

Electrostatic layer-by-layer assembly of poly-3,4-ethylene dioxythiophene functional nanofilms

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Method of electrostatic layer-by-layer assembly is used for preparation of the ultra thin functional films based on anionic complex of poly-3,4-ethylene dioxythiophene (PEDOT) — polystyrene sulfoacid (PSS) on the surface of the transparent indium-tin-oxide substrates. For the first time *N*-cetyl pyridinium chloride (CPC) was used as a cationic surfactant. It has been shown that nanofilms obtained in the presence of CPC demonstrate the optical properties and electrochemical behavior similar to PEDOT-PSS functional films that promises their application in electrochromic devices.

Метод электростатической послойной сборки использован для получения функциональных пленок анионного комплекса поли-3,4-этилендиокситиофена (ПЕДОТ) с полистиролсульфокислотой (ПСС) на поверхности прозрачных индий-станнум оксидных субстратов. В качестве катионного поверхностно-активного вещества впервые использован *N*-цетилпиридиний хлорид (ЦПХ). Показано, что тонкие пленки, полученные в присутствии ЦПХ, демонстрируют оптические свойства и электрохимическое поведение, свойственное функциональным пленкам ПЕДОТ-ПСС, что предполагает возможность их применения в электрохромных устройствах.

1. Introduction

Development of a new generation of functional materials that combine the optical properties of semiconductors with the flexibility, thermoplastic processing and lightness of polymers requires the creation of effective methods for formation of nanoscale films of these materials on the surfaces of various types. For the working out of modern organic displays, flat panels, hybrid solar cells it is needed to obtain thin organic layers with electro-optical and electrochromic properties [1–3] on transparent conducting substrates. Numerous organic

substances exhibit an ability to electrochromic behavior [2], but the conjugated polymers with intrinsic electron conductivity such as polyaniline and its derivatives [4, 5], poly-3,4-ethylene dioxythiophene (PEDOT) [1–3, 6] attract the greatest attention, due to its high conductivity, stability and capacity for reversible color change and thus the optical spectrum under the electric field over a wide region of potentials. Currently, the most promising electrooptical polymer is PEDOT [2, 3, 6, 7], as improved methods of obtaining thin films of this polymer is an important and actual task. To prepare thin layers of PEDOT on conductive surfaces tra-

ditionally it is used the method of electrochemical polymerization of monomer — 3,4-ethylenedioxythiophene [2, 7]. For obtaining PEDOT films practically on any surface recently it is widely used aqueous dispersion of pre-synthesized polymer PEDOT stabilized by polymeric anion of polystyrene sulfonic acid (PSS), which is produced industrially [1–3].

For formation of thin layers from aqueous dispersion of PEDOT-PSS on different surfaces the methods of screen printing [8], inkjet printing [9] and others may be utilized. Conductive layers on glass or other surfaces can be obtained at spreading centrifugation (spin-coating) of PEDOT-PSS dispersion [10, 11]. Also the method of substrate immersion (dip-coating) in the dispersion of PEDOT-PSS [12] is convenient. For a given coating thickness obtaining these techniques require accurate speed control of the substrate removal from solution (dip-coating) or rotation (spin-coating), which is provided by special equipment and automated computer control system.

Similar to these methods a method of layer-by-layer assembly (LBL) [1, 3, 6] is promising because of its simplicity and the possibility of direct control of the film thickness by the number of deposited layers. The method requires no special equipment, thus providing the possibility of forming coatings regardless of the surface type [13] and applying alternating layers of different nature and functionality [1, 3]. LBL method is relatively new and in modern nanotechnology is applied for obtaining films that perform certain functions in an electric field [1–3]. In this case, for reliable film contact with the conductive substrate (electrode) it is necessary to provide sufficient adhesion that is not always achieved in the technology "spin or dip-coating". The above methods are used to form films of PEDOT-PSS [4, 5], but mainly — single layer. However, in the multilayer films obtained by "spin- or dip-coating" the adhesion between the layers is insufficient, which causes nodules and uneven.

The formation of multilayered polymer films via the LBL assembly technique utilizes the electrostatic interaction between oppositely charged molecules of anionic and cationic types. The anionic surfactant creates a negative charge on the surface of substrate, while the cationic surfactant creates a positive one. As rule, the surfactant is selected from a series of polyelectrolytes such as: polydiallyldimethyl ammonium

chloride, polyallylamine hydrochloride, vinylbenzyltrimethyl dodecylammonium chloride (cationic type), polyacrylic acid and polystyrene sulfonate or others (anionic type) [6, 14]. An inclusion of the inert polymer particles into the electrochromic polymer material decreases an optical transmittance and causes of turbidity of the film due to light dissipation or light absorption by globules of polymer electrolyte [6] or insertion of polycation in the layer of PEDOT [14]. Consequently, the optical spectra of PEDOT films unclear, they are difficult to isolate specific absorption band — which reduces the information content of optical studies. In some cases, an increasing the resistivity of multilayer structure almost in order of magnitude takes place [15] by the proper resistance of relatively thick film of the polymer surfactants, which leads to a significant deterioration of the electrochemical activity of the resulting multilayer structure.

One of the ways to improve the technology of LBL assembly of polymer films can be the usage of cationic surfactants with low molecular mass, but this question today is insufficiently studied. Due to the high adsorption activity and small molecular weight as cationic surfactants in technology LBL we first used — *N*-alkyl(cetyl) pyridinium chloride.

The aim was to investigate the physical and chemical properties and patterns of self-assembled multilayer films of PEDOT-PSS on the surface of transparent substrates using *N*-cetyl pyridinium chloride as cationic surfactant.

2. Experimental

Poly-3,4-ethylenedioxythiophene (PEDOT) in the form of aqueous suspension of polymer stabilized by anionic surfactant — polystyrene sulphonic acid (PSS) with a content of 1.3–1.7 % PEDOT-PSS was purchased from the Aldrich. As cationic active surfactant we used the high purity *N*-cetyl pyridinium chloride (CPC) monohydrate (Merck). Chemical structures of the anion stabilized polymer and cationic surfactant are presented in Fig. 1.

All solutions were prepared using twice distilled water at room temperature. Water dispersion of PEDOT-PSS was diluted by water to concentration of 0.08 wt. %. The concentration of CPC was of 0.05 wt. %. The films were assembled on the glass surface, coated with transparent semiconductor surface of ITO (indium-tin-oxide) (SHOTT

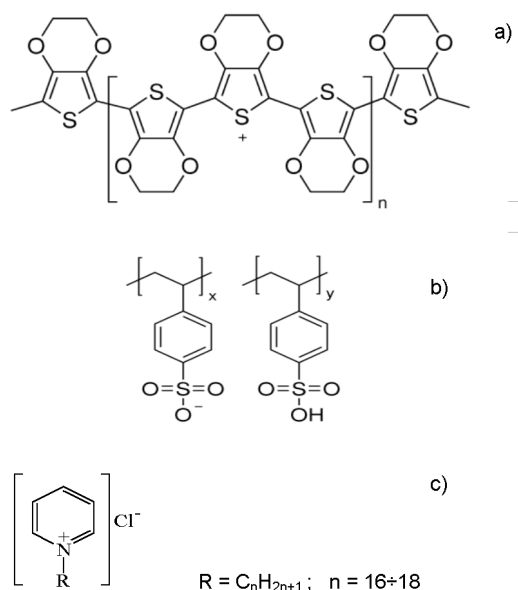


Fig. 1. Structure formula of poly-3,4-ethylene dioxothiophene (PEDOT) (a), polystyrene sulphonic acid (PSS) (b) and cationic surfactant — *N*-cetyl pyridinium chloride (CPC) (c).

Korea), treated with *N*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane to make the substrate surface hydrophilic.

Optical absorption spectra in UV-visible-near-IR region were obtained with spectrophotometer SP-46 at the $T = 293$ K. Film thickness was measured with laser zero-ellipsometer LEF-3M-1 ($\lambda = 632.8$ nm), by 4-bands method [16].

To study an electrochemical activity of the films obtained a three-electrode cell was employed [5]. ITO glass with multilayer polymer nanofilm was used as a working electrode. The counter electrode was platinum wire and as a reference the saturated Ag/AgCl electrode was employed. 0.1 M LiClO₄ solution in acetonitrile was used as a support electrolyte.

3. Results and discussion

The PEDOT-PSS/CPC films were prepared by alternately electrostatic adsorption process. When cationic surfactant — CPC was dissolved in water, it dissociates with formation of surface active cation $[C_nH_{2n+1}NC_5H_5]^+$ which has a high ability to adsorb on the solid surface. The pre-treated positively charged substrate was firstly immersed in the PEDOT-PSS solution for 10 min as counter anion layer to produce a bilayer [6]. Second and next routes of deposition include an immersing in CPC solution, in water, in anionic polymer solution,

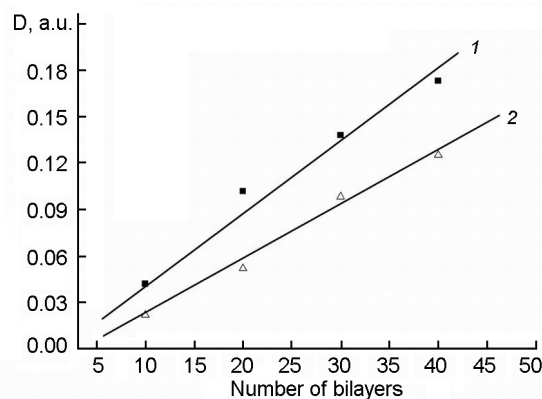


Fig. 2. The relationship between optical absorption of PEDOT-PSS/CPC films and the number of bilayers at $\lambda = 380$ nm (1) and 660 nm (2).

in water and then drying with nitrogen gas after washing with distilled water. The drying procedure between the adsorption of cationic or anionic layers was necessary for obtaining of uniform, self-assembled layers. To monitor the growth process of these LBL multilayers a UV-vis spectroscopy was used.

It was found that the compact uniform films of PEDOT-PSS/CPC with varying thickness were deposited in result of 8–40 routes of alternate adsorption of cationic surfactant and anionic polymer complex. As showed by optical spectroscopy, an increase of the bilayers number during the films formation process leads to rising optical absorption of polymer layer (Fig. 2).

Optical absorption of the films at 380 nm and 660 nm increases uniformly with the bilayer number. It indicates that a progressive assembly runs regularly with almost equal amount of deposition in each cycle. It should be noted that the linear relationship between the film thickness or optical absorption and the number of layers is not always observed in the case of polymeric cationic surfactants such dependence is typically exponential [6].

Simultaneously increasing of absorption intensity by polymer layer with growing its thickness does not change a shape of spectrum, but has certain effect on the position and relative intensity of the absorption bands (Fig. 3).

Multilayer films PEDOT-PSS/CPC obtained from 10 and more bilayers are characterized by absorption spectrum, which consists of two distinct bands: the first with maximum at 380–390 nm indicates the existence of localized polarons and corresponds to $\pi \rightarrow \pi^*$ transition in the chain of

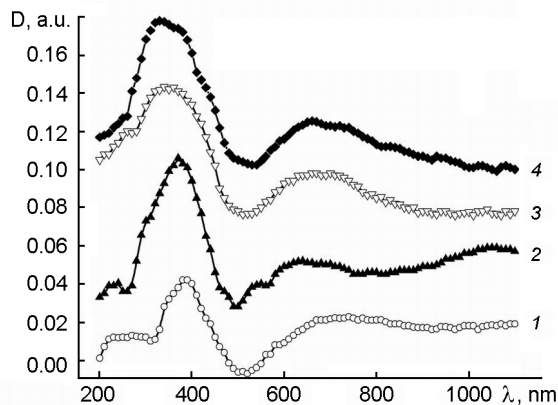


Fig. 3. Absorption spectra of the self-assembled PEDOT-PSS/CPC nanofilms deposited on the ITO substrate by LBL method. Number of bilayers: 10 (1), 20 (2), 30 (3); 40 (4).

conjugation [2, 6, 7]. The second broad band exhibits the maximum at 600–800 nm attributed to vibronic coupling and indicates the possibility of the inter-chain π -stacking interaction of thiophene rings [17]. With increasing film thickness, along with common rising absorption the shift of the first band to short wavelength region with higher energy is observed. For thicker films (30 or 40 bilayers) the second band with maximum at 650–680 nm also exhibits some shift of the absorption to short wavelength region of the spectrum as compared with thinner layers. An existence of the optical absorption at $\lambda > 800$ nm extended to near IR region may be attributed to both polarons and bipolarons (as delocalized charge carriers) which form their own band [18]. The spectra obtained confirm the formed electronic structure of nanofilms as well as that the optical transitions are caused by localized and delocalized charge carries.

To investigate the electrochemical behavior of the multilayer nanofilms of PEDOT-PSS/CPC the method of cyclic voltammetry was employed. Fig. 4 shows cyclic volt-ampere curves obtained for the multilayer PEDOT-PSS/CPC films prepared on the ITO surface by LBL deposition.

Presented cyclic voltammograms demonstrate a high electrochemical activity of the LBL multilayer PEDOT-PSS/CPC film in potential range of $E = -0.2 \dots 1.2$ V with reversible redox maximums in the interval of $E = -0.2 \dots 0.6$ V (Fig. 4). Increase of the anodic and cathode peak current with number of potential sweep scans illustrates the presence of electroactive polymer layer on

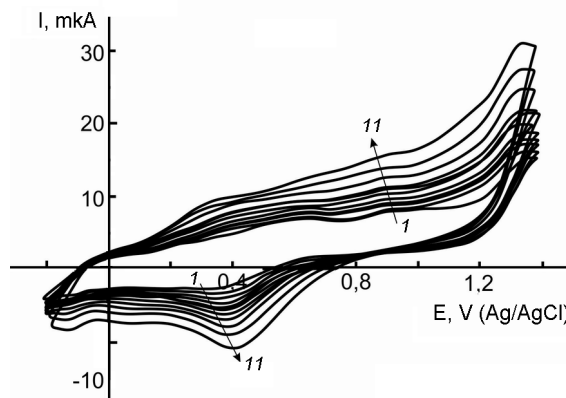


Fig. 4. Cyclic voltammograms of twenty bi-layer PEDOT-PSS/CPC film on the ITO glass plates in 0.1 M LiClO₄ solution in acetonitrile at potential sweep rate of 40 mV/s. The ciphers correspond to number of scan cycles.

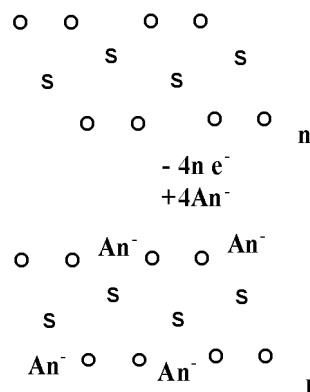


Fig. 5. Scheme of electrochemical reactions in PEDOT-PSS films in the doping-dedoping process (An⁻ — anion of electrolyte, for instance, ClO₄⁻).

the electrode surface and may be caused by electrochemical doping of the films [2, 6]. Redox processes in PEDOT films at potential switching probably carry out by the scheme presented in Fig. 5.

During doping process the color of film changes from blue to light blue (with oxidation) and in the reverse process — to dark blue (during reducing). Electrochemical processes occurring in the film are reversible, and during successive cycling it is no degradation of the electrochemical activity of the film, and vice versa — its growth. Such electrochemical activity is characteristic of the high conducting electrochromic PEDOT/PSS films [[2, 3, 6, 7], that currently regarded as the most promising functional layers for use in the electro-optical devices.

4. Conclusions

It has been found that using *N*-cetyl pyridinium chloride as cationic surfactant, homogeneous PEDOT-PSS films with controlled thickness of 10–60 nm can be obtained by layered assembly. However, unlike to high molecular surfactants there is a linear relationship between the optical absorption of the films and the number of bilayers. Optical absorption spectra of the obtained films characterized by two well-formed bands: at 380–390 nm corresponding to $\pi \rightarrow \pi^*$ transition and other band in the region of $\lambda = 600\text{--}800$ nm indicates the formation of polaron type carriers. The multilayer films obtained in the presence of CPC as cationic surfactant demonstrate a high electrochemical behavior characteristic of high-conductive functional films PEDOT-PSS which promises their application in electrochromic devices.

Thus, the use of the proposed surfactant provides the benefits of technology obtaining and improving the quality of the absorption spectra of PEDOT-PSS films, while ensuring sufficient electrochemical activity of the films in a wide range of potential. The obtained results can be used for layered assembly of PEDOT-PSS also on other surfaces.

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Електростатичне пошарове складання функціональних наноплівки полі-3,4-етилендіокситіофену

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Метод електростатичного пошарового складання використано для отримання функціональних плівок аніонного комплексу полі-3,4-етилендіокситіофену (ПЕДОТ) з полістиролсульфокислотою (ПСС) на поверхні прозорих індій-станум оксидних субстратів. В якості катіонної поверхнево-активної речовини (сурфактанта) вперше запропоновано використання *N*-цетилпіридиній хлориду (ЦПХ). Встановлено, що тонкі плівки, отримані за наявності ЦПХ, виявляють оптичні властивості і електрохімічну поведінку, властиву функціональним шарам ПЕДОТ-ПСС, що передбачає можливість їх застосування в електрохромних пристроях.