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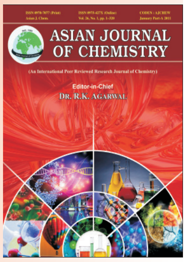

Application of Bismuth Film/Nichrome Electrode for Electrocatalytic Reduction of 4-Nitrophenol

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In this paper, the inexpensive and versatile nichrome was adopted as a substrate to fabricate the bismuth film/nichrome electrode (BNCE). The bismuth film/nichrome electrode was used as the working electrode to investigate the reduction behavior of 4-nitrophenol by cyclic voltammetry and differential pulse voltammetry. The results revealed that bismuth film/nichrome electrode exhibited a sensitive electrochemical response to 4-nitrophenol in pH 5 CH_3COOH-CH_3COONa solution and 4-nitrophenol reduction was observed at -0.466 V *vs*. SCE in one well-defined irreversible peak. The calibration curve with two slopes was obtained in the concentration range of 5×10^{-8} mol/L to 3×10^{-5} mol/L. The detection limit of this method was 5.97×10^{-9} mol/L(S/N = 11). This method had the advantages of low cost, negligible toxicity and high sensitivity. It was successfully applied to determine 4-nitrophenol in lake water sample, with recoveries ranging from 97.5 to 102.1 %.

Keywords: Bismuth film electrode, Nichrome substrate, Differential-pulse voltammetry, 4-Nitrophenol.

INTRODUCTION

4-Nitrophenol (4-NP) has been widely used as raw material or intermediate in the industries of dyestuffs, pharmaceuticals and organic synthesis and it is inevitably released into environment in the process of production and application[1,2]. However, 4-nitrophenol has toxic effects on human beings, animals and plants and is listed as US Environmental Protection Agency priority pollutant[3]. The discharge of 4-nitrophenol is strictly controlled and supervised in many countries due to its toxicity and persistence[4]. In fact, 4-nitrophenol has been found as contaminant in freshwater, in marine and in the atmosphere. Therefore, the detection of this hazardous substance is of great importance, in particular, it is vital to develop simple and effective method for trace analysis of 4-nitrophenol in aqueous solutions, which can help us protect water resources and food supplies[5,6].

In 2000, the bismuth film electrode was proposed by Wang *et al.*[7] as an alternative to mercury electrodes for the trace detection of toxic heavy metal ions. Over the last decade, various new types of bismuth-modified electrodes have been developed exhibiting favourable performance such as very low toxicity, favourable resolution of neighboring peaks, easy renewable surface, *etc.*[8,9]. A range of substrates have been used for bismuth film electrode, including glassy carbon[10,11], carbon paste[12], Au[13] Pt[14]. Nichrome has been previously adopted as a material in the fabrication of different electrodes[15,16], owing to its characteristics such as low-cost, causticity resistance, low thermal expansion and good stability.

In this work, the bismuth film/nichrome electrode (BNCE) was fabricated for voltammetric analysis of 4-nitrophenol and the analytical performance of bismuth film/nichrome electrode demonstrated high sensitivity and reproducibility. Moreover, the experimental conditions were optimized and the method developed was applied to the water samples analysis.

EXPERIMENTAL

Cyclic voltammograms and differential pulse voltammetry were carried out by CHI660C electrochemical workstation (Shanghai Chenhua Instrument Company, China). The three-electrode system consisted of the bismuth film/nichrome electrode as the working electrode, a saturated calomel reference electrode (SCE) serving as a reference electrode and a platinum counter-electrode as a counter electrode. Scanning electron micrograph (SEM) images were obtained with a JSM-6390 LV microscope (JEOL).

The 0.1 mol/L Bi(III) stock solution was prepared by dissolving the proper amount of $Bi(NO_3)_3{\cdot}5H_2O$ in 1 mol/L HNO_3. Less concentrated Bi(III) solutions were attained by dilution using 0.10 mol/L of H_2SO_4. The 4-nitrophenol (Shanghai Reagent Corp. China) working solutions were obtained by appropriate dilution of the stock solution. Acetate buffer solutions were prepared by mixing the appropriate amounts of CH_3COOH and CH_3COONa. All other chemicals were of analytical reagent grade.

Preparation of bismuth film/nichrome electrode: A nichrome rod with 4 mm diameter (A = 0.126 cm^2) was sealed in a plastic tube of matching length. The surface was polished with 0.05 µm alumina slurry and subsequently cleaned in an ultrasonic cleaner with 1:1 nitric acid solution, absolute ethanol and doubly distilled water. Prior to the bismuth deposition, 1×10^{-3} mol/L Bi(III) solution was deoxygenated by purging with pure nitrogen gas for 10 min. Then the nichrome electrode was placed in Bi(III) solution and prepared by cyclic voltammetry sweep between -0.6 V and -0.1 V at a scan rate of 0.01 V/s for 3000 s. After the modification, the bismuth film/nichrome electrode was rinsed with distilled water and used for the following procedure.

Measurement procedure: The three-electrode system was immersed into a 10 mL electrochemical cell, which contained appropriate amounts of 4-nitrophenol in 0.1 mol/L acetate buffer solution. The cyclic voltammogram was recorded between -0.25 and -0.9 V for voltammetric analysis of 4-nitrophenol and the quantitative determination of 4-nitrophenol was developed by operating differential pulse voltammetry from -0.2 to -0.65 V.

RESULTS AND DISCUSSION

Surface morphology characteristic of bismuth film/nichrome electrode: It had been reported three general methods of coating the substrate surface with a bismuth deposit: pre-plating, *in situ* plating, modifying the bulk of an electrode with a bismuth precursor [*i.e.* a Bi(III) compound, such as Bi_2O_3][8]. Pre-plating is more versatile and can be used for any type of analysis. Besides, the forms of bismuth film could be controlled by adjusting the Bi(III) solution concentration and deposition conditions. Consequently, pre-plating was adopted to prepare the bismuth film/nichrome electrode. Fig. 1 showed the low magnifications and the high magnifications scanning electron micrographs of typical regions of the nichrome electrode, before (a) and after (b) the bismuth deposition. The morphologies of bare nichrome and bismuth film/nichrome electrode presented distinct differences. In Fig. 1a, regular grooves distributed on the surface of the bare nichrome electrode and these long, narrow grooves allowed the bismuth to be deposited. As can be seen from Fig. 1b, after the bismuth deposition, the electrode was coated with a thick, porous and dense bismuth layer, which was consisted of bismuth particles with triclinic structure. The size and compactness of the particles and the effective area of the electrode were depended on the deposition conditions.

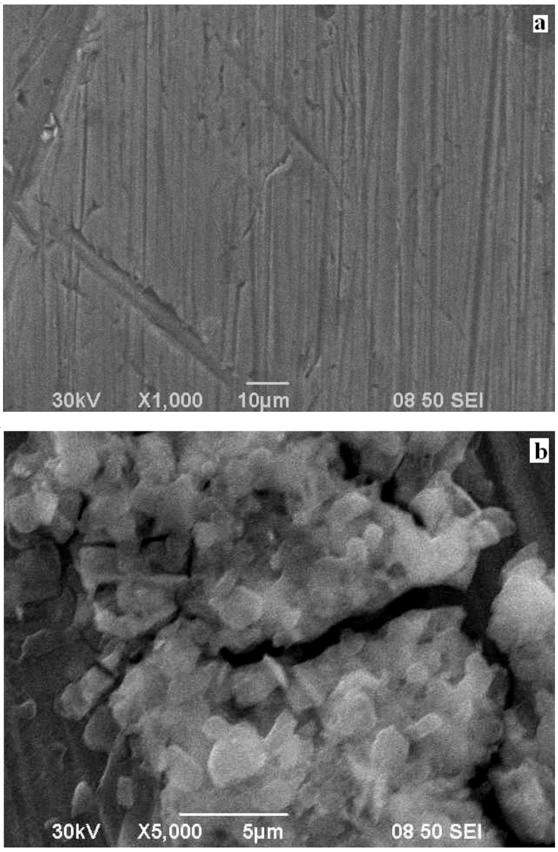


Fig. 1. SEM image on the surface of bare nicochrome electrode and bismuth film/nichrome electrode, (a) Bare nicochrome electrode; (b) bismuth film/nichrome electrode

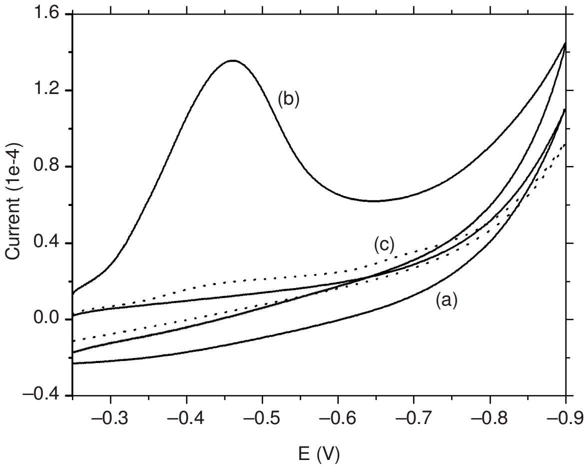


Fig. 2. Cyclic voltammograms of 4-nitrophenol on different electrodes, (a) Bare nichrome electrode (b) bismuth film/nichrome electrode; (c) bismuth film/nichrome electrode in supporting solution $C_{4\text{-NP}}$ = 7 µmol/L; supporting electrolyte: 0.1 mol/L acetate buffer (pH 5); scan rate: 100 mV/s

Voltammetric studies of 4-nitrophenol: Fig. 2 displayed cyclic voltammograms of 7 µmol/L 4-nitrophenol at the bare nichrome electrode and bismuth film/nichrome electrode. No redox peak was observed at the bare nichrome electrode (curve *a*). The same phenomenon was also obtained in acetate buffer solution without 4-nitrophenol at bismuth film/nichrome electrode (curve *c*). After 4-nitrophenol was added into acetate buffer solution (pH 5), a well-defined reduction peak was obtained at -0.466 V on bismuth film/nichrome electrode during the cathodic sweep from -0.25 V to -0.9 V (curve *b*). What's more, no corresponding oxidation peak was observed in the following reverse scan, concluding that the reduction of 4-nitrophenol at bismuth film/nichrome electrode was a totally irreversible electrode process under these experimental conditions. The remarkable enhancement of the current response was clear evidence of the electrocatalytic effects of bismuth film/nichrome electrode on 4-nitrophenol reduction.

Optimization of experimental parameters

Effect of bismuth film on the analytical signal: The cyclic voltammetric response for 7 μmol/L of 4-nitrophenol on bismuth film/nichrome electrode with different film deposition time in the range 1000-5000 s were shown in Table-1. The thickness of bismuth film had a significant effect on the 4-nitrophenol current response, which was controlled by deposition time in this case. The response of 4-nitrophenol increased rapidly with the deposition time of bismuth film up to 3000 s, however, the peak current decreased with much longer deposition time. When bismuth film was thin that possessing only few active centers resulted in the lower current of 4-nitrophenol, while the film became too thick accompanied with lower conductivity also led to a decrease of the signal. In addition, the relative standard deviation was evaluated by seven repetitive determinations of the 4-nitrophenol solution and the minimal value obtained on condition that 3000 s deposition. Therefore, a bismuth film deposition time of 3000 s was used for the subsequent analytical work.

TABLE-1
EFFECTS OF DEPOSITION TIME ON PEAK CURRENTS OF 4-NITROPHENOL

T_{dep} (s)	$I_{4\text{-}NP}$ ($\times 10^{-5}$A)	RSD (%)
1000	2.175	5.38
2000	3.941	4.27
3000	6.572	3.37
4000	5.528	3.70
5000	2.929	4.22

Effects of pH on peak current and peak potential: The voltammetric response for 4-nitrophenol was tested in four different buffer solutions including NH_4Cl, PBS, acetate and borate solution with the same concentration of 0.10 mol/L, the higher currents and the better peak shape of 4-nitrophenol obtained in acetate buffer solution than other solutions. The acetate buffer solution was therefore used as supporting electrolyte.

The influence of pH on 4-nitrophenol reduction was studied in the pH range from 4 to 6. As recorded in Fig. 3, the peak potentials of 4-nitrophenol shifted toward negative linearly with increasing pH values and fitted the following equation: E = -0.19306-0.05454 pH (R = -0.9987), the slope of 54.54 mV pH^{-1} demonstrated that the number of protons and electrons involved in the electro-reduction of 4-nitrophenol was equal. According to the totally irreversible electrode process of 4-nitrophenol and previous literature[17], on bismuth film/nichrome electrode, 4-nitrophenol obtained four electrons and four protons to be 4-(hydroxyamino) phenol and the electroreduction mechanism can be expressed as the first equation in **Scheme-I**.

With the increase of pH, the peak potentials of 4-nitrophenol shifted to the negative direction, indicating that at higher pH it was more difficult for 4-nitrophenol to obtain electrons and be reduced, so with the pH increasing the peak current of 4-nitrophenol should be decreased accordingly. However, as can be seen in Fig. 3, the reduction peak current of 4-nitrophenol increased gradually when the pH value changed from 4 to 5.

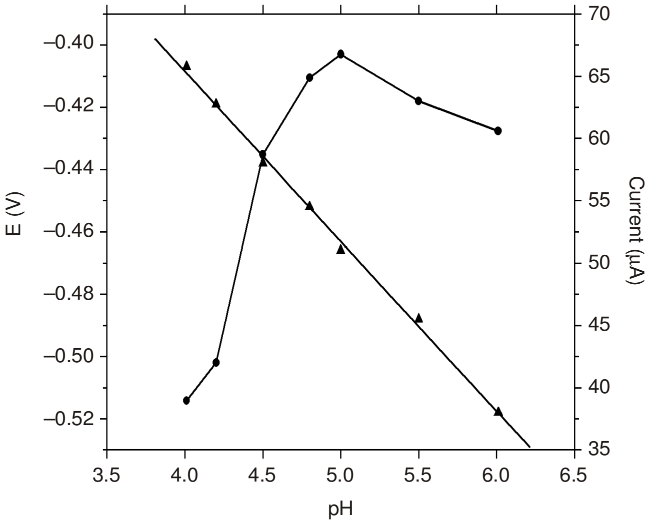
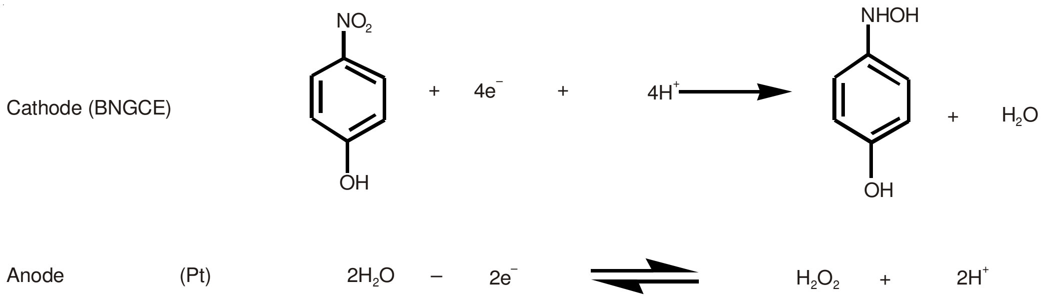


Fig. 3. Effect of buffer solution pH on the current response and potential, $C_{4\text{-}NP}$ = 7 μmol/L; supporting electrolyte: 0.1 mol/L acetate buffer; scan rate: 100 mV/s

The possible reasons of this phenomenon were as follows. Besides 4-nitrophenol in the solution, there were other components such as CH_3COOH, CH_3COO^- and H_2O. Among them, CH_3COOH and CH_3COO can only obtain electrons and be reduced as acetaldehyde, but H_2O will carry out oxidation reaction if the suitable conditions are given. Therefore, in the electrochemical process, 4-nitrophenol conduct reduction reaction at bismuth film/nichrome electrode while the H_2O in the solution lost two electrons to be oxidized at platinum electrode (the second equation in **Scheme-I**). For the H_2O oxidation, the increased concentration of H^+ can partially inhibit the forward reaction. Based on the equal number of protons and electrons transferred principle, the amounts of reduced 4-nitrophenol decreased as well. In contrast, with the pH



Scheme-I: Electrode reaction equations sincreased the concentration of H^+ in solution decreased, but the amounts of H_2O that were oxidized on anode increased, correspondingly the reaction amounts of 4-nitrophenol also increased and led to higher reduction peak current. In conclusion, although the reduced ability of 4-nitrophenol declined with the pH increase from 4 to 5, the peak current of 4-nitrophenol enhanced. When pH > 5, the current response of 4-nitrophenol decreased with further increasing pH, which was in accordance with its declined reduced ability. The maximum current was achieved at pH 5. Thus, the determination of 4-nitrophenol was carried out in pH 5 acetate buffer solution.

Effect of scan rate: The reduction peak current of 7 μmol/L 4-nitrophenol at different scan rates ranging from 10 mV s^{-1} to 200 mV s^{-1} was measured by cyclic voltammetry. As can be seen from Fig. 4, the peak current for reduction of 4-nitrophenol exhibited a linear relation to the square root of the scan rate with the regression equation: $I_p(\mu A) = 251.60568\ v^{1/2}\,(V/s) - 15.08272$ (R = 0.9956). The result demonstrated that the reduction of 4-nitrophenol at the bismuth film/nichrome electrode was a diffusion-controlled process.

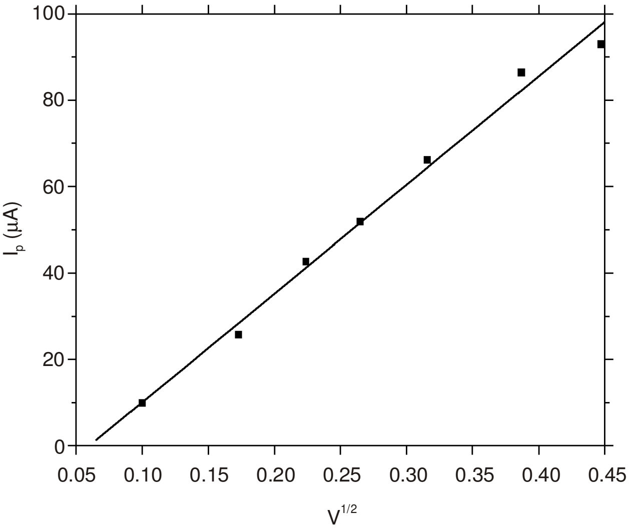


Fig. 4. Linear relationship between I_p and the square root of the scan rate. $C_{4\text{-}NP}$ = 7 μmol/L; supporting electrolyte: 0.1 mol/L acetate buffer (pH 5)

Calibration curve: Fig. 5 showed the differential pulse voltammetry responses of bismuth film/nichrome electrode in increasing concentrations of 4-nitrophenol solution. The reduction peak current was proportional to the concentration of 4-nitrophenol over the range of 0.05 to 0.7 μmol/L and 1 to 30 μmol/L. The linear regression equation was expressed as I (μA) = 6.94611c (μmol/L) + 2.61984 (R = 0.99936) and I (μA) = 1.1861c (μmol/L) + 11.27965 (R = 0.9968), respectively. The detection limit (S/N = 11) was calculated to be 5.97×10^{-9} mol/L, lower than those from Cu_2O nanoparticles modified rotating ring-disk electrode[18], graphene oxide-based electrochemical sensor[19], hydroxyapatite nanopowder modified glassy carbon electrode[20].

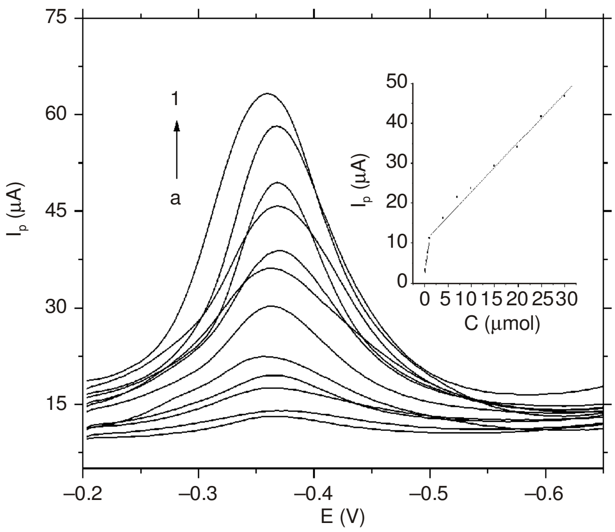


Fig. 5. DPV responses of increasing 4-nitrophenol concentration, from a to l, 0.05, 0.1, 0.4, 0.7, 1.0, 4.0, 7.0, 10, 15, 20, 25, 30 μmol/L, respectively. (Inset: calibration curve) DPV settings: step increment of 4 mV, pulse amplitude of 50 mV and pulse width of 50 ms

Interferences: The interferences of some inorganic ions and organic species in the determination were studied. The tolerable limit of the foreign substance was defined as the deviations produced by them below 5 %. It was found that 400-fold concentration of Na^+, K^+, The presence of 100-fold of Ba^{2+}, Cu^{2+}, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, Br^- had no effects on the reduction peak signal of 7 μmol/L 4-nitrophenol. 5-fold of glucose, 2-fold of phenol and 4-aminophenol also did not interfere with the measurement. The result indicated that bismuth film/nichrome electrode has an excellent selectivity for 4-nitrophenol and the modified electrode might be suitable for analytical application.

Analytical application: The bismuth film/nichrome electrode was finally applied to detect 4-nitrophenol in real water samples from the locality. 5 mL of the lake water and 5 mL 0.2 mol/L acetate buffer solutions were placed in the cell and the analysis was carried out as described above. Then 4-nitrophenol spiked in the water samples was measured. The results listed in Table-2 and it was clear that the recoveries of this method were in the range from 97.5 to 102.1 %, suggesting that the proposed method should be reliable and effective for 4-nitrophenol measurement.

Conclusion

The electrochemical determination of 4-nitrophenol on a bismuth film/nichrome electrode has been investigated. The non-toxic bismuth film electrode exhibited high electrocatalytic activity and good selectivity toward the reduction of 4-nitrophenol. Differential pulse voltammetry was employed for the

TABLE-2
DETERMINATION OF 4-NITROPHENOL IN SAMPLES AND THE RECOVERY (n = 6)

Sample	Measured ($\times 10^{-8}$ mol/L)	R.S.D. (%)	Added ($\times 10^{-8}$ mol/L)	Found ($\times 10^{-8}$ mol/L)	Recovery (%)
4-Nitrophenol	5.58	3.55	6.00	11.43	97.5
			12.00	17.70	101.0
			15.00	20.89	102.1

quantitative determination of 4-nitrophenol and the low detection limit was obtained. The reported results imply a promising application of the modified electrode for trace analysis of 4-nitrophenol in real water samples.

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