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Simultaneous Determination of Epinephrine, Dopamine, Ascorbic Acid and Uric Acid by Polydopamine-nanogold Composites Modified Electrode

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A facile polydopamine (PDA)-nanogold composites modified glassy carbon electrode (GCE) was prepared by a one-pot method and used for the sensitive determination of epinephrine (EP), dopamine (DA), ascorbic acid (AA) and uric acid (UA) simultaneously in this work. Under a mild spontaneous reaction condition, DA as a reducing agent and monomer, and $HAuCl_4$ as an oxidant to trigger DA polymerization and the source of gold nanoparticles, were mixed to yield composites of DA polymer and gold nanoparticles, which were then anchored on GCE by electropolymerization of the remaining DA monomer. The resultant electrode exhibited excellent electrocatalytic redox activities toward EP, DA, AA and UA. Furthermore, although the oxidation peaks of EP and DA at the modified electrode appeared at a same potential of 230 mV, three well-defined oxidation peaks for AA, EP, DA and UA (50, 230, 380 mV) and two non-interference reduction peaks for EP (-150 mV) and DA (190 mV) were presented. By virtue of this interesting phenomenon, for the first time the simultaneous detection of EP, DA, AA and UA using the proposed sensor has been achieved by cyclic voltammetry (CV) and square wave voltammetry (SWV). The calibration curves for EP, DA, AA and UA were acquired in the range of 1.0–80.0 μM, 1.0–80.0 μM, 40.0–1000.0 μM, and 0.8–100.0 μM with the detection limits (S/N = 3) of 0.1 μM, 0.08 μM, 5.0 μM and 0.06 μM, respectively. The proposed method is simple, sensitive and convenient, and was successfully applied to the determination of EP, DA, AA and UA in human blood serum and urine samples.

Keywords: Polydopamine, Nanogold, Epinephrine, Dopamine, Ascorbic acid, Uric acid

1. INTRODUCTION

Both epinephrine (EP) and dopamine (DA) playing essential roles in human health are important catecholamine neurotransmitters in the mammalian central nervous system [1].

Concentrations of plasma catecholamines and their metabolites are often useful for diagnosis and evaluation of therapeutic and pharmacodynamic effects for neurological, psychiatric and cardiovascular disorders [2]. For instance, EP, also known as adrenaline, plays a central role during physical or mental stress and also stimulates a series of actions of the sympathetic nervous system. Abnormalities of DA concentration levels may lead to several diseases such as Parkinson's disease and Schizophrenia. Medically, EP and DA have been used in hypertension, bronchial asthma, cardiac surgery, myocardial infarction and organic heart disease as common emergency healthcare medicine [3]. Therefore, the ability to determine EP and DA has attracted much attention of biological and electroanalytical researchers. However, the main problem of measuring the monoamines by solid electrodes is the overlapping voltammetric signal of themselves and the large excesses of coexisting substances in biological tissues such as ascorbic acid (AA) and uric acid (UA). Similarly, AA, a vital vitamin in human, is known to take part in several biological reactions, and prevents and treats the scurvy, common cold, mental illness, infertility and cancer [4]. UA is the primary end-product of purine metabolism. Abnormal levels of UA in the body are symptoms of several diseases such as gout, hyperuricemia, Lesch-Nyan syndrome, cardiovascular and kidney diseases [5-6]. Till date, many different strategies have been employed for the modification of the electrode surface in order to detect EP, DA, AA and UA with high selectivity and sensitivity [9-35]. Some reports concentrated on simultaneous determination of AA, UA and either EP or DA [10-31], while others tried to deal with differentiating DA and EP [9, 32-35]. To the best of our knowledge, there is not an electrochemical sensor exploited for simultaneous determination of EP, DA, AA and UA.

The aim of this study is to design an electrochemical sensor for determination of EP, DA, AA and UA simultaneously. Recently, the polydopamine (PDA) film, containing amine groups and phenolic hydroxyl groups, has attracted tremendous attention for the reducibility of DA in the process of self-polymerization, its surface-adherent on bulk material surfaces and permselectivity toward electroactive counterions due to the rich charges [36-38]. On the other hand, gold nanoparticle (nanogold) with high surface-to-volume ratio and surface free energy has been used for the nanoelectronic, biological and bioanalytical applications [30-31]. In this work, combining with above merits of PDA and gold nanoparticles, a PDA-nanogold composites modified GCE was fabricated by a one-pot electropolymerization protocol using DA as a reducing agent and a monomer, while $HAuCl_4$ as an oxidant to trigger DA polymerization and gold nanoparticles production. On the basis of the well separation of reduction peaks of EP and DA and that of oxidation peaks of AA and UA at composites modified electrode, a sensitive and rapid electrochemical method for simultaneous determination of EP, DA, AA and UA was set up for routine analysis.

2. EXPERIMENTAL PART

2.1. Apparatus

The electrochemical measurements were performed in a conventional three-electrode cell using CHI440A electrochemical workstation (Shanghai CH Instruments Co., China). Bare or modified

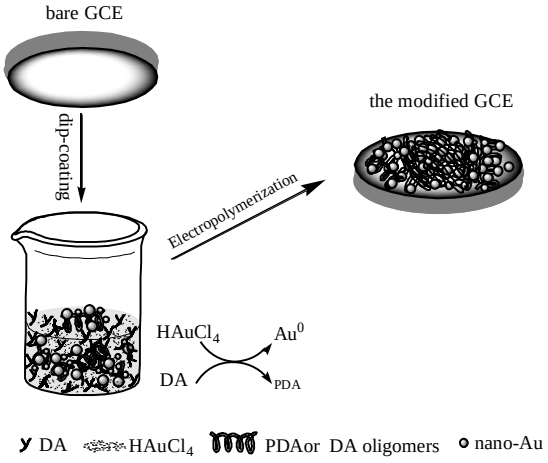
glassy carbon electrode (GCE) (diameter is 4.0 mm) was used as a working electrode. A saturated calomel electrode (SCE) and a platinum wire was performed as reference and counter electrode, respectively. The SEM image was recorded on scanning electron microscope (TESCAN VEGA 3 EasyProbe, Czekh). Various buffer solutions were prepared by PHS-3CT pH meter (Kangyi, Shanghai). All measurements were carried out at a constant temperature (25±1°C).

2.2. Chemicals and solutions

Ascorbic acid was obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Epinephrine, uric acid and 3-hydroxytyramine hydrochloride, chloroauric acid ($HAuCl_4$) were purchased from Sigma-Aldrich (America). Phosphate buffered solutions (PBS) with various pH were prepared by mixing the stock solutions of 0.1 M KCl, 0.1 M KH_2PO_4 and Na_2HPO_4, and used as base solutions for the electrochemical testing. The working solutions of EP, DA, AA and UA were prepared just prior to use. All chemicals used were of analytical grade and doubly distilled water was used throughout.

2.3. Fabrication of the PDA-nanogold composites modified electrode

Prior to modification, the bare GCE was polished with 0.05 μm alumina slurry on the polishing cloth and then rinsed thoroughly with 1:1 HNO_3 solution, acetone and distilled water. The modified electrode was fabricated by a one-pot electropolymerization according to the relevant literature [39] with a little modification.



Scheme 1. Schematic illustration of the construction of the PDA-nanogold composites modified electrode

Scheme 1 shows the fabrication process of the modified electrode. Briefly, the cleaned GCE was soaked in PBS (pH 7.0) containing DA and $HAuCl_4$ (a molar concentration ratio of DA to $HAuCl_4$ of 7: 1) for 5 minutes. Herein, PDA (or DA oligomers), nanogold and PDA-nanogold composites were obtained by means of a mild redox reaction between DA and $HAuCl_4$. Subsequently, cyclic voltammetry was performed between -0.8 to +1. 0 V for 10 cycles at a scan rate of 20 mV/s,

meanwhile, some of the PDA-nanogold composites were electrochemically codeposited onto the GCE surface during the oxidative polymerization of excess DA monomer. Finally, the resultant composites modified electrode was thoroughly washed with distilled water.

2.4. Procedure

The three-electrode system was immersed into 0.05 M PBS containing different concentrations of EP, DA, AA and UA. Then, The CVs and SWVs were recorded in suitable potential range. The quantitative analysis of these compounds could be achieved on the basis of the anodic peak currents of AA and UA and cathodic peak currents of EP and DA.

3. RESULTS AND DISCUSSION

3.1 SEM analysis

Scanning electronic microscopy (SEM) image of the PDA-nanogold composites film was shown in Fig. 1.

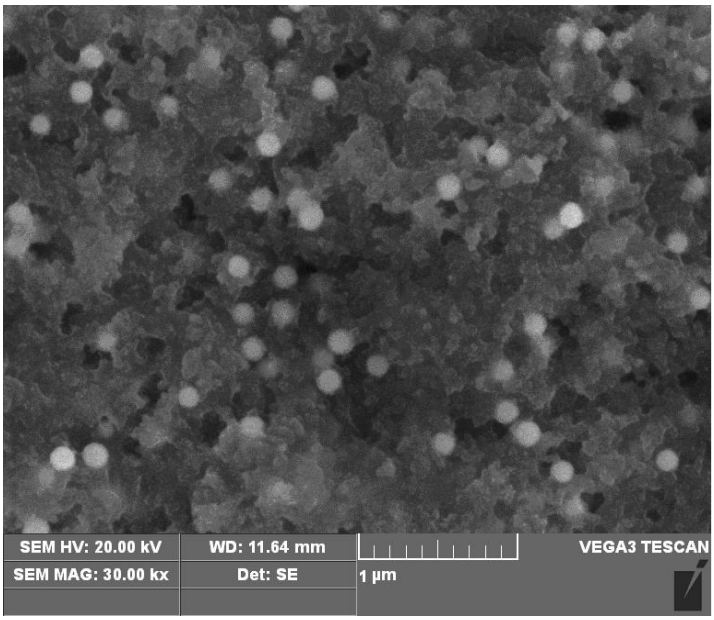


Figure 1. SEM micrograph of the PDA-nanogold composites film

It is clearly seen that the composites film presented a porous and rugged surface with some protuberances of composites aggregation. It is interesting that the gold nanospheres of uniform shape and size (about 100 nm diameter) were formed in or on the composites, which was assumed to surface groups of PDA or DA (for example, amidocyanogen and phenolic hydroxyl) binding to the Au(III)-complex or to the surface of growing gold nanoparticles.

3.2 Individual electrocatalytic activity of DA, AA, EP and UA

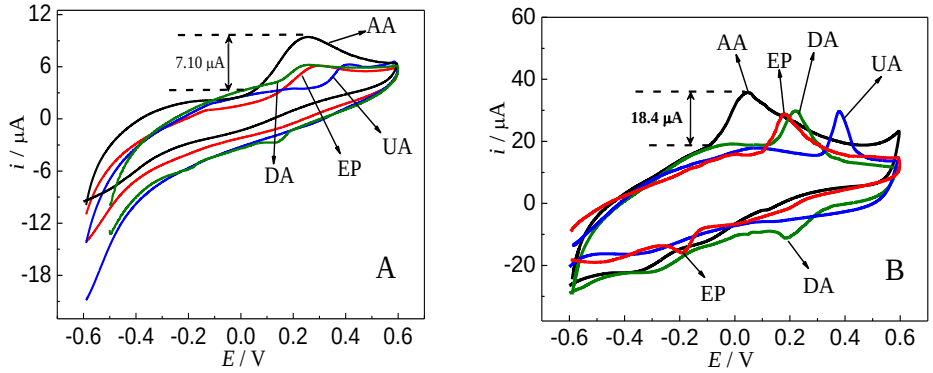


Figure 2. CVs of DA (20.0 μM), EP (30.0 μM), AA (600.0 μM) and UA (30.0 μM) singly at (**A**) a bare GCE and (**B**) modified electrode in PBS (pH 7.0).

The individual electrochemical behaviors of DA, AA, EP and UA at bare GCE (Fig. 2A) and PDA-nanogold modified electrode (Fig. 2B) were investigated by CV. At the bare GCE, the CVs of AA, EP and UA show the irreversible electrochemical behavior and a drawn out oxidation peak at 260 mV, 280 mV and 400 mV, respectively. Also, the CV of DA shows quasi-reversible electrochemical behavior with the oxidation and reduction peak potential at 260 mV and 130 mV, respectively. As is clear, the separation of the oxidation peak potentials for DA, AA and EP is not large enough to obtain good selectivity at the bare GCE. In contrast, the CVs of AA, EP, DA and UA at the modified electrode display the lower oxidation over-potentials and exhibits sharp oxidation peaks at 50 mV, 190 mV, 230 mV and 380 mV with greatly enhanced peak currents around 2.6 times higher than that at the bare GCE, suggesting a strong enhancement in the electron transfer rates of these compounds at the modified electrode (Fig. 2B). Additionally, a quasi-reversible redox pair for EP and a pair of symmetric redox peaks with a smaller peak separation (40 mV) for DA were obtained at the modified electrode, implying that the reversibility was notably improved by the PDA-nanogold composites film. Although EP and DA had similar oxidation potentials at the modified electrode, their reduction peaks appeared at -190 mV and 180 mV, respectively. The results above demonstrated that the PDA-nanogold composites film not only showed excellent catalytic activity for the redox reaction of EP, DA, AA and UA, but also dramatically enlarged the peak separation of the four compounds, hence indicating that individual or simultaneous determination of EP, DA, AA and UA in mixture was feasible.

3.3 Effects of pH on the electrochemical response of EP, DA, AA and UA

The influence of the pH level of the electrolyte on the electrochemical response of EP, DA, AA and UA at the modified electrode was investigated. The results exhibited that the peak potentials of these compounds shifted negatively with the increasing of pH in the range from 4.0 to 9.0, revealing

that protons have taken part in their electrode processes [12]. Although separations between their oxidation peaks diminished slightly with the increasing of pH, the resolution was large enough to distinguish them. In addition, DA and EP had good current responses in weak alkaline solution, but the current responses for AA and UA oxidation were better under acid conditions. Considering the influence of pH on the peak currents mentioned above and pH of physiological condition, pH 7.0 was chosen for the test.

3.4 Electrochemical oxidation of mixture of AA, DA, EP and UA at modified electrode

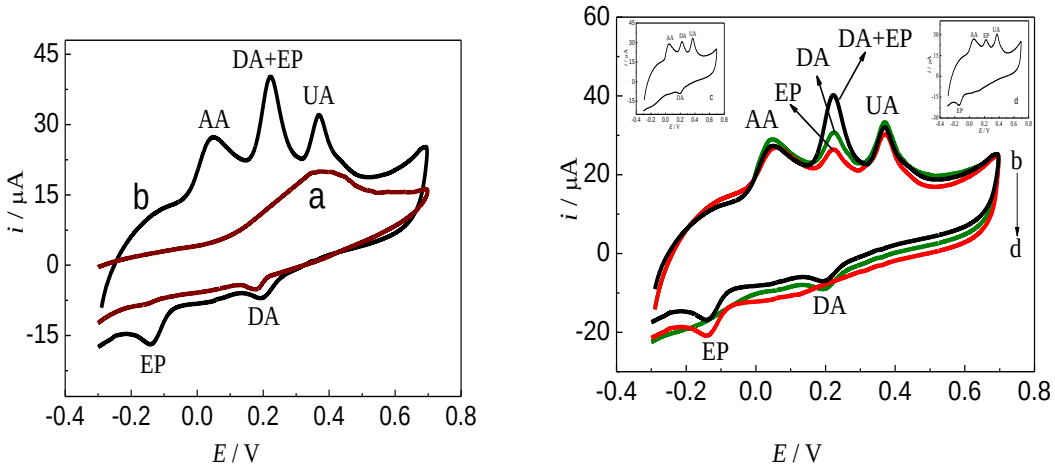


Figure 3. CVs of a mixture containing (a) and (b) EP (20.0 μM)+DA (20.0 μM)+AA (500.0 μM)+UA(30.0 μM); (c) DA (20.0 μM)+AA (500.0 μM)+UA(30.0 μM); (d) EP (20.0 μM)+AA (500.0 μM)+UA(30.0 μM) at the bare GCE (a) and the modified electrode (b, c, d). Scan rate: 50 mV/s.

Fig. 3 shows the CV responses of the bare GCE and the modified electrode in mixture of EP, DA, AA and UA. As seen from Fig. 3a, the bare GCE gives a single broad oxidation peak at around 400 mV and a small reduction peak at 180 mV with poor sensitivity, and fails to distinguish EP, DA, AA and UA in their mixture. In comparison, the modified electrode exhibited high current signals and well-defined three oxidation peaks for AA, DA/EP and UA at 50, 230 and 380 mV, respectively (Fig. 3b). The CVs of EP and DA illustrated both oxidation and reduction peaks in the redox process. Although oxidative peaks overlapped at the same potential for EP and DA, the reduction peaks for EP (-150 mV) and DA (190 mV) were clearly separated from each other. The oxdation peak separations between AA and DA/EP (180 mV), DA/EP and UA (150 mV), coupling with the reduction peak separation between EP and DA (340 mV), are sufficient enough to selective or simultaneous detection of EP, DA, AA and UA in their mixture.

Moreover, the CVs of a mixture of AA, DA and UA (Fig. 3c) and that of AA, EP and UA (Fig. 3d) at the modified electrode are also given. It can be seen that the oxidation peak current of the mixture of EP and DA (Fig. 3b) was equal to the sum of individual peak current of EP and DA. Thus,

based on this phenomenon, the concentrations of EP and DA could also be determined simultaneously according to the reference [9] which was relatively complicated comparing to this work.

3.5 Selective and Simultaneous determination of AA, DA, EP and UA

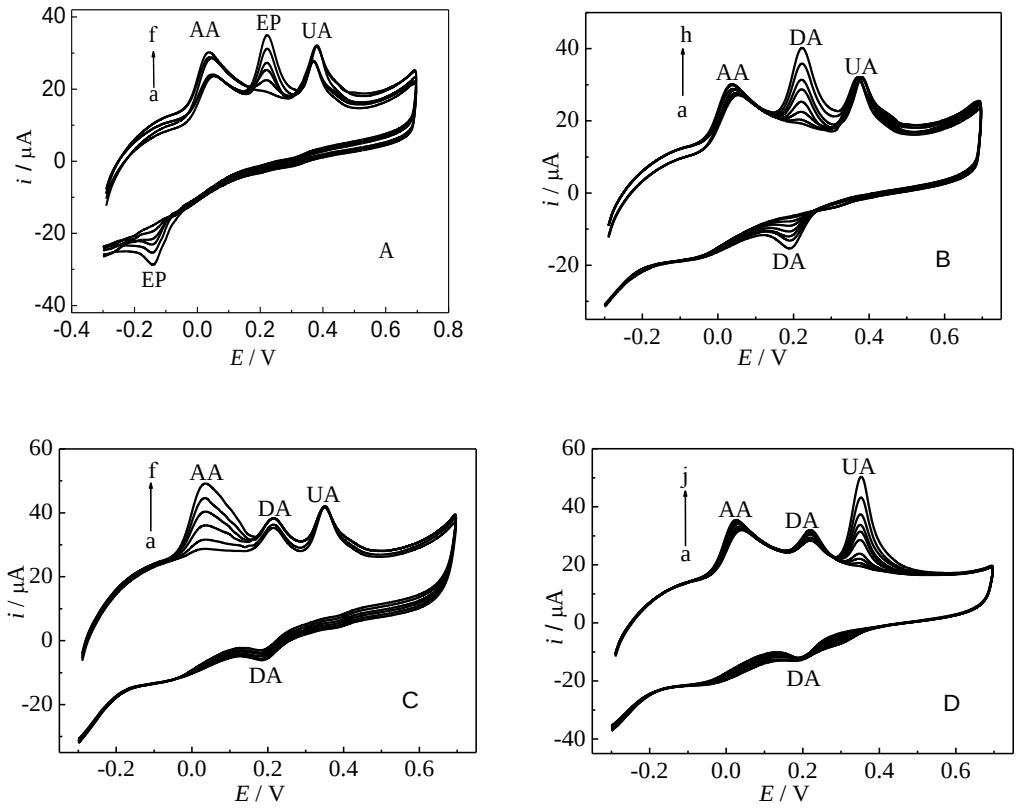


Figure 4. CVs of the mixture containing AA, UA and either EP or DA with different concentrations in PBS (pH 7.0) at the modified electrode. Scan rate: 50 mV/s.(**A**) Containing 600.0 μM AA, 30.0 μM UA and different concentrations of EP (from a to f): 0.8, 4.0, 10.0, 20.0, 30.0, 50.0 μM.(**B**) Containing 600.0 μM AA, 30.0 μM UA and different concentrations of DA (from a to h): 0.8, 1.0, 4.0, 10.0, 20.0, 30.0, 40.0, 60.0 μM. (**C**) Containing 30.0 μM UA, 20.0 μM DA and different concentrations of AA (from a to f): 40.0, 100.0, 300.0, 600.0, 1000.0, 1500.0 μM. (**D**) Containing 600.0 μM AA, 20.0 μM DA and different concentrations of UA (from a to j): 0.6, 1.0, 2.0, 5.0, 10.0, 20.0, 30.0, 50.0, 80.0, 100.0 μM

Fig. 4 depicts the CV responses of the modified GCE towards AA, UA and either EP or DA in the mixture when the concentration of one species changes while the other species keeping constant. As shown in Fig. 4A and 4B, keeping the concentration of AA and UA constant, the oxidation and reduction peak currents of EP (Fig. 4A) or DA (Fig. 4B) are positively proportional to its concentrations. Similarly, Fig. 4C and 3D display that the oxidation peak current of AA (Fig. 4C) or UA (Fig. 4D) increases linearly with the increasing concentrations of AA or UA, while the oxidation and reduction peak currents of DA does not change. Based on the experimental results described

above, the modified electrode could be applied to the simultaneous determination of AA, DA, EP and UA mixture by means of the oxidation peak currents of AA and UA and the reduction peak currents of EP and DA.

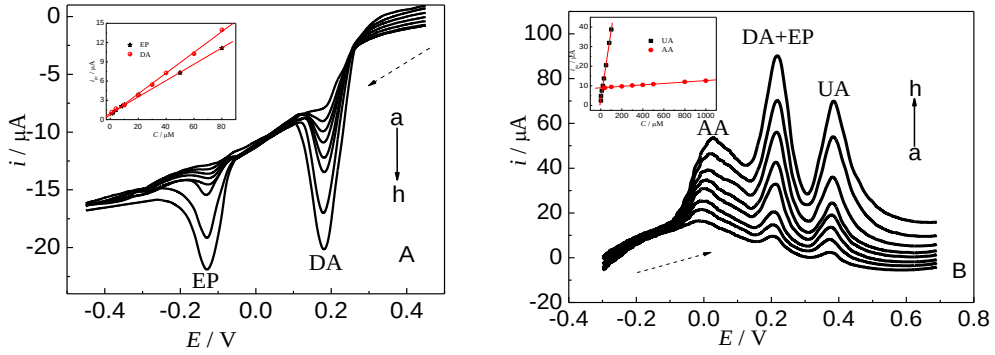


Figure 5. SWVs of the simultaneous determination of EP, DA AA and UA using the modified electrode in PBS (pH 7.0). The concentrations of EP, DA, AA and UA (from a to h) were in the linear range of EP (1.0, 2.0, 4.0, 8.0, 10.0, 20.0, 50.0, 80.0 μM), DA (1.0, 5.0, 10.0, 20.0, 30.0, 40.0, 60.0, 80.0 μM), AA (40.0, 100.0, 200.0, 300.0, 400.0, 500.0, 800.0, 1000.0 μM), and UA (0.8, 2.0, 10.0, 20.0, 30.0, 50.0, 80.0, 100.0 μM). Inset: the plot of peak current vs. the concentrations of EP, DA, AA and UA.

The SWV was used for the simultaneous determination of EP, DA, AA and UA. Fig. 5 illustrates the SWV responses of the proposed electrode towards EP, DA, AA and UA when the concentrations of the four species increase synchronously. It can be seen that the oxidation peak currents for EP and DA and the reduction peak currents for AA and UA increase linearly with their concentrations. The SWV responses of the modified electrode towards the simultaneous determination of these four species are listed in Table 1. The relative standard deviation (RSD) of the peak currents was less than 2.9% for these four species at modified electrode (n = 10). In comparison with other electrochemical sensors, the proposed modified electrode exhibited improved analytical performance as shown in Table 2.

Table 1. Analytical characteristics for the simultaneous determination of EP, DA, AA and UA by the proposed method

Analyte	Linear range (μM)	Linear regression equation (*i*: μA, *C*: μM)	Correlation coefficient	Detection limit (μM)
EP	1.0 -80.0	$i_{pc,\ EP}$ =0.1272 *C*+ 0.9978	0.9990	0.1
DA	1.0 -80.0	$i_{pc,\ DA}$ = 0.1613 *C*+ 0.7967	0.9988	0.08
AA	40.0 -1000.0	$i_{pa,\ AA}$ = 0.0037*C*+ 9.0066	0.9977	5.0
UA	0.8 -100.0	$i_{pa,\ UA}$ =0.3547*C*+ 3.2452	0.9988	0.06

Table 2. Comparison of the proposed method with other electrochemical methods for the simultaneous determination of AA, UA, EP and/or DA.

Electrode	Analytes	Linear range(μmol/L) AA, DA/EP, UA	L.O.D.(μmol/L) AA, DA/EP, UA	Ref./year
Nafion-coated clay/GCE	DA, UA	—, 0-6.0, 0.5-10.0 and 10.0-100.0	— , 0.0027, 0.2	10/1997
PPy–TDS/GE	AA, DA, UA	1.0-500, 1.0-500, 1.0-500	0.6, 0.4, 0.4	11/1998
poly (caffeic acid) / GCE	AA, EP, UA	20.0-1000.0, 2.0-80, 5.0-300.0	7, 0.2, 0.6	12/2006
RNA/GCE	DA, UA	2000.0, 0.37-36, 0.74-73	—, 0.2, 0.36	13/2006
Poly(OB)/GCE	AA, DA, UA	65.0-2000.0, 0.22-7.00, 12.5-400.0	— — —	14/2006
Poly(EBT)/GCE	AA, DA, UA	150-1000, 0.1-200, 10-130	— — —	15/2007
PtAu/GCE	AA, DA, UA	103-1650, 24-384, 21-336	— — —	16/2007
Dopamine/PGE	AA, DA, UA	25.0-500.0, 1.0-20.0, 2.5-30.0	13.0, 0.11, 1.4	17/2008
PMB/SZP/CPE	AA, DA, UA	100-1600, 6-100, 22-350	8.3, 1.7, 3.7	18/2008
PEDOT/Pd/GCE	DA, UA	— , 0.5-1.0, 7.0-11.0	—, 0.5, 7	19/2008
CNF/CPE	AA, DA, UA	6.0-40.0, 0.32-5.6, 2.0-15.2	2.0, 0.04, 0.2	20/2008
oxidized GCE	AA, DA, UA	197.0-988.0, 1.97-9.88, 19.7-98.8	— — —	21/2009
SWCNH/GCE	AA, DA, UA	30.0-400.0, 0.2-3.8, 0.06-10.0	5.0, 0.06, 0.02	22/2009
poly (ACBK)/GCE	AA, DA, UA	50.0-1000.0, 1.0-200.0; 1.0-120.0	10, 0.5, 0.5	23/2009
Nano-$LaFeO_3$/GCE	AA, DA, UA	500-3000, 0.15-800, 100-600	— 0.03 —	24/2009
CDDA/GCE	AA, DA, UA	5.0-240, 5.0-280, 0.1-18.0	1.43, 0.29, 0.016	25/2009
Nano-Pd/PMPy/	AA, DA, UA	50-1000, 0.1-10, 0.5-20	7, 0.012, 0.027	26/2010
Poly(Sulfonazo III)/GCE	AA, DA, UA	0.5-1300.0, 0.05-470.0, 0.2-100.0	0.17, 0.03, 0.11	27/2010
Tiron /GCE	AA, DA, UA	4.0-792.0, 0.2-45.8,0.06-166.0	1.79, 0.07, 0.021	28/2010
Hematoxylin MWCNT/ GCE	AA, EP, UA	133.5-800.0, 13.4-80.0, 26. 0.0	—, 0.024, —	29/2010
nano-Au/p-TA/GCE	AA, DA, UA	2.1-50.1, 0.6-340.0, 1.6-110.0	1.1, 0.05, 0.08	30/2011
GNPs/PImox/GCE	AA, DA, UA	210.0-1010.0, 5.0-268.0, 6.0-486.0	2.0, 0.08, 0.5	31/2012
poly(caffeic acid) / GCE	DA, EP	DA:1.0-35.0, EP:1.0 -35.0	DA:0.1, EP:0.2	9/2007
α-CD/CNT/ GE	DA, EP	DA:2.0-1000.0, EP:1.0-1000.0	DA:1.0, EP:0.5	32/2005
Poly(isonicotinic acid) /CPE	DA, EP	DA:50.0-700.0, EP: 5.0-100.0	DA:20.0, EP:1.0	33/2009
poly(taurine)/ GCE	DA, EP	DA:1.0-800.0, EP: 2.0-600.0	DA:0.1, EP:0.3	34/2009
PAIUCPE	DA, EP	DA:0.8-300.0, EP: 2.0-150.0	DA:0.17, EP:0.33	35/2013
Poly(DA)-nanogold/GCE	DA, EP, AA, UA	1.0-80.0, 1.0-80.0, 40.0-1000.0, 0.8-100.0	0.08, 0.1, 5.0, 0.06	This work

3.6 Interferences, Repeatability and Recovery

The influence of various foreign species on the determination of 500.0 μM AA, 20.0 μM DA, 30.0 μM EP and 30.0 μM UA were investigated. The tolerance limit was taken as the maximum concentration of the foreign substances which caused an approximately ±5% relative error in the determination. The tolerated ratio of the foreign substances to the analytes was 500 for Na^+, Cl^-, K^+; 100 for Mg^{2+}, Ca^{2+}; 30 for L-cystine, glucose, NADH, glutamic acid, glycin and chitosan.

The repeatability of the modified electrode was good. The electrochemical activity of the modified electrode remained 97% after 50 times' measurements. It was also found that the modified electrode showed only about 8% current decrease after 30 days for the storage in dry state at 4 °C. The used modified electrode could be regenerated in PBS of pH 7.0 by CV from -1.0 to +1.0 V at 50 mV/s and the renewed electrode was found to give the stable response for the four components within the error limits.

3.7 Sample analysis

Human serum and urine samples were selected as real samples for analysis by the proposed method. Human serum samples were centrifuged before the experiment. To ascertain the correctness of the results, the standard addition method was applied to the quantitative analysis of EP, DA, AA and UA in real samples. Appropriate amount of samples were diluted to 10 mL mark with 5 mL PBS (0.1 mol/L, pH 7.0) and distilled water for test. The average recoveries of the spiked standard substances ranged between 97 % and 105 %. The results were presented in Table 3.

Table 3. Determination of EP, DA, AA and UA in real samples using SWV (n=6)

sample		Detected (μM)	Added (μM)	Founded (μM)	Recovery (%)	[a] Total value (mM)
Serum	AA	—	100.0	101.5	101.5	—
	DA	—	10.0	10.2	102.0	—
	EP	—	10.0	10.1	101.0	—
	UA	10.5	50.0	59.1	97.2	0.21
Urine	AA	—	100.0	99.7	99.7	—
	DA	—	10.0	9.9	99.0	—
	EP	—	10.0	9.9	99.0	—
	UA	22.5	50.0	74.7	104.4	2.25

a Total value was obtained by multiplying the detected value by the appropriate dilution factor (20 for serum and 100 for urine samples)

4. CONCLUSIONS

For the first time we reported a simple method for simultaneous determination of EP, DA, AA and UA using PDA-nanogold composites modified GCE by a one-pot electropolymerization strategy. The resultant sensor showed the efficient electrocatalytic activity for individual and simultaneous detection of EP, DA, AA and UA with relatively high sensitivity, selectivity and fast response. Moreover, the proposed method was convenient and reusable, and could lead an attractive approach for the determination of real samples.

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