Pedot brushes electrochemically synthesized on thienyl-modified glassy carbon surfaces

Agata Blacha\textsuperscript{a}, Piotr Koscielniak\textsuperscript{b}, Michal Sitarz\textsuperscript{c}, Jacek Szuber\textsuperscript{c}, Jerzy Zak\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Faculty of Chemistry, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland
\textsuperscript{b} Institute of Physics – Centre for Science and Education, Silesian University of Technology, Krzywoustego 2, 44-100 Gliwice, Poland
\textsuperscript{c} Faculty of Automatic Control, Electronics and Computer Science, Silesian University of Technology, Akademicka 16, 44-100 Gliwice, Poland

\textbf{A R T I C L E   I N F O}

Article history:
Received 26 September 2011
Received in revised form 15 December 2011
Accepted 16 December 2011
Available online 24 December 2011

Keywords:
Polymer brushes
Surface-initiated electropolymerization
Electrochemical reduction of diazonium salts
Molecule immobilization
EDOT

\textbf{A B S T R A C T}

The work describes the formation of poly(3,4-ethylenedioxyxothiophene) (PEDOT) brushes attached to thienyl-modified glassy carbon surface (GC) via surface-initiated electrochemical polymerization. The initial modification of the GC electrode was performed by using of three different thienyl-derivatives of aniline that were first converted to the form of diazonium salts. These salts were then electrochemically reduced creating the organic monolayer covalently bound to GC. The surface layer was investigated electrochemically and identified using XPS. The structural conjugation of the resulting monolayer made it possible to initiate the electrochemical polymerization of EDOT from the modified surface. The polymeric structure formed on the thienyl-modified surface reveals a better redox peak separation as compared to the classical polymer film on a bare electrode that can be assigned to its more ordered and uniform structure.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer brushes have become currently of high interest due to their wide range of potential applications, which include areas of the material science as an alternative to conventional methods applied in colloid stabilization, surface tension and friction reduction, in microelectronics, especially sensors, or in biotechnology [1]. There are two main routes of the polymer attachment to the supporting surface leading into the form of brushes, the physical through a simple physisorption or the chemical through a covalent bonding. The first case is not suitable when the strong linkage between polymer and surface is required. Earlier, the most common way for the synthesis of the polymer brushes was the chain bonding to the surface via functional groups, so called “grafting onto” (or “grafting to”) [2]. The main feature of this approach was a low thickness of the obtained films, limited to 1–5 nm. Recently, the most frequent synthesis is the direct surface-initiated polymerization (SIP), classified as “grafting from” technique. The idea behind is to bond an initiator to the surface of the substrate and then to introduce the monomer for the further synthesis. This technique has already been used for polymerization going via different mechanisms: radical [3], atom transfer radical [4], anionic [5], cationic [6], ring-opening metathesis [7] and electrochemical [8].

Various methods of the initiator immobilization have been earlier reported, while the electrochemical reduction of diazonium salts became one of the most interesting recently. The electrografting via diazonium salts reduction has been proposed in 1992 as an universal method of the electrochemical modification of conductive surfaces [9]. Reduction of these salts has been widely investigated due to the possibility of covering with the monolayer of numerous organic compounds for the surfaces of carbon, semiconductors and metals. Since rather gentle conditions of the reduction are required in this process, a possibility of surface modification for easily oxidized metals, like Fe, Cu etc., has been widely opened even on industrial scale. It is believed that the thickness of organic layer can be controlled by means of the conditions selection for the electrochemical synthesis (i.e. controlling time, grafting potential, concentration or charge and concentration) [10].

The electrochemical reduction of diazonium salts has been already applied for the initiator immobilization in the radical polymerization [11]. Moreover, in 2006 Adenier and et al. described the polyphenylene brushes obtained via continuous reduction of benzenediazonium salt [12]. To our knowledge, strategy for the conjugative polymer brushes formation consisting of the electropolymerization starting from the electrografted initiator has not been reported yet.
In our work we report on formation of poly(3,4-ethylenedioxythiophene) (PEDOT) brushes attached to thienyl-modified glassy carbon surface (GC) via surface-initiated electrochemical polymerization. PEDOT was chosen due to its well known, interesting electrochemical and optical properties [13] that have already been applied in antistatic coatings, electrode material solid electrolyte capacitors, sensors, corrosion protection and solar cells [14], etc. The initial modification of the GC electrode was performed using a series of thienyl-derivatives of aniline that were first converted to the form of diazonium salts. The salt was then electrochemically reduced creating the organic monolayer, covalently attached to the surface. Due to its conjugative structure the monolayer molecule could serve as the initiator for separated PEDOT chains formed in the electrochemical process. The surface layer was investigated electrochemically and identified using XPS. The effect of the type of monolayer structure on the electropolymerization process is discussed.

2. Experimental

The aniline thienyl-derivatives used to synthesize of the respective diazonium salts are shown in Scheme 1. (3-Thien-2-yl)aniline (purity 95%), (3T2P), and 3-(thien-3-yl)aniline (purity 97%), (3T3P), were purchased from Maybridge (GB), whereas 4-(thien-2-yl)aniline (purity 97%), (4T2P), was obtained from Aldrich Chemical Co. Tetrabutylammonium tetrafluoroborate (TBABF₄) (Alrich) was used as the electrolyte. Additional reagents for diazotization reaction (40% tetrafluoroboric acid and sodium nitrate, both from POCh, Poland) were analytical grade. Solvents (acetonitrile, diethyl ether, methanol and propan-2-ol) were reagent grade.

2.1. Diazonium salts’ synthesis

The procedure of diazonium salts’ synthesis was adopted from the literature [15]. To dissolve the reactant in the reaction mixture few drops of acetonitrile were added. The resulting precipitate product was washed with a portion of ice-cold diethyl ether and then dried in the desiccator under vacuum for 1 h at room temperature. The dry product was stored in the refrigerator. Typically, the yield of the reaction was better than 63%. The purity of the product was checked by means of ¹H NMR spectroscopy. All spectra were collected with Varian UNITY INOVA 300 apparatus (300 MHz resolution) with DMSO-d₆ used as a solvent. The summary of NMR results is reported below. All three salts appeared to be of high purity with no signs of unreacted substrate or any byproduct.

1 (3T2P): ¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 7.28 (t, 1H, J = 4.2 Hz, H⁴), 7.79 (d, 1H, J = 3.6 Hz, H³), 7.82 (d, 1H, J = 5.1 Hz, H⁵), 8.00 (t, 1H, J = 8.1 Hz, H⁷), 8.56 (d, 2H, J = 8.1 Hz, H⁵⁺⁶), 8.99 (s, 1H, H²).

2 (3T3P): ¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 7.65 (d, 1H, J = 4.8 Hz, H⁴), 7.82 (dd, 1H, J = 4.8 Hz, J = 3.3 Hz, H⁵), 8.02 (t, 1H, J = 8.4 Hz, H⁷), 8.19 (bs, 1H, H⁵), 8.55 (d, 1H, J = 8.4 Hz, H⁴), 8.62 (d, 1H, J = 8.4 Hz, H³), 9.06 (s, 1H, H²).

3 (4T2P): ¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 7.34 (t, 1H, J = 4.5 Hz, H⁴), 8.00 (d, 1H, J = 5.1 Hz, H³), 8.05 (d, 1H, J = 3.8 Hz, H⁸), 8.25 (d, 2H, J = 9.1 Hz, H³⁻⁴), 8.64 (d, 2H, J = 9.1 Hz, H⁵⁻⁶).

2.2. Electrochemical measurements

All electrochemical measurements were carried out using CH Instruments, Inc., Potentiostat Type 660C with glassy carbon (GC) working electrode (Cypress, disk 1 mm diameter) that was polished with emery paper (grit 2000) and with 1 μm alumina (Buehler), then ultrasonicated in deionized water and finally rinsed with isopropanol. A GC rod was used as a counter electrode and Ag wire served as a pseudo-reference electrode. The electrodes mounted in Teflon holder were then located in the 2 mL conical cell. Typically, the sample at mM range concentration in the 0.2 M solution of TBABF₄ in acetonitrile was purged with argon for 15 min, prior the measurement.

The electrochemical reduction of the diazonium salts was conducted by means of cyclic voltammetry (CV) within potential range (−0.8; 0.4) V at the scan rate of 0.1 V/s, starting from 0.4 V. Similar conditions (except the potential range) were applied for electropolymerization (5 mM EDOT solution) and in tests of the modified electrodes in ferrocene or in the pure electrolyte solutions.

2.3. XPS measurements

The XPS spectra were collected using a SPECS XPS spectrometer (background pressure ~10⁻⁶ Pa), equipped with the X-ray source (AlKα, 1486.6 eV; XR-50 Model) and a hemispherical concentric analyzer (PHOIBOS-100 Model). The pass energy was set at 600 eV (for the survey spectra) and 20 eV (for the narrow scans). The take-off angles were 0°, 45°, and 75° in respect to the surface normal. All the reported binding energy (BE) data were calibrated using Au 4f7/2 peak at 83.8 eV. The CASA XPS software was used to analyze the obtained data.

3. Results and discussion

3.1. Surface grafting

The electrografting of GC electrode with molecules able for the further process of EDOT electropolymerization was the first step of the assumed route for the PEDOT brushes formation. Such bifunctional molecules consisting of aniline unit substituted in m- or p-position with thiophene ring attached in its α- or β-position are shown in Scheme 1. They were applied to modify the GC surface after conversion to the form of their diazonium salts. The reduction of the corresponding diazonium salt occurs at the electrode surface under voltammetric conditions as shown in Fig. 1 for the case of 4B2T molecule.

The observed clear and broad irreversible reduction peak occurs at the potential close to −0.20 V vs. Ag during the first cathodic scan, while the consecutive scans result in its reduced peak currents until almost flat CV curve is recorded after several potential cycles.
The irreversible peak characteristic for many diazonium salts was assigned [16] to the process of radical formation accompanied by the evolution of nitrogen molecule. The radical forms a covalent bonding with the surface atom of the electrode making its surface gradually blocked for any further electrode process at the cathodic potentials. The schematic electrode process of 4B2T molecule is shown in Scheme 2. The CV curves recorded under the same conditions for 3B2T and 3B3T diazonium salts were essentially the same as those in Fig. 1.

The shape of the cathodic peak may vary from experiment to experiment, resulting in some pre- or double-peaks, which have been already reported in the literature [17]. As found in these studies, the process on Pt electrodes usually results in clear pre-peaks, whereas at GC surface the CV curves shown in Fig. 1 are more typical. Also, the electrode rinsed after the reduction process reveals some free space on the surface, which can be successfully completed if the reduction is repeated. This clearly suggests a possibility of existence (and removal) for some weakly blocking molecules that cannot be reduced due to not a proper orientation on the surface.

Various electrochemical testing systems were proposed in the literature [18] to detect the surface blocking effect after the formation of surface confined structures. For the covalently bonded molecules in the aprotic solutions of this study a good choice appears to be the ferrocene redox system. As shown in Fig. 2A, its characteristic reversible redox couple is observed in the region (0.35; 0.45) V at bare electrode, whereas a clear decrease in the ferrocene signal occurs when the electrode is gradually covered with the grafting molecules at increasing number of cycles in the diazonium reduction process. It was found that the electrode may attain a stable state of maximum coverage after an extensive reduction consisting of six series of three cycles of modification, although even at half of these scans the electrode becomes practically blocked for the ferrocene reaction.

3.2. Electrochemical and XPS studies of the grafted surfaces

In addition to the simple electrochemical tests for the effectiveness of the grafting process, more information can be provided when applying surface analysis at different states of grafted substrates.

The comparison of XPS spectra obtained for bare GC surface and 4B2T/GCsurf. Surface, shown in Fig. 3, reveals the presence of thienyl sulfur (S 2p at 165 eV) at the modified GC, which evidently confirms the effectiveness of the modification process. Due to the spin–orbit splitting, S 2p signal requires of a deconvolution, which leads to S 2p1/2 and S 2p3/2 peaks (165.5 and 164.2 eV) shown in Fig. 4a, with the peaks’ area ratio (S 2p1/2:S 2p3/2 = 2:1) being in agreement with the literature data [19,20].

Since the carbon C 1s signal for 4B2T/GCsurf sample may arise from both the substrate and the modifying layer itself, it is crucial to investigate the surface by applying various takeoff angles (Fig. 4c and d). Three distinctive maxima at 287.4, 286.5 and 284.9 eV can be distinguished after deconvolution and can be assigned to C–S, C–O, and C–C/C–H, respectively. The oxygen signal recorded by XPS

---

**Fig. 1.** CV curves recorded on GC electrode in 1 mM [4B2TNa]+ BF₄⁻ + 0.2 M TBABF₄ in acetonitrile (red line) and in 0.2 M TBABF₄ in acetonitrile (black line) at 0.1 V/s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

**Scheme 2.** Schematic representation of the electrochemical reduction of (4B2TNa)⁺ on GC to the form of covalently bond monolayer of 4B2T/GCsurf.

**Fig. 2.** CV curves recorded in 1 mM ferrocene solution containing 0.2 M TBABF₄/ACN for the bare GC electrode and for the electrode covered with 4B2T molecules after 3, 9, and 18 cathodic scans in diazonium salt solution; (dashed line) CV was recorded on the 4B2T electrode exposed to potentials destructively oxidizing the attached polymer (see text).

**Fig. 3.** Survey XPS scans on unmodified and 4B2T-grafted glassy carbon surface.
arises from adventitious adsorbed layer, which is usually present on glassy carbon [21]. The peak fitting parameters for C 1s region at different detection angles are summarized in Table 1. The typical decrease in the intensity ratio of (C–C/C–H)/(C–O, C–S) signals with the increase of takeoff angle is observed and can be explained by the lower contribution of the glassy carbon substrate signal to overall carbon signal [22]. Moreover, the C–S signal raise at 75° suggests that the sulfur bounded carbon atoms, C–S, are located in the outermost part of the modifying layer.

Though during the electrochemical reduction of diazonium salts, the nitrogen molecule is evolved and should not be present on the surface, several groups has already observed nitrogen N 1s signal at 400.4 eV in XPS spectrum collected for modified materials. This phenomena may be caused by the formation of hydrazine group bounded via phenol groups present at glassy carbon surface, as stated by Belanger et al. [18], or by multilayers formation via azo-coupling between immobilized phenylene rings and diazonium cation, as stated by Hurley and McCreery [23]. In our case additional peak at 402.6 eV is observed (Fig. 4b), which is believed to come from electrolyte physical adsorption on the surface [24]. The presence of unreduced diazonium salt is excluded due to the absence of the characteristic signals at 403.8 and 405.1 eV [25].

The CV curves recorded at the modified surfaces in electrolyte solution were collected in order to determine basic electrochemical properties, which are crucial for the successful EDOT brushes formation. All the obtained electrode surfaces, 3B2T/GCsurf, 3B3T/GCsurf, and 4B2T/GCsurf exhibit in the supporting electrolyte a broad irreversible anodic peak in the first scan as shown in Fig. 5. It is believed to be partially a result of the thienyl ring oxidation, which is possible due to conjugated character of the attached structures forming the layer. Also, the peak consists of a current which originates from the monolayer oxidative degradation. The

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Fitting parameters for high resolution C 1s spectra of 4B2T/GCsurf at different detection angles.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C–S</td>
</tr>
<tr>
<td>Relative peaks’ area at 0° [%]</td>
<td>6.8</td>
</tr>
<tr>
<td>Relative peaks’ area at 45° [%]</td>
<td>6.5</td>
</tr>
<tr>
<td>Relative peaks’ area at 75° [%]</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Fig. 4. High-resolution spectra with deconvoluted components for S 2p region (a), N 1s region (b) and C 1s region at 0° (c) and 75° (d) take off angles for 4B2T/GCsurf.

Fig. 5. CV curves recorded for the GC electrodes grafted with 3B2T, 3B3T, and 4B2T in 0.2 M TBAFB4/ACN solution at 0.1 V/s.
combination of these two processes explains the resulting, relatively high currents recorded during first anodic scan. Generally, when the surface attached molecules are oxidized they should form the surface radical cation, which in an absence of other reacting molecules around (in solution phase) will tend to form bridges with neighboring surface molecule (or its radical). The last situation was earlier demonstrated for the case of gold attached thiolated aniline [26].

As expected, the values of the thiényl ring oxidation potential are slightly differentiated, depending on the substitution position. An evident structural effect of the conjugation length is observed resulting in the lowest onset potential in case of 4B2T molecule. Typically this value is around 0.8 V, whereas it is nearly 0.15–0.20 V more positive for the other two surface structures. If the applied potential reaches 1.8 V, then all the consecutive background CV curves become practically identical with those recorded for a bare electrode. The test with ferrocene solution shown in Fig. 2 (dashed line) proves that at anodic potentials sufficiently large the attached organic layer can be effectively removed from the electrode surface. This also means that such extensive oxidation of the grafted electrode may finally break the bond with the surface atoms of the electrode. It is worth of note that this kind of oxidation in case of any electropolymerized thin films on bare electrodes leads to the formation of irremovable deposits blocking the electrode surface.

### 3.3. Electrochemical polymerization of EDOT on the grafted surface

When the oxidative potential of the grafted electrode is carefully selected, then a monomer present in the solution phase has a chance to react with the surface cation radical and to form the polymer chain. This kind of the surface-initiated (SI) electrochemical polymerization of EDOT by oxidation of the immobilized molecules was tested for all three monolayers. The CV curves presented in Fig. 6 were recorded for 4B2T/GCsurf electrode during continuous potential scanning in the solution of EDOT. The typical picture illustrating formation of the conductive polymer was obtained, in which gradually increasing current in the entire potential region proves the buildup of electroactive species on the electrode. Since the free surface on the GC is effectively blocked, the polymerization may start only from the generated radical cations of the immobilized molecule. It was found that only in the case of 4B2T/GCsurf the thiényl oxidation makes possible this EDOT SI-electropolymerization. An explanation for the unsuccessful polymerization in other two cases needs to take into account the potentials of the surface radical cation formation. Although there is no direct information what are these values when analyzing CV curves of Fig. 5, an indication of the lowest potential for 4B2T/GCsurf is clear, when analyzing the onset potential values. These potentials come in the order $E(4B2T) < E(3B2T) < E(3B3T)$. The same conclusion might be drawn when considering the conjugation length from the structures of Scheme 1 or UV-vis spectra of the conjugated molecules [27]. This length between the position of attachment (amine group) and the most likely for polymerization the $α$-position of thiényl group is the longest for 4B2T molecule, and the shortest (and disturbed) for 3B3T. Considering UV–vis spectra of these compounds in MeOH at their reduced state (not shown here), we found the most blue-shifted value of $λ_{\text{max}} = 219$ nm for 3B3T, $λ_{\text{max}} = 287$ nm and $λ_{\text{max}} = 303$ nm for 3B2T, and 4B2T molecules, respectively. Thus, the required too high potential of radical cation formation may cause a problem with a stability of the system with the other two grafted molecules for which the polymerization was impossible under the applied conditions.

The PEDOT brush, as compared to PEDOT film on a bare electrode is assumed to be more uniform in its structure and therefore some properties of both films are expected to be different. Considering the electrochemical properties, the structural differences should affect the internal charge transfer mechanism that is likely more complex within randomly deposited film than that in case of all single chains forming brushes attached to the core electrode through initiating monolayer. The comparison of the voltammograms recorded for these two cases, together with the respective backgrounds representing the initial state of each electrode before polymerization, is shown in Fig. 7. The net charges resulting of the redox reaction for both electrodes in the electrolyte have similar values, therefore all the differences between them are easier to distinguish. The GC background evidently lowers the cathodic portion of GC–PEDOT, which makes the last more deformed at that region. Nevertheless, as both CVs clearly indicate, the cathodic current for PEDOT/GCsurf electrode starts to increase at the same potentials as the current forming peak for PEDOT/4B2T/GCsurf case. The peak for first electrode is more broad, besides, its maximum is located at less than 250 mV negative potential, evidently farther than the peak for PEDOT/4B2T/GCsurf is completed. This broader peak may only be interpreted as a result of charge transfer at different rates due to the differentiated nature of the conjugated structures at the SI–PEDOT electrode. In preparation of that electrode, an effort was made (as described above) to reduce as much as possible a free space at the

![Fig. 6. CV curves recorded continuously on 4B2T/GCsurf electrode in 5 mM EDOT with 0.2 M Bu$_4$NBF$_4$/ACN as a supporting electrolyte; the arrows indicate the direction of film growth.](image)

![Fig. 7. CV curves recorded in 0.2 M Bu$_4$NBF$_4$/ACN for (a) PEDOT brush on 4T2B/GCsurf (red line); (b) PEDOT film deposited on bare GC electrode (black line). Background CVs recorded on bare GC and 4B2T/GC electrodes are shown for comparison.](image)
electrode surface providing more uniform film structure, which is a main idea of the conjugated polymer brush. It is worth of note that we have observed CV curves being of similar type as that presented for the PEDOT/GCsurf for the electrodes, which were obtained when the GC electrode was not enough tightly covered with 4B2T layer. At such submonolayer coverage the polymerization process may also start from uncovered electrode surface, providing less defined routes for the charge propagation causing a spreading of the oxidation potentials.

The observed in Fig. 7 effect of the peak separation reduction for the redox reaction may prove of more uniform structure of the conjugative polymer. The final result suggests that formation of polymer brushes of conjugated chains may lead to more ordered polymeric structures.

4. Conclusions

The electrochemical reduction of thienyl-substituted diazonium salts was carried out on glassy carbon yielding covalently attached layer on its surface, which presence was confirmed by means of XPS and cyclic voltammetry. The irreversible oxidation of the attached thienyl group at extended potential range leads to degradation of the surface structure leaving the surface free of any deposits. It was demonstrated that the structure of the preliminary compound has an evident effect on the oxidation potential and consequently the ability of the surface structure to initiate polymerization in a presence of monomer. It was demonstrated that the conjugated structure of the 4T2B/GCsurf surface makes possible the surface-initiated electrochemical polymerization of EDOT. The polymeric structure formed on the 4T2B/GCsurf surface reveals a better redox peak separation as compared to the classical polymer film on a bare electrode that can be assigned to its more ordered and uniform structure. It is believed that this kind of conjugated polymer brush structure may be employed more effectively in a prospect microelectronics or in sensor applications.

References