Electrosynthesis, Characterization, and Application of Poly(3,4-ethylenedioxythiophene) Derivative with a Chloromethyl Functionality

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ABSTRACT: Poly(2-chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine), a chloromethyl functionalized poly(3,4-ethylenedioxythiophene) derivative (PEDOT-MeCl), was synthesized electrochemically via the potentiostatic polymerization of its monomer in dichloromethane solution containing suitable tetrabutylammonium tetrafluoroborate, then it was used for the characterization of film properties and the fabrication of electrochemical sensor. The properties of the resulting PEDOT-MeCl film were characterized by different methods such as cyclic voltammetry, electrochemical impedance spectroscopy, Fourier transform infrared and ultraviolet–visible techniques, scanning electron microscope, and thermogravimetric analysis. The PEDOT-MeCl film displayed a good reversible redox activity, remarkable capacitance properties, good thermal stability, rough, and porous structure, especially fluorescent spectra indicated that PEDOT-MeCl was a blue-emitter with maximum emission centered at 396 and 398 nm. Finally, the PEDOT-MeCl film was employed for the fabrication of the sensing electrode, and dopamine was chosen as a model analyte for the application of the electrochemical sensor. Results indicated that the PEDOT-MeCl film as sensing interface was feasible, and studies of these film properties were very beneficial for studying properties and applications of other poly(3,4-ethylenedioxythiophene) derivative films. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2660–2670, 2013

INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the most stable conducting polymers, has been the main subject of extensive research in the past quarter century due to its versatile properties such as high electrical conductivity, low band gap, good redox activity, high thermal stability, and excellent transparency in the doped state, and it has been of particular significance because of its potential applications in rechargeable batteries, electrochromic display devices, organic light emitting diodes, supercapacitors, antistatic coatings, corrosion inhibitors, printed circuits, smart windows, microwave absorbing materials, and chem/bio sensors.[1–5]

In its well-known study, the one of most attractive properties of PEDOT is that its properties can be tuned by grafting various functional groups. Therefore, different functionalized PEDOT derivatives have widely been studied for their potential different applications in the most recent literature.[6–19] Sallé and co-workers synthesized three fluorinated functionalized 3,4-ethylenedioxythiophene (EDOT) derivatives, and the corresponding fluorinated PEDOT films with dry and chemically immobilized lubrication properties were obtained by electropolymerization.[6] Subsequently, they synthesized a functionalized EDOT derivative bearing a highly nucleophilic thiolate group, and it can take part in reaction with different electrophilic species.[7] Moreover, they also attached crown-tetrathiafulvalenes to an EDOT unit, and the corresponding polymer film had the electroactivity and the cations recognition property.[8] Segura et al.[9–11] have reported the syntheses and electropolymerization of three novel EDOT derivatives covalently functionalized with 9,10-anthraquinone, perylenetetracarboxylic diimide, and 11,11,12,12-tetracyano-9,10-anthraquino-dimethane, the resulting new polymers displayed individual redox and optical properties. Roncali et al.[12] focused on the interest of EDOT as a building block for the synthesis of fluorophores, push–pull chromophores functional π-conjugated systems for nonlinear optics and extended π-donors. Brisset and co-workers synthesized ferrocene-functionalized EDOT derivatives, and these derivatives electrochemically copolymerized

with their precursor.[13] In addition, they also co-electropolymerized this precursor with hydroxymethyl EDOT or two EDOT groups linked by a polyether chain and studied the electrochemical behavior of these polymer films.[14] Yamada et al. synthesized a water-soluble π-conjugated polymer of sulfonyl functionalized PEDOT, and the obtained polymer protected Prussian Blue nanoparticles demonstrated a novel multiple-color pH sensing device.[15] We also developed a new and efficient synthetic route to hydroxymethyl EDOT, and the resulting polymer film from the monomer in aqueous sodium dodecylsulfate micellar solution had good biocompatibility and was used for fabricating the electrochemical vitamin C biosensor.[16] COOH-Functionalized EDOT derivatives were synthesized by Yu and co-workers, and electropolymerized thin PEDOT films exhibited good biocompatibility, very low intrinsic cytotoxicity, and displayed no inflammatory response upon implantation, making them ideal for biosensing and bioengineering applications.[17–19] 2-Chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (EDOT-MeCl), as one of EDOT derivatives, is a versatile intermediate to easily access functionalized EDOT derivatives and their corresponding polymers.[20–24] By these aspects, we might conjecture that polymerization of EDOT-MeCl and properties and characterizations of its polymer should be studied and be necessary for the design and development of novel PEDOT derivatives with a variety of excellent properties. However, so far, there is no report on systematically study of the performances, characterizations of poly(2-chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (PEDOT-MeCl), and including its application.

In this article, PEDOT-MeCl can be polymerized electrochemically by applying a constant potential of $+1.7$ V in dichloromethane (DCM) containing $0.10M$ tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$) (Scheme 1). The electrochemical properties, morphology, and thermal stability of as-prepared PEDOT-MeCl films were studied. And, the structure and performance were characterized by FT-IR spectra, fluorescent spectra, and UV–vis spectra. Moreover, dopamine was used as a model analyte for the application of the as-fabricated electrochemical sensor based on PEDOT-MeCl film (Scheme 2).

EXPERIMENTAL

Chemicals

3,4-Dibromothiophene (98%; Shanghai Bangcheng Chemical Co.), dopamine (DA, 98%; Aladdin Chemistry Co.), copper oxide (CuO, 98%), p-toluenesulfonic acid (≥99.5%), and dichloromethane (DCM; Tianjin Damao Chemical Reagent Factory), potassium iodide (KI, 98%; Shanghai Chemical Reagent Co.), sodium methoxide, methanol anhydrous (Tianjin Fuchen Chemical Reagent Factor), 3-chloro-1,2-propanediol (Wuhan Remote Technology Development Co.), toluene (Shantou Xilong Chemical Industry Co.), disodium hydrogen phosphate dodecahydrate (Na$_2$HPO$_4$ · 12H$_2$O) and sodium dihydrogen phosphate dihydrate (NaH$_2$PO$_4$ · 2H$_2$O) (Sinopharm chemical reagent Co.) were used as received, $0.1M$ phosphate-buffered saline (PBS, pH = 7.0) solution was prepared from $0.1M$ NaH$_2$PO$_4$ · 2H$_2$O and Na$_2$HPO$_4$ · 12H$_2$O. DCM was purified by distillation over calcium hydride before used. Tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$, 99%; Acros Organics) was dried under vacuum at 60°C for 24 h prior to use. All reagents were of analytical grade and used without further purification. Double-distilled deionized water used directly without further purification.

Synthesis of EDOT-MeCl

Under an nitrogen atmosphere, 3,4-dibromothiophene (30 g, 124.00 mmol), sodium methoxide (123.26 g, 30% in methanol, 684.52 mmol), copper oxide (9.86 g, 123.95 mmol), potassium iodide (0.84 g, 5.06 mmol), and methanol (150 mL) were added to a three-necked flask. The mixture was refluxed for 3 days. After this time, another sodium methoxide (123.26 g, 30% in methanol, 684.52 mmol) was added, and the solution was refluxed for another 1 day. Then the solution was allowed to cool to the room temperature and filtered through a sintered glass fritted funnel. The filtrate was then extracted with dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate, the solvent evaporated under vacuum, and the residue purified by column chromatography (silica gel, petroleum ether) to give 15.72 g of a colorless oil (yield 88.02%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 6.19 (s, 2H), 3.86 (s, 6H).

Yield: 88.02%

Global Yield: 54.54%

Yield: 61.96%
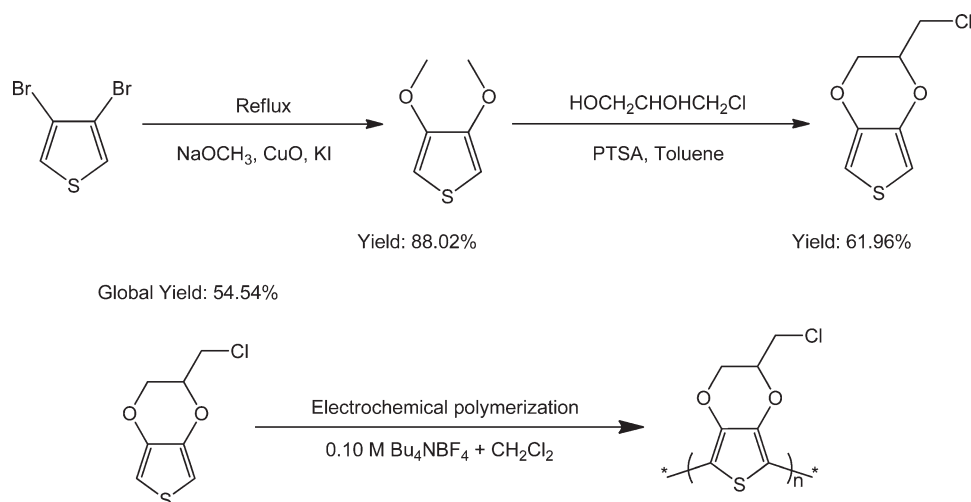
Scheme 1. The two-step synthesis route of EDOT-MeCl, and its electropolymerization.
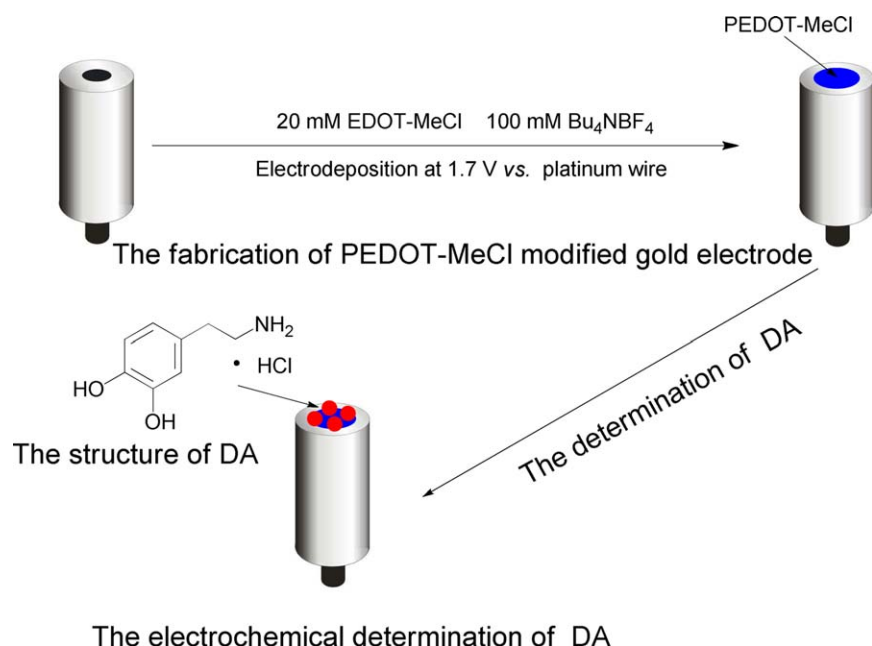
Scheme 2. The electrochemical preparation of the PEDOT-MeCl film modified gold electrode and its DA sensing application. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To a well-stirred solution of 3,4-dimethoxythiophene (16.30 g, 113.05 mmol) in 280 mL of dry toluene, 3-chloro-1,2-propane-diol (25.62 g, 231.77 mmol), and p-toluene sulfonic acid monohydrate (1.6 g, 9.29 mmol) were added under an nitrogen atmosphere. The solution was heated at 90°C for 24 h. Then, another of diol (25.62 g, 231.77 mmol) was added, and the solution was heated at 90°C for another 3 h and was allowed to cool to room temperature. After removal of the solvent, the remaining crude product was isolated by column chromatography (silica gel, hexane/dichloromethane, 8/2, v/v) to give 13.35 g of a white solid (yield 61.96%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 6.37 (s, 2H), 4.35–4.40 (m, 1H), 4.27–4.35 (m, 1H), 4.14–4.18 (m, 1H), 3.65–3.75 (m, 2H).

Electrochemical Measurements

Electrochemical polymerization and examinations were performed in a one-compartment cell with the use of Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control. The gold electrode was used as the working electrode, and the auxiliary electrode and reference electrode were all the platinum wires. The platinum wires above were carefully polished with abrasive paper (1500 mesh), and cleaned by water and acetone successively before each examination. All experiments were carried out under a slight nitrogen overpressure. Finally, the polymer film was dried at 60°C under vacuum for 24 h. The PEDOT-MeCl film was characterized electrochemically in monomer-free DCM containing 0.10M Bu$_4$NBF$_4$.

Preparation of PEDOT-MeCl Modified Electrode

PEDOT-MeCl film was performed by a constant potential of +1.7 V in DCM containing 0.02M EDOT-MeCl and 0.10M Bu$_4$NBF$_4$ at room temperature and the deposition time was 90 s. Then the obtained PEDOT-MeCl film modified gold electrode

was washed repeatedly with deionized distilled water to remove the electrolyte and monomer. Finally, the modified electrode was dried in air.

Electrochemical Determination Procedure

The working electrode served as the PEDOT-MeCl film modified gold electrode, a platinum wire was used as the counter electrode, and the Ag/AgCl as the reference electrode. Prior to the electropolymerization, the gold electrode ($\Phi = 2$ mm) was carefully polished with chamois leather containing 0.05 μm alumina slurry, and was ultrasonically cleaned with deionized distilled water, absolute ethanol and deionized distilled water each for 5 min, respectively. The gold electrode was then immersed into the mixed liquor of concentrated sulphuric acid with hydrogen peroxide in the ratio 7 : 3 for 20 min. Finally, the gold electrode was ultrasonically cleaned in deionized distilled water for 5 min. All potentials were given versus Ag/AgCl. Ten milliliters of phosphate buffer solution (pH 7.0) with different concentrations of DA was transferred into the electrochemical cell. The standard equipment was used for cyclic voltammetry (CV) and differential pulse voltammetry (DPV), cyclic voltammograms (CVs), and differential pulse voltammograms (DPVs) were recorded between −0.2 V to +0.6 V, the peak current was measured, and the scan rates of CV and DPV were 50 mV s^{-1}, and the optimized operating conditions to record DPVs were: pulse amplitude, 50 mV; sample width, 16.7 ms; pulse width, 50 ms; pulse period, 200 ms; sensitivity, 50 μA V^{-1}. Prior to the determination of DA, the cell was deoxygenated by purging with nitrogen for 20 min prior to each experiment. All the experiments were performed at room temperature.

Characterizations

Electrochemical impedance spectroscopy (EIS) experiments were performed in 0.1M KCl solution by using an Autolab Frequency

Response Analyzer System (AUT30; FRA2-Autolab, Echemie, B.V.) connected to a conventional one-compartment three-electrode electrochemical cell, and recorded at the potential of +0.3 V, the deposition time was 90 s, and the frequency range was 10 kHz to 100 mHz, using 5 mM $[Fe(CN)_6]^{3-/4-}$ redox couple as an indicator. Also, CV characterization experiments were further carried out in 5 mM $[Fe(CN)_6]^{4-/3-}$ containing 0.1M KCl. Infrared spectra (FT-IR) of the PEDOT-MeCl film were recorded using Bruker Vertex 70 Fourier spectrometer with samples in KBr pellets, and the PEDOT-MeCl film prepared in DCM containing 0.02M EDOT-MeCl and 0.10M Bu$_4$NBF$_4$ on a platinum gauze electrode at a constant potential of +1.70 V. Ultraviolet–visible (UV–vis) spectra were measured with a Perkin-Elmer Lambda 900 ultraviolet–visible–near-infrared spectrophotometer. With an F-4500 fluorescence spectrophotometer (Hitachi), fluorescence spectra of the monomer and polymer were determined. Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis was performed with a Pyris Diamond TG/DTA thermal analyzer (Perkin-Elmer). Scanning electron microscopy (SEM) measurements were taken using VEGA\\TESCAN Digital Microscopy Imaging, and the polymer film prepared in DCM–Bu$_4$NBF$_4$ on ITO transparent electrode at a constant potential of +1.7 V. pH values were measured with a Delta 320 pH meter (Mettler-Toledo Instrument, Shanghai, China).

RESULTS AND DISCUSSION

Electrochemical Polymerization of EDOT-MeCl

The electrochemical polymerization of EDOT-MeCl was studied in DCM–Bu$_4$NBF$_4$ system. Consecutive CVs of EDOT-MeCl were shown in Figure 1. In the first cycle of CVs, the current densities on the reverse scan were higher than on the forward scan (in the region of from −1.0 to +1.7 V). The formation of this loop could be explained as the characteristics of nucleation process. As compared with EDOT polymerization,[25] during electropolymerization process, the redox peaks of EDOT-MeCl appeared at +0.46 V and +0.16 V, which attributed to the p-doping/dedoping processes of PEDOT-MeCl film formed in previous scans. Upon sequential cycles, redox currents increased, implying that the formed electroactive and conductive layer on the gold electrode surface (light-blue to blue-black as the deposit thickened) was gradually increasing. The broad redox peaks of the as-formed PEDOT-MeCl film could be ascribed to the wide distribution of the polymer chain length or the version of conductive species on the polymer main chain from the neutral state to polarons, from polarons to bipolarons, and finally from bipolarons to the metallic state.

Electrochemistry of PEDOT-MeCl Film

Potentiostatic synthesis was employed to prepare the polymer film for characterization of film. To optimize the applied potential for polymerization, a set of current transients during the electropolymerization of EDOT-MeCl at different applied potentials in DCM–Bu$_4$NBF$_4$. In the inset of Figure 1, the minimum oxidation potential of EDOT-MeCl was +1.62 V. Considering the overall factors affecting the quality of the formed film, such as moderate polymerization rate, negligible overoxidation, regular morphology, and good adherence against the working
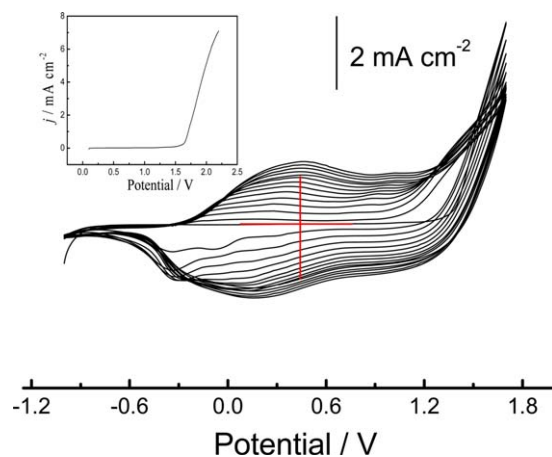
Figure 1. CVs of EDOT-MeCl electropolymerized at potential scan rate of 100 mV s^{-1} in DCM containing 0.1M Bu$_4$NBF$_4$ and 0.02M monomer. Inset: corresponding anodic polarization curve of EDOT-MeCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrode, the selected applied potential was +1.7 V for EDOT-MeCl in DCM containing 0.10M Bu$_4$NBF$_4$.

In order to get a deeper insight into the electroactivity of the obtained polymer film, the electrochemical behavior of PEDOT-MeCl film was investigated carefully by CV in monomer-free DCM–Bu$_4$NBF$_4$ (Figure 2). It could be clearly seen that steady-state CVs of the PEDOT-MeCl film represented broad anodic and cathodic peaks in the monomer-free electrolytes. This was ascribed to the presence of slow diffusion of the counterions inside the film, changes of the film capacitance, and the presence of a wide distribution of the polymer chain length resulting from coupling defects distributed statistically. The peak current densities were linearly proportional to the potential scanning rates (Figure 2 inset), indicating that the redox process
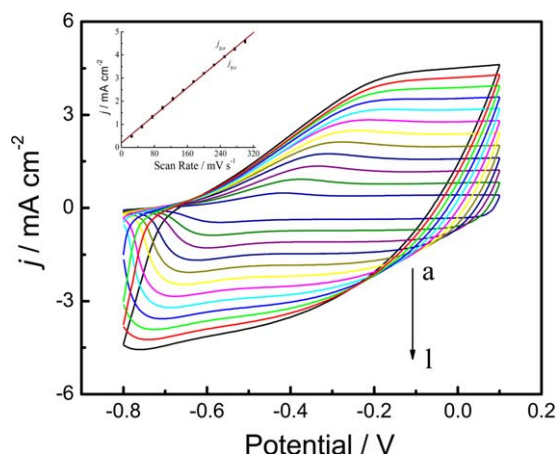
Figure 2. CVs of PEDOT-MeCl film in monomer-free DCM at potential scan rates of (a) 25, (b) 50, (c) 75, (d) 100, (e) 125, (f) 150, (g) 175, (h) 200, (i) 225, (j) 250, (k) 275, (l) 300 mV s^{-1}. Inset: plots of redox peak current densities versus potential scan rates. j_p is the peak current density, $j_{p,a}$ and $j_{p,c}$ denote the anodic and cathodic peak current densities, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was non-diffusional and the electroactive polymer was well adhered to the working electrode surface. Meanwhile, the conducting (oxidized) and insulating (neutral) state without significant decomposition of the materials, indicating high stability of the polymer.
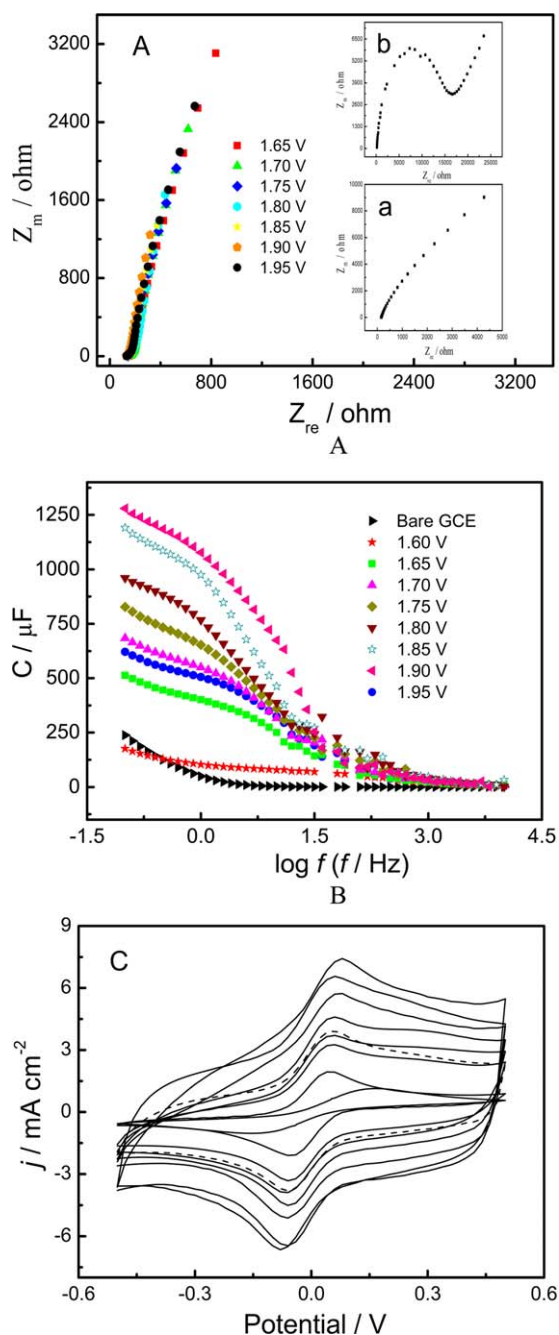
Electrochemical Impedance Spectroscopy

EIS can provide the information on impedance changes of the electrode surface during the modification process. Figure 3(A) was typical Nyquist plots for the deposition of PEDOT-MeCl film in different potentials. The EIS includes a semicircle part and a linear part. The semicircle part at higher frequencies corresponds to the electron-transfer limited process, and the linear

part at lower frequencies corresponds to the diffusion process. As shown in the inset b of Figure 3(A), compared with the bare gold electrode, instead of the semicircle part, the PEDOT-MeCl film modified electrodes were the linear curves, and was almost perpendicular to real part, which implying the PEDOT-MeCl film had a good capacitance behavior.[26] As could be seen from capacitance–frequency plots [Figure 3(B)], the redox capacitance was estimated using the equation $C_{LF} = 1/(2\pi f Z_m)$, where f was the frequency of the impedance and Z_m is the imaginary part of the impedance, with the deposition potentials increased, the capacitance values decreased at low frequencies, which attributed to the deposition potential much more than the minimum oxidation potential, and the PEDOT-MeCl film thickness and film resistance rose, which influenced the electron-transfer rate.

In addition, the real impedance at low frequencies, where the capacitive behavior dominates, was an indication of the combined resistance of the electrolyte and the films including both electronic and ionic contributions.[27,28] The values of the real impedance, imaginary impedance, and capacitance at 100 mHz was given in Table I. It could be seen the trend in change of the real impedance were agreement with that of the imaginary impedance and capacitance for the deposition of PEDOT-MeCl film in different potentials.

Also, Figure 3(C) showed CV response of $[Fe(CN)_6]^{4-/3-}$ at bare gold electrode and PEDOT-MeCl film modified gold electrode. The peak separation (ΔE_p) between the anodic and cathodic peaks at PEDOT-MeCl film modified glod electrodes (20 mV) were smaller than that at bare gold electrode (100 mV), indicating that the reversibility of electrochemical reaction at PEDOT-MeCl film modified gold was improved. Simultaneously, it could be seen the CVs of the full lines (from inner to outer: bare gold electrode, modified electrode in different potential of +1.60 V, +1.65 V, +1.70 V, +1.75 V, +1.80 V, +1.85 V, and +1.90 V, respectively), the response currents at this modified gold electrode were increased apparently with the deposition potential increased. However, the CVs of the dash line, corresponding to the deposition potential of +1.95 V, the current response of the modified electrode was sharply decrease.

electrode for the deposition of PEDOT-MeCl film in different potentials of +1.65 V (■), +1.70 V (▲), +1.75 V (◆), +1.80 V (▼), +1.85 V (★), +1.90 V (◄), +1.95 V (●) recorded in 5 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1M KCl. Inset: bare gold electrode (a), in the deposition potential of +1.60 V (b). (B) Capacitance-frequency plots of the bare gold electrode (▲) and the PEDOT-MeCl film modified gold electrode for the deposition of PEDOT-MeCl film in different potentials of +1.60 V (★), +1.65 V (■), +1.70 V (▲), +1.75 V (◆), +1.80 V (▼), +1.85 V (☆), +1.90 V (▲), +1.95 V (●). (C) CVs of the PEDOT-MeCl film modified gold electrode for the deposition of PEDOT-MeCl film in different potentials. The full lines of CVs are bare gold electrode, modified electrodes for the deposition of PEDOT-MeCl film in different potentials of at +1.60 V, +1.65 V, +1.70 V, +1.75 V, +1.80 V, +1.85 V, +1.90 V from inner to outer, respectively, and the dash line of CVs is PEDOT-MeCl film modified gold electrode in deposition potential of +1.95 V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. (A) Impedance spectra of the PEDOT-MeCl film modified gold

Table I. EIS results of PEDOT-MeCl Film Modified Gold Electrodes for the Deposition of PEDOT-MeCl Film in Different Potentials

Potential (V)	Bare gold	1.60	1.65	1.70	1.75	1.80	1.85	1.90	1.95
Z_{re} at 100 mHz (Ω)	23480	4274	837	618.5	526.1	436.4	373.4	320.2	672.0
Z_m at 100 mHz (Ω)	6688	9030	3105	2329	1925	1657	1336	1245	2553
C_{LF} (mF)	0.2380	0.1763	0.5126	0.6834	0.8269	0.9604	1.191	1.279	0.6209

The results were agreement with electrochemical impedance spectroscopy analysis.

Structural Characterization Analysis

The FT-IR spectra of PEDOT-MeCl films were shown in Figure 4(A). It should be noted that in the spectrum of PEDOT-MeCl the absence of bands at 1061, 921, 919, and 850 cm^{-1}, attributed to the C–H out-of-plane bending vibrations in the EDOT-MeCl monomer spectrum, confirmed the formation of PEDOT-MeCl chains with α, α' coupling. The vibrations at 1582 and 1514 cm^{-1} were attributed to the stretching modes of C=C and C–C in the thiophene ring. The vibration modes of the C–S bond are at 1023, 932, and 776 cm^{-1}. In addition, CH, CHC, and CH$_2$C present at 3117, 3012, and 2930 cm^{-1} were attibuted to out-plane deformation vibration in the fatty acid long-chain. The existence of the 1683, 1661, and 1625 cm^{-1} bands were ascribed to the CO out-plane deformation

vibration. The bands at 1182, 1136, and 1097 cm^{-1} were assigned to the stretching modes of the COCH$_2$–CHOC group, and the band around 966 cm^{-1} was due to the COCH$_2$–CHOC group in-plane deformation mode. The band around 1402 and 1340 cm^{-1} was due to the CH, CH$_2$C group in-plane deformation vibration. The bands of 595 and 560 cm^{-1} were assigned to the C–Cl group in-plane vibration mode, and 774 cm^{-1} was due to the C–Cl group stretching mode. The details of the band assignments of doped PEDOT-MeCl were given in Table II. In addition, the elemental composition of PEDOT-MeCl was confirmed by energy dispersive X-ray spectroscopy EDX [Figure 4(B)].

UV–Vis Spectra Analysis

The as-prepared PEDOT-MeCl film in the doped state was dark blue in color. When the film was dedoped by 25% ammonia for 3 days, its color changed to brownish yellow. In
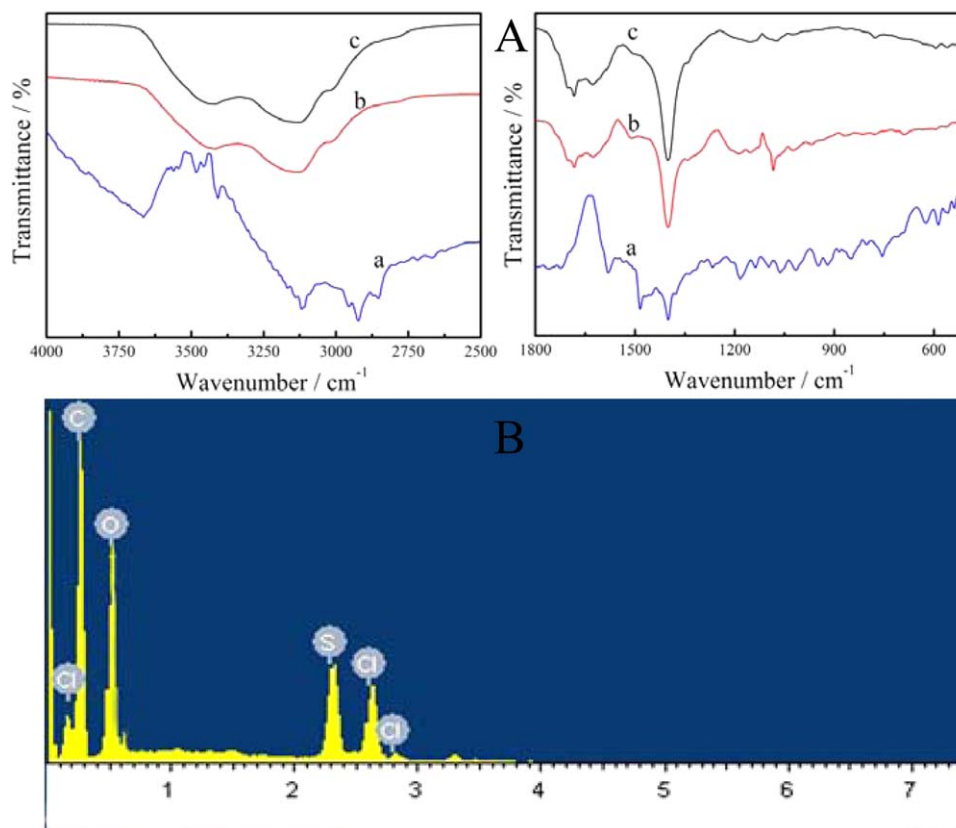
Figure 4. FT-IR spectra (A) of EDOT-MeCl (a), doped PEDOT-MeCl (b), and dedoped PEDOT-MeCl (c), EDX (B) of the PEDOT-MeCl film. The PEDOT-MeCl film was synthesized potentiostatically at +1.70 V versus platinum wire. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
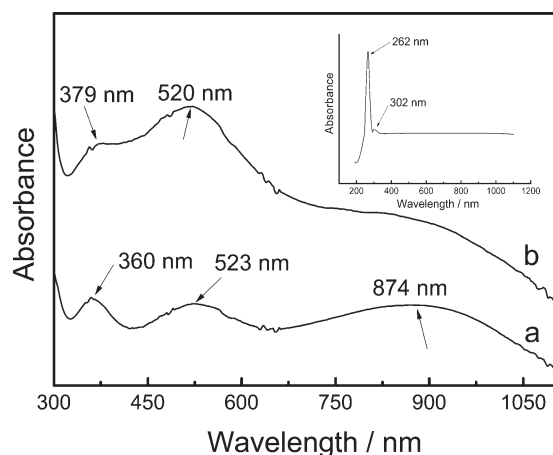
Table II. Assignments of FTIR Spectra of Doped PEDOT-MeCl

Band (cm^{-1})	Assignment
3117	γCH, CHC
3012, 2930	γCH, CH$_2$C
1683, 1661, 1625	γCO
1582, 1514	ν(C=C, C–C)ring
1402,1340	δCH, CH$_2$C
1182, 1136, 1097	νCOCH$_2$–CHOC
1061, 921, 919, 850	γ(C–H)monomer
1023, 932, 776	νC–S
966	δCOCH$_2$–CHOC
774	νC–Cl
595, 560	δC–Cl

ν represents stretching, δ in-plane deformation, and γ out-of-plane deformation.
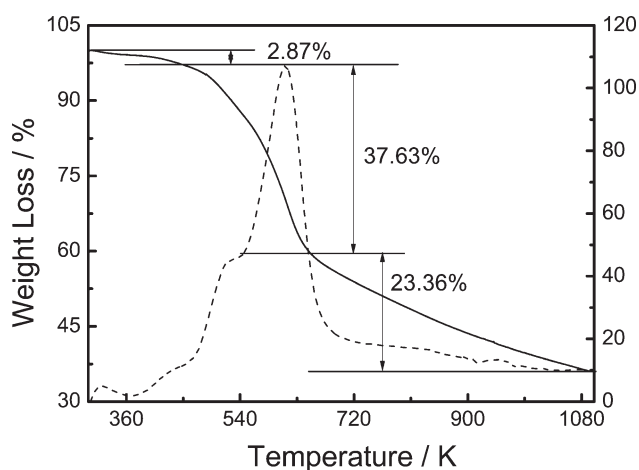

Figure 6. Fluorescence spectra of the doped (a) and dedoped (b) PEDOT-MeCl polymer films coated on an ITO electrode. Inset: fluorescence spectra of EDOT-MeCl monomer in DMSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

addition, the resulting PEDOT-MeCl film was found to be incompletely soluble in DMSO or THF, and also exhibited poor solubility in other solvents such as acetonitrile, and acetone.

UV–vis spectra of the monomer dissolved in DMSO and the resulting polymer film electodeposited on the ITO were examined in Figure 5. The monomer showed a characteristic absorption peak at 262 nm with a shoulder of 302 nm (inset). In contrast, the spectra of the dedoped PEDOT-MeCl film showed not only the absorption at 379 and 520 nm, but also a broad absorption from 796 to 1028 nm [Figure 5(b)]. This implied that the longer wavelength was the absorption, the higher conjugation length was the polymer. On the other hand, the doped PEDOT-MeCl film showed not only the absorption at 360 and 523 nm, but also a much broader absorption from 683 to 1041 nm with their maximum at 874 nm [Figure 5(a)]. This wide peak could be assigned to the absorption of the conductive species such as polarons and bipolarption on the main backbone

of PEDOT-MeCl in the doped state. Generally, these spectral results confirmed the occurrence of the electrochemical polymerization among the monomer and the formation of a conjugated polymer with broad molar mass distribution, and the similaruty of absorption spectra of the polymer in both doped and dedoped states indicated that the doped polymer was very stable. In addition, these sharp absorption peaks at 379, 520, 360, and 523 nm were due to a valence band-conduction band (π–$\pi^\star$) transition.[29]

Fluorescence Spectra

The fluorescence spectra of the monomer in DMSO (Figure 6, inset) and the doped and dedoped polymer films in solid state were illustrated in Figure 6. The monomer exhibited a strong peak at 360 nm. Compared to the monomer, the dominant maximum emission at 396 and 398 nm were used to characterize the spectra of the doped [Figure 6(a)] and dedoped [Figure 6(b)] PEDOT-MeCl, respectively. The small red shifts between

Figure 5. UV–vis spectra of the EDOT-MeCl monomer in DMSO (insert) and the doped (a) and dedoped (b) PEDOT-MeCl polymer films on an ITO electrode. The polymer films were prepared from DCM solutions at the same applied potential of +1.7 V versus platinum wire.

Figure 7. TG/FTG curves of the dedoped PEDOT-MeCl film synthesized potentiostatically at +1.70 V versus platinum wire from DCM after treatment with 25% aqueous ammonia for 3 days.
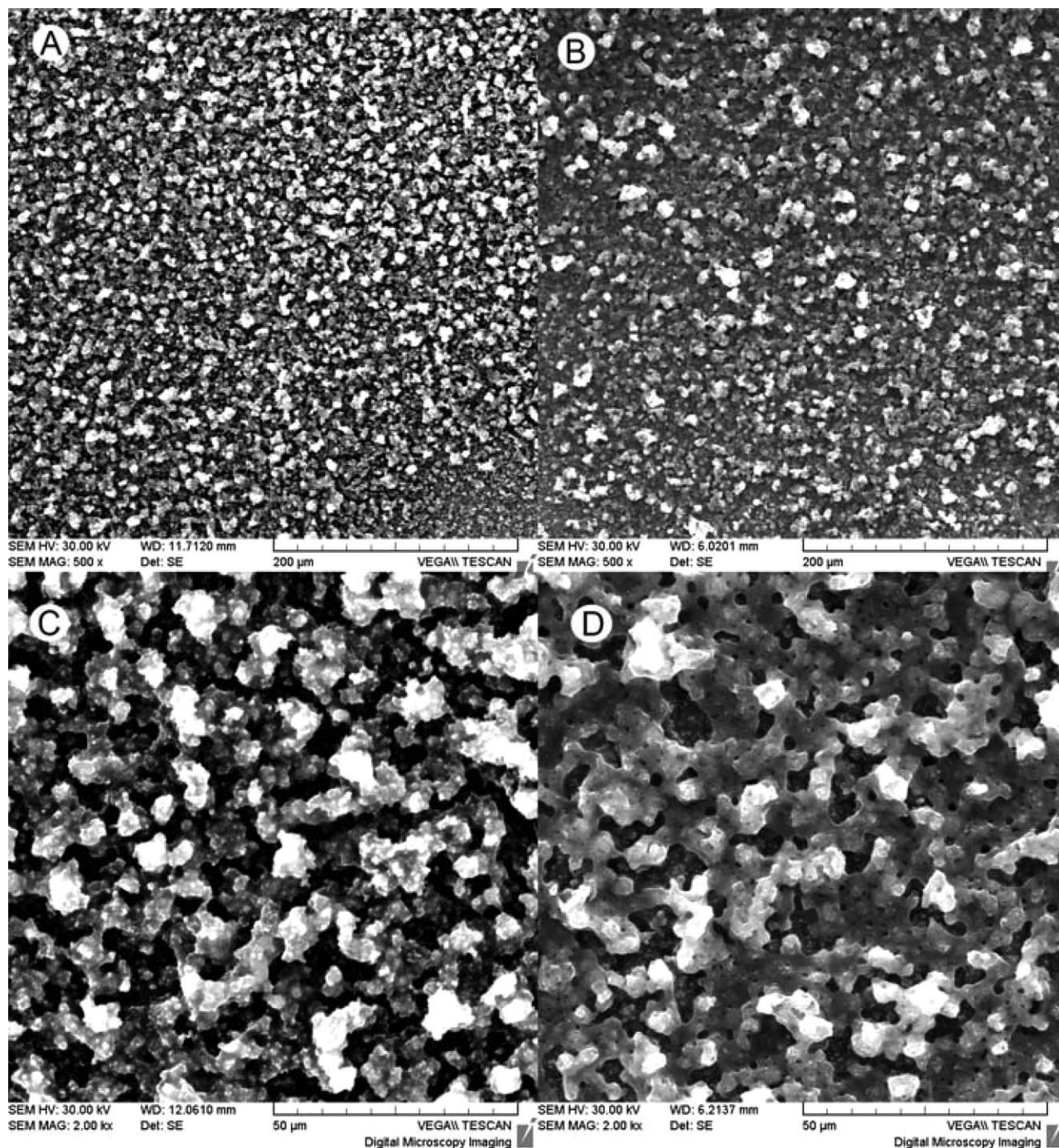
Figure 8. SEM images of (A) the doped PEDOT-MeCl film, (magnification: 500×); (B) the dedoped PEDOT-MeCl film, (magnification: 500×); (C) the doped PEDOT-MeCl film, (magnification: 2000×); (D) the dedoped PEDOT-MeCl film, (magnification: 2000×).

the monomer and the polymer could be clearly seen from Figure 6, which was mainly attributable to the elongation of the polymer delocalized π-electron chain sequence. This further proved the formation of the conjugated backbone of PEDOT-MeCl, in accordance with the UV–vis spectral results. The slight difference between the doped and dedoped PEDOT-MeCl may be the effect of counterion. These results demonstrated that the polymer was a good blue-light emitting materials, indicating some potential applications in organic optoelectronics.

Thermal Analysis

To investigate the thermal stability of the prepared PEDOT-MeCl film, TG and DTG experiments were performed under nitrogen protection at a heating rate of 10 K min^{-1}, as shown in Figure 7. At low temperatures ($T < 447$ K), the polymer initially underwent a small weight decrease of about 2.87%, which may be attributed to evaporation of trace water or other moisture trapped in the polymer. As the temperature continued increasing, a more pronounced weight loss step (37.63%) was observed for 447 K $< T \leq$ 648 K. Simultaneously, the DTG
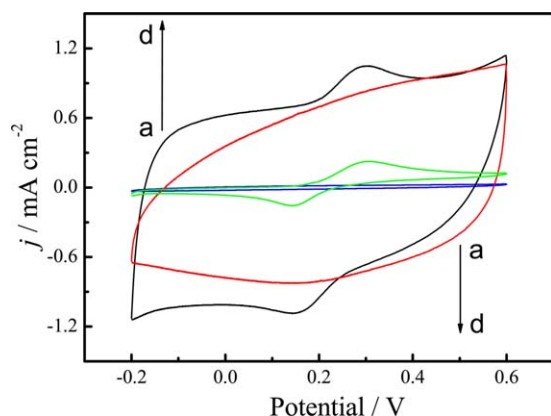
Figure 9. CVs of the PEDOT-MeCl film modified gold electrode in 0.1 M PBS (pH 7.0) containing 0 μM (c) and 50 μM (d) DA, and CVs of the bare gold electrode 0.1 M PBS (pH 7.0) containing 0 μM (a) and 50 μM (b) DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

curve showed that the corresponding maximal decomposition occurred at 612 K. Such a weight loss was closely related to the overflow of some oligomers or with short chain structure. Secondarily, the degradation between 648 and 1091 K amounting to 23.36% was probably caused by the oxidizing decomposition of the skeletal PEDOT-MeCl backbone chain structure. In addition, even when the temperature reached 1091 K, the residual weight of PEDOT-MeCl film was 36.14%, also indicating its good thermal stability. From all these results, it could be logically concluded that as-prepared PEDOT-MeCl film had favorable thermal stability for their potential applications. Also, in comparison of the thermogravimetric behavior of PEDOT in our previous reports,[30,31] the PEDOT-MeCl film has better thermal stability due to the presence of chloro-functional group.

Surface Morphology

Surface morphologies of the doped and dedoped PEDOT-MeCl films were presented in Figure 8. Macroscopically, the doped and dedoped PEDOT-MeCl films on the ITO were homogeneous, compact and rough. In contrast, microscopically, the doped PEDOT-MeCl film resembled cauliflower-like units (A and C), and the dedoped PEDOT-MeCl film resembled coralline algae (B and D).

Electrocatalytic Oxidation of DA

Figure 9 showed CVs of the PEDOT-MeCl film modified gold electrode in PBS with 50 μM DA and without DA. Obviously, an observable anodic peak appeared at approximately +0.31 V versus Ag/AgCl [Figure 9(b,d)] could be ascribed to the oxidation peak of DA, which was very different from in PBS without DA [Figure 9(a,c)], indicating that DA could be oxidized by electrocatalysis. In addition, the corresponding cathodic peak appeared about +0.13 V, which indicated that this electrochemical reaction was a reversible process. In addition, as could be seen, PEDOT-MeCl film could enhance electrocatalytic oxidation of DA in comparison with the bare gold electrode in Figure 9(b) and (d). This was because PEDOT-MeCl film as a conductive polymer could promote the electron transfer.

Electrochemical Determination of DA

Various concentrations of DA were prepared to explore the relationship between peak currents and concentrations of DA by DPV [Figure 10(A)]. The PEDOT-MeCl film modified gold electrode displayed a linear function of the DA concentration range from 0.079 to 672.90 μM. The regression equation was I_{pa} (μA) = 1.8969 − 0.0020c [μM; R^2 = 0.9989; Figure 10(B)]. The current sensitivity was calculated to be 0.002 μA μM^{-1}. At a signal-to-noise ratio of 3 (S/N = 3), the detection limit was found to be 0.0167 μM. As these results meant the prepared electrode exhibited wider linear range and lower limit of detection.[32–34] Also, these results also indicated that the prepared PEDOT-MeCl film modified electrode was successfully employed for the determination of DA.

Repeatability and Selectivity of PEDOT-MeCl Film Modified Au Electrode

In order to test the repeatability of the PEDOT-MeCl film modified gold electrode, 0.5 M DA was added into PBS and successively measured for 20 times using the same PEDOT-MeCl film modified gold electrode (Figure 11). As a result, the relative standard deviation (RSD) was 0.040%, which suggested that the PEDOT-MeCl film modified gold electrode had high repeatability. In addition, PEDOT-MeCl film modified electrodes for determination of
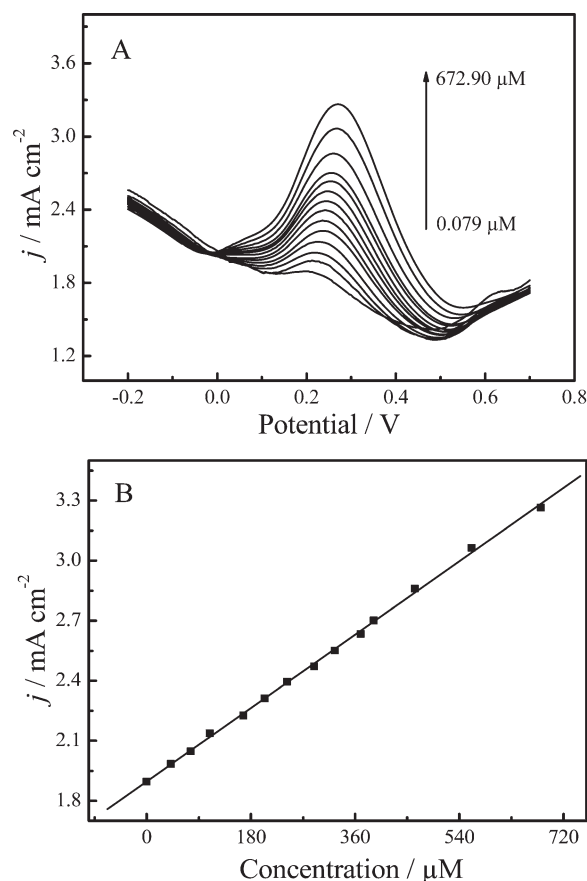
Figure 10. (A) DPV obtained at the PEDOT-MeCl modified gold electrode containing different concentration of DA. (B) The dependence of the anodic peak current density on the concentration of DA (from A) with the relationship observed in the concentration range from 0.079 to 672.90 μM.
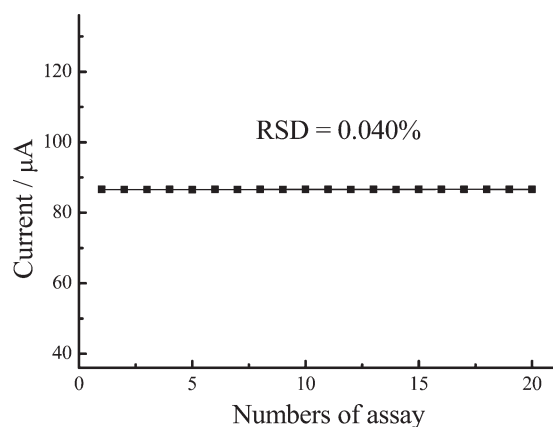
Figure 11. Current responses of the PEDOT-MeCl film modified gold electrode for 20 successive assays in $0.1M$ PBS (pH 7.0) containing $0.5M$ DA.

many analytes were no electrochemical response, especially common interferents and readily oxidizable substance such as ascorbic acid, tryptophan, uric acid, catechol, resorcinol and hydroquinone had bad or no electrochemical response. Moreover, PEDOT-MeCl has great effect on the immobilization of biologically active species due to its high toxicity, PEDOT-MeCl ascorbate oxidase electrode hardly sensing vitamin C. Hence, the PEDOT-MeCl film modified gold electrode had good selectivity.

CONCLUSIONS

EDOT-MeCl was synthesized by the two-step sequence, and polymerized electrochemically in DCM containing Bu_4NBF_4 and monomer. The obtained PEDOT-MeCl film showed good redox activity and stability in corresponding monomer-free electrolyte. Fluorescent spectra indicated that the PEDOT-MeCl film was a good blue-light emitter with maximum emission centered at 396 nm and 398 nm. The thermogravimetric analysis revealed that PEDOT-MeCl film had favorable thermal stability. The surface morphology of PEDOT-MeCl film implied that PEDOT-MeCl film could combine easily with some active molecules. Moreover, dopamine was used as a model analyte for the application of the as-fabricated electrochemical sensor based on PEDOT-MeCl film, the sensor displayed good linear range, low detection limit, pronounced sensitivity, and high repeatability. These satisfactory results implied that the prepared PEDOT-MeCl film modified electrode could be employed for sensing applications.

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REFERENCES

1. Skotheim, T. A.; Reynolds, J. R. Handbook of Conducting Polymers, Conjugated Polymers: Theory, Synthesis, Properties, and Characterization; CRC Press: Boca Raton, **2007**.

2. Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.

3. Groenendaal, L. B.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 855.

4. Elschner, A.; Kirchmeyer, S.; Lovenich, W.; Merker, U.; Reuter, K. PEDOT: Principles and Applications of an Intrinsically Conductive Polymer;, CRC Press: London, **2011**.

5. Kirchmeyer, S.; Reuter, K. *J. Mater. Chem.* **2005**, *15*, 2077.

6. Benedetto, A.; Balog, M.; Rayah, H.; Derf, F. L.; Viel, P.; Palacin, S.; Sallé M. *Electrochim. Acta* **2008**, *53*, 3779.

7. Balog, M.; Rayah, H.; Derf, F. L.; Sallé, M. *New J. Chem.* **2008**, *32*, 1183.

8. Trippé, G.; Derf, F. L.; Lyskawa, J.; Mazari, M.; Roncali, J.; Gorgues, A.; Leillain, E.; Sallé, M. *Chem. Eur. J.* **2004**, *10*, 6497.

9. Segura, J. L.; Gómez, R.; Blanco, R.; Reinold, E.; Bäuerle, P. *Chem. Mater.* **2010**, *18*, 2834.

10. Arias-Pardilla, J.; Otero, T. F.; Blanco, R.; Segura, J. L. *Electrochim. Acta* **2010**, *55*, 1535.

11. Segura, J. L.; Gómez, R.; Reinold, E.; Bäuerle, P. *Org. Lett.* **2005**, *7*, 2345.

12. Roncali, J.; Blanchard, P.; Frèrre, P. *J. Mater. Chem.* **2005**, *15*, 1589.

13. Navarro, A. E.; Fages, F.; Moustrou, C.; Brisset, H.; Spinell, N.; Chaix, C.; Mandrand, B. *Tetrahedron* **2005**, *61*, 3947.

14. Brisset, H.; Navarro, A. E.; Moustrou, C.; Perepichka, L. F.; Roncali, J. *Electrochem. Commun.* **2004**, *6*, 249.

15. Yamada, M.; Ohnishi, N.; Watanabe, M.; Hino, Y. *Chem. Commun.* **2009**, *42*, 7203.

16. Lu, Y.; Wen, Y. P.; Lu, B. Y.; Duan, X. M.; Xu, J. K.; Zhang, L.; Huang, Y. *Chinese J. Polym. Sci.* **2012**, *30*, 824.

17. Arias-Pardilla, J.; Otero, T. F.; Yu, H. H. *Electrochim. Acta* **2011**, *56*, 10238.

18. Ali, E. M.; Kantchev, E. A. B.; Yu, H. H.; Ying, J. Y. *Macromolecules* **2007**, *40*, 6025.

19. Luo, S. C.; Ali, E. M.; Tansil, N. C.; Yu, H. H.; Gao, S. J.; Kantchev, E. A. B.; Ying, J. Y. *Langmuir* **2008**, *24*, 8071.

20. Döbbeli, M.; Pozo-Gonzalo, C.; Marcilla, R.; Blanco, R.; Segura, J. L.; Pomposo, J. A.; Mecerreyes, D. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 3010.

21. Velauthamuty, K.; Higgins, S. J.; Rajapakse, R. M. G.; Bacsa, J.; Zalinge, H. V.; Nichols, R. J.; Haiss, W. *J. Mater. Chem.* **2009**, *19*, 1850.

22. Bu, H. B.; Götz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Blanco, R.; Segura, J. L.; Bäuerle, P. *Chem. Commun.* **2008**, *11*, 1320.

23. Bu, H. B.; Götz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Segura, J. L.; Blanco, R.; Gómez, R.; Bäuerle, P. *Tetrahedron* **2011**, *67*, 1114.

24. Bazaco, R. B.; Gómez, R.; Seoane, C.; Bäuerle, P.; Segura, J. L. *Tetrahedron Lett.* **2009**, *50*, 4154.

25. Liu, M.; Wen, Y. P.; Li, D.; He, H. H.; Xu, J. K.; Liu, C. C.; Yue, R. R.; Lu, B. Y.; Liu, G. D. *J. Appl. Polym. Sci.* **2011**, *122*, 1142.

26. Xu, Y. L.; Wang, J.; Sun, W.; Wang, S. H. *J. Power Sources* **2006**, *159*, 370.

27. Albery, W. J.; Chen, Z.; Horrocks, B. R.; Mount, A. R.; Wilson, P. J.; Bloor, D.; Monkman, A. T.; Elliott, C. M. *Faraday Discuss.* **1989**, *88*, 247.

28. Peng, C.; Jin, J.; Chen, G. Z. *Electrochim. Acta* **2007**, *53*, 525.

29. Tanaka, K.; Shichiri, T.; Yamabe, T. *Synth. Met.* **1986**, *16*, 207.

30. Zhang, S. S.; Hou, J.; Zhang, R.; Xu, J. K.; Nie, G. M.; Pu, S. Z. *Eur. Polym. J.* **2006**, *42*, 149.

31. Wen, Y. P.; Xu, J. K.; He, H. H.; Lu, B. Y.; Li, Y. Z.; Dong, B. *J. Electroanal. Chem.* **2009**, *634*, 49.

32. Alarcón-Angeles, G.; Corona-Avendaño, S.; Palomar-Pardavé, M.; Rojas-Hernández, A.; Romero-Romo, M.; Ramírez-Silva, M. T. *Electrochim. Acta* **2008**, *53*, 3013.

33. Huang, J. S.; Liu, Y.; Hou, H. Q.; You, T. Y. *Biosens. Bioelectron.* **2008**, *24*, 632.

34. Wang, P.; Li, Y. X.; Huang, X.; Wang, L. *Talanta* **2007**, *73*, 431.