An Electrochemical Sensor for Environmental Detection Based on Reduced Graphene Oxide Modified Electrodes

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***Abstract*—The increasing use and associated environmental release of consumed human and veterinary antibiotics have drawn great attention recently. A high percentage of the excreted antibiotics remains in an intact form and enters the natural aquatic systems via the effluent and sludge from wastewater treatment plants, hospitals, and livestock farms. These released antibiotics may lead to bacterial resistance proliferation, contamination or adverse impacts on non-target organisms and microbial ecosystems. Therefore, this situation has created a compelling need to develop sensitive on-site detection techniques for monitoring these antibiotics in the environment. However, delicate instrumentation and complex sample pretreatment requirement of conventional analytical techniques such as spectrophotometry, electrophoresis, and chromatography have hindered their practical applications in real time and in situ sensing task. On the other hand, electrochemical techniques have served as sensitive methods for on-site monitoring with low cost, high efficiency, and minimum sample pretreatment necessity. In the present work, an electrochemical sensor for rapid determination of sulfamethoxazole, one of the most widely used antibiotics, has been developed. Functionalized reduced graphene oxide was used to modify the electrodes owing to its high charge mobility, low background noise, and high surface area. The response was optimized in terms of pH, scan mode, and applied potential. Moreover, the modified electrodes showed great selectivity and stability, and thus collectively, renders it a promising sensor toward detecting sulfamethoxazole in the aquatic system.**

Keywords-electrochemical sensor; emerging contaminants; graphene oxide; environmental detection.

I. INTRODUCTION

Up to 95% of antibiotics could be excreted in an unchanged state from animals and humans [1]. Throughout the conventional biological wastewater treatment processes, many antibiotics such as β-lactams, sulfonamides, trimethoprim, macrolides, fluoroquinolones, and tetracyclines have been reported to remain in the final effluents and be released to the environment [2-4]. Also, treated-wastewater irrigation in arid regions has caused elevated levels of bacterial antibiotic resistance in both aquatic system and treated-wastewater-irrigated soils [1]. These released antibiotic compounds in discharge or reused wastewater have raised increasing concern, owing to their adverse impact to the aquatic environment or proliferation of resistant strains of bacteria [2]. Sulfonamides, one of the most commonly used antibiotic groups, are used for the treatment of urinary-tract infections, pneumocystis pneumonia, chronic bronchitis, meningococcal meningitis, acute otitis, toxoplasmosis, skin and soft tissue infections [5]. Sulfamethoxazole is a representative sulfonamide antibiotic and frequently found in surface water and groundwater worldwide [6, 7]. Given the wide usage of sulfamethoxazole, its real-time and in-situ detection is of great importance. A variety of analytical techniques, including chromatography, spectrophotometry, and electrophoresis, are time-consuming, expensive and pretreatment-needed. On the other hand, electrochemical techniques, which have fast response, low cost, simplicity for operation, are promising for sulfamethoxazole detection. A few studies have used electrochemical approach for determination sulfamethoxazole [5, 8-10]. Herein, we propose an electrochemical sensor for selective detection of sulfamethoxazole based on modified electrodes with functionalized reduced graphene oxide (RGO), owing to its high charge mobility, low background noise, and high surface area. Methods of sample preparation and characterization of the present work are introduced in Section II. Then we demostrate electrochemical responses of the developed sensors for sulfamethoxazole determination in Section III, and finally, we conclude in Section IV.

II. MATERIALS AND METHODS

Chemicals of the highest purity available from Sigma Aldrich (Missouri, USA) [11] and Acros Organics (New Jersey, USA) [12], unless stated otherwise, were used without further purification. Aqueous solutions were prepared in water that purified to ≥ 18.2 MΩ·cm. The pH adjustment was achieved by adding $HClO_4$ and NaOH solutions. Synthesized graphene oxide and reduced graphene oxide were characterized by UV-Vis measurements (HITACHI U-3900 spectrophotometer). The cyclic voltammetry (CV) measurements were performed on

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an electrochemical system (CH Instruments). Graphene oxide (GO) was prepared from purified natural graphite by a modified Hummers' method. Functionalized RGO, N-RGO, was prepared by reducing GO via a solvothermal reaction with ammonia solution.

III. RESULTS AND DISCUSSION

In the UV-Vis absorption spectra (Figure 1 (a)), the absorption peaks at 230 and 300 nm are assigned to the π-π transition of aromatic C=C bonds and C=O bonds, respectively. After the reduction, the absorption peak was red-shifted to 271 nm, indicating a successful GO reduction, in which the conjugated C=C bonds were restored. The electrochemical oxidation of sulfamethoxazole on the bare and modified electrode surfaces was examined, as shown in Figure 1 (b). The relative ordering of CV current has been determined to be N-RGO > bare electrode > GO. In the presence of sulfamethoxazole (50 μM), a relevant increase in the current was observed for N-RGO, as compared to bare electrode and GO modified electrode (Figure 2), implying an enhanced electrochemical response of the N-RGO modified electrode. This indicates a promising sensing feature of N-RGO toward sulfamethoxazole detection.

IV. CONCLUSIONS

In the present work, the characterization and evaluation of functionalized RGO modified electrodes for determination of sulfamethoxazole were performed. The fabricated electrode is promising as an on-site detection tool for point-of-care monitoring of sulfamethoxazole with fast-response, sensitive, and cost-effective characters.

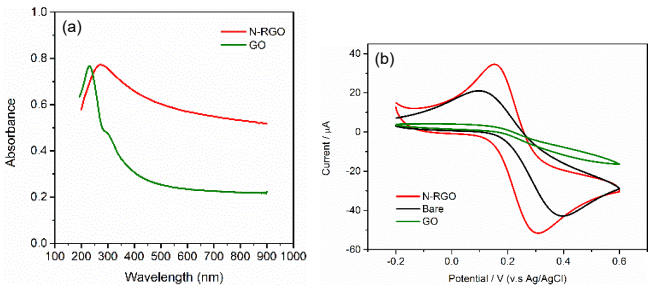

Figure 1. (a) UV-Vis spectra of GO and N-RGO, (b) Cyclic voltammograms of bare electrode, GO, and N-RGO in 0.1 M KCl solution containing 5 mM $[Fe(CN)_6]^{3-}$/ $[Fe(CN)_6]^{4-}$.

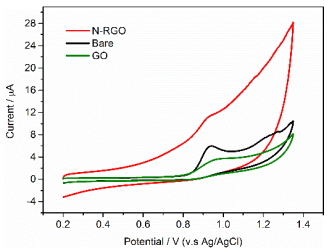

Figure 2. Cyclic voltammograms of bare electrode, GO, and N-RGO in the presence of sulfamethoxazole (50 μM).

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