

AQUEOUS DISPERSION OF SINGLE-WALLED CARBON NANOTUBES BY USING SELF-DOPED POLYANILINE AS DISPERSANT

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ABSTRACT

Single-walled carbon nanotubes (SWCNTs) functionalized with poly(aniline N-butylsulfonate) (PAnBuS), a water-soluble self-doped polyaniline, were prepared by mixing solutions in ex-situ. The interaction between poly(aniline N-butylsulfonate) (PAnBuS) and SWCNTs was investigated by XPS and UV-vis spectroscopy. The morphology of SWCNTs-PAnBuS nanocomposites was investigated by FE-SEM. The SWCNTs-PAnBuS dispersion was exhibited long-term stability in aqueous environments. The sheet resistance of SWCNTs-PAnBuS thin film on a PET substrate was $1\sim 2 \times 10^4 \Omega / \text{sq}$ using four-point probe measurement.

Keywords: self-doped polyaniline, single-walled carbon nanotubes, dispersion

1 INTRODUCTION

Since the discovery of single-walled carbon nanotubes (SWCNTs) in 1991, they have attracted great interest due to their high aspect ratio, small diameter, light weight, and high Young's modulus.[1,2] However, poor solubility of SWCNTs in both aqueous and common organic solvents is a major hindrance for their potential applications. The dispersion and dissolution of SWCNTs are recognized to be an essential step in utilizing them. To obtain the good dispersion, various techniques have been developed to debundle SWCNTs. Recently, carbon nanotubes-polymer composites by using *in-situ* polymerization of inherently conducting polymer (ICP) such as polyaniline have been reported to enhance a dispersion property of carbon nanotubes and allow their new electrical applications.[3,4] Due to their unique properties ICPs have been widely studied as a working component in many fields including rechargeable batteries, light emitting diodes, transistors, molecular sensors, nonlinear optical devices, corrosion protection, and electrochromic display. However, from a practical view point the *in-situ* method has limitations in controlling the ratio of both components easily and in completing functionalizing of SWCNTs in the molecular level. Among ICPs, self-doped polyanilines can be a good candidate to enhance the dispersibility of SWCNT in

aqueous media because of their water solubility, electroactivity, conductivity, and redox activity in a wider pH range.[5] Previously, Kim et al reported the synthesis of poly(aniline N-butylsulfonate) (PAnBuS) *via* either by electrochemical or chemical oxidations of 4-anilino-1-butane sulfonic acid monomer.[6] The PAnBuS shows reversible electrochemical redox behavior, moderate conductivity in the range of $\sim 10^{-3} \text{ S/cm}$, and most of all, excellent solubility in water.

In this paper, a water-soluble self-doped polyaniline, poly(aniline N-butylsulfonate) (PAnBuS), is going to be introduced to disperse SWCNTs. (Figure 1) The SWCNTs functionalized with PAnBuS are expected to exhibit high dispersibility in water, and to form a stable and homogeneous dispersion. Preparation of transparent conductive films (TCF) from the aqueous dispersion of SWCNTs functionalized with PAnBuS will be attempted.[7] Electrical conductivity and other physical properties of the resulting conductive film will be also discussed.

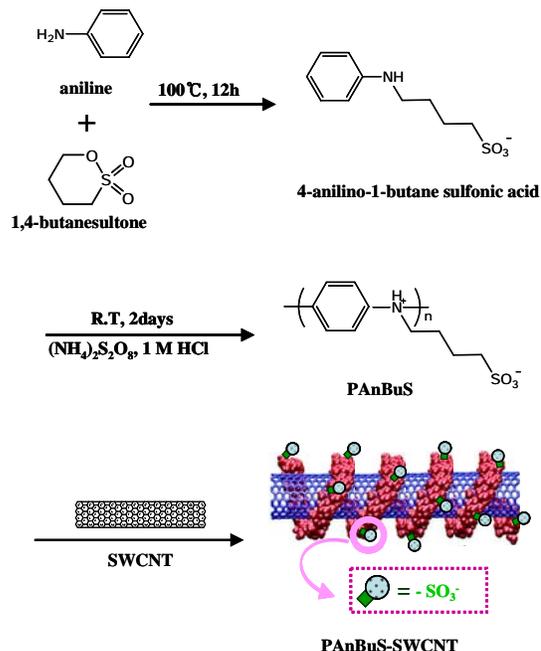


Figure 1 : Preparation route for PAnBuS polymer and a dispersion process of SWCNTs using PAnBuS.

2 EXPERIMENTAL

2.1 Materials

The purified SWCNTs were purchased from Carbon Nanotechnologies Inc. (HiPco SWCNTs, Lot #PO304) and used without further purification. Aniline (Aldrich), 1,4-butane sultone (99+%, Aldrich) and ammonium persulfate (98+%, Aldrich) were used as received.

2.2 Synthesis

A water-soluble self-doped polyaniline, poly(aniline N-butylsulfonate) (PAnBuS) was synthesized by the electrochemical oxidations of aniline N-butylsulfonate, which was readily obtained from aniline and 1,4-butane sultone following a reported procedure.[6] The aniline monomer (0.6 mg) was added to a solution of 1 M HCl (35 %, 0.45 mL) and stirred. Ammonium persulfate (0.66 g) dissolved in deionized water (2.5 mL) solution was dropwisely added to the aniline/HCl solution with stirring. After a few minutes, the dark suspension became green, indicating polymerization of aniline has been started. The solution was further stirred for 48 h at room temperature. The dark-green PAnBuS product was purified by dialysis in deionized water for 3 days, and dried under vacuum for 48 h at 40 °C.

2.3 Dispersion of SWCNTs

As-received SWCNTs were placed in an aqueous solution of PAnBuS, followed by sonication in a bath-type sonicator (300 W, Power Sonic 405, Hwashin Tec.) for 2 h at room temperature. We also isolated solid products of SWCNTs-PAnBuS nanocomposite in order to characterize using XPS and SEM. An aqueous dispersion of SWCNTs-PAnBuS was filtered under 0.2 μm pore membrane filter and sufficiently rinsed with deionized water until the filtrate was colorless. The collected solids were dried under vacuum for 48 h at 60 °C, and stored in a closed container minimizing exposure to moisture in the air.

2.4 Characterization

The UV-vis spectrum of SWCNT dispersed in aqueous PAnBuS solution was recorded using Scinco Co., S-1500 and the result was compared with that of aqueous PAnBuS solution itself. Measurements of the sheet resistance were carried out by four-point probe method (Keithley, 3220/2182A) at room temperature. The morphology studies of the SWCNTs-PAnBuS were performed with field emission scanning electron microscopy (FE-SEM, HITACHI S-4800, Japan) operating at 30 kV and the samples for the measurement were prepared as follows: bath sonicate SWCNTs-PAnBuS in methanol for 20 min,

place one drop of the suspension on the silicon wafer and dry on the hot plate for 80 °C for 10 min. The X-ray photoelectron spectroscopy (XPS) was conducted on an AXIS-NOVA (Kratos Inc.) at using monochromatized Al $K\alpha$ radiation ($h\nu = 1486.6$ eV).

3 RESULTS AND DISCUSSION

A poly(aniline N-butylsulfonate) (PAnBuS) has been successfully synthesized by the electrochemical oxidations of aniline N-butylsulfonate. The dispersion of SWCNTs in water containing PAnBuS was performed by using a typical procedure as described in the experimental section. We observed the dispersed SWCNTs in aqueous PAnBuS solution had not been aggregated even for a month. The pictures of as-received SWCNT and SWCNT-PAnBuS dispersed in water shown in Figure 2 were taken after 30 days since they had been treated under ultrasonic agitation for 1 hour.

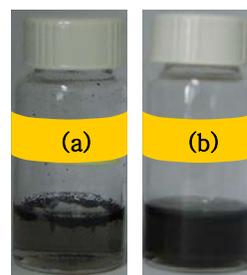


Figure 2 : Aqueous solutions of (a) as-received SWCNTs and (b) SWCNT-PAnBuS.

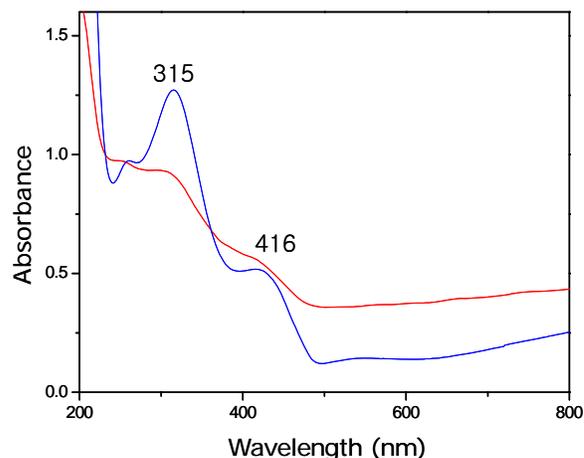


Figure 3 : UV-vis absorption spectra of SWCNT-PAnBuS (red line) and PAnBuS (blue line).

Figure 3 shows the UV-vis spectra of aqueous PAnBuS solution itself (blue line) and dispersed SWCNTs in PAnBuS solution (red line). Two absorption bands at 315 nm and 416 nm of aqueous PAnBuS correspond to π - π^* transitions [8]. The two absorption bands, especially the

band at 315 nm, were significantly decreased upon forming dispersion with SWCNTs. It suggests a change in conformation of the PAnBuS polymer backbone due to the interaction with added SWCNTs. [9]

The formation of SWCNTs-PAnBuS nanocomposites was investigated by X-ray photoelectron spectroscopy (XPS). Since nitrogen atom in PAnBuS would be most highly affected when the PAnBuS molecules were interacted with SWCNTs, we chose the spectra of N(1s) for both PAnBuS and SWCNTs-PAnBuS for XPS study. The XPS spectra of N(1s) of them were depicted in Figure 4. Two peaks of N(1s) (Figure 4(a)) were observed at 399 eV and 401 eV in PAnBuS which corresponded to benzenoid amine (-NH-) and positively charged nitrogen atoms (N⁺), respectively.[10] These peaks were not shown in as-received SWCNTs. (Figure 4(c) After the formation of the SWCNTs-PAnBuS nanocomposites, the peak from positively charged nitrogen atoms was dramatically reduced and the peak from the amine was dominantly appeared. (Figure 4(b) It implies that the SWCNTs-PAnBuS nanocomposites was fabricated *via* a redox reaction.

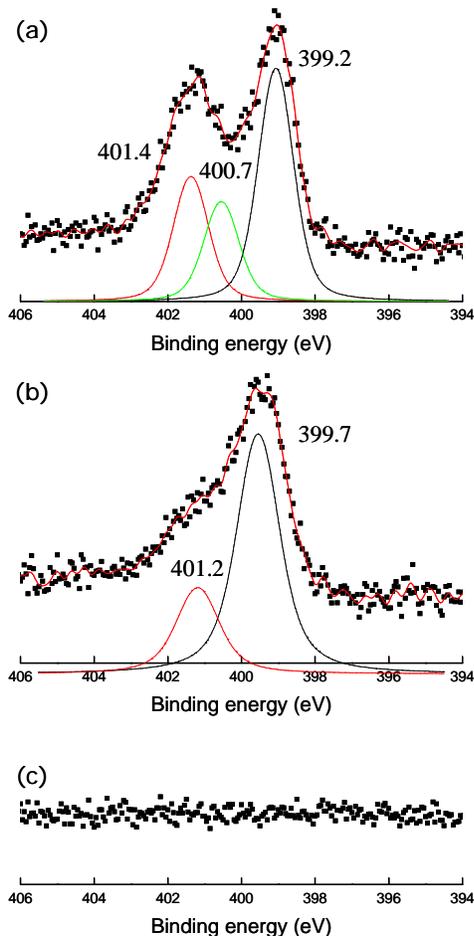


Figure 4 : XPS N(1s) spectra of (a) PAnBuS, (b) SWCNTs-PAnBuS, and (c) as-received SWCNTs

The morphology of SWCNTs-PAnBuS was compared with that of SWCNTs using a field emission scanning electron microscope (FE-SEM). In order to investigate the difference in the surface of SWCNTs and the of SWCNTs-PAnBuS nanocomposites, FE-SEM images were obtained at large area. The surface of the latter (Fig. 5(b)) was seemed to be covered with polymer thin films which were not observed in that of the former (Fig. 5(a)). In addition, bundle diameters of SWCNTs were in the 20 - 50 nm range. By comparison, small bundle sized SWCNTs (less than 20 nm) were frequently observed for SWCNTs-PAnBuS nanocomposites. This explains that the bundled SWCNTs become dispersed into small dimeters through strong chemical interaction between PAnBuS with side-wall of SWCNTs.

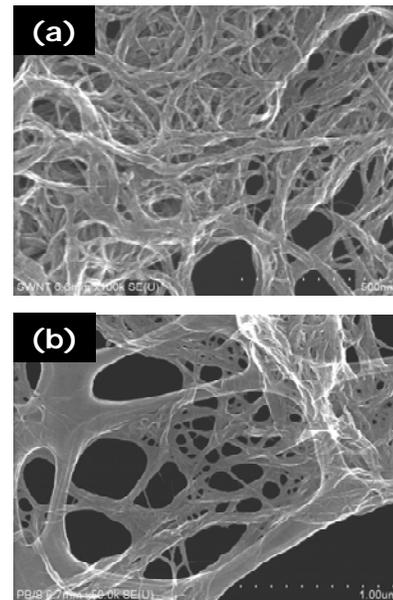


Figure 5 : SEM images of (a) as-received SWCNTs and (b) SWCNTs-PAnBuS.

We attempted to fabricate electrically conducting thin film using the SWCNTs-PAnBuS nanocomposites in order to trace the application possibility for new electrode materials. 3 mg of SWCNTs was added to 10 mL of aqueous solution containing 15 mg PAnBuS under ultrasonic agitation for 10 h. The dark solution was centrifuged at 10,000 g for 10 minutes.[7] The SWCNTs - PanBuS supernatant was sprayed onto polyethylene terephthalate (PET) substrate using an air brush pistol to form a uniformed thin film. The sheet resistance of TCFs prepared from PAnBuS dispersed SWCNTs are in the range of $1\sim 2 \times 10^4 \Omega / \text{sq}$. This values are slightly higher than that of films prepared SDS/SWNT dispersion ($2\sim 8 \times 10^3 \Omega / \text{sq}$) at the same transparency. Even though a conducting polymer was employed to fabricate thin film of SWCNTs, the electrical property was not improved or even detracted.. However, there is more room for enhancing conductivity of thin films, e.g. adding other dopants into conducting

polymers, and improving SWCNT networks in polymer matrix, etc, so that the conductivity of the composite can be enhanced. This study is still on-going for achieving suitable conductivity.

4 CONCLUSIONS

Dispersed and debundled SWCNTs were prepared in an aqueous solution of PAnBuS using a simple mixing procedure under ultrasonic treatment. Unlike the as-received SWCNTs, the synthesized PAnBuS-SWCNTs were completely soluble in water at least for 1 month. This fact implies that the interaction between polymer and carbon nanotubes is strong enough to overcome the van der Waals interaction among SWCNTs. This functionalized complex can be utilized in many applications, especially in fabricating transparent conducting films.

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