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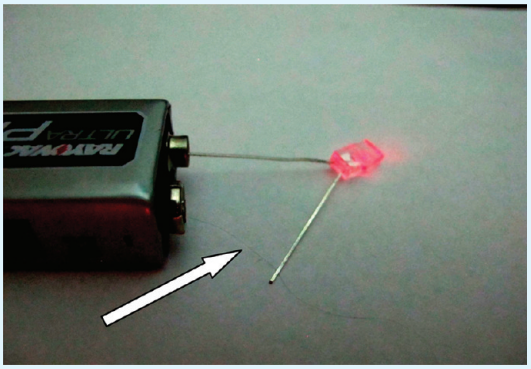
Carbon Nanotube and Graphene Nanoribbon-Coated Conductive Kevlar Fibers

Changsheng Xiang,[†] Wei Lu,[†] Yu Zhu,[†] Zhengzong Sun,[†] Zheng Yan,[†] Chi-Chau Hwang,[†] and James M. Tour*[,†,‡,§]

[†]Department of Chemistry, [‡]Department of Mechanical Engineering and Materials Science, and [§]the Smalley Institute for Nanoscale Science and Technology, Rice University, MS 222, 6100 Main Street, Houston, Texas 77005, United States

Supporting Information

ABSTRACT: Conductive carbon material-coated Kevlar fibers were fabricated through layer-by-layer spray coating. Polyurethane was used as the interlayer between the Kevlar fiber and carbon materials to bind the carbon materials to the Kevlar fiber. Strongly adhering single-walled carbon nanotube coatings yielded a durable conductivity of 65 S/cm without significant mechanical degradation. In addition, the properties remained stable after bending or water washing cycles. The coated fibers were analyzed using scanning electron microcopy and a knot test. The as-produced fiber had a knot efficiency of 23%, which is more than four times higher than that of carbon fibers. The spray-coating of graphene nanoribbons onto Kevlar fibers was also investigated. These flexible coated-Kevlar fibers have the potential to be used for conductive wires in wearable electronics and battery-heated armors.



KEYWORDS: *carbon nanotubes, graphene nanoribbons, Kevlar fiber, spray coating, conductive fiber*

INTRODUCTION

The effort toward producing lightweight fibers that are conductive with superior strength and flexibility continues. Carbon fibers were the first commercialized product with these properties; they have been produced and used in numerous applications for several decades, particularly in the aerospace industry as a material of nonmetal construction. The use of carbon fibers in the automotive industry is growing as their price continues to decline. Carbon fibers are mainly produced from polyacrylonitrile (PAN) and pitch. The process includes stabilization, carbonization and graphitization, each step requiring a specific high temperature range. The final product has high tensile strength (3−7 GPa), modulus (200−500 GPa), and conductivity (556−9090 S/cm).[1,2]

Although the production of carbon fibers brought a revolution to the industry, most applications have been focused on their mechanical properties such as their reinforcing effect in polymer, ceramic and metal composites,[3−5] as well as electrical applications such as cathodic protection, brushes in electrical apparatuses and in lithium ion batteries.[6−8] However, their use in electrical applications as conductive wiring has not been well-explored. One reason is that their electrical conductivity is much lower than that of most metallic wire, but in some applications such as LED lighting and wearable electronics, this is not critical since they do not require very high conductivity. Moreover, carbon fiber is brittle and not easily bent or woven. Because conducting wire has to be bent and fastened to make electrical connections, the brittleness of carbon fiber is a detriment.[9] The elongation at break and the knot efficiency of carbon fiber are less than 2 and 5%, respectively.[2,10] These deficiencies make carbon fiber less attractive in applications such as wearable displays, data managing devices, solar cells, and biomedical sensors.[11−13] Therefore, a conductive and lightweight but more flexible fiber would be valuable in these applications and these fibers could bridge the gap between carbon fibers and conductive metal wires. Carbon nanotube-based fibers have been produced to address this problem[10] but the material and processing cost of carbon nanotube fiber is too high for commercial applications, and their tensile properties are often unattractive.

The idea of coating a conductive material such as carbon nanotubes (CNTs) or metals on the surface of existing flexible commercial fiber has been recently proposed. A CNT-coated fiber could be a good product to solve the brittleness problem; a comparison schematic of metal wires, CNTs fiber, coated fiber and carbon fiber is shown in the Supporting Information, Figure S1. Fugetsu et al.[14] succeeded in coating CNTs on the surface of polyester fibers with the aid of a surfactant. However the coating thickness was only 400 nm, which did not produce a large increase in conductivity. Moreover, the surfactant must be removed from the fiber before use, which make the procedure complicated. Shim et al.[15] produced electronic yarns made by coating CNTs with polyelectrolytes. The as-made yarn was ∼1.5 mm in diameter, yielding a conductivity of 3 S/cm.

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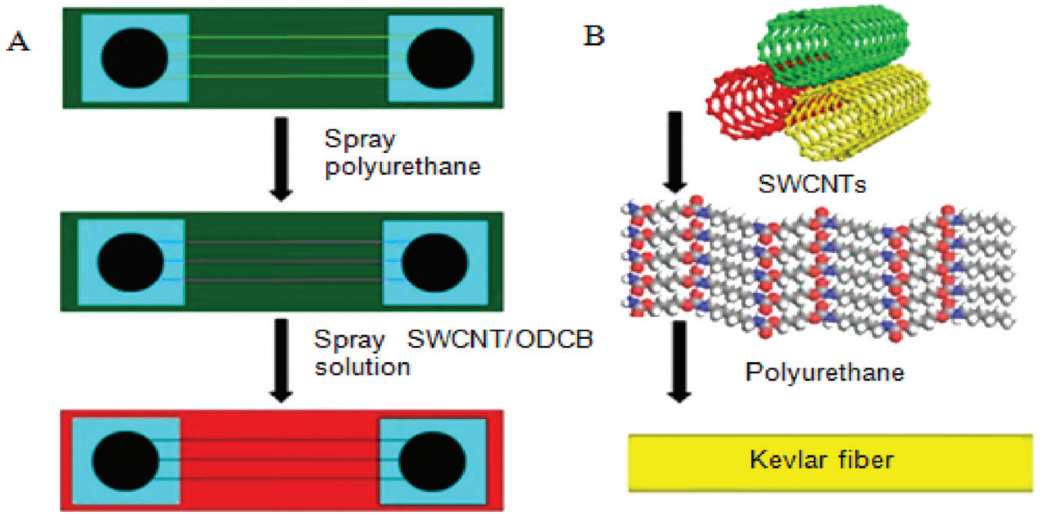

Figure 1. Experimental design. (A) Kevlar fibers (top, yellow, at room temperature) were sprayed with polyurethane to produce polyurethane-coated Kevlar fibers (middle, pink, still at room temperature); that was followed by spraying a SWCNT/ODCB solution onto their surfaces, resulting in the final products (bottom, black, hot plate at 200 °C). (B) Illustration of layer by layer spray coating.

Little et al.[16] used an electrochemical gold plating process to deposit metals onto Kevlar yarns, and the as-made yarn had a conductivity of ~1 S/cm. Liu et al.[17] used electroless deposition of metal particles onto brush-modified cotton yarn to produce a product with a conductivity of 1 S/cm. However, these yarns were not conductive enough to be used as wires in electronic circuits.

Here, we report a facile and inexpensive method for making high performance fibers by layer-by-layer spray coating polyurethane and CNTs or graphene nanoribbons (GNRs) onto Kevlar fibers. CNTs are attractive materials in electronic areas due to their lightweight and high conductivities.[18−20] Kevlar fiber is a unique combination of high flexibility, high modulus, toughness and thermal stability.[21] The fibers disclosed here combine the advantages of conjugated carbon materials and Kevlar fibers, retaining the mechanical properties of Kevlar while exploiting the conductive carbon. The as-produced fibers could be used as conductive wires in some wearable electronics, and could also be woven into a battery-heated armor for military use. This technology could be scaled and could be expanded to Nylon and Dyneema fibers to make other lightweight, tough and conductive fibers.

EXPERIMENTAL SECTION

2.1. Materials. Single-walled carbon nanotubes (SWCNTs), HiPco (Batch #194.3), were obtained from Rice University's Carbon Nanotechnology facility. Multiwall carbon nanotubes (MWCNTs) were generously donated by Mitsui & Co., Ltd. Graphene nanoribbons (GNRs) were synthesized by longitudinal splitting of MWCNTs using potassium vapor.[22] Polyurethane Clearcoat automotive spray paint was obtained from Dupli-color Products Company. Kevlar fiber K29 (diameter = 12 μm) was purchased from DuPont. *O*-dichlorobenzene (ODCB) was purchased from Sigma-Aldrich. The steel airbrush was purchased from Anest Iwata Corporation (Iwata HP-CS). The hot plate was from IKA (C-MAG HP 7).

2.2. Characterization. Scanning electron microscopy (SEM) imaging was performed on a FEI Quanta 400 high resolution field-emission SEM. Mechanical tests were done using an Instron Model 1000; the tension rate was 0.5 mm/min and gauge length was 12 mm; each result was based on 10 samples. The electrical conductivity was measured using a Keithley 2400 with a four-probe configuration, and the electrical conductivity was calculated from the average of 10 different samples. The film thicknesses were determined by SEM or optical microscopy.

2.3. Preparation of Spray-Coated Fibers. As illustrated in Figure 1, carbon tapes were first affixed to microscope slides and the starting Kevlar fibers were parallel mounted on the carbon tapes, followed by covering with another carbon tape on top to secure the fibers. Polyurethane was sprayed on the fibers for 10 s; other polymer-based binders such as epoxy were tried, but their adhesion to the Kevlar fibers was not as good as that of polyurethane. The coating thickness of ~0.5 to 1 μm was measured using an optical microscope. The coated fiber was dried for 3 h at room temperature. SWCNTs (40 mg) were added into ODCB (40 mL) to make a 1 mg/mL suspension. The suspension was sonicated in a bath sonicator (Cole Parmer, model 08849−00) for 2 h to make a homogeneous dispersion. After that, the SWCNT/ODCB solution was poured into the airbrush cup. The airbrush was connected to a nitrogen tank which provided the gas pressure necessary for spraying, and the spray rate was controlled by adjusting the nitrogen flow rate. Finally, the glass slide with the fibers was placed on a hot plate that was set at a surface temperature of 200 °C. The SWCNT/ODCB solution was sprayed on the fibers; once the solution touched the fibers on the hot plate, the ODCB evaporated, leaving SWCNTs on the surface of the fibers. The spraying must be carried out in a well-ventilated fume hood. The spray rate should be constant in order to have uniform coatings. A thickness of ~2 μm SWCNTs was coated on the fiber in 30 s. The coated fibers were removed from the hot plate and cooled for 1 h in the fume hood before the conductivity measurement. The coating procedure was the same for MWCNTs and GNRs.

RESULTS AND DISCUSSION

3.1. Surface Morphology and Electrical Conductivity. Obvious color changes occurred during the coating process. The starting Kevlar was yellow, and it became black after spray-coating a layer of CNTs or GNRs. The uniform surface morphology of a SWCNT-coated Kevlar fiber is shown in Figure 2. The starting diameter was 12 μm, with an average of 0.8 μm of polyurethane and 2 μm of SWCNT coating. The filament had a conductivity of 65 S/cm. In order to demonstrate the conductivity of the SWCNT-coated Kevlar filament, it was used to light a light emitting diode (LED), as shown in Figure 3. More important, the coated filament is only ~18 μm in diameter, which makes it a perfect candidate for use in lightweight miniature electronics and fabrics. The filaments can also be twisted into a bundle for some applications that

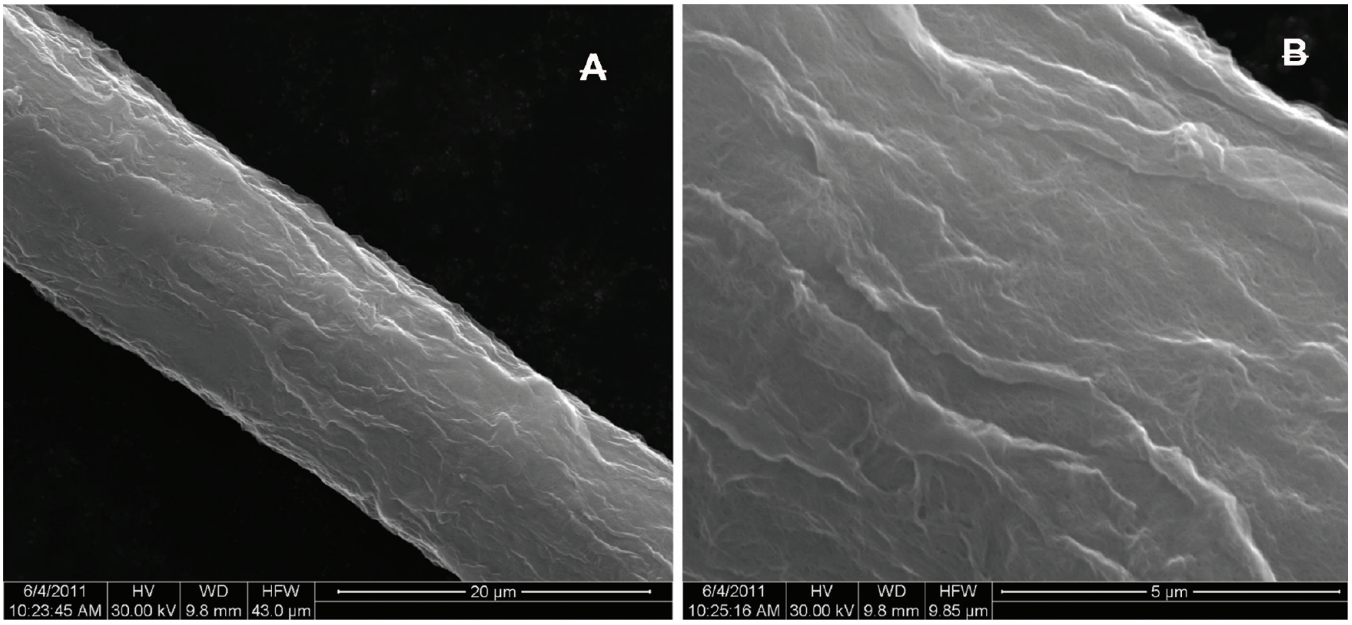

Figure 2. SEM images of (A) a SWCNT-coated Kevlar fiber, scale bar is 20 μm, and (B) enlargement of image in A; scale bar is 5 μm.

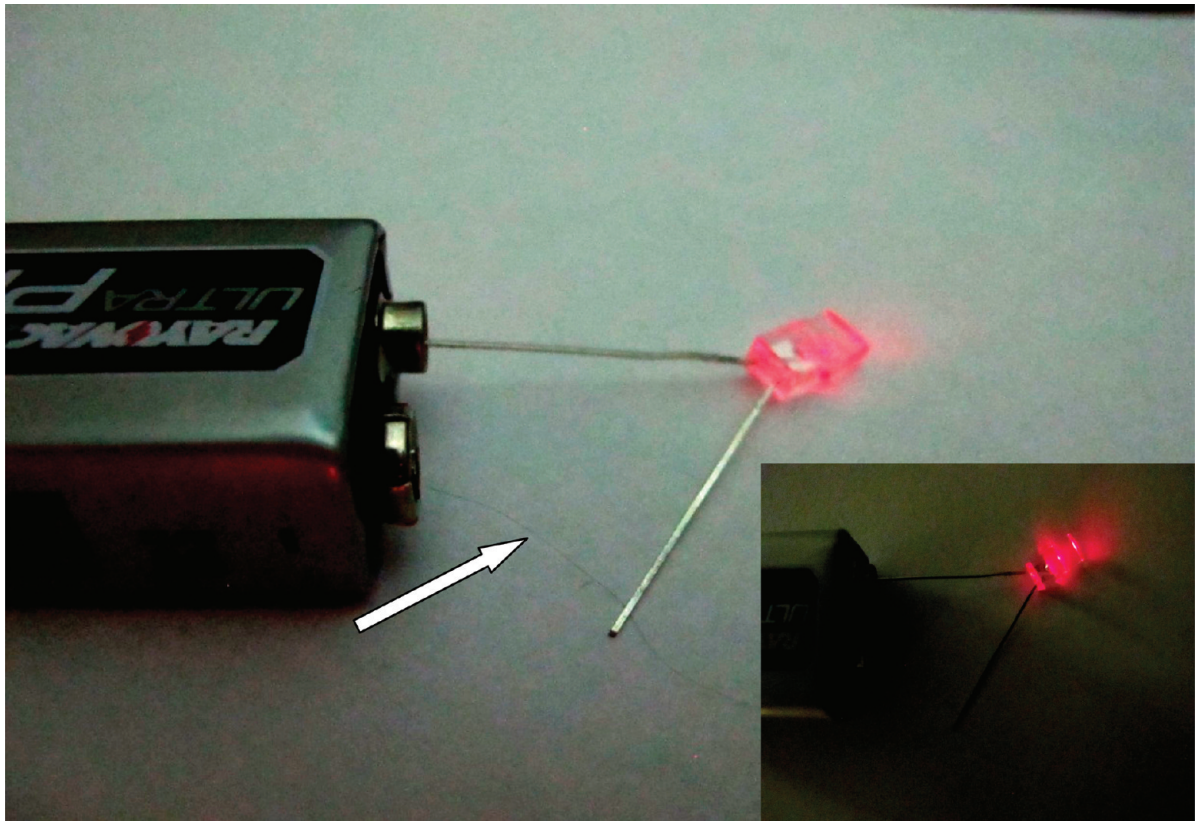

Figure 3. Demonstration of LED emission by using a SWCNT-coated single filament. The white arrow indicates the filament that was knotted to the LED wire and fixed to the battery by carbon tape. The inset is an image taken when the light in the room was turned off.

require lower resistivity cables. The MWCNTs and GNRs were also coated onto Kevlar fibers using the same procedure, and their conductivities were lower than SWCNT-coated fibers, being 9 and 20 S/cm, respectively. In panels A and B in Figure 4, the surface morphologies of the GNR and MWCNT-coated fibers are shown. These morphologies are not as smooth as in the SWCNT-coated fiber because of the larger sizes of the starting aggregates as well as their poor dispersion in ODCB. The length distributions of the tubes and ribbons are shown in Figure S2 in the Supporting Information. However, the conductivity of GNR-coated Kevlar fiber is higher than that of MWCNT-coated Kevlar fiber under the same conditions. Possibly the GNRs have better electrical contact between each other thus lowering the contact resistance relative to the

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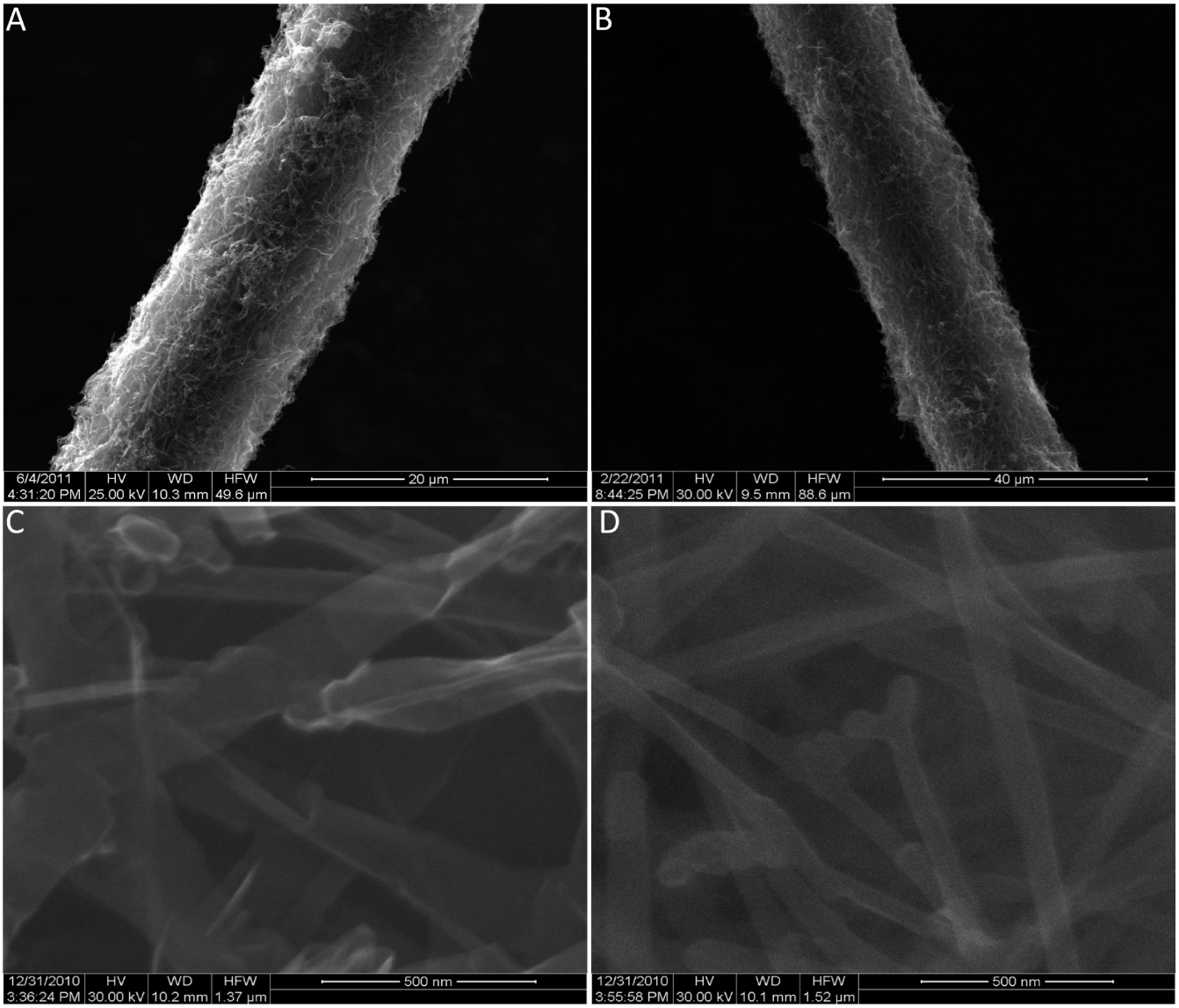

Figure 4. SEM images of GNR and MWCNT-coated Kevlar fibers. (A) A GNR-coated Kevlar fiber; the scale bar is 20 μm. (B) A MWCNT-coated Kevlar fiber; the scale bar is 40 μm. (C) Starting GNRs; the scale bar is 500 nm. (D) Starting MWCNTs; the scale bar is 500 nm.

MWCNTs. SEM images of the starting MWCNTs and GNRs are shown in panels C and D in Figure 4. Electrical conductivities of the fibers are summarized in Table 1.

Table 1. Electrical Properties of CNT and GNR-Coated Kevlar Fibers

solution	diameter[a] (μm)	diameter[b] (μm)	diameter[c] (μm)	σ (S/cm)
MWCNT/ ODCB	12	13.5 ± 0.5	18 ± 2	9
GNR/ODCB	12	13.5 ± 0.5	18 ± 2	20
SWCNT/ODCB	12	13.5 ± 0.5	18 ± 2	65

[a]Starting Kevlar fiber. [b]After coating with polyurethane. [c]After coating with the carbon source.

Representative $I-V$ curves for each carbon-coated Kevlar fiber are provided in Figure S3 in the Supporting Information.

3.2. Mechanical Stability and Electrical Durability. The spray-coated Kevlar fibers do not show any degradation in their mechanical characteristics when compared to the control samples. The mechanical test results are shown in Figure 5A; the breaking load of coated Kevlar fibers is slightly higher than in the control sample, a result of the polyurethane/SWCNT coating. The increase in breaking load was an indication that the adhesion between the Kevlar fiber and the polyurethane/SWCNT coating is quite stable. To further ensure good adhesion, a 10-cm-long SWCNT-coated Kevlar fiber was produced and a 90° bend in the fiber was repeated 50 times. The conductivity was measured after each set of 5 cycles, and only minimal degradation in the conductivity was found, as shown in Figure 5B. Moreover, another 10-cm-long SWCNT-coated fiber was made and washed with water by simple dip washing; it was then dried with blowing air. No dramatic decrease in conductivity was detected after 50 water-washing cycles as shown in Figure 5B. These two tests affirm that SWCNTs adhere well to the Kevlar surface.

In addition, we also studied the durability of the coated fiber after aging. The SWCNT-coated Kevlar fiber was stored in a Petri dish in an ambient atmosphere for 4 months; it was then tested for electrical conductivity and SEM images were

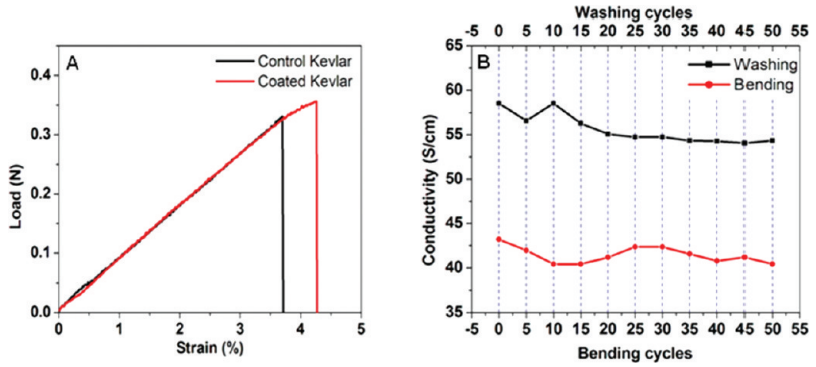

Figure 5. (A) Mechanical properties of control and SWCNT-coated Kevlar fibers. (B) Electrical conductivity of SWCNT-coated Kevlar fibers with 50 cycles of bending or washing.

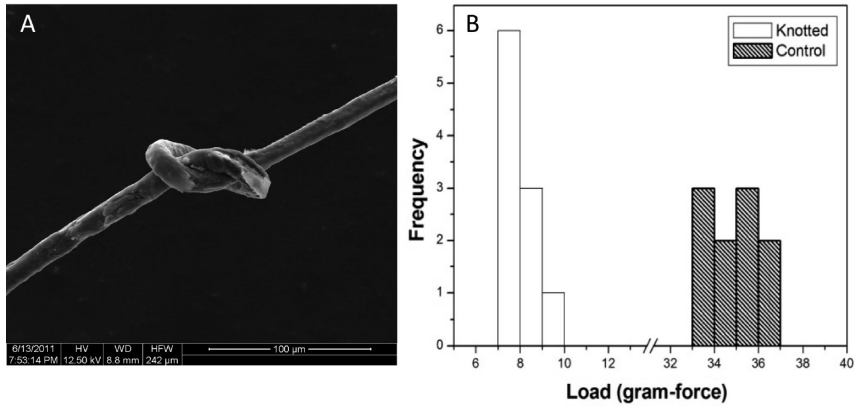

Figure 6. (A) SEM image of a knotted SWCNT-coated Kevlar filament; the scale bar is 100 μm. (B) Breaking load knot-test histogram for SWCNT-coated Kevlar fibers.

obtained. The conductivity was 46 S/cm while the original conductivity was 65 S/cm, and it was still able to be used to light a LED. The SEM images confirmed that SWCNTs did not separate from the fiber surface during aging; see Figure S4 in the Supporting Information. There are at least two reasons for the stability of the coating: (1) the polyurethane was heated to 200 °C, which made it more adhesive, easily binding the SWCNTs to the polyurethane; (2) the surface of the polyurethane was swollen by the ODCB, producing a polyurethane/SWCNT composite.

3.3. Flexibility and Knot Efficiency. In Figure 3, the coated Kevlar filament was connected to the LED by knotting, which is more convenient and less expensive than using conductive adhesives. This unique property makes it more attractive for industrial applications as compared with carbon fibers because carbon fibers lose almost 95% of their strength when they are knotted or even wound around a small diameter cylinder.[10] A terminology called knot efficiency is used to evaluate materials' mechanical properties when they are knotted. Knot efficiency is calculated by dividing the breaking strength of a knotted fiber by the breaking strength of the fiber without knotting.[23] In Figure 6A, an SEM image of a SWCNT-coated Kevlar knot is shown. The SEM contrast is misleading; the film does not delaminate from the fiber upon knotting. Ten samples of both the control and knotted fiber were tested. On the basis of those results in Figure 6B, the knot efficiency of SWCNT-coated Kevlar fibers is calculated to be 23%, which is more than four times higher than that of carbon fibers.

CONCLUSION

The conductive SWCNT-coated Kevlar fiber obtained as described here provides a simple solution for applications that require flexible and conductive yarns, with many parameters exceeding the existing metal-coated yarns and carbon fibers. With 2 μm of SWCNT-coating, the fiber yields a durable conductivity of 65 S/cm. This conductive yarn could be used as conductive wires in wearable electronics, and woven into a battery-heated armor. The filaments can also be twisted into a bundle for high loading and lower resistivity requirement applications. This manufacture process is facile and effective and could be expanded for use on other fibers, and could bridge the gap between carbon fibers and conductive metal wires.

ASSOCIATED CONTENT

Supporting Information

Materials comparison, length distribution, $I-V$ curves, and SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tour@rice.edu.

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