

Self-Assembled Linear Bundles of Single Wall Carbon Nanotubes and Their Alignment and Deposition as a Film in a dc Field

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Abstract: A one-step process of solubilization of single wall carbon nanotubes (SWCNT) in an organic solvent has enabled us to polarize them asymmetrically in a dc electric field. Quaternary ammonium ion-capped SWCNTs readily suspend in organic solvents; under the influence of a dc electric field, they assemble as stretched bundles anchored on the positive electrode. At low dc applied field (~40 V), all of the SWCNTs from the suspension are deposited on the electrode, thus providing a simple methodology to design robust SWCNT films. At higher applied voltages (>100 V), the SWCNT bundles stretch out into the solution and orient themselves perpendicular to the electrode surface. The alignment of these bundles is responsive to the ON–OFF cycles of the applied electric field. The possibility of modulating the alignment of SWCNT in an electric field opens new ways to achieve electrical contacts in nano- to micro-devices.

Introduction

Unique structural identity, mechanical strength, and electronic properties have made carbon nanotubes (CNTs) ideal building blocks of next generation nanodevices.^{1–5} They are potential components in electronic devices and catalytic applications. Individual nanotubes have been extensively studied for application in field emission devices.

A common practice to cast thin films on electrode surfaces of CNT has been a drop cast method that involves applying small amounts of CNT suspension with a surfactant or a polymer binder (e.g., Nafion).⁶ In our earlier studies, we have adopted the electrophoretic deposition method for casting fullerene films⁷ and gold nanoparticles.⁸ Such a method provides a robust coverage of charged particles or molecular clusters on electrode surfaces and employs them in electrocatalytic applications.⁹ Whereas such deposition techniques to cast thin films are useful in designing CNT electrodes, the application of electric field may also enable orientation of CNTs on the electrode surface in a desired direction.

Electric field alignment is a powerful technique that has been shown to orient CNTs along a particular direction during the nanotube growth process.¹⁰ Earlier studies have demonstrated the ability of CNTs to assemble under controlled electric field on electrode surfaces,^{11–13} or to recondense in the flow of a polymer solution to form nanotube meshes.¹⁴ However, orienting CNTs at will in predetermined directions remains a challenge. We report here on the electrophoretic deposition and self-assembly of solubilized CNTs into parallel bundles and their controlled orientation in a dc electric field. Electrophoretic orientation of CNTs in a controlled fashion is likely to pave the way toward utilizing nanotubes in switching devices or electromechanical applications.

Experimental Section

Purified SWCNTs synthesized by the electric arc method (from SES Research) were solubilized by mixing with tetraoctylammonium bromide (TOAB) in THF (10 mg of SWCNTs and 0.13 g of TOAB in 25 mL of THF). Sonication of the mixture for 20–30 min yielded a stable dark suspension. We also solubilized SWCNT in TOAB/THF obtained from another source (Nanocs Inc.). The black suspension was centrifuged at 10 000 rpm for approximately 10 min. The clear supernatant liquid containing unbound TOAB was discarded. This procedure was repeated, and the final centrifugate, after removal of

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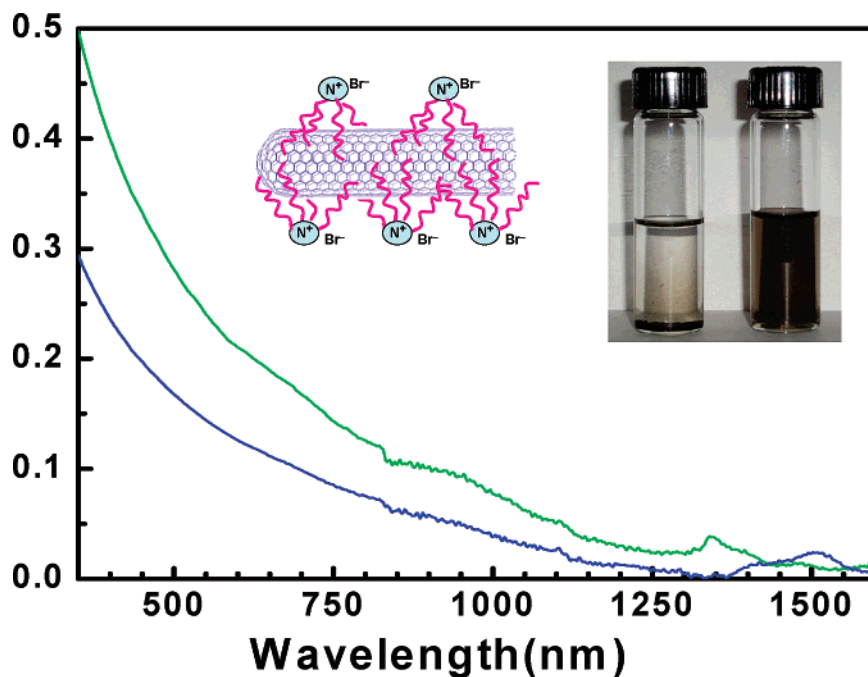


Figure 1. Absorption spectrum of SWCNT solubilized with TOAB in THF solution. The green and blue traces correspond to SWCNT obtained from Nanonics and SES Research. The inset shows the SWCNT in THF before (left) and after solubilization (right) with TOAB.

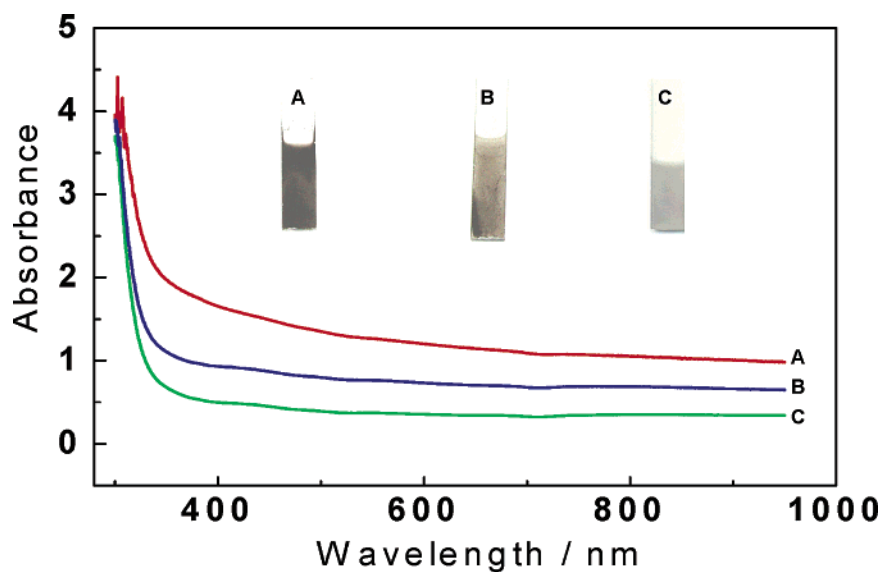


Figure 2. The absorption spectra of SWNT films deposited on a conducting glass electrode of varying thickness. The corresponding electrodes are shown in the inset.

the solvent, was dried. The repeated washing and centrifuging procedure allowed us to discard any unbound TOAB from the SWCNT material. The dried material consisting of TOAB bound SWCNT was readily suspendable in organic solvents. In the present experiments, TOAB bound SWCNT was resuspended in 25 mL of THF and sonicated for 10–15 min. On the basis of weight gain, the capping of 1 mg of TOAB per 10 mg of SWCNT was estimated. It is evident that the quaternary ammonium salt, TOAB, allows solubilization by binding to the SWCNT through hydrophobic interactions of its alkyl chains.

Cyclic voltammetric experiments were carried out using a BAS 100 electrochemical analyzer. Digital images were recorded using an Olympus digital camera. Magnified images were recorded using an Intel QX3 microscope. The microscope was aligned perpendicular to the cell so that images or movies could be recorded during electrophoretic deposition. A low current module of Fluke 415B high voltage power supply was used for applying dc field between the electrodes.

Optically transparent electrodes were cut (0.8×5 cm) from a conducting glass plate obtained from Pilkington.

Results and Discussion

One-Step Solubilization of SWCNTs in THF. Earlier efforts have been made to solubilize various carbon nanotubes in surfactant solutions or by subjecting them to chemical oxidation.^{15–18} The present method of solubilization of SWCNTs in an organic solvent using quaternary ammonium salt is a

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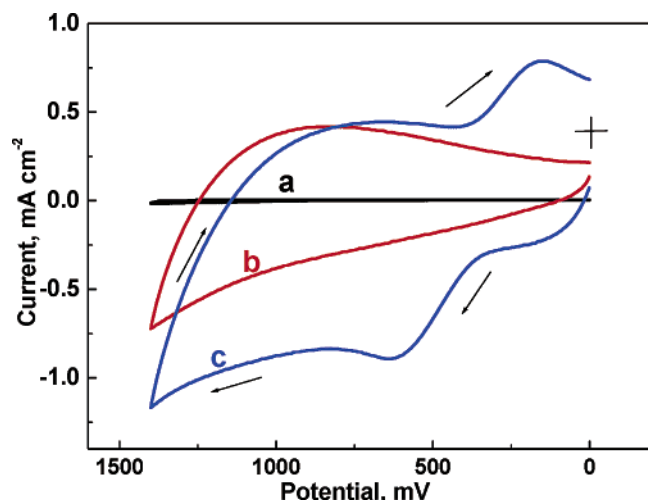


Figure 3. Cyclic voltammograms of SWCNT film deposited on a glassy carbon (GC) electrode. Electrolyte was 0.1 M tetrabutylammonium perchlorate in acetonitrile. (a) Bare GC electrode; (b) SWCNT film deposited on GC electrode; and (c) SWCNT film deposited on GC electrode following its exposure to the ferrocene solution.

simple one-step process that avoids initial treatment of CNT to break the C–C bond or other forms of organic functionalization. The TOAB-modified SWCNT suspension can be dried by evaporating off solvents and can be redispersed in THF using sonication when needed (Figure 1). Thus, this process is convenient to package and store the soluble SWCNT in a bottle. The absorption spectrum of the suspension in THF shows the typical broad featureless absorption in the UV extending into the near-IR region. The lack of spectral features in the infrared region is an indication that these SWCNTs are still bundled in the suspended form.

Electrodeposition of SWCNT on Conducting Glass Electrode Using a Low dc Field (<100 V). Carbon nanotubes constitute an important class of nanostructures that provide the basis for designing electrodes with tailored electrocatalytic or sensing properties. We employed two optically transparent electrodes (OTE) that were kept parallel to each other (~5 mm apart) in an electrophoretic cell. When a dc voltage of ~40 V was applied, we observed a slow movement of carbon nanotubes from the suspension toward the positive electrode. Continued application of dc voltage for 2–3 min resulted in the deposition of SWCNT film on the electrode surface. Figure 2 shows the absorption spectra of three SWCNT films of varying thicknesses deposited on conducting glass electrodes. The thickness of SWCNT films can be increased by increasing the time of electrophoretic deposition. These films are quite robust and are suitable for electrochemical measurements.

We tested the electrochemical response of SWCNT-deposited OTE films by immersing them in an acetonitrile solution containing a ferrocene redox couple for about 30 min and then washing them thoroughly with acetonitrile to remove any unbound ferrocene. The cyclic voltammogram in 0.1 M TBAP solution is shown in Figure 3. Whereas the reversible redox peaks corresponding to the oxidation of ferrocene ($E_{pa} = 560$ mV and $E_{pc} = 200$ mV vs SCE) are seen in the cyclic voltammogram (spectrum c), a large capacitive current seems to dominate in this experiment. From these experiments, we conclude that the SWCNT electrodes exhibit reversible cyclic voltammetric behavior for the adsorbed redox couple, but at the same time they exhibit a double layer charging effect. The large capacitive current of the CNT film was also confirmed from the blank experiments carried out with the CNT film electrode without exposure to ferrocene (spectrum b). The large surface area of the SWCNT film is expected to induce significant

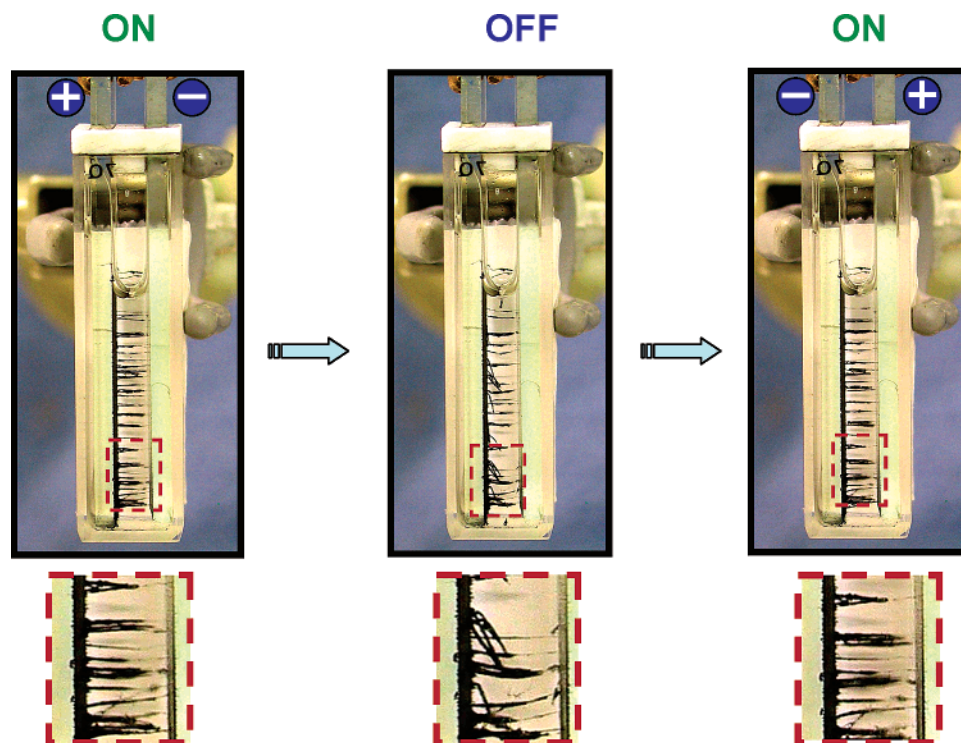


Figure 4. SWCNT-assembly and orientation in response to an applied dc electric field in THF. The left to right sequence corresponds to an ON–OFF–ON cycle of the field with magnified sections at the bottom.

electrochemical double layer charging effects. The oppositely charged ions from the solution that accumulate near the SWCNT surface during the electrochemical cycle contribute to this large capacitive current. The capacitance value obtained by integrating the cyclic voltammogram yields a value of 100 F/g. This value is comparable to the literature value of 80–135 F/g reported for CNT films.^{19–21} Such a large capacitance has made carbon nanotubes attractive candidates for super capacitors.^{21–23}

Alignment of SWCNT at High (>100 V) dc Field. When a dc voltage of >100 V was applied between the two conducting glass electrodes, the nanotubes, instead of undergoing deposition, assembled into linear bundles extending across the space between the two electrodes. These bundles are well separated and aligned perpendicular to the electrode surface. This bundling and alignment effect observed upon application of the high dc voltage is shown in Figure 4. When the dc field is turned off, the aligned nanotubes quickly bend downward. When the field is restored, the tubes align again in the horizontal direction. The sequence in Figure 4 and the enlarged views in the bottom part of the figure show the reproducibility in attaining similar alignments during ON periods. Movie 1 in the Supporting Information shows the alignment of SWCNT bundles in a dc electric field and their response to ON–OFF–ON cycles. It is evident from these experiments that the TOAB-capped SWCNT suspensions in THF become charged under the influence of dc field and align themselves in the electric field. The quaternary ammonium salt that dissociates from the CNT surface compensates the built-in charge around the nanotube. (For example, bromide ions move away from the negatively charged end of CNT and accumulate near the positively charged end of CNT, see Figure 5A).

The high capacitive current observed in the cyclic voltammograms is indirect evidence for the ability of SWCNT to undergo charging when subjected to an externally applied potential. Figure 5B illustrates the mechanism for the assembly of charged SWCNT as linear bundles. During the application of a dc field, the nanotubes become charged asymmetrically, which causes the adsorbed ion pair (tetraoctylammonium bromide) to dissociate and move away from the surface. Both electrostatic and columbic attraction between the nanotubes assists in their assembly as linear bundles. Because of the strong dipole moment along the longitudinal axis, they further align along the direction of the electric field. Indeed, classical, DFT, and molecular dynamics calculations all predict increased charge density at the ends of the charged SWCNTs.^{24,25} Furthermore, oppositely charged counterions (tetraoctylammonium and bromide ions) that rearrange around the charged nanotube bundles screen the charged bundle and provide the stability for the alignment. At low dc field, however, the field is not strong enough to keep them aligned. Under these conditions, cross-

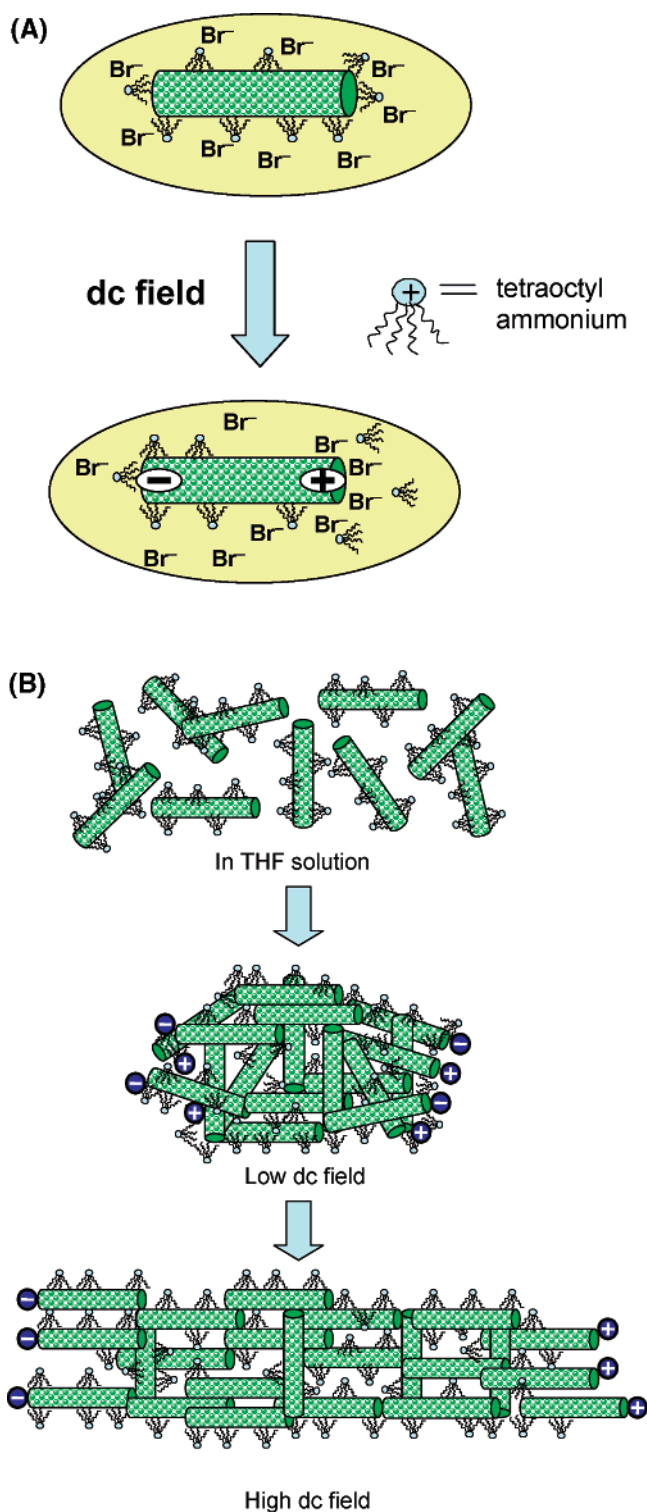


Figure 5. (A) Charge stabilization in CNT by the tetraoctylammonium and bromide ions following the application of the dc field. (B) Schematic illustration of the linear alignment of SWCNT in the dc electric field.

linking of charged nanotubes disrupts the localized field and thus fails to form aligned bundles.

To further probe the alignment process, we employed a portable microscope for photographing the SWCNT bundles during the application of electric field. The magnified images of three different sections of the electrophoretic cell are shown in Figure 6. At the positive electrode, we see firm anchoring of the SWCNT bundles. This is also evident in Figure 4 in which

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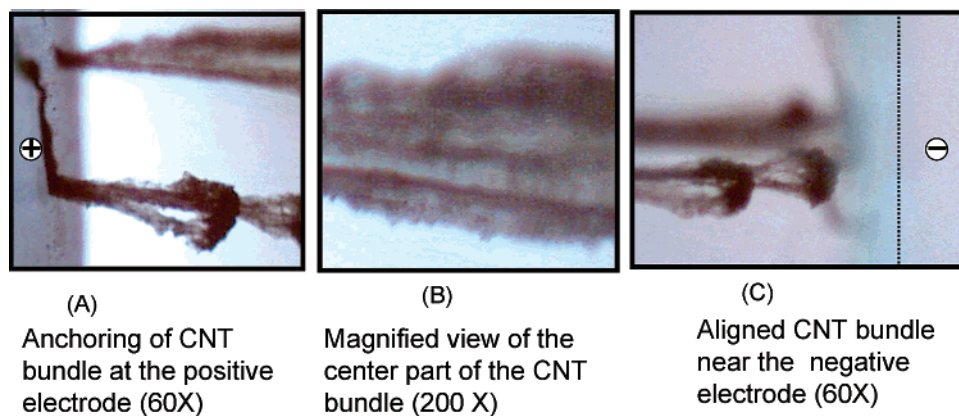


Figure 6. Magnified images of different sections of the aligned bundle of SWCNT. (A) Anchoring of SWCNT at the positive electrode; (B) the distribution and orientation of SWCNT bundles in the center; and (C) stretching of the bundle toward the negative electrode. Note that the bundle does not make any contact with the negative electrode. (See Supporting Information movie 2 for the magnified movement of the aligned bundle near the negative electrode.)

the anchored position at the positive electrode remains firm while the bundles bend downward when the dc field is turned off. Such a strong binding of the SWNT to the positive electrode surface is also reflected in the deposition of SWNT film at low applied dc voltages (see, for example, experiments described in Figure 2). Because the field is mainly localized near the electrode surface, at low dc voltage the nanotubes fail to exhibit any aligning features. Cross-linking of nanotubes in vertical and horizontal directions that occurs near the positive electrode finally results in the deposition as a film.

At higher dc voltages (100–500 V), the field extends further into the solution, and the dipoles formed at the ends align the nanotube bundles along the field direction. With increasing dc voltage, the bundles stretch farther toward the electrode surface. As the opposite end of the bundle stretches out and approaches the negative electrode, it gets repelled. This is visualized from the broadened head of the bundle, which fails to make direct contact with the negative electrode (image C in Figure 6). The strong repulsive force that builds up at the end of the bundle is likely to be responsible for preventing the bundle end from making contact with the negative electrode surface. The interplay between attractive and repulsive interaction near the negative electrode surface causes a wiggling motion of the nanotube bundle. The movie shown in the Supporting Information (movie 2) shows a magnified view of the bundle head movement near the negative electrode surface.

The center part of the bundle in Figure 6B shows a magnified view (200 \times) of SWNT alignment, which illustrates the nature of aggregation of nanotube bundles. A close look at the magnified image reveals that the nanotube bundle consists of several thinner bundles that are vertically cross-linked by smaller bundles. Carbon nanotubes naturally form bundles by van der Waal interactions, and extreme sonication in the presence of an organic capping agent such as surfactant is needed to separate them. Under the application of a dc field, the organic cap rearranges itself to compensate for the accumulating charge, thus paving the way for the nanotube aggregation. The asymmetric charging effects cause these aggregates to form linear bundles and align themselves in the electric field.

We also explored the possibility of transferring the aligned bundles from the solution phase onto a solid support. Once the SWCNT bundles became aligned, following the application of the dc field, we slowly introduced a thin glass slide between

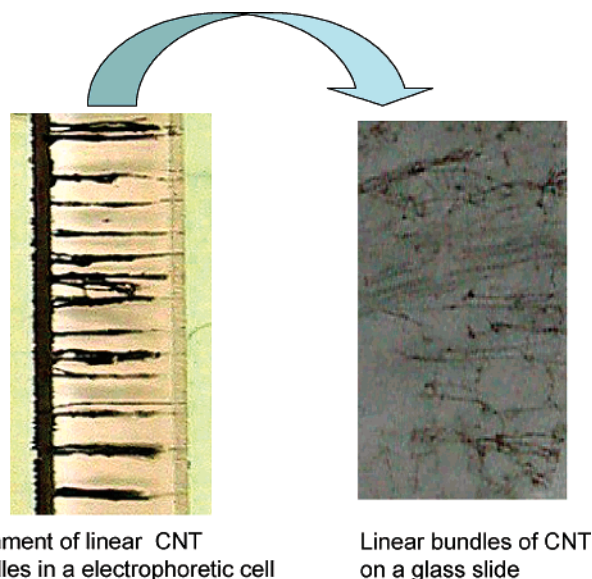


Figure 7. A magnified view of the CNT bundles transferred onto a glass slide.

the two electrodes and carefully lifted out the aligned bundles. Figure 7 (right) shows the transfer of the aligned bundles onto the glass slide. The irregularity in the deposition is due merely to our manual lifting of the slide. Careful control of the deposition procedure should allow better uniformity in the alignment. By carefully optimizing this simple pickup of aligned SWNT bundles on a solid surface, it should be possible to make designed nanostructures with desired orientation.

In summary, we have shown that quaternary ammonium-capped SWCNTs readily suspend in organic solvents. Under the influence of a dc electric field, these nanotubes become charged and assemble as stretched bundles. An increase in the external field increases the process of asymmetric charge buildup along the nanotube: the negative charge at one edge and increasingly more positive charging at the opposite end. The stabilization of the charged CNT bundles by the tetraoctyl ammonium and bromide ions further facilitates their alignment in the electric field.

At low applied dc field, the SWCNTs deposit on the electrode surface as a nanostructured carbon film. The possibility of modulating the alignment of SWCNTs in this configuration opens new ways to achieve electrical contacts in nano- to micro-

devices. Experiments are underway to explore the electrochemical and electrocatalytic properties of the SWCNT-deposited electrodes.

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Supporting Information Available: (A) Movie 1: Response of SWCNT suspension to dc field and visualization of the process of alignment. Bending of SWCNTs during the OFF cycle and realignment during the ON cycle can also be seen at the end of this movie. (B) Movie 2: The wiggling movement of the SWCNT bundle near the negative electrode surface as the attraction and repulsion forces interplay its movement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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