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A self-probing, gate-controlled, molecularly imprinted electrochemical sensor for ultrasensitive determination of *p*-nonylphenol

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ABSTRACT

A novel self-probing, gate-controlled, molecularly imprinted electrochemical sensor for ultrasensitive and highly selective determination of *p*-nonylphenol was prepared, based on a GCE electrode modified with Au nanoparticles and multiwalled carbon nanotubes/reduced graphene oxide nanoribbons (MWCNTs@rGONRs). The molecularly imprinted film was produced using *p*-aminothiophenol as the functional monomer, *p*-nonylphenol as the template molecule and tetrabutylammonium perchlorate as the supporting electrolyte. The modified electrode had specific recognition for the template molecule and very high electrocatalytical activity for electroreduction of the target molecule. The resulting sensor has been successfully used to determine *p*-nonylphenol using cyclic voltammetry and cathodic stripping different pulse voltammetry with detection limits of 0.73 pM ($S/N = 3$) and 4.8 fM ($S/N = 3$), respectively. The method demonstrated extremely high sensitivity and selectivity as well as a wide linear range and could be used to detect *p*-nonylphenol in environmental and food samples.

1. Introduction

Phenolic endocrine disruptors have recently attracted much attention due to their significant toxicity and widespread presence in the environment [1,2]. In particular, *p*-nonylphenol (p-NP) has been widely used as a lubricating oil additive and antioxidant, among other applications [3]. However, p-NP is also a hormone which can interfere with the secretion of estrogen in the human body at the concentrations present in the environment (from pM to nM) and hence can damage the reproductive system [4]. It is therefore a matter of urgency to develop rapid, sensitive and selective techniques to detect p-NP.

Various analytical techniques, including high-performance liquid chromatography [5], liquid–liquid extraction [6], capillary electrochromatography [7], enzyme-linked immunosorbent assay [8,9], chemiluminescence [10] and colorimetry [11] have been used to detect toxic substances. However, these methods usually require complex equipment and time-consuming extraction procedures. In comparison, electrochemical methods have many advantages, including rapid operation, low consumption and high speed [12]. Molecularly imprinted polymer (MIP) electrochemical sensors, which combine molecular imprinting with an electrochemical sensor, have been widely used to determine various kinds of chemicals [13] owing to their intrinsic high sensitivity, chemical stability and selectivity. MIP sensors have two main sensing mechanisms. One is direct redox of the analyte on the electrode surface, accompanied by direct electron transfer, which usually exploits the catalytic ability of the sensor; the other is the so-called "gate-controlled effect", in which the electrode is wrapped with a non-conductive film containing cavities, and the detection process involves incubation of the electrode in analyte solution and subsequent assay in a solution containing redox probes (e.g. $Fe(CN)_6^{3-/4-}$) [14]. Sorption of the analyte inhibits transfer of the probes to the sensor surface, thereby impeding redox of the probes and reducing the redox current. In this paper, we propose a "self-probing, gate-controlled" molecularly imprinted electrochemical sensor which not only has ultrahigh sensitivity and selectivity but is also very simple, without requiring an additional redox probe.

Carbon nanotubes [15–17] and graphene [18–20] have been widely used in electrochemical sensors. Carbon nanotubes/graphene nanoribbons (CNTs@rGONRs), fabricated by partial unzipping of multiwalled carbon nanotubes (MWCNTs), combine the merits of carbon nanotubes and graphene and are promising electrochemical sensing materials due to their large surface area, good electroconductivity and high electrocatalytic activity [21,22]. Au nanoparticles (AuNPs) are also widely used as electrochemical sensing materials in chemical and biological sensing applications [23,24].

In this work, a novel electrochemical sensor for ultrasensitive and highly selective determination of p-NP based on a MIP/AuNPs/MWCNTs@rGONRs/GCE was prepared, and was then successfully used

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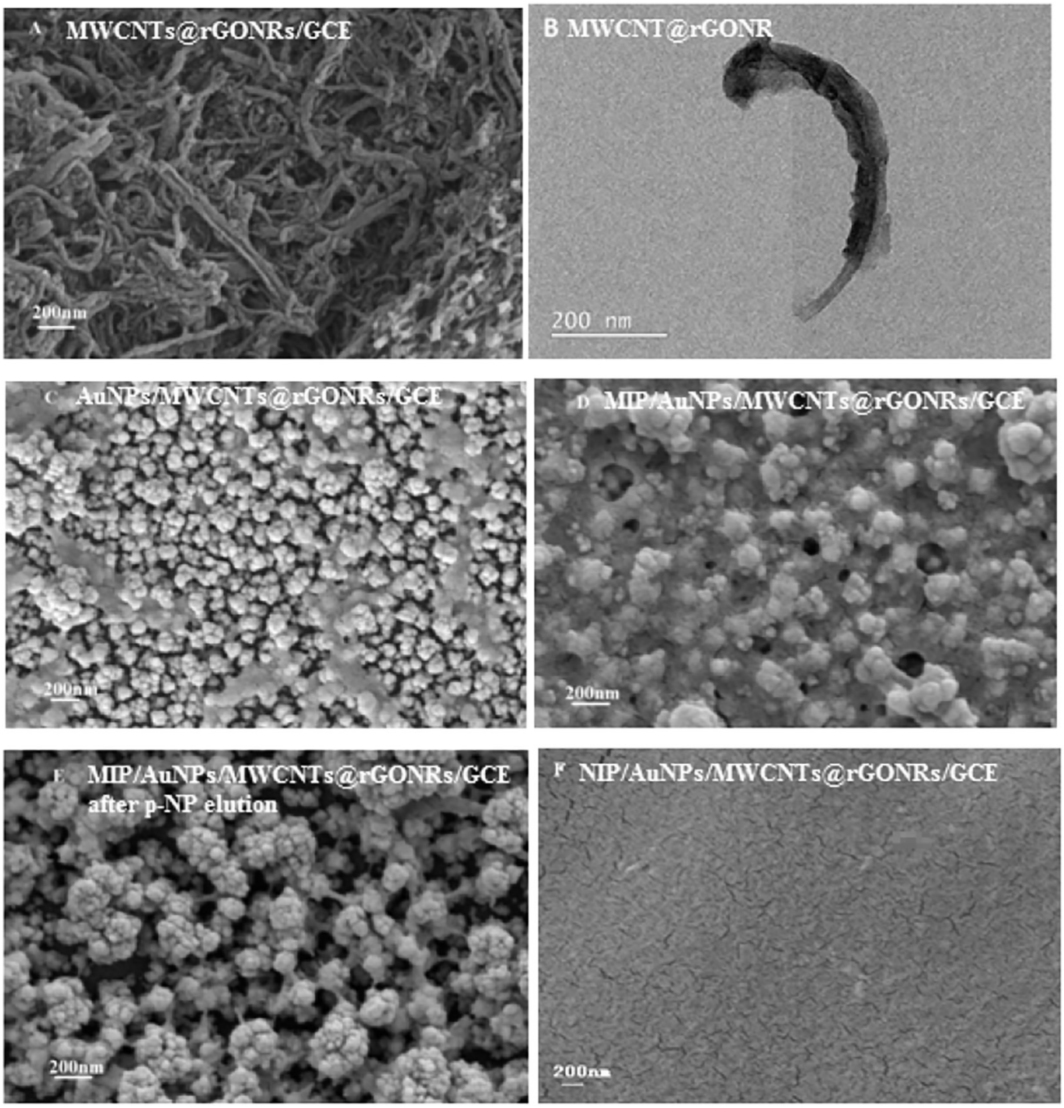

Fig. 1. (A, C–F) SEM images of different modified electrodes and (B) TEM image of a single MWCNT@rGONR.

to detect p-NP in real samples.

2. Experimental

MWCNTs@GONRs prepared using a modified version of a method reported previously [25] were reduced with hydrazine solution to obtain MWCNTs@rGONRs. A MWCNTs@rGONRs-modified GCE electrode was prepared by drop-casting with chitosan (CS) as a cross-linking agent. AuNPs were then electrochemically deposited to produce a AuNPs/MWCNTs@rGONRs/GCE. Finally, a MIP-film-modified AuNPs/MWCNTs@rGONRs/GCE was fabricated by CV scanning, using p-acetamidophenol (p-ATP) as the functional monomer, p-NP as the template agent, and tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. After electropolymerization, the MIP electrode was immersed in an ethanol/water (4:1, v/v) solution containing 0.5 M HCl for a specific time to remove the p-NP template molecules. As a control, a non-imprinted polymer (NIP) electrode, AuNPs/MWCNTs@rGONRs/GCE, was prepared using the same procedure but without the template molecule.

All electrochemical measurements were carried out using a conventional three-electrode system with the modified GCE as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode as the reference electrode.

3. Results and discussion

Fig. 1A shows that the MWCNTs@rGONRs film on GCE possesses a homogeneous network structure, with the MWCNTs showing obvious longitudinal unzipping characteristics and each tube–ribbon structure being wider than its parent MWCNT. The TEM image of a single MWCNT@rGONR (Fig. 1B) shows a tubular structure in the center with lamellae on the sides.

Fig. 1C shows that AuNPs were evenly distributed on the surface of the MWCNTs@rGONRs/GCE, effectively enhancing the specific surface area of the electrode and accelerating electron transfer. After electrochemical polymerization of p-ATP a dense and rough MIP film was formed (Fig. 1D). After the p-NP molecules had been eluted, a large number of pores appeared, suggesting that many effective recognition sites (complementary cavities) had been formed in the MIP film (Fig. 1E). However, there were no cavities imprinted on the surface of the NIP electrode (Fig. 1F).

The electrochemical properties of the different modified electrodes were studied using CV in 0.10 M KCl containing 1 mM $Fe(CN)_6{}^{3-/4-}$. Fig. 2A shows a pair of weak reversible redox peaks on the bare GCE (a). After modification with MWCNTs@rGONRs (b), the peak currents increased significantly due to the good electroconductivity of the MWCNTs@rGONRs. When AuNPs were electrodeposited onto the