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Letter to the editor

Facile fabrication of carbon nanotube forest-like films via coaxial electrospray

A B S T R A C T

Complex fabrication methods for carbon nanotubes limit their potential for scale-up and use in practical applications. This study developed a simple method to deposit multiwall carbon nanotube (MWCNT) forest-like films from polyacrylonitrile and MWCNT solutions by coaxial electrospray. A MWCNT solution was used as the shell flow to generate vertically aligned tree-like structures at mesoscopic scale (~10^{-5} m) on aluminum, silicon, and fiber membrane substrates. These forest-like structures assembled from highly conductive core-shell polymer/MWCNT particles with diameter of about 1 μm. The fabricated MWCNT films show good potential for applications in flexible electronics and as conductive filters.

Carbon nanotubes (CNTs) are nanoscale materials that have unique properties such as high charge mobility, high conductivity, and the potential for low cost production [1]. The electronic properties of disorganized CNT architectures used in bulk composite materials and thin films are limited [2]; however, organized CNTs, especially vertically aligned structures, show good potential for harnessing the properties of individual CNTs in a bulk form. These structures have also drawn considerable attention owing to their porous structures and superior electrical conductivity [3]. CNTs can be manipulated into aligned films and three-dimensional microarchitectures for use as microelectromechanical devices and filters [2,4]. Two methods are commonly used to deposit single wall CNTs (SWCNTs) on flexible substrates, namely, in-situ chemical vapor deposition and solution deposition [1,5–8]. The removal of metallic SWCNTs, in an effective and a scalable manner, is critical to allow large-scale manufacturing for applications including solar cells, supercapacitors, and chemical and biological sensors [5]. However, there remain a number of challenges to processing of vertically aligned CNT films. To fabricate these films on a large-scale at low-cost, we developed a fabrication technique using a coaxial electrospray system to generate CNT particles from polyacrylonitrile (PAN)/dimethylformamide (DMF) and multiwall carbon nanotube (MWCNT)/*N*-methyl-2-pyrrolidone (NMP) solutions. Although the physical phenomenon of the coaxial electrospray still lacks of understanding, such as the complex fluid dynamics in the coaxial jet, it is a promising fabrication technique to produce core-shell nanoparticles and microparticles [9].

The fabrication process of the films was as follows. PAN/DMF (2.5 wt% PAN dissolved in DMF) solution and MWCNT/NMP (5.0 wt% MWCNT with a mean diameter of 16 nm and length of 0.5 μm dispersed in NMP, TCHN-201) dispersion were prepared and received from Toda Kogyo Corp., respectively. A uniformly mixed solution (PAN/MWCNT content ratio: 1: 2) was also prepared by mixing these two solutions at the same weight proportion. The PAN/DMF and MWCNT/NMP solutions were simultaneously injected into the inner and outer needle of a coaxial electrospray apparatus, respectively, as shown in Fig. 1a. Their flow rates were controlled by two syringe pumps (PhD 2000, Harvard Apparatus) fixed at 3.0 μl/min. The internal and external diameters of the inner stainless steel needle were 0.48 and 0.70 mm, respectively, while the internal diameter of the outer needle was 0.80 mm. An aluminum plate was placed 12 cm from the needle tip. Voltages of +5.0 kV and −5.0 kV were applied at the needle tip and the aluminum plate, respectively. During the electrospray process, solvent in the sprayed droplets evaporated, and the particles were deposited electrostatically on a substrate attached to the aluminum plate. We used aluminum foil, silicon wafers, and commercial polymer fiber membranes (made from polypropylene) as substrates to collect samples. The electrospray experiment was conducted under controlled conditions of 30 ± 2 °C and a relative humidity of 45 ± 3%. The amount of solution in each syringe was fixed at 0.50 ml for each sample in the experiment. The experiment was also performed with the inner and outer needles both injected with the same uniformly mixed solution at the same rate.

The morphologies of the prepared films were studied using a scanning electron microscope (SEM,; SU1510, Hitachi, Japan), a field-emission SEM (Hitachi S-5200, Hitachi, Japan), and a high resolution transmission electron microscopy (TEM; JEM-2010, 200 kV, JEOL Ltd., Tokyo, Japan). The composition and resistivity of the films deposited on the silicon wafers was measured by an X-ray diffraction (XRD; D2 Phaser, Bruker, Germany) and a four-probe method (Loresta GP low resistivity meter MCP-T600, Mitsubishi Chemical

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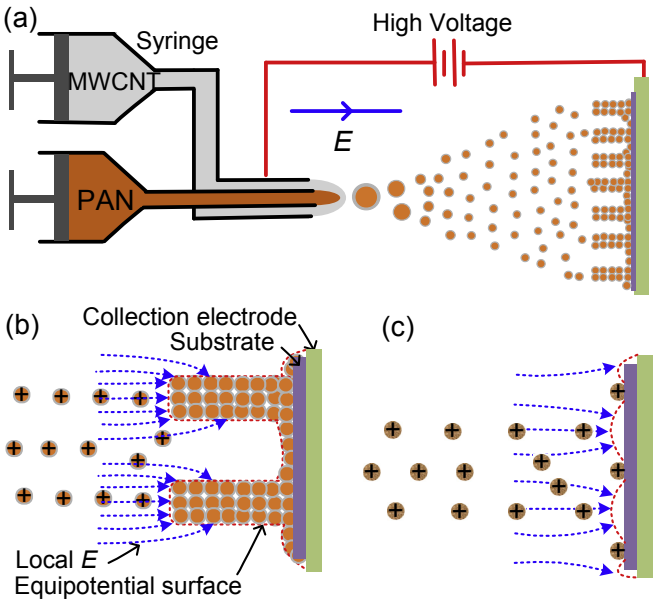

Fig. 1. Schematic of (a) coaxial electrospray system used to fabricate forest films from core-shell PAN/MWCNT particles; and distribution of the local electric field (*E*) during deposition of (b) core-shell particles and (c) uniformly mixed particles. (A colour version of this figure can be viewed online.)

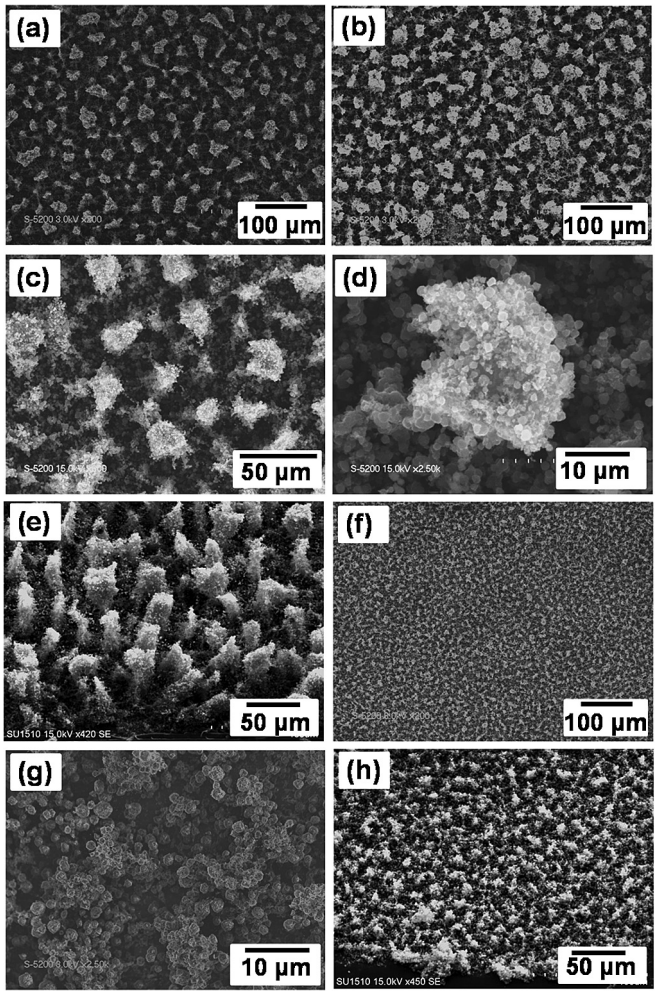

Fig. 2. SEM images of core-shell PAN/MWCNT particles deposited on (a) aluminum, (b–e) silicon substrates, and (f–h) uniformly mixed PAN/MWCNT deposited on a silicon substrate. The high resolution images (c, d) and (g) show detailed structures of the films in (b) and (f), respectively. Images (e) and (h) were obtained at a 45° tilt angle.

Corp., Japan), respectively. All analyses were performed at the center of deposited films.

Fig. 2 shows SEM images of the core-shell PAN/MWCNT particles deposited on the aluminum and silicon substrates, as well as uniformly mixed PAN/MWCNT particles deposited on a silicon substrate. Forest-like structures were formed on the conductive aluminum and semi-conductive silicon substrates by the coaxial electrospray deposition of the core-shell PAN/MWCNT particles (see Fig. 2a–e). Fig. 2e shows that the films were constructed of vertically aligned tree-like structures with height and diameter of about 30 μm and 10 μm, respectively. All the tree-like structures were quasi-uniformly distributed on the substrates. Each individual structure was assembled from particles with diameters of ~1 μm (see Fig. 3a and b). There were many nano-fibrils on the surface of the particles that were generated by coaxial electrospray with the MWCNTs as the shell flow. The inset in Fig. 3b shows that the nano-fibrils are MWCNTs. When PAN and MWCNT were uniformly mixed in solution before the electrospray, no obvious forest-like structure was formed by PAN/MWCNT particles generated by the same fabrication system, as illustrated in Fig. 2f–h. Fig. 3c–d show particles with diameters of also ~1.0 μm and porous surface. The porous surface of the particles is constituted of MWCNT nano-fibrils and nano-particles. Comparing to Fig. 3d, Fig. 3b suggests that the MWCNTs coated on the core part to form a layer. Since the used two solutions are miscible, the MWCNTs in the shell part could be fixed on the PAN core surface after solvent evaporated during the spray process. This suggests that the particle is a core-shell structure with PAN as the core and MWCNTs as the shell for the first case. Additionally, the particles made from uniformly mixed PAN/MWCNT solution are uniformly mixed particles. In other words, the MWCNTs uniformly distributed in the whole particle part for the second case.

The core-shell structure of the particles generated from the coaxial electrospray system was further characterized by XRD, as shown in Fig. 4. We compared the XRD patterns of a MWCNT film, and films formed from the core-shell distributed and uniformly mixed PAN/MWCNT particles. The XRD pattern showed peaks from PAN and CNT assigned as C (002) and C (100). The baseline for the uniformly mixed sample was much higher than that for the core-shell sample because of the effect of PAN on film crystal structure. Furthermore, the relative heights of the CNT peaks of the uniformly mixed sample were lower than those of the core-shell sample. The XRD results suggested that the MWCNT surfaces were coated with PAN in the uniformly mixed sample, while the MWCNTs remained on the surface of the core-shell particles. Thus, the XRD results were consistent with our TEM observations shown in Fig. 3.

The CNT forest film could be fabricated not only on conductive and semi-conductive substrates, but also on insulating substrates, such as commercial polymer fiber membranes (see Fig. 5). Our SEM images showed that the core-shell PAN/MWCNT particles assembled into forest-like structure on a fiber membrane, while uniformly mixed particles were quasi-uniformly distributed on the fiber surface. High resolution images of the particles also showed that the particles either piled up or were quasi-uniformly distributed on fibers in the two samples. These results indicate that our coaxial electrospray technique can be used to fabricate CNT forest-like films on fiber membranes. These structures may be widely applied for water and gas filtration technologies,