alkaline milling of the reed four without EPTAC, which was consistent with our previous work (Liu et al. [2019\)](#page-12-21). In contrast, the zeta potential of LCNFs became positive (+30∼+40 mV) by milling with EPTAC and the maximum of zeta potential reached at $+40.8$ mV. Furthermore, the variation trend of the zeta potential was almost consistent with the variation trend of the quaternary ammonium group content, which further proved that the lignocellulose reacted with the EPTAC. Meanwhile, the introduced high electrostatic repulsion was benefcial to improving the stability of LCNF suspensions. Introduction of positive charge caused **Fig. 5** X-ray difraction data of the reed four and LCNFs with various milling time (**a**, **c**) and molar ratio of EPTAC/hydroxyl (**b**, **d**)

remarkable efect on re-dispersibility of LCNFs. Figure [7c](#page-10-0)–e show the AFM images of redispersed cationic LCNFs (1-M4) by sonication for diferent time. It was found cationic LCNFs could be quickly redispersed in water by short-time sonication (4 min, the yield reached 96%). The fbril width of redispersed LCNFs was around 4 nm, demonstrating excellent re-dispersibility and facilitating their storage and transportation.

Cationic LCNFs applied to paper

One application of the cationic LCNFs is papermaking. When the cationic LCNFs were coated on the paper surface, the pores on the surface of paper were gradually covered with the increasing coating weight of the cationic LCNFs (Fig. S3). The fber on the surface of paper was completely covered with cationic LCNFs and the fber outline became blurred when the coating weight of the cationic LCNFs was 5 g/m^2 . When the coating weight was more than 3 g/ m², the cationic LCNFs formed a dense layer on the paper surface as Fig. S4 shows and the barrier property of paper was greatly improved. The air permeability was decreased signifcantly with the increasing coating weight of cationic LCNFs (Table S1) and the air permeability was lower than 0.01 μm/(Pa s) at the coating weight of 3 g/m^2 , which confirmed again that

Fig. 6 AFM images of prepared LCNFs with EPTAC/hydroxyl molar ratio of **a** 0:1, **b** 1:1, and **c** 2:1

cationic LCNFs formed a barrier layer on the surface of the paper. When cationic LCNFs were applied to paper products, the lignin component was expected to improve the hydrophobicity of paper (contact angle reached 80°, Fig. S5).

The formed dense layer of cationic LCNFs can block oil penetration and the oil resistance of coated paper was characterized by Kit rating. The variation of the Kit rating with the coating weight was shown in Fig. [8](#page-11-11)a. There is a sharp increase in the Kit rating when the cationic LCNFs were coated on the paper surface and the Kit rating reached the maximum of 12/12 at the coating weight of 5 g/m^2 , giving the paper excellent oil-proof performance. The cationic LCNF coated paper-based container had the capability to hold rape oil for 5 days without leakage (Fig. S6). This mainly benefted from the dense layer formed by LCNFs and the positive charge on the LCNFs, which cannot only block the access of oil to penetrate the paper, but also generate electrostatic interactions with oleic acid molecules that prevented oil from permeating and transferring (Long et al. [2015\)](#page-12-25).

The mechanical properties of the paper with and without cationic LCNF coating were tested as the Fig. [8](#page-11-11)b show. The tensile strength of the paper increased with the increasing coating weight. The tensile strength of paper with the coating weight of 9 g/m^2 (22.5 \pm 0.9 MPa) was far beyond that of paper without coated $(9.6 \pm 0.3 \text{ MPa})$. Meanwhile, the Young's modulus of the coated paper also signifcantly increased with the increasing coating weight. The Young's modulus of paper without coating was 0.8 ± 0.2 GPa while the paper with the coating weight of 9 g/m² reached at 1.9 ± 0.1 GPa. It suggested that the cationic LCNFs can strengthen the interactions between cellulose fbers in paper. This was mainly due to the electrostatic interactions and hydrogen bonds formed between the paper fbers and LCNFs. The quaternary ammonium groups of LCNFs were expected to bind with negatively charged hydroxyl on the paper fber surface through electrostatic interactions and hydrogen bonds can be formed between the unreacted hydroxyl groups of LCNFs and the hydroxyl groups on the paper fber surface. The cationic LCNFs acted as a bridge in paper fbers through dual interactions, which leads to the mechanical properties of the coated paper signifcantly improved. Accordingly, the cationic LCNFs can be used as efective paper-strengthening agent. Moreover, the coated paper was also with good antibacterial property and the growth reduction rate against *E. coli* was 93% (Fig. S7), which was conducive to expanding the application of paper.

Fig. 7 Zeta potential of the cationic LCNF suspensions with diferent **a** milling time and **b** molar ratio of EPTAC/hydroxyl, AFM images of the redispersion of freeze-dried cationic LCNFs (1-M4) by sonication for **a** 2 min, **b** 4 min, **c** 10 min

Conclusion

Cationic LCNFs were successfully prepared by the one-pot reaction of reed four and EPTAC under mild alkaline condition. The obtained cationic LCNFs were 2–4 nm wide and several micrometers long. The suspension of cationic LCNFs with a high zeta potential of $+40$ mV showed high dispersion stability and easy re-dispersibility. When cationic LCNFs were coated on paper surface, the hydrophobicity and oil resistance of paper were signifcantly improved. In addition, the tensile strength and Young's modulus of the coated paper can be increased by 144% and 124%, respectively. The cationic LCNFs also endow paper with antibacterial property. This study provides a facile mechanochemical method to achieve value-added material from crop straw.

Fig. 8 a Kit rating and **b** tensile strength and Young's modulus of the paper with and without cationic LCNF coating

Author contributions JL: Investigation, Data curation, Formal analysis, Methodology, Writing-original draft. PX: Investigation and Methodology. SK: Conceptualization, Writing-review and editing. MW: Writing-review and editing, Supervision, Funding acquisition. YH: Supervision, Writingreview and editing.

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Data availability All relevant data are included in this Article and its Supplementary Information. Files.

Declarations

Confict of interest The authors declare no confict of interest.

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

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