



The electrochemical copolymerization of diphenylamine and p-phenylenediamine and its use as a modified electrode for amperometric determination of iodate



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ABSTRACT

In this paper, copolymerization of diphenylamine with p-phenylenediamine was carried out in aqueous sulfuric acid by means of cyclic voltammetric sweep. The obtained copolymer was characterized by cyclic voltammetry (CV), Fourier transform infrared (FTIR), CHNS, energy-dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Electrochemical experiments indicated that the copolymer modified electrode exhibited an excellent sensitivity towards the reduction of iodate, which can be attributed to the electrical conductivity, nanoporous structure of the copolymer composite and an electrostatic interaction between the cationic oxidized (p-doped) copolymer and the anionic iodate. The electrochemical behavior of iodate has been investigated by amperometry and cyclic voltammetry at copolymer modified electrode. Amperometry revealed that there existed a good linear relationship between peak current with the concentration in the range of 50–550 μM and the detection limit of 0.8 μM . This composite film was also successfully applied in determination of iodate in urine.

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1. Introduction

Iodine is an essential micronutrient and has an important role in the normal function of the thyroid gland. Iodine Deficiency Disorder (IDD) is a public health problem in some areas of the world, especially in developing countries [1]. About 740 million people have goiters, but the percentage varies greatly by region (eastern Mediterranean: 32%; Africa: 20%; Europe: 15%; Southeast Asia: 12%; western Pacific: 8%; the Americas: 5%). Surveying communities for goiters is one of the best ways of detecting iodine deficiency, which if not treated, it can cause stillbirths, miscarriages, cretinisms, mental impairments, deafness and dwarfisms [2]. Because of widespread consumption and economical considerations, the salt iodisation is the best way to achieve the virtual elimination of IDD. Iodine is normally added to the salt in the form of potassium iodide (KI) or potassium iodate (KIO_3). The use of potassium iodate is usually preferred as an iodine supplement in iodised salt because of its greater stability in the presence of impurities, humidity, atmospheric oxygen, heat and sunlight [3,4]. Therefore, the determination of iodate (IO_3^-) is one of the important topics in food [5], clinical [6] and biological science

[7]. Various analytical methods have been used to determine IO_3^- , such as spectroscopy [4], chemiluminescence [7], Fluorescence [8] and ion chromatography [9]. However, these methods are generally time-consuming, lack of sensitivity, susceptibility to interference by other substances in analyte samples and difficult for an automated detection. To overcome all these shortcomings, the electrochemical sensors based on modified electrodes are especially promising because of their simplicity, high sensitivity, selectivity and low over oxidation potential in comparison to the bare electrodes [10,11].

Several modified electrodes for the electrochemical determination of iodate have been reported in the literature, such as: carbon based materials [12], metal nanoparticles [13], metal complex [14], metal oxide [15] and conducting polymer [16]. Among these modified electrodes [14,17–19] the polymer-modified electrodes have been used extensively, because of its high sensitivity, selectivity, homogeneity in electrochemical deposition, strong adherence to electrode surface and chemical stability of the film [20–22]. In this paper, we investigated the synthesis of copoly(diphenylamine 2:4 p-phenylenediamine) (copoly(DPA 2:4 PPA)) composite by cyclic voltammetry method on the surface of glassy carbon electrode (GCE). The obtained results show promising practical application of GCE/copoly(DPA 2:4 PPA) electrode as amperometric sensor for iodate determination.

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2. Experimental

2.1. Apparatus

Cyclic voltammetry (CV) and amperometric studies were performed using an Autolab potentiostat–galvanostat model PGSTAT30 (Utrecht, The Netherlands) with a conventional three electrode set-up, in which a modified electrode, an Ag|AgCl|KCl_{sat} and a platinum rod served as the working, reference and auxiliary electrodes, respectively. The working potential was applied in the standard way using the potentiostat and the output signal was acquired by Autolab Nova (version 1.7) software. Electrochemical impedance spectroscopy (EIS) experiments were carried out using a Zahner Zennium workstation in the presence of 5.0 mM Fe(CN)₆^{3/−4} couple (1:1) as the redox probe. An oscillation potential of 5 mV over a frequency range of 100 kHz to 0.1 Hz was applied and the output signal was acquired with the Thales Z (Zennium release) software. Scanning electron microscopy (SEM) was performed with a Philips instrument, Model XL-30. CHNS elemental analysis was performed with an elemental analyzer (The PerkinElmer 2400 Series) Energy-dispersive X-ray (EDX) spectroscopy was performed with shimadzu, Model EDX-720. The infrared spectra were obtained using a Bruker vector 22 Fourier transform infrared (FTIR) spectrometer. Atomic force microscopy (AFM) measurement was made on DME DualScope Scanner DS 95-200 (Herlev, Denmark). All measurements were performed at room temperature.

2.2. Reagents and chemicals

All chemicals were of analytical reagent grade and used without further purification except for diphenylamine (DPA) and P-phenylenediamine (PPA). H₂SO₄, Na₂SO₄, KOH, KCl, KIO₃, K₃[Fe(CN)₆] and K₄[Fe(CN)₆] were obtained from Merck (Darmstadt, Germany). Double distilled water was used throughout.

3. Results and discussion

3.1. Electrochemical copolymerization DPA with PPA

Fig. 1 shows typical multisweep cyclic voltammogram of mixture of 4 mM PPA and 2 mM DPA in 2 M H₂SO₄. There are four anodic peaks at 0.325, 0.475, 0.70, 0.90 V and a shoulder at 0.585 V respectively. The first cycle exhibit a nucleation loop commonly observed when a conducting phase is deposited. The rising current at higher potentials is the oxidation of the monomers to radical cations. The polymerization reaction was subsequently performed by radical-radical coupling [23,24]. The peak current at 0.325 V

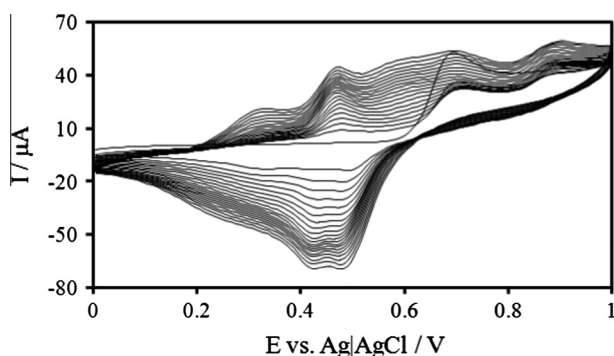


Fig. 1. Cyclic voltammograms of the electrodeposition of a copoly(DPA 2:4 PPA) film in 0.5 M H₂SO₄ solution containing 2 mM DPA and 4 mM PPA, Scan rate: 50 mV/s.

increases very quickly with the increase in the number of potential cycles especially after 5th cycle. This is probably due to the autocatalytic polymerization that causes quick copolymer film growth as the electrolysis process which is also clear from the non-linear relation between the first anodic peak current and cycle number. Based on previous reports for polyaniline and its derivatives [24–26], the peak at lower potential indicates the transformation of the reduced leucoemeraldine salt form into the emeraldine salt form and the peak at higher potential is assigned to the further oxidation into the pernigraniline form. The middle peak was assigned to the presence of crosslinking of polyaniline caused by the reaction of nitrenium species being present as intermediates or to overoxidation products [24–26].

The elemental analysis of prepared polymers was carried out by CHNS and EDX. Table 1.S shows the results of the CHNS analysis. The CHNS analysis indicated that the N/C ratio increased with increasing PPA in copolymer structure in compare with poly diphenylamine (PDPA). Moreover, the S/C ratio increased in copolymer structure in compare with PDPA. So, we can conclude that the p-doping level [27–32] (the negatively charged electrolyte such as SO₄^{2−}, HSO₄[−] that doped in the oxidized polymer structure) in the proposed copolymer is higher than that PDPA. These results are compatible with the EDX results (Fig. S.2).

For further verification, the FTIR spectra of the copolymer and poly diphenylamine (PDPA) were also recorded (Fig. S.3). The absence of a band at 3100 cm^{−1} corresponds to the aliphatic C–H stretching vibrations in the copolymer spectra indicates that the monomer units (DPA and PPA) are para coupled with each other in copolymer structure (shown in Scheme S.1).

The SEM images of GCE/copoly(DPA 2:4 PPA) electrode and GCE/PDPA electrode are shown in Fig. 2. It can be clearly seen that the surface morphology of GCE/copoly(DPA 2:4 PPA) was very porous than that GCE/PDPA.

The surface morphology of the proposed modified electrodes was also characterized by using AFM (Fig. S.4). According to previous reports [33–37], the skewness of the topography height distribution (S_{sk}) and the kurtosis of the topography height distribution (S_{ku}) are the moments of profile amplitude probability density function and is used to measure the profile symmetry about mean line and the measure of surface sharpness, respectively. When the height distribution is symmetrical, S_{sk} is zero. But if the surface has more peaks than valleys, S_{sk} is positive and if the surface is more planar than valleys, S_{sk} is negative. On the other hand, when S_{ku} is 3, it indicates a Gaussian amplitude distribution and surface is called mesokurtic. But if S_{ku} is smaller than 3, the surface is flat and if S_{ku} is higher than 3, surface has more peaks than valleys. Base on the results obtained from AFM software, S_{sk} and S_{ku} values for the GCE/copoly(DPA 2:4 PPA) electrode were 2.23 and 16.8, respectively. In contrast, these values were −0.16 and 2.77, for the GCE/PDPA electrode. Therefore, the surface of the GCE/copoly(DPA 2:4 PPA) electrode was very porous in comparison with the GCE/PDPA electrode (Fig. S.4).

3.2. Electrochemical properties of the electrodes

EIS and CV have been used to characterize the interface properties of surface modified electrodes. The typical impedance spectrum (presented in the form of the Nyquist plot) includes a semicircle portion at higher frequencies corresponding to the electron-transfer-limited process and a linear part at lower frequency range representing the diffusion limited process. The semicircle diameter in the impedance spectrum equals the electron transfer resistance (R_{ct}). This resistance controls the electron transfer kinetics of the redox probe at the electrode interface. Fig 3A displays the Nyquist plots obtained for a GCE (a), GCE/copoly(DPA 2:4 PPA) (b) and GCE/PDPA (c) in a solution containing 5.0 mM Fe(CN)₆^{3/−4}

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