

Enhanced Electrocatalytic Oxidation of Glucose on Nickel Oxides/Graphene Nanoparticles Modified Glassy Carbon Electrode

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Graphene (Gr) modified glassy carbon (GCE) electrode with sequentially electrodeposited nickel oxide nanoparticles (NiO_x) were prepared as effective and stable electrode for electrochemical oxidation of glucose. The electrochemical behavior of the thus prepared electrode towards glucose was examined by voltammetric techniques. The $\text{NiO}_x/\text{Gr}/\text{GCE}$ electrode was prepared by casted Gr onto an electrochemically activated GCE then NiO_x was deposited either from nickel bath containing glucose as additive or not. The thus modified electrode was applied for the electrooxidation of glucose in alkaline medium. The effect of loading level of nickel of modified electrode were investigated as well. Furthermore, the $\text{NiO}_x/\text{Gr}/\text{GCE}$ electrode was morphologically characterized using scanning electron microscopy (SEM). The elemental composition is probed using energy-dispersive X-ray spectroscopy (EDX). The crystallographic orientation is examined using X-Ray diffraction (XRD) technique. The embedding of NiO_x in the Gr enhanced their activity and stability for glucose oxidation reaction. Moreover, the best electrocatalytic activity and stability for glucose was obtained at NiO_x (Glu)/Gr/GCE fabricated from nickel bath containing glucose as compared with the unmodified GCE electrode and NiO_x /Gr/GCE in nickel bath-glucose free. This enhancement is attributed to a synergistic effect between NiO_x (Glu) and Gr, where the NiO_x improve the electrochemical behavior via the formation of Ni^{3+} (NiOOH). The stability of the electrode is enhanced by using grapheme as a substrate for the nickel oxyhydroxide (NiOOH).

Keywords: Nickel- Nanoparticles- Glucose- Electrocatalysis-Graphene.

1. INTRODUCTION

Glucose electro-oxidation reaction has magnetized remarkable inters because of its significance in many potential applications containing clinical diagnostics, food industry [1], glucose fuel cells (FCs) [2], treatment of wastewater [3], biotechnology [4] and glucose sensors [5+6]. So, the expansion of

stable, cheap, and efficient glucose electrocatalysts is very important. Valuable metal-based electrocatalysts have been used in former research such as Pt-multiwalled carbon nanotubes (MWCNTs)[7], Pt–Pb/MWCNT[8], platinum and gold-based electrodes [9,10]. However, there are limits to its use in the practical application because of: its low durability and high cost [11-13]. Thus, the researchers have tended to develop low-cost, high-stability electrical stimuli toward glucose oxidation.

In this respect, many transition metal oxides (MO_x) nanostructured modified anodes such as Co_3O_4 nanofibers [14], Ni NPs [15,16], Fe_3O_4 nanorod arrays [17], MnO_2 [18,19] and CuO nanostructures[20,21] have received intense research attention for glucose electro-oxidation reaction

Recently, since the discovery of graphene, two-dimensional materials have become of great importance as electrical stimuli [14-18,]. This is due to the high graphene activity as a catalyst due to its amazing structural, physical and chemical properties [14, 17,22] such as: chemical stability, exceptional electrical loyalty, high surface area ($\approx 2600 \text{ m}^2/\text{g}$) [15,18], easy operation, high cost of catalytic behavior, and high carrier mobility ($\approx 15,000 \text{ cm}^2/\text{V}\cdot\text{s}$) [17, 23-26], which stimulated the study of electrical catalysis reactions using graphene. However, glucose oxidation reaction used 2D catalysts application uncommon. Thus, a good rostrum for Glucose electro-oxidation reaction is graphene and NiO_x NPs used to give the eminent characteristics.

Graphene-based electrochemical sensors have been used as comprehensive application in electroanalysis enhanced biosensors specificity and sensitivity [23,24,27,28]. In prevalent condition, such sensors were simulated by depositing graphene sheets at the surface of a GCE, followed by the deposition of Ni NPs on the graphene surface [23,24].

In the present work, the simple fabrication of GCE modified with Gr (with the aid of 30 min sonication) through the solution phase approach and deposition of NiO_x nanoparticles for glucose electro-oxidation reaction, designated as NiO_x (Glu)/Gr/GCE (in nickel bath containing glucose). It is compared with the electrode prepared similarly, but from glucose free-nickel bath. It was also compared with NiO_x (Glu)/GCE, i.e., without Gr. Modified electrodes are characterized by cyclic voltammetry (CV) in alkaline medium. Adding glucose to the deposition bath significantly reflected on the electrochemical behavior of the modified electrode towards glucose oxidation. Also including graphene in the underlying substrate enhanced the response of the electrode. The experimental parameters are optimized to sustain the highest electrocatalytic activity towards glucose oxidation. Inclusion of glucose in the deposition bath significantly affect the oxidation of glucose at the modified electrode.

2. EXPERIMENTAL

2.1. Chemicals.

Chemicals of analytical grade were purchased from Sigma Aldrich and were used without further purification. All the solutions used in these experiments were prepared with deionized water.

2.2. Electrochemical Measurements.

Electrochemical experiments were conducted on Gamry Instruments (Potentiostat / galvanostat / ZRA model Reference 600™). A conventional cell with a three-electrode configuration was used in this work, where the modified GCE (NiO_x/Gr/GCE) was used as the working electrode, the silver/silver chloride (Ag/AgCl/ KCl (sat.)) as the reference electrode and a platinum wire as the auxiliary electrode. The GCE (3mm in diameter) was cleaned by mechanical polishing with aqueous slurries of successively finer alumina powder then washed thoroughly with deionized water. All measurements were performed at room temperature (25 °C).

2.3. Preparation of NiO_x/Gr/GCE Electrode.

For the fabrication of Gr/GCE, GCE was modified with 10 μL Gr suspension and subsequently dried at room temperature. After casting of Gr, the Gr/GCE was subjected to oxidation in 0.5 M H₂SO₄ by potential cycling (in the potential range -0.2 to 2 V) at a scan rate of 100 mV s⁻¹. After that, nickel was electrodeposited from a Watts bath (0.02 M NiSO₄ · 6H₂O+ 0.03 M NiCl₂ · 6H₂O + 0.03 M H₃BO₃), either glucose (5mM) containing or glucose free by using five potential cycles in the range from 0 to -1.0 V vs. (Ag/AgCl/ KCl (sat.)) at a scan rate of 50 mV s⁻¹ and at 25°C. Then, the deposited nickel was oxidized by cycling of potential in 0.5 M NaOH solution.

2.4. Characterization.

Characterization of the electrodes was examined by FE-SEM, (QUANTA FEG 250). Also, Dispersive X-Ray Analysis (EDX) analysis, referred to as EDS or EDAX, (PANalytical, X'Pert PRO) operated with Cu target ($\lambda = 1.54 \text{ \AA}$) were used to identify the crystallographic orientation of the nano-NiO_x at bare GCE, NiO_x (Glu)/GCE, and NiO_x (Glu)/Gr/GCE nanoparticles.

3. RESULTS AND DISCUSSION

3.1. Morphological characterizations.

The electrocatalysts prepared atop the surface of the GCE were first investigated by SEM, and EDX. SEM images of nano-NiO_x prepared by a cyclic voltammetry technique described in the experimental section is shown as Fig. 1. Also, using EDX the atomic ratios of C/O/Ni were obtained. In image A, the nanoparticles obtained looks like cauliflower but have many mini diamonds like.

In EDX (plot B), as expected, diffraction peaks of Ni at 0.9, 7.6, and 8.2 KeV are revealed [29]. At image C, NiO_x (Glu)/Gr/GCE electrode which is fabricated similarly to NiO_x (Glu)/GCE electrode but in the presence of graphene. The nanoparticles obtained look like rocks. EDX (plot D), however, presents a smaller ratio of nickel compared with (plot B).

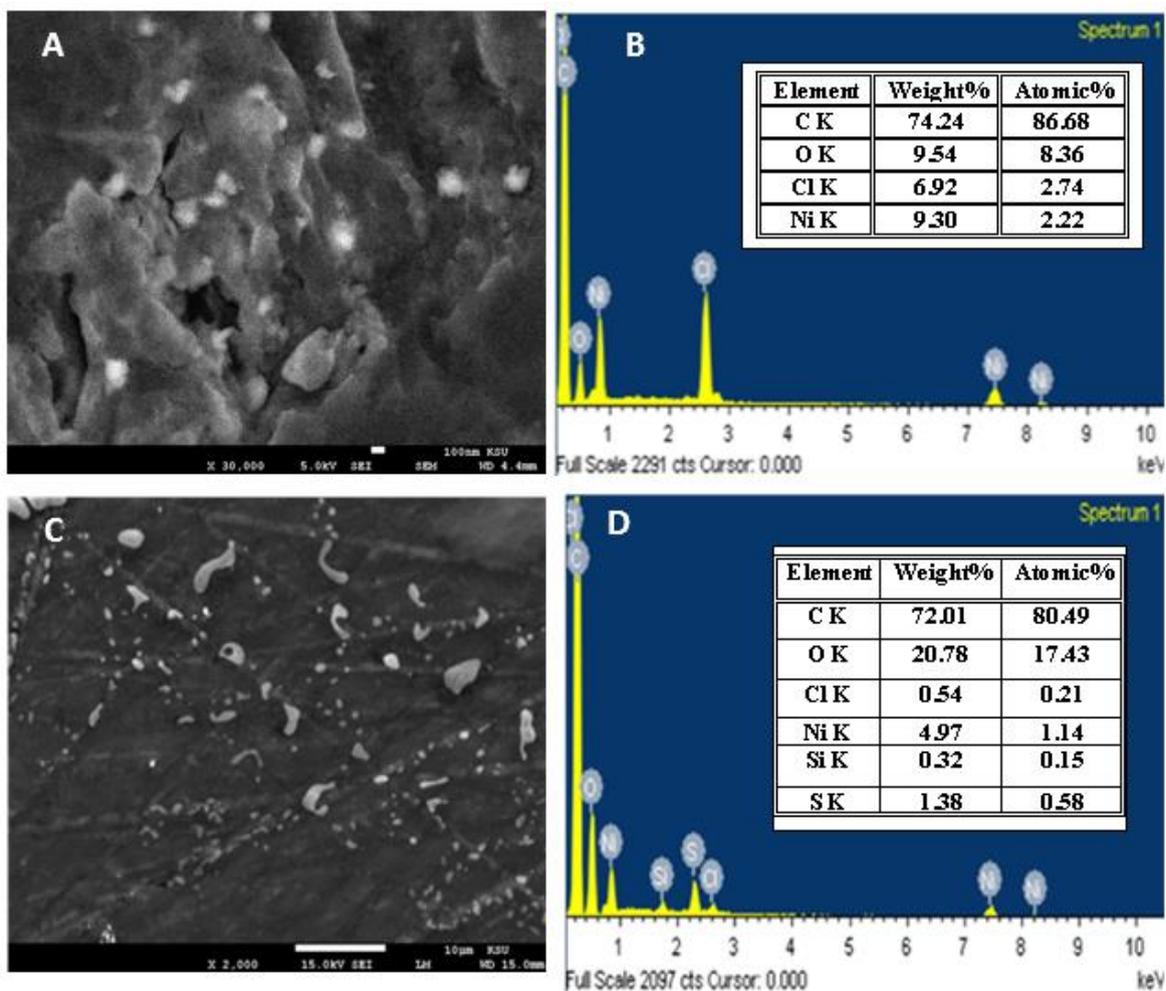


Figure 1. SEM (A, C) and EDX (B, D) of (A, B) NiO_x (Glu)/GCE, and (C, D) NiO_x (Glu)/Gr/GCE electrodes.

3.2. Electrochemical characterizations.

In this work, the GCE was casted by graphene. Then nickel was deposited in the presence and absence of glucose, and then applied for the electrocatalytic oxidation of glucose in alkaline media. (Fig. 2) shows CVs responses obtained (a) NiO_x/Gr/GCE, (b) NiO_x/GCE, (c) NiO_x (Glu)/GCE and (d) NiO_x (Glu)/Gr/GCE electrodes in 0.5 M NaOH. The five potential cycles in the range from 0.0 to -1.0V vs. Ag/AgCl /KCl (sat.) were used to deposit NiO_x nanoparticles onto electrodes. As clearly shown, in (Fig. 2) (curve a), obtained at NiO_x/Gr/GCE electrode in which GCE was electrochemically oxidized and then casted by graphene and subsequently nickel was deposited, the CV is featureless.

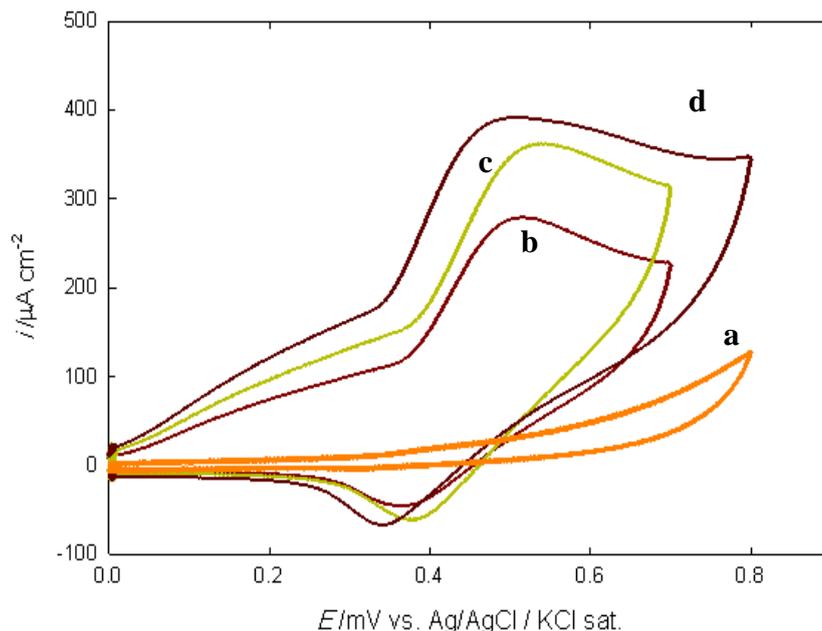


Figure 2. CV obtained at (a) NiO_x/Gr/GCE, (b) NiO_x/GCE, (c) NiO_x (Glu)/GCE and (d) NiO_x (Glu)/Gr/GCE. Scan rate: 100 mV S⁻¹.

Curves b and c shows CV responses obtained at NiO_x/GCE and NiO_x (Glu)/GCE electrodes, respectively. The peak current for nickel couple increases at both electrodes compared with that on the NiO_x/Gr/GCE (a). Probably, the functional groups of the underlying substrate participate in this enhancement [30]. Previously we have reported on the enhancement of glucose electrooxidation by nickel oxide nanoparticles modified electrodes deposited onto a pre-electrodeposited manganese oxide nanoparticles. In the present work the effect of adding additives, typically glucose to the deposition bath is studied [30]. Back to Fig. 2, and comparing curves b and c indicates that including glucose in the deposition bath (curve c) promotes the nickel-nickel oxide redox couple. Curve d, show CV response obtained at NiO_x (Glu)/Gr/GCE electrode. In this case the largest enhancement in the nickel-nickel oxide redox couple is obtained.

Fig. 3 is similar to Fig. 2 but in the presence of 2.5 mM glucose. Table 1 shows data extracted from this figure. The oxidation peak current of glucose increases at NiO_x (Glu)/Gr/GCE electrode (curve d) as compared with NiO_x (Glu)/GCE electrode (curve c). Including of grapheme in the modified electrode enhanced the glucose electrochemical behavior. When grapheme was casted on the electrode, the oxidation peak of glucose is clearly observed and revealed at lower positive potential. Also, the oxidation peak current was doubled compared with that obtained at NiO_x (Glu)/GCE electrode. This indicates that the co-effect of grapheme and NiO_x played an important role in the electrocatalytic oxidation of glucose. The grapheme provides larger surface area for NiO_x as well as for glucose adsorption and assists in faster electrode kinetics [31,32].

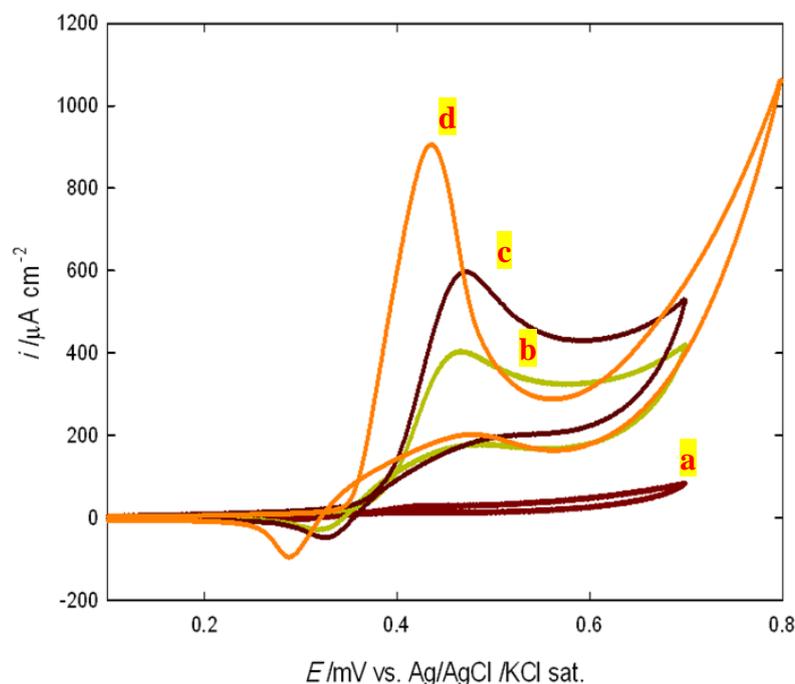


Figure 3. CV obtained at (a) NiO_x (Glu)/GCE, (b) NiO_x/GCE, (c) NiO_x (Glu)/GCE and (d) NiO_x (Glu)/Gr/GCE electrodes in 0.5 M NaOH containing 2.5 mM glucose. Scan rate: 100 mV S⁻¹.

Table 1. Peak potential, peak current and onset potential of glucose oxidation obtained at modified electrodes. Data are extracted from (Fig.3).

Electrode	Peak potential/V	Onset potential/V	Peak current/ μA/cm ²
NiO _x /GCE	0.45	0.35	399
NiO _x (Glu)/GCE	0.46	0.36	616
NiO _x /Gr/GCE	0.43	0.37	31
NiO _x (Glu)/Gr/GCE	0.43	0.34	905

3.3. Effect of loading of nickel oxide nanoparticles.

The extent of NiO_x loading levels at the NiO_x (Glu)/Gr/GCE electrode was examined towards the glucose oxidation reaction and the results are shown in (Fig. 4). A monotonous increase in the peak current of glucose oxidation is observed with the amount of NiO_x. The presence of Gr caused an increase in the anodic peak current of the glucose oxidation reaction at the NiO_x (Glu)/Gr/GCE electrode possibly due to Gr having a large surface area (compared to GCE). This enhances the electrocatalytical activity of the NiO_x/Gr/GCE electrode towards the glucose oxidation reaction.

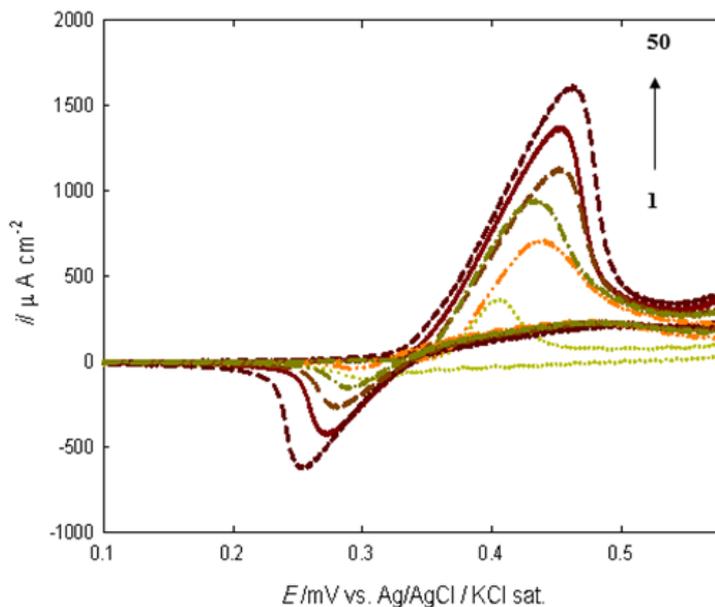


Figure 4. CV obtained at NiO_x (Glu)/Gr/GCE in 0.5 M NaOH containing 2.5 mM glucose, NiO_x was prepared by different potential cycles in the range of 0.1 ~ 0.6 V. Scan rate: 100 mV S⁻¹.

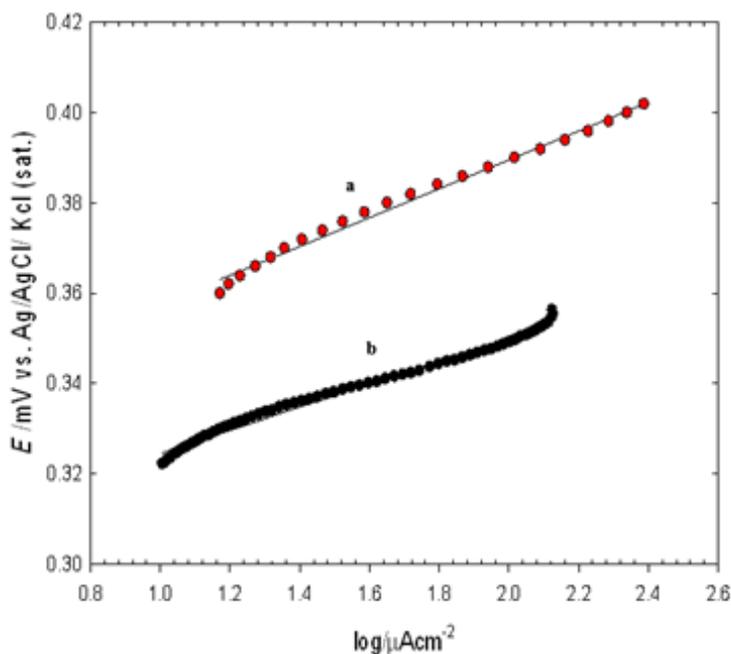


Figure 5. Tafel plots obtained at (a) NiO_x (Glu)/GCE, (b) NiO_x (Glu)/Gr/GCE in 0.5 M NaOH containing 2.5 mM glucose at SR = 5 mV/s.

To get further insight, (Fig. 5) shows Tafel plots obtained at (a) NiO_x (Glu)/GCE, and (b) NiO_x (Glu)/Gr/GCE in 0.5 M NaOH containing 2.5 mM glucose at a scan rate 5 mV/s.

Tafel slopes of ca. 38 mV/dec was obtained at both electrodes. This means the electron transfer represented by Eq. 1. is the rate determining step [33]. The plots confirmed enhanced glucose oxidation on NiO_x (Glu)/Gr/GCE compared to NiO_x (Glu)/GCE.

3.4. Long-term stability of the prepared electrocatalysts.

Graphene when included in electrode modification enhances stability of the modified electrode. The use of graphene as an underlying substrate is thus expected to enhance the redox current and stability of the NiO_x-modified GCE towards the glucose oxidation reaction. Thus, to confirm this, the oxidation current of glucose was recorded at a constant potential of 0.45 V for some time at the two electrodes i.e., NiO_x (Glu)/Gr/GCE (a) electrode and NiO_x (Glu)/GCE (B) electrode (as shown in (Fig. 6). There is a sharp drop in the initial current, followed by a steady current. The initial drop may be due to the rapid oxidation of glucose molecules adjacent to the surface of the modified electrode, and then, the kinetics of the glucose oxidation reaction changes to be a controlled mass transfer-controlled process.

It is clear that the prior casting of Gr over the GCE followed by modification with NiO_x enhances the oxidation of glucose than that obtained at the GCE modified with NiO_x only without pre-casting of Gr. This proves better catalyst optimization in NiO_x (Glu)/Gr/GCE (B) electrode.

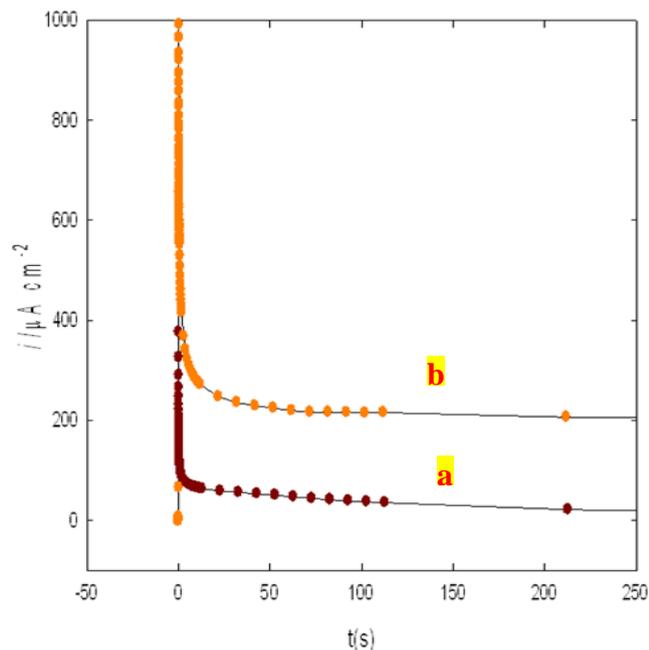


Figure 6. Chronoamperogram obtained at constant potential of 0.45 V at (a) NiO_x (Glu)/GCE, (b) NiO_x (Glu)/Gr/GCE electrodes in 0.5 M NaOH containing 2.5 mM glucose.

Figure 7 shows the function ($I_p/v^{1/2}$) dependency with v obtained at the NiO_x (Glu)/Gr/GCE electrode. As we can see at the higher scan rate from 400 mv/sec, $I_p/v^{1/2}$ does not change significantly

with the scan rate. This behavior is reported as a feature of catalytic reactions [33], i.e., the EC mechanism, represented by Eqs 1 and 2.

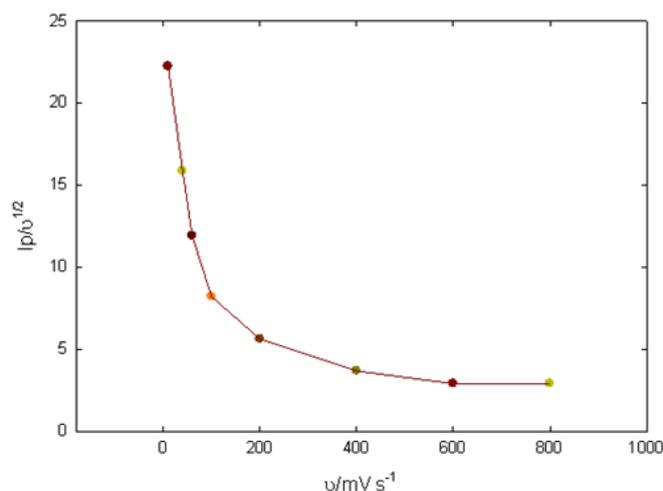


Figure 7. Variation of $I_p/v^{1/2}$ with v for glucose electrooxidation obtained at NiO_x (Glu)/Gr/GCE electrode in 0.5 M NaOH containing 2.5 mM glucose.

4. CONSLUSIONS

Glucose electrooxidation has been studied at NiO_x (Glu)/Gr/GCE modified electrode in which graphene is coated onto glassy carbon underlying substrate and then nickel is deposited subsequently. It has been found that the glucose oxidation reaction critically depends on the involvement of Gr, and the addition of glucose to the nickel deposition bath. The peak current of glucose oxidation is amplified on NiO_x (Glu)/Gr/GCE electrode compared with NiO_x (Glu)/GCE electrode and NiO_x /Gr/GCE. The current transient for glucose oxidation at NiO_x (Glu)/Gr/GCE electrode by applying a constant potential of 0.4 V was larger than that obtained at NiO_x (Glu)/GCE electrode, indicating the activity of the former electrode containing graphene pre-casted before the deposition of Nickel and the prominent role of including glucose in the deposition bath.

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