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A graphene oxide-based electrochemical sensor for sensitive determination of 4-nitrophenol

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ABSTRACT

A graphene oxide (GO) film coated glassy carbon electrode (GCE) was fabricated for sensitive determination of 4-nitrophenol (4-NP). The GO-based sensor was characterized by scanning electron microscope, atomic force microscopy and electrochemical impedance spectroscopy. The electrochemical behaviors of 4-NP at the GO-film coated GCE were investigated in detail. In 0.1 M acetate buffer with a pH of 4.8, 4-NP yields a very sensitive and well-defined reduction peak at the GO-modified GCE. It is found that the GO film exhibits obvious electrocatalytic activity toward the reduction of 4-NP since it not only increases the reduction peak current but also lowers the reduction overpotential. Based on this, an electrochemical method was proposed for the direct determination of 4-NP. Various kinetic parameters such as transfer electron number, transfer proton number and standard heterogeneous rate constant were calculated, and various experimental parameters were also optimized. Under the optimal conditions, the reduction peak current varies linearly with the concentration of 4-NP ranging from 0.1 to 120 μM, and the detection limit is 0.02 μM at the signal noise ratio of 3. Moreover, the fabricated sensor presented high selectivity and long-term stability. This electrochemical sensor was further applied to determine 4-NP in real water samples, and it showed great promise for simple, sensitive, and quantitative detection of 4-NP.

1. Introduction

The analysis of aromatic nitrocompounds such as nitrobenzene, nitrotoluenes and nitrophenols in natural waters and effluents is of prime importance for environmental control due to their appearance from a wide range of activities [1]. These compounds have toxic effect on humans, animals and plants and they give an undesirable taste and odor to drinking water, even at very low concentration [2]. For these reasons, many aromatic nitrocompounds have been included in the environmental legislation. In particular, 4-nitrophenol (4-NP) is one of the nitrophenols cited in the List of Priority Pollutants of the U.S.A. Environmental Protection Agency (EPA) due to its toxicity and persistence [3]. Acute inhalation or ingestion of 4-NP in a short time for humans can cause headaches, drowsiness, nausea and cyanosis [1]. In addition, 4-NP was reported as potential carcinogen, teratogens and mutagen [4], so its application should be strictly controlled and supervised. Unfortunately, 4-NP is still widely used as intermediates in the production of pharmaceuticals, dyestuffs and pesticides, such as fenitrothion and parathion insecticide which can reversely hydrolyze to form 4-NP [5,6]. In addition, 4-NP can also be used as leather fungicide and acid–base indicator [5]. Therefore, 4-NP will be inevitably released into environment to cause pollution during its production and application for agriculture and industry. Therefore, it is very urgent and important to develop simple and reliable method for determination of trace amounts of 4-NP in environment.

Until now, the widely used methods for determination of 4-NP are spectrophotometry [7], fluorescence [8], gas chromatography (GC) [9], capillary electrophoresis [4] and high performance liquid chromatography (HPLC) [10]. Traditional spectrophotometry and colorimetric methods are easily interfered by related compounds. GC methods can sometimes require relatively expensive reagents and need beneficiation and derivatization before analysis and it cannot be used directly to aqueous samples. HPLC and capillary electrophoresis methods are good alternative methods, but they need high cost to buy columns and waste more organic solvents [7]. Thus, there is a demand for new analytical technique with cheap instrument, low cost, simple operation, time saving and real-time detection for 4-NP. Moreover, the easy electrochemical reduction of nitro groups at the aromatic or heterocyclic ring, whose mechanism is discussed in monographs [11], permits very sensitive determinations of a number of genotoxic and ecotoxic nitro-compounds using modern voltammetric techniques at modified electrodes [12]. In this regard, electrochemically analytical technique is an

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alternative to monitor lower concentration of 4-NP in environment. In order to enhance the sensitivity of electrochemical sensors, the working electrode employed in familiar electrochemical technique often needs surface modifying. Recently, Mhammedi et al. [12] used hydroxyapatite modified electrode to investigate the electrochemical behaviors of 4-NP and realize the determination of 4-NP with lower detection limit of 8 nM. Though many other modified electrodes based on carbon nanotubes [13–15], nano-gold [16], silver particles [17] and ionic liquid [18] have been also reported to detect 4-NP with satisfactory results; it is still a challenge to fabricate a new electrochemical sensor based on novel materials with excellent electro-catalysis properties by simpler preparation.

Since the discovery by Geim and co-workers in 2004 [19], graphene, a flat monolayer of sp^2-bonded carbon atoms tightly packed into a two-dimensional honeycomb lattice, and characterized as “the thinnest material in our universe” [19,20], has received considerable attention due to its high surface area ($\sim$2600 m^2/g), high chemical stability, and unique electronic, mechanical properties [21]. This unique nanostructure holds great promise for potential applications in nanoelectronics [22], hybrid [23], lithium ion batteries [24] and sensors [25]. In the past decades, several forms of carbon materials (e.g. C_{60} [23], ordered mesoporous carbon [26], carbon nanofiber [27] and carbon nanotubes [28]) have been used for developing different kinds of electrochemical devices; especially the carbon nanotubes-based electrochemical sensors were most widely investigated. However, several works have demonstrated that graphene usually exhibit better electroanalytical performance than the extensively used carbon nanotubes [29,30]. Graphene oxide (GO), one of the most important derivatives of graphene, also has a large surface area, excellent conductivity and strong mechanical strength. Furthermore, the oxidized rings of functionalized and defective GO sheets contain abundant C—O—C (epoxide) and C—OH groups, while the sheets are terminated with C—OH and —COOH groups [31,32]. Defects of GO may change its electronic and chemical properties. The functionalized and defective GO sheets are more hydrophilic and can be easily dispersed in solvents with long-term stability [33]. Moreover, they are more easily produced in mass quantities as compared with the carbon nanotubes. They may be used to prepare some novel GO-based films, which could facilitate the further manipulation and processing of these materials for developing novel electronic devices, such as chemical sensors and biosensors. Recently, GO-based electrochemical sensors have been developed for the sensitive determination of dopamine [30], caffeine [34], 2,4,6-trinitrotoluene [35] and used as a platform for immobilizing glucose oxidase to construct new glucose biosensors [36].

The aim of this work is to fabricate a novel and stable electrochemical sensor for ultra sensitive determination of 4-NP. The working electrode used in this method was modified with GO which was simply prepared from graphite. Compared with bare electrode, the electro-reduction peak of 4-NP was remarkably heightened at GO modified electrode, and it can be used as an analytical sign for 4-NP determination. The experimental parameters such as the concentration of GO, pH value and accumulation conditions were optimized and the kinetic parameters of the electrode process were detailedly discussed. Finally, this method was successfully applied to determine trace amounts of 4-NP in real water samples with satisfactory results.

2. Experimental

2.1. Reagents

Graphite powder (spectrum pure), H_2SO_4, $KMnO_4$ and H_2O_2 (30 wt%) were obtained from Shanghai Chemical Reagent Co. (China). 4-NP was purchased from Sigma–Aldrich, and its stock solution of 0.01 M was prepared by dissolving the required amount of 4-NP in redistilled water and then kept in darkness at 4 °C. Working solutions were freshly prepared before use by diluting the stock solution. An acetate buffer (pH 4.8) of 0.1 M was always employed as a supporting electrolyte. All other reagents were of analytical reagent grade and used as received. All solutions were prepared with redistilled water, and the solutions were deaerated by bubbling high-purity nitrogen before the experiments. The pH values of the solutions were adjusted with 0.1 M HCl and NaOH.

2.2. Apparatus

All electrochemical experiments were performed on a CHI660D electrochemical workstation (CH Instrumental Co., China) with a conventional three-electrode cell. A bare or modified glassy carbon electrode (GCE, $d = 3$ mm) was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference electrode and auxiliary electrode, respectively. The pH measurements were carried out on PHS-3C exact digital pH meter (Shanghai REX Instrument Factory, China), which was calibrated with standard buffer solution every day. Fourier transform infrared (FTIR) spectra were recorded on a FTIR-8700 infrared sepectrophotometer (Shimadzu, Japan). Scanning electron microscopy (SEM) image was obtained from JSM-6700F field emission SEM system (Jeol, Japan) which was operated at an acceleration voltage of 15.0 kV. Atomic force microscopic (AFM) images were recorded with a Nanoscope IV atomic force microscope (Digital Instruments) using a tapping mode.

2.3. Synthesis of graphene oxide

GO was synthesized directly from graphite by a modified Hummers method [37]. Generally, 1 g graphite was ground with 50 g NaCl for 10 min. NaCl was then dissolved and removed by filtration with water. The remaining graphite was stirred in 23 mL of 98% H_2SO_4 for 8 h. $KMnO_4$ (3 g) was gradually added while keeping the temperature less than 20 °C. The mixture was then stirred at 80 °C for 45 min. Next, the redistilled water of 46 mL was added and the mixture was heated at 105 °C for 30 min. The reaction was terminated by addition of redistilled water (140 mL) and 30% H_2O_2 solution (10 mL). The resulting mixture was washed by repeated centrifugation and filtration, first with 5% HCl aqueous solution and then with distilled water. Finally, the GO product was obtained after dried in vacuum.

2.4. Preparation of modified electrode

For fabrication of modified electrodes, the modifier suspension was prepared by dispersing 10.0 mg GO in 2.5 mL DMF under ultrasonication for 30 min. Prior to modification, a bare GCE was polished to form a mirror-like surface with 0.3 and 0.05 μm alumina slurry on micro-cloth pads, then washed successively with $HNO_3—H_2O$ (1/1 by volume), anhydrous alcohol and redistilled water in an ultrasonic bath and dried in air. Then the prepared suspension of 5.0 μL was coated onto the fresh GCE surface using a micropipette, followed by evaporating the solvent under an infrared lamp. After the solvent was evaporated, the electrode surface was thoroughly rinsed with redistilled water and dried in the air. The obtained electrode was denoted as GO/GCE. In order to eliminate the memory effect, the modified electrode was treated in the blank supporting electrolyte before every measurement by successive cyclic voltammetric sweeps until the steady curve appeared. The modified electrode was stored at 4 °C in a refrigerator when it was not used.