

Electrochemical Fabrication of Polypyrrole Nanofibers and their Characterization

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Abstract

Polypyrrole (PPy) nanofibers have been fabricated on glassy carbon electrode (GCE) using electrochemical technique. Electropolymerization of pyrrole (Py) for the fabrication of PPy nanofibers was occurred on GCE by applying a fixed potential of about 0.85 V for 120 sec in a mild basic solution containing sodium carbonate and sodium perchlorate. In the mild basic media, the monomer, Py, is oxidized on GCE at a potential of about 0.85 V vs. Ag/AgCl and the oxidation product of Py i.e. polypyrrole nanofibers is strictly adsorbed on the electrode surface. Cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy were used for studying the electrochemical and morphological properties of electropolymerized PPy conducting polymer. These techniques confirm the electropolymerization of Py as PPy nanofibers on the electrode surface.

Keywords: Conducting Polymers, Electropolymerization, Polypyrrole, Nanofibers

1. Introduction

As a consequence of having very interesting characteristics and potential applications, the research efforts on conductive polymers, made from heterocyclic monomers, have considerably increased in recent years [1-3]. As an analytical point of view, conducting polymers, due to their imprinting and templating abilities, have been widely used for

the development of highly selective sensors [4-6]. In addition, one of the most interesting characteristics of these conductive polymers is their capacity to store electrical charge, which can be recovered upon demand [7, 8]. On other words, electrically conducting polymers have been found to have higher capacitance because of their capacitive and Faradaic currents contribute to the charge storage. This makes them good candidates as components of advanced rechargeable batteries or super-

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capacitors [8, 9]. However, the main challenge of conducting polymers is their lower cycle-life in charge - discharge duty than carbon-based electrodes because of the instability of redox sites in the polymer backbone [8].

Polypyrrole (PPy) is currently considered as one of the most promising conducting polymers for the development of advanced batteries, due to its good conductivity and stability [1, 3]. PPy is a particularly attractive material for catalyst support because of its large surface area and high electrical conductivity and stability under conditions relevant to the operation of fuel cells or sensors employing an aqueous neutral electrolyte.

PPy can be synthesized by oxidative polymerization of the corresponding monomer, i.e. pyrrole (Py). This may be accomplished either electrochemically or with a chemical oxidizing agent. Electrochemical oxidation methods have various advantages over chemical methods such as simplicity, low cost, better control of PPy formation and finally, no need of additional steps for the separation of oxidant and additives from the product. By applying the potential on the electrode surface dipped in the solution containing monomer, Py can be oxidized and the resulted polymer will be formed on the electrode surface. By controlling the various conditions such as the electrolyte type and its concentration, pH of the solution, and the type of electrochemical technique, various types of PPy including micro [2] and nanofibers [10] can be formed on the electrode surface.

The development of nanostructured polymers has opened up novel fundamental and applied frontiers, which has attracted tremendous interest in recent years. Nanostructured PPy including nanotubules [11], nanowires [12] and nanofibers [10] are of

considerable interest because of their unique properties on account of their finite small size and their larger surface area to volume ratios and have wide-ranging implications to a variety of areas, including biosensors [10], batteries and super-capacitors [8, 9].

In this study, the simple electrochemical method i.e. applying a fixed potential was developed for the fabrication of PPy nanofibers on the glassy carbon electrode (GCE) surface. Electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were used for the characterization of constructed PPy/GCE modified electrode.

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent grade. Pyrrole (Py, Merck) was vacuum-distilled and stored at lower than 5 °C at dark. Other reagents were used as received. The stock solutions of sodium carbonate (Merck, 1.0 M) and sodium perchlorate (Merck, 1.0 M) were prepared by dissolving appropriate amounts of their solids in water and diluting to the mark with water.

2.2. Nano-PPy/GCE fabrication

Glassy carbon electrode with diameter of 2.0 mm was polished with emery paper before use. For the modification of the electrode, GCE was immersed in solution containing 0.1 M sodium carbonate, 0.2 M sodium perchlorate and 0.15 M Py. Then, a fixed potential of about 0.85 V vs. Ag/AgCl reference electrode was applied to the electrode for 120 s. Then, the modified electrode surface was washed three times with perchloric acid (1.0 M) and distilled water for

removing physically adsorbed PPy on the electrode surface.

2.3. Instruments

All electrochemical measurements and polymerizations were performed on an Autolab electrochemical system (The Netherlands) equipped with PGSTAT and GPES software using GCE as working electrode (i.d. 2.0 mm), platinum wire as the counter electrode and an Ag/AgCl as the reference electrode. Scanning electron microscopic (SEM) images of the resulting PPy on the electrode surface were taken on a Philips instrument with an accelerating voltage of about 20 keV.

3. Results and discussion

3.1. The electrochemical oxidation of Py on GCE

Pyrrole (Py) is oxidized on various solid electrodes such as Pt and carbon electrodes at high positive potentials around 0.9 V. On GCE, however, the oxidation of Py is occurred in 0.85 V with a peak shaped oxidation behavior. Fig. 1a shows the cyclic voltammetry (CV) of GCE in solution containing 0.15 M Py, 0.1 M Na₂CO₃ and 0.2 M NaClO₄. At the second cycle, the oxidation peak current of Py was reduced indicating the hindrance of Py oxidation on GCE surface. On the other words, when Py is oxidized on the electrode surface, the polymerized products (Nano-PPy) are strictly adsorbed on the electrode surface causing the Py monomers in solution to difficultly diffuse on the electrode surface. Shifting the Py oxidation potential toward less positive potentials on the partially electropolymerized GCE surface in second cycle probably due to electrocatalytic effect of PPy conducting polymers formed on the

electrode surface at the first cycle (Fig. 1b and c).

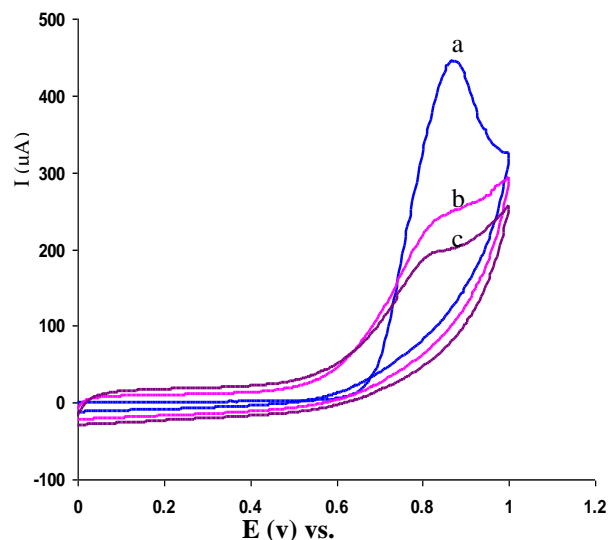


Fig. 1. Cyclic voltammetry of GCE at the scan rate of 0.05 Vs⁻¹ in solution containing 0.15 M Py, 0.1 M Na₂CO₃ and 0.2 M NaClO₄; (a) first cycle, (b) second cycle and (c) third cycle.

3.2. Electrochemical behavior of PPy/GCE modified electrode

Electropolymerization of Py was investigated by applying a fixed potential of 0.85 V for 120 s on GCE immersed in solution containing 0.15 M Py, 0.1 M Na₂CO₃ and 0.2 M NaClO₄. After polymerization process, the modified electrode was cycled in the potential range of -0.6 to 1.0 V at the scan rate of 1.0 Vs⁻¹ for 50 times in 0.1 M Na₂CO₃ solution to obtain stable background currents (treated PPy/GCE). Fig. 2 shows the background currents of GCE (curve a) and treated PPy/GCE in 0.1 M sodium carbonate solution (curve b). Increase in the background current of PPy/GCE in comparison with bare GCE is due to the increase in the surface area of the PPy/GCE modified electrode causing increase in the double layer capacitance and charging currents passed through the electrode surface. However, the cyclic voltammograms of newly

prepared PPy/GCE modified electrode (without treated) in KCl and NaClO₄ electrolytes show a pair of oxidation and reduction peaks (Fig. 2, curves c and d) mainly due to the known process of anions-doping/dedoping process [13]. On the other words, a couple of redox current peaks appearing at the potentials of about 0.4 and -0.13 V (curve d of Fig. 2) corresponds to the doping and dedoping processes of ClO₄⁻ ions in PPy, respectively. These peaks are vanished in alkaline solutions such as sodium carbonate as shown in Fig. 2b, mainly due to the inactivation of PPy nanofibers at these media [14].

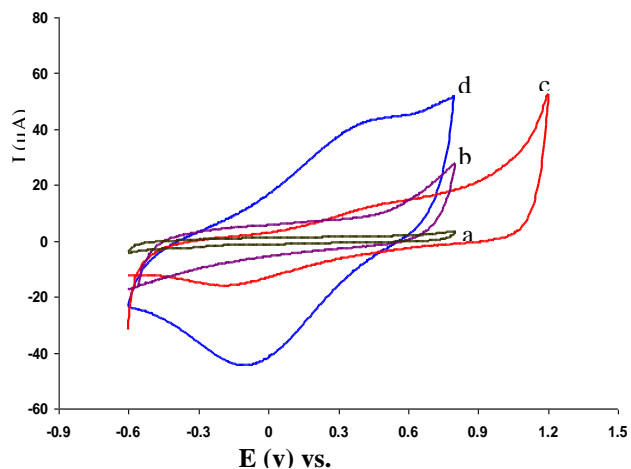


Fig. 2. Cyclic voltammograms of (a) GCE and (b) pretreated PPy/GCE in 0.1 M Na₂CO₃ solution; cyclic voltammograms of newly prepared PPy/GCE (without pretreated) in 0.1 M of KCl (c) and NaClO₄ (d) electrolytes. The scan rates were 0.05 V s⁻¹.

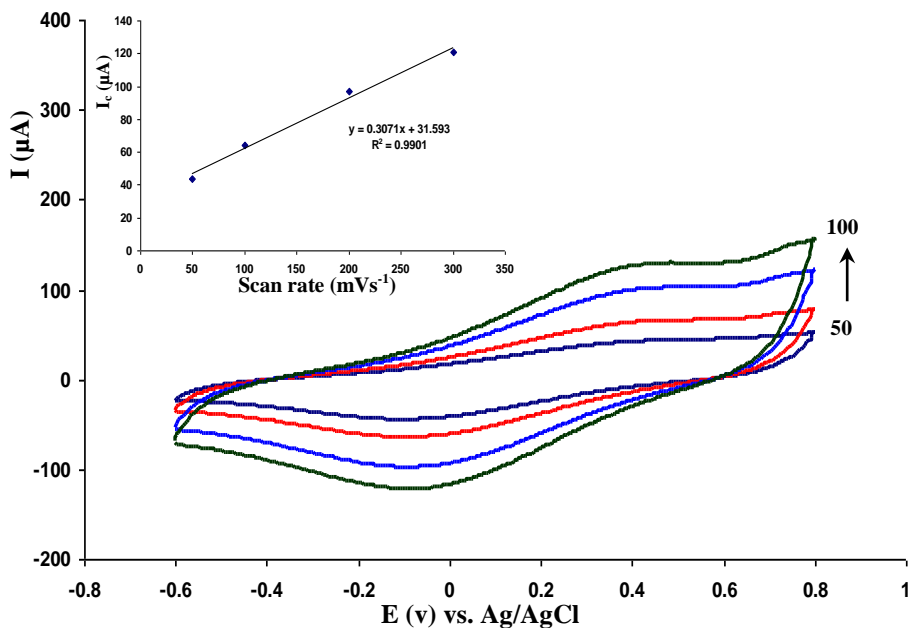


Fig. 3. Cyclic voltammograms of PPy/GCE in 0.2 M NaClO₄ solution at different scan rates of 50, 100, 200 and 300 mVs⁻¹. Inset: Plot of cathodic peak currents (I_c) vs. scan rate.

Fig. 3 shows the cyclic voltammograms of PPy/GCE in 0.2 M NaClO₄ solution at different sweep rates. A linear relationship between cathodic peak current and the potential sweeping rate was observed as shown

in the inset figure, which is characteristic of a thin film electrode [15]. CVs of the constructed Nano-PPy/GCE modified electrode shows that the modified electrode

can be effectively used as capacitor materials [8].

3.3. Scanning electron microscopy of PPy/GCE

SEM was used to characterize the morphology of the PPy prepared by the electrochemical technique. Fig. 4 shows the scanning electron micrograph of PPy nanofibers formed on the GCE electrode surface with the average diameter of about 100 nm. As it is clear, the PPy nanofibers exist in a nearly homogenous three-dimensional network.

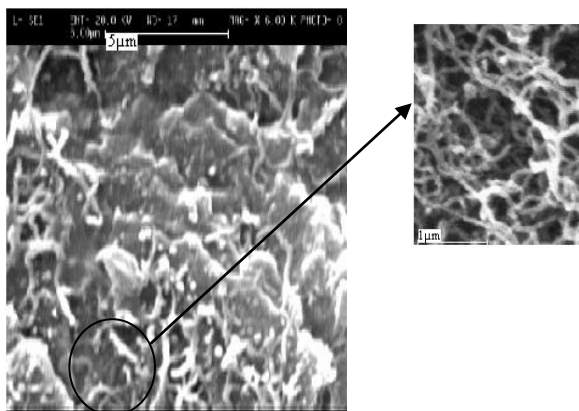


Fig. 4. Scanning electron micrograph of PPy nanofibers formed on the GCE electrode surface.

3.4. Electrochemical impedance spectroscopy of PPy/GCE

Electrochemical impedance spectroscopy (EIS) can provide useful information on the impedance changes of the electrode surface during the fabrication process. The semicircle part at higher frequencies corresponds to the electron-transfer limited process, and the diameter is equal to the electron transfer resistance, which controls the electron transfer kinetics of the redox probe at the electrode

interface. Fig. 5 shows the Nyquist plot of the EIS at GCE (a) and PPy/GCE (b) in 5.0×10^{-3} M $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) as probe containing 0.1 M KCl. Fig. 5a shows that only very small semicircle is observed at GCE, showing a low electron transfer resistance. The Nyquist diagram of the PPy/GCE (Fig. 5b) is the same as GCE with slightly higher electron transfer resistance in comparison with GCE. It means that the PPy film has not obstructed the electron transfer of the redox probe and the electron-transfer resistance was not changed considerably due to the presence of PPy conducting polymer on the electrode surface. This result is attributed to the good conductivity and electrochemical activity of PPy film, the fact that can be deduced from the CV of PPy/GCE (Fig. 2d).

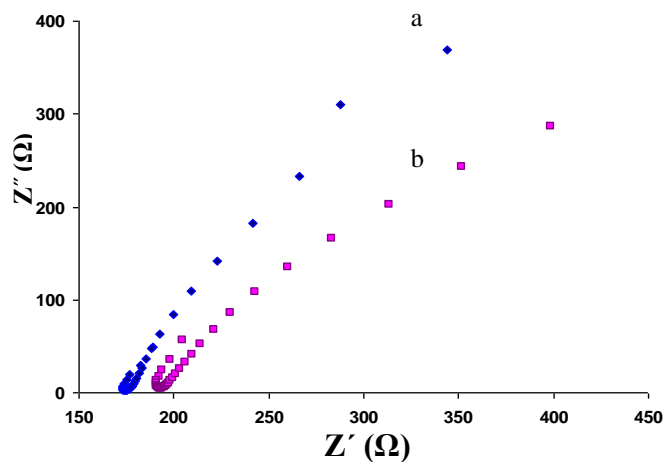


Fig. 5. Nyquist plot of the EIS at GCE (a) and PPy/GCE (b) in 5.0×10^{-3} M $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) as probe containing 0.1 M KCl.

Conclusions

Conductive polypyrrole nanofibers have been simply fabricated on glassy carbon electrode by using the electrochemical method. The proposed method is very simple and the PPy fibers are in the scale of nanometer size about

100 nm. Electropolymerization of pyrrole was done in mild basic media containing sodium carbonate and sodium perchlorate. By controlling the effective factors such as electrolyte composition and the concentration of species therein, the amount of applied potential and time of applying potential were optimized to construct conductive PPy nanofibers on the electrode surface. It is indicated from CVs of the constructed PPy/GCE modified electrode that this electrode can be effectively used as capacitor material. Also, the sensory and biosensory applicability of Nano-PPy/GCE is under investigation.

References

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