

A silver–palladium alloy nanoparticle-based electrochemical biosensor for simultaneous detection of ractopamine, clenbuterol and salbutamol



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ABSTRACT

A multiplexed electrochemical biosensor has been developed for fast and sensitive detection of ractopamine (RAC), salbutamol (SAL) and clenbuterol (CLB) based on reduced graphene oxide (rGO) and silver–palladium alloy nanoparticles (AgPd NPs). In this paper, rGO with high conductivity was used as an electrode material to immobilize artificial antigens and amplify electrochemical signal. AgPd NPs are used to label antibodies and generate a strong electrochemical signal in phosphate buffered saline (PBS) without any other substrates. Screen-printed carbon electrode (SPCE) and competition strategy were adopted to achieve simultaneous detection of RAC, SAL and CLB without cross-talk between adjacent electrodes. This method can simultaneously detect RAC, SAL and CLB ranging from 0.01 to 100 ng mL⁻¹ with detection limits of 1.52 pg mL⁻¹, 1.44 pg mL⁻¹ and 1.38 pg mL⁻¹, respectively. Satisfactory results are achieved in pork sample analysis. The designed strategy provides a promising potential in determination of other biological samples.

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1. Introduction

Ractopamine (RAC), clenbuterol (CLB) and salbutamol (SAL) are a group of β -adrenergic agonists with similar chemical structures and functions. They were originally developed to treat diseases, but side effect of reducing fat levels and increasing muscle protein anabolism were found when they were administered to animals. Recently illegal abuse of β -adrenergic agonists for growth promoting purposes has been widely reported (Shen et al., 2010; Lu et al., 2012). Thus, β -adrenergic agonists have been banned for feeding animals all over the world (Fan et al., 2012). However, driven by economic interests, illegal abuse of β -adrenergic agonists never stopped. The β -adrenergic agonists residue problems have become an increasingly public health concern. To ensure food safety, China and some European countries set strict regulations for these three β -adrenergic agonists as zero tolerances in animal foods (Zuo et al., 2010; Zhang et al., 2012a). Therefore, it is necessary to put forward a sensitive method for the detection of β -adrenergic agonists.

With the advantages of sensitivity, good selectivity and speediness, electrochemical biosensors have been an attractive subject and generally performed as individual test (Zhang et al., 2010; Li et al., 2007; Du et al., 2010). However, in many cases, it is necessary to perform high-throughput and parallel analysis. To meet these requirements, multiplexed electrochemical biosensors

have been developed for simultaneous determination. There are two approaches to achieving simultaneous determination. In the first way, distinguishable signal tags are used for simultaneous determination on single working electrode. For instance, Tang et al. developed a multiplexed electrochemical immunoassay enabling the simultaneous monitoring of α -fetoprotein (AFP) and carcinoembryonic antigen (CEA) using distinguishable signal tags (Tang et al., 2011b). An ultrasensitive aptamer-based multiplexed electrochemical biosensor was developed using coupling distinguishable signal tags (Tang et al., 2011a). In the other way, multiple working electrodes form a multi-electrode array for simultaneous determination. Screen-printed carbon electrode (SPCE) is one of the multi-electrode arrays. It has gained increasing interest as a bioanalytical method with the advantages of simple instrumentation, low cost and convenient miniaturization in recent years. For instance, Du et al. developed a sensor array based on enzyme-functionalized gold nanorod labels for the rapid simultaneous analysis of phosphorylated proteins (Du et al., 2011). Lai et al. reported an ultrasensitive multiplexed immunoassay for multiplexed analysis of human IgG and mouse IgG (Lai et al., 2011). Wu et al. reported a sensor array for multiplexed detection of carbohydrate antigens 153, 125, and 199 (CA 153, CA 125, CA 199) and CEA (Wu et al., 2008).

High sensitivity is always the pursuit of scientific research workers. Various methods have been used for signal amplification to improve the sensitivity. One of the most popular strategies is using enzyme-functionalized nanomaterial as a label to enhance the signal by loading a large amount of enzymes (Preechaworapun et al., 2008;

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Xu et al., 2011; Tang et al., 2010). But enzyme is easy to be inactivated which could affect the stability of the enzyme-based biosensor. Otherwise, electronic mediators such as thionine and ferrocene are also used to generate signal peaks. We have done a lot of research on the electronic mediator in our previous work (Cai et al., 2011; Wei et al., 2010; Li et al., 2011), but leaks of electronic media are difficult to avoid.

Recently, we developed a novel nonenzymatic biosensor for sensitive detection of Microcystin-LR (Wei et al., 2011). The biosensor is constructed using mesoporous PtRu alloy as a label for signal amplification. Eliminating the need for enzyme and electronic mediator, this biosensor strategy is greatly simplified.

Although the need for enzyme and electronic mediator is eliminated, mesoporous PtRu alloy-based biosensor still needs some substrates, because it cannot generate a electrochemical signal by itself. In this case, silver–palladium alloy nanoparticles (AgPd NPs) were found and synthesized. The electrochemical tests indicated that AgPd NPs can generate a strong electrochemical signal in phosphate buffered saline (PBS) without any other substrates. Moreover, the $-NH_2$ groups bind very strongly to Pd NPs (Mandal et al., 2004). And the $-NH_2$ groups are common functional groups of biomolecules, AgPd NPs are thus good electrochemical biomarkers which allows the immobilization of monoclonal antibodies.

Graphene is widespread concerned in electrochemical analysis with large surface area, rich functional groups and good conductivity, but the poor water-solubility of graphene affects its further application. The prepared reduced graphene oxide (rGO) not only exhibits high conductivity, but also can be well dispersed in many solvents. Moreover, the carboxyl-rich rGO can be combined with biomolecules.

Here we report a multiplexed electrochemical biosensor for the rapid simultaneous analysis of RAC, CLB and SAL using competition strategy. Artificial antigens of RAC, SAL and CLB (arti-RAC, arti-SAL and arti-CLB) are respectively immobilized onto three working electrodes by binding to rGO. RAC, SAL and CLB are separately pre-reacted with the corresponding antibody functionalized AgPd nanoparticles (Ab/AgPd NPs). The free Ab/AgPd NPs are finally captured by the corresponding artificial antigen to obtain the competitive electrochemical biosensors. This strategy eliminates the possible negative effects of enzyme and mediator, reduces the cost, realizes the simultaneous detection of the three kinds of β -adrenergic agonists and also ensures enough sensitivity. In addition, SPCE is cheap and easy to realize commercialization. To develop a biosensor for simultaneous detection of β -adrenergic agonists based on SPCE is expected to become a kind of new method in food detection technology.

2. Material and methods

2.1. Reagents and apparatus

The monoclonal antibodies of RAC, CLB, and SAL (anti-RAC, anti-CLB, and anti-SAL), artificial antigens of RAC, CLB, and SAL (arti-RAC, arti-CLB, and arti-SAL), RAC, CLB and SAL were purchased from Beijing Wanger Biotechnology Co., Ltd (Beijing, China). Bovine serum albumin (BSA, 96–99%) was purchased from Sigma (USA) and used as received. N-hydroxysuccinimide (NHS) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) were obtained from Sinopharm Chemical Reagent Limited Corporation (Shanghai, China). All other chemicals were of analytical reagents grade and used without further purification. PBS (0.067 mol L⁻¹, pH 7.0) was used as electrolyte for all electrochemistry measurements. Ultrapure water was used throughout the experiments.

Electrochemical measurements were performed on a CHI 1030B electrochemical workstation (Shanghai CH Instruments Co., China). Transmission electron microscopy (TEM) images were obtained from a JEM-2100 microscope (Japan). Scanning electron microscopy (SEM) images and Energy Dispersive Spectroscopy (EDS) images were obtained from a QUANTA FEG-250 (America). X-Ray Photoelectron Spectroscopy (XPS) images were obtained from an ESCALAB 250.

2.2. Synthesis of rGO

Graphene oxide (GO) was synthesized from natural graphite by a modified Hummers' method (Guo et al., 2010). The rGO were synthesized according to the literature with a slight modification (Ai et al., 2011). The synthesized GO was firstly dispersed in DMF (0.5 mg mL⁻¹) under ultrasonic treatment for 30 min, and then heated in an oil bath (153 °C) for 1 h. Then, the synthesized rGO solution in DMF was filtrated, followed by drying in vacuum and grinding.

2.3. Preparation of AgPd NPs

AgPd NPs were prepared as follows: 0.2 g AgNO₃ and 0.1 g K₂PdCl₆ were added into 10 mL of 5% TritonX-100 aqueous solution. After 30 min stirring at room temperature, the mixture was heated to 70 °C under magnetic stirring until the color of the mixture changed to dark brown. TritonX-100 serves as both a reducing agent and as a protective agent during the reaction. The AgPd NPs were obtained by centrifuging and washing, and then dried under high vacuum overnight. Silver nanoparticles (Ag NPs) and palladium nanoparticles (Pd NPs) are synthesized according to the same method.

2.4. Preparation of Ab/AgPd NPs

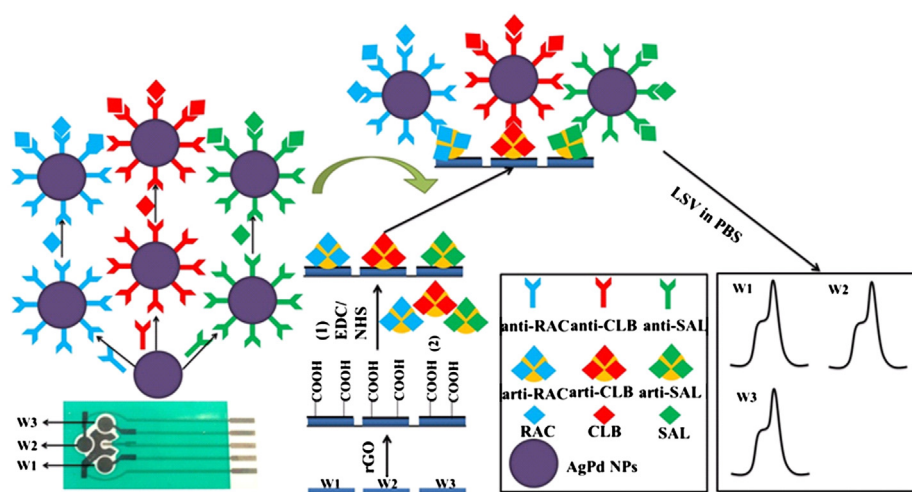
100 μ L of 5 μ g mL⁻¹ antibodies was added to 2 mL of 2 mg mL⁻¹ AgPd NPs solution. The mixture was stirred for 4 h and then centrifuged at 8000 rpm for 10 min to remove excess of antibodies. After discarding the supernatant, the taupe particles were carefully washed; next 1 mL of pH 7.0 PBS solution containing 1% BSA was added, and the mixture was stirred for 4 h, finally recentrifuged and redispersed in 1 mL of pH 7.0 PBS solution. The resulting anti-RAC/AgPd NPs, anti-CLB/AgPd NPs, and anti-SAL/AgPd NPs bioconjugates were prepared and stored at 4 °C.

2.5. Preparation of multiplexed electrochemical biosensor

The multiplexed electrochemical biosensor contains three graphite working electrodes and shares graphite auxiliary electrode and the same Ag reference electrode. The insulating layer printed around the working area constituted an electrochemical microcell. 5 μ L of 1 mg mL⁻¹ rGO was dropped on each working electrode and dried in air. Then 5 μ L of EDC/NHS solution was dropped on each working electrode to form a self-assembled layer. After thoroughly washing with water, the working electrodes were immediately incubated with 5 μ L of 1 μ g mL⁻¹ arti-RAC, arti-CLB, and arti-SAL for 2 h. To prevent nonspecific adsorption, the modified electrodes were incubated in 1% BSA for 1 h to block excess active groups. After washing with pH 7.0 PBS, the multiplexed electrochemical biosensor was stored at 4 °C until use.

2.6. Simultaneous immunoassay procedure

As shown in Scheme 1, a competitive immunoassay was used for simultaneous determination of RAC, CLB and SAL. First a series of standard solutions with different concentrations of RAC, CLB or



Scheme 1. Schematic representation of the multiplexed electrochemical biosensor for the detection of RAC, SAL and CLB.

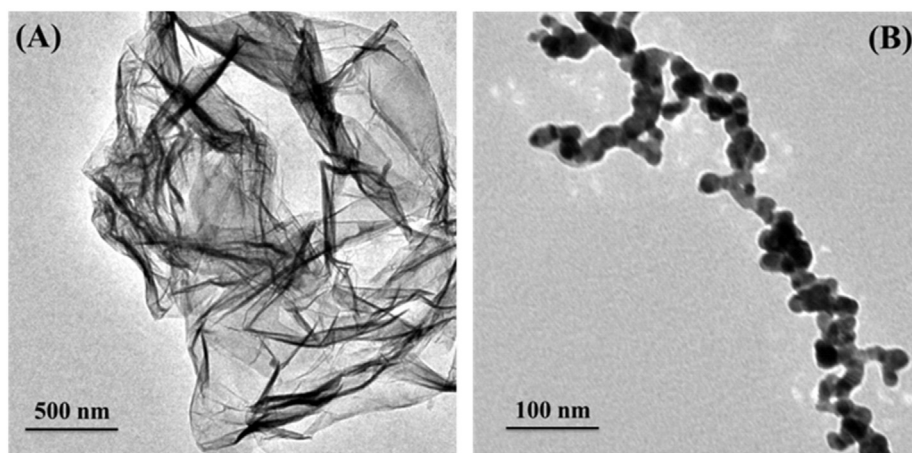


Fig. 1. TEM images of the synthesized rGO (a) and AgPd NPs (b).

SAL were mixed with corresponding Ab/AgPd NPs stock solution to obtain the incubation solutions. Next the incubation solutions were dropped on corresponding working electrodes and incubated for 1 h, and then the residual was removed by washing with PBS. Finally, the electrochemical detection was performed in a 50 μ L of pH 7.0 PBS.

3. Results and discussion

3.1. Characteristics of nano-materials

Fig. 1(a) shows a typical TEM image of the synthesized rGO. The rGO was observed to have a wrinkled, paperlike structure, which provided a large surface area for the immobilization of biomolecules. Fig. 1(b) displays a TEM image of the AgPd NPs; they are granular nanoparticles with an average diameter of 10 nm. Fig. 2(a) is the UV spectra of Ag NPs, Pd NPs and AgPd NPs. As shown in Fig. 2(a), Pd NPs have no absorption peaks, but Ag NPs have a visible absorption peak at about 430 nm (Krishna et al., 2010). AgPd NPs also have no absorption peak. The reason may be that Pd NPs block absorption of Ag NPs. SEM, EDS and XPS were also utilized to confirm the structure of the compounds in Supplementary Figs. S1 and S2.

The electrochemical properties of these three nano-materials were next tested. As shown in Fig. 2(b), an oxidation peak of Ag

NPs at 0.2 V and a weak current peak near 0.1 V were found. The peaks can be attributed to the oxidation of Ag to Ag₂O and Ag₂O to AgO, correspondingly (Huang et al., 2012; Zhang et al., 2012b; Kim et al., 2010; Yang et al., 2007). Pd NPs had no current peak from 0 to 1.0 V. The AgPd NPs had homologous current peaks compared with Ag NPs, but the peak potentials changed and the peak current increased greatly. This may be due to the Pd catalyst redox of Ag. Enhanced electrochemical signal will greatly increase the sensitivity.

3.2. Multiplexed electrochemical immunoassay

Multiplexed electrochemical immunoassay was achieved by performing each electrode as an independent biosensor for specific β -adrenergic agonists. As shown in Fig. 3, pure printed electrodes had only a very low background current in PBS (Curve 1). When rGO was dropped on the working electrode, a significantly increased background current was observed (Curve 2). This indicates that rGO can significantly increase the conductivity of the printed electrodes. anti-RAC and BSA were attached onto the working electrode through a layer of EDC/NHS, and cause the decline of the background current (Curve 3 and Curve 4). Both anti-RAC and BSA can hinder the electron transfer between electrode and solution, which also shows that the fabrication of biosensor is successful. When the biosensor was incubated with anti-RAC/AgPd NPs bioconjugates, the cyclic voltammogram at modified working

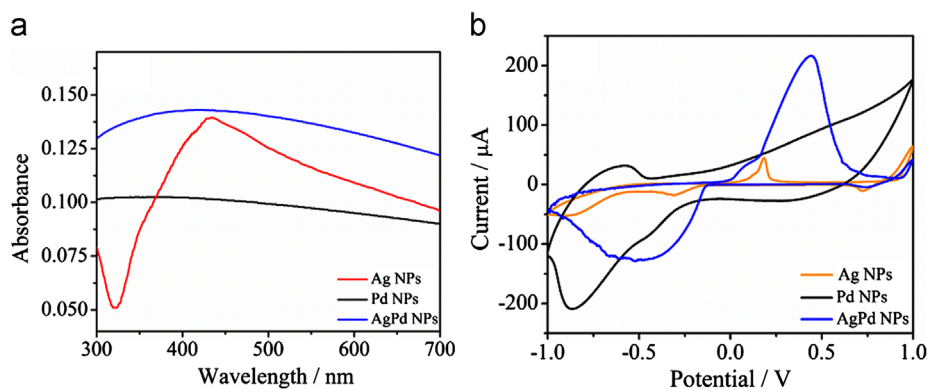


Fig. 2. UV spectra (a) and electrochemical tests (b) of Pd NPs, Ag NPs and AgPd NPs.

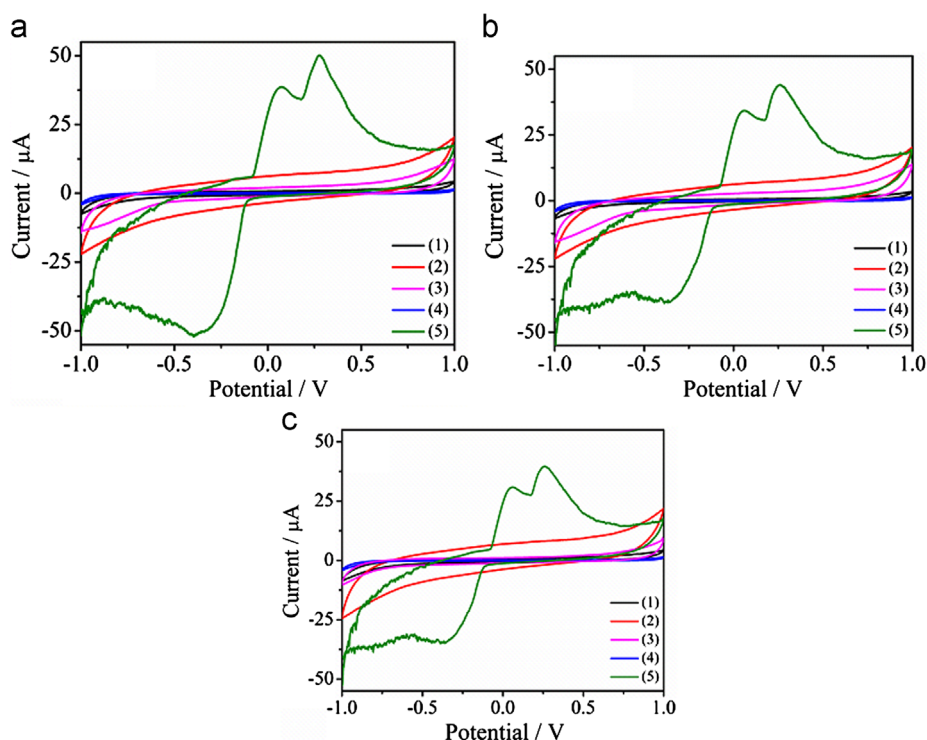


Fig. 3. Multiplexed electrochemical immunoassay procedure for RAC (a), SAL (b) and CLB (c). Cyclic voltammogram of pure SPCEs (1), rGO (2), artificial antigen/rGO (3), BSA/artificial antigen/rGO (4), and Ab/AgPd NPs/BSA/artificial antigen/rGO (5).

electrodes exhibited two anodic peaks (Curve 5), which correspond to the electrochemical oxidation of Ag. Biosensors for CLB and SAL are similar to the biosensor for RAC.

3.3. Evaluation of cross-talk and cross-reactivity between electrodes

Cross-talk generally results from the diffusion of electroactive indicator produced on one electrode to neighboring electrodes. In this work, PBS is the only electrolyte and no electroactive indicator is added. Hence, the possible cross-talk could be well avoided. In order to confirm that the electrochemical cross-talk was not occurring between neighboring electrodes, biosensors for RAC, SAL and CLB were incubated with a series of Ab/AgPd NPs solutions containing only one β -adrenergic agonist and the amperometric responses on the three working electrodes were recorded simultaneously. Only the biosensor for the corresponding β -adrenergic agonist showed a significant decrease in oxidation current while no obviously changed signals were observed on

other working electrodes (Supplementary Fig. S3). The results showed that the simultaneous electrochemical test was possible without influence by adjacent electrodes.

The cross-reactivity, i.e. mutual interference, was also investigated. 100 ng mL⁻¹ SAL and CLB were added into 1 ng mL⁻¹ RAC. Then the solutions were mixed with Ab/AgPd NPs and incubated with RAC biosensor. As shown in Fig. 4(a), the current response was 99.1 μA for the incubation solution containing 1 ng mL⁻¹ RAC and 100 ng mL⁻¹ SAL, and 100.8 μA for the incubation solution containing 1 ng mL⁻¹ RAC and 100 ng mL⁻¹ CLB. As expected, the biosensors having no obviously changed signals were observed compared with the incubation solution containing only 1 ng mL⁻¹ RAC (98.2 μA). The relative tolerances were 0.9% and 2.6%, correspondingly. The biosensors for SAL (Fig. 4b) and CLB (Fig. 4c) were tested using a similar method. The relative tolerances were also less than 5%. Detailed data is shown in Supplementary Table S1. Obviously, the cross-reactivity between these three β -adrenergic agonists and their antibodies was negligible. Thus, simultaneous immunoassay could be performed using the designed biosensor.

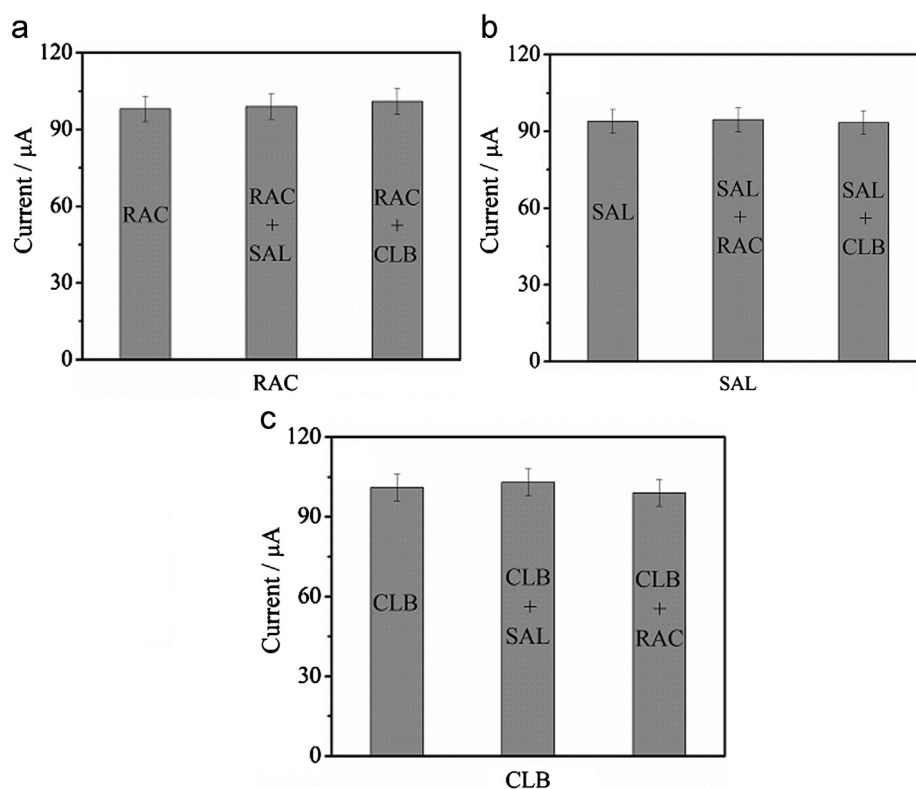


Fig. 4. Mutual interference between the three β -adrenergic agonists. 100 ng mL⁻¹ SAL and CLB were added into 1 ng mL⁻¹ RAC (a), 100 ng mL⁻¹ RAC and CLB were added into 1 ng mL⁻¹ SAL (b), and 100 ng mL⁻¹ RAC and SAL were added into 1 ng mL⁻¹ CLB (c).

3.4. Simultaneous immunoassay

Different concentrations of RAC standard, CLB standard and SAL standard solutions are mixed with AgPd NPs labeled antibodies to obtain the incubation solution. The proposed biosensor was then incubated with the incubation mixture. As shown in Fig. 5, the linear sweep voltammetry (LSV) peaks in three channels decreased with the increase of the concentrations of RAC, SAL and CLB. The linear responses were obtained over the RAC concentration range from 0.01 to 100 ng mL⁻¹ with the detection limit of 1.52 pg mL⁻¹ (a), SAL concentrations range from 0.01 to 100 ng mL⁻¹ with the detection limit of 1.44 pg mL⁻¹ (b), and CLB concentrations range from 0.01 to 100 ng mL⁻¹ with the detection limit of 1.38 pg mL⁻¹ (c), estimated at the 3 σ_B criterion, which were partially lower than those of microarray (0.02 μ g L⁻¹ for SAL and 0.03 μ g L⁻¹ for RAC, Hu et al., 2010), surface plasmon resonance sensor (0.12 ng mL⁻¹ for RAC, Liu et al., 2012) and hapten microarray (0.09 μ g L⁻¹ for CLB, 0.50 μ g L⁻¹ for RAC, and 0.01 μ g L⁻¹ for SAL, Zuo et al., 2010).

3.5. Repeatability, reproducibility and stability

The repeatability and reproducibility of the proposed biosensor were evaluated by intra- and interassay coefficients of variation (CVs). The intra-assay precision of the analytical method was examined by analyzing one biosensor for five replicate determinations in a day at different times. As shown in Supplementary Table S2, the CVs of the intra-assay were 6.1%, 4.7%, and 5.2% at 1.0 ng mL⁻¹ RAC, SAL and CLB, respectively. The interassays were carried out on five different SPCEs. As shown in Supplementary Table S3, the interassay CVs on five biosensors were 7.2%, 6.4%, and 5.9% at 1.0 ng mL⁻¹ RAC, SAL and CLB, respectively. These results demonstrated acceptable reproducibility and precision of the proposed biosensor. When the biosensor was not in use, it was

stored at 4 °C and a test performed every 3–5 days. As shown in Supplementary Table S4, after a month, the response current of the biosensor had no obvious signal change compared to its initial response, suggesting the stability of the biosensor was also good.

3.6. Application in analysis of pork sample

10 mL of pork extract solution was used for sample analysis, which was obtained from 10 g pork through an ultrasonic crushing method. The estimated values were very low, which could be considered as errors. To evaluate the reliability and application potential of the designed biosensor, 0.50 ng mL⁻¹, 5.00 ng mL⁻¹ and 10.0 ng mL⁻¹ of RAC, SAL and CLB were added into the pork extract solution for recovery tests. The results are listed in Supplementary Table S5. As a result, the average recovery of RAC was 97.8–106%, the average recovery of SAL was 96.0–103% and the average recovery of CLB was 97.6–104%, which showed acceptable results for these three β -adrenergic agonists, indicating good accuracy of the proposed method for sample detection.

4. Conclusions

In this work, a novel highly sensitive multiplexed electrochemical biosensor for simultaneous detection of RAC, SAL and CLB was developed using rGO as substrate material and AgPd NPs as signal labels. The rGO was not only used as a substrate for the immobilization of biomolecules, but also promoted the electron transfer of biosensor. AgPd NPs provided a powerful signal that can be used to detect and ensure the sensitivity of the proposed biosensor. Compared with other strategies, the biosensor is rapid, simple, and sensitive. Significantly, the assay does not require sophisticated fabrication and is well suited for high throughput biosensing and application in food analysis and bioanalysis.

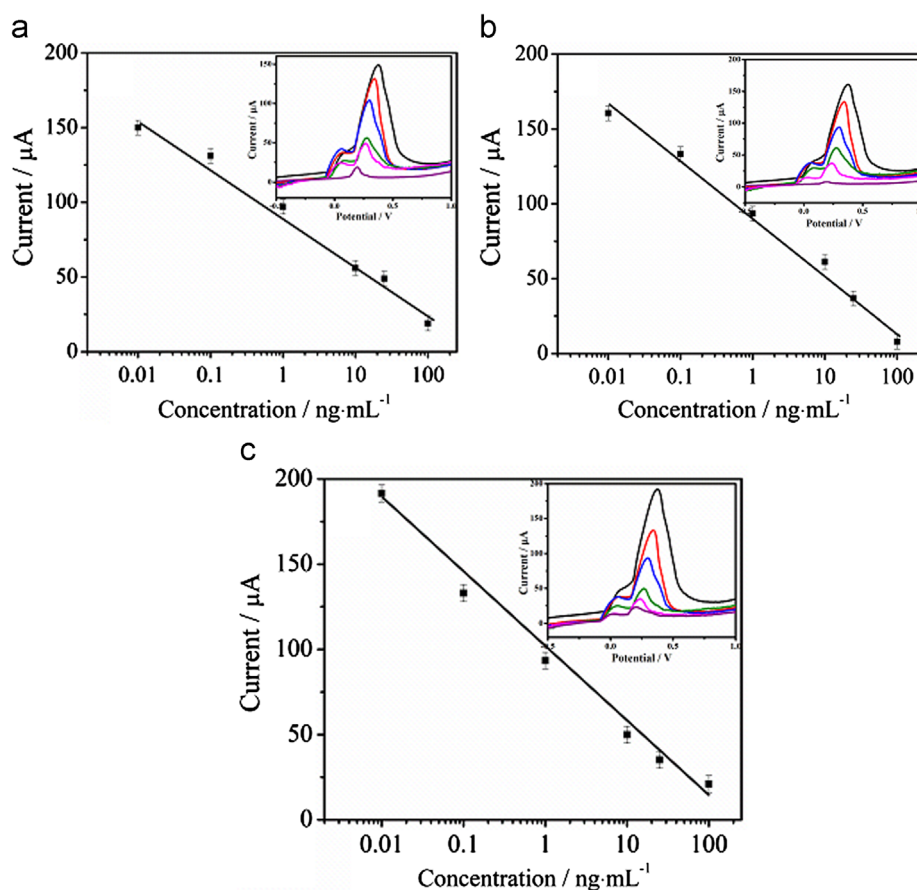


Fig. 5. LSV curves and working curve at the concentrations of 0.01, 0.10, 1.00, 10.0, 25.0 and 100 ng mL⁻¹ in pH 7.0 PBS.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.bios.2013.04.041>.

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