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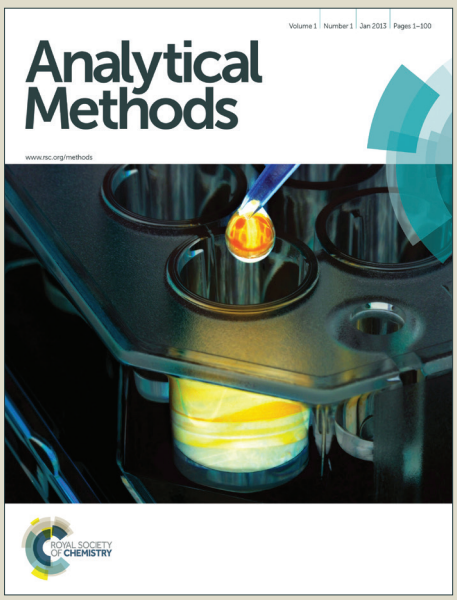

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ARTICLE TYPE

Using AuCo alloy nanoparticles/HS-graphene modified electrode for selective determination of dopamine, ascorbic acid and uric acid

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An electrochemical method for selective determination of dopamine (DA), ascorbic acid (AA) and uric acid (UA) was set up using AuCo alloy nanoparticles/HS-graphene modified electrode. The AuCo alloy nanoparticles (AuCo NPs) was formed on a thiol group functional graphene (HS-GR) modified electrode by an electro-depositing method. The morphology and electrochemical properties of the modified electrode were characterized by scanning electron microscopy (SEM) and electrochemical methods, (such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV)), respectively. The morphology of AuCo NPs was like a cauliflower. The electrochemical experiments revealed that, on the modified electrode, DA, AA and UA had three separate DPV oxidation peaks in pH 4.5 of mcllvaine buffer solutions (MBS). The peak potential separations of DA and AA, DA and UA, AA and UA were 156, 136 and 292 mV, respectively, **which can be used for selective determination each of them in their mixture solution. The linear concentration range of DA, AA and UA were 2.1-21.1 μM, 10.0-100.0 μM and 9.0-60 μM, respectively, with the detection limits (S/N = 3) of 0.1, 4.0 and 1.0 μM. The high selectivity and good sensitivity of the modified electrode made it successfully detect DA in human serum samples.**

Introduction

In recent years, bimetallic alloy nanoparticles (NPs) have drawn particular attention due to their distinctive physical and chemical properties. Compared with monometallic counterparts of them, they often exhibit enhanced performances due to the bifunctional effect and the electronic effect, such as high catalytic activity, good stability, magnetic property and corrosion resistance.[1-7] Among these properties, the catalytic activity is especially noticeable, and some bimetallic NPs, such as AuPt,[8-11] AuAg,[12-14] AuPd,[15, 16] PtPd,[17, 18] PtAg,[19, 20] CoPd,[21] AgCu,[22] and AuCo,[23-25]etc., have been applied in electrochemical research for catalyzing biomolecules with good selectivity and sensitivity.[26] In this work, the cauliflower-like AuCo NPs was synthesized via electro-deposition method and was incorporated with thiol group functional graphene (HS-GR) for selective determination of dopamine (DA), ascorbic acid (AA) and uric acid (UA).

Electrochemical deposition is a facile and general method for preparing bimetallic NPs with many advantages, such as low cost, mild conditions controllability and without complex separation procedures,[27] compared with the methods of vacuum deposition and liquid phase synthesis[28-32] which are usually suffering from demanding heat treatment, severe reaction conditions, or complex process even under mild conditions.

Graphene, a new nanomaterial, has received considerable interest due to its unique structure and extraordinary properties, including large specific surface area, accelerating electron transfer, good biocompatibility and high catalytic activity.[33] Graphene can be used as an ideal platform for growing or anchoring various NPs. However, graphene is hydrophobic due to no functional groups on its surface. Therefore, it usually aggregated or even stack in most of solvents, which seriously restricted its application as substrate material for combining with bimetallic NPs.[34] In order to circumvent the problem, a variety of functionalized graphene were synthesized by connecting functional groups on its surface.[35-38]These groups can make bimetallic NPs directly grow on its surface without using reduction agents. Therefore, the application of functionalized graphene is of great interest for electro-analytical and electro-catalytic researches. Our group has used the aminated Graphene as a platform for incorporating Ag NPs and fabricated an electrochemical biosensor for selective determination of a catecholamine neurotransmitter, epinephrine, in the presence of UA.[39]

DA, a member of the catecholamine neurotransmitters, plays an important role in mammalian central nervous system. The concentration of DA is extremely low (0.01-1μM) in a healthy person. The abnormal levels of DA will lead to brain disorders such as Parkinson and schizophrenia diseases.[40-42] The oxidation potentials of DA are too close with that of the coexistences, such as AA and UA, to be separated, and has a sluggish redox process at bare GCE. Thus, electrochemical assay of DA is still a major challenge for analysts.[43] To solve these problems, various modified electrodes have been developed. These modified electrodes make full use of carbon,[44, 45] ionic liquids,[46] nanotubes,[47] nanowires,[48] nanoparticles,[49, 50] and conducting polymer films.[51-53] However, to best of our knowledge, the use of AuCo NPs incorporated with HS-GR for selective determination of DA, AA and UA has not been reported yet.

Herein, the AuCo NPs was electrodeposited on the surface of HS-

GR with constant potential deposition. The AuCo NPs was anchored on the HS-GR via the thiol groups, which is in favor of improving the electro-deposition efficiency and the stability of the AuCo NPs. The AuCo NPs and HS-GR showed synergistic effects for electro-catalyzing the oxidation of DA, AA and UA in pH 4.5 of mcllvaine buffer solution (MBS). The electrochemical behavior of DA was investigated in detail using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The modified electrode can be used for determination each of DA, AA and UA in their mixture solution with high sensitivity and selectivity.

Experimental section

Regents and apparatus

DA was purchased from National Institute for the Control of Pharmaceutical and Biological Products, Beijing China. $HAuCl_4$ and UA were purchased from Sinopharm Chemical Reagent Co., Ltd., China. *N, N*-dimethylformamide (DMF) and AA were provided by Shantou Xilong Chemical Industry Co., Ltd., China. SH-GR was provided by Nanjing Jicang Nanotechnology Co., Ltd., China. Sodium dodecyl benzene sulfonate (SDBS), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and sodium sulfate anhydrous (Na_2SO_4) were obtained from Tianjin (China) Guangfu Institute of Superfine Chemical Industry, Tianjin (China) Kemiou Chemical Reagent Co., Ltd. and Shanghai (China) Xingta Jinshan County chemical plant, respectively. MBS as supporting electrolyte was prepared by mixing 0.2 M $Na_2HPO_4{\bullet}12H_2O$ and 0.1 M $C_6H_8O_7{\bullet}H_2O$. All chemicals were analytical grade and used without further purification. All solutions in the experiments were prepared with double distilled water.

A CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) was used for all electrochemical experiments involving electro-deposition, CV and DPV at room temperature. The conventional three-electrode system was formed by a working electrode of a GCE or modified GCE, a reference electrode of a saturated calomel electrode (SCE) and a counter electrode of a platinum wire electrode. The pH values of all solutions were measured by a model PHS-3G pH meter (Shanghai INESA & Scientific Instrument Co., Ltd., China).

Fabrication of the modified electrode

Firstly, 2.0 mg HS-GR was dispersed with 1.0 mL DMF and stood for 20 minutes in an ultrasonic bath. Then the suspension of 6.0 μL well-dispersed HS-GR was dripped onto the surface of a GCE and dried under an infrared lamp. The obtained electrode denoted as HS-GR/GCE. Specially, the GCE had been pretreated in advance through polished by 0.05 micron alumina powder on chamois leather, followed by ultrasonic cleaning with ethanol, acetone, and deionized water. The AuCo NPs was synthesized on the HS-GR/GCE according to the reference[54] with little modification. In detail, HS-GR/GCE electrode was immersed into an electrolyte solution containing 1.0 mM $HAuCl_4$, 20 mM $Co(NO_3)_2$, 0.2 M Na_2SO_4 and 0.02 mM SDBS and a constant potential deposition were performed at the constant potential of −0.8 V for 400 s. After that, the resulted modified electrode (AuCo NPs/HS-GR/GCE) was rinsed with double distilled water and then dried naturally at room temperature. Other electrodes such as Co NPs/HS-GR/GCE, Au NPs/HS-GR/GCE and AuCo NPs/GCE were prepared under the same conditions. Additionally, for comparison, another AuCo NPs/HS-GR/GCE was prepared as the same protocol except without SDBS and the resulted modified electrode was denoted by AuCo NPs/HS-GR/GCE (no SDBS).

Processes

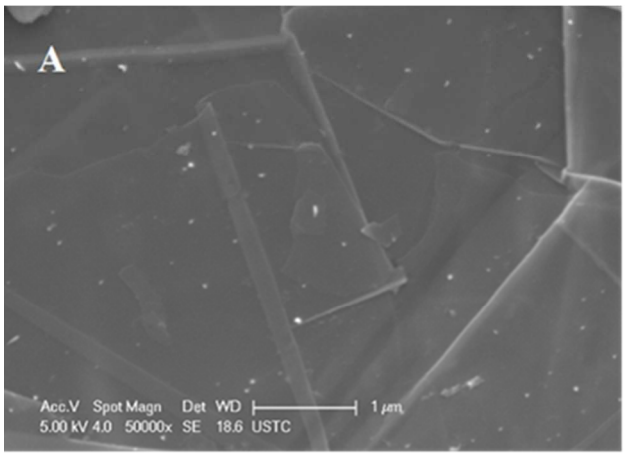
CV measurements were performed in the potential range from 0 to 0.7 V at a scan rate of 100 mV s^{-1} in pH 4.5 of MBS.

DPV measurements were conducted in pH 4.5 of MBS containing different concentrations of DA, UA and AA in the potential range from 0 to 0.6 V. The electro-parameters were as follows: The pulse amplitude was 0.05V; The pulse width was 0.2 s; The sampling width was 0.0167; The pulse period was 0.5 s and the quiet time was 30 s. The solutions of DA, AA and UA need to freshly prepare with MBS and deoxygenated with nitrogen gas for 10 min before use. During determination, a nitrogen atmosphere was maintained over the solutions. All measurements were carried out at room temperature.

Results and discussion

The scanning electron microscopy (SEM) analysis

The SEM images of the surface morphology of the HS-GR/CPE (A) and AuCo NPs/HS-GR/CPE (B) were showed in **Fig.1**. From the **Fig. 1A**, we can see that the surface of the HS-GR/CPE was relatively flat and smooth. However, the surface of AuCo NPs/HS-GR/GCE was rough with many protuberances (**Fig. 1B**), which just like cauliflowers, which significantly increased the surface area of the modified electrode.



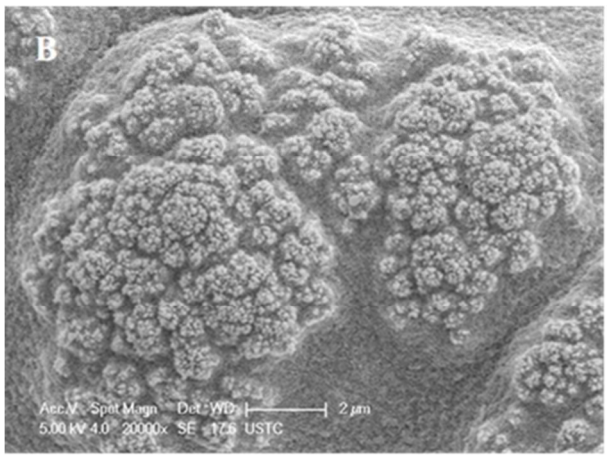


Fig.1.SEM images of HS-GR/GCE (**A**) and AuCo NPs/HS-GR/GCE (**B**)

The electrochemical behavior of DA on the modified electrode

Fig. 2 showed the cyclic voltammograms (CVs) of 0.1 mM DA at 7 types of modified electrodes (GCE, HS-GR/GCE, Co NPs/HS-GR/GCE, Au NPs/HS-GR/GCE, AuCo NPs/GCE, AuCo NPs/HS-GR/GCE (no SDBS) and AuCo NPs/HS-GR/GCE) in MBS of pH 4.5. At the bare GCE, DA exhibited a pair of much poor redox peaks. The peak-to-peak separation (ΔE_p) between anodic (E_{pa}) and cathodic potential (E_{pc}) was 430 mV. When a layer of HS-GR was covered on the bare GCE, the ΔE_p was decreased to 395 mV as well as the anodic peak current increased from 3.746 μA to 4.368 μA. After AuCo NPs were electrodeposited on the surface of HS-GCE (AuCo NPs/HS-GR/GCE), the ΔE_p decreased further (only 134 mV) and the biggest redox peak current was obtained among these 7 types of modified electrodes. Noticeably, the anodic peak current (I_{pa}) was enhanced about 31.85, 27.31 and 1.71 in comparison with that on the bare GCE, HS-GR/GCE and AuCo NPs/GCE, respectively. These revealed that AuCo NPs and HS-GR played synergistic effects for electro-catalyzing the oxidation of DA. Moreover, an interesting thing was that the oxidation peak current of DA was much bigger at the AuCo NPs/HS-GR/GCE than that at the AuCo NPs/HS-GR/GCE (no SDBS), which probably because SDBS promoted the dispersion of AuCo NPs on graphene surface as an anionic surfactant, and the electro-catalytic effect to DA.[55]

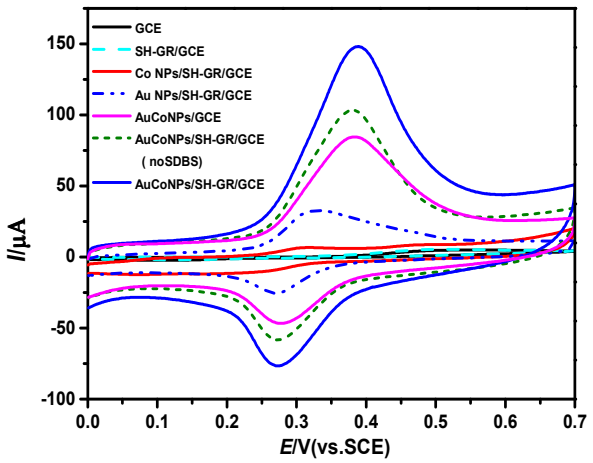
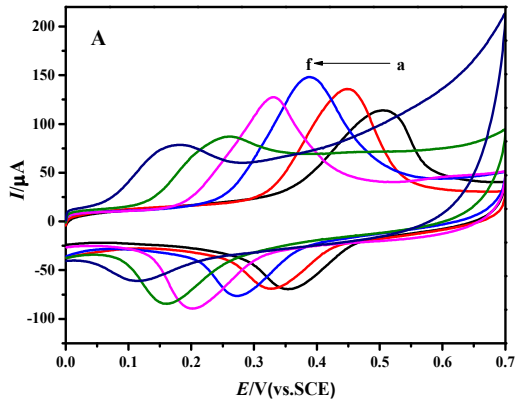


Fig.2. CVs of 0.1 mM DA at GCE, HS-GR/GCE, Co NPs/HS-GR/GCE, Au NPs/HS-GR/GCE, AuCo NPs/GCE, AuCo NPs/HS-GR/GCE (no SDBS) and AuCo NPs/HS-GR /GCE in pH 4.5 of MBS at a scan rate: 100 mV s^{-1}.

Effect of pH on the electrochemical oxidation of DA

The effect of pH of the supporting electrolyte solution on the oxidation of 0.1 mM DA at AuCo NPs/HS-GR/GCE was investigated by CV over the pH range from 2.5 to 7.5, and the results were shown in **Fig.3A**. It could be observed that I_{pa} increased with increasing pH at first, and gradually decreased when pH increases further. Therefore, pH 4.5 was chosen for the follow determination of DA. As shown in **Fig.3B**, E_{pa} shifted negatively and linearly with increasing pH values and linear regression equations could be expressed as E_{pa} = 0.0632pH – 0.6690, r = 0.9982. The slope was near to the theoretical value of 58.5 mV/pH, indicating that the number of electrons and protons participated in the redox reaction of DA was equal.[56]



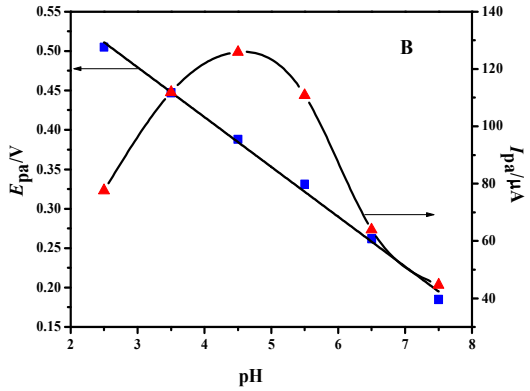


Fig.3. A: CVs of 0.1 mM DA in MBS at different pH values (a-f; 2.5, 3.5, 4.5, 5.5, 6.5, 7.5). Scan rate: 100 mV s^{-1}. **B**: Plots of peak potential and peak current versus pH value.

Effect of scan rates on the electrochemical oxidation of DA

CV was used to study the influence of scan rate (v) on the electrochemical redox of 0.1 mM DA at AuCo NPs/HS-GR/GCE in MBS of pH 4.5. As shown in **Fig.4A**, CVs was dependent on the scan rates ranging from 20 mV s^{-1} to 300 mV s^{-1}. The anodic or cathodic peak currents continuously increased with increasing scan rates. **Fig.4B** showed the anodic or cathodic peak currents had a linear relationship with the square root of scan rate ($v^{1/2}$) with the linear regression equation of $I_{pa}(\mu A) = 9.818v^{1/2}$ ($mV^{1/2}$ $s^{-1/2}$) + 14.20 (r = 0.993) and $I_{pc}(\mu A) = -4.843v^{1/2}$ ($mV^{1/2}$ $s^{-1/2}$) – 1.677 (r = 0.996), respectively, indicating that that the redox process of DA on the modified electrode was a diffusion controlled process.

For an irreversible diffusion controlled process, the following equation (E_q.1) [57, 58] can be used for determination of the electron number (n_α) involved in the rate-determining step.

$$E_p = (0.059/2\alpha n_\alpha)\log v + \text{constant}. \quad (1)$$

Where α was the electron transfer coefficient.

In this research, the linear relationships of E_{pa} = 0.053log$v$ + 0.4495 with r = 0.9914 and E_{pc} = 0.0413log$v$ – 0.2237 with r = 0.9816 were obtained. Therefore, n_α was calculated to be 1.11≈1 according to $0.059/2\alpha n_\alpha$=0.053 assuming α = 0.5.

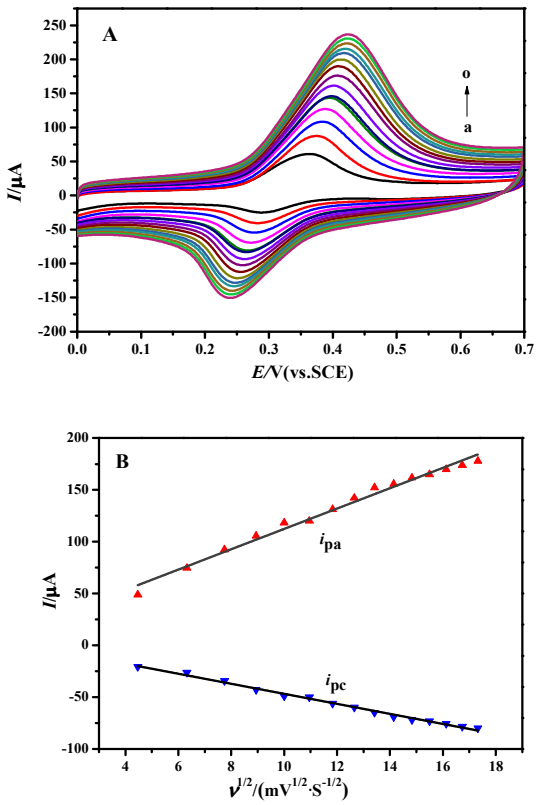


Fig.4 CVs of 0.1 mM DA on the AuCo NPs/HS-GR/GCE at different scan rates (**A**) and the relationship curve of I_p vs. $v^{1/2}$ (**B**). Scan rates (a-o): 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280 and 300 mV s^{-1}.

Determination of DA, AA and UA

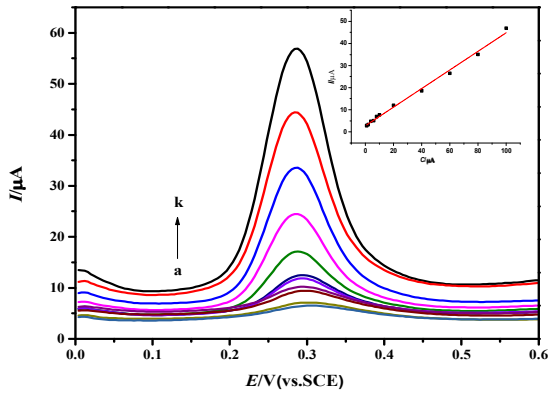


Fig.5. Differential pulse voltammograms of the AuCo NPs/HS-GR/GCE in pH 4.5 of MBS containing different concentrations of DA: a)1.0, b)2.0, c)4.0, d)6.0, e)8.0, f)10.0, g)20.0, h)40.0, i)60.0, j)80.0 and k)100.0 μM of DA. Inset: the calibration curve of DA for concentrations.

Under optimal conditions, the DPV of different concentration of DA at AuCo NPs/HS-GR/GCE in MBS of pH 4.5 was studied. It could be seen from the **Fig.5** that the DPV peak current corresponding to the oxidation of DA was linear with DA concentration in the range of 1.0-100.0 μM. So the linear

regressive equation was represented as $I(\mu A) = 0.4211C_{DA}$ (μM) + 2.745 with r = 0.997. The detection limit (S/N = 3) of DA was 0.03 μM.

AA and UA were two important coexistences with DA. In this method, the DPV responses for different concentrations of UA at AuCo NPs/HS-GR/GCE were shown in **Fig.6A**. As can be seen, the peak current of UA had built up linearly with its concentration over a concentration range: 9.0-60 μM, while the peak currents of 10.0 μM AA and 1.0 μM DA almost keep constant. The linear regression equation was $I(\mu A) = 0.3882C_{UA}(\mu M) - 0.5772$ (r = 0.9983) with the detection limit (S/N = 3) of 1.0 μM. Similarly, **Fig.6B** and **C** displayed the peak currents of AA or DA increased linearly with the increase of their concentrations, respectively. The linear regressive equations of AA and DA were expressed as $I(\mu A) = 0.0966C_{AA}$ (μM) – 0.6526 (r = 0.9981) with detection limits (S/N = 3) of 4.0 μM in the concentration range of 10.0-100.0 μM and $I(\mu A) = 0.8639C_{DA}$ (μM) + 1.450 (r = 0.9998) with detection limits (S/N = 3) of 0.1 μM in the concentration range of 2.1-21.1 μM, respectively. Compared with the other related studies[59-67] (**Table 1**), the present procedure showed a high sensitivity, a low detection limit, convenient and satisfactory application in real samples. Most importantly, the proposed method can be used for simultaneously detection of DA, AA and UA.

Epinephrine (EP) was another important coexistence with DA. However, the electrodes could not be used for selective determination of EP or DA in their mixture solution, although the modified electrode also exhibited good electro-catalytic activity for the oxidation of EP. The modified electrode was allowed to individually measure EP in a concentration range from 1.0 μM to 80.0 μM, the oxidation peak current versus the concentration of EP was linear with the slope of 0.5258 μA μM^{-1}. The detection limit (S/N = 3) was 0.8 μM.

Stability and reproducibility of the modified electrode

The repeatability of the modified electrode was investigated by measuring 10 μM DA in the pH 4.5 of MBS on a batch of five parallel prepared AuCo NPs/HS-GR/GCE or continue measuring 10 μM DA in the pH 4.5 of MBS on the same one electrode for eight times. The relative standard deviations (RSD) of the DPV peak currents were 4.6 % and 6.3 %, respectively. The stability of the fabricated electrode was studied by determining the steady-state response current of 10 μM DA every day, and the RSD of the current responses was 7.2 % (n = 3). These results suggested that the electrode had good reproducibility and stability.

Selectivity for determination of DA, AA and UA

2 mM of $MgSO_4$, $CaCl_2$, NaCl, KCl, $FeCl_3$, $FeSO_4$, serine, threonine, tryptophan, aspartic acid and 20 mM of glucose had no significant effect on the determination of DA, AA and UA, indicating that the proposed electrode exhibited excellent selectivity towards DA, AA and UA.

Table 1. Comparison of some characteristics of the different modified electrodes for the determination of DA

Electrode	S/(μA μM^{-1})			Detection limit (μM)			Fabrication methods	Application	Ref.
	DA	AA	UA	DA	AA	UA		DA	
poly (Evans Blue)/GCE	0.33	0.18	0.038	0.25	0.3	2.0	Electropolymerization	hydrochloride injection solutions	59
GO-PAN/GCE	0.265	0.008	0.209	0.5	150-1050	1	Oxidation polymerization	-	60
poly-CDDA/GCE	0.05	0.11	0.35	0.29	1.43	0.016	Electropolymerization	-	61
NPG/GCE	1.166	-	-	0.017	-	-	Dealloying	-	62
PGE	0.05	0.008	0.016	24	103	21	Anodization	-	63
Pd/CNFs/GCE	0.25	-	-	0.7	1.4	4.5	Electrospinning and thermal treatment	Injectable medicine	64
$(P_2W_{16}V_2$-AuPd/PEI$)_8$	1.916	0.62	-	0.671	0.217	-	LBL	Human serum	65
Sulfonazo III/GCE	0.08	0.006	0.1	0.08	1.7	0.11	Electropolymerization	dopamine injection solution	66
Tiron/GCE	0.33	0.007	0.093	0.07	0.021	1.79	Electropolymerization	Dopamine ampoule	67
AuCo NPs/HS-GR/GCE	0.8639	0.0966	0.388	0.1	4.0	1.0	Electrochemical deposition	Human serum	This work

Abbreviations: GO, Graphene oxide; PAN, Poly-aniline; CDDA, 3-(5-chloro-2-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid; NPG, nanoporous gold; PGE, pyrolytic graphite electrodes; CNFs, carbon nanofibers; $P_2W_{16}V_2$, phosphovanadotungstate $K_8P_2W_{16}V_2O_{62}\cdot 18H_2O$; PEI, Poly-ethylenimine; PGE, pyrolytic graphite electrodes; LBL, layer-by-layer self-assembly; Ref., reference.

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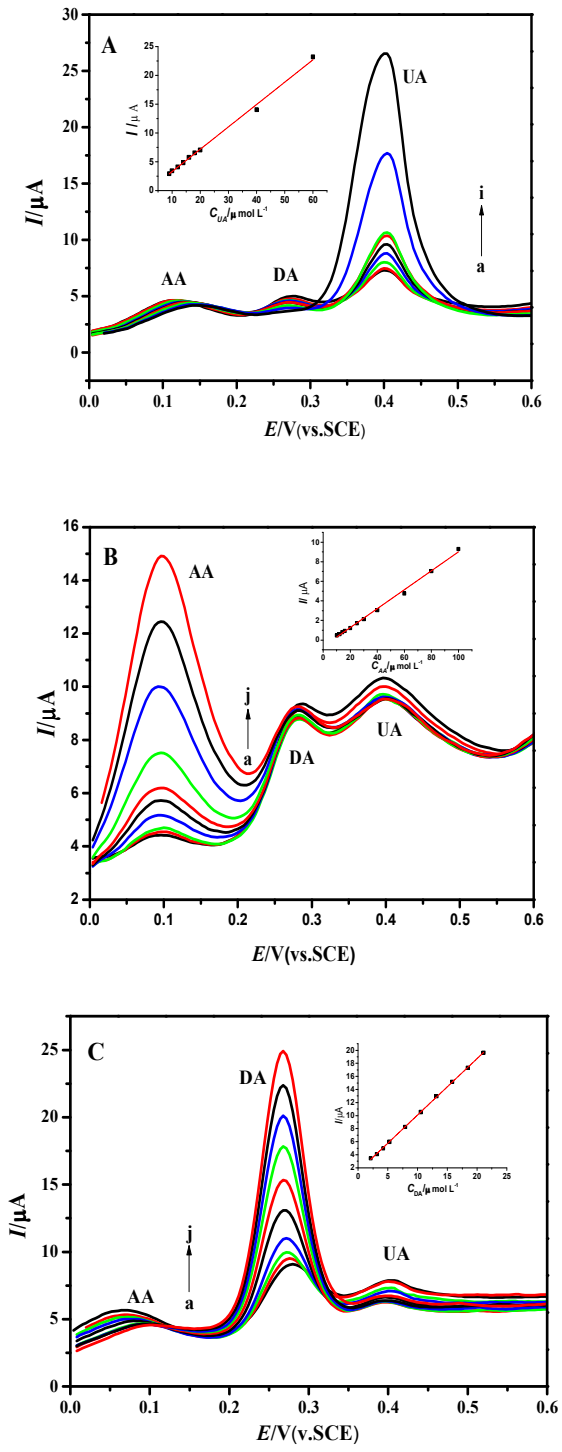

Fig.6. DPVs of the AuCo NPs/HS-GR/GCE in pH 4.5 of MBS (**A**) DPVs of UA concentration (a-I): 9.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 40.0 and 60.0 μM in the presence of 1.0 μM DA and 10.0 μM AA; (**B**) DPVs of AA containing 1.0 μM DA and 6.0 μM UA. AA concentrations (a-j):10.0, 12.0, 14.0, 16.0, 20.0, 25.0, 30.0, 40.0, 60.0, 80.0 and 100.0 μM AA; (**C**) DPVs of DA in the presence of 10.0 μM AA and 4.0 μM UA. DA concentrations (a-j): 2.1, 3.2, 4.2, 5.3, 7.9, 10.5, 13.1, 15.8, 18.5 and 21.1 μM DA. Insets: Calibration plots of UA, AA and DA.

Recovery test

To investigate the practical application of the prepared AuCo NPs/HS-GR/GCE for the determination of DA, the modified electrode was examined by determining the levels of DA in human serum sample. The human blood samples were collected from clinical laboratories and centrifuged 20 min to get upper serum. The gained human serum samples were diluted 10 times with pH 4.5 of MBS without any treatment. Then the serum samples were spiked with DA of standard concentrations (0, 2 and 4 μM) for confirmation. The standard addition method was applied for testing the accuracy of measurement and the results were shown in **Table 2**. The recovery for the standards addition was in the range of 100.9-104.6 %. The results showed that the proposed methods could be successfully used for the determination of DA in human serum sample.

Table 2.Determination of DA in human serum samples (n=3)

Addition (μM)	Found (μM)	Recovery (%)	RSD (%)
0	0.507	–	2.05
2	2.525	100.9	3.44
4	4.690	104.6	3.78

Conclusions

An AuCo NPs/HS-GR/GCE was fabricated by constant potential deposition method. The AuCo NPs/HS-GR/GCE showed excellent catalytic properties for the oxidation of AA, DA and UA, and it could be used for determination each of them in their mixture solutions with wide linear range, high selectivity and sensitivity, good repeatability and stability. Using the proposed modified electrode for determination of DA in human serum, the recovery was in the range of 100.9-104.6 %.

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Notes and references

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