Trade Science Inc.

January 2007 *Volume 3 Issue 4-6*

Analytical CHEMISTRY
An Indian Journal

Full Paper

ACAIJ, 3(4-6), 2007 [180-189]

Electrochemical Behavior Of Dopamine In The Presence Of Ascorbic Acid On A Reduced Au/C_{60} Films Modified Glass Carbon Electrode

Corresponding Author

Ping Zhang
Anhui Wuhu Institute of Drug Control,
Wuhu 241000, (CHINA)

Co-Author

Guang-Chao Zhao
School of Chemistry and Materials Science,
Anhui Normal University, Wuhu 241000, (CHINA)

Received: 16th September, 2006
Accepted: 1st October, 2006

Web Publication Date : 21st December, 2006

ABSTRACT

The Au/C_{60} nanoparticles was modified on the surface of glass carbon electrode by electroreducing the mixture of C_{60} and $HAuCl_4$. SEM an AFM images displayed that the Au/C_{60} nanoparticles was tightly adsorbed on the surface of glass carbon electrode. After electrochemically reduced in 0.1M KOH, the surface of modified electrode was negatively charged which was proved by electrochemical characterization. The modified electrode was demonstrated to catalyze the electrochemical response of dopamine (DA) by cyclic voltammetry. The standard rate constant (K_s) for the electron transfer reaction of DA at the reduced Au/C_{60} films was found to be 1.38×10^{-2} cm/s. Furthermore, the separation between the voltammetric peaks of AA and DA is large, thus the simultaneous determination of AA and DA or the selective determination of DA in the presence of AA is feasible at the modified electrode. A linear response to DA and AA was obtained in the concentration range from 3.2×10^{-6} to 5.0×10^{-4} M and 8.0×10^{-6} to 5.0×10^{-3} M with a correlation coefficient of 0.9986 and 0.9997, respectively. The detection limit for dopamine was 2.0×10^{-7} and 5.3×10^{-6} M for ascorbic acid. The proposed sensor has promising feature such as excellent sensitivity, good selectivity and high stability.

KEYWORDS

The reduced Au/C_{60} films modified electrode;
Dopamine;
Ascorbic acid;
Electrocatalysis.

INTRODUCTION

Dopamine (DA) is the most typical neurotransmitter and plays a significant role in the mammalian central nervous system. Extreme abnormalities of DA concentration levels may lead to several diseases such as Parkinson's disease and schizophrenia and HIV infection[1-3]. Therefore, some methods have been developed to determine the DA[4-9]. Among these, the electrochemical method attracts wide attentions due to their convenient, simple and fast analysis. However, the electrochemical determination of DA was usually affected by the presence of high concentration of ascorbic acid (AA) in the brain[10, 11], which has the almost same oxidation potential range as DA on the solid electrode[13]. So many approaches have been proposed to increase the sensitivity of the determination of DA and eliminate the interference from AA[14-17]. These methods show good selectivity and sensitivity of determination of DA. However, still there is an expanding demand for the development of stable, simple and efficient materials as sensors to determine DA with high sensitivity and selectivity.

In recent years, considerable interest has been shown in the study of synthesis and properties of nanometer-scaled metal particles due to their potential applications in sensors, nanoelectronic devices and catalysts[18-24]. Those nanoparticles were prepared, mainly, through chemical reduction of aqueous solution of the chloro-metallate anion[25, 26], metal vapor synthesis routes[27, 28], or the electrochemical deposition on an inert base[19, 20, 22]. Among these, the electrochemical deposition has received much interest because of its rapidness, convenience and economy. Recently, more and more study groups selected the carbon materials as supports for deposition of metal nanoparticles for its chemical/electrochemical stability, good electrical conductance, high surface area and low surface group contents. Fullerenes, as a new form of carbon, have received numerous theoretical and experimental studies since the discovery of fullerenes in 1985[29] and the first laboratory synthesis in 1990[30]. Due to their nanometer size and interesting properties, fullerenes are also of great interest for many applications such as batteries[31] and chemical sensor[32]. Furthermore, high accessible surface area, unique three dimensions and high stability suggest that fullerenes are suitable support materials for deposition of metal nanoparticles. But still few reports have been published about the application of the fullerenes in this field.

In this paper, we reported the feasibility of forming Au/C_{60} particles on a glass carbon electrode by electrochemically reducing the complexes of fullerene (C_{60}) and Au (III). Based on the experiments, we found that the nanostructured carbon fullerene film served as a favorable support for depositing the Au nanoparticles; in addition, the Au nanoparticles incorporated onto fullerenes can promote the electrochemical activities of the fullerenes in aqueous solution. Furthermore, we investigated the electrochemical response of dopamine at this modified electrode and the results showed the proposed electrode materials exhibited an excellent electrocatalytic activity for the determination of dopamine. We also detected the effect of AA on determination of DA. The results showed the separation between the voltammetric peaks of AA and DA is large. Thus the simultaneous determination of AA and DA or the selective determination of DA in the presence of AA is feasible at the modified electrode. Based on these, an electrochemical method with high sensitivity and excellent selectivity was proposed to detect DA in the presence of AA.

EXPERIMENTAL

Reagents and apparatus

DA and AA (sigma, USA) were used as received. The C_{60} with purity 99.9% was purchased from Tian-an Company (Beijing, China). All other reagents were of analytical grade. The phosphate buffer solution (PBS) was prepared from KH_2PO_4 and K_2HPO_4 (0.1M). The water used throughout was doubly distilled and all experiments were carried out under room temperature.

A pHs-3C digital pH-meter (Shanghai, China) was used to measure the pH values of aqueous solutions. Electrochemical experiments were performed with CHI 660 electrochemical analyzer (CHI, USA) with a conventional three-electrode cell. The image of the surface of the modified electrode was recorded on an AJ-III atomic force microscopy (AFM) (China). The working electrode was a reduced Au/C_{60} modified GC electrode. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the auxiliary electrode, respectively.

Electrodes and preparation

The GC electrode (Φ=3mm) was firstly polished with an alumina slurry and washed successively with triply-distilled water and ethanol in an ultrasonic bath, then 15 cyclic scans were carried out in the potential range of 2.0 to - 2.0V (vs. SCE) in the solution of 1.0 mol/L H_2SO_4. 2 mg C_{60} was dispersed with the aid of ultrasonic agitation in 0.5 mL (1 mg / mL) $HAuCl_4$ acetone solution for 10 minutes. The films were prepared by dropping 20 μL $HAuCl_4$/C_{60} acetone solution onto the surface of GC electrode and dried in air. The modified electrode was firstly cycled in 0.1 M phosphate solutions pH 7.0 in the potential range between + 1.0 ~ - 0.6 V with scan rate 100 mV/s until stable and reproducible voltammograms were obtained. Then the electrode was transferred with washing to another cell containing 0.1M KOH solutions and was cycled in the potential between + 0.8 ~ - 1.0 V with a 100 mV/ s scan rate. Then the reduced Au/C_{60} films modified electrode was performed. All these were done under a N_2 atmosphere.

RESULTS AND DISCUSSION

The electrochemical properties of Au/C_{60} films modified electrode

1 Electrodeposition of Au nanoparticles

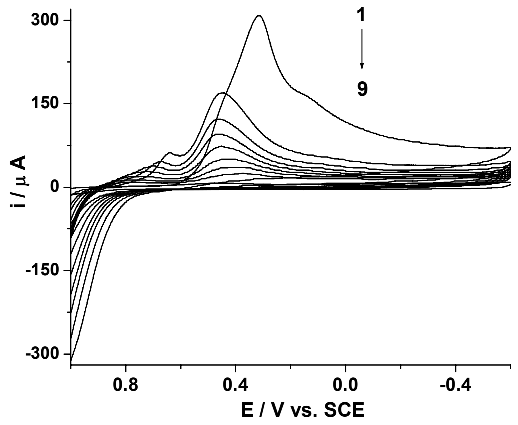

Figure 1: Multicyclic voltammograms of the $HAuCl_4$/C_{60} films modified electrode in 0.1M phosphate buffer solution (pH 7.0). Cycles: from 1 to 9. Scan rate: 100mV/s

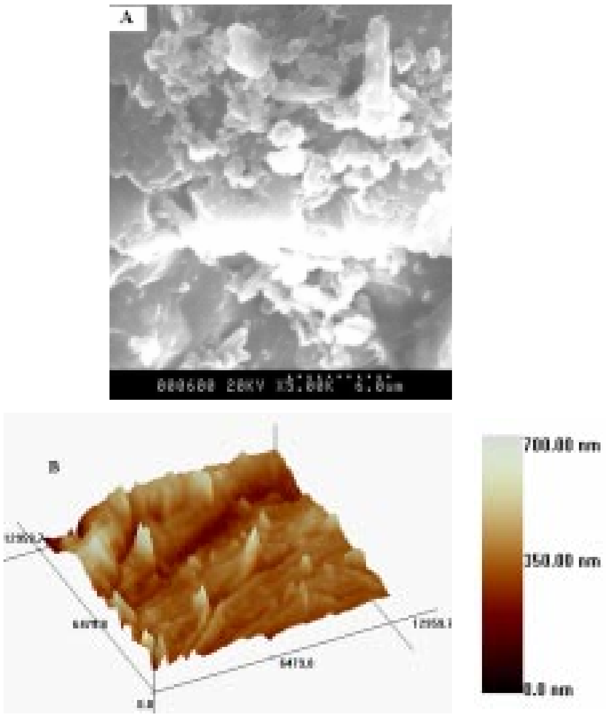

Figure 2: (a): SEM and (b): AFM images of the Au/C_{60} films after cycling in 0.1M phosphate buffer solution (pH 7.0)

20μL acetone solution of C_{60} + $HAuCl_4$ was dropped onto the surface of GC electrode and dried in air. Then, successive cyclic scans were carried out at the potential range of + 1.0 ~ - 0.6 V in 0.1M pH 7.0 phosphate solutions as shown in figure 1. In the initial cycle, a cathodic peak at 0.32 V was observed, which was related to Au (III) reductive reaction (curve 1). At the followed cycle, however, the peak was shifted positively to 0.46 V while the peak current obviously decreased. After 9 cyclic scans, the cathodic peak current and potential value were trended to be constant, which indicated that the Au (III) on the surface of electrode had been reduced fully. After continuous cycles of the modified electrode in 0.1M phosphate solutions pH 7.0 at the potential range + 1.0 ~ - 0.6 V, no obvious changes of the peak current and the peak potential value were observed, which suggested the good stability of the electrode.

Figure 2 showed typical SEM and AFM images of gold nanoparticles incorporated with fullerene films on the electrode. Inspection of the electrode at the end of the multicyclic process reveals that a black deposit is present on the electrode, which we called the Au/C_{60} film. Based on the literature[31] and this experiment, here the fullerene provided a good supported substrate for deposition of the Au nanoparticles.

2 Reduction of the Au/C_{60} films

Figure 3 shows the electrochemical behavior of the Au/C_{60} films modified GC electrode and the bare Au electrode in 0.1M KOH, respectively. When the potential was scanned between + 0.8 and - 1.0V, the Au/C_{60} films showed two reduction peaks and an oxidation peak (Figure 3A). Compared with the bare Au electrode (Figure 3B), the Au/C_{60} films showed a new reduction peak at Epc_2 = - 0.41 V, which is correspond to the reductive result of the C_{60}. In addition, the peaks at Epc_1 = + 0.04 V and Epo_1 = + 0.49 V are associated with the characteristic redox of the Au, which is the same as the bare Au electrode. Hereafter it was reduced in 1M KOH, the Au/C_{60} films on the GC electrode will be referred as the reduced Au/C_{60} films.

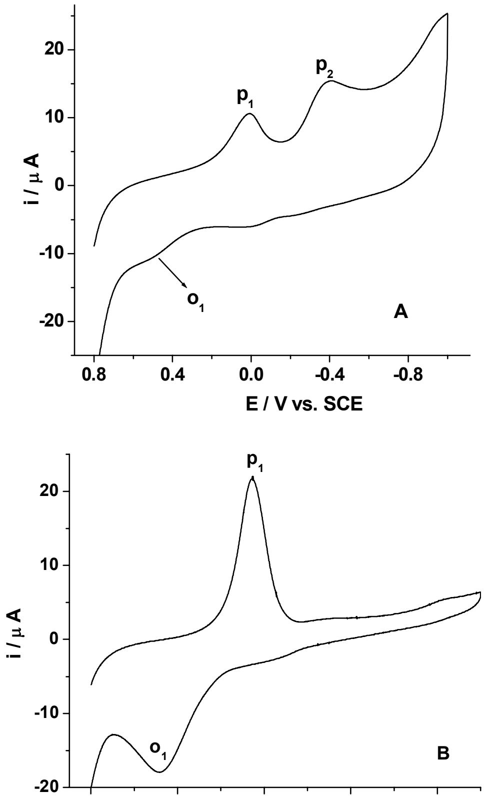

Figure 3: Cyclic voltammograms at (a): the Au/C_{60} films modified GC electrode and (b): the bare Au electrode in 1M KOH. Scan rates were 100 mV/s

3 Electrochemical characterization of electrode surface

Cyclic voltammetry of an electroactive species, such as $Fe(CN)_6^{4-/3-}$ or $Co(bpy)_2^{3+/2+}$ (bpy=2,2'-bipyridine), is a valuable tool for testing the kinetic barrier of the interface[33]. In order to investigate the property of the electrode surface, the CV experiments were carried out in the solutions containing electroactive species $Fe(CN)_6^{4-/3-}$ and $Co(bpy)_2^{3+/2+}$, respectively. Figure 4 showed the cyclic voltammograms obtained from 5mM of $K_3[Fe(CN)_6]$ at the Au/C_{60} GC electrodes and the reduced Au/C_{60} modified electrodes in 0.1M KCl solution, respectively. At the Au/C_{60}-modified GC electrodes, the $K_3[Fe(CN)_6]$ showed a reversible redox response with ΔE_p=109 mV. However, the electron transfer kinetics at the reduced Au/C_{60} modified electrode was found to be sluggish. The peak-to-peak separation turned into 170 mV and the peak current obviously decreased

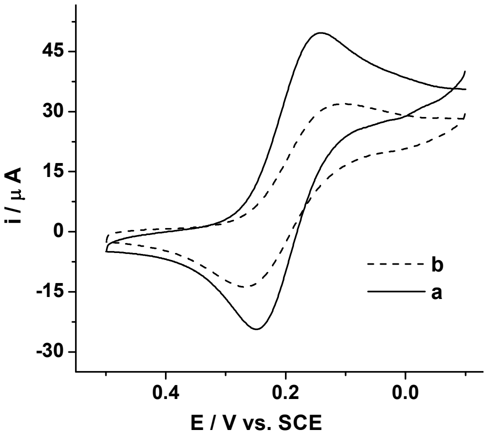

Figure 4: Cyclic voltammograms of 5 mM of $Fe(CN)_6^{4-/3-}$ in 0.1M KCl solution at (a): Au/C_{60}-modified GC electrodes and (b): the reduced Au/C_{60}-modified GC electrodes. Scan rate is 100 mV/s

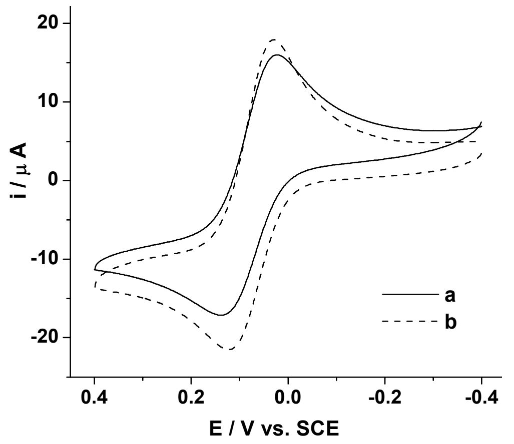

Figure 5: Cyclic voltammograms of 5 mM of Co(bpy)$_2^{3+/2+}$ in 0.1M KCl solution at (a) Au /C$_{60}$-modified GC electrodes and (b) the reduced Au / C$_{60}$-modified GC electrodes. Scan rate is 100 mV/s

(Figure 4b). On the other hand, when the CV experiments were carried out in the solution containing an electroactive species Co(bpy)$_2^{3+/2+}$, the results was different from that obtained in the Fe(CN)$_6^{4-/3-}$ solution. The peak potential obtained at a reduced Au/C$_{60}$ electrode was similar to that obtained at the Au/C$_{60}$-modified GC electrodes, but the peak current at the reduced Au/C$_{60}$ electrode increase obviously (as shown in Figure 5b). Above results suggested that the surface of reduced Au/C$_{60}$ modified electrode would be negative charges, which resulted in repelling the negative redox couple Fe(CN)$_6^{4-/3-}$ and attracting the positive redox couple Co(bpy)$_2^{3+/2+}$.

Electrochemical response of DA at the reduced Au/C$_{60}$ microparticle electrode

Figure 6 depicts the electrochemical behavior of DA at the bare and the reduced Au/C$_{60}$ films modified GC electrode, respectively. At the bare GC electrode, the electrochemical response of DA was poor and the CV of DA demonstrated an irreversible wave with ΔE$_p$, the difference between the anodic peak potential (Epa) and the cathodic peak potential (Epc), 110mV (curve b). However, as shown in figure 6a, the reversibility of the electrode reaction of DA is improved significantly at the reduced Au/C$_{60}$ modified electrode. The ΔE$_p$ value is found to be 30 mV (curve b), which indicates faster electron transfer kinetics at the modified electrode. The formal potential (E$^{0'}$) of DA estimated from the average value of anodic and cathodic peak potential, (E$_{pa}$+ E$_{pc}$)/2, was 0.271 V (vs. SCE) and i$_{pa}$ / i$_{pc}$ was 1.41.

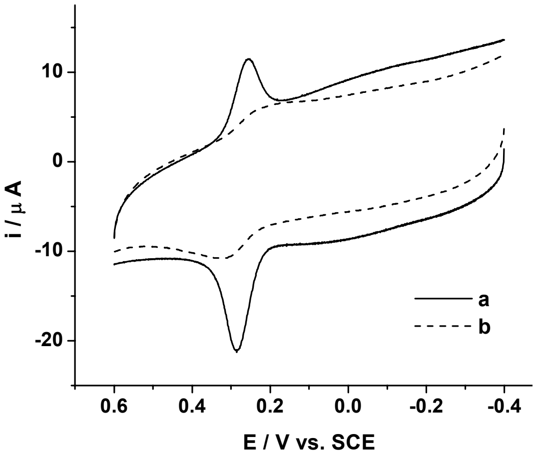

Figure 6: Cyclic voltammograms at (a): the reduced Au/C$_{60}$ films modified electrode; (b): the bare electrode; in the presence of 6.4×10^{-5} mol/L DA and 0.1M phosphate buffer solution (pH 5.0); scan rate: 100mV/s

When the electrode was transferred to the blank supporting electrolyte without DA after measuring a DA solution, it showed a weak voltammetric signal corresponding to the redox reaction of DA, which would disappear in the subsequent sweeps. This indicated DA was weakly adsorbed onto the reduced Au/C$_{60}$ films and it desorbed from the films in the subsequent sweeps.

The effect of scan rate on the anodic and cathodic peak currents of dopamine was investigated. The experiment results indicated that the ip was proportional to the square root of scan rate over the range of 20 ~ 200 mV/s. The linear regression equations were ipc = - 2.252 + 0.6995$\nu^{1/2}$ and ipa = -2.7902 + 0.9325$\nu^{1/2}$ [ip (μA); $\nu^{1/2}$, (mV/s)$^{1/2}$], with correlation coefficients of 0.9958 and 0.9963, respectively. The results indicate that the electron transfer reaction is controlled by the diffusion DA.

According to the Nicholson theory[34,35], the electron transfer rate constant of DA at the reduced Au/C$_{60}$ films, K$_s$ was calculated using the E$_p$ value obtained at higher scan rate.

Figure 7 shows the relationship of Ep and lnν (ν, scan rate, mV/s). The curves approach the straight line at higher rates (6 ~ 20 V/s).

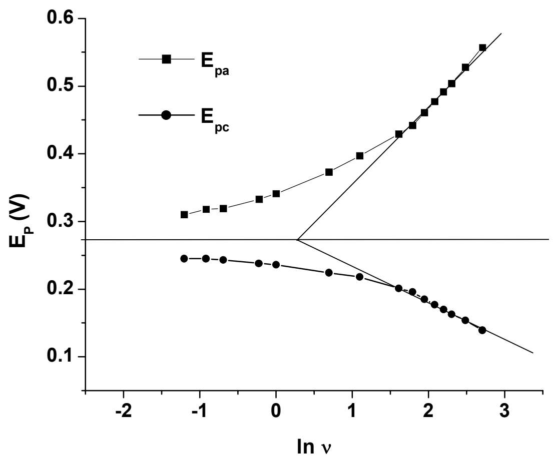

Figure 7: Relationship between the peak potential Ep and the scan rate ln ν with 2.5×10^{-4} M DA at the modified electrode

Based on the slope and the intercept, the standard rate K_s can be obtained according to following equations[35]:

$$E_{pa} = E^{o'} + m[0.78 + \ln(D^{1/2} / K_S) - 0.5\ln m] + 0.5m\ln \nu$$

$$m = RT / [(1 - \alpha)n_\alpha F]$$

$$E_{pc} = E^{o'} - m'[0.78 + \ln(D^{1/2} / K_S) - 0.5\ln m] + 0.5m'\ln \nu$$

$$m' = RT / \alpha n_\alpha F$$

Here the diffusion coefficient D of DA was determined by chronocoulometric method[36,37] and calculated as 4.2×10^{-6} cm^2 / s (25°C) under our experiment conditions. Then the rate constants K_s are calculated to be 1.49 × 10^{-2} cm / s and 1.26 × 10^{-2} cm / s at the reduced Au/C_{60} modified electrode, respectively, and their average is 1.38 × 10^{-2} cm / s, which is 6.2 times than that at the bare GC electrode, demonstrating that the reduced Au/C_{60} films facilitate the oxidation process of DA.

The effect of solution pH on response of DA was studied in 0.1M phosphate buffer solution in the range of 3.0 ~ 8.0. It was found that the response of DA is well behaved in this range, and anodic peak potential of DA shifted negatively with the increasing of pH value. The relation between the peak potential and pH was directly investigated and a linear regression equation Epa (mV) = 551.1 - 52.63 pH; r = 0.9983 and Epc (mV) = 514.7 - 51.51 pH; r = 0.9979 were obtained. The slopes were very close to the theoretical value of -58 mV pH^{-1}. Based on the above results and the literature[38,39], the uptake of electrons is accompanied by an equal number of protons.

Electrochemical response of DA in the presence of AA

AA coexists with DA in the extra-cellular fluid of the central nervous system, and its concentration is much higher than that of DA. It can be oxidized at a potential near to that of DA at most solid electrode, which resulted in an overlapped voltammetric response[13].

To evaluate the sensitivity and selectivity of the present system for determination of DA in the presence of AA, the electrochemical behavior of the mixture of AA and DA at the reduced Au/C_{60} films modified electrode was studied.

Figure 8 shows the cyclic voltammograms obtained for DA and AA coexisting at bare GC electrode and the reduced Au/C_{60} films modified electrode, respectively. Only one broad voltammetric signal was observed at 0.33 V for the mixture AA and DA at the bare GC electrode in 0.1M phosphate buffer solution (pH 5.0) as shown in figure 8a. Therefore it is impossible to use the bare electrode for the voltammetric determination of DA in the presence of AA. However, the reduced Au/C_{60} films modi-

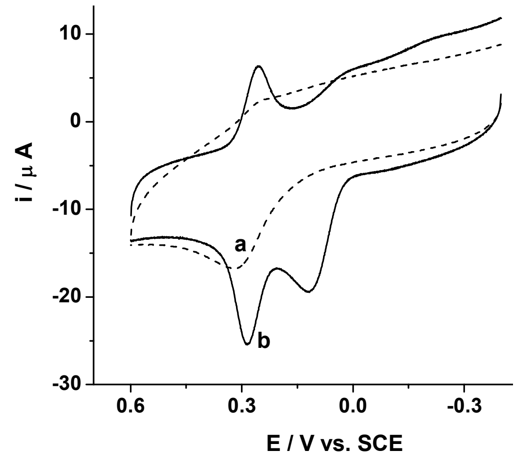

Figure 8: Cyclic voltammograms of a binary mixture containing 1.2×10^{-4} mol/l DA and 4.5×10^{-4} mol/l AA at (a): the bare electrode; (b): the reduced Au/C_{60} films modified electrode; in 0.1M phosphate buffer solution (pH 5.0); scan rate: 100mV/s

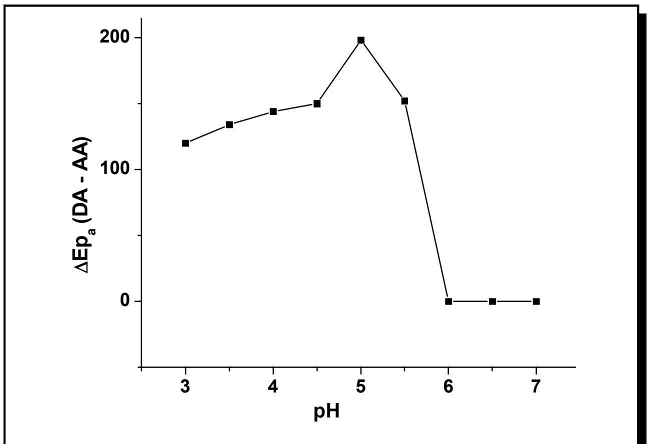

Figure 9: Dependence of the difference of the anodic peak potential between DA and AA, ΔEpa (DA – AA), on pH. The mixture contained 1.2×10^{-4} mol/l DA and 4.5×10-4 mol/l AA at the reduced Au/C60 films modified electrode

fied electrode can separate the mixed voltammetric signals into two well-defined voltammetric peaks at 0.11 and 0.28 V corresponding to the oxidation of AA and DA (Figure 8b), respectively.

To get a better-distinguished voltammogram, the effect of pH was tested with the range 3.0 ~ 8.0 (Figure 9) and the results showed that the difference of the anodic peak potential between DA and AA, ΔE_{pa} (DA-AA), has a maximum value (~200 mV) at pH 5.0. So a pH 5.0 buffer solution was selected as supporting electrolyte for DA determination in the presence off AA in this experiment.

The optimized conditions of the electrode preparation

The effect of the ratio of Au to C_{60} in the mixture on the response of DA was investigated by using differential pulse voltammetry (DPV). With increase of the ratio in the range of 0 ~ 0.15, the peak current of DA increases. When the ratio is more than 0.15, the current obviously decreases. On the other hand, when the ratio is less than 0.15 the response of DA will be obviously affected by AA. According to the experiment results, an optimal ratio of 0.15 was selected in our experiments.

Some amounts of the mixture solutions were dried onto substrates respectively and produced various thickness films. The experiment results showed that there was an optimal response of DA and AA on the electrode with coverage 20 µL $HAuCl_4/C_{60}$ acetone solution.

Simultaneous determination of DA and AA

The difference potential between the two cationic peaks of DA and AA is about 200 mV by DPV voltammograms, which is sufficient enough for the selective determination of DA or simultaneous determination of both DA and AA in a mixture.

Figure 10 exhibits the DPV voltammograms obtained for different concentrations of DA in the presence of AA at the reduced Au/C_{60} films modified electrode. The voltammetric peak of AA was unaltered, whereas the peak current of DA increases linearly with the increasing concentration of DA, confirming that the responses of DA and AA at the modified are independence. The detection limit of DA in the presence of 0.45 mM AA was found to be 0.83 µM with the correlation coefficient of 0.998. So the selective determination of DA in the presence of AA is feasible at the modified electrode.

Figure 11 illustrates the DPV response of the modified electrode while simultaneously varying the concentrations of both AA and DA. The calibration curves for both AA and DA were linear in the range of concentrations (8 to 100 mM for DA and 30 to 350 µM for AA) with correlation coefficients 0.9925

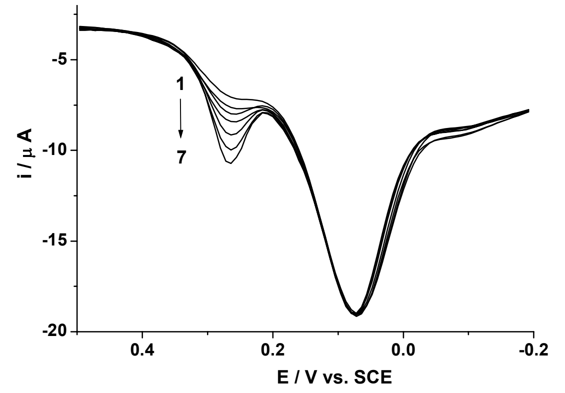

Figure 10: Differential pulse voltammitric curves of DA at modified electrode in the presence of AA (0.45 mM) in 0.1 M PBS (pH 5.0). The concentration of DA is (1) 1.92 µM (2) 2.56 µM (3) 3.20 µM (4) 3.84 µM (5) 4.80 µM (6) 5.76 µM (7) 6.4 µM Scan rate: 4mV/s; pulse amplitude: 50mV; pulse width: 50ms; pulse time: 200ms

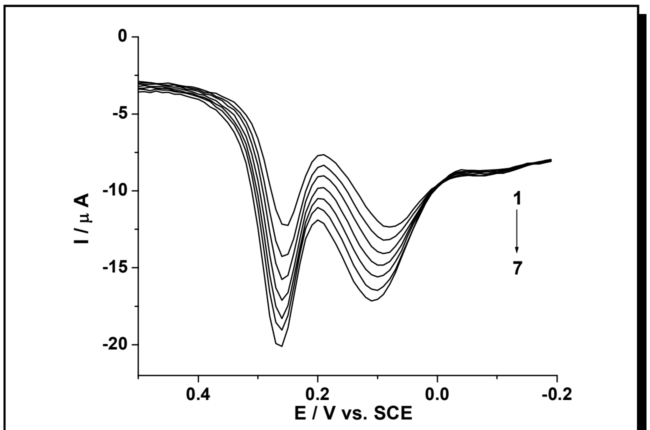

Figure 11: Differential pulse voltammitric curves obtained for AA and DA while simultaneously changing their concentrations of DA in 0.1 M PBS (pH 5.0). [AA]: each addition increased the concentration by 37.5 μM. [DA]: each addition increased the concentration by 9.6 μM. Scan rate: 4mV/s; pulse amplitude: 50mV; pulse width: 50ms; pulse time: 200ms.

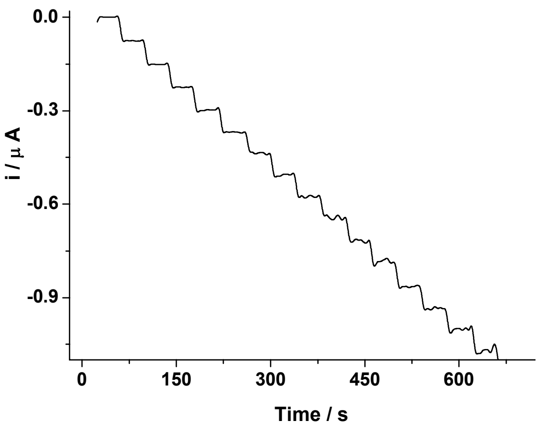

Figure 12: Current-times response of the reduced Au/C_{60} films modified electrode for the successive addition of 6.4 μM DA to the stirring 0.1 M PBS (pH 5.0)

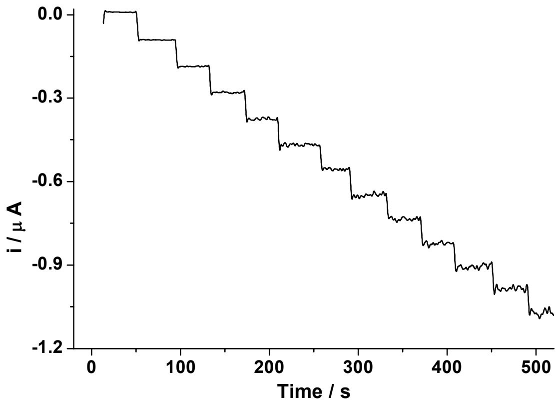

Figure 13: Current-times response of the reduced Au/C_{60} films modified electrode for the successive addition of 36 μM AA to the stirring 0.1 M PBS (pH 5.0)

and 0.9967, respectively, which indicated that the simultaneous determination of DA and AA could be obtained.

DA with positive charges can be attracted to the negatively charged electrode surface while AA with negative charges would be prevented to close to the surface[40]. Under this experimental condition, DA (pK_a 8.9) should exist as cation while AA (pK_a 4.1) should be anion[18]. Here the reduced Au/C_{60} modified electrode showed good sensitivity and selectivity for DA in the presence of AA. The electrostatic interaction is expected to increase the approach of cationic DA to the negative surface and therefore an enhancement in the electron transfer kinetics would be expected at the modified electrode.

Amperometric determination of DA and AA

Figure 12 and 13 depicted the amperonetric current-time response of the reduced Au/C_{60} films modified electrode for the determination of DA and AA, respectively. The response current was measured at a fixed potential in a stirring 0.1 M PBS at a pH 5.0. figure 12 showed the amperonetric response obtained at a potential of + 0.3 V for successive addition of 6.4 μM DA to the stirring 0.1 M PBS (pH 5.0).

The amperonetric current for the successive addition of 36 μM AA at a fixed potential of 0.1 V was shown in figure 13. The reduced Au/C_{60} films modified electrode exhibited rapid response to the changes on the concentration of AA (less than 2s).

The reduced Au/C_{60} films modified electrode showed a linear response to DA in the concentration range from 3.2×10^{-6} to 5.0×10^{-4} M with a correlation coefficient of 0.9986. For AA, the linear range was between 8.0×10^{-6} to 5.0×10^{-3} M and the correlation coefficient was 0.9997. The detection limit for DA was 2.0×10^{-7} and 5.3×10^{-6} M. The relative standard deviation (RSD) for ten successive determinations of 5.0×10^{-5} M DA and 2×10^{-4} M AA were 1.8 and 2.3 %, respectively, indicating the good

TABLE 1: Determination of AA and DA in mixtures

No	DA added (M)	AA added (M)	DA found (M)	Recovery (%)	AA found (M)	Recovery (%)
1	5.0×10^{-6}	2×10^{-4}	5.05×10^{-6}	101.1	1.90×10^{-4}	94.7
2	8.0×10^{-6}	5×10^{-4}	8.40×10^{-6}	105.4	5.29×10^{-4}	105.7
3	2.0×10^{-5}	1×10^{-3}	2.06×10^{-5}	103.1	1.05×10^{-3}	104.8

reproducibility of the present system.

Analysis of mixture of AA and DA in samples

The analytical application of the proposed system for the measurement of AA and DA was studied by analyzing the samples containing known amount of a mixture of AA and DA. Aliquots of the samples were added to the electrolyte solution and the corresponding concentrations were estimated by the calibration graphs. The results were shown in the TABLE 1. A good recovery observed with the present system indicates the reliability of the method for application to monitoring of AA and DA.

Interference studies were also performed with other compounds. As for 5.0×10^{-5} M DA and 2.0×10^{-4} M, no interference could be observed for such compounds as: Cystine (100), Lysine (100), Cysteine (100) and valine (100), NaCl (600), KCl (600), NaBr (400), where the data in brackets were the concentration ratios.

CONCLUSIONS

In the present work, the reduced Au/C_{60} nanoparticles were prepared using an electrochemical technique and developed into a new sensor for the determination of DA. The results indicated that the reduced Au/C_{60} films modified electrode exhibits highly electrocatalytic activity and excellent selectivity for the response of DA in the presence of AA. Furthermore, the separation between the voltammetric peaks of AA and DA is large and thus the simultaneous determination of AA and DA or the selective determination of DA in the presence of AA is feasible at the modified electrode. Based on these, a new sensor was prepared for the determination of DA in the presence of AA. This investigation also develops the electrochemical property of fullerene films and extends the application of Au nanoparticles in aqueous solution.

These attractive features of the proposed electrode suggest the promising applications, which is under progress in our laboratory.

ACKNOWLEDGEMENT

The project was supported by National Natural Science Foundation of P. R.China (No. 20271002) and Anhui Provincial Natural Science Foundation (No. 01044702).

REFERENCES

[1] T.E.Smith, in: T.M.Devlin; 'Textbook of Biochemistry with Clinical Correlation', Wiley/Liss, New York, 929 **(1992)**.

[2] R.M.Wightman, L.J.May, A.C.Micheal; Anal.Chem., **60**, 769A-779A **(1988)**.

[3] J.W.Mo, B.Ogoreve; Anal.Chem., **73**, 1196-1202 **(2001)**.

[4] M.Zhu, X.M.Huang, J.Li, H.X.Shen; Anal.Chim.Acta, **357**, 261-267 **(1997)**.

[5] S.A.Wring, J.P.Hart; Analyst, **117**, 1215 **(1992)**.

[6] L.Virag, R.A.Whittington; J Chromatogr.B, **772**, 267-272 **(2002)**.

[7] C.L.Guan, J.Quyang, Q.L.Liu, B.H.Liu, W.R.G. Baeyens; Talanta, **50**, 1197-1203 **(2000)**.

[8] H.Y.Wang, Q.S.Hui, L.X.Xu, J.G.Jiang, Y.Sun; Anal. Chim.Acta, **497**, 93-99 **(2003)**.

[9] T.Liu, M.X.Li, Q.Y.Li; Talanta, **63**, 1053-1059 **(2004)**.

[10] T.Zetterstrom, T.sharp, C.A.Marsden; U, Ungerstedt, J.Neurochem., **41**, 1769-1773 **(1983)**.

[11] P.Capella, B.Ghasemzadeh, K.Mitchell, R.N.Adams; Electroanalysis, **2**, 175-182 **(1990)**.

[12] F.Gonon, M.Buda, R.Cespuglio, M.Jouvert, J.Pajol; Nature, **286**, 902-904 **(1980)**.

[13] J.M.Zen, G.Ilangovan, J.J. Jou; Anal Chem, **71**, 2797-2805 **(1999)**.

[14] J.Chen, C.S.Cha; J Electroanal Chem, **463**, 93-99 **(1999)**.

[15] M.J.Giz, B.Duong, N.J.Tao; J.Electroanal.Chem., **465**, 72-79 **(1999)**.

[16] J.Oni, T.Nyokong; Anal.Chim.Acta, **434**, 9-21 **(2001)**.

[17] L.Zhang, Y.Sun, X.Lin; Analyst, **126**, 1760-1769 **(2001)**.

[18] G.Schmid; 'Clusters and Colloids', VCH, Weinheim, **(1994)**.

[19] M.O.Finot, G.D.Braybrook, M.T.McDermott; J.Electroanal.Chem., **466**, 234-241 **(1999)**.

[20] M.O.Finot, M.T.McDermott; J.Electroanal.Chem., **488**, 125-132 **(2000)**.

[21] O.Antoine, Y.Bultel, R.Durand; J.Electroanal.Chem., **499**, **(2001)** 85-94 **(2000)**.

[22] D.Guerin, G.S.Attard; Electrochem.Commun., **3**, 544-548 **(2001)**.

[23] M.S.El-Deab, T.Ohsaka; Electrochem.Commun., **4**, 288-292 **(2002)**.

[24] M.S.El-Deab, T.Ohsaka; Electrochim.Acta, **47**, 4255-4261 **(2002)**.

[25] C.W.Chen, T.Takezako, K.Yamamoto, T.Serizawa, M.Akashi; Colloids Surfaces A: Physicochem.Eng. Aspects, **169**, 107-116 **(2000)**.

[26] W.Chen, W.P.Cai, C.H.Liang, L.D.Zhang; Mater.Res. Bull., **36**, 335-342 **(2001)**.

[27] M.Magnusson, K.Deppet, J.O.Malm, J.O.Bovin, L.Samuelson; Nanostruct.Mater., **12**, 45-48 **(1999)**.

[28] P.J.Collier, J.A.Iggo, R.Whyman; J.Mol.Catal. A: Chem., **146**, 149-157 **(1999)**.

[29] H.W.Kroto, J.R.Heath, S.C.O'Brien, R.F.Curl, R.E.Smalley; Nature, **318**, 162-163 **(1985)**.

[30] M.S.Dresselhaus, G.Dresselhaus, P.C.Eklund; 'Science of Fullerene and Carbon Nanotubes', San Diego, Academic Press, **(1996)**.

[31] K.Vinoldgopal, M.Haria, D.Meisel, P.Kamat; Nano Lett, **4**, 415-418 **(2004)**.

[32] M.Csiszar, A.Szucs, M.Tolgyesi, A.Mechler, J.B.Nagy, M.Novak; J.Electroanal.Chem., **497**, 69-74 **(2001)**.

[33] H.Q.Finklea, in: A.J.Bard, I.Rubinstein; 'Electroanalytical Chemistry', **19**, Marcel Dekker, New York, **(1996)**.

[34] S.Richard, Nicholson; Anal.Chem., **37**, 1351-1355 **(1965)**.

[35] S.Richard, Nicholson, S.Irving; Anal.Chem., **36**, 706-723 **(1964)**.

[36] F.R.Anson; Anal.Chem., **38**, 54-59 **(1966)**.

[37] F.R.Anson; Anal.Chem., **36**, 932-935 **(1964)**.

[38] M.D.Hawley, S.V.Tatawawadi, S.Piekarski, R.N. Adams; J.Am.Chem.Soc., **89**, 447 **(1967)**.

[39] M.Zhu, X.M.Huang, J.Li, H.X.Shen; Anal.Chem.Acta, **357**, 261 **(1997)**.

[40] Q.Wang, D.Dong, N.Q.Li; Bioelectrochem., **54**, 169-175 **(2001)**.