



Controlled synthesis of partially reduced graphene oxide: Enhance electrochemical determination of isoniazid with high sensitivity and stability



Xiaofei Zhu^{a,b,1}, Jingkun Xu^{a,1}, Xuemin Duan^{a,*}, Limin Lu^{b,*}, Kaixin Zhang^a, Yongfang Yu^b, Huakun Xing^a, Yansha Gao^a, Liqi Dong^a, Hui Sun^a, Taotao Yang^a

^a School of Pharmacy, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China

^b College of Science, Jiangxi Agricultural University, Nanchang 330045, PR China

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ABSTRACT

Electrochemically reduced graphene oxide (ERGO) based voltammetric sensors have drawn considerable attentions due to their simple preparation process and outstanding electrochemical properties. While quite a lot of work suffers from problems in terms of sensitivity and cycling stability. Here, we demonstrate that the reduction extent of ERGO displays a crucial role in enhancing sensitivity and preventing electrode fouling. To illustrate this, partially reduced and relatively complete reduced ERGO films were prepared via the electrochemical method. The reduction extent was controlled by performing cyclic voltammetry with varieties of reduction cycle numbers. Results indicated that partially reduced ERGO film with 5 reduction cycle numbers (ERGO₅) showed the highest sensitivity towards electrochemical oxidation of isoniazid (INZ) among all the ERGO films with different reduction extents, and acquired better electrode stability as compared with ERGO₁₅. Under the optimal conditions, the peak currents on ERGO₅ modified electrode increased linearly with the concentrations of INZ in the range of 0.09–100 μM. The detection limit of INZ reached 15 nM (S/N = 3). The present work has a guidance meaning in developing ERGO based sensors for detecting other electroactive analytes.

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1. Introduction

Isoniazid (INZ) is an effective anti-tuberculosis drug that has been widely used for chemotherapy of tuberculosis. Unfortunately, frequent use of the drug by patients can induce hepatotoxicity and sometimes even cause death [1,2]. Therefore, it is important to quantify INZ level in human body fluids for effective therapeutic dosages. To date, different methods have been applied to detect INZ, including high performance liquid chromatography (HPLC) [3], fluorimetry [4], spectrophotometry [5], chemiluminescence [6] and capillary electrophoresis [7]. However, these methods suffer from disadvantages, such as expensive facilities, complex sample pretreatment and time-consuming. Electrochemical methods have been proven to be simple, fast, sensitive, and reliable for the determination of numerous electroactive drug components in pharmaceutical dosage forms and biological fluids [8–11]. However, many reported sensors for the electrochemical detection of INZ usually exist problems associated with electrode surface fouling caused by reaction products, which greatly influences their repeatability and sensitivity [12,13]. To meet this challenge, Majidi et al. [14] detected INZ using

an overoxidized polypyrrole modified glassy carbon modified electrode (GCE) to avoid electrode fouling. While Atta et al. [15] developed a PEDOT electrode to detect INZ in the presence of surface active agents. However, these methods are also imperfect in terms of unoptimistic detection limit and large oxidation overpotential. Therefore, it is necessary to develop a method for sensitive detection of INZ without electrode fouling at a low oxidation potential.

Graphene oxide (GO), an important derivatives of graphene, has drawn considerable attention from both the experimental and theoretical scientific communities owing to its large surface area, high electronic features and strong mechanical strength. In particular, GO is highly hydrophilic because of the abundant oxygen-containing groups (carbonyl, carboxyl, hydroxyl and epoxide groups) on basal plane and edges of carbon atoms. With these unique properties, GO become a superior modified material in terms of improving dispersibility, enhancing adsorbability and reducing electrode fouling [16–19]. However, due to the insulativity of GO, GO-based materials usually suffer from sluggish electron transfer and exhibit poor catalytic activity. Therefore, GO is usually reduced into graphene-like material, named reduced GO (RGO). RGO is an ideal material for sensing applications due to its high electrical conductivity, large surface area and the delocalized π -conjugated electrons available on its surface [20–23]. Nevertheless, the potential negative effects of RGO are also evident. Firstly, the high

* Corresponding authors.

E-mail addresses: duanxuemin@126.com (X. Duan), lulimin816@hotmail.com (L. Lu).

¹ These authors contributed equally to this work and should be considered co-first authors.

electrical conductivity and large surface area of RGO usually cause the increase of background currents which becomes the primary limiting factor for trace analyte detection [24]. Secondly, the reduction process may cause decreased sensitivity and unoptimistic stability since electrocatalytic activity and hydrophilicity rely on oxygen-containing groups on RGO surface [25,26].

In fact, there is a transition state between graphene and GO, named partially reduced GO (pRGO). Dong et al. [27] controlled synthesis of electrochemically reduced graphene oxide films with an O/C ratio of less than 6.25% and achieved different thicknesses ranging from a single monolayer to several microns. Lin et al. [28] indicated that controllable electrochemical reduction of GO exhibited higher cycling durability and electrochemical capacitance than chemically reduced graphene and carbon nanotubes. Zhang et al. [26] demonstrated that electro-oxidation of uric acid displayed the highest peak current signal on pERGO modified electrode. Since GO is a good anti-electrode-fouling agents, it is believed that the control preparation of ERGO films with oxygen groups residual could show stabilizing effect in the electrochemical detection of analytes. However, to the best of our knowledge, no literatures have investigated the effect of reduction extent of ERGO on sensitive and stability detection of INZ.

The purpose of this work is to synthesize different extents of ERGO films and investigate their sensing performance towards INZ. The reduction extent of ERGO was controlled by performing cyclic voltammograms (CVs) with different cycles. SEM, TEM, Raman spectra and electrochemical impedance spectroscopy (EIS) were used to characterization of ERGO. Results demonstrated that the pERGO modified electrode not only exhibited low background and high sensitivity towards the electrochemical oxidation of INZ, but also displayed anti-electrode-fouling ability in stability test experiments. Additionally, the developed electrode was successfully applied to practical sample for recovery study with satisfactory results.

2. Experimental

2.1. Chemicals and Materials.

INZ (AR) was purchased from Aldrich. INZ stock solution (5×10^{-3} M) was prepared in double distilled water and stored at 276–281 K. GO was obtained from Nanjing Xianfeng Nano Co. Disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) and sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) were obtained from Sinopharm Chemical Reagent Co. Ltd. All other reagents were of analytical grade. Doubly-distilled water was used throughout the experiments.

2.2. Apparatus

Electrochemical measurements were carried out on a CHI660D electrochemical workstation (Shanghai, China). The conventional three-electrode system consisted of GCE (or modified GCE) working electrode, platinum wire auxiliary electrode and saturated calomel reference electrode (SCE). SEM images were obtained with a Helios NanoLab FESEM/FIB instrument. TEM images were recorded using a Tecnai G2 F30 microscope. Raman spectroscopy (inVia-reflex) was performed with a 633 nm laser. An inert atmosphere was provided by passing N_2 over the solution during the experiments.

2.3. Preparation of GO Modified GCE

0.5 mg GO was dispersed in 1 mL redistilled water by ultrasonating for 2 h and centrifuging for 10 min at 3000 rpm. Prior to modification, GCE was polished with chamois leather containing $0.05 \mu\text{m}$ Al_2O_3 , then cleaned by ultrasonically with doubly-distilled, absolute ethanol and redistilled water, respectively, each for 5 min. To obtain GO modified GCE (GO/GCE), $5 \mu\text{L}$ GO dispersion was dropped on GCE and dried at room temperature.

2.4. Preparation of ERGO

GO on the surface of GCE was electrochemically reduced to RGO by cyclic voltammetry in 0.1 M PBS solution (pH 7.0). The potential window was applied from -1.5 V to 0 V and scan rate was set as 50 mV s^{-1} . The reduction degree of ERGO was controlled by performing certain cycle number of CVs. For comparison, ERGO films with different reduction cycle numbers (1, 3, 5, 7, 9, 11, 13, 15) were prepared and marked as ERGO₁, ERGO₃, ERGO₅, ERGO₇, ERGO₉, ERGO₁₁, ERGO₁₃ and ERGO₁₅, respectively.

3. Results and Discussion

3.1. Construction of Electrochemical Reduced RGO

ERGO films were prepared by cyclic voltammetry in 0.1 M PBS (pH 7.0) electrolyte solution. Fig. 1 displayed electrochemical reduction GO film with a potential window from -1.5 V to 0 V. As shown, an obvious cathodic peak at -1.17 V with a starting potential of -0.75 V can be observed in the first cycle, which was attributed to the reduction of oxygen-containing groups on GO surface [29]. However, in the second cycle, the cathodic peak exhibited a significantly decreased reduction peak, indicating that the reduction of oxygen-containing groups was an irreversible process. It has been reported that totally reduced certain amount of pristine GO (0.5 mg mL^{-1} , $5 \mu\text{L}$) should perform CVs for more than 15 cycles under the same conditions [30,31]. Therefore, a transition state exists between graphene and GO, namely pERGO. Thus, the electrochemical reduction extent of ERGO can be controlled by performing different CV cycles.

3.2. Characterization of GO and ERGO

The morphology and microstructure of related materials were confirmed by SEM and TEM. As can be seen in Fig. 2A, the surface of GO looked like a thin paper with a few wrinkles. While in Fig. 2B, the number and degree of wrinkles were markedly increased, which was highly beneficial in maintaining a high surface area for the electrode since the sheets cannot readily collapse back to a graphitic structure. Fig. 2C and D displayed TEM images of pERGO, clearly exhibiting crack shaped and layered structure. These unique characteristics of pERGO film can provide large conductive surface area and afford more active sites to access analyte molecules. In addition, the residuary oxygen-containing groups on pERGO surface can form hydrogen bond force with analyte molecules and enhance adsorb ability. Therefore, pERGO was a potential electrode material for sensor applications.

Raman spectroscopy is a useful tool to characterize ordered and disordered structures of carbon in graphene. Raman spectrum usually

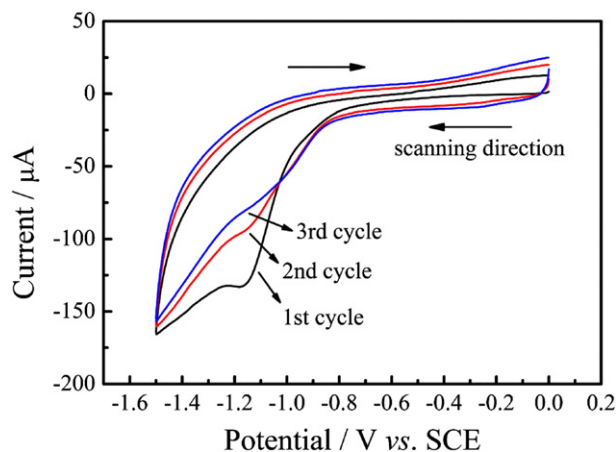


Fig. 1. CVs recorded at 50 mV s^{-1} in 0.1 M PBS (pH = 7.0) at GO/GCE.

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