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Short Communication

A ractopamine electrochemical sensor based on a 3-dimensional macroporous copper electrode modified with a gold coating

Yan Ji[1], *Yuhui Du*[1], *Ling Jia*[1], *Hong Li*[3,4,5,*], *Jiping An*[2,*] *and Bin Qi*[1,*]

[1] Faculty of Chemistry, Northeast Normal University, Changchun, 130024, China
[2] Hospital of Stomatology, Jilin University, Changchun, 130024, China
[3] Key Laboratory of Narcotics Assay and Control Technology, Ministry of Public Security
[4] Public Security Department of Yunnan Province, Kunming, 650220, China
[5] Institute of Forensic Science, Ministry of Public Security, P. R. China
[*]E-mail: qib219@nenu.edu.cn

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Within this work, the direct electrooxidation of Rac on Cu was explored. To enhance the performance of Cu, three hard coatings were investigated: (1) a Au coating (Au@Cu) formed via an electrodeposition process; (2) a 3D-macroporous Cu (3D-Cu) formed by the electrodeposition of Cu (from $CuSO_4$), on a bare Cu surface with H_2 bubbles as a template; and (3) a Au-coated 3D-Cu (Au@Cu3D) prepared by an electrodeposition method. Bare Cu was used as a reference for performance comparison. Au@Cu3D was found to demonstrate the best analytical performance towards the determination of Rac. The detection limit, linear range, reproducibility, stability and real sample analysis results were used to evaluate the analytical abilities of the samples.

Keywords: Ractopamine, electrochemistry, gold coating, Cu

1. INTRODUCTION

Ractopamine (Rac) is an artificially synthesized β-agonist that belongs to the phenolic hydroxyl group [1, 2,]. Originally, Rac was widely used as a treatment for lung diseases and asthma and demonstrated excellent efficacy [3, 4]. Moreover, Rac was also found to improve the weight gain, leanness and feed efficiency of livestock [5, 6]; thus, many farmers used it as a feed additive to promote leanness in animals raised for their meat. However, the consumption of Rac-treated animals may cause cardiovascular and central nervous diseases, which will be a serious threat to human health [7, 8]. Currently, Rac has been banned from promoting growth in animal production in most countries [9]. Some countries have also listed it as a water pollutant. Based on this fact, there is an urgent need to develop an effective method for determining Rac. Currently, to determine Rac, many methods, including gas chromatography–mass spectrometry, high-performance liquid chromatography and immunoassay methods, have been reported [2, 10, 11, 12]. Whereas most of these methods require either an expensive instrument or a long operation time [8], a simple, fast and accurate method is still highly desired.

In recent years, electrochemical methods, based on chemically modified electrodes, may be the preferred approach for detecting Rac. The above approaches have many advantages, including low instrumental cost, efficiency, simplicity and so on. Among these methods, gold nanomaterials have attracted much attention due to their unique physical and chemical properties (including a high electrical conductivity and large specific surface area, excellent biocompatibility, etc.). [13]. Based on these versatile properties, gold materials have been widely used in the electrochemical detection of a variety of toxic substances [14, 15, 16]. For example, Duan et al. developed a method to determine Rac and metaproterenol with a gold nanoparticle-modified glassy carbon electrode as an electrochemical sensor [14]. Yang et al. fabricated a label-free immunosensor based on $Au@Ag_2S$ nanoparticles/magnetic chitosan to determine Rac [15]. Recently, our group constructed an Rac sensor by producing flower-like gold nanostructures on an ordered mesoporous carbon electrode [16].

To date, the performances of copper (Cu) materials in both fundamental research and technical applications have been widely investigated due to their low cost [17, 19]. In contrast to a conventional two-dimensional (2D) plane, a three-dimensional (3D) porous structure has been found to promote charge and mass transport in electrochemical processes due to providing an extremely large specific surface area [18]. Based on this fact, Wang et al. fabricated an electrochemical sensor for Rac determination with 3D $Cu/Cu_2O@rGO$ as the sensing material [19].

In this work, a hard gold coating is cast onto a 3D-Cu surface to construct an Rac electrochemical sensor. The sensor exhibits excellent catalytic performance for the electrochemical oxidation of Rac. Further evaluation results show that the sensor possesses the characteristics of a low detection limit, wide linear range, and good reproducibility and stability, which indicated its potential analytical performance in both environmental evaluation and medical diagnosis applications.

2. EXPERIMENTAL

2.1. Reagents

Rac hydrochloride was obtained from Fluka. Other inorganic chemicals, including $HAuCl_4·3H_2O$, $CuSO_4·5H_2O$, NH_4Cl, H_2SO_4, $NaH_2PO_4·2H_2O$ and $Na_2HPO_4·12H_2O$, were purchased from Beijing Chemical Reagent Co., Ltd. All chemicals were of at least analytical grade and used without further purification [20]. Pork samples were purchased from 5^{Th} Walmart of Changchun, China. A phosphate buffer solution (PBS, pH 7.0, $NaH_2PO_4·2H_2O + Na_2HPO_4·12H_2O$) and other aqueous solutions were prepared with double-distilled water and stored at 4°C [14].

2.2. Instrumentation

All electrochemical experiments were performed at room temperature using a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). A conventional three-electrode system was used for all electrochemical measurements: a Cu-disc electrode, Ag/AgCl electrode and platinum wire electrode served as the working, reference and counter electrodes, respectively. Scanning electron microscopy (SEM) images were obtained using an FEG LEO 1550 (Gemini instrument) [16].

2.3. Preparation of the 3D macroporous Cu electrode

A 3D macroporous Cu (3D-Cu) film was formed on a Cu-disc electrode surface through an electrodeposition procedure. First, the Cu-disc electrode was polished by 2000 grit emery paper and washed to remove surface impurities[21]. Then, the Cu electrode was successively polished to a mirror-like surface with 1.0, 0.3 and 0.05 µm alumina powder and then thoroughly cleaned. Finally, the as-treated Cu electrode was further treated in a solution of 0.05 mol L^{-1} $CuSO_4$ + 0.7 mol L^{-1} H_2SO_4 + 0.01 mol L^{-1} NH_4Cl for 160 s with a potential of -1.0 V[18]. After washing with deionized water, a 3D-Cu electrode was obtained.

2.4. Preparation of the gold coating on a 3D-Cu electrode

A gold coating was cast onto the 3D-Cu electrode via the following procedure. First, the 3D macroporous Cu electrode was immersed into a 0.05 g L^{-1} $HAuCl_4$ solution for 10 s. Then, a - 0.2 V voltage was applied for 180 s. Finally, the as-prepared electrode was washed with deionized water and dried under a nitrogen stream. Thus, a gold-coated 3D macroporous Cu (Au@Cu3D) electrode was successfully obtained.

For comparison, a gold-coated bare Cu (Au@Cu) electrode was prepared in the same way.

3. RESULTS AND DISCUSSION

3.1 Morphologies of the different surfaces

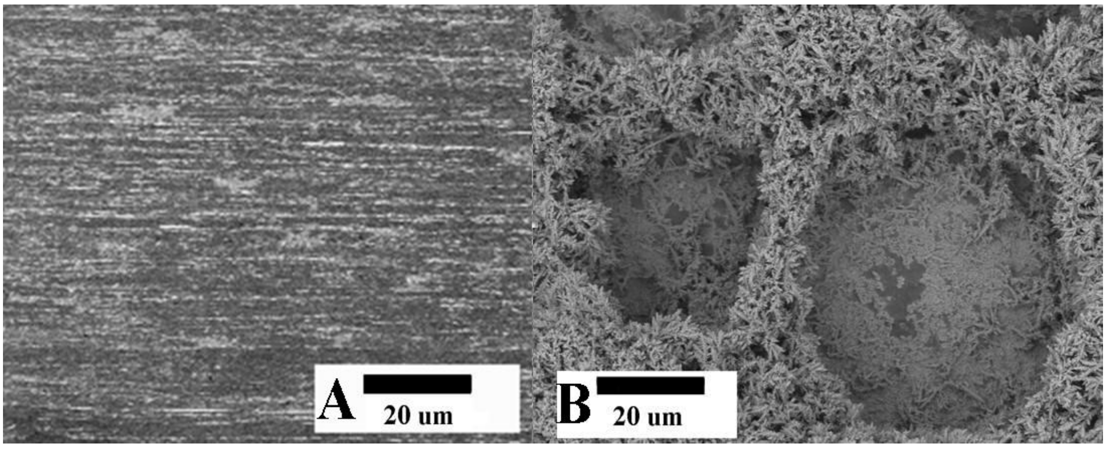

Figure 1. SEM images of bare Cu (A) and 3D-Cu (B)

The morphologies of different Cu surfaces were characterized using SEM. As seen in Fig. 1A, the bare Cu shows a planar surface. The macroporous Cu exhibited an uniform 3D macroporous morphology (Fig. 1B). From the above results, it was rational for us to deduce that compared with that of a planar surface, 3D-Cu possessed a higher surface area and provided more area for the formation of a gold coating.

3.2 Electrocatalytic performance of Cu towards Rac oxidation

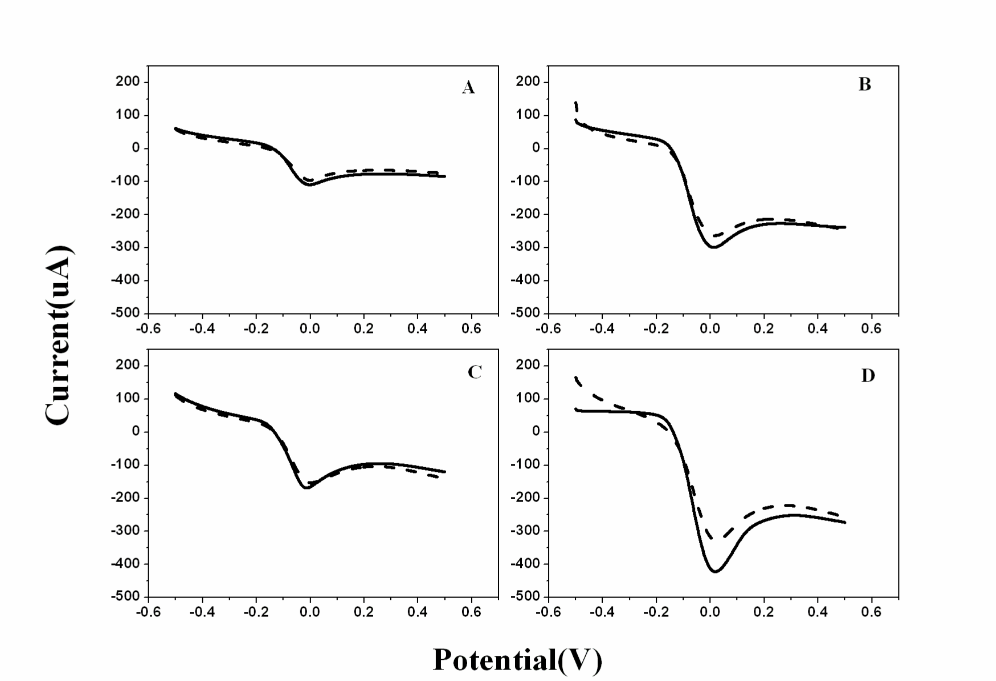

Figure 2. LSV plots of bare Cu (A), 3D-Cu (B), Au@Cu (C) and Au@Cu3D (D) in the absence (dotted line) and presence (solid line) of 0.2 μg ml^{-1} Rac

The electrocatalytic performance of Cu was first characterized using a linear sweep voltammetry (LSV) technique. Fig. 2A and B reveal the LSV curves of Cu with different morphologies obtained in 0.2 μg ml^{-1} Rac. It was found that for both bare Cu (A) and 3D-Cu (B), when there was no Rac in the solution, current responses (dotted line) of approximately 0.0 V were observed. With the addition of Rac, enhanced oxidation currents were obtained (solid line), and the value of 3D-Cu was higher than that of bare Cu, which might result from the relatively high surface area of 3D-Cu compared with that of bare Cu [22, 23].

3.3 Electrocatalytic performance of gold coating-enhanced Cu towards Rac oxidation

The electro-catalytic performance of gold coating-enhanced Cu towards Rac oxidation was also investigated by LSV (Fig. 2C and D). Similar to that for Cu, the corresponding gold-coated Cu also exhibited current responses (dotted line) of approximately 0.0 V. With the addition of Rac, increasing oxidation currents were observed (solid line), and the value of Au@Cu3D was higher than that of bare Cu.

It was also found that under the same experimental conditions, Au@Cu3D exhibited the highest current response towards Rac electrocatalytic oxidation, which suggested that Au@Cu3D might be the best choice for constructing an Rac sensor.

3.4 Electrocatalytic performance of Au@Cu3D

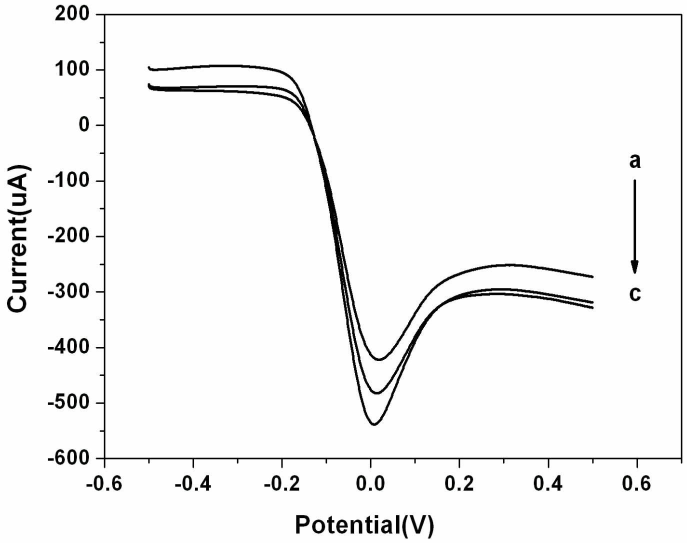

Figure 3. LSV curves of Au@Cu3D in PBS (pH=7) and in the presence of 0.2, 0.4 and 0.8 μg ml^{-1} Rac (from a to c, respectively)

Fig. 3 reveals the LSV curves obtained in a PBS buffer solution with different concentrations of Rac. With increasing Rac concentration, the oxidation peak current clearly increased. Based on this result, there must be some relationship between the Rac concentration and the oxidation current. This indicated that the constructed electrochemical sensor had potential for Rac detection applications.

3.5 Electrochemical determination of Rac

To evaluate the analysis performance of this Rac sensor, a differential pulse voltammetry (DPV) method was performed, and the evaluation result is shown in Fig. 4. Before the DPV operation, Rac was pre−concentrated, and the potential was set to -0.3 V for 25 s. It could be seen from Fig. 4 that with the gradual addition of Rac, the peak oxidation current increased. Data analysis results showed that there was a typical linear relationship between the peak current and Rac concentration, with a correlation coefficient of 0.9999. The linear range of detection was 0.01 to 35.8 μg L^{-1}, and the detection limit was 1.1 μg L^{-1} (S / N = 3) .

Table 1 summarizes a comparison of Rac detection methods for different modified electrode materials. It could be seen that the linear range of this experimental method was comparable to most literature, the detection limit was low, the linear range was large and the stability was good. Therefore, it could be concluded that the Au@Cu3D of the present study was an excellent electrical analysis sensing platform for determining Rac [16].

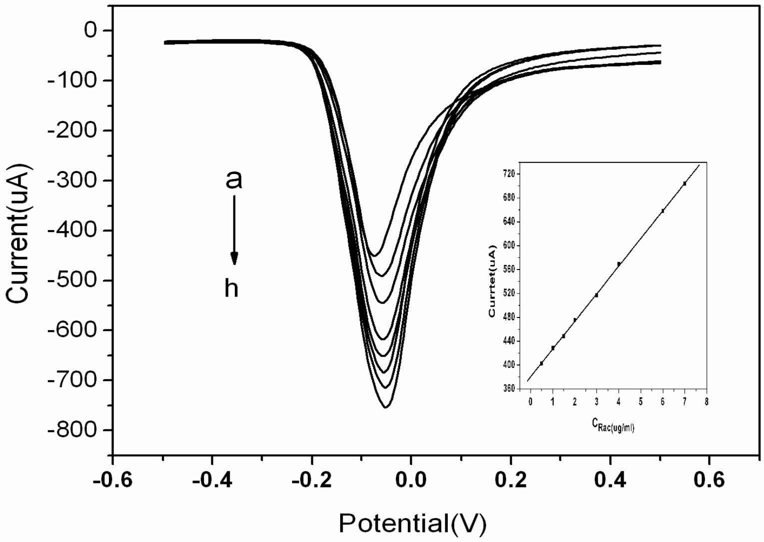

Figure 4. DPV curves of Au@Cu3D in PBS (pH=7) in the presence of 0, 0.1, 0.22, 0.34, 0.44, 0.51, 0.56, and 0.60 µg ml^{-1} Rac (from a to h, respectively)

Table 1. Comparison of methods based on different Au nanomaterials for detecting β-agonists

Electrode	Linear range	LOD (limit of detection)	Test samples	References
Graphene-Nafion/GCE	1.0~18.0 ng/mL	0.81 ng/mL	-	[28]
rGO/AgPd NPs/SPE	0.01~100 ng/mL	0.52 pg/ml	Pork	[29]
AuNPs/PPDA/ Graphene/GCE	1.0×10^{-12}~1.0×10^{-8} mol/L	5.0×10^{-13} mol/L	Pig urine	[24]
OMCs/GCE	0.085~8.0 µmol/L	0.06 µmol/L	Pork	[30]
AuNPs/CS/SPE	0.025~3.0 ng/mL	8.5 pg/mL	Pig urine	[26]
OMCs/AuNPs/SPE	5.0×10^{-11}~1.0×10^{-9} mol/L	4.23×10^{-11} mol/L	Pig urine	[31]
MWNTs/[BMIM]BF4/GCE	1~1 500 ng/mL	0.3 ng/mL	feed	[27]
AuNPs/pdda/GR/CdSe	0.01~1 000 ng/mL	2.6 pg/mL	Pork, feed	[25]
Au@Cu3D	0.01 to 35.8 ng/mL	1.1 ng/mL	Pork meat	This work

3.6 Reproducibility and stability of Au@Cu3D

The reproducibility and stability were two other important parameters to evaluate sensor performance. The above were investigated in our experiments with an amperometric method. The reproducibility of the present sensor was examined by measuring the response currents towards 0.2 μg ml^{-1} Rac solution with Au@Cu3D. The results of 10 parallel experiments revealed that the sensor has good reproducibility with a relative standard deviation (RSD) of 2.36%. The stability of Au@CDs/GCE was checked over a period of one month. It was stored at 4°C in a refrigerator and tested every day for 10 days and then every five days over the next 20 days. For convenience, the mean current response (n=3) of the first day was set to 100%. After one month, the current response of 0.2 μg L^{-1} Rac on Au@Cu3D retained 92.4% of its original value, representing the good stability of the developed electrode.

3.7 Real sample analysis

To test the real sample analysis ability of Au@Cu3D, a fresh pork sample was chosen. Via an ultrasonic crushing method, 10.0 mL of pork (10.0 g) extract solution was prepared to evaluate the reliability and application potential of Au@Cu3D. Considering that the estimated value of Rac content was so low that it could be seen as an error, 0.10 μg mL^{-1} of Rac was added into the pork extract solution for the recovery test. The results showed that the average recovery of Rac was 97.8–103%, which was acceptable for Rac determination and indicated good accuracy of the proposed method for real sample detection.

4. CONCLUSION

In the present work, the analytical performances of bare Cu, Au@Cu, 3D-Cu and Au@Cu3D materials were investigated. The results showed that compared with the other three materials, Au@Cu3D gave the best analytical performance towards Rac determination. The electrochemical Rac sensor constructed on the basis of this hard gold coating displayed a wide linear range, low detection limit and high operating and storage stability, which made Au@Cu3D a promising candidate for both environmental evaluation and medical diagnosis applications.

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