Barrier films to control loss of 9,10-anthraquinone-2-sulphonate dopant from PEDOT films during electrochemical transitions

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A B S T R A C T

We describe a simple approach for the synthesis of stable electroactive poly[3,4-ethylene dioxythiophene] (PEDOT) in an acid medium, by incorporating a redox active dopant like 9,10-anthraquinone-2-sodium sulphonate (AQS) on a glassy carbon (GC) electrode. The modified electrode is responsive up to a pH of 7. The stability of the modified electrode during continuous electrochemical cycling is poor, due to leaching of the dopant from the PEDOT film. Efforts are made to improve the stability of the modified electrode by forming an anionic barrier film on the PEDOT-AQS interface either physically or electrochemically. The modified electrodes were monitored by cyclic voltammetry and Fourier transform-infrared (FT-IR) spectroscopy for the presence of AQS in the film.

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1. Introduction

Conducting polymers are essential components in electrochemical devices because of their electronic conductivity and doping properties. The latter characteristic allows chemists to individually tune the properties of conducting polymers [1]. Various redox-active dopants, like viologens, quinones, tetrathiafulvalene, ferrocenes and polyoxometallates are used as dopants in the conducting polymer matrix to improve the interfacial properties of electrocatalysis, ion sensing and electrochromism [2–6]. The conducting polymers of polyaniline, polypyrrole, and polythiophene derivatives are used as electrode modifiers or as matrices for trapping redox species [5–7]. Among the conducting polymers, PEDOT has received special attention for various applications, including use as a matrix for entrapping enzymes in biosensors, use in electrochromic displays, and use as a hole conductor in solid state devices [8]. There is intense interest in this polymer because of its high-electronic conductivity (ca. 300 S cm^{-1}), regio-regular structure and good chemical stability. The electrocatalytic properties of the modified electrodes can be altered by modification of interfaces with thin films of redox species. Electrochemical modification of glassy carbon/ITO electrodes with redox electron transfer mediators is common practice in electrochemistry [9]. Electrodeposition

provides an easy way to fabricate thin films of conducting polymer matrices with entrapped redox mediators.

There have been attempts to incorporate polyoxometallate electroactive species in conducting polymer thin films. These compounds are multi-centered redox anionic species. The electrocatalytic mediating properties of silicotungstic acid doped PEDOT, for the reduction of molecular oxygen, was reported recently by Kulesza et al. [10]. One advantage of using PEDOT as a matrix for entrapping redox-active species is that, unlike polyaniline, it remains electroinactive in highly acid medium. In other words, the electroactivity of the PEDOT film does not interfere with the redox chemistry of the doped electroactive species. Doping of PEDOT with high-molecular weight anionic polymeric species such as PSS$^-$ (polysyrene sulphonate anion) has been well established [11]. Once incorporated, it is difficult to remove this bulky dopant because it is polymeric. This feature is also responsible for the pseudo-n-doping behavior of electronic conducting polymers [12,13]. However, if the dopant is not big enough (for example, aryl sulphonates), it is likely that, during potential cycling, the dopant will leach out into the solution, which contains smaller anions such as perchlorate.

In this work, we report electropolymerization of EDOT in an acid medium containing AQS. The sulphonate group is highly anionic in nature. Therefore, it can easily be incorporated into the PEDOT film during electropolymerization. The incorporation of an anthraquinone moiety yields a highly reversible symmetric voltammetric peak due to the redox reactions. PEDOT-like films can be used to incorporate anionic redox mediators through counterion

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doping. Initially, it was thought that the molecular/ionic size of AQS was sufficiently bulky to become entrapped. However, it is now realized that leaching through ion exchange with the anions in solution leads to the loss of the redox dopant. After successful doping into PEDOT films, stability studies indicated that AQS⁻ leaches out slowly into solution, leaving PEDOT without AQS. In this process, the solution anion replaced the AQS. In order to control the loss of electroactivity of the entrapped AQS⁻, a macromolecular dopant such as PSS⁻ was employed. This strategy was based on the electrostatic interactions and the relative sizes of AQS⁻ and PSS⁻. A layer of PSS is one of the constituents of the well-known layer-by-layer assembly approach [11]. The polypyrrole-arylsulphonate system is an appropriate example. The electropolymerization of pyrrole in the presence of various aryl sulphonate anions, including AQS⁻, was reported by Wang and MacDiarmid [14], Ahmed et al. [15] and Kuwabata et al. [16]. The properties of the doped films were also studied [14]. Loss of AQS⁻ into the solution was not observed with the use of non-aqueous solvents. These solvents are employed in the examination of the electroactivity of the modified electrodes, as they do not allow anion exchange. The use of non-aqueous solvents facilitated understanding of the two consecutive one-electron transfers taking place in AQS [15]. This finding is in contrast to the results obtained in aqueous solutions. The polyaniline-polyvinyl alcohol-aryl sulphonate systems studied by Nagaoka et al. [17] are interesting. The doped aryl sulphonates were not ejected from the polymer thin film during the chemical oxidation-reduction process. The redox of the composite films is an interdependent action of redox changes in polyaniline and aryl sulphonates. The redox of the PEDOT-AQS described in this work is only due to anthraquinone in acidic solutions. This study presents a detailed method to circumvent the loss of redox-active dopants from the PEDOT thin films during electrochemical cycling.

2. Experimental

Voltammetric experiments were carried out in the three-electrode cell, using a BAS100B work station. The cell contained glassy carbon (GC) (surface area 0.07 cm⁻²) as a working electrode, a platinum (Pt) sheet as a counter electrode and a normal calomel electrode (NCE) as a reference electrode. All reported potentials were referenced to NCE. First, the working electrode was cleaned by polishing with grade 4/0 emery paper. This cleaning was followed by de-greasing with acetone and sonication in distilled water. A Thermo-Nexus 670 model spectrometer was used for FT-IR measurements. All the chemicals used were of Analar grade and the solutions were prepared in fresh MilliQ water (18.2 MΩ). Buffer solutions were prepared using a 0.2 M sodium acetate/0.2 M acetic acid mixture. The pH was adjusted by adding appropriate amounts of HCl or NaOH.

3. Results and discussion

AQS⁻ doped PEDOT films were synthesized electrochemically by potential cycling of a glassy carbon electrode in a solution containing 5 mM EDOT (monomer) and 10 mM AQS (shown in Fig. 1). Potential cycling was carried out in the range of −0.6 to 1.2 V vs. NCE at a scan rate of 50 mV s⁻¹. Electropolymerization of EDOT in the medium containing AQS occurred through electro-oxidation of EDOT at approximately 840 mV vs. NCE. This led to a steep increase in the voltammetric current. From Fig. 1, it is clear that the cyclic voltammetric peak currents increased in both directions, centered around −0.35 V. This increase occurred with an increasing number of cycles, indicating growth of a redox-active film on the surface of the GC. The thickness of the PEDOT-AQS film can be varied by controlling the number of potential cycles or by changing the monomer
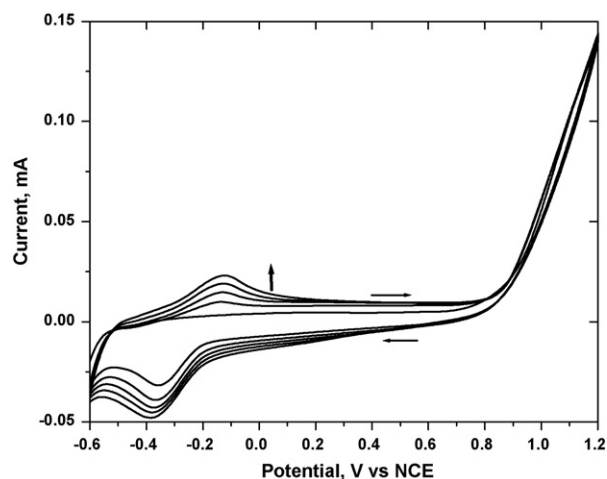

Fig. 1. Cyclic voltammogram showing polymerization of 5 mM EDOT in 10 mM AQS solution, scan rate 50 mV s⁻¹.

concentration in the deposition bath. In contrast to the redox film growth in solutions containing AQS, a featureless flat cyclic voltammogram with an increase in only the non-faradaic current was observed for PEDOT film growth in solution containing LiClO₄.

The films were prepared by varying the cycle numbers. Different thicknesses were observed with an increase in coulombic charge under the redox peaks. The cyclic voltammetric peaks around −0.3 V are due to two-electron transfer in anthraquinone. The peak current increase in both directions can be attributed to the increase in film thickness. This finding suggests an increase in the content of the AQS⁻ dopant in the film. Along with electropolymerization of EDOT, there is doping of a charge-compensating anion from the electrolyte. The PEDOT-AQS modified electrode exhibited a highly reversible redox peak at −0.15 V in 0.5 M H₂SO₄ medium containing no other electroactive species in the background. The redox group in doped AQS (quinol/quinone) is responsible for the highly reversible redox peak seen in the acidic medium (Fig. 2). The reversible redox peak, occurring around 0.15 V, can be ascribed to the reversible redox reaction of the quinone/hydroquinone system [18] in AQS⁻ (Scheme 1). The calculated charge corresponds to 52 mC cm⁻² for films grown for 10 cycles at scan rate of 20 mV s⁻¹.

The redox peak at approximately −0.15 V is highly reversible. This is demonstrated by the small peak-to-peak separation ($\Delta E_p = 20$ mV or less at sweep rates lower than 0.01 V s⁻¹). The peak
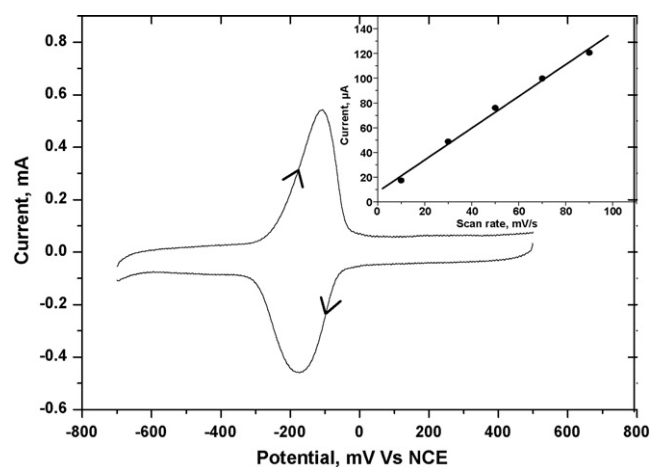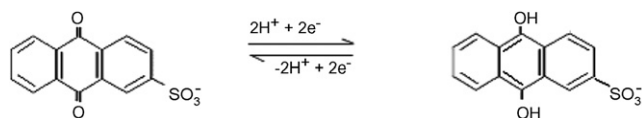

Fig. 2. Cyclic voltammogram showing the redox behavior of AQS doped PEDOT in 0.5 M H₂SO₄ medium at a scan rate of 20 mV s⁻¹. (Inset) Plot of peak current vs. scan rate.

Scheme 1. Redox reactions of AQS doped in PEDOT.

also fulfils another criterion for surface anchored redox species, described in the following equation [19]:

$$I_p = \frac{[n^2 F^2 A \Gamma \upsilon]}{[4RT]} \qquad (1)$$

In this equation, n is the number of electrons involved, F is Faraday's constant, A is the geometrical area of the electrode, υ is the scan rate, R is the gas constant, Γ is surface coverage and T is the absolute temperature. The voltammetric peak current shows a linear dependence with scan rate up to $0.1\,V\,s^{-1}$, confirming ideal surface confined redox entrapped in the PEDOT film as seen from Fig. 2 (inset). However, the peak-to-peak separation of the redox film is found to increase with increasing scan rate. This occurs because the AQS^- anion leaches out of the film during potential cycling. The anion fails to ingress the interior of PEDOT film completely during the reverse cycle at higher scan rates. The electroinactive sulphate ion may also participate in the doping/dedoping process during potential cycling.

3.1. Effect of pH

Platinum is classically used for sensing the pH of solutions in combination with the quinone-hydroquinone redox system [20,21]. The Scholz group instead reports using a pH-sensitive graphite/quinhydrone composite electrode, flow injection potentiometry, solid-composite pH sensors, quinhydrone, solid paraffin, and surface-modified graphite powder composites [22,23]. We attempted to use the GC/PEDOT-AQS interface for its voltammetric response to pH in a series of buffer solutions in the pH range of 1–7. Fig. 3 shows the voltammetric response of the PEDOT-AQS modified electrode in various pH buffers. In a neutral medium (pH 7), the PEDOT-AQS film was redox inactive and turned redox-active only at lower pH values. The mid-peak potential of the redox couple $(E_{pa} + E_{pc})/2$ was found to shift to anodic poten-
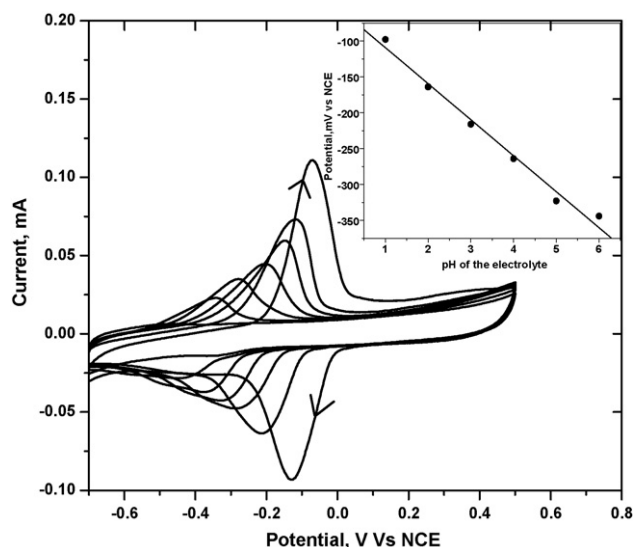

Fig. 3. Cyclic voltammograms showing the pH response of the PEDOT-AQS film at a scan rate of $50\,mV\,s^{-1}$ (voltammetric curves are in the order of decreasing pH from left to right). (Inset) Plot of mid-peak potential vs. pH of the buffer electrolyte.
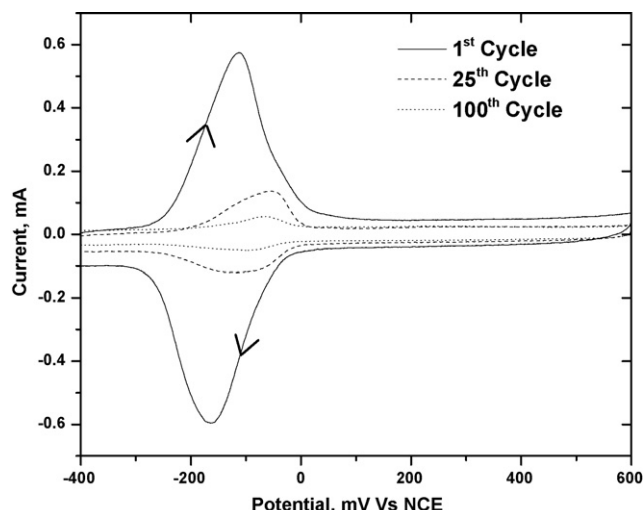

Fig. 4. Cyclic voltammogram showing the instability of PEDOT-AQS up to 100 potential cycles in $0.5\,M\,H_2SO_4$ at scan rate $20\,mV\,s^{-1}$.

tial values with decreasing pH (Fig. 3). The voltammetric peak potential exhibited a near-Nernstian shift of about $52 \pm 2\,mV/pH$ units in the acidic range up to pH 6 (Fig. 3 inset). This finding demonstrates the utility of these films as pH sensors in the acidic range.

3.2. Stability studies

Fig. 4 represents the voltammetric response of the PEDOT-AQS-modified GC during continuous electrochemical cycling in a sulphuric acid solution. A potential range of 0.0–1.0 V was used at a scan rate of $50\,mV\,s^{-1}$. The redox peak current decreased in the anodic and cathodic directions upon electrochemical cycling. This is likely due to the fact that the anionic dopant (AQS^-) slowly leached out of the film into the electrolyte solution. The GC modified with PEDOT-AQS exhibited a featureless voltammetric response after cycling of the modified electrode in H_2SO_4 for more than 100 cycles. This is probably due to the loss of AQS^- into the solution.

In an effort to stabilize the GC-modified PEDOT-AQS film against loss of AQS^-, we attempted to form an anionic barrier film over the PEDOT-AQS film. The anionic barrier was formed either by physical casting of an ionomer film or by electrochemical incorporation.

(a) *Physical method*: Coating the PEDOT-AQS with a layer of anionic Nafion solution.
(b) *Electrochemical method*: Potential cycling of the PEDOT-AQS film in PSS^- electrolyte solution.

The efficacy of the above methods in providing an anionic barrier to the loss of AQS^- from the film is discussed below.

3.3. Physical method

The barrier film can be formed by using Nafion® (tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7-octenesulphonic acid copolymer dissolved in ethanol), which is a polyelectrolyte with sulphonic acid groups. A thin film of Nafion can be cast on the modified electrode by adding a few microliters of dilute Nafion solution onto the modified electrode and allowing it to dry for two hours in air. This thin film may act as a barrier for the egress of AQS^- from the PEDOT-AQS film. From Fig. 5, it is clear that the modified electrode retains about 70% of its electroactivity, after continuous potential cycling for more than 100 cycles at a scan rate of $50\,mV\,s^{-1}$. Nafion coating
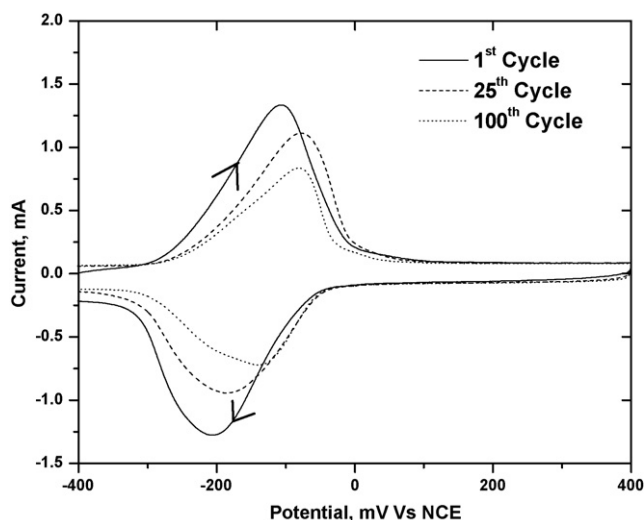
Fig. 5. Cyclic voltammogram showing the stability of PEDOT-AQS up to 100 potential cycles after casting Nafion on the electrode in 0.5 M H$_2$SO$_4$ at scan rate 20 mV s^{-1}.

Fig. 6. Cyclic voltammogram showing the stability of PEDOT-AQS up to 100 cycles after electrochemical treatment in Na-PSS electrolyte in 0.5 M H$_2$SO$_4$ (scan rate 20 mV s^{-1}).

is known to remove the interference of ascorbates, urates, and other compounds in glucose sensors by preventing anionic species from getting to the film [24]. The anionic interferants are screened out by the charge-selective nature of the Nafion membranes. In our study, we utilized the charge-selectivity of Nafion to prevent the anionic dopant from leaching out of the modified electrode. This type of "reverse approach" has not yet been attempted in the literature of modified electrodes. The effectiveness of this approach in improving the stability of the modified electrode towards electrochemical cycling is demonstrated in this simple experiment. The cation-exchange polymer (Nafion) that forms a layer on the surface of the electrode works as a stabilizing layer for the charged conducting polymer via electrostatic interactions [25]. Hence, its macromolecular nature provides a barrier which prevents leaching of the anionic dopant from the polymer film.

3.4. Electrochemical method

The conducting polymer films are doped with PSS$^-$ (i) during polymerization, via electro-oxidation of the monomer in the presence of PSS$^-$ or (ii) by potential cycling in a solution. In our study, we treated the PEDOT-AQS-modified GC by electrochemical cycling in the range of 0.0 V to 1.0 V in a medium containing bulky PSS$^-$ (MW 70,000), for five cycles at a scan rate of 50 mV s^{-1}. This resulted in a few outer layers of the modified electrode being doped with PSS$^-$. This thin PSS$^-$ layer is expected to act as an anionic barrier layer. The treated electrode showed a significant increase in stability when cycled in 0.5 M H$_2$SO$_4$. The PSS$^-$ treated film retained more than 85% of its redox activity after 100 cycles in 0.5 M H$_2$SO$_4$ (Fig. 6). To the best of our knowledge, the use of a thin anionic barrier film to retain the electroactivity of a dopant has not been previously reported in the literature.

The two methods were compared as described below. The PEDOT-AQS-modified electrode retained maximum redox activity after 100 potential cycles, using electrochemical treatment in a solution of PSS$^-$ (Fig. 7). This comparison suggests that PSS$^-$ solutions are more electrochemically effective in providing stable PEDOT-AQS films. It is interesting to note that even when PEDOT was made neutral, AQS$^-$ anions continued to stay in the film when PSS$^-$ was an outer layer. It is likely that a few outer layers of PEDOT undergo PSS$^-$ doping in exchange for AQS$^-$. It appears that incorporation of macromolecular PSS$^-$ dopant into the electro-oxidized PEDOT is more effective in bringing about a barrier than a physical
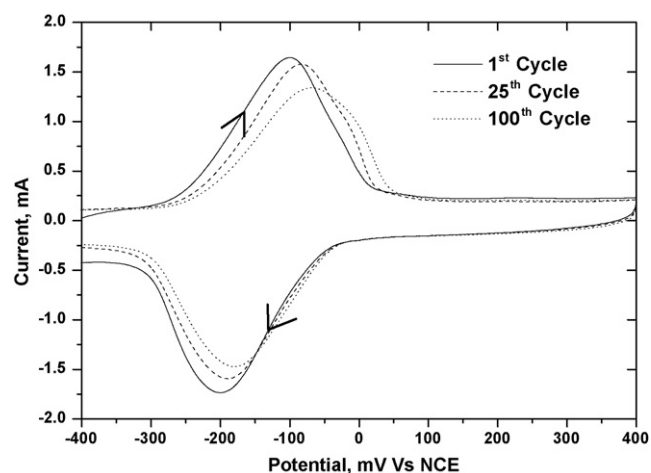
coating of Nafion. This may explain the improved retention of AQS$^-$ in PEDOT in the electrochemically treated films.

A FTIR spectrum of the PEDOT-AQS coated with PSS is shown with the spectra of AQS and Na-PSS in Fig. 8. The absorption due to –O–C–O– was observed around 1200 and 1068 cm^{-1}. The aromatic C–H stretching appears at 3050 cm^{-1}. The vibration present at <1000 cm^{-1} is due to =C–H out-of-plane bending vibration in EDOT. The stretching bands around 1486, 1598 and 1682 cm^{-1} are due to =CH and C=C of PEDOT. The peak corresponding to aliphatic C–H stretching, present at 2877 cm^{-1}, indicates that PEDOT is doped with PSS$^-$. The absorption peak at 1276 cm^{-1} can be assigned to the vibration of the sulphonyl group (S–O). The peak at 1750 cm^{-1} is assigned to the C=O of AQS. The peaks observed around 974, 835 and 684 cm^{-1} show the C–S bond in the thiophene molecule. Thus, FT-IR studies revealed the presence of both PSS and AQS in the polymer film [26,27].

The increased stability of PEDOT-AQS films shown in this work could be useful in several applications. One application is the production of H$_2$O$_2$ through an anthraquinone route [28–30]. Work toward achieving this goal is currently underway in our laboratory.
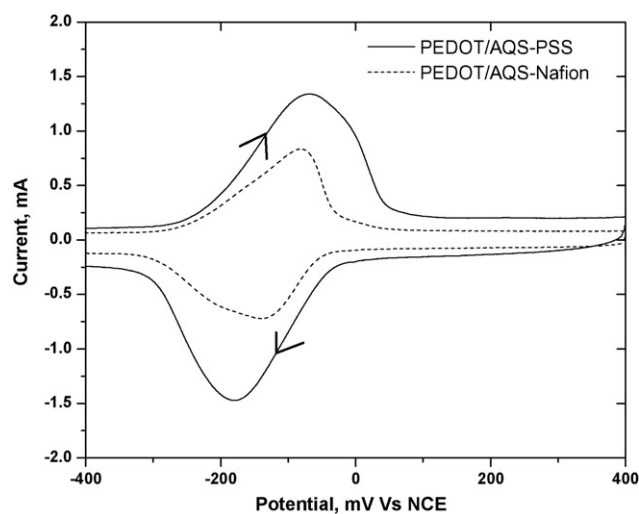

Fig. 7. Stability comparison of PEDOT-AQS modified by Nafion casting (physical) and PSS$^-$ treatment (electrochemical) after 100 cycles in 0.5 M H$_2$SO$_4$ at the scan rate 20 mV s^{-1}.
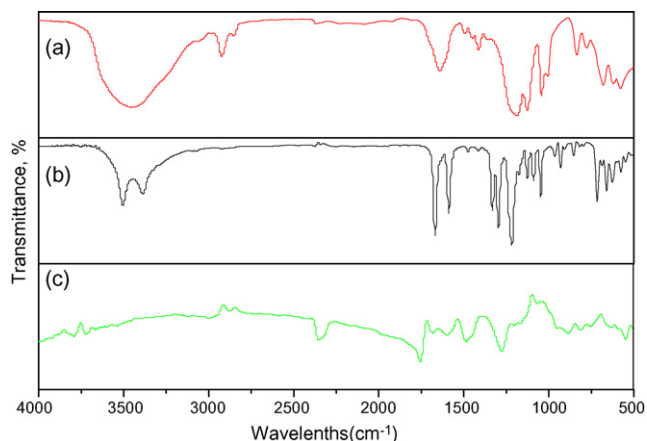
Fig. 8. FTIR spectra of (a) Na-PSS; (b) AQS in KBr and (c) PSS⁻ modified PEDOT-AQS on an ITO glass plate for 20 cycles followed by cycling for five cycles in Na-PSS containing electrolyte.

Acknowledgement

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