

## Synthesis of Graphene Oxide modified Polyaniline and its electrochemical application for detection of Nitric Oxide

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### Abstract

Nitric oxide plays a crucial and important role in cellular physiology and also functions as a human cancer signaling molecule. Nitric oxide (NO) also exhibits antimicrobial and antitumor properties. However, conventional detection methods have their own limitations in the detection of NO at low concentrations because of its high reactivity and low lifetime. Here, we report a strategy to graphene oxide (GO)-modified polyaniline with efficiency to detect NO at a low concentration by electrocatalytic method. For this study we prepared graphene oxide –polyaniline (GO-PANI) which has higher stability and stronger catalytic activity towards the oxidation of nitric oxide (NO). The synthesized compound was characterized by field emission scanning electron microscopy (FESEM) and UV-visible spectroscopy. With further modification of Nafion, the determination of NO in PBS with different concentration. This investigation offers a different method for determination of NO.

**Keywords:** Graphene oxide (GO), Polyaniline(PANI), Nitric oxide(NO), Sensing ,Cyclic Voltammetry .

### 1. Introduction

Nitric oxide (NO) has been extensively researched as a result of impact on air pollution, particularly on biological systems. Numerous physiological and pathological processes include it<sup>1</sup>The aberrant generation of NO has an impact on several critical biological activities and contributes to a variety of illnesses<sup>2</sup>.Arteriosclerosis,hypertension ,brain

attack, Paralysis agitans and diabetes mellitus (type I and II) can all result from the under or over production of NO<sup>3,4</sup>. It is crucial from an industrial, biochemical, and medical standpoint either in vivo or in vitro testing to measure the NO produced in healthy and unhealthy tissues<sup>5</sup>. As a result, identification of NO is critical in these fields. The measurement of NO is challenging due to the hydrophobic free radical's automatic chemical reactivity and short half-life (about 6 seconds)<sup>2-6</sup>.

Due to its superior attributes, including its quick response, high sensitivity, low cost and most importantly, its suitability for both in vivo and in vitro detection, the electrochemical approach is frequently used<sup>8-11</sup>. Other techniques include fluorescence, chemiluminescence, electron spin resonance spectroscopy and UV-visible spectroscopy. Recently, a lot of research has been done on how to modify electrodes with nonmaterials to increase the sensitivity of electrochemical sensor<sup>12</sup>. As a result of exceptional biocompatibility, a significant productiveness, good conducting ability, intriguing digital transmission capability, and extraordinarily crucial significant particular dimension, graphene is gathered significant interest in electrochemical NO sensors<sup>13-16</sup>. Chemical and electrochemical processes are used to prepare graphene.

A toxic chemical reagent, such as hydrazine, is utilized in a chemical method to reduce graphene oxide (GO) to graphene. The electrochemical approach is high precise and environmentally responsible than this method<sup>17</sup>. Graphene-metal nanocomposites have recently been studied for electrochemical sensors<sup>18-20,29</sup>.

Polyaniline (PANI) is unique among conducting polymers due to its ease of production, excellent conductivity, stability, and low cost<sup>21-22</sup>. Many substrates have been detected using PANI-based electrochemical sensors<sup>23-25</sup>.

Here, an electrochemically reduced graphene oxide (ErGO)-PANI-enhanced Ag electrode was used to create a sensitive and stable NO sensor. The field emission scanning electron microscopy (FESEM) and UV-vis spectroscopy were utilized to explain the rGO-PANI-Ag NPs nanocomposite. To stop interfering species from penetrating the redesigned electrode, a Nafion coating was applied. Using cyclic voltammetry (CV) and chronoamperometry (CA) techniques, the response of the electrochemical and electrocatalytic reaction the resulting Nafion/ PANI-rGO/Ag electrode was studied. It was discovered that the modified electrode had excellent NO oxidation capability.

## 2. Experimental Methods

### 2.1. Materials

Graphite fine powder and aniline were purchased from Sigma Aldrichin. In order to create phosphahate buffer saline solutions (BS,0.1M,pH 7.4) 80g of NaCl ,2g KCl ,14.4g Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> in one liter distilled water and used as supporting electrolyte <sup>2</sup>.All solutions are prepared using double distilled water.

### 2.2. Preparation of NO Standard Solutions

NO was produced by drop wise addition of 2M H<sub>2</sub>SO<sub>4</sub> into a saturated NaNO<sub>2</sub> solution .This gas was formed by adding 2M H<sub>2</sub>SO<sub>4</sub> drops at a time into a glass flask that already contained saturated NaNO<sub>2</sub> solution .The generated gas was continuously passed through 5%(w/v) pyrogallol solutions in the saturated and 10% (W/V) potassium hydroxide solutions, respectively, to remove oxygen and nitrogen oxides. The full process took place inside the glove box .The glove box and all equipments were meticulously degassed with nitrogen gas for 30min to remove O<sub>2</sub> because the generated NO could react quickly with O<sub>2</sub>.At 20°C,the solutions saturated NO concentration was 1.8mM .10mL of deoxygenated PBS (pH 7.0 ) containing 0.1NaCl was bubbled with produced NO gas for 30min to produce a saturated NO solution .These prepared substance were stored in a glass flask with a rubber stopper ,a light – bocking curtain, and foil-wrapped foils.

### 2.3. Preparation of PANI-GO

GO was created using Hummer's method from graphite<sup>27</sup>.Chemical oxidative polymerization was used for producing the PANI-GO nanocomposite<sup>28</sup>. 17ml of DDW were mixed with 2mg of aniline ,10mg of GO and 0.2mL of 1M HCl for 30min at room temperature.After 4hours of continuous stirring ,10mg of ammonium peroxydisulfate was added to the suspension.Final product was autoclaved at 120° C for 3h.

## 3. Result and Discussion

### 3.1. Spectroscopic Study

A UV –vis measurement utilized to describe the manner in which the GO-PANI compositewas produced.The UV-visible spectra of GO,PANI and GO-PANI composite

appear in Fig 1. The  $n \rightarrow \pi^*$  transition of C=O groups and  $\pi-\pi^*$  transition of aromatic C=C bonds respectively, are related to the two distinctive absorption peaks at 230nm and 300nm that are present in GO. As can be seen, when GO-PANI is used as compared to GO, the maximum absorption peak is discovered to red shift towards 270nm. This change shows that the electronic conjugation in graphene sheets has been refreshed. The transfer of the shared electrons from the polymerization of aniline to the nearby oxygen-containing species on GO is one conceivable reduction mechanism<sup>28</sup>. Additionally, a peak at 320nm is seen, denoting the formation of PANI.

### **3.2. Surface Characterization**

The morphology of the synthesized materials was evaluated using the FESEM technique Fig .2 Graphene oxide has uniform and neat sheets. On the other hand, the graphene oxide /polyaniline composites Fig .2B is observed as non-uniform sheets in which polyaniline is positioned between the sheets, which indicates the formation of polyaniline particles on flat and uniform graphene oxide sheets<sup>28</sup>.

### **3.3. Electrochemical process and amperometric reaction of NO on Nafion /GO/GO-Polyaniline/Ag Electrode**

Fig .3 demonstrates cyclic voltammograms of the Nafion/GO/GO-PANI Ag electrode in absence and presence (different concentrations) of NO in oxygen-free 0.1 M PBS (pH 7.0) solution with a scan rate of  $100\text{mVs}^{-1}$ . In accordance with Fig PBS does not exhibit a redox peak at pH 7.0, whereas based on the applied voltage range (0 to 1V) the modified electrode showed no response in the absence of NO but an oxidation peak current in +0.8V when NO was present. When compared to the absence of NO, a significant increase in the oxidation peak suggests that NO is being oxidized electrocatalytically. Based on the outcomes, the chronoamperometry (CA) experiments in Fig 4 were performed with a +0.8V applied potential in comparison to the reference electrode<sup>26-27</sup>.

## **4. Conclusion**

In a broader sense we constructed a selective NO sensor based on GO-GO PANI hybrid compound. The interference compounds ( $\text{NO}^{2-}$ , AA and  $\text{H}_2\text{O}_2$ ) were eliminated by nafion. In addition, this compound sensor exhibits high sensitivity and stability, fast response and excellent selectivity for NO identification even with competing species available. The

methodology placed out in this work might serve as a foundation for further investigation to improve the accuracy and speed of NO detection in biological systems, highly conductive polymer-graphene nanocomposites are being used in sensors and biosensors.

Figures

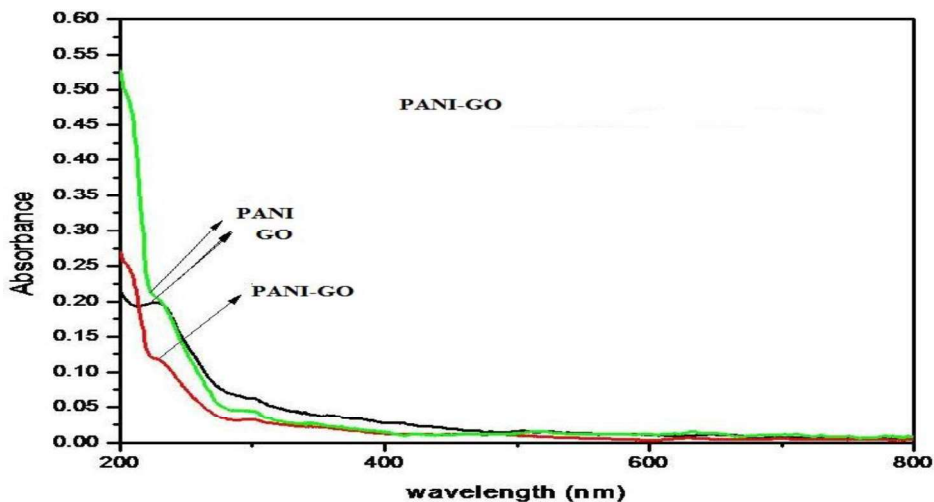


Fig .1 UV-visible Spectra of Graphene oxide /Polyaniline ,Graphene Oxide – Polyailine

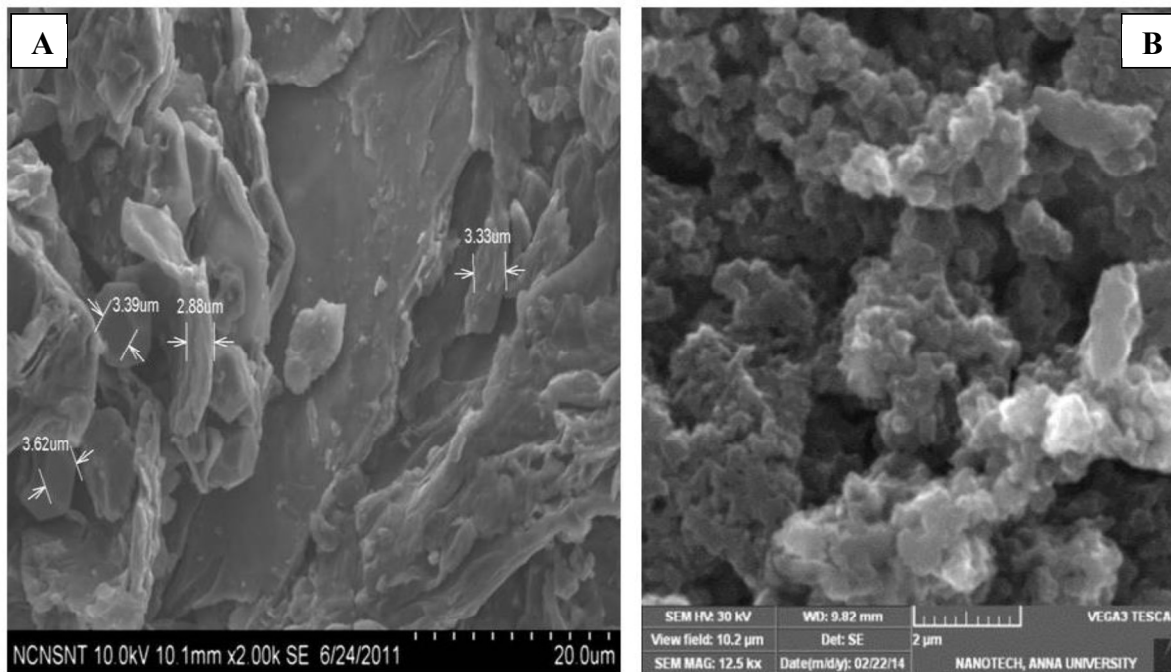


Fig .2 FE-SEM images of Graphene oxide and Graphene Oxide – Polyailine

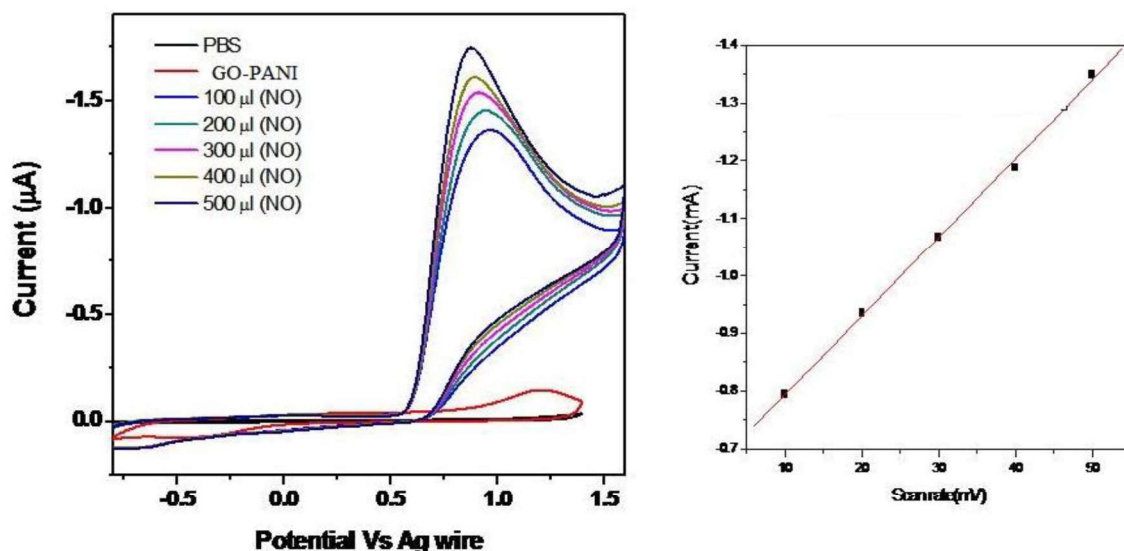


Fig .3 CVs were performed using graphene oxide-PANI for 0 mM of NO in PBS (curve 1), and 0.2 mM of NO in PBS with an graphene oxide-PANI and Ag electrode . Scan rate: 0.05 v/s B) Peak current versus scan rate plot for CVs of 0.2 mM of NO in PBS using the graphene oxide-PANI.

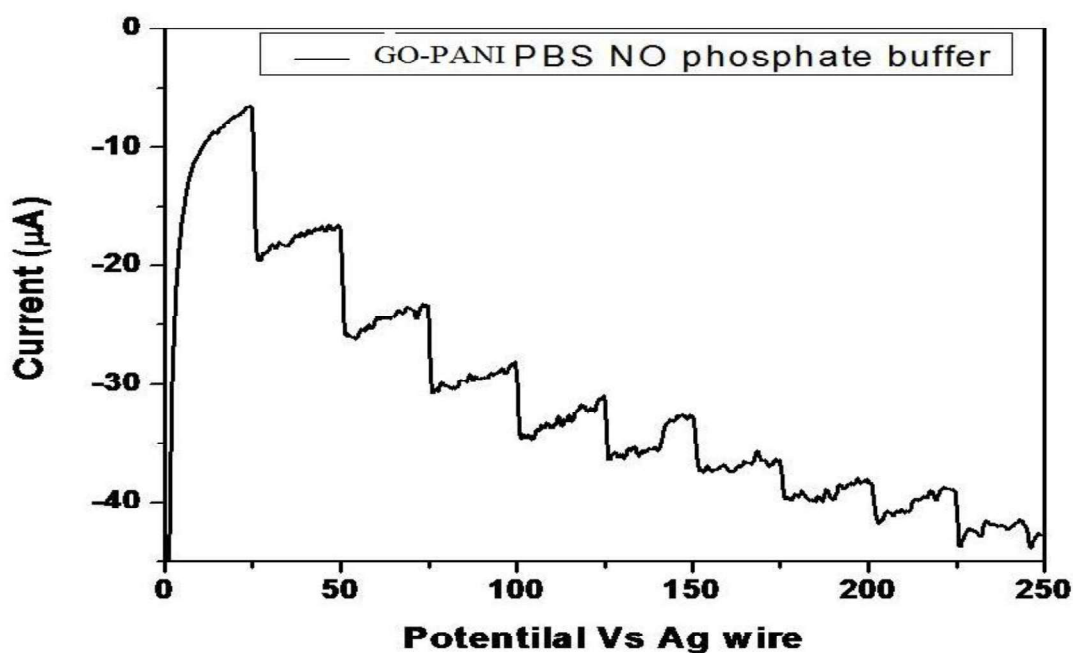


Fig .4 Amperometric action for the Nafion/PANI-GO electrode to successive infusions of NO into 10 mL of stirring 0.1 M PBS (pH 7.0) at an applied potential of +0.8 V (vs. Ag/AgCl).

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