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Electrochemical, electrochromic behaviour and effects of supporting electrolyte on nano-thin film of poly (3,4-ethylenedioxy thiophene)

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ABSTRACT

3,4-Ethylenedioxy thiophene is polymerized electrochemically in p-toluene sulphonic acid (a), phosphate buffer (b) and borax buffer (c) on glassy carbon and Indium tin oxide (ITO) surface. The scan rate dependence studies of the polymer redox processes were carried out. A linear relationship was observed between the peak current and scan rate with good correlation, $r^2 = 0.998$ indicating adsorption controlled behaviour of polymer film. The SEM photograph showed the differences in surface morphology of polymers modified electrode. The XRD studies revealed semi-crystalline nature of doped polymers. Spectroelectrochemical behaviors of Indium tin oxide coated glass electrode covered with thin film of poly-3,4-ethylenedioxythiophene a, b, c in 0.1 M KCl were obtained at different electrode potentials between 1100 and 200 nm. Poly-3,4-ethylenedioxythiophene-a, poly-3,4-ethylenedioxythiophene-b and poly-3,4-ethylenedioxythiophene-c film exhibits transparent clear blue, opaque violet and dark maroon colours respectively at reduced potential. Further probing the potential between 400 mV and 800 mV coated film shows greenish blue colour for poly-3,4-ethylenedioxythiophene-a, poly-3,4-ethylenedioxythiophene-b and poly-3,4-ethylenedioxythiophene -c shows opaque violet and yellowish maroon colours respectively. Increasing the applied potential between 1000 mV and 1200 mV over oxidation of polymer film shows dark greenish blue for poly-3,4-ethylenedioxythiophene -a, dark brown for poly-3,4-ethylenedioxythiophene-b and transparent red colour for poly-3,4-ethylenedioxythiophene-c. Electrochromic parameters such as colouration efficiency, response time and optical contrast were calculated for all three films.

1. Introduction

Electrochromic materials undergo change in their absorbance of heat and visible light when a small current or voltage is passed through them. Electrochromic materials are highly desirable, as they are the potential candidates for applications in display devices. Conducting or conjugated polymers have been found to be more promising as electrochromic materials because of their better stability, faster switching speeds, and easy processing compared to the inorganic electrochromic materials. Conducting polymer-modified electrodes can be obtained by electropolymerization of the monomer on the electrode surface. Polythiophene is a relatively stable conducting polymer but the synthesis by electrochemical initiation is very difficult because of the high oxidation potential of thiophene. This problem has been overcome by the introduction of 3,4-ethylenedioxythiophene. This monomer is oxidized at 1.1 V versus (Ag/AgCl)/V which is 1.0 V less than that of thiophene. The polymer is found to be very stable in oxidized and reduced states and switches between opaque blue to transparent blue colors in 2.2 s. The band gap of the polymer is 1.6 eV. These interesting properties attracted the attention of researchers from academic and industrial laboratories that resulted in application of this polymer in various electrochromic devices [1], capacitors [2–4], photovoltaic devices [5], organic polymer solar cell [6–14], transistors [15–18], light emitting diodes [19,20] actuators [21,22] batteries [23], sensors [24–32], and trace analysis has been reported [33]. Spectral and optical performance of electrochromic poly(3,4-ethylenedioxythiophene) (PEDOT) deposited on transparent conducting oxide coated glass and polyethylene tetraphthalate (PET) film substrate was reported [34]. PEDOT with a dendritic substituent was synthesized and characterized [35]. They have reported that the polymer was found to be electroactive with a contrast of 67%. Au nano-brush membranes were prepared using a modified template method and they immobilized PEDOT films membrane by electropolymerization [36]. They have reported that the PEDOT film on the nano-brush electrode showed

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higher electrochromic coloration compared to the PEDOT film on an Au planar electrode. Electrochromic devices based on complementary layers of PEDOT and Prussian blue by use of a free standing proton conducting polymer electrolyte has been reported [37]. Electrochromism and redox behavior of PEDOT films electropolymerized from an aqueous micellar solution encompassing the monomer (EDOT) and dopant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) have been extensively studied [38]. Copolymers of PEDOT and diclofenac with surfactants such as SDS and CTAB were synthesized [39]. They have reported that the optical contrast ($\Delta\%T$) at λ_{624} is 78 for Poly (EDOT-co-DCF), 86 for Poly (EDOT-co-DCF)/SDS and 88 for Poly (EDOT-co-DCF)/CTAB. In the present work we have polymerized 3,4-ethylenedioxythiophene(EDOT) by doping tosyl ion(a), phosphate ion(b) and borate ion(c) and studied its electrochemical behaviour and electrochromic behaviour. The formed PEDOT films were characterized by SEM, XRD and EDAX. The conductive nature of the film was studied by impedance spectroscopy. The films formed were well adherent and highly stable in all ranges of pH.

2. Experimental

2.1. Materials

Electrochemical workstation (CH650C instruments, USA) was employed for all electropolymerization studies presented in this work. The solution of 0.01 M EDOT was prepared in deionized water. A single compartment three-electrode system was used for the cyclic voltammetric studies. PEDOT films were prepared on glassy carbon electrode surface and ITO plate by number of cycling method. The conducting PEDOT modified electrode was used as working electrode, platinum foil as counter electrode and Ag/AgCl/0.1 M KCl, as reference electrode. EDOT was purchased from Aldrich. The aqueous supporting electrolyte solutions 0.1 M H_2SO_4 (pH 1.0), Buffer (pH 4.0), 0.1 M KCl (pH 7.0), Buffer (pH9.2), 0.1 M NaOH (pH 13.0) were prepared and used. All the solutions were prepared using ultrapure water (SG International, Germany). Purging and blanketing of nitrogen were done for analyte solutions placed in an electrochemical cell of 25 mL capacity for 20 min under stirred conditions. Then various voltammograms were recorded. To get reproducible results, great care was taken in the electrode pretreatment. The glassy carbon electrode was pretreated in two ways namely mechanical polishing over a velvet micro-cloth with an alumina suspension and electrochemical treatment by applying a potential of +1.5 V for 2 s. The electrochemical pretreatment was done in the same supporting electrolyte solution in which the measurements were carried out.

2.2. Preparation of PEDOT coated electrode

The electrochemical polymerization is often found to be the preferred method for preparing electrically conducting polymers in view that polymer film with good quality can be prepared readily from the adequate monomer using simple apparatus. The thickness of the films are easily controlled by the deposition charge and the products are directly obtained in their conducting states. PEDOT was obtained by the electrooxidation of the 0.01 M EDOT solution in 0.1 M p-toluene sulphonic acid (a), phosphate buffer (b) and borax buffer (c) by the cyclic voltammetric method, cycled between the potentials −0.6 and +1.0 V (versus Ag/AgCl/0.1 M KCl) at the scan rate of 0.05 V s^{-1}(Fig. 1). The initial scan polarity was fixed as positive side. Thickness of the films was controlled by the number of cycles. Then the electrode had been repeatedly washed with ultrapure water (SG International, Germany) and cycled in monomer free supporting electrolyte (pH 1.0) before it was used.

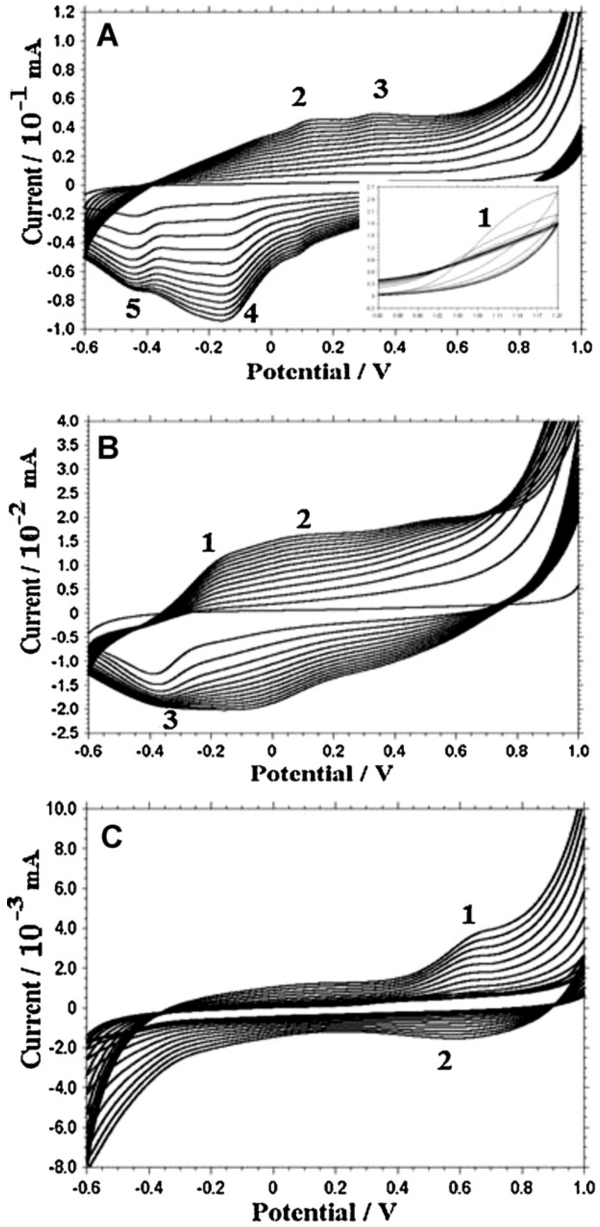

Fig. 1. Cyclic voltammogram of 0.01 M EDOT in (A) acidic (B) neutral and (C) basic medium at a scan rate of 0.05 V s^{-1}.

3. Results and discussion

3.1. Electrochemical growth of polymer

Growth of PEDOT was studied in aqueous media containing three different supporting electrolytes in the potential range from −600 to 1200 mV at scan rate of 50 mV s^{-1} using cyclic voltammetry. For tosyl doped PEDOT (a), the monomer underwent oxidation and around 1140 mV (Fig. 1A, 1) in the first cycle but the peak current decreased in the subsequent cycles and the intermediates, diradical dication/bipolaron produced in the oxidation of monomer reacted with another molecule of monomer and produced radical cation called as polaron. These radical cations underwent redox reaction much easily and oxidation peak appears at 140 mV (Fig. 1A, 2) and 350 mV (Fig. 1A, 3). Because of this redox behavior, reduction of the monomer takes place around −150 mV (Fig. 1A, 4) and −430 mV (Fig. 1A, 5). The intensity of the newer