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Effects of surfactants on spinning carbon nanotube fibers by an electrophoretic method

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Abstract

Thin fibers were spun from a colloidal solution of single-walled carbon nanotubes (SWNTs) using an electrophoretic method. Sodium dodecylbenzenesulfonate (NaDDBS) was chosen as a surfactant and showed good performance owing to its special chemical structure. The highest spinning velocity reached 0.5 mm s^{-1} . The resulting SWNT fibers had a tensile strength of 400 MPa and a conductivity of 355 S cm^{-1} . Their mechanical and electrical properties were markedly improved after adding NaDDBS as the dispersant in water.

Keywords: carbon nanotube, fiber, electrophoretic assembly, tensile strength, conductivity

 Online supplementary data available from stacks.iop.org/STAM/11/065005/mmedia

1. Introduction

Over the past decade, carbon nanotubes (CNTs) have attracted much interest owing to their unique properties [1–6]. They are an extremely strong material with both high electrical and thermal conductivities, and are therefore a potential filler for polymer composites. CNTs with a length of 1–30 μm are commercially available in dry powder form. The conversion of CNT powder into macroscopic fibers would strongly promote CNT applications. Such fibers can be assembled using the *van der Waals* force between the CNT bundles. Their mechanical properties are mainly determined by the CNT quality [7] and they can be improved by adding poly-acrylonitrile (PAN) [8], polyvinyl alcohol (PVA) [9] and other polymers. Macroscopic CNT fibers are easy to handle; they can be used to reinforce polymer composites and give them anisotropic properties.

CNT fibers can be fabricated by direct chemical vapor deposition (CVD) [10–12], dry spinning [13, 14], wet spinning [15–22] and other methods. Wet spinning yields CNT fibers of high purity with tunable characteristics, because

it allows the selection and purification of the raw CNT powder [23] as well as their alignment [24–26]. However, this method uses organic solvents such as dimethylformamide (DMF) or tetrahydrofuran (THF) as the dispersion medium, which may pose environmental problems. In some studies, superacids were used to dissolve single-walled carbon nanotubes (SWNTs) and the colloidal solution could be used to make fibers [27, 28], but handling such oxidative materials is dangerous. Our group developed an electrophoretic method to make thin fibers with a diameter ranging from 0.2 to 2 μm in an aqueous solution [25]. The tensile strength of the fibers was 65 MPa and the electrical conductivity was 80–200 S cm^{-1} when using CVD SWNTs [29]. In this process, SWNTs are first aligned in water using an alternating current (ac) electric field. Inhomogeneity of the field drives the aligned SWNTs towards the high-field region near a sharp tungsten needle tip. By gradually withdrawing the needle, SWNTs were continuously precipitated at the electrode. A fiber with a small and uniform diameter was formed, and it was compressed and aligned by the capillary pressure of the water interface [25].

The limitation of this method is the difficulty of dispersing SWNTs in water without the aid of surfactants owing to the poor wettability of SWNTs [30]. Sodium dodecyl sulfate (SDS) is commonly used to disperse SWNTs in water [31, 32], but it could not be used to form continuous fibers in our experiments. After experimental screenings, sodium dodecylbenzenesulfonate (NaDDBS) was found to support the electrophoretic method and to disperse SWNTs in high concentration [33–37].

Here, we report the effects of surfactants on the spinning SWNT fibers. We used surfactants to disperse SWNT powders in water and then drew fibers from the resulting stable colloidal solution. When broken, the fibers could be extended by redipping them in the solution. This property should be useful for the scale-up fabrication.

2. Materials and methods

2.1. Acidic treatment of SWNT powder

The SWNT powder (90 wt%, length 5–30 μm) was purchased from Cheap Tubes Inc., USA, and separately treated by two methods: (i) C-SWNTs, sonication in 4 : 1 H_2SO_4 : HNO_3 for 2 h and (ii) R-SWNTs, refluxing in 6 N HNO_3 for 24 h. Then, the SWNT powder was collected by filtration and dried in vacuum at room temperature. The dried powder can be stored in a vacuum cabinet for a long time.

2.2. Preparation of the colloidal solution

The SWNTs treated by acids were dispersed in deionized water by adding a surfactant at a concentration of 0.5–1%. The surfactants used were NaDDBS (~80%, Sigma, USA), SDS (> 99%, Sigma-Aldrich, USA), poly (sodium 4-styrenesulfonate) (PSS, average molecular weight ~ 70 000, Aldrich, USA), sodium alginate (Aldrich, USA), polyethylene glycol (PEG-400, Wako, Japan), PEG-4000 (Wako, Japan) and poly (vinylpyrrolidone) (PVP, Aldrich, USA). The SWNT dispersion formed a stable colloidal solution after 2 h of sonication; it was diluted with deionized water or the surfactant solution. No flocculation or sedimentation was observed within 2 h and this stability was required for the next assembly process.

2.3. Preparation of tungsten wires

A tungsten wire (diameter 0.15 mm, Nilaco, Japan) was electrochemically etched with a KOH solution. The etched part of the wire had a sharp conical shape with an angle of less than 20° . If the tungsten wire was not sufficiently sharp, the SWNT fibers could not be formed because of the large tensile force at the interface between the solution and the wire end.

2.4. Electrophoretic assembly of SWNT fibers

A drop of SWNT colloidal solution was put in a copper cylinder with a pit, and the drop formed a dome as shown in figure 1(e). The SWNT fibers are usually fabricated at

ambient temperature. The evaporation of the aqueous drop can be ignored in this experiment. The tungsten wire was fixed on a motorized stage controlled with the Labview program. Alternating current (10 V, 2 MHz) was applied between the copper vessel and the tungsten wire. The sharp tip of the wire was then immersed in the SWNT dispersion contained in the copper vessel using the motorized stage. Then, the tip was withdrawn from the solution at a constant velocity. The SWNT fiber was continuously formed as shown in figures 1(e) and (f) and in the video clip (available from stacks.iop.org/STAM/11/065005/mmedia).

2.5. Electrical properties of the SWNT fibers

The current–voltage (I – V) curve was measured using a Keithley 6517 electrometer controlled by the Labview program. The diameter of the fibers was measured with a scanning electron microscope (SEM, JEOL JSM-6500).

3. Results and discussion

3.1. Acid treatment and surfactant selection

After sonication in 4 : 1 H_2SO_4 : HNO_3 mixed acids, the SWNTs acquire carboxylic and hydroxyl groups and become dispersible in water at low concentration even without a surfactant. However, this treatment also cuts SWNTs into segments shorter than 1 μm , which degrades the final quality of the produced fibers. The cut SWNTs could be dispersed in a stable 10 mg l^{-1} colloidal solution without any surfactants, but when the concentration was increased, serious flocculation and sedimentation that would hinder the fiber formation occurred [29]. Meanwhile, 6 N HNO_3 treatment kept the tubes nearly intact owing to the gentle character of acidic erosion, that is the length of the R-SWNTs was not shortened by the treatment. Because of the poor wettability, R-SWNTs could form stable colloidal solutions only with the addition of a surfactant.

Continuous SWNT fibers could not be drawn when SDS was used as the surfactant—only a small SWNT bundle could be attached to the tungsten needle after several dippings. When the needle with a short SWNT bundle was reimmersed in the colloidal solution, the SWNT bundle dissolved in the solution. Similar results were obtained for nonionic surfactants such as PEG-400, PEG-4000 and PVP. For PSS and sodium alginate, the fibers could sometimes reach 100 μm in length, but not longer.

When NaDDBS was used as the surfactant, SWNTs could be dispersed at relatively high concentrations (1 g l^{-1} for the C-SWNTs and 0.2 g l^{-1} for the R-SWNTs), and long fibers could be drawn under the same condition as above. The colloidal solutions prepared with NaDDBS were stable for about one month; when the solutions were kept for a longer period, the quality of the fibers produced from them would deteriorate. Before the fiber preparation, sonication is required to refresh the dispersion. The interaction with SWNTs is different for SDS (figure 1(a)) and NaDDBS (figure 1(b)). The latter has a benzene ring and interacts mainly via π – π bonds that seem to be more compatible with the ac electrical

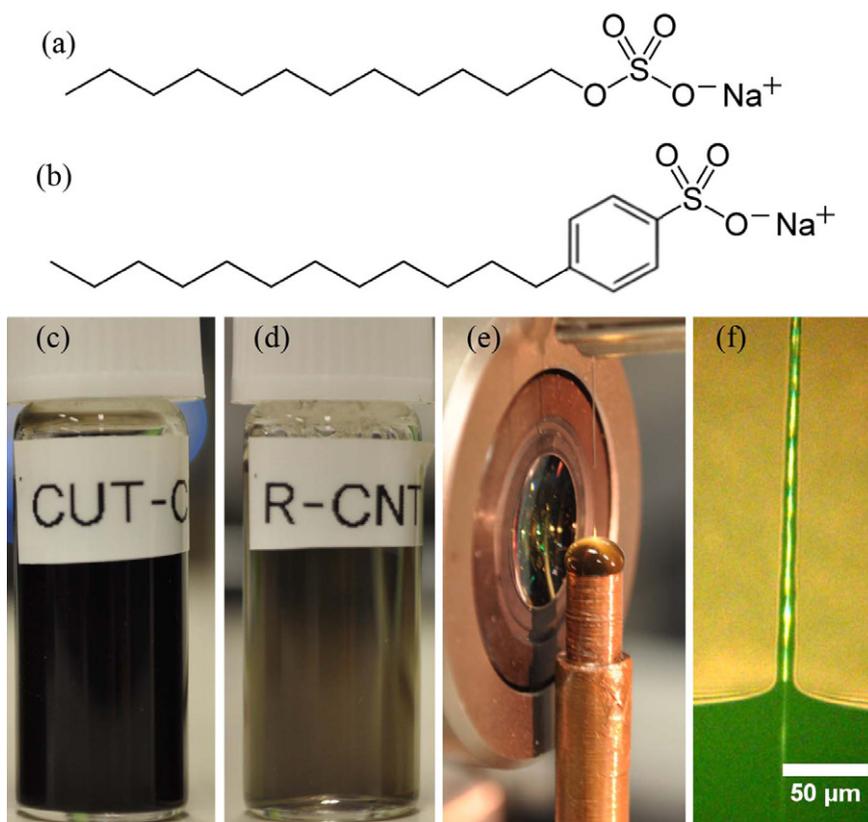


Figure 1. Molecular structures of (a) SDS and (b) NaDDBS and colloidal solutions of (c) 1.1 g l^{-1} C-SWNT and (d) 0.26 g l^{-1} R-SWNT; (e) is a photo of a typical experiment showing the fiber drawn from a drop of a colloidal solution filled in the pit of a copper rod; (f) is an optical microscopy image of the fiber.

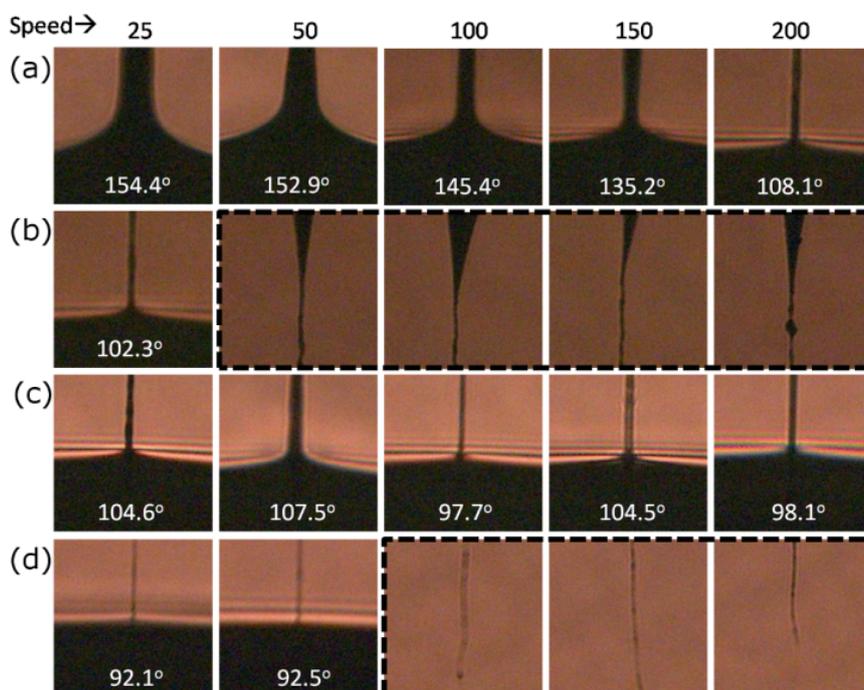


Figure 2. Snapshots of the interface between the formed SWNT fiber and the colloidal solution. (a) C-SWNT, concentration 1.1 g l^{-1} ; (b) C-SWNT, concentration 22 mg l^{-1} ; (c) R-SWNT, concentration 78 mg l^{-1} ; (d) R-SWNT, concentration 7.8 mg l^{-1} . From left to right, the drawing velocities are $25, 50, 100, 150$ and $200 \mu\text{m s}^{-1}$. Each photo has a dimension of $72 \times 72 \mu\text{m}^2$. For the photos marked by the dashed rectangles, the contact angle was close to 90° .

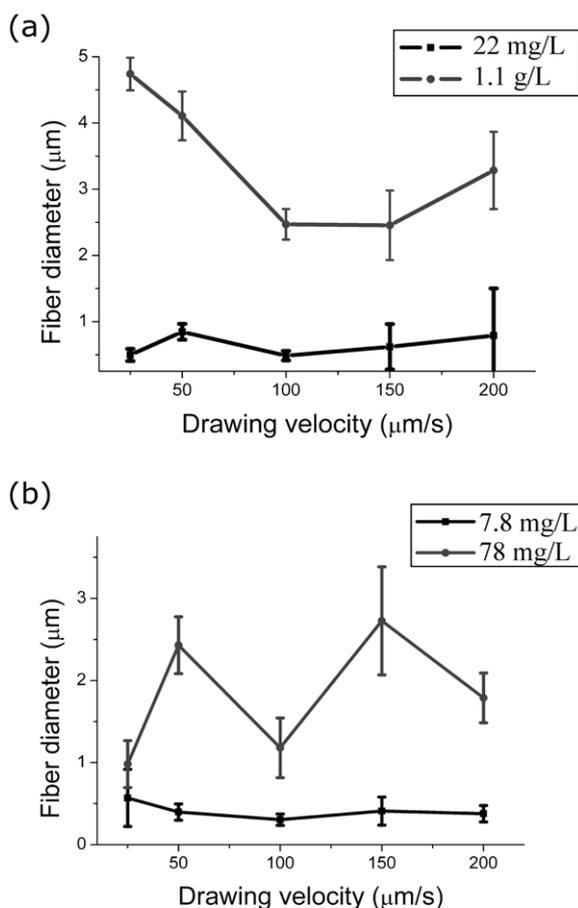


Figure 3. Dependences of the fiber diameter on the SWNT concentration in the solution and on the drawing velocity for (a) C-SWNT and (b) R-SWNT.

field. Besides, the surface tension at the interface between the formed SWNT fiber and the solution is very low for SDS. The contact angles were always close to 90° under this condition; thus, no continuous fibers could be made when SDS was used as the surfactant. Wrapping SWNTs by large molecules such as PSS may also decrease the interaction between the SWNT bundles, thereby hindering their assembly under the electrophoretic field.

Impurities or large agglomerates in the colloidal solution negatively affect the fiber production by the electrophoretic method. Therefore, the SWNT colloidal solution was stored overnight to eliminate the agglomerates by sedimentation. The final stable colloidal solutions are shown in figures 1(c) and (d). In the electrophoretic process, the solution formed an axially symmetrical meniscus around the formed SWNT fiber, where the contact angle is determined by the interfacial energy. The meniscus between the SWNT colloidal solution and SWNT fiber is very important for the continuous formation of the fiber, as the fiber becomes thin and porous upon drying. The dynamic contact angle was measured during the withdrawing process by analyzing photographs. It could range from 90° to 160° depending on the solution concentration and withdrawing velocity, and the angles wider than 120° promoted the formation of continuous fibers.

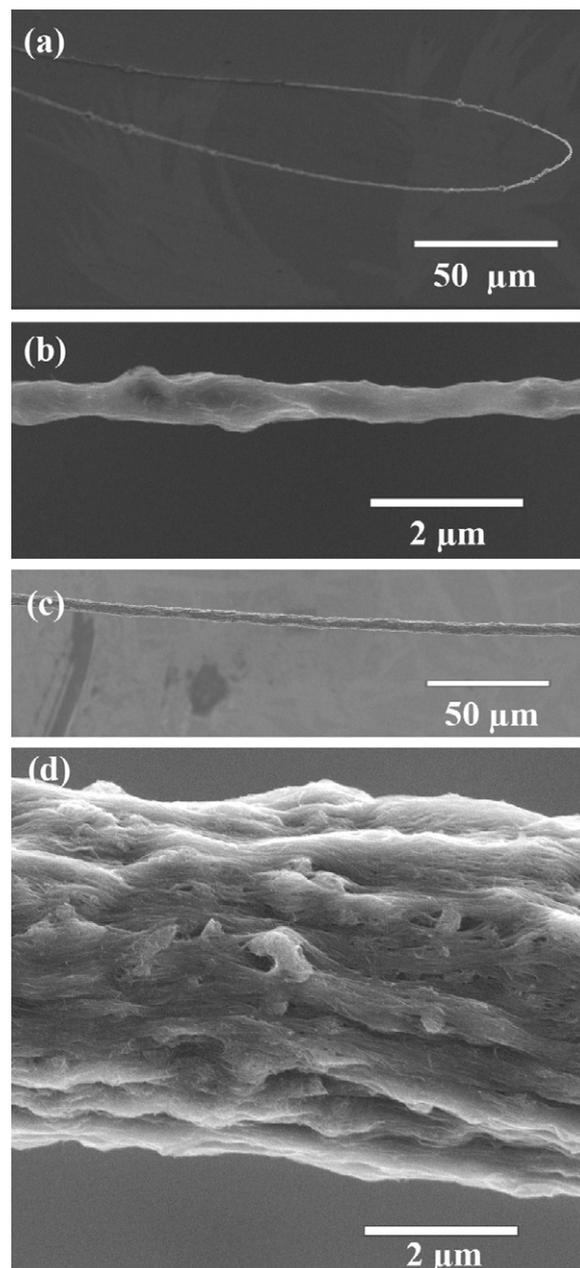


Figure 4. SEM images of the SWNT fibers prepared at SWNT concentrations of (a, b) 22 mg l⁻¹ C-SWNT and (c, d) 1.1 g l⁻¹ C-SWNT.

3.2. Drawing velocity

The velocity of the motorized stage could be changed in our experiment between 2 and 1000 μm s⁻¹. Higher velocities resulted in more uniform and less porous fibers, but also increased the possibility of breaking the fibers by the tensile force between the fibers and the colloidal solution. Higher velocities also resulted in smaller contact angles, thereby increasing the chance of terminating the fiber formation as shown in figure 2. When using the velocity of 1 mm s⁻¹ and a highly concentrated SWNT solution, the contact angle was nearly 90° and the fibers were breaking at a length shorter than 100 μm. However, when the contact angle was kept above 120°, the formation of SWNT fibers was

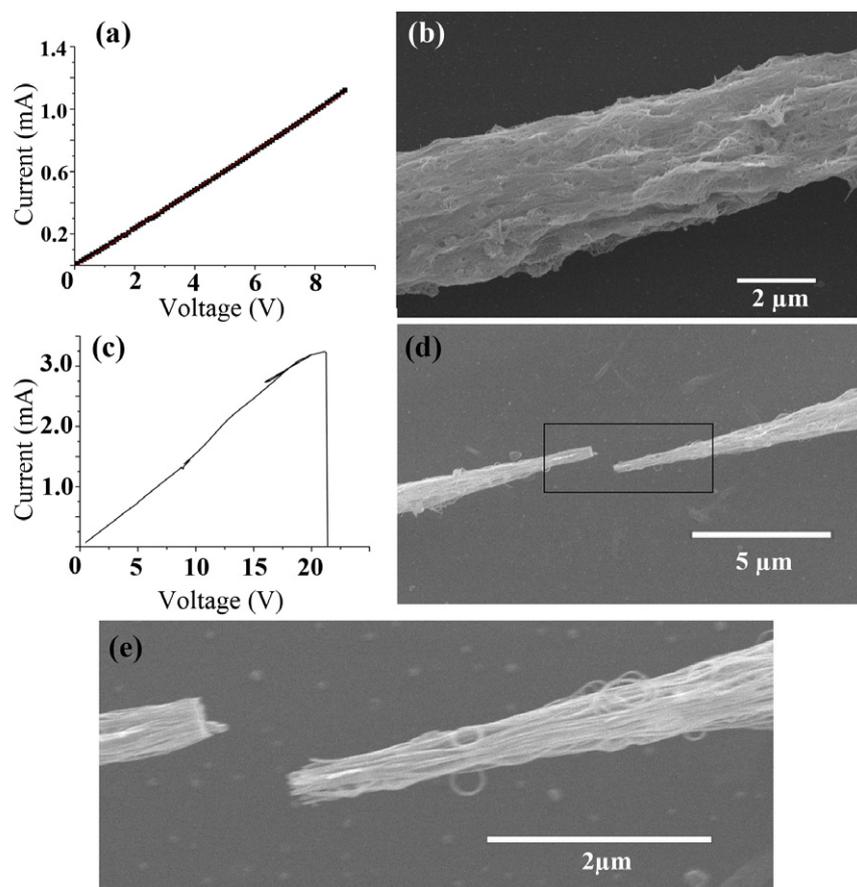


Figure 5. (a) I - V curve of an R-SWNT fiber at low voltages, (b) SEM image of the fiber, (c) I - V curve when increasing the applied voltage until failure, (d) broken point on the fiber, (e) magnification of squared area in (d). Most of the SWNT bundles at the broken point were burned off.

rather stable, as shown in the video clip (available from stacks.iop.org/STAM/11/065005/mmedia).

After applying ac voltage, the SWNT bundles were redistributed between the two electrodes in the colloidal solution, and the SWNT network was formed before the fibers were drawn from the solution [38]. A higher drawing velocity would require a stronger electrical field, so that the network could be maintained upon drawing.

After the obtained SWNT fibers were dried in vacuum, their diameters were measured with SEM. The results shown in figure 3 suggest that the drawing velocity has little effect on the fiber diameter, which could be explained by the existence of the SWNT network between the two electrodes before the fiber formation. The SWNT density in the network should markedly affect the final fiber diameter, which was determined mainly from the concentration of the colloidal solution.

3.3. Concentration of colloidal solution

Highly concentrated SWNT colloidal solutions could be prepared with NaDDBS for the SWNT fiber fabrication, and they could be diluted using water or the surfactant solution. The decrease in the SWNT concentration resulted in smaller contact angles, as shown in the photos in figure 2, and in thinner fibers as shown in figure 3. At the highest tried concentration of 1.1 g l^{-1} for C-SWNTs, the contact angle

reached 154.4° at the drawing velocity of $25 \mu\text{m s}^{-1}$, and the obtained SWNT fiber after drying had a diameter of $4.8 \mu\text{m}$. When the SWNT solution was diluted to 22 mg l^{-1} , the contact angle decreased to 102.3° and the fiber diameter to about $0.5 \mu\text{m}$ at the same drawing velocity. Only short SWNT fibers could be drawn from the diluted SWNT colloidal solution when the drawing velocity was increased to above $50 \mu\text{m s}^{-1}$ —the contact angles were approximately 90° and the fiber formation became unstable. SEM images in figure 4 reveal that the additional surfactant did not change the morphology as compared with the previous results obtained without any surfactants [29]. The preferred orientation of the SWNT bundles was parallel to the long axis of the fiber, as shown in figure 4(d). Some pores were observed on the fiber surface.

Similar tendencies were observed for the R-SWNT colloidal solutions (figure 3(b)): the contact angle decreased as the concentration decreased and was nearly 90° at 7.8 mg l^{-1} , and the obtained fibers had a diameter of 0.2 – $0.5 \mu\text{m}$. At a high concentration of 78 mg l^{-1} , the diameter increased to 1 – $3 \mu\text{m}$.

The relation between the solution concentration and the fiber thickness was nonlinear, particularly at high concentrations, and thus, factors other than concentration may affect the fiber formation. In addition, sparse sampling (three

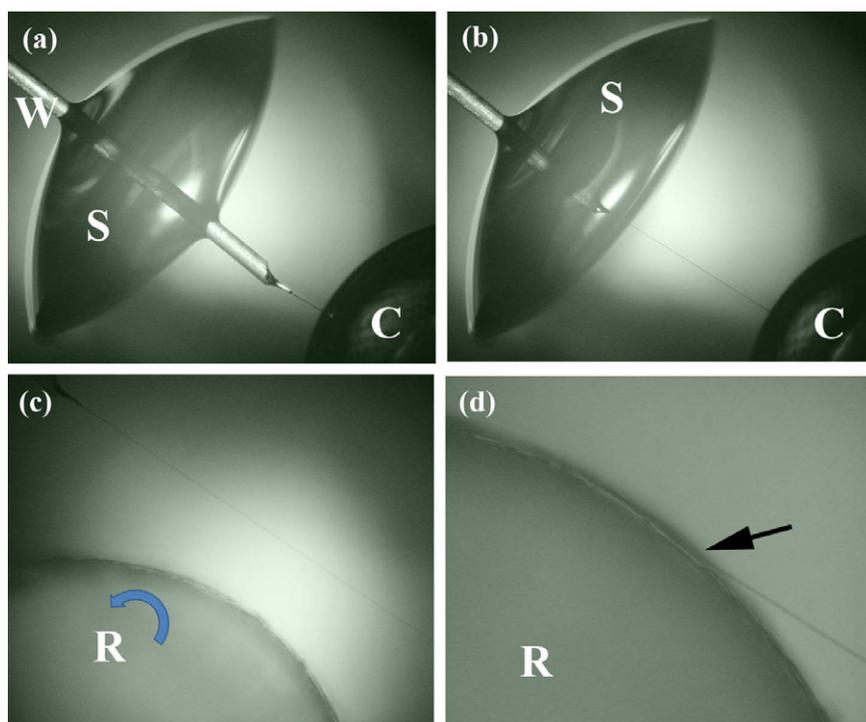


Figure 6. Rolling of the SWNT fiber. (a) The tungsten wire (W) passed through the saline solution in a metal ring (S). (b) The SWNT fiber passed through the saline solution. (c, d) The SWNT fiber is approached by a rotating Teflon rod (R) and the tungsten wire is withdrawn; the rod continues to draw the SWNT fiber. The arrow marks the contact where the fiber attaches to the rod. C marks the SWNT dispersion.

repetitions) produced much scatter in the dependences of the fiber diameter on the concentration and withdrawing velocity.

3.4. Conductivity and tensile strength of the fibers

The electrical conductivity of the obtained fibers was measured using the two-probe method, connecting the fiber to gold wires (diameter 0.03 mm) with the silver paste. The contact resistance could be ignored because of the large contact area. The I - V curves reveal higher conductivity for the R-SWNT than the C-SWNT fibers. The conductivity reached 355 S cm^{-1} (figure 5(a)), which is higher than that of the unprocessed SWNTs (about 100 S cm^{-1}) and our previous values of about 80 – 200 S cm^{-1} [29]. The fibers could sustain a current density larger than 10^7 A cm^{-2} (figure 5(c)). At the burning point, shown in figures 5(d) and (e), the current removed some of the SWNT bundles that led to failure—the curly bundles around the broken point suggest that some bundles were broken by a sudden force.

The tensile strength was also improved in the R-SWNT fibers. Using the silicon cantilever, we estimated the tensile strength of a 200-nm-thick R-SWNT fiber as larger than 400 MPa, which is almost six times higher than our previous values [29]. These results show that the tube quality in the colloidal solution markedly affects the properties of the obtained fibers.

3.5. Rolling of SWNT fibers

When the fiber became longer, it would bring a larger solution drop, so that less voltage could be applied to the

fiber. Furthermore, straight line spinning has practical length limitations. To solve these problems, the ac current was supplied not directly to the wire (W in figure 6(a)), but through a metal ring and a saline solution drop (S) in it. The tungsten wire with the SWNT fiber was slowly drawn through the ring. The results show that no significant changes in the fiber occurred when it passed through the saline solution (figure 6(b)), but the saline solution had passed electricity to the newly forming fiber segment. After the formed fiber segment passed through the saline solution, it was approached by a rotating rod (figure 6(c)) and rolled onto it (figure 6(d)). This modification allowed us to continuously draw the fiber by replenishing the feeding solution in a way similar to the production of spider silk, and it was actually designed on the basis of the spider silk gland.

3.6. Sorted SWNTs

Colloidal solutions of metallic (IsoNanotubes-M) and semiconducting SWNTs (IsoNanotubes-S) were provided by Nanointegris Inc., USA. This company used a patented ultracentrifugation technique to separate the metallic and semiconducting SWNTs [39]. The provided colloidal solutions (10 mg l^{-1}) contained some surfactant and were rather stable. The color was blue for metallic and pink for semiconducting SWNT solutions. Only short fibers could be drawn from these solutions by the electrophoretic method, as shown in figure 7. These short SWNT fibers may be used as electrochemical sensors or electron emission sources [40, 41].

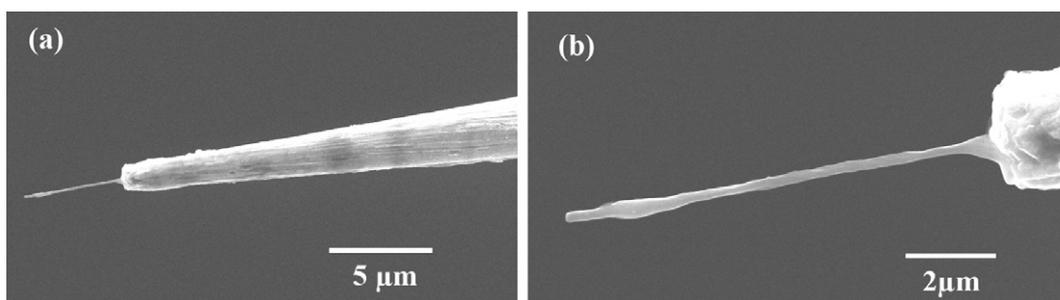


Figure 7. SEM images of a metallic SWNT bundle attached to a blunt tungsten needle.

4. Conclusions

In summary, several surfactants were used to disperse acid-treated SWNTs resulting in stable colloidal solutions with different concentrations. SWNT fibers were drawn from these solutions by the electrophoretic method. When SDS was used as the surfactant, short SWNT bundles could be attached to the tungsten tip, which could then be used as an electron emission source. In contrast, long, uniform, porous SWNT fibers with diameters ranging from 0.2 to 5 μm could be obtained with NaDDBS. A study of their formation as a function of SWNT concentration in the solution and drawing velocity revealed that continuous fiber fabrication requires high contact angles between the formed SWNT fibers and the solution. This method can possibly be scaled up to spin long SWNT fibers under ambient conditions. No superacids or harmful solvents are needed for this process, making it environment-friendly. The produced SWNT fibers can potentially be used in fabrics or polymer fillers.

Acknowledgments

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