



An electrochemical sensor based on polyelectrolyte-functionalized graphene for detection of 4-nitrophenol



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ABSTRACT

A novel electrochemical sensor based on poly(diallyldimethylammonium chloride) (PDDA) functionalized graphene (PDDA-G) composite film has been developed for the detection of 4-nitrophenol (4-NP). The PDDA-G was successfully prepared and characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Due to PDDA-G has more functional groups which were beneficial for the absorption of 4-NP by electrostatic interaction, it was found that the sensitivity for 4-nitrophenol was remarkably improved at the PDDA-G nanocomposite film modified GCE. The experimental parameters such as the pH of buffer solution, the scan rate, the accumulation time and potential were optimized. Under the optimum experimental conditions, this sensor had a wide linear range over 4-NP concentration from 0.06 μM to 110 μM with a detection limit of 0.02 μM ($S/N = 3$). Furthermore, the PDDA-G sensor not only exhibited good stability with adequate reproducibility and accuracy, but also demonstrated efficiency in the detection of 4-NP in water samples. It was expected that this method has great promise for simple, sensitive, selective detection of 4-NP.

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1. Introduction

Graphene, emerging as a true two-dimensional single atomic sheet of graphite with sp^2 -bonded carbon atoms closely packed in a hexagonal structure, has garnered tremendous attention owing to its high surface area ($\sim 2600 \text{ m}^2/\text{g}$), excellent chemical stability, outstanding electrical conductivity, exceptional physicochemical, electronic and mechanical properties [1,2]. Due to its great deal of advantages, graphene has found its way into various applications such as nanoelectronics [3,4], electrodes [5,6], supercapacitors [7], sensors [8–10], and memory devices. Several approaches have been presented to synthesize graphene, including chemical vapor deposition (CVD) [11,12], plasma enhanced chemical vapor deposition [13], solvothermal method, exfoliation and cleavage of natural graphite, and so on [14–16]. However, graphene nanosheets are apt to agglomerate during the chemical conversion course, even would back to graphitization just due to Van der Waals forces and π - π stacking, this has seriously hindered its further development [17]. To address this issue, several ways have been committed to ameliorate its electronic, soluble, and electrochemical properties including covalent and non-covalent functionalization methods. Compared to covalent

methods, non-covalent strategies are attracting more and more attention as they allow for enhanced solubility, and superior electrochemical properties. Therefore, some polymers and macromolecular compounds have been utilized to stabilize graphene sheets, and the non-covalent functionalization with polyelectrolyte become a preferable one of these focus approaches [18].

Poly(diallyldimethylammonium chloride), PDDA, not only an electronic conducting polymer but also a strong ionic polymer, has been found to be attractive for combining with other materials as the functional macromolecule, especially used to functionalize graphene sheets [19–21]. In particular, PDDA has excellent binding capability with graphene and could maintain the electronic structure of graphene. As an effective material for the functionalization of graphene, PDDA exhibits superior conductivity, solubility and biocompatibility [22]. Accordingly, the positively charged PDDA-functionalized graphene (PDDA-G) has been employed as a matrix to anchor some negatively charged materials for fabricating multifunctional and application-directed composites [23,24]. Meanwhile, it has more functional groups which are beneficial for adsorbing the analytes by electrostatic interaction [25]. The resultant PDDA-functionalized/adsorbed graphene was shown to possess dramatically enhanced activities towards electrochemical catalysis [26]. Therefore, the PDDA-G not only acquires a perfect dispersion but also serves as a sort of favorable material to modified electrodes.

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Nitrophenols and their derivatives because of their extensive use as raw materials in chemical processing industries and exhibiting mutagenic, cyto- and phyto-toxic effects, are the major priority pollutants in the industrial effluent. As a kind of refractory organic pollutant which result from the production processes of pesticides, insecticides, synthetic dyes and herbicides [27], these compounds have severe toxicity to humans, animals as well as plants. The degradation of NPs by biological treatment is difficult and requires long incubation time since the presence of nitro-group which causes the aromatic compound a strong chemical stability and resistance to microbial degradation. Therefore, it is particularly significant for the analysis of nitrophenols in the Environment. 4-Nitrophenol (4-NP), one of the most ubiquitous and abundant nitrophenol, which has been included in the list of Priority Pollutants of the USA [28], the maximum permissible limit is less than 20 ppb. Based its serious harm to the environment and human beings, to develop an effective determination method of 4-NP in the environmental protection is very important. Literature reveals that there are various methods have been used to detect 4-NP and applied in real samples, such as liquid chromatography [29,30], chemiluminescence [31], UV-vis spectrophotometry [32] as well as other combined use [33,34]. Despite these methods have the characteristics of high efficiency and resolution, however, the expensive instrument cost, time consuming, quite harsh requirements for part of the instruments of the testing environment and some other factors, such as field, real-time online detection due to restricting by various environment and conditions, limited the development of these approaches. Throughout all of the above, there is a need to develop a cost effective, less time consuming technique which can effectively monitor the analyst in the sample. Recently, electrochemical sensing techniques were used to detect 4-NP for its excellent performance, high sensitivity and easy operability [35–38], but it is still a challenge to fabricate a new electrochemical sensor based on novel materials with excellent electroanalytical performance by simpler preparation [39].

Herein, the aim of this work is to fabricate a novel and simple electrochemical sensor for sensitive determination of 4-NP. In this work, PDDA-G composite film was synthesized by facile chemical process and used to determine 4-nitrophenol efficiently. Compared to the bare electrode and graphene modified electrode (GN-G/GCE), the electrochemical response of 4-NP in PDDA-G composite film has improved greatly. Several influential factors such as the effects of pH value and scan rate and accumulation time, were investigated. We demonstrate here that the PDDA-G composite modified electrode (PDDA-G/GCE) exhibit excellent analytical performance towards 4-NP and successfully applied to determine trace amounts of 4-NP in real water samples with satisfactory results.

2. Experimental section

2.1. Reagents and materials

Graphite (99.99% SP-1, Bay carbon) with average particle size of 45 μm , PDDA (20%), Potassium thiosulfate ($\text{K}_2\text{S}_2\text{O}_8$, 99.5%), potassium permanganate (KMnO_4 , 99.5%), phosphorus pentoxide (P_2O_5), concentrated sulphuric acid (H_2SO_4 , 98%), hydrated hydrazine (99%), Hydrogen peroxide (H_2O_2 , 30%) were purchased from Sigma-Aldrich. 4-NP was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjing, China). 1 mM stock solution of 4-NP was prepared by dissolving 4-NP into ultrapure water, and then stored at 4 °C in a refrigerator. Phosphate buffer solutions (PBS) of 0.2 M for different pHs were prepared by mixing stock solutions of 0.2 M KH_2PO_4 and 0.2 M K_2HPO_4 and adjusting the pH with 0.2 M H_3PO_4 or 0.2 M K_3PO_4 . All other reagents and solvents were of analytical grade and used without further purification. All chemicals were prepared with ultrapure water.

2.2. Equipments

Electrochemical measurements were carried out on a CHI 832 electrochemical analyzer (Chenhua Instrument Company, Shanghai, China) with a conventional three-electrode cell comprised of an Ag/AgCl (saturated KCl) electrode and a platinum wire were used as reference electrode and auxiliary electrode, respectively. A bare or modified glassy carbon electrode (GCE, $d = 3 \text{ mm}$) were used as working electrode. UV-vis absorption spectra were taken by absorption mode with a UV-1102 UV-vis spectrophotometer (Shanghai, China). Fourier transform infrared (FTIR) spectra were recorded on a FTIR-8700 infrared spectrophotometer (Shimadzu, Japan), Transmission Electron Microscope (TEM) image was taken with a JEM-3010 transmission electron microscope (JEOL Co., Ltd., Japan) and X-ray Diffraction (XRD) study was conducted by D/max-2400 (Rigaku Co., Japan).

2.3. Synthesis of PDDA-functionalized graphene

Graphite oxide (GO) was prepared from graphite powder by a modified Hummers method [40,41]. The GO aqueous dispersion was obtained from graphite oxide by ultrasonication for 3 h and centrifugation at 3000 rpm for 20 min to remove any unexfoliated GO, and then dispersed in water to yield a yellow-brown dispersion. Subsequently, the homogeneous GO dispersion (1 mg/mL, 50 mL) was mixed with 1 mL PDDA (20%) solution and stirred for 2 h, followed by the addition of 1.5 mL hydrazine hydrate and after being vigorously stirred for a few minutes, allowed to react for 3 h at 100 °C in Teflon autoclave. The final product (PDDA-G) was collected through centrifugation and further washed with ultrapure water. To obtain the unfunctionalized graphene, the above procedure was adopted just in the absence of PDDA.

2.4. Preparation of PDDA-functionalized graphene modified electrode

Prior to the surface modification, the glassy carbon electrode (GCE) was polished with 0.3 μm and 0.05 μm alumina slurries, rinsed with water and ethanol, and finally subjected to ultrasonic agitation for 1 min in ultrapure water and dried under nitrogen gas. The PDDA-G was dissolved in ultrapure water at a concentration of 1 mg/mL with the aid of ultrasonic agitation for 6 h, resulting in a homogeneous black suspension. Finally, 5 μL PDDA-G solution was deposited on the fresh prepared GCE surface. The modified electrode was dried in the room temperature and stored at 4 °C in a refrigerator if not be used. The obtained electrode was noted as PDDA-G/GCE. Graphene modified electrode (GN/GCE) was constructed in the similar manner described above.

3. Results and discussion

3.1. Characterizations of PDDA-G

Fig. 1A displayed the TEM and HRTEM image of PDDA-G. As shown, the morphology of PDDA-G was clearly exhibited some slightly folding of the nanosheets. Meanwhile, some aggregations of the nanosheets can be observed in HRTEM (inset of Fig. 1A) image of PDDA-G.

The XRD pattern (Fig. 1B) showed that the graphite existed a strong characteristic peak centered at 26.4° (curve a). After oxidation, GO (curve b) exhibited a new characteristic peak at 10°, while the characteristic peak of graphite was absent, suggesting that the graphite had been oxidized completely. After the reduction with hydrazine, the diffraction peak at 10° disappeared and a broad peak around 25° was observed (curve c), indicating the completely reduction of GO and the exfoliation of the layered PDDA-G [42].

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