Synthetic Metals 206 (2015) 115–119

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Synthesis of twisted ribbon-like carbon, carbon microtubes and carbon rod from mercerized cotton fiber

Jin Won Yu [a,b], Yong-Mun Choi [a], Seung Min Kim [a], Jae-Kwan Lee [b], Nam-Ho You [a], Munju Goh [a,*]

[a] Carbon Composite Materials Research Center, Institute of Advanced Composites Materials, Korea Institute of Science and Technology (KIST), Chudong-ro 92, Bongdong-eup, Wanju-gun, Jeollabuk-do 565-905, Republic of Korea
[b] Department of Carbon Materials, Chosun University, Gwangju 561-756, Republic of Korea

ARTICLE INFO

Article history:
Received 23 April 2015
Received in revised form 6 May 2015
Accepted 14 May 2015
Available online 23 May 2015

Keywords:
Carbon Microtube
Microporous materials
Nanostructures
Structural materials
Electron energy loss spectroscopy (EELS)
Surfaces

ABSTRACT

In this study, we used mercerized cotton fibers as carbonization precursors to fabricate carbon materials having different structures. The morphologies of the synthesized carbon materials were successfully controlled by varying the mercerization time. Twisted ribbon-like carbon structures, carbon microtubes, and carbon rods could be synthesized by carbonizing non-mercerized cotton fibers, cotton fibers mercerized for 40 min, and fully mercerized cotton fibers (*i.e.*, fibers mercerized for 60 min), respectively. Interestingly, along with the morphological changes, the specific surface areas of these carbon materials were also changed to 203.7, 726, and 276.7 m^2/g, respectively. This method of fabricating carbon materials should lead to the synthesis of novel, structured carbon materials with various functionalities as it exploits both the natural structure of cotton fibers and artificial chemical processes.

1. Introduction

Many of the unique and exquisite hierarchical structures found in nature are still difficult to synthesize artificially. Cellulose, which is the most abundant material in the biosphere, is the primary constituent of wood and plants. It has a unique nanostructure that allows it to perform important life-sustaining functions. Natural structures such as that of cellulose have provided compelling insights and are proving to be of great use in various applications. For example, highly porous carbon materials were successfully manufactured from porous coconut shells [1]. Further, a metal microcoil was fabricated using a helically structured vascular plant [2].

Cotton fibers (CtFs) consist of a cuticle, a primary wall, a secondary wall, and a lumen. Most of the cellulose exists in the primary and secondary walls. Many hundreds of celluloses gather and form microfibrils. The primary and secondary walls of CtF consist of a number of microfibrils wrapped around the fiber axis. The lumen, which is located in the center of the secondary wall, is a hollow channel that carries nutrients for growth [3]. A cotton fiber has natural twists along its entire length; these are called convolutions. Interestingly, the shapes of the lumen and the convolutions are chemically changeable by treating the fibers with a high-concentration aqueous sodium hydroxide solution. This process is called mercerization [4]. Mercerization has been employed in the cotton industry to prevent cotton fabric from shrinking and to give it a lustrous appearance [5].

Recently, cellulose was used as a carbonization precursor after being heat treated at a high temperature [6,7]. If one could use mercerized CtF as a carbonization precursor while ensuring that they retain their morphology even after their conversion to a carbon material, it would become possible to use them to synthesize microtube-like carbon materials. It is likely that we could easily produce carbon microtubes by using exploiting both the natural structure of CtF and chemical modification methods.

2. Experiment

Cotton yarn was purchased from a commercial source, and CtF was prepared from the yarn. Mercerization was performed by dipping the CtF into a 15 wt% aqueous NaOH solution. The CtF were soaked at room temperature for 10, 20, 40, or 60 min, and washed with the deionized (DI) water. The mercerized CtF (M-CtF) subjected to the alkaline treatment for 10, 20, 40, and 60 min are referred to as M-CtF(10), M-CtF(20), M-CtF(40), and M-CtF(60), respectively. Next, samples of the M-CtFs were neutralized by

---

[*] Corresponding author. Tel.: +82 63 219 8141; fax.: +82 63 219 8139.
E-mail address: goh@kist.re.kr (M. Goh).

http://dx.doi.org/10.1016/j.synthmet.2015.05.017

being dipped into a 5 wt% aqueous HCl solution. The neutralized M-CtF were washed with DI water and dried for 12 h at room temperature. The carbonization of the CtF and M-CtF samples was performed using an electric furnace (KDF75, Denken Co., Ltd., Japan). The CtF and M-CtF samples were heated to 800 °C at a heating rate of 10 °C/min and then were kept at 800 °C for 1 h under flowing argon gas. After the completion of the carbonization process, the electric furnace was allowed to cool to room temperature, and the samples were removed from the furnace. The carbonized CtF and M-CtF samples are referred to as C-CtF and CM-CtF, respectively. The morphologies of M-CtF and CM-CtF were observed using field-emission scanning electron microscopy (FESEM) (Nova NanoSEM 450, FEI Co., USA). The crystallinities of the porous carbon materials were investigated using transmission electron microscopy (TEM) (Tecnai G2 F20, FEI Co., USA). An elemental analyzer (vario MICRO cube, Elementar Analysensysteme, Germany) was used to analyze the changes in the elemental contents of the CM-CtF samples. The porosities of the samples were determined through N_2 adsorption analyses performed at 77 K using a volumetric adsorption measurement system (BELSORP-max, BEL Japan, Inc., Japan); the system was pre-evacuated for 6 h at 573 K and 10^{-4} Pa. The electrical conductivities of the samples were measured using the four-point probe method (FPP-RS8, Dasol Engineering Co., Ltd., Korea). The distance between the electrodes was 2 cm, and each sample type was tested 30 times.

3. Results and discussion

The changes in the morphology of the CtF during mercerization were examined using SEM (Fig. 1). Before mercerization, the CtF exhibited a flat and twisted, ribbon-like structure, as can be seen in Fig. 1a; as noted previously, such structures are called convolutions. The cross section has a distorted, bean-like shape. Further, crushed lumens can be seen between the sandwiched secondary walls in the inset of Fig. 1a. During the mercerization process, the most significant shape changes were seen in the cross sections of the CtF. Further, convolutions were formed, the lengths of the CtF decreased, and their diameters increased. With an increase in the mercerization time, the twisted convolutions gradually disappeared. The cross sections deformed and became oval shaped after mercerization for 10 min (see Fig. 1b). Moreover, the hollow-channeled lumens also became oval. After mercerization for 40 min, the oval-shaped cross sections became almost round, and the convolutions became disentangled (see Fig. 1c). Further, the structures of the squashed lumens also changed, and the lumens became round. Finally, in M-CtF(60), which were mercerized for 60 min, the hollow channel shrank and disappeared (Fig. 1d). As a result, the ribbon-like CtF transformed gradually into oval and round tubes, eventually becoming round rods, during the mercerization process.

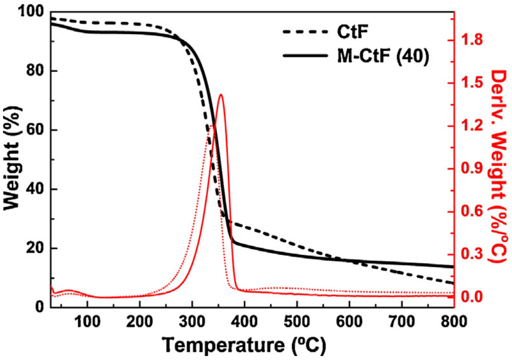

Fig. 2. TGA and DTA curves of CtF and M-CtF(40).

Thermogravimetric/differential thermal analyses (TG–DTA) of the CtF and M-CtF samples were performed using a TA Q50 system (TA Instruments, USA) under a flow of nitrogen gas at a heating rate of 5 °C/min. Fig. 2 shows the TG and DTA curves of CtF and M-CtF (40). All the samples exhibited a small degree of weight loss in the low-temperature range, that is, for temperatures below 110 °C; this was owing to the evaporation of the water in the samples. During the heating process, all samples exhibited primary decomposition peaks at 200–400 °C, as can be seen from the DTA curves. However, there was a difference in the maximum decomposition temperatures of CtF and M-CtF(40), which were 335 and 355 °C, respectively. This difference may be related to the differences in the crystallinities or crystal structures of the CtF and M-CtF samples. It is rationalized that sodium hydroxide breaks the hydrogen bonds between the different cellulose types, causing the crystalline part of cellulose to swell during the mercerization process. After the completion of the mercerization process, the lattice of the crystal structure of the CtF transformed from the cellulose-I type to the cellulose-II type [8]. X-ray diffraction (XRD)

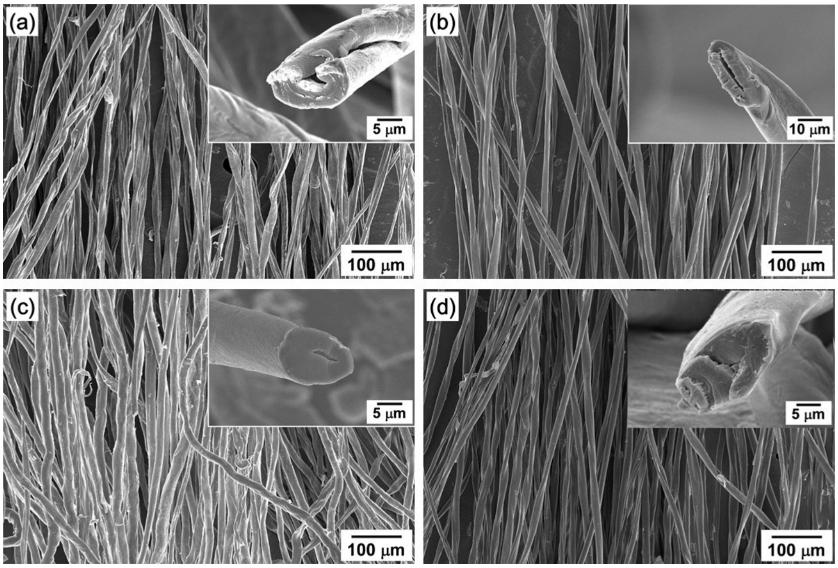

Fig. 1. SEM images of the (a) CtF and (b–d) M-CtF samples: (b) mercerization time of 10 min; (c) mercerization time of 40 min; and (d) mercerization time of 60 min.