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Polyaniline nanotubules obtained in room-temperature ionic liquids

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Abstract

Polyaniline (PANI) nanotubules were synthesized electrochemically on a modified ITO glass in the room-temperature ionic liquid (IL), 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BMIPF_6$) containing 1 M trifluoroacetic acid. Tubular structures of PANI with the diameter of ~120 nm were shown by scanning electron microscopy. The resulting PANI from this IL media is further characterized by Raman and Fourier transform infrared spectra, which show that the PANI nanotubules are in the conducting form. This provides a possible IL media to functionalize conducting PANI with, for example, single wall carbon nanotubes for the application of organic photovoltaics and light emitting diodes.

Keywords: Polyaniline; Electropolymerization; Ionic liquids; Organic photovoltaics and light emitting diodes

1. Introduction

Conducting polymers are attracting significant interest worldwide due to their applications in organic electronics such as light emitting diodes, transistors and photovoltaics [1–3]. Polyaniline (PANI) is one of the most studied conducting polymers due to its high stability and wide range of conductivity [4,5]. The electropolymerization of aniline in aqueous electrolytes has been thoroughly studied [6–8]. In the view of technological application of PANI from electrochemical synthesis, the choice of electrolyte is essential for the material property and its further functionalization. Improved electrolyte should simultaneously meet the following requirements [9]: (1) High ionic conductivity; (2) low volatility; (3) Large electrochemical windows (>1 V) over which the electrolyte is inert (i.e., neither oxidized nor reduced) at the electrode; (4) Thermal stability and environmental friendliness. Room-temperature ILs meet all above requirements. In addition, ILs are free from solvents thus they can prevent side reactions caused by solvent molecules with moderately stable radical cations generated during electropolymerization [10]. There are several reports on the synthesis of conducting polymers in ILs [11–17]. However, few reports on electropolymerization of aniline in room-temperature ILs were published [18,19]. Since better electrochemical stability of PANI in 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BMIPF_6$) has been observed [20], $BMIPF_6$ containing 1 M trifluoroacetic acid (CF_3COOH) was selected as the ionic liquid media to perform the electropolymerization. Green PANI nanotubules were obtained on modified ITO glass in our experiment. The use of ITO glasses is very important for the further applications in organic photovoltaics and light emitting diodes.

Generally speaking, electrochemically obtained conducting polymer tubules are more rigid and uniform than those obtained by chemical synthesis [21]. Doping anions may influence the conformation and oxidation state of PANI. The surface morphology of PANI formed in $EMICF_3SO_3$ is smooth [19], whereas PANI nanotubules were obtained in our system. This may be due to the doping anion effect to the structures. Bulky anions such as BF_4^-, PF_6^- and CF_3COO^- belong to the similar group

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which promotes the formation of compact PANI nanotubules [21]. The morphology and structure of the resulting PANI were characterized by SEM, Raman and Fourier transform infrared (FTIR). Raman and FTIR spectra were elaborately discussed in this paper. To the best of our knowledge, Raman spectrum for PANI synthesized from room-temperature ILs has never been reported.

2. Experimental

Aniline (>99.5%), was obtained from Fluka and CF_3COOH (99%) from Aldrich. $BMIPF_6$ ($\geqslant$ 98%) was bought from Solvent Innovation. All chemicals were used as received.

0.2 M aniline and 1.0 M CF_3COOH were added in $BMIPF_6$. This electrolyte was homogenously mixed in an ultrasonic oscillator for 10 min to become a yellowish viscous liquid. The polymerization was carried out in a three-electrode quartz cuvette cell by cyclic voltammetry. Ag/AgCl wire was used as reference electrode and platinum wire as counter electrode. The potential was controlled by an Autolab (PGSTAT 20) and scanned between −0.3 and 1.5 V with scan rate of 50 mV/s for 50 scans. The modified ITO glass (MITO) with aniline silane (cut as 3 cm × 1 cm slide) was used as working electrode. The detail modification procedure has been described before [22]. MITO is reported to enhance the electropolymerization of PANI and its sulphonated derivatives [22,23].

The morphology of the obtained PANI film was studied by scanning electron microscopy (SEM), which was from Leica Cambridge Instruments. The film was then further characterized by Raman and FTIR spectra. The excitation wavelength of 780 nm (Renishaw, NIR diode laser) was used for Raman analysis. The spectrometer was always calibrated against a Si standard (520 cm^{-1}) before measurements. FTIR measurement was performed with Bruker IFS 66/S spectrometer equipped with a seagull^{TM} variable angle reflectance accessory (Harrick Scientific). 2000 interferograms were recorded with incidence angle 80° and a resolution of 4 cm^{-1}. MCT detector was cooled with liquid nitrogen and the sample holder was purged with N_2.

3. Results and discussion

Electropolymerization of aniline was done by cyclic voltammetry in $BMIPF_6$ containing aniline monomer and trifluoroacetic acid. Fig. 1 shows the cyclic voltammograms obtained during electropolymerization for the 1st, 10th, 25th and 50th scan. The first scan (Fig. 1a) is a typical response from the initiation of polymerization to create radical cations, and the current onset is at about 0.67 V. The electrochemical window is obviously enlarged compared with the one in aqueous media. With increasing number of scans from 10th to 50th, the current increases with the anodic peak value blue-shifted and cathodic peak value red-shifted. The increasing oxidation and reduction currents in Fig. 1 indicate the growth of the polymer film.

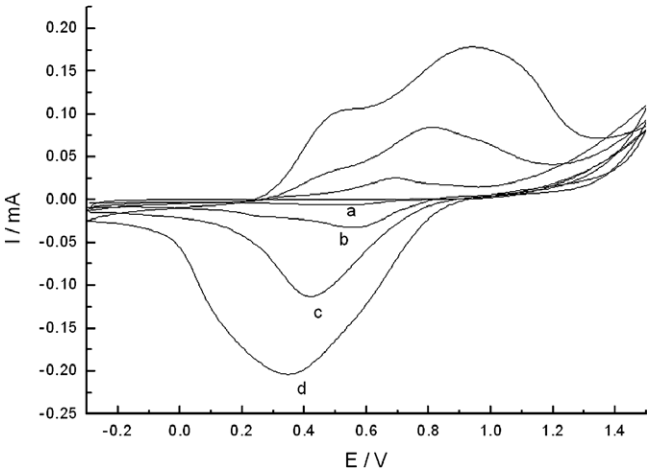

Fig. 1. Cyclic voltammograms obtained during electropolymerization of 0.2 M aniline in $BMIPF_6$ containing 1.0 M CF_3COOH for the (a) 1st scan, (b) 10th scan, (c) 25th scan, and (d) 50th scan. The potential was cycled between −0.3 and 1.5 V (vs. Ag/AgCl) at a scan rate of 50 mV/s.

Due to high viscosity of ILs, the reaction products will be accumulated near the surface of MITO electrode, which will facilitate the electropolymerization rate of aniline [16,18]. A green film was finally formed on the MITO substrate.

As shown in Fig. 2, the surface morphology from pure MITO (Fig. 2a) and the resulting PANI film (Fig. 2b) on MITO were observed by SEM. Fig. 2b illustrates that tubular PANI structures were formed on MITO after electropolymerization. The diameter of the PANI nanotubules is ~120 nm and some granules are also formed around the tubular structures.

The Raman spectrum (Fig. 3) was taken after electropolymerization. The existence of bands at 1575 and 1462 cm^{-1} are attributed to C=C ring stretching and C=N stretching from the quinoid unit respectively [24]. A strong Raman band at ca. 1326 cm^{-1} was observed and assigned to $C-N^+$ stretching vibrations of the semiquinone radicals. Generally speaking, the existence of peaks in the range of 1300–1400 cm^{-1} is inherently associated with the protonation process via poly-semiquinone radical formation mechanism [25]. This means that the obtained PANI nanotubules are in the conducting form. The bands at 1557, 1215, 1147 and 802 cm^{-1} are assigned to C—C stretching, C—N stretching of benzenoid rings, C—H in plane bending of the quinoid rings, and the quinoid ring deformation individually [24]. Meanwhile, the broadband around 802 cm^{-1} also indicates the existence of the mixture of various torsion angles between aniline rings [21].

Fig. 4 shows the FTIR spectrum of the PANI film. The absorbance bands at 1578 and 1469 cm^{-1} correspond to stretching deformations of quinoid and benzenoid rings respectively [26]. Bands at 1386, 1252 and 807 cm^{-1} are assigned to C—N stretching, $C-N^+$ stretching and C—H out of plane vibration [27]. The increasing absorbance in the spectrum region of 1800–3000 cm^{-1} is attributed to free charge carriers in the doped polymer [26]. The band at

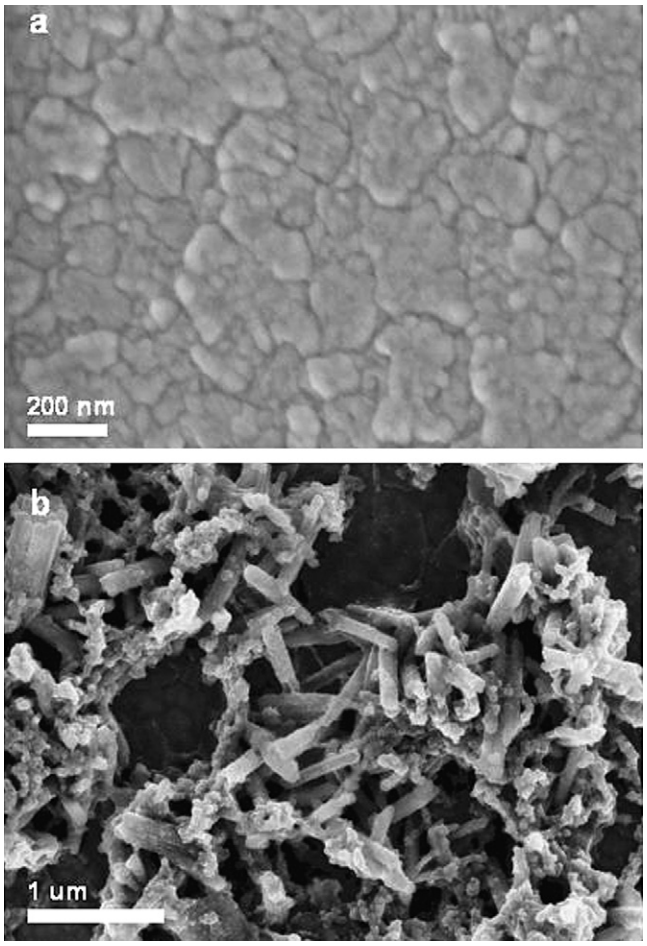

Fig. 2. SEM images of (a) modified ITO glass (MITO) and (b) PANI synthesized from $BMIPF_6$ containing 1.0 M CF_3COOH.

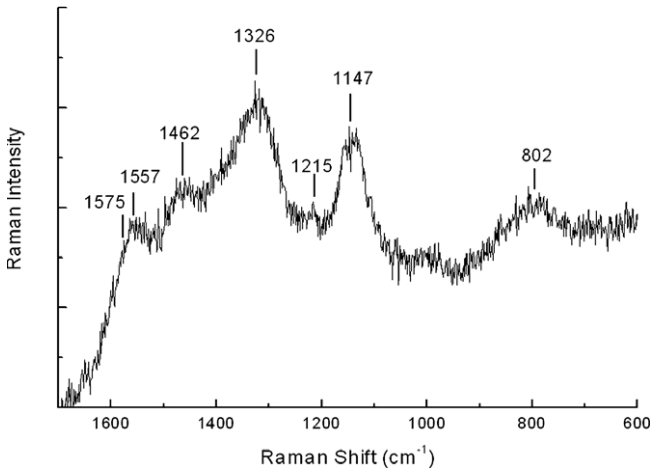

Fig. 3. The Raman spectrum of the PANI film electropolymerized from $BMIPF_6$ containing 1.0 M CF_3COOH.

1177 cm^{-1} was attributed to be an electronic-like band and was considered to measure the degree of delocalization of electrons [28]. The intensities of the bands at 1608 and 1178 cm^{-1} was observed to increase with increasing acidity of the media during *in situ* FTIR–ATR experiments by

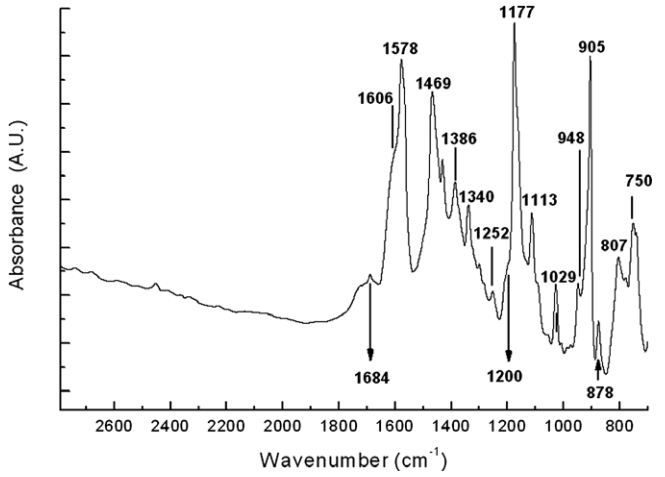

Fig. 4. The FTIR spectrum of the PANI film electropolymerized from $BMIPF_6$ containing 1.0 M CF_3COOH.

Ping [29] and the characteristic band of conducting protonated form is observed at 1252 cm^{-1} [5]. The evidences above prove that the PANI electropolymerized in $BMIPF_6$ is conducting (emeraldine salt form), which is in good agreement with the previous results from Raman spectroscopy. However, the intensity of the quinoid ring stretching vibration at 1578 cm^{-1} is little more than that of the benzenoid related band at 1469 cm^{-1}, indicating the existence of a higher amount of quinoid structure unit in the polymer chain. This means that the PANI film synthesized in this ionic liquid media may compose some small amount of non-conducting forms such as emeraldine base and/or pernigraniline forms, which have more quinoid structures in the backbone. The characteristic bands assigned to the emeraldine base form are at 1578, 1386, and 1340 cm^{-1}; and the bands of emeraldine salt form occur at 1606, 1469, 1252, and 1177 cm^{-1} [22,29]. The bands in the range of 948–807 cm^{-1} belong to P—F vibrations from PF_6^- anions in ILs [30]. The absorption bands at 1684 and 1200 cm^{-1} are assigned to C=O and C—F stretching vibrations from the anions of CF_3COO^- [18]. This implies that CF_3COO^- may be also doped to the PANI backbone besides PF_6^- from ILs.

It is essentially important to keep PANI in its conducting form as p-type material for its application in organic electronics (e.g. organic photovoltaics). The tangled bundles of n-type single wall carbon nanotubes (SWNTs) have been reported to be well individualized in ILs such as $BMIPF_6$ due to 'cation-π' interactions [31]. Our experiment provides a possible way to functionalize large amount of SWNTs with conducting PANI nanotubules on MITO glasses electrochemically.

4. Conclusions

A novel electrolyte, $BMIPF_6$ containing 1.0 M CF_3COOH, was applied to electropolymerize aniline on MITO glass. The resulting PANI has a tubular structure

with the diameter of ~120 nm. Both Raman and FTIR spectra confirmed that the resulting PANI is in its conducting state. This electrochemical method to synthesize conducting PANI on MITO in ILs will have an important potential application in organic photovoltaics and light emitting diodes.

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