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A Facile and Novel Synthetic Route to Gold Nanoparticles Using Cefazolin as a Template for a Sensor

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Electrochemical synthesis of gold nanoparticles on the surface of pyrolytic graphite electrode and preparation of GNPs using cefazolin as a template in aqueous solution was proposed. The gold nanoparticles were characterized by scanning electron microscopy, transmission electron microscopy, spectrophotometry, powder X-ray diffraction spectra and cyclic voltammetry. The currents for dopamine at GNP/PGE prepared by electrochemistry deposition and absorption method are more than that of dopamine at bare PGE. The catalysis of gold nanoparticles for dopamine was demonstrated.

Keywords: synthesis, gold nanoparticles, cefazolin

1. INTRODUCTION

Gold nanoparticles (GNPs) are particarly attractive for numerous investigations by virtue of the facile synthesis and their applications. To maximize the efficiency of GNPs on the surface of carriers in the applications of biological and chemical sensors [1, 2], microelectronics [3, 4], catalysis [5, 6], and data storage [7, 8], etc., the well-controlled particle size and efficient particle dispersion are necessary. The strategies for immobilization of GNPs layers onto the surfaces include electrostatic links and covalent bonding. The surfaces with functional groups (COOH, OH, SH, NH_2) are suitable substrate for the merging of GNPs [9-12]. Therefore, the selection of the stabilizing reagent is an interesting topic.

Cefazolin, known as cefazolin sodium, is a broad-spectrum cephalosporin antibiotic and its molecular formula is $C_{14}H_{13}N_8NaO_4S_3$. In present work, cefazolin as a stabilizing reagent was used for

electrochemical synthesis of GNPs on the surface of pyrolytic graphite electrode (PGE) and preparation of GNPs in aqueous solution. The characterization of GNP was studied and the catalysis of GNP/PGE for dopamine was demonstrated.

2. EXPERIMENTAL

2.1. Reagents

All reagents used herein were of analytical grade. Doubly distilled water was used throughout. 0.1 mol·L^{-1} phosphate buffer solution (PBS) was prepared by dissolving 0.1 mol NaCl and 0.1 mol Na_2HPO_4 in the double-distilled water of 1000 mL and adjusted desired pH values with 6 mol·L^{-1} HCl or 1 mol·L^{-1} NaOH.

2.2. Preparation of GNPs

The PGE with a diameter of 3 mm was polished with 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with water, and then sonicated in ethanol and water for 10 min, sequentially. The PGE was immersed in the mixture of $HAuCl_4$ (2.0 mg·mL^{-1}), H_2SO_4 (0.5 mol·L^{-1}) and cefazolin sodium (0.4 mg·mL^{-1}), cycled between -1.00 and 0.80 V for five times, and then washed in doubly distilled water. Thus the cefazolin@GNPs on the surface of PGE was obtained. In the typical synthetic process of cefazolin@GNPs in aqueous solution, 0.150 g of $NaBH_4$ were dissolved the mixture of 2.0 mg·mL^{-1} $HAuCl_4$, 0.5 mol·L^{-1} H_2SO_4 and 0.4 mg·mL^{-1} cefazolin sodium. The solution was stirred with a magnetic stirrer for 10 min to ensure that the $NaBH_4$ completely dissolved; the black cefazolin@GNPs were soon produced, and followed by centrifugal separation, washing with absolute alcohol and drying in vacuum at 40 °C for 6 h.

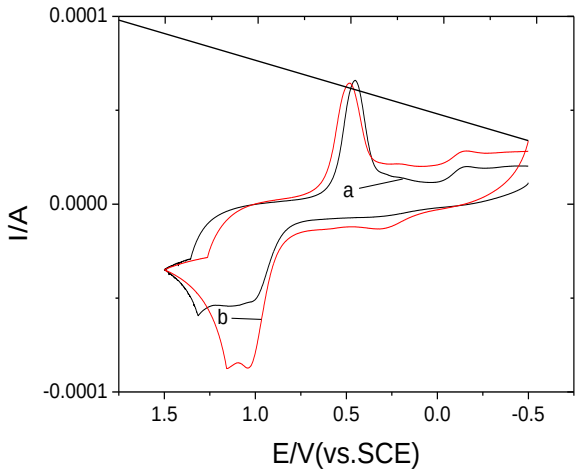
2.3. Characterization of GNPs

For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The GNPs modified PGE was used as working electrode, a platinum wire served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The cefazolin@GNPs was characterized by scanning electron microscopy (SEM) (S-4800, HITACHI, Japan), spectrophotography (UV-1750, Shimadzu, Japan) and transmission electron microscopy (TEM) (JEM 2100, JEOL, Japan). Powder X-ray diffraction (XRD) spectra was recorded on a Switzerland ARL/X'TRA X-ray diffractometer rotating anode with Cu-Kα radiation source (λ = 1.54056 ˚ A).

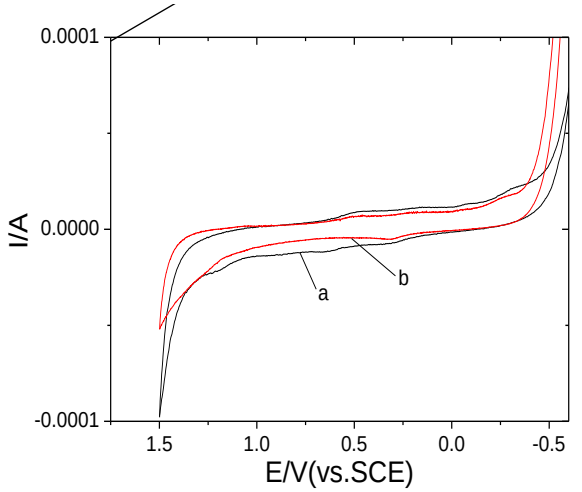
3. RESULTS AND DISCUSSION

3.1. Cyclic voltammograms of GNPs

The Cyclic voltammograms (CVs) of cefazolin@GNPs obtained by electrochemical synthesis on the surface of PGE in 0.1 mol·L^{-1} PBS of pH 7.3 is shown in Fig. 1A. The oxidation peak of cefazolin@GNPs was found at 1.029 V, and the reduction peak was observed at 0.479 V. To remove cefazolin on the surface of GNPs, the cefazolin@GNPs modified PGE was rinsed in 5 mol·L^{-1} H_2SO_4 aqueous solution and doubly distilled water for 10 min, sequentially, The oxidation current of the rinsed GNPs increases, and the reduction potential shifted to positive direction, indicating that the cefazolin on the surface of GNPs could prevent the oxidation of GNPs, and the cefazolin was removed. The CVs of cefazolin at PGE are shown in Fig.1B, a weak oxidation peak at 1.216V and a reduction peak at 0.496 V were found, indicating that cefazolin is stable in the progress of electrochemical synthesis of GNPs on the surface of PGE.



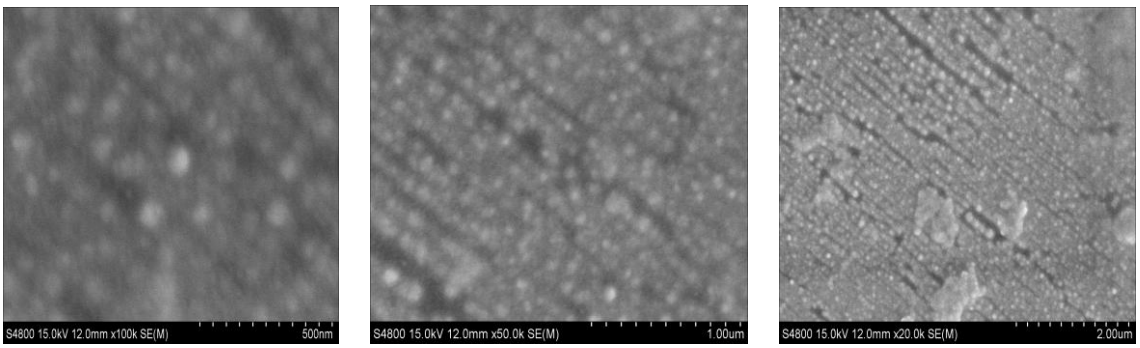
A



B

Figure 1. A: CVs of cefazolin@GNPs (a) and the rinsed GNPs (b). Supporting electrolyte: 0.1 mol·L^{-1} PBS of pH7.3. B: CVs of 0.4 mg·mL^{-1} cefazolin sodium at PGE (a) and blank PGE (b), supporting electrolyte: 0.5 mol·L^{-1} H_2SO_4.

3.2. SEM and TEM images of GNPs



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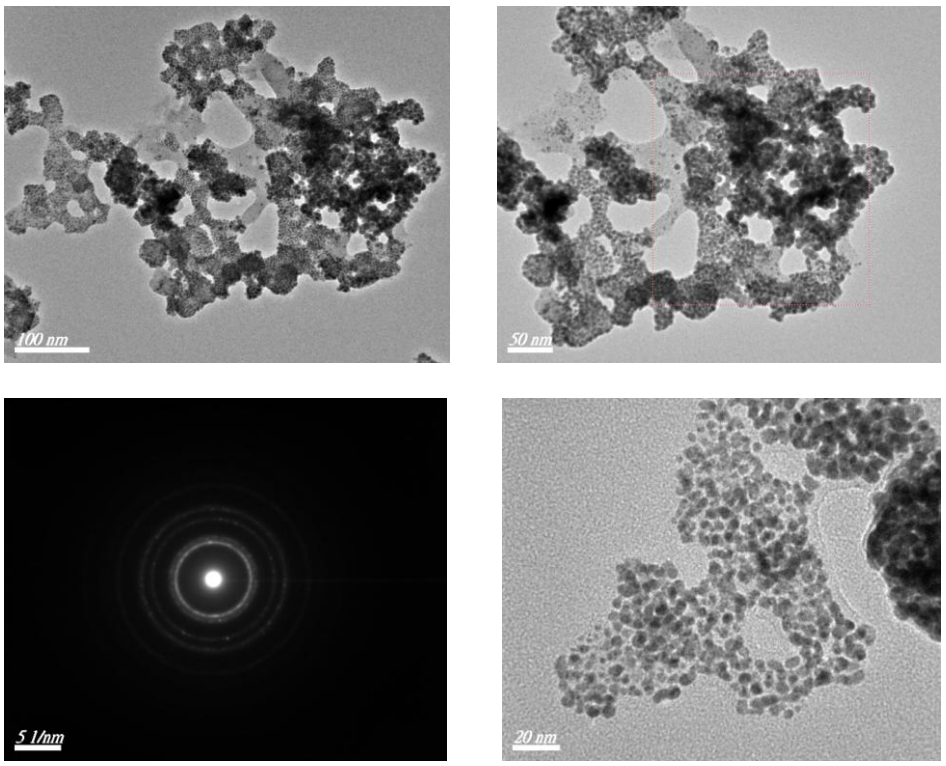

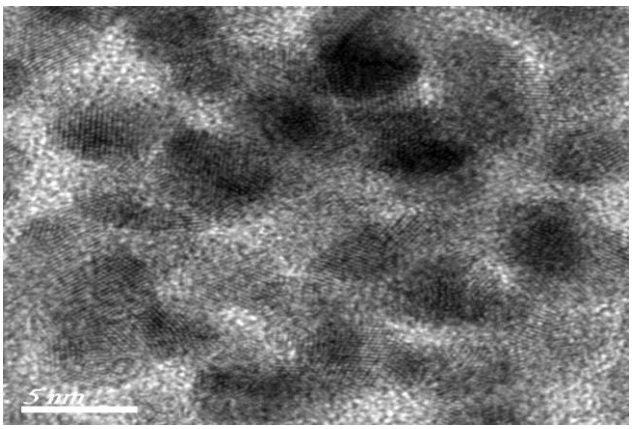

B

Figure 2. SEM (A) and TEM (B) images of GNPs

SEM images confirm the formation of a layer of cefazolin@GNPs on the surface of PGE. The linear cefazolin@GNPs on the surface of PGE was observed in Fig. 2A, indicating that the well dispersion of cefazolin@GNPs on the surface of PGE was obtained. The TEM of cefazolin@GNPs obtained from aqueous solution are shown in Fig.2B, the size of cefazolin@GNPs is about 5 nm. The cefazolin@GNPs on the PGE surface is similar to the preparation of cefazolin@GNPs in aqueous, the large nanoparticles on the PGE surface is composed of small GNPs.

3.3. XRD pattern of GNPs

The powder XRD pattern of cefazolin@GNPs obtained from aqueous solution is shown in Fig. 3. The major diffraction peaks can be indexed as the gold face-centered cubic (fcc) phase based on the data of the JCPDS file (JCPDS no.04-0784) [13]. The diffraction peaks of GNPs appeared at 38.8°, 44.5°, 65.0°, and 78.1°can be assigned to (111), (200), (220), and (311) crystalline plane diffraction peaks of gold, respectively.

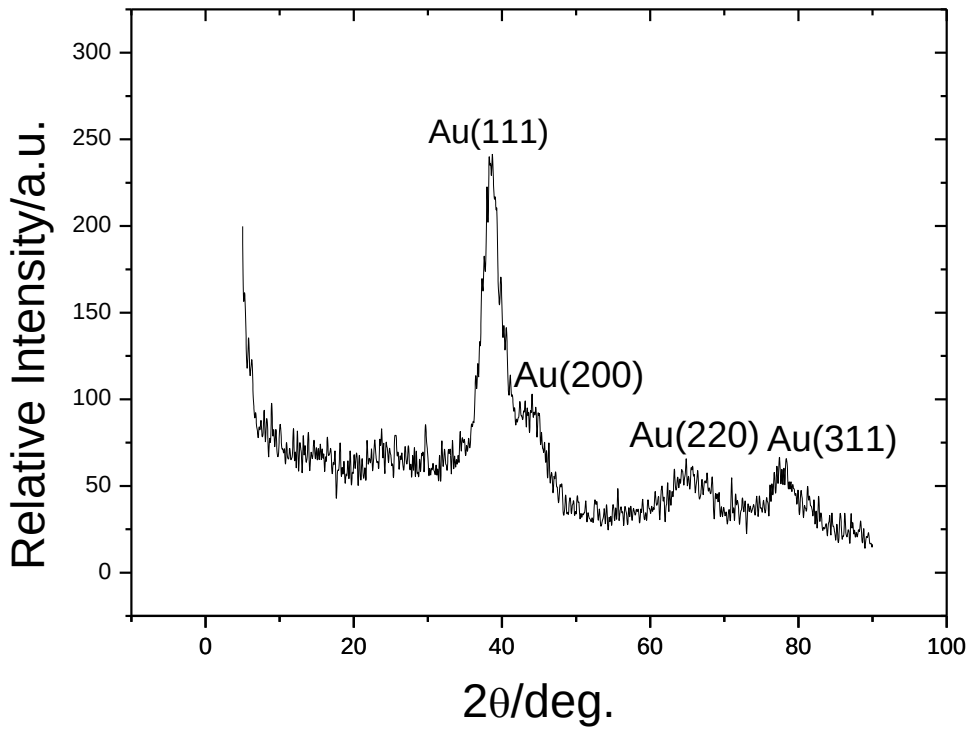

Figure 3. XRD pattern of GNPs obtained from aqueous solution

3.4. UV spectra of GNPs

Fig. 4 shows the UV–vis absorption spectrum of the cefazolin@GNPs obtained from aqueous solution. A band centered at ca. 562 nm appears, characteristic of surface Plasmon absorption on the cefazolin@GNPs.

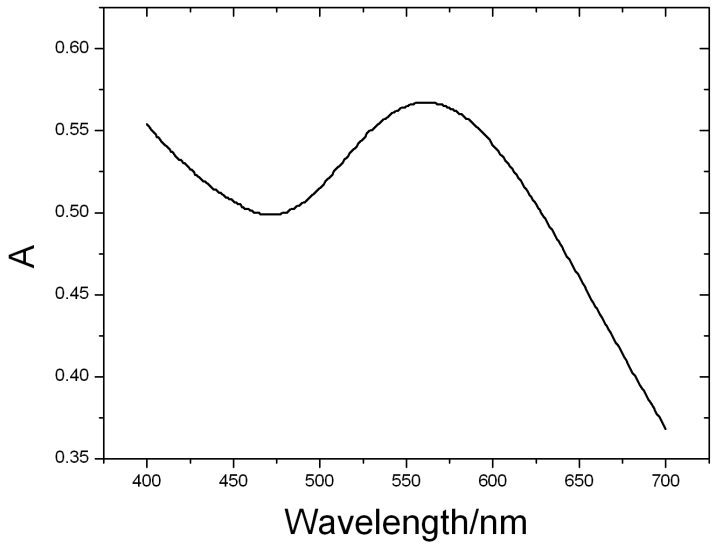

Figure 4. UV spectra of GNPs in absolute alcohol

3.5. CVs of GNPs modified PGE in the $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ system

The CVs of GNPs modified PGE in the $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ system was shown in **Fig. 5**. The real active surface area will be estimated. In a reversible process, the following Randles-Sevcik formula [14] at 298 K has been used: $i_p = 2.69 \times 10^5 n^{3/2} A C_o D_o^{1/2} \nu^{1/2}$.

From the slope of the plot of oxidation current (i_p) versus $\upsilon^{1/2}$, the electrode surface area of the cefazolin@GNPs/PGE, rinsed GNPs/PGE and the bare PGE is 0.115, 0.110 and 0.095 cm^2, respectively, indicating that the microscopic area of the rinsed GNP/PGE increased and was about 1.16 times larger than the microscopic area of the bare PGE.

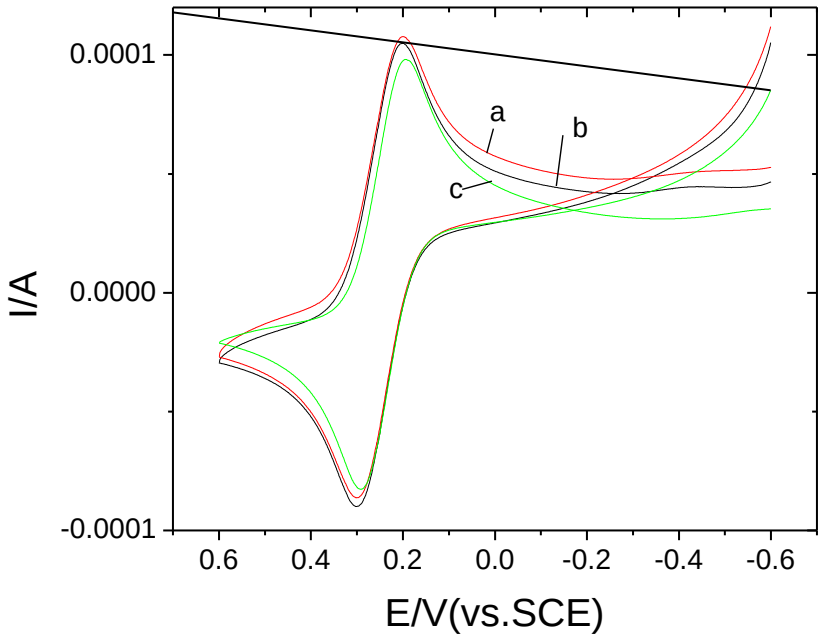

Figure 5. CVs of 5 mmol·L^{-1} $K_4[Fe(CN)_6]$ at the cefazolin@GNPs/PGE (a), rinsed GNPs/PGE (b) and bare PGE (c). Supporting electrolyte: 0.1 mol·L^{-1} KCl.

3.6. Comparison of two methods for preparation of the modified electrode

Dopamine is a very important catecholamine neurotransmitter in the mammalian central nervous system and is often monitored electrochemically in vivo with microfiber electrodes. The oxidation of such compounds is interesting, and this process occurs in the human body. Catecholamine drugs are also used to treat hypertension, bronchial asthma, and organic heart disease and are used in cardiac surgery and myocardial infarction [15, 16]. An understanding of the electrochemical reactions of dopamine is necessary to develop a method for studying their physiological function and to aid diagnosis of some diseases, because in clinical medicine it is often desirable to develop an electroanalytical method to study electron transfer processes. Numerous observations of the electrochemical behavior of dopamine and its analogs, such as epinephrine, have been made by many research groups [17–24]. However, it is still of great interest in the development of more efficient and stable materials for the electrocatalytic oxidation of dopamine and its analogs.

For studying the catalysis of modified electrode for dopamine, two methods were used for preparation of the modified electrode. The absorbing method is usually used for the preparation of the modified electrode [25, 26]. Cefazolin@GNPs solution of 5 μL was placed directly onto the cleaned PGE surface to form GNPs film, after 24 hours storage in the air, the PGE was rinsed thoroughly with water for 10 minutes, thus cefazolin@GNP/PGE prepared by absorbing method was obtained. Another rinsed GNP/PGE obtained by electrochemical synthesis is used.

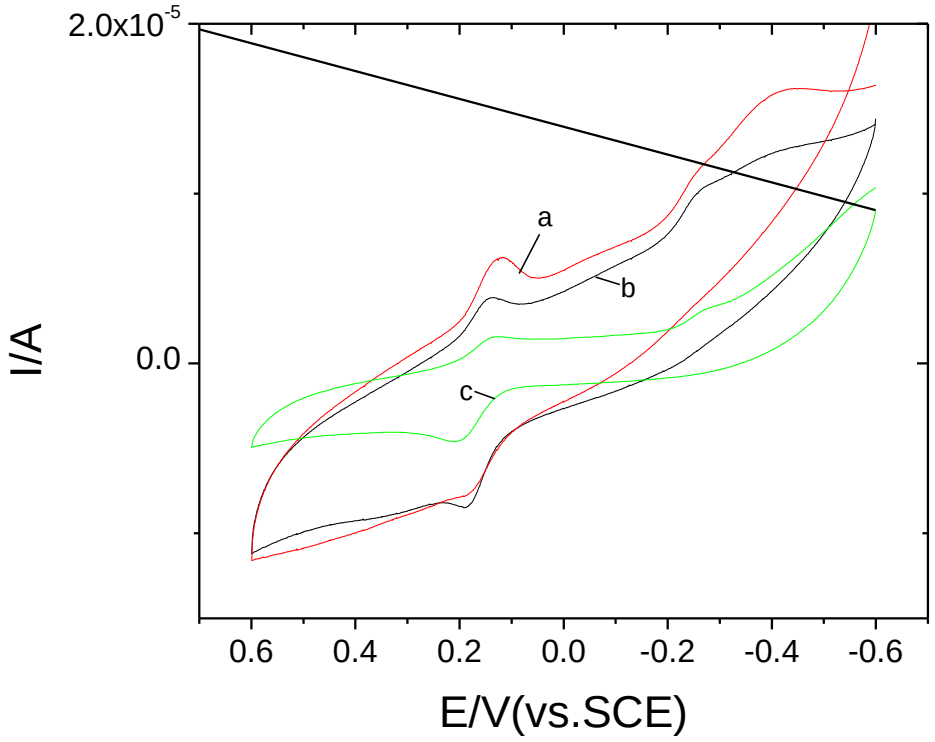

Figure 6. CVs of 10.0 mg·L^{-1} dopamine at cefazolin@GNP/PGE prepared by absorbing method (a), the rinsed GNPs/PGE (b) and bare PGE (c). Scan rate: 100.0 mV·s^{-1}.Supporting electrolyte: 0.1 mol·L^{-1} PBS of pH 7.3.

The CVs of dopamine at bare PGE, cefazolin@GNP/PGE prepared by absorbing method and rinsed GNP/PGE were shown in Fig. 6. The oxidation peak potential for dopamine at bare PGE appeared at 0.206 V, the reduction peak was found at 0.138 V and its oxidation peak currents was 2.552 μA. While the oxidation potential for dopamine at cefazolin@GNP/PGE prepared by absorbing method and rinsed GNP/PGE were observed at 0.184 and 0.187 V, their oxidation peak currents are 3.077 and 4.493 μA, and their reduction peak appeared at 0.122 and 0.146 V, respectively. The results is in agreement with the previous work [1,2]. The potential difference of reduction peak at the cefazolin@GNP/PGE prepared by absorbing method, rinsed GNPs/PGE and bare PGE is 68, 41 and 62 mV, respectively. The notably increased peak current and decreased peak potential deference demonstrate that the two modified electrodes can be used as a catalytic mediator to facilitate the electron transfer of dopamine oxidation, which is essential for the sensitive quantitative determination of dopamine. The phenomena exhibit that the catalysis ability of GNPs on the surface of PGE prepared by electrochemical deposition is stronger [27]. The results may be ascribed to the well dispersion of GNPs on the surface of GCE prepared by electrochemical deposition. To characterize the reproducibility and stability, the two kinds of modified electrode was used continuously for ten days and storing under ambient conditions. The rinsed GNP/PGE retained 95.2% of its initial peak current response with relative standard deviation (RSD) of 1.7% (n = 12) in 10.0 $mg \cdot L^{-1}$ dopamine. However, the cefazolin@GNP/PGE prepared by absorbing method retained 86.5% of its initial peak current response with RSD of 3.8 % (n = 12) for a dopamine concentration of 10.00 $mg \cdot L^{-1}$.The results indicate that the rinsed GNPs/PGE prepared by electrodeposited exhibits several attractive features such as the high sensitivity, long-term stability and good reproducibility.

4. CONCLUSIONS

The GNPs on the surface of PGE was prepared in the presence of cefazolin and its characterization was studied in this paper. The well-dispersed ceftriaxone@GNPs could be obtained on the surface of PGE indicating that cefazolin is an excellent stabilizing reagent. The catalysis for dopamine of GNP/PGE modified by electrode deposition is better than that of modified by absorption method. The electrochemical synthesis of GNPs on the surface of PGE is simple, cheap, and rapid, and the rinsed GNP/GCE has a good reproducibility and repeatability.

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