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Synthesis of Gold Nanoparticles Using Cefopernazone as a Stabilizing Reagent and Its Application

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Synthesis of gold nanoparticles using cefopernazone as a stabilizing reagent for a sensor was proposed. The gold nanoparticles were characterized by scanning electron microscopy, transmission electron microscopy, infrared spectrometry, ultraviolet- visible spectrophotometry, powder X-ray diffraction and cyclic voltammetry. The catalytic properties of gold nanoparticles on the glassy carbon electrode for dopamine were demonstrated. The results indicate that gold nanoparticle the modified electrode by means of electrochemical synthesis has an excellent repeatability and reproducibility.

Keywords: gold nanoparticles, cefopernazone, catalytic properties

1. INTRODUCTION

Gold nanoparticles (GNPs) have received great interests due to their attractive electronic, optical, and thermal properties as well as catalytic properties and potential applications in the fields of physics, chemistry, biology, medicine, and material science and their different interdisciplinary fields [1]. The reduction of $HAuCl_4$ is the most used methods for the preparation of GNPs in aqueous solution, and the molecule with functional groups (COOH, OH, SH, NH_2) is suitable cap for the preparation of GNPs [2-5], reductants such as ascorbic acid [6], citrate [7–9], and borohydride [10, 11] have been used in this reaction. Electrochemical deposition of metal nanoparticles has been found as better alternative because of their flexibility in controlling the size and coverage of the metalnanoparticles [12, 13].The adsorption method is used commonly for preparation of the sensor [14-18], the materials such as GNP- multi-walled carbon nanotubes [14], GNP-chitosan [15], Au–Ag

alloy nanoparticles [16], GNP-ssDNA [17], GNP-poly-eriochrome [18] have been proposed for the sensors. However, when stirring the solution for renewing the modified electrode, the materials on the surface of GCE removed easily due to the preparation of sensors by means of adsorption method. Cefoperazone, formerly known as cefoperazone sodium, is a sterile, semisynthetic, broad-spectrum, parenteral cephalosporin antibiotic for intravenous or intramuscular administration. It is the sodium salt of 7-[(*R*)-2-(4-ethyl-2, 3-dioxo- 1-piperazinecar boxamido)-2-(*p*-hydroxyphenyl)acetamido-3-[[(1-methyl-*H*-tetrazol-5-yl)thio]methyl]-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylate [19].

In present work, cefopernazone as a stabilizing reagent was used for electrochemical synthesis of GNPs on the surface of glassy carbon electrode (GCE) and preparation of GNPs in aqueous solution for the sensor. The catalysis of GNPs for dopamine at GNP/GCE was demonstrated. The electrochemical synthesis of GNPs on the surface of glassy carbon is simple, cheap, and rapid.

2. EXPERIMENTAL

2.1. Materials

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

2.2. Preparation of GNPs

The GNPs were deposited at a voltage of −0.2 V for 30 s on the surface of GCE that was immersed in the mixture of $HAuCl_4$ (2.0 $mg.mL^{-1}$), H_2SO_4 (0.5 M) and cefopernazone sodium (0.4 $mg.mL^{-1}$), and then washed in doubly distilled water. In the typical synthetic process of GNPs in aqueous solution, 0.150 g of $NaBH_4$ were dissolved into the mixture of 2.0 $mg.mL^{-1}$ $HAuCl_4$, 0.5 $mol.L^{-1}$ H_2SO_4 and 0.4 $mg.mL^{-1}$ cefopernazone sodium. The solution was stirred with a magnetic stirrer for 10min to ensure that the $NaBH_4$ completely dissolved; the black 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

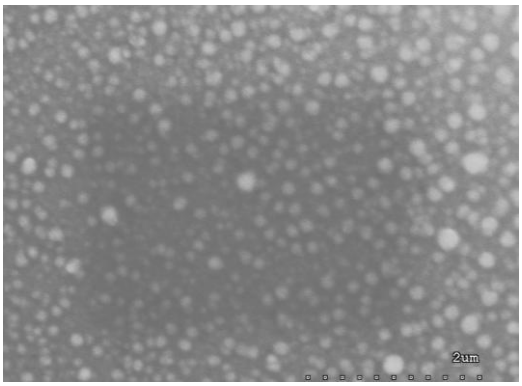
For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The GNP modified GCE was used as working electrode, a platinum wire served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. A S—3000N/EMAX—250 scanning electron microscope (SEM) (HITACHI, Japan) was used to study the shape and particle size of GNPs on the surface of GCE. The samples examined in the transmission electron microscope (TEM) were prepared by dispersing these samples in absolute alcohol followed by

ultrasonic vibration for half an hour. A drop of the dispersed sample was placed onto a copper grid coated with a layer of amorphous carbon. A JEM 2100 transmission electron microscope (JEOL, Japan) was used to study the shape and particle size of the samples. The electronic absorption spectra were obtained using a Shimadzu UV-1750 ultraviolet-visible spectrometer (Japan). Powder X-ray diffraction (XRD) spectra were recorded on a Switzerland ARL/X'TRA X-ray diffractometer rotating anode with Cu-Kα radiation source (λ = 1.54056 ° A). IR spectra were measured by a NICOLET NEXUS470 spectrometer in the frequency range 4000–400cm^{-1}.

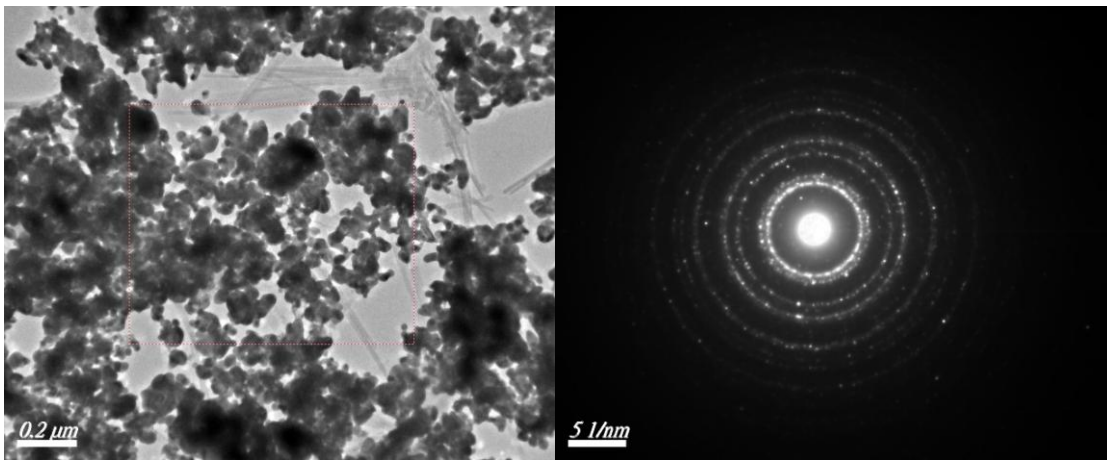
3. RESULTS AND DISCUSSION

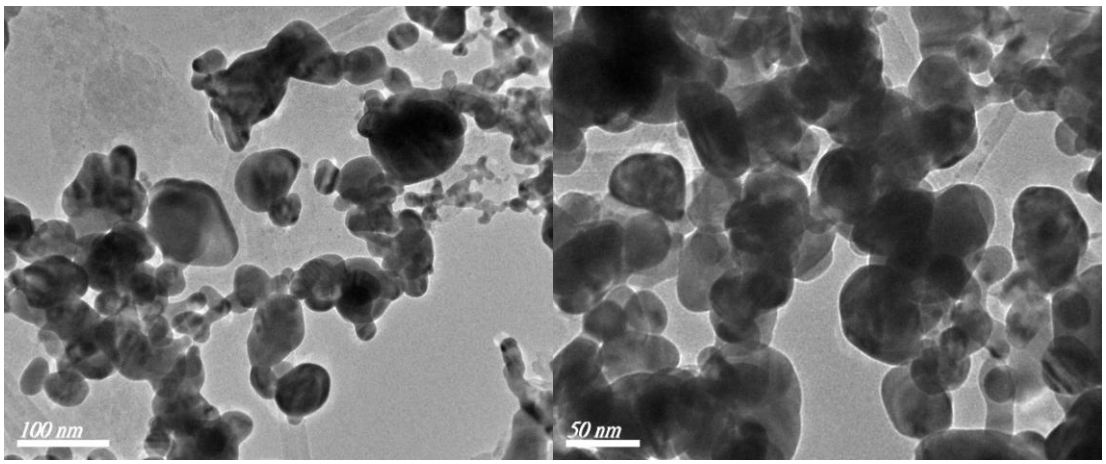
3.1. SEM and TEM images of GNPs

SEM images confirm the formation of a layer of GNPs on the GCE surface, several GNPs on the surface of GCE were observed in Fig. 1a, indicating that the well dispersed GNPs on the surface of GCE were obtained; the size of GNPs on the surface would be controlled by the electrochemical depositing time of $HAuCl_4$ and reduction potential.



a





b

Figure 1. SEM (A) and TEM (B) images of GNPs

The TEM images of GNPs obtained from aqueous solution were shown in Fig. 1b, the size of GNPs is about 25～100nm, the diffraction ring indicated that the GNPs of polycrystalline structure were obtained. The GNPs on the GCE surface are similar to those in aqueous. From the molecular structure of cefopernazone it can be seen that the gold atoms of surface of GNPs adsorb the negative ions (cefopernazone) with the polar groups such as carbonyl, carboxyl, and hydrophobic phenyl [19], the degree of ionization for cefopernazone is controlled by the concentration of sulphuric acid. Therefore, the cefopernazone@GNPs on the surface of GCE are well dispersed.

3.2. XRD of GNPs

The powder XRD pattern of the GNPs from aqueous solution is shown in Fig. 2. 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) [20].

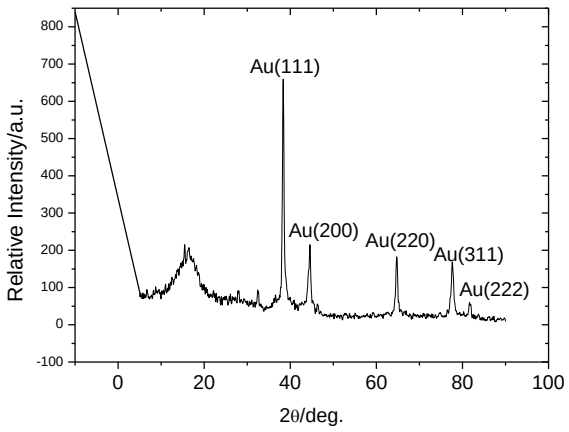


Figure 2. XRD pattern of GNPs obtained from aqueous solution

The diffraction peaks of GNPs appeared at 38.4°, 44.6°, 64.7°, 77.7°, and 81.5°, which can be assigned to (111), (200), (220), (311) and (222) crystalline plane diffraction peaks of gold, respectively. The results are in agreement with our previous work[22-25].

On the nanometer scale metals (most of them are face-centered cubic, or fcc) tend to nucleate and grow into twinned and multiply twinned particles with their surfaces bounded by the lowest-energy (111) facets [21]. Other morphologies with less stable facets have only been kinetically achieved by adding chemical capping reagents to the synthetic systems [26-29].

3.3. IR spectra of GNPs

The IR spectra of GNPs from aqueous solution and cefopernazone are shown in Fig. 3. From the IR spectra of cefopernazone, the bands at 3437,3345,3246 and 3110cm^{-1} could be assigned to the stretching vibrations of NH and OH, the bands of stretching vibrations of CH were found at 2940, 2898, and 2819 cm^{-1}, the band of stretching vibrations of C=O appeared at 1762, 1734, and 1649 cm^{-1}[30-32], and the peak at 1535cm^{-1} was associated with the torsional vibrations of aromatic hydrocarbon ring, the bands at 1393 and 1350cm^{-1} could be assigned to stretching vibrations of CN, and band of breath vibration of aromatic hydrocarbon ring was observed at 1045cm^{-1} [33].

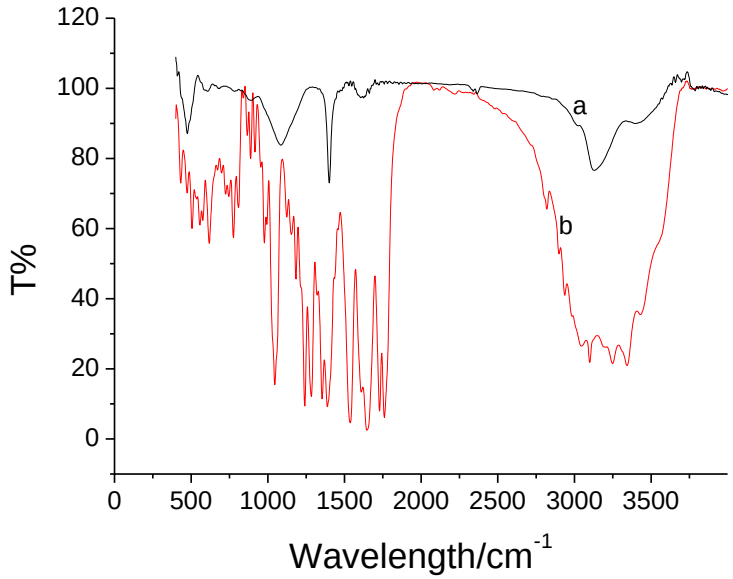


Figure 3. IR spectra of GNPs obtained from the surface of GCE (a) and cefopernazone (b)

However, the IR spectra of GNPs obtained from GCE, only the strong bands were observed. the bands of stretching vibrations of NH were found at 3423 and 3132 cm^{-1}, the bands at 1763 and 1613 cm^{-1} could be assigned to the stretching vibrations of C=O, and the bands of stretching vibrations of CN and the aromatic hydrocarbon ring were found at 1399 cm^{-1} and 1089 cm^{-1}, respectively, indicating cefopernazone was assembled on the surface of GNPs.

3.4. Cyclic voltammograms of GNPs

The Cyclic voltammograms (CVs) of GNPs on the surface of GCE in 0.1 M PBS of pH 7.3 are shown in Fig.4. The oxidation peak of cefopernazone@GNPs was found at 1.046 V, and the reduction peak was observed at 0.461 V. To remove cefopernazone on the surface of GNPs, the cefopernazone@GNPs modified GCE stirred with a magnetic stirrer was rinsed in 5 mol.L^{-1} H_2SO_4 aqueous solution and doubly distilled water for 10 min, sequentially. The peak potential of the rinsed GNPs shifted to positive direction, the oxidation current increases, and the reduction current decreases, indicating the cefopernazone on the surface of GNPs is removed. The CVs of cefopernazone at GCE are shown in Fig.4 (Insert Fig.), a oxidation peaks was observed at 1.113 V, which assigned to the sulphur atoms in cefopernazone; the reduction peak of cefopernazone in a neutral medium (phosphate buffer, pH 7.0) with CV, differential pulse voltammetry (DPV) and square-wave voltammetry (SWV) was found at about –1.1V [34], while no reduction peak was found in this paper, indicating that cefopernazone is stable under electrochemical synthesis of cefopernazone@GNPs at -0.2 V.

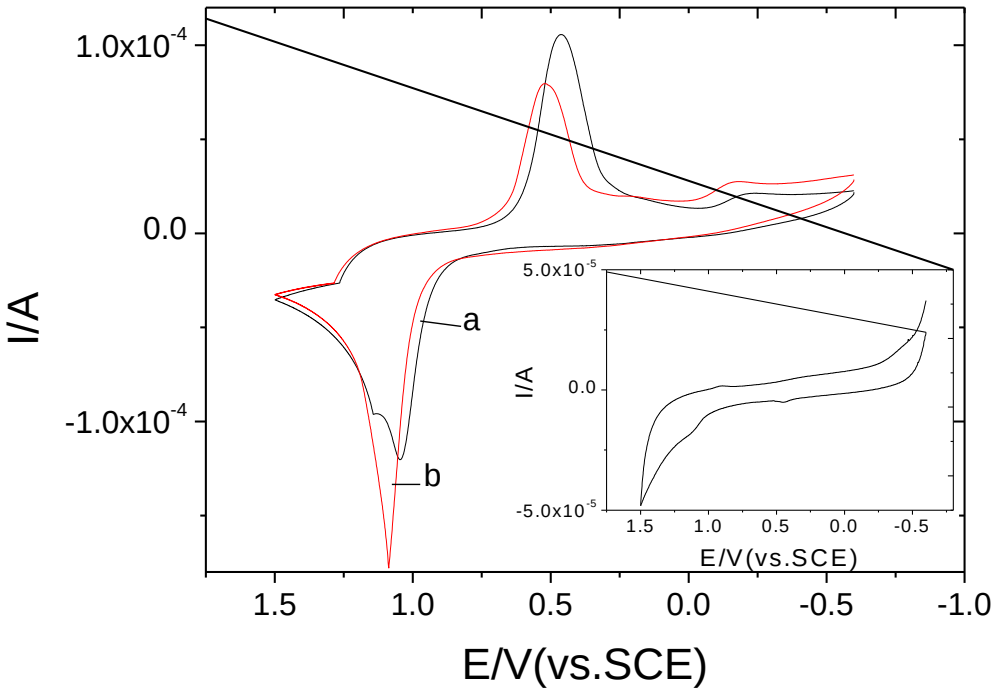


Figure 4. CVs of cefopernazone@GNPs (a) and the rinsed GNPsGNPs (b). Supporting electrolyte: 0.1 mol.L^{-1} PBS of pH7.3. Insert Figure: CV of 0.4mg/mL cefopernazone sodium at GCE, supporting electrolyte: 0.5 mol.L^{-1} H_2SO_4。

3.5. UV spectra of GNPs

Fig. 5 shows the UV absorption spectrum of the GNPs obtained from aqueous solution. A broad band centered at ca. 600nm appears, characteristic of surface plasmon absorption on the GNPs.

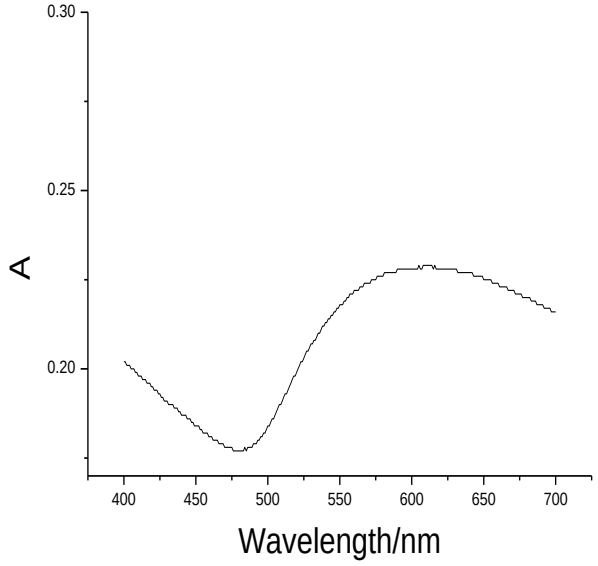


Figure 5. UV-spectra of GNPs in absolute alcohol

3.6. Electrochemical catalysis of GNP and application

Dopamine is important in the regulation of sodium balance and blood pressure via renal mechanisms [35]. The affinity of dopamine for its receptors is in the nanomolar range; higher concentrations occupy other G-protein-coupled receptor [35]. Circulating dopamine concentrations (picomolar range) are not sufficiently high to activate dopamine receptors, but high nanomolar concentrations can be attained in dopamine-producing tissues (e.g., renal proximal tubule, jejunum). The concentration of dopamine is controlled by not only the taking drugs but also the human emotion. Therefore, the determination of dopamine in blood is important.

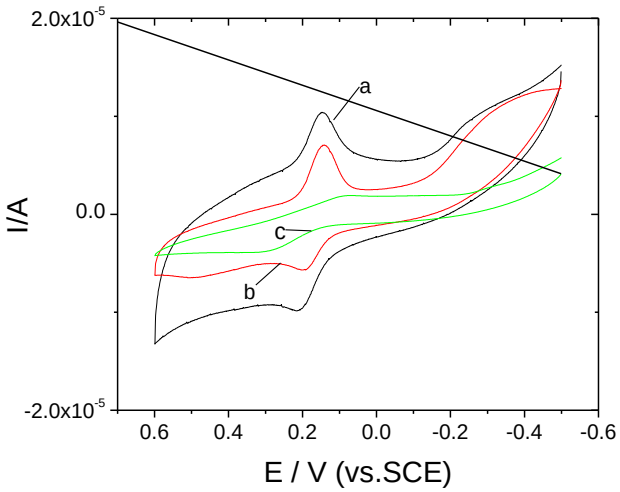


Figure 6. CVs of 10.0 mg.L^{-1} dopamine at cefopernazone@GNP/GCE (a), the rinsed GNP/GCE (b) and bare GCE (c). Scan rate: 100.0 mV.s^{-1}.Supporting electrolyte: 0.1 mol.L^{-1} PBS of pH 7.3.

The CVs of dopamine at bare GCE, cefopernazone@GNP/GCE and rinsed GNP/GCE are shown in Fig.6, respectively.

The peak and current of dopamine at bare GCE, cefopernazone@GNP/GCE, and rinsed GNP/GCE are summarized in Table 1. The oxidation potential for dopamine at the rinsed GNP/GCE and cefopernazone@GNP/GCE are less than that of dopamine at bare GCE, and their currents are higher than that of dopamine at bare GCE. However, the oxidation currents for dopamine at the cefopernazone@GNP/GCE are higher than that of dopamine at the rinsed GNP/GCE, and the reduction currents for dopamine at the cefopernazone@GNP/GCE are lower than that of dopamine at the rinsed GNP/GCE, indicating that cefopernazone catalyze the electro-oxidation of dopamine due to the formation of hydrogen bond between nitrogen atoms in cefopernazone and hydroxyl groups in dopamine. The reduction currents decrease due to the disappearance of hydroxyl groups in cefopernazone.

Table 1. Peak and current of dopamine

Electrode	Oxidation peak(V)	Oxidation current (μA)	Reduction peak (V)	Reduction current (μA)
Bare GCE	0.286	1.834	0.073	0.955
GNP/ GCE	0.192	3.437	0.141	4.893
cefopernazone@GNP/GCE	0.216	5.432	0.146	4.197

To assess the applicability of the proposed method, the GNP/GCE was used to determination of the content of dopamine injection by applying CV method. The oxidation peak currents of dopamine at GNP/GCE were proportional to dopamine concentrations in the range of 0.10mg.L^{-1} to 1.80 mg.L^{-1} in 0.1M PBS of pH 7.3. The linear regression equation is obtained as c (mg.L^{-1})=0.2731 I_{pa} (μA) - 0.2183 (R=0.998). The detection limit (3σ/slope, where σ is the standard deviation of the intercept and s is the slope of the calibration curve) observed for dopamine is 0.09 mg.L^{-1}. 1-5.00 μL of 1g.L^{-1} dopamine injection was diluted to 5.0 ml with 0.1M PBS of pH 7.3. The recoveries were in the range from 97.8 to 102.0%. Using this standard addition method, the content for the diluted dopamine is obtained to be 0.22～1.03 mg.L^{-1} with RSD of 1.7～2.2% (n=6). The working range and detection limit are close to the reports [36-40].

3.7. Comparison of two preparation methods for the sensor

On using the rinsed GNP/GCE daily and storing under ambient conditions over a period of 2 month, and after stirring at 500rpm/min with a magnetic stirring apparatus for 2h, the electrode retained 98.5% of its initial peak current response with relative standard deviation (RSD) of 2.4% (n=25) for a dopamine concentration of 10.00 mg.L^{-1}, which shows long-term stability of the film modifier on the surface of GCE. The results indicate that the rinsed GNP/GCE has an excellent

repeatability and reproducibility. However, the GNPs obtained from aqueous solution was dropped on the surface of GCE as the adsorption method, followed by storage at 14 °C for 24h, after stirring at 500rpm/min with a magnetic stirring apparatus for 2h the modified GCE retained 78.5% of its initial peak current response with relative standard deviation (RSD) of 4.7% (n=25) for a dopamine concentration of 10.00 $mg.L^{-1}$. The results indicate that the modified electrode has an excellent repeatability and reproducibility.

4. CONCLUSIONS

The GNPs on the surface of GCE and in aqueous solution using cefopernazone as a stabilizing reagent were prepared in this paper, and the catalysis of GNPs for dopamine was demonstrated. The electrochemical synthesis of GNPs on the surface of glassy carbon is simple, cheap, and rapid, and the rinsed GNP/GCE has an excellent repeatability and reproducibility.

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