A novel composite of reduced graphene oxide and molecularly imprinted polymer for electrochemical sensing 4-nitrophenol

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ARTICLE INFO

ABSTRACT

A novel composite of reduced graphene oxide and molecularly imprinted polymer (RGO-MIP) was prepared using free radical polymerization and used as a recognition element in the construction of an electrochemical sensor for 4-nitrophenol (4-NP). RGO was achieved through the incomplete reduction of graphene oxide, and then 4-NP molecules were adsorbed at RGO surface due to their good affinity based on their hydrogen and π-π bonding interaction. Subsequently, selective copolymerization of methacrylic acid and ethylene glycol dimethacrylate was further carried out at RGO surface to prepare RGO-MIP. The properties of RGO-MIP sensor for 4-NP, such as special binding, response time, and recognition ability were investigated in detail. The results demonstrated that the RGO-MIP sensor not only possessed a short response time, but also a good selectivity and binding capacity for 4-NP, which enabled the RGO-MIP sensor with higher current response than that of non-imprinted polymer, traditional MIP and RGO. The RGO-MIP sensor had a wide linear range over 4-NP concentration from 0.01 to 100.0 μM with a detection limit of 0.005 μM. Furthermore, the RGO-MIP sensor not only exhibited good stability with adequate reproducibility and accuracy, but also demonstrated efficiency in the detection of 4-NP in water samples.

1. Introduction

Graphene, a two-dimensional monolayer of carbon atoms arranged in honeycomb lattice, has received extensive attention due to its unique properties [1–3]. The graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO), offer a wide range of possibilities to synthesize functional materials for various applications [4,5]. RGO can be prepared in large quantity through chemical or thermal reduction of GO. It possesses a higher conductivity compared with GO [6], which holds a great promise for electrochemical sensing applications. In recent years, RGO-based hybrid materials, including the composites of RGO and polymers [7,8], have been widely researched for various applications [4,5]. In the preparation of these composites, RGO is usually applied as the reinforcing element in a polymer matrix. Besides, through the combination between RGO and different polymers, the composites usually exhibit some novel properties, such as good

dispersibility [9], high conductivity [10], and excellent thermal stability [11]. Molecularly imprinted polymer, which is tailor-made for a target molecule, is considered as a competitive candidate to combine with RGO. The composite of RGO and molecularly imprinted polymer possesses a good conductivity, as well as a high adsorption capacity and good specificity for the target molecule.

Molecular imprinting is used to create recognition sites that are chemically and sterically complementary to the target molecules in a synthetic polymer [12,13]. However, molecularly imprinted polymer (MIP) prepared by the conventional technique has some disadvantages, such as incomplete template removal, low-affinity binding and slow mass transfer [14,15]. In recent years, surface imprinting technique has received extensive attention, because it can provide the advantages of favorable selectivity, fast association/dissociation kinetics, some unique physicochemical properties and desired application. Therefore, some groups have reported surface MIP composites based on supporters, such as Fe_3O_4 nanoparticles [16], Fe_3O_4@Au multifunctional nanofibers [17], carbon nanotubes [18], quantum dots [19] and SBA-15 [20]. In recent years, GO and its derivatives have been demonstrated to be good candidates as supporters for preparing surface MIP composites. These supporters mainly included GO [21], GO-magnetite

[22], GO/SiO$_2$ [23] and graphene/congo red (GSCR) [24]. Li and co-workers first synthesized GO-MIP composite by reversible addition and fragmentation chain transfer (RAFT) polymerization for specific recognition for 2,4-dichlorophenol [21]. Qiu's group reported GO-magnetite-MIP composite using RAFT polymerization for chemiluminescence sensing epinephrine [22]. Our group prepared surface MIP composites for dopamine recognition on the basis of GO/SiO$_2$ as a supporter [23]. In addition, Mao et al. used free radical polymerization (FRP) to prepare a composite of GSCR-MIP for electrochemical sensing dopamine [24], in which congo red was functionalized onto graphene (the complete reduction of GO) to prepare GSCR to adsorb dopamine molecules. In this paper, RGO was prepared by incomplete reduction of GO, which possesses some residual oxygen-containing groups and a better electrocatalytic activity compared with GO. So RGO with residual oxygen-containing groups can easily adsorb 4-nitrophenol (4-NP) molecules, which can create more recognition sites during the polymerization process [25]. In addition, FRP has been successfully utilized to covalently graft polymer chains on graphene-based materials by macromolecular radical addition to the reactive carbon-carbon double bonds [24,26]. Therefore, it is interesting to adopt RGO as a supporter to prepare a composite of RGO and MIP (RGO-MIP).

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 [27]. Acute ingestion or inhalation of 4-NP for humans may cause headaches, drowsiness, nausea and cyanosis [28]. The United States EPA has provided the allowed limit of 4-NP in drinking water at 0.43 μM [29]. Based on the above description, it is important to develop simple and reliable method for the determination of 4-NP in environmental water samples. Herein, a novel composite of RGO-MIP was synthesized using FRP and used as a molecular recognition element to construct 4-NP electrochemical sensor. RGO was prepared through the incomplete reduction of GO. 4-NP molecules were adsorbed at RGO surface due to their good affinity based on hydrogen bond and π-π stacking interaction, and subsequently, selective copolymerization of methacrylic acid and ethylene glycol dimethacrylate was further carried out at RGO surface. The RGO-MIP composite was characterized by Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), scanning electronic microscopy (SEM), and Raman spectroscopy. The properties of RGO-MIP sensor for 4-NP, such as special binding, response time, and selective recognition ability using differential pulse voltammetry (DPV) were investigated. An electrochemical sensor fabricated by modifying RGO-MIP composite on the glassy carbon electrode (GCE) surface was employed to recognize 4-NP from its analogs and detect the concentration of 4-NP. The sensor based on RGO-MIP composite was applied to the determination of 4-NP in water samples.

2. Experimental

2.1. Materials and apparatus

Nitrobenzene (NB), 2,4,6-trinitrotoluene (TNT) (1 mg mL^{-1} in acetonitrile), 2,4-dinitrotoluene (DNT), 1,3-dinitrobenzene (DNB) and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma-Aldrich. Methacrylic acid (MAA) was obtained from TCI Co., Ltd. and distilled under reduced pressure to remove inhibitors. 4-NP, graphite powder (spectral grade) and 2,2-azobisisobutyronitrile (AIBN) were obtained from Sinopharm Group Chemical Regent Co., Ltd. Other chemicals used were of analytical grade, and purchased from Sinopharm Group Chemical Regent Co., Ltd. (Shanghai, China). Phosphate buffer solution

(PBS, 0.1 M, pH = 5.5) was prepared from NaH$_2$PO$_4$ and Na$_2$HPO$_4$. Double-distilled water was used throughout the experiments.

FTIR spectroscopy was performed on NEXUS 670 Fourier transform infrared spectrometer (Nicolet, USA). TGA was conducted on a TGA/SDTA851e instrument from room temperature to 700 °C with a heating rate of 10 °C min^{-1} in the nitrogen flow (Mettler Toledo Co., Switzerland). Raman spectra were measured using Senterra R-200L Raman spectrometer with a 532 nm line of laser source (Bruker, Germany). Surface morphological images were taken by a HITACHI S-4800 scanning electronic microscopy (Hitachi Co. Ltd., Japan). Electrochemical measurements were performed on a CHI 660c electrochemical workstation (CH Instruments Co., Shanghai, China) with a conventional three electrode system comprising platinum wire as auxiliary electrode, saturated calomel electrode as reference electrode and the modified or unmodified GCE (3 mm diameter) as working electrode, containing a 10 mL of glass cell.

2.2. Preparation of RGO-MIP

GO was prepared using a modification of Hummers and Offeman method from graphite powders [30,31]. RGO was synthesized by incomplete reduction of GO. Briefly, 0.1 g of GO was added to 200 mL of water, followed by sonicating for 2 h. Then, 0.1 mL of ammonia (28% w/w) and 1.4 mL of hydrazine (80% w/w) were added to the GO resultant dispersion. After being vigorously stirred for a few minutes, the reaction mixture was stirred for 1 h at 95 °C. After this, the mixture turned its color from brown to black, which indicated the reduction of GO to RGO.

RGO-MIP was prepared by the method of FRP. In brief, 0.08 g of RGO and 0.1 mmol of 4-NP were added to 30 mL of methanol. Then, 0.4 mmol of MAA was dissolved into the above solution and this mixture was stirred for 2 h to form a complex of template molecule and functional monomer. 2.0 mmol of EGDMA and 20 mg of AIBN were added into the above solution. The resulting solution was stirred with nitrogen for 15 min. The temperature was increased to 60 °C, and the reaction was allowed to proceed for 24 h. The resulting product of RGO-MIP was collected and eluted by a mixture of methanol/acetic acid (9:1, v/v) to remove the templates. For comparison, the composite of RGO and non-imprinted polymer (RGO-NIP) was prepared by the same procedure, only without using the template molecule in the polymerization process.

For comparison, traditional MIP was prepared by the same procedure, only without using RGO in the polymerization process.

2.3. Electrochemical measurements

The GCE was polished with 0.05 mm alumina slurry, followed by rinsing with twice-distilled water, and then treated by ultrasonication in nitric acid (1:1, v/v), 1 M NaOH, acetone, and twice-distilled water. 5 mg of RGO-MIP (or RGO-NIP) was dispersed in 1 mL of 1 M HAc containing 0.5% chitosan (w/w) by ultrasonication for 30 min. The above suspensions (5 μL) were dropped on the clean GCE surface and dried at room temperature. PBS (0.1 M, pH = 5.5) was used as the supporting electrolyte. The electrolyte solution was purged with nitrogen for 10 min and maintained under nitrogen atmosphere during the measurements. The modified electrodes were incubated in 5 mL of 4-NP solution for 5 min and measured by DPV in PBS.

3. Results and discussion

3.1. Preparation and characterization of RGO-MIP

Fig. 1 presents illustration of the preparation procedure for RGO-MIP and detection process for its electrochemical sensor. Details of the preparation could be found in the experimental section.