Morphology and electrical properties of electrochemically synthesized pyrrole–formyl pyrrole copolymer

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A direct electrochemical copolymerization of pyrrole–formyl pyrrole (Py–co-FPy) was carried out by oxidative copolymerization of formyl pyrrole and pyrrole in LiClO 4 aqueous solution through galvanostatic method. The (Py–co-FPy) copolymer was characterized using Fourier-transform infrared spectroscopy (FT-IR), field emission scanning electron microscope (FESEM), energy-filtering transmission electron microscope (ETEM), thermal gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The FESEM images showed that the synthesized copolymer had a hollow whelk-like helixes structure, which justifies the enhancement of charge transportation through the copolymer film. Cyclic voltammetry studies revealed that the electrocatalytic activity of synthesized copolymer has improved and the surface coverage in copolymer enhanced 1.6 times compared to polypyrrole alone. Besides, (Py–co-FPy) copolymer showed 2.5 times lower electrochemical charge transfer resistance (Rct) value in impedance spectroscopy. Therefore, this copolymer has a strong potential to be used in several applications such as sensor applications.

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1. Introduction

Conducting polymers have obtained significant attention in various fields due to their amazing electrochemical and mechanical characteristics such as low ionization energy, electrical conductivity, and low energy optical transitions [1–3]. Among conducting polymers, polypyrrole is one of the most famous ones, which has been used in several applications such as batteries [4,5], sensors and biosensors [6–11], electrochromic displays [12,13], light-emitting diodes [14,15], capacitors [16,17], enzyme electrodes [18–20] and membrane [21,22]. Based on final application, different methods can be used to synthesize polypyrrole, for instance, chemical [23], electrochemical [24], photochemical [25] and electrospinning [26] polymerization. However, electropolymerization is a more preferred method, since the films’ thickness can be controlled and it is possible to obtain homogeneous films directly on the electrode surface [27].

Furthermore, considerable attention has been focused on the copolymers, due to their amazing electrical, physical, and electrochemical characteristics [28–35]. Recently, chemical copolymerization of formyl pyrrole (FPy) and pyrrole (Py) using acidic catalysts in the copolymerization was reported [36–38]. Fig. 1 shows the structural formula of (Py–co–FPy) copolymer.

To the best of our information, there is no report regarding electro-copolymerization of (Py–co–FPy) in the literature. In this study, (Py–co-FPy) copolymer was successfully prepared via electro-copolymerization process in an aqueous solution containing pyrrole, formyl pyrrole and lithium perchlorate (LiClO 4 ). The synthesized copolymer showed high electrochemical activity and improved the surface coverage in compare with PPy alone. The conjugated structure between Py and FPy in the presence of methine group can cause the enhancement of conductivity compared to polypyrrole [35]. Moreover, the impedance data revealed that the (Py–co–FPy) copolymer has 2.5 times lower charge transfer resistance (Rct) compared to (PPy).

2. Experimental

2.1. Reagents

Chemicals including pyrrole, formyl pyrrole and lithium perchlorate were analytical reagent grade and purchased from Merck (Germany). All aqueous solutions were prepared using deionized water with resistivity of ~18 MΩ cm. All glass apparatus were kept

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in 1.0 mol L⁻¹ nitric acid when not in use. Pyrrole was purified by vacuum distillation, shielded from light and kept at 4 °C until the electro-copolymerization solution was prepared.

2.2. Instruments

All electrochemical studies were performed using a Galvanostat–Potentiostat; Autolab 302N controlled by Nova 1.10 software, Metrohm, Switzerland. A three-electrode cell was used for all the measurements; a glassy carbon electrode GCE with a diameter of 3 mm as the working electrode, a platinum auxiliary electrode and a saturated calomel as the reference electrode (SCE) (BAS Inc., Japan). Surface evaluation was performed by field emission scanning electron microscopy (FESEM) in a Hitachi SU8000 (Japan) microscope and the energy-filtering transmission electron microscope (EFTEM) LIBRA 120 equipped with an Olympus SIS ITEM Version 5.0 (build 1243) (Carl Zeiss, Germany). The Fourier transform infrared (FTIR) spectra of the modified electrode were obtained using a Perkin–Elmer (Frontier FT-IR/FIR Spectrometer) armed with attenuated total reflectance (ATR) sampling tool. The X-ray photoelectron spectroscopy (XPS) spectra for polypyrrole and copolymer were obtained using OMICRON Nanotechnology, model DAR400, Germany with Al Kx 1486.7 (Dual anode) at working pressure 5.5 × 10⁻¹¹ Torr, with CASA XPS software. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 4000 instrument at a heating rate of 10 °C/min in N₂ atmosphere.

2.3. Preparation of modified electrodes

The (Py–co-FPy) copolymer film was prepared by electro-copolymerization on a glassy carbon electrode GCE with the diameter of 3 mm, using chronopotentiometry mode [39,40] at 480 µA for 200 s. The electro-copolymerization was carried out in an aqueous solution with a transparent brownish color; containing 0.1 M pyrrole, 0.1 M formyl pyrrole (FPy) and 0.1 M LiClO₄ that was purged by nitrogen gas for 1 min prior to electro-copolymerization. The (Py–co-FPy) copolymer film formed a dark greenish color on the surface of glassy carbon electrode. It has been reported that the chemically synthesized (Py–co-FPy) copolymer has a green color [35–37]. Similar conditions were applied for (PPy) preparation and a black film was coated on the surface of GCE.

2.4. Electrochemical impedance spectroscopy (EIS)

The EIS recorded in 1.0 M H₂SO₄ solution in the frequency range of 0.1 Hz to 100 KHz was followed by applying a signal amplitude of 5.0 mV (around the open circuit potential). The validity of fitting to the corresponding circuit was evaluated by minimizing the Chi-squared (χ²) to 10⁻⁴.

3. Results and discussion

3.1. Field emission scanning electron microscopy (FESEM) and energy-filtering transmission electron microscope (EFTEM)

Fig. 2(a) shows the structure of polypyrrole-coated electrode. Fig. 2(b) and (c) shows the (Py–co-FPy) copolymer with many
whelk-like helixes, which most of the (Py–co-FPy) copolymer whelks have a small hole on their apices with an average diameter about 45 nm, which provides large surface area, with more available active sites and high catalyst properties. Moreover, the whorls on the bodies of (Py–co-FPy) copolymer whelk have well-ordered periodic nanostructures that provides a great high ratio of surface to volume. Besides, comparing (PPy) and (Py–co-FPy) copolymer indicates that (PPy) has a typical califlower morphology, but after incorporating FPy through the copolymerization, a whelk-like helix shape is formed and this confirms the effect of FPy in the copolymerization process. Chen et al. [41] reported the electrochemical polymerization of pyrrole in the presence of a surfactant with whelk-like helixes poly(pyrrole) on a glassy carbon electrode with an average base diameter about 1.0 μm. Baleg et al. [29] synthesized whelk-like helixes structure of 2 poly(propylene imine)-co-poly(pyrrole) conducting dendrimeric star copolymer on a platinum electrode, without presence of surfactant via electro-copolymerization of pyrrole in an aqueous 0.1 M LiClO₄ medium. Comparing the works of Chen et al. [41] and Baleg et al. [29] with the present study reveals that the (Py–co-FPy) copolymer whelks have a smaller hole on their apices which provides larger surface area, with more available active sites and high catalyst properties. Fig. 2(d) shows the EFTEM images of (Py–co-FPy) copolymer coated on a glassy carbon electrode after dispersing in water. As it is clear, similar whelk-like helixes structure is observed.

3.2. Fourier transform infrared spectroscopy (FT-IR)

Fig. 3(a)–(c) shows the FT-IR spectra of (Py–co-FPy) copolymer, PPy, and formyl pyrrole monomer. The broad band (A) between 3350 and 3450 cm⁻¹ is associated to N–H stretching. The peaks (B) at 2916 and 2812 cm⁻¹ are attributed to saturated C–H stretching [36–38]. These peaks in (Py–co-FPy) copolymer became very weak because of the increase of the conjugated structure in the copolymer backbone [36–38]. Conversely, the peaks in (C) region, between 1950 and 2100 cm⁻¹ are more intense due to consecutive presence of alkene in (Py–co-FPy) copolymer. It was revealed that peak (D) at 1625 cm⁻¹ was observed only in formyl pyrrole monomer. This peak can be attributed to carbonyl group and its disappearance confirms the formation of (Py–co-FPy) copolymer. The peak (E) at 1525 cm⁻¹ corresponds to C=O stretching of the pyrrole ring and the peak (F) appeared at 1450 cm⁻¹, which is related to C=N stretching, were suggesting the formation of conjugate configuration in the (Py–co-FPy) copolymer [36–38]. The peak (G) observed at 1278 cm⁻¹ is due to C=CH₂ stretching [36–38]. Moreover, the peak (H) at 1026 cm⁻¹ can be related to C–N stretching of amine group. The peak (I) at 940 cm⁻¹ is related to out-of-plane vibrational deformation of C–H in methine group and this peak proves that methine bonds between FPy and Py were formed in the copolymer and peak (J) at 866 cm⁻¹ is related to aromatic C–H out-of-plane deformation vibration [36–38].

3.3. Electrochemical study of modified electrodes in the sulfuric acid solution

Fig. 4(a) presents the cyclic voltammograms of the bare glassy carbon electrode, (b) PPy and (c) the (Py–co-FPy) copolymer coated electrode in a solution containing 1.0 M H₂SO₄ at the scan rate of 50 mV s⁻¹. As can be seen from Fig. 4(b) and (c), both modified electrodes show redox peaks while there is no significant peak for bare electrode (Fig. 4(a)). However, in compare to the PPy electrode, the electrode coated with (Py–co-FPy) copolymer shows greater response. Moreover, ∆Eₚ (Eₚ,a − Eₚ,c) for (Py–co-FPy) copolymer is about 300 mV less than PPy. Therefore, as can be seen from Fig. 4(b) and (c), (Py–co-FPy) copolymer has a higher electrochemical reversibility than PPy; mainly because the electron transfer of copolymer is higher than that of electrodes coated by PPy. While
positive potential is applied, the counter ions are carried on to balance the positive charge \((1)\) of \((\text{Py–co-FPy})\) copolymers (doping). On the other hand, once enough negative potential is adapted to the \((\text{Py–co-FPy})\) copolymers \((2)\), the counter ions are taken out (de-doping) \([39,42]\).

\[
\begin{align*}
(\text{Py–co-FPy})_h &\xrightarrow{\text{oxidation}} (\text{Py–co-FPy})^n_+ + e^- & (1) \\
(\text{Py–co-FPy})^n_+ &\xrightarrow{\text{reduction}} (\text{Py–co-FPy})_h & (2)
\end{align*}
\]

Fig. 5(a) presents the cyclic voltammograms of \((\text{Py–co-FPy})\) copolymers coated electrode at different scan rates in a range of \(5–70\) \text{mV s}^{-1} in 1.0 M \(\text{H}_2\text{SO}_4\) solution. As can be seen in Fig. 5(a), with increasing the scan rate values, well-defined and potential scan rate dependent peaks appeared in the voltammograms. The peak-to-peak potential separation deviates from the theoretical value of \(0\) and slightly increases at higher potential scan rates. In the electrochemically synthesized copolymer, with varying the potential from \(5\) to \(30\) \text{mV s}^{-1}, the peaks shift for anodic and cathodic reaction varied from \(320\) to \(691\) \text{mV} and \(-98\) to \(-372\) \text{mV}, respectively. This peak-to-peak deviation can be either due to the charge-transfer kinetics limitation between the electrolyte ions in each modified electrode or the non-equivalent sites presented in each modified electrode \([43,44]\). Fig. 5(b) presents the linear dependence of both the anodic and cathodic currents in voltammograms on potential sweep rate at low values of \(5–30\) \text{mV s}^{-1}. The linear enhancement of the redox peak currents with increasing of scan rates confirms that the reaction of electrode is controlled by surface layer in all modified electrodes. Eq. (5) can be obtained by re-expressing Laviron’s equations (3) and (2). From the average slope of the linear part of the anodic and cathodic peak currents in Fig. 5(b) versus the potential scan rate, and using the Eq. (4), the surface coverage \((\Gamma)\) of the electroactive species of the modified electrodes can be estimated:

\[
\begin{align*}
I_p &= \frac{n^2F^2AT\nu}{4RT} & (3) \\
Q &= nFAT & (4) \\
I_p &= \frac{nFQ\nu}{4RT} & (5)
\end{align*}
\]

where \(A\) is the electrode area (cm²), \(Q\) is the quantity of charge (C) calculated from the average of both anodic and cathodic peak area of the voltammograms, \(\Gamma\) is the surface coverage of the electrode reaction substance (mol cm⁻²), \(I_p\) is the peak current (A) and \(\nu\) is the potential scan rate (V s⁻¹). \(F, R, n\) and \(T\) have their usual significance. The average surface coverage \(\Gamma\) is estimated by considering the average of both cathodic and anodic currents to be \(1.34 \times 10^{-6}\) mol cm⁻², for modified \((\text{Py–co-FPy})\) copolymers coated electrode. Similar calculations were applied for modified PPy coated electrode and the surface coverage \(\Gamma\) by considering the average of both cathodic and anodic currents is estimated to be \(8.5 \times 10^{-7}\) mol cm⁻².

The peak currents of the cyclic voltammograms are linearly dependent to the square root of the potential scan rate at the higher potential scan rates \((30–70\) \text{mV s}^{-1}), Fig. 5(c). This suggests that the diffusion of electrolyte anions in the bulk of the copolymer is the rate-limiting step at high potential scan rates \([45]\). From the average slope of the linear part of the anodic and cathodic peak currents versus the square root of the potential scan rate in Fig. 5(c) and using the Randles–Sevcik equation \((6)\), the diffusion coefficients of \(\text{SO}_4^{2-}\) can be calculated \([43]\):

\[
I_p = (2.69 \times 10^5)n^{3/2}ACD^{1/2}\nu^{1/2}
\]

where \(D\) and \(C\) are the diffusion coefficient and active sites concentration, respectively. The diffusion coefficient of \(\text{SO}_4^{2-}\) is estimated to be \(3.06 \times 10^{-7}\) cm² s⁻¹ for \((\text{Py–co-FPy})\) copolymer. Similar calculations were applied for the modified PPy coated electrode and the diffusion coefficient of \(\text{SO}_4^{2-}\) is estimated to be \(5.74 \times 10^{-8}\) mol cm⁻². The diffusion coefficient of \(\text{SO}_4^{2-}\) for \((\text{Py–co-FPy})\) copolymer is about 5.2 times greater than PPy.

### 3.4. Electrochemical impedance spectroscopy (EIS) study

Electrochemical impedance spectroscopy (EIS) is a useful method for investigating the interfacial properties of polymer film/electrolyte interface. The measurement proceeds by applying a low amplitude alternating voltage \(V\):

\[
V = V_m \sin(\omega t + \varphi_1)
\]

where \(\omega\) is defined as angular frequency and \(V_m\) the signal amplitude. This input signal leads to a sinusoidal output current \(I\):

\[
I = I_m \sin(\omega t + \varphi_2)^2
\]

where \(\varphi\) is the phase angle and \(I_m\) the signal amplitude. The electrochemical impedance \(Z\) is defined as:

\[
Z = r = \frac{V}{I(t)} = \frac{V_m \sin(\omega t + \varphi)}{I_m \sin(\omega t + \varphi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} = Z_r + jZ_i
\]

Here \(Z_r\) and \(Z_i\) are defined as the imaginary and the real part of the impedance \([46,47]\). The Nyquist diagrams of GCE, (b) the PPy, and (c) the (PPy–co-FPy) copolymer in 1.0 M \(\text{H}_2\text{SO}_4\) solution. The results indicated that the charge transfer resistance significantly decreases with modification of GCE by PPy. High conductivity of PPy is responsible for decreasing the charge transfer \([48]\). As can be seen in Fig. 6(b) and (c), the semicircle diameters of \((\text{Py–co-FPy})\) copolymer \((31.42)\) and PPy \((81.62)\) clearly show that the \((\text{Py–co-FPy})\) copolymer layer can enhance electron transfer. This also indicates that the conducting \((\text{Py–co-FPy})\) copolymer facilitated the flow of ions through the copolymer onto the surface of the electrode. The results confirm that \((\text{Py–co-FPy})\) copolymer layer can improve the electron conduction 2.5 times higher than PPy. For simulating the impedance behavior of PPy and \((\text{Py–co-FPy})\) copolymer from the experimentally obtained impedance data, Randles circuit model was used. Several parameters were used for modeling the equivalent circles. These parameters are the charge transfer resistance of bulk electrolyte \((R_b)\), charge transfer resistance of electrode surface/solution \((R_s)\), double layer capacitance \((Q)\) and Warburg element \((W)\). Due to the non-ideal nature of the electrode and for optimizing the fit to the experimental data, constant phase
element was used [49–51]. The following order is observed for charge transfer resistance of modified electrodes:

\[
\text{GCE} > \text{PPy} > \text{(Py–co-FPy) copolymer}
\]

The simulation data of all of the modified electrodes are given in Table 1.

The impedance parameters in Table 1 were obtained by fitting the equivalent circuit shown in Fig. 6(d) and (e), where the fitting error was <5%.

The surface coverage (\(\theta\)) of 99.99% was obtained for the (Py–co-FPy) copolymer on the GCE electrode. The value was estimated from the \(R_{\text{ct}}\) value using the formula [29],

\[
\theta = 1 - \frac{R_{\text{ct}}^{\text{modified}}}{R_{\text{ct}}^{\text{bare electrode}}} \times 100
\]

3.5. Thermal gravimetric analysis (TGA)

Fig. 7 displays the thermal gravimetric analysis of PPy (a) and Py–co-FPy copolymer (b). As it is clear the thermal stability of Py–co-FPy copolymer is higher than that of PPy in the temperature range of 30–800 °C. By increasing the temperature, the degradation of PPy and Py–co-FPy copolymer starts at about 236 °C and 220 °C respectively. A large weight reduction for PPy and Py–co-FPy copolymer observed at 275 °C and 308 °C respectively. The complete decomposition temperature for PPy and Py–co-FPy copolymer.
copolymer is about 660 °C and 720 °C respectively. These results show that the Py–co-FPy copolymer has more thermal stability compared to polypyrrole.

3.6. X-ray photoelectron spectroscopy (XPS) of polypyrrole and Py–co-FPy copolymer

The low-resolution XPS spectra of polypyrrole and Py–co-FPy copolymer are shown in Fig. 8(a) and (b) respectively. These spectra of polypyrrole and (Py–co-FPy) copolymer consist of three peaks, namely, C 1s around 285 eV, N 1s around 400 eV and O 1s around 530 eV.

The deconvolution of the C 1s core level spectrum of polypyrrole Fig. 8(c) and Py–co-FPy copolymer Fig. 8(d) show two Gaussian components. The main C 1s peak at 284.7 eV is corresponded to α- and β-carbons in Py [52] and formylpyrrole rings for both PPy and Py–co-FPy copolymer. The peak at 287.5 eV of PPy can be related to the branching carbon [53–55], C≡N [56], =C−NH+ (polaron) defects [52], and C−OH [52]. The carbon peak at 288.5 eV of Py–co-FPy copolymer is derived from =C−N+ (bipolaron) defects [52,54,55,57–62]. The observed shifting at higher binding energy side of the main C peak of Py–co-FPy copolymer can be due to the conjugated structure between Py and PPy in the presence of methine group.

The N 1s spectra of polypyrrole and Py–co-FPy copolymer is only derived from N of pyrrrole or formyl pyrrrole, due to the absence of N in dopant (LiClO₄) used. In Fig. 8(e) and (f) the main N peaks centering at 400 eV is related to the neutral N at the pyrrrole [55] and formyl pyrrrole ring (−NH−) respectively. In the case of Py–co-FPy copolymer, this peak is not symmetric. The small shoulder which observed at about 2 eV lower binding energy side of the main N peak of copolymer can be attributed to =N− [33]. The copolymer shows a peak at about 0.5 eV higher binding energy binding energy side of the main N peak (400.5 eV) is attributed to −NH+−. On the other hand in the case of polypyrrole the 2.4 eV higher binding side of the main N peak (402.4 eV) peak can be related to =NH+, a bipolaron charge carrier species [55,63].

The O 1s signal in the XPS spectrum of polypyrrole is given in Fig. 8(g). The peak centered at 532 eV can be attributed to C=O of polypyrrole defects. The O 1s signal in the XPS spectrum of Py–co-FPy copolymer is shown in Fig. 8(h). The two peaks at 530.4 and 531.6 eV can be attributed to C=O in the copolymer. The peak located at 532.5 eV may be attributed to the oxygen contribution of bound water and copolymer-oxidized parts [55,63]. The hydrophilic property of this copolymer has already reported [35] and this property may be correlated to the peak found at 532.5 eV.

### 4. Conclusions

The electro-copolymerization of (Py–co-FPy) was successfully carried out in an aqueous solution containing monomers of (Py), (FPy), and LiClO₄. The FESEM study revealed that this copolymer has several whelk-like helices structures; most of the whelks have a small hole on their apices with an average diameter about 45 nm, which can be a reason for the enhancement of charge transportation through the copolymer film. Moreover, the conjugated structure between Py and PPy in the presence of methine group causes the improvement of conductivity compared to polypyrrole. It was revealed that the Py–co-FPy copolymer has more thermal stability compared to polypyrrole. This copolymer exhibits

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**Table 1**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$R_s$ (Ω)</th>
<th>$R_n$ (Ω)</th>
<th>C (μF)</th>
<th>Q (μmhos)</th>
<th>W (μmhos)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>17.6</td>
<td>$1.8 \times 10^6$</td>
<td>2.63</td>
<td>–</td>
<td>$3.99 \times 10^3$</td>
<td>–</td>
</tr>
<tr>
<td>PPy</td>
<td>20.8</td>
<td>81.6</td>
<td>–</td>
<td>$1.56 \times 10^3$</td>
<td>–</td>
<td>0.74</td>
</tr>
<tr>
<td>Py–Fpy copolymer</td>
<td>17.3</td>
<td>32.4</td>
<td>–</td>
<td>$2.35 \times 10^3$</td>
<td>7.86</td>
<td>0.67</td>
</tr>
</tbody>
</table>

**Fig. 8.** Wide region XPS spectra of (a) polypyrrole and (b) (Py–co-FPy) copolymer, (c) C 1s spectrum of polypyrrole, (d) C 1s spectrum of (Py–co-FPy) copolymer, (e) N 1s spectrum of polypyrrole, (f) N 1s spectrum of (Py–co-FPy) copolymer, (g) O 1s spectrum of polypyrrole and (h) O 1s spectrum of (Py–co-FPy) copolymer.
interesting properties and has a strong potential to be used in several applications such as sensors.

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References


