

DNA Functionalized Carbon Nanotubes as Active Stabilizers: Enhanced Stability of Conducting Polymer Composites

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ABSTRACT

Short lifetime has been a thorny problem for chemical and biosensors, and light emitting devices consisting of organic (polymer) materials. In this work, a *water-soluble* self-doped polyaniline nanocomposite was fabricated by *in-situ* polymerization of 3-aminophenylboronic acid monomers in the presence of single-stranded DNA dispersed- and functionalized- single-walled carbon nanotubes. For the first time, we found that carbon nanotubes act as novel *active stabilizers*. This is possibly due to DNA functionalization: they reduced the polyaniline backbone from the unstable, degradable, fully oxidized pernigraniline state to the stable, conducting emeraldine state, which significantly improves the chemical stability of the self-doped polyaniline against the harsh UV irradiation.

Keywords: carbon nanotubes, DNA, self-doped polyaniline, composite, UV irradiation, stability

1 INTRODUCTION

Conjugated polymers received a renewed intense interest in the fabrication of numerous light and/or foldable electronic devices, such as light emitting devices, electrochromic displays, rechargeable batteries, microelectronic devices, protection coatings and chemical/biosensors. However, the relative low conductivity, mechanical strength, and stability severely limit conducting polymers for practical applications. Environmental stability is an essential determinant of a device's lifetime. Currently, very little effort has been expended on this subject.

Inspired by the remarkable electronic and thermal conductivity and the superior mechanical properties of carbon nanotubes (CNTs), tremendous efforts have been made over the past decade to prepare polymer and CNT composites with an aim of synergistically combining the merits of each individual component. Herein, for the first time, we exploit the special redox chemistry of carbon nanotubes for improving the stability of conducting polymers under harsh UV irradiation. We fabricated a *water-soluble* self-doped polyaniline/carbon nanotube nanocomposite by *in-situ* polymerization of the 3-aminophenylboronic acid monomers in the presence of single-stranded DNA dispersed- and functionalized- single-walled carbon nanotubes (SWNTs). We found that not only was the electrical performance of the conducting polymer

dramatically improved as predicted, the composite also shows remarkable enhanced stabilization under UV irradiation. Such stabilization effect is of academic interest and practical importance. Short lifetime has been a significant problem in devices consisting of organic (polymer) materials. Incorporation of carbon nanotubes into such devices may help develop organic photonic systems with longer life spans and thus commercial value.

2 EXPERIMENTAL SECTION

2.1 Materials

Purified HiPco single-walled carbon nanotubes (SWNT) were purchased from Carbon Nanotechnologies. Single stranded DNA (ssDNA) with sequence d(T)₃₀ was purchased from Integrated DNA Technologies. Ammonium persulfate (APS; 98%), potassium fluoride, 3 – aminophenylboronic acid hemisulfate salt (ABA; ≥ 95%) were purchased from Aldrich. Sulfuric acid was purchased from Pharmco. All chemicals were used as received without further purification.

2.2 Dispersion of SWNTs into water solution

Single-walled carbon nanotubes were dispersed in water using a method previously described by Zheng et al. Briefly, 11 mg of purified HiPco SWNT was suspended in aqueous ssDNA solution. This mixture was kept at 0°C with an ice-water bath and sonicated with a Sonics Vibra-cell (at 30% amplitude) for 30 minutes. After sonication, the sample was centrifuged with a Beckman centrifuge at 5000g to remove undispersed SWNT. After centrifugation, the sample was also dialyzed several times with a Centricon centrifugal filter unit with a molecular weight cutoff of 50kDa to remove free ssDNA. The resulting solution contains DNA – dispersed carbon nanotubes (ssDNA/SWNT) at a mass concentration of 200 – 500 mg/L.

2.3 *In-situ* fabrication of a self-doped polyaniline/ss-DNA/SWNTs nanocomposites

A typical synthetic procedure for the preparation of a water soluble poly (anilineboronic acid)/ssDNA/SWNT nanocomposite (ssDNA/SWNT/PABA) in the presence of fluoride is as follows: An aqueous solution of 40mM ABA

and 40mM potassium fluoride was prepared with 0.05M sulfuric acid. A known quantity of ssDNA/SWNT (178.15 μ l for 0.2%, 890.75 μ l for 1%) with a concentration of 250.35 mg/L was added to the ABA solution bringing the total volume to 3mL. The quantity of ssDNA/SWNT added is the weight percent based on the amount of ABA monomers in the mixture. The mixture was then purged with nitrogen for 30 minutes to remove dissolved oxygen. 0.38mL of 40mM APS, the oxidizing agent, was slowly added to this mixed solution over a period of 70 minutes to initiate the polymerization process. This reaction was carried out at 0°C under nitrogen bubbling for an additional 5 hrs. The mixture was left to react overnight in the refrigerator at 4°C. The same protocol was applied for the synthesis of pure PABA except ssDNA/SWNT was not added into the polymerization solution. The formed polymer was centrifuged at 4000g for 30 minutes to remove the water soluble oligomers and monomers from the mixture. This process was repeated several times. Dialysis was then performed to remove free DNA and other salts from the solution. This process was repeated until the pH of the formed polymer solution was adjusted to approximately 3.5.

2.4 Ultraviolet irradiation of self-doped polyaniline/ss-DNA/SWNTs nanocomposites

The following steps were taken to expose the polymer nanocomposites with ultraviolet (UV) light: A known quantity of the polymer solutions were dissolved in de-ionized water. Using UV-Visible spectroscopy, the absorbance intensity of the polymer peak for the three polymer samples (pure PABA, 0.2% ssDNA/SWNT/PABA composite, and 1% ssDNA/SWNT/PABA composite) were adjusted to approximately the same intensity to keep the polymer concentration the same. The three polymer solutions, in quartz cuvettes, were then placed 4cm from each other and 7cm from a 3UV multi-wavelength lamp light source (Ultraviolet Products). The three samples were then irradiated for different lengths of time and characterized using UV-Visible spectroscopy (UV-Vis), Fourier Transform Infrared spectroscopy (FTIR), and conductance measurements. All UV-Vis spectra were obtained using a Cary 500 UV-Vis-NIR Spectrophotometer in double beam mode. All FTIR spectra were obtained using a Spectrum Spotlight FTIR Imaging System with a spectral resolution of 4 cm^{-1} . All conductance measurements were obtained using an Electrochemical Workstation CHI 760C.

3 RESULTS AND DISCUSSION

3.1 Improved stability of ss-DNA/SWNT/PABA nanocomposite

Oxidation of the PABA backbone causes a change in its structure. This change is represented by a decrease in conductance due to the conversion of benzenoid units to the more reactive quinoid units in the PABA backbone. Therefore, the conductance can be monitored as a function of time using an Electrochemical Workstation CHI 760C. Thin films were prepared by adding 5 μ l of the polymer composites to pre-patterned silicon chips in a layer-by-layer fashion and the conductance was measured until the percolation point was reached. After percolation, the three polymers on the silicon chips were subjected to UV irradiation light at 365nm, the wavelength where the π - π^* electron orbital transition occurs along the backbone of the PABA polymer chain. The conductance was monitored for pure PABA, 0.2% ssDNA/SWNT/PABA, and 1% ssDNA/SWNT/PABA as a function of UV irradiation time. Figure 1a shows a typical I-V curve for pure PABA after 150 minutes of UV light irradiation.

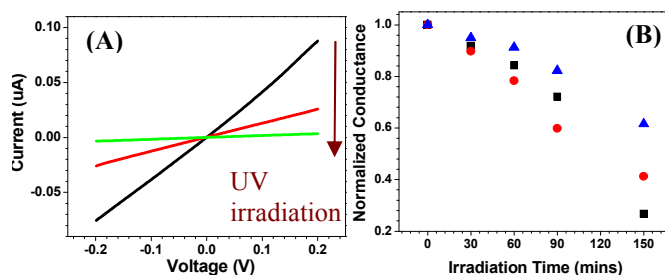


Figure 1: (a) I-V curve of pure PABA irradiated for 0 (black), 60 (red), and 150 mins (green). (b) Normalized relative conductance decrease for pure PABA (black), 0.2% ssDNA/SWNT/PABA (red), 1% ssDNA/SWNT/PABA (blue). Larger percentage of SWNT in the in-situ polymerized solution yields more stable composite.

The normalized relative conductance decrease is shown in Figure 1b. Pure PABA showed the largest relative decrease in conductance (73.31%) compared to 1% ssDNA/SWNT/PABA (38.40%) and 0.2% ssDNA/SWNT/PABA (58.79%) after UV light irradiation. These results reveal that the amount of ssDNA/SWNT added to the polymerization process affects the stability of the formed polymer nanocomposite. In order to understand this phenomenon further, we used UV-Visible spectroscopy and FTIR spectroscopy to study the electronic and molecular structures of the formed polymers before and after UV irradiation.

A typical UV - Vis spectrum of PABA in the emeraldine oxidation state contains three absorption bands of interest. The first absorption peak at \sim 266nm is characteristic of ABA monomers, free ssDNA, and certain polyaniline degradation products such as hydroquinone, p-benzoquinone, and p-aminophenol.¹ The second peak at \sim 390nm originates from the π - π^* electron orbital transition in the benzenoid rings along the backbone of the PABA

chain and also from oligomers. The last absorption peak of interest is at $\sim 800\text{nm}$. This peak is caused by the intrachain electron excitation of the polymer.

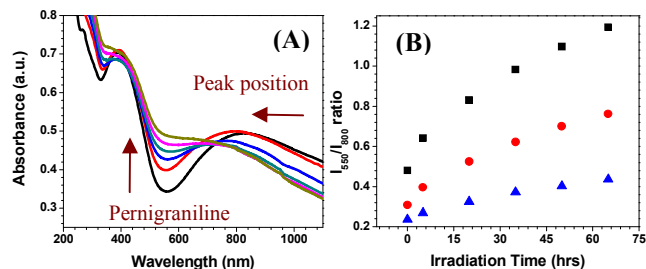


Figure 2: (a) UV – Visible spectra of pure PABA after exposure to UV light irradiation for 0 (black), 5 (red), 20 (blue), 35 (green), 50 (pink), and 65 hours (olive). (b) Pernigraniline to emeraldine ratio at different irradiation time periods for pure PABA (black), 0.2% ssDNA/SWNT/PABA (red), and 1% ssDNA/SWNT/PABA (blue). The values for pernigraniline and emeraldine were obtained by fitting Gaussian curves and taking the total area under these curves. Higher percentage of SWNT used during the in-situ polymerization process results in less pernigraniline state produced under UV irradiation.

Figure 2a shows the UV-Vis spectra of pure PABA at different UV irradiation times. As shown in the figure, UV irradiation induces significant changes in the UV-Vis spectra. The increase in absorbance at $\sim 266\text{nm}$ is due to the oxidation of the PABA backbone, resulting in an increase in concentration of ABA monomers and PABA degraded products such as hydroquinone, p-benzoquinone, and p-aminophenol. Similarly, the increase in absorbance at $\sim 550\text{nm}$, attributed to the non-conductive pernigraniline oxidation state of PABA and to quinoneimines, indicates oxidation of the emeraldine state of PABA to the pernigraniline state and thus the degradation of the polymer chain. Furthermore, irradiation of the PABA nanocomposite shows a decrease in absorbance and a blue shift of the absorption band at $\sim 800\text{nm}$, attributed to the emeraldine state of PABA. The decrease in absorption at $\sim 800\text{nm}$ is consistent with the increase in absorption at $\sim 550\text{nm}$, verifying that the emeraldine state is oxidized to the pernigraniline state. The conjugation length of the conducting PABA polymer can also be qualitatively determined from the UV spectrum by examining the emeraldine peak position. It is well documented that longer wavelengths of the emeraldine peak position indicates longer PABA conjugation length and thus higher conductivity.

The emeraldine peak position of pure PABA blue shifts (149nm) much more compared with the PABA nanocomposites containing 0.2% wt SWNT (45nm) and 1% wt SWNT (24nm) after 65 hours of UV light irradiation. The conjugation length of the polymer produced and thus

the conductivity is preserved more efficiently in the presence of harsh UV light with higher concentration of SWNT.

In addition, the stability of the produced polymer can be determined by analyzing the amount of pernigraniline ($\sim 550\text{nm}$) to emeraldine ($\sim 800\text{nm}$) in the solution, as shown in figure 2b. The increasing pernigraniline to emeraldine ratio for the three polymers verify the degradation of the PABA polymer chain with UV light irradiation. In addition, it shows that the amount of quinoid units in the polymer chain increases as irradiation time increases. The percent increase of the pernigraniline to emeraldine ratio for pure PABA, 0.2% ssDNA/SWNT/PABA, and 1% ssDNA/SWNT/PABA are 148.0%, 127.6%, and 84.9% respectively. The UV-Vis data shown are consistent with conductance measurements; increasing the concentration of ssDNA/SWNT in the in-situ polymerization process yields a polymer nanocomposite with higher stability.

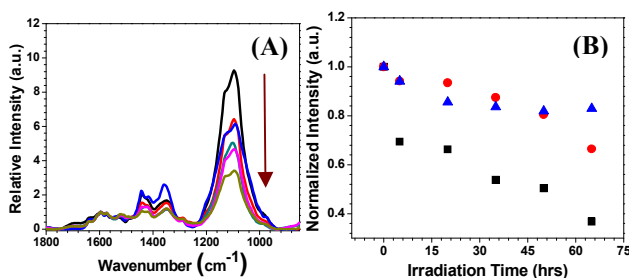


Figure 3: (a) FTIR spectra of pure PABA after exposure to UV light irradiation for 0 (black), 5 (red), 20 (blue), 35 (green), 50 (pink), and 65 hours (olive). (b) Relative decrease in intensity of the “electronic-like” peak ($\sim 1100\text{nm}$) at different irradiation times for pure PABA (black), 0.2% ssDNA/SWNT/PABA (red), 1% ssDNA/SWNT/PABA (blue).

Furthermore, FTIR spectroscopy was used to study and characterize molecular structural changes of the polymers after exposure to UV irradiation. Figure 3a shows the FTIR spectra of pure PABA at different UV irradiation times. The strong absorption band at 1100cm^{-1} can be attributed to the “electronic-like band” and is a measure of the degree of delocalization of electrons, and thus conductivity. The absorption band at 1596cm^{-1} can be attributed to the C=C stretching in the quinoid type ring and the absorption band at 1440cm^{-1} is from mixed C-C stretching, C-H, and N-H bending vibrations of the benzenoid ring.

A general relative decrease in the “electronic-like” peak is seen, indicating that the conductivity of the polymers decreases with increasing UV irradiation time. In addition, the amount of benzenoid units in the polymer chain, represented by the intensity band at 1440cm^{-1} , shows a decrease with increasing irradiation time. This indicates the oxidation of PABA from the emeraldine state, which has

more benzenoid units than quinoid units, to the pernigraniline state. The relative intensity decrease of the “electronic-like band” for the three polymers was calculated. After 65 hours of UV light irradiation, pure PABA showed the greatest relative decrease in intensity (63.2%) compared to 0.2% ssDNA/SWNT/PABA (33.6%) and 1% ssDNA/SWNT/PABA (17.0%). This reveals that pure PABA experiences the greatest conductivity loss compared to the composites containing SWNT. Furthermore, as the concentration of SWNT increases, the polymer produced has greater stability.

The absorption bands corresponding to the quinoid ring at 1596 cm^{-1} and the benzenoid ring at 1440 cm^{-1} can be expressed as an intensity ratio (I_{1596}/I_{1440}). This quinoid to benzenoid ratio can provide information on the degree of oxidation of the polymer. Figure 3b shows the quinoid to benzenoid intensity ratio of pure PABA, 0.2% ssDNA/SWNT/PABA, and 1% ssDNA/SWNT/PABA at different irradiation times. 1% ssDNA/SWNT/PABA showed almost no change ($\sim 0.9\%$ increase) in the quinoid to benzenoid ratio, indicating that its molecular structure is relatively unaffected by UV irradiation even after 65 hours of exposure. The quinoid to benzenoid ratio, however, increased 1.9 times for 0.2% ssDNA/SWNT/PABA and over 2.5 times for pure PABA. This shows that as the concentration of ssDNA/SWNT used in the in-situ polymerization decreases the amount of quinoid units formed in the polymer chain increases under UV irradiation and thus makes the formed polymer less stable.

3.2 Proposed Mechanistic Aspect and Role of the ssDNA/SWNTs

The mechanism of the chemical degradation of polyaniline induced by UV irradiation has been discussed in literature.² In the presence of dissolved oxygen, the amine units in the polyaniline backbone were oxidized to imine units. The polyaniline is converted from the conductive, half oxidized emeraldine state to the non-conductive and fully oxidized pernigraniline state. Under UV light irradiation, this oxidation process is accelerated. In the pernigraniline form, polyaniline contains quinoid units which are easily hydrolyzed by water, producing various degraded products such as hydroquinone and p-aminophenol. To our knowledge, there have not been any studies on the degradation mechanism of PABA; we assume that PABA experience similar degradation process as polyaniline. The results from our UV-Vis and FTIR study of the molecular structure of PABA after different UV irradiation time periods support this assumption.

However, the data shown from the conductance measurements, UV-Vis, and FTIR spectra all lead to the conclusion that PABA/SWNT nanocomposites are much more stable as the concentration of ssDNA/SWNT is increased during the in-situ polymerization process. The exact mechanism of how the ssDNA/SWNTs enhance the chemical stability of the PABA under UV irradiation is still

under investigation in our group. We hypothesize that this is due to the reductive ability of ssDNA/SWNTs, which can reduce the nonconductive pernigraniline to the stable and highly conductive emeraldine state (Figure 4) and making the polymer more stable and less susceptible to hydrolysis. Therefore, the molecular structure and thus the conductivity of the polymer are largely preserved. As the concentration of SWNT is increased, this stabilizing effect is more prominent, as supported by the conductance, UV-Vis, and FTIR data. In this process, the SWNTs are also oxidized. Reduction of the oxidized carbon nanotubes by water or hydroxide ions would complete the cycle.^{3,4}

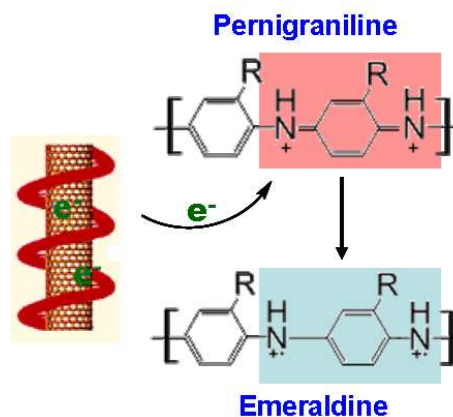


Figure 4: Proposed stabilization mechanism of ssDNA/SWNT during the in-situ polymerization process.

In summary, not only was the electrical performance of the conducting polymer dramatically improved by *in-situ* polymerization of 3-aminophenylboronic acid monomers in the presence of single-stranded DNA dispersed- and functionalized- single-walled carbon nanotubes (SWNTs), the composite also showed remarkable enhanced stabilization under UV irradiation. This may possibly be due to the reductive capability of the carbon nanotubes functionalized with DNA. The enhanced stability would greatly help develop organic photonic systems with longer life spans and thus commercial value.

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