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Fabrication and densification of high performance carbon nanotube/copper composite fibers

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ABSTRACT

An effective method to fabricate CNT/Cu composite fibers through combined physical vapor deposition (PVD) and drawing treatment is presented in this work. Dense copper films with various thicknesses were coated on CNT fibers using the PVD method for different deposition periods. One of the resulting films with ~5 μm average thickness was subjected to drawing treatment. The results show that the density of CNT/Cu composite fibers was improved by 56% after the drawing treatment. Meanwhile, the alignment of the CNT fibers beneath the copper film showed improvement, as measured by polarized Raman spectrometry. The optimization in densification and alignment result in an increase of the tensile strength for the CNT/Cu composite fibers, from 258 ± 9 MPa to 515 ± 11 MPa (by 100%). Moreover, the electrical conductivity and ampacity increased from (7.64 ± 1.18) × 10^6 S/m and (5.76 ± 0.36) × 10^3 A/cm^2 to (1.37 ± 0.10) × 10^7 S/m (by 79%) and (1.09 ± 0.06) × 10^4 A/cm^2 (by 89%), respectively. Overall, these findings reveal that copper films play an important role in enhancing the tensile strength and current density, as well as reducing the electric resistance.

1. Introduction

Carbon nanotube (CNT) possesses high strength, good electrical conductivity, elevated thermal conductivity, and many other interesting functional properties [1,2]. Composed by millions of CNTs, CNT fibers are important macroscopic materials with broad application prospects [3]. These materials have now been widely used in many applications, including composites [4,5], capacitors [6,7], sensors [8,9], and wires [10–12].

A number of methodologies have been developed to fabricate CNT fibers. These include wet spinning [13], spinning from aligned CNT arrays [14], twisting from CNT films [15], and floating catalyst chemical vapor deposition (FCCVD) [16]. The FCCVD-based methods have been demonstrated to be promising due to their low-cost and ability for continuous production [17]. However, the tensile strength of the as-prepared fibers fabricated by FCCVD is often lower than the other engineering fibrous materials, such as carbon and SiC fibers [18].

To improve the tensile strength, several methods have been proposed for CNT fibers. Stretching is one effective process due to its effect on alignment optimization, through which the tensile strength could be improved by more than 100% [19]. Pressuring is another frequently used process to improve tensile strength by increasing the density and friction between CNT bundles [20,21]. The mechanical densification processes combine stretching with the pressing method and have been adopted to strengthen CNT fibers, including drawing [22,23], rolling [24], multiple steps stretching-pressing [19], manual rolling in spatula [25], or a combination of these processes [26,27]. The alignment and density optimizations after processing yield remarkable improvements in the mechanical properties of CNT fibers. Very high tensile strength of post-treated CNT fibers was reported as 4.34 GPa, which is close to that of the T700 carbon fiber [24].

The electrical conductivity of CNTs fibers can also be enhanced when treated by simultaneous stretching and pressing processes to reach high values ranging from (1.82–2.24) × 10^6 S/m [24]. However, these values are still lower than those recorded for metal conductors, such as copper (5.9 × 10^7 S/m) and gold (4.5 × 10^7 S/m).

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To further improve the electrical conductivity, the CNTs were compound with the metals with high electrical conductivity, such as Cu [28,29], Au [28,30], Ag [30,31], Pd [32], etc. In these metals, copper is the most promising one for its low cost. CNT fibers coated with copper using electrodeposition to yielded an electrical conductivity value close to that of copper (3×10^7 S/m for (fiber diameter)/(copper layer thickness)=(13 μm)/(6–7 μm)) [28]. Nonetheless, the density of the copper layer (6 g/cm^3) fabricated by electrodeposition was much lower than its pure counterparts [33], thus the corresponding electrical conductivity of the CNT/Cu composite fibers is also lower. On the other hand, the introduction of copper reduces the tensile strength of the whole fiber for its lower strength [33]. Therefore, novel fabrication processes of CNT/Cu composite fibers are required to enhance the electrical conductivity and their strength simultaneously.

In this study, a series of smooth and dense copper films with various thicknesses were coated on the CNT fibers using physical vapor deposition (PVD). The drawing treatment was adopted to improve the density of the CNT/Cu composite fibers. The structure and morphology of the resulting CNT fibers and CNT/Cu composite fibers, before and after the drawing treatment, were characterized and analyzed. Furthermore, tensile tests, electrical conductivity, and ampacity measurements were conducted to evaluate the effect of copper films and drawing treatment on the mechanical and electrical properties.

2. Materials and experimental methods

2.1. Fabrication of CNT/Cu composite fibers

The CNT fiber was synthesized by means of the FCCVD method [34] and was used in this work for the subsequent study. The specific surface area of the CNT fiber was measured by surface area and pore size distribution analyzer (AutoSorb 6ISA, Quantachrome Instruments, American) using Brunauer-Emmett-Teller (BET) method, as described in Refs. [35,36].

The magnetron sputtering instrument (TRP-450, SKY Technology Development Co., Ltd., Shenyang, China) was used to coat a copper film on the CNT fibers surface using PVD method. During the PVD process, the CNT fiber was winded in a frame as a coating substrate. The frame could rotate along its axis at the speed of 0–15 r/min (Fig. 1(a)). Three couples of copper plate (99.99%, Beijing Founde Star Science and Technology Co., Ltd., Beijing, China) were used as targets. The thickness of the resulting copper film was adjusted by controlling the deposition time. In this work, deposition periods of 0.5 h, 1 h, 1.5 h and 2 h were utilized.

2.2. Densification of CNT/Cu composite fibers

The drawing treatment was applied to the CNT/Cu composite fibers deposited for 0.5 h. The CNT/Cu composite fiber was drawn through a small die hole at a speed of 20–100 mm/min, as shown in Fig. 1(b). A series of drawing dies with decreasing hole size, from 140 μm to 100 μm, were used in sequence during the drawing process. The decrease in the hole diameter was 5 μm between two adjacent steps.

2.3. Structural characterization

In order to reveal the morphology of the cross section, sample was prepared by a few steps. First, the CNT/Cu composite fibers were adhered to a metal plate, and then mounted using the mixed solution of epoxy resin (E44) and triethanolamine. After the epoxy resin became hardened, the sample was ground by SiC sand paper initially (#400 ~ #2000) and followed by polishing with diamond suspensions (0.5 μm particle size).

The structures of prepared fibers were examined by a field emission scanning electron microscopy (FE-SEM, Model S-4300, Hitachi, Japan) equipped with an energy-dispersive X-ray (EDX) spectrometry system. The acceleration voltage was 15–20 kV. Secondary electron SEM images were taken to record the structure morphologies. The structure of carbon nanotubes was examined by a transmission electron microscopy (TEM, JEL-2100, JEOL Ltd., Japan) under an acceleration voltage of 200 kV. The roughness of the pristine CNT fibers and composite fibers were characterized by the atomic force microscope (AFM, Multimode 8, Bruker Corporation, Germany). The roughness of the surface was measured in an area of 5×5 μm^2 using the contact mode. At least 3 samples of each type of fiber were measured. The structural quality of the produced CNT fibers was assessed by Raman spectrometry (Raman, LabRAM HR Evolution, HORIBA Ltd., Japan) with a wave length of 532 nm. For the composite fiber, the copper film was partially peeled off from the CNT fiber by tweezers with the assistance of a magnifying glass. The quality of the exposed CNT fibers was then assessed by the ratio of the intensities of G-band (I_G) and D band (I_D). The degree of alignment of the CNT fibers was measured by polarized light source in the Raman spectrometry. During the polarized Raman detection, the intensities of G-band in both directions, parallel and perpendicular to the CNT fiber axis ($I_{G\parallel}$ and $I_{G\perp}$), were collected. The ratio of $I_{G\parallel}/I_{G\perp}$ was then calculated to characterize the alignment degree.

2.4. Density estimation

The content of Cu was measured by thermal gravimetric analysis

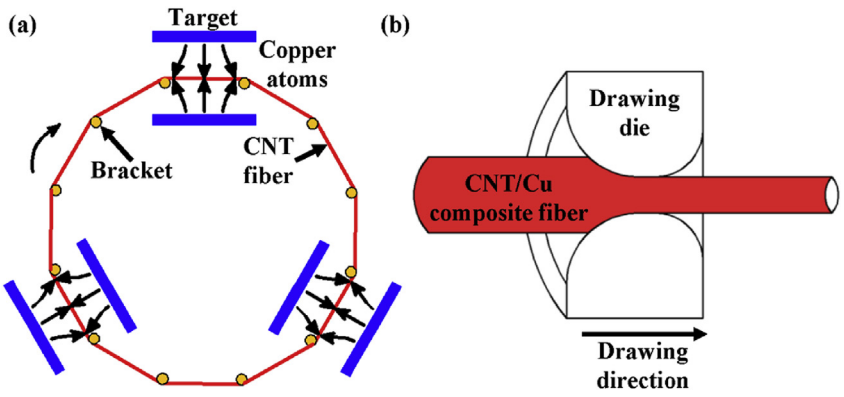

Fig. 1. Schematic of (a) PVD of copper on the CNT fiber, and (b) drawing treatment processing for CNT/Cu composite fiber. (A colour version of this figure can be viewed online.)