Simultaneous reduction of graphene oxide (GO) and formation of rGO/Gly-Gly composite for sensitive detection of Cu$^{2+}$ ions

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Abstract. Here, we report the sensitive detection of copper (Cu$^{2+}$) ions using field-effect transistor (FET) based on reduced graphene oxide/glycylglycine (rGO/Gly-Gly) composite. The simultaneous reduction of graphene oxide (GO) using glycylglycine, and formation of rGO/Gly-Gly confirmed by employing X-ray diffraction (XRD), Ultraviolet–visible (UV-vis) spectroscopy, and fourier-transform infrared spectroscopy(FTIR). The formation of rGO/Gly-Gly composite was confirmed by FTIR spectroscopy. Further, the sensing channel was fabricated with rGO/Gly-Gly and explored for the electrical detection of Cu$^{2+}$ ions between the concentration range of 100 ppb to 600 ppb. Present study recommends that rGO/Gly-Gly are encouraging for low-cost, portable, and real-time detection of heavy metal ion sensors.

1. Introduction

In the last several decades, due to ever-increasing industrial activities, humans have come under direct exposure to various heavy metals such as mercury, iron, cobalt, zinc, copper, lead, cadmium, etc. through contaminated water. Some of these heavy metals like iron, copper, zinc, etc. are required by the human body in lower quantities, and its presence at higher levels can cause toxic effects on human health. Among these, copper is one of the most toxic heavy metals. Wilson’s disease and Indian Childhood Cirrhosis are examples of severe chronic liver disease, which results from a predisposition to the hepatic accumulation of copper [1]. Moreover, the excess amount of copper can cause anemia, cystic fibrosis, diabetes, Adreno-cortical hyperactivities allergies, autism, kidney disorder, alopecia, etc. [2]. Hence, a proper detection of copper ion in water is important. A number of techniques have been developed over the years for copper ion detection, including photoelectrochemical, fluorescent chemosensing, colorimetric detection, photo electrochemical, fluorometric sensing, fluorescence sensing, electrochemical [3–11]. However, the aforementioned techniques...
techniques are time consuming, require experienced staff handling of these instruments, expensive and non-portable.

A possible alternative to overcome the shortcomings of these techniques is FET measurement. This method is simple, least time consuming, and does not require trained personal for its handling, thus provides a potential sensing platform that meets day to day demand for sensor technology [12]. Research in polypeptide based heavy metal ion sensors has gained significant traction in recent years for copper ion detection [13,14]. Herein, we demonstrate a simple, eco-friendly, and one step modification method to fabricate a FET sensor for Cu\(^{2+}\) detection in the concentration range of 100 to 600 ppb.

2. Experimental

2.1. Materials

All the chemicals for synthesis GO and rGO/Gly-Gly used in this research were of analytical grade or higher standard. Graphite powder was purchased from Molychem, GlycylGlycine (Gly-Gly) was purchased from Thermo Fisher Scientific. Phosphoric acid (H\(_3\)PO\(_4\)), sulfuric acid (H\(_2\)SO\(_4\)), hydrogen peroxide (H\(_2\)O\(_2\)), potassium permanganate (KMnO\(_4\)) were procured from Sigma Aldrich.

2.1.1 Synthesis of graphene oxide (GO)

The graphene oxide (GO) was synthesized by adopting a modified Hummers method from pure graphite powder. In brief, 90 ml of H\(_2\)SO\(_4\) and 10 ml of H\(_3\)PO\(_4\) were added together and stirred for 30 minutes. The 1 g of graphite powder was added into 6 g of KMnO\(_4\), and this mixture then added slowly into the acidic solution under constant stirring. This mixture was stirred for 11 hours until the solution converted to dark green. The reaction was terminated by adding 8 ml of H\(_2\)O\(_2\) and stirred for 10 minutes. After the addition of H\(_2\)O\(_2\), an exothermic reaction occurred, and let it cool down to room temperature. The solution was centrifuged at 8000 rpm for 30 minutes. After centrifugation, the supernatant was decanted away, and the precipitate was washed repeatedly with HCl and deionized (DI) water three times. Then, the obtained GO was dried in an oven at 80 °C for 24 hours.

2.1.2 Reduction of GO using Gly-Gly di-peptide and composite formation (rGO/Gly-Gly)

Simultaneous reduction of GO using Gly-Gly and composite formation of rGO/Gly-Gly was carried out as per the procedure mentioned elsewhere [15]. Briefly, 5 mg of GO dissolved in 10 ml of DI water, and 10 ml of Gly-Gly was mixed in 20 ml DI water. These two solutions were mixed in another beaker. Then very minute quantities of NaOH powder were added until the pH was 10. The solution was stirred for 3 hours, after which we get a faint yellow-colored solution, as shown in scheme1 (a). Then the beaker was kept in an oven at 90° C for 15 hours; then, the solution turns blackish in color, which indicates that the GO has reduced successfully reduced as shown in scheme 1 (b). Further, the solution was centrifuged at 7000 rpm for 30 minutes, and then the precipitate was collected as rGO/Gly-Gly composite.
3. Results and Discussion

3.1 X-ray diffraction analysis

The reduction of GO using Gly-Gly was confirmed by X-ray diffraction characterization with Brucker (D8 Advance, Germany) using Cu Kα radiation at the power of 40 kV and 40 mA (λ = 1.54059 Å). The diffraction peak for GO at 2θ = 9.8° confirms the d-spacing of 9.39Å, which infers that the GO has interlinked through carboxyl and hydroxyl functional groups evident that GO successfully synthesized. The reduction of GO might be possible due to amino (NH2) groups present in the Gly-Gly. The GO diffraction peak at 2θ = 9.8° disappear after completion of the reduction process, and a broad peak at approximately 2θ = 24.6° appeared, as shown in figure 1. It indicates that the removal of oxygen-containing functional groups from GO and rGO synthesized successfully.

3.2 UV-vis Spectroscopy Analysis

UV–Vis spectra of GO and rGO was recorded using Jasco V-750 UV-Visible spectrophotometer in the wavelength range of 190-900 nm to evaluate the degree of GO reduction. As shown in figure 2, the sharp absorption peak at 230 nm exhibits a π–π* transition associated with C=C in GO. However, the presence of an additional shoulder peak of n-π* at 295 nm is associated with C=O, which confirms the presence of oxygen functional groups in the GO sample. After the GO reduction, the main distinctive absorption peak red-shifted to 290 nm and shoulder peak at 295 nm disappeared due to the removal of oxygen functional groups from the GO material and restoring its conjugated structure.

The optical band gap values of GO and rGO/Gly-Gly were calculated using the Tauc plot and showed in figure 2 (b, c). The relation between absorption coefficients (α) and the incident photon energy (hv) is given by

\[ αhv = A(hv - Eg)n \quad ------ \quad (a) \]

where, α - absorption coefficient calculated from UV-vis absorption data, A - optical constants for indirect and direct transitions, hv – energy (eV), Eg - bandgap energy, n - frequency. For direct allowed transition n = 1/2 and for indirectly allowed transition n = 2 and for directly forbidden transition n = 3/2. In order to define the desirable indirect band transitions, the graphs were drawn between hv and (αhv)² and the corresponding band gaps values were obtained from extrapolating the straight line on hv axis at α = 0. The optical band gap values of GO and rGO/Gly-Gly was achieved to be 4.47 eV and 2.98 eV. The bandgap of GO approximately matches with reported literature [16].
3.3 Fourier-transform infrared spectroscopy (FTIR) analysis

FTIR spectra were recorded to analyze the functional groups in the GO and composite of rGO/Gly-Gly. The GO peak appears at 1727 cm\(^{-1}\) for C=O attributed to the carbonyl and carboxylic groups and another peak at 1055 cm\(^{-1}\) for C-O assigned to the carbonyl, carboxylic, and epoxy groups. These verify the occupancy of oxygen-containing groups in the GO. The peak at 1625 cm\(^{-1}\) increased to 1639 cm\(^{-1}\), and the peak at 1723 cm\(^{-1}\) nearly vanished after reduction, indicating the elimination of the C=O groups. These outcomes prove the formation of rGO and simultaneous adsorption of Gly-Gly over the surface of rGO, as evidenced by the peak observed at 1400 cm\(^{-1}\) attributed to C-N, the nitrogen atom is from Gly-Gly molecules which indicates that the rGO/Gly-Gly composite formed successfully.

3.4 Electrical Characteristics

Electrical characterization and FET sensing experiments were conducted to detect heavy metal ions employing Keithley 4200 SCS integrated probe station (Ecopia). Depending on the oxidation degree, the electronic features of GO deviate from insulating to semiconducting, and eventually behind to semi-metallic. GO is typically insulating because of two reason: i) Due to large concentration of oxygen-containing functional groups, it demolishes the symmetry of the material and, make it electrically insulating, with a bandgap of up to 3.6 eV ii) the oxygenated groups destroy π bonds in graphene. In our case, the energy bandgap for GO was achieved to be 4.47 eV. Hence, electrical characteristics for GO are not shown in the present study. The current-voltage (I-V) characteristics curve of rGO/Gly-Gly recorded between the potential window –1 to 1 V with the step of 0.05 V.
I-V curve exhibited semiconducting nature as shown in figure 4 (a). In the output characteristics curve \((I_{DS} - V_{DS})\), the gate potential was applied by varying \(V_{GS} = 0-30\) V with the step of -10 V. As a result of that, the increase in drain current was observed as gate potential increases, as depicted in figure 4 (b). Transfer characteristics curve \((I_{DS} - V_{GS})\) at constant drain voltage \(V_D = -20\) V shown in figure 4 (b). \(I_{DS}-V_{GS}\) curve exhibited p-type behavior. The threshold voltage was found to be \(V_{TH} = 1.5\) V and current on/off ratio \(10^2\). The carried mobility was achieved to be 1.34 cm\(^2\) V\(^{-1}\) s\(^{-1}\). The carrier mobility was calculated in the saturation regime according to the following relation:

\[
I_D = \left(\frac{WCi}{2L}\right) \mu (V_G - V_T)^2
\]

where, \(I_D\) - drain current, \(\mu\) - charge carrier mobility, \(Ci\) - capacitance per unit area of the dielectric layer (SiO\(_2\), 300 nm, \(Ci = 11\) nF cm\(^{-2}\)), \(V_G\) - gate voltage, \(V_T\) - threshold voltage, \(W=200\) µm & \(L=50\) µm is the width and length of the channel respectively.

![Figure 4](image_url)  
**Figure 4.** I-V plot (a) output characteristics\((I_{DS}-V_{DS})\) at \(V_{GS} = 0\) to -30 V (b) transfer characteristics\((I_{DS}-V_{GS})\) at \(V_{DS} = -20\) V (c) of rGO/Gly-Gly.

### 3.5 Detection of Cu\(^{2+}\) ions

The drain current was monitored to depict the sensing behavior of the FET sensor. The drain current \(I_{DS}\) of the rGO/Gly-Gly sensor at a constant drain voltage \(V_{GS}\) and the gate voltage \(V_G\) (-0.2 V) was measured as the sensor exposed to water and concentration of 100-600 parts per billion (ppb) Cu\(^{2+}\) ion solution, as shown in figure 5. The Cu\(^{2+}\) ions stock solution of 1000 ppb concentration
was prepared by adding chloride salts in deionized water and diluted as per the necessity of various concentrations for the design of sensing experiments.

The drain current of the FET sensor increases due to the binding of Cu\(^{2+}\) ions to the carboxylate functional group of the Gly-Gly molecules after subsequent exposure to the Cu\(^{2+}\) ion solution. The binding of Cu\(^{2+}\) ions with carboxylic acid groups can produce variations in the charge carrier concentration in rGO/Gly-Gly composite [15,17].

4. Conclusions

In summary, we have demonstrated a FET sensor for the detection of Cu\(^{2+}\) ions based on a facile and environmentally friendly method for the reduction of GO using Gly-Gly and simultaneous formation of rGO/Gly-Gly composite. The sensor was tested between the concentration range of 100 to 600 ppb of Cu\(^{2+}\) ions. The sensor channel material (rGO/Gly-Gly) exhibits stable sensing performance under aqueous medium. The achieved detection limit was well below WHO recommendations (2 ppm for copper ions).

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