Microchim Acta (2011) 174:345–352
DOI 10.1007/s00604-011-0632-1

ORIGINAL PAPER

Determination of dopamine with improved sensitivity by exploiting an accumulation effect at a nano-gold electrode modified with poly(sulfosalicylic acid)

Juan Li · Jia Chen · Xiaoli Zhang

Received: 22 February 2011 / Accepted: 30 May 2011 / Published online: 7 June 2011

Abstract We describe a glassy carbon electrode modified with nano-gold and a film of poly(sulfosalicylic acid) that was obtained by electropolymerization of sulfosalicylic acid. The electrochemical characteristics of the electrode were investigated by using (a) the anionic hexacyanoferrate, and (b) the cationic ruthenium-trisbipyridyl systems as redox probes. The electrode displayed selective and enhanced electroanalytical response towards dopamine (DA), obviously because DA (which is cationic) is accumulated at the electrode, while anions such as ascorbic acid (AA) do not and in fact are being repelled. A 2000-fold molar excess of AA is tolerated after a 120-s accumulation time followed by stripping detection at pH 6.5. Response is linear with the concentration of DA in the range from 0.05 to 5 μM, and the detection limit is 7 nM (at an S/N of 3) even in the presence of 100 μM concentrations of AA.

Keywords Polymer film incorporated nano-gold modified electrode · Electropolymerization · Electrodeposition · Voltammetry · Dopamine · Preconcentration

Introduction

Dopamine (DA) is an important neurotransmitter in the mammalian central nervous system and some serious diseases such as Huntington's chorea, schizophrenia and Parkinsonism are related to low levels of DA. Therefore, it is very important to develop simple and rapid method for the sensitive determination of DA in routine analysis [1–3]. DA could be oxidized electrochemically under specific potential at conventional electrodes due to its electrochemical active groups, phenolic hydroxyls. Hence, voltammetric techniques have been proved to be advantageous for detection of DA [4–6]. However, an important disadvantage in electrochemical detection of DA is the interference of AA because of oxidation potential of AA close to that of DA [7], and the electrode surface can also be readily fouled by accumulation of product from oxidation of DA. In addition, the irreversibility of DA's electrochemistry, and AA coexistance in very high concentrations (2–3 orders of magnitude higher than that of DA in biological fluid) results in that the detection of DA gives a poor and nearly unavailable sensitivity using conventional electrodes [8]. Various modified electrodes have been prepared and used to solve these problems; such as, self-assembled monolayer [9–12], polymer film [13–17], nanoparticles [18–21] and composite material [22–25] modified electrodes. In all of these modifications, electrochemical polymerization is a simple and effective approach to prepare polymer modified electrodes (PMEs). The PMEs have many advantages in the detection of bio-molecules owing to its selectivity, sensitivity, chemical stability as well as controllable preparation of the film [26]. Besides, the negatively charged polymer film modified electrode can allow the cationic DA toward the electrode and repel the anionic AA, considering DA exists in the cation form (pK_a=8.87) while AA is in the anionic form (pK_a=4.10) in biological environment [7]. Several groups have reported the efforts in utilizing various negatively charged polymer film modified electrodes for the detection of DA [15, 27, 28]. However, the procedures of fabrication,

Electronic supplementary material The online version of this article (doi:10.1007/s00604-011-0632-1) contains supplementary material, which is available to authorized users.

J. Li · J. Chen · X. Zhang (✉)
School of Chemistry and Chemical Engineering,
Shandong University,
Jinan 250100, China
e-mail: zhangxl@sdu.edu.cn

the selectivity and sensitivity of the electrodes should not be neglected in practical analysis. Therefore, it is essential to explore a simple and effective strategy for the sensitive detection of DA.

Recently, gold nanoparticles as a kind of special sensing material of chemical modified electrodes showed copacetic electrocatalytic activity owing to their excellent electronic quality. And they have been used to fabricate electrochemical sensors and biosensors [19–21]. In our previous work, the nano-Au/GCE was obtained by electrodeposition for simultaneous voltammetric determination of dihydroxybenzene isomers [29].

Based on the above factors, in this work, we have tried to make poly (sulfosalicylic acid) film incorporated nanogold modified electrode (PSA-nano-Au/GCE) and study the selective detection of DA in coexisting large amount of AA. Moreover, other three negatively charged films such as poly aspartic acid (PAA), poly glycine (PG) and poly histidine (PH) incorporated respectively nanogold modified electrode, i.e. PAA-nano-Au/GCE, PG-nano-Au/GCE and PH-nano-Au/GCE, were also obtained and used to detect DA. A novel experiment mode based on the difference of adsorbabilities between DA and AA on the modified electrode was developed. The new method possesses obvious benefit such as lower detection limit and good selectivity.

Experimental

Chemicals

Dopamine was purchased from Sigma-Aldrich, (St. Louis, MO, USA, http://www.sigmaaldrich.com). Ascorbic acid, $HAuCl_4$, sulfosalicylic acid, aspartic acid, glycine and histidine were obtained from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China, http://gyjthxsj.b2b.hc360.com). All chemicals were of analytical reagent grade and used without further purification. Phosphate buffer solutions (PBS) with different pH values were prepared by mixing 0.10 M Na_2HPO_4 and 0.10 M NaH_2PO_4 and pH values were adjusted by addition of 1.0 M H_3PO_4 and/or NaOH solution. Freshly prepared solution of DA and AA were used in all experiments. Doubly distilled water was used throughout the experiments.

Apparatus

A CHI 800 electrochemical analyzer (Shanghai Chenhua Instrument Company, China, http://chi.instrument.com.cn) was used to perform electrode characterization and voltammetric measurements. A conventional three-electrode system was employed with a saturated calomel electrode (SCE) as the reference electrode, a platinum wire as the auxiliary electrode and a bare or modified glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode. All potentials in the text were against SCE.

Preparation of the modified electrode

The glassy carbon electrode was polished subsequently with 0.5 and 0.05 μm alumina slurry, then thoroughly rinsed with water and sonicated in ethanol and distilled water in turn. After being cleaned, the electrode was continuously cyclic voltammetry scanned from −1.5 to 2.0 Vat 100 mV s^{-1} for 20 cycles in 1.0 mM sulfosalicylic acid aqueous solution to form poly sulfosalicylic acid film on the electrode surface. Followed, this electrode was taken out and rinsed with water, then was immersed into 0.1 M KNO_3 containing 0.4 gL^{-1} $HAuCl_4$, electrodeposition from $HAuCl_4$ was conducted for 60 s at −0.2 V. Finally, the resulting electrode, PSA-nano-Au/GCE, was activated by several successive cyclic voltammetric scanning from −0.5 to 1.0 V with 100 mV s^{-1} in phosphate buffer solution (pH 6.5) until a steady voltammogram was obtained. After the same processes, PAA-nano-Au/GCE, PG-nano-Au/GCE and PH-nano-Au/GCE, were also obtained.

Analytical procedure

Firstly, the PSA-nano-Au/GCE electrode was immersed into the solution of DA and AA for 120 s accumulation, then taken out and the stripping detection in another phosphate buffer solution without DA and AA (blank PBS). The voltammograms were recorded from −0.2 to 0.6 Vand the peak height was measured as a signal (I_p). The all experiments were carried out at room temperature.

Results and discussion

The electropolymerization of SA and voltammetric characteristics of PSA film incorporated nano-gold modified electrode (PSA-nano-Au/GCE)

Figure 1 dispalyed the continuous cyclic voltammograms of sulfosalicylic acid (SA) electrochemical polymerization over the potential range of −1.5 to +2.0 V for 20 cycles at a scan rate of 100 mV s^{-1} in phosphate buffer (pH 7.4), and the inset was the scanning electron microscope image (SEM) of PSA-nano-Au/GCE. All the redox peak currents increased gradually with incessant scans indicating the formation and growth of an electroactive layer on the GCE surface. After the tenth cycles, these anodic and cathodic peak currents tended to be stable, implying that the polymerization had reached saturation. Meanwhile, it also can be observed that the GCE surface presented a dark blue

film. These phenomena demonstrated that polymer film have formed on the GCE surface. Followed, the as-prepared PSA film modified electrode was immersed into 0.1 M KNO_3 solution containing 0.4 gL^{-1} $HAuCl_4$ for electrodeposition of gold via a constant potential −0.2 V (vs. SCE) for 60 s. Finally, the resulting electrode, PSA-nano-Au/GCE, was obtained.

Because SA palys an important role in the process of determination, the optimization of the PSA film thickness was also investigated. With the polymerizing cycles increasing, the electroresponse of DA increased at first, which may be attributed to the fact that more negatively charged groups could be immobilized on the electrode. But when the polymerizing cycles is more than 20, the current begins to fall. This could be explained that an increase in thickness of the film would prevent the electron transfer. Therefore, 20 cycles was used in the experiments.

To investigate the electrochemical properties and ionic selectivity of the modified layer, a cyclic voltammetric study for the PSA-nano-Au/GCE was performed utilizing a negatively charged redox probe, $Fe(CN)_6^{3-/4-}$, and a positively charged probe, $Ru(bpy)_3^{2+}$. Figure 2a showed the cyclic voltammograms of 5.0 mM $Fe(CN)_6^{3-/4-}$ at bare GCE and PSA-nano-Au/GCE. As could be seen, the voltammetric response of $Fe(CN)_6^{3-/4-}$ at PSA-nano-Au/GCE (curve b) was as reversible as that at the bare GCE (curve a) but a slight increase in peak current. A possible reason might be owing to the joint action of nano-gold and negatively charged polymer film. Firstly, nano-gold played an important role in the enhancement of peak current and improvement of electron transfer reaction due to the good conductivity, excellent electrocatalytic ability. Second, the repulsive interaction between the negatively charged electrode surface and negatively charged $Fe(CN)_6^{3-/4-}$ weakened the response of $Fe(CN)_6^{3-/4-}$, which both of opposite factors resulted in the ensemble with slight change. On the contrary, the negatively charged electrode surface ought to attract the positively charged probe, $Ru(bpy)_3^{2+}$, which was expected that the electron-transfer reaction would be enhanced because the attractive interaction. This indeed was confirmed in Fig. 2b, The voltammetric response of 1.0 mM $Ru(bpy)_3^{2+}$ at the PSA-nano-Au/GCE (curve b) increased greatly, which was about 2 orders of magnitude higher than that at the bare GCE (curve a). These results proved the presence of negatively charged monolayer on the electrode surface. Meanwhile, above results also demonstrated that the PSA film incorporated nano-gold modified electrode possessed the ionic selectivity, which predicted a potential application in selective determination of DA in the presence of AA.

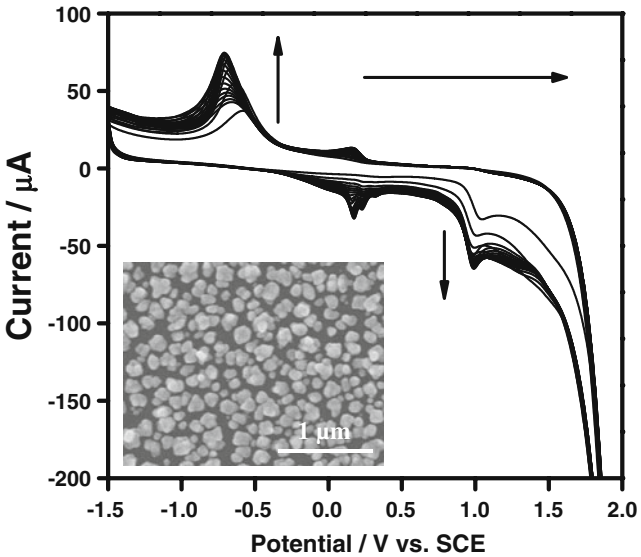

Fig. 1 Cyclic voltammograms of sulfosalicylic acid in polymerization process from 1 to 20 cycles. Sulfosalicylic acid: 1.0 mM; scan rate: 100 mV s^{-1}; pH=7.4. The inset was the SEM image of PSA-nano-Au/GCE

Electrochemical behaviors of DA and AA at the PSA-nano-Au/GCE

Figure 3 was the electrochemical responses of single component (curve a and b) and mixed components (curve c and d) of DA (1 μM) and AA (100 μM) in 0.1 M PBS (pH 6.5) at bare GCE and PSA-nano-Au/GCE. As can be seen, that at bare GCE, the single componen of DA gave a very weak oxidation peak approximate to 0.23 V (curve a), while solitary AA also showed a wide and insensitive oxidation peak at 0.26 V (curve b). When DA and AA coexisted in the same solution, their oxidation peaks overlaped to form a broad peak at about 0.26 V (curve c). However, at PSA-nano-Au/GCE (curve d), two well-defined oxidation peaks appeared at 0.195 V and 0.015 V, corresponding to DA and AA, respectively. The increase in peak current as well as the separation in the peak potential at PSA-nano-Au/GCE might be correlated not only with the speed of electron transfer but also with the type of electrochemical-controlled process. And they ought to be the result of two factors: first, the polymer film changed greatly the properties of electrode surface through the anionic carbonyl and sulfonic groups of sulfosalicylic acid. Second, the unique physicochemical properties of nano-gold significantly enhanced the active electrode surface area.

The possible reaction process of DA at the PSA-nano-Au/GCE followed the mechanism in Scheme S1 (Electronic Supplementary Material, ESM). The corresponding cyclic voltammogram was shown in Fig. S1 (ESM). When the DA is oxidized, its oxidation product, dopaminequinone, can undergo follow-up ring closure reaction, leading to leucodopaminechrome, which in turn is oxidized to dopaminechrome [17].

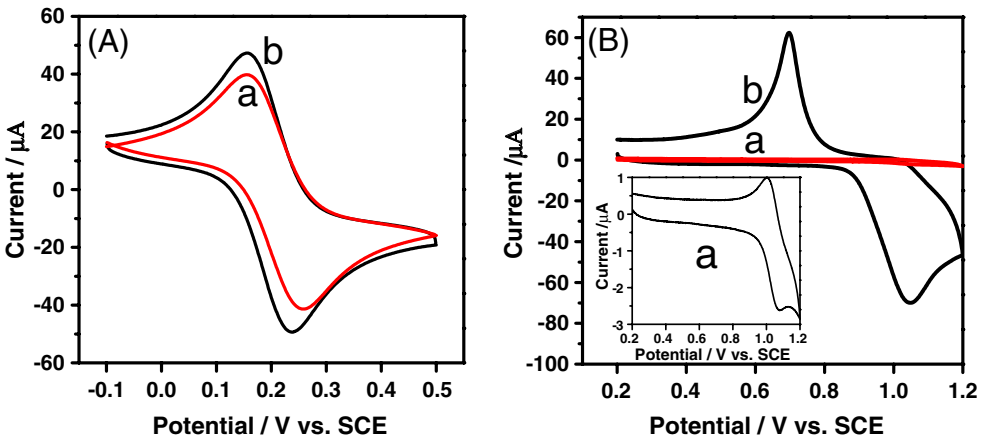

Fig. 2 Cyclic voltammograms of (**a**) bare GCE, (**b**) PSA-nano-Au/GCE in (A) 0.1 M KNO_3 with 5.0 mM $[Fe(CN)_6]^{3-/4-}$ and (B) 0.2 M Na_2SO_4 with 1.0 mM Ru $(bpy)_3^{2+}$. The inset in (B) was the amplified response of curve (**a**)

To determine the type of the controlled process of DA and AA at PSA-nano-Au/GCE, the effects of scan rate on the oxidation peak current of DA and AA were studied separately. The peak current of DA (5 μM) increased linearly with the scan rate in the range from 40 to 240 mV s^{-1} with equation: $I_p/\mu A = 0.06044\nu/\text{mV s}^{-1} + 0.1987$, the correlation coefficient was 0.9989, demonstrating that the oxidation of DA at the PSA-nano-Au/GCE was an adsorption-controlled process. The peak current of AA (500 μM) was proportional to the square root of the scan rate (20–240 mV s^{-1}): $I_p/\mu A = 0.85\nu^{1/2}/(\text{mV s}^{-1})^{1/2} + 5.1$, and the correlation coefficient R was 0.9973, suggesting that the electrode reaction of AA was a diffusion-controlled process.

The effect of accumulation time on oxidation peak current of DA (5 μM) and AA (50 μM) was determined respectively (shown in Fig. S2, ESM). It was clear that the peak current of DA (curve a) increased remarkably within the first 2 min and then enhanced slowly. Further increase in accumulation time did not increase the amount of DA at the electrode surface owing to surface saturation, and the peak current remained constant. This phenomenon was due to the special interaction between DA and the negatively charged modified layer, which improved the ability of the electrode to adsorb electroactive DA. There was only a slight increase in the peak current of AA (curve b), which demonstrated that the PSA-nano-Au/GCE had poor adsorbability towards AA.

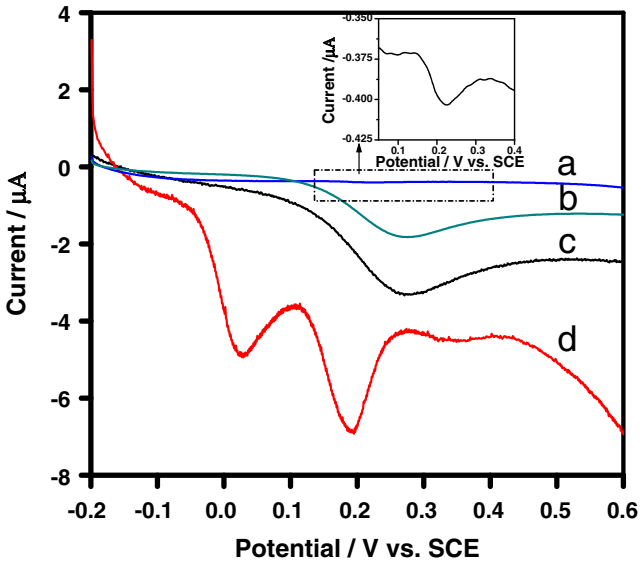

Fig. 3 Voltammetric curves of single component of (**a**) 1 μM DA, (**b**) 100 μM AA and (**c**,**d**) mixed components of 1 μM DA and 100 μM AA in phosphate buffers at (**a**–**c**) bare GCE, and (**d**) PSA-nano-Au/GCE. Scan rate=100 mV s^{-1}

A further adsorption experiment was made. When the PSA-nano-Au/GCE was immersed into an AA solution for 120 s preconcentration, no response of AA was observed during the stripping detection in a blank PBS. However, after the same procedure with a DA solution, the response of DA could still be observed. This result made it is feasible that the selective determination of DA in the presence of AA.

Figure 4 depicted the results of cyclic voltammetric responses of DA in two different modes. At mode I: when the PSA-nano-Au/GCE was immersed into the solution of DA and AA for 120 s accumulation and then stripping detection in the PBS with DA and AA (curve a). It could be noticed that the oxidation peak of DA and AA all appeared and partly overlapped when DA coexisted with 1000-fold excess of AA. Namely, the detection of DA should suffer from the interference of AA in this case. However, at mode II: after the same 120 s accumulation, the stripping detection was performed in a blank PBS (curve b), only one oxidation peak corresponding to DA was observed on the voltammogram, while that of AA was not. This result confirmed that PSA-nano-Au/GCE only selectively adsorbed DA in the coexisting solution of both. Besides, the result also indicated that the oxidation peak current of DA at mode II (curve b) was about 1.6-fold compared with that at mode I (curve a).

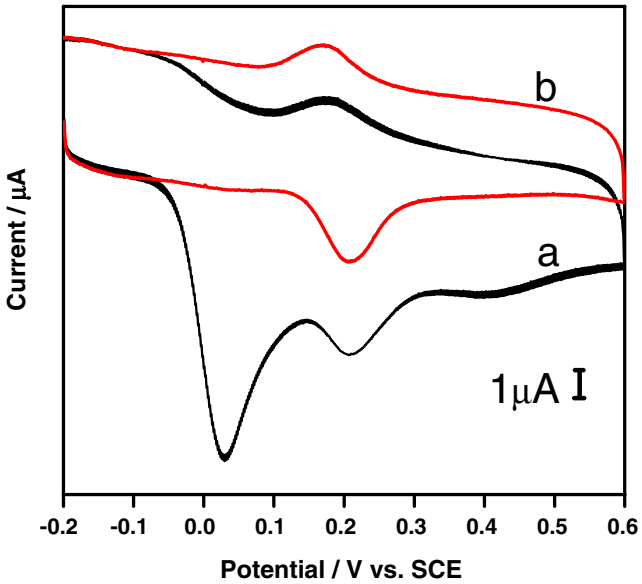

Fig. 4 Cyclic voltammograms of preconcentrated PSA-nano-Au/GCE in the phosphate buffer solution (**a**) with or (**b**) without DA and AA. Accumulation time =120 s. Scan rate=100 mV s^{-1}

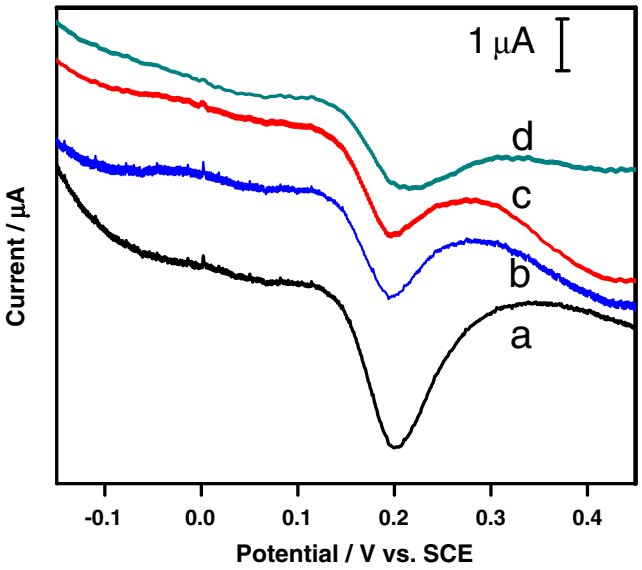

Fig. 5 Voltammetric curves of preconcentrated (**a**) PSA-nano-Au/GCE, (**b**) PAA-nano-Au/GCE, (**c**) PG-nano-Au/GCE, (**d**) PH-nano-Au/GCE in the phosphate buffer solution without DA and AA. Accumulation time =120 s. Scan rate=100 mV s^{-1}

Based on the above studies, the glassy carbon electrode modified with the negatively charged polymer incorporated nano-gold exhibited excellent electrochemical response to DA. Four different polymers incorporated respectively nano-gold modified eletrode were fabricated and investigated in order to compare the electroresponse for DA. Figure 5 showed the results of stripping detection of preconcentrated (a) PSA-nano-Au/GCE, (b) PAA-nano-Au/GCE, (c) PG-nano-Au/GCE and (d) PH-nano-Au/GCE in blank PBS. It can be seen, that four modified electrode all exhibited excellent selectivity towards DA. Compared with other three modified electrode (curve b, c and d), the PSA-nano-Au/GCE (curve a) was the optimal for the electrochemical detection of DA. The possible reason might be that the molecular of sulfosalicylic acid has both negatively charged group, carbonyl group and sulfonic group (COO^- and SO^{3-}), therefore, the PSA-nano-Au/GCE carried the more profuse negative charge, which resulted in the more stronger electrostatic interaction between modified electrode and DA.

Selective determination of DA in the presence of AA

Since differential pulse voltammetry (DPV) has a higher current sensitivity, it was employed in selective determination of DA in the presence of AA at PSA-nano-Au/GCE and estimate of the lower limit of detection. Before the determination, the PSA-nano-Au/GCE was first accumulated for 120 s in various concentrations of DA in coexisting 100 μM AA. The determination was performed with a DPV technique in a blank PBS. After every measurement, the PSA-nano-Au/GCE electrode was cleaned with several voltammetric cycles in 0.1 M PBS in order to clear entirely the residue of DA so as to renew the electrode surface. Figure 6 showed the DPV responses for various concentrations of DA at the PSA-nano-Au/GCE electrode. The inset of Fig. 6 demonstrated that the DPV peak height was linearly related to DA concentration over the range of 50 nM to 5 μM in presence of 100 μM AA. Optimization of the experimental conditions yielded a detection limit of 7 nM (based on S/N=3). A comparison of the advantages and disadvantages with other electrochemical methods for the determination of DA was listed in Table 1.

The stability of the PSA-nano-Au/GCE was tested by measuring voltammetric currents during repetitive DPV measurements. Without renewing the electrode surface, the electrode retained 91% of its initial activity even after the eighth determination. When the electrode was stored in the phosphate buffer (pH 6.5) at room temperature, the current reponse remained 92% after 1 week. To ascertain the reproducibility of the PSA-nano-Au/GCE, four same GCE were modified to obtain the PSA-nano-Au/GCE, and their responses towards DA was tested. The relative standard deviations of the peak currents were found to be 3.74%. Such a good stability and reproducibility is acceptable for most practical applications.

Interference study

The effects of some organic and inorganic species coexisting with DA were investigated. No interference occurred in the presence of substance as following: 200-fold uric acid, 200-

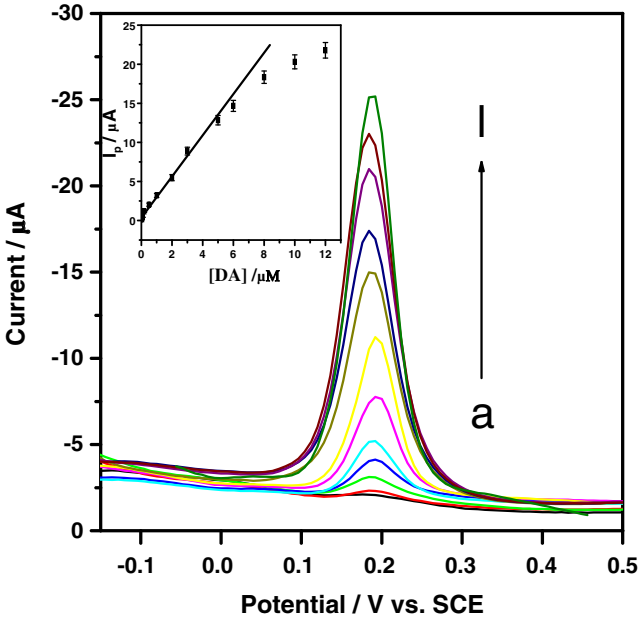

Fig. 6 Differential pulse voltammetric responses of various concentrations of DA at PSA-nano-Au/GCE in phosphate buffer solution (pH= 6.5) without DA and AA. The PSA-nano-Au/GCE was first accumulated for 120 s in various concentrations of DA coexisting 100 μM AA. The DA concentrations (**a**) 0.05, (**b**) 0.1, (**c**) 0.2, (**d**) 0.5, (**e**) 1.0, (**f**) 2.0, (**g**) 3.0, (**h**) 5.0, (**i**) 6.0, (**j**) 8.0, (**k**) 10.0, (**l**) 12.0 μM. Inset was the relation between the peak currents and the DA concentrations. Scan rate: 50 mV s^{-1}, pulse amplitude: 20 mV, pulse width: 60 ms

Table 2 Selective determination of DA in injection (n=6)

DA Injection	Recommended (mg)	Found (mg)	RSD (%, n=6)	Added (μg)	Recovery (%)
I	20.0	19.8	3.1	10	98.6
II	20.0	20.1	2.6	20	98.4

fold glucose, 100-fold tartaric acid, 200-fold citric acid, 1000-fold sodium chloride, 1000-fold potassium nitrate, 500-fold magnesium sulfate, with the deviations below 5%.

Analytical application

The dopamine hydrochloride injection samples (standard content of DA 10 mg mL^{-1}, 2 mL per injection) were purchased from a local pharmacy, and diluted to 50 mL using PBS (pH 6.5). One hundred microlitres of the diluted injection solution and 1.0 mL AA standard solution (10 mM) were added to a series of 10 mL measuring flasks and made up to volume with PBS. The content of DA was obtained by the standard addition method, and the results are shown in Tables 2. In order to testify the accuracy of this method, standard DA solution was spiked in the sample and the analytical procedure repeated. The recovery values were acceptable, revealing that this method is accurate and effective.

Table 1 Comparison of PSA-nano-Au/GCE with reported methods

Ref.	Modified electrode	method	Linear range (μM)	Detection limit (μM)	Coexistance amount of AA	Sample
[9]	Polypyrrole-Congo Red modified GCE	DPV	0.5–100	0.01	0.4 μM DA can be sensed in the presence of 250-fold excess of AA	not mentioned
[12]	EDTMP-ZrO_2 modified Au electrode	DPV	0.015–4	0.009	500 μM AA does not affect	not mentioned
[22]	β-CD-MWNTs/polyaniline modified GCE	DPV	0.1–1000	0.012	Excess AA does not affect	injection
[23]	MWCNTs-Quercetin-Nafion modified GCE	Amperometric method	1.4–300	1.4	AA has not contributed any significant current response for the equimolar mixture of AA and DA	Human serum
[24]	Nafion-coated clinoptilolite modified GCE	DPASV	0.05–10	0.01	3 μM DA can be sensed in the presence of 200-fold excess of AA	not mentioned
[30]	graphene modified electrode	DPV	4–100	2.64	1000 μM AA does not affect	not mentioned
[31]	mesoporous silica modified CPE	DPV	0.4–25	0.1	500 μM AA does not influence the oxidation signal of 1 μM DA	injection
[32]	Sodium dodecyl sulfate modifiedCPE	DPV	0.5–800	0.05	Excess AA does not affect	injection
[33]	EDTA-RG/Nafion modified GCE	DPV	0.2–25	0.01	the presence of 500–1000 times higher AA does not interfere with the anodic peak of DA	not mentioned
This work	poly (sulfosalicylic acid)/ nano-gold modified GCE	DPV	0.05–5	0.007	0.05 μM DA can be sensed in the presence of 2000-fold excess of AA	injection

CPE carbon paste electrode; *GCE* glassy carbon electrode; *DPV* differential pulse voltammetry; *DPASV* differential pulse anodic stripping voltammetry; *EDTA-RG* ethylenediamine triacetic acid modified reduced graphene; *EDTMP* ethylenediamine-tetramethylene phosphonic acid; *β-CD* β-cyclodextrin; *MWNTs* multi-walled carbon nanotubes

Conclusions

A novel PSA-nano-Au/GCE modified electrode was fabricated by simply electropolymerizating and electrodepositing. The resulting electrode combined the catalytic properties of nano-gold with the selectivity of the polymerized film, and it exhibited a high selective and enhanced electroanalytical response toward DA. Besides, the experimental results also demonstrated that AA had no interference for the detection of DA owing to the selective adsorption of DA on the PSA-nano-Au/GCE. Although the selective determination of DA was also achieved on the other electrodes, the PSA-nano-Au/GCE electrode holded some advantages in a way that it could be easily prepared, recycled, highly anti-fouled, and could entirely eliminate the interference from the coexistence of large amount of AA.

Acknowledgements This project was supported by the National Natural Science Foundation of China (Grant No. 20975061), the National Basic Research Program of China (Grant No. 2007CB936602) and the Natural Science Foundation of Shandong Province in China (Grant No. Y2008B20).

References

1. Wightman RM, May LJ, Michael AC (1988) Detection of dopamine dynamics in the brain. Anal Chem 60:769A
2. Martin C (1998) The Parkinson's puzzle—new developments in our understanding of Parkinson's disease have generated a number of promising new treatments for this disabling condition. Chem Br 34:40
3. Mo JW, Ogorevc B (2001) Simultaneous measurement of dopamine and ascorbate at their physiological levels using voltammetric microprobe based on overoxidized poly(1,2-phenylenediamine)-coated carbon fiber. Anal Chem 73:1196
4. Wang J, Tuzhi P, Golden T (1987) Amperometric detection of cationic neurotransmitters at nafion-coated glassy carbon electrodes in flow streams. Anal Chim Acta 194:129
5. Wiedemann DJ, Kawagoe KT, Kennedy RT, Ciolkowski EL, Wightman RM (1991) Strategies for low detection limit measurements with cyclic voltammetry. Anal Chem 63:2965
6. Salimi A, Abdi K, Khayatian GR (2004) Amperometric detection of dopamine in the presence of ascorbic acid using a nafion coated glassy carbon electrode modified with catechin hydrate as a natural antioxidant. Microchim Acta 144:161
7. Shams E, Babaei A, Taheri AR, Kooshki M (2009) Voltammetric determination of dopamine at a zirconium phosphated silica gel modified carbon paste electrode. Bioelectrochem 75:83
8. Zhang M, Gong K, Zhang H, Mao L (2005) Layer-by-layer assembled carbon nanotubes for selective determination of dopamine in the presence of ascorbic acid. Biosens Bioelectron 20:12170
9. Shahrokhian S, Zare-Mehrjardia HR (2009) Electrochemical Synthesis of Polypyrrole in the Presence of Congo Red; Application to Selective Voltammetric Determination of Dopamine in the Presence of Ascorbic Acid. Electroanalysis 21:157
10. Sun YX, Wang SF (2006) Simultaneous Determination of Dopamine and Ascorbic Acid at a Triazole Self-Assembled Monolayer-Modified Gold Electrode. Microchim Acta 154:115
11. Shervedani RK, Bagherzadeh M, Mozaffari SA (2006) Determination of dopamine in the presence of high concentration of ascorbic acid by using gold cysteamine selfassembled monolayers as a nanosensor. Sens Actuators B 115:614
12. Zheng M, Zhou Y, Chen Y, Tang YW, Lu TH (2010) Electrochemical behavior of dopamine in the presence of phosphonate and the determination of dopamine at phosphonate modified zirconia films electrode with highly antifouling capability. Electrochim Acta 55:4789
13. Ates M, Castillo J, Sarac AS, Schuhmann W (2008) Carbon fiber microelectrodes electrocoated with polycarbazole and poly(carbazole-co- p -tolylsulfonyl pyrrole) films for the detection of dopamine in presence of ascorbic acid. Microchim Acta 160:247
14. Zhang YZ, Jin GY, Yang ZS, Zhao H (2004) Determination of Dopamine in the Presence of Ascorbic Acid Using a Poly (Amidosulfonic Acid) Modified Glassy Carbon Electrode. Microchim Acta 147:225
15. Balamurugan A, Chen SM (2007) Poly (3, 4-ethylenedioxythiophene-co- (5-amino-2-naphthalenesulfonic acid)) (PEDOT-PANS) film modified glassy carbon electrode for selective detection of dopamine in the presence of ascorbic acid and uric acid. Anal Chim Acta 596:92
16. Zhao H, Zhang YZ, Yuan ZB (2002) Determination of dopamine in the presence ascorbic acid using poly(hippuric acid) modified glassy electrode. Electroanalysis 14:1031
17. Hou SR, Zheng N, Feng HY, Li XJ, Yuan ZB (2008) Determination of dopamine in the presence of ascorbic acid using poly(3,5-dihydroxy benzoic acid) film modified electrode. Anal Biochem 381:179
18. Yuan S, Chen W, Hu S (2005) Fabrication of TiO_2 nanoparticles/surfactant polymer complex film on glassy carbon electrode and its application to sensing trace dopamine. Mater Sci Eng C 25:479
19. Zhang L, Jiang X (2005) Attachment of gold nanoparticles to glassy carbon electrode and its application for the voltammetric resolution of ascorbic acid and dopamine. J Electroanal Chem 583:292
20. Raoof JB, Kiani A, Ojani R, Valiollahi R, Rashid-Nadimi S (2010) Simultaneous voltammetric determination of ascorbic acid and dopamine at the surface of electrodes modified with self-assembled gold nanoparticle films. J Solid State Electrochem 14:1171
21. Zhang YF, Li BX, Chen XL (2010) Simple and sensitive detection of dopamine in the presence of high concentration of ascorbic acid using gold nanoparticles as colorimetric probes. Microchim Acta 168:107
22. Yin T, Wei W, Zeng J (2006) Selective detection of dopamine in the presence of ascorbic acid by use of glassy-carbon electrodes modified with both polyaniline film and multi-walled carbon nanotubes with incorporated beta-cyclodextrin. Anal Bioanal Chem 386:2087
23. Chen PY, Vittal R, Nien PC, Ho KC (2009) Enhancing dopamine detection using a glassy carbon electrode modified with MWCNTs, quercetin, and Nafion. Biosens Bioelectron 24:3504
24. Senol A, Sibel KA, Azmi T (2005) A sensitive determination of dopamine in the presence of ascorbic acid using a nafion coated clinoptilolite-modified carbon paste electrode. Anal Bioanal Chem 383:695
25. Lai GS, Zhang HL, Han DY (2008) Electrocatalytic oxidation and voltammetric determination of dopamine at a Nafion/carbon-coated iron nanoparticles-chitosan composite film modified electrode. Microchim Acta 160:233
26. Xu L, Chen W, Mulchandani A, Yan Y (2005) Reversible superhydrophobic to superhydrophilicconversion of conducting polymer films. Angew Chem Int Ed 44:6009
27. Zhao H, Zhang Y, Yuan Z (2001) Study on the electrochemical behavior of dopamine with poly (sulfosalicylic acid) modified glassy carbon electrode. Anal Chim Acta 441:117

28. Huang PF, Wang L, Bai JY, Wang HJ, Zhao YQ, Fan SD (2007) Simultaneous electrochemical detection of dopamine and ascorbic acid at a poly(*p*-toluene sulfonic acid) modified electrode. Microchim Acta 157:41
29. Han L, Zhang XL (2009) Simultaneous voltammetry determination of dihydroxybenzene isomers by nanogold modified electrode. Electroanalysis 21:124
30. Kim YR, Bong S, Kang YJ, Yang Y, Mahajan RK, Kim JS, Kim H (2010) Electrochemical detection of dopamine in the presence of ascorbic acid using graphene modified electrodes. Biosens Bioelectron 25:2366
31. Sun D, Xie XF, Zhang HJ (2010) Surface effects of mesoporous silica modified electrode and application in electrochemical detection of dopamine. Colloids Surf Biointerfaces 75:88
32. Zheng J, Zhou X (2007) Sodium dodecyl sulfate-modified carbon paste electrodes for selective determination of dopamine in the presence of ascorbic acid. Bioelectrochem 70:408
33. Hou SF, Kasner ML, Su SJ, Patel K, Cuellari R (2010) Highly Sensitive and Selective Dopamine Biosensor Fabricated with Silanized Graphene. J Phys Chem C 114:14915