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Carbon Nanofibers Prepared by the Carbonization of Self-Assembled Cellulose Nanocrystals

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Abstract: In this study, we fabricated fibrous carbon materials by using self-assembled cellulose nanocrystal fibers as the precursor. Cellulose nanocrystals at low concentrations, which were isolated from commercial microcystallline cellulose by a sulfuric acid treatment, were self-assembled into fibrous cellulose particles during the frozen process. After a stabilization process, the cellulose nanocrystal fibers were carbonized at 1,000 ºC. Field-emission scanning electron microscopy, Raman spectroscopy, and wide-angle X-ray diffraction analysis were used to confirm the formation of amorphous carbon fibers from the cellulose nanocrystal fibers.

Keywords: cellulose nanocrystals, self-assembly, carbonization, carbon fibers.

Introduction

Fibrous carbon materials have attracted considerable attention from both academic and engineering communities and have been contemplated for use in numerous applications.[1,2] Since the 1960s, carbon fibers have been developed from various carbon precursors prepared by the melt-spinning process of polyacrylonitrile, isotropic and anisotropic mesophase pitches, phenolic resins, and cellulose derivatives. Over the past decade, various fabrication methods, such as chemical vapor deposition and arc-discharge techniques, have been employed to produce fibrous carbon materials with diverse structures and properties, such as carbon nanotubes.[3,4] More recently, the use of electrospinning technique has been explored to prepare nanofibrous carbon materials by producing nanofibers, which are subsequently subjected to the carbonization process.[2]

Cellulose, the most abundant renewable polymer on the earth, can be converted to highly crystalline nanostructures, termed as cellulose nanocrystals (CNs). CNs are obtained by cleaving cellulose fibrils along the transverse direction and by disrupting amorphous regions under controlled acid hydrolysis. The cellulose fibrils used for obtaining the CNs can be obtained from various sources, such as cotton,[5,6] wood,[7,8] grass,[9] tunicates,[10,11] and bacteria.[12] The width and length of the CNs are reported in the range 5-20 nm and 100 nm-several micrometers, respectively. The dimensions of the CNs vary according to the origin of cellulose and acid hydrolysis conditions, such as time and temperature. Because of their exceptionally high specific strength and modulus, low density, chemical tunability, renewability, and low cost, CN has been mainly investigated for their application as reinforcement nanofillers in polymer nanocomposites.[13-16] Recently, new attempts have been undertaken to extend the applications of CNs by fabricating microstructured CN foams using the freeze drying technique.[17,18] During the freezing of the CN solution, after being expelled from growing ice crystals, suspended CNs can become organized into ordered structures at the spaces between the ice crystals. The subsequent removal of the solvent from the frozen sample under vacuum allows for the formation of the porous CN form. Dash *et al.* prepared CN foams with a uniform layered structure and investigated the relationship between the freezing rate and the pore morphologies of the CN architectures.[17] Han *et al.* reported the fabrication of aligned layers and oriented ultrafine fibers from aqueous suspensions of CNs with various concentrations, particle sizes, surface charges, and crystal structures.[18] They confirmed the formation of self-assembled fibers at low concentrations, *i.e.*, below 0.05 wt% *via* strong hydrogen bonds and van der Waals forces.

In the present study, fibrous carbon materials were obtained from self-assembled CN fiber precursors. CNs with a length of 190±24 nm and a width of 14±2 nm were prepared from commercial microcystallline cellulose (MCC) by sulfuric acid treatment. Cellulosic fibers with diameters ranging from dozens of nanometers to sub-micrometers were formed by self-assembly from low concentration aqueous solutions of CNs during freeze drying. The CN fibers were carbonized at 1,000 ºC after a stabilization process. Field-emission scanning electron microscopy (FESEM), Raman spectroscopy, and wide-angle X-ray diffraction (XRD) analysis were used to confirm the formation of amorphous carbon fibers from the CN fibers. This novel

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approach we have proposed to fabricate carbon fibers may provide further opportunities extend the applications of CNs.

Experimental

Materials. MCC powder was purchased from Sigma Aldrich. Sulfuric acid (DC Chemical Co. Ltd., Korea, 95%) was used to produce the CNs.

Preparation of CNs. Ten grams of MCC powder was hydrolyzed using 64 wt% sulfuric acid (*i.e.*, 8.75 mL of sulfuric acid solution per gram of the pulp) at 45 °C for 1 h with continuous stirring. After diluting with decuple deionized water, the resulting CNs were collected and purified by repeated centrifugation (at 9,500 rpm for 30 min) and dialysis for seven days. The CN suspension was dispersed by unltrasonication for one hour at ambient temperature using an ultrasonic generator (Kyungill Ultrasonic Co., Korea) with a nominal frequency of 28 kHz and a power of 600 W. The concentration of the resulting CN suspension was about 0.7 wt%. The obtained CN aqueous suspensions were diluted to 4 concentration levels (*i.e.*, 0.1, 0.05, 0.03, and 0.01 wt%) and lyophilized to obtain self-assembled CNs.

Carbonization of CNs. The diluted CN suspensions were frozen in a freezer at -16 °C for a day to provide enough time for self-assembly to occur during the freezing process. The freeze-dried CN samples with concentrations of 0.05 and 0.01 wt% were initially stabilized using the following heating schedules in a tubular furnace under an ambience of air -5 °C min^{-1} to 100 °C, 2 h dwell; 1 °C min^{-1} to 150 °C, 2 h dwell. The stabilized CN samples were carbonized by heat treatment at 1,000 °C for 180 in nitrogen atmosphere. The temperature was achieved by heating at the rate of 1 °C min^{-1}.

Characterization. Transmission electron microscopy (TEM, CM200, Philips, Netherlands) was used to examine the morphology of the CNs. A single drop of the diluted suspension of CNs was placed onto a carbon coated grid and stained by placing one drop of a 2 wt% solution of uranyl acetate onto a carbon coated grid directly. Thermogravimetric analysis (TGA) was carried out from room temperature to 800 °C at a heating rate of 10 °C min^{-1} with TA instruments Q50 under an Ar atmosphere. The morphology of the prepared materials was examined by FESEM (S-4200, Hitachi, Japan) at an accelerating voltage of 15 kV after the samples were precoated with a homogeneous Pt layer through ion sputtering (E-1030, Hitachi, Japan). XRD (Rigaku DMAX 2500) analysis of the carbon material was performed using CuK_α incident X-radiation (wavelength λ=0.154 nm) from a generator operated at 40 kV and 100 mA. Raman spectroscopy (Jobin Yvon, excitation wavelength=514 nm, France) was used to determine the structure of carbon.

Results and Discussion

Cellulose is a linear semicrystalline polymer consisting of β-1,4-linked *d*-glucopyranose units. In nature, cellulose consists of alternating highly ordered crystalline regions foamed by intra and intermolecular hydrogen bonds and less ordered amorphous regions.[19] CNs can be prepared by breaking down cellulose into elementary crystalline domains by removing the amorphous cellulose segments through acid hydrolysis. In the present study, TEM analysis was used to confirm the formation of CNs by sulfuric acid hydrolysis. As shown in Figure 1, the TEM image of the CNs sample exhibited the presence of rod-like structures with an average length of 190±24 nm and an average width of 14±2 nm, which is similar to the dimensions of CNs reported elsewhere.[20,21]

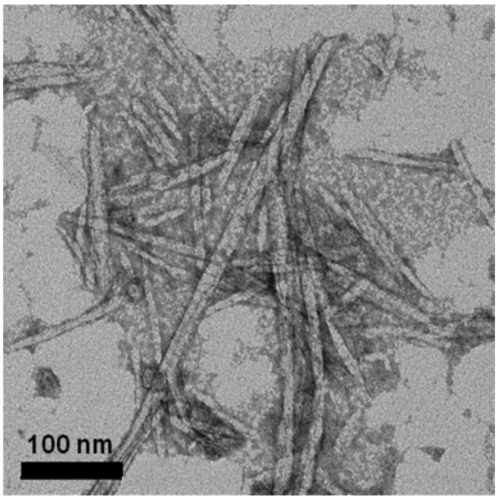

Figure 1. TEM image of the CNs prepared by acid hydrolysis.

Because of the inclusion of negatively charged sulfate groups originating from the sulfuric acid treatment,[22] the formation of hydrogen bonding between the individual CNs was limited. Hence, the CN dispersion was stable and homogeneous in an aqueous solution. Therefore, during the freezing process, the suspended CNs could be organized into ordered structures, which after being rejected from the growing ice crystals, moved to the spaces between the ice crystals. And then the CNs rejected from the growing ice crystals could be rearranged and self-assembled into ordered structures through the hydrogen bonds and van der Waals forces.[17,18] The morphologies of the self-assembled CNs obtained by freeze-drying of CN suspensions of different concentrations were observed using FESEM analysis (Figure 2). When the concentration of the CN solution was decreased from 0.1 to 0.01 wt%, the morphology of the materials changed from a layer structure consisting of perforated sheets to nanofiber structures. From 0.1 wt% CN solution, a porous structure with ordered layers was obtained. In the material obtained from 0.05 wt% CN solution, layers and fibers were observed to coexist. Further, solutions with CN concentrations below 0.03 wt% led to the formation of fibrous structures in which the fiber diameter decreased from submicron to hundreds of

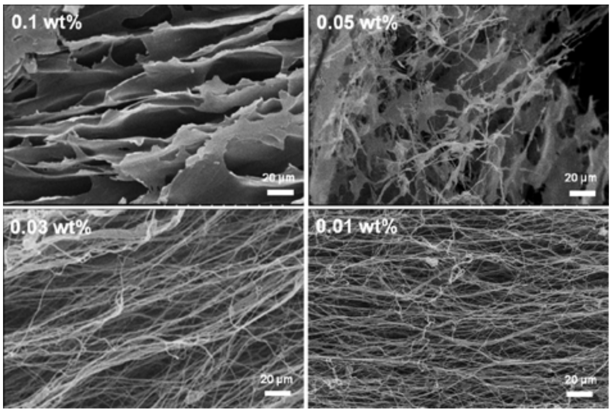

Figure 2. FESEM images of the freeze-dried CNs obtained from suspensions with concentrations 0.1 wt%, 0. 05 wt%, 0.03 wt%, and 0.01 wt%.

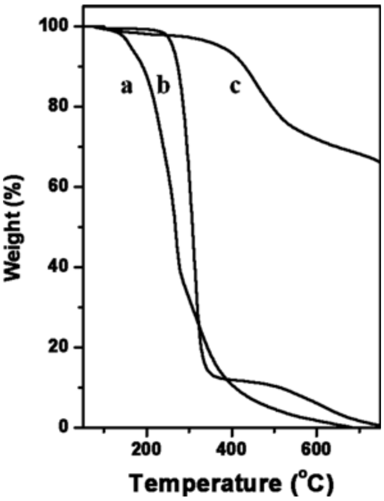

Figure 3. Results of TGA (10 °C/min in air) of (a) CNs, (b) commercial MCC and (c) CNs after stabilization at 150 °C in air for 120 min.

nanometer with decrease in concentration. From our observations, we assume that CNs can form fibrous structures by self-assembly during the initial stages of the freezing process, and sheet-like structures are subsequently formed by merging of adjacent fibers. Therefore, when solutions with low concentrations were used, fibers could have remained in the product because of the excessively large space between fibers, which reduces the probability of neighboring fibers encountering each other. Compared to the results of similar research by Han *et al.*,[18] the morphologies of fibers and the concentrations required to fabricate fibers are slightly different in the present work. This is mainly because of the differences in the dimensions of the CNs and the freezing conditions.

The CN fibers prepared by freeze-drying of the CN suspension were carbonized at 1,000 °C after stabilization. To synthesize carbonaceous materials from cellulose substances with improved yield and properties, it is important to stabilize the precursor by dehydration and by the formation of double bonds and conjugated double bonds at a certain temperature in an oxidative atmosphere.[23] For optimizing the stabilization conditions, the thermal properties of the CNs were investigated using TGA. In case of MCC (Figure 3(b)), a weight loss between 220 and 360 °C was observed, which is similar to that observed in the case of native cellulose, as reported elsewhere.[23] However, as shown in Figure 3(a), the thermal degradation of CNs was initiated at a lower temperature (around 125 °C) because of the introduction of sulfate groups onto the CNs by sulfuric acid treatment, which decreases the decomposition temperature of cellulose.[24,25] Therefore, the stabilization of CNs was carried out at 150 °C in this study. After stabilization in air, the stabilized CNs showed seldom weight loss before 240 °C, which is temperature at which the thermal scission of cellulose begins (Figure 3(c)), suggesting that the stabilization reactions were complete.

The FESEM images of the carbonized CN fibers prepared from suspensions with CN concentration of 0.03 and 0.01 wt% are shown in Figure 4. The pyrolyzed CN fibers showed a decrease in the average diameter and assumed a crooked shape because of the caused by shrinkage during carbonization. However, the fiber morphology was retained and the fibrils showed nanomicron and submicron diameters.

To confirm the conversion of CNs into carbon structured material, XRD and Raman spectroscopy were undertaken.

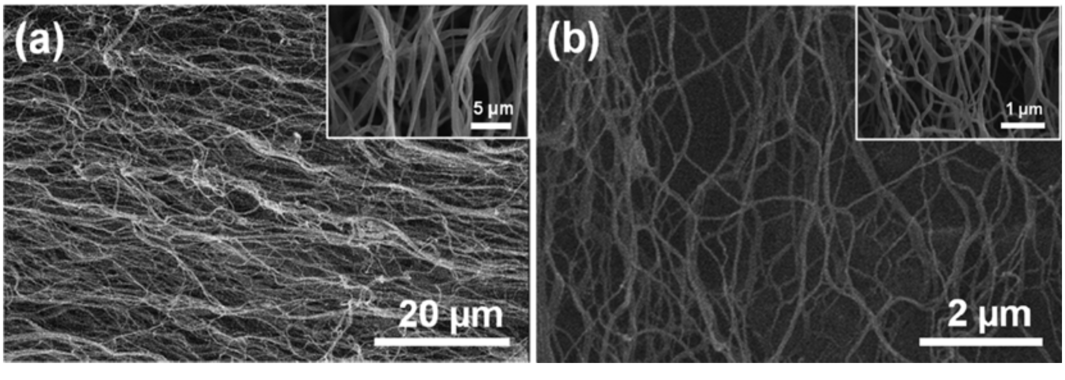

Figure 4. FESEM images of carbonized CN nanofibers prepared from (a) 0.03 wt% and (b) 0.01 wt% suspensions.

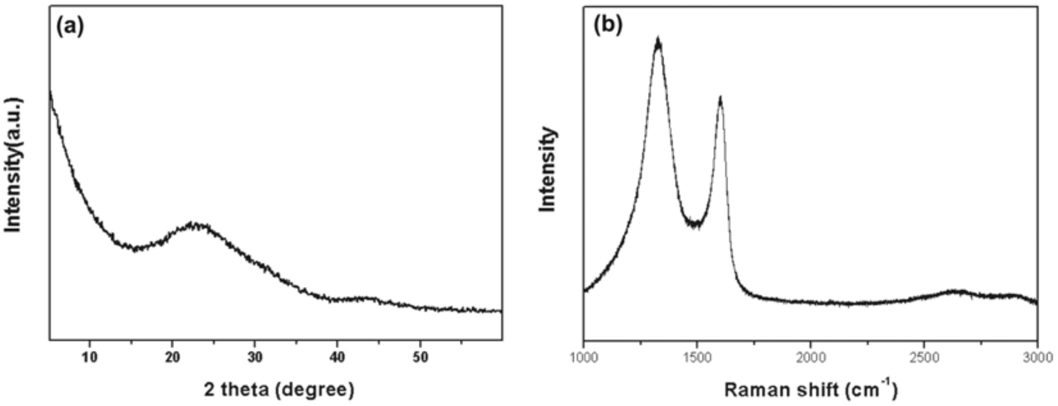

Figure 5. (a) XRD pattern and (b) Raman spectrum of nanofibrous carbon.

The XRD pattern of the fibrous carbons is presented in Figure 5. Two broad diffraction peaks broad peaks in the region 2θ=20°-25° and around 42° corresponding to reflections from the (002) and (100) planes, respectively, are indicative of the presence of an amorphous carbon structure. Also, the Raman spectrum (Figure 5) revealed typical resonance bands related to the presence of amorphous carbon structures with a broad D band centered at 1320 cm^{-1} and a smaller G band at 1580 cm^{-1}.

Conclusions

In this work, an interesting approach was used to fabricate carbon fibers using the self-assembling behavior of CNs. Using a sulfuric acid treatment, CNs with a length of 190±24 nm and a width of 14±2 nm were prepared and subjected freeze-drying process to fabricate fiber structures. During the freeze-drying process, CNs self-assembled into nanomicron and submicron fibers when CN suspensions of low concentrations were used. After carbonization at 1,000 °C, the pyrolyzed CN fibers maintained the fiber morphology which is demonstrated by the FESEM images. Raman spectroscopy and wide-angle XRD analysis were used to confirm the formation of amorphous carbon fibers from the CN fibers. In our future studies, we intend to explore the applications of carbon fibers obtained from self-assembled CN fibers with more advanced and organized structures.

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