

Cellulose nanofibrils aerogels generated from jute fibers



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ABSTRACT

In this work, we report the cellulose nanofibrils extracted from the pristine jute fibers via the pre-treatments followed by the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation and mechanical disintegration. The effects of pretreatments by using the NaOH solution and dimethyl sulfoxide solvent on the fiber morphology and macro/micro-structures were investigated by polarizing microscope and synchrotron radiation wide/small-angle X-ray scattering (WAXS/SAXS). The cellulose nanofibrils exhibit a diameter ranging from 5 nm to 20 nm and a length of several micrometers, which have been assembled into cellulose aerogels by the lyophilization of as-prepared nanofibrils dispersions with various concentrations. The results indicated that the hierarchical structures of as-prepared cellulose aerogels were dependent on the dispersion concentrations. The WAXS results show that the typical cellulose aerogels are coexistence of cellulose I and cellulose II, which has a great promise for many potential applications, such as pharmaceutical, liquid filtration, catalysts, bio-nanocomposites, and tissue engineering scaffolds.

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1. Introduction

In recent years, large-scale assembly of the nanomaterials with the size less than 100 nm at least in one dimension (1D) in the form of nanoparticles, nanofibers, nanowires, nanobelts, nanotubes, graphenes, etc., using as the building blocks into a well-controlled macroscopic configuration has aroused considerable attentions in the materials research area as a result of the development of nanoscience and nanotechnology, which is of great importance to the practical applications for these nanomaterials (Deng et al., 2012; Li, Yang, Feng, Yuan, & Su, 2012; Li et al., 2013; Lin et al., 2012; Liu et al., 2012; Liu, Shen, Luo, Wang, & Sun, 2013). For instance, the nanotubes and graphenes have been assembled into the continuous fibers, yarns with excellent mechanical properties, large-scale ultra-flyweight aerogels and sheets with multi-functionality (Cong, Ren, Wang, & Yu, 2012; Gui et al., 2010; Xu, Sun, Zhao, & Gao, 2013; Zhao et al., 2012).

Recent environmental issues and the creation of recycle-based and sustainable societies have driven the fundamental researches and applications of these materials with non-toxicity, biodegradability, sustainability and renewability in the coming decades (Isogai, Saito, & Fukuzumi, 2011). Fortunately, nature has created the most ubiquitous renewable polymer resource, cellulose,

available today, which occurs in wood, cotton, long vegetable fibers and other plant-based materials serving as the dominant reinforcing phase in plant structures (Klemm, Heublein, Fink, & Bohn, 2005). Nano-scaled cellulose fibers, i.e. cellulose nanofibrils, cellulose nanocrystals, and cellulose nanowhiskers, derived from the cellulose crystalline regions consisting of tightly packed cellulose chains together with a width of 2–50 nm, are embedded in a matrix of amorphous cellulose, hemi-cellulose and lignin, which have been extensively investigated using as new cellulose based building blocks in various areas of applications during the past decade (Habibi, Lucia, & Rojas, 2010; Isogai et al., 2011; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Siró & Plackett, 2010).

Up to now, cellulose nanofibrils extracted from the various cellulosic resources such as wood (Abe, Iwamoto, & Yano, 2007; Chen, Yu, Li, Liu, & Li, 2011), wood pulp (Ma, Burger, Hsiao, & Chu, 2011), cotton (Heath & Thielemans, 2010), cotton linter (Elazzouzi-Hafraoui et al., 2008), bacterial cellulose (Liang et al., 2012), ramie (Zoppe, Peresin, Habibi, Venditti, & Rojas, 2009), sisal (De Rodriguez, Thielemans, & Dufresne, 2006), flax (Cao, Dong, & Li, 2007), tunicate (Iwamoto, Isogai, & Iwata, 2011), jute (Cao, Ding, Yu, & Al-Deyab, 2012; Das et al., 2010), and sugarcane bagasse (Mahanta, Leong, & Valiyaveetil, 2012) via two main processing processes involving acid hydrolysis and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation have been widely studied, which are fully reviewed by some publications (Habibi et al., 2010; Isogai et al., 2011; Moon et al., 2011). In view of the environmental protection as well as government

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regulations in some areas, the great importance and developmental prospect of reasonable utilizing plant fibers with a short growth cycle, rather than wood fibers from the growing trees, has become increasingly momentous (Cao et al., 2012). Therefore, the development of a facile method for the controllable fabrication of cellulose nanofibrils using as building blocks for the construction of macroscopic nanomaterials assemblies from the plant fibers is what we are hunting for.

Jute, a kind of abundant natural biodegradable fibers, is widely grown in some Asian areas such as China, India and Bangladesh, which occupies the second place in terms of world production level of cellulosic fibers apart from the cotton (Cao et al., 2012; Mwaikambo, 2006). In the jute fibers, the molecules are highly oriented parallel to one another in fibrils, which is similar to other natural fibers, but they spiral round the fiber, thus reducing the degree of orientation parallel to the fiber axis (Morton & Hearle, 1993). The spiral angle of jute fiber is relatively larger than that of the other bast fibers (e.g. flax, ramie, and hemp) (Mwaikambo, 2006), which is favorable to the extraction of cellulose crystallites that are so called cellulose nanofibrils.

In the light of the large throughput, short growth cycle, renewability, biodegradability, biocompatibility as well as the typical structure of spiral angle in jute fibers mentioned above, developing a facile processing procedure with pollution-free, low cost and high efficiency for the generation of jute nanofibrils is significative to the promising candidates for bio-nanocomposites, electronic industry, pharmaceutical, filtration, tissue engineering, catalysts, etc. Although previous work on the generation of jute micro/nanofibrils via acid hydrolysis route and other processing routes has been reported, the unambiguously individual jute nanofibril was seldom unfold before our eyes instead of the nanoparticles presented (Cao et al., 2012; Das et al., 2010, 2011). In these reports, few have illustrated the effects of pretreatment processes on the formation of nanofibrils. In this work, we will report a simple procedure of the pretreatment processes combined with a TEMPO-mediated oxidation process for the generation of individual jute nanofibril. Moreover, the as-prepared jute nanofibrils using as building blocks are assembled into macroscopic aerogels with a well tunable porous structure.

2. Experimental details

2.1. Materials

The pristine jute fibers were obtained from Redbud Textile Tech. Inc., China as a gift and sufficiently dried in vacuum drying oven. The other starting materials including sodium hydroxide (NaOH, 97%), dimethyl sulfoxide (DMSO, spectroscopically pure grade), 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO, 98%), NaBr, Na₂CO₃ (99.5%), NaClO solution, ethanol absolute were purchased from Shanghai Aladdin Chemical Regent Inc., China.

2.2. Preparation of samples

Pristine jute fibers were grinded into powder with ~1 mm particle size and heated at 90 °C for 5 h in a 15 wt% NaOH solution. After completely washed with deionized water and dried in 70 °C for 24 h, the mass was then soaked in DMSO (liquor ratio 1:15) and heated at 70 °C for 3 h in a water bath according to the previous report (Cao et al., 2012). Again after fully washed with a 2 wt% Na₂CO₃ solution and deionized water successively, the mass was dried at 70 °C for 24 h and the jute fibers were named as pretreated jute fibers. Another 3 bundles of un-grinded jute fibers (about 80 mm in length) were pretreated by the above same method and marked as pristine jute fiber, jute fiber/NaOH, jute fiber/NaOH/DMSO, respectively.

The pretreated jute fibers (1.0 g) were dispersed in water (100 g). Then NaBr (0.20 g) and TEMPO (0.04 g) were both dissolved in the suspension. The reaction was started by the addition of a 12 wt% NaClO solution (18.0 g) under stirring for 3 h. The pH value was kept between 10.0 and 10.5 (Isogai et al., 2011) monitored with a pH meter, by adjusting with a 2 wt% NaOH solution. The reaction was stopped by adding ethanol absolute (5 mL), followed by continuously stirring for 20 min. The final product was washed ten times with deionized water by successive centrifugations (10,000 rpm for 5 min). The generated oxidized jute fiber cellulose jelly with different amounts (1.0, 3.0, 6.0, 9.0, and 18.0 g, respectively) was dispersed in 100 mL deionized water followed by high-speed homogenization (at 9000 rpm for 10 min) and ultrasound sonicated (for 5 min). 1.0 g jute fiber cellulose jelly was dried by a vacuum oven at 90 °C for 24 h and 0.03 g solid content was left. Therefore, the concentrations of these jute cellulose nanofibrils suspensions were calculated to be 0.03, 0.09, 0.18, 0.27, and 0.54 wt%, respectively. The as-prepared aqueous suspensions were kept in a refrigerator at 4 °C for further use.

The jute cellulose nanofibrillar aerogels were prepared by the method of freeze-drying. 50 mL of each obtained cellulose nanofibrils aqueous suspension was poured into a cylindrical mold and subjected to freeze-drying using a freeze-drier (FD-1D-80, Beijing BoYiKang Experimental Equipments Ltd., Co., China) to allow frozen water in the cellulose materials to sublime directly from the solid phase to the gas phase. The cold trap temperature was –50 °C and the vacuum was below 80 mTorr during the freeze-drying process.

2.3. Characterizations

The dimensions of pristine jute fibers, jute fibers/NaOH, jute fibers/NaOH/DMSO were observed by a polarizing microscope (Leica DM2500P) with a digital camera. Optical photographs of fiber bundles were taken by a digital camera (Sony A580L).

The synchrotron radiation wide-angle X-ray scattering (WAXS) experiments were performed at the synchrotron radiation small-angle X-ray scattering (SAXS) beamline (BL16B) in Shanghai Synchrotron Radiation Facility (SSRF). The wavelength used was 0.124 nm. The sample-to-detector distances were 102.0 mm and 2030 mm for WAXS and SAXS, respectively. A 2D MAR165 CCD (MAR USA, Inc.) was used for data collection. Three bundles of well-oriented jute fibers (pristine jute fibers, jute fibers/NaOH, and jute fibers/NaOH/DMSO) were arranged and placed in a sample holder with the fiber direction perpendicular to the direction of incident X-ray. The image acquisition time of every sample was 600 s. The 2D WAXS pattern was processed with the software package FIT2D. The data of blank air were collected to correct for air scattering.

The transmission electron microscopy (TEM) (Tecnai G2 F20 S-TWIN) equipped with a Gatan 1K × 1K CCD camera and an EDX detector was used to take the TEM micrographs. The accelerating voltage was 100 kV. 1.00 g oxidized jute fiber cellulose jelly was dispersed in 99.0 g ethanol absolute, followed by high-speed homogenization (at ~9000 rpm for 10 min). About a 10 μL of the 1 wt% cellulose nanofibrils ethanol dispersion was mounted on a glow-discharged carbon-coated Cu grid. Excess solution was absorbed by clean filter paper and stand for drying by natural evaporation. The surface morphology of the aerogels was examined by a field emission scanning electron microscopy (SEM) (FEI Company). The sample was cut into a piece with the analyzed volume of 5 mm × 5 mm × 10 mm. The 3D microtomography experiment was carried out at the X-ray imaging and biomedical application beamline (BL13W1) of SSRF. The pixel resolution was 3.7 μm × 3.7 μm × 3.7 μm.

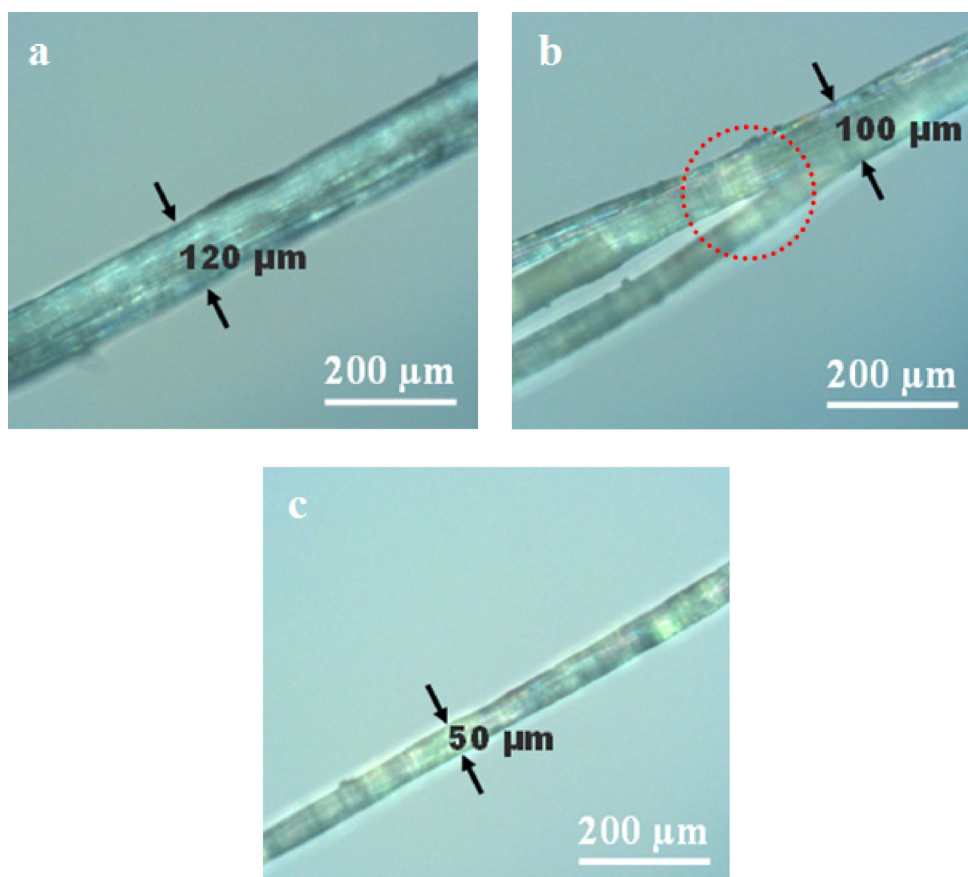


Fig. 1. Optical images of the (a) pristine jute fibers, (b) jute fibers pretreated by NaOH solution and (c) jute fibers pretreated by NaOH solution and DMSO solvent successively.

3. Results and discussion

3.1. Effects of pretreatments on the morphology of jute fiber

Jute fibers, as shown in Fig. 1a, often contain a larger proportion of non-cellulosic impurities, approximately 25%, such as hemi-cellulose, lignin, which serve as cementing materials distributed throughout the entire body of the fibers, and other minor components liking pectin, waxes, fats, inorganic salts (Mohanty & Misra, 1995), etc. Therefore, to extract the cellulose nanofibrils from jute fibers, the non-cellulosic impurities must be removed by some appropriate processes. The pristine jute fibers before and after treatment by a 15 wt% NaOH solution at 90 °C for 5 h are shown in Fig. 1a and b, respectively, indicating that the long strands comparing small individual fibers bonded together were broken down into smaller fibers. A clearly observation of the fiber diameter reduction of jute fibers by the pretreatments can be seen from Fig. 1. The alkali treatment acted on the pristine jute fibers (120 μm) can contribute to removing hemi-cellulose, surface impurities, and a part of lignin from the fibers, as well as the inter-molecular hydrogen bonding, leading to the decrease of fiber diameter (100 μm) and the formation of forficate jute fibers as marked by the dotted circle in Fig. 1b. Similar results have been reported by previous work (Cho, Kim, Song, & Hong, 2011). The succedent DMSO, a kind of strong hydrogen bonding-breaking agent, treatment further contributed to the breakage of inter-molecular hydrogen bonding and dissolution of interior and external non-cellulose materials, resulting in a further dimensional diminution of the jute fibers (Fig. 1c). The function of DMSO was to swell the jute fibers (Das et al., 2010).

3.2. SAXS results

To investigate the evolution of macromolecular and micro-structural parameters of jute fibers caused by pretreatments, the samples were examined by SAXS of SSRF. Fig. 2a–c presents the SAXS patterns of jute fibers from different pretreatments. Fig. 2a shows that the scattering pattern of the pristine jute fibers has much sharper and more elongated equatorial streak in intensity than that of the pretreated fibers (Fig. 2b and c), which shows an increasing central diamond shape of diffuse scattering. This result can be ascribed to much more nanofibrils were presented in the jute fibers after these treatments due to the removal of non-cellulosic components (Nishiyama et al., 2003).

Fig. 2d provides the relation of q^2 vs. $I(q) \cdot q^4$ obtaining from SAXS 2D scattering data through integrating in the range of -25° to $+25^\circ$. As can be seen, the curves of pristine jute fibers and treated by NaOH exhibit a negative deviation according to the Porod's Law, indicating the fibers were of non-ideal, two-phase structure (Sinha & Rout, 2008; Stribeck & Martinez-Vazquez, 2007). Furthermore, the curve of jute fibers treated by NaOH shows less deviation than that of pristine fibers. The reason for this is that the pristine jute fibers contain crystalline cellulose and other non-cellulosic components that can be regarded as two phases of cellulose phase and non-cellulose phase. The non-cellulose phase and some non-crystalline constituents were reduced due to the alkali treatment, resulting in the less obvious phase discrimination of these two phases (Sinha & Rout, 2008). Moreover, the curve of jute fibers treated by NaOH and DMSO successively displays a positive deviation, implying much more cellulose phase existed in the as-prepared fibers.

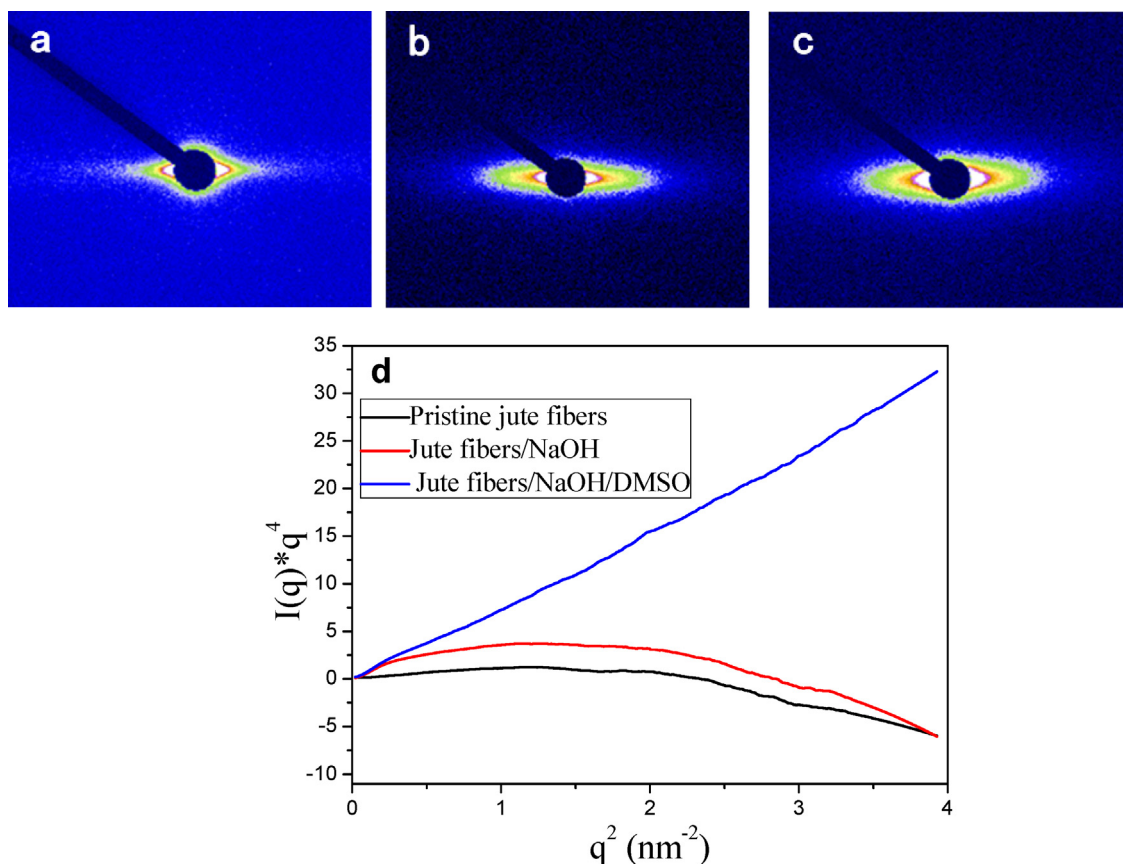


Fig. 2. SAXS patterns of the (a) pristine jute fibers, (b) jute fibers pretreated by NaOH solution, (c) jute fibers pretreated by NaOH solution and DMSO solvent successively, and (d) the corresponding $I(q) \cdot q^4 \sim q^2$ curves.

3.3. WAXS results

As can be seen from Fig. 3a in the equatorial direction, there are three characteristic diffractions assigned (110), (200), and (004) corresponding to cellulose I. The reflections of (110) and (200) were obviously changed after the alkali and DMSO treatments implied by the reflection arcs elongated along the fiber direction, and furthermore, the (110) reflection gradually split into two reflections as (10 $\bar{1}$) and (101) (Fig. 3b and c). In the meridional direction, a clear transformation of the reflection (022) ($2\theta = 27.88^\circ$) was presented. Integrated data from the 2D detector images as shown in Fig. 3d and e. The new scattering peaks of cellulose II (with the blue indices of lattice plane) presented after the pretreatments of pristine jute fiber. The diffraction peak cellulose I-(110) ($2\theta = 15.69^\circ$) separated into cellulose II-(101) corresponding to the 2θ peak position at 15.03° and cellulose I-(10 $\bar{1}$) ($2\theta = 16.44^\circ$) (Fig. 3d) (Klemm et al., 2005). Meanwhile, the diffraction peak cellulose I-(022) ($2\theta = 28.01^\circ$) was converted into cellulose II-(022) positioned at 27.88° , and cellulose I-(140) peaked at 45.64° , exhibiting a left shift into cellulose II-(141) with the new peak at 45.33° (Fig. 3e) (Cao et al., 2012; Das et al., 2010; Sinha & Rout, 2008). These clearly reveal the fact that during the pretreatment processes, some parts of cellulose I (namely I β) were converted into cellulose II, for the reason that the structure of cellulose tended to be more stable, which enabled cellulose II to be preferable for jute fiber in NaOH solution and DMSO solvent in high temperature (no less than 70°C) (Klemm et al., 2005). The transformation of cellulose I to cellulose II requires a change in the hydrogen-bonding network between cellulose unit cell, which has been known as an irreversible change (Moon et al., 2011).

3.4. TEM images of the jute nanofibrils

The jute cellulose nanofibrils were obtained through the mechanical disintegration of the jute fiber cellulose jelly stemmed from the TEMPO-oxidized jute fibers treated by the NaOH solution, NaOH solution and DMSO solvent successively, respectively. The inset of Fig. 4a shows a photo of jute nanofibrils aqueous suspension with a concentration of 0.09 wt%, which exhibits homogeneous with a high transparency. To observe the dimension of jute cellulose nanofibrils, a drop of nanofibrils ethanol dispersion with a concentration of 1 wt% was mounted on a glow-discharged carbon-coated Cu grid examined by TEM. The TEM images indicate that the jute nanofibrils have a length of several micrometers and a diameter ranging from 5 nm to 20 nm (Fig. 4). This result is different from the previous reports of the jute nanofibrils exhibiting an elliptical shape with a diameter of 146 nm and a length of 950 nm obtained by acid hydrolysis method (Das et al., 2010). In addition, the nanofibrils generated from the jute fibers treated by NaOH solution and DMSO solvent successively (Fig. 4c and d) exhibit much larger diameter than that from the jute fibers treated by NaOH solution only (Fig. 4a and b). It can be concluded that the jute cellulose nanofibrils were successfully extracted from the pristine jute fibers via the TEMPO-oxidation method in combination with the pretreatments by the NaOH solution, NaOH solution and DMSO solvent successively, respectively.

Previous work showed that the treatment process by DMSO solvent was essential for the generation of nanofibrils with the spherical- and elliptical-shape as well as much larger length to diameter ratio (Cao et al., 2012; Das et al., 2011, 2010). Whether the DMSO is need for the preparation of nanofibrils, the authors have not provided the experiments and elucidations in these reports.

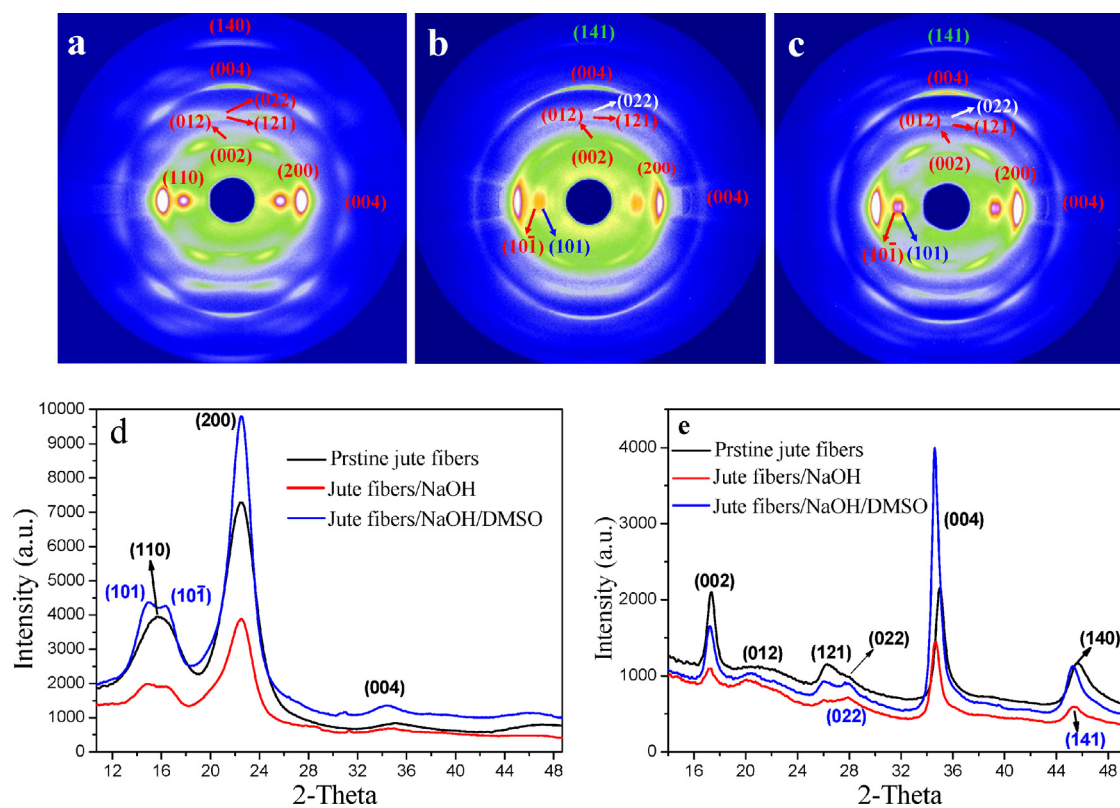


Fig. 3. 2D WAXS patterns of the (a) pristine jute fibers, (b) jute fibers pretreated by NaOH solution, (c) jute fibers pretreated by NaOH solution and DMSO solvent successively, 1D $I \sim 2\theta$ integrated curves of the (d) equatorial direction and (e) meridional direction from the corresponding WAXS patterns.

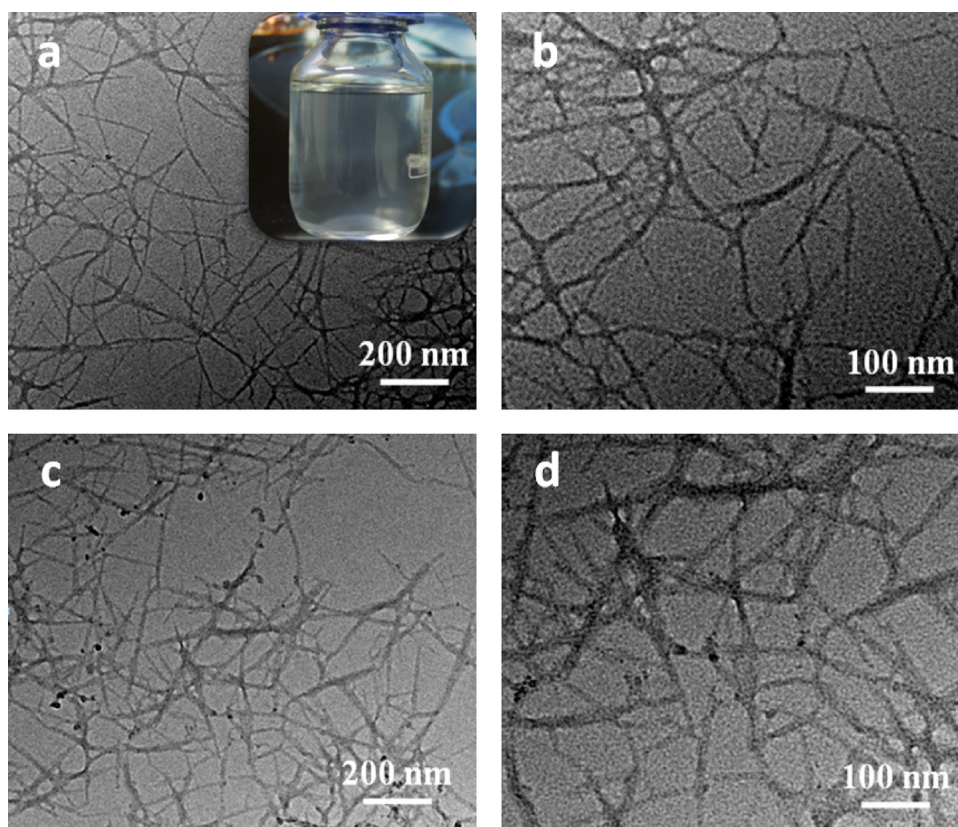


Fig. 4. TEM images of cellulose nanofibrils generated from the jute fibers treated by the (a and b) NaOH solution only, (c and d) NaOH solution and DMSO solvent successively. (The inset of (a) shows a photo of jute nanofibrils aqueous solution with a concentration of 0.09 wt%. (b) and (d) are the high magnifications of (a) and (c), respectively.)

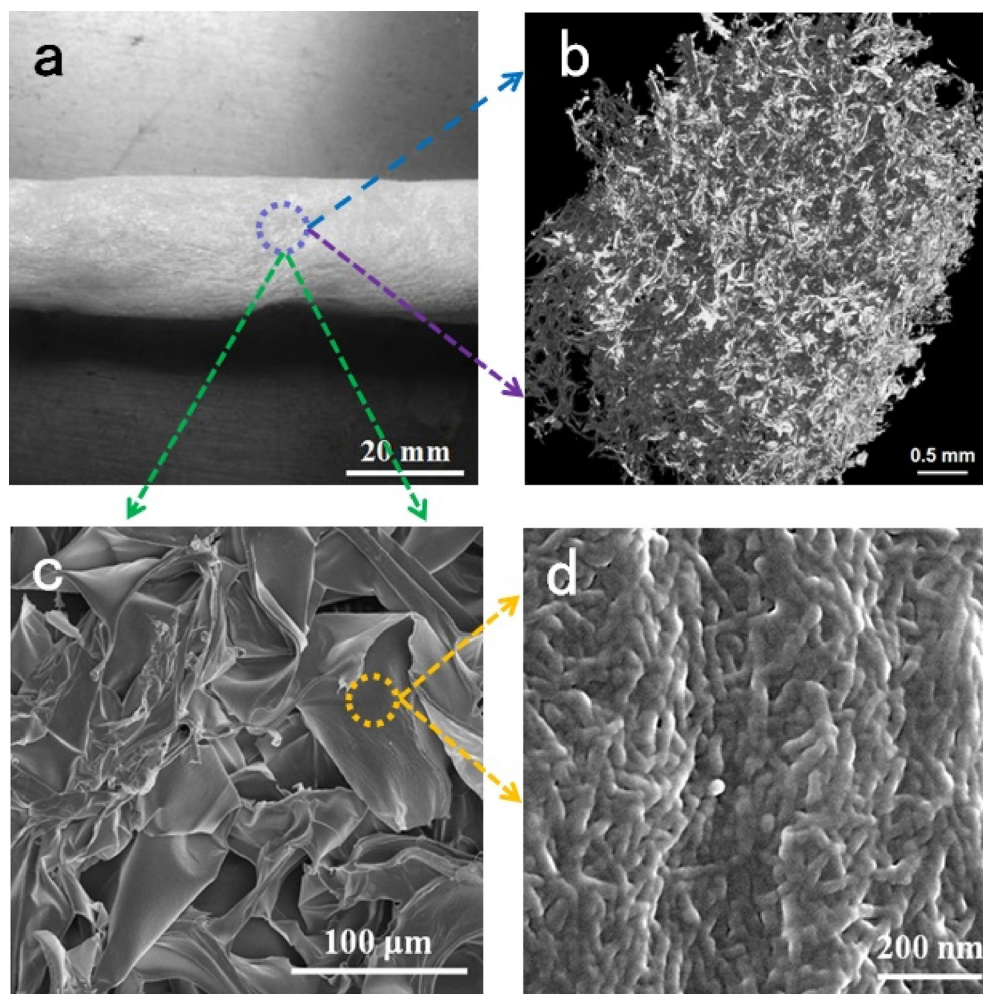


Fig. 5. (a) A photo of the cellulose aerogel comprising jute nanofibrils. (b) A 3D microtomography image of the jute nanofibrils aerogel. (c and d) FE-SEM images of the jute nanofibrils aerogel with different magnifications.

In our work, it is showed that the nanofibrils can be generated from the jute fibers treated by the sole NaOH solution. Furthermore, the morphology of these nanofibrils prepared from the two different pretreatment processes has no obvious differences. The result demonstrated that the treatment of DMSO solvent is not essential, thus, the extraction process of nanofibrils can be directly from the treated jute fibers by the NaOH solution.

The simplified generation process of jute nanofibrils can be attributable to the removal of impurities in pristine jute fibers mainly by the NaOH solution and the DMSO solvent treatment was only further to split the bundle jute fibers individually as displayed in the foregoing section. Therefore, the jute nanofibrils can be generated from jute fibers only treated by the NaOH solution without another treatment processes, thus, it is time-saving, cost-saving and less contaminates discharged. Since the crystallinity and cellulose components including cellulose I and cellulose II of the fibers can be tuned by the alkali treatment (Liu & Hu, 2008), it is expected that the crystallinity and cellulose components of the resultant nanofibrils as well as their macroscopic assemblies are also tunable. Further study is under our investigation.

3.5. Morphology of the jute nanofibrils aerogels

To construct the macroscopic nanomaterials assemblies via using jute nanofibrils as building blocks, the selected jute

nanofibrils dispersions with various concentrations were poured into a cylindrical mold and subjected to freeze-drying, respectively. Fig. 5a shows a typical shaped macroscopic aerogel consisting of jute nanofibrils obtained from the lyophilization of a 0.54 wt% aqueous dispersion. The X-ray phase contrast microtomography at BL13W beamline of SSRF was used to investigate the 3D microstructures of the aerogel with non-destructivity on the sample. Fig. 5b provides the 3D microtomography image of the aerogel, which presents that numerous lamellar structures exist in the aerogel, resulting in the formation of 3D porous structures in the range from several micrometers to a few tens micrometers.

Fig. 5c and d shows the FE-SEM images of the aerogel with different magnifications. As can be noted, the abovementioned lamellar structures are composed of a great deal of thin membrane layers, which are sparsely stacked forming many large voids among them. A magnification image of the thin membrane as shown in Fig. 5d indicates that the membrane is actually composed of numerous random orientated nanofibrils with the diameter ranging from several nanometers to a few tens nanometers. The result is consistent with the TEM examination in previous section. Moreover, the jute nanofibrils were stacked very closely, forming a numerous pores or cracks in the nanometer range.

A possible formation mechanism of the jute nanofibrils aerogel with 3D porous network and 2D membrane-like skeleton

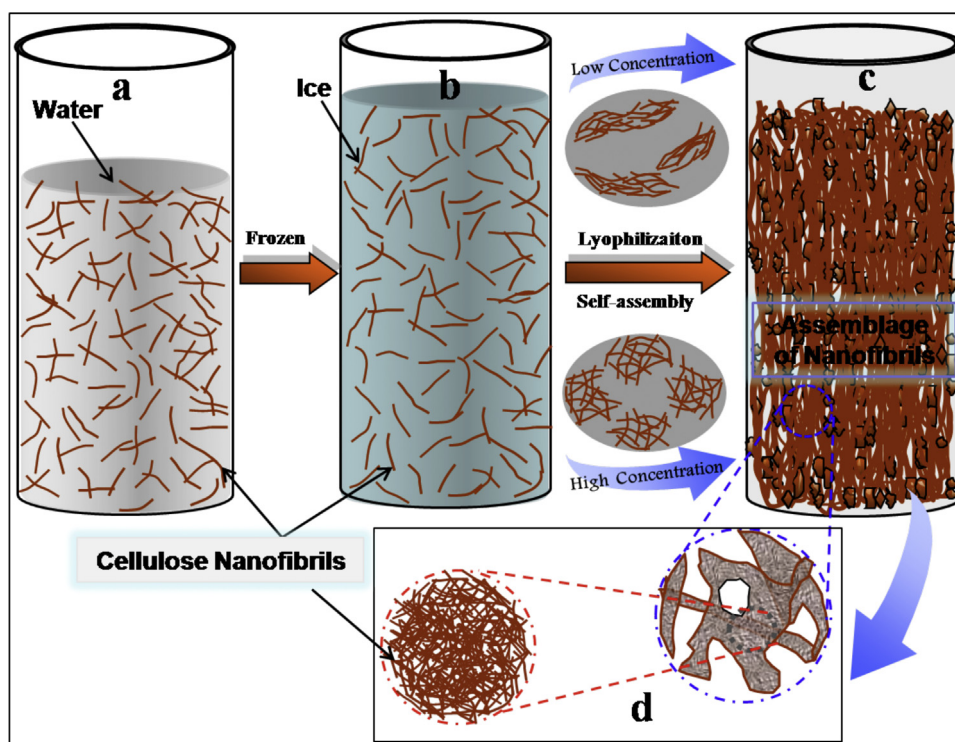


Fig. 6. Scheme of the possible formation mechanism of jute nanofibrils aerogel by the lyophilization: (a) homogeneous aqueous solution of jute nanofibrils; (b) jute nanofibrils in freezing ice; (c) jute nanofibrils aerogel. (d) Hierarchical structures of the jute nanofibrils aerogel.

microstructure is shown in Fig. 6. As can be noted in Fig. 6a, the jute nanofibrils are dispersed in the deionized water, which forms a stable and homogeneous aqueous solution due to the inter-electrostatic repulsion caused by the negatively charged carboxylate groups on the surfaces of cellulose nanofibrils (Isogai et al., 2011). In the process of freezing an aqueous suspension, the suspended nanofibrils are organized in the intervening space between growing ice crystal fronts, resulted in the formation of an ordered structure after the sublimation of ice crystal templates (Aulin, Netrval, Wågberg, & Lindström, 2010; Chen et al., 2011; Han, Zhou, Wu, Liu, & Wu, 2013; Lee & Deng, 2011; Minaberry, Chiappetta, Sosnik, & Jobbagy, 2013; Minaberry & Jobbágy, 2011; Romeo et al., 2012; Zhang et al., 2005).

It is reasonable to know that the hierarchical structures formed in process of sublimation were affected by the concentrations of cellulose nanofibrils in aqueous solution. It was reported that the nanofibrils were well ordered into a large bundle due to the high specific surface area and strong hydrogen bonds (Gutiérrez et al., 2007; Han et al., 2013; Zhang et al., 2005). For a suspension with a relatively high concentration, the space among the bundles was decreased, and the physical cross-linking among the nanofibrils of neighboring bundles occurred, which enabled the strong hydrogen bonds to be formed among the bundles during the lyophilization process (Fig. 6b and c). Meanwhile, the ice crystal formation also caused the coagulation of the nanofibrils (Chen et al., 2011). Thus, a 2D membrane-like skeleton structure was obtained as shown in Figs. 6d and 5c. For a low concentration, the space between nanofibrils bundles became larger as the decreasing of suspension concentration, leading to the weakening of hydrogen bonding and interfacial attraction between the bundles, which tended to larger pores and microfibers formed in final aerogel (Han et al., 2013). Fig. 7 provides the SEM images of as-prepared nanofibrils aerogel from much more dilute suspensions,

indicating larger pores, microfibers and smaller 2D membrane-like skeletons were formed gradually. Our results are observed to mutually agree with the previous work (Aulin et al., 2010; Chen et al., 2011; Han et al., 2013; Heath & Thielemans, 2010; Lee & Deng, 2011).

3.6. WAXS results of the jute nanofibrils aerogel

The 2D WAXS pattern of as-prepared jute nanofibrils aerogel exhibits a ring pattern as shown in the inset of Fig. 8, indicating a random orientation of the fiber axis of the jute cellulose nanofibrils on the horizontal plane of the aerogel. It is clearly shown that several diffraction peaks similarly assigned to the cellulose I crystal planes (002), (102), (200), (004), and (140), corresponding to the angles of 17.42°, 20.97°, 22.58°, 35.24°, 45.79°, respectively (Han et al., 2013). This result is attributed to the carboxylate groups formed by TEMPO-mediated oxidation are selectively linked on pretreated jute fibers surfaces without any internal cellulose crystallites (Isogai et al., 2011). Diffractions from cellulose II are also presented in the jute nanofibrils aerogel at angles of 28.89°, 30.75°, and 41.87° representing cellulose II crystal planes (112), (201), and (140), respectively, indicating the coexistence of cellulose I and cellulose II in the aerogel, which is ascribed to the pretreatments by NaOH and DMSO successively that removed the impurities and amorphous regions of pristine jute fibers and transformed the partial cellulose I into cellulose II simultaneously during the production process (Habibi et al., 2010). However, some shifts of the cellulose I peaks are observed in Fig. 8, the reason for this shifts may be caused by the disintegration of surface modified jute nanofibrils with carboxylate groups. Similar result was also found in the preparation of quaternized cellulose nanofibrils by Pei, Butchosa, Berglund, and Zhou (2013).

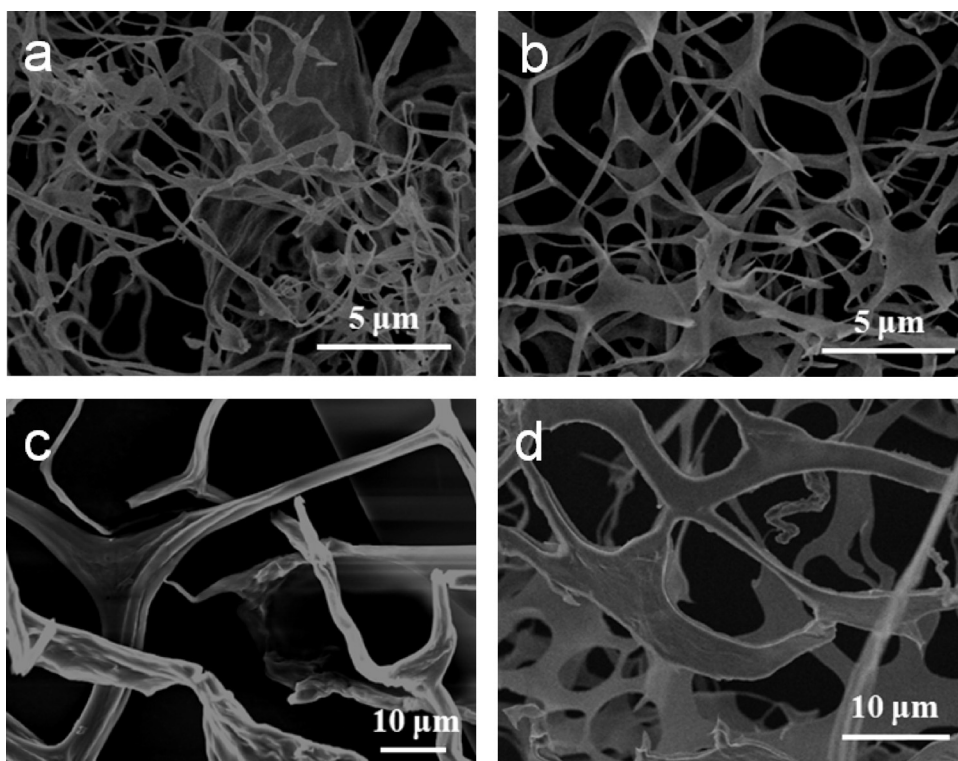


Fig. 7. FE-SEM images of the jute nanofibrils aerogel formed from the suspensions with various concentrations of (a) 0.03 wt%, (b) 0.09 wt%, (c) 0.18 wt% and (d) 0.27 wt%.

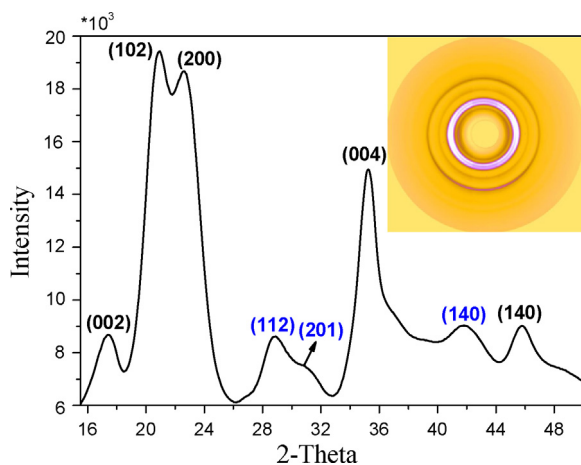


Fig. 8. 1D integrated WAXS curve and (inset) 2D WAXS pattern of jute nanofibrils aerogel.

4. Conclusions

In summary, we have successfully extracted the jute nanofibrils from the pristine jute fibers via the pretreatments by the sole NaOH solution, NaOH solution and DMSO solvent successively, respectively, followed by the TEMPO-oxidation and mechanical disintegration. The nanofibrils with a diameter ranging from 5 to 20 nm and a length of several micrometers using as the building blocks have been assembled into cellulose aerogels with controllably hierarchical 3D porous structures by a green approach of lyophilization. The result shows that the typical cellulose aerogels are coexistence of cellulose I and cellulose II, which has a great promise for many potential applications, such as pharmaceutical, liquid filtration, catalysts, bio-nanocomposites, and tissue engineering scaffolds.

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