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Electrochemistry Communications 9 (2007) 206–210

electrochemistry communications

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Electrochemical functionalization of single walled carbon nanotubes with polyaniline in ionic liquids

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Received 17 August 2006; received in revised form 8 September 2006; accepted 14 September 2006

Abstract

Single walled carbon nanotubes (SWNTs) are covalently functionalized during the electropolymerization of aniline in ionic liquids. In our experiment, 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BMIPF_6$) containing 1 M trifluoroacetic acid (CF_3COOH) was selected as the ionic liquid media to separate SWNTs and to perform the electropolymerization of aniline within. The morphology of the resulting composite material of SWNT and polyaniline (PANI) was studied by scanning electron microscopy (SEM). Covalent bonding was evidenced by the increase of intensity ratio of the D band vs. G band in the Raman spectrum, whilst SWNTs may also be incorporated as big dopant anions to the PANI backbone. This paper provides a novel method by which large amount of SWNTs (15 mg/ml) can be modified by aniline electrochemically. p-type conducting polymer and n-type SWNTs can be thus copolymerized and applied to organic photovoltaics.

Keywords: Single walled carbon nanotubes; Polyaniline; Ionic liquids; Electrochemical functionalization; Organic photovoltaics

1. Introduction

Carbon nanotubes have attracted intense attention for their extraordinary mechanical and electronic properties. Reliable methods to functionalize the carbon nanotubes will extend their applications and may implant new functions that cannot otherwise be acquired by pristine ones. There are many different ways to functionalize carbon nanotubes chemically [1–3]. Electrochemical functionalization will provide an efficient, clean, and more versatile alternative. Since single walled carbon nanotubes (SWNTs) are n-type materials, SWNTs/conjugated polymer devices have been demonstrated to have good photovoltaic properties [4–6]. Polyaniline (PANI) as a good electron donor is unique among the conjugated polymers, because its electrical properties can be reversibly tuned by both charge transfer doping and protonation [7]. Carbon nanotubes can be covalently functionalized or doped to PANI [8–11]. In these reports, small amount of tangled carbon nanotubes were used either as modified electrode materials in electrochemical modification [9,11] or as additives, which were mixed with conducting polymers during chemical polymerization [8,10]. We introduce here a novel electrochemical method to functionalize rather large amounts of SWNTs in ionic liquids (ILs). This method offers a possibility to produce PANI–SWNTs donor–acceptor dyads, which can be applied in organic electronics.

2. Experimental

$BMIPF_6$ ($\geqslant$98%) was bought from Solvent Innovation and the structure is shown in Scheme 1. Aniline (>99.5%) was obtained from Fluka and CF_3COOH (99%) from Aldrich. All chemicals were used as received. SWNTs were purchased from Nanoport Co. Ltd. (Shengzhen, China) with inner diameter <2 nm and length 5–15 μm. They were

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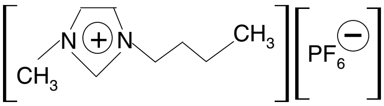
doi:10.1016/j.elecom.2006.09.008



Scheme 1. The chemical structure of 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BMIPF_6$).

purified by refluxing in 3 M HNO_3 for 48 h, and then filtered through a 0.45 μm pore size nylon membrane with the aid of a pump and thoroughly washed with deionized water (ELGA, 18.2 MΩ cm). The materials were then dried under vacuum at 60 °C for 12 h before use.

ITO glasses (Planar International) with thickness of 1 mm were cut to 3 cm × 1 cm slides, and then cleaned by ultrasonication in separate solutions of acetone, ethanol and water for 10 min each. Afterwards, both the sides of the ITO glass were further cleaned in a plasma cleaner (Harrick, PDC-001) for another 10 min. The cleaned ITO glasses were then conditioned for 5 h in piranha solution, which was a mixture of concentrated sulphuric acid and hydrogen peroxide (30%) with a volume ratio of 7:3. This was done in order to produce more hydroxyl groups on the ITO surface. The ITO glasses were then washed with a large amount of water and dried under nitrogen gas. The surfaces for these pre-treated substrates were modified by immerging them in a methanol solution containing 10 mM aniline silane for 24 h. The ITO substrates modified with aniline silane (MITO) were then washed thoroughly with methanol and dried under nitrogen gas at room temperature before use.

The electropolymerization was carried out in a three-electrode quartz cuvette cell in SWNT-IL matrix. SWNT-IL matrix were prepared by the following procedure: 15 mg SWNTs (purified before use) and 1 ml $BMIPF_6$ was ground for 15 min, then 0.2 M aniline and 1.0 M CF_3COOH were added and ground thoroughly. MITO was used as working electrode, Ag/AgCl wire as reference electrode and platinum wire as counter electrode. MITO was reported to enhance the electropolymerization and improve the surface morphology of PANI and its sulfonated derivative [12,13]. The potential was controlled by an Autolab (PGSTAT 20) and scanned between −0.3 V to 1.5 V with a scan rate of 50 mV/s for 50 or 300 cycles.

The morphology of the SWNT–PANI composite film was studied by scanning electron microscopy (SEM; Leica Cambridge Instruments). It was then further characterized by Raman spectroscopy. The Raman spectra were measured with a Renishaw–Raman imaging microscope (with Wire^{TM} v1.3 Raman software) connected to a Leica DMLM microscope, the excitation wavelength of 780 nm was chosen for Raman analysis. This excitation is in resonance with tubes that have diameters of 1.0–1.2 nm [14], which matches the average diameter of SWNTs in our study. The spectrometer was always calibrated against a Si standard (520 cm^{-1}) before measurements.

3. Results and discussion

SWNTs usually existing as tangled bundles are difficult to dissolve in both aqueous and organic media. However, they can be well separated in ILs due to 'cation–π' interactions [15]. This gives the possibility to functionalize large amount of SWNTs electrochemically. There are only a few reports on electropolymerization of aniline in ILs [16–18], resulting in better electrochemical stability of PANI in ILs [16].

In our case, electropolymerization of aniline was done by cyclic voltammetry (CV) on MITO in the SWNT-IL matrix, which contains aniline monomer and trifluoroacetic acid. The CVs obtained during electropolymerization for the 1st, 50th and 300th cycle are shown in Fig. 1. The first cycle (Fig. 1a) is a typical response from the initiation of PANI polymerization to produce positive anilinium radicals, whilst the 50th cycle (Fig. 1b) seems like a response from pure anode resistance. The current is almost doubled and the slope of the current–voltage relationship is increased to almost 55° when the cycle number is up to 300 as shown in Fig. 1c. This phenomenon can be explained if the SWNT-IL matrix near to the MITO anode is considered as a three dimensional (3D) working electrode, where SWNTs have the same functions as carbon particles in the carbon paste electrode. The concept of IL-type carbon paste electrode has been proposed by Liu et al. [19] and Zhang et al. [20].

The morphology of the resulting SWNT–PANI composites was characterized by scanning electron microscopy (SEM). As a comparison, SEM images from MITO and purified SWNTs are illustrated in Fig. 2a and b. SEM image from the clean unmodified ITO glass can be seen in Fig. 2e. The purified SWNTs were pasted on a ITO chip. Fig 2b shows that pure SWNTs are randomly oriented, and some of them are in the bundled form. When dispersed in ILs and electropolymerized with aniline for 50 cycles

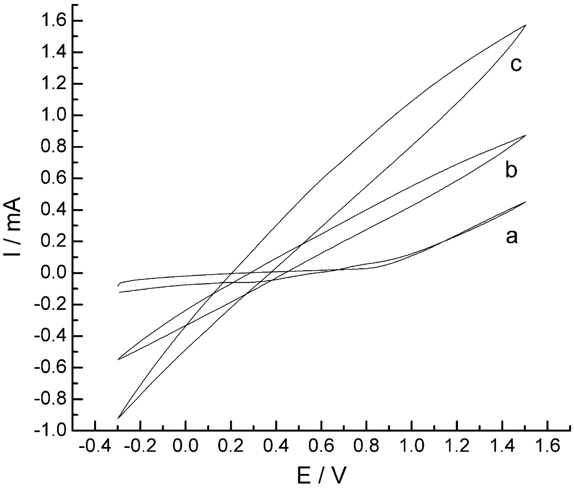


Fig. 1. Cyclic voltammogram for the electropolymerization of aniline with SWNTs in ILs: (a) 1st, (b) 50th and (c) 300th cycle.

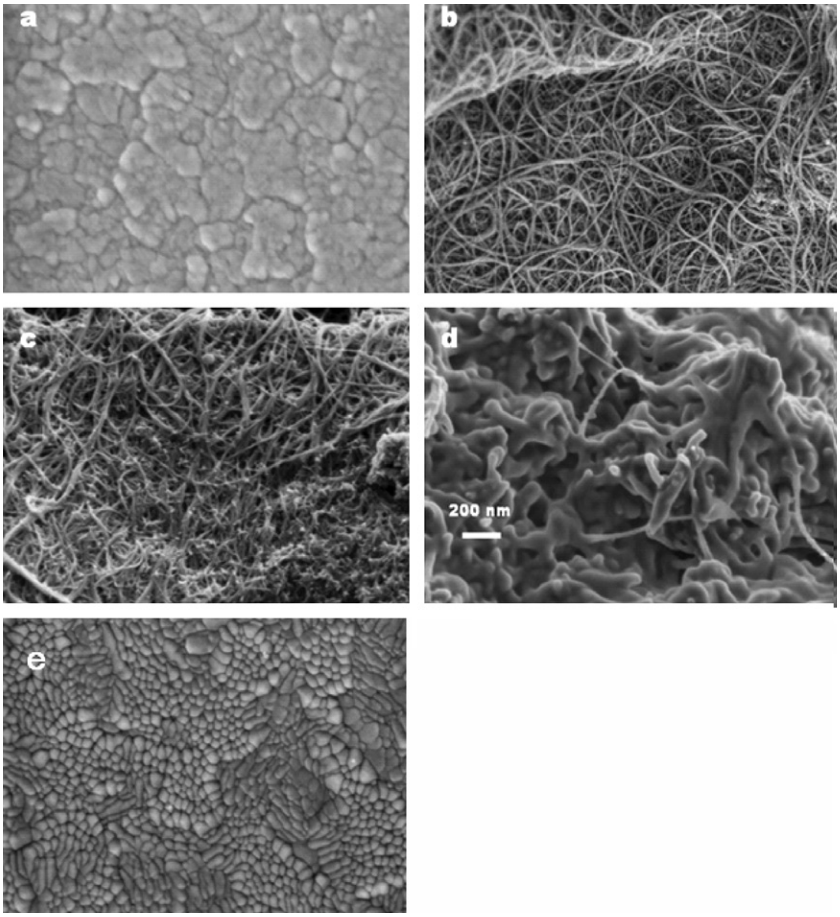


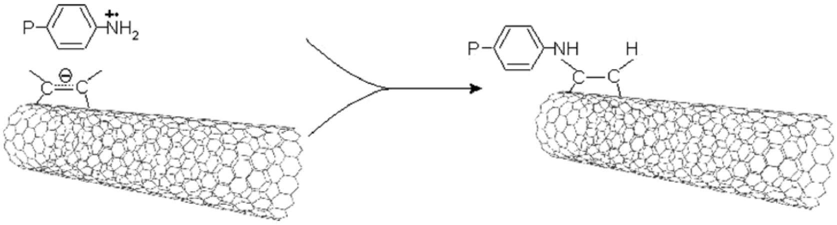
Fig. 2. SEM image of (a) modified ITO glass surface (MITO); (b) purified SWNTs; (c) SWNT modified with PANI (electropolymerization for 50 cycles); (d) SWNT modified with PANI (electropolymerization for 300 cycles); (e) bare ITO glass surface.

(Fig. 2c), some of the SWNTs on the surface are covered by PANI granules. As the number of cycles was increased to 300 (Fig. 2d), PANI seems to wrap around SWNTs and the whole surface was coated with PANI. In other words, SWNTs function like small working electrodes in ionic liquid media and thus facilitate electropolymerization of aniline on their own surface.

There are two possible interactions between PANI and SWNTs. First, the positively charged aniline radical during electropolymerization can be covalently bonded to the carbon surface of SWNTs [10,21] as shown in Scheme 2. Besides covalently bonding, Zengin et al. [8] have reported that SWNTs can also be incorporated as doping anions in the PANI backbone.

Raman spectroscopy was employed to verify the interaction, and the spectra have been separated from each other in order to clarify the spectral changes. Signal intensities from SWNTs (Fig. 3a–c and e) have been increased for easier comparison.

The Raman spectra (except for those shown in Fig. 3a and b) were taken after electropolymerization. In Fig. 3d, all Raman bands belong to PANI. The existence of peaks at 1578 cm^{-1} and 1476 cm^{-1} are associated with C=C ring stretching and C=N stretching from the quinoid unit [22]. The $C–N^{+\cdot}$ stretching vibrations of the semiquinone radicals give a strong Raman band at ca. 1336 cm^{-1}, which confirms that the obtained PANI is in the conducting form [23]. C–H in plane bending of the quinoid rings at



Scheme 2. Covalent bonding. P can be H (in case of monomer cation), or longer aniline repeating units (in case of oligomer cations).

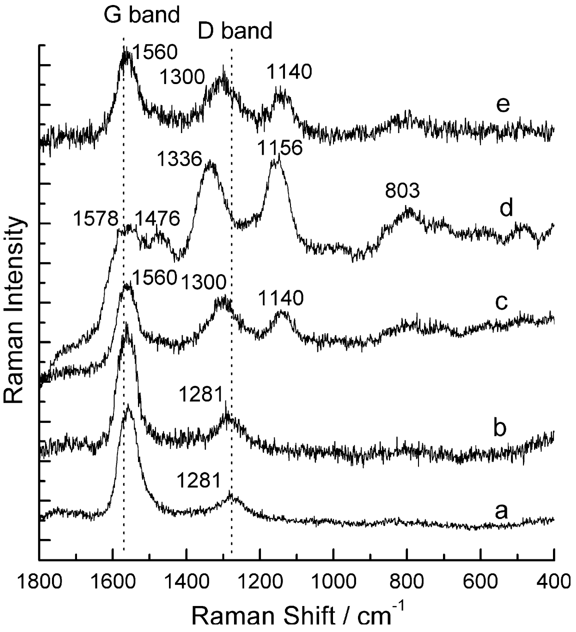


Fig. 3. Raman spectra of (a) pure SWNT, (b) 15 mg/ml SWNT and 0.2 M aniline in ILs containing 1 M CF_3COOH, (c) SWNT functionalized with PANI (after 50 cycles), (d) SWNT functionalized with PANI (after 300 cycles), (e) SWNT functionalized with PANI (after 300 cycles) washed by acetone.

1156 cm^{-1} and the quinoid ring deformation at 803 cm^{-1} can also be observed [22]. It has to be pointed out that there are also Raman signals from PANI after electropolymerization for 50 cycles. However, PANI does not fully cover the surface and the spectrum shown in Fig. 3c is taken in a spot where PANI is not interfering with the SWNT signal. The increase in number of cycles from 50 to 300 leads to the total disappearance of the SWNT signal in the Raman spectra, i.e. the whole surface is covered by PANI after 300 cycles (Fig. 3d). This, together with the SEM images, confirms that SWNT-IL matrix in the vicinity of MITO anode functions as a working electrode and PANI grows on the SWNT surface. The PANI films containing SWNTs (Fig. 3d) were washed thoroughly by acetone to wash off ILs and some parts of loosely bonded PANI in order to enhance the Raman signal originating from the modified SWNTs. The spectrum shown in Fig. 3e was measured at the place where short oligomers of PANI had been washed off and therefore they would not contribute to a large extent to the measured Raman spectra.

SWNTs have characteristic G and D bands in the Raman spectra. G band belongs to the tangential modes at 1540–1300 cm^{-1} [14]. The bands at ca. 1560 cm^{-1} in Fig. 3a–c and e are assigned to G bands. Another characteristic of SWNTs, the D band, is always present of 1270–1300 cm^{-1}. It is caused by disorder-inducing parameters, mainly from covalent modification. The bands of 1281 cm^{-1} in Fig. 3a and b and bands of 1300 cm^{-1} in Fig. 3c and e are assigned to D bands. The Raman spectra of the SWNT exhibited noticeable changes upon modification, most importantly an increase in the relative intensity of the D band *vs.* G band. This is known to be sensitive to disorder mainly caused by covalent bonding [14]. In order to get a detailed overview of the changes upon modification, the intensity ratio (I_D/I_G) of the D band (I_D) and the G band (I_G) was calculated. The I_D/I_G ratio for pure SWNT (Fig. 3a) is 0.15, for SWNTs dispersed in ILs (Fig. 3b) it is 0.21, for both SWNTs covered with PANI (Fig. 3c and e) the ratio is $\sim$ 0.75. The D band increased slightly when SWNTs were dispersed in ILs (Fig. 3b). This might be caused by the distortion from the weak π–π interaction between SWNTs and ILs containing aniline monomer and trifluoroacetic acid. This non-covalent interaction is quite weak and I_D/I_G ratio does not differ much. The D bands are blue shifted after the electropolymerization and I_D/I_G ratio increased sharply to $\sim$ 0.75 in Fig. 3c and e. This implies that covalent bonding takes place upon modification. The I_D is usually comparable to or even larger than I_G in covalent functionalization [24,25]. Lefrant et al. [26] have reported that the band at ca. 1165 cm^{-1} confirms the presence of covalently functionalized SWNTs composite with PANI (the insulating form of emeraldine base). The Raman bands at 1140 cm^{-1} in Fig. 3c and e may therefore possibly originate from the covalent functionalization of SWNTs with conducting PANI.

The results show that PANI has been covalently bonded to the SWNT, which is evidenced by the change in D band intensity in the Raman spectra. However, SWNTs may also be incorporated as charge compensating (counter) anions in the PANI backbone during the electropolymerization process.

4. Conclusions

In conclusion, a novel electrochemical method to functionalize large amount of SWNTs with conducting polymers (PANI) in ILs was developed. $BMIPF_6$ containing 1 M trifluoroacetic acid was chosen as the media to disperse SWNTs and electropolymerize aniline. Covalent bonding between SWNTs and PANI was confirmed by Raman spectroscopy. This method offers possibility to produce a donor–acceptor dyad (PANI–SWNT) in an easy way, which is essentially important for the study of the electron transfer mechanism between donor and acceptor compounds and for the design of highly efficient organic photovoltaics.

Acknowledgement

This work is part of the activities of the Åbo Akademi Process Chemistry Centre within the Finnish Centre of Excellence Programme (2000–2011) supported by the Academy of Finland.

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