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Electrocatalytic oxidation of hydrazine at overoxidized polypyrrole film modified glassy carbon electrode

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Abstract

Electrocatalytic oxidation of hydrazine (HZ) was studied on an overoxidized polypyrrole (OPPy) modified glassy carbon electrode using cyclic voltammetry and chronoamperometry techniques. The OPPy-modified glassy carbon electrode has very high catalytic ability for electrooxidation of HZ, which appeared as a reduced overpotential in a wide operational pH range of 5–10. The overall numbers of electrons involved in the catalytic oxidation of HZ, the number of electrons involved in the rate-determining and diffusion coefficient of HZ were estimated using cyclic voltammetry and chronoamperometry. It has been shown that using the OPPy-modified electrode, HZ can be determined by cyclic voltammetry and amperometry with limit of detection 36 and 3.7 μM, respectively. The results of the analysis suggest that the proposed method promises accurate results and could be employed for the routine determination of HZ.

Keywords: Hydrazine; Overoxidized polypyrrole; Voltammetric behavior

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1. Introduction

Conducting polymer films have been widely studied for applications in chemical sensors and biosensors. Polypyrrole (PPy) is one of the most extensively used conducting polymers for constructing of bioanalytical sensors and modified electrodes [1]. Applications of PPy to trace metal determinations by voltammetry have generally required an immobilization of a selective chemical reagent onto/into the polymer film, such as PPy covalently modified with *N*-carbodithionate ligating groups [2] or incorporation of anionic reagents into the polycationic oxidized PPy film during the pyrrole electropolymerisation process [3–6].

The use of non-conducting polymers with permselective properties in enzyme entrapment applications is another effective alternative for the construction of interference-free biosensors [7]. In this sense, the irreversible overoxidation of PPy films allows to obtain a non-conducting film with remarkable permselectivity stemming from size- and anion-exclusion properties, owing to the permeability of the polymer and to the generation of anionic groups in the polymer backbone with high electron density that act as a barrier against the diffusion of anionic species into the film [8,9]. Overoxidized PPy films acquire properties that resemble those of non-conducting polymers, but offer an additional advantage of the control of the film thickness during the electropolymerization process in contrast with non-conducting polymers that exhibit self-limited growing and afford only modest enzyme loads owing to the small film thickness achieved [10].

Hydrazines (HZ) are important compounds of interest in chemical and pharmaceutical industries. They are employed in areas such as fuel cells, herbicides, catalysts, rocket propellants and so on. There are several electrochemical methods for determination of hydrazine in the literature with different detection limit, pH, linear range and the potential of hydrazine oxidation. Table 1 summarized details of the methods from available references along with their analytical parameters and compared them with the proposed electrode in this work.

Previously we have used the overoxidized polypyrrole–GC electrode to elcrocatalysis and determination of isoniazid, a derivative of HZ [27]. In this work, a glassy carbon electrode coated with overoxidized polypyrrole (OPPy) film for electro-

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Table 1
The reported electrodes from the literature and the proposed one for electrocatalytic determination of hydrazine, their common analytical parameters and the references

	Electrode	Modifier	Electrochemical method	E_p	pH	Linear range (μM)	LOD	References
1	Glassy carbon	Chlorogenic acid	Cyclic voltammetry	240	–	50–1000	–	[11]
2	Glassy carbon	Fe–tetraaminophthalocyanine	Cyclic voltammetry	−300	13	1–10000	–	[12]
3	Glassy carbon	Pyrocatechol violet	Amperometry	240	7.5	5–40	4.2	[13]
4	Cylindrical carbon fiber microelectrodes	Rhodium	Flow injection with amperometric detection	0, 300, 500	7.5	5–1000	0.62	[14]
5	Carbon nanotube powder microelectrodes	–	Amperometric	90	7	1–10000	–	[15]
6	Glassy carbon	Cobalt pentacyanonitrosylferrate	Cyclic voltammetry	500	-	0–12000	–	[16]
7	Glassy carbon	Cobalt phthalocyanine	Cyclic voltammetry	150	13.3	2000–20000	–	[17]
8	Carbon paste	Hybrid copper–cobalt hexacyanoferrate	Cyclic voltammetry	240	7	100–12000	–	[18]
9	Glassy carbon	Hydroquinone salophen derivatives	Cyclic voltammetry	212	–	10–400	1.6	[19]
10	Gold electrode	Iron phthalocyanine	Osteryoung square wave voltammetry	350	7	0.13–0.92	5	[20]
11	Glassy carbon	Pyrogallol red	Linear sweep voltammetry	200	9	5–600	2	[21]
12	Glassy carbon	Hematoxylin on the multi-wall carbon nanotube	Amperometric	203	7	2–122.8	0.68	[22]
13	Glassy carbon	*o*-Aminophenol	Amperometric	110	9	2–20	0.5	[23]
14	Carbon fiber microelectrode	Co and Cu hexacyanoferrate	Potentiometric	550	7	1–1000	0.5	[24]
15	Carbon ceramic composite electrode	Chlorogenic acid	Amperometric	250	8	0.1–1000	0.02	[25]
16	Carbon	Copper–palladium alloy nanoparticle	Flow injection	200	7.4	2–100	0.27	[26]
	Glassy carbon	Overoxidized polypyrrole	Amperometric	265	9	1.3–2000	3.6	This work

catalytic determination of HZ has been developed as a simple, sensitive, rapid and new assay method for HZ.

2. Experimental

2.1. Reagents and instrumentation

HZ and other reagents were of analytical grade supplied by Merck. Pyrrole is purified by double distillation and stored in a refrigerator and prevented from light. Deionized water was used for the preparation of all solutions. The background electrolyte solution was prepared from potassium chloride. The pH of solutions was adjusted to 9 with ammonia buffer. A glassy carbon disk electrode with 2 mm diameter was used as working electrode. A platinum wire was employed as counter electrode and a saturated calomel electrode (SCE) served as the reference electrode and all potentials in the text refer to it (all electrodes obtained from Azar Electrode Co., Urmia, Iran). Voltammograms were obtained with PGSTAT 20 Autolab potentiostat from ECO Chemie (the Netherlands).

2.2. Preparation of modified electrode

The glassy carbon electrode was polished with 0.05 μm alumina in water slurry using a polishing cloth and deionizied water. The polished electrode was placed in a 0.5 M NaOH solution and the electrochemical activation of the electrode was performed by potentiostatic method at 0.9 V for 100 s. This electrode was used for preparation of modified electrode.

Overoxidized polypyrrole were prepared for characterization in two polymerization/overoxidation steps. Polypyrrole was first elctropolymerized on the GC by using cyclic voltammetry method. In this procedure potential was scanned from −0.2 V to 0.8 V at the scan rate of 50 $\mathrm{mVs^{-1}}$ for four times. The polymerizing solution was 0.05 M pyrrole and 0.1 M $LiClO_4$ in deionized water. PPy was then overoxidized by scanning potential from −0.3 V to 0.8 V versus SCE at the scan rate of 10 $\mathrm{mVs^{-1}}$ for eight times in 0.5 M NaOH.

3. Results and discussion

Fig. 1a shows the voltammograms recorded for the overoxidation process of PPy. There is a prominent peak at approximately 390 mV during the first cycle. During the second and third cycles, however, featureless voltammograms were recorded (Fig. 1b and c). This indicates that an irreversible electrochemical transformation of the polymer film has been achieved during the first cycle. This transformation is accomplished by a loss of conjugation and hence electronic conductivity [10,13,27] and a net electronegative character is imparted to the polymer film and it then undergoes permselective behavior resulting in overoxidized films [28]. Also at this process, the surface of electrode is activated.