Accessory Publication

Vapour phase polymerization of pyrrole and 3, 4ethylenedioxythiophene using iron(III) 2,4,6trimethylbenzenesulfonate

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XPS Analysis

The XPS spectrum of PPy doped with trimethylbenzenesulfonate is shown in Figure 1 and analysis of the traces indicated the presence of four distinct peaks, CI, CII, CIII and CIV. The peak CI in the C1s spectrum is due to the presence of aromatic carbons in the iron(III) trimethylbenzenesulfonate and β -carbon atoms in the PPy. The peak CII at 285.6 eV is due to the contribution of α -carbon atoms in the pyrrole units involved in electrostatic interaction with the anion and the C-N interactions. The C-O/C-S bands can be seen at 286.3 eV and the CIV peak at 288.5-289.1 eV is due to the presence of C=O or O-C=O bonds. A similar peak assigned to C=O bonds is observed in the XPS spectrum of PPy synthesized here (refer Figure 1). The presence of carbonyl group is also indicated in the Raman spectrum of PPy, as shown in Figure 1. The presence of carbonyl peak in Raman and XPS spectra of PPy films may be due to the oxidation of 2-butanol or from the carbonyl stretches in the underlying PET substrate.



Figure 1: XPS spectrum of PPy film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate



Figure 2: XPS spectrum of PEDOT film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate

The XPS C1s spectrum for PEDOT film is as shown in Figure 2. The peak CI at 285 eV is due to C-C/C-H carbon species. The band at CII 286.5 eV is due to C-O/C-S bonds. The peak at 288 and 289.5 eV is due to carbonyl group formed due to oxidation of 2-butanol or due to carbonyl stretches of underlying PET substrate as discussed in earlier work ^[1]. The peaks in the C1s spectrum are in accordance with that reported by Winther-Jensen *et al.* for VPP PEDOT films ^[2].

Cyclic voltammetry

The CV traces indicated that the PPy and PEDOT polymer films had strong responses to changes in voltage. This is in agreement with the conclusions reached by Winther-Jensen *et al.* who reported that vapor phase polymerization leads to films with fewer defects and higher mobilities ^[3]. They also reported larger responses to changes in voltage in the CVs of PEDOT films. The cyclic voltammogram of electropolymerised PEDOT reported by Garreau *et al.* also showed a shape identical to the CV of PEDOT-trimethylbenzenesulfonate reported here ^[Error! Reference source not found.]. The electrochemical behaviour of PPy and PEDOT was quite different, see Figure 3 – Figure 8.

The CV of PEDOT films scanned from 0.8 V to -1.2 V *versus* Ag/AgCl reference electrode showed a complex series of reduction and oxidation processes, which is typical of a base inhibited PEDOT film^[21]. The PEDOT film shows a larger response and the shape of the base inhibited VPP PEDOT synthesized using iron(III) trimethylbenzenesulfonate here is similar to what has been reported by Winther-Jensen *et al.*^[2] for base inhibited VPP PPy synthesized using iron(III) *p*toluenesulfonate. The potential difference between the anodic peak and cathodic peak decreased as the scan rate of the voltammetry was decreased from 100 mV/s to 10 mV/s for PPy and PEDOT films.

The electrochemical behavior of the PPy films was less complex, and as is typical of PPy, there is a cathodic peak at -0.17 V *versus* SCE and an anodic peak at -0.5 V *versus* SCE at a scan rate of 100 mV/s and the cathodic peak shifts to -0.36 V versus SCE and the anodic peak shifts to -0.43 V *versus* SCE at a scan rate of 10 mV/s. PPy and PEDOT films show slow charge transfer and the separation of cathodic potential peak and anodic potential peak becomes smaller as the scan rate is lowered. In summary, the CVs of PPy and PEDOT show that films are electroactive and they show good electrochromism during oxidation and reduction.



Figure 3: Cyclic voltammograms of PPy film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate. CVs were recorded at a sweep rate of 100 mV/s with the polymers deposited on ITO glass immersed in aqueous electrolyte (0.1 NaMSA)



Figure 4: Cyclic voltammograms of PPy film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate. CVs were recorded at a sweep rate of 50 mV/s with the polymers deposited on ITO glass immersed in aqueous electrolyte (0.1 NaMSA)



Figure 5: Cyclic voltammograms of PPy film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate. CVs were recorded at a sweep rate of 10 mV/s with the polymers deposited on ITO glass immersed in aqueous electrolyte (0.1 NaMSA)



Figure 6: Cyclic voltammograms of PEDOT film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate. CVs were recorded at a sweep rate of 100 mV/s with the polymers deposited on ITO glass immersed in aqueous electrolyte (0.1 NaMSA)



Figure 7: Cyclic voltammograms of PEDOT film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate. CVs were recorded at a sweep rate of 50 mV/s with the polymers deposited on ITO glass immersed in aqueous electrolyte (0.1 NaMSA)



Figure 8: Cyclic voltammograms of PEDOT film synthesized by VPP using iron(III) 2,4,6trimethylbenzenesulfonate. CVs were recorded at a sweep rate of 10 mV/s with the polymers deposited on ITO glass immersed in aqueous electrolyte (0.1 NaMSA)

REFERENCES

- Subramanian, P.; Clark, N. B.; Spiccia, L.; MacFarlane, D. R.; Winther-Jensen, B.; Forsyth, C., *Synthetic Metals*, **2008**, 158, 704.
- Winther-Jensen, B.; Norrman, K.; Kingshott, P.; West, K., Plasma Processes and Polymers, 2006, 239, 84.
- Winther-Jensen, B., Forsyth, M., West, K., Andreasen, J. W., Bayley, P., Pas, S., MacFarlane, D. R., *Polymer*, 2008, 49, 481.
- 4. Garreau, S.; Louarn, G.; Bruisson, J. P.; Lefrant, S., Macromolecules, 1999, 32, 6807.
- 5. Winther-Jensen, B.; Breiby, D. W.; West, K., Synthetic Metals, 2005, 152, 1.