L-cysteine-nano-gold modified glassy carbon electrode and its application for determination of dopamine hydrochloride

Yang Song, Yuan-Zhi Song*, An-Feng Zhu & Hui Zhong

*College of Materials Science and Engineering, Beijing University of Chemical Technology, Peking 100029, People’s Republic of China
Email: songyuanzhi@126.com

Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry & Chemical Engineering, Huaiyin Normal University, Huai An 223300, People’s Republic of China

Received 8 March 2011; revised and accepted 20 June 2011

A sensor based on l-cysteine-gold-nanoparticle modified glassy carbon electrode has been prepared. Electrochemical behaviour of dopamine hydrochloride at l-cysteine-gold-nanoparticle modified glassy carbon electrode is investigated. A simple, sensitive, and inexpensive method for determination of dopamine hydrochloride is proposed.

Keywords: Electrochemistry, Sensors, Modified electrode, Gold, Dopamine hydrochloride

Gold nanoparticles (GNs) are particularly attractive for several investigations due to their facile synthesis, the large specific surface area, high surface free energy, good conductivity, optical properties, high chemical ability, favourable biocompatibility, and catalytic applications. L-cysteine exhibits excellent electrochemical activity and the use of l-cysteine for the preparation of self-assembled monolayers on gold surfaces has been reported widely in many literatures.

Dopamine is the immediate precursor of epinephrine in the body. Exogenously administered, it produces direct stimulation of beta-1 receptors and variable stimulation of alpha receptors (peripheral vasoconstriction). It causes a release of norepinephrine from its storage sites. These actions result in increased myocardial contraction and increased renal blood flow and sodium excretion. Dopamine hydrochloride injection as a drug is a clear, practically colourless, sterile, pyrogen-free, aqueous solution of dopamine HCl for intravenous infusion after dilution.

In present work, a simple, sensitive, and inexpensive sensor based on l-cysteine-gold-nanoparticle (CGN) modified glassy carbon electrode (GCE) is prepared. Electrochemical behaviour of dopamine hydrochloride at the CGN modified electrode is investigated.

Experimental

All reagents used herein were of analytical grade. Doubly distilled water was used throughout. Phosphate buffer solution (0.1 M) was prepared by dissolving 0.1 mol NaCl and 0.1 mol Na₂HPO₄ in 1000 mL doubly distilled water of and adjusting to the desired pH values with 6 M HCl or 1 M NaOH.

For all electrochemical experiments, a CHI660B electrochemical analyzer (CHI, A) was employed. The electrochemical cells consisted of a three-electrode system. The CGN composite-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. The l-cysteine-gold-nanoparticles were characterized by transmission electron microscopy (JEM 2100, JEOL, Japan).

The GCE was polished with 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with doubly distilled water, and then sonicated in ethanol and doubly distilled water for 10 min, sequentially. The gold nanoparticles were deposited at a voltage of −0.2 V for 30 s on the clean GCE that was immersed in HAuCl₄ solution (2 mg mL⁻¹), and then washed in doubly distilled water. The obtained gold nanoparticles-modified GCE was immersed in 1 mg mL⁻¹ l-cysteine solution for 24 h, and then washed in doubly distilled water. Before the voltammetric measurements, the modified electrode was cycled between −0.6 and 0.6 V (scan rate 100 mV. s⁻¹) in 0.1 M phosphate buffer solution of pH 7.3 several times until reproducible responses were acquired.

Results and discussion

TEM images confirm the formation of a layer of film on the GCE surface. The TEM image of CGN (Fig. 1) shows several l-cysteine-gold-nanoparticles on the surface of the glassy carbon electrode, indicating that l-cysteine-gold-nanoparticles have been assembled on the electrode surface.

The cyclic voltammetry (CV) of l-cysteine-gold-nanoparticles-modified GCE in the K₃Fe(CN)₆–
The system is shown in Fig. 2. Compared with the bare GCE, the gold nanoparticles-GCE and the l-cysteine-gold-nanoparticles-modified GCE show higher peak current.

The increase in voltammetric response of ferrocyanide is simply due to the intrinsic properties of the CGN, which produce a larger peak current than the bare GCE. In a reversible process, the Randles-Sevcik formula has been used to estimate the active surface area,

\[ i_{p,a} = 2.69 \times 10^5 n^{3/2} A C_0 D_o^{1/2} v^{1/2} \]

where, \( i_{p,a} \) refers to the anodic peak current, \( n \) is the electron transfer number, \( A \) is the microscopic surface area of the electrode, \( D_o \) is the diffusion coefficient of \( K_4[Fe(CN)_6] \), \( C_0 \) is the bulk concentration of \( K_4[Fe(CN)_6] \), and \( v \) is the scan rate (V s\(^{-1}\)). From the slope of the plot of oxidation current (\( i_{p,a} \)) versus \( v^{1/2} \), the electrode surface areas of the CGN-modified GCE, gold nanoparticle-modified GCE and the bare GCE were found to be 0.084, 0.071 and 0.060 cm\(^2\), respectively, indicating that the microscopic area of the CGN-modified GCE increased significantly and was about 1.40 times larger than that of the bare GCE.

The oxidation peaks for dopamine hydrochloride at bare GCE, GN modified GCE and CGN modified GCE are observed at 0.447, 0.255 and 0.223 V (Fig. 3), respectively, while the reduction peak for dopamine hydrochloride at bare GCE, GN modified GCE and CGN modified GCE are found at 0.018, 0.084 and 0.095V, respectively.

The oxidation peaks for dopamine hydrochloride at CGN-modified GCE is less than that of dopamine hydrochloride at bare GCE and GN modified GCE, while the reduction peak for dopamine hydrochloride at CGN-modified GCE is more than that of dopamine hydrochloride at the GN-modified GCE and bare GCE, with increase in its peak current. The electrochemical response of CGN-modified GCE in 0.1 M phosphate buffer solution of pH 7.3 is shown in Fig. 3(Inset). It can be seen that no oxidation peaks of blank CV are found on the bare GCE, GN-modified GCE and CGN-modified GCE. These results indicated that the CGN-modified electrode promoted the electrochemical oxidation/reduction of dopamine hydrochloride by considerably accelerating the rate of electron transfer.

The CV investigations for 50.0 mg L\(^{-1}\) dopamine hydrochloride were carried out on the surface of the CGN-modified GCE in buffered solution of pH 7.3 at different potential sweep rates. Figure 4 illustrates the influence of scan rate on the CVs of 50.0 mg L\(^{-1}\) dopamine hydrochloride in the range of 10–1000 mV s\(^{-1}\).
The linear relationship between peak current (oxidation current: $I_{pa}$; reduction current: $I_{pc}$) of 50.0 mg L$^{-1}$ dopamine hydrochloride and $v^{1/2}$ in the range of 10 – 300 mV s$^{-1}$ (Fig. 4, inset) indicates a diffusion controlled process on the surface of the modified electrode. The regression equations for this relationship are obtained as: $I_{pa} = -51.7000 \cdot v^{1/2} - 4.7996$ ($r = 0.998$) and $I_{pc} = 46.0650 \cdot v^{1/2} + 0.1988$, $r = 0.990$ ($I$: µA; $v$: V s$^{-1}$).

The relationship between the oxidation peak current and the concentration of dopamine hydrochloride was examined by CVs on the surface of CGN modified GCE (Fig. 5). Under the earlier mentioned optimum conditions, the oxidation peak currents are proportional to dopamine hydrochloride concentrations in the range of 2.0 mg L$^{-1}$ – 110.0 mg L$^{-1}$ in 0.1 M phosphate buffer solution of pH 7.3. The linear regression equation was obtained as $c$ (mg L$^{-1}$) = 2.5868 (µA) – 6.6329 ($R = 0.996$). The detection limit (3σ/slope, where $\sigma$ is the standard deviation of the intercept and $s$ is the slope of the calibration curve) observed for dopamine hydrochloride was 0.3 mg L$^{-1}$.

The repeatability of the modified electrode was investigated at a fixed dopamine hydrochloride concentration of 50.0 mg L$^{-1}$. The relative standard deviation (RSD) for the peak currents in CVs based on six replicates was 1.2 %, indicating excellent repeatability of the response of the modified electrode. Also, on using the CGN-modified GCE daily and storing under ambient conditions over a period of 2 weeks, the electrode retained 98.3 % of its initial peak current response for a dopamine hydrochloride concentration of 50.0 mg L$^{-1}$, which shows long-term stability of the film modifier on the surface of GCE. The results indicate that the modified electrode has excellent repeatability and reproducibility.

To assess the applicability of the proposed method, the CGN modified-GCE was used to determine the content of dopamine hydrochloride in injections by the proposed method. Dopamine hydrochloride injection (2.00 – 10.00 µL in 10.0 g L$^{-1}$) was diluted to 5.00 mL with 0.1 M phosphate buffer solution of pH 7.3, and analysed by the standard addition method with the proposed CGN modified-GCE. The recoveries were in the range of 99.7 – 102.4 % RSD of 1.6 – 2.3% ($n = 6$).

In conclusion, it has been demonstrated that modification of GCE with CGN is a simple and effective method for obtaining highly sensitive electrodes for determination of dopamine hydrochloride. The procedure enables preparation of highly stable and reproducible uniform modifier films, which leads to considerable enhancement in repeatability and reproducibility in the voltammetric measurements. High sensitivity and improved detection limit of the CGN modified GCE are promising for the determination of dopamine hydrochloride injection.
Acknowledgement
This research was supported by the National Science Foundation of China (Grant No. 20975043) and Jiangsu Higher Institution Key Basic Research Projects of Natural Science (Grant No. 7KJA15012).

References