Synthesis and characterization of Ni nanoparticles-dispersed graphene oxide and N-*doped* phenolic polymer composite electrode for glucose sensors

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ABSTRACT

At present, development of electrochemical sensors for biomolecules, based on inexpensive and stable carbonaceous electrodes is of prime interest. In this study we have developed for the first time reduced graphene oxide in situ dispersed with Ni-nanoparticles and N-doped phenolic polymer-based composite (Ni-rGO/P) as the working electrode, which also serves as the substrate for poly acryl amide (PAA) used as the recognition element for glucose. Notably, PAA was electrochemically grown on Ni-rGO/P. Nitrogen doping (N-doping) was performed using melamine. The prepared materials were characterized using various spectroscopic techniques such as SEM, EDS and XRD. Electrochemical impedance spectroscopy and cyclic voltammetry were used for electrochemical characterization, e.g. measurements of solution and charge transfer resistances, electrochemical active area, and studying electron transfer mechanism for bio-sensing. Tested with differential pulse voltammetry, the PAA_Ni-rGO/P sensor showed remarkable linearity ($R^2 = 0.99$) over $0.03 - 250$ mg dL^{-1} glucose concentration, high reproducibility (number of experiments = 500, RSD < 5%). The present method and materials can be used for the development of enzymatic as well as non-enzymatic electrochemical sensors for the various other important inorganic and organic analytes.

Keywords: electrochemical sensor, Ni-nanoparticles, reduced graphene oxide, N-doping, composite electrode.

1 INTRODUCTION

Selective and accurate measurement of glucose, a biomarker of diabetes mellitus and hyperglycaemia is a challenging task and is highly important in clinical diagnosis [1]. The electrochemical measurements using enzyme as recognition element is s promising technique showing high sensitivity, selectivity and fast response [2]. However, these are expensive and highly temperature and pH sensitive [3]. The use of commercial expensive electrodes with relatively higher resistance is also the drawback. Therefore, development of selective non-enzymatic electrochemical sensors based on different conductive carbonaceous electrode material paves a new way to overwhelm the above problem.

In the last decade, graphene-based materials such as graphene, reduced graphene oxide (rGO), carbon nano fibres [4,5] etc. have been widely used as the electrode materials in many electrochemical sensors because of their high electrical conductivity and mechanical stability. Reduced graphene oxide (rGO) is easy to prepare, and disperse in the polymeric substrate [6]. With the advancement in nanotechnology, different metal nanoparticles (NPs) such as Au, Ni [7,8] etc. and metal oxide NPs [9] were used as the non-enzymatic recognition element. These sensors showed promising electro-chemical characteristics, but poor selectivity and high detection limit are the major drawbacks [10]. However, use of transition metal and metal oxide NPs can increase the electrical conductivity of the electrode material. Thus the transition metal NPs-rGO nanocomposite material may provide a new domain in the preparation of efficient carbonaceous electrode material.

In the present study, we have prepared a novel Ni NPs-dispersed reduced graphene oxide and N-*doped* conductive polymer nanocomposite (Ni-rGO/P) and used as sensor electrode with electrochemically grown polyacrylamide (PAA) nano-film as the glucose recognition element for the first time. The Ni NPs catalyzed the growth of stable PAA nano-film on Ni-rGO/P surface and also acted as an electro-catalyst. The prepared materials were tested for different physicochemical characteristics such as metal loading, surface morphology etc. and electrochemical characteristics such as impedance, electro-active area etc. using different physic-chemical and electrochemical methods.

2 MATERIALS AND METHODS

2.1 Chemicals and Apparatus

Glucose was purchased from Tata Chemicals (India). Acrylamide, graphite, phenol and other chemicals were purchased from Sigma-Aldrich (India). All the chemicals are of analytical grade. All the gases (99.9% pure) were supplied by Sigma Gases (India). All the solutions were prepared using ultrapure water (Milli-Q system, USA). All the electrochemical experiments were performed using a potentiostat (AUTOLAB 302N, The Netherlands) in a three electrode assembly, with a Pt rod and an Ag/AgCl (0.3 M) electrode as an auxiliary and reference electrodes, respectively. The prepared electrodes were used as working electrode (WE).

2.2 Preparation of Ni-rGO/P electrode

Graphene oxide was prepared using Hummers method [11] from graphite using potassium permanganate as the oxidizing agent in concentrated sulphuric acid (98%) in presence sodium nitrate. Next, 1 g of prepared GO was suspended in

50 mL 0.4 M nickel nitrate ($Ni(NO_3)_2.6H_2O$) solution (under optimized condition) using sonication, and the suspension was centrifuged. The residue was calendared and dried in room temperature (30 °C). The prepared film was then reduced at 550 °C (from TPR data) and used as electrode material (Ni-rGO).

A phenolic polymeric resin was prepared using the method according to an earlier reported study [12], with formaldehyde as cross linking agent as well as solvent, triethylamine as initiator and melamine as N-*doping* agent. The entire reaction was performed at 60 °C under continuous stirring (240 rpm). At the incipience of gel formation, 1 g Ni-rGO/P (optimized) was mixed into the polymeric solution, and the gel was casted on a Teflon petri dish followed by drying at 60 °C. The dried film was cut into rectangular shapes and used as working electrode (Ni-rGO/P).

2.3 Electrochemical Study

The PAA film was electrochemically grown on the Ni-rGO/P surface by immersing it in the 0.01 M monomer solution (aqueous acrylamide solution) using cyclic voltammetry (CV) in the three electrode assembly using Ni-rGO/P as WE. The electro-polymerization techniques was performed with an optimized scan rate (50 mV s^{-1}) for 60 CV cycles (optimized) over -1.0 to +1.0 V potential window. The prepared film (PAA_Ni-rGO/P) was thoroughly washed and used for the electrochemical measurements.

3 RESULTS AND DISCUSSION

3.1 Surface Morphology

Scanning electronic microscopic (SEM) images of GO film, and PAA_Ni-rGO/P were acquired using a Field Emission Scanning Electron Microscope (MIRA3, TESKAN) and are presented in Figure 1(a-b). A wrinkled thin film like surface was observed for GO composed with few layers, totally different from graphite images (made of thick staked film, data not shown here), confirming the formation of GO (Figure 1a). A porous homogeneous film was observed in the SEM image of PAA_Ni-rGO/P, confirming uniform growth of the nano film at the surface of Ni-rGO/P (Figure 1b). Energy-dispersive X-ray spectroscopy was also performed for the Ni-rGO/P nanocomposite (Figure 1c). The data confirmed the presence of Ni in the nanocomposite.

3.2 XRD

X-ray diffraction analysis of rGO and Ni-rGO were performed using a X-ray Diffraction Spectrophotometer, and the data are presented in Figure 1d. The data for GO showed the presence of (002 kα1) and (002 kα2) planes at around 25.4 and 39.2°, respectively corresponding to graphitic nature similar to the planes present in graphite. In addition to the earlier mentioned planes, peaks corresponding to (111), (200) and (220) planes at 4.8, 52.8 and 76.3□, respectively were also observed confirming the bulk FCC lattice of Ni NPs. An additional peak corresponding to (002) amorphous planes related to GO was also observed in rGO data which is absent in Ni-rGO, confirming the effective reduction of the rGO in presence of Ni NPs.
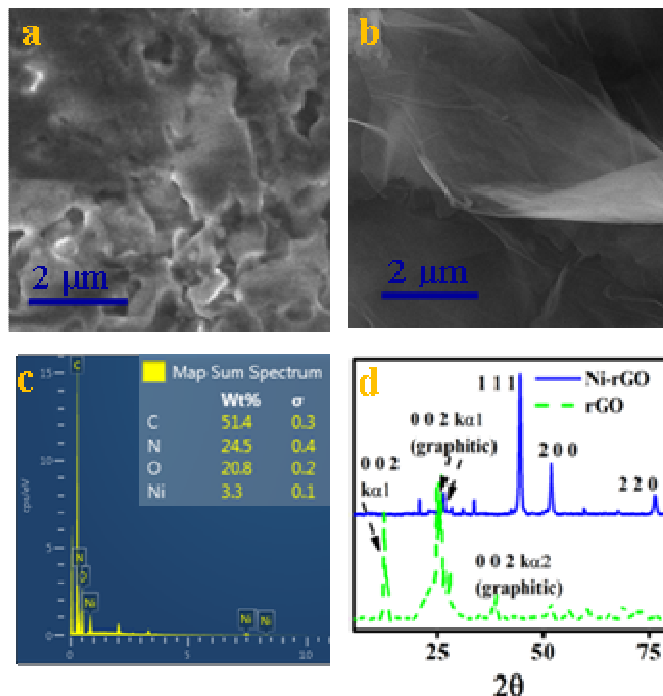

Figure 1: SEM images of (a) GO and (b) PAA_Ni-rGO/P; (c) EDS of Ni-rGO/P; and (d) XRD data of rGO and Ni-rGO.

3.3 Impedance and Electro-active Area Measurement

Impedance components, namely solution resistance (Rs) and charge transfer resistance (Rct) of the different electrodes – N-doped polymer, Ni-rGO/P and PAA_Ni-rGO/P were determined using Electrochemical Impedance Spectroscopy and the data are presented in Table 1. The Rs value was measured to be similar for both of Ni-rGO/P and PAA_Ni-rGO/P. However, the Rct value was found to be lesser in the former electrode as compared to the latter material, indicating the presence of ionic resonating structure of grown PAA.

Table 1 Electrochemical Properties

Electrochemical Properties	Sensor/Electrode		
	N-doped polymer	Ni-rGO/P	PAA_Ni-rGO/P
Rs (Ω)	~100	~35	~35
Rct (Ω)	~1780	~585	~560
Electro-active area (cm^2)	negligible	~3.1	~2.85

CV method was used to determine electro-active area of the prepared electrode materials in 500 nM aqueous $K_4[Fe(CN)_6]$ performed at 10 mV s^{-1} over -1.0 to 1.0 V. The electro-active area per unit geometrical area was determined from the CV data using Randles-Sevcic equation [13] –

$$I_p = 0.4463\ c\ (n\ F)^{1.5}\ (v\ D)^{0.5}(R\ T)^{-0.5} \qquad (1)$$

, where, I_p is peak current observed in CV, A; $n = 1$; D (diffusion co-efficient) = 7.6 x 10^{-10} cm^2 s^{-1}, F is Faraday's constant, c is molar concentration and v is scan rate, mV s^{-1}. The data showed a high electro-active area for both of PAA_Ni-rGO/P and Ni-rGO/P with a relatively higher value for the former electrode (Table 1).

3.4   Measurement of Glucose

Differential pulse voltammetric (DPV) method was used to measure the concentration of glucose in a 40 mL synthetic test solution (prepared in 0.1 M phosphate buffer solution of pH 7.0) using the prepared PAA_Ni-rGO/P sensor. All DPV experiments were performed with optimized deposition time (3 s) over -1.2 to 1.0 V potential window at 10 mV s^{-1} and the measurement data for different glucose concentration is presented in Figure 2a. The data showed a linear increase in peak current with increase in glucose concentration (R^2 = 0.99).

Reproducibility of the data was determined using the DPV measurements in the 50 mg dL^{-1} glucose solution for multiple times under the same DPV conditions (Figure 2b). A decrease in the response was observed after 300 consecutive measurements using a single PAA_Ni-rGO/P sensor.
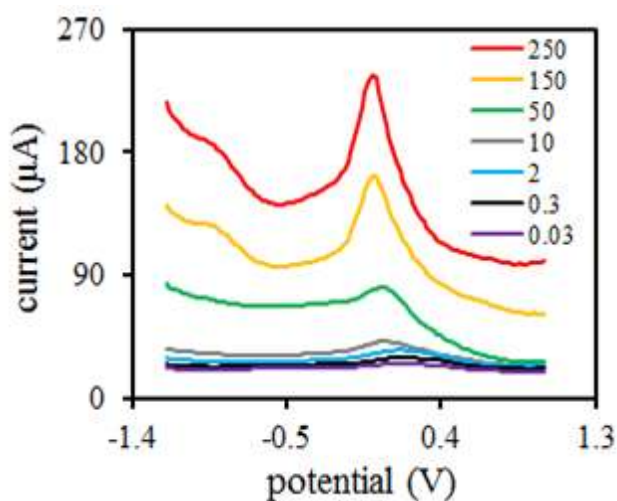

Figure 2: DPV responses measured at different glucose concentration (mg dL^{-1})

4   CONCLUSIONS

The Ni-rGO/P electrode was successfully developed, showing promising electrochemical characteristics viz. high electro-active area and low impedances because of the metal-graphene-conductive polymer network present in the material. The PAA nano film was electrochemically grown from the acrylamide monomer, and successfully used for the glucose recognition and measurement in its first such application. Presence of PAA nano film in the sensor also enhanced the electro-active area of the electrode material by ion-analyte interaction. The prepared sensor showed its applicability over a linear range (R^2 = 0.99) of concentration of 0.03 – 250 mg dL^{-1} (Signal to noise ratio = 3:1) for the precise and accurate measurement of glucose. The prepared PAA_Ni-rGO/P sensor can be used for the point of care monitoring of glucose. The proposed materials and method can be explored for the development of the other electrochemical sensors.

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