

Electrochemical Behavior of 2, 4-Dinitrophenol at Multi-Walled Carbon Nanotube-Modified Glassy Carbon Electrode and Its Application

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Received: 17 December 2012 / Accepted: 4 January 2013 / Published: 1 February 2013

The electrochemical behavior for 2, 4-dinitrophenol at multi-walled carbon nanotube-modified glassy carbon electrode is investigated in this paper. A new, simple, sensitive and inexpensive method for determination of 2, 4-dinitrophenol in soil is proposed. The accuracy and reproducibility of the determination method for 2, 4-dinitrophenol was evaluated. This method was satisfactorily applied for the determination of 2, 4-dinitrophenol in soil. The concentration ranges are 0.001 to 0.05mM, and the detection limit is 1.44×10^{-4} mM for 2, 4-dinitrophenol.

Keywords: 2, 4-dinitrophenol, soil, multi-walled carbon nanotube, cyclic voltammetry

1. INTRODUCTION

2,4-dinitrophenol (DNP) is primarily used for making dyes, wood preservatives, photographic developers and explosives. Nitrophenols presented in wastewater, river and atmosphere are considered to be important environmental contaminant and highly toxic to humans, animals and plants [1-3]. The major site of degradation is the soil, where microorganisms metabolize it [4]. A fast, sensitive and selective analytical method to detect DNP will be of great significance in the environmental treatment. Spectrophotometry [5], differential pulse voltammetry (DPV) [6], cyclic voltammetry (CV) [7, 8], reversed-phase liquid chromatography (RPLC) [9], liquid chromatography-Mass spectrum-mass spectrum (LC-MS-MS) [10] and gas chromatography (GC) [11] have been used for the determination of DNP. However, all methods mentioned above are time-consuming or lower sensitivity.

Since carbon nanotubes (CNTs) were discovered in 1991, CNTs have attracted much attention of researchers [12]. The modification of electrode substrates with multi-walled carbon nanotubes (MWCNTs) has been documented to result in high sensitivities, promotion electron-transfer, low detection limits, resistance to surface fouling and reduction of over potentials. It has been reported that MWCNT modified electrodes were successfully applied to study and determine many organic molecules [13-16].

In this work, the electrochemical behavior of DNP is investigated, and a new, simple, sensitive and inexpensive method for determination of DNP in soil is proposed.

2. EXPERIMENTAL

2.1. Chemicals

Multi-walled carbon nanotubes (MWCNTs) were purchased from Shenzhen Nano-Technologies Port Co. Ltd. (China). All other reagents were analytical grade. Double-distilled water was used throughout. 0.1M phosphate buffer solution was prepared by dissolving 0.1mol NaCl and 0.1mol Na₂HPO₄ in the double-distilled water of 1000mL and adjusting desired pH values with 6 M HCl or 1M NaOH.

2.2. Instrumentation

For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, USA) was employed. The electrochemical cells consisted of three electrodes, a 3 mm diameter glassy carbon disc electrode (GCE) and MWCNT composite modified GCE were used as working electrode. A platinum wire served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode.

2.3. Preparation of multi-walled carbon nanotubes and modified GCE

The MWCNTs was purified in boiling concentrated nitric acid for 4 h, followed by rinsing with deionized water, and drying under ambient atmosphere. Open-end MWCNTs with hydrophilic surface were thus obtained. Before modification, the GCE was polished with 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with doubly distilled water, and then sonicated in ethanol and doubly distilled water for 10 min, sequentially. The modifier suspension was prepared by dispersing MWCNTs in 5.0 ml of N, N-dimethylformamide under sonication for 30 min. The MWCNT modified GCE was prepared by casting 5 μL of the mentioned above black suspension on the GCE surface using a micropipette and left to dry at room temperature. Before the voltammetric measurements, the modified electrode was cycled between -1 and 1 V (scan rate 100 $\text{mV} \cdot \text{s}^{-1}$) in 0.1 M phosphate buffer solution for several times until acquiring the reproducible responses.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of DNP at MWCNT/GCE

The electrochemical response of DNP at MWCNT/GC electrode and bare electrode in 0.1 M phosphate buffer solution of pH 7.3 is shown in Fig.1.

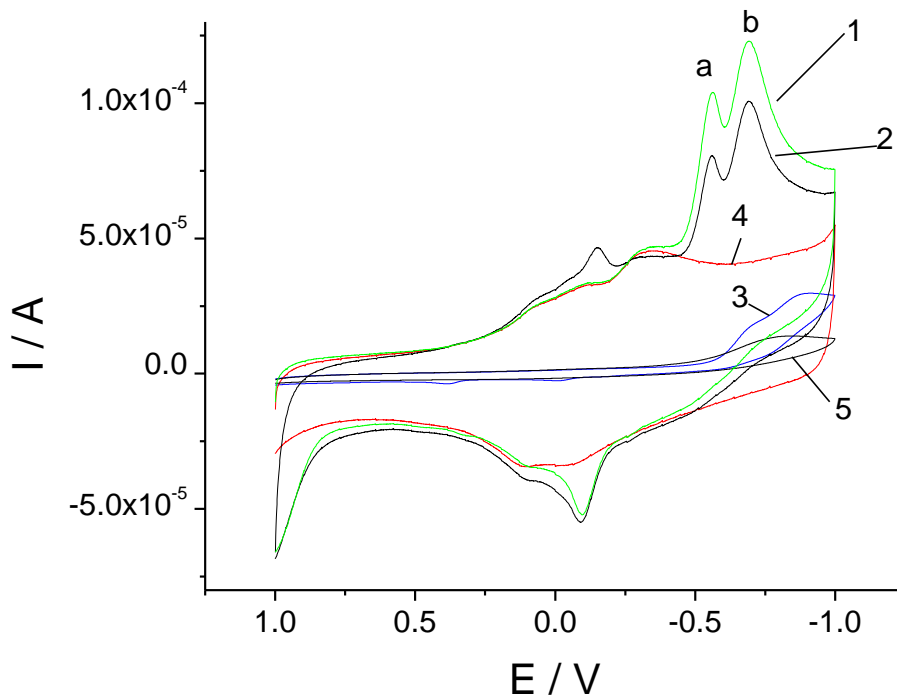


Figure 1. CVs of 0.25mM DNP at MWCNT/GCE (1: the first circle; 2: the second circle) and bare GCE (3), CVs of MWCNT/GCE (4) and bare GCE (5). Supporting electrolyte: 0.1M phosphate buffer with pH 7.3; Scan rate: $100\text{mV}\cdot\text{s}^{-1}$; Accumulation volume of $1\text{mg}\cdot\text{ml}^{-1}$ MWCNTs suspension: $5\mu\text{l}$.

Two reduction peaks for DNP at bare GCE are observed at -0.703 and -0.886V . However, the reduction peaks of DNP at MWCNT/GCE are observed at -0.556V (Peak a) and -0.697V (Peak b), and an oxidation peak appears at -0.092V . The reduction peaks were ascribed to the reduction of $-\text{NO}_2$ and the oxidation of $-\text{OH}$. The results are in agreement with the previous work [6]. On the second cycle, a new reduction peak is observed at -0.152V , which is ascribed to the reduction of $\text{C}=\text{O}$. The reduction peak potential of DNP at MWCNT/GCE shifted to positive potentials, and the peak current increased, indicating that the MWCNT modified electrode promoted the electrochemical reduction of DNP by considerably accelerating the rate of electron transfer. Purified MWCNTs were functionalized with $-\text{OH}$ and $-\text{COOH}$ [17], which could interact with hydroxyl groups and nitro groups in DNP to form hydrogen bond. The π - π conjugated bonds between MWCNTs and DNP probable increase the reaction current. The MWCNT interface had a large surface area, a great deal of active sites, better conductivity and favorable electrocatalytic power, all of them led to the dissimilar conjugation effect of DNP with the bare electrode interface.

3.2. Amount of the modifier

The reduction current of DNP at modified electrode can be affected by the amount of MWCNTs on the electrode surface [18]. This can be controlled by using the same volume ($5\mu\text{L}$) of the suspensions with the different concentrations of MWCNTs, casted on the surface of GCE. The experiments showed that the reduction peak current for 0.25mM DNP increased quickly by increasing the concentration of MWCNT suspension deposited on the surface of GCE up to $1.0\text{ mg}\cdot\text{mL}^{-1}$. Further increase, caused a gradual decrease in the peak current of DNP with increase in background current. As a result, $5\mu\text{L}$ of $1.0\text{ mg}\cdot\text{mL}^{-1}$ MWCNT suspension was selected as optimum volume for preparation of the modified electrode.

3.3. Influence of pH

The influence of pH on the electrochemical behavior of DNP was investigated at different pH values in the range of 4.0 to 8.0. Fig. 2 shows the CVs of 0.25mM DNP on the surface of the modified electrode over the discussed pH range at the scan rates of $100\text{ mV}\cdot\text{s}^{-1}$.

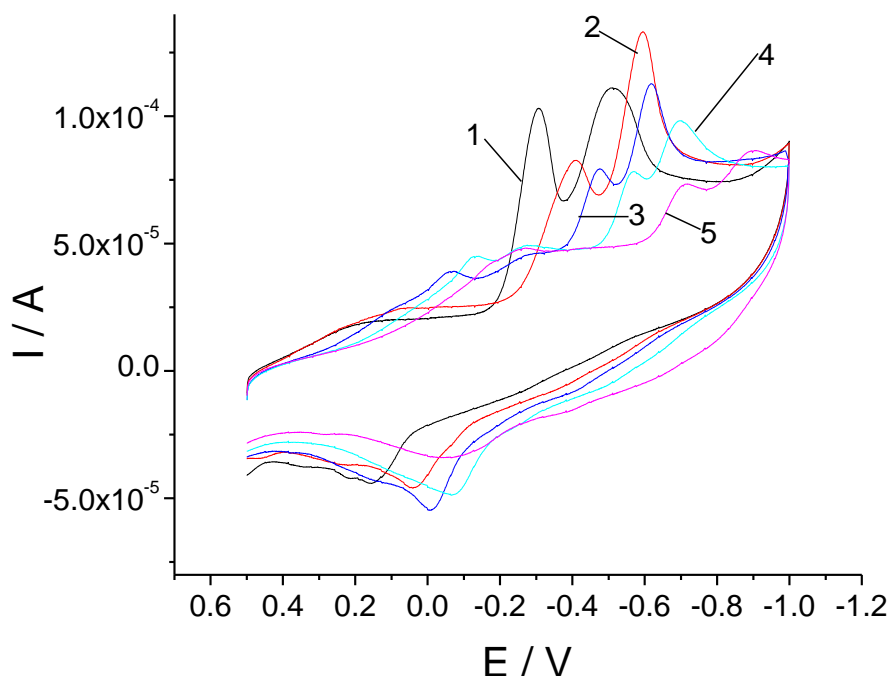


Figure 2. Influence of pH on the shape of peak, pH: 4.0 (1), 5.0(2), 6.0(3), 7.0(4) and 8.0(5). Other conditions are as in Fig. 1.

It was found that the peak potential shifted negatively with pH increasing. Good separation peak and most peak current of DNP in phosphate buffer solution of pH 5.0 were observed, this result is consistent with the good separation peak and peak current of DNP at GC electrode in HAc–NaAc

buffer of pH 5.8 with the surfactant of cetyltrimethyl ammonium bromide [6]. In order to obtain stable pH and higher sensitivity the phosphate buffer solution of pH 5.0 was used as supporting electrolyte in all voltammetric determinations.

3.4. Effect of potential scan rate

The CV investigations for DNP were performed on the surface of the MWCNT/GCE in buffered solution of pH 5.0 at different potential sweep rates. Fig. 3 illustrates the influence of scan rate on the CVs of DNP in the range of 10 to 800 mV.s⁻¹.

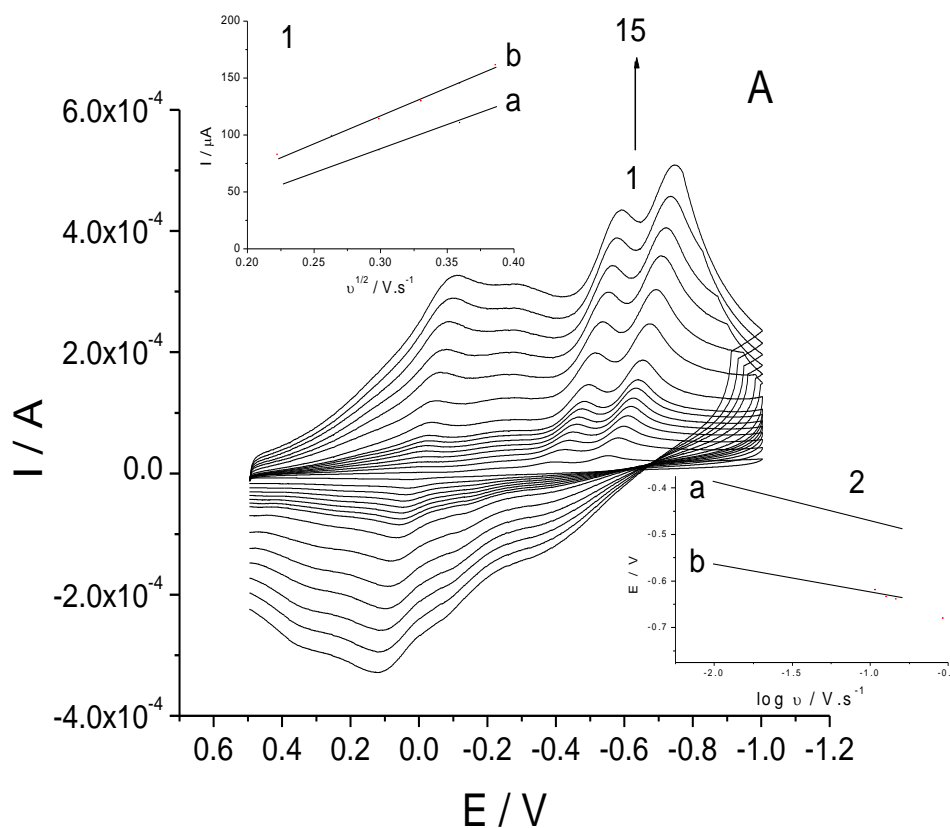


Figure 3. CVs of 0.25mM DNP at MWCNT/GCE with different scan rates, (1) – (15) were 10, 30, 50, 70, 90 110, 130, 150, 200, 300, 400, 500, 600, 700 and 800 mV.s⁻¹, respectively. Insert: plot of the peak current against scan rates for Peak a and b, and plot of the peak potential against logarithm of scan rates for Peak a and b, respectively; Supporting electrolyte: 0.1M phosphate buffer with pH 5.0 ; Other conditions are as in Fig. 1.

Two linear equations between the peak current and scan rate for Peak a and b (Fig. 3, insert Fig.1.) were obtained as:

$$\text{Peak a: } I_a = 407.814 v - 8.9928, R^2 = 0.998 \tag{1}$$

$$\text{Peak b: } I_b = 317.854 v - 11.465, R^2 = 0.995 \quad (2)$$

The linear relation between the current (I) and scan rate (v) for Peak a and b in the range of 10 to $200\text{mV}\cdot\text{s}^{-1}$ indicated that at sufficient potential, the reaction involves mass transport and depends on DNP concentration, which was ideal case for quantitative applications. The linear relation between the current and scan rate indicates an adsorption-controlling process on the surface of the modified electrode [6]. The peak current of Peak b is more than that of peak a, thus Peak b is selected for determination of DNP.

The relationship between the reduction peak potential and scan rate for Peak a and b is also shown in Fig. 3 (Insert Fig.2). It can be seen that the reduction peak potential of shifts negatively with increasing scan rate. There are linear relationship between E and the logarithm of the scan rate for Peak a and b in the range of 10 to $600\text{mV}\cdot\text{s}^{-1}$. The regression equations for the relationship are obtained as:

$$\text{Peak a: } E_a (\text{V}) = -0.0721 \log v (\text{V}\cdot\text{s}^{-1}) - 0.5354, R^2 = 0.963 \quad (3)$$

$$\text{Peak b: } E_b (\text{V}) = -0.0509 \log v (\text{V}\cdot\text{s}^{-1}) - 0.6685, R^2 = 0.975 \quad (4)$$

Such a behavior reveals the irreversible nature of the reduction process for DNP [18].

The adsorption products of DNP affected the peak shape, thus the scan rates of $100\text{mV}\cdot\text{s}^{-1}$ were selected for determination of DNP.

3.5. Linearity range and the detection limit

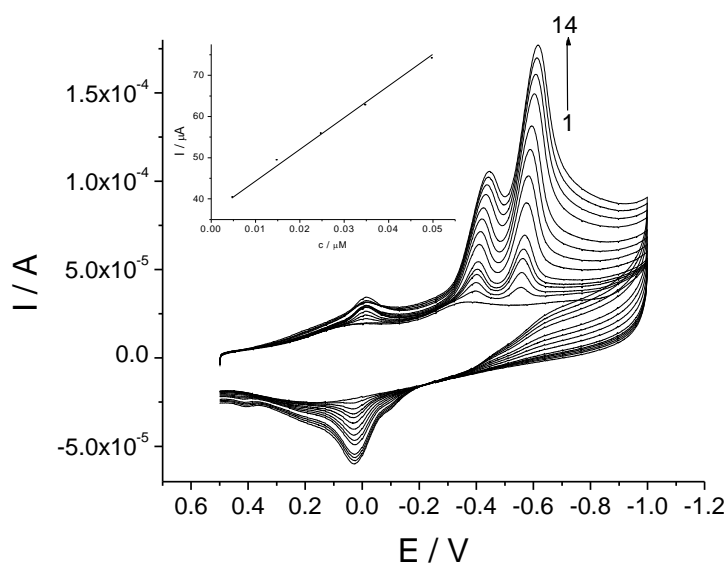


Figure 4. CVs of different content DNP at MWCNT/GCE, (1) – (14): the contents of DNP were 0, 000, 0.005, 0.015, 0.025, 0.035, 0.050, 0.100, 0.150, 0.200, 0.250, 0.300, 0.350, 0.400 and 0.450mM, respectively. Insert: plot of the peak current against the concentration for Peak b. Other conditions are as in Fig. 3.

Under the previous mentioned optimum conditions, the relationship between the reduction peak current and the concentration of DNP was examined by CV on the surface of MWCNT/GCE, and the results were shown in Fig.4. It can be seen that the reduction currents of peak b were proportional to DNP concentrations in the range of 0.001 to 0.05mM in 0.1 M phosphate buffer solution of pH 5.0. The linear regression equations were obtained as

$$c \text{ (mM/L)} = 0.0014 I \text{ (}\mu\text{A)} - 0.0503, R^2=0.998. \quad (5)$$

The detection limit ($3\sigma / \text{slope}$, where σ was the standard deviation of the intercept and s was the slope of the calibration curve) observed for DNP was 1.44×10^{-4} mM, which is lower than 2.4×10^{-7} M [6].

3.6. Repeatability of the modified electrode

The repeatability of the modified electrode was investigated by repetitive recording at a fixed DNP concentration of 0.25mM. The relative standard deviation (RSD) for the peak currents in CVs based on 6 replicates was 1.6%, indicating excellent repeatability of the response of the modified electrode. Also, on using the MWCNT/GCE daily and storing under ambient conditions over a period of 2 weeks, the electrode retained 95.3% of its initial peak current response for DNP concentration of 0.25mgM, indicating that the excellent MWCNT/GCE is obtained and superior to hidepowder-modided carbon paste electrode for DNP [19].

3.7. Determinations in soil

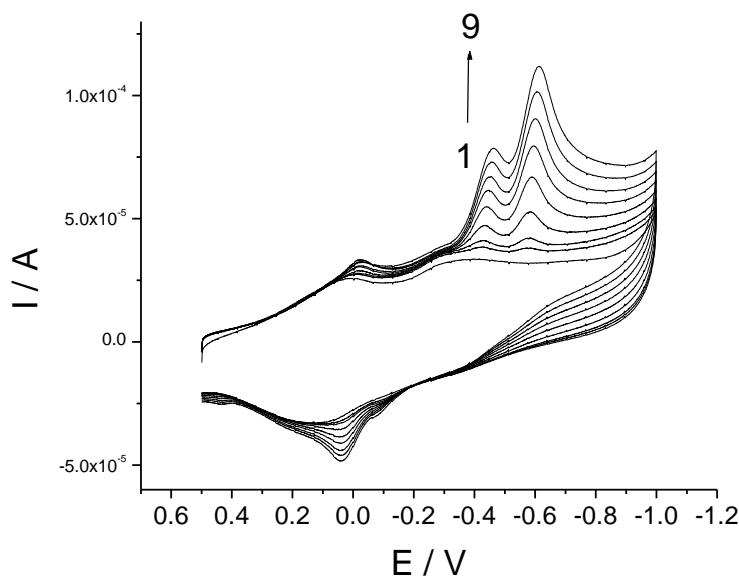


Figure 5. CVs of soil sample and added standard samples, (1) - (9) were 0.000, 0.005, 0.015, 0.050, 0.100, 0.150, 0.200, 0.250 and 0.300mM, respectively.

The MWCNT/GCE was used to determination of the content of DNP in soil by applying CV method. 2.0000 g of soil added into 10.0 ml of 0.1M phosphate buffer solution of pH5.0 and sonicated for 30min, then centrifugated at 4000 r/min for 10min. The filtered solution was used to determine the concentration of DNP. The CVs of sample and added standard samples are shown in Fig.5. The determination results using the standard addition method were shown in Table 1. The recoveries were in the range from 97.0 to 106.5%. Using this standard addition method, the content of DNP in soil was obtained to be 0.00~0.004mM with the relative standard deviation (RSD) of 0.0~4.0% (n=6).

Table 1. Recovery and RSD% for 2, 4-dinitrophenol in soil by the proposed methods

No.	Sample ^a (mM)	RSD ^a (%)	added (mM)	Found ^a (mM)	Recovery ^a (%)
1	0.000	0.0	0.010	0.0097	97.0
2	0.002	4.0	0.020	0.0230	105.0
3	0.003	3.1	0.030	0.0324	98.0
4	0.004	2.7	0.040	0.0466	106.5

^aaverage of six replicate measurements

3.8 Interference

The influence of some organic compounds and inorganic salts was tested. If the presence of an interferent altered the average current signal of DNP by less than $\pm 5\%$, we considered that caused no interference. The results show 500-fold of K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Pb^{2+} , Ni^{2+} , Mn^{2+} , Na^+ , NH_4^+ , Cu^{2+} , Zn^{2+} , NO_3^- , Cl^- , F^- , I^- , CO_3^{2-} and Br^- , 300-fold of oxalic acid and humic acid, did not interfere on the determination, while p-nitrophenol and o-nitrophenol interfered severely. This suggests the modified electrode had certain resistance to some interference, indicating that this method is superior to spectrophotometry [5].

4. CONCLUSIONS.

In present work, the mechanism for DNP at MWCNT/GCE is proposed in this paper. It was demonstrated that modification of GCE with MWCNTs is a simple and effective method for obtaining highly sensitive electrodes for determination of DNP. The procedure enables preparation of highly stable and reproducible uniform modifier films, which leads to a considerable enhancement in repeatability and reproducibility in the voltammetric measurements. High sensitivity and improved detection limit of the MWCNT/GCE are promising for the determination of trace amounts of DNP in soil.

ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation of China (No. 20975043), The authors gratefully acknowledge the financial support of the National Science Foundation of China (grant No. 21003065), the Open Science Foundation for Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials (grant no. JSKC11091), the Open Science Foundation for Jiangsu Key Laboratory for Biomass-based Energy and Enzyme Technology (grant No. JSBEET1207), and the Science Foundation for Huaiyin Normal University (grant no. 11HSGJBZ13)

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