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Nickel hydroxide nanoparticles-reduced graphene oxide nanosheets film: Layer-by-layer electrochemical preparation, characterization and rifampicin sensory application

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ABSTRACT

Electrochemical deposition, as a well-controlled synthesis procedure, has been used for subsequently layer-by-layer preparation of nickel hydroxide nanoparticle-reduced graphene oxide nanosheets (Ni$(OH)_2$–RGO) on a graphene oxide (GO) film pre-cast on a glassy carbon electrode surface. The surface morphology and nature of the nano-hybrid film (Ni$(OH)_2$–RGO) was thoroughly characterized by scanning electron and atomic force microscopy, spectroscopy and electrochemical techniques. The modified electrode appeared as an effective electro-catalytic model for analysis of rifampicin (RIF) by using linear sweep voltammetry (LSV). The prepared modified electrode exhibited a distinctly higher activity for electro-oxidation of RIF than either GO, RGO nanosheets or Ni$(OH)_2$ nanoparticles. Enhancement of peak currents is ascribed to the fast heterogeneous electron transfer kinetics that arise from the synergistic coupling between the excellent properties of RGO nanosheets (such as high density of edge plane sites, subtle electronic characteristics and attractive π–π interaction) and unique properties of metal nanoparticles. Under the optimized analysis conditions, the modified electrode showed two oxidation processes for rifampicin at potentials about 0.08 V (peak I) and 0.69 V (peak II) in buffer solution of pH 7.0 with a wide linear dynamic range of 0.006–10.0 μmol L^{-1} and 0.04–10 μmol L^{-1} with a detection limit of 4.16 nmol L^{-1} and 2.34 nmol L^{-1} considering peaks I and II as an analytical signal, respectively. The results proved the efficacy of the fabricated modified electrode for simple, low cost and highly sensitive medicine sensor well suited for the accurate determinations of trace amounts of rifampicin in the pharmaceutical and clinical preparations.

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1. Introduction

It is very important to develop simple, sensitive and accurate methods for detecting active ingredients, since drug monitoring plays an important role in drug quality control and this has a great impact on public health. Besides, development of sensing systems is the main application of nanomaterials, since they can enhance the analytical performance of such devices [1]. Graphene, the basic of carbon-based nanomaterials, is a one-atom-thick planar sheet of sp^2 bonded carbon atoms densely arranged into a 2D honeycomb crystal lattice [2–4]. Thanks to a high specific surface area (theoretically 2630 m^2/g for single-layer graphene) [5], large amounts of edge-planes/defects [6], a high electron transfer rate (15,000 $cm^2/V\,s$) [7], strong mechanical strength and both excellent thermal and electrical conductivities [8], graphene sheets are also ideal materials for electrochemical sensing and biosensing [9,10]. Graphene oxide (GO), a precursor for graphene synthesis, consists of a hexagonal ring-based carbon network having both (largely) sp^2-hybridized carbon atoms and (partly) sp^3-hybridized carbons, which bear oxygen functional groups in the form of hydroxyl and epoxy moieties on the basal plane, with smaller amounts of carboxyl, carbonyl, phenol, lactone and quinone at the sheet edges. These can be viewed as oxidized regions disrupting the extended sp^2 conjugated network of the original honeycomb-lattice structured graphene sheet [11]. Reduced graphene oxide (RGO), product of partially reduction of GO, comprises of nanometer-sized 'islands' of sp^2 graphene separated by invariably residual oxygen-functionalized groups and sp^3 bonding remaining (oxygen fraction around or below 10%), and other defects and vacancies are introduced during reduction [12]. Partial electrochemical reduction of GO provides this importunate for the electrochemist to control the optimal balance between the levels of reduction that can give a reasonable number of functional

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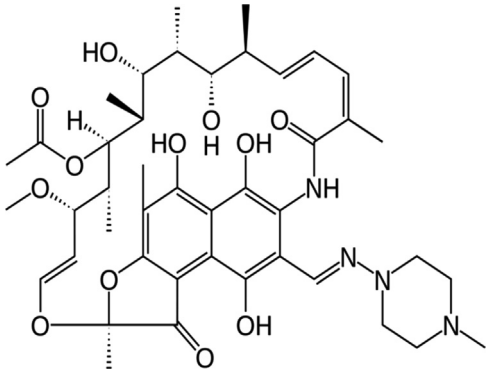

Scheme 1. Chemical structure of rifampicin (RIF).

oxygen groups and defects for electron-transfer reaction while maintaining an appropriately high level of conductivity in the RGO [13,14].

Direct electrochemical deposition of inorganic crystals especially metal nanoparticles, on highly conductive graphene-based substrates, is an attractive approach for thin film based applications, which rising nanocomposites with larger active surface areas and improved electron transport, as an ideal material for the fabrication of electrochemical sensors [14,15]. In this area, various experimental parameters including salt solution concentration, potential and time of deposition can be manipulated to control the nucleation and growth rate of the metal NPs [16].

Rifampicin (RIF), 3-[(4-methyl-1-piperazinyl) imino] methyl rifamycin (Scheme 1) belongs to the class of macrocyclic antibiotics, which contains a naphthohydroquinone ring spanned by a highly substituted aliphatic bridge, and differ from one another in the type and location of the substituent on their aromatic ring. RIF is the most important antibiotic of groups widely used in the treatment of tuberculosis, Hansen's disease (HD) and other serious infections such as HIV, which inhibits bacterial DNA-dependent RNA polymerase. Drug-monitoring in patients during anti-tuberculosis therapy is important, especially in AIDS patients, owing to a global increase in the prevalence of drug-resistant tuberculosis [17–19].

Due to its important role in numerous pathological processes, several analytical methods have been reported in the literature for the rifampicin detection [20–22]. Among these, electrochemical methods have attracted great interest because of their simplicity, rapidness and high sensitivity in detecting RIF without requiring tedious pretreatments [17–19,23–27].

In the present work, we develop a simple and versatile in situ approach for the fabrication of a nano-structured thin film (as a modifier) on the surface of a glassy carbon electrode (GCE) by coating it with a thin layer of GO and then partial electro-reduction to RGO by applying constant potential, following it with electro-deposition of $Ni(OH)_2$ nanoparticles, which is capable of forming a uniform and stable thin film on the surface of the electrode. The properties of the $Ni(OH)_2$–RGO thin film electrode were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) methods. The resulting electrochemical sensor under the optimum conditions (electro-deposition and other experimental parameters) is conveniently applied to determination of RIF with a nanomolar detection limit. Excellent features, like a low detection limit, wide linear dynamic range and high sensitivity of the modified electrode proved the successful application of this sensor for the voltammetric determination of RIF in pharmaceutical preparations and human blood serum samples.

2. Experimental

2.1. Chemicals and reagents

Graphene oxide (GO) was ordered from Graphene Supermarket (Graphene Laboratories, Inc. USA). Rifampicin (RIF) was taken kindly from Excir Daru pharmaceutical company (Tehran, Iran). All other chemicals were of analytical reagent grade from Merck. All aqueous solutions were prepared with doubly distilled deionized water. Stock solutions of RIF were freshly prepared as required in N-dimethylformamide (DMF) solution. The working solutions were prepared by diluting the stock solution with phosphate or acetate buffer solutions. In these experiments, 0.1 mol L^{-1} acetate was used for preparation of pHs 4.0 and 5.0, and 0.1 mol L^{-1} phosphate buffer solution (PBS) for pHs 3.0, 6.0, 7.0 and 8.0. Tablets of RIF (300 mg per tablet) were purchased from local pharmacies. Fresh frozen human blood serum was obtained from Iranian Blood Transfusion Organization. A 2% (v/v) of pure methanol was added to the serum sample. After vortexing each of the samples for 2 min, the precipitated proteins were separated by centrifugation for 10 min at 10,000 rpm. Then, this sample was diluted 10-fold and spiked with the different amounts of standard RIF without extraction for further treatments and applied for the recovery tests in the spiked samples. Each sample was run in triplicate and relative standard deviation (RSD) for each sample was calculated.

2.2. Apparatus

Electro-deposition of reduced graphene oxide (RGO) and $Ni(OH)_2$ nanoparticles on RGO and also voltammetric experiments were performed using a Metrohm potentiostat/galvanostat model 797 VA. A conventional three-electrode system was used with a GC working electrode (unmodified or modified), a saturated Ag/AgCl reference electrode and a Pt wire counter electrode. A digital pH/mV/ion meter (CyberScan model 2500) was used for preparation of the buffer solutions. Scanning electron microscopy (SEM) images were obtained with a VEGA\\TESCAN scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (EDS, RONTEC, QUANTAX). Atomic force microscopy (AFM) experiments were carried out in ambient condition using Veeco CP Research instrument using Si cantilever. X-ray photoelectron spectra (XPS) recorded with an Mg or Al X-ray source at the energies of 1486.6 eV or 1253.6 eV, respectively. Electrochemical impedance spectroscopy (EIS) measurements were performed with a Potentiostat/Galvanostat EG&G model 273 A (Princeton Applied Research, USA) equipped with a Frequency Response Detector model 1025 (Power Suite software), which was used with a frequency between 100 MHz and 10 kHz and a 5 mV rms sinusoidal modulation in 0.1 mol L^{-1} KCl solution containing 1 mmol L^{-1} of both $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ (1:1 mixture) at the $E_{1/2}$ of the $[Fe(CN)_6]^{3-/4-}$ (0.13 V vs. Ag/AgCl). Voltammetric experiments were carried out in buffered solutions of RIF drug that were deoxygenated by purging with pure nitrogen (99.999% from Roham Gas Company). Nitrogen gas was also flowed over the surface of the test solutions during the experiments.

2.3. Electrochemical preparation of modified electrode

The stable GO aqueous solution was achieved by dispersion of 2.0 mg portion of the GO in 2.0 mL H_2O and homogenized ultrasonically for 5 min. Compared to other insoluble carbon nanostructures like RGO and carbon nanotubes, the negative electrostatic repulsion from ionized carboxylic and phenolic groups of GO made it much easier in applying for electrode coating and modification. Before the modification, the GCE was polished with 0.1 mm alumina slurry on a polishing cloth, rinsed thoroughly with water, sonicated

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