Construction and Mechanism of Bacterial Cellulose With High Carbon Yield By a Stretching Orientation Method

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Research Article

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Abstract

Bacterial cellulose (BC) decomposes easily and the carbon residue rate is low. These factors critically restrict its application in fabricating cellulosic carbon materials. Therefore, in this paper, a simple and facile method to improve the BC carbon yield is proposed based on the stretching orientation of BC. By controlling the degree of BC deformation, the orientation and crystallinity of the BC can be adjusted, thereby sensitively affecting the graphitization degree and carbon yield of carbonized BC. Samples were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Raman scattering, and low-field nuclear magnetic resonance (LNMR). The results indicated that when the pre-stretched strain was 40%, the crystallinity and graphitization degree of BC improved, and the carbon yield increased significantly in comparison to that of untreated BC. Thus, a low-cost, facile, and environmentally friendly method of increasing the carbon yield of BC was developed in this study.

1. Introduction

Carbonized bacterial cellulose (CBC), which has the advantages of fibrous structure, 3D porous network, high specific surface area, and high porosity, has been widely studied and employed in diverse applications related to adsorption, catalysis, and electrochemistry (Chen et al. 2013; Ma et al. 2020). However, the molecular chains of cellulose are depolymerized, and the carbon is removed in the form of carbon monoxide, carbon dioxide, or aldehydes. Previous studies found that the total carbon yield was not close to the theoretical carbon yield of cellulose 44.4% (Byrne et al. 2014; Spörl et al. 2017). The low yield greatly limits the application of cellulose to attain carbon materials. Consequently, improving the carbon yield of cellulose is a core issue in the production of cellulosic carbon materials.

Presently, the commonly used methods of improving the carbon yield of cellulose include the use of a slow heating rate and carbonization additives (Brunner Paul et al. 1980; Wu et al. 2008; Li et al. 2019; Zahra et al. 2020; Gao et al. 2021). Furthermore, the addition of inorganic salts cellulose leads to an enhanced carbon yield (Frank et al. 2014). For example, Li et al. (Li et al. 2019) showed that the carbon yield of cellulose increased up to 31.4% when NH$_4$H$_2$PO$_4$ was used as a fire retardant. Collard et al. (Collard et al. 2015) observed that impregnated metals could catalyze rearrangement reactions and promote char formation form the cellulose. Ionic liquid-derived cellulose fibers were reported to achieve a carbon yield of 36% by weight (81.1% of the theoretical value); however, the mechanical properties of the carbon fibers deteriorated (Byrne et al. 2014). Although these methods can enhance the carbon yield, dangerous and expensive carbonizing auxiliaries and complex equipment greatly limit the large-scale production of cellulosic carbon materials for industrial applications. Therefore, a low-cost, facile, and environmentally friendly method is urgently needed to increase the carbon yield of cellulose.

In this study, we developed a facile method to improve the carbon yield of cellulose. BC hydrogel, which is an abundant, renewable and low-cost resource, was selected as the raw material. Highly aligned BC nanofibers were successfully fabricated using simple pre-stretching processes. The morphology, structure, and crystallinity of the samples were characterized and analyzed by scanning electron
microscopy (SEM), FTIR, X-ray diffraction (XRD), and LNMR. The orientation of the molecular chains improved because of the orderly arrangement of BC nanofibers along the direction of stretching. This improved the crystallinity, carbon yield, and graphitization degree of the pre-stretched BC. The method is environmentally friendly, inexpensive, and easy to scale owing to the use of a natural cellulose precursor and simple preparation process.

2. Experimental Section

2.1. Materials

The BC hydrogel with a cellulose content of 1 wt% was purchased from Hainan Yide Food Industry Co., Ltd., China. Instruments include tensile testing machine (CZ-8000A) and freeze-drying machine (XLG-10-50B).

2.2. Preparation of pre-stretched BC

A piece of uniform BC hydrogel was cut into a rectangular shape of size 50 mm × 20 mm × 4 mm. Before mechanical stretching, the strip of BC hydrogel was immersed in deionized water for 2 h to reduce the effect of cutting on the boundaries and restore the original microstructure. Then, the BC hydrogels were stretched at the 30 mm/min speed by a tensile testing machine (CZ-8000A, China) to strains of 10, 20, 30, 40 and 47% respectively (BC tensile fracture). When the mechanical force was removed, hydrogels were difficult to maintain a high alignment structure due to the elastic effect of the network. After mechanical stretching, the strip of stretched-BC hydrogel was fixed in both ends of the tablet to prevent shrinking. The samples were freeze-dried for 24 h to obtain highly aligned BC and original BC by using the unstretched sample as control. The resulting BC with pre-stretched strain 0, 10, 20, 30, 40 and 47% were designated as BC-0, BC-1, BC-2, BC-3, BC-4 and BC-5, respectively.

2.3. Preparation of CBC

Figure 1 showed the schematic diagram of carbonized pre-stretched BC. The BC hydrogel was mechanically stretched to form highly ordered nanofibers within BC. To examine the effect of the pre-stretching on the carbonized BC, the CBC was prepared at high temperature. At room temperature, the samples were heated to 400°C at a heating rate of 2°C/min and continuously carbonized them for 1 h, and then heated them to 500°C at a heating rate of 5°C/min and continuously carbonized them for 2 h. After cooling down, the carbonized pre-stretched BC were denoted by CBC-0, CBC-1, CBC-2, CBC-3, CBC-4, CBC-5, respectively. The carbon yield (%) was calculated from the following Eq. (1):

\[
\text{Carbonyield (\%)} = \frac{M_1}{M_0} \times 100\% \quad (1)
\]

Where \( M_0 \) represents the mass of BC before carbonization, \( M_1 \) represents the mass of BC after carbonization.

2.4. Characterization
The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, Hitachi SU8010) at a magnification of 10000.

Thermal degradation of the samples was analyzed by the thermogravimetric (TA Instruments, SDTQ600) in the N$_2$ atmosphere from 25 to 700°C at 10°C/min heating rate.

The FTIR spectra (FTIR, AVATAR370) of the samples was recorded for characterizing the functional group structure of the samples from the range of 525 cm$^{-1}$ to 4000 cm$^{-1}$ with a 4 cm$^{-1}$ resolution.

The X-ray diffraction (XRD, Rigaku Ultima IV) was applied to characterize the crystallinity and structure of the samples from a 2$\theta$ of 10° to 50° at a step size of 0.03°. The crystallinity index (CrI) was calculated using Jade software version 6.0 as the following Eq. (2) (Segal L et al. 1959):

$$\text{CrI (\%)} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

Where $I_{002}$ represents the maximum crystallization peak in the crystallization area, and $I_{am}$ represents the diffraction intensity of 2$\theta$ = 18° which corresponds to the amorphous part of cellulose.

$^1$H-LNMR spectra was recorded on a Low-field Nuclear Magnetic Resonance (LNMR PQ001, Suzhou Niumag) at a resonant frequency of 21.0 MHz, a magnet strength of 0.5 T, and a magnet temperature of 32°C.

The graphitization degree of the samples was characterized by Raman spectra (HORIBA Scientific LabRAM HR Evolution) in the excitation wavelength 514 nm over the range of 500 cm$^{-1}$ to 4000 cm$^{-1}$.

### 3. Results And Discussion

#### 3.1. Basic structure of the BC

BC hydrogel has high toughness, and this provides a structural basis for the stretching orientation of BC. Mechanical stretching was performed to test the maximum stretching strain of the BC hydrogel, as shown in Fig. 2a. The stress–strain curve of the BC hydrogel indicates that the stretching strength was up to 0.67 MPa and the breaking strain was 47%. TG and DTG analyses were performed to determine the weight loss and decomposition of BC during pyrolysis. As shown in Fig. 2b, the decomposition occurred in three stages. The mass loss in the first stage occurred at approximately 200°C, which is attributed to the evaporation of water in the BC. The weight loss in the second stage occurred at 200 ~ 400°C, which is mainly attributed to the decomposition of cellulose, indicating that the main pyrolysis degradation starts at approximately 280°C and is completed at approximately 390 °C. In this temperature range, the non-carbon elements H and O in the cellulose molecules are decomposed and volatilized; therefore, the rapid weight loss is as high as 88%. In the third stage, the weight loss occurred at 400 ~ 500°C, which might
correspond to the decomposition of the " residue " decomposed from the initial stage of heating and further decomposition into carbon and volatile matter.

As shown in Fig. 2c, the main absorption peaks of functional groups such as OH, -CH, -CH$_2$, and C-O-C, were removed or decreased during the carbonization process. After carbonization, the hydroxyl groups left the cellulose by dehydration, and the carbon remained on the cellulose skeleton. When the carbonization temperature reached 500°C, the BC weight loss rate was not obvious (Fig. 2b). Broido (Broido et al. 1975) also proposed a pyrolysis reaction model of cellulose and suggested that a low temperature was beneficial to the formation of carbon. Hence, the carbonization temperature was set to 500°C in this experiment.

3.2. Morphology and structure of pre-stretched BC

The morphology of the mechanically stretched BC structures was analyzed by SEM, as shown in Fig. 3. In contrast with the original BC sample (Fig. 3a), when the pre-stretched strain was only 10%, oriented BC nanofibers were initially observed in the local area of the BC (Fig. 3b). The network structure area of the aligned BC nanofibers gradually expanded as the pre-stretched strain increased. When the pre-stretched strain reached 40% (Fig. 3e), the BC nanofibers were highly aligned and had an obvious orientation along the stretching direction. When the pre-stretched strain reached 47%, the BC broke because of the increase in internal stress, and the BC nanofibers were fractured and shrank along the stretched direction. The SEM images demonstrate that in the range of 0 ~ 47% pre-stretched strain, single BC nanofibers gradually aggregated to form dense nanofiber bundles. The nanofiber bundles gradually formed a highly ordered structure, the orientation degree of the BC nanofibers increased, the porosity of the BC membrane decreased, and finally, the original random network structure disappeared.

FTIR spectroscopy was used to investigate the specific functional groups and structures of the samples. Fig. 4 shows the characteristic peaks of pre-stretched BC. The broad peak at 3350 cm$^{-1}$ indicates O-H stretching and bending vibrations of type I cellulose, at 2900 cm$^{-1}$ for the -CH stretching vibrations, at 1426 cm$^{-1}$ for -CH$_2$ stretching vibrations and 1050 cm$^{-1}$ for C-O-C stretching vibrations of the sugar ring (Ul-Islam et al. 2013; Fan et al. 2016). There was no variation between the infrared functional groups of the pre-stretched BC and original BC, indicating that mechanical stretching did not affect the basic BC functional group structure.

Figure 5b shows the crystallinity of the pre-stretched BC samples, which was calculated by using the Segal formula (Segal L et al. 1959). Compared to that of the original BC, the crystallinity of the pre-stretched BC samples increased with increasing pre-stretched strain. In particular, the pre-stretched strain was 40%, the crystal structure was highly aligned and had an obvious orientation; further, and the crystallinity reached the maximum value of 93.76%. When the pre-stretched strain exceeded 40%, the crystallinity of BC-5 was lower than that of BC-4.
The change in the crystallinity of pre-stretched BC was analyzed by SEM images. With the increase in pre-stretched strain along the stretching direction, the number of highly aligned BC nanofibers increased, and the distance between cellulose nanofibers shortened as the pre-stretched strain increased. These factors contributed to an increase in the bonding area between nanofibers. Notably, this increase in bonding area was (1) beneficial to the formation of hydrogen bonds between adjacent nanofibers and (2) improved the orientation degree and crystallinity of the cellulose molecular chains. However, the failure of BC entailed fractures and a less ordered orientation of the cellulose molecular chains, and the crystallinity decreased. In short, the crystallinity of BC can be improved within a suitable range of pre-stretched strain.

LNMR technology, also called time-domain NMR, can monitor the relaxation signal of hydrogen protons according to the characteristics of molecular motion (Chen et al. 2019). Hydrogen bonds and C-H bonds constrained the hydrogen protons, thereby reducing their degree of freedom and transverse relaxation time. Therefore, the strength of hydrogen bonds was evaluated by the variation in the transverse relaxation time of the pre-stretched BC.

The bond energy of the O-H bonds was higher than that of the C-H bonds; therefore, the transverse relaxation time of the hydrogen protons in the O-H bonds was shorter than that of the hydrogen protons in the C-H bonds. In Fig. 6a, the peaks corresponding to the shorter and longer transverse relaxation times represent the hydrogen protons of the O-H and the C-H bonds, respectively. As the pre-stretched strain increased from 0 to 47%, the transverse relaxation time of hydrogen protons was prolonged and then shortened, indicating that the hydrogen bonds first strengthened and then weakened.

The changes in the relaxation time of the hydrogen protons in the O-H bonds shown in Fig. 6b were integrated into a molecular structure diagram. The relaxation time of the O-H bonds were: 1.05 ms (BC-0), 0.64 ms (BC-4), 0.85 ms (BC-5) at pre-stretched strains ranging from 0–47%. The presence of hydroxyl groups was beneficial to the formation of intrachain and interchain hydrogen bonds. Hydrogen bonds retain the connection between adjacent cellulose chains, which play a key role in the deformation and failure behavior of cellulosic materials. Upon increasing pre-stretched strain to 40%, the number of hydrogen bonds between the molecular chains of cellulose increased. When the pre-stretched strain reached 47%, the failure of BC nanofibers caused the breaking of hydrogen bonds, and the relaxation time of hydrogen protons in the O-H bonds was close to that in the initial state. This result indicates that hydrogen bonds between the molecular chains of cellulose tended to form within the appropriate pre-stretched strain range. The cellulose molecules were connected by intermolecular hydrogen bonds to form a regular structure, which is consistent with the previously discussed crystallinity analysis results.

3.3. Morphology and structure of CBC

Figure 7 shows SEM images of carbonized pre-stretched BC samples. Compared to the uncarbonized BC samples shown in Fig. 3, it was found that the CBC still retained the 3D nanofiber network structure, ribbon-like interconnections, and highly ordered arrangement after carbonization at 500 °C. The porous structure of CBC was significantly smaller, the nanofibers were denser, and shrinkage was observed. This shrinkage is attributed to the removal of small molecules and non-carbon substances after carbonization.
Figure 8a shows the carbon yield of pre-stretched BC. It is notable that with the increase in pre-stretched strain from 0 to 40%, the carbon yield of pre-stretched BC gradually increased. In particular, when the BC pre-stretched strain reached 40%, the carbon yield increased to its highest value of 8.14%, a significantly increase of 89% over the original BC carbon yield of 4.31%. This result indicates that the carbon yield of BC could be increased within the appropriate range of pre-stretched strain. Moreover, based on the analyses of hydrogen bonds and crystallinity, changes in crystallinity and hydrogen bonds corresponded to variations in the carbon yield. These results indicates that carbon might be more likely to occur in the high-crystallinity cellulose material or the ordered region of cellulose, thereby promoting the carbon yield.

a to f are CBC-0, CBC-1, CBC-2, CBC-3, CBC-4 and CBC-5

The CBC samples were subjected to Raman spectroscopy. As shown in Fig. 8b, two prominent characteristic peaks namely the D peak and G peaks, were observed at 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\), respectively (Zhang et al. 2019). In general, the D peak is attributed to defects and a disordered of carbon structure, and the G peak is ascribed to the in-plane tangential vibrations of the graphitic structure (Xi et al. 2019; Cheng et al. 2020). The relative intensity ratio of the D and G peaks (\(\frac{I_D}{I_G}\)) can be applied to estimate the extent of defects and disorder degree of graphite, and a smaller \(\frac{I_D}{I_G}\) ratio indicates a higher graphitization degree in the carbon materials. Fig. 8b shows that the G peak of the sample gradually increases with increasing the pre-stretched strain. The \(\frac{I_D}{I_G}\) radio were 0.86 for CBC-0, 0.82 for CBC-1, 0.78 for CBC-2, 0.76 for CBC-3, 0.75 for CBC-4, and 0.77 for CBC-5. Specifically, the lowest radio obtained of for CBC-4 (\(\frac{I_D}{I_G} = 0.77\)) indicates that CBC-4 had few defects and an excellent graphitization degree. The graphitization degree of BC increased with increasing pre-stretched strain for the following reasons: The dense and aligned structure was conducive to the removal of BC defects, and a material with highly oriented molecules was favorable for graphitization in the high-temperature carbonization process.

4. Conclusions

In summary, this article proposes a facile, economical, and environmentally friendly method to increase the BC carbon yield by mechanical stretching, freeze-drying, and carbonization. It is notable that the prepared CBC showed an excellent graphitization degree without the addition of chemicals to the BC. Mechanical stretching affected the carbon yield and graphitization degree in the cellulose materials. The results indicate that the orientation and crystallinity of the pre-stretched cellulose were improved compared to those of the original cellulose, thereby improving the carbon yield and graphitization degree. Although the effect of the degree of crystallinity on the carbon yield of BC through carbonizing process remains to be further studied, this study provides a feasible strategy for improving the carbon yield of BC. It can not only reduce cost and protect the environment, but also provides basic data for the preparation of carbon materials.

Declarations
Conflict of interest

The authors declare that they have no conflict of interest.

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Figures

Figure 1

Schematic illustration for carbonized pre-stretched BC
Figure 2

a is stretching stress–strain curves of BC hydrogel, b is TG and DTG curves of the BC and c is FTIR spectra of BC-0 and CBC-0

Figure 3

SEM images of pre-stretched BC: a to f are BC-0, BC-1, BC-2, BC-3, BC-4, and BC-5
Figure 4
FTIR spectra of pre-stretched BC

a is XRD patterns and b is crystallinity of pre-stretched BC

Figure 5

Figure 6
a is LNMR spectra of pre-stretched BC and b is schematic diagram of hydrogen proton relaxation time in pre-stretched BC

Figure 7

SEM images of carbonized pre-stretched BC: a to f are CBC-0, CBC-1, CBC-2, CBC-3, CBC-4 and CBC-5
Figure 8

a Carbon yield of pre-stretched BC and b Raman patterns of the CBC