



## A novel sensor for electro catalytic determination of two nitro aromatic compounds

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**Abstract:** In this study a modified glassy carbon electrode (GCE) coated with a mixture of multi-wall carbon nanotube (MWCNT), 1, 4-dihydroxy anthra quinone (Q) and chitosan (C) has been used for electro catalytic determination of nitrobenzene (NB) and 1, 2-dinitro phenyl hydrazine (DNPH). The results obtained by using this electrode were compared with those obtained by the application of different modified GCE with MWCNT, Q, C, MWCNT-Q, MWCNT-C and Q-C under the same conditions. Also the effective parameters such as pH and scan rate of modified electrode were studied. The modified electrode showed electro catalytic activity for the reduction of DNPH and NB with the domination of overpotential of about 100 mV and 50 mV for DNPH and NB compared with that for a bare electrode in cyclic volt ammo grams and an increase in peak current. The calibration curves were linear from  $5.0 \times 10^{-6}$  to  $7.9 \times 10^{-5}$  M ( $r=0.992$ ,  $n=12$ ) and ( $5.0 \times 10^{-6}$  to  $1.7 \times 10^{-4}$  M ( $r=0.993$ ,  $n=14$ ) for DNPH and NB, respectively. The values of recovery for three samples obtained between 94.0 and 102.3. This newly modified electrode was applied to determination of NB and DNPH in spiked natural water samples.

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### 1. Introduction

Nitro aromatic compounds have been widely used in the industries for the production of aniline, aniline dyes, explosives, pesticides and drugs, and also as a solvent in products like paints, shoes and floor metal polishes "(M. Latifoglu and et al, 2003)". As a toxic and suspected carcinogenic nitro aromatic compounds such as nitrobenzene released to environment poses a great threat to human health. Even at low concentrations, it may present high risks to environment, "(D.S. Bhatkhande and et al, 2003)". The strong electron affinity of nitro reduces the electron cloud density of benzene ring and thus makes nitrobenzene very stable. Therefore, nitrobenzene is listed as one of prior pollutants by many countries. Nitro aromatic compounds are often difficult to donate electron due to the low electron cloud density in their benzene ring, so the oxidation of nitro aromatic compounds is very difficult to achieve. Furthermore, the oxidation of nitrobenzene may produce some more toxic dead-end products like picolinic acid, "(S.F. Nishino, and et al 1993)". Therefore, reductive technologies attracted more and more attention recently "(E.K. Nefso and et al, 2005)".

In this research we are applied MWCNT for modification of electrode because obviously MWCNT as a magical material, because their uniqueness and have received excellent attention for the preparation of electrochemical sensor, as it was extensively reviewed. "(M. Trojanowicz and et al, 2005)", "(J. Wang, 2005)", "(N. Li, J. Wang and et al, 2003)", "(C.E. Banks and et al, 2006)", "(J. Wang, 2005)", "(M. Valcarcel and et al, 2005)".

### 2. Material and Methods

All the electrochemical measurements were carried out with a Electroanalyser. The three-electrode system consisted of a modified GCE, a SCE reference electrode, and a platinum auxiliary electrode. All potentials were referred to the SCE.

Two 10<sup>-2</sup>mol l<sup>-1</sup> stock solutions of DNPH and NB were prepared by direct dissolution of DNPH and NB in acetonitril and store in the dark. The chitosan solution (8%) was prepared by dissolving 0.8 g chitosan in 10 ml acetic acid. CNTs were functionalized by sonification treatment in a mixture of sulfuric acid and nitric acid (3:1) for 6 h at room temperature. Functionalized MCNTs (fMCNTs) were washed with dowble distilled water (DDW) and

separated by centrifugation. “(S. Hoon Baek and et al, 2008)”. 1, 4-Dihydroxy anthraquinone, 1, 2-Dinitro phenyl hydrazine, Nitrobenzene, Acetonitrile (AN), purchased. All experiments were carried out at room temperature (about 15 °C).

First make a solution of Q (0.05mg) in 2.5ml acetonitril and then added 25mg of MWCNT and agitation with ultrasonic to give a black suspension, now 0.5ml of this suspension mixed with 0.1ml of chitosan solution (0.5%). Before being modified, the GCE was polished with 0.3 and 0.05  $\mu\text{m}$  aluminum slurry, rinsed thoroughly with DDW, then ultrasonically cleaned with  $\text{H}_2\text{SO}_4(1\text{M})$  for 5 min, finally rinsed with DDW, and dried under an infrared lamp. After the GCE was cooled, it was smeared evenly with 6  $\mu\text{L}$  of a MWCNT–chitosan–anthraquinone (0.5%) solution by a micro-syringe, and then dried under an infrared lamp for 10 min. After cooling, the MCQ/GCE could be used.

A phosphate buffer solution (PB) 0.3 M (pH= 1.5) was used as the supporting electrolyte and each DNPH and NB was added to the sample cell. The solution was purged with nitrogen for 2 minutes. In the cyclic voltammetric (CV) study, the electrode was scanned between 0 and -1V.

### 3. Results

The CV former component of electrode shown in fig.1 at the QMC/GCE the CV demonstrated two reversible wave with half peaks potential ( $E_{1/2}$ ) respectively at -0.032 and -0.327 V. As shown in fig.1 the values of  $i_{pa}$ ,  $i_{pc}$  for QMC/GCE is more than of this values for Q/ GCE respectively because chitosan promote electron transfer in the matrix. “(Zhang M and et al, 2005)”, “(Zhang M and et al, 2005)”, “(Zhang M and et al, 2004)”.

The behavior of DNPH at a bare GCE and QMC/GCE was studied by cyclic voltammetry. Figure 2 shows the cyclic voltammogram obtained for  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> DNPH in PB solution (PH=1.5). With the bare GCE, current peak is low with value of potential -0.458 v range studied, evidencing the high overpotential of DNPH reduction. In voltammogram obtained with modified electrode the value of current enhanced extremely and potential of peak (77 mv) shifted toward more positive values. Hence, the presence of CNTs leads to a decrease in the over potential of reduction of DNPH and effectively catalyzes its reduction. This is probably due to the combined effect of a large effective surface area of CNTs, their electronic structure, and the topological defects present on the tube surface, “(G Jurmann and et al, 2007)”. The large surface area is also responsible for the higher background current of the modified electrode as

compared to that of the bare GCE. Experiments have been performed in a variety of electrolytes and PH. The results showed that the CNT catalyzed reduction of DNPH takes place only in moderately to highly acidic media (PH=1.5). Therefore, it is suspected that it is DNPH that is actually reduced on the modified electrode.

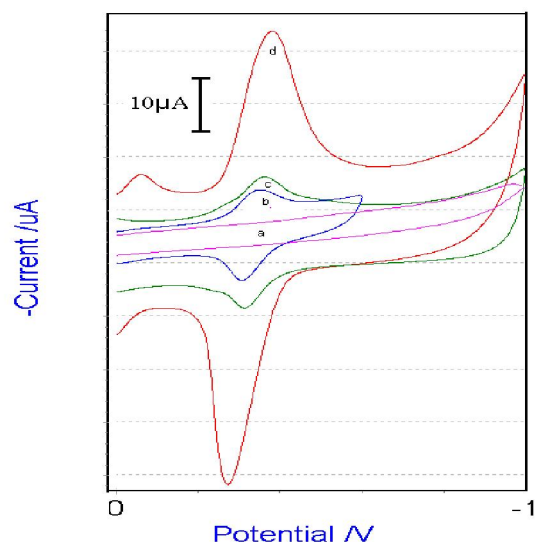


Fig 1. The CV former component of electrode in 0.3M PB (PH=1.5), Scan rate=100mv/sec

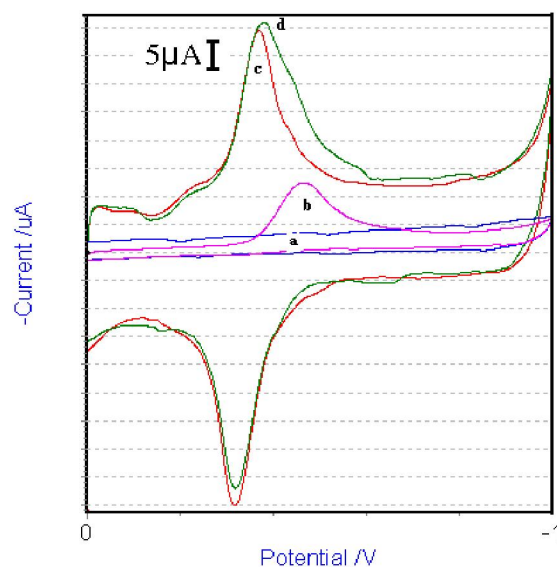


Figure 2. Cyclic voltammogram With the bare GCE and QMC/GCE in absence and presence  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> DNPH in PB solution (PH=1.5).

A series of cyclic voltammograms obtained at different scan rates for a typical DNPB concentration showed that the anodic and cathodic peak current ( $i_{pa}$ ,  $i_{pc}$ ) were proportional to the square root of scan rate ( $v^{1/2}$ ) ( $r = 0.987$ ,  $0.983$  respectively). In addition, at lower concentration of DNPB, the  $i_{pc}$  of the QMC/GCE in DNPB solution did not increase with the increase of immersed time. The results suggested that the oxidation and reduction of DNPB was undergoing a diffusion-controlled process.

The amount of modifier on the surface of electrode affected the  $i_{pa}$  and  $i_{pc}$ . Fig 3. showed that the  $i_{pa}$ ,  $i_{pc}$  enhanced when the amount of MWCNT increased, which probably because of the presence of electro-reactive sites which increased with the amount of MWCNTs, "(C.E. Banks and et al, 2005)", "(C.E. Banks and et al, 2004)". When the concentration of MWCNTs in the modifier surpassed 0.5ml, the  $i_{pa}$ ,  $i_{pc}$  of nitrite fell. These because the film on the electrode surface was too thick, which prevented the electron transfer between nitrite and electrode. In this paper, 0.5ml MWCNTs in the Q-chitosan-MWCNT modifier was used as optimum amount for voltammetric determination of DNPB, NB.

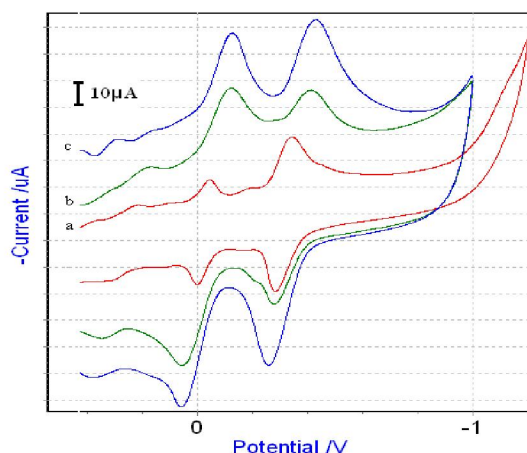


Fig. 3. The cyclic voltammogram of QMC/GCE prepared with ratios contains a) 0.1 ml of mix (MWCNT, Q) b) 0.3 ml of mix (MWCNT, Q), c) 0.5 ml of mix (MWCNT, Q) with 0.1 ml chitosan in 0.3M PB (pH=1.5), Scan rate=100mv/sec

A series of standard solutions of DNPB were determined by CV (shown in fig 4.). The,  $i_{pc}$  was linearly related to DNPB concentrations over the range of  $5.00 \times 10^{-6}$ –  $7.94 \times 10^{-5}$  mol  $l^{-1}$  with a correlation coefficient of  $r^2 = 0.992$  respectively.

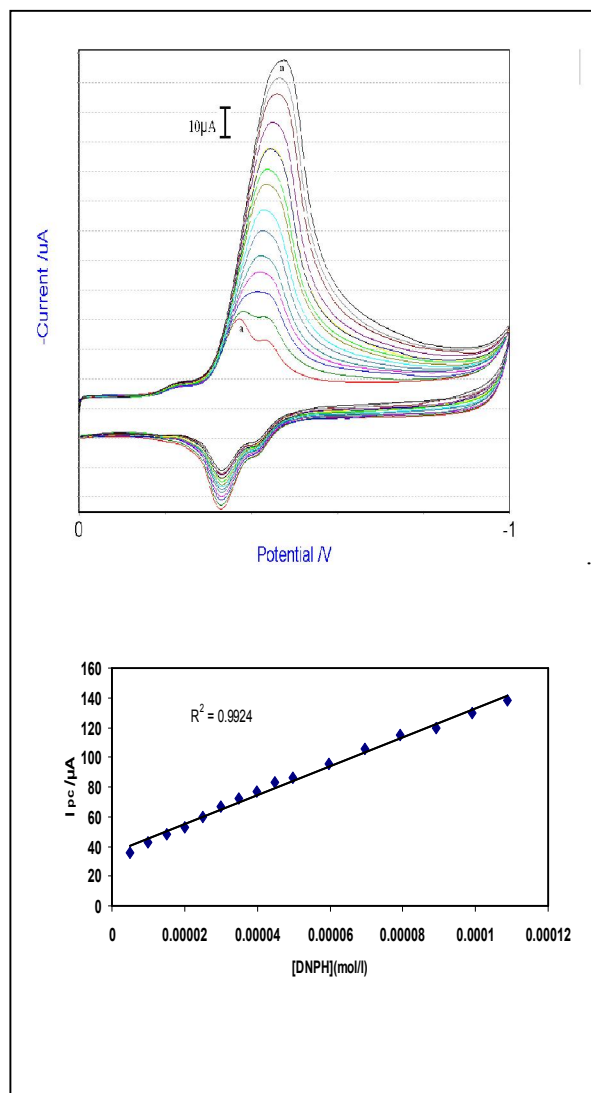


Fig. 4. Cyclic voltammograms of QMC/GCE, at scan rate 100 mVs<sup>-1</sup> with increasing DNPB concentration (from a to n) 0.0, 5.0, 10, 15, 20,25,30,35,40, 45, 50, 60, 70 and 80 mM of DNPB in pH 1.5 phosphate buffer solution. Inset, plot of peak current vs. DNPB concentrations.

Figure 5 shows the cyclic voltammetric responses of bare GCE and QMC/GCE in the presence of  $5.0 \times 10^{-6}$  M NB at a scan rate of 100mV s<sup>-1</sup>. At the bare GCE, a small and broad cathodic peak at the potential of -0.051 V was observed (curve b), while at the BGCE, a significant reduction peak appeared at about -0.478 V (curve a). Though the potential is more positive than the reduction peak at

the bare GCE, the peak current is of about six fold enhancement. With an increase of NB concentration, the reduction current increased, accompanied by the evidently negative shift of the peak potential (curve b). These results suggest that QMC film has an excellent electrochemical activity toward the reduction of NB, and that the electrochemical behavior varies slightly with the substrate concentration. Fig 6. Shows cyclic voltammograms of QMC/GCE in solutions containing different concentrations of NB and the inset shows the plots of cathodic current vs. NB concentration. The plot of cathodic current vs. NB concentration was linear in the concentration range  $5 \times 10^{-6}$  -  $1.67 \times 10^{-4}$  M, and  $R^2=0.995$ .

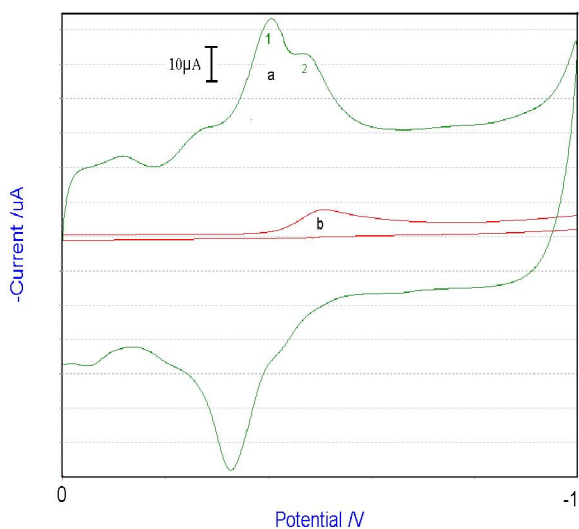


Figure 5. Cyclic voltammetric responses of a) QMC/GCE and b) bare GCE in the presence of  $5.0 \times 10^{-6}$  M NB at a scan rate of  $100 \text{ mV s}^{-1}$  in pH 1.5 phosphate buffer solution.

The effect of the solution pH on the current response for  $5.0 \times 10^{-6}$  M NB in 0.1 M PB was examined. Acidic conditions are more favorable for a good response and the maximum current is obtained at pH 2.0. Therefore, pH 2.0 was adopted for the NB determination.

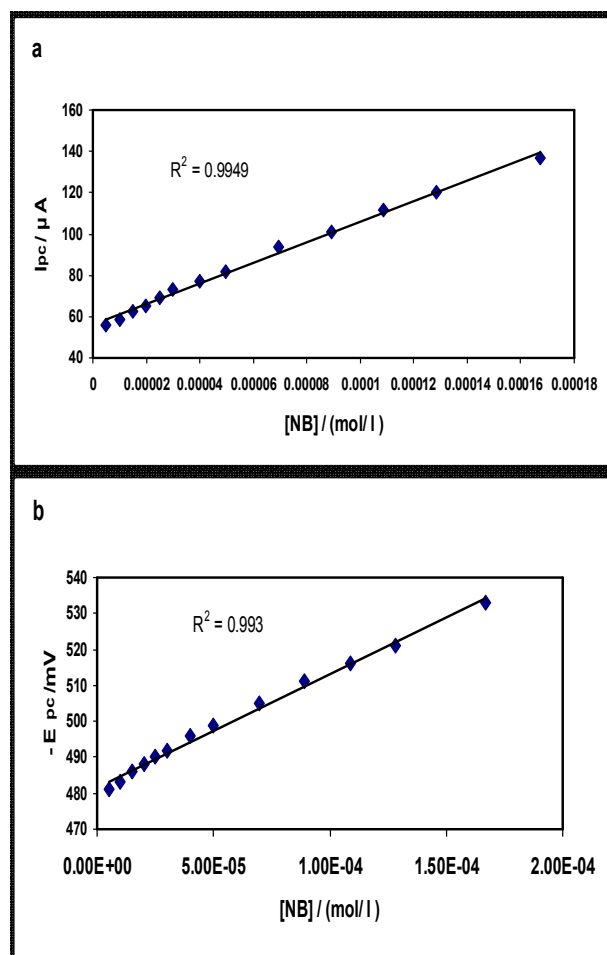


Fig 6. Cyclic voltammograms of QMC/GCE, at scan rate  $100 \text{ mV s}^{-1}$  with increasing NB concentration (from a to n) 0.0, 5.0, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70 and 80 mM of NB in pH 1.5 phosphate buffer solution. Inset, plot of a) peak current b) potential cathodic vs. NB concentrations.

To check the validity of the proposed procedure for DNPB and NB in 3 samples Water, the recoveries of added DNPB and NB, were determined. All the samples were prepared by adding 2mL fresh water samples to the cell and diluted to 20mL with the supporting electrolyte solution and each recovery was calculated by comparing the results obtained before and after adding the DNPB and NB standard solutions. The amounts of DNPB and NB in the samples, and their recoveries, are shown in Tables 1 and 2 this results evidenced the reliability of the method.

Table 1. Determination of DNPH in 3 samples water

| samples       | Added(molL <sup>-1</sup> ) | Found(molL <sup>-1</sup> ) | Recovery(%) |
|---------------|----------------------------|----------------------------|-------------|
| Mineral water | 5.0×10 <sup>-6</sup>       | 4.987×10 <sup>-6</sup>     | 99.7        |
| Well water    | 5.0×10 <sup>-6</sup>       | 5.14×10 <sup>-6</sup>      | 102.8       |
| City water    | 5.0×10 <sup>-6</sup>       | 4.83×10 <sup>-6</sup>      | 96.9        |

Table 2. Determination of NB in 3 samples water

| samples       | Added(molL <sup>-1</sup> ) | Found(molL <sup>-1</sup> ) | Recovery(%) |
|---------------|----------------------------|----------------------------|-------------|
| Mineral water | 5.0×10 <sup>-6</sup>       | 4.85×10 <sup>-6</sup>      | 97          |
| Well water    | 5.0×10 <sup>-6</sup>       | 5.136×10 <sup>-6</sup>     | 102.7       |
| City water    | 5.0×10 <sup>-6</sup>       | 4.94×10 <sup>-6</sup>      | 94          |

#### 4. Discussions

The CNT in modified electrode acts as an efficient catalyst for electrochemical reduction of nitrobenzene and 1, 2-dinitro phenyl hydrazine. Thus this modified electrode is a highly sensitive sensor for monitoring two nitro aromatic compounds.

Obviously this result is reproducible for 3 sample waters. The responsibility of this electrode is good and needs a very short time.

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#### References

- [1] M. Latifoglu, M.D. Gurol, *Water Res.* 37 (2003) 1879.
- [2] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. *Water Res.* 37 (2003) 1223.
- [3] S.F. Nishino, J.C. Spain, *Appl. Environ. Microbiol.* 59 (1993) 2520.
- [4] E.K. Nefso, S.E. Burns, C.J. McGrathb, J. *Hazard. Mater.* B123 (2005) 79.

- [5] M. Trojanowicz, M. Szewczynska, *TrAC-Trend. Anal. Chem.* 24(2005) 92.
- [6] J. Wang, *Electroanalysis* 17 (2005) 7.
- [7] N. Li, J. Wang, M. Li, *Rev. Anal. Chem.* 22 (2003) 19.
- [8] C.E. Banks, R.G. Compton, *Analyst* 131 (2006) 15.
- [9] J. Wang, *Analyst* 130 (2005) 421.
- [10] M. Valcarcel, B.M. Simonet, S. Cardenas, E.B. Suarez, *Anal. Bioanal. Chem.* 382 (2005) 1783.
- [11] S.Hoon Baek, B. Kim, K.Do Suh, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 316 (2008) 292–296
- [12] Zhang M, Gorski W. *J Am Chem Soc*(2005)127:2058–9.
- [13] Zhang M, Gorski W. *Anal Chem* (2005)77:3960–5.
- [14] Zhang M, Smith A, Gorski W. *Anal Chem* (2004)76:5045–50.
- [15] G Jurmann, D.J. Schiffrin, Kaido Tammeveski *Electrochim Acta* 53 (2007) 390–399
- [16] C.E. Banks, T.J. Davis, G.G. Wildgoose, R.G. Compton, *Chem. Commun.* 7 (2005) 829.
- [17] C.E. Banks, R.R. Moore, T.J. Davis, R.G. Compton, *Chem. Commun.* 16 (2004) 1804.

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