Biosensors and Bioelectronics 100 (2018) 341–347

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

A novel molecularly imprinted electrochemical sensor based on graphene quantum dots coated on hollow nickel nanospheres with high sensitivity and selectivity for the rapid determination of bisphenol S☆

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A R T I C L E I N F O

Keywords:
Molecularly imprinted polymers
Electrochemical sensor
Hollow nickel nanospheres
Graphene quantum dots
Bisphenol S
Electrochemical determination

A B S T R A C T

In this paper, a novel molecularly imprinted electrochemical sensor (MIECS) based on a glassy carbon electrode (GCE) modified with graphene quantum dots (GQDs) coated on hollow nickel nanospheres (hNiNS) for the rapid determination of bisphenol S (BPS) was proposed for the first time. HNiNS and GQDs as electrode modifications were used to enlarge the active area and electron-transport ability for amplifying the sensor signal, while molecularly imprinted polymer (MIP) film was electropolymerized by using pyrrole as monomer and BPS as template to detect BPS via cyclic voltammetry (CV). Scanning electron microscope (SEM), energy-dispersive spectrometry (EDS), CV and differential pulse voltammetry (DPV) were employed to characterize the fabricated sensor. Experimental conditions, such as molar ratio of monomer to template, electropolymerization cycles, pH, incubation time and elution time were optimized. The DPV response of the MIECS to BPS was obtained in the linear range from 0.1 to 50 μM with a low limit of detection (LOD) of 0.03 μM (S/N = 3) under the optimized conditions. The MIECS exhibited excellent response towards BPS with high sensitivity, selectivity, good reproducibility, and stability. In addition, the proposed MIECS was also successfully applied for the determination of BPS in the plastic samples with simple sample pretreatment.

1. Introduction

Bisphenol S, [4, 4′– sulfonyldiphenol], has been commonly used as the substitute for bisphenol A to produce polycarbonate plastic with multifarious applications such as optical, electrical, automotive, media, and electronics equipment, packaging, appliances, medical, and construction (Eladak et al., 2015). The replacement of dimethylmethylene ($C(CH_3)_2$) group of BPA by the sulfonyl (SO_2) group of BPS (Fig. S1) (Boucher et al., 2016) offers several benefits, such as higher rigidity, increased resistance to organic solvents, improved dimensional stability, and better wetting of glass reinforcements (Lotti et al., 2011; Molina-Molina et al., 2013). However, studies show that BPS retains similar estrogenic activity, shows increased environmental persistence (Mathew et al., 2014) and the ability of developing chronic diseases, including obesity, diabetes, atherosclerosis, genital malformation, hepatic disturbances, and even cancers (Helies-Toussaint et al., 2014). Up to now, the methods of detecting BPS mainly depend on chromatographic analysis like LC-ESI-MS (Yang et al., 2014), UHPLC-MS/MS (Vela-Soria et al., 2014), P-GC-MS (Becerra and Odermatt, 2012) and online-SPE-HPLC-MS/MS (Zhou et al., 2014b). Although these techniques detect BPS in the water environment with high accuracy and are based on common analytical methods, they also require complex pretreatment steps, time-consuming analysis, expensive instruments, and well-trained operators (Zhu et al., 2016). Hence, it is of great importance to find a more convenient way to detect BPS with high sensitivity and selectivity.

With high selectivity, excellent robustness, chemical stability and practicability (Kor and Zarei, 2016; Rezaei et al., 2013), the MIPs have been widely developed to recognize some particular target molecules in recent years. MIPs are typically synthesized by polymerizing functional monomers in the presence of a template molecule (Li et al., 2015a). After the template molecules are extracted from the MIPs, the MIPs forms the cavities of the specific molecule so that the MIPs can recognize the target molecule by strong chemisorption (Liu et al., 2017a). MIECS combines molecularly imprinted technique (MIT) and electrochemical sensor. It has attracted much attention and has been

☆ The authors wish it to be known that, in their opinions, Hanbing Rao and Xun Zhao should be regarded as joint First Authors.

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http://dx.doi.org/10.1016/j.bios.2017.09.016
Received 17 July 2017; Received in revised form 2 September 2017; Accepted 12 September 2017
Available online 15 September 2017
0956-5663/

widely used to detect different molecules (Rao et al., 2017; Xia et al., 2016). However, the poor conductivity and electrocatalytical activity of the MIECS leads to lower sensitivity. As a result, many efforts have been made to enhance its conductivity by using electrocatalytical nanocomposites (Liang et al., 2017; Rao et al., 2017), conductive functional monomers and functionalized conductive nanocomposites, such as pyrrole (Wang et al., 2014; Yang et al., 2016), and monomeric graphene quantum dots (Prasad et al., 2017).

Different metal nanoparticles/nanowires, such as Au, Pt, Ni nanoparticles/ nanowires (Atar et al., 2016; Beluomini et al., 2017; Lu et al., 2013b; Shervedani et al., 2014) and PtAu, AuAg bimetallic nanoparticles (Cui et al., 2015; Thanh et al., 2017; Zhang et al., 2017), have been used to enhance electrocatalytical activity of MIECS. In particular, hNiNS prepared by electrodeposition offer lower price, better electron-transfer rate, better-controlled, and easier in-situ preparation (Li et al., 2015b; Liu et al., 2017b), when compared to Ni nanoparticles (D'Addato et al., 2012) and other noble metal nanoparticles (Cui et al., 2015) that are modified on a flat electrode. For example, Liu et al. (2017b) and Li et al. (2015b) used flaked hollow nickel nanospheres and 3D nanoporous nickel skeleton as an electrode modifier to serve as the loading platform for MIPs to enhance its conductivity, which allowed to detect metronidazole and dopamine with a remarkably low detection limit.

GQDs are 0 D nanomaterial converted by 2 D graphene (Neubeck et al., 2010) under hydrothermal conditions (Wang et al., 2011). GQDs have stable luminescence, chemical stability, suitable conductivity, as well as low toxicity (Tan et al., 2016; Zhu et al., 2012a, 2012b) with diameter less than 10 nm (Roushani and Abdi, 2014). Zhao et al. (2011) and Mahmoud Roushani and Roushani and Abdi (2014) have reported that GQDs were used to fabricate the electrochemical sensor based on the strong interaction between single-stranded DNA and GQDs and combine with riboflavin as a novel type of nanocomposite for detecting persulfate, respectively.

Herein, we constructed a novel MIECS based on hNiNS coating GQDs and MIP film for BPS quantitative analysis. As shown in Scheme 1, the GQDs were coated on hNiNS were and used as electrode modifications to increase the active area, improve the conductivity, and enhance the electrochemical response for sensitively detecting BPS. The proposed sensor was constructed via electropolymerization of pyrrole in the presence of BPS template molecules onto the surface of a glassy carbon electrode modified with the hNiNS coating GQDs. After the template molecules were extracted from the MIP film, the senor could detect BPS molecules through DPV based on hydrogen bonding and π-π stacking interactions. The resulting new modified electrode showed high sensitivity, selectivity, good reproducibility, stability, and a wide detection range. Furthermore, the proposed electrochemical sensor was successfully applied to detect BPS in different plastic samples.

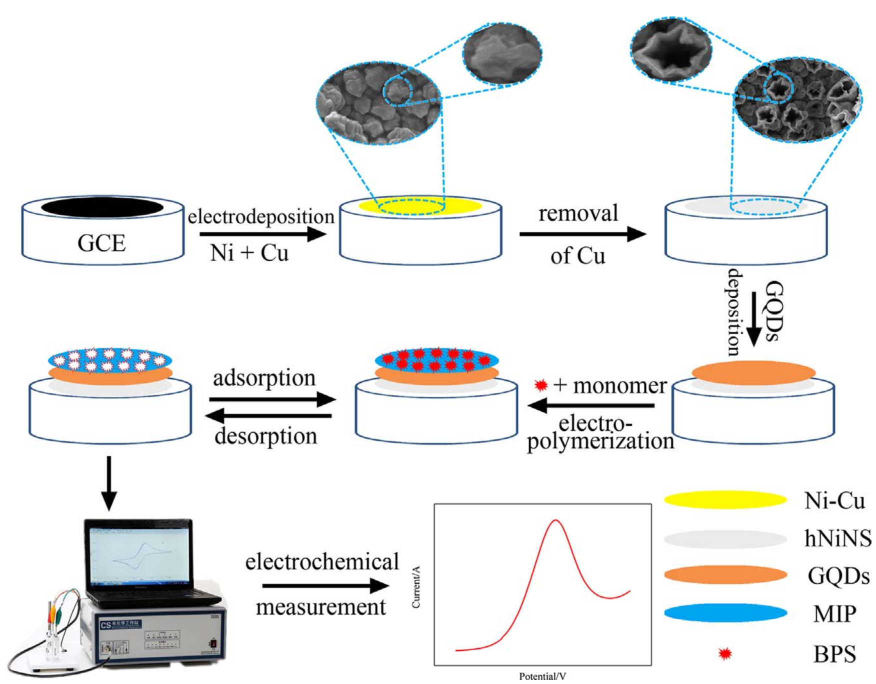
2. Experimental

All reagents and apparatus required for the experiment, and detailed experimental steps were included in the Supporting information.

3. Results and discussion

3.1. Surface characterization of the different electrodes

The surface morphologies and element distribution of different electrodes were characterized by SEM and EDS. As shown in Fig. 1**A** and Fig. S2A, the Ni-Cu alloy modified electrode is composed from small alloy blocks. According to results from EDS, the atomic ratio of Ni and Cu is close to 1:2, which can be explained by the fact that it is easier to reduce and form particles from Cu^{2+}. After dealloying Cu from the Ni-Cu alloy, the small alloy blocks were transformed into hollow nickel nanospheres (Fig. 1**B**), while the ratio of Ni to Cu was changed into 6:1 (Fig. S2B). To achieve GQDs modification, the GQD nanoparticles were coated on a uniform nanocomposite layer formed on the hNiNS/GCE (Fig. 1**C**). Fig. 1**D** and **E** respectively show the SEM images of the BPS-imprinted polypyrrole film and non-imprinted polypyrrole film on the hNiNS/GQDs/GCE. It can be seen, that the MIP film has a more porous and rougher surface than the non-imprinted polymer (NIP) film. The formed cavities after elution of organic solvent and electrochemical elution on the polypyrrole film are likely caused by the structure of target molecule, BPS. As a result, MIP film demonstrated better adsorption ability than the NIP film (Rao et al., 2017).



Scheme 1. Schematic illustration of the preparation of hNiNS/GQDs/GCE and electrochemical detection process.