

# Amperometric Determination of 4-Nitrophenol at Multi-Walled Carbon Nanotube-Poly(Diphenylamine) Composite Modified Glassy Carbon Electrode

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In this work we report the fabrication of multi-walled carbon nanotube-poly(diphenylamine) (MWCNT-PDPA) composite film modified glassy carbon electrode (GCE) and its application for the electrochemical reduction of 4-nitrophenol (4-NP). Diphenylamine (DPA) was polymerized on the MWCNT modified GCE by cyclic voltammetry (CV) in 5 M H<sub>2</sub>SO<sub>4</sub>. The surface morphology of MWCNT-PDPA was studied using Scanning Electron Microscopy (SEM). The interfacial electron transfer phenomenon at the modified electrode was studied using electrochemical impedance spectroscopy (EIS). 4-NP showed a well defined reduction peak at -0.71 V (vs. Ag/AgCl electrode) at the MWCNT-PDPA modified GCE. The MWCNT-PDPA composite film showed good electrocatalytic behavior towards the reduction of (4-NP) in pH 7. The MWCNT in MWCNT-PDPA film enhanced the reduction peak current by several times. The peak current increased linearly with 4-NP concentration. The amperometric determination of 4-NP at the composite film modified electrode showed linear range from  $8.9 \times 10^{-6}$  M to  $1.43 \times 10^{-3}$  M. These results show that the proposed composite film modified electrode may be developed for potential application in real sample analysis.

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**Keywords:** 4-nitrophenol, multi-walled carbon nanotube, diphenylamine, cyclic voltammetry, amperometry

## 1. INTRODUCTION

4-nitrophenol is an important compound used in the synthesis of many organic dyes, fungicide, pesticide, industrial chemicals and pharmaceutical products. These industries are sources of 4-NP releasing into the environment. It is not easily degradable and hence it exists in the environment, especially in groundwater for long time [1]. 4-NP poses a threat to living beings due to their

carcinogenic and recalcitrant properties [2]. Therefore it is very important to develop efficient methods for the determination of 4-NP in environment. Many electrochemical methods have been used for the determination of 4-NP due to their low cost, high sensitivity and fast results. Cyclic voltammetry [3-7] have been an effective tool for the study of electrochemical reduction and determination of 4-NP and various electrodes. Determination of 4-NP by electrochemical reduction and oxidation process by SWV [8, 9] and DPV [10, 11] have shown high sensitivity and good linearity.

Carbon nanotubes (CNT) have been extensively used in electrode modification for electrochemical studies, due to their high specific surface area, excellent structural, electronic and mechanical properties. In many cases CNT is used after pretreatment or functionalization. Previous reports show that electrodes modified with pretreated CNT exhibit very good catalytic activity towards the electrochemical oxidation of substances like phenolic compounds [12-14] alkaloids [15] etc. The fouling of the electrode surface is one of the problems faced in the electrocatalysis of phenolic compounds. Another problem is that the nitro phenols undergo oxidation at higher potentials around +1.0 V which destabilizes the matrix easily. Therefore, CNTs are modified with conducting polymers or other electroactive substances for improving sensitivity and the linear range of detection [16]. Poly (diphenylamine) (PDPA) is a conducting polymer similar to aniline in structure, but has some differences in properties. Diphenylamine (DPA) can be polymerized by CV [17-19] and pulse potentiostatic method [20]. Baibarac et al. [21] synthesized polydiphenylamine/single walled carbon nanotube (PDPA/SWNT) composites by CV and a detailed mechanism of electrochemical polymerization has been reported. In this work, we report the application of MWCNT-PDPA film modified GCE for the cathodic determination of 4-NP by cyclic voltammetry and by amperometry in pH 7.

## 2. EXPERIMENTAL

### 2.1 Apparatus

The cyclic voltammetric experiments were conducted on CHI 611A electrochemical workstation. A conventional three electrode system was used for cyclic voltammetry (CV) with GCE modified with MWCNT, PDPA and MWCNT-PDPA as working electrodes, a thin Pt wire as counter electrode and Ag/AgCl (sat. KCl) as reference electrode. EIS measurements were performed using IM6ex ZAHNER (Kroanch, Germany). SEM was performed using a Hitachi S-3000 H Scanning Electron Microscope. The amperometric experiments were performed using CHI 750 potentiostat with analytical rotator AFMSRX (PINE Instruments, USA).

### 2.2 Reagents and materials

MWCNTs with O.D. 10 – 15 nm, I.D. 2–6 nm, length 0.1–10  $\mu\text{m}$  was obtained from Sigma–Aldrich. Diphenylamine (99+%, A.C.S. reagent) and 4-nitrophenol were obtained from Aldrich Chemical Company Inc., USA. 0.1 M phosphate buffer solution (PBS) was prepared from 0.1 M

$\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  in doubly distilled deionized water to get a pH of 7. Inert atmosphere was set by passing  $\text{N}_2$  over the solution during experiment. All the experiments were conducted at  $25^\circ\text{C} \pm 2$ .

### 2.3 Preparation of MWCNT-PDPA composite modified electrode

As purchased MWCNT was hydrophobic in nature and could not produce a stable and homogeneous dispersion in aqueous media. MWCNT was pretreated and functionalized by following the procedures reported earlier [22, 23]. 150 mg of MWCNT was heated at  $350^\circ\text{C}$  for 2 h and cooled to room temperature. Then it was ultrasonicated for 4 h in concentrated HCl to remove impurities like amorphous carbon and metal catalysts.

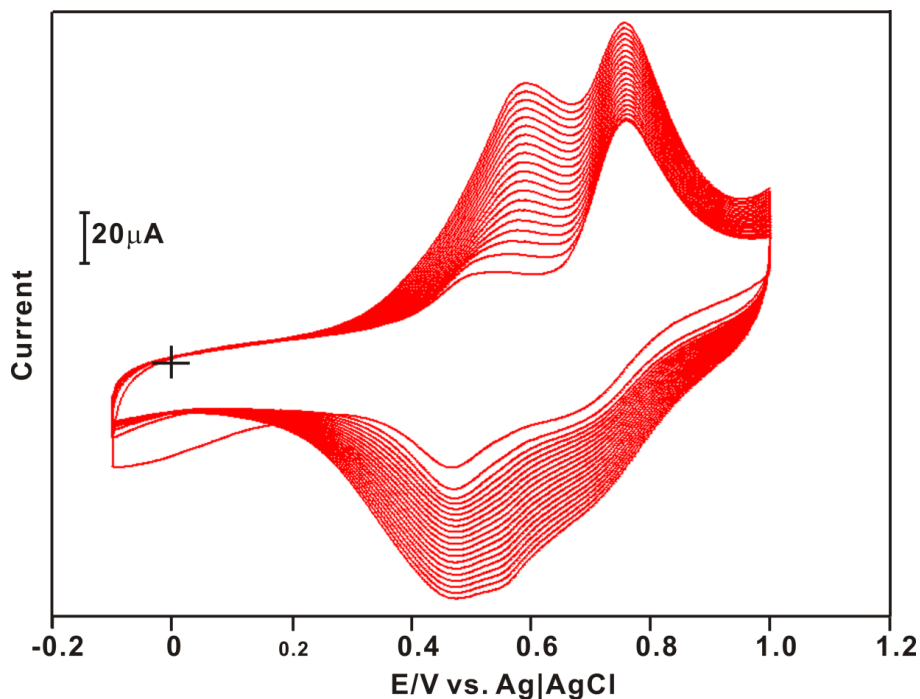
It was filtered and washed thoroughly with deionized water until the pH of the washing was 7. The filtered MWCNT was dried at  $100^\circ\text{C}$ . Carboxylation of the MWCNT was done by sonicating the pretreated MWCNT in a mixture of sulfuric acid and nitric acid in 3:1 ratio for 6 h. It was then washed several times with deionized water until the washing was neutral. GCE was polished using  $0.05 \mu\text{m}$  alumina slurry and Buehler polishing cloth. To fabricate the MWCNT-PDPA modified electrodes, 1 mg of the functionalized MWCNT was dispersed into 1 mL of doubly distilled deionized water by ultrasonication for 30 minutes. A well dispersed homogeneous solution of MWCNT was obtained.  $3 \mu\text{L}$  of MWCNT dispersion was drop casted onto the well polished GCE and dried. Electropolymerization of DPA was done on MWCNT-GCE by continuous cycling in a three electrode system by cyclic voltammetry.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Electropolymerization of DPA

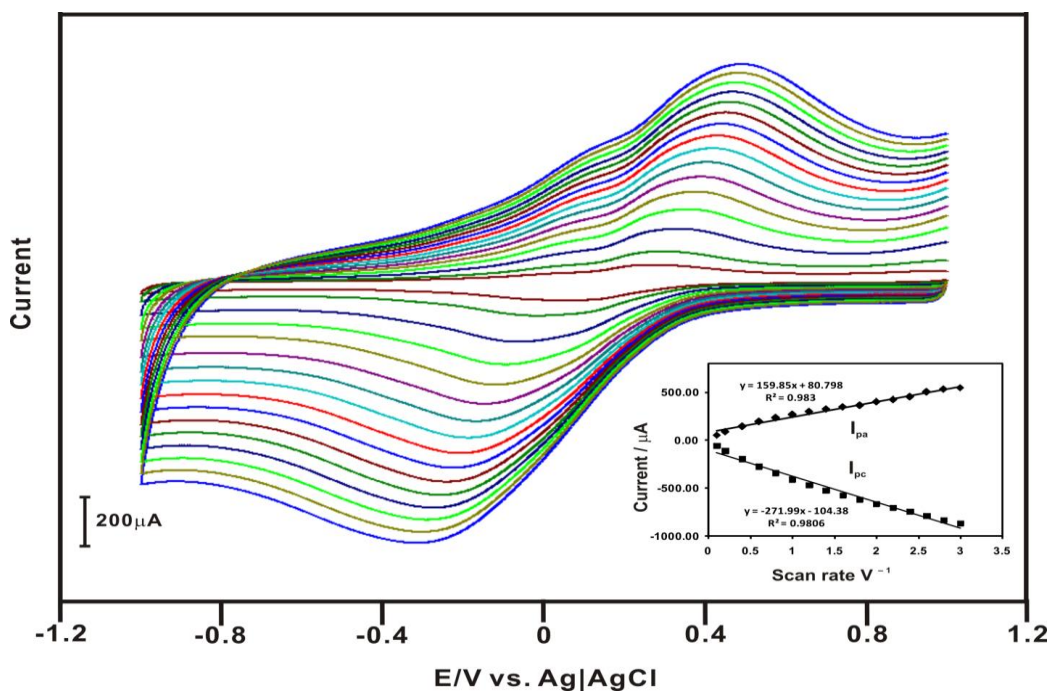
Fig. 1 shows the cyclic voltammogram of the electropolymerization of DPA on MWCNT-GCE. CV was recorded by continuous potential cycling for 20 cycles in the range of  $-0.1$  to  $1.0 \text{ V}$  vs. Ag/AgCl (sat KCl) at a scan rate of  $0.1 \text{ Vs}^{-1}$  in  $5 \text{ M H}_2\text{SO}_4$  containing  $1 \times 10^{-3} \text{ M}$  monomer concentration. The continuous growth of PDPA exhibits two redox processes. The first oxidation peak appears at  $0.59 \text{ V}$  and the second one appears at  $0.76 \text{ V}$  during the anodic scan. The oxidation peak at  $0.59 \text{ V}$  is due to the removal of one electron from the amino group to form a positively charged N, N'-diphenylbenzidine type ion radical ( $\text{DPA}^{+\bullet}$ ) [24]. Then, a removal of proton from two such monomer radicals dimerizes to form a dimer of DPA.

The coupling takes place at the para position [18]. Further oxidation leads to the growth of PDPA chain. A detailed mechanism for electropolymerization of DPA was previously reported by Wu et al. [25]. During negative scan, the polymer is reduced by the protonation of the nitrogen atom in the backbone of the polymer. The reduction peaks appear at  $0.47$  and  $0.69 \text{ V}$  during the cathodic scan. The anodic and cathodic peak currents increase with the number of cycles indicating the deposition of the conducting material on the electrode surface.



**Figure 1.** Electropolymerization of DPA on GCE for 20 cycles in  $N_2$  saturated 5 M  $H_2SO_4$  containing  $1 \times 10^{-3} \text{ mol L}^{-1}$  monomer concentration in the potential range of  $-0.1$  to  $1.0$  V. Scan rate:  $0.1 \text{ Vs}^{-1}$ . Inner to outer are cycle 1 to 20.

### 3.2 Electrochemical behavior of MWCNT-PDPA film



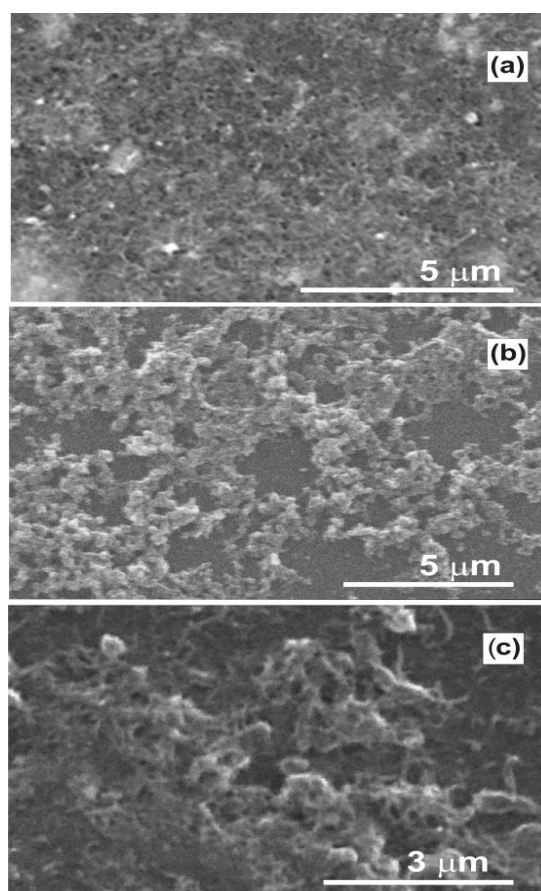
**Figure 2.** Cyclic voltammograms recorded at MWCNT- PDPA/GCE in  $N_2$  saturated 0.1 M PBS (pH 7) at different scan rates; inner to outer is  $0.1$  to  $3 \text{ Vs}^{-1}$ . The inset shows the linear dependence of cathodic peak current ( $I_{pc}$ ) and anodic peak current ( $I_{pa}$ ) on scan rates.

The electrochemical behavior of the deposited PDPA on MWCNT-PDPA was studied by CV. The MWCNT-PDPA/GCE was washed and dried. Then it was transferred to  $N_2$  saturated 0.1M PBS (pH 7). Cyclic voltammograms were recorded at various scan rates in the potential range  $-0.1$  to  $1.0$  V. DPA would generate electroactive sites during the electropolymerization process [24]. The CV responses of GCE/MWCNT-PDPA at different scan rates are shown in fig.2. Both  $I_{pc}$  and  $I_{pa}$  increase linearly with the scan rate.

The linear dependence of  $I_{pc}$  and  $I_{pa}$  with the scan rate is given in the inset of fig.2. This result shows that MWCNT-DPA composite film has electroactive sites and shows the redox peaks in pH 7. The redox peak potentials shift significantly with the increase in scan rates. That is, the peak potential separation,  $\Delta E_p$  depends on the scan rate. These results show that the redox couple exhibited by the MWCNT-PDPA film is not reversible and surface confined. The film exhibits good linear relationship between  $I_{pc}$  and  $I_{pa}$  in such a wide range of scan rate from  $0.1$   $Vs^{-1}$  to  $3$   $Vs^{-1}$ . This indicates the good stability of the film in pH 7.

### 3.3 Surface morphological characterization of various films using SEM

Fig. 3 shows the SEM images of MWCNT, PDPA, MWCNT-PDPA films coated on indium tin oxide electrodes (ITO) with same experimental conditions as mentioned in section 3.1.

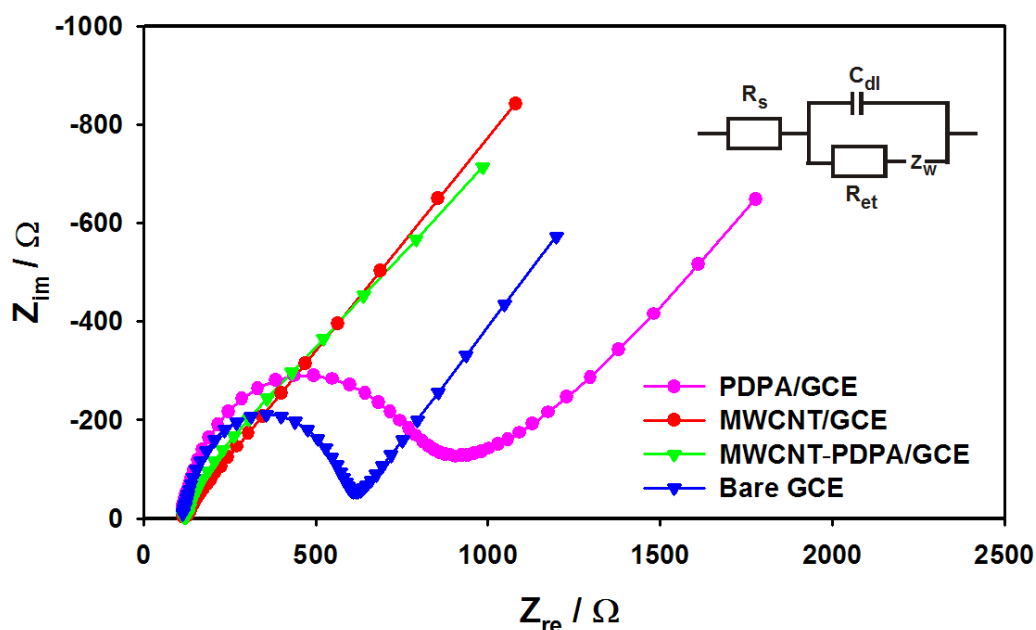


**Figure 3.** SEM images of a) MWCNT, b) PDPA and c) MWCNT-PDPA films

The images show different surface morphology among the various films. Fig.3 (a) shows the uniform distribution of MWCNT on the ITO surface. Fig.3 (b) shows the PDPA globules distributed over the ITO surface. The PDPA formed on the surface is not a continuous uniform thin film. This is in accordance the previous report by Comisso et al. [26] for electropolymerization of PDPA homopolymer. However, it can be seen that the PDPA film a lot of cavity like structures. It is reported earlier that continuous film of PDPA cannot be prepared by cyclic voltammetry [27]. This could be due to the solubility of the oligomers from the electrode surface. Fig. 3 c) shows the SEM image of MWCNT-PDPA composite film on ITO surface.

### 3.4 EIS studies of different films

Conducting polymers, polyelectrolytes, surfactants, nanomaterials or semiconducting materials coated on the electrode surface change the double layer capacitance and interfacial electron transfer resistance of the corresponding electrode. Impedance spectroscopy can reveal the interfacial changes due to the surface modification of electrodes [28].The electrochemical impedance properties of the bare GCE, MWCNT, PDPA, MWCNT-PDPA modified GCE were recorded in 5 mM  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  in PBS and are represented as Nyquist plot ( $Z_{im}$  vs.  $Z_{re}$ ) in fig.4. The inset of fig. 4 shows the Randles equivalence circuit model used to fit the experimental data. Where  $R_s$  is the electrolyte resistance,  $R_{et}$  is charge transfer resistance,  $C_{dl}$  is double layer capacitance and  $Z_w$  is Warburg impedance. The semicircle appeared in the Nyquist plot indicates the parallel combination of  $R_{et}$  and  $C_{dl}$  resulting from electrode impedance [29]. The semicircles obtained at lower frequency represent a diffusion limited electron transfer process and those at higher frequency represent a charge transfer limited process. The Nyquist plot of various films obtained from EIS measurements are given in fig. 4.

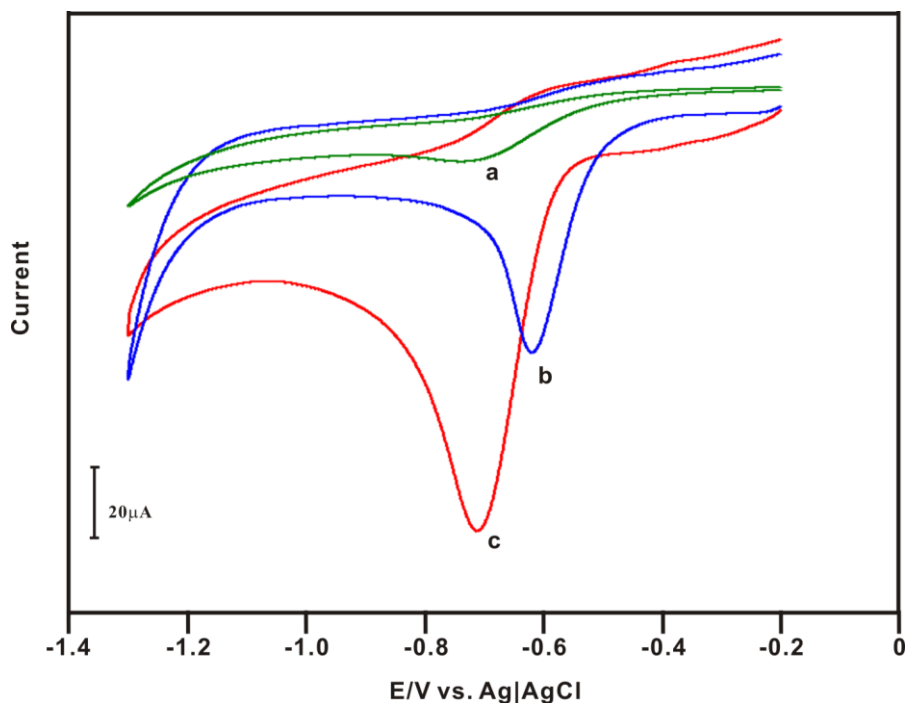


**Figure 4.** EIS of bare, MWCNT, PDPA, MWCNT-PDPA modified GCE in 5mM  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  in 0.1 M PBS pH 7. Applied AC voltage: 5mV, frequency: 0.1 Hz to 100 kHz.

Bare GCE and PDPA-GCE exhibit a semicircle at lower frequency region showing significant resistance towards the electron transfer process at the electrode surface. Whereas, MWCNT and MWCNT-PDPA modified GCE exhibit a very small semicircle region indicating very low impedance of the films. The low impedance of these two films is due to the high conducting nature of MWCNT. Also, it indicates that the PDPA deposited over the MWCNT and GCE surface does not hinder the transfer of electrons.

### 3.5 Electrochemical behavior of 4-NP at various electrodes

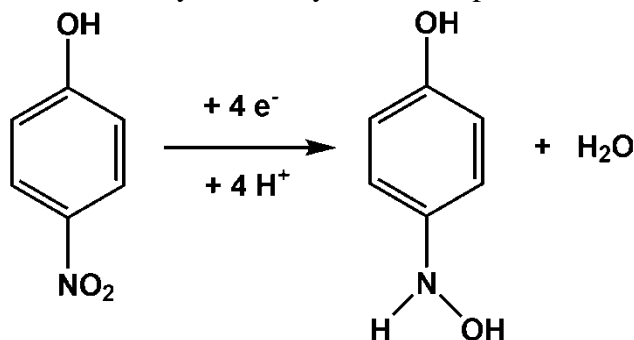
The electrochemical behaviour of 4-NP at various electrodes in the potential range  $-0.2$  to  $-1.3$  V in  $0.1$  M PBS (pH 7) is shown in fig. 5. At bare GCE (curve a) 4-NP undergoes an irreversible reduction at  $-0.942$  V with respect to Ag/AgCl (sat. KCl) with a cathodic peak current ( $I_{pc}$ ) of  $1.39 \times 10^{-5}$  A. The cathodic peak is due to the reduction of the nitryl group of the 4-Nitrophenol to form 4-hydroxylaminophenol by a  $4e^-/4H^+$  transfer electrochemical reduction process [30-32]. 2-nitrophenol also undergoes electrochemical reduction by a similar mechanism [33].



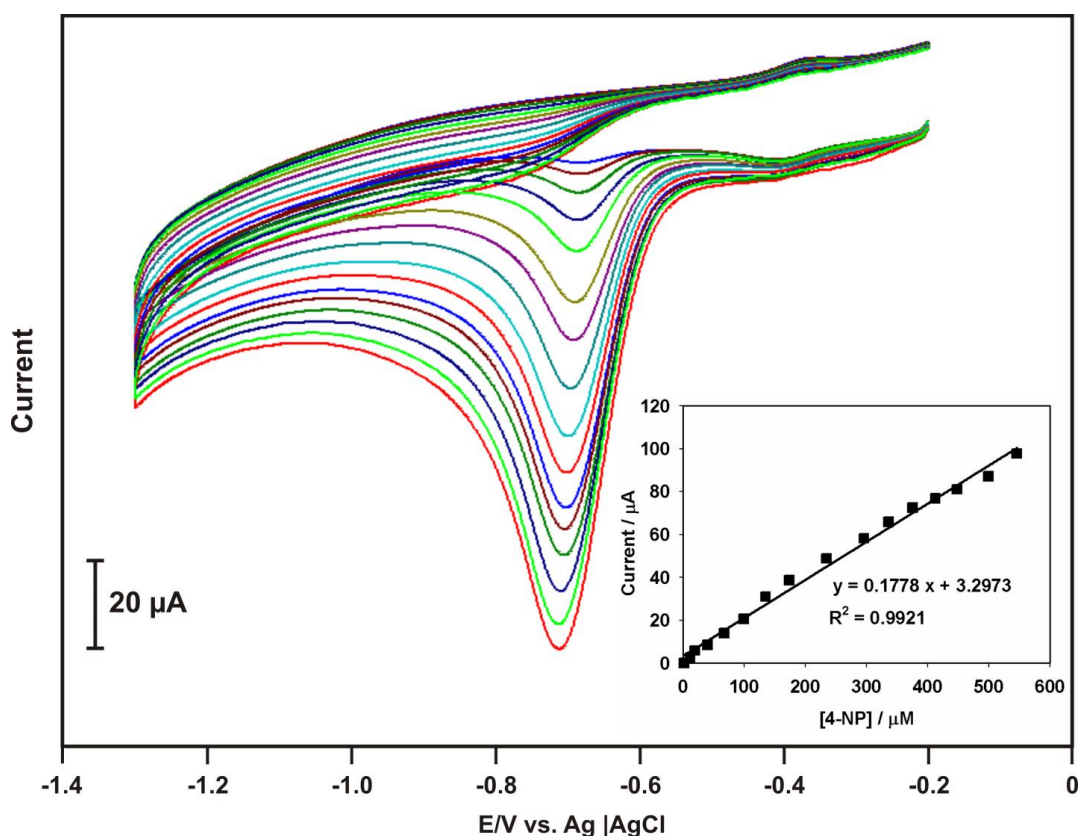
**Figure 5.** Cyclic voltammograms of  $5.46 \times 10^{-4}$  M 4-NP at different electrodes in  $0.1$  M PBS (pH 7) at the scan rate of  $0.1 \text{ V s}^{-1}$ . a) bare GCE, b) MWCNT/GCE, c) MWCNT-PDPA/GCE.

At CNT/GCE (curve b), the cathodic peak potential ( $E_{pc}$ ) appears at  $-0.619$  V with  $I_{pc}$  of  $5.9 \times 10^{-5}$  A. Compared to bare GCE, the peak potential is shifted positively by  $0.322$  V and the current is increased by  $4.24$  times. At MWCNT-PDPA/GCE, the reduction peak appears at  $-0.711$  V with  $I_{pc}$   $1.01 \times 10^{-4}$  A which is  $7.27$  times increase when compared to bare GCE. The mechanism of the

irreversible reduction of 4-NP at MWCNT-PDPA/GCE is shown in scheme 1. The significant increase in peak current indicates the electrocatalytic activity of the composite film.



**Scheme 1.** Reduction of 4-NP at MWCNT-PDPA/GCE in 0.1M PBS (pH 7)



**Figure 6.** Cyclic voltammograms obtained for various concentrations of 4-NP at MWCNT/PDPA modified GCE in 0.1M PBS pH 7 in the potential range  $-0.2$  to  $-1.3$  V. Scan rate:  $0.1 \text{ Vs}^{-1}$ . Concentration range - inner to outer: 1.99, 11.9, 40.3, 67.1, 99.1, 135, 173.5, 234.3, 336, 375, 412.4, 448.1, 499.5, 545.8  $\mu\text{M}$ . The inset is the linear dependence of  $I_{pc}$  on the 4-NP concentration.

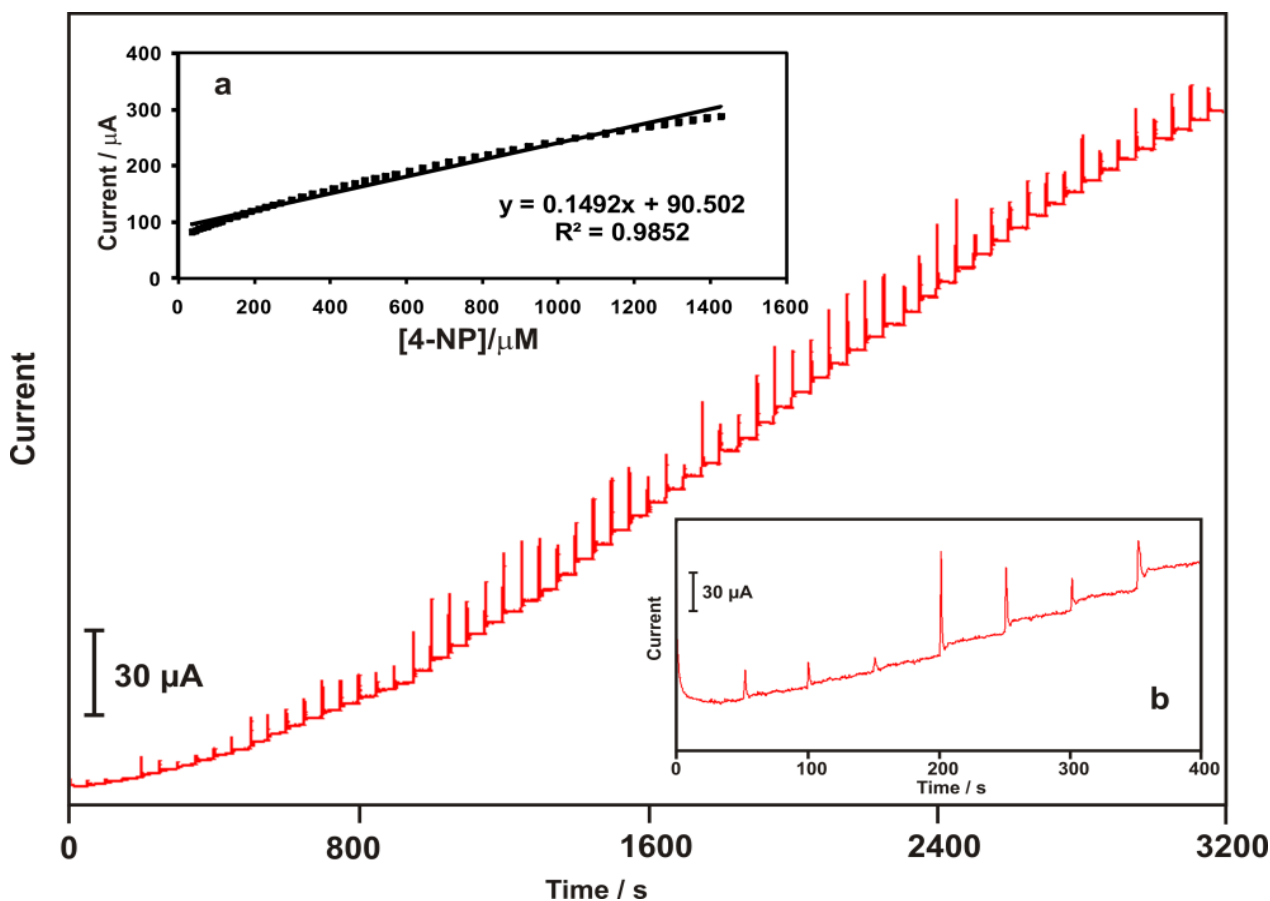
The cyclic voltammetric response of various concentrations of 4-NP is given in fig.6.  $I_{pc}$  increased linearly with the increase in concentration of 4-NP from 1.99 to 546  $\mu\text{M}$  at MWCNT-PDPA/GCE. The dependence of  $I_{pc}$  on the concentration of 4-NP is shown in the inset of fig.6. The



linear increase of  $I_{pc}$  fits the equation  $I_{pc} (\mu A) = 0.1778 C (\mu M) + 3.2973$ , regression coefficient ( $R^2$ ) = 3.2973. The linear response shows the stability and promising electrocatalytic application of the proposed film. Above the linear range, the poor response of the electrode may be due to the increase in concentration of the products formed during the electrochemical reduction at the electrode surface. Hence, we employed hydrodynamic amperometry to improve the linear range of the film. Amperometric response of the film is discussed in detail in section 3.6

### 3.6 Amperometric determination of phenol at GCE/MWCNT-PDPA

Rotating disc electrode is a hydrodynamic electrochemical technique which involves the convective mass transport of reactants and products at the electrode surface, when the electrode is rotated at a specific speed [34]. The amperometric response of 4-NP at MWCNT-PDPA modified rotating disc GCE is show in fig. 7. The RDE surface area was  $0.236 \text{ cm}^2$ . The experiment was conducted in  $N_2$  saturated 0.1M PBS (pH 7) at an applied potential of  $-0.71 \text{ V}$  with a rotation rate of 1200 RPM.  $1 \times 10^{-2} \text{ M}$  4-NP solution in PBS (pH 7) was added at regular intervals of time. Electrocatalytic reduction of 4-NP occurs at RDE in a totally mass transfer controlled condition.



**Figure 7.** Amperometric  $i-t$  curve of 4-NP at MWCNT/PDPA modified rotating disc GCE in the applied potential of  $-0.71 \text{ V}$  for the addition of  $4.9 \times 10^{-7}$  to  $1.6 \times 10^{-3} \text{ M}$  4-NP in  $N_2$  saturated 0.1M PBS (pH 7). Rotation rate: 1200 RPM. The inset “a” shows the plot of linear dependence

of current on 4-NP concentration. Inset “b” is the enlarged view of amperometric response for the addition of  $4.9 \times 10^{-7}$  to  $3.9 \times 10^{-6}$  M 4-NP.

For every addition of 4-NP, a quick response was observed and the reduction current increases linearly up to 3200 s which is equal to  $1.573 \times 10^{-3}$  M 4-NP. The response time is 5 s. Inset (a) of fig. 7 shows the linear dependence of the current on the concentration of 4-NP in the linear range. The linear dependence of the amperometric response on concentration fits the equation  $I (\mu\text{A}) = 0.1492 C (\mu\text{M}) + 90.502$ , regression coefficient ( $R^2$ ) = 0.9852. The film shows the linear range of detection of 4-NP from 8.9  $\mu\text{M}$  to 1.5 mM 4-NP. The sensitivity of the film towards the reduction of 4-NP is  $0.6322 \mu\text{A} \mu\text{mol}^{-1}\text{cm}^{-2}$ . This shows the stability of the proposed electrode and the efficient amperometric response which could be applied for real sample analysis.

#### 4. CONCLUSION

In this study, we reported the fabrication of MWCNT-PDPA composite modified GCE and its application for electrochemical reduction of 4-NP in pH 7. DPA was successfully electropolymerized onto MWCNT modified GCE by cyclic voltammetry in 5 M  $\text{H}_2\text{SO}_4$ . The surface morphology of PDPA and MWCNT-PDPA films were characterized by SEM. The study shows PDPA is formed as polymer globules on the surface of the electrode and not as a continuous smooth film. The MWCNT-PDPA composite film enhanced the reduction peak current of 4-NP by 7.27 times than that of bare GCE. The amperometric determination studies showed that the composite film has quick response and a very good linear range.

#### ACKNOWLEDGEMENT

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