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Hyun Suk Kim [a], Minsung Kang [a], Hyoung-Joon Jin [a], In-Joo Chin [a], Hyoung Jin Choi [a] & Jinsoo Joo [b]

[a] Department of Polymer Science and Engineering, Inha University, Incheon, Korea

[b] Department of Physics, Korea University, Seoul, Korea

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# Carbon Nanotube-Organized Polymeric Fibers and Measurement of Their Electrical Conductivity

**Hyun Suk Kim**
**Minsung Kang**
**Hyoung-Joon Jin**
**In-Joo Chin**
**Hyoung Jin Choi**
Department of Polymer Science and Engineering, Inha University, Incheon, Korea

**Jinsoo Joo**
Department of Physics, Korea University, Seoul, Korea

*This study developed a simple, potentially mass-producible and environment-friendly method for incorporating carbon nanotubes onto the surface of polymeric single fibers by adsorption in water containing surfactants. The carbon nanotubes used in this study were multiwalled carbon nanotubes (MWCNTs) that had been synthesized using a thermal chemical vapor deposition method. The MWCNTs were sonicated in an aqueous solution of non-ionic polyoxyethylene octyl phenyl ether in order to prevent agglomeration due to van der Waals attractions. The electrical conductivity of the MWCNT-adsorbed fibers at room temperature ranged from* $6.2 \times 10^{-3}$ *S/cm to* $6.0 \times 10^{-2}$ *S/cm, which suggests that the MWCNTs were adsorbed uniformly and densely along the fiber.*

**Keywords:** adsorption; composite fibers; electrical conductivity; multiwalled carbon nanotubes; surfactants

## INTRODUCTION

Conducting fibers are becoming of increasing importance not only because of their electrical and mechanical properties from

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Address correspondence to Hyoung-Joon Jin, Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea. E-mail: hjjin@inha.ac.kr

fundamental viewpoints but also because of their applications in electromagnetic interference shielding or conducting textiles [1–3]. Many researchers have used conducting polymers directly or have incorporated conducting materials such as carbon nanotubes (CNTs) into a polymer matrix to increase the conductivity of conducting micro- and nanofibers [4,5].

Since their discovery by Ijima in 1991 [6], CNTs have attracted enormous interest on account of their excellent mechanical and electrical properties [7]. CNTs are used as reinforcing additives into polymeric materials and their composites have potential applications in many industrial areas. In addition, the good electrical properties of CNTs can increase the conductivity of non-conducting polymers [8–10]. Fibers containing CNTs are generally produced by wet spinning or electrospinning methods [4,5,11,12]. However, the appropriate homogeneous dispersion of CNTs in fibers for practical applications of this unique material has been rarely achieved.

Silk fibers have been investigated over the past 10 years because of their unusual mechanical properties as well as their biocompatibility. Spider dragline silk is the strongest known natural fiber, and is used by the spider as the safety line and as the frame thread of as orb-web. These fibers are three times as tough as synthetic fibers and are five times stronger by weight than steel [13].

This study fabricated conducting fibers using multiwalled carbon nantotubes (MWCNTs) adsorbed on single silk fibers. The electrical conductivity and the surfaces of the MWCNTs-adsorbed fibers were examined.

## EXPERIMENTAL

### Materials

We collected the spider dragline silk fibers from the orb-web spiders (*Araneus ventricosus*) and the sericin extracted insect silk fiber from the domesticated silkworm cocoons (*Bombyx mori*). The MWCNTs (Iljin Nanotech Co., Korea) synthesized by a thermal chemical vapor deposition (CVD) method was used.

### Purification of MWCNTs

The purity of the as-received MWCNTs was 97%. The impurities in the MWCNTs (such as metallic catalysts) were removed by treating them with 3 M $HNO_3$ at 60°C for 12 h, followed by a refluxing in 5 M HCl at 120°C for 6 h [13]. The purity of the acid-treated MWCNTs,

as measured by thermogravimetric analysis (TGA, Polymer Lab., TGA1000, UK), was 99%. Acid-treatments are known to introduce carboxylic functional groups to the MWCNT surface [14,15].

## Preparation of MWCNT Dispersion

The purified MWCNTs were dispersed in pure water, using non-ionic polyoxyethylene octyl phenyl ether (Triton X-100) and anionic sodium dodecyl sulfonate (SDS) as surfactants (0.3 wt%). Ultrasound was then applied to the MWCNT dispersion for 7 h at 25°C using a ultrasonic generator (Kyungill Ultrasonic Co., Korea) with a nominal frequency of 28 kHz and a power of 600 W.

## Adsorption of MWCNTs on Single Silk Fibers

Single silk fibers were fixed on a frame, as shown in Figure 1. Single silk fibers were immersed in a glass bath containing the MWCNT dispersion for 15 s, rinsed briefly (60 s) in deionized water and dried under ambient conditions.

## Measurement of DC Conductivity

The four-probe method was used to measure the electrical properties of the MWCNTs-adsorbed single fibers. A Keithley 237 source measurement unit (SMU) was used to determine the electrical properties. The one strand of a sample was fixed onto a slide glass, and then four thin gold wires (50 μm thick and 99.99% pure gold) were laid vertically onto the samples. Another cleaned small glass was placed onto the gold wires and pressed for better electrical contact. All the measurements were performed in the open air. The measurements

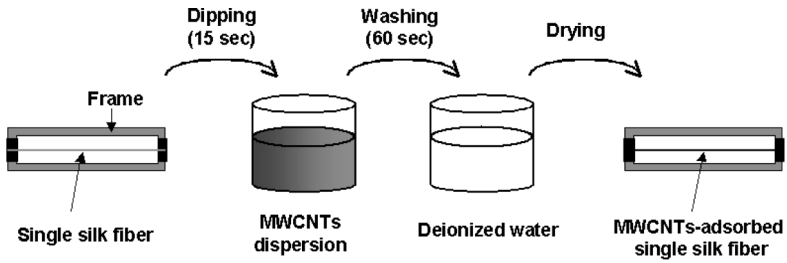


**FIGURE 1** Schematic diagram of the process of adsorbing carbon MWCNTs on the surface of the fibers.

were repeated to confirm the electrical uniformity of the samples. A micrometer, optical microscope, and scanning electron microscopy (SEM) images were used to determine the dimensions of the samples such as the diameter (10 μm ~ 15 μm) and length (1 mm).

## RESULTS AND DISCUSSION

In the as-synthesized MWCNTs, individual MWCNTs were found within an amorphous material in the form of bundles, which were several hundred micrometers long. The MWCNTs were entangled with impurities such as metal catalysts that formed large submicron aggregates. The MWCNTs were purified using a two-step purification procedure including oxidation, as described in the experimental section, which effectively removed the impurities such as metal particles, as shown in Figure 2.

A surfactant was used to disperse the MWCNTs in an aqueous media in order to prevent the MWCNTs from aggregation due to substantial van der Waals forces. Two types of surfactants, Triton X-100 and SDS, were used to disperse the purified MWCNTs, which resulted in homogenous black ink-like solutions after ultrasonication.

Figure 2 shows that the MWCNTs are densely adsorbed on the surface of the single silk fibers, which were obtained when the MWCNTs were dispersed in an aqueous solution of Triton X-100. Interestingly, virtually no MWCNTs were adsorbed on the surface of fibers when an ionic surfactant (SDS) was used. It was very recently reported that the interactions between the surfactant molecules and the CNT surface are mostly hydrophobic in nature [16–18]. Therefore, the electrostatic repulsion between the charged headgroups of the surfactant molecules adsorbed on the silk fiber and MWCNT surfaces, respectively, may be responsible for the absence of the adsorbed MWCNTs on silk fiber surfaces. In addition, the non-ionic surfactant molecules could potentially serve as the link between the MWCNTs and silk fibers, providing hydrophobic interactions that would enhance a more intimate contact at the interface between silk fiber and MWCNTs. Although the exact reason for the good adhesion of the MWCNTs on the fibers when Triton X-100 was used is unclear, it should be noted that the choice of surfactant is critical for inducing the required interactions between the polymers and the MWCNTs. We also examined the cross section of the MWCNT adsorbed fibers after fracture in liquid nitrogen (Fig. 2). Two different domains could be distinguished, which included a core silk fibroin and an external shell of adsorbed MWCNTs.

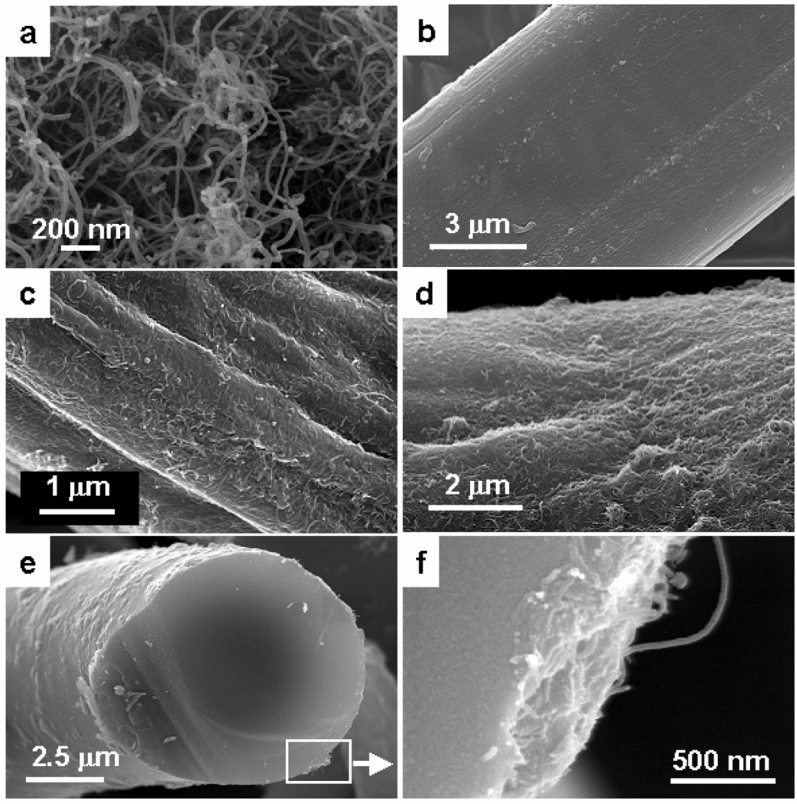


**FIGURE 2** High resolution SEM images of (a) the purified MWCNTs, (b) native silkworm silk fiber, (c) MWCNT-adsorbed silkworm silk fiber, (d) MWCNT-adsorbed spider silk fiber, and (e) and (f) the fractured surface of MWCNT-adsorbed spider silk fiber.

The electrical properties of the single silk fibers were determined by measuring the DC conductivity ($\sigma_{DC}$) using the 4-probe method to eliminate the contact resistance (Fig. 3). The measured electrical conductivity is summarized in Table 1. The data shows that the conductivity of the silkworm silk fibers was higher than the spider silk fibers. This means that the MWCNTs adsorbed more densely on the surface of the silkworm silk fibers than on the spider silk fibers. The electrical conductivity of the silkworm silk fibers was $6.0 \times 10^{-2}$ S/cm, which was the highest value obtained. This was attributed to the fact that the outer shell comprised of MWCNTs on the silk fiber surfaces.

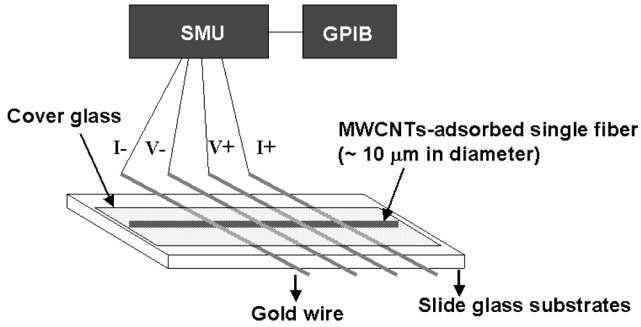


**FIGURE 3** Four probe measurement of the DC conductivity of the MWCNT-adsorbed single silk fibers.

**TABLE 1** Electrical Conductivity of the MWCNTs-Adsorbed Single Silk Fibers

| | Spider dragline silk fiber | Silkworm silk fiber |
|---|---|---|
| Conductivity (S/cm) | $6.2 \times 10^{-3}$ | $6.0 \times 10^{-2}$ |

## CONCLUSIONS

Electrically conductive single silk fibers were prepared using a simple dip-coating method in aqueous MWCNTs dispersion with surfactants. When Triton X-100 was used, the MWCNTs were well adhered to the surface of single silk fibers, which improved their conductivity up to $6.0 \times 10^{-2}$ S/cm. Therefore, a combination of the excellent electrical properties of MWCNTs and the good mechanical properties of the single silk fibers can lead to significant advances in the development of new materials such as conducting textiles.

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