



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: [www.elsevier.com/locate/talanta](http://www.elsevier.com/locate/talanta)

# Molecularly imprinted polymer grafted graphene for simultaneous electrochemical sensing of 4, 4-methylene diphenylamine and aniline by differential pulse voltammetry



Ningning Chen<sup>a</sup>, Li Chen<sup>b</sup>, Yuxiao Cheng<sup>b</sup>, Kai Zhao<sup>a</sup>, Xiaohong Wu<sup>b</sup>, Yuezhong Xian<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, East China Normal University, 500 Dongchuan Road, Shanghai 200241, China

<sup>b</sup> Shanghai Entry-Exit Inspection and Quarantine Bureau, Shanghai 200135, China

## ARTICLE INFO

### Article history:

Received 22 May 2014

Received in revised form

29 August 2014

Accepted 3 September 2014

Available online 16 September 2014

### Keywords:

Molecular imprinting polymers

Graphene

Aromatic amines

Electrochemical sensor

## ABSTRACT

A sensitive and selective electrochemical sensor based on molecular imprinting polymers grafted graphene (MIPs-G) was developed for simultaneous measurement of 4, 4-methylene diphenylamine (MDA) and aniline by differential pulse voltammetry (DPV). MIPs-G was synthesized via free radical polymerization reaction using MDA and 4-vinyl pyridine as template molecule and functional monomer respectively. The obtained nanocomposites were characterized by transmission electron microscope, scanning electron microscope, Fourier transform infrared spectrometry, Raman spectroscopy and thermal gravimetric analysis. After removal template molecules, MIPs-G was used as electrode material for aromatic amines measurements. Due to the high binding affinity towards MDA and the  $\pi$ - $\pi$  interaction with aniline, the MIPs-G based electrochemical sensor can be used for simultaneous detection of MDA and aniline by DPV. Under the optimized condition, the oxidation potentials for MDA and aniline were observed at 0.62 and 0.72 V, respectively. Moreover, MIPs-G modified glassy carbon electrode shows linear response towards MDA and aniline simultaneously over the range of 1.0 to 15  $\mu$ M. The MIPs-G based electrochemical sensor has been applied for simultaneous measurement of MDA and aniline in plastic tableware.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Since the concept of molecular imprinting was first realized by Dickey in 1949 [1], molecular imprinting technology has become a well-established approach to generate molecular recognition materials (molecularly imprinted polymers (MIPs)) with tailor-made selective recognition sites [2]. Due to high specificity, low cost, ease of preparation, thermal and chemical stability, MIPs have attracted considerable interest in a variety of fields, such as chromatographic separations [3], biomimetic sensors [4], solid-phase extraction [5], drug delivery [6], and catalysis [7] etc. MIPs have artificial antibody-like recognition ability because they bear cavities that are complementary in size, shape, and chemical functions to a target molecule. However, traditional MIPs suffer from some drawbacks such as high diffusion barrier, low-rate mass transfer, low binding capacity and poor site accessibility because of their high cross-linking nature [8]. In recent years, to overcome these drawbacks, a surface imprinting technique on nanomaterials has been developed to enable the recognition sites at the surface or in the proximity of the surface [9].

It has been proved that the nanostructured MIPs own the advantages of favorable selectivity and fast association/dissociation kinetics. For example, the nanostructured materials with a large surface area and high porosity, such as nanoparticles [10,11], nanowires [12], nanotubes [13,14], nanofibers [15,16], are excellent candidates for MIPs by surface imprinting.

Recently, graphene has attracted tremendous attention since it is mechanically exfoliated and observed by Novoselov and coworkers in 2004 [17]. Its unique thermal, electronic, mechanical properties and high specific surface area endow graphene with various applications in scientific and technological fields [18]. Moreover, as the thinnest nanomaterial ever discovered, graphene shows great promise as a versatile platform for MIPs with excellent performances, such as the high binding capacity, fast binding kinetics, good accessibility to the target species, low mass-transfer resistance, and easy removal of template molecules, etc. It is because that the atomic-thick structure of graphene could make most of template molecules situate at the surface [19]. Numerous methods have been made to synthesize graphene-based MIPs (MIPs-G), including atom transfer radical polymerization [20], reversible addition fragmentation chain transfer polymerization [19], free radical polymerization (FRP) [21] and electrochemical polymerization [22]. Due to its applicable to almost all of vinyl monomers with simple operation, FRP shows obvious

\* Corresponding author. Tel./Fax: +86 21 54340046.

E-mail address: [yzxian@chem.ecnu.edu.cn](mailto:yzxian@chem.ecnu.edu.cn) (Y. Xian).

advantages in synthesis MIPs-G [23]. The applications of MIPs-G in adsorption [24], optosensing [25] and electrochemical recognition [26–30] were reported.

Aromatic amines are a class of toxic substances and represent one of the most important classes of environmental pollutants. In addition, aromatic amines have been widely used as raw materials in the manufacture of plastic tableware. Major types of aromatic amines in the plastic tableware are 4, 4-methylene diphenylamine (MDA) and aniline [31]. MDA and aniline have been identified as potential carcinogen by International Agency for Research on Cancer, and are limited to ppb levels in natural waters [32]. Therefore, it demands reliable, sensitive and rapid analytical methods for the measurement of MDA and aniline. Gas chromatography, liquid chromatography and capillary electrophoresis were reported to separate and detect aromatic amines [33–35]. These methods have the advantage of high-efficient separation, however, complicated procedure (for instance, chemical derivation) and expensive instruments are required. In view of time consuming and easy operation, there are growing needs to seek some other sensitive and rapid methods. Electrochemical method has emerged as fast and efficient tool for the analysis of aromatic amines [36,37]. However, as a disadvantage, this method has poor selectivity because of the similar structure of MDA and aniline. In this work, we describe a new strategy for simultaneous detection of MDA and aniline using MIPs-G as electrode material and the procedure is illustrated in [scheme 1](#). MDA was used as the template and adsorbed on the surface of graphene through the  $\pi$ - $\pi$  interaction [38], and 4-vinyl pyridine (4-VP) could pre-polymerize with template molecules via hydrogen bonds and van der Waals interaction [39]. After the thermal decomposition of 2, 2'-azobis (2-methylpropionitrile) (AIBN), free radicals would occur and the polymerizations begin to form MIPs-G nanocomposites. After removal of template molecules (MDA) through linear sweeping voltammetry, MIPs-G was used as electrode materials for simultaneous detection of MDA and aniline. MDA is binding preferentially at imprinting cavities and is oxidized electrochemically due to the high affinity and fast kinetics to uptake the template molecules. As for aniline, it is adsorbed on graphene via  $\pi$ - $\pi$  stacking and then electrochemically oxidized. Due to the difference on surrounding environment, the electrochemical responses of MDA and aniline at MIPs-G modified electrode can be discriminated easily.

## 2. Materials and methods

### 2.1. Reagents

Graphene (physical reduction, Nanjing XFNano Chemicals, China), MDA (99.5%, Shanghai J&K Chemicals, China). Ethylene glycol dimethacrylate (EGDMA) and 4-VP were purchased from Aldrich and were distilled under reduced pressure to remove

inhibitors. AIBN (99%) was purchased from Aladdin Chemicals (Shanghai, China). Other chemicals were purchased from Sino-pharm Chemical Reagent Company. Phosphate buffer solution (PBS) was prepared with  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ . The solutions of MDA and aniline ( $1.0 \text{ mmol L}^{-1}$ ) were made by ethanol.

### 2.2. Apparatus

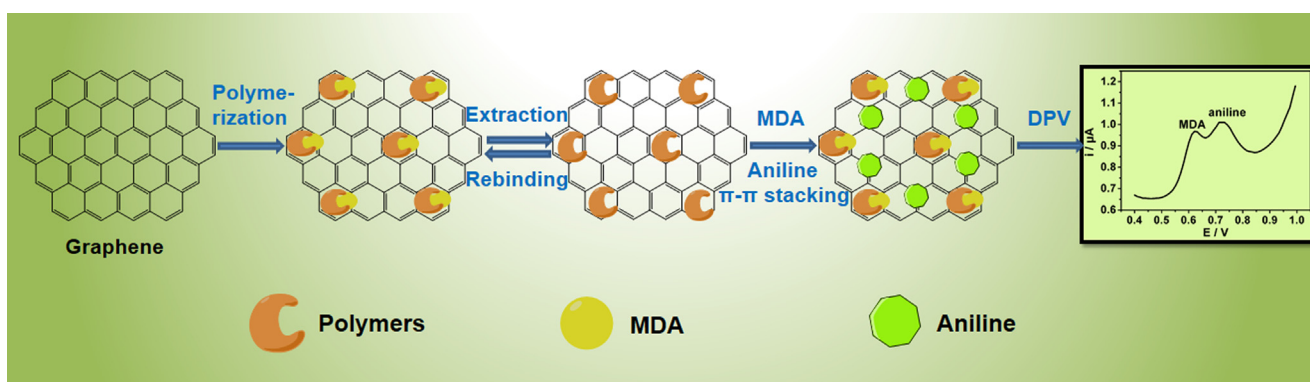
The surface morphological images were characterized by transmission electron microscope (TEM, TECNIG20, 200 KV) and scanning electron microscope (SEM, HITACHI S-4800). Fourier transform infrared (FTIR) spectra were performed on a NEXLIS FTIR (Nicolet, USA). Raman measurements were carried out using a confocal microprobe Raman system (LabRam II, Dilor, France). Thermal gravimetric analysis (TGA) was conducted on a SDTA851 TGA analyzer (Mettler Toledo, Switzerland) with temperature ranging from room temperature to  $700 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in the nitrogen flow.

Electrochemical measurements were conducted with a computer-controlled Autolab (TYPE III, Netherlands) electrochemical workstation at room temperature. A glassy carbon electrode (GCE,  $d=3 \text{ mm}$ ) or modified-GCE was used as working electrode, with a platinum wire as auxiliary electrode and a saturated calomel reference electrode (SCE).

The official method based on liquid chromatography was performed on Agilent 1200 with a diode array detection (DAD) system. The DAD monitoring wavelength was set at 240 nm. An Eclipse Plus C18 column ( $4.6 \times 250 \text{ mm}$ ,  $5 \mu\text{m}$ ) was used for separation and the injection volume was  $10 \mu\text{L}$ . The stationary phase was a mixture of water and acetonitrile (9:1, v/v) at a flow rate of  $1.0 \text{ mL min}^{-1}$ .

### 2.3. Synthesis of MIPs-G

MDA molecules were used as the template and the synthesis route of MIPs-G was described as follows. Firstly, 20 mg graphene were dispersed in 20 mL mixed solution of trichloromethane and acetonitrile (v/v, 1:3). Then, 0.2 mmol MDA was added into the solution and mixed by ultrasonic for about 30 minutes until MDA was homogeneously dispersed. After that, 0.8 mmol 4-VP, 4.0 mmol EGDMA, and 30 mg AIBN were added and the resultant mixture was stirred at  $60 \text{ }^\circ\text{C}$  for about 24 hours under the nitrogen protection. The resulting products were collected through centrifugation and washed thoroughly with methanol. Finally, the materials were dried under vacuum at  $55 \text{ }^\circ\text{C}$  for 12 hours. As controlled samples, non-imprinted polymers (NIPs-G) were also synthesized by the same protocol of MIPs-G but in the absence of MDA.



**Scheme 1.** The synthesis route for MIPs-G via FRP and the electrochemical sensing of MDA and aniline.

Download English Version:

<https://daneshyari.com/en/article/1242002>

Download Persian Version:

<https://daneshyari.com/article/1242002>

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