Electropolymerization of 3,4-Ethylenedithiathiophene in the Green Binary Solvent System of Water and Ethanol

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The electrosynthesis of poly(3,4-ethylenedithiathiophene) (PEDTT), which is the sulfur analogue of the well-known poly(3,4-ethylenedioxythiophene) (PEDOT), is investigated in green binary solvent system of deionized water and anhydrous ethanol (1:1 by volume) contained poly(sodium-p-styrenesulfonate) (PSSNa) as the surfactant and $LiClO_4 \cdot 3H_2O$ as supporting electrolyte . The polymer obtained from this medium showed good electrochemical behavior, stability, electrochromic properties and could be partly dissolved in dimethylsulfoxide, tetrahydrofuran, chloroform, etc. Electrochemical impedance studies were performed on Pt/PEDTT/electrolyte system. From the Nyquist plots of the PEDTT film, the electroactivity of the polymer starts to increase from 1.0 V. FT-IR and UV-vis-NIR spectra indicated that the polymerization of monomer occurred mainly at 2,5 position. Cyclic voltammetry and spectroelectrochemistry studies demonstrated that PEDTT can be reversibly oxidized and reduced accompanied by obvious color changes from grass green to golden brown, these properties indicate that the polymer showed favorable electrochromic performance. Fluorescent spectral studies indicated that the polymer was a green-light emitter. TG and DTG analyses showed that the as-formed PEDTT films had good thermal stability.

1. INTRODUCTION

3,4-Ethylenedioxythiophene (EDOT) is the most intensively investigated monomer in the past decade because of the very high conductivity and excellent environmental stability of its polymer

poly(3,4-ethylenedioxythiophene) (PEDOT).[1-3] Therefore, PEDOT and its derivatives have been attracting great attention with their outstanding electronic properties. They are characterized by low energy-gap values, low oxidation potentials, and high electrical conductivity and stability in the oxidized (p-doped) state. These characteristics make p-doped PEDOT films suitable as electrodes and interfacial hole conducting layers in various types of organic electronic devices, for example, in light emitting diodes, solar cells, and antistatic or electrochromic coatings.[3-5]

Scheme 1. Synthesis route and scheme for PEDTT

Poly(3,4-ethylenedithiathiophene) (PEDTT, scheme 1), as the all-sulfur analog of PEDOT, each thiophene ring is functionalized with an ethylenedithia substituent. Since firstly reported by Kanatzidis and coworkers in 1995,[6] much of the research associated with PEDTT has entailed its incorporation with other conjugated structures or introduced other functional groups into its structure [7-14]. The PEDTT and its derivatives have found possible applications as the electron donor materials in photovoltaic devices [7-11,15,16], and as the cathode active materials for rechargeable lithium batteries with better cathode capacity than PEDOT [17]. In addition, the presence of sulfur atoms in EDTT, replacing the oxygen atoms of EDOT, does not provide a simple explanation for the very different properties of the two monomers. For example, EDTT has a lower oxidation potential compared with EDOT, it was expected to important electron donating mesomeric effects by sulfur.[6,18,19]

Water is a most ideal medium for synthetic chemistry from the aspects of operational costs, safety, and greening,[20-24] but many organic materials are water-insoluble or only sparingly soluble. To overcome the solubility problem in water, synthetic processes employing surfactant-stabilized emulsions and suspensions have been developed. As a conventional synthetic method, electrochemical polymerization of aromatic heterocyclic compounds with concurrent polymer film deposition has played a very important role in polymer science and it has been proved to be an especially effective method for the preparation of high-quality conjugated polymer film. However, it still is in the development stage to fulfill its potential as a "green" methodology. In this situation, the electrochemical transformations of immiscible materials in aqueous electrolytes have been also investigated.[25-27] As reported in the literatures [28-31], conducting polymers has been widely studied in aqueous media, such as polypyrrole, polyaniline and PEDOT. However, electrochemical polymerization of EDTT was only in organic electrolytes [6,32,33] or ionic liquid[34]. In order to develop new polymerization system and to expand the application fields of PEDTT, the mild conditions used for electrochemical polymerization in aqueous solution are perfect choice and ideal for

incorporation of enzymes, antibodies or even whole living cell. Based on these considerations above, water still seems to be more attractive for the large scale synthesis of PEDTT and their usage in biosensor field than any other solvent from the viewpoint of cost, handling and safety.

In this paper, a preliminary study was carried out on the electrochemical polymerization of EDTT in binary solvent system of water-ethanol (1:1 by volume) contained poly(sodium-p-styrenesulfonate) (PSSNa) as the surfactant and $LiClO_4 \cdot 3H_2O$ as supporting electrolyte. Note here that to the best of our knowledge, the electrochemical polymerization of EDTT in binary solvent system has not been reported so far. Besides, the structural characterization, electrochemistry, spectroelectrochemistry, fluorescence, and other properties of the as-formed PEDTT film, such as electroactivity and thermal stability, were minutely researched.

2. EXPERIMENTAL

2.1. Materials

We synthesized EDTT following our previous work [35] and distilled under reduced pressure before use. Poly(sodium-p-styrenesulfonate) (PSSNa, 98%, M_w=30000, Alfa aesar), $LiClO_4 \cdot 3H_2O$ (99%, Sinopharm Chemical Reagent Co.,Ltd), ethanol, 25% ammonia and concentrated sulfuric acid (Jinan Chemical Reagent Company) were used as received without further purification. Dimethyl sulfoxide (DMSO, analytical grade) was a product of Tianjin Bodi Chemicals Co., Ltd. Other reagents were all analytical grade and used as received without further treatment.

2.2. Electrosynthesis and Electrochemical Tests

The electrochemical tests and polymerization of the monomers were performed in a one-compartment cell using a potentiostat-galvanostat (model 263A, EG&G Princeton Applied Research) under computer control. For electrochemical tests, the working and counter electrodes were Pt wire with a diameter of 1 mm and stainless steel wire with a diameter of 1 mm, respectively. They were placed 5 mm apart during the tests. To obtain a sufficient amount of the polymer films for characterization, ITO or Pt and stainless-steel sheets with surface areas of 4 and 6 cm^2 each were used as the working and counter electrodes, respectively. These electrodes were carefully polished with abrasive paper (1500 mesh), cleaned successively with water and acetone, and then dried in air before each experiment. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode, and it revealed sufficient stability during the experiments. The polymer films were grown potentiostatically, and their thickness was controlled by the total charge passed through the cell, which was read directly from the current-time (I-t) curves by computer. In order to remove the electrolyte and oligomers/monomer, the electropolymerized films were rinsed in mixtures of ethanol and water containing increasing amounts of water and finally pure water. For spectral analyses, the polymer films were dedoped with 25% ammonia for 3 days and then washed repeatedly with pure water. Finally, the polymer film was dried at 60 °C under vacuum for 24 h.

2.3. Apparatuses

Electrochemical and spectroelectrochemical studies were carried out on a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) and a Cary 50 UV-vis-NIR spectrophotometer under computer control. Infrared spectra were recorded using a Bruker Vertex 70 Fourier transform infrared (FT-IR) spectrometer with samples in KBr pellets. The fluorescence spectra were determined with an F-4500 fluorescence spectrophotometer (Hitachi). Gel permeation chromatography (GPC) measurements of the samples were performed in tetrahydrofuran with a Waters Breeze GPC system. Thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA thermal analyzer (Perkin-Elmer).

Spectroelectrochemical measurements were carried out to consider absorption spectra of these polymer films under applied potentials. The spectroelectrochemical cell consisted of a quartz cell, an Ag/AgCl electrode (RE), a Pt wire (CE), and an ITO glass as the transparent working electrode (WE). All measurements were carried out in the mixed electrolyte of deionized water and anhydrous ethanol (1:1 by volume) contained poly(sodium-p-styrenesulfonate) (PSSNa) as the surfactant and $LiClO_4 \cdot 3H_2O$ as supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1. Cyclic Voltammetry
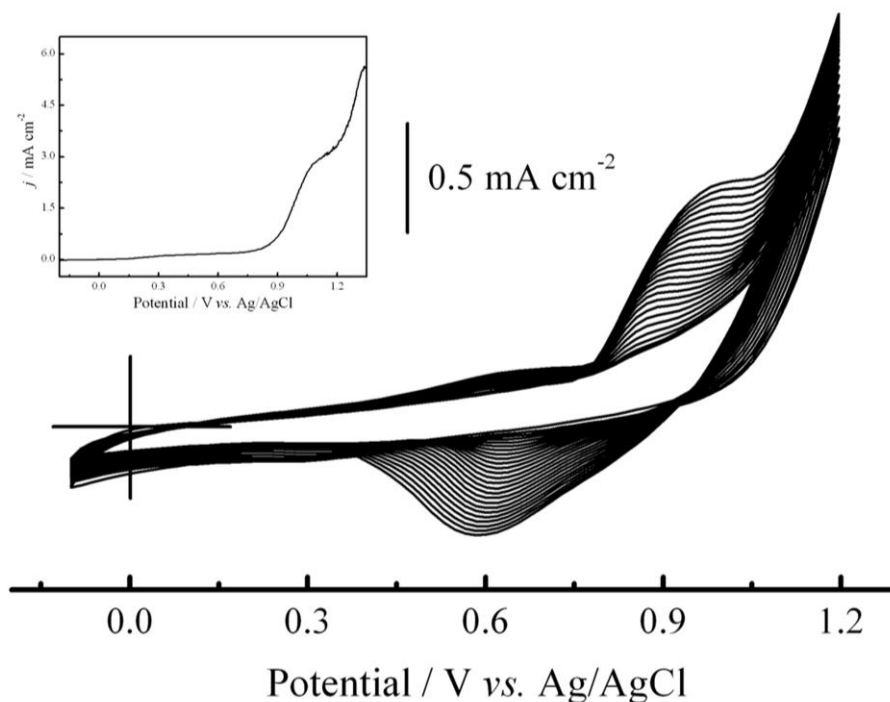
Figure 1. Cyclic voltammograms and anodic polaritiong curve (inset) of EDTT (0.02 mol/L) in deionized water-ethanol (V:V=1:1)-$LiClO_4 \cdot 3H_2O$ (0.02 mol/L)-PSSNa (0.05 mol/L), Potential scan rate: 100 mV s^{-1}

Cyclic voltammetry (CV) is a very useful method which qualitatively reveals the reversibility of electron transfer during the electropolymerization, and also examines the electroactivity of the polymer films because the oxidation and reduction process can be monitored in the form of a current–potential diagram.[36] The potentiodynamic electropolymerization of EDTT was carried out in the mixed electrolyte of deionized water and anhydrous ethanol (1:1 by volume) contained poly(sodium-p-styrenesulfonate) (PSSNa) as the surfactant and $LiClO_4 \cdot 3H_2O$ as supporting electrolyte. The representative electrochemical growth revealing the electrochemical performance of monomer and the formation of corresponding polymers was given in Fig. 1. From the first cycle (or from the anodic polarization curve, inset of Fig. 1), the onset oxidation potential (E_{onset}) of EDTT was approximately at 0.91 V vs. Ag/AgCl (1.15 V vs. SCE in CH_3CN/0.1 M Bu_4NClO_4 [6]). As the potential scanning continued, the oxidation and reduction peaks were observed near 0.9 and 0.6 V vs. Ag/AgCl. The increases of the redox wave currents (Fig. 1) implied that the amount of the polymer electrodeposited increased on the working electrode with CV proceeding. The broad redox waves of the polymer may be ascribed to the wide distribution of polymer chain length or the conversion of conductive species on the polymer main chain from the neutral state to the metallic state. The potential shift of the wave current maximum provided information about the increase in the electrical resistance of the polymer film and the over potential needed to overcome the resistance.

3.2. Structural Characterization
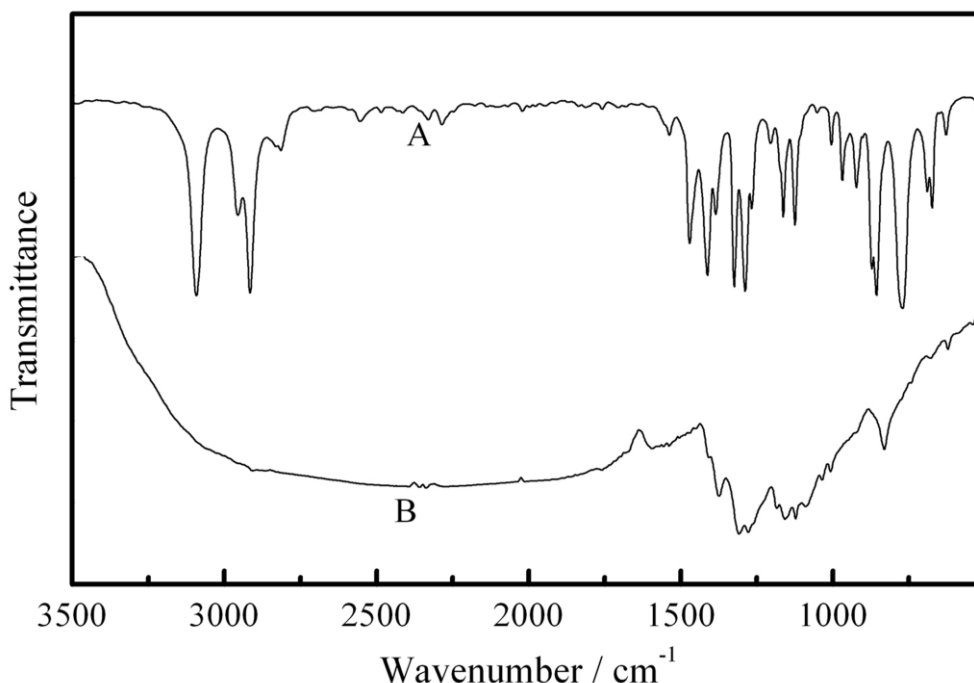
Figure 2. FT-IR spectra of the EDTT (A) and the dedoped PEDTT (B) film

Vibrational spectra can provide much structural information for conducting polymers, especially for insoluble and infusible polymers. A comparison of the evolution of the vibrational

modes appearing in conducting polymers and in some simpler related molecules acting as references usually facilitates the interpretation of the experimental absorption spectra. FT-IR spectra of the EDTT monomer and the corresponding neutral PEDTT were recorded to elucidate the structure of PEDTT and interpret the polymerization mechanism, as shown in Fig. 2. As can be seen from Fig. 2, the absorption bands in the spectra of the dedoped polymer were obviously broadened in comparison with those of the monomer, similar to those of other conducting polymers reported previously.[31,37] This was mainly due to the wide chain dispersity of the resulting product composed of oligomers/polymers. The peak at 3093, 2916 and 773 cm^{-1} for EDTT (Fig. 2A) was produced by C-H vibration of the 2,5-position in the thiophene ring. These peaks were disappeared in the spectrum of PEDTT (Fig. 2B). These spectral changes implied the occurrence of the polymerization happened at C(2) and C(5) positions of the thiophene ring, in agreement with the previously reported results.[6,31] The stretching of the ethylenedioxy ring appeared as a large peak at 1323 and 1288 cm^{-1} in both EDTT and PEDTT with no detectable change in intensity or wavelength, indicating that the ethylenedioxy ring was not destroyed during the electropolymerization. The possible polymerization mechanism of EDTT is illustrated in Scheme 2. The initiation step involves the anodic oxidation of EDTT monomers to radical cations in the vicinity of the anode. Then radical cations dimerize and deprotonate. After the deprotonation step, the dimer is reoxidized and couples with another radical cation. Deprotonation and reoxidation follow, and the process continues with the formation of oligomer species. Once the chain length of the oligomers exceeds the solubility limit of the solvent, precipitation occurs and nuclei deposit on the anode. Then the above steps proceed continuously. Finally, PEDTT film electrodeposits on the surface of the electrode. The rate of polymerization is limited by the diffusion of monomers to the anode surface during the propagation stage. The deprotonation steps in the above mechanisms are believed to produce an acidic environment in the region of the anode.
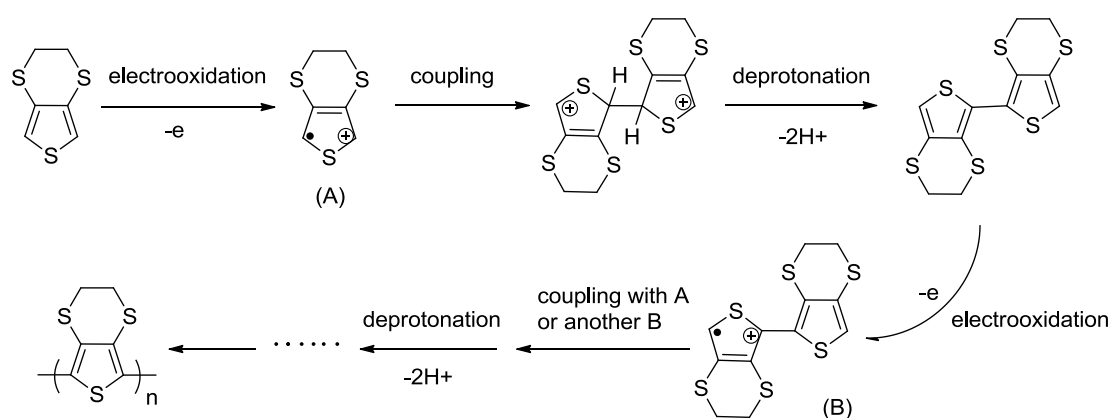

Scheme 2. Possible polymerization mechanism for EDTT

3.3. Electrochemistry of PEDTT Films

In order to get a deeper insight into the electroactivity and environmental stability of PEDTT films, the electrochemical behavior was determined carefully by cyclic voltammetry in monomer free

deionized water and anhydrous ethanol (V:V=1:1) - $LiClO_4 \cdot 3H_2O$ (0.02 M) and concentrated sulfuric acid, as shown in Fig. 3A and B, respectively.
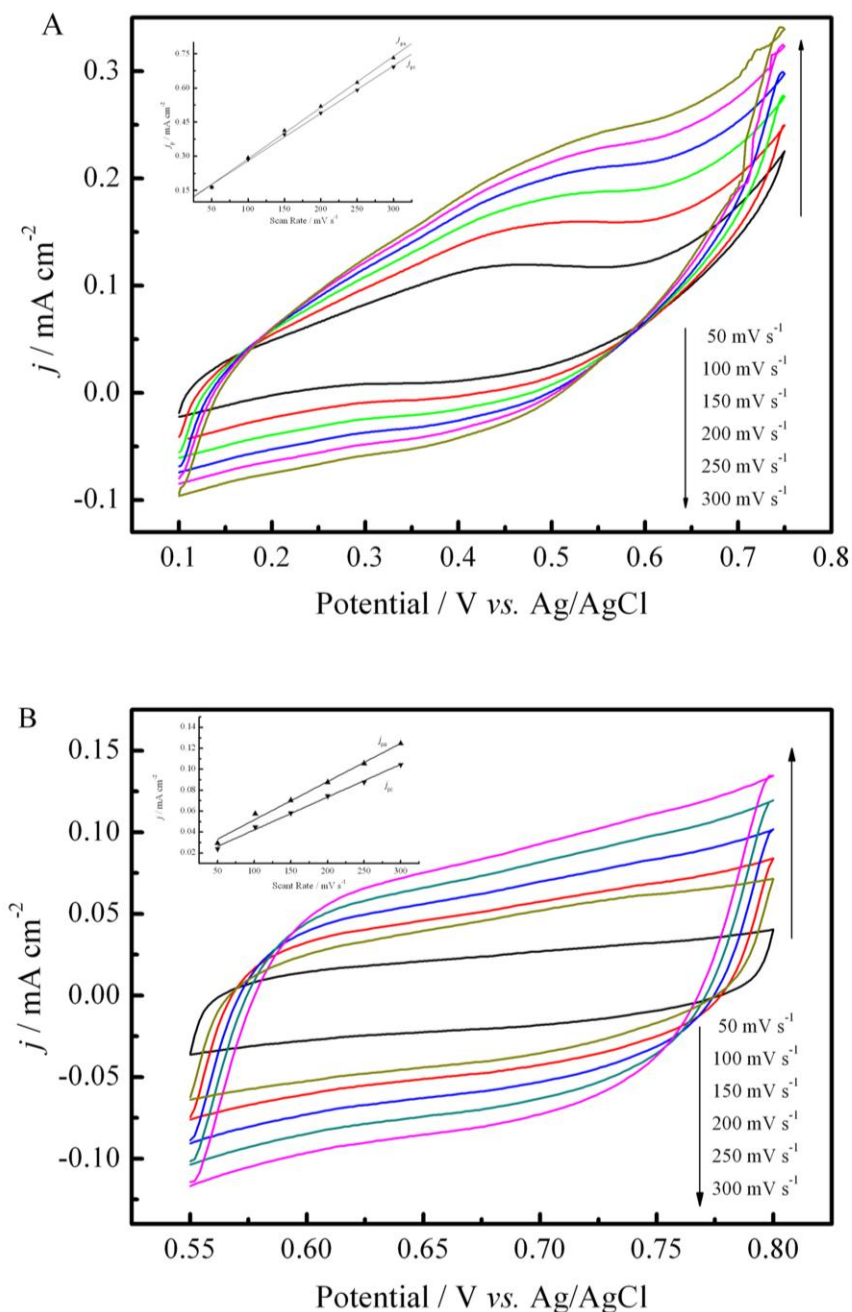

Figure 3. Cyclic voltammograms of PEDTT films in deionized water- ethanol (V:V=1:1) containing $LiClO_4 \cdot 3H_2O$ 0.02 mol/L (A) and concentrated sulfuric acid (B) at different potential scan rates

Similar to the results reported previously [34-39], the steady-state CVs displayed broad anodic and cathodic peaks (Fig. 3A and B) and the peak current densities were proportional to the potential scan rates (inset in Fig. 3A and B), indicating that the redox processes were not controlled by diffusion limits and the electroactive polymers were well adhered to the working electrode surface. Furthermore,

the films could be cycled repeatedly between the conducting (oxidized), and insulating (neutral) states without significant decomposition, indicating the high redox stability of PEDTT films. The polymer film could be oxidized and reduced from 0.45 V (anodic peak potential, Ea) to 0.36 V (cathodic peak potential, Ec) in deionized water and anhydrous ethanol (V:V=1:1) - LiClO$_4$·3H$_2$O (0.02 M) (Fig. 3A) and from 0.73 V (Ea) to 0.64 V (Ec) in concentrated sulfuric acid (Fig. 3B). All these results described above indicate that the as-prepared PEDTT films have good redox activity and high structural stability.

The ac impedance technique, with a wide range of applicable frequencies, is a powerful method for the investigation of electrochemical processes, which involves several steps occurring at different rates. Therefore, the ac impedance of PEDTT films in monomer free deionized water and anhydrous ethanol (V:V=1:1) - LiClO$_4$·3H$_2$O (0.02 M) is measured, as shown in Fig. 4. Fig. 4 illustrates the complex plane impedance plots of the polymer in the range of 0.2–1.2 V. In the Nyquist plots, polymer shows very little almost negligible electroactivity in the range of 0.2–0.8 V. Values of the imaginary part are very large and capacitance values are very small in this region, starting from 1.0 V phase angle starts to increase and reaches its maximum value at 1.2 V. This is indicating that the electroactivity of the polymer starts to increase from 1.0 V.
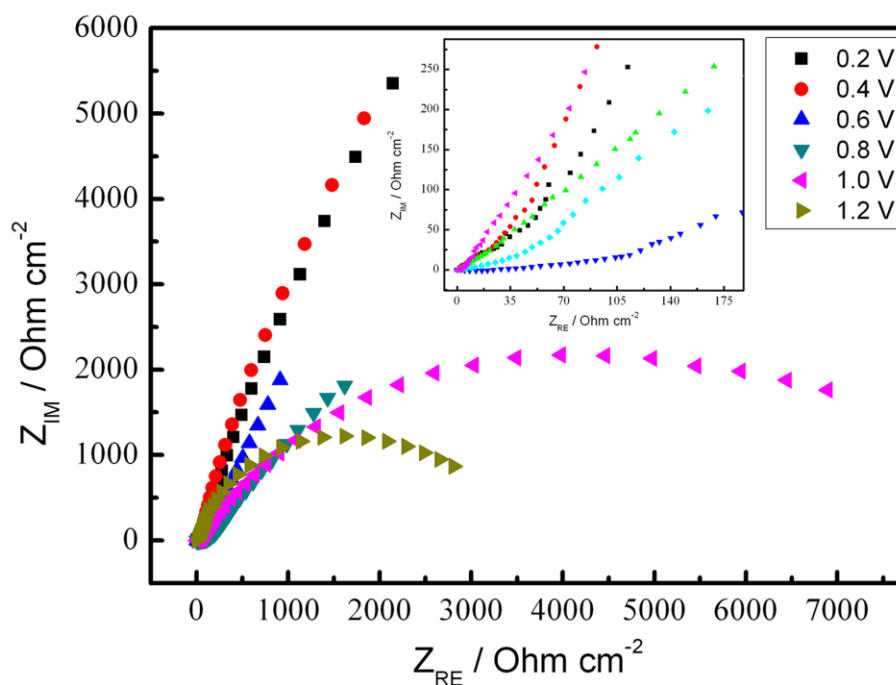
Figure 4. Electrochemical impedance spectroscopy of PEDTT-modified electrode measured at 0.2-1.2 V in deionized water-anhydrous ethanol (V:V=1:1) containing LiClO$_4$·3H$_2$O (0.02 mol/L)

3.4. Spectroelectrochemical Properties of PEDTT Films

Optoelectrochemical studies of the polymers were utilized to elucidate the electronic structure and the nature of electrochromism in the electrochromic polymers because polarons, bipolarons, and π-dimers all factor into their respective optical changes.[40] The electrooptical properties of the polymer films were investigated using the changes in electronic absorption spectra at various applied voltages.

PEDTT films were cast on an ITO-coated glass slide, and a home-made electrochemical cell was built from a commercial UV-visible cuvette. The cell was placed in the optical path of the sample light beam in a UV–vis–NIR spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control in deionized water and anhydrous ethanol (V:V=1:1) - $LiClO_4 \cdot 3H_2O$ (0.02 M) solution. As each potential was stepped, the absorption in the visible regime began to decrease, whereas that in the NIR regime increased, indicating the creation of lower energy charge carriers at the expense of $\pi–\pi^*$ transition.[41]

The spectroelectrochemistry of PEDTT film upon oxidation is presented in Fig. 5 as a series of UV–vis–NIR absorbance curves and the corresponding colors of electrochemically prepared films correlated to electrode potentials. Stepwise oxidation of the polymer (increasing applied voltage from 0.1 to 1.2 V) showed the fading of absorbance at 572 nm and typical evolution of peaks at more than 660 nm. As previously reported in acetonitrile,[32] the spectral changes, taking place at ca.1.9–2.2 eV (650-560 nm), is a general observation for many counterions employed, such as ClO_4^-, PF_6^-, BF_4^-, $CF_3SO_3^-$, etc. Moreover, the corresponding color of PEDTT film was golden brown in the reduced state (Fig. 5, top right inset) and grass green in the oxidized state (Fig. 5, top right inset).
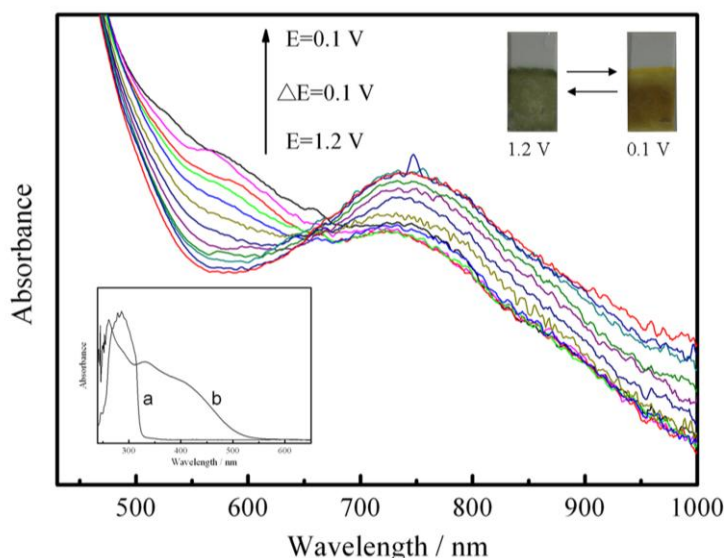

Figure 5. Spectroelectrochemistry for PEDTT on ITO coated glass in deionized water-anhydrous ethanol (V:V=1:1) containing $LiClO_4 \cdot 3H_2O$ 0.02mol/L. Inset: UV-visible spectra of EDTT (a), dedoped PEDTT (b) in DMSO

The doped and dedoped PDBTO films were both partly soluble in common organic solvents at room temperature, such as DMSO, acetonitrile, chloroform, and THF. The soluble part of PEDTT in THF showed a number-average molar mass (Mn) of about 4550, comparable with the results of electrosynthesized PEDTT in CH_3CN/0.1 M Bu_4NClO_4 or $BmimPF_6$ reported previously.[6,34] However, they exhibited better solubility in DMSO. UV-vis spectra of the monomers and the resulting polymers in DMSO were examined, as shown in Fig. 5, bottom left inset. Compared with the monomer of EDTT, PEDTT dissolved in DMSO showed two broad absorption bands centered at 342 nm and

416 nm (Fig. 5b), in well accordance to the results (341 and 419 nm) reported by Kanatzidis and others previously.[6,35] The overall absorption of the polymer tailed off to approximately 554 nm in comparison with that of the monomer (about 322 nm for EDTT), mainly due to the formation of the conjugated polymer chain. The low-energy peaks with an onset around 554 nm have an absorption maximum at 416 nm for soluble PEDTT, which is a result of the π–π* absorption transition,[42] slightly higher than previous results (518 nm). This could be attributed to the absorption of longer chain sequences due to the higher polydispersity of as-formed PEDTT. From the onset of the absorption of PEDTT, the band gap of the polymer was determined to be 2.24 eV, which is comparable to the reported optical band gap prepared in acetonitrile (2.2 eV). This indicates that the PEDTT prepared in aqueous solution can be compared with the organic systems.

3.5. Fluorescence Spectra

The fluorescence emission spectra of the EDTT and the dedoped polymers PEDTT were determined in DMSO at room temperature, as shown in Fig. 6. From Fig. 6A, it can be seen that the emission spectrum emerged at 375 nm (excited at 370 nm).
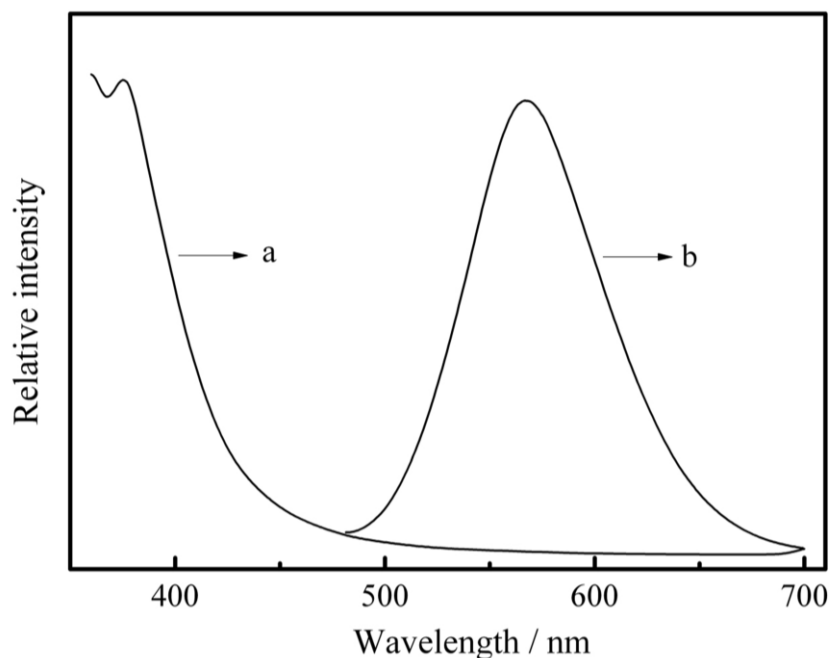

Figure 6. The fluorescence spectra of EDTT (a) and the dedoped PEDTT (b) in DMSO

In comparison, a dominant maximum at 568 nm characterized the emission spectrum of the soluble dedoped PEDTT when excited at 472 nm (Fig. 6B). The bathochromic shift between the EDTT and the dedoped PEDTT (about 193 nm) can be clearly seen from the figure. It is mainly attributable to the elongation of the delocalized π-electron chain sequence resulting from the electropolymerization of the thiophene units. The emission peak of the as-formed PEDTT showed a red shift of about 16 nm

compared with that of PEDTT obtained by chemical oxidative polymerization or electropolymerization in $CH_3CN/0.1$ M Bu_4NClO_4 [6]. This phenomenon can be ascribed to the higher polydispersity of the polymer. Due to the resulting polymer composed of oligomers/polymers with wide chain dispersity, the emission peaks of these components with different polymerization degrees overlap one another and produce broad emissions with hyperstructures, in well accordance with the results of UV–vis spectra.

3.6. Thermal Properties of the Polymers

Thermal degradation behavior of conducting polymers is very important for their potential applications. For most conducting polymers, the skeletal decomposition temperatures are usually low, generally reported to be lower than 600 K, which hinders their practical uses in various fields. To investigate the thermal stability of the newly obtained polymer, thermogravimetric and differential thermogravimetric (DTG) analytical experiments were performed under a nitrogen stream at a heating rate of 10 K min^{-1}, as shown in Fig. 7. It can be seen that at low temperatures (T < 432 K), the polymer initially underwent a small weight decrease of about 2.35%, which may be attributed to water evaporation or other moisture trapped in the polymer according to many authors.[34-38] With the gradual increasing of the temperature, a more pronounced weight loss step (about 38.35%) was observed for 432 K < T < 696 K, which may be caused by the volatilization of a few oligomers trapped in the films and the partly oxidizing decomposition of the skeletal polymer backbone chain structure. The following degradation after 696 K was probably caused by the overflow of the oligomers decomposed from PEDTT mentioned previously. Simultaneously, from the DTG curve (Fig. 7B), the corresponding maximal decomposition existed at 635 K. From these results, it is clear that the as-prepared PEDTT has good thermal stability.
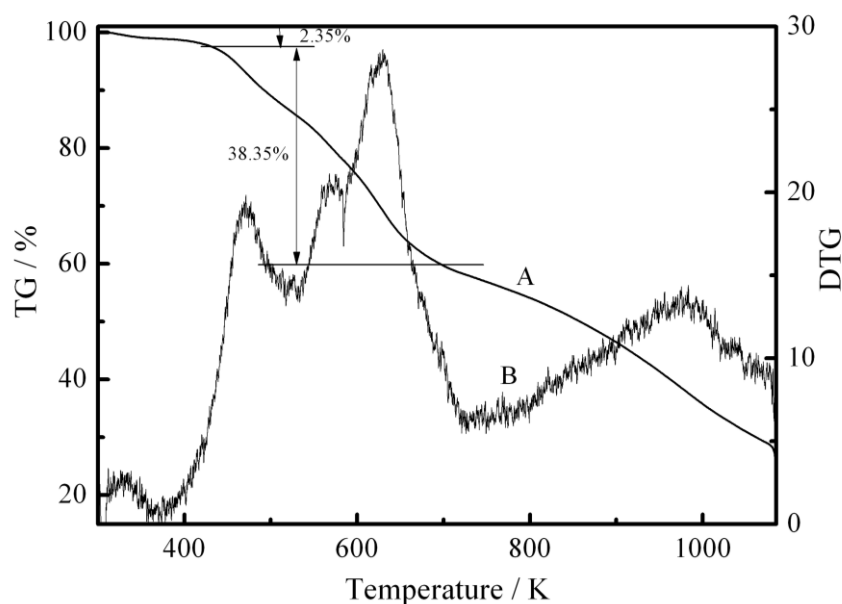
Figure 7. TG and DTG curves of the dedoped PEDTT film

4. CONCLUSIONS

High quality PEDTT films were electrochemically synthesized at low monomer concentrations in green binary solvent system in the presence of a surfactant, Poly(sodium-p-styrenesulfonate). PEDTT films showed good redox activity and structural stability even in concentrated sulfuric acid. The as-formed PEDTT film was minutely studied by FT-IR, UV–vis spectroscopy, fluorescence and thermal analysis. In comparison with prepared in traditional organic solvent and $BmimPF_6$, PEDTT films electrosynthesized in green binary solvent system with comparable or even better property. Moreover, PEDTT was found to possess electrochromic nature with its color changing from golden brown to grass green and low switching voltages than prepared in organic solvent or $BmimPF_6$. These results indicate that PEDTT from green binary solvent system is very promising as an optoelectronic material and may find application in organic electronic devices and electrochemical sensors.

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