

*Full Paper*

## **A Comparative Study of Electrochemical Behaviors of 1-nitroso-2-naphthol on Glassy Carbon and Platinum Electrode Surfaces by Cyclic Voltammetry**

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**Abstract-** In the present work, electrochemical and spectroelectrochemical behaviors of 1-nitroso-2-naphthol has been studied by cyclic voltammetry and electrochemical impedance spectroscopy techniques in non-aqueous media. Cyclic voltammetric studies of 1-nitroso-2-naphthol in acetonitrile containing 100 mM tetrabutylammonium tetrafluoroborate on glassy carbon and platinum electrodes were performed between 0.0 mV and +2600 mV potential range at 100 mV s<sup>-1</sup> scan rate with 10 cycles. Anodic peaks were observed at 475.3 mV, 958.9 mV, 1395 mV and 2103 mV for 1-nitroso-2-naphthol on the glassy carbon electrode surface vs. Ag/Ag<sup>+</sup> reference electrode. The surface characterizations were carried out by using cyclic voltammetry and electrochemical impedance spectroscopy techniques in both aqueous and non-aqueous media. Electrochemical behaviors of 1-nitroso-2-naphthol on glassy carbon and platinum electrode surfaces were compared.

**Keywords-** 1-Nitroso-2-naphthol, Modified Electrode, Cyclic Voltammetry, Glassy Carbon Electrode, Platinum Electrode

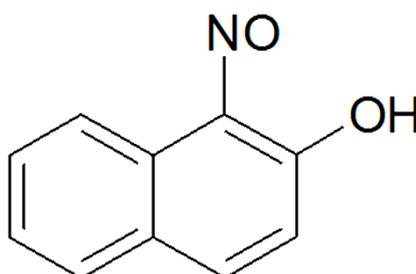
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## 1. INTRODUCTION

Electrochemical methods are based on the direct oxidation or reduction of substrate onto an electrode surface. Electrode reactions are very suitable for analytical applications due to their requirements of high potential [1]. Moreover, these surfaces can be modified by a reductive substrate for analytical applications. Recently, the application of inorganic modified electrodes has increased [2-4].

Electrochemical determination methods have been considered as one of the fastest and cheapest techniques in analytical quantitative determination of different analytical species [5]. Also the maintenance of a clean, reproducible electrode surface is of critical importance in making meaningful electro analytical measurements [6], but in most cases the electrode behavior degrades with time due to adsorption of impurities from the solution or chemical changes to the electrode surface [7].

Several studies were carried out by using 1-nitroso-2-naphthol (Scheme 1). A sensitive procedure is presented for the voltammetric determination of nickel. The procedure involves an adsorptive accumulation of nickel 1-nitroso-2-naphthol complex on a bismuth film electrode prepared *ex situ* by electrodeposition [8]. Gledhill and van den Berg [9] used CLE-CSV with the competitive ligand 1-nitroso-2-naphthol to examine Fe speciation in seawater collected from the North Sea. Demir Mülazımoğlu et al. [10] used 1-nitroso-2-naphthol for the determination of copper (II) and zinc (II) in drinking water using ICP-AES after preconcentration. Krzan et al. [11] used 1-nitroso-2-naphthol in the potential region 0 to +1.0 V vs. Ag/AgCl reference electrode using glassy carbon and platinum electrodes shows a reversible redox couple by cyclic voltammetry. 1-nitroso-2-naphthol was used as a complexing ligand to study Fe speciation and the kinetic interaction of  $\text{Fe}^{3+}$  with excess organic ligands in sea water [12].



**Scheme 1.** Chemical structure of 1-nitroso-2-naphthol

The aim of this study, 1-nitroso-2-naphthol was covalently modified on glassy carbon and platinum electrode surfaces by electrochemical oxidation in non-aqueous media. Electrochemical and spectroelectrochemical behaviors of 1-nitroso-2-naphthol were

investigated by cyclic voltammetry and electrochemical impedance spectroscopy. Cyclic voltammetric studies of 1-nitroso-2-naphthol on glassy carbon and platinum electrode surfaces were performed between 0.0 mV and +2600 mV potential range at 100 mV s<sup>-1</sup> scan rate with 10 cycles. The presence of 1-nitroso-2-naphthol at glassy carbon and platinum electrode surfaces were characterized by cyclic voltammetry and electrochemical impedance spectroscopy.

## 2. EXPERIMENTAL SECTION

### 2.1. Chemicals

1--nitroso-2-naphthol (NN), Tetrabutylammonium tetrafluoroborate (NBu<sub>4</sub>BF<sub>4</sub>), potassium chloride (KCl), acetonitrile (CH<sub>3</sub>CN, HPLC grade) and other chemicals were obtained from Riedel de Haën (Seelze, Germany) or Sigma-Aldrich (Buchs SG, Switzerland), chemical companies and so no further purification was performed. Ultra pure quality of water with a resistance of 18.3 MΩ cm (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used in preparations of aqueous solutions, cleaning of the glassware and polishing the electrodes. In all experiments, the electrodes were kept in CH<sub>3</sub>CN when they were not in use. All the experiment solutions were prepared at 1 mM concentration. Solutions were thoroughly deoxygenated by purging with purified argon gas (99.99%) for 10 min prior to the electrochemical experiments.

### 2.2. Electrochemical equipment and apparatus

Electrochemical measurements were performed with GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA), using a standard cell with three electrodes. The cyclic voltammetry (CV) technique was applied with PHE200 Physical Electrochemistry software, electrochemical impedance spectroscopy (EIS) was applied with EIS300 Electrochemical Impedance Spectroscopy software. The working electrodes were a glassy carbon (GC) electrode BAS (Bioanalytical Systems, West Lafayette, IN, USA) model MF-2012 (3.0 mm dia.) and a platinum (Pt) electrode BAS model MF-2013 (1.6 mm dia.). The reference electrodes an Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) (BAS Model MF-2042) for non-aqueous media and a Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous media were used. Pt wire (BAS Model MW-1032) was used as counter electrode.

### 2.3. Polishing and GC Carbon and Pt Electrodes

The GC electrode, geometric area of the former was 0.071 cm<sup>2</sup> and O-ring delimited area of the latter was 3.0 mm dia., surfaces were prepared for the experiments by polishing to gain a mirror-like appearance, first with fine wet emery papers (grain size 4000) and then with 1.0 μm and 0.3 μm alumina slurry on micro cloth pads (Buehler, USA). After the initial

polishing, the GC electrodes were resurfaced with 0.05  $\mu\text{m}$  alumina slurry. First, in the following order, the GC electrodes were sonicated both in an ultrasonic water bath (Bandelin RK 100, Germany), and then in 1:1 (v/v) isopropyl alcohol (IPA) and  $\text{CH}_3\text{CN}$  (IPA+ $\text{CH}_3\text{CN}$ ) mixture for 5 min [13]. In all experiments, the electrodes were kept in  $\text{CH}_3\text{CN}$  when they were not in use. Electrode surfaces were sonicated with  $\text{CH}_3\text{CN}$  before and after each treatment.

The size of Pt working electrode was 1.6 mm dia. Prior to the surface modification, the Pt electrode was polished on a polishing cloth with wet alumina powders, starting with 0.3  $\mu\text{m}$  particle size and then with finer grades down to 0.05  $\mu\text{m}$ . It was then rinsed with ultrapure water and sonicated for 5 min [14].

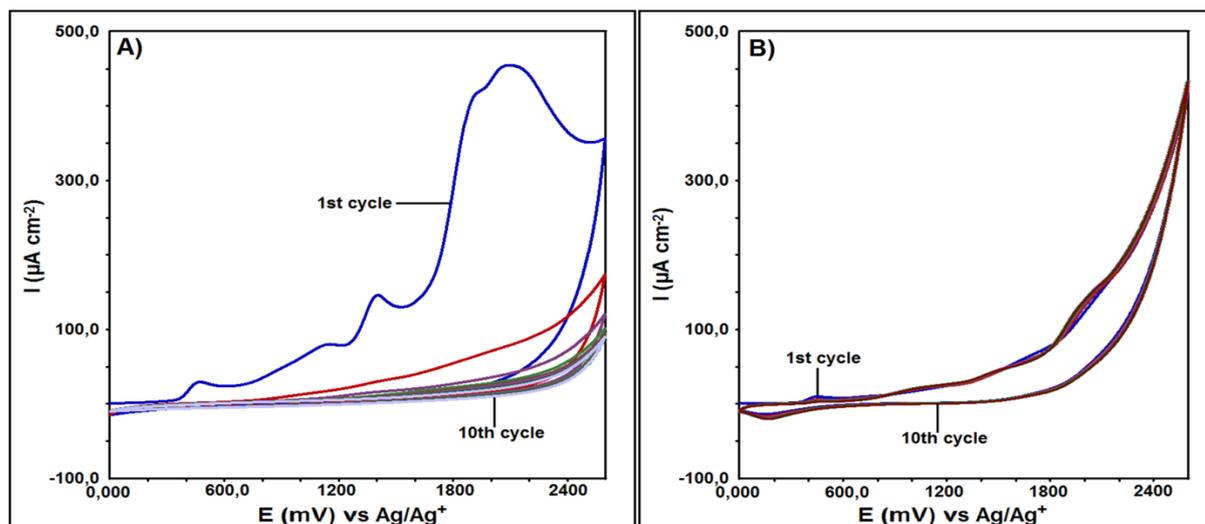
### 3. RESULTS AND DISCUSSION

#### 3.1. Modification of GC and Pt electrode surfaces with NN

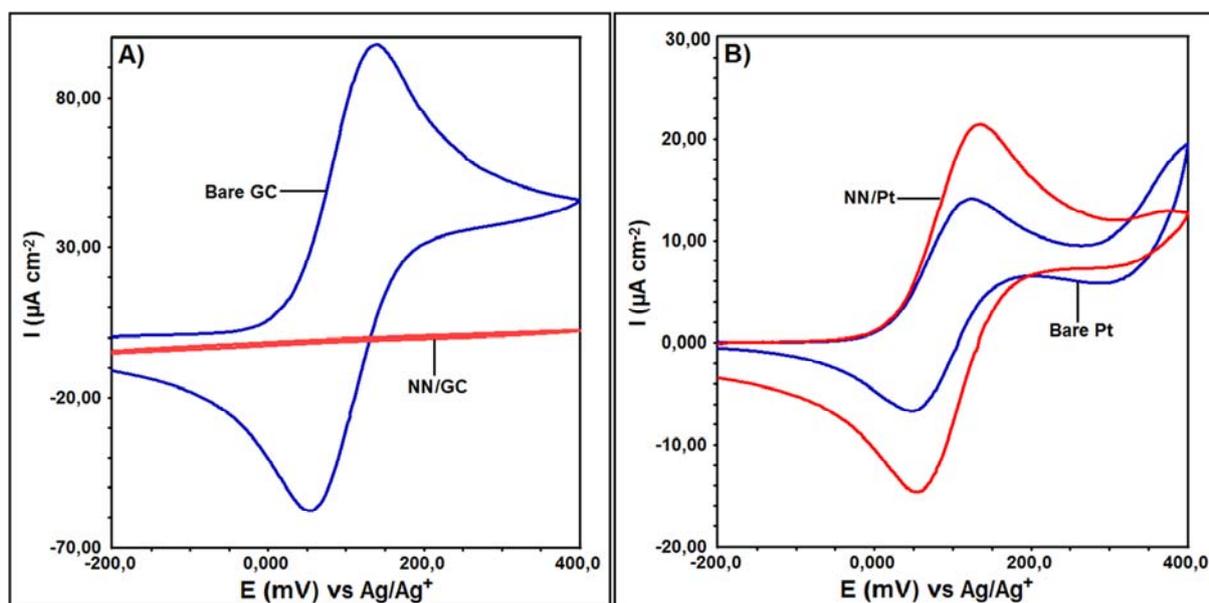
Cyclic voltammetric experiments were performed using 1 mM NN solution in  $\text{CH}_3\text{CN}$  containing 100 mM  $\text{NBu}_4\text{BF}_4$  in the range from 0.0 mV to +2600 mV potential range at 100  $\text{mV s}^{-1}$  scan rate with 10 cycles in non-aqueous media vs.  $\text{Ag}/\text{Ag}^+/(10 \text{ mM AgNO}_3)$ . As can be clearly seen from Fig. 1-A, NN was modified onto GC electrode surface and NN was not modified onto Pt electrode surface (Fig. 1-B). Four irreversible anodic peaks were observed at 475.3 mV, 958.9 mV, 1395 mV and 2103 mV for NN on the GC electrode surface vs.  $\text{Ag}/\text{Ag}^+$  reference electrode.

#### 3.2. Characterization of NN/GC and NN/Pt electrode surfaces by CV and EIS

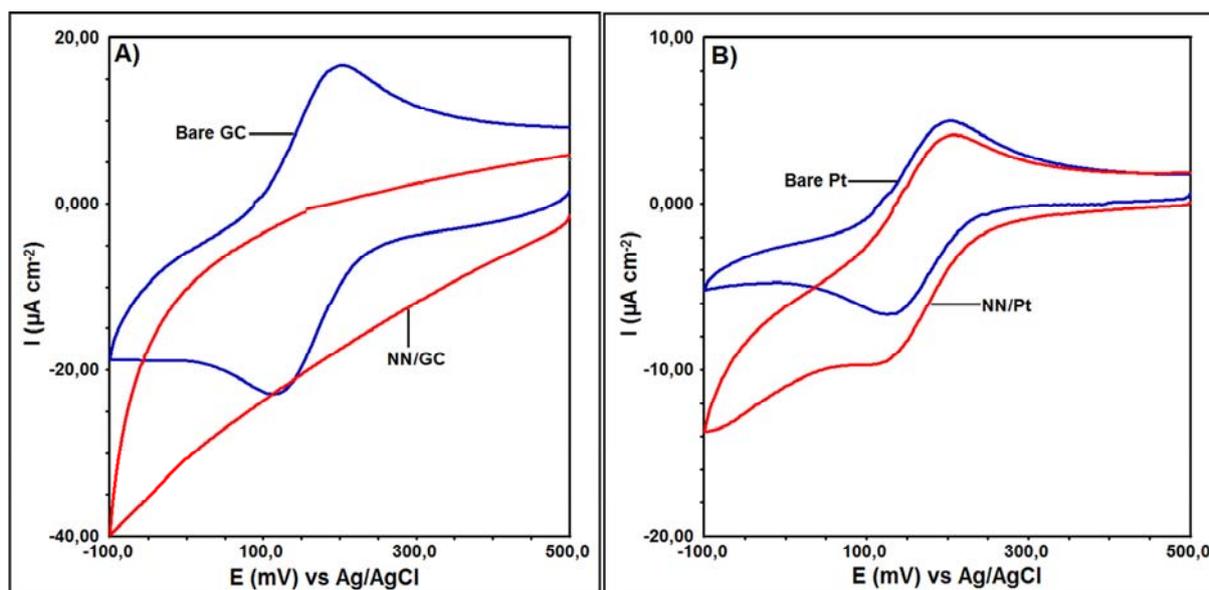
Surface characterizations after the modification process were carried out by CV and EIS. In the characterizations with CV, 1 mM ferrocene solution in 100 mM  $\text{NBu}_4\text{BF}_4$  was carried out the potential range from -200 mV to +400 mV in non-aqueous media and 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  in Britton-Robinson (BR) buffer solution, pH 2, was performed the potential range from +500 mV to -100 mV in aqueous media at scan rate of 100  $\text{mV s}^{-1}$ . Fig. 2 and Fig. 3 were shown in the voltammograms of ferrocene and  $\text{Fe}(\text{CN})_6^{3-}$ , respectively. All potentials are referenced vs.  $\text{Ag}/\text{AgCl}/(3 \text{ M KCl})$  for aqueous media and  $\text{Ag}/\text{Ag}^+/(10 \text{ mM AgNO}_3)$  for non-aqueous media. When the voltammogram obtained in ferrocene and  $\text{Fe}(\text{CN})_6^{3-}$  is overlaid with the voltammogram obtained for bare GC electrode, it is clear that the modified surfaces are not allow electron transfer. However, Pt working electrode surface is allowing electron transfer.



**Fig. 1.** Cyclic voltammograms of 1 mM NN in CH<sub>3</sub>CN containing 100 mM NBu<sub>4</sub>BF<sub>4</sub> vs. Ag/Ag<sup>+</sup>/(10 mM AgNO<sub>3</sub>) onto the GC (A) and Pt (B) working electrodes. Potential range from +0.0 mV to +2600 mV, scan rate is 100 mV s<sup>-1</sup>

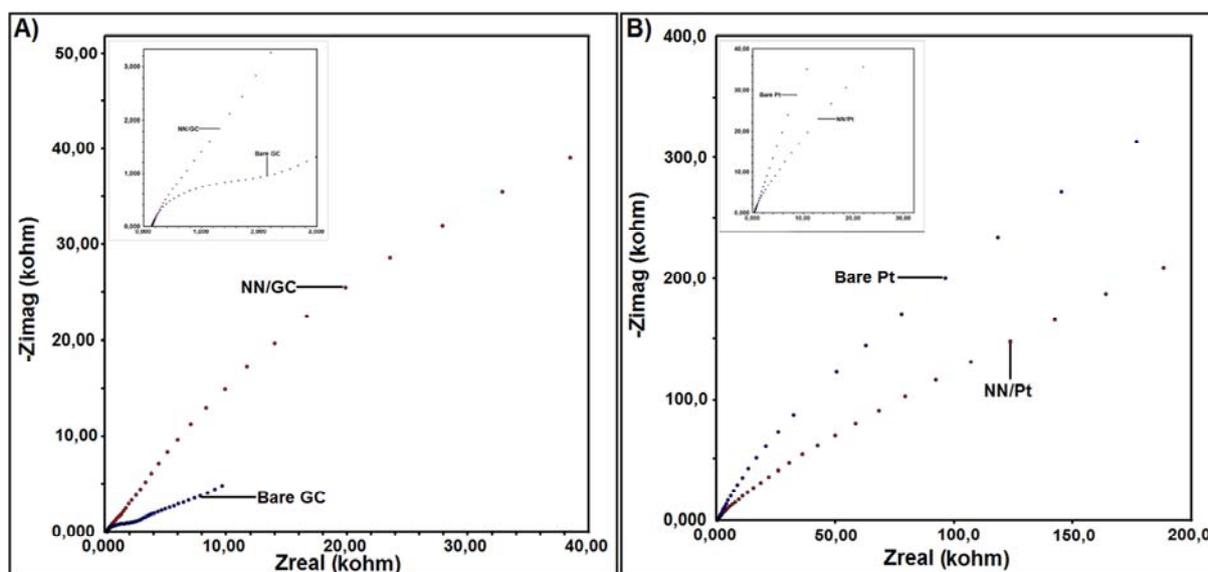


**Fig. 2.** Overlapping cyclic voltammograms for 1 mM ferrocene redox probe solution vs. Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) in CH<sub>3</sub>CN containing 100 mM NBu<sub>4</sub>BF<sub>4</sub> at 100 mV s<sup>-1</sup> scan rate (A, GC; B, Pt working electrodes)



**Fig. 3.** Overlapping cyclic voltammograms for 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  redox probe solution vs. Ag/AgCl/3 M KCl reference electrode in BR buffer solution, pH=2, at  $100 \text{ mV s}^{-1}$  scan rate (A, GC; B, Pt working electrodes)

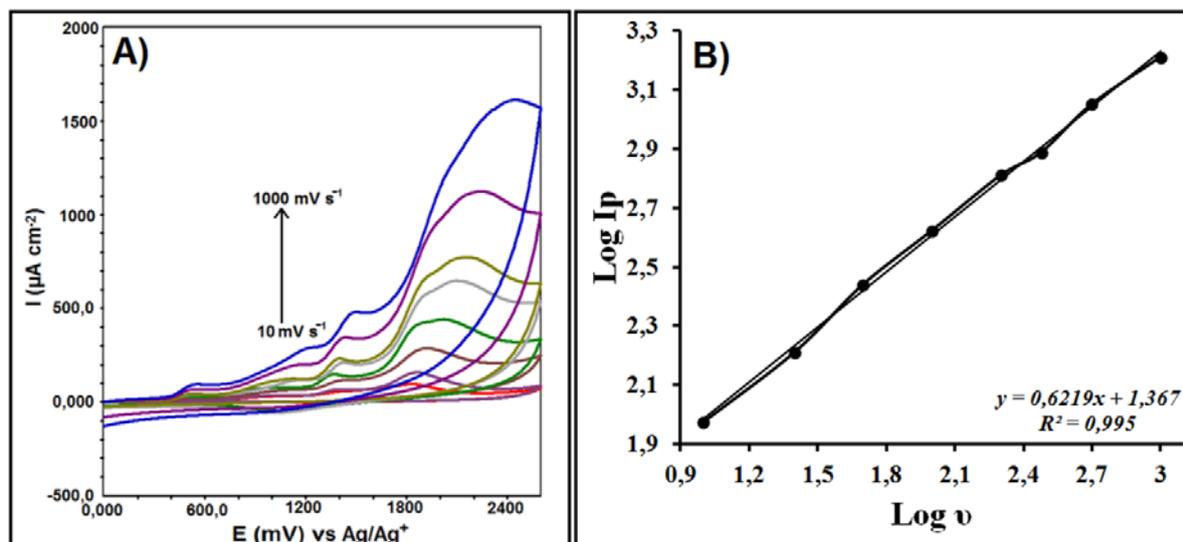
No peak is observed on the voltammogram of the surface characterization tests performed by ferrocene and ferricyanide on electroinactive surfaces on GC electrode. In current research, NN/Pt surface is electroactive. This result is an expected one and an evidence for binding of NN on GC electrode surface. Similar result can be seen in the Nyquist test done by EIS (Fig. 4). The characterization with EIS technique was carried out with a Gamry Reference PCI4/750 potentiostat by EIS 300 software. For the EIS measurements performed in 100 mM KCl containing 1.0 mM equiv.-molar ratio of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ , a sine wave potential alteration at 5 mV amplitude superimposed on a formal potential of the redox probe of 220 mV was applied, a wide frequency range from 100.000 Hz to 0.05 Hz was scanned and the Nyquist plots were recorded.



**Fig. 4.** Nyquist plots for electrochemical impedance spectra of 1 mM  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  redox couple solution in 100 mM KCl at the frequency range of 100.000–0.05 Hz at 10 mV wave amplitude, on GC (A) and Pt (B) working electrodes

### 3.3. Effect of scan rate

The surfaces obtained after characterization processes were evaluated and then it was presupposed that the surface obtained after the modification in non-aqueous media on GC electrode was suitable for the application. In non-aqueous media, it was examined that whether the molecule has binded to the electrode surface through diffusion-controlled or not. For this purpose, by using NN solution prepared in the 100 mM  $\text{NBu}_4\text{BF}_4$  at 10, 25, 50, 100, 200, 300, 500 and 1000  $\text{mV s}^{-1}$  scanning scans, voltammograms with a single cycle potential range from +0.0 mV to +2600 mV with the CV were obtained. These voltammograms as seen in Fig. 5-A were compared by overlaying. Values used for the graph of scan rate logarithm drawn against the peak current values obtained using these voltammograms and logarithm of peak current showing that the molecule bounds to the surface as the diffusion-control are shown in Fig. 5-B.

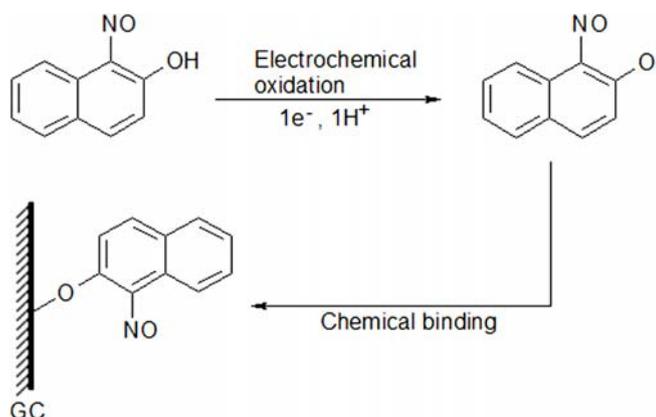


**Fig. 5.** A) Overlapping cyclic voltammograms of different scan rate for 10, 25, 50, 100, 200, 300, 500 and 1000  $\text{mV s}^{-1}$  with a GC working electrode. B) Plot of logarithm of peak current versus logarithm of scan rate dependence of the cyclic voltammetric response at a modified GC electrode

### 3.4. Electrografting NN onto the GC electrode surface

Only a single resonance hybrid exists for both the NN anion and radical, since calculations converge on only one structure regardless of whether the structure of the phenol was used for the input. There is no evidence of the preceding tautomeric equilibrium on the voltammetric behaviors of NN [11].

After the oxidation of -OH group in solution (E mechanism), GC electrode surface was found to be electroinactive from the chemically grafting process (C mechanism) is given in Scheme 2 (EC mechanism).



**Scheme 2.** Modification mechanism of NN at GC electrode surface (in  $\text{CH}_3\text{CN}$  containing 100 mM  $\text{NBu}_4\text{BF}_4$ )

#### 4. CONCLUSION

By the use of NN for the modification of GC electrode surface, an electroinactive surface was obtained in this study. Modification process has been carried out by using CV, electrochemical and spectroelectrochemical surface characterization processes have been done by using CV and EIS. The following step of this research will be the use of this developed electrode as a chemical sensor electrode for the quantitative determination of polyphenolic molecules and metal samples in different media.

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