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## Q1 Application of nanosized gold and graphene modified carbon ionic liquid electrode for the sensitive electrochemical determination of folic acid

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### ABSTRACT

In this study a new electrochemical folic acid (FA) sensor was proposed by using gold nanoparticles (AuNPs) and graphene (GR) modified carbon ionic liquid electrode (CILE) as the working electrode. GR and AuNPs were directly electroreduced on the surface of CILE to get the modified electrode, which exhibited excellent electrochemical performances due to the specific characteristics including higher conductivity and larger surface area. The modified electrode showed excellent electrocatalytic ability to the oxidation of FA with an irreversible oxidation peak appeared at +1.05 V (vs. SCE) in pH 5.5 phosphate buffer solution. Electrochemical behaviors of FA on the modified electrode were carefully investigated with the electrochemical parameters calculated. Under the optimal conditions and by using differential pulse voltammetry, the oxidation peak currents were linear to FA concentration in the range from 0.01  $\mu\text{mol L}^{-1}$  to 50.0  $\mu\text{mol L}^{-1}$  with the detection limit as 2.7  $\text{nmol L}^{-1}$  (3 $\sigma$ ). The proposed method was successfully applied to the FA tablet sample determination with satisfactory results.

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### 1. Introduction

Folic acid (FA) is an important component of the hemopoietic system, which acts as the coenzyme that controls the generation of ferroheme [1]. The decrease of the concentration of FA in human body fluids could result in some diseases such as gigantocytic anemia, leucopenia, devolution of mentality, and psychosis, and increase the possibility of heart attack and stroke [2]. Because FA and vitamin B<sub>12</sub> can participate in the nucleotide synthesis, cell division and gene expression, so the diminished folate status would be associated with enhanced carcinogenesis [3]. Different kinds of analytical methods have been devised for the measurement of FA, such as spectrophotometry [4], capillary electrophoresis [5] and HPLC [6]. Due to the electroactivity of FA, electrochemical methods have been used for the detection of FA with the advantages including less expensive instruments, more convenient procedure, good selectivity and sensitivity [7,8]. For example, Fernandez et al. investigated the adsorption behaviors of FA on the mercury electrode with adsorptive stripping voltammetry [9]. Prasad et al. fabricated a hyperbranched molecularly imprinted polymer-immobilized pencil graphite electrode for the electrochemical detection of FA [10]. Xiao et al. applied a single-walled carbon nanotube-ionic liquid (IL) paste electrode for the sensitive voltammetric determination of FA [11]. Arvand et al. fabricated a gold nanoparticle (AuNP) modified carbon paste electrode (CPE) for the detection of FA [12]. Recently Babakhanian

et al. developed a  $\alpha$ -polyoxometalate–polypyrrole–AuNP modified gold electrode for the electrochemical detection of FA [13]. Taherkhani et al. fabricated a ZnO nanoparticle and IL modified electrode for the voltammetric determination of FA in food and pharmaceutical samples [14]. Jamali et al. described a nanoalloy (Pt:Co) and IL modified CPE for the voltammetric determination of FA in food samples [15].

Recently graphene (GR) has been the research focus due to its specific characteristics such as extremely high thermal conductivity, good mechanical strength, high mobility of charge carriers, large specific surface area and outstanding electrical properties [16,17]. The preparation and applications of GR and its related composite have also been reviewed [18]. Among various methods for the synthesis of GR based composite, electrochemical methods have been reported as an efficient procedure with the advantages including green, fast and easy to control without the usage of dangerous reagents. The oxygen-containing group on graphene oxide (GO) can be directly reduced by electrochemical method to get the electrochemical reduced GO (ERGO) [19]. In addition, other nanoparticles can also be deposited on the surface of ERGO to give a composite material at the same time [20,21]. Chen et al. prepared the GR-based composite by electrochemical methods and applied to the fabrication of electrochemical devices [22]. Our groups also investigated the electrochemical application of GR–metal nanocomposite in the field of protein electrochemistry [23] or electrochemical DNA sensor [24].

IL has exhibited many specific properties such as high ionic conductivity and wide electrochemical windows, which can be used as a new kind of binder/modifier for chemically modified electrodes [25,26]. Karimi-Maleh's group applied various nanomaterials and the mixture

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with IL to prepare a modified CPE, which were applied to detection of electroactive compounds in different samples [27–29]. By incorporating IL into the CPE, the fabricated carbon ionic liquid electrode (CILE) had exhibited many advantages such as easy preparation, good reversibility, high sensitivity and the ability to lower the overpotential of electroactive compounds. Therefore CILE has been used as the working electrode in the field of electrochemical sensor [30,31].

In this paper a CILE was prepared by using N-hexylpyridinium hexafluorophosphate (HPPF<sub>6</sub>) as the modifier and the binder [25], and further used as the working electrode. Then GR and AuNPs were electrodeposited on the surface of CILE by potentiostatic electroreduction to get a nanocomposite modified electrode, which exhibited better electrochemical performance with good stability. Electrochemical behaviors of FA on the modified electrode were carefully investigated and a new electrochemical method for the sensitive determination of FA was further developed.

## 2. Experimental

### 2.1. Apparatus

All the electrochemical experiments including cyclic voltammetry, differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were performed on a CHI 750B electrochemical workstation (Shanghai CH Instrument, China). A conventional three-electrode system was used, which was composed of an Au/ERGO/CILE as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. Scanning electron microscopy (SEM) was recorded on a JSM-7100 F scanning electron microscope (Japan Electron Company, Japan).

### 2.2. Reagents

HPPF<sub>6</sub> (>99% Lanzhou Greenchem, ILS, LICP, CAS, China), FA (Aladdin Chem. Ltd., Co., China), chloroauric acid (HAuCl<sub>4</sub>, Shanghai Chem. Plant, China), graphite powder (average particle size 30 μm, Shanghai Colloid Chem. Ltd., Co., China) and graphene oxide (GO, Taiyuan Tanmei Ltd., Co., China) were used as received. 0.1 mol L<sup>-1</sup> phosphate buffer solution (PBS) with various pH values was used as the supporting electrolyte. All the other chemicals used were of analytical reagent grade and doubly distilled water was used in the experiments.

### 2.3. Fabrication of the modified electrode

CILE was fabricated according to the former reported procedure [25]. In detail 3.2 g of graphite powder and 1.6 g of HPPF<sub>6</sub> were mixed thoroughly in a mortar, and further heated at 80 °C for 10 min to form a homogeneous carbon paste. Then a portion of the carbon paste was filled into one end of a glass tube (Φ = 4 mm) and a copper wire was inserted through the opposite end to establish an electrical contact. Prior to use, a mirror-like surface can be obtained by polishing the electrode on a weighing paper.

The Au/ERGO/CILE was further prepared based on a reported procedure [23]. In brief, a freshly prepared CILE was placed in the 1.0 mg mL<sup>-1</sup> GO dispersion with a magnetic stirring and N<sub>2</sub> bubbling. By applying the potential of -1.3 V for 300 s, a stable ERGO film can be formed on the surface of CILE (ERGO/CILE). Then AuNPs were further electrodeposited on the surface of ERGO/CILE by applying the potential of -0.4 V for 300 s in a 5.0 mmol L<sup>-1</sup> HAuCl<sub>4</sub> solution. The fabricated Au/ERGO/CILE was rinsed with doubly distilled water and dried in air for further usage.

### 2.4. Electrochemical procedure

The three-electrode system was inserted into a 10 mL electrochemical cell containing 0.1 mol L<sup>-1</sup> PBS and certain amount of FA solution.

After accumulating at open circuit for 450 s, cyclic voltammetric scan was recorded in the potential range from 0.6 V to 1.6 V. As for the DPV experiments, the instrumental parameters were selected as follows: pulse amplitude, 0.05 V; pulse width, 0.05 s; sample width, 0.0167 s; pulse period, 0.2 s; and quiet time, 2 s.

## 3. Results and discussion

### 3.1. SEM images of the modified electrode

Fig. 1 shows the SEM images of nanomaterial modified electrodes. The formation of ERGO film on the CILE surface could be observed on the SEM image with the layered structure appeared (Fig. 1A). Electrochemical reduction is a simple and efficient method for the preparation of nanomaterial modified electrode and the oxygen functionalities of GO can be directly reduced on the electrode surface at the negative potential. After electrodeposition of AuNPs on the ERGO/CILE surface, a dendritic structure appeared on the interface (Fig. 1B). The enlarged image further proved the formation of gold nanomaterial on the electrode surface (Fig. 1C), which exhibited an interesting dendritic structure along the branches of bone-axis. Therefore SEM results indicated that the nanostructured gold was deposited on the surface of ERGO.

### 3.2. Electrochemical properties of the modified electrodes

Electrochemical performances of different modified electrodes were investigated by various electrochemical techniques such as cyclic voltammetry and EIS. Cyclic voltammograms of CILE (curve a), ERGO/CILE (curve b) and Au/ERGO/CILE (curve c) were recorded in a 1.0 mmol L<sup>-1</sup> [Fe(CN)<sub>6</sub>]<sup>3-</sup> solution with the results shown in Fig. 2A and all the cyclic voltammetric data are summarized in Table 1. On CILE a pair of well-defined redox peaks appeared (curve a), indicating CILE exhibited excellent electrochemical performances due to the good electrochemical properties of IL in the CPE. On ERGO/CILE the redox peak currents increased with the decrease of ΔE<sub>p</sub> value (curve b), which could be ascribed to the formation of ERGO on the CILE surface. The good conductive GR on the electrode surface can result in the fast electron transfer with increase of the effective surface area. On Au/ERGO/CILE the biggest redox peaks appeared (curve c), which indicated the formation of AuNPs on the electrode. AuNPs with high conductivity can be directly electrodeposited on the electrode surface and the presence of ERGO can provide larger effective surface area for the formation of AuNPs. Therefore the electrochemical responses of [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> were further enhanced on the modified electrode. Also with the modification of ERGO and AuNPs step-by-step on the CILE surface, the redox peak currents increased gradually with the decrease of ΔE<sub>p</sub>, indicating that the electrochemical reaction of ferricyanide was enhanced with fast electron transfer rate. Therefore the Au/ERGO nanocomposite on the surface of CILE could provide a specific interface with higher conductivity and larger surface area.

EIS results can further provide the interfacial information during the modification process. The semicircle diameter of Nyquist plot reflects the electron transfer resistance (R<sub>et</sub>), which is resulted from the electron transfer of the redox probe [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup>. The AC voltage amplitude was set as 5 mV and the applied potential was 202 mV. By using a 10.0 mmol L<sup>-1</sup> [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> solution as the electrochemical probe, the Nyquist plots of different modified electrodes were recorded with the results shown in Fig. 2B. Here Z' and Z'' are the real variable and the negative value of the imaginary variable of impedance. The R<sub>et</sub> value of CILE (curve a), ERGO/CILE (curve b) and Au/ERGO/CILE (curve c) were got as 151.2 Ω, 46.8 Ω and 17.36 Ω, respectively. The gradually decrease of the interfacial resistance also proved that the presence of ERGO and AuNPs on the electrode surface could greatly decrease the resistance of electrode interface due to the excellent conductivity. The gradually decrease of interfacial resistance proved that the formation of high conductive ERGO and AuNPs on the CILE surface step-by-step.

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