



## Original Research

## Molecularly imprinted polymer/graphene oxide modified glassy carbon electrode for selective detection of sulfanilamide

Xiaobing Wei<sup>a,b</sup>, Xinhua Xu<sup>a,\*</sup>, Wen Qi<sup>c</sup>, Ying Wu<sup>c</sup>, Lihong Wang<sup>d</sup><sup>a</sup> School of Materials Science and Engineering, Tianjin University, Tianjin 300350, China<sup>b</sup> Analysis and Testing Center, Shandong University of Technology, Zibo, Shandong 255000, China<sup>c</sup> Beijing Key Laboratory of Energy Nanomaterials, Advance Technology & Materials Co, Ltd, China Iron & steel Research Institute Group, Beijing 100081, China<sup>d</sup> School of Agricultural and Food Engineering, Shandong University of Technology, Zibo, Shandong 255000, China

## ARTICLE INFO

## Keywords:

Graphene oxide  
Sulfanilamide  
Molecularly imprinted polymer  
Electrochemical detection

## ABSTRACT

A novel sensitive electrochemical sensor based on a glassy carbon electrode (GCE) modified with molecularly imprinted polymer (MIP) and graphene oxide (GO) was developed. The MIP/GO material was prepared by precipitation polymerization in the presence of sulfanilamide as template molecule. The MIP/GO based electrochemical sensor was characterized using scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV). The results indicated that the sensor exhibited good affinity and excellent electrochemical response for sulfanilamide. Under optimized conditions, the oxidation peak current intensity of sulfanilamide showed two linear dynamic ranges from 10 to 1000 ng mL<sup>-1</sup>, and the standard deviation was less than 5% using SWV method. The sensor displays good stability, reproducibility, and high sensitivity. It can be further applied to quantify sulfanilamide in milk.

## 1. Introduction

Graphene, a new carbon material, shows promising applications in scientific and technological fields owing to its novel properties such as exceptional thermal and mechanical properties, high electrical conductivity [1–4]. Graphene oxide (GO), the oxidation form of graphene, bears two-dimensional plane and lots of electroactive oxygen containing functional groups and disorder on the basal planes and edges [5,6]. It possesses the properties of large surface area and good chemical stability, especially, the excellent solubility and the convenience of preparation, which make it an ideal material for the modification of electrodes, and can be widely used for electrochemical detection [7,8]. Moreover, in order to obtain selective detection of targets in complex samples, some special recognition elements such as antibody are usually emerged with graphene materials to modify the electrodes. Molecularly imprinted polymer (MIP) is a type of synthesized polymer material, which is a man-made polymer with predetermined selectivity toward some given analytes or a group of structurally related species [9,10]. MIP has been widely utilized for separation and detection purpose as molecular recognition material because of some outstanding advantages such as predetermined recognition ability, mechanical and chemical stability, relative ease and simple synthesis procedures

[11,12]. Furthermore, MIP/GO composite has been developed which can process the synergistic effect of MIP and GO. And GO can be used as reinforcement in polymer composites, potentially ensuring a drastic improvement of composite performances [13,14].

Recently, due to the frequent occurrence of excessive drug residues in food events, people pay widespread attention to drug residues in food detection [15,16]. Sulfonamide is a synthetic antibacterial, which is widely used in veterinary medicines. In order to treat the domestic animal disease, drugs are usually used excessively, causing food contamination and leading to negative effects to human health [17]. Therefore, developing sensitive method for the determination of sulfanilamide is essential. Traditional detection methods usually include high performance liquid chromatography, chromatography-mass spectrometry and so on [18]. However, these instruments are not fit for the popular use because of their high cost, strict pretreatment methods and complex detection. Accordingly, interest in electrochemical methods has increased for its simplicity, high sensitivity, good stability, low-cost instrumentation and onsite monitoring [19,20]. Therefore, the electrochemical determination of sulfanilamide has been widely used in food detection.

In the present study, a novel sensor of sulfanilamide was fabricated based on molecularly imprinted polymer combined with graphite oxide

Peer review under responsibility of Chinese Materials Research Society.

\* Corresponding author.

E-mail address: [xhxutju@gmail.com](mailto:xhxutju@gmail.com) (X. Xu).<http://dx.doi.org/10.1016/j.pnsc.2017.05.001>

Received 6 January 2017; Received in revised form 25 April 2017; Accepted 4 May 2017

Available online 30 May 2017

1002-0071/© 2017 Chinese Materials Research Society. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

modified on glassy carbon electrode (MIP/GO/GCE). Sulfanilamide molecules were imprinted to create specific places in the polymer matrix for selective stereo chemical recognition. The sensitivity of the sensor could be enhanced by an increase in the electrochemical conductivity and in the surface area provided by the use of GO. With this method, the developed sensor can improve the selectivity and sensitivity to sulfanilamide. The electrochemical performance of the modified electrode was evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV). And further a MIP/GO/GCE was developed for the selective detection of sulfanilamide residues.

## 2. Experimental

### 2.1. Preparation of graphite oxide

GO was prepared by oxidation of natural graphite powder according to the modified Hummers method [21–23]. Briefly, graphite (1.5g) was added to concentrated sulfuric acid (80 mL) under stirring at room temperature, then sodium nitrate (1.5g) was added, and the mixture was cooled to 0 °C. Under vigorous agitation, potassium permanganate (12.0g) was added slowly. Successively, the reaction system was transferred to a 35 °C water bath for about 2 h, forming a thick paste. Then, 120 mL of deionized water was added to keep the temperature of the suspension 98 °C and the solution was stirred for another 15 min. An additional 200 mL of water was added followed by a slow addition of 15 mL of H<sub>2</sub>O<sub>2</sub> (30%), then all added in the mixture. After reaction, the mixture was filtered and washed with 1: 10 HCl aqueous solution (250 mL) to remove metal ions followed by repeated washing with water and centrifugation to remove the acid. The obtained brown dispersion was then subjected to 60 min of centrifugation at 3000 rpm to remove aggregates. Finally, it was purified by dialysis for 1 week to remove the remaining salt impurities for the following experiments.

### 2.2. Preparation of MIP/GO

The MIP/GO was synthesized as follows: 0.17g of sulfanilamide and 0.34 mL of MAA were added into a round-bottom flask with three necks (100 mL) containing 40 mL of acetonitrile. The mixture was incubated for one night at room temperature for pre-polymerization. Then, 4 mmol of DVB, 1 mmol of AIBN and 2.4g of GO were added. The mixture was sonicated for 20 min before purging with a stream of nitrogen for 15 min and sealing the bottle. The reaction was allowed to proceed at 60 °C for 24 h. At the end of this period, the reaction mixture had the appearance of gray precipitation. After the polymerization, the template was removed by centrifugation (3000 rpm) using the mixture solution of methanol/acetic acid (9: 1, v/v) to wash the polymerization for several times until the template molecule could not be detected by HPLC. Finally, the MIP/GO were dried in vacuum at 60 °C for 6 h, grinded and saved in sealing.

Non-imprinted polymer (NIP) was synthesized under the same conditions, except for the addition of sulfanilamide in the polymerization process. MIP was prepared by the same procedure, only without using GO in the polymerization process.

### 2.3. Characterization

Scanning electron microscopy (SEM, Sirion200, FEI) and transmission electron microscopy (TEM, JEM-1011, FEI) were used to study the morphology and structure of the composite with acceleration voltage of 100 kV and magnification 20000x. The chemical composition and the crystal structure analysis were investigated by X-ray diffraction (XRD, D8ADVANCE, Bruker AXS, Germany) with scanning angle of 5–90° and produced by copper target X-ray wavelengths  $\lambda=1.54 \text{ \AA}$ . Raman spectra were carried out from 2500 to 200 cm<sup>-1</sup> with a laser excitation at 532 nm (EQUINOX 55, Bruker, Germany). Fourier trans-

form infrared spectrometer (FT-IR, Nicolet 5700, Thermo Electron Corporation) was explored with the scanning range of 500–4000 cm<sup>-1</sup>.

### 2.4. Preparation of modified electrode based on MIP/GO

Prior to modification, a bare glass carbon electrode (GCE) was polished carefully using alumina polishing powders with particle sizes of 1.0, 0.3, and 0.05  $\mu\text{m}$ , respectively, followed by sonication in ultrapure water and desiccation under a high-purity N<sub>2</sub> stream to obtain a mirror surface. The electrode was then activated in sulfuric acid 0.5 M using CV at 100 mv s<sup>-1</sup> between -0.2 V and +1.6 V, for 20 cycles. The GCE was scanned by CV from -0.1 to +0.6 V in [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> solution (1 mmol L<sup>-1</sup>) until repeating cyclic voltammograms occurred and voltage difference less than 95 V between the electrodes. Finally the electrode was washed with deionized water and allowed to dry at room temperature before use.

The process for the construction of the modification electrode MIP/GO/GCE was depicted as follows. Firstly, MIP/GO composite was diluted in the chitosan aqueous solution (0.03 mg mL<sup>-1</sup>, pH=2.5) and the solution was sonicated and mixed sufficiently. Then, moving 10  $\mu\text{L}$  dispersion on the center of GCE by using pipette. Finally, the electrode was allowed to dry at room temperature before use. The other modified electrodes (MIP/GCE and NIP/GCE) were prepared under the same experimental conditions.

All the electrochemical measurements were carried out on a CHI760E electrochemical workstation (Chenhua Instrument Shanghai Co. Ltd, China) with a conventional three-electrode system at room temperature, consisting of a bare glassy carbon electrode (4 mm diameter) as the working electrode, a Ag/AgCl electrode as reference electrode and a platinum wire electrode as the counter electrode, respectively. Electrochemical measurements of the modified electrodes were performed by using different electrochemical techniques including CV, EIS and SWV.

Sulfanilamide was dissolved with a mixture of methanol/deionized water (1: 9, v/v) and then diluted with NaAc-HAc buffer solution (pH = 5.2). Electrolyte solutions were prepared at 0, 10, 20, 40, 100, 200, 400, 600, 800 and 1000 ng mL<sup>-1</sup>, respectively.

## 3. Results and discussion

### 3.1. Characterization of graphene oxide

GO was prepared by oxidation of natural graphite powder according to the modified Hummers method. The oxygen-containing functional group such as carboxyl and carbonyl has been introduced to graphene successfully. Graphene oxide aqueous solution was dark brown, but turned in black solid with large-sized lamellar structure after drying. As shown in Fig. 1a, the morphology of the GO was characterized by SEM and the GO showed laminated structure and overlapping of flake layers on the surface. The TEM image of GO is shown in Fig. 1b where the overlapping of flake layers was observed and GO processed irregular shape and different sizes.

The X-ray diffraction (XRD) was used to further study the structure of the graphite and the graphene oxide. The results are shown in Fig. 2a. The natural graphite reveals a characteristic height centered at  $2\theta=26.6^\circ$  [24]. For GO, the diffraction peak located at approximately  $12.30^\circ$  and the d-spacing is about 0.9 nm, which is assigned to the (002) plane [25,26]. The crystal structure of the graphene in highly structured monolayer of carbon atoms tightly packed had changed for the oxidization, where oxygen-containing functional groups had been introduced with the overlapping of flake layers, making the increase of the interlayer spacing of graphene as the power decreased. Raman spectroscopy can well characterize graphene materials for evaluating ordered and disordered structural features. In general, the D band is assigned to characterize defects and disorders of graphitic domains, whereas the G band is attributed to the E<sub>2g</sub> mode of sp<sup>2</sup> carbon

Download English Version:

<https://daneshyari.com/en/article/5450447>

Download Persian Version:

<https://daneshyari.com/article/5450447>

[Daneshyari.com](https://daneshyari.com)