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Enhancement of the electrochemical behavior of CuO nanoleaves on MWCNTs/GC composite film modified electrode for determination of norfloxacin

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ABSTRACT

A novel and facile (single-step) method was developed for the synthesis of CuO nanoleaves in the presence of a cationic polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA) at pH 10.5. The mechanism and self-assembly for the formation of CuO nanoleaves are discussed. The structure and morphology of CuO nanoleaves are characterized by means of Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopic (TEM) studies. The CuO/MWCNTs modified glassy carbon (GC) electrode was fabricated via the drop-casting of CuO nanoleaves suspension on MWCNTs/GC surface. In order to investigate the electrochemical behavior of norfloxacin, cyclic voltammetry (CV) and differential pulse voltammetric analysis (DPV) were carried out and compare the oxidation behavior on CuO/MWCNTs/GC, MWCNTs/GC and bare GC. The electrocatalytic oxidation of norfloxacin was studied (pH 7.2) on CuO/MWCNTs/GC electrode and found an irreversible behavior in the range from 0 to +1.1 V with an oxidation peak at 0.91 V in physiological conditions. The quantitative detection of norfloxacin was obtained with a limit of detection of 3.21×10^{-7} M within a linear range from 1 μM to 47.7 μM.

1. Introduction

Norfloxacin [1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinolonecarboxylic acid] belongs to fluoroquinolone class of synthetic antibiotics which exhibits broad activity against gram-negative bacteria and marginal activity against gram-positive bacteria [1]. Norfloxacin is used effectively in both human and veterinary therapeutic medicines for the treatment of a wide variety of diseases caused by urinary, respiratory and gastrointestinal tract infections [2,3]. Norfloxacin has been associated with rare cases of sensory or sensorimotor axonal polyneuropathy resulting in paresthesias, hypoesthesias, dysesthesias, and weakness [4]. In clinical trials, norfloxacin related adverse effects have been minimal, while these effects were mild and included disturbances of the gastrointestinal tract and in the central nervous system resulting in tremors, restlessness, nervousness, hallucinations, paranoia, depression, insomnia, and rarely suicidal thoughts or acts [5]. The most commonly reported side effects include nausea, vomiting, anorexia, dizziness, headache, drowsiness, depression, and a bitter taste in the mouth [6]. Therefore, it is necessary to develop a sensitive analytical method for the determination of norfloxacin in biological samples and in pharmaceutical formulations. There have been numerous techniques reported in the literature such as UV–vis spectrophotometry [7], spectrofluoriometry [8], HPLC [9], capillary electrophoresis [10] and electro chemiluminescence [11] for the determination of norfloxacin. However, in many such techniques certain disadvantages include: time consuming, tedious sample pretreatment and involvement of expensive reagents are subject to interferences. To overcome these disadvantages, there is a need for fast sensitive and cost effective method for the successful determination of pharmaceutical drugs arises.

In this context, electrochemical methods have received considerable interest because of the high sensitivity, selectivity and their ability to minimize the interferences. The electrochemical oxidation of norfloxacin usually involves a large overpotential at the surface of the bare electrodes, and therefore, the determination of norfloxacin tends to suffer interferences from other oxidizable compounds. In order to circumvent these interferences, chemically modified electrodes have attracted immense importance because of fast electron rate transfer, decrease in overpotential with minimal surface fouling and reduce the overpotential of the oxidizing species. Recently, Ghoneim et al. [12] investigated the electrochemical behavior of norfloxacin on GC electrode at its oxidation peak, +0.95 V. Goyal et al. [13] reported the electrochemical oxidation of norfloxacin on edge plane and basal plane pyrolytic graphite electrode with oxidation peak at +0.95 V. Xie et al. [14] have recently reported a poly(methyl red) film modified GC for the oxidation

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of norfloxacin at +1.12 V, which is attributed to the overlapping of interfering species on the bare electrodes. To overcome these difficulties, electrodes modified with nanocomposites have been explored [15,16]. Among the most promising designs, those involving the fabrication of carbon nanotubes along with metal oxide nanoparticles are especially exhibit remarkable electrocatalytic properties by enhancing the electrode conductivity, facilitating the electron transfer and the anti-fouling capability reduce the overpotential at the modified electrode [17,18].

Recently, considerable efforts have been developed toward the synthesis of CuO nanoparticles to enhance their existing applications in batteries [19], gas sensors [20], magnetic storage media [21], solar cells [22] and biosensors [23]. The synthesis of CuO nanostructures with well-defined shapes and sizes (nanorods, nanowires, nanotubes, nanosheets, nanowhiskers, nanoshuttles, nanoneedles and nanoleaves) by a simple and inexpensive route remains a great challenge [24]. There are numerous methods reported in the literature for the synthesis of CuO nanoleaves. Xu et al. [25] reported a transition process for the synthesis of 2D CuO nanoleaves from 1D $Cu(OH)_2$ nanowires, Xiang and coworkers [26] were reported the self-assembled synthesis of various hierarchical CuO morphologies at various pH values. Recently, Zhao et al. [27] synthesized 2D CuO nanoleaves using surfactant in aqueous medium at room temperature. Even though, there is a need for the development of a facile and desirable method for the synthesis of CuO nanostructures. In this context, PDDA stabilized nanostructures (can act as both stabilizing and reducing agent) have significant advantage such as single step, low temperature and cost effective method for the synthesis of desired nanostructures compared to other methods reported. Metallic Cu nanoparticles are not enough stable for the electrochemical determination because it can be easily oxidized in aqueous medium. Herein, the modification of an electrode by CuO nanostructures is an essential way to enhance the selectivity and sensitivity of the electrochemical method [28]. To the best of our knowledge, the study involving the fabrication of copper oxide nanostructures modified electrode for electrochemical determination of norfloxacin are not reported in literature.

Therefore, in this paper considerable effort has been taken toward the fabrication of PDDA stabilized CuO nanoleaves incorporated MWCNTs/GC nanocomposite film modified electrode for electrochemical oxidation of norfloxacin. The methods of cyclic voltammetry and differential pulse voltammetry of the CuO/MWCNTs/GC modified electrode for the electrochemical determination of norfloxacin are described. The obtained CuO/MWCNTs/GC modified electrode exhibits excellent electrochemical activity for the determination of norfloxacin.

2. Experimental procedure

2.1. Chemicals and reagents

Poly(diallyldimethyl)ammonium chloride (PDDA) ($M_w = 5000$–20,000, 25 wt% in water), copper chloride ($CuCl_2$) anhydrous, multiwalled carbon nanotubes (MWCNTs), and sodium hydroxide (NaOH) pellets were purchased from Sigma–Aldrich. Phosphate buffer (0.1 M, pH 7.2) solution (PBS) prepared with Na_2HPO_4 and NaH_2PO_4 were used as supporting electrolyte. All chemicals and reagents used in the experiments were of analytical grade and used without further purification. All the solutions were prepared by using double distilled water.

2.1.1. Tablet sample preparation

Five tablets (400 mg norfloxacin per tablet, obtained from local drug store) of norfloxacin pharmaceutical formulation were accurately weighed and finely ground in a mortar until a fine and homogeneous powder resulted. The powdered tablets were dispersed in 100 mL standard flask with 0.1 M hydrochloric acid (HCl). The content of the mixture was sonicated for 10 min until most of the sample get dissolved and centrifuged at 6000 rpm for 10 min and filtered using Whatmann filter paper. The resulted solution was further diluted to the required concentrations.

2.1.2. Instrumentation analysis

All the electrochemical measurements were performed on PGSTAT-12 electrochemical workstation, (AUTOLAB, The Netherlands BV). The measurements were based on a three electrode system, with a glassy carbon (GC) electrode of geometric area (0.07 cm^2), being used as a working electrode, a Pt wire in the form of a spiral with high geometrical surface area (~20 cm^2) was used as a counter electrode and saturated calomel electrode (SCE) as the reference electrode. Prior to each experiments GC surface was polished with increasingly finer grade alumina powders (1, 0.3 and 0.05 μm) down to mirror polish, sonicated for about 15 min in double distilled (DD) water, degreased with acetone and washed with copious amount of DD water. All the solutions were purged with analar grade nitrogen for atleast 30 min prior to each electrochemical measurement and a nitrogen environment was maintained throughout the experiments.

The UV–vis spectrum was procured using Perkin-Elmer (Lambda 650) UV-Visible diffuse-reflectance spectrophotometer, using barium sulfate as reference. FT-IR spectra were recorded for pure PDDA and PDDA stabilized CuO nanoleaves as KBr pellets using BRUKER (TENSOR 27) in the region 4000–400 cm^{-1} with the resolution of 4 cm^{-1}. The morphology of the CuO nanoleaves was observed by utilizing a TECNAI-G^2 (model T-30) S-twin high resolution transmission electron microscope (HRTEM) operated at an accelerating voltage of 300 kV. Field emission scanning electron microscopy (FESEM) images were obtained using a Hitachi SU6600. X-ray diffraction (XRD) results were collected by using BRUKER D8 advance X-ray diffractometer with monochromatic Cu Kα radiation ($\lambda = 1.5418$ Å). The X-ray photoelectron spectroscopy (XPS) was performed using an OMICRON Nanotechnology, Germany. Interpretation of electrochemical impedance spectroscopy (EIS) measurements were analyzed by fitting the experimental impedance spectra to the theoretical model represented by an equivalent electric circuit using AUTOLAB PGSTAT12 (Eco chemie, B.V., The Netherlands) controlled by Frequency Response Analyzer (FRA 4.9) software. The electrochemical impedance spectra were recorded in the frequency range from 1 MHz to 1 Hz, at the formal potential of the $[Fe(CN)_6]^{3-/4-}$ redox couple. The R_{ct} values are calculated using curve fitting analysis. The peak potential for cyclic voltammogramm was obtained from PGSTAT12 (Eco chemie, B.V., The Netherlands) Potentiostat/Galvanostat controlled by General Purpose Electrochemical System (GPES 4.9) software.

2.2. Synthesis of CuO nanoleaves

In a typical method for the preparation of CuO nanoleaves, an appropriate amount of PDDA solution was mixed with ethanol/water (4:6, v/v) and then 1 mL of 0.01 M $CuCl_2$ was added dropwise into the solution with a molar ratio of 10:1. The pH of the reaction mixture was adjusted to 10.5 by adding an aqueous solution of 0.1 M NaOH. The reaction was then heated to about 60 °C for 1 h under nitrogen atmosphere. The color of the solution changed from yellowish to dark brown indicating the formation of CuO nanostructures. Finally, the dark brown precipitate was separated by centrifugation, washed with ethanol and DD water and dried at 60 °C.