



A novel electrochemical sensor based on poly(*p*-aminobenzene sulfonic acid)-reduced graphene oxide composite film for the sensitive and selective detection of levofloxacin in human urine



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ABSTRACT

To develop the sensitive and selective levofloxacin sensors with simple preparation process, the novel poly(*p*-aminobenzene sulfonic acid)-reduced graphene oxide (poly(*p*-ABSA)-rGO) composite film-based electrochemical sensor was facilely and rapidly prepared by one-step electrochemical method without the expensive and troublesome electrode modification procedure. The poly(*p*-ABSA)-rGO composite film was found to possess remarkable catalytic activity on the oxidation of levofloxacin. Electrocatalytic performance of the as-prepared sensor could be dramatically improved by optimizing the synthesis conditions of composite film. Based on the synergetic effect of organic conductive polymer poly(*p*-ABSA) and rGO, the proposed sensor exhibited excellent electrocatalytic activity of levofloxacin, high sensitivity, low detection limit (0.12 μM), wide linear range and excellent selectivity. Further, the fabricated sensor was successfully applied onto the determination of levofloxacin in real human urine samples and showed good reliability for real samples assay. Based on the simple construction process and excellent electrocatalytic performance, the proposed poly(*p*-ABSA)-rGO film-based sensor demonstrated the potential for the extensive applications on electroanalysis and bioelectrocatalysis.

1. Introduction

Levofloxacin, a member of the quinolone-type drugs, is generally used as a broad spectrum antibiotics for a variety of infections in human and animals [1]. However, the rampant use of levofloxacin frequently increases the risks of some diseases, such as tendon injury, heart disease, pseudomembranous colitis and muscle wasting [2,3]. In addition, the excessive use of levofloxacin in grazing and aquaculture has led to drug residues in food source, which may be toxic to humans. The use of levofloxacin can also cause the antimicrobial resistance of bacteria in human and animals [4]. Therefore, it is important to monitor the amount of levofloxacin in biological fluids for rational use of antibiotics as well as human health. Because levofloxacin undergoes limited metabolism and is mainly excreted through urination in the form unchanged levofloxacin [5], many reported methods were based on the determination of levofloxacin in urine, such as fluorometric method [6], high performance liquid chromatography [7–10], capillary electrophoresis [11], nuclear magnetic resonance [12,13], flow-injection spectrophotometric method [14] and chemiluminescence [15,16]. But most of methods encounter with some drawbacks, including expensive instruments, long analysis time, low sensitivity and complicated sample

pretreatment. Recently, electrochemical sensors have been widely applied on the determination of levofloxacin [17–22], due to the simple operation and equipment, low cost, short analysis time and high sensitivity [23–27]. However, it is still needed to develop the sensitive and selective sensors with simple preparation process.

With the development of nanotechnology, various nanomaterials have been widely used on analytical chemistry [28,29]. Graphene, an interesting two-dimensional carbon nanomaterial with high conductivity and catalytic activity, has been extensively applied to the development of various sensors [30–32]. In general, reduced graphene oxide (rGO) can be obtained by the chemical reduction of graphene oxide (GO), where many toxic reductants are employed and are harmful to human health and environment. Alternatively, rGO can also be prepared by electrochemical reduction of GO in mild conditions without dangerous chemicals [33]. Such rGO from electrochemical methods has shown relatively strong conducting properties and catalytic activity [34,35]. However, the conventional methods might lead to an inevitable aggregation of obtained rGO in aqueous solution and then the decrease of the effective surface area [36]. With the rapid development of organic polymer [37–42], conducting polymers have also been widely used in electrochemical sensors, due to the easy synthesis,

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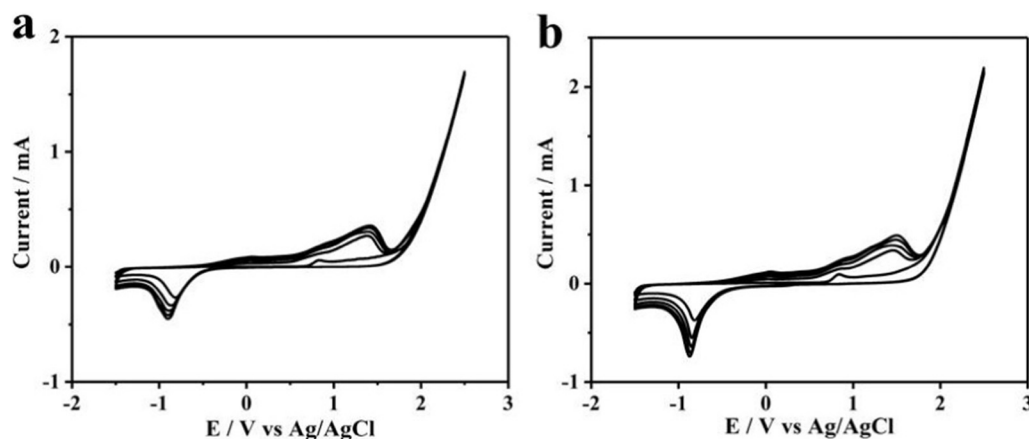


Fig. 1. Cyclic voltammograms of (a) *p*-ABSA, and (b) *p*-ABSA and GO on GCE in phosphate buffer (pH 7.0, 0.1 M) at 150 mV s⁻¹.

low cost, high environmental stability, and variable electrical conductivity [43–45]. Nowadays, the hybridization of conducting polymers with rGO is attractive for combining the advantages of both components and improving the water dispersivity of rGO [46–49]. So far, various types of conducting polymers-rGO nanocomposites have been synthesized to enhance the electrochemical activity, such as polystyrene/rGO [50], polypyrrole/rGO [51], polyaniline/rGO [52] and polyimidazole/rGO composites [53]. Among numerous conducting polymers, poly(*p*-aminobenzene sulfonic acid) (poly(*p*-ABSA)) has been widely studied, due to its excellent properties including large numbers of π - π bonds, electron-rich N atoms and high electron density [54,55]. However, there is few report about composites of rGO and poly(*p*-ABSA) for applications of electrochemical sensors [56]. In addition, reduction of GO and polymerization of *p*-ABSA were generally segregated. Therefore, it is urgent need to develop the one-step synthesis method of poly(*p*-ABSA)-rGO composite film.

Here, for the first time, a novel electrochemical levofloxacin sensor based on the poly(*p*-ABSA)-rGO composite film was rapidly fabricated by using a simple one-step strategy. Combining the advantages of both poly(*p*-ABSA) and rGO, the as-prepared sensor showed high sensitivity, low detection limit, wide linear range, excellent selectivity and good reliability in real urine samples for the detection of levofloxacin.

2. Experimental

2.1. Chemicals and materials

Levofloxacin and *p*-ABSA were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Aqueous GO dispersion (5 g L⁻¹) was purchased from Graphene supermarket (USA). All reagents were of analytical grade and were used without purification. All aqueous solutions were prepared with Milli-Q water (18.2 M Ω cm), which was obtained from a Millipore water purification system.

2.2. Fabrication of electrochemical sensors

For the fabrication of poly(*p*-ABSA)-rGO/glassy carbon electrode (GCE) electrode, the bare GCE was sequentially polished with 0.3 and 0.05 μ m Al₂O₃ slurry on a polishing cloth, sonicated in ethanol, and rinsed with water. The poly(*p*-ABSA)-rGO composite film was prepared on GCE by cyclic voltammetry (CV) between -1.5 and 2.5 V at a scan rate of 150 mV s⁻¹ for 5 cycles in phosphate buffer (pH 7.0, 0.1 M) containing 2.0 mM of *p*-ABSA and 0.1 mg mL⁻¹ GO. The control electrodes (poly(*p*-ABSA)/GCE and rGO/GCE) were prepared in the same process. Then the electrodes were rinsed by water and stored in 4 °C before use.

2.3. Apparatus and electrochemical measurements

The surface morphology of as-prepared modified electrode was observed by the scanning electron microscopy (SEM) S-4800 (Hitachi, Japan) with an accelerating voltage of 15 kV. Electrochemical experiments were carried out on a CHI660D electrochemical workstation (Chenhua Instruments Co., Shanghai, China). CV and linear sweep voltammetry (LSV) were conducted at room temperature in sodium acetate buffer (0.1 M, pH 4.5) under a conventional three-electrode system with a modified GCE as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrochemical impedance spectroscopy (EIS) was conducted in [Fe(CN)₆]^{3-/4-} solution containing 0.1 M KCl.

3. Results and discussions

3.1. Fabrication and characterization of poly(*p*-ABSA)-rGO composite film

To facilely prepared the poly(*p*-ABSA)-rGO composite film, the electropolymerization of *p*-ABSA and the electroreduction of GO were simultaneously performed by one-step electrochemical method (Fig. 1). There were nearly not observable distinction between two CV curves, but a slightly higher oxidation peak current was observed during electropolymerization of *p*-ABSA with GO, which might be attributable to π - π stacking interactions between GO and aromatic rings of *p*-ABSA.

To research the morphology and structure of poly(*p*-ABSA)/rGO film, SEM assays were conducted for the poly(*p*-ABSA)-rGO film, poly(*p*-ABSA) film and rGO film on GCE. As shown in Fig. 2, the poly(*p*-ABSA)-rGO film was flat and poly(*p*-ABSA) and rGO uniformly dispersed onto the GCE. More importantly, the proposed preparation process of poly(*p*-ABSA)-rGO/GCE sensor was simple and timesaving.

3.2. Electrocatalytic behavior of poly(*p*-ABSA)-rGO film electrode

The impedance of the modified electrode was investigated by recording EIS data of the bare GCE, poly(*p*-ABSA)-rGO/GCE and the poly(*p*-ABSA)/GCE in the solution containing [Fe(CN)₆]^{3-/4-}. As shown in Fig. 3, electron-transfer resistance (R_{et}) of the bare GCE was 23 k Ω , while poly(*p*-ABSA)/GCE showed larger R_{et} (1670 k Ω), indicating the polymer did a big impediment on the electron transfer between electrode and the redox probes in the solution. For poly(*p*-ABSA)-rGO/GCE, R_{et} obviously decreased to about 900 Ω , implying rGO was introduced into polymer membrane and remarkably improved the conductivity of the modified electrode, because of excellent conductivity of rGO.

To research the active surface area of the poly(*p*-ABSA)-rGO/GCE, CV of modified electrode was conducted in 1 mM K₃Fe(CN)₆ solution at different scan rates (Fig. 4). For the reversible process, electrical

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