

# A reagentless non-enzymatic hydrogen peroxide sensor presented using electrochemically reduced graphene oxide modified glassy carbon electrode



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## ABSTRACT

Herein, we report a simple, facile and reproducible non-enzymatic hydrogen peroxide ( $H_2O_2$ ) sensor using electrochemically reduced graphene oxide (ERGO) modified glassy carbon electrode (GCE). The modified electrode was characterized by Fourier transform infrared (FT-IR), UV–Visible, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. Cyclic voltammetric (CV) analysis revealed that ERGO/GCE exhibited virtuous charge transfer properties for a standard redox systems and showed excellent performance towards electroreduction of  $H_2O_2$ . Amperometric study using ERGO/GCE showed high sensitivity ( $0.3 \mu A/\mu M$ ) and faster response upon the addition of  $H_2O_2$  at an applied potential of  $-0.25 V$  vs. Ag/AgCl. The detection limit is assessed to be  $0.7 \mu M$  ( $S/N = 3$ ) and the time to reach a stable study state current is  $<3 s$  for a linear range of  $H_2O_2$  concentration ( $1-16 \mu M$ ). In addition, the modified electrode exhibited good reproducibility and long-term stability.

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## 1. Introduction

Graphene is a carbon allotrope that consists of a flat monolayer of  $sp^2$  bonded carbon atoms, which are arranged in a honeycomb lattice. Since the discovery of graphene in 2004, the single atomic layer carbon material has reaped tremendous attention from researchers across the globe due to its outstanding properties, such as high surface area [1], strong Young's modulus [2], good thermal conductivity [3], outstanding electrical conductivity [4], and optical transparency [5]. Due to these fascinating properties, graphene has found its way in numerous applications, including energy conversion/storage systems [6,7], electrocatalysis [8] and electronic devices [9].

So far, plethora methods are existing for graphene preparation, among which reduction of graphene oxide (GO) may be the facile approach [10]. There are vast numbers of itineraries available for GO reduction, such as chemical reduction [11], thermal reduction [12], photocatalytic reduction [13] and electrochemical reduction. Typically, the chemical reduction of GO involves the usage of strong reducing agents, such as hydrazine [14], dimethylhydrazine [15], metal hydrides [16] and hydroquinone [11]. The excessive use of strong reducing agents contaminates the resulting product that is harmful to human health and environment [17,18]. The thermal reduction route requires high temperature to remove the oxygen functionalities that results in high

production cost in addition to tedious experimental control. Photocatalytic reduction of GO depends on the presence of photoactive materials under ultraviolet irradiation. In contrast, the electrochemical reduction of GO is a relatively simple approach to reduce GO to graphene on a large scale compared to the aforementioned methods [19]. This approach is often compared with electrochemical exfoliation approach due to similarity of exploiting the external power source to yield graphene in solid forms and occurring in solution phase. However, it should be noted that, electrochemical reduction of GO is aimed at restoring some of the original properties of pristine graphene and exploiting new functionalities at the reduced GO. The graphene produced from this approach is more appropriately known as 'electrochemically reduced graphene oxide (ERGO)' as its properties differ from pristine graphene due to the presence of several residual oxygen functionalities on the carbon basal plane. In recent years, the electrochemical GO reduction has received much more attention, since it is considered a 'green approach', further thin films of graphene can be prepared by this method on conducting substrates [20–23]. In this work, a facile approach is projected for the synthesis of high quality graphene in large scale by electrochemical reduction of GO. The present method is having the following foremost advantages: it is new-fangled, fast, green and non-toxic solvents are employed; therefore this will not result in contamination of the resulted product.

Hydrogen peroxide is a well-known oxidizing agent and by-product of large number of oxidase enzymes. It plays an important role in the production of textile, organic compounds and in food industries [24,

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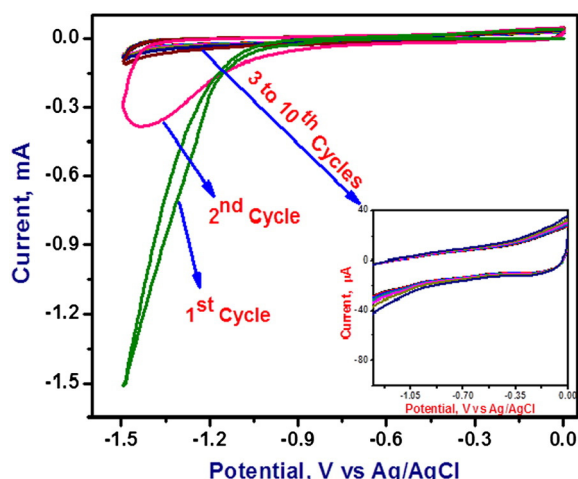


Fig. 1. Cyclic voltammograms of GO film in 0.1 M PBS at a scan rate of 50 mV s<sup>-1</sup>.

25]. In addition, it is also used as a signalling molecule to control various biological processes such as vascular remodelling, immune cell activation and root growth in living organisms [26]. Hence, there is a huge demand and immense interest to create a high sensitive, low cost and stable H<sub>2</sub>O<sub>2</sub> sensor. So far, various analytical approaches including potentiometric titration and electrochemical methods have been used for H<sub>2</sub>O<sub>2</sub> detection [27,28]. Recently, Zhang et al. highlighted the recent advances in electrochemical enzymatic and non-enzymatic H<sub>2</sub>O<sub>2</sub> detection [29]. However, direct electrochemical reduction or oxidation of H<sub>2</sub>O<sub>2</sub> at a bare solid electrode is highly sluggish and requires large overpotential [30]. In order to decrease the overpotential and increase electron transfer kinetics several enzyme based electrochemical biosensor approaches are in vogue using horseradish peroxidase [31], cytochrome C [32] and haemoglobin [33]. These enzyme modified electrodes usually suffer from high cost, short lifetime, inherent instability and difficult immobilization procedure [34]. Also, enzyme based detection methodologies are often complicated and dependent on pH and temperature. Thus, an electrochemical H<sub>2</sub>O<sub>2</sub> sensor particularly reagentless cum non-enzymatic approach holds a leading position among various bio-sensing protocols and hence it is imperative to develop a non-enzymatic H<sub>2</sub>O<sub>2</sub> sensor in this work.

To the best of our knowledge, there has been no report on ERGO modified electrode for reagentless cum non-enzymatic H<sub>2</sub>O<sub>2</sub> determination. Firstly, GO is prepared using modified Hummer's method and drop cast on GCE. The modified electrode was electrochemically

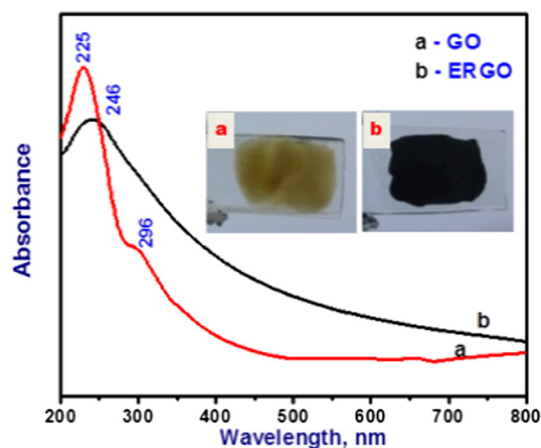


Fig. 2. UV–Vis absorption spectra of GO (a) and ERGO (b). Inset showed the colour change from light brown (GO) to black (ERGO). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

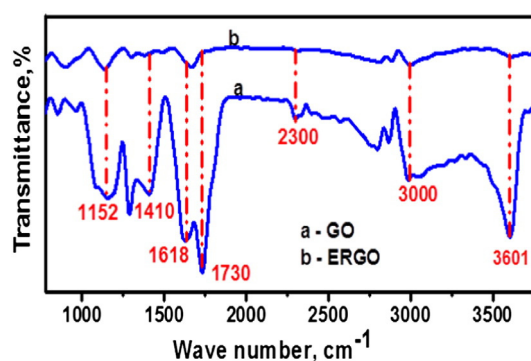


Fig. 3. FT-IR spectroscopy analysis of (a) GO and (b) ERGO.

reduced using CV technique. The resulted electrode (ERGO/GCE) showed a high activity towards H<sub>2</sub>O<sub>2</sub> reduction with a negligible interference in the presence of other electroactive species.

## 2. Experimental section

### 2.1. Chemicals

All chemicals were purchased from global suppliers. Graphite powder, nitric acid (HNO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), sodium nitrate (NaNO<sub>3</sub>), potassium permanganate (KMnO<sub>4</sub>), hydrochloric acid (HCl) and H<sub>2</sub>O<sub>2</sub> (30% v/v aqueous solution) were obtained from Sigma Aldrich or Merck. All the chemicals were used as received without further purification. 0.1 M phosphate buffer solution (PBS) [pH-7.0] was prepared by mixing standard stock solutions of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. All the experiments were performed at room temperature (~25 °C). Aqueous solutions were prepared using Milli Q water (18.2 MΩ·cm).

### 2.2. Synthesis of graphene oxide (GO) & electrochemically reduced graphene oxide (ERGO)

Graphene oxide was prepared from graphite powder using modified Hummer's method [35]. Briefly, graphite powder (2.0 g) was added in 50 mL of concentrated H<sub>2</sub>SO<sub>4</sub> in a 250 mL beaker under vigorous agitation at ice cold condition. Subsequently, NaNO<sub>3</sub> (2.0 g) and KMnO<sub>4</sub> (6.0 g) were slowly added into the beaker in a sequence manner and this mixture was heated at 35 °C for 24 h. The slurry was diluted with 80 mL of deionized water and temperature was kept under 50 °C. Then, 20 mL of H<sub>2</sub>O<sub>2</sub> was added in a dropwise manner into reaction mixture. The product obtained was washed with 1:10 HCl acid solution and followed by deionized water until the solution pH attained a value of 6.5. The resulted solid was dried in a vacuum oven at 40 °C for 48 h and then crushed into fine

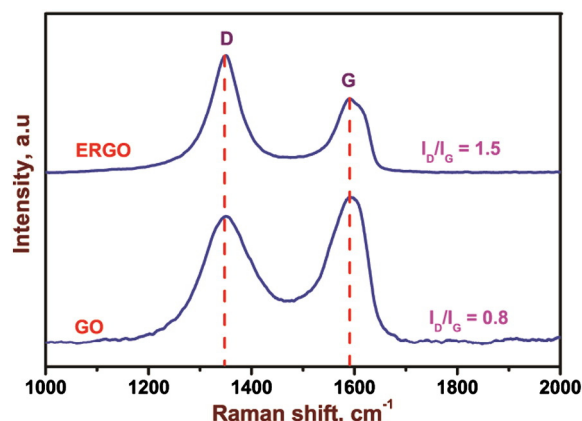


Fig. 4. Raman spectra analysis of respective materials.

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