



# Tuning the reduction extent of electrochemically reduced graphene oxide electrode film to enhance its detection limit for voltammetric analysis



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## ABSTRACT

Electrochemically reduced graphene oxide (ERGO) films find growing interest as voltammetric sensors for trace detection of electroactive analytes due to their easy preparation and unique electrochemical properties. Here, we demonstrate that the reduction extent of the ERGO film, is a crucial determinant of the concentration detection limits of such ERGO-based voltammetric sensors. To show this, we prepared a series of ERGO films with various reduction extents through electro-reduction at different reduction potentials, examined their background currents and electrocatalytic activities by using dopamine (DA) as a model analyte. Results showed that the background current response on the ERGO modified electrode monotonically increased with increasing reduction extent of the ERGO film, whereas the highest electrocatalytic activity towards the oxidation of DA was observed on the partially electrochemically reduced graphene oxide (pERGO) film. Because of its relatively low background current and high electrocatalytic activity, the pERGO modified electrode exhibited the lowest concentration detection limit for DA and a simple voltammetric sensing platform for trace detection of DA has been developed. These results highlight the important role of the reduction extent of ERGO film in determining the detection limits of ERGO film modified electrodes as voltammetric sensors. We believe that our findings could be also of value in the further developing ERGO-based sensors for trace voltammetric detection of other electroactive analytes.

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## 1. Introduction

Reduced graphene oxide (RGO) nanosheets have been widely used as electrode materials for voltammetric sensors owing to their excellent electrocatalytic activities originated from the large number density of functional groups (epoxy, hydroxyl and carboxylic groups) and large specific electroactive surface [1–4]. The common methods to prepare RGO nanosheets employ graphite oxide to be exfoliated and followed by thermal or chemical reduction to obtain thermally reduced graphene oxide or chemically reduced graphene oxide (CRGO) [5,6]. Although these methods are suitable for massive production, their disadvantages are also evident: the thermal treatment requires specific equipment for controlling the preparation conditions of high vacuum and heat, while the chemical reduction usually uses dangerous reducing reagents such as sodium borohydride, hydrazine or aluminium hydrides.

To address these limitations, electrochemical methodologies have recently been proposed as feasible alternatives to the chemical and thermal reduction of GO [7–10]. For electro-reduction of GO to produce the electrochemically reduced graphene oxide (ERGO), two different protocols of solid-state [7,8] and solution-based [9,10] electro-reduction have been reported. The latter is characterized by direct electro-deposition of RGO onto an electrode surface from a GO suspension and the former consists of electro-reduction of a GO solid-state film coated on an electrode substrate. As compared to the thermal and chemical reduction, such electro-reduction methods exhibit advantages of simple instrumentation, operating at a low temperature and requiring not any dangerous (aluminium hydride) or toxic (hydrazine) chemical reagents. In addition, the solid-state electro-reduction technique allows for exact control over the degree of reduction process, which can thus provide an easy route to controllably tune the surface composition and electrochemical property of ERGO films [11].

Because of their ease in preparation and the retained electrochemical properties of RGO materials, ERGO films are increasingly employed in the recent development of voltammetric sensors for

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trace detection of electroactive analytes. For example, pristine ERGO film electrodes were reported for voltammetric determination of hydroquinone [9], uric acid [12], dopamine [13], ascorbic acid [14], DNA bases [15], allopurinol [16] and caffeine [17]. Also, ERGO-based nanocomposites by integrating ERGO with polymers [18,19], metal nanoparticles [20–22] and carbon nanotube [23] have been used as modified materials for the design of different voltammetric sensing platforms. Despite many sensor examples, the previous studies paid little attention to the effect of the reduction extent of ERGO film on the trace detection performance of such ERGO-based voltammetric sensors. In fact, a full electro-reduction of the reducible oxygen groups of a GO film was usually applied in the reported ERGO-based sensor systems, most possible in order to achieve a high electrical conductivity and large surface area of the ERGO film. Although a large electrode surface area can give the increased total current response for a given analyte concentration, two potential negative effects will arise from the full reduction extent of the ERGO film. Firstly, a large electrode surface area generally leads to the increased background current, which acts as the primary limiting factor for trace concentration detection [24]. And secondly, the ERGO film with a large reduction extent (corresponding to a little amount of oxygen groups on the film) may exhibit the decreased current sensitivity (current per unit electrode surface area for unit analyte concentration) owing to its reduced electrocatalytic activity resulted from the reduced numbers of oxygen groups [25,26] during electro-reduction. It is therefore highly desired to perform a systemic study of the reduction extent-dependent detection limits of the ERGO-based voltammetric sensors for better trace detection performance.

Herein, we aim to demonstrate the key role of the reduction extent of ERGO film in determining the detection limits of ERGO-based voltammetric sensors. To this end, we prepared a series of ERGO films with various reduction extents by using different reduction potentials during electro-reduction. Dopamine (DA), a voltammetrically active neurotransmitter, was introduced as a model analyte for evaluating the various concentration detection limits on these different types of ERGO film electrodes. Particularly, we focused on the dependence of the background current and the electron transfer activity, the two crucial factors determining the detection limit of voltammetric analysis, on the reduction extent of ERGO film. Results demonstrate that the background current increases monotonically with increasing reduction extent of ERGO film whereas the highest heterogeneous electron transfer activity of DA is observed on the partially electrochemically reduced graphene oxide (pERGO) film. As a result of its relative low background current and high electro-catalytic activity towards the electro-oxidation of DA, the pERGO film electrode shows the best concentration detection limit for voltammetric analysis of DA.

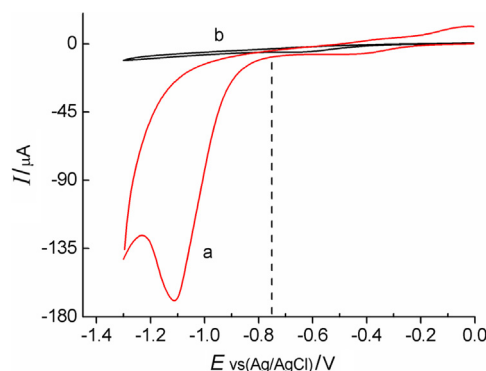
## 2. Experimental

### 2.1. Chemicals and materials

Graphene oxide nanosheets (with C/O ratio 2.2:1, thickness 0.55–1.2 nm and diameter 0.5–3  $\mu\text{m}$ ) were commercially obtained from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). Dopamine (DA), ascorbic acid (AA) and Uric acid (UA) were supplied by Sigma-Aldrich. Phosphate buffer solution (PBS, pH = 7.0, 1/15 mol L<sup>-1</sup>) was prepared with Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. All solutions were prepared using 18.2 M $\Omega$  cm ultrapure water and all reagents are of analytical grade.

### 2.2. Instrumentations and measurements

Electrochemical measurements were performed at room temperature using an electrochemical workstation of CHI 660A (CH



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

Instructions, Austin, TX, USA). A three-electrode cell system including a glassy carbon (GC) working electrode (3 mm diameter), a platinum wire counter electrode and an Ag/AgCl (3 mol L<sup>-1</sup> KCl) reference electrode was used with an electrolyte solution of 10 mL. Before cyclic voltammetric (CV) or square wave voltammetric (SWV) measurements of DA, the working GC electrode was immersed in the electrolyte solution to preconcentrate DA on the electrode surface under magnetic stirring for 2 min, a time period optimized by recording CV oxidation peak current of 2  $\mu\text{mol L}^{-1}$  DA at different time intervals (data not shown). SWV Parameters were pulse height of 25 mV, frequency of 10 HZ and step height of 4 mV. The morphology of the ERGO film was characterized using a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) at an accelerating voltage of 5.0 kV.

### 2.3. Fabrication of ERGO film electrodes

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

## 3. Results and discussion

### 3.1. Preparation and characterization of ERGO films

ERGO films with different reduction extents were prepared through electro-reduction of the GO films drop-coated on GC substrates under different reduction potentials in PBS electrolyte solution. The electrochemical behavior of GO film was first investigated to obtain appropriate potential parameters for electro-reduction (Fig. 1). In agreement with the previous reports, the GO film electrode (curve a) shows a well-defined, irreversible reduction peak starting from -0.75 V, while not any voltammetric wave is observed on the control bare GC electrode (curve b) in the potential range of -0.75 ~ -1.30 V. This irreversible reduction wave can be attributed to the reducible oxygen functionalities of the GO film (including epoxy, peroxy and aldehyde groups) [8,27]. Moreover, because the magnitude of this reduction peak is directly proportional to the amount of reducible oxygen groups, it can therefore be used as an indicative signal for characterizing the reduction extent of the ERGO film (ERGO films with low amounts of the remaining reducible oxygen groups corresponding to high reduction extents).

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