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Effect of acidification conditions on the properties of carbon nanotube fibers

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ABSTRACT

Carbon nanotube (CNT) fibers prepared by dry-spun method were functionalized by mixture of nitric and sulfuric acids. The effects of acidification conditions on the electrical conductivity and tensile properties of CNT fibers were investigated. A strong, high conductive CNT fiber was obtained under the optimal mixture ratio and processing time, with a electrical conductivity and tensile strength up to 3.2×10^4 S/m and 1103 MPa, respectively. It showed that the acids densified the surface of the CNT fiber and introduced functional groups onto the tubes, both of which contributed to the conductivity improvement of the CNT fiber. The infrared spectroscopy, Raman and fracture analysis indicated that acidification process resulted in two competitive effects on the tensile properties of CNT fibers, one was the positive contribution by the enhancement of interactions between CNTs through the densification and functional groups, and the other was the negative effect due to the structural destruction of the tubes.

1. Introduction

Carbon nanotube (CNT) is a kind of lightweight material with remarkable mechanical, electrical and thermal properties [1]. Recently, high performance macroscopic structures based on CNTs had attracted a lot of attention among researchers, since they can be handled much more conveniently than individual CNTs. Among them, CNT fibers showed a wide range of potential applications such as structural fibers, composites, multifunctional fabrics, and devices [2,3]. Several processes were established to fabricate CNT fibers [4,5], including coagulated from CNT solution, spinning from a vertically aligned CNT array, directly spinning from a CNT aerogel formed in a chemical vapor deposition (CVD) reactor. However, mechanical properties of the obtained CNT fibers were much lower than those of individual CNTs [4]. Therefore, many studies had been devoted to modify original CNT fibers to obtain improvements in mechanical, optical or electrical properties.

Acidic oxidation method is an effective strategy to purify and functionalize the surface of CNTs [6–9]. Mirershadi et al. [10] revealed that suitable molarity of acid and immersion time were necessary to purify the carbon nanotubes. Although tremendous studies have devoted to the topic of acid functionalization of individual CNTs, the effect of acid introduction on the performance of hierarchical CNT fibers is quite a new issue, of great significance but in its infancy. Meng et al. [11] increased the tensile strength and electrical conductivity of CNT fibers by an acid treatment for electrochemical applications by adding acid during the preparation of CNT fibers. However, it is not clear whether the acid treatment is efficient using a post-preparation method and how the acidification processing conditions affect the structure and tensile properties of CNT fibers, which is critical for the wide application of CNT fibers and is the main problem this paper aiming to solve.

In this study, the CNT fibers were prepared by dry-spun from vertically aligned CNT arrays, which were modified by mixture of nitric and sulfuric acids. The effects of mixture ratio and acidification time on the electrical and mechanical properties of CNT fibers were investigated. Fourier transform infrared spectroscopy (FTIR) analysis and Raman spectra were employed to analyze the chemical modification effect of the acids. Scanning electron microscope (SEM) was performed to examine the tensile failure surfaces of the fibers after various acidification conditions. Moreover, the optimal acidification conditions on the properties of CNT fibers were concluded.

2. Experimental

2.1. Materials

Continuous CNT fibers used in this study were spun by drawing and twisting a CNT sheet from vertically aligned CNT arrays which

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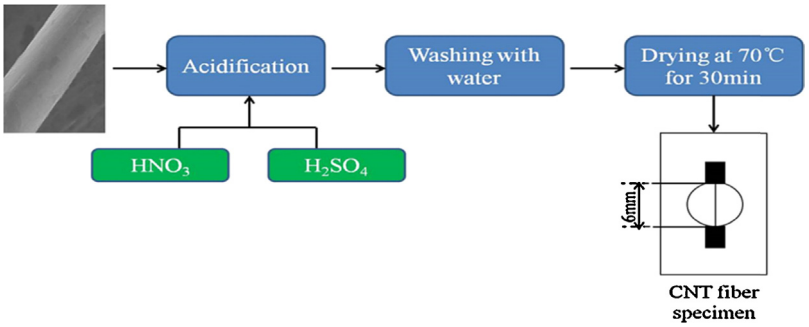

Fig. 1. The schematic of acidification procedure of CNT fiber.

were synthesized on SiO_2/Si wafers by a sustained chemical vapor deposition method [12]. The CNTs in the array were of 2–3 walls, 320 μm in length and less than 6 nm in diameter. To densify the CNT fiber, a drop of ethanol was applied at the tip of the triangular CNT sheet before twisting during the spinning [13]. Nitric and sulfuric acids were provided by Chinasun Specialty Products Co., Ltd.

2.2. Strategies of acidification

The mixture of nitric and sulfuric acids was used to acidify the CNT fibers.

Fig. 1 presents the schematic of acidification procedure. Before modification, the pristine CNT fiber was glued onto a paper mold with a gage length of 6 mm. The nitric and sulfuric acids were mixed with different ratios. Then the pristine CNT fiber was acidized in the mixed acids for a while, following by a 10 min washing process using deionized water. At last, the obtained CNT fiber was dried in a vacuum at 70 °C for 30 min. To optimize the acidification process of CNT fibers, different acidification time and different mixed ratios of nitric and sulfuric acids were conducted, as listed in Table 1. All of the acidized CNT fibers were washed with deionized water except for those specially stated.

2.3. Characterization

The CNT fiber diameter was measured by the optical diffraction method using 532 nm green laser [14,15]. During test, the laser was irradiated on a CNT fiber vertically to form the diffraction stripes. Then, the distance l between the two dark stripes which were closest to the center of the diffraction stripes was measured. The CNT fiber diameter R was calculated from l by Eq. (1)

$$R = \frac{\lambda L}{l} \tag{1}$$

where λ is the wavelength of laser, L is the distance between the fiber and the center of the diffraction stripes.

Table 1
Various acidification processing conditions for the CNT fibers.

CNT fiber specimen	Acidification time (min)	Mixed ratio of nitric and sulfuric acids
I	3	1:3
II	15	1:3
III	25	1:3
IV	15	1:0
V	15	1:1
VI	15	1:2
VII	15	0:1

The electrical conductivity σ of CNT fiber was calculated from electrical resistance [15–17] by Eq. (2)

$$\sigma = \frac{l}{RS} \tag{2}$$

where R is the electrical resistance, measured using a digital multimeter by dropping a tiny silver glue on the two ends of tested fiber, S is the cross-sectional area of the fiber, calculated from the fiber diameter, l is the gage length of the test fiber.

Tensile tests were conducted on a MTS Nano Bionix Universal Testing System (Oak Ridge, Tennessee), with an extension speed of 0.001 mm/s. The samples were mounted on paper tabs with a gauge length of 6 mm [18]. In the present study, the top 8–10 highest results of each sample were taken to calculate the average strength and to mark the error bars. After the tensile test, the morphology of fiber surface and fracture region was probed by SEM with CamScan-Apollo 300-Field Emission Scanning Electron Microscope at 15 kV.

To obtain FT-IR spectrometer samples, CNT fibers were mechanically mixed to the KBr powder and pressed into discs shape. FT-IR was used to analyze the changes in the surface chemical bonding and structure in the frequency range of 3750–1000 cm^{-1}. Spectrometer used was a Nicolet 6700.

The CNT structure was characterized by Raman spectra using a JY LabRam HR 800 micro-Raman spectroscope. The apparatus included a He–Ne laser providing 632.8 nm monochromatic light, a grid monochromator with 1800 grooves/mm and a CCD electrical cooled multichannel detector. The spectrometer was calibrated on the 520.7 cm^{-1} band of single crystalline silicon (1 0 0). Each spectrum was recorded via an 100× objective in backscattering geometry. The spectra were processed by the software package Labspec and by origin.

3. Results and discussion

3.1. Effect of acidification time on the property of CNT fiber

The effect of acidification time on the performance of CNT fibers was examined, with the mixture ratio of nitric to sulfuric acids fixing at 1:3, shown by the CNT fibers I, II, and III in Table 1. The electrical conductivity and tensile test results were shown in Fig. 2.

Fig. 2(a) indicated that the conductivity of CNT fibers was significantly improved after acidification. It increased from 2.1×10^4 S/m for pristine CNT fiber to 2.6×10^4 S/m after 3 min acidization. After a 15 min acidization, the conductivity of the CNT fiber reached 2.8×10^4 S/m, which increased by 33% comparing with the pristine one. Longer acidization time tended to result in lower conductivity of the CNT fiber, e.g. it began to decrease to 2.5×10^4 S/m after 25 min treatment, nevertheless still higher than that of the pristine one. Functional groups on the CNTs were tested by FTIR. Fig. 3 showed that functional groups