Enhanced Conductive Fiber of Multiwalled Carbon Nanotubes Templated Carbonization of Cellulose

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It has been reported that a conductivity of 100 S/cm of carbonized cellulose is obtained when the carbonization temperature is higher than 2000 °C. However, such high temperatures require expensive equipment and are energy consuming. In this study, carbonized multi-walled carbon nanotubes (MWCNTs)/cellulose composites fibers with a conductivity of 105 S/cm were prepared. They were prepared based on cellulose (in the carbonization temperature 1000 °C), a naturally abundant and low-cost material. The mechanism of improving electrical conductivity was studied. The MWCNTs played the role of a conductive bridge between the nano-carbonization cellulose blocks. As the template of cellulose graphitization, MWCNTs not only can improve the degree of cellulose graphitization but can also change the microstructure of carbonization cellulose from nano-spheres to sheets. This preparation method can be applied to other carbon materials to make highly conductive fibers or various conductive structure materials, such as a conductive film or an aerogel. This study broadens the application of cellulose in the field of electricity. The obtained conductive fibers have great potential in a range of applications, such as wearable electronics and low-cost energy storage.

Keywords: Cellulose; MWCNTs; Carbonized cellulose fibers; Conductivity

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INTRODUCTION

Conductive fibers have attracted considerable attention because of their potential applications in flexible solar cells, super capacitors, batteries, wearable electronics, micro-robotics, and epidermal and implantable medical devices (Chen *et al*. 2011; Lee *et al*. 2012; Cheng *et al*. 2013; Lee *et al*. 2013; Ren *et al.* 2013a,b).

Cellulose is a biocompatible, biodegradable, and renewable natural polymer from the most abundant green plants. In the field of ion exchange, catalysis, energy storage, carbon fiber fabrication, water purification, green electronics, and life sciences, cellulose is an important precursor to form carbonaceous materials (Phan *et al*. 2006; Sammons *et al*. 2013; Frank *et al*. 2014). Cellulose can be carbonized at high temperatures in a specific atmosphere (Lu *et al*. 2013). In previous studies, when the carbonization temperature is 1000 °C, the conductivity of carbonization cellulose is 30 S/cm (Rhim *et al*. 2010). Although the carbon structure is formed during such carbonization, the conductivity of carbonized cellulose material is low. Increasing the carbonization temperature enhances the conductivity of carbonized materials by improving the graphitization degree of the carbonized product (Wang *et al.* 2014). A conductivity of 100 S/cm is obtained when the carbonization temperature is higher than 2000 °C (Rhim *et al*. 2010). However, high temperatures require expensive equipment and energy consumption.

Carbon nanotubes (CNTs) exhibit excellent mechanical, electronic, optical, and magnetic properties due to their special structure (Iijima 1991; Dai 2002; Bianco *et al*. 2005; Jorio *et al*. 2008). Carbon nanotubes are single-walled (SWCNT) or multi-walled (MWCNT). The conductivity of SWCNTs is 10^6 S/cm, which is higher than that of copper.

The conductivity of MWCNTs is 3×10^4 S cm^{-1} (Collins and Avouris 2000; Li *et al*. 2007). Due to the different technology required for preparation, SWCNTs are more expensive than MWCNTs.

There have been many studies on the introduction of high conductivity of MWCNTs into cellulosic fibers (Zhang *et al*. 2019). Hamedi *et al.* (2014) used CNTs and nanocellulose to prepare conductive fiber and conductive nanopaper. Lee *et al.* (2016) prepared conductive fiber with the highest conductivity of 2.7 S/cm with 0.5 to 30% MWCNTs and 5% cellulose.

The present study aimed to facilitate the conductivity of carbonized cellulose materials. Carbonized MWCNTs/cellulose composites fibers were prepared, and high electrical conductivity of carbon nanotubes was introduced into carbonized cellulose fiber. MWCNTs act as a template to improve the degree of carbonization of carbonized cellulose.

EXPERIMENTAL

Materials

Cellulose powder was purchased from Inner Mongolia University (Hohhot, China). 1-allyl-3-methylimidazolium chloride (AmimCl) was purchased from Lanzhou Yulu Fine Chemical Co. Ltd., (Lanzhou, China). The MWCNTs were purchased from Nanjing XFNANO Co. (Nanjing, China). The average conductivity of the MWCNTs is 2.13×10^4 S/cm. The other reagents applied in this experiment were analytical grade.

Methods

Preparation for MWCNTs/cellulose fiber (Zhang et al. 2018)

First, 0.6 g cellulose was added to 8 mL AmimCl. The mixture was stirred for 2 h at 100 °C under nitrogen. The MWCNTs were added to the mixtures to final concentrations of 0 wt% and 10 wt%. The mixture was ground for 10 min and then ultrasonically stirred at 100 ℃ for 30 min in a vacuum. The MWCNTs/cellulose composite fibers were spun from the solution using dry-jet wet-spinning. The mixture was added to a vacuum oven for debubbling, heated to 100 °C, incubated for 15 min, and extruded into a distilled-water coagulation bath with nitrogen through a single-hole spinneret. Subsequently, the fibers were soaked in distilled water for 24 h and rinsed with distilled water at least 5 times to ensure removal of AmimCl. The fibers were dried for 48 h at 80 °C in a vacuum. During fiber drying, gentle tension was applied at the end of the fiber to improve fiber arrangement.

Preparation of highly conductive fiber

The MWCNTs/cellulose fiber was carbonized at a high temperature in an atmosphere furnace (Ar atmosphere). During the heating process, the temperature was increased from room temperature to 400 °C at a rate of 30 °C/h, then further increased to 1000 °C with at a rate of 200 °C/h. Afterwards, the samples were held at 1000 °C for 2 h. The MWCNTs/cellulose fibers were replaced with cellulose fibers, then the carbonized cellulose fibers were obtained.

Characterization techniques

Scanning electron microscopy (SEM) images of the fractured surfaces of the fibers were captured on a Hitachi S4800 microscope (Tokyo, Japan) operating at 10 kV. Before observation, the fibers were fractured after freezing in liquid nitrogen, and the fracture surface of the fibers was coated with a platinum layer. Electrical conductivity of the fibers was measured at room temperature on a Solartron 7081 precision voltmeter (London, England) with a four-probe method. The morphology and graphitization of fibers were performed by transmission electron microscopy (TEM) using an FEI Tecnai G2 20 device

(Hillsboro, America) with an accelerating voltage of 200 kV. The X-ray diffraction (XRD) was performed using XRD diffractometer (Omicron Nanotechnology, ESCA-14, Berlin, Germany). Raman spectra were recorded with a Horiba LabRAM HR 800 spectroscope (Paris, France) using a 532 nm laser.

RESULTS AND DISCUSSION

Morphology and Structure of Carbonized Fibers

Figure 1 shows the SEM images of the cross-sectional fracture of carbonized cellulose fiber and carbonized MWCNTs/cellulose fiber. In the carbonized cellulose fiber, many microspheres in the fiber were observed, which is a typical morphology of carbonized cellulose (Li *et al*. 2014). These nanospheres possess less percolation between building blocks, which leads to the lower conductivity of fiber. Additionally, the fiber was porous. The porous structure was mainly due to the volume and morphology change of cellulose during the carbonized process. In the carbonized MWCNTs/cellulose fiber, there were some sheets formed and MWCNTs in the fiber, instead of microspheres. The sheets formed possessed more percolation between building blocks compared to the microspheres, which was good for electronic transmission. In addition, the MWCNTs played the role of a conductive bridge between carbonization cellulose blocks. Meanwhile, vacancies and topological defects always appeared on MWCNTs. The coating layer of carbonized cellulose can repair the vacancies and topological defects on MWCNTs, which can further improve the conductivity. In addition, the fiber was more porous, potentially because of the different changes in volume and morphology of cellulose and MWCNTs during carbonization. This porous structure of the fibers offers potential applications in the field that need both high conductivity and high surface area.

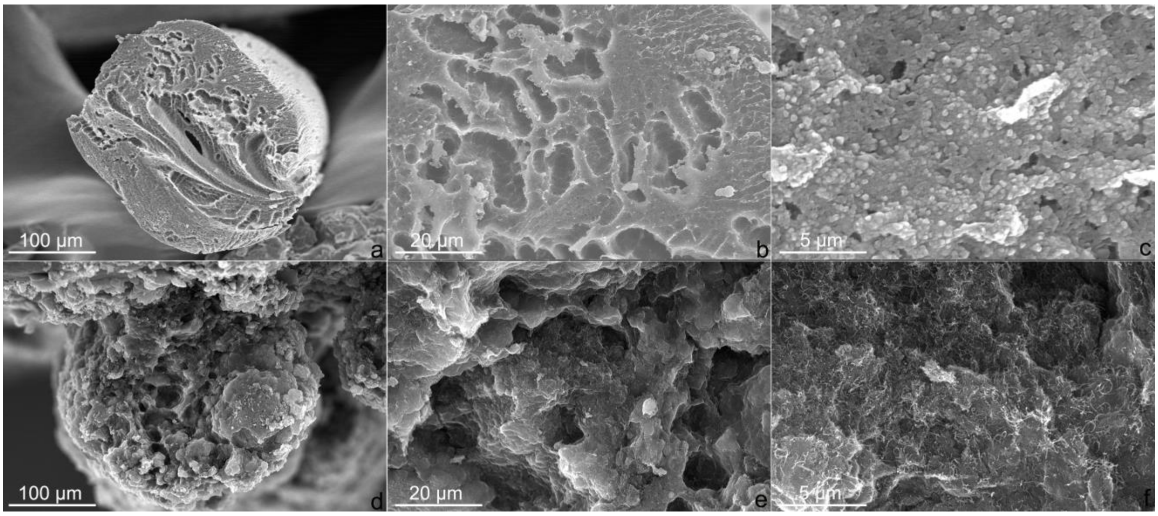

Fig. 1. SEM images of the cross-sectional fracture of carbonized cellulose fiber at (a) low resolution and (b, c) high resolution and the cross-sectional fracture of carbonized MWCNTs/cellulose fiber at (d) low resolution and (e, f) high resolution

Graphitization and Electrical Properties of Carbonization Fibers

The average conductivity of the carbonized MWCNTs/cellulose composites fiber and carbonized cellulose fiber was 105 S/cm and 27 S/cm (Table 1), respectively. With further characterization by TEM, as can be seen in the TEM images of carbonized MWCNTs/cellulose composites fiber, the MWCNTs were linked between carbonization cellulose blocks. Gaps between carbonization blocks can hinder electron transport. However, for the carbonized MWCNTs/cellulose composites fiber, MWCNTs were present spanning the gaps of carbonization blocks. The MWCNTs played the role of a conductive bridge between carbonization cellulose blocks, which facilitated the electron transportation between building blocks, leading to a high conductivity.

Table 1. Electrical Conductivity and I D/I G Ratio of Carbonized MWCNTs/cellulose Fiber and Carbonized Cellulose Fiber

	Electrical conductivity	I D/I G ratio
Carbonized MWCNTs/cellulose fiber	105 S/cm	0.89
Carbonized cellulose fiber	27 S/cm	0.98

Figure 2b shows that large amounts of lattices were homogeneously distributed in the carbonized MWCNTs/cellulose composites fiber. However, in the carbonized cellulose fiber (Fig. 2e), the carbonized product had a large amount of amorphous carbon with a small region of graphitic lattices. Mesquita *et al*. (2013) reported similar results for cellulose nanocrystals carbonization. This result indicated that the carbonized cellulose blocks in the carbonized MWCNTs/cellulose composites fiber had a higher degree of graphitization, which was confirmed by the fast Fourier transform (FFT) pattern. This effect could be caused by MWCNTs acting as a template for cellulose carbonization during the graphitization process, which enhanced the degree of graphitization of carbonized cellulose, leading to a high conductivity of the MWCNTs/cellulose composites fiber.

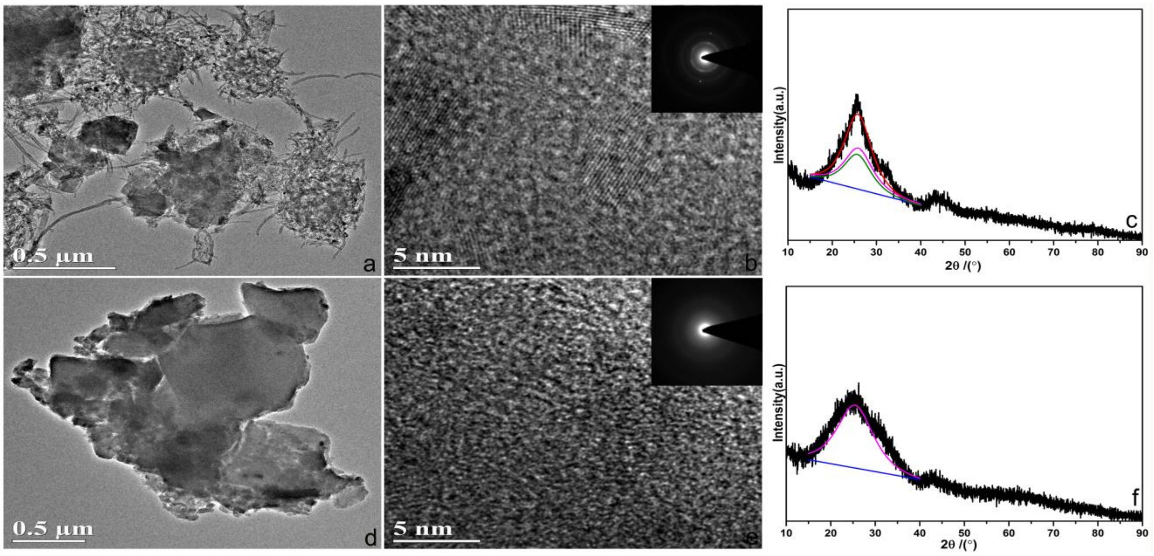

Fig. 2. The TEM images and FFT pattern of carbonized MWCNTs/cellulose composites fiber (a and b) and carbonized cellulose fiber (d and e). XRD analysis of carbonized MWCNTs/cellulose composites fiber and carbonized cellulose fiber (c and f)

The XRD studies of the carbonized MWCNTs/cellulose composites fiber and carbonized cellulose fiber were conducted to investigate the degree of graphitization of carbonized cellulose (Fig. 2c and 2f). The degree of graphitization can be characterized by the interplanar distance (d_{002}) of the carbonized materials. The degree of graphitization increased with a decrease in the crystal plane spacing. The interplanar spacing of the amorphous carbon and the ideal graphite crystal were 0.3440 nm and 0.3354 nm, respectively. The graphitization degree of carbonized materials increases with the decrease of crystal plane spacing and the increase of diffraction angle. This relationship is demonstrated by Eq. 1 (Bragg’s equation),

$$d_{002} = \lambda / 2 \sin \theta \qquad (1)$$

where d_{002} is the interplanar distance, λ is the wavelength of the incident wave, and θ is the diffraction angle of crystal plane. The XRD studies of the carbonized cellulose fiber showed that the fiber exhibited a diffraction peak at 25.46°. The X-ray diffraction of carbonized MWCNTs/cellulose fiber was deconvoluted to 25.9° and 25.71°, which were characteristic of the crystal structure of carbon nanotube and carbonization cellulose, respectively. The diffraction peak of carbonization cellulose moved from 25.46° to 25.71°, which indicated that the graphitization degree of the carbonization cellulose was increased. This effect could be caused by the MWCNTs, which may have promoted the graphitization of cellulose. Figure 3 shows the Raman spectrum of carbonized MWCNTs/cellulose composites fiber and carbonized cellulose fiber. The Raman spectra of carbon materials in the range of 800 to 2000 cm^{-1} are mainly composed of D-bands and G-bands. The D-band at 1337 cm^{-1} was caused by defects and curvature in the nanotube lattice of nanotubes. The G-band at 1577 cm^{-1} occurred because of the plane vibration of the C-C bond (Baskaran *et al*. 2005). The integral area ratio of the D-bands and G-bands (I D/I G) can be used to evaluate the degree of structural defects in carbon materials (Li *et al*. 2009). As shown in Table 1, the I D/I G ratio of carbonized cellulose fiber was 0.98, which was higher than that of a carbonized MWCNTs/cellulose composites fiber (0.89). This indicated that the degree of graphitization for carbonized MWCNTs/cellulose composites fiber was higher than that of carbonized cellulose fiber.

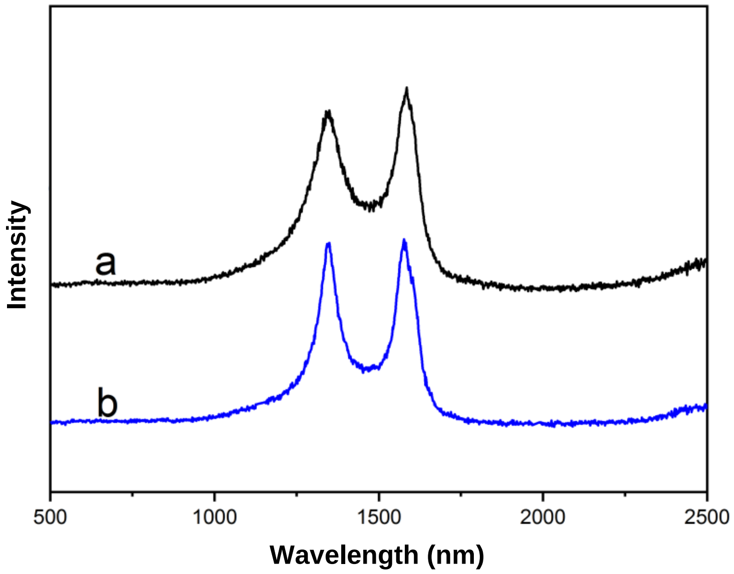

Fig. 3. Raman spectra of (a) carbonized MWCNTs/cellulose composites fiber and (b) carbonized cellulose fiber

CONCLUSIONS

1. Carbonized MWCNTs/cellulose composites fibers were prepared. The conductivity of the fiber was 105 S/cm.
2. In the SEM images of the cross-sectional fracture of carbonized MWCNTs/cellulose fiber, there were both sheets and MWCNTs, instead of microspheres in carbonized cellulose fiber. Also, the fiber was more porous.
3. The sheets formed of carbonized MWCNTs/cellulose fiber possessed more percolation between building blocks compared to the microspheres in carbonized cellulose fiber, which was good for electronic transmission. Meanwhile, the MWCNTs played the role of a conductive bridge between carbonization cellulose blocks.

4. With further characterization by TEM, the carbonization cellulose blocks in the carbonized MWCNTs/cellulose composites fiber had a higher degree of graphitization as compared to the carbonized cellulose fiber. This was confirmed by the FFT pattern, XRD, and Raman spectrum.

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REFERENCES CITED

Baskaran, D., Mays, J. W., and Bratcher, M. S. (2005). "Noncovalent and nonspecific molecular interactions of polymers with multiwalled carbon nanotubes," *Chem. Mater.* 17(13), 3389-3397. DOI: 10.1021/cm047866e

Bianco, A., Kostarelos, K., Partidos, C. D., and Prato, M. (2005). "Biomedical applications of functionalised carbon nanotubes," *Chem. Commun.* 7(5), 571-577. DOI: 10.1039/b410943k

Chen, T., Wang, S. T., Yang, Z. B., Feng, Q. Y., Sun, X. M., Li, L., Wang, Z. S., and Peng, H. S. (2011). "Flexible, light-weight, ultrastrong, and semiconductive carbon nanotube fiber for a highly efficient solar cell," *Angew. Chem. Int. Ed.* 50(8), 1815-1824. DOI: 10.1002/anie.201003870

Cheng, H. H., Liu, J., Zhao, Y., Hu, C. G., Zhang, Z. P., Chen, N., Jiang, L., and Qu, L. T. (2013). "Graphene fibers with predetermined deformation as moisture-triggered actuators and robots," *Angew. Chem. Int. Ed.* 52(40), 10482-10486. DOI: 10.1002/anie.201304358

Collins, P. G., and Avouris, P. (2000). "Nanotubes for electronics," *Sci. Am.* 283(6), 62-69. DOI: 10.1038/scientificamerican1200-62

Dai, H. (2002). "Carbon nanotubes: Synthesis, integration, and properties," *Accounts Chem. Res.* 35(12), 1035-1044. DOI: 10.1021/ar0101640

Frank, E., Steudle, L. M., Ingildeev, D., Spörl, J. M., and Buchmeiser, M. R. (2014). "Carbon fibers: Precursor systems, processing, structure, and properties," *Angew. Chem. Int. Ed.* 53(21), 5262-5298. DOI: 10.1002/anie.201306129

Hamedi, M. M., Hajian, A., Fall, A. B. Hakansson, K., Salajkova, M., Lundell, F., Wagberg, L., and Berglund, L. A. (2014). "Highly conduction, strong nanocomposites based on nanocellulose-assisted aqueous dispersion of CNTs," *ACS Nano* 8(3), 2467-2476. DOI: 10.1021/nn4060368

Iijima, S. (1991). "Helical microtubules of graphitic carbon," *Nature* 354, 56-58. DOI: 10.1038/354056a0

Jorio, A., Dresselhaus, G., and Dresselhaus, M. S. (2008). *Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications*, Springer-Verlag Berlin Heidelberg, Berlin, Germany.

Lee, J. A., Shin, M. K., Kim, S. H., Cho, H. U., Spinks, G. M., Wallace, G. G., Lima, M. D., Lepró, X., Kozlov, M. E., Baughman, R. H., *et al.* (2013). "Ultrafast charge and discharge biscrolled yarn supercapacitors for textiles and microdevices," *Nat. Commun.* 4, 1970-1978. DOI: 10.1038/ncomms2970

Lee, M., Chen, C. Y., Wang, S., Cha, S. N., Park, Y. J., Kim, J. M., Chou, L. J., and Wang, Z. L. (2012). "A hybrid piezoelectric structure for wearable nanogenerators," *Adv. Mater.* 24(13), 1759-1764. DOI: 10.1002/adma.201200150

Lee, T.-W., Han, M.-J., Lee, S. -E., and Jeong, Y. G. (2016). "Electrically conductive and strong cellulose-based composite fibers reinforced with multiwalled carbon nanotube containing multiple hydrogen bonding moiety," *Composites Science and Technology* 123, 57-64. DOI: 10.1016/j. compscitech.2015.12.006

Li, L., Meng, L., Zhang, X., Fu, C., and Lu, Q. (2009). "The ionic liquid-associated synthesis of a cellulose/SWCNT complex and its remarkable biocompatibility," *J. Mater. Chem.* 19(22), 3612-3617. DOI: 10.1039/b823322e

Li, Q. W., Li, Y., Zhang, X. F., Chikkannaavar, S. B., Zhao, Y. H., Dangelewicz, A. M., Zheng, L. X., Doorn, S. K., Jia, Q. X., Peterson, D. E., *et al.* (2007). "Structure-dependent electrical properties of carbon nanotube fibers," *Adv. Mater.* 19(20), 3358-3363. DOI: 10.1002/adma.200602966

Li, Y., Zhu, H., Shen, F., Wan, J., Han, X., Dai, J., Dai, H., and Hu, L. (2014). "Highly conductive microfiber of graphene oxide templated carbonization of nanofibrillated cellulose," *Adv. Funct. Mater.* 24(46), 7366-7372. DOI: 10.1002/adfm.201402129

Lu, X. W., Pellechia, P. J., Flora, J. R. V., and Berge, N. D. (2013). "Influence of reaction time and temperature on product formation and characteristics associated with the hydrothermal carbonization of cellulose," *Bioresource Technol.* 138, 180-190. DOI: 10.1016/j.biortech.2013.03.163

Mesquita, J. P., Reis, L. S., Purceno, A. D., Donnici, C. L., Lago, R. M., and Pereira, F. V. (2013). "Carbon-clay composite obtained from the decomposition of cellulose nanocrystals on the surface of expanded vermiculite," *J. Chem. Technol. Biot.* 88(6), 1130-1135. DOI: 10.1002/jctb.3952

Phan, N. H., Rio, S., Faur, C., Coq, L. L., Cloirec, P. L., and Nguyen, T. H. (2006). "Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications," *Carbon* 44(12), 2569-2577. DOI: 10.1016/j.carbon.2006.05.048

Ren, J., Bai, W., Guan, G., Zhang, Y., and Peng, H. (2013a). "Flexible and weaveable capacitor wire based on a carbon nanocomposite fiber," *Adv. Mater.* 25(41), 5965-5970. DOI: 10.1002/adma.201302498

Ren, J., Li, L., Chen, C., Chen, X. L., Cai, Z. B., Qiu, L. B., Wang, Y. G., Zhu, X. R., and Peng, H. S. (2013b). "Twisting carbon nanotube fibers for both wire-shaped micro-supercapacitor and micro-battery," *Adv. Mater.* 25(8), 1155-1162. DOI: 10.1002/adma.201203445

Rhim, Y. R., Zhang, D., Fairbrother, D. H., Wepasnick, K. A., Livi, K. J., Bodnar, R. J., and Nagle, D. C. (2010). "Changes in electrical and microstructural properties of microcrystalline cellulose as function of carbonization temperature," *Carbon* 48(4), 1012-1024. DOI: 10.1016/j.carbon.2009.11.020

Sammons, R. J., Collier, J. R., Rials, T. G., Spruiell, J. E., and Petrovan, S. (2013). "Orientation of carbon fiber precursors from 1-butyl-3-metylimidazoluim chloride cellulose solutions," *J. Appl. Polym. Sci.* 128(2), 951-957. DOI: 10.1002/APP.37906

Wang, L. P., Schütz, C., German, S. A., and Titirici, M. M. (2014). "Carbon aerogel from bacterial nanocellulose as anodes for lithium ion batteries," *RSC Adv.* 4(34), 17549-17554. DOI: 10.1039/C3RA47853J

Zhang, H., Dou, C., Pal, L., and Hubbe, M. A. (2019). "Review of electrically conductive composites and films containing cellulosic fibers or nanocellulose," *BioResources* 14(3), 7494-7542.

Zhang, S., Zhang, F., Pan, Y., Jin, L., Liu, B., Mao, Y., and Huang, J. (2018). "Multiwall-carbon-nanotube/cellulose composite fibers with enhanced mechanical and electrical properties by cellulose grafting," *RSC Adv.* 8(11), 5678-5684. DOI: 10.1039/c7ra11304h

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