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Modification of carbon paste electrode with NiO/graphene oxide nanocomposite and ionic liquids for fabrication of high sensitive voltammetric sensor on sulfamethoxazole analysis

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ABSTRACT

A high sensitive electrochemical nanostructure sensor based on NiO/graphene oxide nanocomposite-ionic liquids (1-methyl-3-butylimidazolium bromide; 1M3BIB) modified carbon paste (NiO/GO/1M3BIB/CPE) electrode has been developed for trace analysis of sulfamethoxazole (SMTZ). NiO/GO was synthesized by co-precipitation method and characterized with different methods such as scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical response was found to be linearly proportional to SMTZ concentration in the range from 0.08–550 μM with a regression coefficient of 0.9935 and a detection limit of 0.04 μM. The novel sensor has been successfully applied for the assay of SMTZ in pharmaceutical and biological samples.

1. Introduction

Antibiotics are a type of antimicrobial compounds that used in the treatment and prevention of bacterial infection. There are many antibiotics drugs in world that used for treat kind of diseases. Sulfamethoxazole (as a sulfonamide antibiotics category drugs) is a useful and usual drug in combination with trimethoprim to treat infections such as urinary tract infections, and traveler's diarrhea. The mechanism of action of sulfamethoxazole is as a Cytochrome P450 2C9 Inhibitor. The SMTZ residues in foods of animal origin may lead to thyroid cancer and some other diseases [1]. The benefits and risks of SMTZ have encouraged us to measurement of it in pharmaceutical and biological samples. In between, application of electrochemical based methods has more attention because fast response, low cost, high sensitivity and good selectivity in trace analysis [2–10].

The interest in developing electrochemical sensing devices for using in trace compound analysis in biological, pharmaceutical, environmental samples quickly growing in the recent decades [11–19]. Voltammetric sensors based on modified electrodes were used for analysis of a wide range of materials in the recent years [20–24]. Nanostructure based materials have a good conductivity for electrochemical investigation due high surface area [25–30]. Presence of this type of materials with nanoscale size can be help to increasing conductivity modified electrode [31–34]. On the other hand, ionic liquids/nanomaterials modified electrodes can be improved quality of voltammetric sensors for trace and high sensitive determination of electroactive compounds in biological and pharmaceutical samples [35–41]. Therefore, scientists used this kind of voltammetric based modified electrodes for increase the quality of electrochemical analysis in the recent years [42–48].

As yet, based on our best knowledge, no published paper has been reported on the voltammetric determination of SMTZ using ILs modified nanomaterials electrode, which is the focus of the present study. In this work, we describe a suggestion strategy for the determination of SMTZ using carbon paste electrode containing of NiO/Graphene oxide (NiO/GO) plus a room temperature ionic liquid (i.e. 1-methyl-3-butylimidazolium bromide). The proposed sensor showed good electrocatalytic and accumulative effect on SMTZ. NiO/GO/IL/CPE shows advantages in terms of sensitivity, reproducibility, and selectivity. Finally, we evaluate the analytical performance of the suggestion sensor for SMTZ determination in drug and urine samples.

2. Experimental

2.1. Chemicals and reagents

Analytical-grade ethanol, graphite powder and phosphoric acid, NaOH were obtained from Merck (Darmstadt, Germany). Sulfamethoxazole, $Ni(NO_3)_2 \cdot 6H_2O$ and paraffin were procured from Sigma-Aldrich. All solutions were prepared using double distilled water having a

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specific conductivity of 0.4–0.9 μS. A stock standard solution (0.01 M) of each SMTZ was prepared by dissolving 0.025 g of SMTZ in 10 mL of double distilled water in a volumetric flask and stored at 4 °C in the dark.

2.2. Apparatus

The voltammetric experiments were performed with a computer-controlled potentiostat/galvanostat Autolab controlled by the GPES software EcoChemie, Netherland. The three-electrode configuration was used comprising the modified carbon paste electrode, as the working electrode, a Pt wire electrode as an auxiliary electrode and an Ag/$AgCl/KCl_{sat}$ reference electrode.

2.3. Synthesis of GO/NiO/NPs

Graphene nanosheets were prepared by oxidizing graphite using Hummers' Method [49]. In the first step, 1 g of purified GO were dispersed into distilled water solution of NaOH (0.25 M; 50 mL) by ultrasonication for 45 min. The second step is the supporting of NiO/NPs on GO by a direct deposition process. In the constant magnetic stirring, the solution of Ni $(NO_3)_2 \cdot 6H_2O$ (0.25 M; 25 mL) was added drop wise to the solution of GO at 30 °C through a dropping funnel. The rate of addition of the salt solution was kept approximately at 35 mL/h. After completion of the precipitation procedure, the mixture was stirred at room temperature for 18 h, washed and filtered continually with distilled water (pH 7.0), and dried at 100 °C. The solid samples were then calcined at 400 °C for 2 h.

2.4. Sensor preparation

NiO/GO/1M3BIB/CPE was prepared by mixing of 0.2 g of 1-methyl-3-butylimidazolium bromide 1M3BIB, 0.80 g of the liquid paraffin, 0.2 g of GO/NiO/NPs, and 0.8 g of graphite powder. Then the mixture was mixed well for 70 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare NiO/GO/1M3BIB/CPE. Unmodified carbon paste electrode was prepared by hand-mixing of 1.0 g of graphite powder plus paraffin at a ratio of 70:30 (*w*/*w*) and mixed well for 75 min until a uniformly wetted paste was obtained.

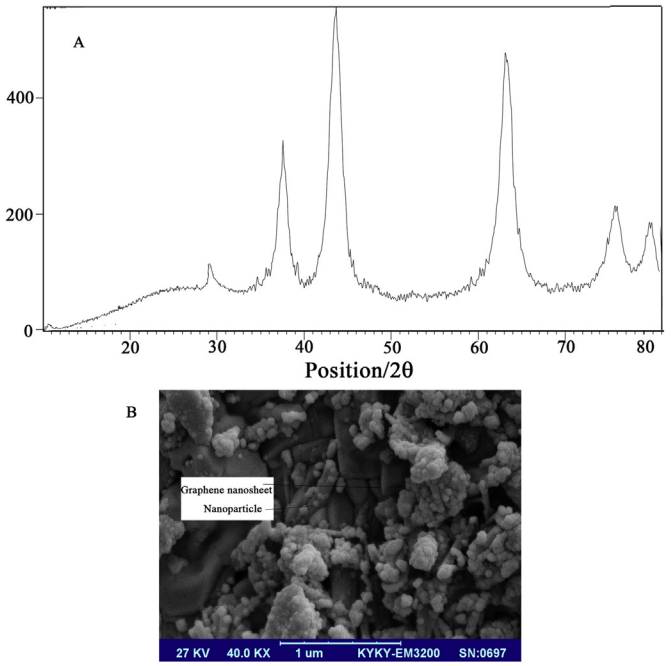

Fig. 1. XRD patterns of as-synthesized NiO/GO nanocomposite.

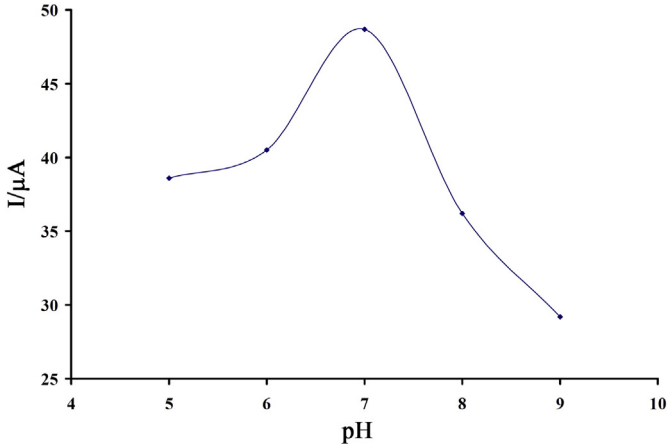

Fig. 2. Current–pH curve for electro-oxidation of 500 μM SMTZ at NiO/GO/1M3BIB/CPE with a scan rate of 100 mV s^{-1}.

2.5. Real sample preparation

Urine samples were stored in a refrigerator (at 4 °C) immediately after collection. Ten milliliters of the sample was centrifuged for 30 min at 2000 rpm. The supernatant was filtered using a 0.45 μm filter and then it was diluted 5 times with the phosphate buffer of pH 7.0.

The tablet (with different labeled name such as Cotrim and Bactrim; 400 mg SMTZ and 80 mg trimethoprim) solution was prepared by completely grinding and homogenizing seven tablets of it. Then, suitable amount of each tablet powder was accurately weighed and dissolved in 100 mL water by ultrasonication. In continuous, the mixture was filtered on an ordinary filter paper, 10 mL of which was subsequently transferred into a 50-mL volumetric flask and diluted to the mark with buffer solution (pH 7.0).

3. Result and discussion

3.1. Nanocomposite characterization

The XRD patterns of the NiO/GO showed diffraction peaks absorbed at 2θ values (Fig. 1). The prominent peaks were used to calculate the grain size via the Scherrer equation ($D = K\lambda/(\beta \cos\theta)$). The grain size of the NiO nanostructure was 18 nm, and the peaks were observed at the (111), (200), (220), (311) and (222) planes. These peaks

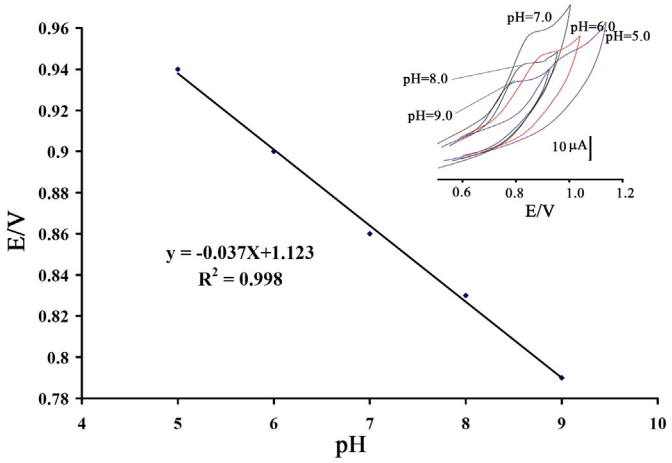

Fig. 3. Plot of potential, E, vs. pH for the electro-oxidation of 400 μM SMTZ at a surface of NiO/GO/1M3BIB/CPE. Inset: influence of pH on cyclic voltammograms of SMTZ at a surface of the modified electrode (pH 5–9, respectively).