

# Sensitive detection of uric acid on partially electro-reduced graphene oxide modified electrodes



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## ARTICLE INFO

### Article history:

Received 5 November 2013

Received in revised form 5 December 2013

Accepted 7 December 2013

Available online 19 December 2013

### Keywords:

Uric acid

Reduced graphene oxide

Electro-reduction

Voltammetric sensor

## ABSTRACT

Reduced graphene oxide (RGO) material-based modified electrodes are increasingly employed as voltammetric sensors for detection of uric acid (UA), an important biologically active molecule. While substantial research efforts have used chemical doping, formation of hybrids to improve the electrocatalytic activities of RGO-related electrode films and thus the sensitivity for UA detection, little attention was paid to the effect of oxygen functionalities of RGO itself. Here, we demonstrate that the content of oxygen groups in RGO electrode films is an important determinant of the current response for UA oxidation on the RGO modified electrodes. To show this, RGO films with various amounts of oxygen functionalities were prepared through electro-reduction at different reduction potentials and their electrocatalytic activities for UA oxidation were examined in detail. The partially electro-reduced graphene oxide (pERGO) electrode film with intermediated content of oxygen functionalities was found to exhibit the highest current sensitivity towards the oxidation of UA. By using this class of pERGO modified electrodes, a simple voltammetric sensing platform for sensitive detection of UA was developed and adopt for analyzing UA in urine samples with satisfactory results. These findings highlight the important effect of oxygen groups in RGO film on the electrocatalytic property of RGO modified electrodes and thus can be helpful for the development of more sensitive RGO-based voltammetric sensors for other electroactive molecules.

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## 1. Introduction

Uric acid (UA) is an end product of purine metabolism and primarily presents in urine and blood. Abnormal levels of UA are important indicators for the diagnosis of several diseases such as gout, hyperuricemia, leukemia and Lesch-Nyhan syndrome [1]. Therefore, it is clinically significant to develop sensitive and effective detection techniques for analysis of UA. Since UA is voltammetrically active, electrochemical analysis based on electro-oxidation of UA on an electrode surface represents an attractive method for its detection. Substantial recent research efforts have used reduced graphene oxide (RGO)-based modified electrodes to develop electrochemical sensing platforms for detection of UA. For example, unfunctionalized RGO materials prepared through chemical, thermal and electrochemical reduction of graphene oxides were used to make RGO modified electrodes and the voltammetric performances of these different types of RGO films for UA detection were comparatively studied [2–5]. Similarly, nitrogen-doped RGO modified electrodes were shown as electrochemical sensing platforms for detection of UA [6–8]. Significant efforts

have also gone into the development of UA voltammetric sensors using RGO-based nanocomposites by integrating RGO with metal nanoparticles [9–15], polymers [16–21] and organic functional molecules [22,23]. Through tuning the electrocatalytic properties of RGO-based electrode films towards the electro-oxidation of UA by chemical doping or formation of nanocomposites, different detection sensitivities for UA have been reported in these systems. These previous studies, however, paid little attention to the content of oxygen functional groups of RGO itself, an important factor for determining the electrochemical properties of RGO materials [24,25]. In fact, the influence of the content of oxygen functionalities in RGO film on the electrocatalytic activities of RGO-based modified electrodes towards the electro-oxidation of UA molecules has not been explored, most probably due to the lack of a simple and effective procedure for total control the extent of GO reduction process to reproducibly produce RGO materials with controllable amounts of oxygen functionalities. For example, most of the reported RGO-based voltammetric sensors have used chemically reduced graphene oxide (CRGO) materials to prepare the sensing interfaces for UA. The mechanisms for chemical reduction of GO with chemical reagents to produce RGO, however, are rather complicated and rely on several factors including concentration, temperature and time, which makes it very difficult to precisely tune all these factors to obtain a RGO material with desired content of oxygen functionalities.

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Recently, electro-reduction methodologies have already been shown to be simple and effective alternatives to chemical reduction of GO for fabricating RGO material [26–28]. Compared to chemical reduction techniques, electro-reduction of GO possesses several important advantages such as operating at room temperature, not requiring dangerous chemicals and use of simple instrumentation. Most importantly, electro-reduction methods can provide exact control over the extent of GO reduction process through easy and precise tuning the amount of electrons supplied for the reduction of oxygen functionalities on GO. Here, to explore the important effect of oxygen functionalities in RGO film on the electrochemical property of RGO modified electrodes, we employ electro-reduction technique to prepare electro-reduced graphene oxide (ERGO) films with various contents of oxygen functionalities and investigate their electrocatalytic activities towards electro-oxidation of UA. We have used different reduction potentials to control the reduction extent of GO films deposited on glassy carbon substrates and ERGO films with different content of oxygen functionalities have been successfully obtained in a simple, controllable way. Electrochemical oxidation behaviors of UA on these ERGO films were systematically studied and our results demonstrated that the partially electro-reduced GO (pERGO) modified electrode obtained under a middle electro-reduction potential exhibited the highest sensitivity towards the electro-oxidation of UA. Based on this type of pERGO modified electrode, we have developed a simple voltammetric sensor for sensitive detection of UA.

## 2. Experimental

### 2.1. Chemicals and materials

Graphene oxide powder (with nanosheet thickness of 0.55–1.2 nm, diameter of 0.5–3  $\mu\text{m}$  and C/O ratio of 2.2:1) was commercially supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (Chengdu, China). Uric acid (UA) and ascorbic acid (AA) were purchased from Sigma-Aldrich. Phosphate buffer solution (PBS, 1/15 mol L<sup>-1</sup>, pH = 7.0) was prepared with NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>. UA standard test solution (with concentration level of  $\mu\text{mol L}^{-1}$ ) was prepared by diluting UA stock solution (0.1 mol L<sup>-1</sup> UA in 0.2 mol L<sup>-1</sup> NaOH) with 1/15 mol L<sup>-1</sup> PBS. All reagents are of analytical grade and all solutions were prepared using 18.2 M $\Omega$ -cm ultrapure water. Human urine samples were collected from the laboratory personnel and diluted to 10<sup>3</sup> times using PBS without further treatment.

### 2.2. Instrumentations and measurements

Electrochemical measurements were carried out on an electrochemical workstation of CHI 660A (CH Instructions, Austin, TX, USA) at room temperature. The employed three-electrode cell system consisted of a glassy carbon (GC) working electrode (3 mm diameter), an Ag/AgCl (3 M KCl) reference electrode and a platinum wire counter electrode. All electrochemical experiments were performed using a 10 mL electrolyte solution. Prior to cyclic voltammetric (CV) or square wave voltammetric (SWV) measurements of UA, the working electrode was immersed in the electrolyte solution to preconcentrate UA on the electrode surface for 3 min under magnetic stirring. The employed enrichment time of 3 min was optimized by recording CV oxidation peak current of UA at different time intervals (data not shown), and a saturation current value was observed after enrichment of UA for 3 min. Parameters for SWV measurements were step height of 4 mV, pulse height of 25 mV and frequency of 10 Hz. The morphology of the ERGO modified electrode was characterized using a field-emission scanning

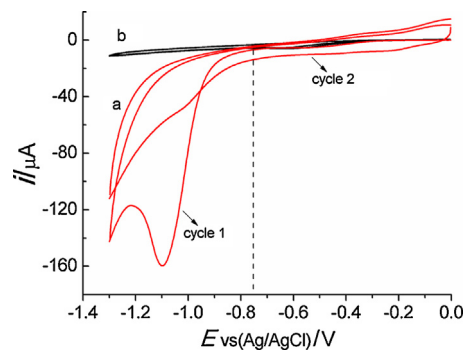


Fig. 1. Cyclic voltammograms recorded at 100 mV s<sup>-1</sup> in 1/15 mol L<sup>-1</sup> PBS (pH = 7.0) at GC-GO (a) and GC (b) electrodes.

electron microscope (FE-SEM, S-4800, Hitachi, Japan) at an accelerating voltage of 5.0 kV.

### 2.3. Fabrication of GC-ERGO modified electrodes

For fabrication of GC-ERGO modified electrodes, GC substrates were mechanically polished using 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub> powder, ultrasonically rinsed with ethanol and water (each for 5 min), and then dried under N<sub>2</sub> blowing. A 5  $\mu\text{L}$  of 0.5 mg mL<sup>-1</sup> GO suspension (prepared through ultrasonic dispersing of GO powder in ultrapure water for 1 h) was dropped on the cleaned GC surface and allowed to dry at room temperature for 12 h. The dried GO film was then electro-reduced in the 1/15 mol L<sup>-1</sup> PBS solution under a given reduction potential for 2 min to obtain the GC-ERGO modified electrode.

## 3. Results and Discussion

### 3.1. Characteristics of GC-ERGO modified electrodes

A two-step procedure consisted of drop coating GO onto a GC substrate surface and electro-reduction of the GO film in PBS supporting electrolyte was employed to prepare the GC-ERGO modified electrode. To obtain proper potential parameters for electro-reduction of GO films, we first investigated the electrochemical behavior of GO films in PBS solution. As shown in Fig. 1, a well-defined reduction peak starting from -0.75 V is observed on the GC-GO modified electrode (cycle 1, curve a). Control experiment reveals that the bare GC electrode shows not any voltammetric wave in the potential range of -0.75 ~ -1.30 V (curve b), indicating that the reduction peak is from the reduction of electroactive oxygen functionalities of the GO film. It can also be observed that such an electro-reduction reaction is irreversible since the second voltammetric scan curve (cycle 2, curve a) exhibits a remarkably decreased reduction wave due to the decreased amounts of oxygen functionalities on the film after the first reduction scan. These results are in good agreement with the previous reports [26–28] that GO films deposited on conductive substrates such as GC electrode surfaces could be irreversibly electro-reduced to form ERGO films through voltammetric scan among the reduction potential region of oxygen groups on the GO films. Additionally, as the intensity of the reduction peak is directly related to the amount of oxygen functionalities [26,29], it therefore can provide a quantitative signal for characterizing the content of oxygen functionalities remaining on the ERGO film.

We then prepared a series of GO-ERGO modified electrodes through electro-reduction of GO films for a fixed time of 2 min under various reduction potentials of -0.80, -0.85, -0.90 and -0.95 V. SEM image of the GC-ERGO surface (prepared using a reduction potential of -0.85 V) displays the crumpled and flake

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