

# Study on Electrochemical Behavior of Ortho-Aminophenol on Nano-Gold/Carbon Nanotubes Composite Modified Electrode

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**Abstract:** The aim of this work was to construct a novel modified electrode based on Au nano-particles and carbon nanotube for studying the electrochemical behavior of ortho-aminophenol (OAP). A sensitive oxidation peak of OAP at the potential of 0.352V was observed in HAc-NaAc-PHP buffer solution. The effect factors of the electrochemical response of OAP were optimized by linear sweep voltammetry (LSV). Under the optimum conditions, a linear calibration curve of the peak current of OAP and concentration was obtained in the range of  $4.0 \times 10^{-7} \sim 2.0 \times 10^{-4}$  mol/L. The oxidation peak current increases direct proportionally with the square root of scanning speed, which indicates that the electrochemical oxidation process of OAP on this modified electrode is diffusion-controlled process. The diffusion coefficient ( $D$ ) could be estimated and the result was  $5.42 \times 10^{-7}$   $\text{cm}^2 \cdot \text{s}^{-1}$  by employing chronocoulometry. The charge transfer rate constant ( $k_s$ ) was also discussed and the result was  $7.85 \times 10^{-4}$   $\text{cm} \cdot \text{s}^{-1}$ . Concurrently, based on the experiment results, the electrode reaction process of OAP with one electron and one proton was proposed.

**Keywords:** Ortho-aminophenol; Au nano-particles; Multi-walled carbon nanotube; Au electrode; Voltammetry

## 1. INTRODUCTION

Ortho-aminophenol (OAP) is an important chemical substance, widely used in the dye, pharmaceutical, and biological industries as an intermediate in the production of dyes and pharmaceuticals [1]. It is a key component in industrial effluent from printing and dyeing plants, which is not biodegradable and has serious toxic and contaminative effects. Being industrial pollutants with toxic effects, it can penetrate through the skin and membranes of human, animals and cause genotoxic, mutagenic and hepatotoxic effects [2, 3]. Therefore, the determination of aminophenol has been become an important environmental challenge.

Some analytical techniques have been employed to separate and determinate aminophenol, including gas chromatography [4], high performance liquid chromatography [5], capillary electrophoresis [6], spectrophotometry [7]. Generally speaking, chromatography and electrophoresis have disadvantages, for instance, expensive instrument and time-consuming. Spectrophotometry is inconvenient and has low sensitivity. Electrochemical measurement possesses advantages, such as rapid detection, remarkable sensitivity, and low cost. Electrochemical methods have been used to detect some phenol pollutants in the recent years [8-10]. To the best of

our knowledge, voltammetric determination of OAP by using Au nano-particles/multi-walled carbon nanotube composite modified Au electrode (AuNPs/MWCNT/Au) has not been reported yet.

Since carbon nanotube was discovered, this new material has attracted much attention because of good electrical conductivity, strong adsorptive ability, and excellent biocompatibility [11]. A subtle electronic behavior of CNTs reveals that they have the ability to promote electron-transfer reactions [12]. Nanosized particles of precious metals have better catalytic characteristics compared with conventional particles because they have high conductivity and high surface-to-volume ratio [13]. In this work, a novel composite modified electrode that combined special characteristics of CNTs and Au nanosized particles was fabricated. The electrochemical response of OAP at AuNPs/MWCNT/Au has been investigated. The results have shown that this modified electrode has a good electrocatalytic effect on the oxidation of OAP. The proposed method has been successfully used to determine the content of OAP in the simulated waste water.

## 2. EXPERIMENTS

### 2.1. Apparatus and Reagents

All electrochemical experiments were performed using a CHI 660D Electrochemical Analyzer (CH Instrument, USA). The

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working electrode was a modified Au electrode ( $0.071\text{cm}^2$ ). A platinum wire was used as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. All the potentials were reported versus SCE. Transmission electron microscopy (TEM) analysis was performed using a JEM 2100 microscope (JEOL Ltd., JAPAN). The pH values of the solutions were recorded with a PHS-3C Digital pH-meter (Shanghai Yidian Science Instrument Company, Shanghai, China). All experiments were performed at the room temperature ( $25^\circ\text{C}\pm 1$ ).

Multi-walled carbon nano-tube (MWCNT) was obtained from Nano-material Company of Shenzhen, China.  $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$  was purchased from Shanghai Chemical Reagent Factory, China. A  $1.0\times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$  stock solution of Ortho-aminopheno (Tianjin Damao Chemical Reagent Factory, China) was prepared in ethanol and then stored in the dark at  $4^\circ\text{C}$ . 0.2% (w %) Chitosan (CTS) was fabricated by dissolving an appropriate amount of CTS in 1% (v/v) acetic acid solution. Other chemicals were of analytic grade reagents without further purification. The water used in our experiment was redistilled water.

## 2.2. Fabrication of the modified electrode

Au nano-particles (AuNPs) collosol was prepared according to the previous report [14]. The gold nanoparticles with different diameters were obtained by employing different amount of sodium citrate in the reaction process. The average diameters of AuNPs were measured by TEM. AuNPs collosol was stored at a refrigerator under  $4^\circ\text{C}$ .

MWCNT was purified by using the other's procedure [15]. 4 mg purified MWCNT was dispersed into 4 mL mixing solution (containing 2.0 mL Au collosol, 1.2mL anhydrous ethanol and 0.8 ml 0.2% CTS) and sonicated for about 30 min to produce a homogeneous AuNPs/MWCNT suspension. Before modification, bare Au electrode was mechanically polished with  $0.05\mu\text{m}$  aluminum slurry, rinsed and sonicated (2 min) successively in 1:1  $\text{HNO}_3\text{-H}_2\text{O}$  (v/v), anhydrous ethanol and redistilled water.  $4.5\mu\text{L}$  dispersion was coated onto the surface of Au electrode and the solvent was evaporated at room temperature. Then, AuNPs/MWCNT composite modified Au electrode was fabricated successfully.

## 2.3. Experiment procedure

In the consequent experiments, AuNPs/MWCNT/Au electrode was used as the working electrode. The three-electrode system was transferred into electrolytic cell containing an appropriate amount of OAP in 10 mL pH=4.8 HAc-NaAc-PHP buffer solution. Linear sweep voltammetric curves within  $0\sim 0.7\text{V}$  potential window were recorded, and the oxidation peak was measured at 0.352V. After each measurement, in order to remove the previous deposits completely, this modified electrode was refreshed by 20 times cyclic voltammetric sweeps in blank buffer solution.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of AuNPs and composite suspension

The sizes of AuNPs prepared by above-mentioned procedure were measured by TEM. When the amounts of sodium citrate are 1.0, 0.7, 0.4mL in the preparation process, the average diameters of AuNPs is measured as 17nm, 25nm, 38nm by TEM, respectively.

To evaluate the influence of the sizes of AuNPs on the electro-

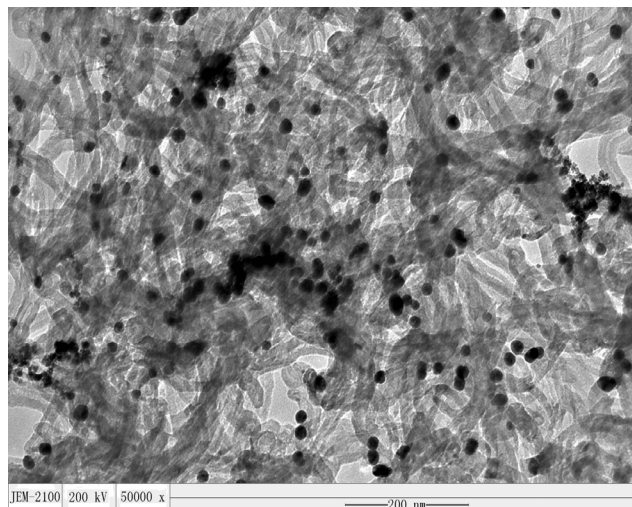


Figure 1. TEM image of the composite suspension

chemical behavior of the composite modified electrode, electrochemical measurements were conducted in HAc-NaAc-PHP buffer solution (pH 4.8) containing 0.1M KCl and 5mM  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  was used as a redox probe. The experiment results demonstrate that the redox peak current of this probe at the modified electrode prepared with 17 nm diameter AuNPs and MWCNTs are distinct higher than those at the other modified electrodes.

The morphology of the composite suspension was also characterized by TEM. Fig.1 depicts TEM picture of one kind of the composite suspension. Many nanocarbon tubes with diameters ranging from 20 to 30 nm are observed. From the image, it also can be seen that AuNPs adheres to the walls of carbon nanotubes and the average diameter of AuNPs is 17 nm.

### 3.2. Electrochemical behaviors of OAP at the different electrodes

Cyclic voltammograms of OAP in pH=4.8 HAc-NaAc-PHP buffer solution at the different electrodes are shown in Fig.2. No oxidation or reduction peak was found at AuNPs/MWCNT/Au electrode (curve a) in the blank supporting electrolyte. In the presence of  $5.0\times 10^{-4}\text{ mol/L}$  OAP, there is obvious oxidation peak at the potential of 0.395V, and no corresponding reduction peak is observed for OAP at the bare Au electrode within the potential window from 0 to 0.7V (curve b), suggesting that the electrode reaction of OAP under these conditions is totally irreversible. Compared with bare Au electrode, a sensitive oxidation peak is found at 0.352 V, and the peak potential shifts negatively 43 mV (curve c). The oxidation peak current of OAP at AuNPs/MWCNT/Au electrode increases significantly. AuNPs-MWCNT film coated Au electrode leads to a decrease in the over-potential of the oxidation of OAP and the increase of the oxidation peak. The subtle electronic behaviors of carbon nanotubes have the ability to promote electron-transfer reactions, and the high surface area of Au nanoparticles has better catalytic characteristics. The composite nanomaterial modified electrode that was prepared in this work combined the special advantages of AuNPs and MWCNT. The experi-

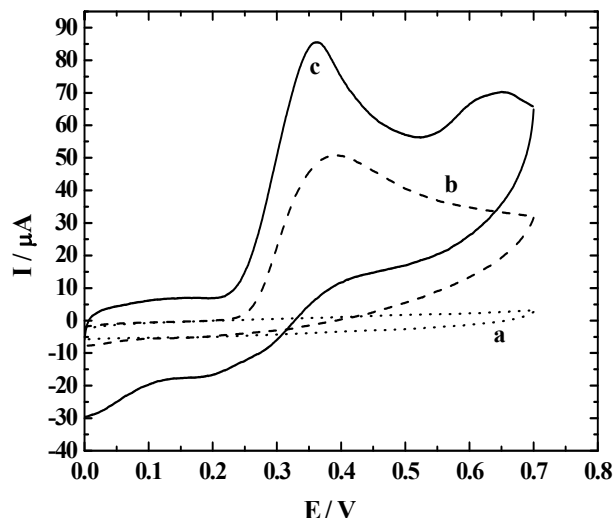


Figure 2. Cyclic voltammograms of OAP in pH=4.8 HAc-NaAc-PHP at different electrodes: (a) AuNPs/MWCNT/Au electrode+blank solution; (b) Au electrode+ $5.0 \times 10^{-4}$  mol/L OAP, (c) AuNPs/MWCNT/Au electrode+ $5.0 \times 10^{-4}$  mol/L OAP, scan rate:  $0.1 \text{ V} \cdot \text{s}^{-1}$

ment result indicated that this modified Au electrode enhanced the determination sensitivity of OAP.

### 3.3. Optimization of the measurement conditions

#### 3.3.1. Optimizing of supporting electrolyte and choice of pH

The oxidation peak potential and peak current for OAP might be affected by the electrolyte solution. The effect of some different electrolytes, such as tartaric acid-tartrate sodium, HAc-NaAc, HAc-NaAc-PHP, PBS, PBS-KCl, HCl-KCl and  $\text{NH}_3\text{-NH}_4\text{Cl}$  on the voltammetric responses was investigated. The results showed that the oxidation peak potential ( $E_{p,a}$ ) of OAP was lower and the peak current ( $I_{p,a}$ ) was higher in HAc-NaAc-PHP. Therefore, HAc-NaAc-PHP was chosen as the supporting electrolyte.

The influences of solution pH on the oxidation peak potential and peak current were examined by LSV from pH4.2 to pH 7.1. The dependence of the peak potential on pH can be expressed by the following equation:

$$E_{p,a} = 0.554 - 0.050 \times \text{pH} \quad (R=0.997) \quad (1)$$

As seen in equation (1),  $E_{p,a}$  shifts negatively with increasing pH, suggesting that proton is involved in the electrode reaction. It also indicated that equal protons and electrons were involved in the oxidation of OAP.

From pH 4.2 to pH4.8, with the increase of pH, the peak current increases gradually, and achieves a maximum at pH=4.8. Then,  $I_{p,a}$  decreases slightly with increasing pH. Therefore, pH=4.8 HAc-NaAc-PHP solution was chosen as the supporting electrolyte.

#### 3.3.2. Influence of the amount of AuNPs/MWCNT modifier

The amount of AuNPs/MWCNT suspension on the surface of Au electrode directly determines the thickness of AuNPs/MWCNT

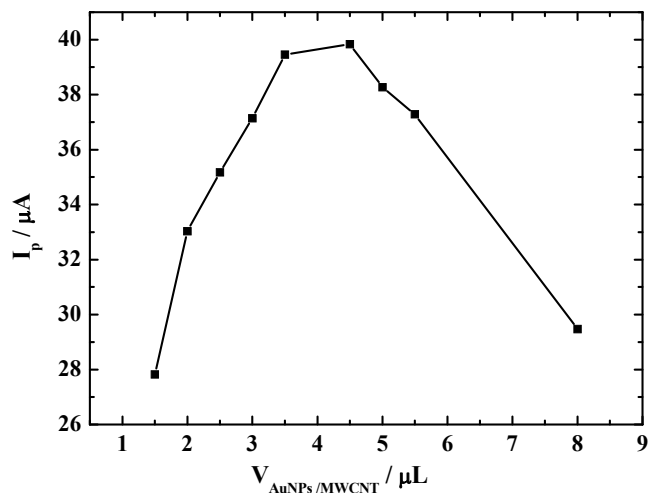


Figure 3. Effect of the modifier amount on the oxidation peak current.

film, and the latter will influence the voltammetric response of OAP. The effect of the amount of modifier on the peak current is depicted in Fig.3. The oxidation peak current of OAP increases with increasing the amounts of AuNPs/MWCNT dispersion within the range from 1.5 to 4.5  $\mu\text{L}$ . However, if further increasing the amount of AuNPs/MWCNT suspension, the oxidation peak current conversely shows gradual decline. This phenomenon is probably due to the reason that AuNPs/MWCNT film becomes thicker and blocks the mass transport and electron transfer. Owing to the uncompensated resistive effects or the lower of the charge transfer rate, the peak current decreases. So electrodes prepared with the optimum coating film of 4.5  $\mu\text{L}$  were used in all subsequent experiments.

#### 3.3.3. Effect of scan rate

The effect of scan rates on the peak currents of OAP at AuNPs/MWCNT/Au electrode in pH=4.8 HAc-NaAc-PHP solution were investigated by LSV. The peak current varies linearly with the square root of scan rate from 10~160  $\text{mV/s}$ . The linear regression equation is as follows:

$$I_p = 0.266 + 1.911 \times v^{1/2}, \quad (R=0.9980) \quad (2)$$

It indicates a diffusion-controlled oxidation process occurring at AuNPs/MWCNT/Au electrode. The linear plot of  $E_p$  versus  $\ln v$  was obtained, and could be expressed by the equation (3).

$$E_p = 0.427 + 0.027 \ln v, \quad (R=0.995) \quad (3)$$

The anodic peak potential shifts to more positive values with increasing scan rate. The linear relationship of  $E_p \sim \ln v$  of an irreversible process obeys the following equation[16]:

$$E_p = E_0 + \frac{RT}{\alpha n F} \left\{ 0.780 + 0.5 \ln \frac{\alpha n F D v}{RT} - \ln k_s \right\} \quad (4)$$

Based on the slope of  $E_p$  with  $\ln v$ , the number of electrons ( $n$ ) involved in the oxidation of OAP can be evaluated. The slope of the plot in equation (3) is 0.027. Here  $\alpha n$  is calculated to be 0.48,

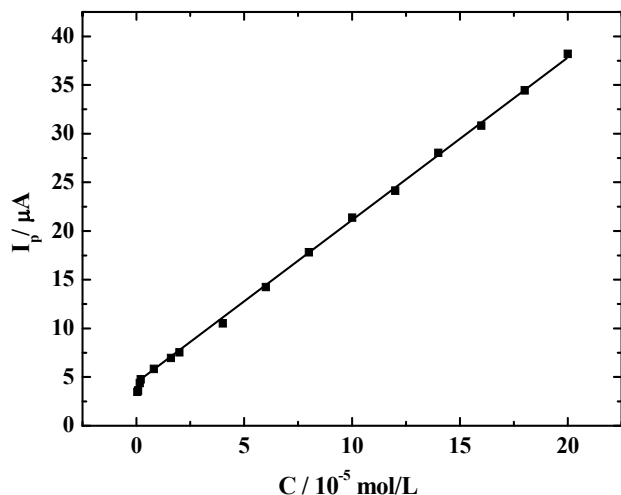


Figure 4. Linear relationship between  $I_{p,a}$  and concentration.

Generally, the electron transfer coefficient ( $\alpha$ ) is about 0.5 in the totally irreversible electrode process. Therefore, the value of  $n$  is calculated to be 1, indicating that one electron is involved in the oxidation of OAP. Combining the result of Section 3.3.1, we know that one proton takes part in the oxidation process of OAP.

The standard heterogeneous rate constant can be calculated from Eq.(4). Under the low scan rate (0.01–0.06V/s),  $E_p$  has linear relationships with the scan rate. The linear equation was as follows:  $E_p = 0.3159 + 0.6086v$ , ( $R=0.992$ ).  $E_0$  in Eq. (4) can be gained when the plot of  $E_p \sim v$  was extrapolate to y-axis ( $v \rightarrow 0$ ). Combining the intercept of plot of  $E_p$  versus  $\ln v$  and the diffusion coefficient ( $D$ ) of OAP, the standard heterogeneous rate constant ( $k_s$ ) of OAP at the modified electrode can be obtained, and the results are  $E_0=0.3159V$ ,  $k_s=7.85 \times 10^{-4} \text{ cm} \cdot \text{s}^{-1}$  (25°C), respectively.

### 3.4. Calibration graph

The relationships between the oxidation peak current and the concentration of OAP were examined by employing LSV. The peak current ( $I_{p,a}$ ) is proportional to the concentration of OAP from  $4.0 \times 10^{-7}$  to  $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  with a linear regression equation of  $I(\mu\text{A}) = 4.031 + 1.699 \times C$  ( $R=0.9996$ ,  $C, 10^{-5} \text{ mol/L}$ ), as shown in Fig.4. The detection limit of OAP is estimated to be  $1.3 \times 10^{-7} \text{ mol/L}$  according to  $S/N=3$ .

### 3.5. Reproducibility and stability of composite modified Au electrode

Under the optimum condition, five AuNPs/MWCNT/Au electrodes were used to measure  $1.0 \times 10^{-5} \text{ mol/L}$  OAP. Relative standard deviation (RSD) of the measurement of five modified electrodes was 3.53%, which indicating that the fabrication of the modified electrode has a good reproducibility. The long-term stability of the AuNPs/MWCNT/Au electrode was also evaluated in 10 days. The AuNPs/MWCNT/Au electrode was employed to detect OAP once every day, and then stored in the air. The experimental results indicated that the current responses deviated only 3.75 % at the tenth day, as depicted in Fig.5, which revealing that the AuNPs/MWCNT/Au electrode fabricated by this way

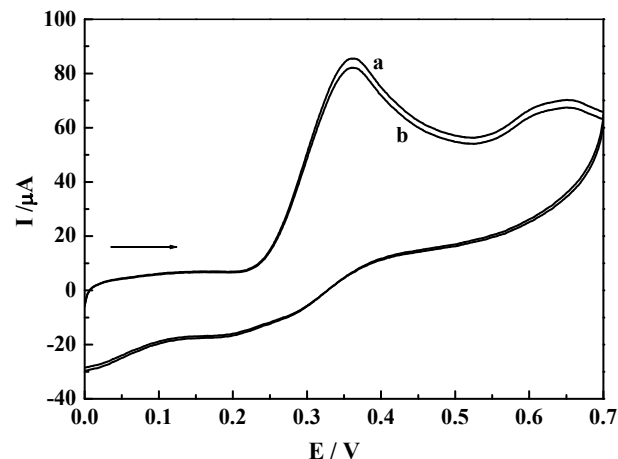


Figure 5. Cyclic voltammograms of  $5.0 \times 10^{-4} \text{ mol/L}$  OAP at AuNPs/MWCNT/Au electrode: (a) voltammetric response at the same day, (b) voltammetric response at the tenth day.

possesses long-term stability.

### 3.6. Interferences

To evaluate the interferences of foreign species on the determination of OAP at  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  level, a systematic study was carried out. 100-fold concentrations of  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Hg}^{2+}$ , resorcinol and Hydroquinone have no influences on the signals of  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  OAP, with deviation below 5 %. However, 100 fold p-Nitrophenol has definite influence on the determination of OAP. Therefore, this method has good selectivity to the determination of OAP.

### 3.7. Determination of OAP in simulated waste water

Under the optimum conditions, the determination of OAP in the simulated waste water was carried out by LSV. Simultaneously, in order to examine the suitability of this method, known amounts of OAP were added into the simulated sample and the same procedure was applied. The recovery of the measurement is in the range from 95.4 % to 100.2%, as shown in Tab.1, which suggesting that the proposed method is accurate and reliable.

### 3.8. Diffusion coefficient

Before to obtain the diffusion coefficient of OAP, firstly, we need get the real surface area of the AuNPs/MWCNT/Au electrode. Here  $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$  was used as the measurement substance. The oxidation peak current was  $6.123 \mu\text{A}$  in our experiment. The real surface area of this modified electrode can be calculated according to the Randles-Savcik equation [17]. The result is  $0.2417 \text{ cm}^2$ , which is larger than that of the bare Au electrode ( $0.071 \text{ cm}^2$ ). This experiment result indicated that the surface area was enhanced dramatically after modification.

Chronocoulometry was often employed to calculate the diffusion coefficient ( $D$ ). The plot of  $Q$  against  $t$  is depicted in Fig.6. After the subtraction of the background charge, the linear plot of  $Q$  against  $t^{1/2}$  could be obtained, and can be described as the following equation:

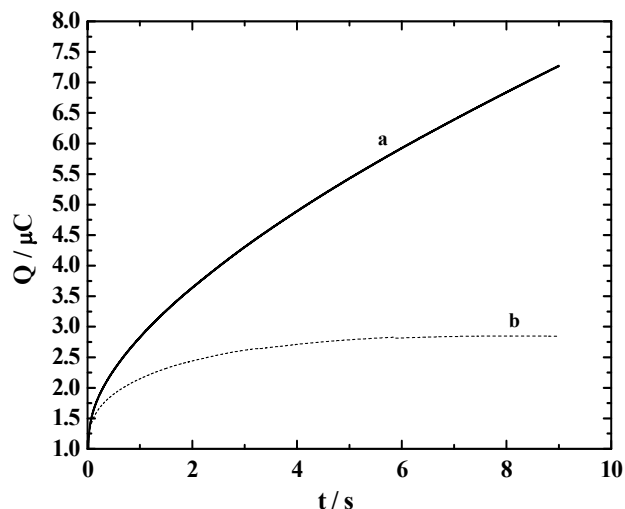


Figure 6. Chronocoulometry of OAP at AuNPs/MWCNT/Au electrode, (a),  $1.0 \times 10^{-4}$  mol·L<sup>-1</sup> OAP, (b), the blank solution.

$$Q(\mu\text{C}) = -1.582 + 1.937t^{1/2} \quad (5)$$

According to the integrated Cottrell equation [18].

$$Q = 2nFACD^{1/2}t^{1/2}\pi^{-1/2} \quad (6)$$

The diffusion coefficient of OAP can be estimated from the slope of the plot of  $Q$  versus  $t^{1/2}$ , where  $A$  is the surface area of the working electrode,  $C$  is the concentration of OAP,  $D$  is the diffusion coefficient of OAP, other symbols have their usual significance. In this work,  $A = 0.2417\text{cm}^2$ ,  $C = 0.1\text{mmol}\cdot\text{L}^{-1}$ ,  $n = 1$ , and the slope of the plot of  $Q$  versus  $t^{1/2}$  is  $1.937\mu\text{C}/\text{s}^{1/2}$ . Thus, the value of  $D$  was calculated to be  $5.42 \times 10^{-7}\text{cm}^2\cdot\text{s}^{-1}$ .

### 3.9. Electrode reaction

Combining the results of Section 3.3.1 and Section 3.3.3, a conclusion can be drawn that the oxidation of OAP is a one-electron and one-proton irreversible electrode reaction. The probable electrode reaction of OAP is as follows:

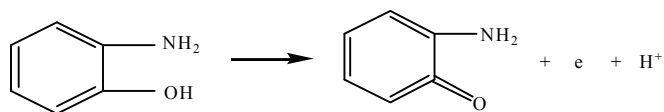


Table 1. Determination of OAP in simulated waste water

Sample No.	Added amount ( $10^{-4}$ mol/L)	Measured total amount ( $10^{-4}$ mol/L)	Recovery amount ( $10^{-4}$ mol/L)	Recovery (%)
1	0.5	4.478	0.478	95.6
2	1.0	4.967	0.967	96.7
3	1.5	5.496	1.496	99.7
4	2.0	5.908	1.908	95.4
5	2.5	6.505	2.505	100.2

## 4. CONCLUSION

In this paper, a novel modified electrode, namely AuNPs/MWCNT/Au electrode, was developed for studying the electrochemical behavior of OAP. This modified electrode significantly enhanced the oxidation peak current and decreased the oxidation peak potential of OAP. It was found that the oxidation of OAP is a one electron and one proton totally irreversible and diffusion-controlled electrode process. The heterogeneous rate constant ( $k_s$ ) and the diffusion coefficient of  $D_R$  of OAP were calculated to be  $7.85 \times 10^{-4}\text{cm}\cdot\text{s}^{-1}$  and  $5.42 \times 10^{-7}\text{cm}^2\cdot\text{s}^{-1}$ , respectively.

## 5. ACKNOWLEDGMENTS

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