Improve Contacts in Carbon Nanotube Networks by In situ Polymerization of Thin Skin of Self-Doped Conducting Polymer

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ABSTRACT

The overall conductivity of SWNT networks is dominated by the existence of high resistance and tunneling/Schottky barriers at the intertube junctions in the network. Here we report that *in-situ* polymerization of a highly conductive self-doped conducting polymer "skin" around and along single stranded DNA dispersed- and functionalized- single wall carbon nanotubes can greatly decrease the contact resistance. The polymer skin also acts as "conductive glue" effectively assembling the SWNTs into a conductive network, which decreases the amount of SWNTs needed to reach the high conductive regime of the network. The conductance of the composite network after the percolation threshold can be two orders of magnitude higher than the network formed from SWNTs alone.

Keywords: carbon nanotubes, DNA, self-doped polyaniline, composite

1 INTRODUCTION

There is increasing enthusiasm for the use of single walled carbon nanotube (SWNT) networks as conductive flexible electrodes and sensing materials. However, the experimentally measured conductivities of the SWNT networks are significantly lower than the conductivity of a SWNT rope. Previous studies demonstrate the existence of high resistance and tunneling/Schottky barriers at the intertube junctions, which dominates the overall film conductivity in the network.

Herein, we report that the conductivity of SWNT networks can be dramatically improved by *in-situ* polymerization of a thin layer of self-doped conducting polymer (polyaniline boronic acid, PABA) around and along the carbon nanotubes. The formed conducting polymer improves the contacts between the SWNTs and it also acts as a "conductive glue or zipper", which effectively assembles the SWNTs into a conductive network and decreases the amount of SWNTs needed to reach the high conductive regime of the network. The conductance of the composite network beyond the percolation threshold can be two orders of magnitude higher than the network formed from SWNTs alone. In addition, the thin layer of conducting polymer provides a powerful functionality for a variety of potential applications, including flexible sensors.[1] We also found that the enhancement highly depends on the methods to coat the thin layer of the polymer onto the carbon nanotubes.

2 EXPERIMENTAL SECTION

2.1 *In-situ* fabrication of a self-doped polyaniline/ss-DNA-SWNTs nanocomposite

The materials used and the protocol for the dispersion of SWNT into water solution are described in our previous work.[2] A typical procedure for the preparation of a solution of ss-DNA/SWNTs/PABA nanocomposite by *in-situ* polymerization approach is as follows: 50 μL of ABA solution (50 mM) and KF (40 mM) in 0.05 M H_2SO_4 was added to 2.5 mL of the ss-DNA/SWNTs solution (70 mg/L) in 0.05 M H_2SO_4. The solution was bubbled with nitrogen for 30 min at 0 ºC to remove the dissolved oxygen. The chemical polymerization of ABA was then initiated by adding 11.34 μL of 37.5 mM $(NH_4)_2S_2O_8$ (APS) (in 0.05 M H_2SO_4) drop-wise to the mixture. It is important to note that the amounts of ABA and APS were determined from titration experiments to make sure only a thin layer of PABA is produced around and along the carbon nanotubes. The polymerization was carried out at 0 ºC with nitrogen bubbling for 7 h and another 43 h in a refrigerator (4 ºC). The obtained composite solution is referred to as "*in-situ* polymerized composite". For the "seed" approach, the polymerization conditions were kept the same, except 11.34 μL of 37.5 mM APS was first added to pre-oxidize the same amount of ss-DNA/SWNTs, followed by addition of 50 μL of ABA solution (50 mM). The obtained composite solution is termed "seed composite". A neat poly (aniline boronic acid) (PABA) was fabricated by a recipe described in our previous work, which was demonstrated to produce PABA with longer conjugation length.[2] A composite of ss-DNA/SWNT/PABA was prepared by mixing 50 μL of the preformed neat polymer solution with 2.5 mL of the ss-DNA/SWNTs (70 mg/L) in 0.05 M H_2SO_4. The resulting solution is so called "postmixture composite". All the composites, neat PABA, and ss-DNA/SWNTs solutions were dialyzed to remove excess salts before conductance measurements.

2.2 Characterization

Percolation-like conductive behaviors of the composites and ss-DNA/SWNT alone were prepared and studied by measuring the conductance of the films in a layer-by-layer approach on a pre-patterned Si chip. Each layer was prepared by adding 2 µL of the dialyzed solution (10 mg/L of SWNTs) onto a Si chip and dried under vacuum. The Si chip was fabricated at Air Force Research Labs and the distance between two facing gold electrodes is 2 µm. The conductance of the composites was measured with an Electrochemical Workstation CHI 760C.

The conductance was also studied by a four point-probe approach. Films with different thickness were prepared from the corresponding composite and ss-DNA/SWNT solutions by vacuum filtration using Anodisc 47 inorganic membranes with 200nm pores (Whatman Ltd). To evaluate the impact of the conducting polymer skin on the conductivity of the carbon nanotube network, the thickness of each film were prepared with different composite solutions while maintaining the concentration of the carbon nanotubes. After filtration, the thin films were dried in vacuum for 15 – 20 minutes. The sheet conductance was determined by a 302 manual Four Point Resistivity Probe (Lucas Labs).

The morphology of the resulting composites, neat polymer, and the ss-DNA/SWNT films was characterized by a Nanoscope III A (Digital Instruments) operating with tapping mode in ambient air. The thickness of PABA on the carbon nanotubes was measured from high resolution transmission electron microscope (TEM) (Libra 120 Energy Filtering TEM, Zeiss) operated at 200kV. Samples were prepared for imaging by placing a drop of aqueous composite solution on TEM grids and wicking away the liquid after 2 minutes. Electronic and molecular structures of the PABA in the pure polymer and the composites were measured by a Spectrum Spotlight FTIR Imaging System (Perkin Elmer instruments) and a Cary 500 UV-Vis-NIR Spectrophotometer operating in double beam mode.

3 RESULTS AND DISCUSSION

3.1 Electrical properties of the composite and ss-DNA/SWNT films

Figure 1a shows the room-temperature percolation behavior of the ss-DNA/SWNTs network and the composite films. At the third layer, the *in-situ* fabricated composite reaches its percolation threshold while the ss-DNA/SWNT film just begins to have measurable current. At this percolation point, the conductance of the *in-situ* polymerized composite is 5 orders of magnitude higher than that of the ss-DNA/SWNT film. There is no detectable current for the composites prepared by post-mixing and "seed" method. According to the percolation mechanism, multiple conducting channels have formed in the *in-situ* polymerized composite film and the tube-tube junctions begin to dominate its overall resistance, whereas space between conducting sticks is still the governing factor for the other three samples.

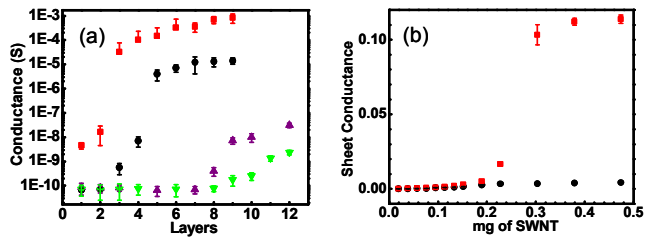

Figure 1. (a) Conductance of in-situ polymerized composite (■), ss-DNA/SWNTs (●), post mixture (▲), and "seed"composite (▼) as a function of layers of the composites and ss-DNA-SWNT. Each layer corresponds to 2 µL of solution with a concentration of SWNT at 10mg/mL. The conductance was measured by a two probe approach. Each data points presented here was an average of 18 pair of electrodes on five silicon chips. (b) Conductance of *in-situ* polymerized composite (■), ss-DNA/SWNTs (●) measured by a four probe approach. Each data point presented here was an average of 10 measurements.

The films reached their percolation threshold at 3, 6, 10 and 11 layers for in-situ polymerized composite, ss-DNA/SWNTs, post-mixture and "seed" composite, respectively. After percolation, the conductance of the *in-situ* polymerized composite is ~10^2-fold, ~10^5-fold, and ~10^6-fold higher than that of the ss-DNA/SWNTs, post-mixture and "seed" composite, respectively. Based on the percolation theory for randomly arranged conducting sticks, above the percolation threshold, the overall resistance of the film is dominated by intertube junctions in the conducting channels. The significant difference in conductance illustrates that only the *in-situ* polymerized PABA remarkably improved the intertube contacts, while the pre-formed PABA and the *in-situ* polymerized PABA by "seed" approach did not.

To eliminate the influence of electronic contacts between the electrodes and the composite on the electrical measurements, the percolation behavior was also studied by a four probe approach with a probe distance of 1mm. The conductance of the composite prepared by the "seed" method and postmixture approach is beyond the sensitivity of the measurement setup. Figure 1b shows that the sheet conductance of the *in-situ* polymerized composite network increased 40 times compared to that of ss-DNA/SWNT alone. In contrast to two-probe measurements, it seems that the in-situ polymerized conducting polymer skin did not decrease the amount of SWNTs needed to reach the high conductive regime of the network. This discrepancy may be related to the geometry-dependent percolation behavior of the carbon nanotube networks, which has been studied by Kumar et al and Ural groups recently. With larger distances between the source and drain electrodes, the percolation

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probability of the carbon nanotubes, defined as the probability of finding at least one conducting path between the source and drain electrodes, decreased more dramatically compared to the small ones. In this work, the distance between the two electrodes is around 2 μm in the two-probe measurement, 500 times shorter than the distance between the probes in the four-probe measurements (1mm). It is possible that the length of the "glued" tubes by self-assembling during the polymerization is still too short compared to 1 mm, while it is comparable or longer than 2μm.

Molecular structures of PABA in the composites. We used Fourier Transform Infrared (FTIR) spectroscopy to systematically study the molecular structures of PABA in the composites fabricated from different approaches. Figure 2 shows the FTIR spectra of the four samples: in-situ polymerized composite, neat PABA, "seed"-composite, and postmixture. IR characteristic bands of polyaniline are observed at 1574, 1478, and 1120 cm^{-1}, corresponding to quinoid, benzenoid, and C=N stretching (-N=quinoid=N-, "electron-like band") modes, respectively. The peak at 1210 cm^{-1} is related to the antisymmetric stretching vibration of the PO^{2-} in DNA. The spectra also exhibit characteristic vibrations at 1510 and 1340 cm^{-1}, assigned to the B-N and B-O stretching mode. The calculated ratio for the absorption intensity of quinoid to benzenoid ring modes (I_{1574}/I_{1478}) in the pure PABA is 3.5, which suggests that the percentage of quinoid units is much higher than that of benzenoid units for the neat PABA film. However, the ratio of I_{1574} to I_{1478} decreases to 1.5 for PABA in the in-situ fabricated composite, indicating that the relative amount of quinoid units decreased in the PABA when polymerized in the presence of ss-DNA/SWNTs. This result is consistent with our previous work,[2] indicating that the PABA exists more in the fully oxidized pernigraniline state in pure PABA, and more in the conductive emeraldine state in the composite.

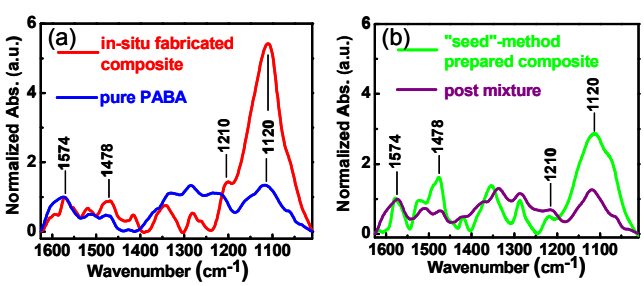

Figure 2. Normalized Fourier-transform IR spectra of (a) *in-situ* polymerized composite (red) and pure PABA (blue); (b) "seed" composite (green) and postmixture (purple). After the baseline correction at two points (1626 and 1010 cm^{-1}), all IR spectra are normalized as the standard peak (quinoind) at 1574 cm^{-1}.

The ratio of relative intensities of quinoid to benzenoid ring modes (I_{1574}/I_{1478}) in the post mixture is 3.4, which is similar to the neat PABA (3.5), indicating the neat PABA weakly interact with the ss-DNA/SWNTs in the composites. The results demonstrate that the PABA in the postmixture composite exists in the non-conductive pernigraniline state.

A striking difference among the four spectra in Figure 2 is found in -N=quinoid=N- stretching at ~1120 cm^{-1}. The peak has been described by MacDiarmid et al. as the "electronic-like band" and is considered to be a measure of the degree of delocalization of electrons along polyaniline backbone and thus it is a characteristic peak of polyaniline conductivity. There is a dramatic intensity increase of the "electronic-like band" in the *in-situ* polymerized composite, as shown in Figure 2a. This remarkable increase suggests that PABA in the *in-situ* polymerized composite has higher conductivity compared to the neat PABA. The composite fabricated by the postmixture approach shows similar low intensity of the "electron-like band" as the neat PABA, indicating that conductivity of the PABA in the postmixture composite may be similar to the neat PABA.

Unexpectedly, the relative intensity of the "electron-like band" in the composite prepared by the "seed" approach is 2.9, much higher than that of the neat PABA and the postmixture composite (1.3). The ratio of relative intensities of quinoid to benzenoid ring modes (I_{1574}/I_{1478}) in the composite prepared the "seed"-method is 0.9, much lower than that of the neat PABA and the postmixture composite (3.5, and 3.4 respectively). The results indicated that the PABA in the composite fabricated by the "seed" approach also existed in the conductive emeraldine states. Therefore, the conductivity of the PABA should be higher than the PABA in the postmixture composite, even though lower than that of the composite prepared by *in-situ* polymerization with the intact ss-DNA/SWNTs. However, the conductance measurements described above did not show this trend, indicating that there are other uncovered factors that determine the overall macroscopic conductivity of the films in addition to the modified tube-tube contacts.

Atomic force microscope (AFM) and high resolution transmission electron microscope (HRTEM) images in Figure 3 shows the third layer of the different samples (ss-DNA/SWNTs, *in-situ* polymerized composite, postmixture and "seed" composite) that have been prepared layer-by-layer from the corresponding solutions with a SWNT concentration of 10 mg/L. At this percolation point, as shown in Figure 1a, only the composite fabricated by *in-situ* polymerization with the intact ss-DNA/SWNTs reached the percolation threshold studied by two-probe measurements. The composites fabricated by postmixture and "seed" method showed no detectable current by our detection instruments. Figure 3a shows the morphology of the films prepared from ss-DNA/SWNT alone. Most of the SWNTs are individual (~2 nm diameter), with some bundled structures (~17 nm). The nanotubes appear randomly oriented. Most of the tubes remain isolated from each other, with some jointed tubes. Figure 3b is a typical AFM image of the *in-situ* polymerized composite. Remarkably, individual ss-DNA/SWNTs are replaced by

long fibers (most of the fibers are longer than 4 μm). These fibers are randomly arranged and self-assembled into a network. The diameter of the fibers ranges from 3 nm to 20 nm measured by high resolution TEM (Figure 3c). From the TEM images it is noted that some of the fibers are composed of individual nanotubes with a polymer coating of 1 to 3 nm in thickness. Some of the fibers are carbon nanotubes bundles, which are composed of carbon nanotubes with polymer coating.

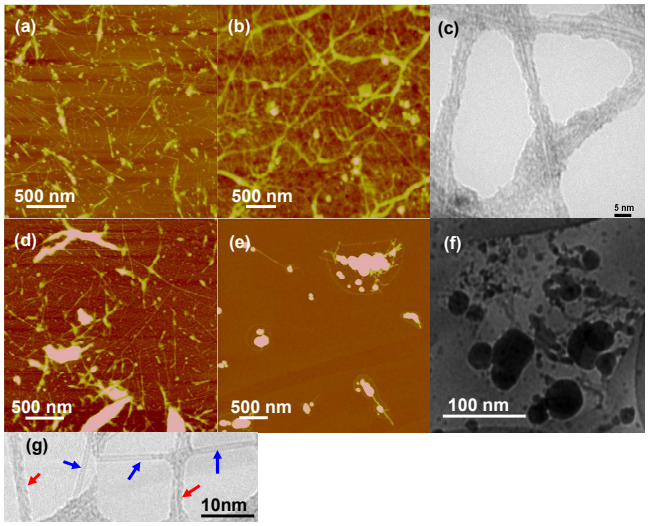

Figure 3. AFM images of the third layers of the films prepared from (a) ss-DNA/SWNTs, (b) *in-situ* polymerized composite, (d) postmixture and (e) "seed"composite. The concentration of SWNT in all these samples is 10 mg/L. TEM images of *in-situ* polymerized composite (c), "seed" composite (f) and postmixture (g).

The pre-polymerized PABA didn't show the tendency to self-assemble the carbon nanotubes into networks (Figure 3d). The arrangement and the spatial distribution of the carbon nanotubes in the postmixture composite are very similar to that of ss-DNA/SWNT alone. In the AFM image, there are large bright regions (~60 nm in height), which are suspected to be the neat PABA without being uniformly mixed with the SWNTs. From the study by high resolution TEM (Figure 3g), we found that while some of the tubes were not coated, some were coated with a 1-3 nm layer of polymer. In the conductance experiment, we found the conductance of the postmixture network dramatically decreased and the percolation threshold of the SWNT networks largely increased (3 fold) (Figure 1). After the percolation threshold, the conductance of the postmixture composite is three orders of magnitude lower than the network prepared from SWNT alone, and is five orders of magnitude lower than the network formed from the in-situ polymerized PABA composite. Combined with the FTIR results, showing that the PABA exists in the non-conductive pernigraniline state in the postmixture composite and conductive emeraldine state in the *in-situ* polymerized composite, this morphological study strongly suggest that the electronic and molecular structure, and therefore the conductivity of the interfacial PABA on the SWNTs can modulate the overall electronic performance and percolation behavior of the SWNT films. Compared to the simple postmixture process, the *in-situ* polymerization process also facilitates SWNTs self-assembling to highly conducting networks, which also largely contributes to the highly improved conductance and the low percolation threshold of the *in-situ* polymerized composite. This result soundly supports the hypothesis discussed earlier in this work.

The morphological study of the "seed" composite (Figure 3e, f) revealed our curiosity pertaining to why the conductance is even lower than the postmixture. In contrast to the PABA *in-situ* polymerized in the presence of the intact ss-DNA/SWNTs, the PABA in the "seed" composite did not interlink the nanotubes into a conductive network. Instead, the PABA induced severe aggregation of the nanotubes into large particles (as large as 1μm). This aggregation dramatically changed the effective length/diameter aspect ratio of the carbon nanotubes, which is known to impact the conductivity and percolation behavior of the carbon nanotube films. Therefore, even though the PABA in the "seed" composite may has higher conductivity compared to that of PABA in the postmixture, the aggregated carbon nanotubes makes the conductivity of the "seed" composite even lower than the postmixture composite. We conclude that not only do the molecular structure of the polymer, but also the arrangement or distribution of carbon nanotubes in the composites determines the overall macroscopic electronic property and percolation behavior of the composites.

Summary. The electrical performance of SWNT network can be significantly improved by *in-situ* polymerization of a thin layer of PABA on the intact ss-DNA/SWNTs. However, the fabrication process rigorously impacts the electronic and molecular structure of the produced PABA in the composites, and also the arrangement or lateral distribution of the carbon nanotubes in the composites. Understanding these reaction characteristics is important to effectively optimize the fabrication parameters and ensure the formation of SWNT networks in a controllable fashion for a variety of potential applications.

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