



## Development of Reduced Graphene Oxide / Polyaniline (Rgo/Pani) Composite As Novel Modified Electrode for Heavy Metal (Lead II) Detection

## KEYWORDS

Graphene, Polyaniline, Lead

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**ABSTRACT** Graphene oxide(GO), Reduced Graphene Oxide(RGO) and Reduced Graphene Oxide- Polyaniline(RGO/PANI) composites were chemically synthesized and characterized by UV-vis, XRD and FT-IR techniques. The results reveal that there was a strong interaction between RGO and polyaniline chains. The average grain size of RGO/PANI composite was found to be 10-15 nm, which is confirmed by XRD analysis. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements demonstrated that the resulted RGO/PANI was electroactive. A glassy carbon electrode was modified with RGO/PANI to give an electrode for the selective determination of lead(II) via differential pulse voltammetry. The use of RGO/PANI with their extraordinary electrical conductivity and strong adsorption ability warrants high sensitivity and excellent selectivity for lead(II). The modified electrode shows enhanced reproducibility for lead(II). It responds linearly to lead(II) in the 1 to 30 nM concentration range (with a correlation coefficient of 0.9992) after a 10-min accumulation time.

### 1. Introduction:

Recently, great effort has been focused on developing advanced supercapacitors by exploring novel electrode materials with high performance. [1]. At present, carbon-based materials (active carbon, carbon nanotubes, and graphene [2] are usually employed as electrode materials for electrical double layer capacitors because of their excellent electrical conductivity and large surface area. Transition metal oxides [3] and lightweight conducting polymers [4] with high specific capacitance is usually used as electrode materials of pseudocapacitors. In order to obtain high performance electrode materials, nanocomposites of conducting polymers and carbon-based materials have been investigated because they combine the unique properties of individual material and show their special synergistic effects that can be used in electrode materials of supercapacitors. Graphene is known as a new class of two dimensional carbon material, according to its unique nanostructure, excellent mechanical properties, unusual electronic and transport properties [5]. Researchers mainly focused on the preparation and functionalization of graphene layers to improve their solubility, dispersibility, mechanical properties and electrochemical activity [6]. Graphene oxide (GO) has recently attracted increasing research attention as a composite with polymers. The graphite nanosheets contain several oxygen functional groups, including hydroxyl, epoxy, carbonyl, and carboxyl groups. All of these groups render graphite oxide nanosheets with strong hydrophilic characters and electrical insulation. Therefore, they must be reduced to remove oxygen-containing moieties and restore their graphitic structure to yield electrically active GO nanosheets. Meanwhile, the nanocomposites of conducting polymers based on reduced GO (GOR) have a tendency to exhibit synergistic properties. These properties, such as enhancement in electrical conductivity and electrochemical cyclability, derived from both components and polymer nanocomposites, form a new class of organic/inorganic hybrid materials with layered GOR. This layer is where the inorganic fillers are dispersed into the polymer matrix at the nanoscale level. These resulting materials tend to exhibit superior physical and mechanical properties compared

with their corresponding pure polymers with small amounts of layered graphite [7]. In recent years, attention has been given to the potential application of polyaniline (PANI) in chemical and biological sensors due to its high yield in redox process, gas sensing ability, optimum performance at room temperature, response to a wide range of volatile organic compounds (VOCs) environmental stability,

etc. [8]. The interfacial interaction between GO and polymer matrix is a crucial factor to improve the properties of the polymer composites. Therefore, different strategies have been used to increase the interfacial interaction between GO and the polymer matrix, such as using surfactants [9] and the covalent functionalization of GO [10] in order to attach the organic groups to the surface of the GO grafted with the polymer matrix to obtain a uniform and stable dispersion of GO in the polymer matrix. A homogenous dispersion and good interfacial interaction strongly enhance the properties of the composite.

### 2. Materials and Method:

#### 2.1. Materials:

Natural graphite has been purchased from Sigma Aldrich. Sulfuric acid, hydrochloric acid, ethanol and hydrogen peroxide are purchased from Samchun Pure Chemical Co. Ltd, Korea. Potassium permanganate (oxidizing agent) has been purchased from Junsei Chemical Co. Ltd, Japan and hydrazine monohydrate (reducing agent) has been purchased from TCI, Japan. Aniline monomer, having a molar mass of 67 g mol<sup>-1</sup> and density of 0.97 g cm<sup>-3</sup>, is purchased from Sigma Aldrich .

#### 2.2. Preparation of graphene oxide (GO)

GO was synthesized from natural graphite (crystalline, 300 mesh) by a modified Hummers method [40]. Graphite (5 g) and NaNO<sub>3</sub> (5 g) were mixed with 230 mL of H<sub>2</sub>SO<sub>4</sub> (98%) in a 1000 mL beaker. The mixture was stirred within an ice bath. Under vigorous stirring, potassium permanganate (15 g) was added slowly to the suspension in 1 h. The reaction system was stirred at room temperature for 5 days forming a thick paste. As the reaction progressed,

the mixture gradually became pasty, and the color turned into light brownish. At the end, 1000 mL of 1% H<sub>2</sub>O<sub>2</sub> was slowly added to the pasty with vigorous agitation turning the color of the solution from brown to yellow. Then the GO was suction filtered, washed with copious amounts of 5% HCl aqueous solution and deionized water and finally redispersed in water for next use. Exfoliation was carried out by sonicating the GO dispersion under ambient condition for 30 min.

### 2.3. Reduction of GO

In a typical experiment, 3.5 mL of ammonia solution (25%) and 0.5 mL of hydrazine monohydrate (99%) were added into 500 mL of diluted GO dispersion (1.5 mg/mL) and then the mixture was heated at 95°C for 2 h under vigorous stirring. Once the reaction is completed, the reduced graphene oxide (RGO) were collected by filtration as a black powder, washed with copious amounts of deionized water.

### 2.4. Preparation of RGO-PANI

In a typical synthesis of RGO-PANI, aniline (1.05 mmol) and RGO(100 mg) were dispersed in 40 mL of 0.2 M HCl aqueous solution under ultrasonication. A fresh solution of ammonium peroxydisulfate (APS, 0.54 mmol) in 20 mL of 0.2 M HCl solution was rapidly transferred to the above solution containing aniline and RGO. The polymerization reaction was carried out for 12 h at room temperature without any disturbance. The dark green precipitate was filtered off, washed with deionized water and ethanol several times, and dried at 80°C for 24 h. The RGO-PANI synthesized. Herein, the pure PANI was synthesized chemically in the absence of GN via the similar procedure above.

### 2.5. Preparation of the Modified Electrodes

A certain amount of GO-PANI was ultrasonicated in distilled water to form a homogenous dispersion. Then, 5 mL of the above solution was drop-cast onto the surface of a freshly polished glassy carbon electrode and dried in ambient atmosphere for 12 h. The PAN, GO and GS modified electrodes were prepared by using the same procedure and the corresponding modified electrodes were denoted as RGO-PANI/GCE, RGO/GCE and GO/GCE, respectively

## 3. Result and Discussion:

### 3.1. FT-IR Characterization:

Fig. 1 A, B and C present the FTIR spectra of GO, RGO and RGO-PANI, respectively. As shown in Figure 2, the spectrum of GO illustrates the presence of C-O at 1050 cm<sup>-1</sup>, C-O-C at 1216 cm<sup>-1</sup>, C-OH at 1377 cm<sup>-1</sup>, and C=O in carboxylic acid and carbonyl moieties at 1707 cm<sup>-1</sup>. The peak at 1626 cm<sup>-1</sup> may be attributed to skeletal vibrations of unoxidized graphitic domains [41]. For reduced graphene oxide 1725 C=O (carbonyl/carboxy); 1576 C=C (aromatics); 1413 C-O (carboxy); 1122 C-O (epoxy); 1023 C-O (alkoxy). In comparison peaks due to oxygen functional groups are almost entirely removed in reduced graphene oxide. The FT-IR spectrum of RGO-PANI has shown that the above analysis indicates that the surface of the GO was completely wrapped in PANI, so there is no peak around 1700 cm<sup>-1</sup> which is due to C=O vibration. In this system, graphene oxide played a key role during the polymerization process. GO served as the hard template during the growth of RGO-PANI composites.

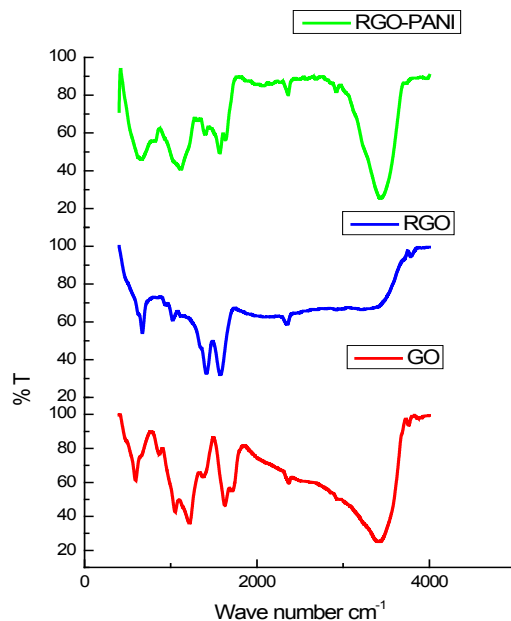


Fig. 1 FT-IR spectrum of GO, RGO and RGO/PANI

### 3.2. UV Characterization:

Typical UV-vis spectra of GO, RGO, RGO-PANI are shown in Fig. 2. The UV-VIS spectra of GO exhibits a maximum absorption peak at about 223 nm, corresponding to  $\pi-\pi^*$  transition of aromatic C-C bonds. The absorption peak for reduced GO had red shifted to 270 nm. This phenomenon of red shift has been used as a monitoring tool for the reduction of GO.

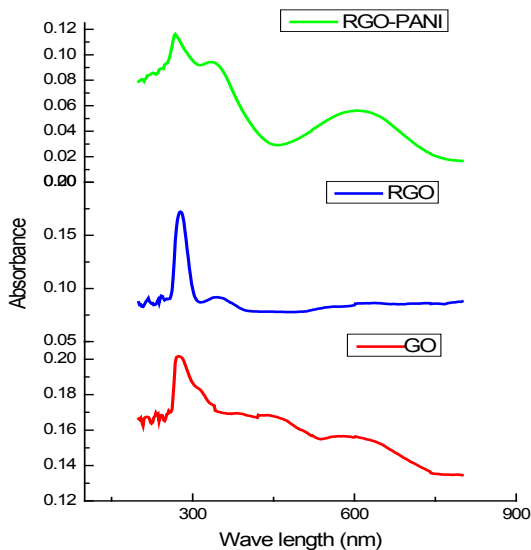


Fig. 2 UV- Vis spectrum of GO, RGO and RGO/PANI

### 3.3 XRD Characterization:

XRD pattern of GO (Fig. 3B) reveals an intense, sharp peak centered at  $2\theta = 10.03^\circ$ , corresponding to the interplanar spacing of 0.88 nm of GO. In the case of RGO/PANI composites, the peak of GO stacking disappeared, indicating that the GO had almost no aggregation and was fully used as the substrate for the PANI to produce hierarchical nanocomposites. Two new broad peaks of RGO/PANI nanocomposites centered at  $2\theta = 15.92^\circ$  and  $43^\circ$  corresponding to

the interplanar spacing of 15nm, which are the characteristic from Bragg diffraction equation.

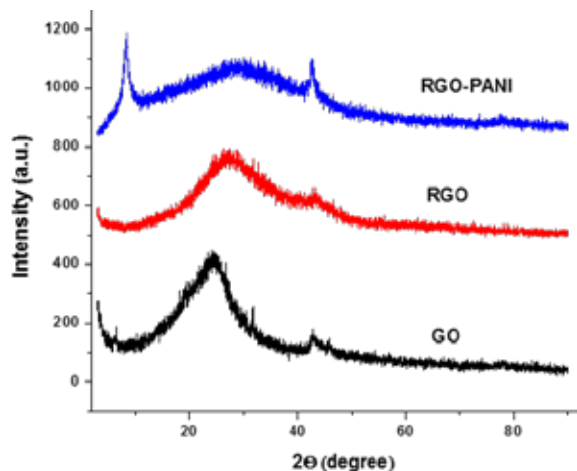


Fig. 3 X-ray diffraction spectrum of GO, RGO and RGO/PANI

### 3.4 Cyclic voltammetric studies:

cyclic voltammetric behaviour of RGO/PANI modified glassy carbon electrode in 0.1 M acetate buffer solution. Previously the RGO/PANI modified GCE is immersed in a buffer solution containing 5  $\mu\text{M}$  Pb(II) ions for 10 min. After accumulation, the modified electrode is rinsed with distilled water and transferred to a lead free acetate buffer solution (pH 4.5). Due to the size selectivity, the Pb(II) ion are incorporated in the ionophore shows a well-defined anodic (-0.476 V) and cathodic (-0.656 V) voltammetric peaks. In the absence of Pb(II) ion in the acetate buffer solution, no such peaks are observed that clearly demonstrates the incorporation of Pb(II) ion in the solution.

### 3.5 Optimization of experimental parameters:

Figure 4 illustrates the effect of pH of the supporting electrolyte on the Pb(II) peak current at RGO/PANI modified glassy carbon electrode. The peak current is found to minimum at pH 4.0 to 5.0 and reaches a maximum value at around pH 4.5. After that the peak current decreased notably while increasing the pH up to 8.0, which is due to the hydrolysis of Pb(II) takes place at higher pH values. Hence, a pH value of 4.5 was selected for subsequent measurements.

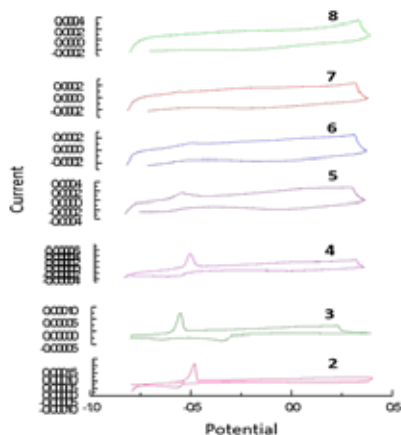


Fig. 4 Cyclic voltammograms of RGO/PANI modified glassy carbon electrode in

### 0.1 M acetate buffer solution with pH variation from 2.0 to 8.0 containing 5 $\mu\text{M}$ Pb(II)

### 3.6 Determination of lead(II) at RGO/PANI modified glassy carbon electrode:

Figure 5 shows the DPV of varying lead concentration ranging from  $10^{-2}$  to  $10^{-10}$  mM in 0.1 M acetate buffer solution at RGO/PANI modified GCE. The corresponding figure revealed that the peak current increases linearly with Pb(II) ion. The correlation coefficient of Pb (II) was found to be 0.9992 and the calculated limit of detection is 1 nM. The analytical performance of this modified electrode for Pb (II) electroanalysis is comparable or superior to many typical analogues previously reported. The current response at RGO/PANI modified electrode did not vary considerably even after one week under ambient circumstances shows of high stability.

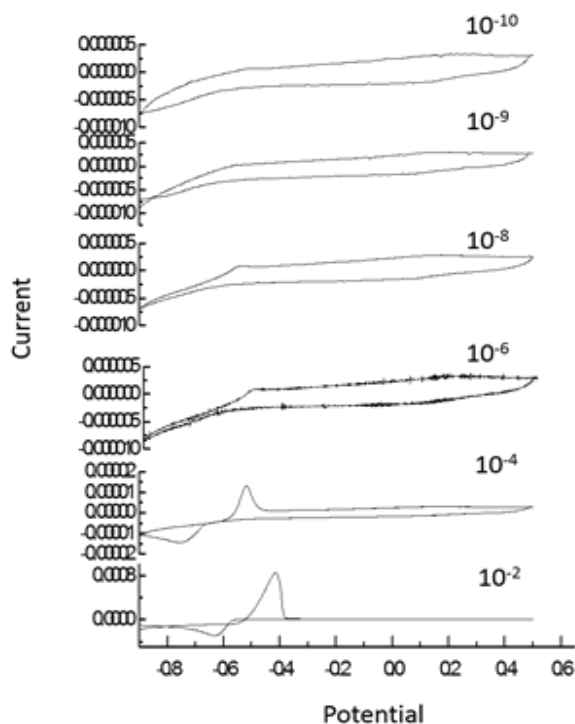


Fig. 5 Cyclic voltammograms of RGO/PANI modified glassy carbon electrode in 0.1 M acetate buffer solution with variation from  $10^{-2}$  to  $10^{-10}$  containing 5  $\mu\text{M}$  Pb(II)

## 4. CONCLUSION

In this present work, Graphene oxide(GO), Reduced Graphene Oxide(RGO) and Reduced Graphene Oxide- Polyaniline(RGO/PANI) composites were chemically synthesized and characterized by UV-vis, XRD and FT-IR techniques. The use of RGO/PANI with their extraordinary electrical conductivity and strong adsorption ability warrants high sensitivity and excellent selectivity for lead(II). The modified electrode shows enhanced reproducibility for lead(II).

## 5. Acknowledgment

The authors are thankful to the management of Bishop Heber College for their kind support to do this work.

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