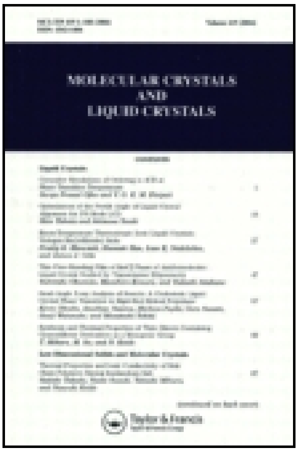

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Electrosynthesis of Electrochromic Poly-3,4-ethylenedioxythiophene – Polyaniline Hybrid Layers

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The poly-3,4-ethylenedioxythiophene (PEDOT) – polyaniline (PANI) electrochromic films are obtained by the electrochemical polymerization of EDOT on the indium tin oxide (ITO) surfaces modified by a thin film of PANI. It is shown that the anode synthesis of PEDOT on the ITO electrode modified by PANI leads to a significant improvement of the contrast ratio and changes a potential limit of the electrooptical activity of the obtained layer as compared with the individual polymer films.

Keywords Electrochemical polymerization; electrochromic film; polyaniline

Introduction

A great interest in opto-electronic devices based on conducting polymers such as "smart windows," optical memories, IR-switching, electrochromic displays [1–5] requires a creation of electrochromic materials working in a wide spectral range – from the near UV region to the visible and near IR-ones. Such devices are based on the electrochromic effect – the changes in the optical spectrum (and color) in a polymer layer under an external electric field [2]. The conjugated polymers based on heterocyclic compounds, particularly, poly-3,4-ethylenedioxythiophene (PEDOT), exhibit electrochromic transitions in a wide potential range [1] with mono color change observed from light blue in the doped state to dark blue in the undoped state with contrast ratio near 30–40% [3]. An interesting multichromic material is a polyaniline (PANI) characterized by a high electrochemical activity in the anode potential range [6,7], but it contrast ratio also is not high (27–30%). The aim of the work is the investigation of the possibility to improve the electrochromic properties of polymer films by the electrochemical anode synthesis of PEDOT on the electrode surface modified by polyaniline.

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Experimental

Materials

The monomers 3,4-ethylenedioxythiophene (EDOT) and aniline purchased from the Aldrich Chemical Co. were used. All solutions were prepared on distilled acetonitrile. As a supporting electrolyte, anhydrous $LiClO_4$ was employed. Films were obtained on the transparent surface of indium-tin-oxide glass (SCHOTT, Korea) with a resistance of 20 Ohm/sq. with a visible transmission of >80%.

Instrumentation

Optical absorption spectra in the UV-visible-near-IR region were obtained with a spectrophotometer SP-46 in the spectral range 320...900 nm at $T = 293$ K. To study the electrochromic properties of the films, a quartz cell disposed in the work camera of a spectrophotometer and connected by the three-electrode circuit with a potentiostat PI-50M has been used. The film thickness was estimated by an interferometer MII-4. The film morphology was studied with help of an optical microscope "Micromed XS-2610."

Film formation methods

The polymer films on the ITO surface were obtained by the electrochemical polymerization of a 0.1 M EDOT solution in acetonitrile in the presence of 0.1 M $LiClO_4$ under the potential cycling between 0 and 1.5 V at the sweep rate $v = 20$ mV/s. The sweep cycle number (N) regulated the film thickness. The glass plate (an area of 2.5 cm^2) coated by ITO was used as a working electrode. The counter electrode acted as a platinum wear, whereas Ag/AgCl was used as a reference electrode.

Results and Discussion

During the process of electrochemical polymerization of EDOT on the ITO electrode surface, a monomer oxidation in the first cycle of sweeping was observed at the potential $E = 1.1 - 1.3$ V (Fig. 1). The repetitive sweeping of the potential causes the appearance of an irreversible anodic peak at $E = 0.4 - 0.5$ V. The peak current grows with the cycle number (N), which evidences the formation of an electroactive polymer layer on the electrode surface.

The PEDOT films of a controlled thickness (280–320 nm) were electrodeposited on the ITO surface as a result of 15–20 cycles of the potential scanning between −0.2 and +1.2 V. The chemical structure of PEDOT is presented in Figure 2(a).

As found by optical microscopy, the PEDOT film obtained on the ITO surface is characterized by a structural disordering with the formation of dark-blue microcrystals embedded in the amorphous polymer matrix (Fig. 3a). This film loses its electrochemical activity in repetitive cycles of the electrochemical doping-dedoping process (Fig. 3b) due to, perhaps, the disordered amorphous – crystalline structure of the main mass of PEDOT and to the absence of a significant electrical contact between the semiconductor ITO surface and the conjugated polymer layer of PEDOT.

The copolymerization of PEDOT with other conducting polymers or polyelectrolytes results in improving the functional properties of the films and giving them

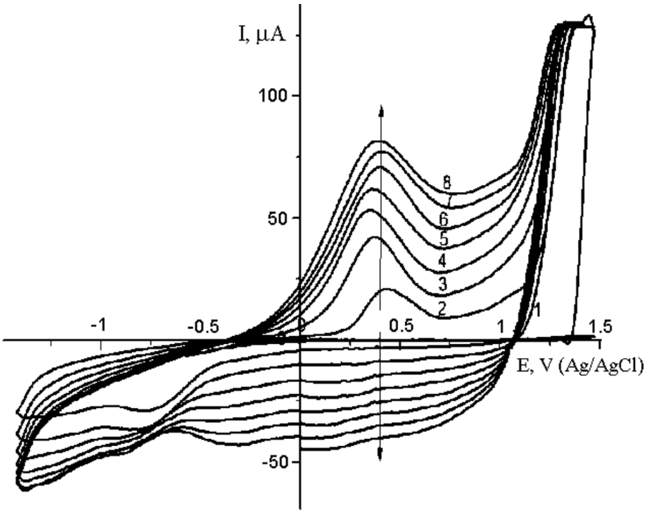
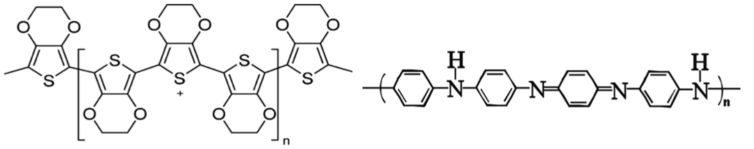


Figure 1. Cyclic voltammograms obtained on the ITO electrode during the electrochemical polymerization of a 0.1 M EDOT solution in 0.1 M $LiClO_4$ in acetonitrile. Sweep rate is 20 mV/s. The ciphers indicate a number of the potential sweeping.

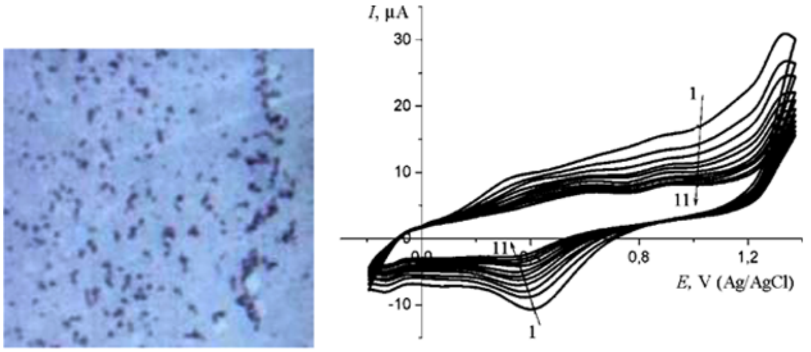
new features by changing the electron structure of a polymer [8–11]. To improve the PEDOT film morphology and the adhesion to the electrode surface, we studied a possibility of the electrochemical polymerization of EDOT on the modified ITO surface. The electrode surface was modified by a thin PANI layer obtained by the electrolysis of a 0.01 M aniline solution in acid electrolyte at a current density of $0.05\,mA/cm^2$ for 20 s. As was previously shown by electron microscopy [12], a PANI layer 50–60 nm in thickness obtained under such conditions is uniform and fully amorphous. In the optical microscopic investigation, a layer of PANI has a uniform compact morphology and green color, which suggests that PANI is in a high conductive emeraldine-color form (chemical structure is shown in Fig. 2b).

The obtained PANI layer exhibits a high electrochemical activity in the potential interval $E = -0.2$–1.2 V (Fig. 4, drop line). For the PANI layer in an acetonitrile electrolyte, two main peaks of the anode current and two corresponding peaks of the cathode current are observed. The anode waves may be assigned to the oxidation of the nonconductive leucoemeraldine form of PANI into a conductive emeraldine cation-radical at $E = 0.25$–0.45 V with the next oxidation to a bication ($E > 0.5$ V) and the formation of a pernigraniline form at $E > 1.0$ V [13].



(a) (b)

Figure 2. Chemical structure of poly-3,4-ethylene dioxythiophene (a) and polyaniline (b).



(a) (b)

Figure 3. (a) Optical microphoto (x 500) of the obtained PEDOT film on the ITO glass; (b) cyclic voltammograms of a PEDOT film in a 0.1 M $LiClO_4$ acetonitrile solution at $\nu = 40\,mV/s$. The ciphers correspond to the number of scan cycles.

A process of electrochemical polymerization of EDOT on the PANI modified electrode proceeds in the interval of *E* corresponding to potentials of PANI electrochemical activity. In this potential range, a polymer is in a highly conductive polaron-bipolaron state [14] and serves as a mediator of the electron transfer between electrode surface and EDOT monomer molecules. An electrocatalytic action of polyaniline nanolayer leads to a reduced oxidative potential of EDOT and flowing the polymerization in the potential range from 0.5 to 1.0 V.

It may be suggested that, as a result of the EDOT chemosorption on a PANI nanolayer and the electron transfer between the electrode surface with the conductive PANI layer and EDOT monomer molecules, the graft copolymerization leading to the formation of a PEDOT-PANI hybrid layer can proceed. This would lead to a significant improvement of the adhesion of polymer films to the electrode surface and a change of their optical properties.

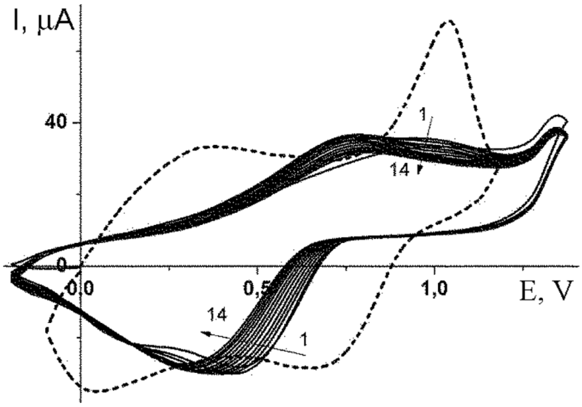
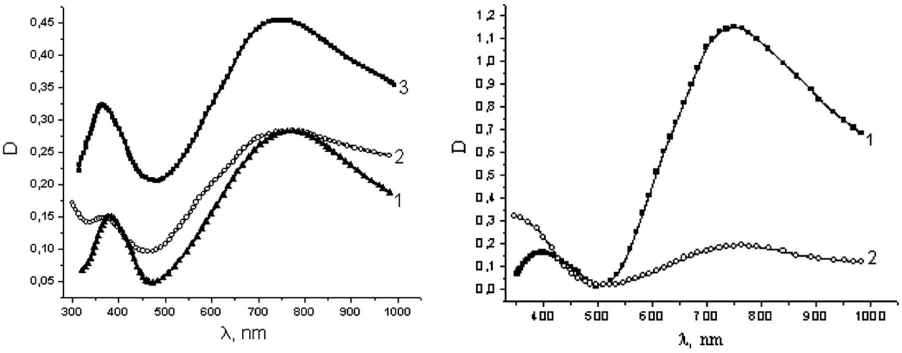


Figure 4. Cyclic voltammograms obtained during the electrochemical polymerization of 0.1 M EDOT in 0.1 M $LiClO_4$ in acetonitrile on the ITO electrode coated with a PANI layer (60 nm in thickness) at a sweep rate of 20 mV/s. The ciphers indicate the cycle number (*N*). Drop line corresponding to a PANI film in a blank solution in of 0.1 M $LiClO_4$ in acetonitrile.



(a) (b)

Figure 5. (a) Optical spectra of polymer films on the ITO surface: 1 – PEDOT, 2 – PANI, 3 – PEDOT-PANI. (b) Optical spectra of a PEDOT – PANI film on the ITO surface at the cathodic and anodic polarizations: $E = -0.6\,\mathrm{V}$ (1); $E = +0.8\,\mathrm{V}$ (2). The thickness of films is $320 \pm 25\,\mathrm{nm}$.

The optical spectra of the individual and obtained hybrid layers are characterized by two main absorption bands at $\lambda = 380$–$400\,\mathrm{nm}$ ($\pi - \pi^*$ transition in the band gap) and $\lambda = 700$–$750\,\mathrm{nm}$ (absorption of free carriers in the polaron – bipolaron band [6,7]).

The optical spectrum of the hybrid layer repeats generally the spectrum shape and the characteristics of absorption bands for the PEDOT layer (Fig. 5a, curve 1) with some "red" shift in the position of the absorption maxima and a significantly higher optical density.

The evidence of the "hybrid" formation is a color as that of a "sea wave" for the obtained layer and its ability to electrochromic transitions in a wide potential range from $E = -1.1\,\mathrm{V}$ to $E = +1.2\,\mathrm{V}$. Such an interval of electrochromic transitions is significantly different from that observed for PANI films: from $-0.2\,\mathrm{V}$ (colorless leucoemeraldine) to 0.2–0.4 (green emeraldine form) 0.6–0.8 V green-blue mixed emeraldine-pernigraniline and near 0.9 V – dark blue and black pernigraniline [6,7] and does not align with the interval of PEDOT electrochromic transitions [10]. Simultaneously, a significantly higher contrast ratio achieves 60–70% at a wavelength of 750 nm which is a very good performance for organic electrochromic displays [1,2].

Conclusion

The EDOT polymerization on a PANI nanolayer occurs in the potential range corresponding to the electrochemical activity of PANI served as a mediator of the electron transfer from the electrode to a monomer molecule. The electrosynthesis of PEDOT on the PANI-modified ITO electrode leads to a significant improvement of the contrast ratio and the electrooptical activity of the hybrid layer as compared with individual polymer films.

Acknowledgment

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