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Electronic properties of carbon nanotube/fabric composites

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Abstract

Single walled carbon nanotube (SWNT)/fabric composite materials were manufactured using two simple manufacturing processes. The first method is direct deposition of SWNTs by either a spray method or by incubation; the other is a Quasi-Langmuir–Blodgett (QLB) transfer technique. The composite retains high mechanical strength (governed by the fabric), and good electrical properties (determined by the nanotubes). We measure the DC electrical conductivity of the composite fabric to be 5.33 S/cm for the sprayed tubes, 13.8 S/cm for the incubated SWNTs, and 8 S/cm for the QLB transferred tubes; these values are limited not by the nanotube network, but by the surface roughness of the fabric itself. Measurements of the conductivity up to 1 MHz reveal a transport process that proceeds along a random network, with barriers separating the various nanotubes. The material is resistive both to changes in temperature (range of 0–80 °C) and mechanical deformations. The conductivity of the composite decreases by less than 10% when bent around a cylinder of 1 cm diameter.

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Keywords: Carbon nanotube network fabric composite

1. Introduction

Networks of carbon nanotubes are emerging as a material that is relevant from both a scientific and an applications viewpoint, both in stand alone applications or when combined with other materials. Nanotube–polymer composites, for example, have been thoroughly explored [1,2], with embedded nanotubes enhancing the mechanical and electronic properties of the polymer matrix. Two dimensional networks of conducting nanoscale wires such as carbon nanotubes have been fabricated before on a variety of smooth surfaces, such as glass [3], polymers [4], and inorganic oxides [5]. Such networks show two dimensional (2D) percolation features, and evidences of a transport process that proceeds through thermally activated charge hopping between the various nanotube segments [6,7].

In this communication we describe the fabrication and examination of the conducting properties of carbon nanotube networks on a ‘‘rough’’ surface, exemplified by a nonconducting fabric. This composite material has – aside from the interest as a model system for diffusive charge transport along two interpenetrating networks – significant application potential. Lightweight, conducting, wearable fabric can and will be used for microwave absorption, static charge dissipation, resistive and microwave heating, Electromagnetic Interference (EMI) Shielding [8,9], and – in its patterned form – wearable antennas, and interconnects. Functionalized carbon nanotubes have been shown to operate as extremely sensitive sensors for the selective detection of both gases [10] and biomolecules [11]; these sensors will in the future be incorporated as wearable sensors that can be fabricated directly onto various fabrics.

2. Experimental

To fabricate our conducting fabric material, we used two major coating strategies: direct deposition through spaying/incubation, and the QLB thin film deposition tech-

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nique (first demonstrated by Armitage et al. [3]). In both cases, we used purified arc SWNTs (P2) bought from Carbon Solutions, with no additional purification steps. Both methods involve the application of a well dispersed solution of SWNTs to a fabric surface. To make this solution, we use 0.2–0.5 mg/ml of nanotubes in an aqueous solution of 1% sodium dodecyl sulfate (SDS). This solution is mixed by high powered sonication from a probe sonicator for 1 h and 40 W to form a surfactant stabilized suspension. These suspensions are stable for time periods on the order of months with no visible tube flocculation.

One method for direct deposition of the nanotubes in solution onto almost any surface is through a spraying technique, where a dilute (0.01–0.02 mg/ml) solution of well dispersed nanotubes is sprayed through a fine mist onto the substrate of interest. The nanotubes are sprayed onto the fabric surface using a Paasche airbrush, with the fabric heated to 100 °C to avoid forming large droplets and small pools of liquid, which would decrease the film uniformity. The fabric is then soaked in water for 10 min to remove residual SDS. One can also perform a simple incubation and soak the fabric in the nanotube solution directly, under gentle stirring, followed by a water rinsing. Another method used to coat the fabric is the QLB technique, which involves first vacuum filtering the solution of carbon nanotubes in SDS through a porous alumina filter (Whatman, 20 nm pore size), followed by the re-deposition of the film by flowing water over the filter and allowing the film to break free and float on the water's surface, where it can be re-deposited onto the fabric substrate [3].

All resistance measurements were made using a two probe measurement with a Keithley 2400. Frequency dependent conductivity measurements up to 1 MHz were made using an Agilent 4284A LCR meter. SEM imaging was performed using a Hitachi S4700 Field Emission SEM with 1.5 kV and 5 μA emission current.

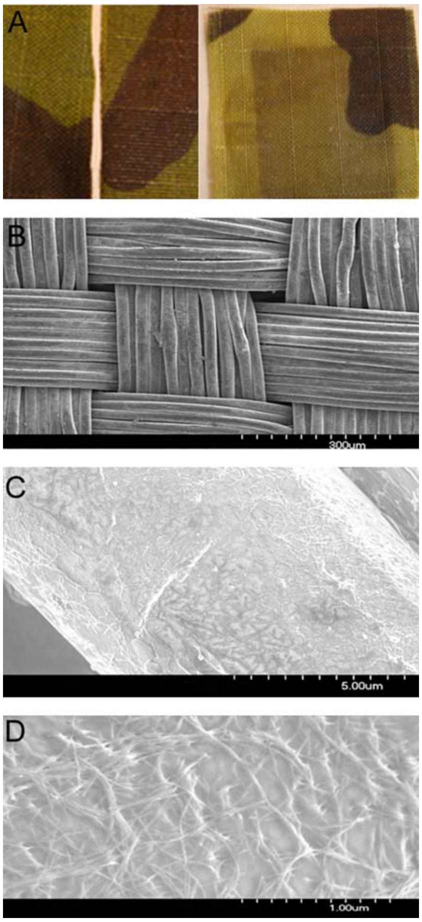

Fig. 1. Optical (A) and SEM (B–D) image of the sprayed nanotube fabric. The optical photograph shows from left to right: fabric with no nanotubes, fabric with incubated layer of 29 kΩ/sq, and fabric with square shaped sprayed area of nanotubes (darker region in middle) yielding about 75 kΩ/sq. SEM image in (B) shows fabric fiber morphology. (C) Shows the tubes coating one of the fibers. The distribution of nanotubes along each fiber in the bundle is non-uniform, but about one monolayer. (D) Shows image zoomed in on one fiber, revealing nanotube bundle sizes between 20–30 nm in diameter and 0.5–2 μm long.

3. Results and discussion

The spray deposition technique is a simple and cheap method for coating a fabric surface with nanotubes. It can make patterns down to the resolution of the spray mist, can be easily scaled up for large area applications, and can be used on almost any surface compatible with water. The results are films of controllable sheet resistance and, for films that are relatively thin, films that retain high transparency. Fig. 1A shows the fabric with a square shaped region in the middle sprayed with nanotubes (far right, darker square in the middle of the fabric has been sprayed), and Fig. 1B–D shows SEM images of the sprayed fabric at increasing magnification. The optical image of the sprayed, conductive fabric shows the camouflage pattern showing through the mostly transparent nanotube layer; it has been shown in previous work that nanotube films can be transparent, as well as conductive [5]. For our hand-held sprayer, the films are not perfectly uniform (film uniformity defined as the variation in nanotube density (NT/Area) over the surface of the fabric). The nanotube density can be determined directly from SEM images, as well as indirectly from measurements of the sheet resistance at various locations of the fabric, since the sheet resistance should be proportional to the network density when well above the percolation threshold [5]. The film shown in Fig. 1A has a sheet resistance of 75 kΩ/sq ± 10 kΩ/sq over the area of the fabric surface sprayed (we used a piece of fabric about 5 cm by 5 cm which can be scaled up for applications). The uniformity of the films will be determined by the droplet size in the spray mist, as well as the spatial distribution of droplets in the mist. These two parameters can be controlled in industrial applications to make films of extremely high uniformity. The nanotube density can be finely controlled by adjusting both the volume of liquid sprayed onto the fabric, and the initial concentration of nanotubes in the aqueous solution.

A simple incubation technique where fabric is soaked in nanotube solution for varying amounts of time under gentle stirring yields fabric that has a higher conductivity than with the spray technique, and has mostly uniform distribution of tubes, but leaves some dark patches where the tubes stick very well to the fabric. Fig. 1A shows a piece of fabric with no nanotubes (far left) and after incubation overnight (middle). The sheet resistance for this fabric is 29 kΩ/sq average where there is a monolayer coverage, with some more dense (thicker) patches of tubes down to 5–10 kΩ/sq that appear visibly darker.

By controlling the density, one can control the sheet resistance ($R_\square$) of the sample. Using the thickness (t) of our nanotube layer, coupled with the measured sheet resistance, one can calculate the DC conductivity of the sample, by using Eq. (1):

$$\sigma_{DC} = 1/(R_\square * t). \tag{1}$$

Using a sheet resistance of 29 kΩ/sq for the incubated fabric and 75 kΩ/sq for the sprayed fabric, and assuming about a one monolayer thick network (with a nanotube bundle size of 25 nm), we calculate a conductivity of 13.8 S/cm for the incubated nanotube films on the fabric and 5.33 S/cm for the sprayed films. It has been shown in previous work [12] that two dimensional nanotube films sprayed onto a flat surface (quartz or plastic) have a conductivity of 150–200 S/cm, which is over one order of magnitude higher than for our films on fabric. The reason for this discrepancy is most likely due to the roughness and curvature of the fabric surface causing poor contact between the SWNTs on separate threads within the fabric. The trend that incubated fabrics have higher conductivity than the sprayed fabric is understandable as the incubation technique allows more intimate contact between the nanotubes in solution and the threads in the fabric, while the spray technique may have some threads masking those beneath them in the weave pattern, thus causing gaps in the nanotube coating. One can use the fabric in simple circuits as shown in Fig. 2, where a battery is hooked in series with an LED and a piece of fabric, which acts as a simple wire or interconnect; application of a voltage across the fabric circuit causes the LED to light.

The second method for nanotube network film deposition involves the re-deposition of a nanotube network from the surface of an alumina filter to the fabric surface. We can make nanotube network films with a conductivity of 1600 S/cm, using a vacuum filtration method to deposit tubes on an alumina filter [13]. However, when we redeposit the film from the filter to the fabric surface using the QLB technique, we measure the conductivity of the film to be about 8 S/cm, which is a decrease in the conductivity by a factor of 200. That is to say, the conductivity, of the same exact SWNT network, is more than two orders of magnitude worse on the rough surface of the fabric, than the smooth surface of the filter. The morphology of the fabric surface makes a significant difference in the film conductivity; discontinuities, crossing threads, and gaps in the fabric itself leads to a dramatic increase in resistance over the nanotube network film on a smooth surface.

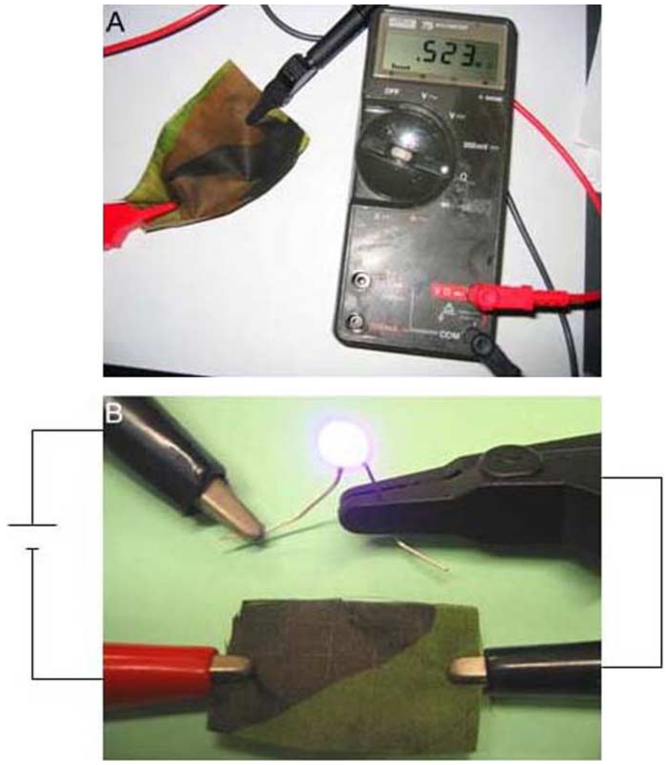

Fig. 2. Conducting fabric can be used as interconnects along a piece of clothing. Here, (A) shows the measurement of the resistance of a thin layer of nanotubes sprayed onto the fabric and (B) shows a circuit set up to light an LED with a battery, using a piece of fabric as a simple wire in series with the battery and LED.

Previous studies of conducting fabric have been done using PEDOT [14] and aniline [15] polymerized on nylon 6 fabric; they yielded maximum conductivities of 2 S/cm and 0.06 S/cm respectively. Fabric coated with polypyrrole by Electrochemical Polymerization yielded conductivity up to 10 S/cm [16]. The nanotube network/fabric composites presented in this paper have competitive conductivities, as shown in Table 1. Nanotube networks are also stable in air and practically insoluble in water once deposited on the fabric. Conducting polymers like polypyrrole are also insoluble in water and concentrated acids, and air

Table 1
Conductivities of various materials on both flat (filter/PET) and rough (fabric) surfaces

Type of surface	Coating type	Conductivity (S/cm)
Flat surface	Nanotubes on filter [13]	1600
	Nanotubes sprayed [12]	150–200
Fabric surface	Nanotubes transferred from filter	8
	Nanotube incubated	13.8
	Nanotubes sprayed	5.33
	PEDOT polymerized [14]	2
	Aniline polymerized [15]	0.06
	Polypyrrole ECP on COP [16]	10

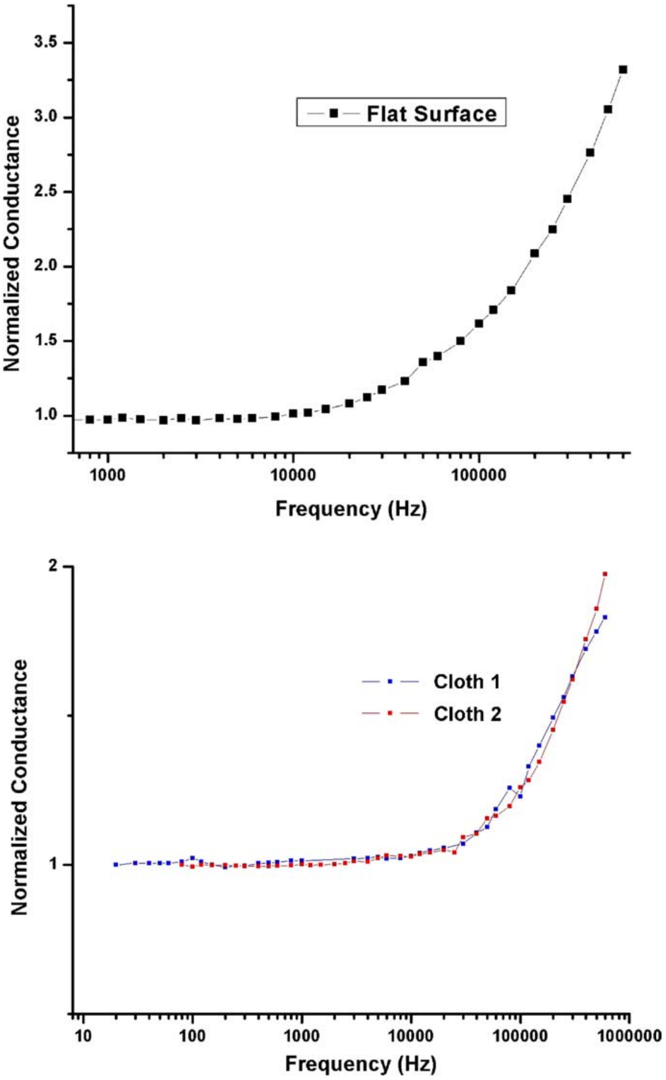

Fig. 3. Frequency dependence of the conductivity. The increasing conductivity with increasing frequency gives evidence of a transport process that proceeds via hopping over (random) barriers. In our system, the tube–tube interconnect provides a random barrier height for electron transport.

stable, but are degraded by oxidants and alkaline solutions. Carbon nanotubes are robust under most weather conditions, and show very little change in conductivity in temperature ranges from −20 °C to 80 °C. Almost no change of the conductivity of the network was found under repetitive bending of the fabric, indicating that the nanotube network is resistive to mechanical distortions. The conductivity of the network decreases by less than 10% when the fabric is wrapped around a cylinder that has a 1 cm diameter.

The overall frequency dependence of the DC conductivity of the nanotube network on the fabric surface is similar to that observed on nanotube networks on flat surfaces [14]. Fig. 3 shows the frequency dependence of the normalized conductance out to 1 MHz for both a flat (filter) and rough (fabric) surface. The increasing conductance with increasing frequency gives evidence of a transport process that proceeds along a random network with barriers separating the various nanotubes.

4. Conclusion

We have fabricated a carbon nanotube network on a rough surface, a fabric. The network has excellent mechanical (determined by the fabric) and electrical properties (determined by the nanotube network), indicating its significant application potential, when combined with wearable photovoltaic or active electronic devices.

The properties of the coated fabric are comparable to conducting polymer coated fabrics. We expect that significant improvement can be made by inter-dispersing the network during fabric production into the fabric matrix itself, creating a more dense – and maybe a three dimensional – network, instead of the two dimensional network that resides on the surface of the fabric. This should significantly aid the conductivity as the limiting factor at this point seems to be topological gaps in the fabric between threads. Also, one can optimize the choice of fabric towards one with a flatter surface. In addition, the network can be modified towards a specific purpose. For example, recognition molecules that are sensitive to different analytes can be attached to the carbon nanotubes themselves to make wearable chemical and biological sensors.

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