Current Applied Physics xxx (2016) 1–9

Contents lists available at ScienceDirect

Current Applied Physics

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

Multifunctional characterization of carbon nanotube sheets, yarns, and their composites

Thuy Kieu Truong [a, b], Yourack Lee [a, b], Dongseok Suh [a, b, *]

[a] IBS Center for Integrated Nanostructure Physics, Institute for Basic Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea
[b] Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea

ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form
19 April 2016
Accepted 20 April 2016
Available online xxx

Keywords:
Carbon nanotube sheet
Carbon nanotube yarn
Carbon nanotube forest
Magnetoresistance
Artificial muscle

ABSTRACT

Carbon nanotube (CNT) based macroscopic objects such as dry-state free-standing sheets and yarns have attracted much attention during more than a decade for their multifunctional features. Thanks to their lightweight, highly conductive, mechanically strong and flexible properties, various applications had been explored so far. However, because of the difficulties in the spinnable CNT forest growth, the sample availability in the academic fields has been quite limited. In this report, various properties of CNT sheets, yarns, and their composites were experimentally presented using the samples prepared from the spinnable CNT forest grown in the newly installed, acetylene-based, chemical-vapor-deposition chamber system. Clear observation of the dimensional effect on the charge transport through CNTs, the enhancement of electro-mechanical actuation owing the volume-expandable infiltration material inside CNTs, and other exemplary evaluations proved the versatility of this macroscopic assembly as well as the good quality of our sample.

1. Introduction

Applications of carbon nanotube (CNT) have been explored from the level of individual nanotubes to that of macroscopic objects in the form of sheets, yarns or composites with other materials in the field of, for example, electronic textiles and artificial muscles [1–3]. Especially for large scale usages, it is important to make the remarkable properties of individual nanotubes manifested even in the macroscopic articles [3–5]. Due to the intrinsic one-dimensional nature of nanotube, alignment of CNTs is one of the crucial factors making the beneficial characteristics of individual nanotubes retained up to the macroscopic stage [5,6]. For this purpose, free-standing sheets of highly aligned CNT arrays have been investigated due to its ultra-flexile, aerogel-like mechanical properties [7]. They come from the vertically-grown CNT forest spinnable by the mechanical-pulling, and do not require other ingredients such as binder for further scale-up. Multifunctional properties of this CNT sheet had been studied in terms of its unique combination of electrical, optical and mechanical features [8,9], demonstrating its usage as loudspeakers, incandescent display, touch screens, polarizer, electrodes for batteries and supercapacitors, CNT sheet and polymer composites [3,10–15].

Furthermore, twisting of those sheets can produce CNT yarn consisting of nanotubes and their bundles that are highly aligned along the yarn axis [5]. This yarn is lightweight, electrically conductive, and mechanically strong enough to be used as a superfiber or an artificial muscle [5,16,17]. Additionally, these have been widely investigated as a host material for many applications [18,19]. In more details, the outstanding tensile and torsional actuation of CNT yarn driven by the double-layer charge injection inside electrolyte was improved to the stage of an electrolyte-free dry-state actuation [17]. And the large actuation in the coiled structure made another observation showing the importance of coiled yarn in terms of the amplification of strokes in artificial muscles for practical applications [20,21]. In another aspect, these approaches induced a solvent-driven actuation by hybridizing the yarn with elastomer in contact with the solvent resulting in the volume expansion of the elastomer up to 400%, which might be useful in the area of robotics, prosthetic, and medical devices [21,22].

In this paper, we address the current trends in this field and compare them to our results obtained from the newly synthesized spinnable CNT forest and the following sheet, yarn and coiled yarn. Firstly, the fabrication methods of these materials are provided on the basis of the dry-state spinning process. Secondly, their general

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[*] Corresponding author. Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea.

E-mail address: energy.suh@skku.edu (D. Suh).

http://dx.doi.org/10.1016/j.cap.2016.04.023
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Please cite this article in press as: T.K. Truong, et al., Multifunctional characterization of carbon nanotube sheets, yarns, and their composites, Current Applied Physics (2016), http://dx.doi.org/10.1016/j.cap.2016.04.023

properties are examined in the structural, electrical and mechanical aspects, which are also related to their appropriate applications. Lastly, two intriguing phenomena of this macroscopic system are carefully investigated. One is the electrical transports of CNT sheets and yarns under magnetic field in transverse and longitudinal configurations studying its nature of low-dimensional electrical conduction. The other is an exemplary test of their electro-mechanical actuation in the combination with paraffin. The detailed description for each topic and analysis will help the understanding of this interesting material and open the possibilities for broader applications.

2. Fabrications, physical properties and exemplary applications

2.1. Fabrication

The main properties of CNT system are governed by its basic structure whether the number of walls is single, double or more in addition to its chirality. However, due to the difficulties of chirality control during the growth of CNTs, the number of walls seems to be a more practical control parameter in the CNT characterization [23–25]. In the market point of view, the cost of multiwalled CNT is lower than that of single-walled CNT because of the simplicity in the production process [23,26]. For the production of bulk CNT system having the shape of sheet or yarn, individual CNTs are assembled in a large scale using the wet or dry methods. For example, CNT sheets have been produced using a method similar to the ancient paper-making technique, involving the dispersion of nanotubes in aqueous solution containing surfactants followed by the filtration of the sheets using a micro/nano-porous filter [9,27]. Other solution-based processes include the Langmuir–Blodgett technique using CNT's hydrophobicity, the self-assembly, the dip coating method, and the electrophoretic deposition on a conductive substrate [9,28–31]. One of the drawbacks of the wet methods mentioned above is the possibility of undesired effects on CNTs by chemical residues added during the wet processes, which consequently require the post treatment process such as high temperature annealing. Some of them are not feasible for large scale applications.

The continuous fabrication of CNT sheets using a floating catalyst method was introduced in the year of 2004, where aerogel-like ultra-long CNT bundles are formed and entangled inside the chemical vapor deposition (CVD) zone. Such floating CNT bundles are collected continuously using the wind-up assembly out of CVD machine [32]. This method has been progressed until now, producing a commercial level macroscopic CNT objects such as sheets and yarns. Alternatively, a solid state technique was developed by pulling CNT sheets from CNT forest [7,27]. Unlike the case of the floating catalyst method, CNT bundles inside the sheet are quite well aligned due to the mechanical drawing. The driving force to take a thin, horizontally-aligned CNT layer out of a vertically grown CNT forest is the van der Waals interaction between long CNT bundles and interconnecting nanotubes [33]. This solid-state approach is advantageous in the aspects of better alignment and less contamination [34]. However, the length of CNT sheet is limited by the finite size of CNT forest on the substrate in the present technology. On the contrary, the floating-catalyst method is suitable for the continuous production of CNT sheet in the large scale.

In the case of CNT yarn production methods, all require spinning/twisting steps such as wet spinning, direct dry spinning, or solid-state spinning [7,32,35]. Especially in the case of solid-state spinning, the yarn is fabricated by the twist of the sheet drawn from CNT forest [7,8]. Here, the final states of the yarn are determined by the process parameters such as the width of CNT sheet and the number of twists [8]. Moreover, a stacked multi-layer sheets can be used to form a thick and strong yarn [21]. The number of CNT sheet layers as well as the applied tension determines the yarn diameter. Excessive twist insertion into the yarn results in the formation of coiled structure due to an imbalance between the twist and the yarn tension [36].

Our fabrication methods of CNT sheets and yarns are graphically illustrated in Fig. 1. Firstly, from a CNT forest that was vertically grown on a silicon wafer substrate as shown in Fig. 1(a), multi-layer CNT sheets were prepared using the stepper motor as in Fig. 1(b). Initially, we touched one edge side of CNT forest using a knife and pulled a sheet from the forest. The continuous layer of CNT sheet was mechanically drawn from the CNT forest. The front end of that CNT layer was attached to the U-shaped supporting jig combined with the stepper motor. The number of stacked CNT sheet layers was proportional to the number of rotation of the stepper motor. These stacked CNT sheets were twisted to form the yarn as in

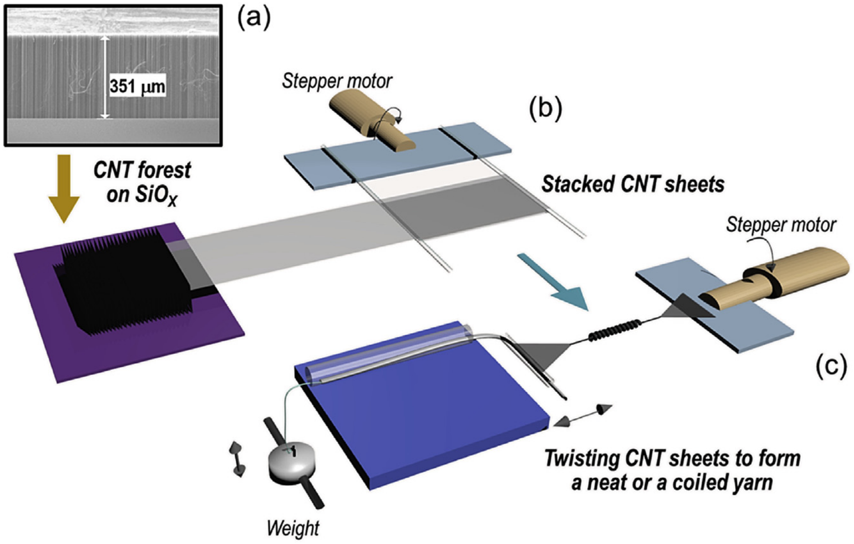

Fig. 1. (a) Scanning electron microscope image of the vertically-grown CNT forest spinnable to form a sheet and a yarn. (b) Schematic illustration of the apparatus designed for CNT sheet drawing, and (c) that of the home-made system for CNT yarn twisting.

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