Electrochemical production of Graphene Oxide and its application as a novel Hydrogen Peroxide sensor

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Abstract
Herein, graphene oxide is produced by electrochemical oxidation method from graphite rod to examine its hydrogen peroxide sensing ability. The electrochemically produced graphene oxide is characterized by SEM. A few layers of Graphene Oxide (GO) sheets and corrugations in graphene sheets appeared intensely crumpled and folded into a typical wrinkled structure after electrochemical oxidation. Electrochemical measurements are carried out cyclic voltammetry (CV) and chronoamperometry (CA) on graphene oxide and graphite. As a result, graphene oxide exhibits the highest performance toward electrochemical oxidation of H\textsubscript{2}O\textsubscript{2} in 0.1 M phosphate buffered solution (PBS). In addition, CA is employed for the determination of H\textsubscript{2}O\textsubscript{2} at the applied potential of 0.0 V (vs. Ag/AgCl). The electrochemical sensor exhibits fast and selective responses to H\textsubscript{2}O\textsubscript{2} concentration.

Keywords: Electrochemical; Graphene Oxide; Graphite; Hydrogen Peroxide; Nonezymatic Sensor.

INTRODUCTION
Graphene is an allotrope form of carbon consisting of a single layer carbon in hexagonal crystal lattice, separated from 3D structured graphite. Graphene is known as the first two-dimensional structure and thinnest material at one atom thick and incredibly strong about 200 times stronger than steel with its superior performance and potential applications [1-7]. Graphene production techniques have been known as mechanical cleavage, chemical peeling, epitaxial growth, Hummers method, sublimation of 4H-SiC, chemical vapor deposition (CVD), and electrochemical reduction [8-11]. Among these methods, electrochemical reduction is a cheap, short-time, and simple method [12]. Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) is a typical product of oxidase based on enzymatic reactions and a substrate for peroxidases. Furthermore, H\textsubscript{2}O\textsubscript{2} is a widespread and environmentally friendly oxidant for organic synthesis. H\textsubscript{2}O\textsubscript{2} emits only water as a byproduct and shows high atomic yield. As a result, it is widely used in food production, chemical synthesis, fuel cells, and pharmaceutical analysis due to its strong oxidizing properties. Therefore, the precise determination of H\textsubscript{2}O\textsubscript{2} is an important focus [13-18]. Different analytical techniques and methods based on titrimetry, spectrophotometry, chromatography, chemiluminescence, and fluorescence have been developed for the determination and quantification of H\textsubscript{2}O\textsubscript{2} [16, 19-21]. Among these methods, the electrochemical method has been focused on more and more attention on the account of its great advantages such as high sensitivity and selectivity, rapid response, and low cost [22-25]. Recently, graphene has been offered great potential in electrochemical sensor applications due to its exceptional physicochemical properties, including large surface area, higher electron conductivity, and better biocompatibility [26]. Furthermore, graphene is a promising carbon material, widely used for the preparation of hybrid...
nanomaterials owing to its distinct electronic, mechanical, and chemical properties [25, 27-31]. For instance, N’Diaye et al. [32] reported that Rh nanoparticles on the graphene support revealed great sensitivity towards $\text{H}_2\text{O}_2$. Similarly, Asif et al. [33] reported that graphene oxide supported MgO-Al$_2$O$_3$ nanocomposite was a promising material, prepared by low cost and low temperature facile method for the electrochemical determination of $\text{H}_2\text{O}_2$. Zhao et al. [34] investigated that graphene oxide (GO) AuNC nanocomposites were prepared layer-by-layer assembly method and this material had good sensitivity towards to $\text{H}_2\text{O}_2$.

At present, GO was prepared via electrochemical method from graphite rods. These rods were characterized by surface analytical techniques such as SEM measurements. To investigate their $\text{H}_2\text{O}_2$ sensor activities, cyclic voltammetry (CV) and chronoamperometry (CA) techniques were employed.

EXPERIMENTAL

Materials and Equipments

Graphite rods purchased from Auto Pencil company (2B, diameter= 2 mm). $\text{H}_2\text{SO}_4$ was supplied from Sigma-Aldrich. Potentiostat, Ag/AgCl reference electrode, and Pt wire electrodes were purchased from CH Instruments. Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware were washed with acetone and copiously rinsed with distilled water.

Electrochemical production of Graphene oxide

Graphite rods were used in order to produce GO rods by anodization technique applied via cyclic voltammetry (CV). Graphite rods were rinsed with water and dried at room temperature. Anodization measurements on the graphite rod working electrode were carried out in a conventional three electrode glass cell under the control of CHI 660 E potentiostat. On the other hand, Pt wire and Ag/AgCl (3 M KCl) electrodes were employed as counter electrode and reference electrode, respectively. First of all, to compare the $\text{H}_2\text{O}_2$ electrooxidation activities of the graphite and GO electrodes, cyclic voltammograms were taken in 0.1 M phosphate buffer solution (PBS) with 10 mM $\text{H}_2\text{O}_2$ at $-1-1$ V with a scan rate of 50 mV s$^{-1}$. Following this, further CV measurements were performed on GO electrode at varying $\text{H}_2\text{O}_2$ concentrations. Amperometric measurements were executed in a 0.1 M PBS under stirred condition. Following this, response current was related with the change value between the steady-state current and background current.

The interference experiments were also carried out in 0.1 M phosphate buffer solution by adding 0.5 mM $\text{H}_2\text{O}_2$, 0.5 mM ascorbic acid, 0.5 mM uric acid, and 0.5 mM $\text{H}_2\text{O}_2$, respectively.

RESULTS AND DISCUSSION

Characterization

Scanning Electron Microscopy (SEM) images of graphite and Graphene Oxide (GO) were

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Scan Rate</th>
<th>$\text{H}_2\text{SO}_4$ Solution</th>
<th>Precondition (s)</th>
<th>Potential range (V)</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO rod</td>
<td>0.1 V/s</td>
<td>1.0 M</td>
<td>3600</td>
<td>-0.85:1.2</td>
<td>C V</td>
</tr>
</tbody>
</table>
given in Fig. 1a-b and Fig. 2a-b, respectively. GO sheets are folded into a wrinkled structure after electrochemical oxidation (see Fig. 2a-b). This wrinkled structure could provide enhanced mechanical properties, reduced surface energy, and increased surface roughness and area.

**Electrochemical measurements of graphite and graphene oxide electrodes**

The electrocatalytic reduction of hydrogen peroxide ($\text{H}_2\text{O}_2$) was studied on graphite and graphene oxide (GO) electrodes. The cyclic voltammetric responses for the reduction of 5 mM $\text{H}_2\text{O}_2$ at graphite and GO electrodes in N$_2$-saturated 0.1 M phosphate buffered solution (PBS, pH=7.5) at scan rate of 50 mV s$^{-1}$ were displayed in Fig. 3. The current density for $\text{H}_2\text{O}_2$ oxidation on GO was 2.5 times higher than the one for graphite. The improved electrochemical activity of GO may also result from electronic state change of graphite after electrochemical oxidation [16, 33, 35, 36].

As a result, GO exhibited higher $\text{H}_2\text{O}_2$ oxidation and reduction current than graphite. Further experimental studies were performed to examine the effect of $\text{H}_2\text{O}_2$ concentration on GO rod electrode for $\text{H}_2\text{O}_2$ oxidation and reduction. As shown in Fig. 4 (a,b), the oxidation and reduction currents gradually increases with rising the $\text{H}_2\text{O}_2$
Amperometric measurements were performed to obtain an amperometric response of GO by the successive additions of H$_2$O$_2$ at varying potentials (Fig. 5). One could note that the best response was obtained at 0.0 V potential. The LOD values were calculated the methods given in the literature [37]. As seen Fig. 5b, the sensor has a linear response range of 0.5 mM to 25 mM with a sensitivity of 11 µAmM$^{-1}$cm$^{-2}$ ($R^2$=0.99). Moreover, the limit of detection (LOD) was 0.0975 mM. As a result, the GO could be used for the preparation of an

Fig. 3. CVs for the GO and Grafit in N$_2$-saturated 0.1 M PBS at varying 5 mM H$_2$O$_2$ concentration scan rate: 50 mV s$^{-1}$.

Fig. 4. CVs for the GO in N$_2$-saturated 0.1 M PBS at varying (a) 0-10 mM (b) 10-100 mM H$_2$O$_2$ concentrations scan rate: 50 mV s$^{-1}$.
amperometric H$_2$O$_2$ sensor with prompt response, high sensitivity, and wide linear range. Table 2 shows the comparison of linear range, detection limit, applied potential, and sensitivity of GO rod with other hydrogen peroxide sensors reported in literature. As seen Table 2, the analytical performances of GO rod is nearly equivalent the other enzyme or non enzymatic H$_2$O$_2$ sensors in one or more categories [38-39]. Furthermore, GO rod exhibited good sensitivity in the literature studies compared with the support material and metal studies [16, 20, 24, 28, 32, 33, 35, 36, 41-47].
Sample repeatability is an important parameter for the determination of H₂O₂ sensor sensitivity. In the present study, four samples were prepared and measured at the same conditions by CV. Results were given in Fig. 6. The repeatability of graphite oxide was performed using 20 mM H₂O₂ (Fig.6). Sample repeatability test for H₂O₂ detection for four successive runs on the same solution gave a RSD of 5 %.

The selectivity of the proposed H₂O₂ sensor was investigated in the existence of some various interferents such as ascorbic acid (AA) and uric acid (UA). Interference of these compounds to H₂O₂ sensor was examined by comparing the amperometric responses at 0.0 V. These responses were measured by successive additions of 0.5 mM H₂O₂, AA, UA, and H₂O₂. As shown in Fig. 7, the interferents give negligible signal changes [16, 35, 49-51].

**CONCLUSIONS**
Herein, graphite was electrochemically oxidized and as a result graphene oxide (GO) was obtained. GO and graphite was characterized by Scanning Electron Microscopy (SEM). GO sheets and corrugations in graphene sheets appeared intensely crumpled and folded into a typical wrinkled structure after electrochemical oxidation. Furthermore, electrochemical measurements were performed to investigate the electrochemical sensing ability of GO. Optimized sensor revealed fine analytical parameters such as linear range from 0.5 mM to 25 mM, lower detection limit (0.0975 mM), and 11 µA mM⁻¹ cm⁻² sensitivity. Furthermore, GO rod exhibited good sensitivity in the literature studies compared with the support material and metal studies. In conclusion, the study of the preparation, characterization, and employment of these catalysts as sensor led to the following conclusions and insights:

- GO could be easily prepared from the electrochemical oxidation of graphite. GO is efficient material for H₂O₂ electrooxidation activity compared to graphite.
- The morphology of GO and graphite were characterized by SEM. These measurements revealed that GO was prepared, successfully. In addition, the H₂O₂ sensing ability of GO is better than graphite due to corrugations in graphene sheets.
- The sensor exhibits a comprehensive performance, including good sensitivity, low detection limit, and wide linearity toward the detection of H₂O₂.

**CONFLICT OF INTEREST**
The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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