

Glassy carbon electrode modified with poly(methyl orange) as an electrochemical platform for the determination of 4-nitrophenol at nanomolar levels



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ABSTRACT

In this study, poly(methyl orange) (PMO) was synthesized by electrodeposition onto a glassy carbon electrode (GCE), and the resulting structure was examined for the determination of 4-nitrophenol (4-NP). Cyclic voltammetry revealed that the PMO-modified GCE (PMO/GCE) exhibited excellent electrocatalytic activity for the oxidation of 4-NP in a 0.5-M phosphate buffer solution. In contrast, the bare GCE showed no oxidation peak. Interestingly, PMO/GCE exhibited an oxidation peak at approximate 0.93 V, and the background current was higher than that of the bare GCE. Furthermore, the developed electrochemical sensor exhibited a linear relationship with the 4-NP concentration from 600 nM to 10 μM, and the limit of detection was 170 nM (signal/noise = 3). The sensor demonstrated excellent selectivity, good stability, and reproducibility. It was applied to the determination of 4-NP in water samples by the standard addition method and gave recoveries of 99.2–100.9%.

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1. Introduction

Organic pollutants represent a serious threat to the environment worldwide and adversely affect human health. Because they persist for long periods of time, these pollutants have exerted unforeseen effects on human health and the environment and can accumulate and pass from one species to the next through the food chain [1]. The improper disposal of materials containing these chemicals leads to problems. Phenols and their derivatives are considered serious, ubiquitous pollutants in water and soil [1].

Phenolic compounds enter natural water bodies in the effluents of various chemical industries, such as the rubber, dye, pharma, detergent, resin, paper, and petrochemical industries, which use these compounds as precursors or intermediates. The water discharged from these industries contains highly toxic substances that enter human food chains and lead to a variety of disorders ranging from infertility to death. As a result, these substances are included in the list of priority pollutants [1]. Among phenolic pollutants, many nitrophenols (NPs) not only affect the respiratory and central nervous system but also induce cancer at higher doses. Therefore, these phenolic industrial effluents must be identified and treated before being discharged into the environment. Thus, the development of reliable techniques for the determination of phenols and substituted phenols in wastewater is highly important.

Analytical techniques such as spectrophotometry, fluorimetry, and chromatography [2–7] have been used for the determination

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of NPs. Among these methods, electrochemical methods have been determined to be reliable because of their simple instrumentation, high sensitivity, and cost effectiveness. Electrochemical methods constitute a group of analytical techniques based on two pathways: reduction and oxidation. A variety of reduction-based methods has been reported in the literature [8–11]. However, to date, very few studies have focused on the oxidative determination of 4-NP [12,13]. The advantage of oxidative determination is that, unlike reductive determination, no prerequisite procedure is needed to analyze 4-NP. In electroanalytical studies, conducting polymers are used to detect analytes rapidly because of their ease of polymerization. Electrochemical polymerization is generally achieved by oxidizing monomers under an external potential [14]. Recently, Reddy et al. reported the electrochemical polymerization of methyl orange (MO) for the detection of L-dopa [15]. Although poly(methyl orange) (PMO) has been used in various applications, few studies have investigated its application for the electrochemical detection of analytes. Indeed, previously, no attempt was made to utilize PMO for the electrochemical detection of 4-NP.

In the present study, we reported the electropolymerization of MO on the surface of a glassy carbon electrode (GCE) using cyclic voltammetry (CV) and the application of the resulting structure for the electroanalytical determination of 4-NP. The PMO-modified GCE (PMO/GCE) exhibited a limit of detection (LOD) of 170 nM, the linear response from 600 nM to 12 μ M, improved better anti-interference ability, and good sensitivity.

2. Experimental

2.1. Materials

4-NP and MO were purchased from Sigma-Aldrich. All other chemicals were of analytical grade and used as received unless otherwise specified.

2.2. Fabrication of PMO/GCE

Prior to electrochemical polymerization, the GCE was polished using 1- μ m, 0.3- μ m, and 0.05- μ m alumina slurries in sequence; washed ultrasonically in ethanol and deionized water for 10 min, and dried at room temperature. The electrode pretreatment was performed as described in our previous report [16]. The electro-deposition of PMO onto the GCE was conducted at a scan rate of 50 mV s^{-1} in the given potential range from +0.6 to +1.2 V versus a saturated calomel electrode (SCE) for 30 CV cycles in 0.1-M phosphate buffer solution (PBS) containing 0.1-mM MO. After electro-deposition, the electrode was thoroughly washed with deionized water.

2.3. Electrochemical measurements

A three-electrode system (CHI 1103A electrochemical workstation) was used to evaluate the electrochemical performance of PMO/GCE. The electrochemical performance of the catalyst-modified GCE was evaluated by CV and differential pulse voltammetry (DPV) in 0.1-M PBS (pH 5). PMO/GCE was used as the working electrode, and a Pt wire electrode was used as the counter electrode. All potentials were measured versus an SCE. DPV experiments were conducted at a scan rate of 50 mV s^{-1} in the range of -0.4 to 0.4 V with a pulse amplitude of 0.025 V and a pulse interval of 0.05 s.

3. Results and discussion

Methyl orange was subjected to electropolymerization in the

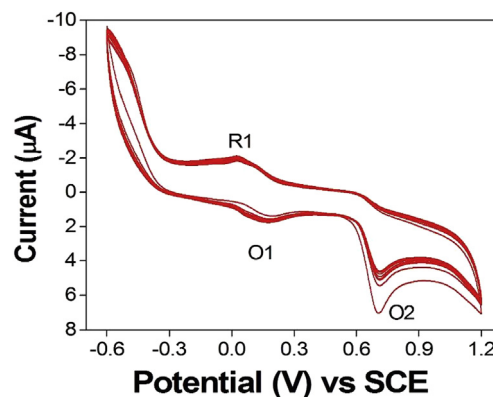
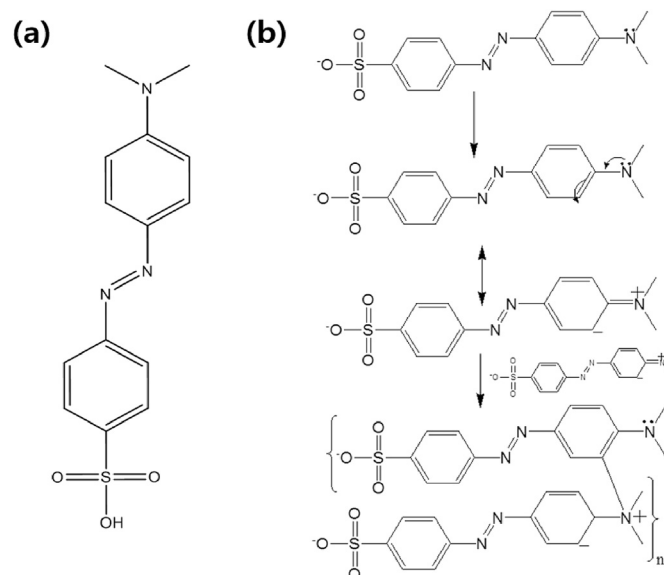


Fig. 1. CV curve of MO electropolymerization: 0.1-mM MO, 0.05-M PBS, 30 cycles from -0.6 to +1.2 V versus SCE at 50 mV s^{-1} .

potential range from -0.6 to +1.2 V for 20 cycles. Fig. 1 illustrates the CV analysis of MO polymerization on the GCE in 0.1-M PBS (pH 7). The CV curve shows oxidation and reduction peaks in the given potential ranges from 0.7 to 0.6 V and from 0.16 to 0.02 V, respectively. The peak observed in the potential range of 0.7 to 0.6 V is related to the oxidation of MO, whereas the other peak (0.16–0.02 V) is attributed to the formation of PMO. During the electrochemical process, the number of CV cycles gradually decreased as the cycle time increased.

A plausible electropolymerization mechanism is shown in Scheme 1 and is consistent with the existing literature [15]. The -Nme₂ group of MO can bind to the GCE because of the adsorptive nature of the electrode surface.

Fig. 2a shows the CV curves of PMO/GCE at different pH values. The voltammetric profiles collected from -0.2–0.8 V display reversible oxidation and reduction peaks. As shown in Fig. 2a, the redox peaks disappeared as the pH increased from 3 to 11, and the oxidation peak current decreased as the proton concentration decreased. Thus, the optimal pH was in the range of 3–5. When the electrolyte pH value is over 5 or below 3, it may affect the sensitivity and conductivity of PMO at the electrode surface. The morphological analysis of PMO/GCE was performed using scanning



Scheme 1. (a) Structure of MO and (b) mechanistic pathway of the electrochemical polymerization of MO at the GCE surface.

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