Int. J. Electrochem. Sci., 12 **(2017)** 861 – 875, doi: 10.20964/2017.02.29

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

One Step Electrodeposition of Graphene-Au Nanocomposites for Highly Sensitive Electrochemical Detection of Salbutamol

Xiu-Chun Guo[1,†], *Hai-Hui Wang*[2,†], *Xuan-Jie Chen*[1], *Zhao-Yang Xia*[1], *Wen-Yi Kang*[1], *Wen-Hui Zhou*[2,*]

[1] Institute of Chinese Materia Medica, Henan University, Kaifeng 475004, China.
[2] The Key Laboratory for Special Functional Materials of MOE, Henan University, Kaifeng 475004, China.
[*]E-mail: zhouwh@henu.edu.cn, zhouwh@foxmail.com
† These two authors contributed equally to this work.

Received: 29 October 2016 / *Accepted:* 8 December 2016 / *Published:* 30 December 2016

A simple and available strategy was developed for one step electrodeposition of graphene-Au (G-Au) nanocomposites which could be used for highly sensitive electrochemical detection of salbutamol. G-Au nanocomposites were simultaneously deposited on glassy carbon electrode by one step electrodeposition method. This resulting G-Au nanocomposites modified electrode was characterized by different methods. Compared to graphene or Au nanoparticles (AuNPs) modified electrodes, this G-Au nanocomposites modified electrode dramatically promote the electrooxidation of salbutamol on electrode surface and significantly enhance the differential pulse voltammetry (DPV) current response towards salbutamol. In addition, this one step electrodeposition method improved the stability of the modified G-Au nanocomposites layer. This constructed G-Au nanocomposites based electrochemical sensor exhibits high sensitivity and good selectivity for salbutamol, which may introduce by the synergistic effect of G-Au nanocomposites. Under optimized conditions, the constructed salbutamol sensor showed two linear dynamic ranges (0.05-10 μM and 20- 200 μM). The linear range and sensitivity of the proposed salbutamol electrochemical sensors are better than other reported values. Moreover, this electrochemical sensor has been successfully applied to the determination of salbutamol in salbutamol sulfate injections with satisfied recoveries (95.4 % to 103.1 %) and precision (1.5 % to 4.6 % of RSD).

Keywords: Salbutamol; Graphene-Au nanocomposites; One step electrodeposition; Electrochemical sensor.

1. INTRODUCTION

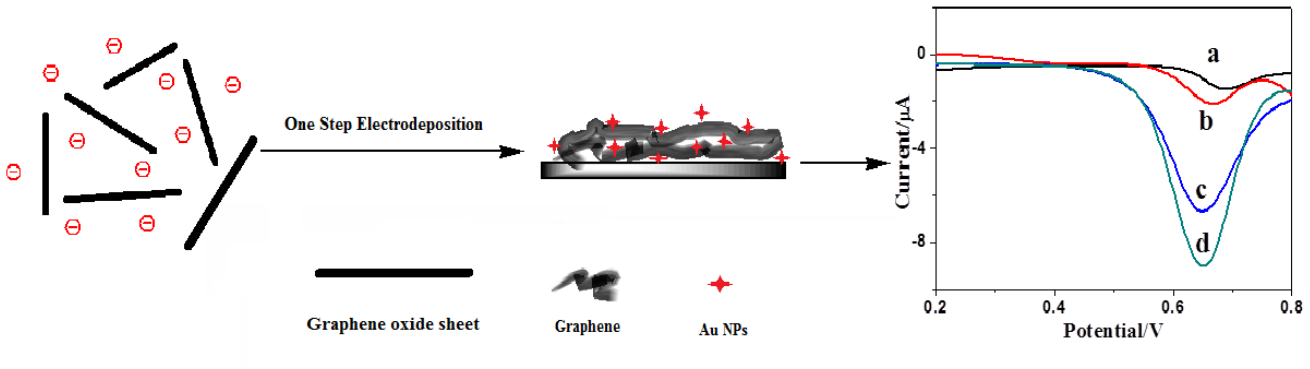
Salbutamol belongs to general class of β_2-adrenergic agonists which was originally developed for the treatment of bronchial asthma, chronic obstructive pulmonary disease and other allergic

diseases associated with respiratory pathway [1]. Moreover, salbutamol has been frequently reported to be abused as a "lean meat agent", since it could improve growth rate and reduce carcass fat when fed to animals [2]. It is worth noting that salbutamol accumulates easily in animal organs and can enter the human body through the food chain. Though salbutamol is generally well tolerated, long time and high dose intake salbutamol may still pose serious dangers to human with symptoms of muscular tremor, cardiac palpitation, nervousness, headache, muscular pain, dizziness, nausea, vomiting, fever and chills. Therefore, the use of salbutamol in animal feed has been banned in most countries [3]. Especially, all β-agonists are banned as feed additives for growth promotion in animals in both European Union and China [4,5]. Therefore, a reliable, rapid and selective determination method for salbutamol is extremely important and highly demanded.

Up to now, different methods have been reported for the detection of salbutamol including immunosensor [6], capillary electrophoresis (CE) [7-8], atomic absorption spectroscopy (AAS) [9], electrochemical method [1,10], chemiluminescence [11], gas chromatography-mass spectrometry (GC-MS) [12-13], high performance liquid chromatography (HPLC) [14-15] and liquid chromatography mass spectrometry (LC-MS) [16] etc. Though these methods are proven widely accepted and have shown creditable reliabilities, most of these techniques are complex as many steps are involved for sample preparation and skilled expertise are also required to get significant results. In comparison, electrochemical method offers the advantages of great speed, simplicity, low cost and short analysis time. So, electrochemical method has attracted more and more researcher's attention in chemicals sensors and biosensors [17]. In most cases, bare gold and glassy carbon electrode only give weak redox peaks, so they cannot resolve conventional electrochemical problems. Electrochemical methods based on Nafion and carbon nanotube modified electrodes showed that modified electrodes are superior to unmodified electrodes in terms of sensitivity and reliability [18-19]. Nowadays, graphene has recently attracted tremendous interest because of its unique thermal, mechanical and electrical properties [20-21]. One of the promising applications of graphene is electrochemical sensing [21-24]. Because every atom in the graphene sheet is a surface atom, molecular interaction and thus electron transport through graphene can be highly sensitive to adsorbed molecules [25]. As another star material, Au nanoparticles also have attracted much interest in catalysis and sensors because they can provide excellent catalytic activity and a hospitable environmental for biomolecules or chemical pollutions [26-28]. Recently, graphene-based nanocomposites have shown potential applications in the area of chemical sensors because they can improve the performance of graphene-based sensors [24,28-31]. Graphene-Au nanocomposites have been attempted to modify the electrode to design highly sensitive, selective and stable electrochemical sensors [28,30,31]. For sensing applications, the method for deposition of active materials on electrodes is most crucial. Until now, the traditional method to obtain graphene-based modifier films on electrodes is drop-casting, which shows bad stability of modifier layer. Though nafion could be used to improve the stability of modifier layer, the poor electrical conductivity of nafion is also a serious issue [32].

In this work, G-Au nanocomposites were simultaneously deposited on glassy carbon electrode by one step electrodeposition method. Then, G-Au nanocomposites modified glassy carbon electrode was used to develop an electrochemical senor for highly sensitive electrochemical detection of salbutamol. This G-Au nanocomposites modified electrode significantly enhanced the DPV current

response and selectivity towards salbutamol, which may be introduced by the synergetic effect of graphene and Au nanoparticles. The stability of the modified nanocomposites layer is also improved. To the best of our knowledge, this work represents the first attempt using G-Au nanocomposites by one step electrodeposition method for electrochemical detection of salbutamol.



Scheme 1. Schematic illustration for one step electrodeposition of graphene-Au nanocomposites and use for salbutamol detection.

2. EXPERIMENTAL

2.1. Apparatus and Materials

Electrochemical measurements like cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed by a CHI660E electrochemical workstation (Chen Hua Instruments Co., Shanghai, China). Flake graphite, salbutamol [IUPAC name: (*RS*)-4-[2-(*tert*-Butylamino)-1-hydroxyethyl]-2-(hydroxymethyl)phenol], epinephrine were purchased form Alfa Aesar. Unless stated otherwise, all other chemicals were of analytical reagent grade and were used as received. All water used was obtained from a Millipore Milli-Q purification system. Salbutamol sulfate injections were obtained from local commercial sources.

2.2. Preparation of G-Au nanocomposites modified electrode

Graphite oxide was synthesized from natural flake graphite by the Hummers method [33]. The prepared graphite oxide powder was exfoliated in a pH 6.5 phosphate buffered saline (PBS) solution by ultrasonication to form a 1.0 mg/mL graphene oxide (GO) colloidal dispersion. $HAuCl_4$ was drop-wise added to GO colloidal dispersion under vigorous ultrasonication, obtaining a 1.0 mg/mL GO and 100 μmol/L $HAuCL_4$ colloidal dispersion. Then, ultrasonication was continued for 2h. Prior to modification, the glassy carbon electrode surface was polished to a mirror-like smoothness with an aqueous slurry of 0.3 μm and 0.05 μm alumina powder on a damp silk cloth, and then cleaned with ethanol and water. The electrodeposition of G-Au nanocomposites was performed by using cyclic

voltammetry method. A conventional three-electrode cell were used at room temperature with glassy carbon electrode (GCE) (surface area = 0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrodes as reference electrode, and platinum wire as counter electrode. The cyclic voltammetry was conducted for electrochemical deposition on GCE surface in the potential range from -1.4 to 0.6 V at a scan rate of 50 mV/s for 25 cycles. After the electrodeposition, the GCE electrode with G-Au nanocomposites deposit was washed with distilled water to remove electrolyte adhered.

In order to select optimal electrode modification method, we also prepared different graphene films modified GCE electrodes by drop-casting and electrodeposition method, respectively. For drop-casting method, the GCE electrode surface was coated with 7 μL of 1.0 mg/mL GO suspension and dried under infrared lamp for 10 min to obtain graphene modified GCE. For electrodeposition method, GCE was placed in GO colloidal dispersion and then CV was performed for electrodeposition graphene in the potential range from -1.4 to 0.6 V at a scan rate of 50 mV/s for 25 cycles.

3. RESULTS AND DISCUSSION

3.1. Select of electrode modification methods and materials

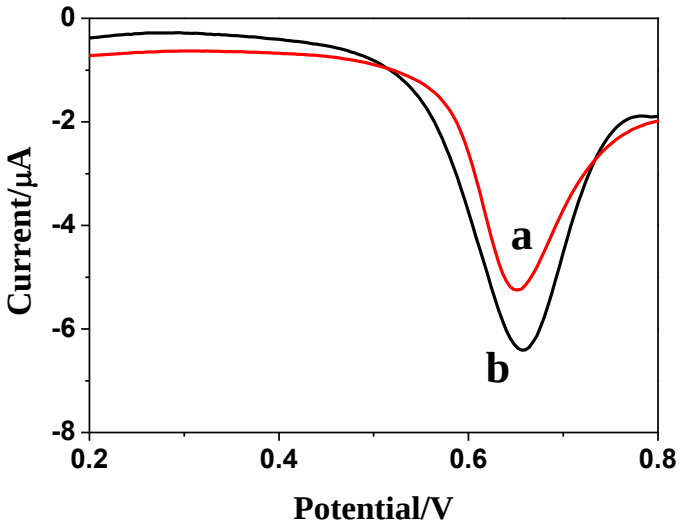


Figure 1. DPV responses of graphene modified GCEs from different methods immersed in 50 μM salbutamol solution. (a, drop-casting method; b, electrodeposition method)

For sensing applications, the deposition methods of graphene significantly affect the performance of graphene-based electrochemical sensor. So far, graphene films on electrodes usually were obtained by drop-casting method from graphene oxide solution, which leads to stability issue. In order to select optimal electrode modification method, different graphene films modified GCE electrodes were integrated into electrochemical sensors for salbutamol and compared. The performance of different graphene modified GCEs was invested by DPV method in 50 μM salbutamol solution. As shown in Figure 1, the DPV oxidation current of graphene modified GCE by electrodeposition method

towards salbutamol is higher than that of modified GCE by drop-casting method. We recognize that the status of graphene deposited on GCEs by different methods can not completely consistent. However, this result still gives us valuable information to construct electrochemical sensors based on electrodeposited graphene.

The stability of the graphene modified GCEs is an important concern for its further application. So, freshly prepared graphene modified GCEs by different methods were continuous soaked in same PBS solution for different times (2h, 4h and 6h) and then performed for the DPV measurement in 50 μM salbutamol solution. As shown in Figure 2, there was no visible deterioration after continuous soaking for 6 hours for graphene modified GCE prepared by electrodeposition method. Meanwhile, graphene modified GCE prepared by drop-casting method almost lost all its response towards salbutamol. So, electrodeposition method is a better choice than drop-casting method for graphene deposition and modification. In this work, unless stated otherwise, the deposition and modification of graphene on GCE was achieved by electrodeposition method.

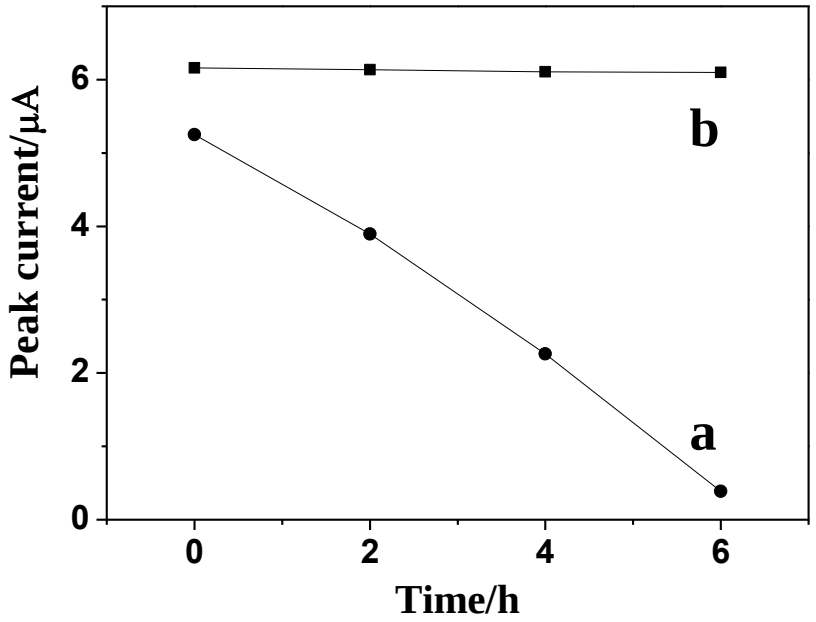


Figure 2. DPV peak currents of graphene modified GCEs prepared by different methods after continuous soaking in PBS solution for different time towards 50 μM salbutamol. (a, drop-casting method; b, electrodeposition method)

As is known to all, nanometer materials modification can enhance the electronic transmission ability and catalytic activity of the resulted electrode. In order to obtain high performance electrode, different materials (AuNPs, graphene, G-Au nanocomposites) were deposited on GCEs. The cyclic voltammograms for AuNPs (a), graphene (b) and G-Au nanocomposites (c) deposition on GCEs were shown in Figure S1. Cathodic current peak at about -0.2 V ($[AuCl_4]^-$) and -0.8 V ($[AuCl_2]^-$) confirm the electrochemical reduction of gold nanoparticles on GCEs [34]. While, cathodic current peak at about -1.2 V confirm the electrochemical reduction of GO to form graphene on GCEs [35]. The optical

photograph of bare GCE (a), AuNPs (b) and G-Au nanocomposites (c) modified GCEs were shown in Figure S2. The bare GCE has a silvery work area. After electrodeposition large amount of gold, the modified GCE showed golden lustre. While, G-Au nanocomposites modified GCE shows dark gray. G-Au nanocomposites were further also confirmed by TEM (Figure S3) and SEM (Figure S4). We can see that AuNPs were randomly distributed on graphene sheets. Raman spectrum of electrodeposited graphene and G-Au nanocomposites were shown in Figure S5. Raman spectrum for graphene sheets exhibit the regular two peaks, corresponding to the D band line (~1330 cm^{-1}) and the G band (~1585 cm^{-1}). Raman Spectra for G-Au nanocomposites showing the presence of AuNPs on graphene enhances the intensity of D and G bands, suggesting the formation of G-Au nanocomposites [36].

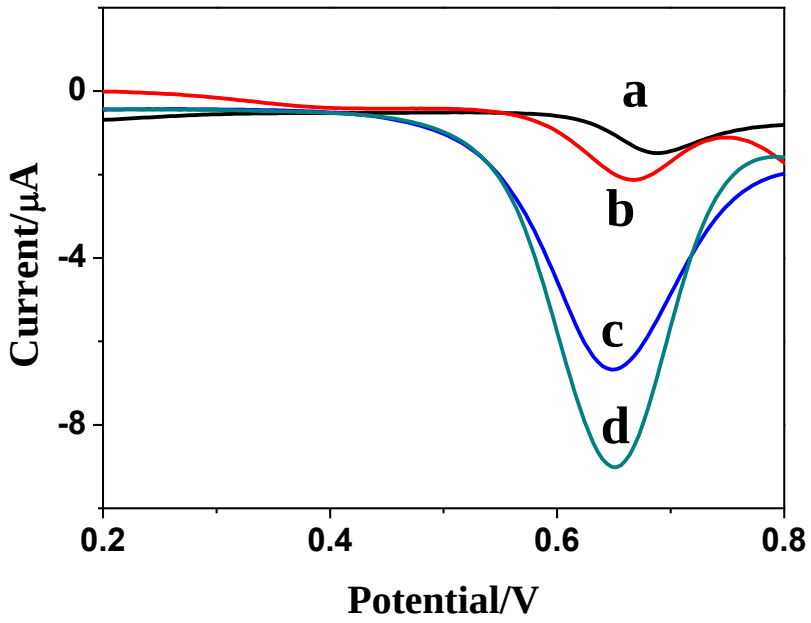


Figure 3. DPV responses of bare (a), AuNPs (b), graphene (c) and G-Au nanocomposites (d) modified GCEs immersed in 50 μM salbutamol solution.

The electrochemical response of different materials modified GCEs toward salbutamol was studied by using DPV method (shown in Figure 3). It's apparent that all the modified GCEs displayed higher current response than that of bare GCE. The oxidation peaks of salbutamol at bare GCE, AuNPs, graphene and G-Au nanocomposites modified GCEs were observed at 0.69 V, 0.67 V, 0.65V and 0.64 V, respectively. The anodic peaks shifted to lower potential after modification, which may be caused by the high catalytic activity of the modified materials. The peak currents of salbutamol at bare GCE, AuNPs, graphene and G-Au nanocomposites modified GCEs are 0.959, 1.725, 6.162 and 8.494 μA, respectively. The graphene modified GCE possess much higher peak current than that of AuNPs modified GCE, which may be caused by higher specific surface area and catalytic activity of graphene than AuNPs. Obviously, the G-Au nanocomposites modified GCE displayed the highest current response among all modified GCEs. Interestingly, the peak current of salbutamol at G-Au nanocomposites modified GCE is higher than the sum of the peak currents at graphene and AuNPs

modified GCEs. This phenomenon may be explained by the synergistic catalysis effect of graphene and AuNPs on the surface of GCE. Therefore, G-Au nanocomposites were selected as the modifier layer to fabricate electrochemical sensor for highly sensitive detection of salbutamol.

3.2. Optimization of experimental conditions

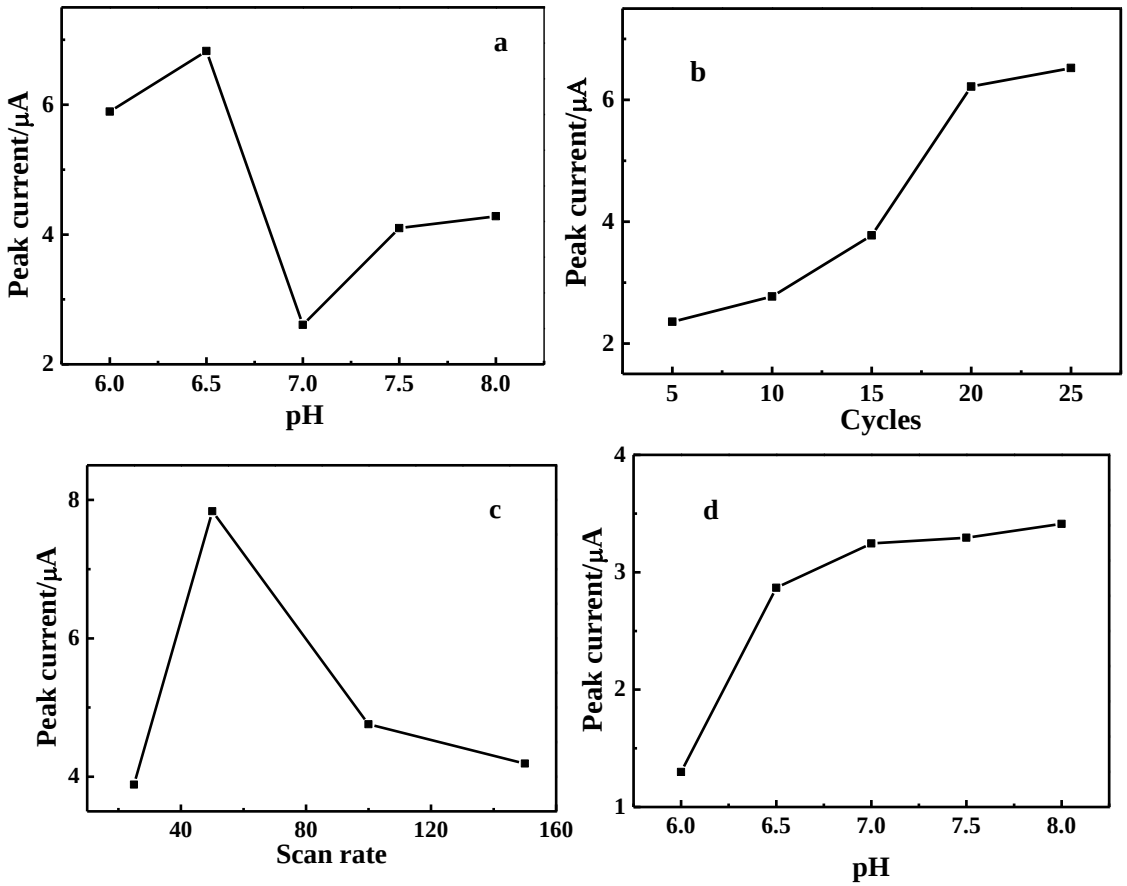


Figure 4. Effects of electrodeposition solution pH values (a), CV cycles of electrodeposition (b), CV scan rates of electrodeposition (c) and supporting electrolyte solution pH values (d) on DPV peak current values. (The concentration of salbutamol solution is 50 μM)

In order to obtain an optimal G-Au nanocomposites layer, thus enhancing sensitivity and selectivity of the modified electrochemical sensor, optimization experiments should be performed to optimize the performance of the proposed sensor. In this work, different influencing factors including pH value of the electrodeposition solution, electrodeposition cycles and scan rates were detailed investigated. The dependence of pH on the current responses was investigated in pH values of electrodeposition solution between 6.0 and 8.0 and shown in Figure 4a. It was obvious that the current responses increased with the increase of pH at the beginning (acid media). The lowest current response was obtained at pH 7.0. In alkaline conditions, the current responses also increased with the increase of pH. Meanwhile, the current responses of the modified electrode electrodeposited in alkaline conditions are all lower than that of electrodeposited in acid conditions. The highest current response was

obtained at pH 6.5. This phenomenon may be explained that the optimal deposition condition of graphene is quite different from that of Au nanoparticles. Therefore, pH 6.5 PBS solution was used in the present work. The thickness of the G-Au nanocomposites layer would increase with the increase of the scan cycles of electrodeposition, which should significantly affect the sensitivity of the electrochemical sensor. The effect of scan cycles with different numbers on the performance of G-Au modified GCE was tested by using the DPV measurements. As shown Figure 4b, the current responses increased with the increase scan cycles up to 25 cycles. At high scan cycles, the increase of scan cycles did not increase the current responses notably. Higher scan cycles lead to more extensive electrodeposition of G-Au nanocomposites, which would cause the formation of a thicker modifier layer with less accessible sensing sites. Higher scan cycles also lead to higher electrodeposition time. Therefore, 25 cycles was used in the present work. The electrodeposition scan rate also has a significant influence on the peak current of salbutamol on G-Au nanocomposites modified GCE. As shown in Figure 4c, G-Au nanocomposites modified GCE prepared at a scan rate of 50 mV/s displayed the best current response towards salbutamol. At a slower scan rate, quite compact G-Au nanocomposites layer could be formed. Compact G-Au nanocomposites could decrease the number of accessible sensing sites, leading to relative low sensitivity towards salbutamol. However, a faster scan rate may form a loose and thick G-Au nanocomposites layer, which also leads to a low recognition capacity towards salbutamol. Therefore, the optimum scan rate was chosen to be 50 mV/s. The performance of one electrochemical sensor is also influenced by the supporting electrolyte solution used for the test. G-Au nanocomposites modified GCE was tested by DPV method in PBS solution with the pH value range from 6.0 to 8.0. It was obvious that the current responses increased with the increase of pH of PBS solution in Figure 4d. The lowest current response was obtained at pH 6.0. However, the current responses do not changed obviously at neutral and alkaline conditions. Considering the G-Au nanocomposites modified GCE was obtained at pH 6.5, pH 7.0 PBS solution was used in the present work.

3.3. Determination of salbutamol

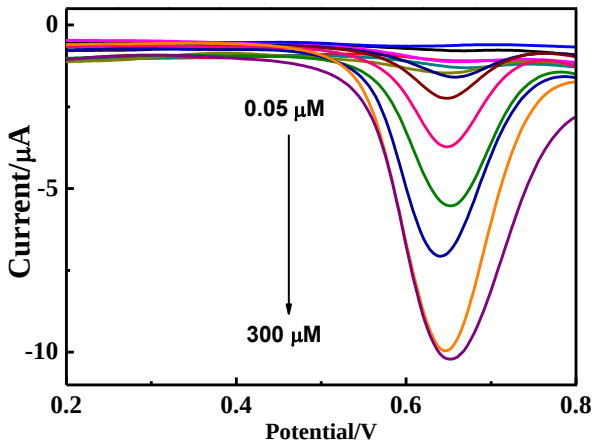


Figure 5. DPV responses of G-Au nanocomposites modified GCE to different salbutamol solutions. Salbutamol concentration range covered 0.05 to 300 μM.

Under optimized conditions, the DPV responses of salbutamol solutions in the concentration range of 0.05 to 200 μM were investigated. As shown in Figure 5, the DPV responses of G-Au nanocomposites modified GCE increased as the concentration of salbutamol increased in the range from 0.05 to 200 μM. Obviously, the peak current is not linear to salbutamol concentration over the whole range of 0.05 to 200 μM. Non-linearity of the oxidation peak current vs. salbutamol concentration dependence in the whole concentration range maybe mainly due to the gradual saturation of accessible active sites in the G-Au nanocomposites.

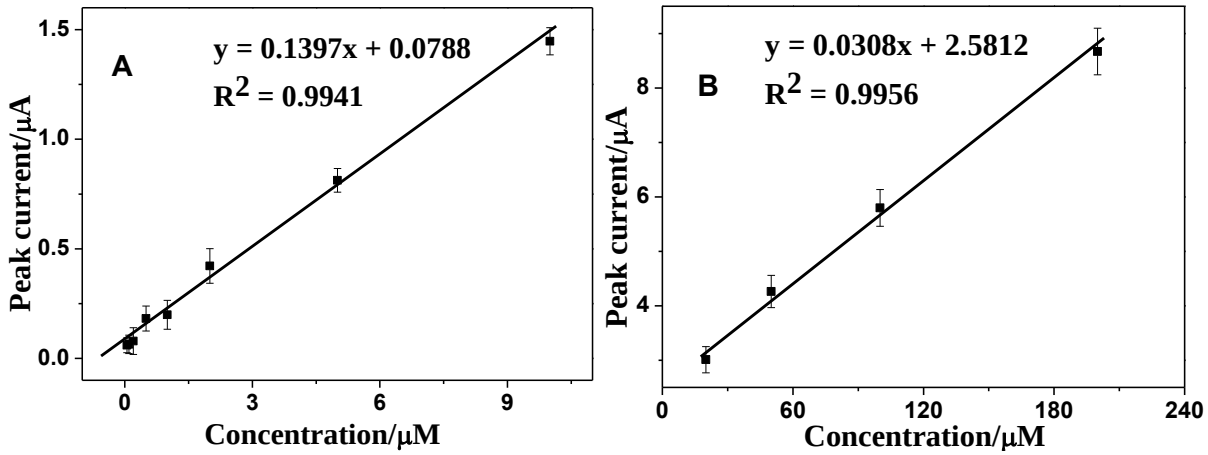


Figure 6. Calibration plots of DPV responses via the concentration of salbutamol. (A, 0.05 μM to 10 μM; B, 20 μM to 200 μM)

The oxidation peak current values were extracted from the DPV responses of G-Au nanocomposites modified GCE to different salbutamol solutions and shown in Figure 6. The peak currents of salbutamol showed two linear dynamic ranges from 0.05 μM to 10 μM with regression equation of y=0.1397x+0.0788 (R^2=0.994, n=3) and 20 μM to 200 μM with regression equation of y=0.0308x+2.5812 (R^2=0.9956, n=3). The difference in slopes of calibration curves may be ascribed to the difference about specific surface area, electronic transmission ability and catalytic activity of graphene and Au nanoparticles. Due to higher specific surface area, electronic transmission ability and catalytic activity of graphene on GCE surface, relatively higher sensitivity can be expected. At low concentration, peak current of salbutamol is preferentially produced by graphene. So, it is comprehensible that the slope of the first calibration curve is relatively high. While at high concentration, peak current of salbutamol can also be produced by Au nanoparticles. Due to the decrease of specific surface area, electronic transmission ability and catalytic activity of Au nanoparticles, sensitivity towards salbutamol dramatically decreased and the slope of the calibration decreased remarkably. Moreover, a comparison of analytical parameters of the proposed G-Au nanocomposites modified GCE with other similar salbutamol electrochemical sensors has been summarized and given in Table 1 [1,3,10,38-47]. From Table 1, it was found that the proposed method shows relatively higher sensitivity or wider linear range than other reported salbutamol electrochemical sensors. Though carbon paste electrodes [45-46] and monoclonal antibodies based

electrochemical sensors show relatively higher sensitivity than our proposed method, their repeatability and/or stability issues can not be ignored, which may hinder their use in salbutamol detection.

Table 1. Comparison table for salbutamol with various modified electrodes.

Modified electrode	Modification method	Linear range (μM)	Reference
MWNTs-Au/GCE	drop-casting	0.09-7	[1]
Poly taurine/ZrO_2/GCE	electrodeposition	5-220	[3]
G/GCE	drop-casting	0.4-30	[10]
PASA/GCE	electrodeposition	2-100	[37]
CNTs/GCE	drop-casting	0.1-33	[38]
SWNT/EPPGE	drop-casting	0.05-2.5	[39]
MnO_2/RGO@NF	Spraying and electrodeposition	0.042-1.463	[40]
NsCuHcFe-CNT/GCE	drop-casting	5-25	[41]
P-Gr-P/GCE	drop-casting	0.03-180	[42]
GP-PEDOT:PSS/SPCE	screen print	5-550	[43]
MWNT/GCE	drop-casting	0.8-10	[44]
Fe_2TiO_5/CPE	mixing	0.0002-0.025	[45]
MIP/CPE	mixing	0.001-0.055	[46]
AgPd/anti-SAL/GCE	drop-casting	0.0004-0.4	[47]
G-Au/GCE	electrodeposition	0.05-200	This work

3.4. Selectivity, repeatability and stability of the G-Au nanocomposites modified GCE sensor

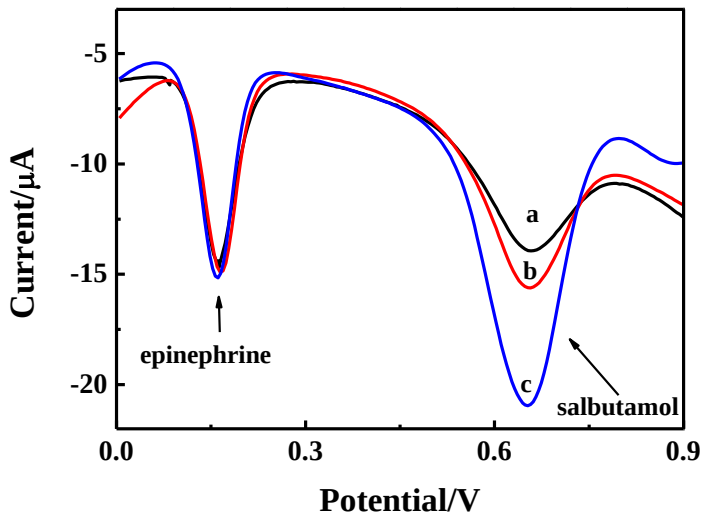


Figure 7. The selectivity of the G-Au nanocomposites modified GCE to different salbutamol and epinephrine mixtures. (the concentration of epinephrine is 100 μM; the concentrations of salbutamol are 50, 100 and 200 μM.)

To confirm the selectivity of the proposed G-Au nanocomposites modified GCE sensor, we selected epinephrine as the interference of salbutamol (They are all belongs to β-agonists). The concentration of the tested interference was fixed at 100 μM, while the concentration of salbutamol was ranged from 50 μM to 200 μM. Figure 7 shows the DPV of the mixture solution of salbutamol and epinephrine. Salbutamol shows oxidation peak at 0.64 V, while epinephrine shows oxidation peak at 0.18 V. The separation of the peak potential for salbutamol and epinephrine is 480 mV. The large separation of the peak potential allows selective determination of salbutamol in the presence of epinephrine or simultaneous detection of them in their mixture. This result suggested that the proposed G-Au nanocomposites modified GCE sensor possessed excellent selectivity towards salbutamol.

The repeatability of the proposed G-Au nanocomposites modified GCE sensor was evaluated by using the same electrode for 10 repeated analyzes of 50 μM salbutamol solutions. The current response showed a relative standard deviation of 3.1 %, indicating very good repeatability. The stability of the G-Au nanocomposites modified GCE sensor was investigated by different ways. When the G-Au nanocomposites modified GCE sensor was exposed to surrounding atmosphere for 20 days at room temperature, the electrochemical sensor also reserved 90.9 % of its original response to 50 μM salbutamol. The stability of the G-Au nanocomposites modified GCE is also evaluated within 2 weeks by recording the DPV current responses once each day. The DPV current of salbutamol on G-Au nanocomposites modified GCE also retained 90.02 % of its initial current after 2 weeks. These results demonstrated that the prepared G-Au nanocomposites modified GCE sensor had excellent repeatability and stability.

3.5. Detection of salbutamol in salbutamol injections by the proposed G-Au nanocomposites modified GCE electrochemical sensor

In order to assess the suitability of the developed G-Au nanocomposites modified GCE electrochemical sensor for the determination of salbutamol in complex matrix, salbutamol sulfate injections were analyzed using the developed sensor.

Table 2. Detection of salbutamol in salbutamol sulfate injections (n=3)

Contain (μM)	Added (μM)	Detected (μM)	Recovery (%)	R.S.D (%)
5	1	5.91	98.5%	1.50 %
5	3	7.85	98.1%	1.90 %
50	0	50.75	101.5%	1.55%
50	10	57.24	95.4%	4.61%
50	20	71.47	102.1%	2.15%
50	50	103.10	103.1%	3.10%

The labeled value for salbutamol is about 0.24 mg/mL (1 mM). The original salbutamol sulfate injection was diluted by 20 and 200 times with PBS solution (pH=7) to form two different salbutamol sulfate solutions with known concentrations (5 μM and 50 μM). We spiked these two different salbutamol sulfate solutions with known concentrations of salbutamol sulfate. At last, the

concentrations of salbutamol were determined by the proposed G-Au nanocomposites modified GCE electrochemical sensor, and the results were listed in Table 2. As shown in Table 2, the recoveries ranged from 95.4 % to 103.1 % and relative standard deviation (RSD) ranged from 1.5 % to 4.6 %, suggesting an acceptable detection result for salbutamol analysis in real samples.

4. CONCLUSIONS

In this work, we presented a simple and available strategy to fabricated G-Au nanocomposites modified GCE sensor by one step electrodeposition for highly sensitive detection of salbutamol. Compared traditional drop-casting method, the proposed electrodeposition method could solve the stability issue of modifier layer on GCEs. The prepared G-Au nanocomposites modified GCE electrochemical sensor displayed excellent stability, sensitivity, selectivity and repeatability towards salbutamol. Furthermore, the proposed G-Au nanocomposites modified GCE was applied for the determination of salbutamol in commercially available salbutamol sulfate solutions. The satisfied results indicated that G-Au nanocomposites will be a promising electrode modification material for the measurement of salbutamol in other complex matrix as well as in pharmaceutical and food.

SUPPORTING MATERIAL:

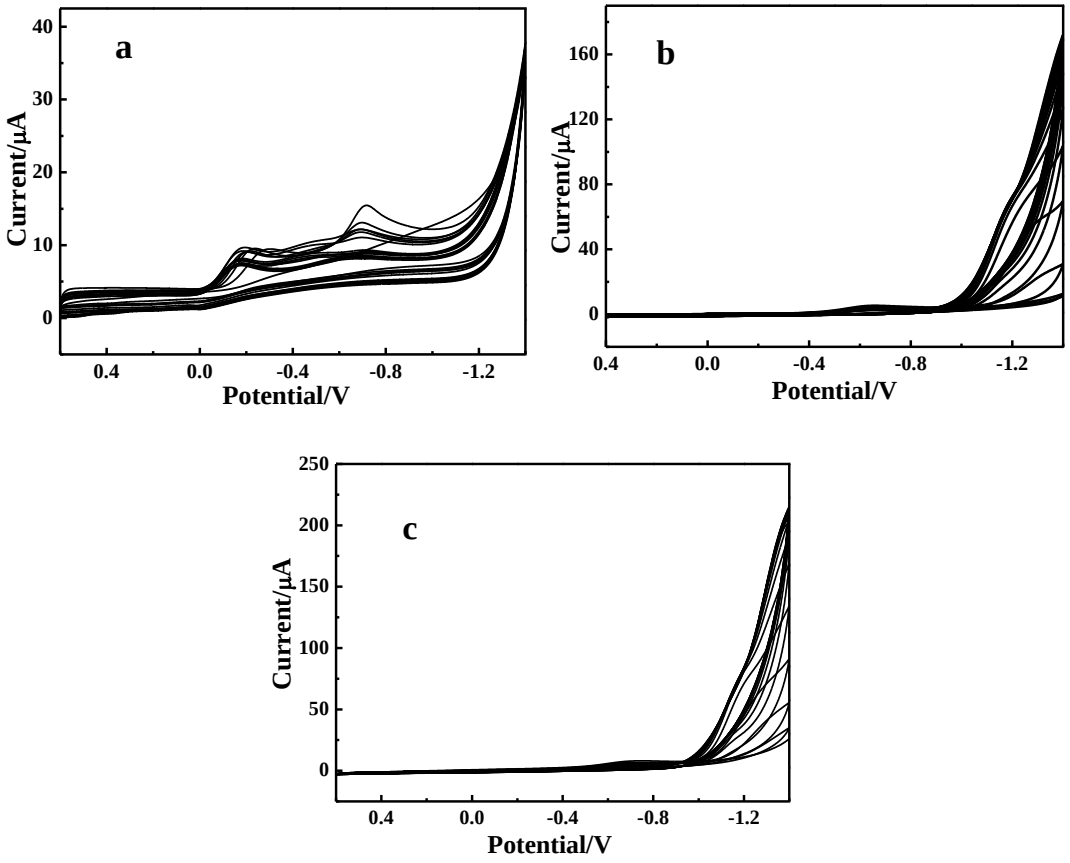


Figure S1. Cyclic voltammograms for AuNPs (a), graphene (b) and G-Au nanocomposites (c) deposition on GCEs.

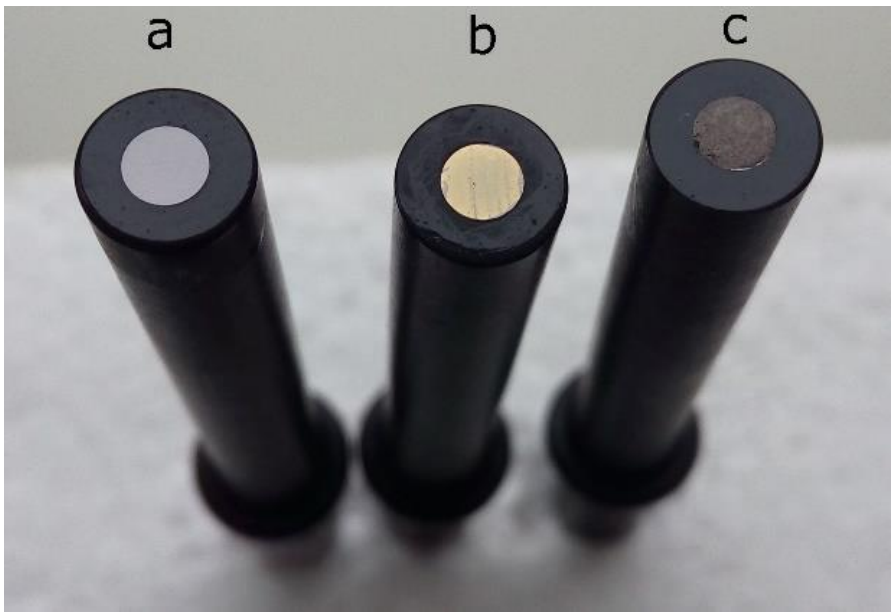


Figure S2. Optical photograph of bare GCE (a), AuNPs (b) and G-Au nanocomposites (c) modified GCEs

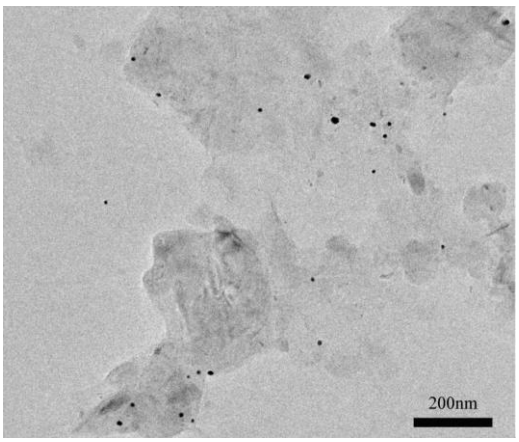


Figure S3. TEM image of G-Au nanocomposites.

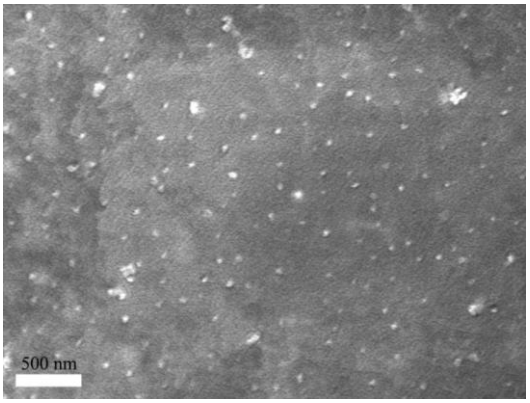


Figure S4. SEM image of G-Au nanocomposites.

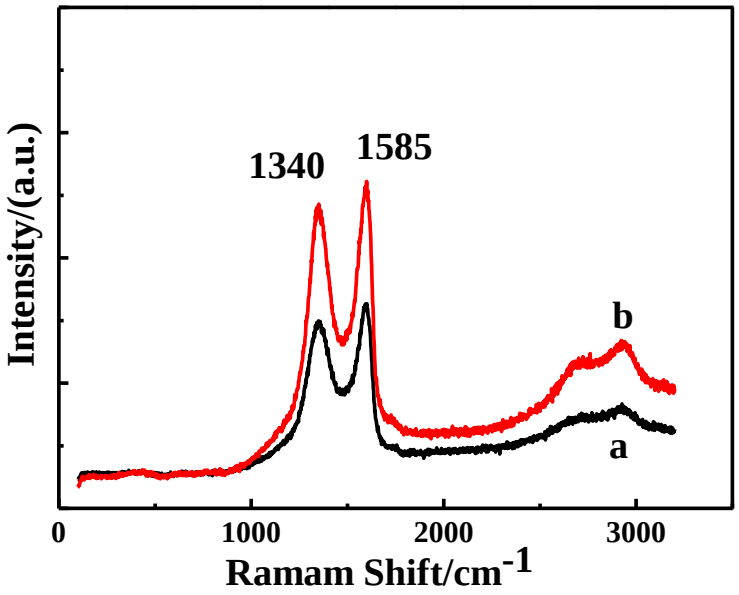


Figure S5. Raman spectrum of electrodeposited graphene (a) and G-Au nanocomposites (b) .

ACKNOWLEDGEMENT
This study was funded by the Joint Talent Cultivation Funds of NSFC-HN (U1204214), the National Natural Science Foundation of China (21203053), the Innovation Research Team of Science and Technology in Henan province (16IRTSTHN019), the Young Key Teacher Foundation of Henan Province's Universities (2015GGJS-022), the Key Scientific Research Project of Henan Province's Universities (16A360017), the Science and Technology Development Project of Kaifeng (1503006) and the Scientific Research Foundation of Henan University (B2010079 and B2011037).

References

1. Y. F. Li, Z. Ye, P. L. Luo, Y. Li and B. X. Ye, *Anal. Methods*, 6 (2014) 1928.
2. C. Crescenzi, S. Bayoudh, P. A. G. Cormack, T. Klein and K. Ensing, *Anal. Chem.*, 73 (2001) 2171.
3. M. Rajkumar, Y. S. Li and S. M. Chen, *Colloid. Surface. B*, 110 (2013) 242.
4. European Communities, *Off. J. Eur. Communities*, 125 (1996) 3.
5. Ministry of Agriculture of the People's Republic of China, No. 235 Bulletin of the Ministry of Agriculture of the People's Republic of China (2003).
6. Y. P. Chen and M. X. Xie, *RSC Adv.*, 5 (2015) 95401.
7. A. Esquisabel, R. M. Herandez, A. R. Gascon, M. Igartua, B. Calvo and J. L. Pedraz, *J. Pharmaceut. Biomed.*, 16 (1997) 357.
8. S. Sirichai and P. Khanatharana, *Talanta*, 76 (2008) 1194.
9. R. M. Nejem, M. M. Issa, M. H. AL-Kholy, A. A. Saleh, A. A. Shanab, R. I. S. Staden and H. Y. Aboul-Enein, *RSC Adv.*, 5 (2015) 57164.
10. Y. L. Zhou, H. Q. Zhang, Z. Chang, B. X. Ye and M. T. Xu, *Int. J. Electrochem. Sci.*, 11 (2016) 5154.
11. C. A. Lindino and L. O. S. Bulhoes, *Talanta*, 72 (2007) 1746.
12. M. I. Saleh, Y. M. Koh, S. C. Tan and A. L. Aishah, *Analyst*, 125 (2000) 1569.
13. B. Bocca, M. Fiori, C. Cartoni and G. Brambilla, *J. AOAC Int.*, 86 (2003) 8.
14. F. G. Xu, Z. J. Zhang, Y. Tian, H. Y. Jiao, J. B. Liang and G. Q. Gong, *J. Pharmaceut. Biomed.*, 37

(2005) 187.
15. A. Aresta, C.D. Calvano, F. Palmisano and C.G. Zambonin, *J. Pharmaceut. Biomed.*, 47 (2008) 641.
16. J. Blanca, P. Munoz, M. Morgado, N. Méndez, A. Aranda, T. Reuvers and H. Hooghuis, *Anal. Chim. Acta.*, 529 (2005) 199.
17. D. W. Kimmel, G. LeBlanc, M. E. Meschievitz and D. E. Cliffel, *Anal. Chem.*, 84 (2012) 685.
18. D. Boyd, J. R. B. Rodriguez, A. J. M. Ordieres, P. T. Blanco and M. R. Smyth, *Analyst*, 119 (1994) 1979.
19. C. Karuwan, A. Wisitsoraat, T. Maturos, D. Phokharatkul, A. Sappat, K. Jaruwongrungsee, T. Lomas and A. Tuantranont, *Talanta*, 79 (2009) 995.
20. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 306 (2004) 666.
21. Y. X. Liu, X. C. Dong and P. Chen, *Chem. Soc. Rev.*, 41 (2012) 2283.
22. C. S. Shan, H. F. Yang, J. F. Song, D. X. Han, A. Ivaska and L. Niu, Anal. Chem., 81 (2009) 2378.
23. M. Zhou, Y. M. Zhai and S. J. Dong, *Anal. Chem.*, 81 (2009) 5603.
24. H. Zhu, *Int. J. Electrochem. Sci.*, 11 (2016) 4007.
25. A. Rochefort and J. D. Wuest, *Langmuir*, 25 (2009) 210.
26. L. X. Wang, J. Bai, X. J. Bo, X. L. Zhang and L. P. Guo, *Talanta*, 83 (2011) 1386.
27. X. H. Lu, P. F. Wang, X. G. Wang and Y. B. Guo, *Int. J. Electrochem. Sci.*, 11 (2016) 5279.
28. F. O. G. Olorundare, D. Nkosi and O. A Arotiba, *Int. J. Electrochem. Sci.*, 11 (2016) 7318.
29. J. Yang, S. Y. Deng, J. P. Lei, H. X. Ju and S. Gunasekaran, *Biosens. Bioelectron.*, 29 (2011) 159.
30. F. Cui and X. L. Zhang, *J. Electroanal. Chem.*, 669 (2012) 35.
31. Y. K. Ye, S. Ding, Y. W. Ye, H. C. Xu, X. D. Cao, S. Liu and H. J. Sun, *Microchim. Acta*, 182 (2015) 1783.
32. L. M. Lu, X. B. Zhang, G. L. Shen and R. Q. Yu, *Anal. Chim. Acta.*, 715 (2012) 99.
33. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 80 (1958) 1339.
34. T.H. Tsai, S. Thiagarajan and S.M. Chen, *J. Appl. Electrochem.*, 40 (2010) 493.
35. H. L. Guo, X. F. Wang, Q. Y. Qian, F. B. Wang and X. H. Xia, *ACS Nano*, 3 (2009) 2653.
36. K. Jasuja and V. Berry, *ACS Nano*, 3 (2009) 2358.
37. L. J. Li, L. B. Yu, H. Cheng, Q. F. Chen, F. M. Wu, T. Chen, X. Y. Zhu, H. X. Kong and J. L. Wu, *Anal. Lett.*, 40 (2007) 3290.
38. K. C. Lin, C. P. Hong and S. M. Chen, *Sens. Actuators B*, 177 (2013) 428.
39. R. N. Goyal, S. Bishnoi and B. Agrawal, *Int. J. Electrochem.*, 2011 (2011) 373498.
40. M. Y. Wang, W. Zhu, L. Ma, J. J. Ma, D. E. Zhang, Z. W. Tong and J. Chen, *Biosens. Bioelectron.*, 78 (2016) 259.
41. M. Latwal, P. Chandra, S. R. Ali, *J. Appl. Electrochem.*, 44 (2014) 1127.
42. X. F. Zhu, X. M. Duan, J. K. Xu, L. M. Lu, K. X. Zhang, H. K. Xing, Y. S. Gao, T. T. Yang and W. M. Wang, *New J. Chem.*, 40 (2016) 302.
43. C. Karuwan, C. Sriprachuabwong, A. Wisitsoraat, D. Phokharatkul, P. Sritongkham and A. Tuantranont, *Sens. Actuators B*, 161 (2012) 549.
44. Y. L. Wei, Q. Zhang, C. Shao, C. Li, L. P. Zhang and X. L. Li, *J. Anal. Chem.*, 65 (2010) 398.
45. A. M. Attaran, M. Javanbakht, F. Fathollahi and M. Enhessari, *Electroanal.*, 24(2012) 2013.
46. T. Alizadeh and L. A. Fard, *Anal. Chim. Acta.*, 769 (2013) 100.
47. H. Wang, Y. Zhang, H. Li, B. Du, H. M. Ma, D. Wu and Q. Wei, *Biosens. Bioelectron.*, 49 (2013) 14.