

Unique Roles of DNA-Wrapped SWNTs: *In-situ* Fabrication of A Water-Soluble, Self-Doped Polyaniline Nanocomposite

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ABSTRACT

Due to the remarkable electrical conductivity and superior mechanical properties of carbon nanotubes (CNTs), as well as the rich optical, electronic and electrochemical properties of conducting polymers, nanocomposites of conducting polymers and CNTs have been pursued with an aim to synergistically combine their individual components. We demonstrate for the first time the use of single stranded DNA wrapped single walled carbon nanotubes (ss-DNA/SWNTs) to *in-situ* fabricate a water-soluble nanocomposite of self-doped polyaniline/SWNTs. Due to their unique surface and electronic properties, the ss-DNA/SWNTs performed multiple roles in the greatly enhanced performance of the self-doped polyaniline [poly(aniline boronic acid) (PABA) in this work] both during and after the polymerization, which makes this work unique compared to previously reported conducting polymer/carbon nanotube composites[1,2].

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

1 INTRODUCTION

Recently, by electrochemical polymerization of 3-aminophenylboronic acid on a gold electrode surface in the presence of the ss-DNA/SWNTs[3], we found that polymerization speed was greatly increased compared to growth of PABA in the absence of ss-DNA/SWNTs. More importantly, the stability of this self-doped polyaniline is greatly improved: the redox properties of the polyaniline backbone are preserved in neutral solutions (pH = 7.4), which increases the utility of polyaniline in biosensor applications. We demonstrated this idea by detecting dopamine in neutral solutions — the detection limit reaches 10^{-11} M, 6 orders of magnitude lower than that of the electrodes modified with PABA alone.

In this work, we fabricate *water-soluble* self-doped polyaniline nanocomposite by chemical polymerization of 3-aminophenylboronic acid in the presence of the ss-DNA/SWNTs. Similar to the electrochemical polymerization process, the polymerization speed greatly increased in the presence of the ss-DNA/SWNTs, as monitored by *in-situ* UV-Vis spectroscopy. Using UV-Vis and FTIR spectroscopies to study the molecular structure of the PABA in the nanocomposite, we found that the polyaniline backbone was in the stable emeraldine state

instead of the unstable, degradable pernigraniline state. Conductivity measurements demonstrated that the conductivity of the nanocomposite in the doped state is 25 S cm^{-1} , 370 times higher than the neat PABA film fabricated under the same conditions. After dedoping with ammonia, the conductivity of the neat PABA film is below $10^{-6} \text{ S cm}^{-1}$. The nanocomposite is still conductive *after dedoping* and the conductivity is 2.2 S cm^{-1} , which is 37 times higher than the *doped* neat PABA.

We believe that the ss-DNA/SWNTs performed multiple roles in the greatly improved performance of the self-doped polyaniline both during and after the polymerization. First, they acted as *catalytic molecular templates* during polymerization of self-doped polyaniline so that not only was the polymerization speed increased, but also the quality of the resulting polymer was greatly improved. Second, they functioned as novel *active stabilizers* after the polymerization: they readily reduced the unstable, fully oxidized pernigraniline form to the stable emeraldine state of polyaniline due to their catalytic reductive ability. Furthermore, the ss-DNA/SWNTs also acted as *conductive* polyanionic doping agents in the resulting film, which showed enhanced conductivity and electrochemical activity. We envision that the self-doped polyaniline nanocomposite solution will find a wide range of applications, such as in biosensors, conductive coatings, foldable micro- or macroelectronics, etc., which are currently being pursued by our group.

2 EXPERIMENTAL SECTION

2.1 Materials

3-Aminophenylboronic acid hydrochloride salt, potassium fluoride and all other chemicals were of analytical grade purity and were used as received from Aldrich Chemicals Inc., Milwaukee, WI. All solutions were prepared using nanopore water ($18.2 \text{ M}\Omega$) (Nanopure water, Barnstead), which was also used to rinse and clean the sample after polymerization and before any type of characterization.

2.2 Dispersion of SWNTs into water solution

Purified single-walled carbon nanotubes were purchased from Carbon Nanotechnologies, Inc. Houston, TX and dispersed into water using the method described by Zheng et al[4], resulting in DNA-dispersed nanotube solutions at a mass concentration around $\sim 30 \text{ mg/L}$. AFM images show

that ss-DNA/SWNTs have a length distribution from 50 to 1,000 nm with diameters around $1.3 \text{ nm} \pm 0.2 \text{ nm}$, measured from the cross section of the SWNT in the AFM images. If we consider a single ss-DNA molecule to be of 0.4 nm in height, (although the diameter of DNA should be around 2 nm in theory, it is only 0.3-0.4 nm in most of the AFM measurements[5]) the diameter of the carbon nanotubes is around 0.8-1.1 nm, which is consistent with HiPco tubes.

2.3 *In-situ* fabricate water solution of self-doped polyaniline/ss-DNA-SWNTs nanocomposite

A typical synthetic procedure for the preparation of a water solution of ss-DNA/SWNTs/PABA nanocomposite is as follows: 3-Aminophenylboronic acid hydrochloric salt (ABA) (50mM) and potassium fluoride (40 mM) were dissolved in 0.5 M H_2SO_4 . 0.8 mL of the ss-DNA/SWNTs solution with a concentration of 8 mg/L was then added to 2 mL of the prepared monomer solutions. The solution was bubbled with nitrogen for 30 min at 0°C to remove the dissolved oxygen. The chemical polymerization of ABA was initiated by adding 0.0125 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS) (in 0.5 M H_2SO_4 + 40 mM KF) as an oxidant drop-wise to the mixture. The polymerization was carried out at 0°C under nitrogen bubbling for 12 h. For *in-situ* UV-Visible study, all experiments were performed at 16°C to avoid condensing water onto the cuvet. Control experiments were also performed to fabricate neat poly (aniline boronic acid) (PABA) under the same conditions, except without adding ss-DNA/SWNTs into the monomer solution.

2.4 UV-Vis and Fourier Transform Infrared (FTIR) spectra

All UV-Vis absorption spectra were obtained at a Cary 500 UV-Vis-NIR Spectrophotometer with double beam mode. FTIR spectra were measured on a Spectrum Spotlight FTIR Imaging System (Perkin Elmer instruments). The water solutions of the neat PABA and composite, fabricated at 0°C , were centrifuged for 10 minutes at 10000g, and the resulting pellets were evenly re-dispersed into 18.2 M Ω nanopore water. This procedure was repeated 3 times to remove the sulfuric acid and monomer remaining in the solutions. Thin films of neat PABA and composite were prepared on a calcium fluoride substrate from the respective purified solutions. All FTIR spectra were obtained in the range of 750-1700 cm^{-1} (with 2 cm^{-1} spectral resolution).

2.5 Conductance measurements

0.5 μL of the composite (or the neat PABA) solution fabricated at 0°C was placed onto a prepatterned Si chip and dried under air. The gap distance between two gold electrodes on the Si chip is 1.5 μm . The resulting junctions of Au-nanocomposite-Au or Au-PABA-Au was rinsed with

nanopore water 5 times to remove the sulfuric acid and monomer and then dried under nitrogen. The conductance of the neat PABA and composite were measured with a Keithley 6517 multimeter and data were recorded by a Yokogawa 708 oscilloscope. A measurement scheme is shown in the inset of Figure 4.

3 RESULTS AND DISCUSSION

3.1 Enhanced stability

Figure 1 shows the UV-Vis spectra of the composite solution (1a) and the neat PABA solution (1b), which were polymerized at 0°C for 12 hours. Two broad peaks are visible with maxima at 390 nm and 686 nm for the neat PABA solution. The peak at 390 nm shifts to 383 nm and that at 686 nm shifts to 756 nm for the composite. This data suggests that the produced PABA both in the neat polymer and the composite is either in the fully oxidized pernigraniline state or emeraldine salt state[6,7]. That the polyaniline backbone in the composite absorbs light at longer wavelengths indicates that either the PABA in the composite has longer conjugated structures or it is in the more conductive and stable emeraldine salt state, while the PABA in the neat PABA exists more as the fully oxidized pernigraniline state.

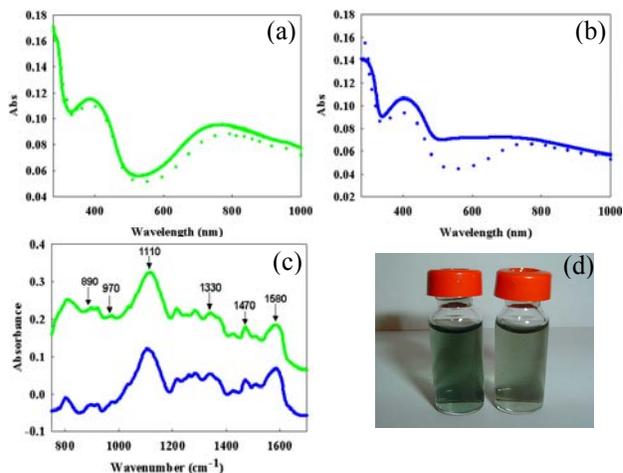


Figure 1. UV-Vis spectra of: (a) the PABA/SWNT composite and (b) the neat PABA before (—) and after (...) treatment with NaBH_4 . (c) FTIR spectra of the neat PABA (blue line) and the composite (green line). (d) A picture of the Composite (Left) and PABA (Right) solutions.

To understand the molecular structure of the PANI backbone in the neat PABA and the composite, we used FTIR to examine films prepared from the respective solutions. Figure 1c shows the FTIR spectra for the neat PABA (blue line) and the composite (green line). Both spectra exhibit the characteristic C=C stretching vibrations of the benzenoid ring at 1470 cm^{-1} and of the quinoid ring at 1580 cm^{-1} . The ratio of the relative intensities of quinoid to benzenoid ring modes (I_{1580}/I_{1470}) in the neat PABA is

1.3, which suggests that the percentage of quinoid units is higher than that of benzenoid units in the neat PABA film. This result is consistent with the previous report[7]. However, the ratio of I_{1580}/I_{1470} surprisingly decreases to 1.0 in the composite, indicating that the relative amount of quinoid units decreased and benzenoid units increased in the PABA when polymerized in the presence of the ss-DNA/SWNTs. Taken together with the UV-Vis spectroscopy results, the FTIR results further indicate that the PANI backbone exists mostly in the fully oxidized pernigraniline state in the neat PABA, and mostly in the emeraldine state in the composite.

To further support this conclusion and to understand if the PANI backbone has a longer conjugation length in the composite, we reduced the composite and the neat PABA with NaBH_4 , and then compared their resulting UV-Vis absorption properties. Figure 1 shows the UV-Vis spectra of the neat PABA and the composite before and after NaBH_4 treatment. For the neat polymer, the peak at 686 nm (fig. 1b solid blue line) greatly shifts to 760 nm (fig. 1b dash blue line), and for the composite, the peak at 756 nm (fig. 1a solid green line) slightly increases to 770 nm (fig. 1a dash green line). These results further reveal that before reduction, most of the PABA in the composite exists in the emeraldine state and in the neat polymer exists in the more oxidized pernigraniline state. After reduction, the composite absorbs at a slightly longer wavelength, indicating that the PANI backbone has longer conjugated structures in the composite.

Aromatic molecules are known to interact strongly with the basal planes of graphitic surfaces via π - π stacking. It is theoretically expected and experimentally demonstrated that the strong interaction between carbon nanotubes and PANI promotes and/or stabilizes the quinoid ring structure, i.e. the PABA in a composite should have more quinoid units than neat PABA[1,2]. Our unexpected results may be due to the catalytic reductive ability of ss-DNA/CNTs[8]. It is commonly believed that carbon nanotubes are relatively good electron acceptors, and PANI is considered to be a good electron donor, and therefore "charge transfer" occurred from PANI to carbon nanotubes in the composite. However, due to the electron donating ability of the DNA molecules, the ss-DNA/SWNTs are very different from bare carbon nanotubes, they are effective electron donors, and therefore possess reductive ability. The chemical potential of the polymerization initiator, APS, is 2.0 V, high enough to oxidize emeraldine to pernigraniline. However, due to the reductive ability of the ss-DNA/CNTs, the pernigraniline produced during the polymerization was readily reduced to the emeraldine state. Therefore, "charge transfer" also occurred between the two species in the composite, but in the opposite direction as initially assumed, i.e. electrons transferred from the ss-DNA/SWNTs to the PANI backbone.

It is well known that pernigraniline is not stable in acid solutions. PABA polymerized *in-situ* with ss-DNA/SWNTs existing in the more stable emeraldine state suggests that

the ss-DNA/SWNTs would greatly enhance the chemical stability of the film. In our earlier study[3], we indeed found that the PABA had much more enhanced electrochemical stability when *in-situ* electrochemically polymerized in the presence of ss-DNA/SWNT compared to the neat PABA film. Therefore we draw the conclusion that the catalytic reductive ability of the ss-DNA wrapped carbon nanotubes improved the quality and stability of the composite.

3.2 Increased Polymerization Speed

Due to the highly conjugated nature of the polyaniline backbone of PABA, it possesses UV-Vis absorbance spectra different from that of the 3-aminophenylboronic acid monomer. Therefore the amount of PABA formed during oxidative polymerization of 3-aminophenylboronic acid can be monitored as a function of time with UV-Vis spectroscopy.

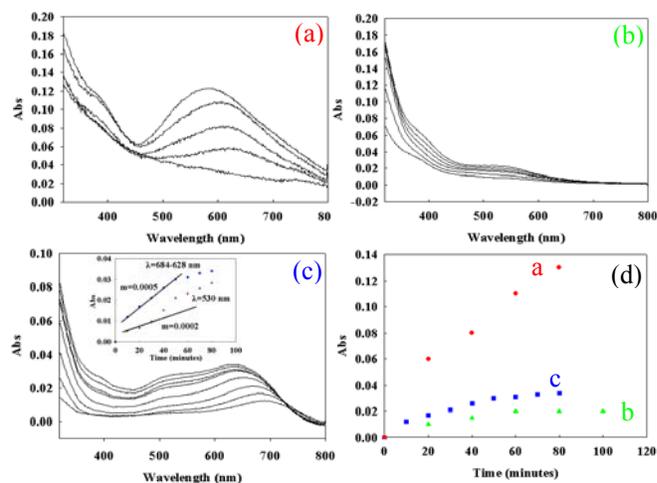


Figure 3: UV-Vis spectroscopy to monitor the polymerization processes at 16°C, (a) the SWNT:ABA weight ratio is 1:200, 0.01 M ABA. (b) 0.05M ABA without SWNTs, (c) the SWNT:ABA weight ratio is 1:50, 0.0025M ABA. (d) The peak intensity as a function of time.

Figure 3b represents the UV-Visible absorption spectrum recorded at various time intervals for the polymerization of 0.05 M ABA. The spectrum, during the course of polymerization, showed two broad bands at 390 nm and 530 nm (Fig. 3b) that increased in intensity as time progressed. The 530 nm band can be assigned to the electronic transition of the quinoid rings present in the PABA. The λ_{max} of the peak at 530 nm was lower compared to the PABA polymerized in 0°C. This blue shift is reasonable since it is known that polymerization at higher temperature produces more branched PANI with a shorter conjugation length.

When the polymerization was performed in the presence of a small amount of ss-DNA/SWNT (SWNT:ABA weight ratio is 1:200, 0.01 M ABA), the UV-Vis spectra also showed two broad bands during the polymerization. However, interesting observations were

noted. First of all, the intensity of the peak in the red region remarkably increased with time. Figure 3d (line a) shows the peak intensity in the red region as a function of time. Since the absorbance reflects the concentration of PABA formed in the reaction mixture (even though the peak position blue-shifts with time), the slopes of the curves reflect the polymerization rates under varying conditions. From this curve we can easily see that the polymerization is 32 times faster with ss-DNA/SWNTs than without, even though the concentration of ABA monomers was 5-fold more concentrate. Secondly, the λ_{\max} is much larger compared to the neat PABA solution. It was 622 nm in the very beginning, and gradually shifted to 576 nm. Finally, this band stabilized at 530 nm, the same position that appeared in the polymerization of ABA without ss-DNA/SWNTs. These results may indicate that in the ss-DNA/SWNT/ABA mixture, PABA was first polymerized along carbon nanotubes, thereby having longer conjugation lengths, and existed mainly in the emeraldine state. As time went on, the PABA fully covered the ss-DNA/SWNTs and therefore, the influence of the ss-DNA/SWNTs on the polymerization became diminished and more free PABA was produced. By decreasing the monomer concentration to 0.0025 M to increase the CNTs/monomer ratio to around 1:50, we can clearly see two different polymer structures (fig. 3c) simultaneously, which support our assumption described above.

The mechanism for the polymerization of aniline has been proposed as oxidative polymerization of aniline. The polymerization can be divided into three steps: initiation, propagation, and termination. The role of the DNA-wrapped carbon nanotubes on the rate of polymerization can be determined by considering the influence of ss-DNA/SWNTs on each step of polymerization. ss-DNA/SWNTs likely significantly speed up the initiation step: first, the ABA monomers pre-adsorb along the SWNTs, which results in a high local concentration of the monomers. Second, due to the high electron density of the ss-DNA/SWNTs, they may donate electrons to the monomers to make the monomers oxidation easier than that of the free monomers. Pre-alignment of the monomers along the ss-DNA/SWNTs also facilitates the propagation step of the polymerization. Last, the bulky structure of the carbon nanotubes may slow down the termination process by preventing collision of the radicals, which facilitate further the propagation and growth of the polymer. Therefore longer conjugated structures were produced with increased polymerization speed in the presence of ss-DNA/SWNTs as demonstrated by UV-Vis spectroscopy.

3.3 Improved Conductance

Figure 4 shows the current-voltage (*I-V*) curves measured on the films prepared from the composite and neat PABA solution. They all showed ohmic behavior between -0.1 V and 0.1 V. Remarkably, upon doping the electrical conductivity of the neat PABA film is 0.068 S

cm^{-1} , and for the nanocomposite it is $\sim 25 \text{ S cm}^{-1}$, 370 times higher than the neat PABA film fabricated under the same conditions. After dedoping with ammonia, the conductivity of the neat PABA is below $10^{-6} \text{ S cm}^{-1}$, which is beyond our current measurement setup, while the nanocomposite is still conductive in the dedoped state. Its conductivity decreased 11 times to 2.5 S cm^{-1} , but is still 37 times higher than the conductivity of neat PABA films in the doped state. This enhanced conductivity further indicates that the PABA exists in the more conductive and stable emeraldine state in the composite. More importantly, ss-DNA/CNTs may serve as “conducting bridges,” connecting PABA conducting domains and increasing the effective percolation.

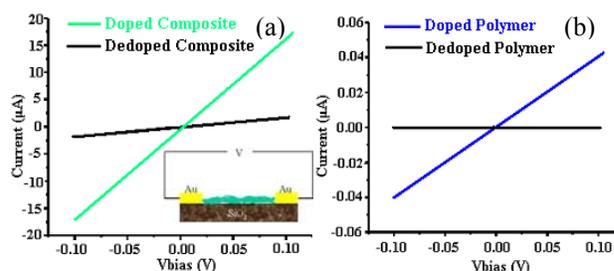


Figure 4: *I-V* characteristics of $\sim 70 \text{ nm}$ thick films, which have an area of $\sim 2 \text{ }\mu\text{m} \times 0.5 \text{ mm}$. Currents are for four electrode pairs. a) PABA-ss-DNA/SWNTs composite film. b) neat PABA composite film.

In summary, the ss-DNA/SWNTs performed multiple roles, i. e. active stabilizer and catalytic molecular template, conductive doping agents or conducting bridges in the greatly improved performance of the self-doped polyaniline both during and after the polymerization, which were investigated using UV-Vis spectroscopy, FTIR spectroscopy, and conductivity measurements.

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