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A disposable molecularly imprinted electrochemical sensor based on screen-printed electrode modified with ordered mesoporous carbon and gold nanoparticles for determination of ractopamine

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ABSTRACT

The following paper describes a surface molecular self-assembly strategy used to imprint the electropolymerized molecular imprinted membrane (MIM) on the surface of the screen-printed electrode (SPE) modified with ordered mesoporous carbon material (OMC) and gold nanoparticles (AuNPs) for determination of ractopamine (RAC). A SPE modified with OMC and AuNPs is assembled and tested. Electrochemical and morphological investigations highlight the effective performance of such a modified SPE in rate of electron-transfer and electroactive surface (0.1270), which is more than that of bare SPE (0.0305), AuNPs/SPE (0.0601), OMC/SPE (0.0798). Electropolymerizable ρ-Aminothiophenol (ρ-ATP) and dummy-template Ritodrine (RIT) were first assembled on the AuNPs/OMCs/SPE surface. And subsequently, the MIM was formed by electropolymerization, the recognition sites matching RAC were obtained after the removal of RIT. Cylic voltammetry (CV), differential pulse voltammetry (DPV), electrochemical impedance spectra (EIS) and scanning electron microscopy (SEM) were used to characterized the MIM sensor. Factors that affected the performance of the MIM sensor were discussed and optimized. Under the optimal conditions, the DPV current response was linear with the logarithm (log) concentration of the RAC in the range from $5 \times 10{-}11$ to $1 \times 10{-}9$ mol L^{-1} ($R2 = 0.9911$) with the detection limit of $4.23 \times 10{-}11$ mol L^{-1} ($S/N = 3$). The sensor had rapid equilibrium incubation time (100 s), high binding affinity and selectivity towards RAC. The average recovery of RAC from the swine urine was excellent ranging from 95.7% to 99.3%.

1. Introduction

Ractopamine (RAC), an effective artificially synthesized beta-agonist, possesses the capability of promoting animal growth through accelerating accretion of skeletal muscle mass and decreasing the deposition of body fat [1,2]. Unfortunately, this compound is illegally applied as a nutrient reparsing agent within the Chinese livestock industry to divert nutrients from fat deposition to muscle production [3]. Numerous poisoning potential effects and hazards of RAC have been reported, including cardiopalmus, tachycardia, anxiety, bewilderment and muscle tremors [4,5]. This compound has been banned in the Europe Union (EU) as well as some Asian countries and regulations have been established to strictly control the illegal use of RAC due to the strong likelihood of adverse side effects to consumers [6]. The United Nations Food and Agriculture Organization (UNFAO) has revised regulations for the animal drug residues enacting a maximum residue limit of 10 ng g^{-1} (29.5 nmol L^{-1} kg^{-1}). An announcement was issued by the Ministry of Agriculture of People's Republic of China on April 27, 2008 that no beta-agonists were to be present in the tissue of edible animal. Therefore, rapid and portable techniques to determine RAC residues in animal samples are necessary to ensure food safety.

Until recently, several conventional techniques, such as high-performance liquid chromatography (HPLC) [7,8], liquid chromatography/tandem mass (LC-MS) [9,10], gas chromatography–mass spectrometry (GC–MS) [11,12], Raman Spectroscopy [13] and immunoassays [14] have been reported. These confirmatory methods can provide reproducibility and satisfactory sensitivity for both qualitative and quantitative analysis and detections. However, they are time-consuming and expensive apparatus are needed, thus rendering them applying in the aspect of real time detection. The screen-printed electrode (SPE) is recognized for its effectiveness in the development of portable sensors to be used in electroanalysis [15] due to its low cost and applicability to mass production [16,17]. Compared with conventional electrodes, SPEs present several advantages as they are highly versatile, user-friendliness, cost-effective and they permit accurate, sensitive, and reproducible sensors' development by working with low volumes [18]. Gradually, SPEs are attracting more and more attentions as effective devices for the development of portable sensors to be used in electroanalysis [19,20].

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In recent years, the application of molecularly imprinted membrane (MIM) to determine drug residues has been an attractive alternative due to the advantages of easy preparation, favorable stability and selective recognition sites [21,22]. The simplest solution to further increase the amount of effective recognition sites on the surface of SPE is to provide higher electroactive area through modifying nanoparticles on the electrodes' surface. The nanoparticles have attracted extraordinary research interest due to their unique and advantageous applications in different fields [23,24]. Highly ordered mesoporous carbons (OMCs), a type of carbon materials, have been attracting more and more attentions due to their high specific surface area, extremely well-ordered pore structure and volume. Their applications have been expended to catalysis [25,26], energy storage [27] and electrochemical sensor [28]. So far, several studies have been reported based on OMCs for electrochemical determination of various substances, including metolcarb [29], nitrophenol isomers [30], dopamine [31], glutathione and cysteine [32], uric acid [33], hydrazine [34]. Despite the overwhelming potential of OMCs, their applications in electroanalytical for determination of RAC have been reached a little [31,35]. X. Yang et al. [36] described an electrochemical methods for determination of RAC at OMCs modified electrode with a detection limit of 0.06 μmol L^{-1}. A formation of flowerlike gold nanostructure on OMCs electrode was proved for determination of RAC [37]. Au nanoparticles (AuNPs) have been widely used to increase the surface area and amount of effective recognition sides on the surface of electrodes due to their high biocompatibility of conductivity and large specific surface [38]. In particular, AuNPs represent interesting nanosized materials capable to effectively active photocatalytic performance [39].

Studies have shown that RAC itself has slightly electrochemical sensing signals which will lead to structure changes in the step of electropolymerization [36]. Therefore, the structure analogue Ritodrine (RIT), which boasts almost no electrochemical response signal, is chosen as the dummy template molecule during the period of electropolymerization of MIMs due to its similar structure size and functional groups with RAC.

The aim of this research is to develop a rapid, convenient and portable electrochemical sensor of high sensitivity for the determination of RAC. In order to improve the electrochemical performance, we double-modified SPE with OMCs and AuNPs to increase its electroactive area. We were able to successfully fabricate a rapid, sensitive, cost-effective, and portable electrochemical SPE sensor based on MIMs on P-ATP-AuNPs/OMCs/SPE to detect RAC. Though some papers about fabricating electrochemical SPE sensor to detect RAC have been reported [40,41]. This is the first time that we combined portable SPE modified with OMCs and AuNPs with MIM by using the dummy template RIT. Zhang Hongcai et al. developed an amperometric sensor based on multi-walled carbon nanotubes and MIM for determination of RAC [6]. Compared with the methods above, the sensor this work developed could decrease the detection limit by nearly 100 folds for the reasons that we adopted electropolymerization instead of thermal polymerization and furthermore we modified SPE with OMCs and AuNPs to get higher electroactive surface area electrode as well as increase the number of effective binding cavities. The sensor had rapid equilibrium incubation time (100 s), high binding affinity and selectivity towards RAC. The average recovery of RAC from the swine urine was excellent and ranged from 95.7 to 99.3%. Electrochemical and morphological investigations highlight the effective performance of such a modified SPE in electroactive surface (0.1270), which is more than that of bare SPE (0.0305), AuNPs/SPE (0.0601), OMC/SPE (0.0798).

2. Materials and Methods

2.1. Materials

Tetrachloroaurate acid (III) ($HAuCl_4$), ρ-Aminothiophenol (ρ–ATP), Dodecanethiol (DOD) and Tetrabutylammonium perchlorate (TBAP) were purchased from Sigma. Ractopamine (RAC) and Ritodrine (RIT), as the hydrochloride salt, were purchased from Shanghai Civil Chemical Industrial Co., Ltd. OMCs were purchased from Najing XFNANO Technology Co., Ltd. All the reagents were analytic grade.

2.2. Apparatus

SPEs and the linking device corresponding were purchased from Shanghai Molybdenum Electronic Technology Co., Ltd. Electrochemical measurements were performed using electrochemical workstation CHI-760C (Chenhua, Shanghai, China) connected to a personal computer. The surface morphology of the SPE modified was observed by using scanning electron microscrope (SEM) (Hitachi TM3030, Japan).

2.3. Fabrication of AuNPs/OMCs/SPE

Before the modification of OMCs, a bare SPE was scanned cyclic-potentially in solution of 2.5 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ in the potential window between −0.2 V and +0.6 V for several circles. The working area of the SPE was covered by 10 μL of the OMCs suspension (1.0 mg/ml in DMF) and dried in the environment over 45 °C to remove the solvent. And then washed the OMCs/SPE by ultrapure water and dried it at room temperature for the next deposition of AuNPs. To electrochemically deposit AuNPs on the working area of OMCs/SPE, the OMCs/SPE was immersed in 0.589 mol L^{-1} aqueous $HAuCl_4$ solution containing 0.1 mol L^{-1} H_2SO_4 and treated at potential −0.2 V constantly for 80 s. After being washed several times with ethanol and ultrapure water, the AuNPs/OMCs/SPE was dried under nitrogen.

The modification of ρ-ATP was carried out by methods reported in literature [42–44]. The pretreated AuNPs/OMCs/SPE was immersed into 100 mmol L^{-1} solution of ρ-ATP in ethanol. After reacting for 24 h at room temperature, the SPE was then taken out and washed with ethanol and ultrapure water. Then, we immersed the ρ-ATP modified AuNPs/OMCs/SPE into the solution of 5 mmol L^{-1} RIT for 4 h. Through hydrogen bonded between the amino groups ($-NH_2$) of ρ-ATP and the nitrogen/oxygen atoms of RIT, RIT molecules were assembled onto the ρ-ATP modified AuNPs/OMCs/SPE accordingly.

2.4. Fabrication of the MIM-AuNPs/OMCs/SPE

The AuNPs/OMCs/SPE with ρ-ATP and RIT assembled on the surface of working area was immersed in electrolyte solution containing 30 mmol L^{-1} ρ-ATP, 5 mmol L^{-1} RIT, 0.589 mmol L^{-1} aqueous $HAuCl_4$ and 50 mmol L^{-1} TBAP. After deoxygenizing for 10 min by bubbling nitrogen, the electropolymerization was carried out using 20 consecutive cyclic scans in the potential window between −0.2 V and 1.2 V. Then the imprinted polyaminothiophenol (PATP)-AuNPs/OMCs/SPE was immersed into an ethanol solution containg 0.05 mol L^{-1} DOD for 24 h to fill defects in the imprinted layer. After the electropolymerization, the imprinted PATP-AuNPs/OMCs/SPE was rinsed with 2 mol L^{-1} H_2SO_4 three times for 25 min to remove the RIT template, thus obtaining the MIM-AuNPs/OMCs/SPE. Then, the MIM-AuNPs/OMCs/SPE was washed with ethanol and ultrapure water and subsequently dried under nitrogen. As a control, the NIM-AuNPs/OMCs/SPE was fabricated in the same way without adding template RIT molecule.

2.5. Electrochemical Measurements

The MIM-AuNPs/OMCs/SPE was dipped into 0.1 mol L^{-1} KCl that contained the desired concentration of RAC for 100 s, carefully washed with ultrapure water and then dipped 100 μL volume of 2.5 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ solution. The current responses of different modified SPEs were recorded by CV and DPV measurements in potential window between −0.2 V and +0.6 V. The EIS was scanned in 2.5 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ at the formed potential of 0.25 V with a frequency range of 1–10^5 Hz and a signal amplitude of 5 mV.