Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3357-3363

Amperometric Determination of Dopamine on a Glassy Carbon Electrode Chemically Modified with Cobalt Pentacyanonitrosylferrate

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A cobalt pentacyanonitrosylferrate modified glassy carbon electrode (GC/CoPCNF) was prepared by electrochemical method. The prepared GC/CoPCNF electrode was showed a reversible peak with formal potential of 0.52 V *vs.* SCE in 0.25 M KNO_3 with 50 mVs^{-1} scans rate. The electrochemical behaviour and stability of the modified electrode were studied by cyclic voltammetry. The experimental results were showed that the GC/CoPCNF electrode is stable within a pH range of 2-8. The modified electrode was exhibited good electrocatalytic activity toward oxidation of dopamine. The effect of pH and applied potential on the electrocatalytic activity of the modified electrode investigated. According to the experimental results the best potential for the amperometric determination of dopamine was 0.70 V *vs.* SCE. The calibration plot was linear from 10 μM up to 110 μM (r = 0.993) with a good response time (10 s). The detection limit of modified electrode as an amperometric sensor is 8 μM.

Key Words: Dopamine, Cobalt pentacyanonitrosylferrate, Electrocatalysis, Electrocatalytic oxidation, Amperometric determination, Glassy carbon electrode.

INTRODUCTION

Since Neff[1,2] first deposited Prussian Blue (PB) in the form of a film on solid electrodes, interest in the analogues of this compound has increased and various transition metal cations used with hexacyanoferrate to fabricate metal hexacyanoferrate modified electrodes. Recently modified electrodes have received increased attention during two decade, because of their application in electrocatalysis[3-6], biosensor systems[7-10], ion selectivity[11-14] and solid-state battery[15,16]. The metal pentacyanonitrosylferrates (MPCNF), as a class of polynuclear mixed valence compounds, also have attracted

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much attention for the preparation of thin films on electrodes in the last years[17-26] and ability to catalyze electrochemical reactions. The MPCNF modified electrodes used for electrocatalytic oxidation of iodide[21], nitrite[22], sulfite[23,24], dopamine[26], ascorbic acid[17,20] and in this studies, M at MPCNF modified electrode was Ni[19-21,24,26], Pd[18,22,], Co[17,23]. They act as mediators in electron transfer from substrate to electrode materials and the most important feature of the chemically modified electrodes (CMEs), are the electrocatalysis of slow electron transfer reactions. The modified electrodes enhance the rate of electron transfer by reducing the over potential associated with a reaction, therefore such electrocatalysis enables a high current density (*i.e.* increased sensitivity) to be obtained for a poor kinetic reaction at a potential close to the equilibrium potential. Several neurotransmitters such as dopamine are electroactive and therefore can be detected electrochemically. The fact that dopamine and other catecholamines are easily oxidizable compounds makes their detection possible by electrochemical methods based on anodic oxidation. Previous workers[27-30] used the modified electrode to study of dopamine oxidation. However, the product of the oxidation of dopamine can cause electrode surface fouling and the electrochemical response of dopamine become irreversible or qusi-reversible with a large peak-to-peak separation.

EXPERIMENTAL

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP-2063 electrochemical analysis system, Behpajooh. Iran) at room temperature. A conventional three-electrode cell was used at room temperature. A saturated calomel electrode, platinum wire and a glassy carbon disk modified electrode of 0.0314 cm^2 surface area were used as reference, auxiliary and working electrodes, respectively. $CoCl_2$, $Na_2[Fe(CN)_5NO]$ (nitroprusside), KNO_3 and dopamine were of analytical grade from Merck and used without further purification. All solutions were prepared with double distilled water. A solution of 0.25 M KNO_3 was used as a supporting electrolyte.

Modified electrode construction: The glassy carbon electrode surface was polished with 0.05 μm alumina powder on the wet polishing cloth. The polished electrode was rinsed with distilled water for several times. For preparation of the modified electrode, first the metallic cobalt was deposited from a 20 mM $CoCl_2$ + 0.1 M KNO_3 (plating solution) on the glassy carbon electrode by applying a constant cathodic current of 0.1 mA for 10-40 s depending on the desired thickness. The glassy carbon electrode covered by metallic cobalt was immersed in 0.25 M KNO_3 + 50 mM $Na_2[Fe^{2+}(CN)_5NO]$ solution (derivatization solution) and derivatized by cycling the electrode potential between -0.2 and 0.75 V until a stable voltammogram observed (about 30 cycles with potential scan rate of 50 mV/s). The total surface coverage of the electrode, Γ^0, was determined from the area under anodic cyclic voltammograms of GC-CoPCNF electrode.

RESULTS AND DISCUSSION

Electrochemical behaviour of modified electrode: The preparation of the CoPCNF/GC modified electrode is carried out in two-step involving the deposition of metallic cobalt on the GC surface and then derivatization the deposited cobalt to CoPCNF. The plating step may be achieved by amperostatic or potentiostatic procedures using optimized conditions ($CoCl_2$ concentration, current density, applied potential and plating time). The primary experiments showed that the low current density and prolonged plating duration is most convenient. We have chosen a 20 mM $CoCl_2$ solution, current density of 3 mA cm^{-2} or applied potential of -1.15 V and the plating duration of 15-30 s. The derivatization step was also carried out with either amperostatic or potentiodynamic methods. We have found that for the amperostatic derivatization, a 0.05 M $Na_2[Fe(CN)_5NO]$ + 0.25 M KNO_3 solution, using the low current density of - 4 mA cm^{-2} is suitable. Similarly for the potentiodynamic derivatization it is found that sweeping the electrode potential between -0.2 and + 0.75 V for about 30 cycles with a scan rate of 50 mV/s yields a good modifier layer.

Cyclic voltamogramms of CoPCNF-modified glassy carbon electrode between 0 and 1 V exhibit a pair of peaks with a formal potential, $E^{o'} = (E_{pa} + E_{pc})/2$, of 520 mV *vs.* SCE. Since, the Co^{2+} cations in the modifying film are not expected to be electroactive in the potential range examined, 0.1-1.1 V, the electrode reaction should be attributed to the Fe(II, III) portion of CoPCNF. At lower scan rates ($\nu < 200$ mV/s) the anodic peak currents (I_{pa}) are linearly proportional to the scan rate (ν), which is expected for surface confined redox processes. However, at higher scan rates ($\nu > 200$ mV/s), the plot of I_{pa} *vs.* $\nu^{1/2}$ indicates diffusion-controlled processes, which may be related to the relatively slow diffusion of K^+ into the modified layer. As seen in Fig. 1A (curve b) the ratio I_{pa}/I_{pc} remains almost unity, as expected for a surface-type behaviour. The voltammograms exhibit a pair of peaks with a peak potential separation, $\Delta E = E_{pa} - E_{pc}$, of 25 mV at a scan rate of 20 mV/s. The surface coverage of electroactive species in the modified layer, Γ, can be evaluated from the following equation:

$$\Gamma = Q/nFA \qquad (1)$$

where Q is the background corrected charge obtained by integration of anodic peaks (ν = 20 mV/s), A is the electrode surface area, F is the Faraday constant and n is the number of electrons (one electron here), the calculated surface coverage was 2×10^{-8} mol cm^{-2}. It should be pointed out that the calculated surface coverage is an efficient attribute (per cross section of the electrode) and does not reflect the actual amount of CoPCNF per area of exposed glassy carbon.

Electrochemical oxidation of dopamine: The CoPCNF films on the glassy carbon electrode showed an excellent electrocatalytic activity toward the oxidation of dopamine in 0.25 M KNO_3 as supporting electrolyte. The cyclic voltammograms of the GC electrode (curve a) and GC/CoPCNF electrode in the absence (curve b) and presence of 20 mM dopamine (curve c, d) in 0.25 M KNO_3 are shown in Fig. 1A. As can be seen after addition of 20 mM dopamine, an increase in the anodic peak current is observed, whereas the cathodic peak have depressed This behaviour is typical of that expected for mediated oxidation, the cyclic voltammograms for dopamine on a bare GC and GC/CoPCNF in presence and absence of 20 mM dopamine are shown in Fig. 1A (curve c and d). At the bare GC electrode, the oxidation of dopamine oxidation occurs around 0.75 V *vs.* SCE (curve c) and the electron transfer kinetics in comparison to GC/CoPCNF is slow, owing to fouling of the electrode surface by the adsorption of oxidation product of dopamine. As can be seen from Fig. 1 (curve c and d), an increase in the oxidation peak current accompanied by a negative shift (about 230 mV) in the peak potential was observed for the oxidation of dopamine at GC and GC/CoPCNF electrodes. The height of the anodic peak increases with increasing dopamine concentration and the plot of Ip *versus* dopamine concentration between 0.1-20 mM is linear (Fig. 1B).

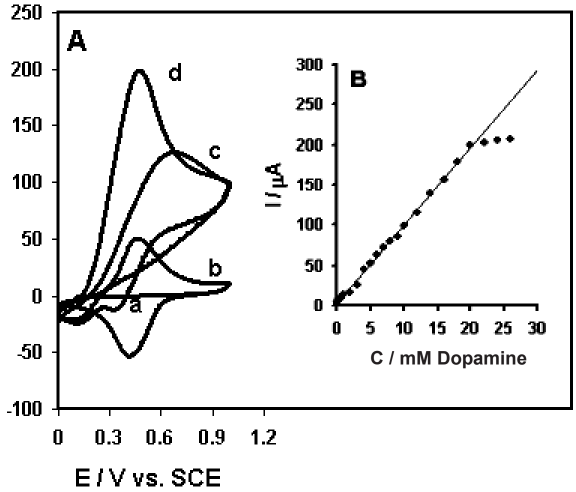

Fig. 1. (A) Cyclic voltammograms of a) GC electrode b) GC/CoPCNF in absence and c,d) in the presence of 20 mM dopamine in a 0.25 M KNO_3 solution. Scan rate of 20 mV/s (B) Variation of the anodic peak currents *vs.* dopamine concenteration

Effect of pH on electrocatalytic activity: Fig. 2 shows the effect of pH on voltammetric effect of the modified electrode. The effect of pH on electrochemical behaviour of GC/CoPCNF was studied in 0.25 M KNO_3 + 0.1 M phosphate buffer (with K^+ cation). The experimental results show that the modified electrode exhibits best voltammetric response in pH about 7. At higher pHs the peak current decreases. It may be due to hydrolysis of the modified electrode film and in lower pHs also the peak current decreases. It may be due to the competition effect of H^+ cation.

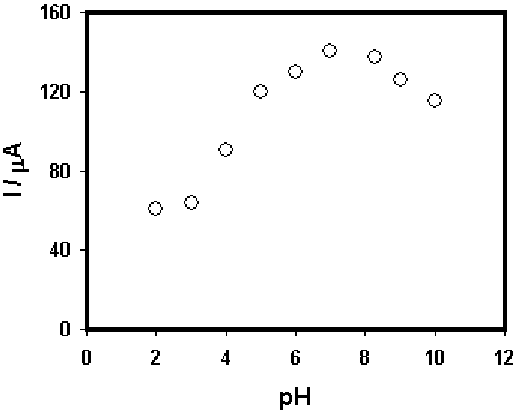

Fig. 2. The anodic peak currents of a GC/CoPCNF electrode in 0.25 M KNO_3 + 0.1 M phosphate buffer (with K^+ cation) *versus* pH. Scan rate: 50 mV/S

Stability of the modified electrode: The stability of GC/CoPCNF electrode was studied by cyclic voltammetry in 0.25 M KNO_3 solution. The modified electrode exhibits one pair of peaks at 0.52 V *vs.* SCE. Scanning of the potential of the modified electrode between 0-1 V *vs.* SCE for 100 continuous scan, shows only 12 % decrease in the heights of peaks was observed. On the other hand cyclic voltammetry with an electrode stored in air at room temperature for about 1 month showed that the decrease of the peak current was less than 3 % after 100 cycle in 0.25 M KNO_3. The experimental results also indicates that the GC/CoPCNF film is stable in the -1 to 1.5 V *vs.* SCE (oxidation potential of the solvent) (Fig. 3).

Hydrodynamic amperometry: Hydrodynamic amperometry for dopamine oxidation on GC/CoPCNF was studied to investigate application of the GC/CoPCNF electrode in flow system (Fig. 4). The hydrodynamic voltammograms were performed in stirred solution, while the steady state current measured at fixed value of the potential. A low response to dopamine oxidation was observed at a bare GC electrode. However, at a modified electrode an enhanced response to dopamine oxidation was obtained. The

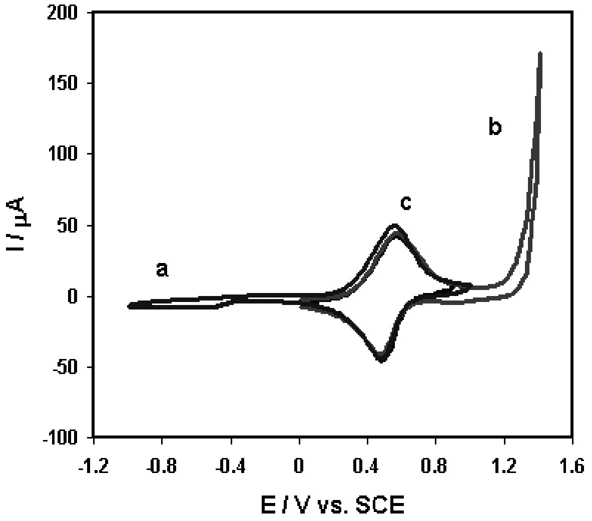

Fig. 3. Cyclic voltammograms of GC/CoPCNF in 0.25 M KNO_3 in potential range of (a) -1 to +1 V (b) 0 to 1.4 (c) 0 to 1.2 V *vs.* SCE, Scan rate: 100 mV/s

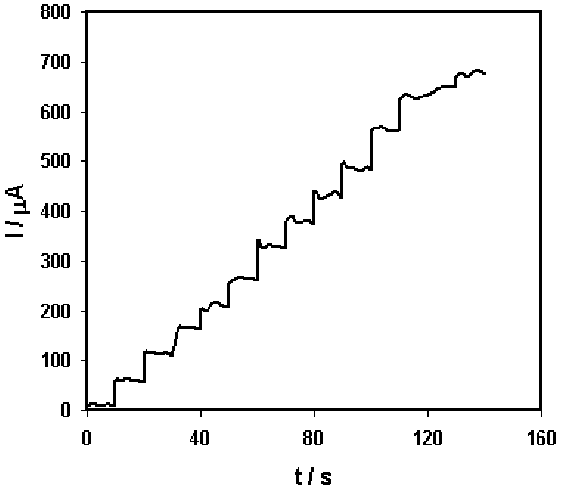

Fig. 4. Typical amperogram showing the current response for successive additions of dopamine to 10 mL 0.25 M KNO_3 (pH = 7) to prepare dopamine solution range 10-110 mM applied potential: 0.7 V

effect of potential on catalytic oxidation of dopamine also studied. The results show that in the presence of 10 mM of dopamine in the potential range of 0.0 to 1.0 V a plateau at 0.7 V appeared, so the 0.7 V *vs.* SCE in stirred solution of 0.25 M KNO_3 was applied to GC bare and modified electrode. The modified electrode showed a linear response for dopamine determination in the concentration range of 10-110 µM, with detection limit (as 3 times of background current) of 5 μM, the response time was 10 s. The standard addition technique was used for determining dopamine content the dopamine hydrochloride injection solution. This procedure was repeated 4 times and the relative standard deviation obtained was < 5 %. Standard dopamine solutions in dopamine hydrochloride injection solution were added and the above analytical procedure repeated. The recovery was between 96.8 and 103.5 % for 5 measurements.

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(*Received*: 17 March 2007; *Accepted*: 30 January 2008) AJC-6262