



Short communication

Facile preparation of poly (diallyldimethylammonium chloride) modified reduced graphene oxide for sensitive detection of nitrite

Fugang Xu ^{*}, Miao Deng, Ying Liu, Xincan Ling, Xueyi Deng, Li Wang ^{*}

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, People's Republic of China

ARTICLE INFO

Article history:

Received 18 June 2014

Received in revised form 22 July 2014

Accepted 22 July 2014

Available online 31 July 2014

Keywords:

Graphene

Nitrite

Electrochemical sensor

Poly (diallyldimethylammonium chloride)

Nanocomposite

ABSTRACT

In this communication, a sensitive electrochemical nitrite sensor was constructed based on poly (diallyldimethylammonium chloride) (PDDA) functionalized reduced graphene oxide (PDDA-rGO). The preparation of PDDA-rGO is quite facile, and the PDDA-rGO exhibits good dispersity and high stability in water, together with good conductivity and positive surface charge. All these factors lead to a greatly enhanced catalysis of PDDA-rGO for the nitrite oxidation compared with that of unmodified rGO or bare glassy carbon electrode. Based on PDDA-rGO, an electrochemical nitrite sensor with low overpotential (0.75 V), wide linear range (0.5 μM –2 mM), low detection limit (0.2 μM), good stability and selectivity was fabricated, which exhibited satisfied recovery for detecting nitrite in drinking water.

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1. Introduction

Reliable, sensitive and economic method to detect nitrite is of great importance for human health and environment protection [1,2]. Among various techniques for nitrite sensing [3], electrochemical sensor has attracted considerable attentions due to its simple operation, low cost, high sensitivity, and fast response [4,5]. Usually, oxidation is preferred for nitrite detection as the major interferences from reduction of nitrate and molecular oxygen in cathodic determination of nitrite are avoided [6]. However, the oxidation of nitrite often requires high potentials (>0.9 V) at bare electrode and exhibits poor response. To resolve this problem, various functional nanomaterials have been explored to modify the electrode to lower overpotential and improve sensitivity for nitrite sensing [7,8].

At present, graphene and graphene based hybrid materials are widely used to construct various electrochemical sensors due to the large surface area, high conductivity of graphene and its synergistic interaction with other nanomaterials [9–12]. Specifically, many nitrite sensors have been constructed from graphene–metal [13], graphene–metal oxide [14], graphene–polymer hybrids [15]. These sensors display good performance such as high sensitivity and low detection limit. However, the effective and uniform anchoring of nanomaterials on graphene is difficult and tedious; in addition, decorating graphene with nanocatalysts such as Au or Pt elevates the cost of the sensor. While so much attention paid on the integration of graphene with other nanomaterials, advanced sensors based on doping or modification

graphene itself may be overlooked [16]. Previously, graphene modified by alkaline metal K (K-rGO) [17] or produced by chemical reduction (CR-GO) [18] was explored for nitrite sensing. These works demonstrate that graphene or rationally modified graphene itself could be a good alternative for electrochemical sensor. However, the preparation of K-rGO (48 h) or CR-GO (24 h) is time-consuming; in addition, metal K is not safe and cannot be used in aqueous solution [17]; CR-GO suffers from low sensitivity and narrow response linear range for nitrite detection [18]. Thus, new functionalized graphene should be facilely produced for sensitive, fast and economic detection of nitrite.

In this study, polyelectrolyte PDDA functionalized graphene nanosheet (PDDA-rGO) was prepared within 30 min and used for the sensitive detection of nitrite without loading any other nanomaterials as catalysts. PDDA functionalized graphene retains the large surface area, good conductivity of graphene, and displays enhanced adsorption towards anion nitrite and thus largely improves its catalysis for the oxidation of nitrite. Finally, a sensitive and stable electrochemical sensor based on PDDA-rGO was constructed and successfully achieved the detection of nitrite in buffer solution and real water sample. Our results indicated that rationally functionalized graphene can be explored to construct advanced electrochemical sensors.

2. Experimental

2.1. Reagents

Poly (diallyldimethylammonium chloride) (PDDA) was purchased from Sigma-Aldrich (USA). Sodium nitrite and other reagents were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). All reagents

^{*} Corresponding authors. Tel./fax: +86 791 88120861.

E-mail addresses: fgxu@jxnu.edu.cn (F. Xu), lwang@jxnu.edu.cn (L. Wang).

were of analytical grade and used without further purification. Ultrapure water purified by a Millipore-Q System (18.2 M Ω cm) was used as solvent.

2.2. Apparatus

All electrochemical measurements were performed on a CHI 760D electrochemical workstation (Shanghai, China) at room temperature, using a conventional three-electrode system (bare or modified glassy carbon electrode (GCE) as working electrode; platinum wire as auxiliary electrode and saturated calomel electrode as reference electrode). Phosphate buffer saline (10 mL, 0.1 M, pH 7.4 or 4.5) was employed as the supporting electrolyte solution for the electrochemical experiments.

2.3. Preparation of graphene derived materials modified electrodes

Graphene oxide (GO) was synthesized according to a modified Hummers' method. PDDA-rGO was prepared according to a previous method with some modification [19]. Typically, 15 mg GO was dispersed in 40 mL H₂O and then 10 mL PDDA (0.2 wt.%) and 10 mL N₂H₄·H₂O (4 wt.%) was added. The introduction of PDDA induced the aggregation of GO at first, as more PDDA was added and with the help of sonication, the mixture became homogeneous again. Then the mixture was heated to 100 °C and reacted for 30 min at this temperature. Thus prepared PDDA-rGO was centrifuged, washed with Milli-Q water, and finally re-dispersed into 30 mL water to obtain 0.5 mg/mL PDDA-rGO. Unmodified rGO (UM-rGO) was prepared in similar approach except that no PDDA was added. For comparison, rGO modified with negatively charged surfactant sodium dodecyl-benzene-sulfonate (SDBS) was also prepared in a similar way to that of PDDA-rGO, except that 50 mg SDBS instead of PDDA was added to functionalize rGO. Then, 8 μ L of PDDA-rGO or UM-rGO or SDBS-rGO was cast on a polished GCE

(3 mm in diameter) and dried at room temperature. Thus prepared modified electrodes were defined as PDDA-rGO/GCE, or UM-rGO/GCE.

3. Results and discussion

3.1. Preparation of UM-rGO and PDDA-rGO

The oxidation–exfoliation–reduction method may be the most widely used approach to prepare graphene due to its high efficiency and mass production. IR spectra show oxy-groups of GO including –OH (3429 cm⁻¹), C=O (1732 cm⁻¹), C–OH (1400 cm⁻¹) and C–O (1070 cm⁻¹) disappear or greatly decrease in intensity for UM-rGO and PDDA-rGO (Fig. 1A), indicating the reduction of GO with N₂H₄. Moreover, the peaks at 2924 cm⁻¹ (–CH_n–), 1463 cm⁻¹ (–CH₂–), and 1113 cm⁻¹ (C–N) of PDDA-rGO correspond to the characteristic bands of PDDA (Fig. 1A), implying the modification of rGO with PDDA. Raman spectroscopy reveals the D/G ratio of GO (1.08) increases to 1.36 for PDDA-rGO and 1.52 for rGO (Fig. 1B), which also demonstrates the reduction of GO and the reduced graphite domain size. The similar peak position and D/G ratio of PDDA-rGO and UM-rGO demonstrates the interaction between PDDA and rGO is not strong enough to drastically change the electronic structure of rGO, which is critical to preserve the unique properties of graphene. Although the interaction is mild, it greatly improves the dispersity and stability of rGO. Previous yellowish GO turns into black suspension after reduction (Inset of Fig. 1B). However, the suspension of UM-rGO is not stable, and it easily aggregates, contaminates the tube and cannot be re-dispersed (inset of Fig. 1B) after washing procedure. SEM image shows UM-rGO aggregated into thick wrinkles (Fig. 1C), thus the surface area of UM-rGO should be greatly decreased. In contrast, the black suspension of PDDA-rGO is quite stable and homogeneous (inset of Fig. 1B); thin film with few wrinkles formed after it was dried (Fig. 1D), thus

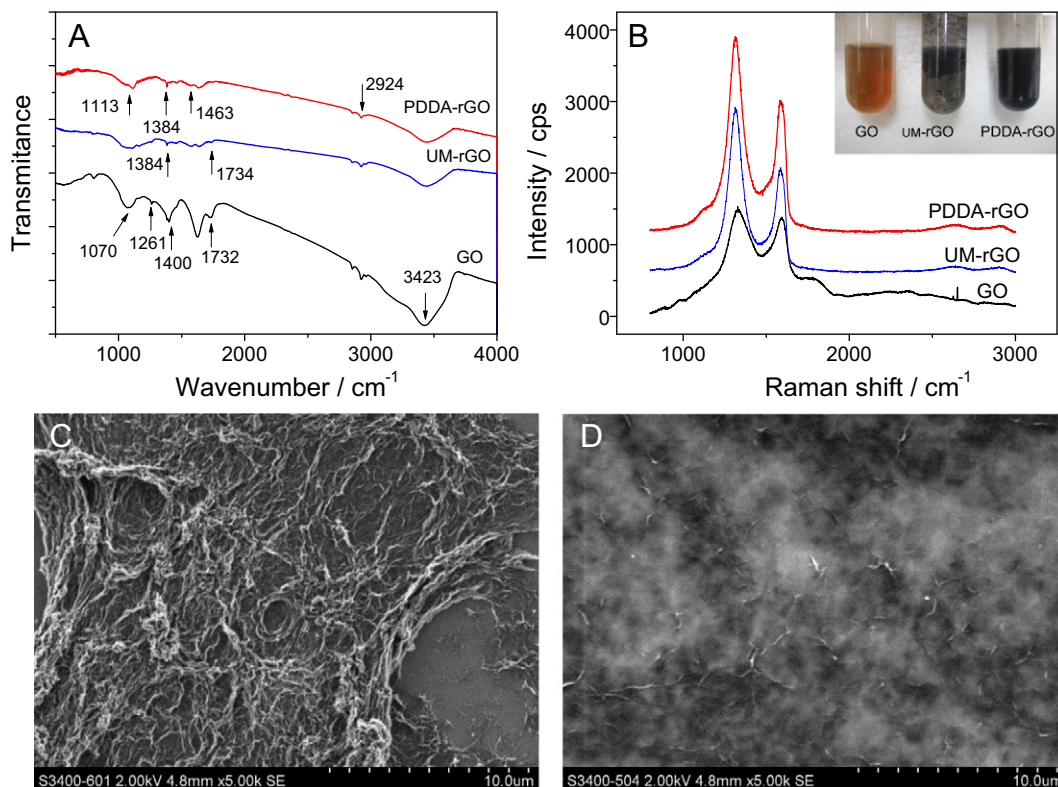


Fig. 1. (A) IR spectra and (B) Raman spectra of graphene derived materials; SEM images of UM-rGO (C), and PDDA-rGO (D). Inset of B is photographs of corresponding materials.

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