

Fabrication of Poly(3,4-ethylenedioxythiophene)-Polysaccharide Composites

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ABSTRACT: Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with a series of anionic polysaccharides such as carboxymethyl cellulose, sodium hyaluronate, xanthan gum, pectin, gellan gum were prepared by electropolymerization in aqueous solutions. Some other dopants of potassium nitrate, potassium sulfate, sodium poly(styrenesulfonate), and sodium polyacrylate were used in comparison with the anionic polysaccharides. The electrochemical properties and stability of the obtained PEDOT films were also investigated. It was found that indium tin oxide (ITO) conductive glass could be used as the working electrode of the electropolymerization of EDOT and that

the dopant had a great influence on polymerization potential and overoxidation potential. These charged biomolecules of anionic polysaccharides were found to facilitate electropolymerization of EDOT instead of common doping anions as counterion. The electroactive PEDOT films doped with anionic polysaccharides showed stable electrochemical properties, good texture, and adhesion properties to the ITO conductive glass. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 855–863, 2012

Key words: conducting polymers; polyanion; polysaccharides; biomaterials; electrochemical polymerization

INTRODUCTION

Conducting polymers, especially those based on polyanilines, polypyrroles, polythiophenes, and polyphenylenes, have received significant attention throughout the course of the past three decades owing to their tunable electro-optical properties and high degree of processability. Among the many materials that have been developed during this period, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most successful polythiophene derivatives because of its interesting properties.^{1,2} PEDOT-based polymers are currently, and will in the future be, applied in many fields such as polymeric light-emitting diodes,³ conducting polymer-based actuators,⁴ supercapacitor,⁵ corrosion protection,⁶ antistatic coatings, transparent electrodes for inorganic electroluminescent devices (indium tin oxide, ITO replacement), sensors, rechargeable batteries, electrochromic windows, and photovoltaic devices, etc.^{7–9} PEDOT is one of the few organic conducting polymers that has

successfully found its way from a laboratory curiosity into multiple technical applications.^{10,11}

Over the last 50–70 years there have been many reports indicating that electrical stimulation of tissues can elicit enhanced cellular activity. There are many tissues that have been targeted for regeneration, including nerve, bone, skin, liver, heart, cartilage, vascular, tendon, and ligament.¹² Tissue engineers are interested in making interactive scaffolds that not only perform a mechanical and physical role, but also a biological function. It is clear that electrical stimulation *in vivo* and *in vitro* leads to enhanced regeneration of some tissues including peripheral nerves.^{13–15}

While some inorganic salts and synthetic polymers such as potassium nitrate, potassium sulfate, and sodium poly(styrenesulfonate) (PSS), etc. have been used as dopants to prepare conducting polymers, some charged biomolecules, especially anionic polysaccharides may also possess the same effect. It has been reported that conjugated polymers of polypyrrole and PEDOT doped with polysaccharides of hyaluronic acid (HA) and heparin can be used as potential tissue engineering and neural electrode material.^{16–19} Polysaccharides are naturally produced polymers of simple sugar building blocks with inherently desirable bioactivity, biocompatibility, and biodegradability. It has been reported that conducting polymer-polysaccharides composites could be electroactive, biodegradable, and biocompatible

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materials and thereby could be used to enhance the regeneration of severed peripheral nerves and other tissues.^{20–22} As one of the most important derivatives of cellulose, carboxymethyl cellulose (CMC) is a typical anionic polysaccharide, whose chains are linear β (1 \rightarrow 4)-linked glucopyranose residues.²³ HA is one of the most important and ubiquitous glycosaminoglycan in vertebrate bodies with unbranched molecular chain composed of a repeating disaccharide unit of D-glucuronic acid and N-acetyl-D-glucosamine having the property of polyelectrolytes.²⁴ The primary structure of xanthan gum is a linear (1–4) linked-D-glucose backbone (as in cellulose) with a trisaccharide side chain on every other glucose at C-3, containing a glucuronic acid residue linked (1–4) to a terminal mannose unit and (1–2) to a second mannose that connects to the backbone.²⁵ Pectin is a high molecular weight heteropolymer containing a majority of galacturonic acid units that may be free (or as a simple salt with sodium, potassium, calcium, or ammonium) or naturally esterified with methanol.²⁶ Gellan gum is a linear and anionic heteropolysaccharide, the primary structure of which is composed of a linear tetrasaccharide repeat unit.²⁷ All the abovementioned polysaccharides have been widely used in food and pharmaceuticals, etc.

In this work, several kinds of PEDOT films doped with a series of anionic polysaccharides of CMC, HA, xanthan gum, pectin, and gellan gum were prepared by electropolymerization in aqueous solution. Some other dopants of potassium nitrate, potassium sulfate, PSS, and sodium polyacrylate (PAA-Na) were also used in comparison with these charged biomolecules. FTIR/structural analysis was conducted to confirm the successful electropolymerization of EDOT and that all the anions were successfully incorporated in the resulting PEDOT films. The electrochemical properties, morphology, and adhesive properties of the resulted PEDOT films were also investigated.

EXPERIMENTAL

Materials

EDOT was kindly provided by Beili Pharm Raw Material Co., Ltd. (Suzhou, China), and the purity was 99.9%. Xanthan gum (GRINDSTED® Xanthan 80) used in this study was of food grade (Viscosity 1200–1600 mPa s, 24°C, 1%KCl, Brookfield LVT, 60 rpm, spindle 3), and the pectin (GRINDSTED® Pectin FB 220) was a low-ester one, both of which were kindly provided by Danisco-China Co., Ltd. (Kunshan, China). Gellan gum was provided by Zhejiang DSM Zhongken Biotechnology Co., Ltd. (Tongxiang, China). It is a low-acetyl gellan gum, and its weight average molecular weight (M_w) is 5×10^5 . CMC was

purchased from ACROS Organics; its M_w and the degree of substitution (DS) are 2.5×10^5 and 1.2, respectively. The HA sample (M_w 1.27×10^6) was obtained from Freda Biochemistry (China) in the form of sodium salt originated from bacterial fermentation. Sodium PSS (M_w 1×10^5) was purchased from Shanghai Herochem Biology and Chemical Reagent Co., Ltd. (Shanghai, China). PAA-Na (M_w 3×10^7) was purchased from Sinopharm Chemical Reagent Co., Ltd. (shanghai, China). Potassium sulfate, potassium nitrate, and other reagents were analytical grade, and purchased from Sinopharm Chemical Reagent Co., Ltd. (shanghai, China). All the solid materials were vacuum dried at room temperature for 48 h before use.

Preparation and characterization of the PEDOT films

Electropolymerization of the EDOT monomer to form PEDOT polymer films were performed at 25°C under N₂ on a CHI604B Electrochemical Workstation using potentiostatic method (1.2 V, 600 s). A three-electrode cell was used containing an ITO or metal working electrode, a platinum counter electrode (2.0 \times 7.0 mm²), and a saturated calomel electrode (SCE) as reference electrode. The working electrodes were sealed by wax to provide a working area of 1.0 \times 1.0 cm². All the electrodes were washed by Milli-Q water, acetone, and alcohol in turn and dried in air at room temperature before use. Solutions for the experiments were prepared by adding 5 mmol EDOT into 60 mL 0.5% (weight) (polyanionic electrolytes) or 0.01 mol/L (inorganic salts) electrolytes aqueous solutions, and then agitated vigorously for 2 h. The obtained films were washed by Milli-Q water, dried in air at room temperature.

Infrared spectral (IR) spectra of the obtained PEDOT films were recorded on a Paragon 1000 FTIR spectrophotometer (Perkin-Elmer, Inc., Waltham, Massachusetts, USA). The surface morphology analysis on PEDOT films were performed with a Hitachi S-2150 scanning electronic microscope (SEM, Japan).

RESULTS AND DISCUSSION

The working electrodes

Linear sweep voltammetry (LSV) method was used to choose a suitable electrode for electropolymerization of EDOT. Stainless steel, aluminum (Al), copper (Cu), and ITO conductive glass were chosen as the working electrodes, respectively. Solutions for the experiments were prepared by adding 5 mmol EDOT into 60 mL 0.01 mol/L KNO₃ aqueous solution. Figure 1 shows the LSV curves of EDOT on different working electrodes. From 1.0 to 1.8 V, almost

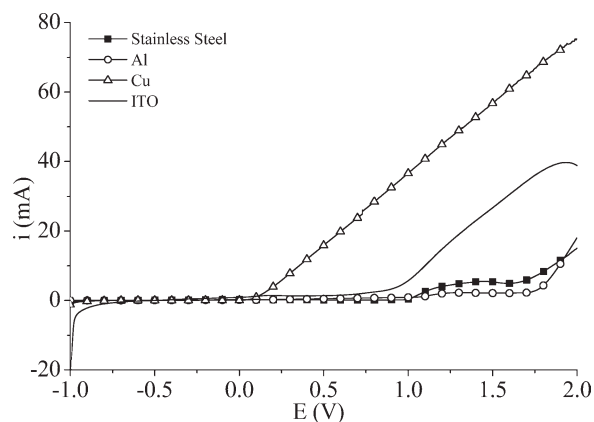


Figure 1 LSV Curves of EDOT on different electrodes in 0.01 mol/L KNO_3 solution at a scan rate of 0.05 V/s.

no current passed through the Al electrode, which is due to the protection of the dense oxide film on the surface of the metal.^{28,29} A sudden change of current began at 1.8 V, and white floccules generated as the electric potential increased. This was because the electrical breakdown of aluminum oxide film occurred at about 1.8 V, and without the protection of the dense oxide film, the Al substrate was electrochemically oxidized. The anode polarization of Cu electrode began when the electric potential was as low as 0.1 V, and blue floccules were observed as the electric potential further increased. There was no anode passivation observed in the scanning range. Stainless steel electrode had good stability before 1.0 V. However, when the electric potential was higher than 1.55 V, the current increased significantly, and anode polarization occurred. For ITO conductive glass, there was no current passing through it until the electric potential reached 0.8 V. Subsequently, PEDOT began to deposit on the surface of the electrode. An oxidation peak appeared at 1.9 V, which is related to the overoxidation and decomposition of PEDOT.³⁰

When the scanning finished, while no PEDOT was observed on the aluminum and copper electrodes, and only a bit of PEDOT appeared discontinuously on the stainless steel electrode, a homogeneous, adherent, black film was obtained on the ITO conductive glass electrode. This fact indicated that ITO conductive glass was suitable for the electrochemical polymerization of EDOT in aqueous solution.

Effect of pH of the solutions

LSV method was also used to choose a suitable pH of the solutions for electrochemical polymerization of EDOT, in which an ITO working electrode was adopted. The pH of the system was adjusted by adding 0.1 mol/L HNO_3 or 0.1 mol/L KOH solutions. It was found that at acidic conditions, EDOT

had lower polymerization and overoxidation potentials. This phenomenon was attributed to that the acid can catalyze oligomerization of EDOT and that the polymerization of the oligomer can be completed at lower potentials.³¹ It was also found that the electropolymerization could not occur if the pH of the solution was higher than 13, which was due to that the electrochemical polymerization of EDOT was based on the cationic polymerization mechanism.³² Excessive OH^- can capture EDOT^{++} or redox couple ($\text{EDOT}/\text{EDOT}^{++}$), thus hinder the reaction.³³ In the present work, the pH range for film forming was 6–8 except PAA-Na system, in which PEDOT film can only be formed under acidic conditions.

Cyclic voltammetric behaviors of EDOT in electrolyte solutions

Cyclic voltammetry (CV) analyses of the EDOT solutions were performed at 25°C to see the growth of PEDOT built through electrochemical deposition on the electrode. Figure 2 shows the cyclic voltammogram of EDOT in 0.01 mol/L KNO_3 solution with three runs. In the first cycle, the oxidation of monomer of EDOT to form a monolayer of the polymer took place at a higher potential; on the next two cycles, propagation of polymer chains and polymer precipitation were the main processes,³⁴ in which the oxidation of EDOT could take place at lower potentials. Similar behaviors were observed for EDOT in other electrolyte solutions.

Polymerization potential

The applied potential is one of the most significant parameters in the electropolymerization process. Therefore, experiments to find the highest and lowest potential values at which it is possible to obtain polymer films with satisfactory characteristics were carried out. If the electropolymerization reaction

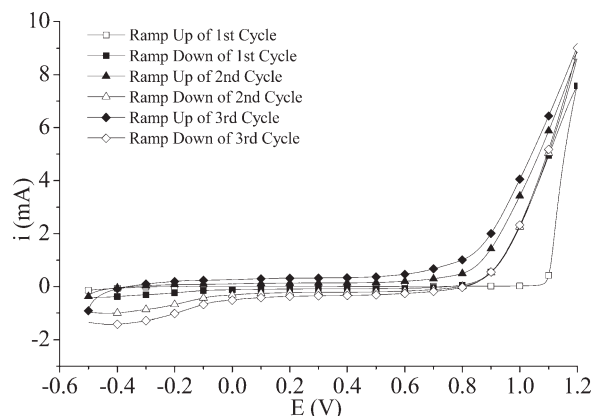


Figure 2 Cyclic voltammogram of EDOT in 0.01 mol/L KNO_3 solution at a scan rate of 0.05 V/s.

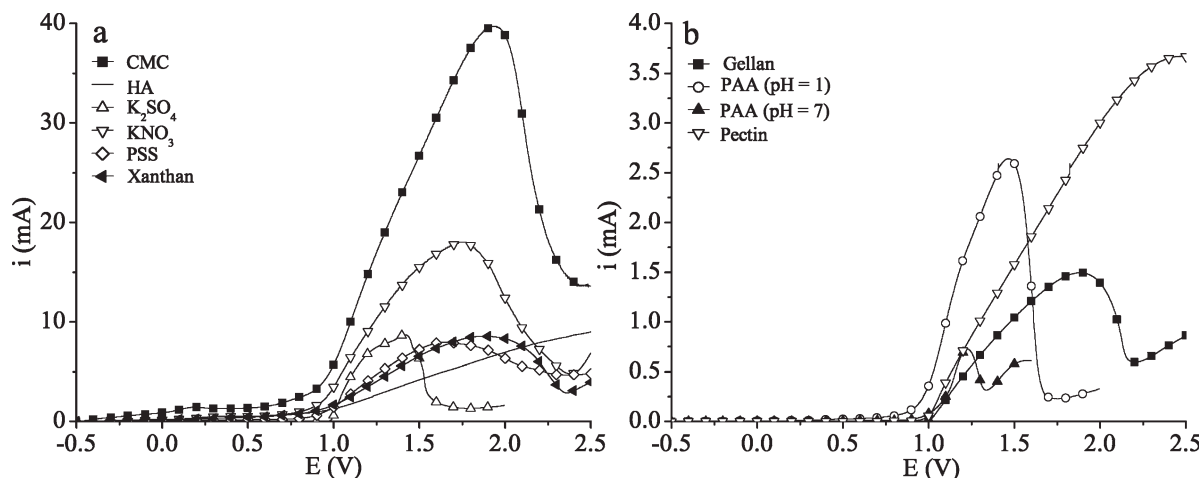


Figure 3 LSV Curves of EDOT in different electrolyte solutions at a scan rate of 0.05 V/s.

takes place at a low enough potential, the chain propagation preceding the start of deposit formation occurs for a long period of time, generating a big amount of low-weight oligomers.³⁵ On the other hand, PEDOT can be overoxidized at higher potentials, and the overoxidation may lead to the decrease of the conductivity of the conducting polymer and even the destruction of the polymer films.³⁰ Therefore, the suitable polymerization potential for the electrosynthesis of the EDOT was chosen by LSV method. Figure 3 shows the LSV curves of EDOT in different electrolyte solutions. Here, solutions for the experiments were prepared by adding 5 mmol EDOT into 60 mL 0.5% (weight) (polyanionic electrolytes) or 0.01 mol/L (inorganic salts) electrolytes aqueous solutions.

It can be seen in Figure 3(a,b) that all the LSV curves of EDOT in the nine kinds of electrolyte solutions had abrupt changes in current at about 0.95 V and oxidation peaks, which are in agreement with previously reported data.^{32,35} The abrupt change in current is related to the oxidation of monomer, adsorbed³⁰ or not³² on the electrode surface. The oxidation peak is related either to the oxidation of EDOT species diffusing close to the electrode (and/or dimers or oligomers formed during the first step), or to the overoxidation of the PEDOT film if an enough amount of polymer was deposited on the electrode.³⁶

According to Figure 3(b), the overoxidation potential for PAA (pH = 7) system was only 1.22 V, indicating that compared with others, PAA-doped PEDOT was inclined to be overoxidized at lower oxidation potential and thus the conductivity of the formed film was lost. The viscosity of PAA-Na system was much higher than others, which is detrimental to the transmission of electric charges in it, resulting in the stop of chain reaction prematurely. Anions can be doped in the backbone of the poly-

mer as compensation charges when overoxidized. PAA-Na has more charged groups than other dopants, so the oxidation can take place at a lower potential.³⁷

In addition, as shown in Figure 3, compared with other electrolytes, both pectin and HA systems had a higher oxidation and overoxidation potential. This fact indicated that the oxidation of EDOT and the overoxidations of PEDOT in pectin and HA systems were more difficult than others.

Taking account into the above influencing factors, to ensure an effective polymerization of EDOT and prevent the overoxidation of PEDOT, the polymerization potential should be higher than the oxidation potential (~ 0.95 V) and lower than the overoxidation potential. Therefore, potentiostatic experiments were performed at 1.0 V and 1.2 V, respectively, by polarizing the electrode for 600 s. At 1.0 V, after 600 s, there were black films formed on the surface of the working electrodes in KNO_3 , K_2SO_4 , PSS, and CMC solutions that have lower viscosities. For pectin, HA, gellan, PAA-Na, and xanthan solutions, which have higher viscosities, there were only little uncontinuous black substance formed on the surface of the working electrodes. At 1.2 V, after 600 s, dense black films were generated on the surface of the working electrodes in all the solutions except PAA-Na (pH 7). When the pH of the PAA-Na solution was adjusted from 7 to 1, it was found that the oxidation potential decreased and overoxidation potential increased to 1.46 V. After potentiostatic polymerizing at 1.2 V for 600 s, a dense black PEDOT film was also obtained on the electrode.

Infrared spectral analysis

Infrared spectral (IR) spectra were recorded on a Paragon 1000 FTIR spectrophotometer (Perkin-Elmer, Inc., USA) in the wavenumber range of 500–

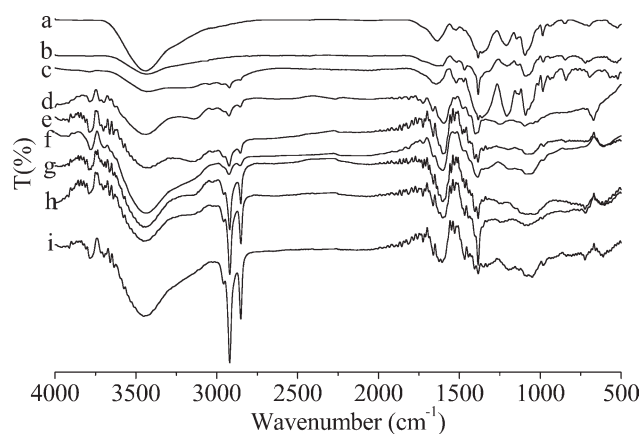


Figure 4 FTIR spectra of PEDOT doped with different electrolytes (a: K_2SO_4 , b: KNO_3 , c: PSS, d: pectin, e: HA, f: PAA, g: gellan, h: CMC, i: xanthan).

4000 cm^{-1} . As showed in Figure 4, in the infrared spectra of all the various kinds of electrolytes doped PEDOT films, the basic characteristic bands of PEDOT can be found. The peaks at $1540\text{--}1480\text{ cm}^{-1}$ were attributed to asymmetric $C_\alpha=C_\beta$ stretching,

and the peak at 1440 cm^{-1} was assigned to symmetric $C_\alpha=C_\beta$ stretching. The peak at 1384 cm^{-1} was ascribed to $C_\beta-C_\beta$ stretching, and the peaks originated from the stretching in the alkylenedioxy group were observed at 1208 cm^{-1} .³⁸ The vibrations at ~ 1320 and 1510 cm^{-1} were attributed to C—C or C=C stretching of quinoidal structure of thiophene ring and ring stretching of thiophene ring, respectively. C—S bonds in the thiophene ring were also seen at $980, 833,$ and 685 cm^{-1} .^{39,40} Vibrations at $1185, 1140\text{--}1125, 1090\text{--}1070\text{ cm}^{-1}$, and $1060\text{--}1045\text{ cm}^{-1}$ were originated from C—O—C bond stretching in the ethylenedioxy group.^{41,42}

In the IR spectra of KNO_3 , K_2SO_4 , and PSS doped PEDOT films, the absorption peaks at $722, 840,$ and 1380 cm^{-1} were assigned to NO_3^- , and the peaks at $620, 728,$ and 1142 cm^{-1} belonged to K_2SO_4 .⁴³ The peaks at 1043 and 1296 cm^{-1} were attributed to the absorption of the $-SO_3H$ group.⁴⁰ These proved that the obtained PEDOT was in the doped state. In spectra for films doped by other polyanions, the absorption band at 1607 cm^{-1} was due to the asymmetrical COO^- stretching vibration, whereas the band at

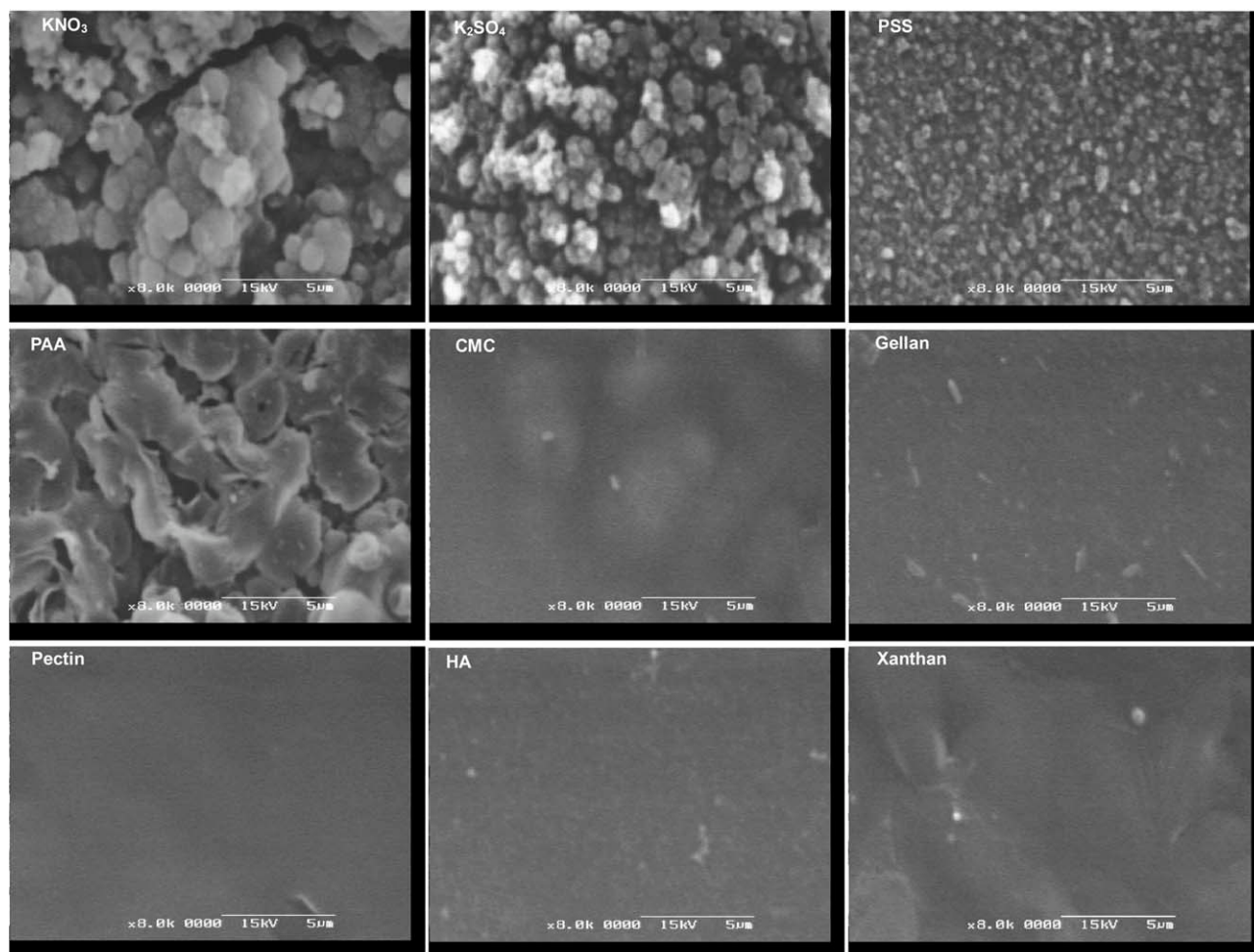


Figure 5 SEM images of PEDOT films doped with different electrolytes.

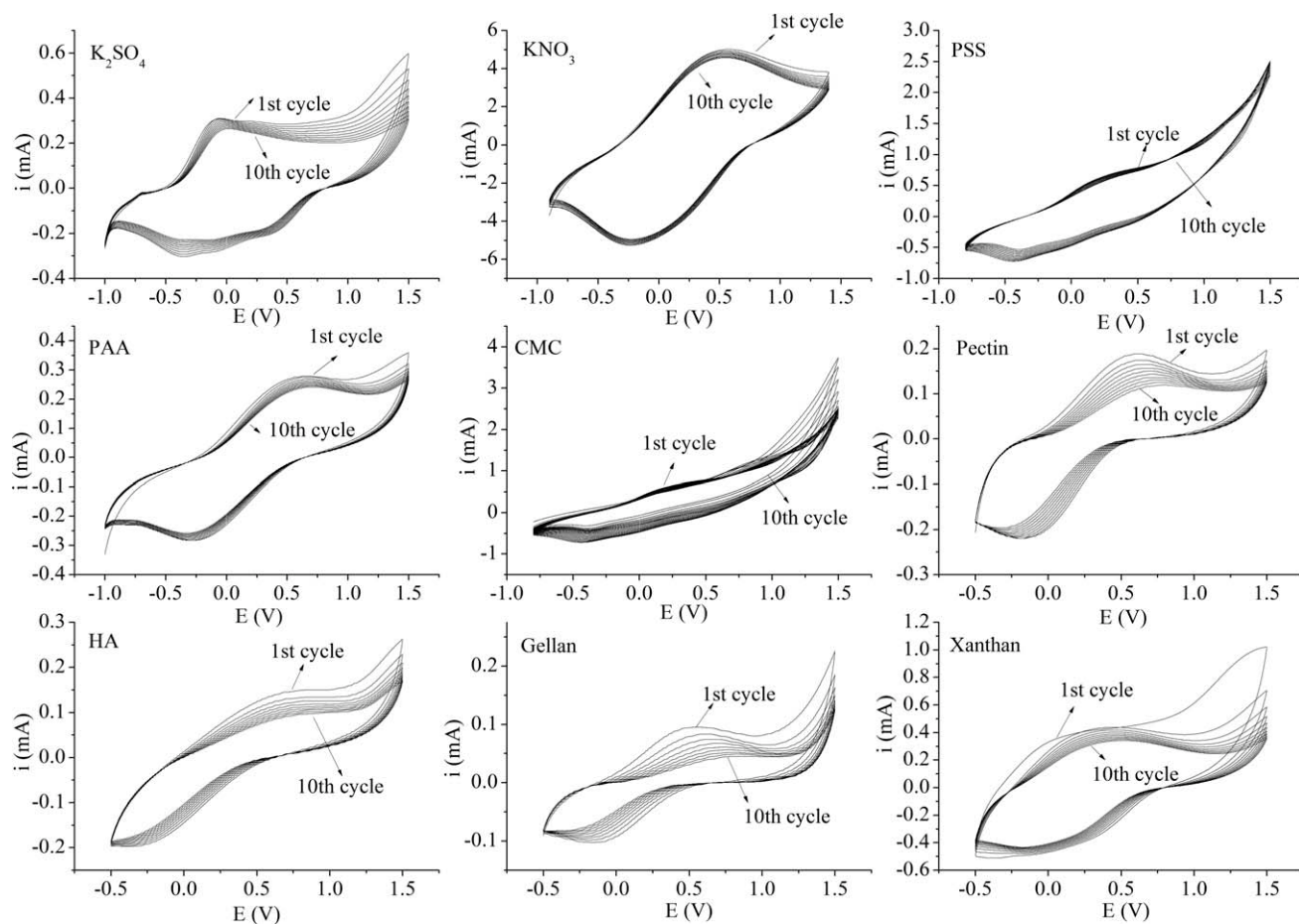


Figure 6 Cyclic voltammogram of PEDOT films doped with different electrolytes at a scan rate of 0.05 V/s.

1432 cm^{-1} was due to the symmetrical COO^- stretching vibration,⁴⁴ which proved that the resulting PEDOT films were doped by polyanions with carboxyl groups. In addition, the broad band at about 3440 cm^{-1} was assigned to the stretching vibration modes of OH groups and the two peaks at 2920 cm^{-1} and 2850 cm^{-1} were assigned to the stretching vibration modes of CH_2 . These infrared spectra confirmed that all the anions were successfully doped into the PEDOT films.

Surface morphology analysis

Figure 5 exhibits the SEM images of PEDOT films doped by different electrolytes which resulted in different morphologies. While the films doped with inorganic salts were porous with a cauliflower-like morphology, the films doped with polysaccharides were well textured and compact, which should be related to the high molecular weight, electron-rich groups, strong steric hindrance of polyanions, and the high viscosities of the polysaccharide solutions. A slower doping process might result in a denser film. Meanwhile, the departure of polyanions was relatively difficult due to their big size. The polysac-

charides with high molecular weights could be immobilized and therefore, the obtained composite films were more uniform, dense, and smooth.

Electrochemical behavior of PEDOT films

It is known that at high potentials, oxidation can occur in position 3- or 4- of the thiophene rings, thus degrading the conducting polymer by breaking the conjugation in the polymer backbone. The presence of a substituent such as the alkylendioxy group avoids this type of degradation. Therefore, PEDOT is considered as one of the most stable conducting polymers reported to date.^{11,45} In the present work, CV was used to investigate the electrochemical stability of PEDOT doped with different electrolytes. CV measurements of the PEDOT films were performed in 0.01 mol/L KNO_3 solution at a scan rate of 0.05 V/s. Cyclic voltammograms of PEDOT films doped with different electrolytes are shown in Figure 6. During CV measurements, the coating underwent reduction and oxidation due to movement of counterions in and out of the PEDOT coatings. It is known that the reduction potentials of conducting polymers are strongly affected by

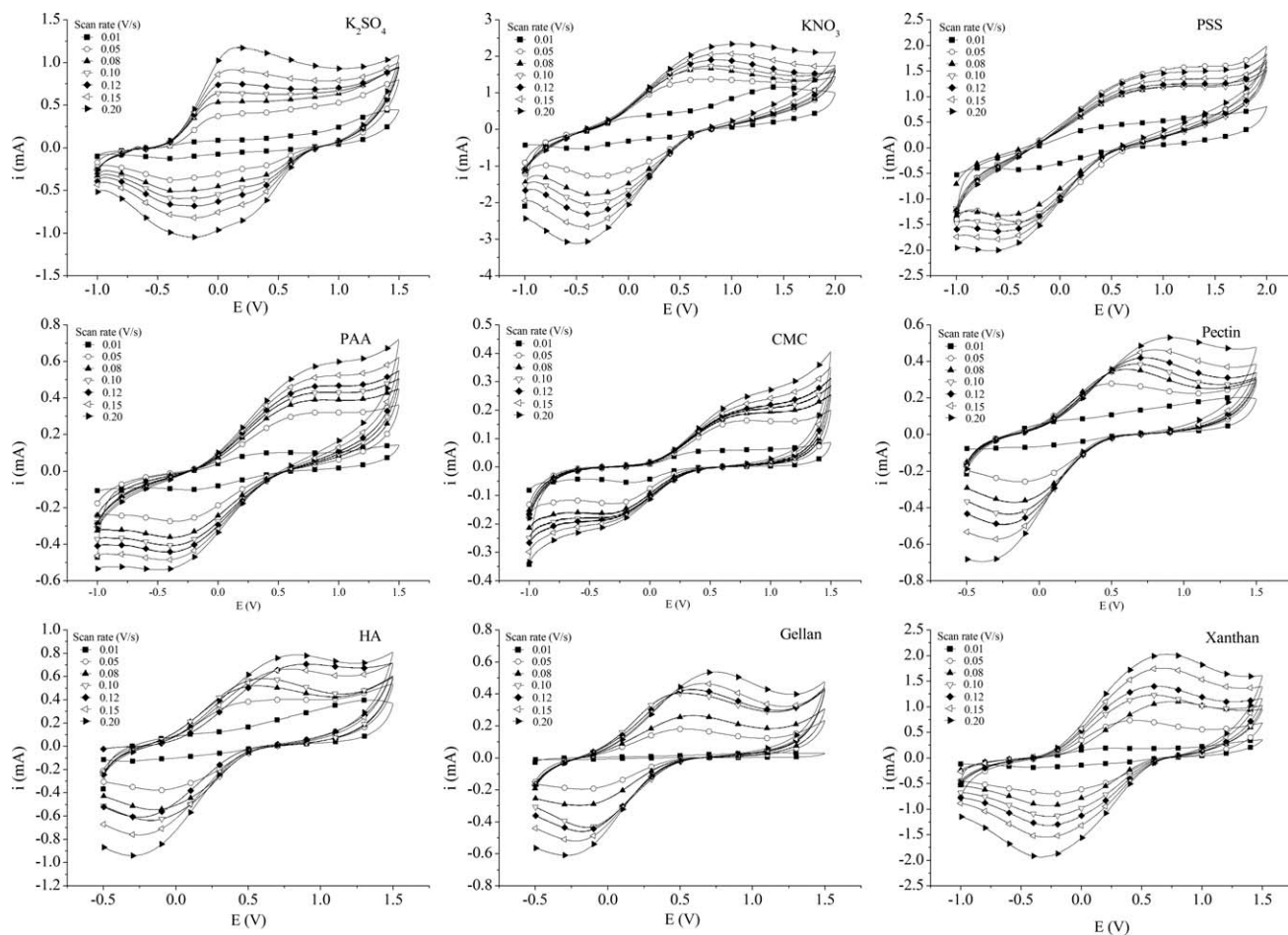


Figure 7 Cyclic voltammogram of PEDOT films doped with different electrolytes at various scan rates.

electrosynthesis conditions, the identity of the dopant anion used, and the nature of the switching electrolyte. The reduction potentials of the PEDOT films doped with different electrolytes were -0.36 V (K_2SO_4), -0.23 V (KNO_3), -0.43 V (PSS), -0.30 V (PAA), -0.41 V (CMC), -0.20 V (pectin), -0.38 V (HA), -0.24 V (gellan), and -0.33 V (xanthan), respectively. Lower reduction potentials can give the polymers remarkable stability in the conducting, oxidized form and renders them immune to strong biological reducing agents.⁴⁶ According to Figure 6, the cyclic voltammograms of PEDOT films doped with every kind of electrolytes showed only very small changes through multiple cycles. This demonstrates the good electrochemical stability of PEDOT-polyanion composites.⁴⁷

Figure 7 shows the CV curves of PEDOT films doped with different electrolytes at different scanning rates from 0.01 to 0.2 V/s. Obviously, these copolymer films were cycled repeatedly between doped and dedoped states without significant decomposition, indicating the high stability of PEDOT films.^{48–50} Figure 8 shows that the peak currents are directly proportional to the potential scan

rates, indicating that electrochemical processes are not diffusion controlled, in agreement with other reports on PEDOT films.^{48,51–53} In addition, these processes are reversible, even at very high scan rates. These experimental results also demonstrated that the PEDOT films were electroactive and adhered well to the electrode.^{48,53}

Delamination resistance test

Delamination resistance tests for the PEDOT films were carried out based on the International Standard ISO 2409 : 2007(E),⁵⁴ which describes a test method for assessing the resistance of paint coatings to separation from substrates when a right-angle lattice pattern is cut into the coating, penetrating through to the substrate. The property measured by this empirical test procedure depends, among other factors, on the adhesion of the coating to either the preceding coat or the substrate. The number of cuts in each direction of the lattice pattern is six, and the spacing of the cuts in each direction is 1 mm. According to the standard, it was found that PEDOT doped with inorganic salts could be classified to 3–5

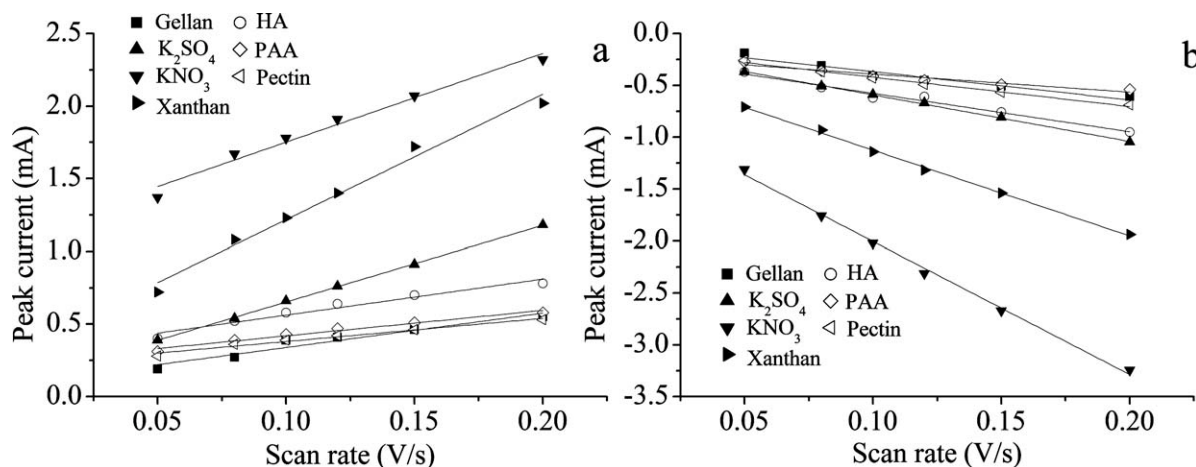


Figure 8 Peak current of PEDOT films doped with different electrolytes at various scan rates (a: oxidation, b: reduction).

classification, i.e., the coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A crosscut area greater than 15% is affected, whereas the PEDOT doped with polysaccharides could be classified to 0–2 classification, i.e., the edges of the cuts are completely smooth or the coating has flaked along the edges but the crosscut area not greater than 15% is affected. PEDOT films doped with polysaccharides had good peel strength in comparison with those doped with inorganic salts, which should be related to the high molecular weight of polysaccharides that enhances the cohesiveness of the films.

CONCLUSIONS

Stable, well textured PEDOT films doped with anionic polysaccharides were prepared by potentiostatic polymerization. The optimum working electrodes, potential range, and pH to obtain the electroactive PEDOT films were determined from the experiments of LSV. The FTIR spectra confirmed that all the anions were successfully doped into the PEDOT films. ITO conductive glass was suitable for the electrochemical polymerization of EDOT in aqueous solution and the potential should be about 1.2 V which was between the oxidation potential and the overoxidation potential of EDOT in the solutions used. It was found that at acidic conditions, EDOT had lower polymerization and overoxidation potentials, and the optimum pH range for film forming was 6–8 except PAA-Na system, in which PEDOT film could only be formed under acidic conditions. Experimental results showed that the dopant had a significant influence on the electrochemical synthesis and the property of the PEDOT film. The PEDOT films doped with natural anionic polysaccharides

were smoother and denser than those doped with inorganic salts and synthetic polyanions, processing stable electrochemical properties and better adhesion properties to the ITO conductive glass.

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