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Electrochemically Reduced Graphene Oxide/ Neodymium Hexacyanoferrate Modified Electrodes for the Electrochemical Detection of Paracetomol

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The Electrochemically reduced graphene oxide (ERGO)/ Neodymium Hexacyanoferrate (NdHCF) film has been successfully fabricated on the glassy carbon electrode (GCE) and ITO using cyclic voltammetry. The morphology of the as-prepared ERGO/NdHCF composite was investigated by scanning electron microscopy (SEM). Fabricated film modified GCE has been successfully employed for the detection of P-acetoaminophenol in lab analysis and as well as in real paracetomol drug samples. The ERGO/NdHCF film modified GCE successfully detects the P-acetoaminophenol with the detection limit of 14.22 μM in lab samples. Also, the proposed film successfully detects the real sample Paracetomol drug with a detection limit of 3.2 μM respectively.

Keywords: Electrochemically Reduced graphene oxide, Neodymium Hexacyanoferrate, electro oxidation, P-acetoaminophenol, Electroanalysis, Electrochemistry.

1. INTRODUCTION

In recent years, considerable attention has been attracted towards the modification of electrode with transition metal hexacyanoferrate resulting to their wide applications[1,2] in electrocatalysis, electrochromism, ion-selective electrodes, anticorrosion, and memory devices since 1978 Neff reported Prussian blue modified electrodes for analytical applications[3].In particular, transition metal hexacyanoferrate have increased a greater interest as a materials in chemical sensors because of their attractive properties. Nickel [4], tin [5], osmium [6], lanthanum [7], terbium [8], cerium [9], yttrium [10] and Neodymium hexacyanoferrate films [11-13] have been reported as sensor materials.

Other than Neodymium hexacyanoferrate, Graphene based electrochemical sensors have exhibited excellent analytical performance for the detection of biomolecules due to its attractive mechanical, electronic and thermal properties. It also have some unique electrochemical properties such as fast electron transfer, excellent conductivity and wide potential windows [14,15].We have prepared reduced graphene oxide using the electrochemical method, which has low cost , high sensitivity and without using any toxic solvents[16].

Acetoaminophenol or paracetomol is a widely used analgesic drug. It is used for the relief of moderate pain for headache, backache and also used for reduction of fevers [17, 18].There are many analytical techniques have been employed for the detection of acetoaminophenol such as spectrophotometric [19, 20], HPLC [21], Flow injection analysis [22] and electrophoresis [24] .Comparing with above methods, we need a simple, highly sensitive and low cost instrument for the detection of acetoaminophenol. Electrochemical methods are found to be convenient, reliable, cheapest and important one for the acetoaminophenol detection [25-26]. Metal hexacyanoferrate modified electrodes have been widely studied for their interesting electrochemical applications [27-30]. To the best of our knowledge, there is no report on electrochemically reduced graphene oxide(ERGO)[31-32] and Neodymium hexacyanoferrate(NdHCF) composite modified film for the electrocatalytic oxidation of P-acetoaminophenol[33-34].

In this report, we have fabricated the electrochemically reduced graphene oxide (ERGO)/ Neodymium hexacyanoferrate (NdHCF) film on GCE and ITO by using cyclic voltammetry (CV). Surface morphological study has been analyzed using scan electron microscopy (SEM). Fabricated ERGO/NdHCF film modified GCE showed significant response for the detection of acetoaminophenol in lab and real samples using Linear sweep voltammetry.

2. EXPERIMENTAL

2.1. Reagents

Graphite powder was purchased from Sigma-Aldrich. Neodymium (III) chloride hexahydrate were purchased from Aldrich. Potassium Ferri cyanide and potassium chloride was purchased from sigma Aldrich. Paracetomol drug were purchased from near hospital and p-acetoaminophenol were obtained from sigma Aldrich Company. The supporting electrolyte used for all electrochemical experiment is pH 3 phosphate buffer solution prepared by using 0.05 M potassium hydrogen phthalate. All the reagents were used for the experiments prepared by utilizing doubly distilled water. Electrochemical experiments were carried out using a single compartment, three-electrode cell apparatus under nitrogen atmosphere.

2.2. Apparatus

Electrochemical measurements like cyclic voltammetry (CV) and linear sweep voltammetry (LSV) was performed by a CHI 1205A electrochemical analyzer. A conventional three-electrode cell

were used at room temperature with glassy carbon electrode (GCE) (Surface area =0.07 cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphological of the film was studied by SEM (Hitachi S-3000H, Japan). Indium tin oxide (ITO) thin film coated glass electrodes have been used for SEM. Electrochemical impedance studies (EIS) were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co KG, Germany).

3. RESULTS AND DISCUSSION

3.1. Fabrication and characterization of ERGO/ NdHCF Modified electrode

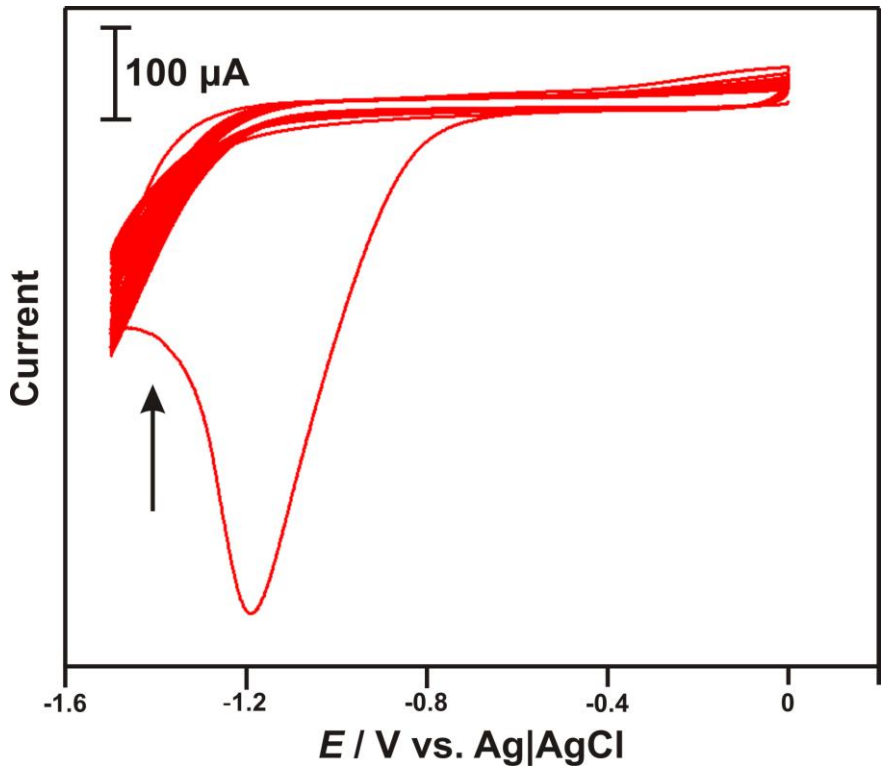

Figure 1. Cyclic Voltammogram of Electrochemical reduction of 0.5 mg/ml Graphene oxide 30 cycles in 0.05 M PBS (pH 5) solution in the plot of Potential Range between -1.5 to 0 V at the scan rate of 0.03 V/S.

Graphite oxide was prepared by Hummers method [35]. As prepared, graphite oxide was dispersed in water and sonicated for 2 hours, to form exfoliated graphene oxide (GO). The prepared GO (0.5 g/ml) was well dispersed in water. About 8 µl of GO was drop casted on the pre-cleaned GCE and dried at room temperature. The GO modified GCE was transferred to an electrochemical cell containing 0.05 M PBS (pH 5) solution. 30 successive cyclic voltammograms were performed in the potential range between 0 and -1.5 V at the scan rate of 30 mV s^{-1} (see fig.1). During the first cathodic

potential scan, a large cathodic peak appears at -1.0 V with an onset potential of -0.75 V. After several cycles, this cathodic peak disappeared completely, attributed to the reduction of oxygen moieties at the GO basal plane [36].The GO sheets are mostly decorated with epoxy and hydroxyl groups on the basal plane, while carbonyl and carboxyl groups are located at the edges [37]. The Electrochemically reduced graphene oxide (ERGO) modified GCE was dried in air for few minutes.

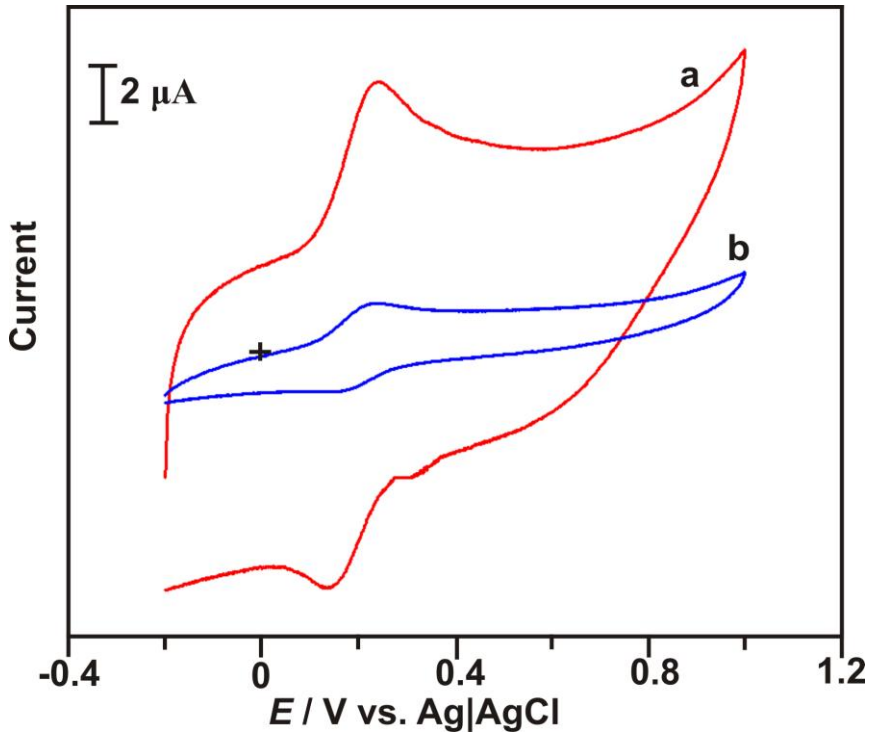

Figure 2. Cyclic voltammogram signals of a) Neodymium hexacyano ferrate/ERGO/GCE b) Neodymium hexacyano ferrate/GCE.

Neodymium Hexacyanoferrate (NdHCF) used in this work was prepared according the procedure reported in the literature [38]. 5 mM neodymium (III) chloride hexahydrate and 5 mM of potassium ferricyanide were dissolved in 0.1 M KCl solution. Then 10 µl of as prepared NdHCF was drop casted on the ERGO modified GCE to obtain ERGO/NdHCF modified electrode. To verify the NdHCF deposition process, only NdHCF film has been drop casted on the GCE (Fig2). In the only NdHCF deposition process, specific redox peaks were obtained at 0.231 V. These results clearly reveal that, the presence of electrochemically reduced graphene oxide (ERGO) increases the redox peak current and were successfully employed on the GCE.

3.2. Different scan rate studies

Figure 3. Shows the CVs recorded for the ERGO/NdHCF/GCE in N_2 saturated pH 3 PBS at different scan rates. The ERGO/NdHCF composite film exhibits well defined redox peaks at the scan rate of 100 mV s^{-1}. Both these redox peaks exhibit a linear dependence on scan rates. The redox peak

current and peak potential (ΔE_p) increased with increase in scan rates between 0.01 – 0.1 Vs^{-1}, which confirmed the surface confined redox process. The linear dependence of I_{pc} and I_{pa} peaks of the different scan rates is shown in the inset of figure 3.

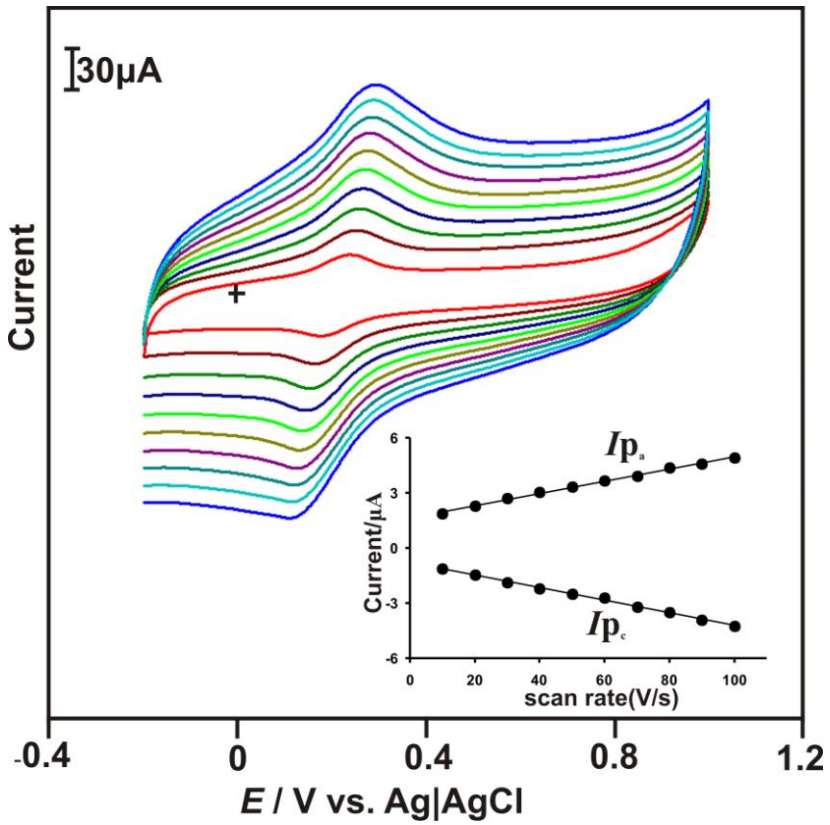

Figure 3. Different Scan rates of electrochemically reduced graphene oxide and Neodymium Hexacyano ferrate modified electrode in pH 3 at various scan rates from 0.01 to 0.1 V/S. Inset shows current vs. scan rate plot at pH 3.

3.3. Impedimetric and SEM analysis

The ERGO/NdHCF modified film has been examined by using electrochemical impedance analysis (see fig.4). Electrochemical impedance analysis is generally studied by utilizing an equivalent circuit model, which suites and associates with the electrochemical properties of the film modified GCE. Nyquist plot of electrochemical impedance spectra generally explicates the electron transfer nature of the film. Here Figure 4 displays the Nyquist plots of the bare (curve a) and ERGO/NdHCF film (curve b) modified GCEs in pH 3 PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$. Here the respective semicircle parameters correspond to the electron transfer resistance (R_{et}) and the double layer capacity (C_{dl}) of the film. As can be seen in Figure 4, bare GCE exhibits a semi circle area (R_{et} = 1017 Ω) which is larger than the ERGO/NdHCF film (R_{et} = 541 Ω). This shows that the ERGO/NdHCF film possesses the lower electron transfer resistance comparing with the bare GCE which enhances the electron-transfer kinetics process as a faster one and more suitable for the electrocatalytic activities, respectively.

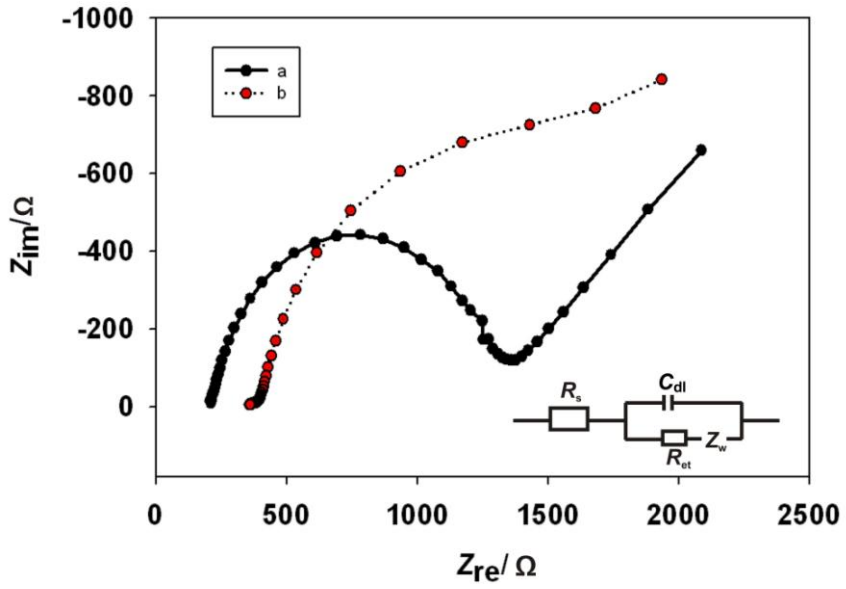

Figure 4. EIS response of (a) bare and (b) film modified GCE in pH 7 PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$. Inset shows the simple Randles circuit model for the ERGO/NdHCF film.

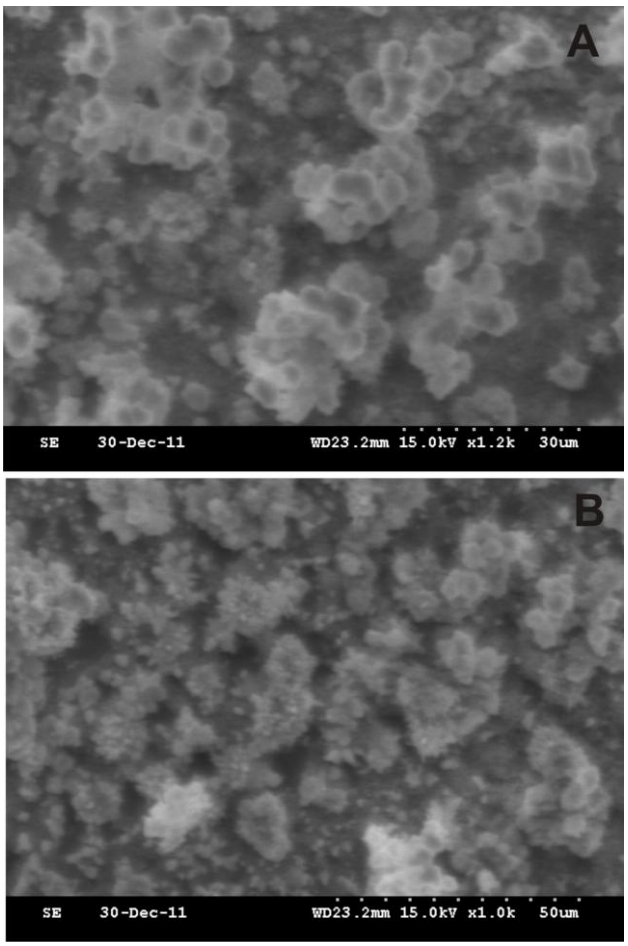

Figure 5. SEM images of the ERGO/NdHCF film modified ITO (magnifications (30 μm) and (50 μm)).

Further a simplified randles circuit model (Fig 4(inset)) has been used to fit the impedance spectra. Here the simplified randles circuit model well suites with the impedance spectroscopic results and the fit model error for the film was found as 7.3%. Finally the electrochemical impedance spectroscopic analysis clearly illustrates the electrochemical behavior of the ERGO/NdHCF film, respectively.

In Fig.5 the ERGO/NdHCF film modified ITO has been employed for the SEM analysis. Figure 5(A) and (B) shows the large scale view [(30 μm)] and magnified views [(50 μm)] of electrodeposited ERGO/NdHCF film modified ITO. Based on Fig. 3(A) and (B) we can clearly see the existence of electrodeposited ERGO particles on the ITO surface. Here the NdHCF has been co-deposited as thin film on the ITO surface. Finally SEM results clearly explicate the surface morphological nature of the ERGO/NdHCF film.

3.4. Electrochemical detection of paracetomol at ERGO/NdHCF modified GCE

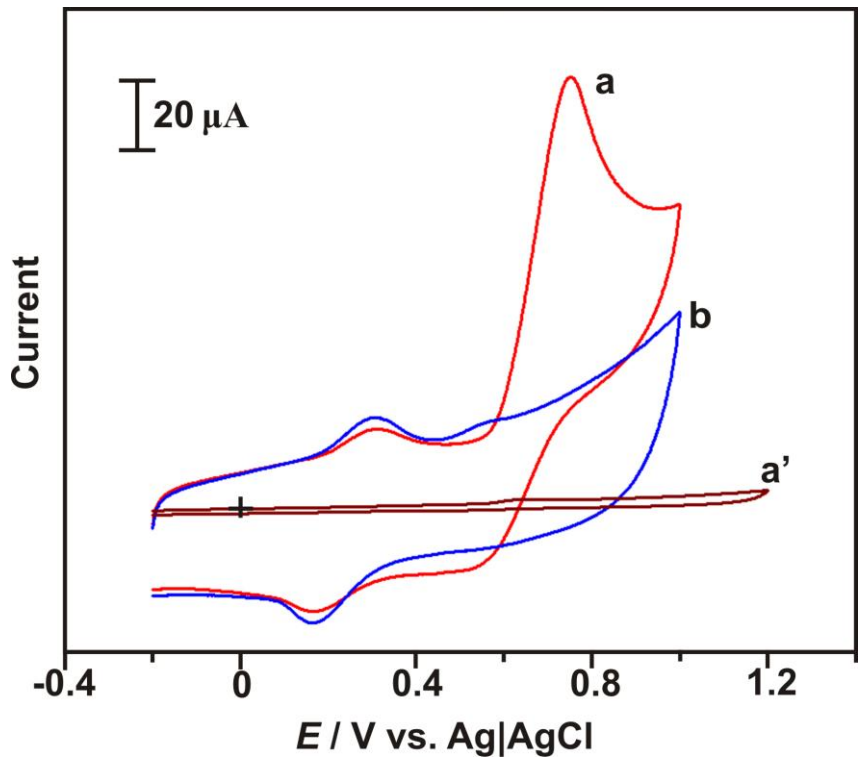

Figure 6. Electro catalytic response of P-acetoaminophenol at high concentration in pH 3 at a) ERGO and Neodymium hexacyano ferrate modified GCE, b) Neodymium hexacyano ferrate modified GCE, a') Bare GCE.

Electrochemical detection of paracetomol has been examined using CV and LSV techniques. At first, CV has been employed for the detection of. Figure 6 curve a shows CV response of the ERGO/NdHCF modified GCE for the electrochemical detection of at higher concentration in pH 3.0 PBS. Here, the P-acetoaminophenol oxidation signal appears at 0.75 V. Curve b displays only for the NdHCF modified GCE it does not shows any obvious response for the detection of paracetomol. At the

same time, bare GCE shows diminished current response for the detection of (curve a'). This shows that modified GCE possesses capability for detection of. In the next step, ERGO/NdHCF modified GCE has been employed for the LSV detection of P-acetoaminophenol.

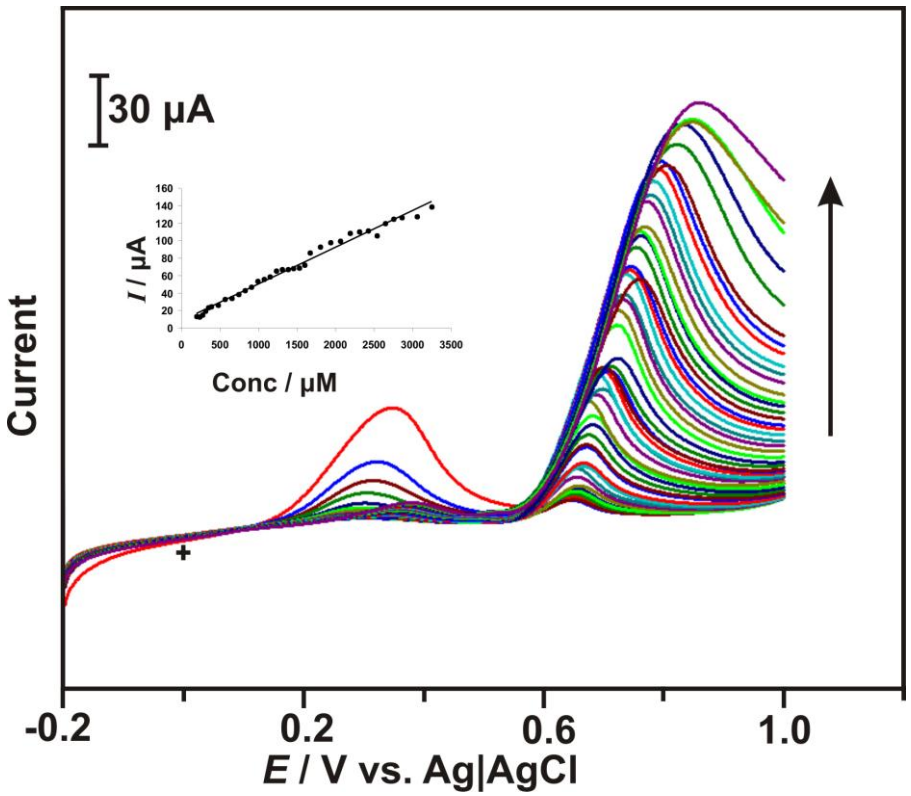

Figure 7. LSV of Electrochemically reduced graphene oxide and Neodymium hexacyano ferrate modified electrode for the different concentrations of P-acetoaminophenol (Lab sample) in pH 3. Inset shows a current Vs. Concentration plot of P- acetoaminophenol.

In figure.7 the electrochemical detection signal of appears at the 0.65 V. For the continuous additions of the ERGO/NdHCF film shows well distinguished anodic oxidation peaks which linearly dependent on the increasing concentrations of, respectively. This result validates the capability of the proposed film will be suitable for the detection of in the certain linear ranges in pH 3.0 PBS. The inset of Figure7 shows the current versus calibration plot for the detection. The sensitivity and the detection limit of the detection at the film modified GCE was found as 0.531 µA $\mu M^{-1}cm^2$ and 14.22 µM, respectively.

In the next step, the -modified GCE has been employed for the detection of in real samples. Commercially available paracetomol drug was used for the real sample analysis process. As expected, the modified GCE shows the oxidation signals of paracetomol at 0.684 V in figure.8. The sensitivity and detection limit of the ERGO/NdHCF film for the paracetomol, detection was found as 0.1367 µA $\mu M^{-1}cm^2$ and 3.2 µM. This shows that the proposed film holds the capability to detect the P-acetoaminophenol in real samples.

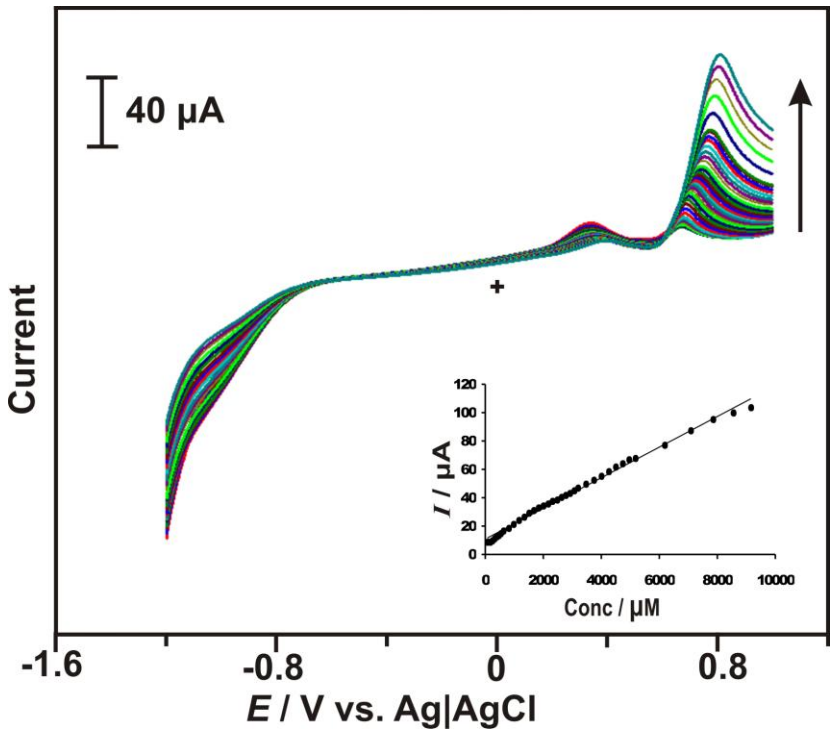

Figure 8. LSV of electrochemically reduced graphene oxide and Neodymium hexacyano ferrate modified electrode for the different concentrations of P-acetoaminophenol (Real sample) in pH 3. Inset shows a current Vs. Concentration plot of P- acetoaminophenol.

3.5. Stability studies

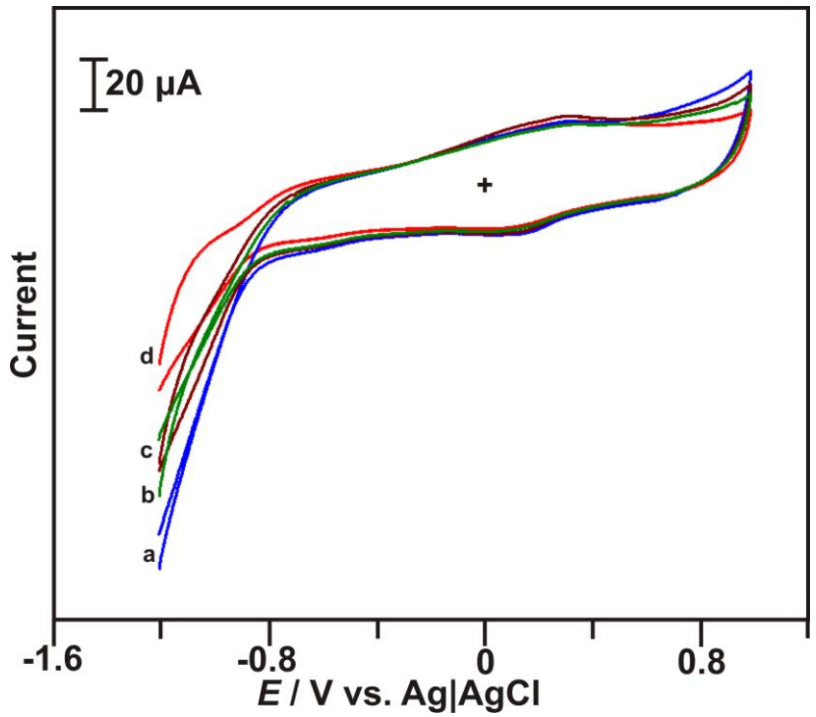

Figure 9. Cyclic response of ERGO and Neodymium hexacyano ferrate modified GCE in the pH 3 PBS a) first day b) second day c) second day after 6 hours and d) Third day.

Stability of the ERGO/NdHCF film modified GCE was investigated by storing it in air at 4 ºC and further checking the back-ground current response in pH 3.0 PBS. It was stable for 2 days and few gradual decreases occurred in the reduction and oxidation peak potentials (Fig.9). Further by increasing the amount of Neodymium Hexacyanoferrate and other factors, we can improve the stability of this type of modified electrodes.

4. CONCLUSIONS

In conclusion, we have successfully fabricated the ERGO/NdHCF using the cyclic voltammetry and employed for the detection of p-acetoaminophenol using CV and LSV. The proposed film shows the p-acetoaminophenol detection signals at the stipulated conditions. Not only limited to lab sample, the proposed film modified GCE also employed for the p-acetoaminophenol in real samples. . Based on these results, we conclude that the ERGO/NdHCF could be employed as the electrochemical sensor for the detection and determination of p-acetoaminophenol.

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