

Construction of a Novel Sensor Based on Electropolymerization of Carmine for Voltammetric Determination of 4-Nitrophenol

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ABSTRACT: 4-Nitrophenol (4-NP) has been determined with voltammetric technique based on a novel sensor fabricated by electropolymerization of carmine on a glassy carbon electrode (GCE). An obvious reduction peak located at about -0.700 V and a couple of redox peaks that were not well-defined were observed in the potential range of -1.00 to 0.600 V. Compared with its voltammetric behavior on a bare GCE, the reduction peak potential shifted positively and the peak current increased significantly. All experimental parameters were optimized and linear sweep voltammetry was proposed for its determination. In the

optimal conditions, the reduction peak current was proportional to the 4-NP concentration over the concentration range from 5.00×10^{-8} to 1.00×10^{-5} mol L $^{-1}$, and the detection limit was 1.00×10^{-8} mol L $^{-1}$ after 200 s of accumulation. The high sensitivity and selectivity of the sensor was demonstrated by its practical application for the determination of trace amounts of 4-NP in lake water. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3271–3277, 2007

Key words: electropolymerization; carmine; 4-nitrophenol; sensor

INTRODUCTION

Phenolic compounds are products of many industrial processes, including plastics, paints, drugs, pesticides, resins, antioxidants, paper, and cellulose, and have been widely released into natural and wastewater.¹ The environmental concern for phenol pollution resulted from the high toxicity of many substituted phenolics to mammals, fish, and other aquatic life.² 4-Nitrophenol (4-NP), an aromatic phenolic compound which is a hazardous substance that has high environmental impact due to its toxicity and persistence, has been included in the Environmental Protection Agency List of Priority Pollutants.³ The importance of 4-NP determination was related to the degradation pathway of several organophosphorous pesticides such as fenitrothion, methyl-parathion, ethyl-parathion, etc. They were decomposed in soils and waters, producing 4-NP as an intermediate or final product of the reaction.^{4,5} Additionally, 4-NP was widely used in the manufacturing of one of the most popular analgesics (acetaminophen), pesticides, and dyes, and processing of leather. Hence, the determination of 4-NP in water samples becomes of paramount importance and obviously there is a strong interest for developing efficient methodologies for its determination in complex matri-

ces. Moreover, the potential for accidental releases during these industrial processing activities required analytical tools/devices to monitor 4-NP on-line.

Many procedures have been reported for its determination, such as gas chromatography,⁶ high performance liquid chromatography,⁷ liquid chromatography associated with mass spectroscopy,⁸ and capillary electrophoresis.^{9,10} Although sensitive and selective, they are time-consuming, expensive, and require skilled personnel and therefore are unsuitable for on-line or field monitoring.¹¹ The versatility of electrochemical techniques and the smallest detection limits as well as their low acquisition costs are reasons for their wide applications in the determination of phenolic compounds. Different approaches have been accomplished in the field of electrochemistry, including basically the chemical modification and/or using immobilized enzymes for this purpose.^{12,13} In addition, hanging mercury drop electrode (HMDE) electrode^{14,15} has also been proposed for 4-NP determination based on its well-known four-electron reduction process.^{16,17} With differential pulse voltammetry, 4-NP in seawater had been measured and could potentially be used for on-line monitoring.¹⁸ A comparison between the analytical performance of a HMDE and a boron-doped diamond (BDD) electrode for the quantification of 4-NP in spiked pure and natural waters has also been reported.¹⁹

In recent years, dye molecules have been widely used as mediators to study the electrocatalytic reduc-

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tion of nitro compounds.^{20,21} In general, the derivatives of dyes covalently bound to an aromatic ring could decrease their proton-donor ability, resulting in improved catalytic activity.²² Polymerization of dyes could form a crosslinked oligomer, which leads to the enhancement of its electrocatalytic ability.²³ Many redox dyes such as methylene blue,^{24,25} methylene green,²⁶ and brilliant cresyl blue²⁷ have been employed as mediators. Carmine, which was invariably applied in conjunction with a mordant, is a valuable dye. However, carmine polymer has rarely been used as a mediator to facilitate the electrochemical reaction of any compounds.

In the present article, a novel sensor based on electropolymerization of carmine on a glassy carbon electrode (GCE) was developed for 4-NP. On the sensor, 4-NP was reduced at about -0.700 V, and a peak current higher than that on a bare GCE was obtained. Based on this, an electrochemical measurement was proposed for the direct determination of 4-NP. Compared with other methods^{9,11,17} developed for 4-NP, the sensor possesses a lower detection limit, a rapid response, excellent reproducibility, simplicity, and low cost.

EXPERIMENTAL

Apparatus

All electrochemical experiments were carried out on a CHI-660A electrochemical workstation (CH Instrument Inc., USA) with a three-electrode system. The working electrode used here was a glassy carbon electrode (GCE) modified with electropolymerization of carmine. A platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode against which all potentials were measured.

Reagents

4-Nitrophenol (4-NP) was obtained from Shanghai reagent Company (Shanghai, China). Stock standard solution of 4-NP was prepared from ethanol and stored in a refrigerator until further use. An aqueous solution was prepared daily by simple dilution of the stock solution with 0.100 mol L⁻¹ phosphate-buffered solution (pH = 6.0). Carmine was purchased from Fluka (Switzerland); its chemical structure is shown in Figure 1. Other chemicals used were of analytical grade, and all compounds were used without further purification. All solutions were prepared with redistilled water.

Preparation of the sensor

A GCE (2.00 mm in diameter) was polished to a mirror finish with polish paper and 0.300 – 0.050 μ m alumina slurry, and cleaned thoroughly in an ultra-

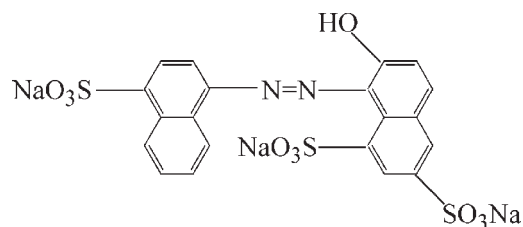


Figure 1 Chemical structure of carmine.

sonic cleaner with 1 : 1 nitric acid solution, alcohol, and redistilled water, sequentially. Electropolymerization of carmine on the GCE was carried out in 1.00 mol L⁻¹ H₂SO₄ solution containing 1.00×10^{-3} mol L⁻¹ carmine with a constant potential of 1.60 V. Because the electropolymerization is carried out in a positive potential, 1.60 V, both $-N=N-$ and $-OH$ can be oxidized to give free-radicals to form polymer. Thus, the structural formula for the polymer of carmine is difficult to be confirmed. After 20 min, the surface of the modified electrode was washed with ethanol to remove the unreacted carmine monomers. Then the film was washed by distilled water to remove physically adsorbed material, and subsequently transferred to a clean test tube.

Sample preparation

Lake water was filtered with 0.45 - μ m membrane filters, and the pH value was adjusted with KH₂PO₄ and Na₂HPO₄. Then, a known amount of 4-NP stock solution was spiked into it, and was used for the electrochemical determination.

Electrochemical measurements

Electrochemical determination of 4-NP was carried out in a voltammetric cell with 10 mL of supporting electrolyte solution. Standard 4-NP stock solution was added by micropipette according to the requirement. Voltammograms were recorded after a 5-s quiescence period. Accumulation was accomplished with stirring at a constant potential of 0.00 V. Linear sweep voltammogram from -0.100 to -1.00 V was recorded for the determination of 4-NP. The reduction peak current applied for the analysis was measured at -0.700 V. The same procedure was applied in the samples analysis and all electrochemical experiments were carried out at room temperature (20 ± 2)°C. Removal of oxygen was achieved by using high purity N₂. Prior to and after each measurement, the sensor was reactivated by five successive cyclic voltammetric sweeps between 0.200 V and $+1.20$ V in a 0.100 mol L⁻¹ phosphate-buffered solution (pH 6.0) to produce a reproducible electrode surface.

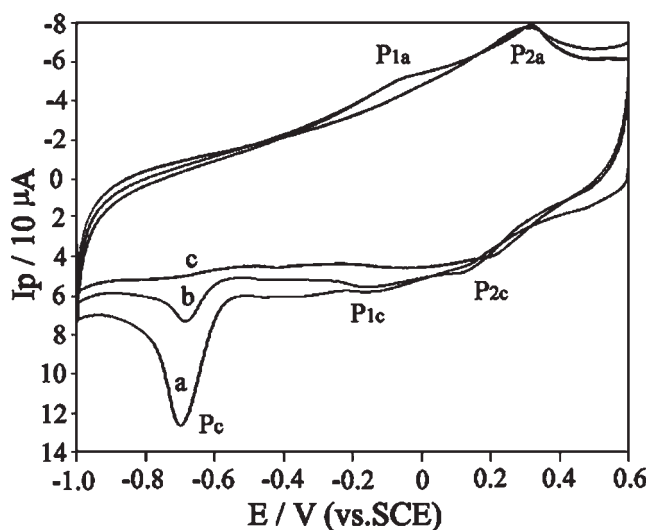
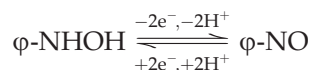
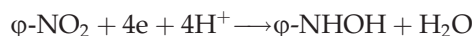


Figure 2 Voltammograms for a sensor in 0.100 mol L^{-1} phosphate buffer (pH 6.0) with (curves a and b) and without (curve c) $5.00 \times 10^{-5} \text{ mol L}^{-1}$ 4-NP. Curves a and b represent the first and the second cycle respectively.

RESULTS AND DISCUSSION

Voltammetric behavior of 4-NP on the sensor

Cyclic voltammetric response of $5.00 \times 10^{-5} \text{ mol L}^{-1}$ 4-NP on the sensor is shown in Figure 2. An obvious reduction peak (Pc) located at about -0.700 V and a couple of redox peaks (P1a and P1c) that are not well-defined were observed in the potential range of -1.00 to 0.600 V . According to the currently accepted mechanism,^{12,17} the reduction peak (Pc) should be attributed to a four-electron transfer reduction of the nitro group ($\phi\text{-NO}_2$) to give the hydroxylamine derivative. It can be reoxidized to the nitroso compound at more positive potential (P1a). Under subsequent cycling, the nitroso group is reversibly reduced to respective hydroxylamine (P1c). Therefore, the electrochemical reactions of 4-NP at the polycarmine film electrode included these steps:



The reduction peak current in the second sweep (curve b) decreased remarkably when compared with that of the first sweep (curve a), while in the successive sweeps, its peak current decreased gradually. The facts indicated that the reduction of 4-NP at the poly(carmine) film electrode is a totally irreversible process. The great decrease in the reduction peak current might be caused by the electropolymer-

ization of 4-NP or the adsorption of its reductive products on the carmine polymer film, so that the electrode surface was inactivated. In the case of the redox reaction of $\phi\text{-NHOH}/\phi\text{-NO}$, no obvious variations in the peak current were observed in the successive cyclic voltammetric sweeps. Moreover, the peak-to-peak potential is only 70 mV . Therefore, they should be corresponding to a quasi-reversible process.

Compared with the voltammogram of the sensor in 0.100 mol L^{-1} phosphate buffer (pH 6.0) in absence of 4-NP (curve c), another couple of redox peaks (P2a and P2c) would be ascribed to the redox reaction of carmine polymer film. Voltammetric behavior of 4-NP on a bare GCE was also investigated in 0.100 mol L^{-1} phosphate buffer, and only a shoulder-peak was observed at -0.770 V when the 4-NP concentration was controlled at $5.00 \times 10^{-5} \text{ mol L}^{-1}$. The reduction peak current was also lower than that obtained on the sensor. Seventy millivolt of peak-to-peak potential separation and five times higher peak current obtained on the sensor indicated that the carmine polymer film can facilitate the reduction of 4-NP.

Linear sweep voltammetry was further applied to study the electrochemical behavior of 4-NP on the sensor. From the voltammograms shown in Figure 3, in the potential range from -0.100 to -1.00 V , no redox peaks were observed on the sensor in 0.100 mol L^{-1} phosphate buffer in the absence of 4-NP (curve c). However, a reduction peak corresponding to the reduction of $\phi\text{-NO}_2$ was recorded either on the sensor (curve a) or on a bare GCE (curve b). The shape of the reduction peak and the peak

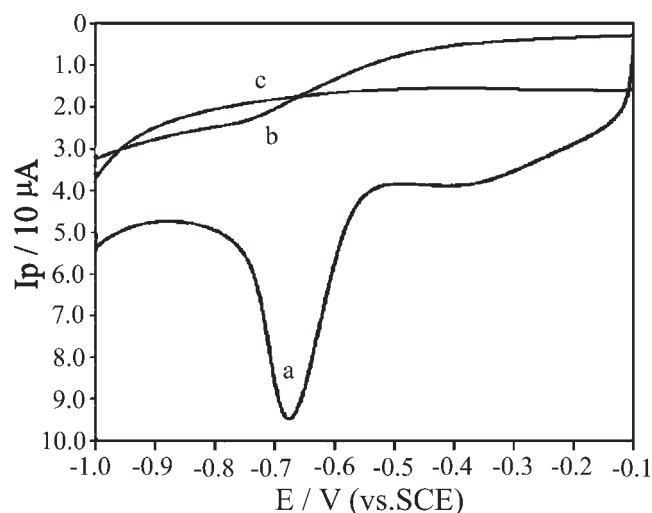
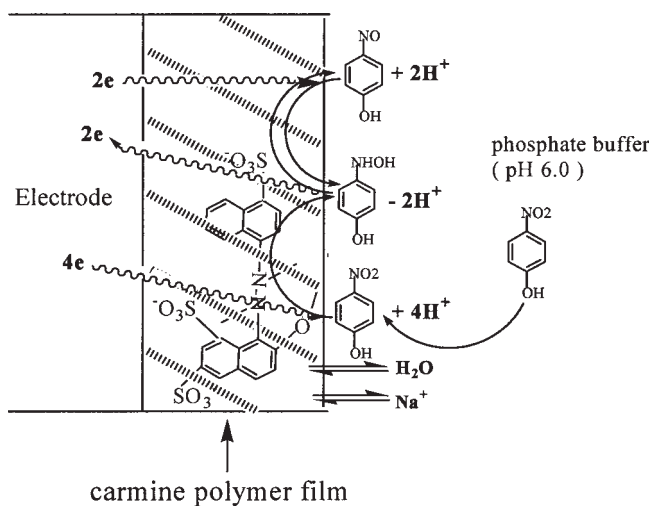


Figure 3 Linear sweep voltammograms for $1.00 \times 10^{-5} \text{ mol L}^{-1}$ 4-NP on the sensor (a) and a bare glassy carbon electrode (b). Curve c represents linear sweep voltammogram of the sensor in 0.100 mol L^{-1} phosphate buffer (pH 6.0) in the absence of 4-NP. Scan rate, 100 mV s^{-1} .



current obtained on the sensor were superior to that on a bare GCE. The remarkable peak current enhancement was undoubtedly attributed to the extraordinary properties of the polymer film, such as high aspect ration and strong adsorption ability. According to Figure 1, there are two naphthyl groups in the chemical structure of carmine, and they will also be present in the polymer of carmine. Moreover, there is a phenyl group in the structure of 4-NP. Therefore, during the process of preconcentration, 4-NP can be accumulated to the surface of the electrode via “ π - π ” hydrophobic interaction and/or hydrogen bond with the poly(carmine) film to enhance the current response. The likely chemical process between the carmine polymers and 4-NP is shown in Scheme 1.

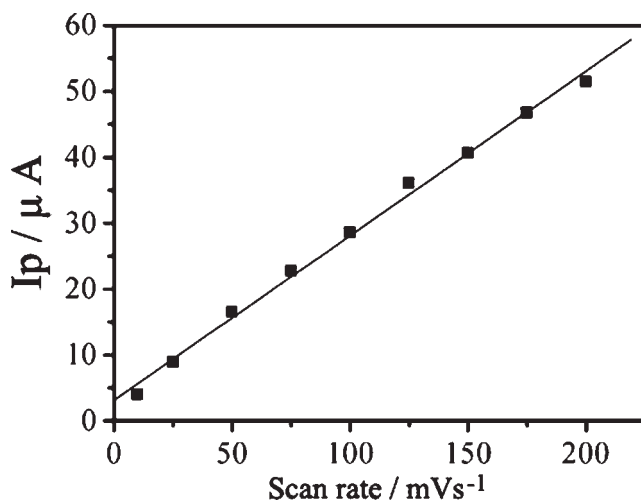


Figure 4 Dependence of the reduction peak current (I_{Pc}) on the scan rate. Supporting electrolyte, 0.100 mol L⁻¹ phosphate buffer (pH 6.0); 4-NP concentration, 5.00×10^{-6} mol L⁻¹.

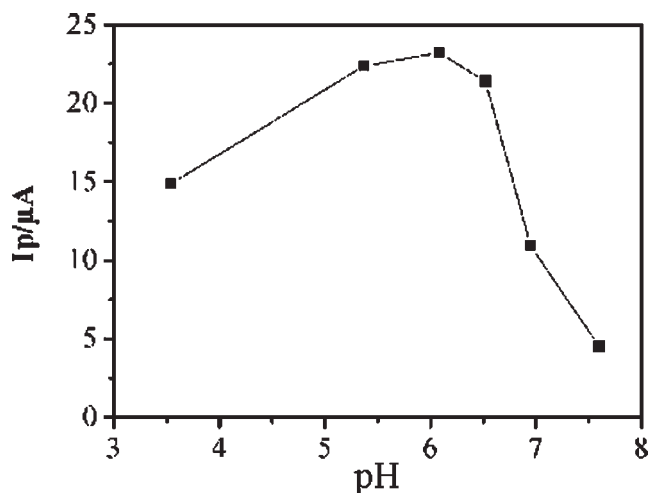


Figure 5 Effect of pH on the reduction peak current of 5.00×10^{-6} mol L⁻¹ 4-NP on the sensor.

Effect of scan rate

Scan rate is an important parameter in electrochemical research and has obvious influence on the electrochemical behavior of substrates. As shows in Figure 4, the reduction peak current (I_{Pc}) of 4-NP increased with the increasing scan rate and exhibited a linear relationship to the scan rate, v , with a linear regression equation $I_{Pc} (\mu A) = 0.250v (\text{mV s}^{-1}) + 3.96$ and a correlation coefficient of 0.998. This electrochemical behavior reflected an adsorption process of 4-NP at the polymer film electrode, and indicated that the electrode reaction is adsorption-controlled rather than diffusion-controlled.

With an increase in v , the peak potential (E_{Pc}) shifted negatively. According to Laviron's conclu-

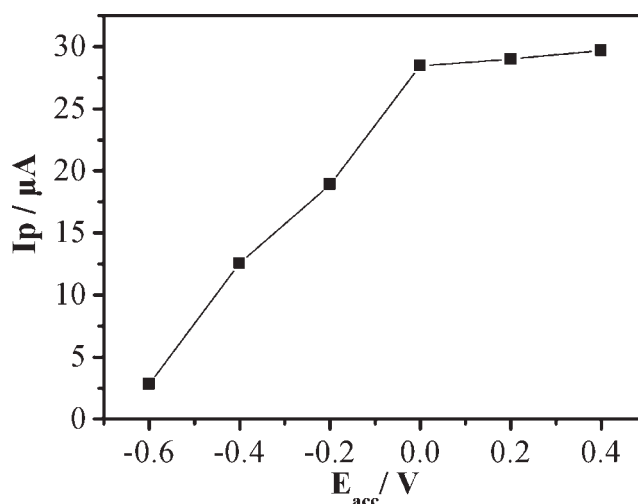


Figure 6 Effect of the accumulation potential on the reduction peak current for 5.00×10^{-6} mol L⁻¹ 4-NP in 0.100 mol L⁻¹ phosphate buffer (pH 6.0).

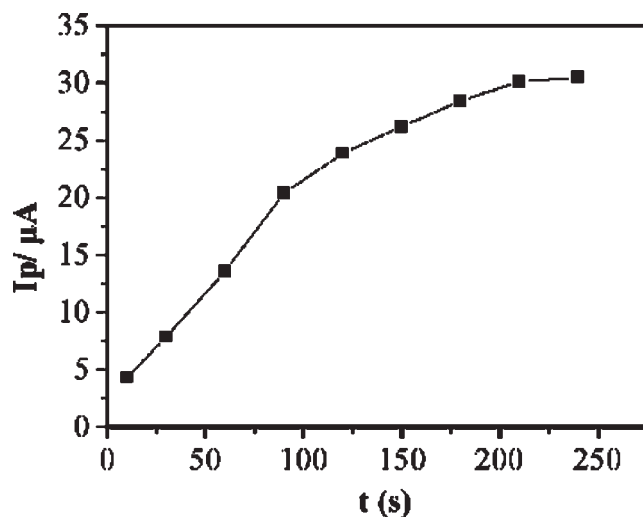


Figure 7 Dependence of the reduction peak current on the accumulation time.

sion, the relationship between E_{Pc} and v was examined. The potential was found to depend linearly on the logarithm of v , as shown in the following equation: $E_{Pc} = -0.0800 \log v - 0.510$ (v , scan rate, mV s^{-1} ; $r = 0.997$). However, at a scan rate higher than 200 mV s^{-1} , the plot deviated from the linearity.

Optimization of parameters for the 4-NP determination

Supporting electrolytes and pH value are critical for the voltammetric responses of 4-NP. A 0.100 mol L^{-1} phosphate buffer was used as supporting electrolyte solution to investigate the effect of the solution pH on the peak potential and the peak current of 4-NP. The reduction peak potential (E_{Pc}) corresponding to the reduction of $\phi\text{-NO}_2$ showed a linear dependence on pH value between 3.54 and 7.60. The equation relating E_{Pc} to pH was $E_{Pc} = -0.0510 \text{ pH} - 0.390$ ($r = 0.996$). According to the Nernst equation $E = 59.2 m/n \text{ pH}$ (where m , n is corresponding to the transference number of proton and electron, respectively), a slope of 51.0 mV/pH suggested that the transference number of protons and electrons was equal in the electrochemical process. This result was consistent with the electrochemical reaction of nitro-

containing compounds such as parathion²⁸ and fenitrothion.²⁹

Figure 5 shows the dependence of the peak current (I_{Pc}) on solution pH. A maximum current response was reached at a pH value of about 6.0, and a decrease in current was observed when the pH value of the solution was more than 6.0. The best results, with respect to the current enhancement, were obtained at pH 6.0. Therefore, phosphate buffer (pH 6.0) was selected as a supporting electrolyte solution for the determination of 4-NP on the sensor.

Influence of accumulation potential and time on the reduction peak current

Effects of the accumulation potential (E_{acc}) and the accumulation time (t_{acc}) on the voltammetric response were examined. As shown in Figure 6, the reduction peak current (I_{Pc}) decreased obviously when the accumulation potential was more negative than 0.00 V, and an almost stable peak current was obtained in the potential range of 0.00–0.400 V. Thus, the optimum E_{acc} should be 0.00 V for analytical estimation of 4-NP. The influence of the accumulation time on the reduction peak current of $5.00 \times 10^{-6} \text{ mol L}^{-1}$ 4-NP has also been investigated and the results are illustrated in Figure 7. The reduction peak current increased greatly within the first 200 s and then levels off, suggesting that the adsorption of 4-NP has reached a saturation state at the surface of the sensor. Therefore, 200 s was selected as optimum accumulation time for the determination of 4-NP on the sensor.

The stability of the sensor was evaluated by measuring the reduction peak current of $5.00 \times 10^{-6} \text{ mol L}^{-1}$ 4-NP on the sensor. The sensor was used daily and stored in the redistilled water in the refrigerator. The reduction peak currents measured at different periods are shown in the Table I. As can be seen, over a period of three weeks, there is only a deviation of 4.06% from its original current response. The results indicated that the sensor possesses long-time stability. The reproducibility for the determination of $5.00 \times 10^{-6} \text{ mol L}^{-1}$ 4-NP solution on the sensor was investigated and a relative standard deviation (RSD) of 2.48% was obtained for nine parallel mea-

TABLE I
Evaluation of the Stability for the Determination of $5.00 \times 10^{-6} \text{ mol L}^{-1}$ 4-NP at the Sensor

Period	Peak currents (μA)	Average (μA)	RSD (%)	Deviation (%)
Original	27.98, 28.49, 28.52	28.33	1.07	
One week	27.23, 28.03, 28.68	27.98	2.60	1.23
Two weeks	27.06, 26.90, 28.34	27.43	2.89	3.16
Three weeks	27.95, 26.89, 26.69	27.18	2.49	4.06

surements. The reproducibility for the fabricated sensors was evaluated by measuring the peak current of 5.00×10^{-6} mol L⁻¹ 4-NP at the sensor. Six sensors were independently constructed for this purpose, and a RSD of 2.69% has been calculated from the measured peak current (each sensor has been used to determine 5.00×10^{-6} mol L⁻¹ 4-NP three times, and the average value was applied for the calculation of RSD).

Study of the interfering species on the current response indicated that the sensor provides a higher selectivity for the determination of 4-NP. For 5.00×10^{-6} mol L⁻¹ 4-NP determination, 100-fold excess concentration of Cd²⁺, Pb²⁺, Cu²⁺, Hg²⁺, K⁺, Zn²⁺, Mg²⁺, Ca²⁺, Fe³⁺, Fe²⁺, and Al³⁺ did not interfere. The possible interfering species, such as dopamine, ascorbic acid, acetaminophen, tyrosine, vitamin B, glucose, and cholesterol, were tested by adding these compounds to the solution in the ratio of 10:1. The error made by each interferent was less than 3.00%. However, nitro aromatic compounds, e.g., 2-nitroso-1-naphthol, *o*- and *m*-nitrophenol, and *o*- and *m*-dinitrobenzene, nitrobenzene, can readily be reduced on the surface of the sensor and brought on a positive interference for electrochemical determination of 4-NP.

Analytical application

The reduction peaks (I_{pc}) of 4-NP at 1.00×10^{-8} , 5.00×10^{-8} , 1.00×10^{-7} , 5.00×10^{-7} , 1.00×10^{-6} , 2.00×10^{-6} , 5.00×10^{-6} , 7.00×10^{-6} , 1.00×10^{-5} , and 2.00×10^{-5} mol L⁻¹, which were obtained with linear sweep voltammetry in the potential range of -0.100 to -1.00 V after accumulation 200 s, were employed for the analytical purpose. Figure 8 shows the calibration curve for the determination of 4-NP.

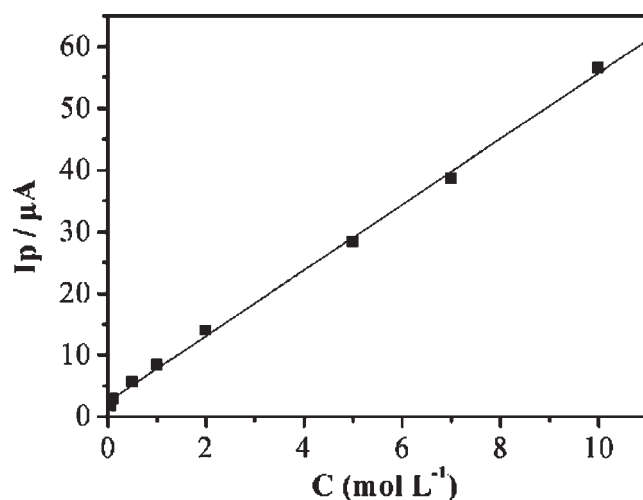


Figure 8 Calibration curve for the determination of 4-NP on the sensor.

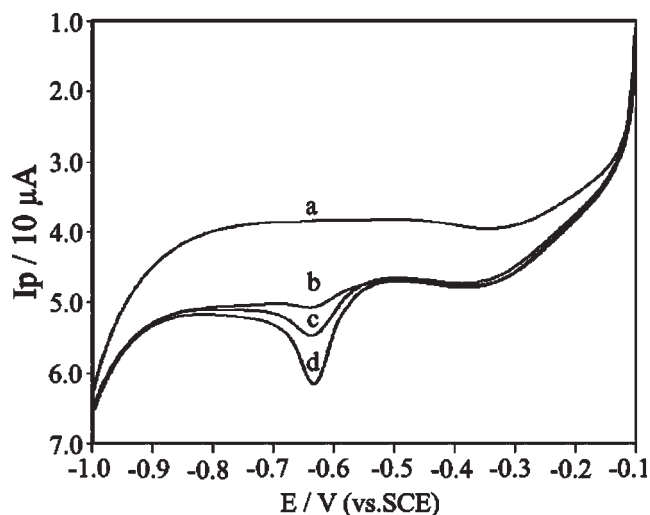


Figure 9 Voltammograms from typical analysis of 4-NP in lake-water samples. Curve a represents a lake-water sample without 4-NP spiked. Curves b, c, and d represent the voltammograms of lake-water samples spiked with 3.00×10^{-7} , 1.00×10^{-6} , and 2.00×10^{-6} mol L⁻¹ 4-NP respectively.

Under the optimal conditions, a linear relationship between the reduction peak current and the 4-NP concentration was observed over the concentration of 5.00×10^{-8} to 1.00×10^{-5} mol L⁻¹. Variation of peak current (I_{pc}) with the concentration of bulk 4-NP gives a straight line following the equation I_{pc} (μA) = 5.33 C (μmol L⁻¹) + 2.44 ($r = 0.999$). For the concentration of 4-NP higher than 2.0×10^{-5} mol L⁻¹, the peak current increases only slightly and approaches a constant value because of the saturate adsorption of 4-NP on the electrode surface. The minimum detectable concentration of 4-NP was estimated to be 1.00×10^{-8} mol L⁻¹ ($S/N = 3$).

Because of its high sensitivity, 4-NP was determined repeatedly in samples of lake water by using the recommended method. The analytical procedure was applied as described earlier. Figure 9 shows the voltammograms from typical analysis of 4-NP in

TABLE II
Determination of 4-Nitrophenol in Lake-Water Samples

No. of samples	4-NP added (μM)	4-NP found (μM)	Recovery (%)
1	0.3	0.293	97.7
		0.302	100.6
		0.289	96.3
2	1	0.956	95.6
		0.984	98.4
		0.992	99.2
3	2	1.95	97.5
		2.07	103.5
		1.89	94.5

lake-water samples. As curve a shows, none of the lake-water samples analyzed contained any 4-NP, and so they had to be spiked with the analyte at a certain concentration, and the results are summarized in Table II. The recovery of the spiked 4-NP was observed to be good for the determinations.

CONCLUSIONS

Based on an electropolymerization of carmine film, a voltammetric sensor has been successfully fabricated for the determination of 4-NP. The successful determination of 4-NP spiked into lake-water samples suggested that it was a promising electrochemical device for the detection of 4-NP in environmental samples.

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