Polymer 50 (2009) 2999–3006

Contents lists available at ScienceDirect

Polymer

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

Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanical properties

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ARTICLE INFO

Article history:
Received 16 February 2009
Accepted 11 April 2009
Available online 6 May 2009

Keywords:
Electrospinning
Nanofibers
Carbon fibers

ABSTRACT

Carbon nanofibers with diameters of 200–300 nm were developed through stabilization and carbonization of aligned electrospun polyacrylonitrile (PAN) nanofiber bundles. Prior to the oxidative stabilization in air, the electrospun PAN nanofiber bundle was tightly wrapped onto a glass rod, so that tension existed during the stabilization. We also investigated several carbonization procedures by varying final carbonization temperatures in the range from 1000 to 2200 °C. The study revealed that: (1) with increase of the final carbonization temperature, the carbon nanofibers became more graphitic and structurally ordered; (2) the carbon nanofiber bundles possessed anisotropic electrical conductivities, and the differences between the parallel and perpendicular directions to the bundle axes were over 20 times; and (3) the tensile strengths and Young's moduli of the prepared carbon nanofiber bundles were in the ranges of 300–600 MPa and 40–60 GPa, respectively.

1. Introduction

Carbon fibers possess high mechanical strengths and moduli, superior stiffness, excellent electrical and thermal conductivities, as well as strong fatigue and corrosion resistance; therefore, they have been widely used for numerous applications particularly for the development of large load-bearing composites. Conventional carbon fibers are prepared from precursors such as polyacrylonitrile (PAN) [1,2]; and the fibers typically have diameters ranging from 5 to 10 μm. To prepare carbon fibers with diameters in the nanometer range, the method of chemical vapor deposition (CVD) has been investigated [3]. However, the CVD method involves a complicated chemical and physical process thus the associated cost is inevitably high; additionally, the CVD method is only capable of producing relatively short fibers which are difficult to align, assemble, and process into applications. The rapidly developing technique of electrospinning provides a straightforward and cost-effective approach to produce fibers with diameters ranging from sub-microns to nanometers [4–7]. The electrospun PAN nanofibers are uniform with diameters of approximately 330 nm [8,9], which is more than 30 times smaller than their conventional counterparts. The subsequent thermal treatments, including stabilization and carbonization, convert the PAN precursor nanofibers into carbon nanofibers that are very long (continuous) probably with desired microstructural, electrical, mechanical, and other properties. Similar to the carbon nanofibers prepared by the CVD method as well as other one-dimensional carbonaceous nanomaterials such as carbon nanotubes, the electrospun PAN-based carbon nanofibers can be utilized for making hierarchical nanostructures [10,11], super-capacitors [12,13], filters [8], nanocomposites [14], catalyst supports for rechargeable batteries and/or fuel cells [15,16], and optoelectronics [17].

In the recent decade, several research efforts have been attempted to develop carbon nanofibers from electrospun precursors and to explore their potential applications [8,9,18,19]. However, microstructures and the related mechanical and/or electrical properties of the electrospun carbon nanofibers are still largely unknown. It is noteworthy that the reported carbon nanofibers were prepared exclusively from randomly overlaid electrospun nanofiber mats, so that tension could not be applied to the fibers during the thermal treatments. It is well known that applying tension during thermal treatments, particularly during stabilization, is crucial for the development of carbon fibers with high mechanical strength; i.e., if the stabilization is carried out without tension, the resulting carbon

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doi:10.1016/j.polymer.2009.04.058

fibers are mechanically weak [1,2]. Additionally, the reported electrospun carbon nanofibers were prepared without optimization of thermal treatment procedures, and the carbonization was conducted in the relatively low temperature range of less than 1200 °C. Therefore, the reported electrospun carbon nanofibers possessed mechanical (and probably electrical) properties that were far lower than predicted [9]. In this study, we developed an experimental method to prepare the electrospun PAN precursor nanofibers in the form of an aligned nanofiber bundle. The bundle was then tightly wrapped onto a glass rod, so that tension existed in a certain degree during the oxidative stabilization in air. Although tension was not applied during the subsequent carbonization, it is well known that applying tension during stabilization minimizes the requirement for tension during carbonization [1,2]. We also varied the final carbonization temperature in the range from 1000 to 2200 °C. The microstructures, electrical conductivity, and mechanical properties of the aligned carbon nanofiber bundles were systematically investigated.

2. Experimental

2.1. Materials

PAN homopolymer (weight-average molecular weight $M_W = 150{,}000$ g/mol, catalog number: 181315), *N*,*N*-dimethylformamide (DMF, catalog number: 227056), and acetone (catalog number: 34850) were purchased from the Sigma Aldrich Co. (Milwaukee, Wisconsin). Dodecylethyldimethylammonium bromide with the purity of 99.8% was purchased from the Tianjin Yongda Chemical Reagents Development Co. (Tianjin, China). The chemicals were used without further purification.

2.2. Electrospinning and collection of aligned PAN nanofiber bundles

PAN was first dissolved in DMF to prepare a 10 wt.% solution; subsequently, 5 wt.% acetone and 0.01 wt.% dodecylethyldimethylammonium bromide were added into the PAN solution to obtain the spinning solution. Our study indicated that the addition of acetone and dodecylethyldimethylammonium bromide could effectively prevent the formation of beads and/or beaded nanofibers [20], resulting in uniform electrospun PAN nanofibers with diameter of ~330 nm. The experimental set-up for electrospinning is schematically shown in Fig. 1. The spinning solution was held in a vertical syringe with a stainless steel needle having an orifice of 0.55 mm. The needle was electrically connected to a positive high voltage power supply purchased from the Gamma High Voltage Research, Inc. (Ormond Beach, Florida). A laboratory-built 30 cm diameter metal disc with the rim width of 1 cm was placed at 22 cm (from the tip of the needle to the surface of the rim) below the syringe as the collector, and the disc was electrically connected to a negative high voltage power supply also purchased from the Gamma High Voltage Research, Inc. Electrospinning was carried out in an open environment inside a fume hood at the room temperature; during electrospinning, a positive high voltage of 20 kV was applied to the needle while a negative high voltage of −2 kV was applied to the metal disc. Electrospun nanofibers were collected on the rim of the disk covered with aluminum foil. The rotational speed of the disk during electrospinning was set at 1500 rpm, making the rotational velocity at the surface ~24 m/s; and the solution flow rate of 1.5 ml/h was maintained using a digitally controlled, extremely accurate, positive displacement syringe pump (model number: KDS 200) purchased from the KD Scientific Inc. (Holliston, Massachusetts). The process was extremely stable, and the electrospinning jet could run steadily without breaking for many hours; the obtained bundle on the aluminum foil was thus made of aligned PAN nanofibers. The mass per unit area of the collected nanofiber bundle was controlled at ~10 g/m^2.

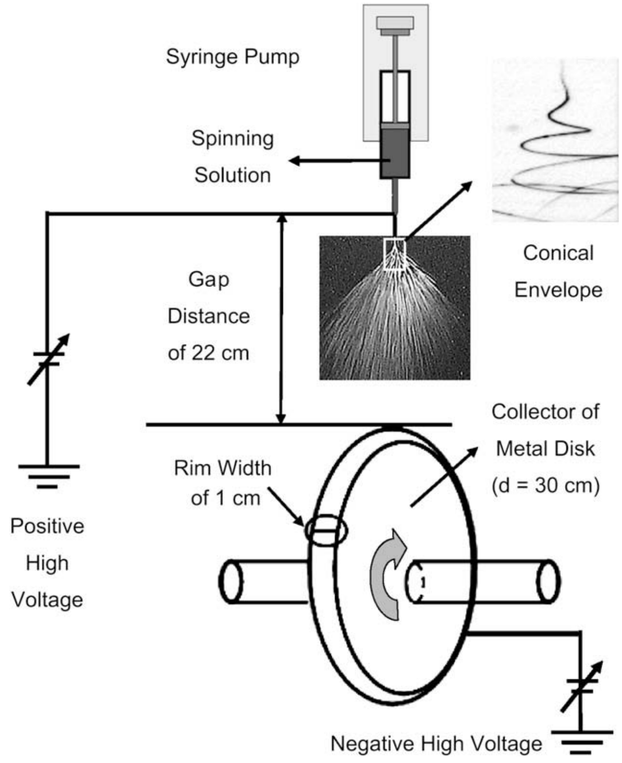

Fig. 1. Schematic representation of the electrospinning setup.

2.3. Stabilization and carbonization

The electrospun PAN nanofiber bundle could be easily peeled from the aluminum foil after being immersed in distilled water. The stabilization and low-temperature carbonization were conducted in a Lindberg 54453 heavy duty tube furnace purchased from the TPS Co. (Watertown, Wisconsin). A constant flow of air was maintained through the furnace during the stabilization. Prior to stabilization, the peeled electrospun PAN nanofiber bundle was dried and then tightly wrapped onto a glass rode with diameter of 2 cm; therefore, tension existed in a certain degree during the stabilization. The stabilization was carried out by heating the wrapped PAN nanofiber bundle from the room temperature to 280 °C with the heating rate set at 2 °C/min, followed by holding the temperature at 280 °C for 3 h to allow the stabilization to complete. The stabilized nanofiber bundle was subsequently un-wrapped and then carbonized at a relatively low temperature of 1000 °C in an inert (high purity nitrogen gas) environment with the heating rate set at 2 °C/min. Finally, the 1000 °C carbonized PAN nanofiber bundles were further carbonized in vacuum (~6 Pa) at relatively high temperatures of 1400 °C, 1800 °C, and 2200 °C. A Lindberg high temperature reactor with inside diameter and depth of 12 cm and 25 cm, respectively, was used for conducting the high-temperature carbonization; and the heating rate was set at 5 °C/min. All of the carbonized PAN nanofiber bundles were held at the respective final temperatures for 1 h to allow the carbonization to complete.

2.4. Characterization

A Quanta 200 Scanning Electron Microscope (SEM) was employed to examine the morphologies of the as-electrospun, stabilized, and carbonized PAN nanofibers at an acceleration voltage of 20 kV. Prior to SEM examinations of the as-electrospun and stabilized PAN nanofibers, the specimens were sputter-coated with gold to avoid charge accumulations. A JEM-2010 Transmission Electron Microscope (TEM) was employed to study the carbonaceous structures in the carbonized PAN nanofibers. TEM specimens were prepared by dispersing the nanofibers onto lacey carbon films supported on 200-mesh copper grids. The microstructures of the carbonized PAN nanofibers as well as the structural conversions resulted from stabilization and carbonization were investigated by a Renishaw inVia Raman Spectrometer and a Siemens D5000 X-Ray Diffractometer (XRD). The X-ray tube operating at 40 kV and 40 mA with the CuKα radiation (wavelength $\lambda = 0.154$ nm) was used; and the XRD profiles were recorded with the 2θ angles ranging from 5° to 40° at the scanning speed of 5°/min.

The electrical conductivities of the carbonized PAN nanofiber bundles in both parallel and perpendicular directions were measured with a Shanghai-PC9A digital micro-ohmmeter. Cross-section areas of the nanofiber bundles ("A") were determined by the widths and thicknesses of the samples, while the sample thicknesses were calculated using the masses per unit area of the nanofiber bundles and the reported densities of carbon fibers prepared at the same carbonization temperatures [21]. The electrical conductivity ("σ") was calculated using the equation of "$\sigma = L/AR$", where "R" is the electrical resistance of the nanofiber bundle in "ohms", "A" is the cross-section area of the nanofiber bundle in "cm^2", and "L" is the distance between the two electrodes in "cm" [22].

Mechanical properties of the carbon nanofiber bundles were measured according to a reported method [23] at a crosshead speed of 0.5 mm/min using a computer-controlled mechanical testing machine (QTEST™/10) purchased from the MTS Systems Corp. (Eden Prairie, Minnesota). Prior to testing the mechanical properties, two small pieces of double stick tape were placed at the opposite sides on a square cardboard frame with the outside size of "1.5 cm × 1.5 cm" and the inside size of "1 cm × 1 cm"; both ends of the nanofiber bundle were then attached onto the tapes. Subsequently, a super glue of ethyl-2-cyanoacrylate was added onto the tapes to ensure a strong bonding of the nanofiber bundle. To prevent the specimen from sticking to the clamps of the mechanical testing machine, the specimen was finally covered by a piece of paper with the same shape as the cardboard frame. During testing, the frame was cut at both sides without the tapes, leaving the aligned nanofiber bundle alone for measuring the mechanical properties.

3. Results and discussion

3.1. Morphology and microstructure

The SEM images of "A", "B", "C", and "D" in Fig. 2 shows the representative morphologies of the as-electrospun, stabilized, low-temperature (1000 °C) carbonized, and high-temperature (2200 °C) carbonized PAN nanofiber bundles, respectively. The PAN precursor nanofibers in the as-electrospun bundle were uniform without microscopically identifiable beads and/or beaded nanofibers [20]; and the fiber diameters were approximately 330 nm. Although most PAN nanofibers were aligned along the rotational direction, the

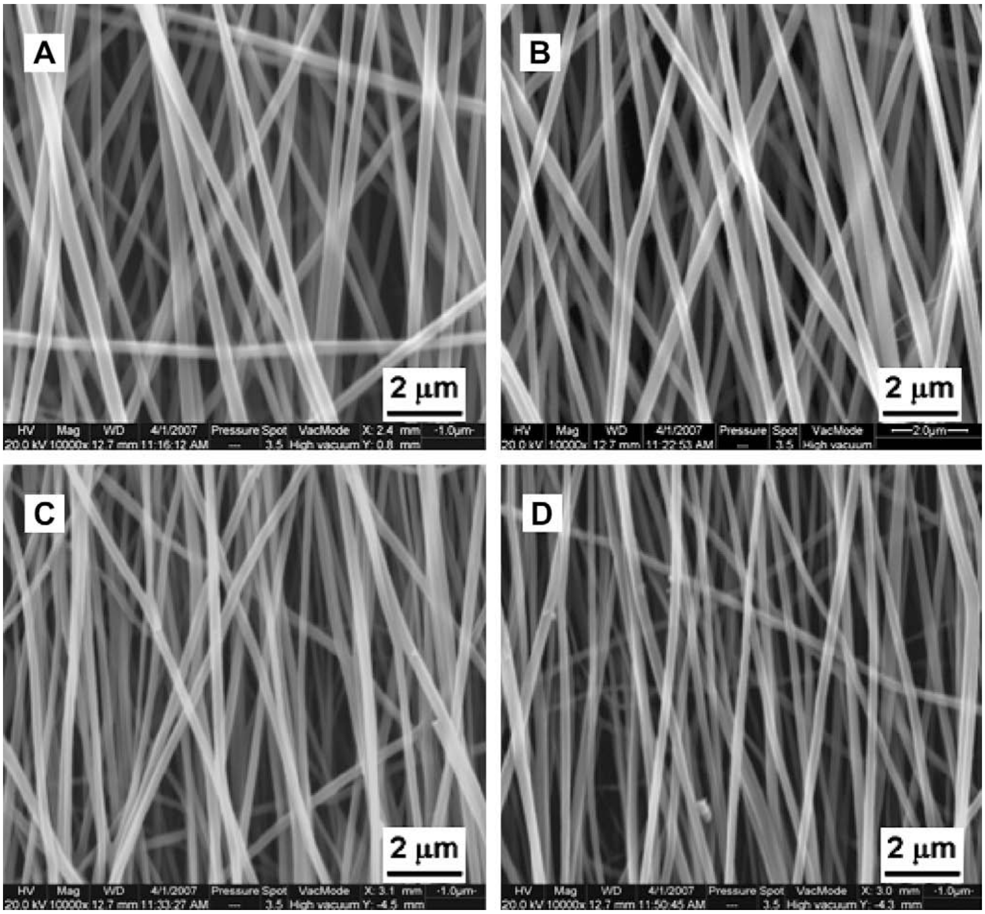

Fig. 2. SEM images showing the representative morphologies of (A) as-electrospun PAN nanofiber bundle, (B) stabilized PAN nanofiber bundle, (C) low temperature (1000 °C) carbonized PAN nanofiber bundle, and (D) high temperature (2200 °C) carbonized PAN nanofiber bundle.

overall degree of nanofiber alignment in the bundle was far from perfect. It is noteworthy that by using only a roller (or similar devices), it is unlikely to achieve a high degree of nanofiber alignment since the formation of electrospun nanofibers results from the "bending instability" [24], which makes the traveling path/trajectory of the electrospinning jet complicated and chaotic. Before high-speed digital cameras were available, visual observations and home video images (taken at 30 frames per second) of electrospinning were interpreted as the evidence that electrospinning was a process that split the primary jet into many smaller jets, as shown by the home video image in Fig. 1. The splitting jets were believed to emerge from a region at the end of the straight segment (known as the "Conical Envelope"). After employing a 2000 frame per second high-speed digital camera with exposure time set at less than a millisecond, it became evident that the "Conical Envelope" consisted of one continuous, looping, spiraling, and gradually thinning jet, as shown by the high-speed digital image in Fig. 1. The lines seen in the visual observations and in the home video images were due to the rapid movement of bright specular reflection spots on the bending jet. The morphologies of the stabilized and carbonized PAN nanofibers were similar to those of the as-electrospun nanofibers except for discrepancies in diameters. The average diameter of the stabilized PAN nanofibers appeared to be almost the same as that of the as-electrospun nanofibers, while the average diameters of the 1000 °C and 1800 °C carbonized PAN nanofibers were reduced to 250 nm and 220 nm, respectively. During stabilization, the PAN macromolecules in the as-electrospun nanofibers absorbed oxygen from air and went through chemical changes that resulted in cyclization of PAN macromolecules and led to formation of a ladder-like polymeric structure, which no longer melted and therefore could retain the fiber morphology in the subsequent carbonization [1,2]. During carbonization, a variety of gases (e.g., H_2O, N_2, HCN, and others) were evolved and the carbon content increased to 90 wt.% or higher; the process therefore led to the reduction of fiber diameter and the formation of three-dimensional carbonaceous structures.

The TEM images of "A" and "B" in Fig. 3 show the representative microstructures of the 1000 °C and 2200 °C carbonized PAN nanofibers, respectively. The selected regions in the left images were further examined at higher magnifications as shown in the right images. It was evident that the 2200 °C carbonized PAN nanofibers were graphitic, and the graphene sheets stacked together to form ribbon-shaped structures. Such structures did not exist in the 1000 °C carbonized PAN nanofibers, of which the carbonaceous structure was primarily turbostratic and the sheets of carbon atoms were haphazardly folded and/or crumpled together. The acquired microstructural results were consistent with what were found in the conventional carbon fibers [1,2]. The longitudinal directions of the ribbon-shaped graphitic structures in the 2200 °C carbonized PAN nanofibers were not perfectly parallel to each other, and they were not perfectly parallel to the fiber axis either. This was probably due to

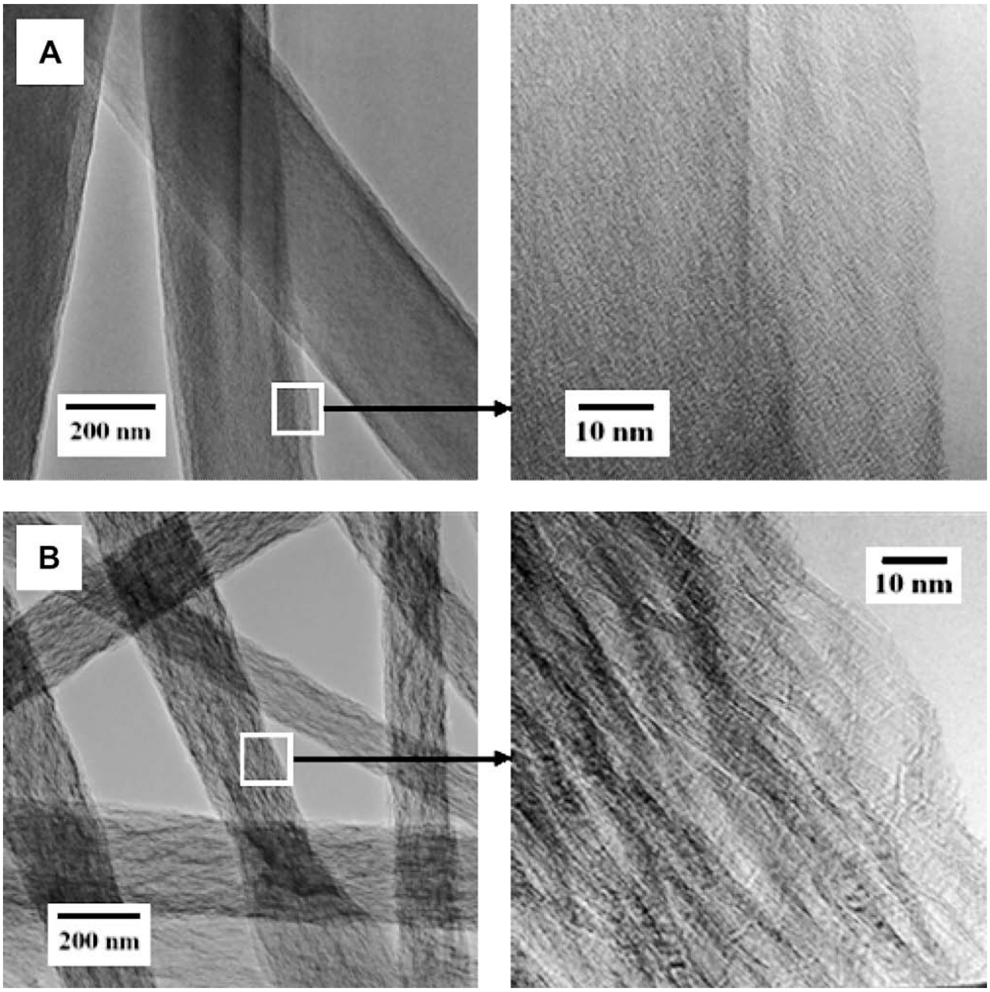

Fig. 3. TEM images showing the representative microstructures of (A) low temperature (1000 °C) carbonized PAN nanofibers, and (B) high temperature (2200 °C) carbonized PAN nanofibers.

the following two reasons: (1) unlike the conventional PAN precursor fibers, the electrospun PAN precursor nanofibers were not stretched. It is well-known that the stretching process can significantly improve the structural orientation along the fiber axes, and the orientation in the precursor fibers can be retained in the resulting carbon fibers. (2) Although tension existed in a certain degree during stabilization for making electrospun carbon nanofibers in this study, the tension value was not optimized and was probably smaller than that for making the conventional carbon fibers.

XRD was employed to further investigate the macromolecular and crystalline structures in the prepared carbon nanofibers and their electrospun precursors. As shown in Fig. 4, the as-electrospun PAN nanofibers (curve "A") showed a strong diffraction peak centered at the 2θ angle of 16.8° and a weak diffraction peak centered at the 2θ angle of 28.6°; these two peaks represented the X-ray reflections of the (100) and (110) crystallographic planes in PAN [9]. After stabilization (curve "C"), the (100) peak disappeared while a broad diffraction peak centered at the 2θ angle of 25.3° emerged; this new peak represented the formation of ladder-like polymeric structures in the stabilized PAN [1,2]. Contrastively, the XRD curve "B", which was acquired from the conventional ~10 μm diameter PAN precursor fibers (the Special Acrylic Fibers (SAF 3K) provided by the Courtaulds, Ltd in the UK) after the same stabilization treatment, showed the (100) peak, although the intensity of the peak was significantly lower than that prior to the stabilization. This indicated that almost all nitrile groups in the electrospun PAN nanofibers reacted while some nitrile groups in the SAK 3K fibers still remained. This was probably due to the fact that the diameters of the electrospun PAN nanofibers were much smaller than those of the SAF 3K fibers. Since oxidative stabilization is a diffusion-controlled process and the diffusion of molecules including oxygen and stabilization by-products was much easier and/or faster in the nanofibers, the stabilization of the electrospun PAN nanofibers could be completed faster and more thoroughly than that of the SAF 3K fibers. The XRD curves of "D", "E", "F", and "G" were acquired from the carbonized PAN nanofibers with the final carbonization temperatures set at 1000 °C, 1400 °C, 1800 °C, and 2200 °C, respectively. The diffraction peak around the 2θ angle of 25° ~ 26° was attributed to the (002) crystallographic plane of graphite crystallites [1,2,21,25]. With increase of the final carbonization temperature, the intensity and sharpness of this peak gradually increased; additionally, the peak also slightly shifted to higher degree. According to the "Bragg Equation" and the "Scherrer Equation" as shown below [21], the average interplanar spacing "$d_{(002)}$" and crystallite size parameter "L_c" could be determined using the XRD results.

$$d_{(002)} = \frac{\lambda}{2\sin\theta}$$

$$L_c = \frac{0.9\lambda}{\beta\cos\theta}$$

where "θ" was the scattering angle, "λ" was the wavelength of X-ray, "β" was the width of the diffraction peak measured at half its height in radian, and the coefficient (pre-factor) of "0.9" was included in "Scherrer's Equation" because the Gaussian distribution was adopted. The calculated values of "$d_{(002)}$" and "L_c" are shown in Table 1. It was evident that the "$d_{(002)}$" value decreased while the "L_c" value increased with increase of the final carbonization temperature. This indicated that the carbonization treatment consolidated the sheets of carbon atoms and thereby reduced the average interplanar spacing; additionally, the carbonization treatment also allowed graphite crystallites to undergo structural rearrangements to become larger and more ordered. For example, the 1800 °C carbonized PAN nanofibers had the "L_c" and "$d_{(002)}$" values of 4.25 nm and 3.46 Å, respectively. The crystal size parameter was consistent with the reported values (3.5–4.5 nm) acquired from the conventional carbon fibers, indicating the small diameter of electrospun PAN nanofibers did not vary the "L_c" value in the resulting carbon nanofibers. The "$d_{(002)}$" value of 3.46 Å in the 1800 °C carbonized PAN nanofibers, however, was slightly larger than the interplanar spacing of 3.35 Å observed in the naturally occurring graphite [26]. This was reasonable since the PAN-based carbon fibers were structurally turbostratic in general; although a high carbonization temperature could produce graphitic structures, these structures were not as perfect and/or ordered as those in the naturally occurring graphite.

Raman spectroscopy is another powerful tool to investigate microstructures [21,27,28]. The Raman spectra of carbonaceous materials have two characteristic bands including (1) "D-band", centered at the wavenumber of ~1340 cm^{-1} that is related to disordered turbostratic structures, and (2) "G-band", centered at the wavenumber of ~1580 cm^{-1} that is related to ordered graphitic structures. The positions of these two bands are irrelevant to the carbonization temperature, and the intensity ratio (known as the "R-value") of the "D-band" to the "G-band" indicates the amount of structurally ordered graphite crystallites in the carbonaceous materials [28]. The Raman spectra of "A", "B", and "C" in Fig. 5 are acquired from the carbon nanofibers with the final carbonization temperatures set at 1400 °C, 1800 °C, and 2200 °C, respectively. The "G-band" was attributed to the "E_{2g2} C=C stretching vibrations" in the graphite crystallites [28], and the band was correlated to the (002) diffraction peak in the XRD curve. The "D-band", on the other hand, was attributed to the turbostratic and/or disordered carbonaceous structures. It was evident that the "R-values" of the carbon nanofibers decreased with increase of the final carbonization temperature, indicating disordered carbonaceous components were converted into more ordered graphite crystallites.

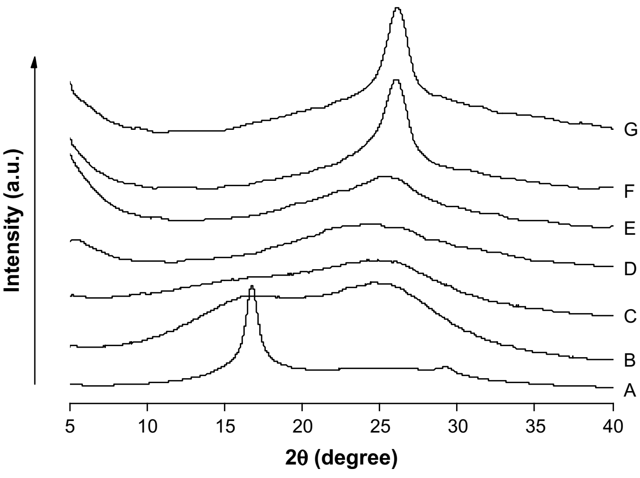

Fig. 4. XRD curves of (A) as-electrospun PAN nanofibers, (B) stabilized commercial PAN (SAF 3K) precursor fibers, (C) stabilized PAN nanofibers, (D) 1000 °C carbonized PAN nanofibers, (E) 1400 °C carbonized PAN nanofibers, (F) 1800 °C carbonized PAN nanofibers, and (G) 2200 °C carbonized PAN nanofibers.

Table 1
The average interplanar spacing "$d_{(002)}$" and crystallite size parameter "L_c" of electrospun carbon nanofibers calculated from XRD results.

Carbonization temperature (°C)	$2\theta_{(002)}$ (°)	β (radian)	L_c (nm)	$d_{(002)}$ (Å)
1000	24.6	0.163	0.882	3.62
1400	25.3	0.123	1.17	3.52
1800	25.8	0.0339	4.25	3.46
2200	25.9	0.0291	4.94	3.44

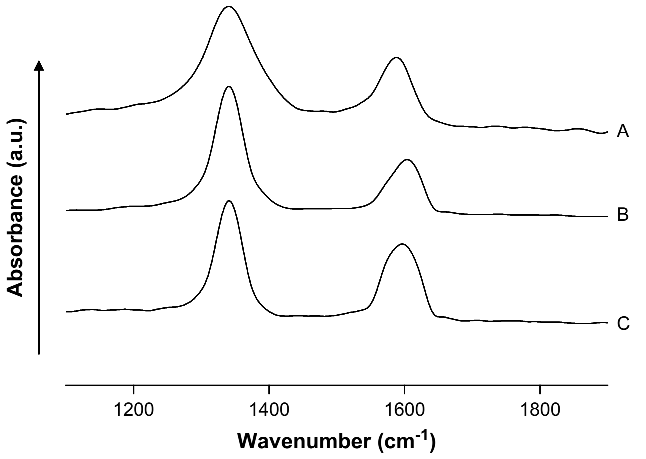

Fig. 5. Raman spectra of (A) 1400 °C carbonized PAN nanofibers, (B) 1800 °C carbonized PAN nanofibers, and (C) 2200 °C carbonized PAN nanofibers.

3.2. Electrical conductivity

Electrical conductivity of carbonaceous materials is important for applications such as super-capacitors and catalyst supports. As shown in Fig. 2, the electrospun PAN-based carbon nanofibers prepared in this study possessed reasonably good alignment in the bundles. The electrical conductivities of the nanofiber bundles carbonized at 1000 °C, 1400 °C, 1800 °C, and 2200 °C were measured in both parallel and perpendicular directions to the bundle axes. As shown in Fig. 6, the nanofiber bundle carbonized at 1000 °C had electrical conductivities (mean ± standard deviation, $n = 6$) of (180 ± 6) S/cm in the parallel direction and (7.7 ± 0.8) S/cm in the perpendicular direction; thus the discrepancy of electrical conductivities in the two directions was over 20 times. This was because the carbon nanofibers in the bundles only had occasional contacts with neighboring nanofibers, despite some did entangle with others; electrons could move readily along the nanofibers while their transfer in the direction perpendicular to the bundle axis was impeded. Such a discrepancy of electrical conductivities was significantly larger than what was reported previously by Ra and coworkers [29], suggesting that the nanofibers prepared in this study had much higher degree of alignment along the bundle axis. For the nanofiber bundle carbonized at 2200 °C, the electrical conductivities in parallel and perpendicular directions increased to (840 ± 15) S/cm and (61 ± 5) S/cm, respectively, suggesting that the microstructures became more graphitic and ordered. Intriguingly, when the final carbonization temperature was increased from 1000 to 2200 °C, the electrical conductivity in the parallel direction was increased by ~367%, whereas that in the perpendicular direction was increased by ~692%; this indicated that higher carbonization temperature apparently improved the contact among the entangled nanofibers in the bundle. It is noteworthy that the electrical conductivity of a nanofiber bundle cannot be directly interpreted as the electrical conductivity of the individual nanofibers in the bundle; this is because the electrical conductivity of a bundle is determined not only by the conductivity of individual nanofibers in the bundle but also by the contacts and/or entanglements among the nanofibers.

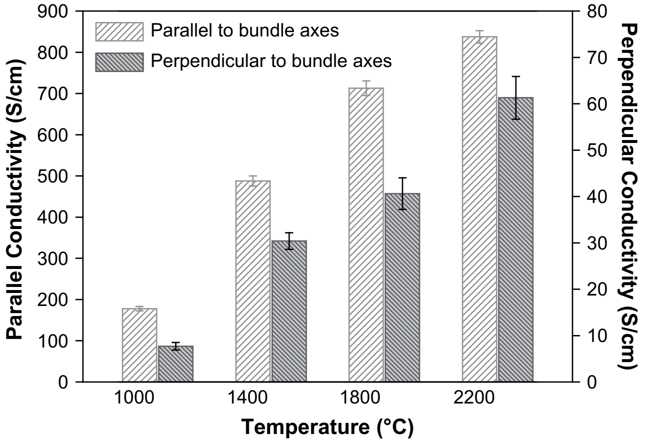

Fig. 6. Electrical conductivities of electrospun carbon nanofiber bundles in both parallel and perpendicular directions.

3.3. Mechanical properties

Mechanical properties of the electrospun carbon nanofiber bundles were measured using the method described in the Experimental Section, and the results are shown in Fig. 7. Both tensile strength and Young's modulus became substantially higher with increase of the final carbonization temperature. The 1000 °C carbonized nanofiber bundle had the tensile strength and Young's modulus (mean ± standard deviation, $n = 6$) of (325 ± 15) MPa and (40 ± 4) GPa, respectively. For the 2200 °C carbonized nanofiber bundle, the tensile strength and Young's modulus were increased to (542 ± 45) MPa and (58 ± 6) GPa, respectively. Thus, the tensile strength was improved by ~67%, while Young's modulus was improved by ~45%. Similar to electrical conductivity, mechanical properties of the bundles cannot be directly interpreted as those of individual carbon nanofibers in the bundles. The tensile strengths and Young's moduli of commercially available PAN-based carbon fibers (such as the T-series carbon fibers produced by the Toray Industries, Inc.) are 3–7 GPa and 200–400 GPa [1,2], respectively; both are approximately an order of magnitude higher than the acquired results for bundles. Generally speaking, the mechanical properties of the prepared electrospun carbon nanofiber bundles are attributed to two factors including (1) the mechanical properties of individual carbon nanofibers in the bundles, and (2) the alignment of carbon nanofibers in the bundles. In order to measure the mechanical properties of individual carbon nanofibers, the testing methods for measuring mechanical properties of carbon nanotubes may be appropriate, and such study is in progress. It is well-known that the moduli of carbon fibers can be improved by increasing the carbonization temperature; however, the increase of tensile strength with higher carbonization temperature is abnormal since the strongest PAN-based carbon fibers usually possess turbostratic microstructures instead of highly graphitic microstructures [1,2]. This is probably due to the reason that the acquired moduli were

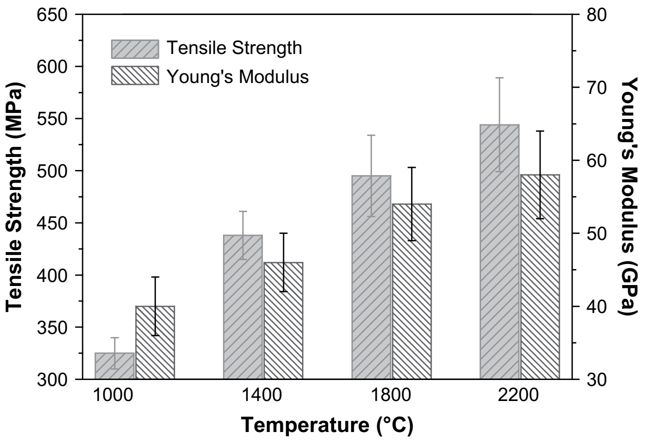

Fig. 7. Tensile strengths and Young's moduli of electrospun carbon nanofiber bundles.

measured from the bundles instead of the individual nanofibers; as described before, higher carbonization temperature may result in stronger binding and/or improved contacting at the locations among the entangled nanofibers thus can prevent the nanofibers from separating and/or slipping with each other.

Although the mechanical properties of individual electrospun carbon nanofibers prepared in this study have not been acquired, we speculate that they are unlikely to be superior for the following three reasons: (1) PAN copolymer, instead of homopolymer, has to be used as the precursor in order to develop carbon nanofibers with superior mechanical properties. This is because the PAN homopolymer contains highly polar nitrile groups, hindering the alignment of macromolecular chains during spinning (particularly during fiber stretching); additionally, the stabilization of PAN homopolymer occurs at a relatively high temperature, and the reaction is difficult to control due to a sudden evolution of heat. This surge of heat can cause the scission of PAN macromolecular chains and make the resulting carbon fibers mechanically weak. (2) The as-electrospun PAN precursor nanofibers have to be stretched to significantly improve the structural orientation. It is noteworthy that the rapid elongation of an electrospinning jet occurs in the solution or gel state [24]. Although highly extended macromolecular chains are expected to exist during electrospinning (particularly during "bending instability"), these chains could relax afterwards, especially if the collected nanofibers still contain enough solvent(s) to allow the movement/relaxation of elongated macromolecules [6]. Additionally, the stretching process may also result in untying and straightening of the nanofibers in the bundle, thus convert the as-electrospun loosely aligned PAN nanofiber bundle into the highly aligned and extensively stretched PAN nanofiber bundle. And (3) the thermal treatment procedures and conditions, particularly the tension values during stabilization and carbonization, have to be optimized. This could be readily accomplished if the highly aligned PAN precursor nanofiber bundles could be developed, and this is a goal of future work.

4. Conclusions

In this study, a PAN homopolymer ($M_w = 150{,}000$ g/mol) was electrospun into nanofibers; and the nanofibers were collected as aligned bundles using a laboratory-built metal disk with the rim width of 1 cm. The electrospun PAN nanofibers were uniform with diameters of approximately 330 nm and contained no microscopically identifiable beads and/or beaded-nanofibers. The electrospun PAN nanofiber bundles were used as the precursor to prepare carbon nanofiber bundles through thermal treatments including stabilization and carbonization. Prior to oxidative stabilization in air, the PAN nanofiber bundle was tightly wrapped onto a glass rod, so that tension existed during the stabilization. We also varied the final carbonization temperature in the range from 1000 to 2200 °C. The microstructures, electrical conductivity, and mechanical properties of the aligned carbon nanofiber bundles were systematically investigated. The study revealed that: (1) the average diameter of the stabilized PAN nanofibers appeared to be almost the same as that of the as-electrospun nanofibers, while the average diameters of the carbonized PAN nanofibers were significantly reduced; (2) with increase of the final carbonization temperature, the carbon nanofibers became more graphitic and structurally ordered; the microstructure of the low-temperature (1000 °C) carbonized nanofibers was primarily turbostratic and the sheets of carbon atoms were haphazardly folded and/or crumpled together, while the microstructure of the high-temperature (2200 °C) carbonized nanofibers was graphitic and the graphene sheets stacked together to form ribbon-shaped structures; (3) the carbonized PAN nanofiber bundles possessed anisotropic electrical conductivities, and the discrepancies between the parallel and perpendicular directions to the bundle axes were over 20 times; (4) the tensile strengths and Young's moduli of the carbon nanofiber bundles were in the ranges of 300–600 MPa and 40–60 GPa, respectively; and (5) both electrical conductivities and mechanical properties of the carbon nanofiber bundles increased with the increase of the final carbonization temperature. It is noteworthy that the electrical conductivities and mechanical properties of the carbon nanofiber bundles cannot be directly interpreted as those of individual nanofibers in the bundles. In order to develop carbon nanofibers with superior mechanical properties particularly tensile strength, the electrospun PAN precursor nanofibers have to be extensively stretched; the stabilization (and probably carbonization as well) has to be conducted under optimal tension; and the PAN copolymer instead of homopolymer has to be used as the precursor. The electrospun carbon nanofibers with superior mechanical and electrical properties are expected to be an innovative type of nanomaterials with many potential applications.

Acknowledgements

HH thanks the supports from the National Natural Science Foundation of China (Grants No.: 20674034 and 20874041), the Ministry of Education of China (Grant No.: 707038), and the Bureau of Science and Technology of Jiangxi Province in China (Grant No.: 050008). HF thanks the supports from the National Aeronautics and Space Administration of the United States (Grant No.: NNX07AT52A), the Department of Energy in the United States (Grant No.: DE-FG02-08ER64624), and the National Science Foundation of the United States (Grant No. CBET-0827844).

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