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Cyclic Voltammetry Determination of Epinephrine with a Nano-gold Modified Glassy Carbon Electrode in the Presence of High Concentration Ascorbic Acid

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Abstract: Nano-gold (NG) modified glassy carbon electrodes (GCEs) were used for determination of epinephrine (EP) in the presence of high concentration ascorbic acid (AA) by cyclic voltammetry (CV). This modified electrode can not only catalytically oxidize EP and AA, but also separate the catalytic peak potentials of EP and AA by about 183.5 mV. In pH = 7.0 ogisogate byffer solution, the linear range of epinephrine was $5 \times 10^{6} \sim 1 \times 10^{-4}$ mol/L.

Keywords: Nano-gold, glassy carbon electrode, epinephrine, ascorbic acid, cyclic voltammetry.

As we know, there are usually some problems in electrochemical analysis with bare electrode to detect neurotransmitters. One is low electron transfer rate and the other is interfering compounds, such as ascorbic acid. So some kinds of modified electrodes have been successfully employed to promote the efficiency of electrochemical analysis[1-4], such as Nafion modified electrode[5,6] and SAM modified electrode[7]. They can attract positively-charged neurotransmitters while repulse negatively-charged compounds, *e.g.* ascorbic acid, due to their negatively-charged surface.

Herein, we studied the electrochemical behavior of epinephrine at the nano-gold particles modified glassy carbon electrode by cyclic voltammetry. This modified electrode has been proved to be of catalytic effect to the epinephrine and ascorbic acid due to the biocompatibility of nano-gold. The peak potentials of epinephrine and ascorbic acid could be separated by about 183.5 mV, which is large enough for selective detection of epinephrine in the presence of ascorbic acid. This maybe also based on electrostatic interactions due to the negatively-charged surface of nano-gold which was reduced by citric acid[8].

Experimental

Equipment and reagents

Electrochemical measurements were carried out on an EG & G Princeton Applied

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Research Corporation (PARC) model 283 Potentiostat/Galvanostat (U.S.A) with a nano-gold modified glassy carbon electrode as working electrode, an Ag/AgCl/KCl (3 mol/L) and a platinum wire as reference and counter electrodes, respectively. In this paper all potentials are given *versus* Ag/AgCl/ KCl (3 mol/L) reference electrode unless otherwise written.

Epinephrine and ascorbic acid were obtained from Sigma and Chemical Reagent Company of Shanghai. Solutions of EP and AA were prepared in 0.1 mol/L phosphate buffer solution (PBS) which was previously deaerated with high purified nitrogen for 10 min, respectively. All other reagents are analytical grade and used without further purification. Quartz double-distilled water was used for all solutions.

Preparation of the nano-gold modified glassy carbon electrode

The 6 nm nano-gold particles were prepared according to the method of Natan[9]. The nano-gold modified glassy carbon electrode (ϕ = 3 mm, BAS, USA) was obtained according to literature[10], labeled as NG/GCE and immersed in PBS before use.

Results and Discussion

Electrochemical behavior of EP

Figure 1 CV curve of 1×10^{-3} mol/L EP at (a) bare GCE and (b) NG/GCE (scan rate:100 mV/s)

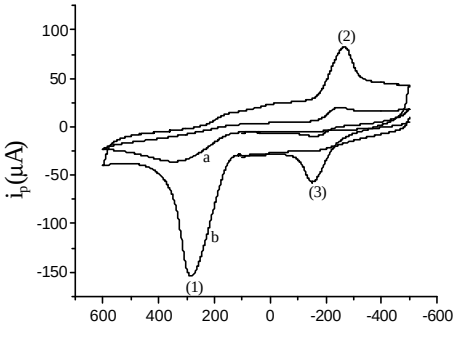
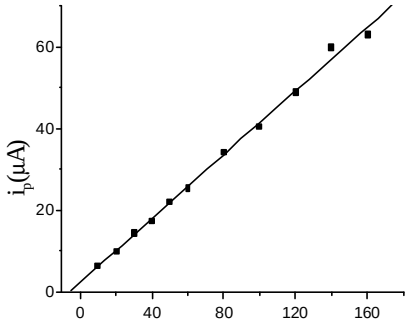


Figure 2 Relationship between oxidation peak current of EP and scan rate



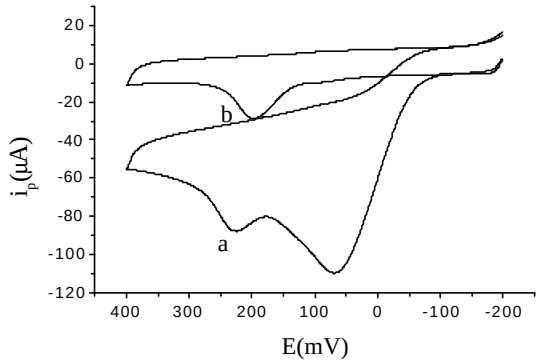
scan rate v=10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160 mV/s

Figure 1 shows the cyclic voltammograms of the 1×10^{-3} mol/L EP at bare GCE (curve a) and NG/GCE (curve b). Peak (1) is in accord with the oxidation of EP to the open-chained quinone, and peak (2) corresponds to the reduction of the cyclized product, *i.e.* adrenochrome to leucoadrenochrome, while peak (3) is that of the reoxidation of leucoadrenochrome to adrenochrome[11]. As shown in curve b of **Figure 1**, the current of peak (1) is about 4 times to that in curve a, while the potential of peak (1) shifts to negative by about 54.5 mV compared with that in curve a, which are the clear evidences of the catalytic effect of the NG/GCE toward epinephrine.

CV peak current response obtained at the NG/GCE was found to be linearly proportional to the scan rate in the range of 5 to 160 mV/s (**Figure 2**), which illustrated that the electrode process was concerned with the surface reaction process. Furthermore, after scanning in 1×10^{-3} mol/L EP for one cycle, the NG/GCE scanning in 0.1 mol/L PBS (pH = 7.0), the well-defined voltammetric peak was still observed (CV not shown). This also illustrated that the EP has been adsorbed on the surface of NG/GCE. The total surface concentration of $\Gamma = 3.84 \times 10^{-10}$ mol/cm^2 of EP on the NG/GCE surface can be calculated, according to the equation: $i_p = n^2F^2 \Gamma vA/4RT$[12].

Cyclic voltammogram of EP and AA mixture

Figure 3 CV curves of NG/GCE scanning in EP + AA mixture solution and PBS



(a) 5×10^{-5} mol/L EP + 5×10^{-3} mol/L AA mixture solution and
(b) 0.1 mol/LPBS after scanning in 5×10^{-5} mol/L EP and 5×10^{-3} mol/L AA mixture for one cycle (scan rate: 100 mV/s)

Figure 3a is the CV curve of the mixture of 5×10^{-5} mol/L EP and 5×10^{-3} mol/L AA at NG/GCE which indicates that NG/GCE can separate the oxidation peak by about 183.5 mV, this is large enough for selective determination of EP. Furthermore, because there was no adsorption of AA on the surface of NG/GCE (**Figure 3b**), we applied the following method to achieve the selective determination of EP. After scanning in EP and AA mixture for one cycle, the electrode was rinsed with water, then scanned in 0.1 mol/L PBS. After that no oxidation peak of AA could be observed but the oxidation peak of EP was still observed. So this CV response can be applied to the detection of EP.

Effect of pH on the oxidation peak of EP

The effect of pH on the oxidation peak potentials and peak currents were investigated. The potential shifted to lower values as the pH increased according to the equation: E_p (mV) = 692.7-69.1 pH. The peak current increased with increasing pH values from

2.0 to 8.0 and reached a maximum at pH 8.0, then decreased quickly with further increasing of the pH values. This was coincident with the previous report[13]. But we still selected pH 7.0 as the metrical condition in the subsequent experiments due to its similarity to environment in human body.

Relationship of peak current and EP concentration

Relationship of peak current and EP concentration was investigated with NG/GCE scanning in various concentration of EP ($c = 5 \times 10^{-6}$, 1×10^{-5}, 5×10^{-5}, 1×10^{-4} mol/L). The oxidation peak current was found to be linearly proportional to the concentration of EP in the range of 5×10^{-6} to 1.0×10^{-4} mol/L ($R = 0.996$).

Conclusion

In this paper, the electroanalysis of EP in the presence of high concentration of AA has been performed at a nano-gold modified GC electrode. We found that the NG/GCE could not only catalytically oxidize EP and AA, but also separate the catalytic peak potentials of EP and AA by about 183.5 mV, which was large enough to the selective determination of EP in presence of high concentration AA. This may be also based on the electrostatic reaction. This novel method might be applied to sensing neurotransmitters in the living organism

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