Chinese Chemical Letters Vol. 13, No. 8, pp 765 – 768, 2002
http://www.imm.ac.cn/journal/ccl/html

Nanosized SnO_2 Particles Dispersed on a Graphite Electrode for Selective Detection of Dopamine and Ascorbic Acid

Jun LIU[1,2], Zong Hua WANG[1], Yi Ming WANG[1], Guo An LUO[1]*, Han Wen SUN[2]

[1]Department of Chemistry, Tsinghua University, Beijing 100084
[2]Department of Chemistry, Hebei University, Baoding 071002

Abstract: A novel nano-SnO_2/graphite electrode has been prepared *via* polishing procedure to produce active and stable surface. The modified electrode resolves the overlapping voltammetric response of dopamine and ascorbic acid into two well-defined peaks by 230 mV. The mechanism of discrimination of dopamine from ascorbic acid is discussed. Dopamine and ascorbic acid can be determined simultaneously with the modified electrode. The electrode shows good sensitivity, selectivity and stability.

Keywords: Nano-SnO_2/graphite electrode, dopamine, ascorbic Acid.

Introduction

Dopamine (DA) plays a crucial role in the central and peripheral nervous system of human beings and mammals, so its detection with high selectivity and sensitivity is of great significance in the investigation of its physiological functions and diagnose of nervous diseases resulted from abnormal metabolite[1]. The main and foremost difficulty is the interference of ascorbic acid (AA), which is oxidized at almost the same potentials as DA on solid electrodes. As a result, a great deal of approaches has been used to overcome the problem. The choice of an electrode material is greatly influenced by the morphological aspects of its surface, because the electrooxidation rates strictly depend on the actual chemical and physical status of the electrode surface. Metal oxides dispersed on glassy carbon (GC) electrodes showed some favorable features in electrooxidative catalysis of ascorbic acid, oxalic acid[2] and catechol[3]. Nanosized materials can exhibit unique features in the electric, optical, magnetic and catalytic aspects[4]. Very recently, ultrafine TiO_2 coated graphite electrodes used for voltammetric separation DA and AA have been established by our group[5]. In this study, a good electrode substrate modified by polishing nanosized SnO_2 particles on a graphite electrode, designated as nano-SnO_2/graphite, is firstly described. The nano-SnO_2/ graphite electrode has many advantages with regard to sensitivity and selectivity for the detection of DA and AA.

*E-mail: galuo@chem.tsinghua.edu.cn

Preparation of nano-SnO_2/graphite electrode

The graphite electrode (12.56 mm^2) was polished with 600-grit SiC paper, 0.3 and 0.05 m Al_2O_3 slurry and then ultrasonically cleaned in doubly distilled water and ethanol for 5 min, respectively, and dried with a stream of highly purified nitrogen. The graphite electrode was lightly repolished with nanosized SnO_2 particles with the average particle size at 15 nm, and rinsed with doubly distilled water. The electrode was immediately used for experiments.

Results and Discussion

Figure 1 showed one cathodic peak and anodic peak emerged in the curves. Comparing with the case at bare electrode, the cathodic peak potential of DA shifted from 0.21 V to 0.27 V (*vs.* SCE), while the anodic peak potential was similar to that of bare electrode (0.34 V), meanwhile, the cathodic and anodic peak currents both increased. These results indicated that the SnO_2/graphite electrode exerted an electrocatalytic effect on DA. The redox reaction of dopamine can be expressed as:

$$\text{Dopamine} \rightarrow \text{Dopaminequinone} + 2H^+ + 2e^-$$

Figure 1 Cyclic voltammograms of 2.0×10^{-4} mol/L DA at nano-SnO_2 /graphite (a) and bare (b) electrode in 5.0×10^{-2} mol/L phosphate buffer solution. Scan rate: 50 mV s^{-1}.

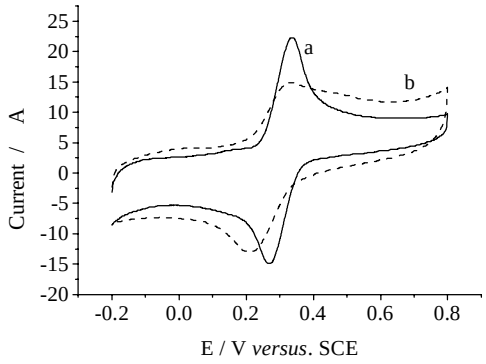
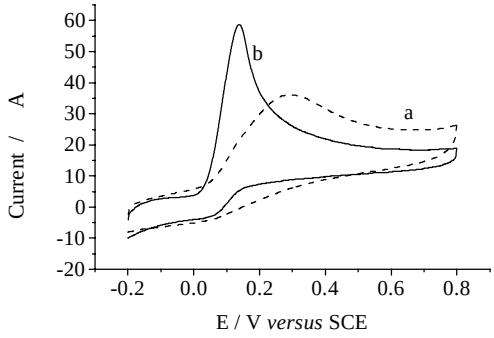


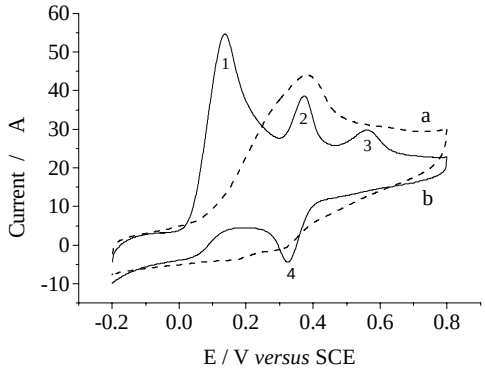
Figure 2 showed the cyclic voltammograms of AA at the bare and SnO_2/graphite electrode. A broad anodic peak appeared at 0.29 V on the bare electrode (**Figure 2a**). The SnO_2/graphite electrode exhibited effective electrocatalysis toward AA, resulting that the peak current increased as well as the peak potential shifted to 0.138 V with a spiky peak (**Figure 2b**). In the present buffer solution, AA existed as an anion, and the SnO_2/graphite electrode carried higher concentrations of negatively-charged surface functional groups (*e.g.* –OH, -COOH). The hydrophilic oxygen-rich groups enhanced electrostatic repulsion toward AA, resulting the peak potential of AA shifted negatively.

Figure 2 Cyclic voltammograms of 1.0×10^{-3} mol/L AA at bare (a) and nano-SnO_2/graphite (b) electrode. Conditions as Figure 1.



Pyrolytic graphite has two kinds of crystal faces, edge and basal. A perfect basal surface is one layer of carbon atoms in the graphite array. The edge surface is composed of the layer ends and is generally covered with surface oxides[6]. Some oxygen-rich groups (*e.g.* carboxylic) may be introduced on freshly polished graphite electrode[7]. The presence of a three-dimensional reaction zone at the electrode surface improved electrocatalysis area and the nanosized SnO_2 dispersed enhanced the transfer of charge, which might eventually lead to the increase of sensitivity and selectivity of DA and AA.

Figure 3 Cyclic voltammograms of 2.0×10^{-4} mol/L DA and 1.0×10^{-3} mol/L AA in mixture at bare (a) and nano-SnO_2/ graphite (b) electrode. Conditions as Figure 1.



When DA and AA coexisted in the sample, a rather broad anodic peak was observed at 0.38 V on bare graphite electrode (**Figure 3a**). SnO_2/graphite electrode resolved the overlapping voltammetric response into two well-defined anodic peak 1 and peak 2 (**Figure 3b**) at 0.138 V and 0.375 V, corresponding to the oxidation of AA and DA, respectively. Compared to them in solution alone, the anodic peak potential of AA unchanged, but the peak current decreased a little; however the anodic (peak 2) and cathodic (peak 4) peak potentials of DA shifted to 0.375 V and 0.324 V, respectively, and ΔEp was decreased from 0.061 V to 0.051 V. The separations between the two

anodic peak potentials of DA and AA were about 230 mV in CV and, which might be large enough for simultaneous determination of DA and AA. In addition, an additional very small irreversible peak 3 appeared at 0.560 V. This might be taken into consideration the interaction between AA and DA[8,9].

Two linear graphs are obtained in the range 1.0×10^{-6} to 1.1×10^{-3} mol/L and 3.0×10^{-6} to 3.1×10^{-3} mol/L for DA and AA, respectively. The detection limits (3σ) are 2.2×10^{-7} mol/L for DA and 1.1×10^{-6} mol/L for AA by CV. Using DPV mode, under optimum conditions, the catalytic peak current was linearly related to DA concentration over the range of $6.2\times10^{-7}\sim6.2\times10^{-5}$ mol/L in the presence of 1.0×10^{-3} mol/L AA with correlation r=0.994. The detection limit (3σ) was 2.2×10^{-8} mol/L. Accordingly, determination of low concentration level of DA in the presence of a high concentration of AA was possible. This behavior could be very valuable for in *vivo* applications since the AA content in brains is much more than that of catecholamines.

As an example for the analytical performance at the nano-SnO_2/graphite electrode, dopamine hydrochloride injection solution was determined. The results are acceptable when compared with those given by the classical method[10].

An interference of fresh rabbit brain tissue homogenate as a matrix was experimented. The results showed that rabbit brain tissue homogenate had no effect on electrocatalytic behavior toward to DA and AA at nano-SnO_2/graphite electrode, this may be useful for *in vivo* studies of neurotransmitters.

References

1. J. O. Rinne, T. Myllykyla, P. Marjamaki, *Brain Res.*,**1991**, *547***.**167.
2. S. J. Dong, T.Kuwana, *Chinese J.Applied Chem.*,**1985**, *3*.34
3. J. Zak, T. Kuwana, *J.Am.Chem.Soc.*,**1982**,*104*,5514.
4. C. R. Martin, D.T.Mitchell. *Anal.Chem.*,**1998**,May 1.323A.
5. Q. W. Li, Y. M. Wang, G. A. Luo. *Materials Science and Engineering C,***2000,** *11*.71.
6. K. S. E. Liu, R. J. Lagow. *J. Am.Chem.Soc.*,**1976,***12* (8).8271.
7. F. Anson, W. Z. Huang (Ed.). *Elctrochmistry and electroanalysis chemistry*. Peking University Press, Beijing, **1983,**p.90
8. J. J. Sun, J. J. Xu, J. H. Q. Fang, H. Y. Chen. *Bioelectrochem.Bioenerg.*,**1997,***44*.45
9. A. Ciszewaki, G. Milczarek. *Anal Chem.*,**1999,** *71*.1055.
10. Editorial Committee of the Ministry of Health of P.R.China,*Pharmacopeia of P.R.China.*Part 2, Chemical Industry Press, Beijing, **1995**, p.609.

Received 16 November, 2001