

Full Paper

Electrochemical Determination of 3,5-dinitrobenzoic Acid in the Presence and Absence of CTAB at Multi-walled Carbon Nanotubes Modified Glassy Carbon Electrode: A Voltammetric Study

Gujapaneni Venkataprasad, Tukiakula Madhusudana Reddy*, Pinjari Shaikshavali, Palla Gopal and Palakollu Venkata Narayana

Electrochemical Research Laboratory, Department of Chemistry, S.V.U. College of Sciences, Sri Venkateswara University, Tirupati-517502, Andhra Pradesh, India

*Corresponding Author, Tel.: +91-877-2289303

E-Mail: tmsreddysvu@gmail.com

Received: 5 October 2016 / Received in revised form: 3 May 2017 /

Accepted: 21 May 2017 / Published online: 30 June 2017

Abstract- In this work, the glassy carbon electrode (GCE) was modified with multi-walled carbon nanotubes (MWCNTs) by drop casting process, and it was used as a working electrode for the electrochemical determination of 3,5-dinitrobenzoic acid (3,5-DNBA) in an electrolytic solution containing a cetyl trimethyl ammonium bromide (CTAB). This process was examined by using differential pulse voltammetry (DPV) and cyclic voltammetry (CV) techniques. The modified electrode showed an excellent electrocatalytic activity and sensitivity towards the investigation of 3,5-DNBA reduction behavior in the presence of CTAB. The electrochemical process was irreversible and was controlled by adsorption. The effect of pH, scan rate and concentration were studied at the surface of MWCNTs/GCE. The electrochemical behavior of 3,5-DNBA was studied in the presence and absence of CTAB at MWCNTs/GCE in PBS having pH 6.5. The LOD (limit of detection) and LOQ (limit of quantification) of 3,5-DNBA was found to be as 4.94×10^{-6} M, 1.65×10^{-5} M respectively. The surface coverage area concentration (Γ) of MWCNTs/GCE was calculated and was found to be as 1.3146×10^{-8} mole/cm². By using electrochemical impedance spectroscopy (EIS), the interfacial electron transfer behavior of 3,5-DNBA was studied at different types of electrode surfaces.

Keywords- 3,5-DNBA, MWCNTs, CTAB, CV, DPV, EIS

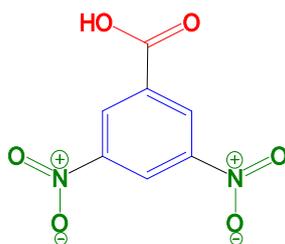
1. INTRODUCTION

N, N, N, N –Cetyl trimethyl ammonium bromide (CTAB) is also known as cationic surfactant. CTAB plays an important role in the formation of a complex between ligand and metal ions [1]. CTAB forms micelles in aqueous solution and has two ends, namely hydrophobic head and hydrophilic tail. Due to its unique molecular structure, it is widely used in the study of various parameters in electroanalytical techniques [2,3]. Micelles act as selective masking agents for the increase of selectivity and sensitivity in several electrochemical processes [4] and it is also used for the preparation of electrochemical sensors [5].

Imija in 1991 first discovered the carbon nanotubes (CNTs) by using transmission electron microscope (TEM) [6]. CNTs are the allotropes of carbon having cylindrical structure and are categorized into single-walled (SW) and multi-walled carbon nanotubes (MWCNTs). CNT consist of the carbon and has sp^2 hybridization [7]. MWCNT has high electrical properties, such as low detection limits, high sensitivity, reduction of over potentials [8,9] and inter-connectivity [10]. Due to the above properties, MWCNTs are used for the modification of electrodes, in order to increases the electron transfer rate by decreasing the over potentials of various electroactive species in redox-reactions [11,12,13]. CNTs play an important role in the preparation of electrochemical biosensors [14], enzymatic electrochemical biosensors [15] and the functionalized CNTs was also used as a grafting of polymers [16].

3,5-Dinitrobenzoic acid is an organic compound used as a corrosion inhibitor and in photography [17]. Scheme-1 shows the structure of 3, 5-DNBA, consisting of carboxylic acid group in ipso position and two nitro groups at meta positions with a positive charge on two nitrogen atoms and negative charge on two oxygen atoms. The cyclic voltammetric technique is used for the determination of various electrochemical active species. An electrochemical study and mechanism of 3,5-DNBA at GCE was carried by Gopal et al [17]. In the present investigation a novel electrochemical sensor was used for the electrochemical determination of 3,5-DNBA in the presence of CTAB with the help of electroanalytical techniques like CV, DPV and EIS.

To the best of our knowledge, there were no results found for the electrochemical determination of 3,5-DNBA at MWCNTs/GCE in the presence of CTAB. The main aim of the present work is to develop a simple, sensitive and convenient electrochemical method for the determination of 3,5-DNBA at MWCNTs/GCE in presence of CTAB. This electrochemical investigation involves the adsorption of surfactant (CTAB) at the surface of MWCNTs/GCE for the enchantment of electrochemical properties of the electrode [18].



Scheme 1. The molecular structure of 3,5-Dinitrobenzoic acid

2. EXPERIMENTAL

2.1. Instruments

A CH Instrument model number 1200 A was used to carry out all the cyclic voltammetric (CV) measurements and CHI 660D electrochemical instruments were used for the EIS and DPV measurements, which was connected to a personal computer. An Electrochemical cell consisted of three types of electrodes, i) modified glassy carbon electrode (GCE) as a working electrode (at which reaction of interest occurs), ii) Ag/AgCl electrode as a reference electrode (which maintains constant potential) and platinum wire as a counter/auxiliary electrode (which measure the current). The various pH values of the buffer solution were measured by using Elico U 120 pH meter with the combination of pH CL 51 B electrode.

2.2. Chemical Reagents

3,5-Dinitrobenzoic acid was from Riedel-de Haen, Germany. The stock solution of 3,5-DNBA was prepared by dissolving in ethanol solution. A stock solution of 10 mM was prepared and stored in cool temperature. N, N, N, N- Cetyl trimethyl ammonium bromide (CTAB) was from HIMEDIA and dissolved in distilled water to make 1% solution. Multi-walled carbon nanotubes (MWCNTs) were obtained from Dropsens, Edificio CEEI, Llanera (SPAIN). By using $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and Na_2HPO_4 , 1 M Phosphate buffer solution was prepared.

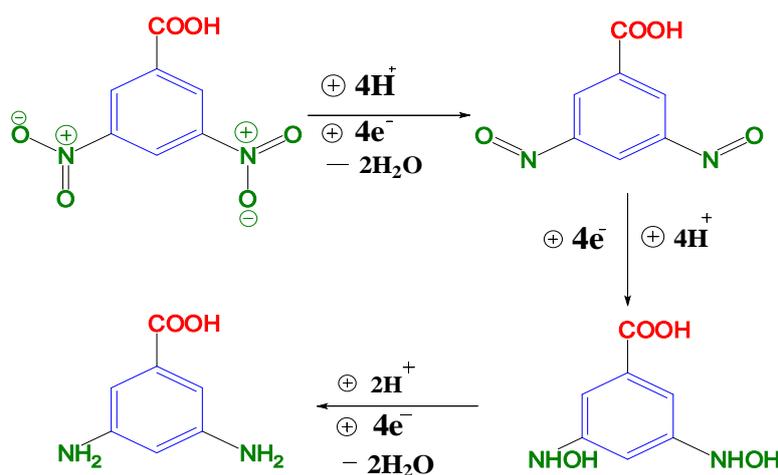
2.3. Preparation of modified glassy carbon electrode (MWCNTs/GCE)

Prior to the modification of GCE, the surface of the bare GCE was polished with 1.0, 0.5 and 0.3 μm alumina slurry on micro cloth pads and then rinsed with doubly distilled water to obtain a mirror-like surface of GCE, then 1 mg/1 ml of MWCNTs were dissolved in ethanol and sonicated for 5-min to get a homogeneous suspension. 5 μL of MWCNTs was drop cast onto the surface of GCE by using a micropipette and air dried at room temperature and hereafter the resulted electrode is denoted as MWCNTs/GCE and used as a working electrode.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical behavior of 3,5-DNBA at MWCNTs/GCE in the presence and absence of CTAB

The electrochemical studies of 3,5-DNBA were carried at MWCNTs/GCE in the presence of CTAB in (pH 6.5) PBS by using CV and DPV techniques. Both the techniques (CV & DPV) gave two enhanced reduction peaks towards the determination of 3,5-DNBA at MWCNTs/GCE in the presence of CTAB. In the forward scan, we have observed two reduction peaks and there were no peaks in the reverse scan suggesting an irreversible process [19,20]. Among the two reduction peaks, one peak corresponds to the reduction of nitro (-NO₂) groups into hydroxylamine (-NHOH) groups and other corresponds to the reduction of hydroxyl amine (-NHOH) groups into amine (-NH₂) groups and the mechanism was explained in scheme.2, the detailed mechanism of 3,5-DNBA was explained by Gopal et al. [17]. The electron transfer rate towards the determination of 3,5-DNBA at different electrodes (MWCNTs/GCE & bare GCE) in presence and absence of CTAB was showed in Fig. 1. In Fig. 1, at bare GCE (curve-a), we have observed a poor reduction peak current response for 3,5-DNBA and at the same electrode (curve-b) in presence of CTAB in PBS gave enhanced reduction peak currents for 3,5-DNBA and the electron transfer rate was fast due to the presence of CTAB (cationic surfactant) in PBS, which accumulates on the surface of bare GCE and attracts more analyte particles towards the surface of GCE, hence the reduction peak current was increased. At MWCNTs/GCE (curve-c), in the absence of CTAB in PBS solution, we have observed enhanced reduction peak currents for 3,5-DNBA, which was due to the fact that MWCNTs have large surface area and good electrical conductivity.



Scheme 2. The reduction mechanism of 3,5-DNBA

At the same electrode (curve-d), in the presence of CTAB in the PBS solution gave excellent enhanced reduction peak currents for 3,5-DNBA in comparison with above three peaks (a, b

& c), the reason was, due to the accumulation of CTAB onto the electrode surface which intern attracted more analyte molecules towards the MWCNTs/GCE surface. An excellent enhancement of the reduction peak currents and electron transfer rate towards the determination of 3,5-DNBA was achieved at MWCNTs/GCE in presence of CTAB.

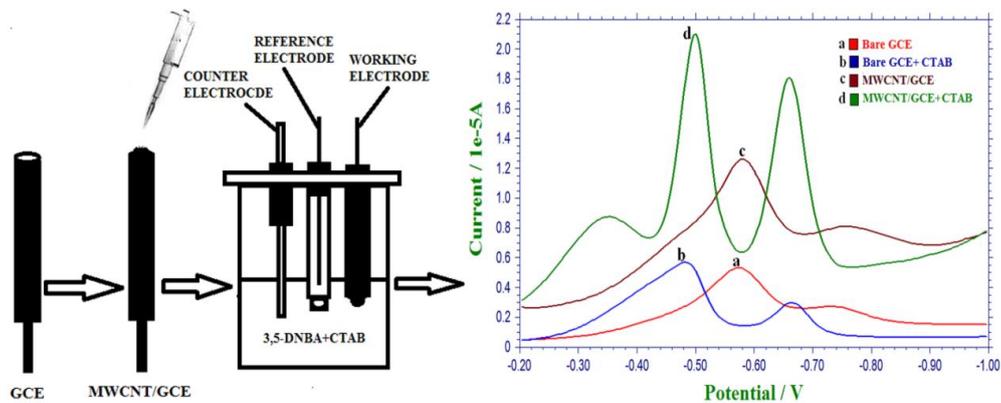


Fig. 1. The electrode reaction at bare and (MWCNTs/GCE) modified GCE in presence and absence of CTAB towards the determination of 3,5-DNBA

3.2. Effect of pH

Fig. 2a shows the effect of pH of PBS containing CTAB towards the determination of 1 mM of 3,5-DNBA at MWCNTs/GCE. This was studied in the pH range from 5.0 to 8.0 with the help of CV technique.

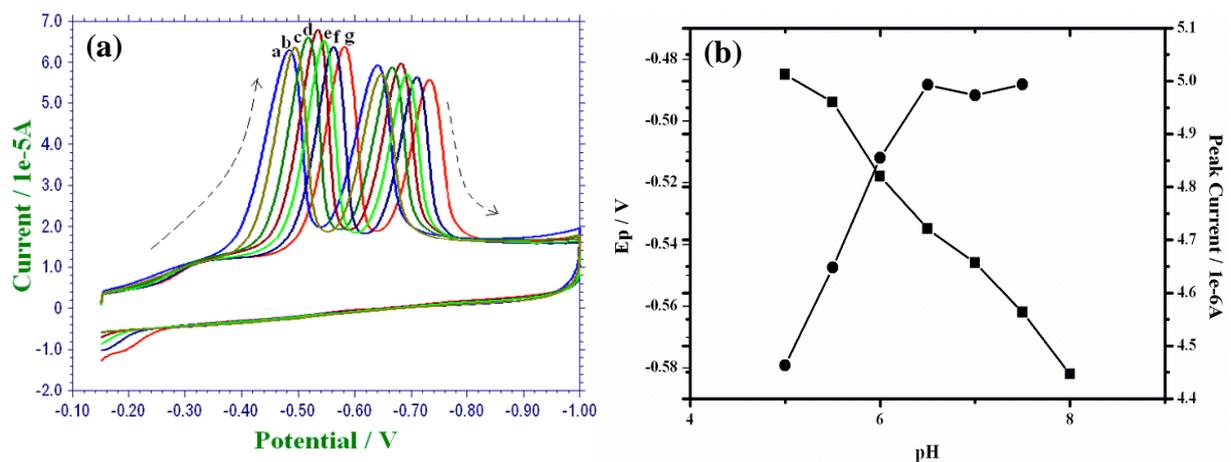


Fig. 2. (a) Cyclic voltammograms of 1×10^{-3} M 3,5-DNBA obtained at MWCNTs/GCE in 1 M PBS containing 5 μ L CTAB at the different pH values pH 5.0 (a), pH 5.5 (b), pH 6.0 (c), pH 6.5 (d), pH 7.0 (e), pH 7.5 (f) and pH 8.0 (g) at a scan rate of 100 mV s^{-1} ; (b) The Calibration plot of pH vs. peak current (circle) & E_p (square)

From Fig. 2a, there was an increase in the peak currents by increasing the pH range from pH 5.0 to 6.5, on a further increase of pH beyond 6.5 the peak current started to decline, which was due to the protonation effect [17,21]. At lower pH (in acidic medium) of the PBS, the 3,5-DNBA contains sufficient protons and these protons were attracted onto the surface of MWCNTs/GCE, which intern facilitates in producing enhanced reduction peak currents. On increasing the pH (basic medium) of the PBS, reduction peak currents were decreased which was due to the less availability of the protons. We observed better peak currents at pH 6.5 and this pH was chosen for further electrochemical studies. A plot of pH against peak potentials (E_p) and Peak currents is shown in Fig. 2b.

3.3. Characterization of MWCNTs/GCE with $K_3[Fe(CN)_6]$

Fig. 3, shows the response of the bare GCE (a) and MWCNTs/GCE (b) in the presence of 1 mM $K_3[Fe(CN)_6]$ at 100 $mV s^{-1}$ scan rate in 0.1 N KCl (buffer) solution. The MWCNTs/GCE showed enhanced redox peak currents which were due to the large surface area of MWCNTs, hence MWCNTs/GCE was chosen for further studies. The Randles-Sevcik eq. (1), was used to calculate the 'D' (diffusion coefficient) of the redox process of $K_3[Fe(CN)_6]$.

$$I_p = (2.69 \times 10^5) n^{1/2} A D^{1/2} \nu^{1/2} C_0 \quad (1)$$

From eq.(1), where ' I_p ' is the cathodic peak current in μA , ' n ' is the number of electrons ($n=1$) for $K_3[Fe(CN)_6]$, ' ν ' is the scan rate ($\nu=100 mV s^{-1}$) and ' C_0 ' is the concentration of $K_3[Fe(CN)_6]$. ' D ' is the diffusion coefficient and was found to be as $1.7938 \times 10^{-6} cm^2/sec$.

The amount of MWCNTs immobilized on the surface of the GCE was calculated by using eq. (2) [22,23] and it was found to be as $\Gamma = 1.3146 \times 10^{-8} molcm^{-2}$.

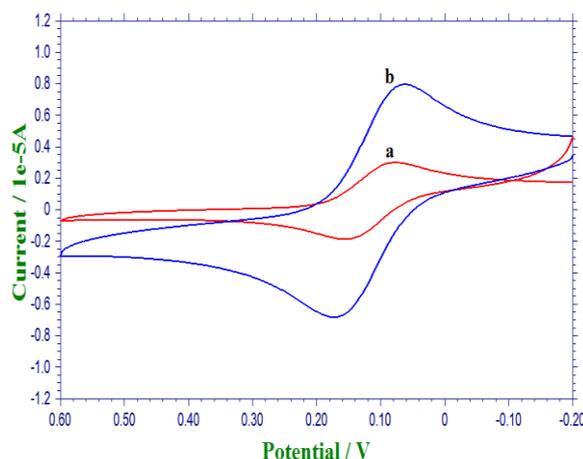


Fig. 3. Cyclic voltammograms of 1 mM $K_3[Fe(CN)_6]$ at bare GCE (a) and MWCNTs/GCE (b) in presence of 0.1 N KCl solution at scan rate 100 $mV s^{-1}$

$$\Gamma = I_p / 4RT/n^2 F^2 A \nu \quad (2)$$

Where ‘ Γ ’ is the concentration of surface coverage area (MWCNTs/GCE) of the modified electrode, ‘ I_p ’ is the peak currents ($I_p = 8.674 \times 10^{-5} \text{ A}$), ‘ ν ’ is the scan rate (100 mV s^{-1}), ‘ R ’ is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), ‘ F ’ (96500 C mol^{-1}) is the faraday constant, ‘ T ’ is the temperature (300 K) in kelvins and ‘ n ’ ($n=1$) is the number of electrons transferred.

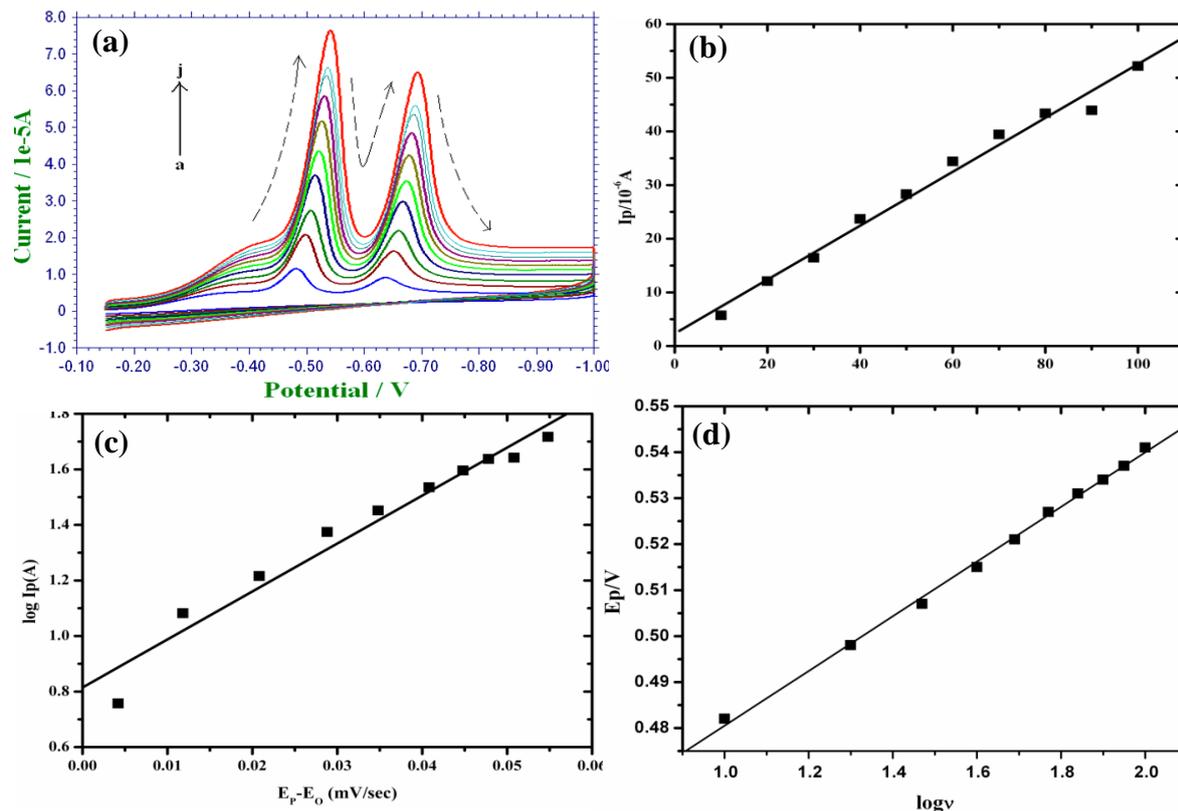


Fig. 4. (a) Cyclic voltammograms of $1 \times 10^{-3} \text{ M}$ 3,5-DNBA obtained at MWCNTs/GCE in PBS of pH 6.5 containing $5 \mu\text{L}$ CTAB at scan rates 10 mV s^{-1} (a), 20 mV s^{-1} (b), 30 mV s^{-1} (c), 40 mV s^{-1} (d), 50 mV s^{-1} (e), 60 mV s^{-1} (f), 70 mV s^{-1} (g), 80 mV s^{-1} (h), 90 mV s^{-1} (i) and 100 mV s^{-1} (j); (b) Calibration plot for the scan rate (mV s^{-1}) vs. I_p (in A); (c) Calibration plot for $\log \nu$ vs. E_p ; (d) Calibration plot of $E_p - E_o$ vs. $\log I_p$ for calculating the energy transfer coefficient (α)

3.4. Scan rate study

The effect of scan rate was studied at MWCNTs/GCE with 1 mM of 3,5-DNBA in the presence of CTAB ($5 \mu\text{L}$) in 1 M PBS (pH 6.5) by using CV. Fig. 4a shows the increases in the reduction peak currents of 3,5-DNBA with the increase in scan rates from 10 to 100 mV/s . From Fig.4b, a plot was drawn between scan rate and peak current, as a result a correlation coefficient $R=0.99347$ was observed and the electrode reaction process and was found to be controlled by adsorption process [24,25,22]. A scan rate of 100 mV s^{-1} was

chosen for all the calculations, because it contains maximum faradaic currents and minimum non-faradaic currents [26].

From fig.4c (E_p vs $\log v$), we have calculated the heterogeneous rate constant ' k_s ' by using eq. (3) and it was found to be as $k_s=2.57308 \times 10^{-6}$ cm/sec. From fig.4d ($\log i_p$ vs E_p-E_o), the energy transfer coefficient ' α ' was calculated and it was found to be as $\alpha=0.4525$. The number of electrons involved in the rate determining step ($n=0.7939$) was calculated by using eq. (4).

$$E_{pc} = E_O - m[0.78 + \ln(D^{1/2}/k_s) - 0.5 \ln m] - 0.5 \ln v \quad (3)$$

$$m = RT/\alpha n_a F \quad (4)$$

3.5. Effect of concentration

By using DPV technique, the effect of concentration for 3,5-DNBA was studied from 5 μL to 100 μL (fig.5a) in presence of (5 μL) CTAB in 1 M PBS (pH 6.5) at the surface of MWCNTs/GCE. From Fig. 5a, it can be seen that the cathodic peak current increases gradually with increase in the concentration of 3,5-DNBA. Fig.5b, shows a plot between the concentration of 3,5-DNBA in μML^{-1} and peak currents (I_p) in μA , with a linear regression equation of $I_p(\mu\text{A}) = -0.56803 + 0.07679 C_{(3,5\text{-DNBA})}(\mu\text{M})$ and a correlation coefficient of $R=0.99843$ [27]. The LOD and LOQ values were calculated by using eq.(5) & (6) [25,28] and the values were found to be as 4.9440×10^{-6} M and 1.6480×10^{-5} M respectively.

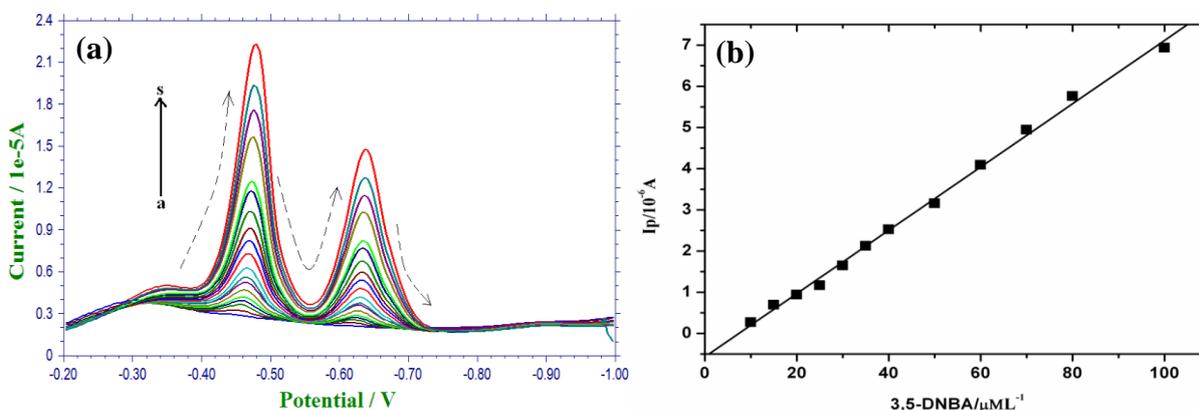


Fig. 5. (a) The differential pulse voltammograms of 3,5-DNBA at concentrations 5 μM (a), 10 μM (b), 15 μM (c), 20 μM (d), 25 μM (e), 30 μM (f), 35 μM (g), 40 μM (h), 50 μM (i), 60 μM (j), 70 μM (k), 80 μM (l), 100 μM (m), 120 μM (n), 140 μM (o), 180 μM (p), 220 μM (q), 260 μM (r) and 300 μM (s) in PBS (pH 6.5) containing 5 μL of CTAB.; (b) The plot between different concentrations of 3,5-DNBA (in $\mu\text{M L}^{-1}$) vs. I_p (in A)

$$\text{LOD}=3S_b/m \quad (5)$$

$$\text{LOQ}=10S_b/m \quad (6)$$

Where, 'S_b' is the standard deviation of mean values of peak currents and 'm' is a slope of the calibration curve.

3.6. Role of MWCNTs and surfactant(CTAB)

MWCNTs and surfactant (CTAB) played an important role in the electrochemical determination of 3,5-DNBA in PBS of pH 6.5 at the surface of GCE. From Fig. 6a, the MWCNTs/GCE in presence of CTAB in solution showed an increased (enhanced) reduction peak currents towards the determination of 3,5-DNBA, this was due to the fact that the surfactant i.e. CTAB is of cationic in nature, that forms micelle aggregates in aqueous solution (PBS). This property influences the transportation of more analyte particles towards the surface of the MWCNTs/GCE and alters the electron transfer rate, there by increases the reduction peak currents of 3,5-DNBA. The modified electrode has the property of more conductivity, catalytic activity, large active surface area, and also CNTs has the cloud of electrons surrounding its walls by this nature which attracts more charged particles towards itself [16] and promotes the electron transfer rate in determining 3,5-DNBA. This effect was not observed in the case of bare glassy carbon electrode (GCE). Fig. 6b shows the bar diagram of peak currents towards the reduction of 3,5-DNBA at bare and MWCNTs/GCE. The different types of electrodes have the different types of electron transfer rate order i.e. bare GCE < bare GCE/CTAB < MWCNTs/GCE < MWCNTs/GCE/CTAB.

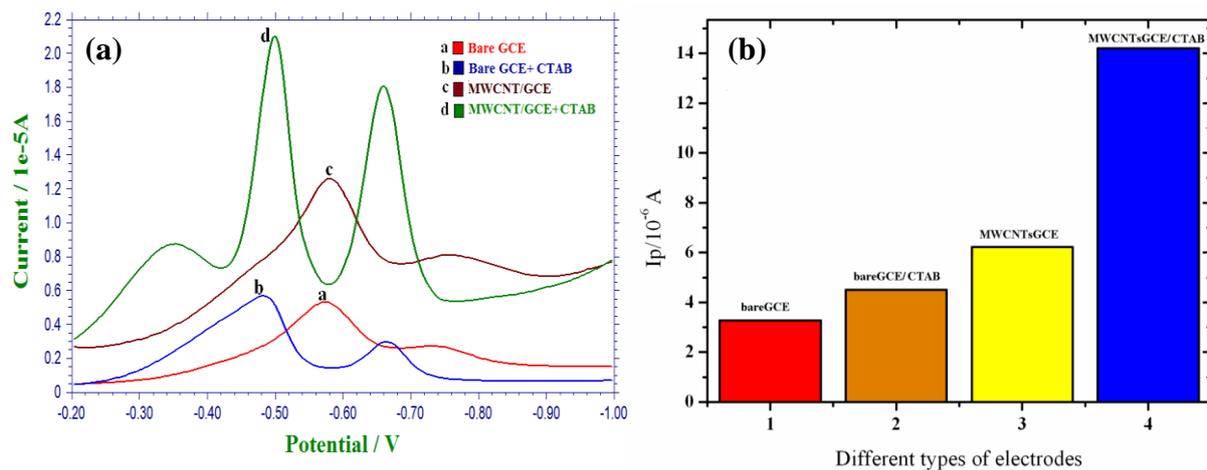


Fig. 6. (a) The differential pulse voltammograms of 1×10^{-3} 3,5-DNBA in PBS of pH 6.5 at bare GCE (a), at bare GCE in the presence of 5 μL of CTAB (b), at MWCNTs/GCE (c), at MWCNTs/GCE in the presence of 5 μL of CTAB (d) at a scan rate of 100 mV s^{-1} ; (b) The bar diagram of 1×10^{-3} 3,5-DNBA in PBS of pH 6.5 at bare GCE and MWCNTs/GCE in the presence and absence of CTAB

3.7. Investigation of MWCNTs/GCE at Electrochemical impedance spectroscopy (EIS)

EIS is an effective electroanalytical technique used for the investigation of electron transfer properties at the chemically modified electrode. Typically, the impedance spectrum has the semicircular part and linear part, where the semicircle represents charge transfer resistance and linear part represents diffusion of the analyte towards the electrode surface. If the linear part has more slope value, then this indicates the diffusion of analyte towards the electrode surface and the current response was mainly due to the diffusion process. In this work, by using EIS the surface nature of bare GCE and MWCNT's/GCE at 3,5-DNBA in presence and absence of CTAB was examined. In Fig. 7a, a Nyquist plot (Z'' Vs Z') shows a distinctive impedance diagram for bare GCE and MWCNT's/GCE in presence and absence of CTAB in a solution. From the Fig. 7a, it is clear and the impedance response of 3,5-DNBA was found to be different after the presence of CTAB in the solution at MWCNT's/GCE. From Fig. 7a, the bare GCE (a) has a very low slope value for the linear part of the curve and the slope of bare GCE in presence of CTAB (b) was quite high when compared to bare GCE (a). On the other hand at the MWCNT's/GCE (c) and MWCNT's/GCE in presence of CTAB (d), the slope value for MWCNT's/GCE in presence of CTAB (d) was very high (high diffusion means high electron transfer) when compared to MWCNT's/GCE (c).

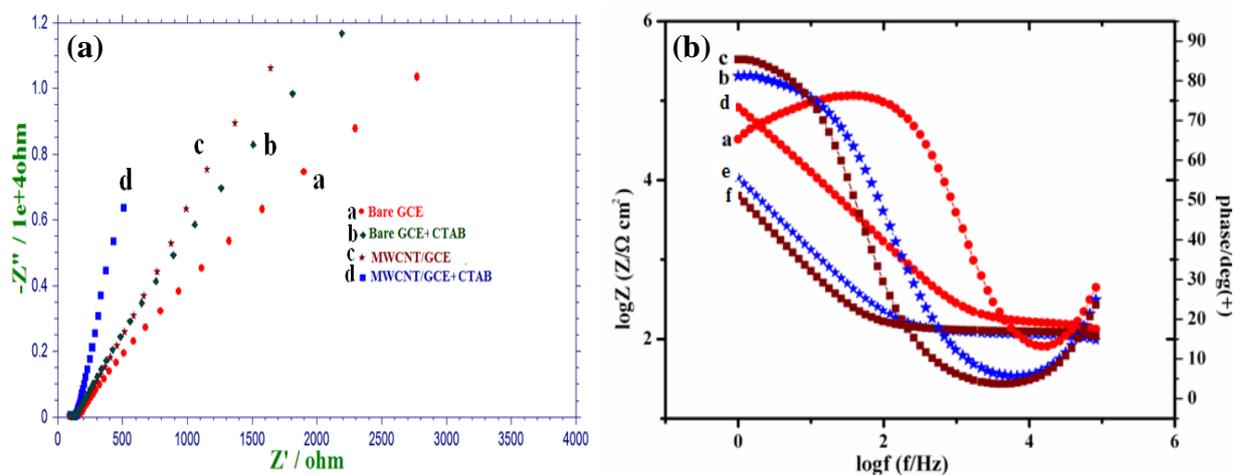


Fig. 7. (a) The Nyquist plot of 1×10^{-3} 3,5-DNBA in PBS of pH 6.5 at bare GCE (a), at bare GCE with 5 μ L of CTAB in PBS (b), at MWCNTs/GCE (c), at MWCNTs/GCE with 5 μ L of CTAB in PBS (d); (b) The bode plot for different types of electrodes: bare GCE (a), MWCNTs/GCE (b), MWCNTs/GCE/CTAB (c)

Among the all, the modified novel electrochemical sensing electrode (MWCNT's/GCE in presence of CTAB) has high diffusion, hence it showed more electron transfer rate. Fig. 7b is the bode plot for different types of electrodes in which 'a' represents bare GCE, 'b' represents MWCNTs/GCE and 'c' represents MWCNTs/GCE/CTAB [28]. From the bode plot, the curves a (red coloured), b (blue coloured) and c (brown coloured) represents the plot

between $\log f$ (f/Hz) vs $\log Z$ ($Z/\Omega \text{ cm}^2$), on the other hand the curves e (red) , f (blue) and g (brown) represents the plot between $\log f$ (f/Hz) vs phase/deg(+).

4. CONCLUSION

In this work, we conclude that the modified (MWCNTs/GCE) electrode showed an excellent electrocatalytic activity (more conductivity) and sensitivity towards the determination of 3,5-DNBA in presence of CTAB in PBS. The effect of scan rates study of 3,5-DNBA revealed that the system was irreversible and controlled by adsorption process. The electroanalytical measurements like 'D' and 'Γ' of the modified electrode were calculated. EIS studies concluded that the MWCNTs/GCE in presence of CTAB in PBS was more suitable for the determination of 3,5-DNBA.

Acknowledgement

One of the authors G. Venkataprasad is grateful to the University grants commission (UGC), New Delhi, India for providing financial assistance through basic scientific research fellowship for meritorious students (BSR-RFMS).

REFERENCES

- [1] N. R. Lakshmi, S. M. Kumar, and B. M. Chamy, Res. J. Chem. Sci. 3 (2013) 29.
- [2] S. S. Shankar, B. E. K. Swamy, and B. N. Chandrashekar, J. Mol. Liq. 168 (2012) 80.
- [3] C. F. Valezi, G. R. Mansano, E. H. Duarte, L. H. D. Antonia, C. R. T. Tarley, and E. R. Sartori, Sens. Actuators B 205 (2014) 234.
- [4] R. A. Dar, P. K. Brahman, S. Tiwary, and K. S. Pitre, Colloids. Surf. B 98 (2012) 72.
- [5] Y. Mao, Q. Fan, J. Li, L. Yu, and L. Qu, Sens. Actuators B 203 (2014) 759.
- [6] L. Yang, C. Tang, H. Y. Xiong, S. F. Wang, and X. H. Zhang, Bioelectrochemistry 75 (2009) 158.
- [7] C. B. Jacobs, M. J. Peairs, and B. J. Venton, Anal. Chim. Acta 662 (2010) 105.
- [8] A. R. Fakhari, and H. Ahmar, Anal. Methods 3 (2011) 2593.
- [9] K. Kor, and K. Zarei, J. Electroanal. Chem. (2014).
- [10] B. Dong, B. L. He, C. L. Xu, and H. L. Li, Mate. Sci. Eng. B 143 (2007) 7.
- [11] B. C. Janegitz, R. Pauliukaite, M. E. Ghica, C. M. A. Brett, and O. F. Filho, Sens. Actuators B 158 (2011) 411.
- [12] S. Wang, F. Xie, and G. Liu, Talanta 77 (2009) 1343.
- [13] M. Arvand, and T. M. Gholizadeh, Sens. Actuators B 186 (2013) 622.
- [14] L. Agui, P. Y. ez-Sedeno, and J. M. Pingarron, Anal. Chim. Acta 622 (2008) 11.
- [15] P. Raghu, T. M. Reddy, P. Gopal, K. Reddaiah, and N. Y. Sreedhar, Enzyme. Micro. Tech. 57 (2014) 8.

- [16] P. Y. Sedenó, J. Riu, J. M. Pingarrón, and F. X. Rius, *Trends in Anal. Chem.* 29 (2010) 9.
- [17] P. Gopal, T. M. Reddy, K. Reddaiah, P. Raghu, and P. V. Narayana, *J. Mol. Liq.* 178 (2013) 168.
- [18] C. F. Valezi, E. H. Duarte, G. R. Mansano, L. H. D. Antonia, C. R. T. Tarley, and E. R. Sartori, *Sens. Actuators B* 205 (2014) 234.
- [19] J. C. Abbar, and S. T. Nandibewoor, *Colloids. Surf. B* 106 (2013) 158.
- [20] S. Chitravathi, B. E. K. Swamy, G. P. Mamatha, and B. N. Chandrashekar, *J. Mol. Liq.* 172 (2012) 130.
- [21] T. M. Reddy, K. Balaji, S. Reddy, and J. Reddy, *Croatica-Chem. Acta* 79 (2006) 253.
- [22] K. Reddaiah, T. M. Reddy, Y. S. Rao, P. Raghu, and P. Gopal, *Mate. Sci. Eng. B* 183 (2014) 69.
- [23] P. Raghu, T. M. Reddy, K. Reddaiah, L. R. Jaidev, and G. Narasimha, *Enzyme. Mic. Tech.* 52 (2013) 377.
- [24] K. Reddaiah, T. M. Reddy, P. Raghu, and B. E. K. Swamy, *Anal. Bioanal. Electrochem.* 4 (2012) 122.
- [25] T. M. Reddy, K. Balaji, and S. J. Reddy, *J. Anal. Chem.* 62 (2007) 168.
- [26] P.V. Narayana, T.M. Reddy, P. Gopal, K. Reddaiah and P. Raghu, *Res. J. Chem. Sci.* 4 (2014) 37.
- [27] P. Raghu, T. M. Reddy, K. Reddaiah, B. E. K. Swamy, and M. Sreedhar, *Food Chem.* 142 (2014) 188.
- [28] P. Gopal, T. M. Reddy, P. Raghu, K. Reddaiah, and P.V. Narayana, *Anal. Bioanal. Electrochem.* 6 (2014) 183.