Measurement 127 (2018) 175–186

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Fabrication of high performance disposable screen printed electrochemical sensor for ciprofloxacin sensing in biological samples

Kasarla Ramakrushna Reddy[a], Pradeep Kumar Brahman[a,*], Lakkavarapu Suresh[a,b]

[a] Electroanalytical Lab, Department of Chemistry, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Guntur, Andhra Pradesh 522502, India
[b] Department of Biotechnology, Koneru Lakshmaiah Education Foundation, Vaddeswaram, Guntur, Andhra Pradesh 522502, India

ARTICLE INFO

Keywords:
Gold nanoparticles
Ciprofloxacin
Cyclic voltammetry
Nanocomposite
Electrochemical sensing

ABSTRACT

In this paper, we report a facile one step electrochemical method to synthesize a highly sensitive nanocomposite film based on gold nanoparticles (AuNPs) and chitosan (CHI) polymer on disposable screen printed electrode (SPE). We have demonstrated that AuNP/CHI composite film based fabricated sensor exhibited distinctly higher electrochemical behavior towards oxidation of ciprofloxacin (CF) due to excellent conducting properties of the gold metal nanoparticles incorporated in chitosan matrix. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and square wave voltammetry (SWV) were used for electrochemical characterization of modified electrodes. Morphological characterization was carried out by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). AuNP/CHI/SPE sensor displayed excellent conductive properties for CF oxidation with higher oxidation current, which enabled us to employ AuNP/CHI/SPE as an electrochemical sensor for CF detection. Electrochemical parameters were optimized and kinetic parameters at AuNP/CHI/SPE were also explored. CF showed good linearity at proposed sensor over the range of 0.1–150 μM with detection limit of 0.001 μM. Further, fabricated sensor showed good stability, selectivity and sensitivity. Finally sensor was successfully employed for CF determination in biological samples.

1. Introduction

Quinolones are synthetic antimicrobial agents widely used against both gram-positive and gram-negative bacteria. They can prevent DNA replication by inhibiting the action of bacterial DNA gyrase enzymes [1]. Ciprofloxacin (CF) is one of the most routinely prescribed fluoroquinolones owing to its broad-spectrum antimicrobial activity and is widely administered to humans and livestock [2,3]. Unlike other antibiotics CF can be induced by both parenteral and oral mode. It has tendency to get absorbed and distributed throughout fluids and tissues easily. This drug is being applied to cure various infectious diseases such as urinary tract, respiratory tract and gastrointestinal tract, skin and soft tissue infections [4].

During the past two decades scientists have paid extensive attention towards the sensitive detection and recognition of chemical and biological molecules [5–10]. For sensitive detection electrochemical sensors have become versatile tool owing to their notable detection sensitivity, selectivity, stability and excellent repeatability [11–16]. The designing and development of novel electrochemical sensors have opened new channels and promising approaches in the field of electrochemistry. However, lot of research work is still needed to make electrochemical sensors as real and trust worthy detection tools. Over the past two decades modified electrodes have been used as sensor for the electrochemical determination of various electroactive molecules [17–23]. Modification of electrodes to achieve high sensitivity, selectivity and compatibility requires extensive study. Excellent performance of modified electrodes/sensors depends upon various modifiers such as conducting polymers, carbon materials, metal nanoparticles and redox mediators.

Chitosan (CHI) is a biopolymer derived from chitin containing one amino group and two hydroxyl groups which makes it to be used as a modifier [24]. Chitosan is one of the cationic polymers and has a various potential applications such as in treatment of waste water, drug delivery, biomedical sciences, pharmaceuticals, cosmetics and food science [11]. It also has several useful properties in biosensor fabrication such as, biocompatibility, good adsorption tendency, easy thin film formation of electrode surface and enough mechanical strength. CHI does not exhibit electrical conductivity hence it is generally combined with conducting materials like, carbon nanotubes, graphene, conducting polymers, redox mediators (ferrocene, hydroquinine, methylene blue etc.) and metal nanoparticles to enhance its properties for sensing applications [24–28]. Modified electrodes based on metal

* Corresponding author.
E-mail address: drpkt@kluniversity.in (P.K. Brahman).

https://doi.org/10.1016/j.measurement.2018.05.078
Received 2 January 2018; Received in revised form 22 May 2018; Accepted 23 May 2018
Available online 24 May 2018

nanoparticles (MNPs) exhibit enormous utility in the analysis of electroactive species due to their extreme catalytic tendency, controlled diffusion process, high surface area, high sensitivity and selectivity. Among all metal nanoparticles, gold nanoparticles (AuNPs) have been used extensively in the modification of electrodes in past two decades. Literature reveals that synthesis of AuNPs is very simple and they have excellent adsorption and catalytic character [29–31].

Analysis of drugs has attracted extensive attention since it is important aspect of pharmaceutical industries. Presently CF is determined in biological fluids and pharmaceuticals using conventional methods such as high-performance liquid chromatography (HPLC) [32,33], spectrophotometry [34], spectrofluorimetry [35] and chemiluminescence method [36] etc. Most of these methods require tedious and time consuming steps, costly columns, high purity solvents, sophisticated labs, skilled person and analysis involves complicated pretreatment steps to carry out experiments. Since CF is electroactive molecule therefore it can be determined by electroanalytical techniques. Electroanalytical techniques are an immersing analytical tool for qualitative and quantitative determination of various electroactive molecules in the field of pharmaceuticals and environmental monitoring [37–40]. Their wide range applications are attributed to comparatively cheap instrumentation, reasonable accuracy, high sensitivity, low cost, rapidity and low detection limit for the analysis of several molecules [41–43]. There are few reports available in the literature for the determination of CF using electrochemical methods. Such as Garbellini et al. [44] determined CP using boron doped diamond electrode with the linearity range of 0.5–60 μM and detection limit of 0.44 μM. Gayen et al. [45] fabricated an electrochemical sensor employing multi-walled carbon nanotubes dispersed in a porous nafion film on to a boron-doped diamond electrode for the determination of CP in waste water. The presented analytical curve was linear in two different ranges 0.005–0.05 μM and 0.05–10 μM, with limit of detection value of 0.005 μM. Zhang et al. [46] reported voltammetric determination of CP using poly(alizarin red)-graphene composite film modified glassy carbon electrode. The obtained linear curve was in the range of 0.04 to10 μM with LOD value of 0.01 μM. Shan et al. [47] proposed CdS quantum dots modified glassy carbon electrode for the determination of CP in biological fluids. The presented analytical curve was linear in the concentration range from 0.1 to 10 μM with LOD value of 0.022 μM. Ensafi et al. [48] presented $MgFe_2O_4$-MWCNTs modified glassy carbon electrode as electrochemical sensing of CP. The obtained analytical curve presented a linear concentration range of 0.1–1000 μM with a LOD value of 0.01 μM. Kingsley et al. [49] developed an adsorptive stripping differential pulse voltammetry employing copper zinc ferrite nanoparticles modified carbon paste electrode for the determination of CP in the presence of paracetamol. The developed method was found linear in the concentration rage of 0.91–4700 μM with LOD value of 0.0026 μM. In general most of these sensors/electrodes are suffering with low sensitivity and selectivity. Most of these sensors involve glassy carbon electrode as substrate for deposition of modifiers to fabricate sensors which involves polishing and cleaning procedures. In addition to this, these papers involve different synthesis procedures to prepare nonomaterials and eventually modified electrodes which lead to use of various solvents/chemicals. Most of the reported electrodes are based on non disposable electrodes and therefore limit their applicability for onsite detection of CP. In the present work, we propose disposable screen printed electrode modified with AuNPs and CHI composite film based sensor for the analysis of CF in biological samples using very simple procedure. Firstly CHI was manually drop casted on SPE and then AuNPs were electrodeposited on CHI modified SPE without any reducing agents. The whole process took 40 min to fabricate electrochemical sensor. The proposed sensor showed excellent conductivity, good electrochemical behavior, wide concentration range, high selectivity and sensitivity, large electrode surface area and excellent adsorbing character. To the best our knowledge this is the first report for CF determination using AuNP/CHI/SPE electrode.

2. Experimental part

2.1. Apparatus

The electrochemical (voltammetric, square wave voltammetric, chronocoulometric and impedance) experiments were carried out using Metrohm Autolab Potentiostat/Galvanostat electrochemical system (Model No. 204) with NOVA software. A working electrode (modified and unmodified screen printed electrode), auxiliary electrode (platinum wire) and reference electrode (Silver-Silver Chloride) combined in three electrode system was used to perform all electrochemical experiments. The pH of test samples was recorded using systronic-362 μpH meter.

2.2. Chemicals and reagents

Authentic ciprofloxacin was procured from Himedia Pvt. Ltd, Vijayawada, India. A standard solution of 1×10^{-3} M was made by dissolving the substance in distilled water and kept at low temperature when not in use. Screen printed electrodes were purchased from Sinsil International Pvt. Ltd Hyderabad, India. Biological samples (serum, plasma and urine) were arranged from local Pathology Lab, Vijayawada, India. $HAuCl_4$ and chitosan were purchased from Himedia Pvt. Ltd, Vijayawada, India. All substances required for supporting electrolytes preparation i.e. *ortho*-phosphoric acid, disodium hydrogen phosphate, sodium dihydrogen phosphate, tris-HCl, acetic acid, boric acid, sodium acetate, sulfuric acid and sodium hydroxide were of analytical reagent grade (Himedia Pvt. Ltd. Vijayawada, India). 0.1 M phosphate buffer solution was prepared by mixing calculated amount of disodium hydrogen phosphate and sodium dihydrogen phosphate with distilled water. To prepare acetate buffer solutions, successive additions of 0.2 M acetic acid and 0.2 M sodium acetate were made with water. Tris-HCl buffer solutions were prepared by dissolving tris-HCl in water and pH was adjusted by adding dilute HCl and NaOH. To prepare Britton-Robinson buffer solutions, 0.04 M H_3BO_3, 0.04 M CH_3COOH and 0.04 M H_3PO_4 solutions were mixed and titrated with 0.2 M NaOH to get desired pH. The interfering substances such as vitamin-C, $CaCl_2$, KCl, NaCl, uric acid, paracetamol, epinephrine, dopamine and $MgCl_2$ were of analytical reagent grade. The concentration of stock solutions of interfering agents was 1.0×10^{-4} M.

2.3. Designing of electrochemical sensor

0.5% CHI solution was prepared by adding 50 mg of CHI in 10 ml of 1% CH_3COOH and sonicated for complete dissolution. pH of CHI solution was maintained 4–5 by adding dilute NaOH solution [50]. 0.2 mM $HAuCl_4$ precursor solution of was prepared with the help of distilled water. Fabrication of AuNP/CHI/SPE sensor was done two steps. In the first step 5 μL CHI solution (optimized volume) was manually casted on pretreated SPE surface and allowed to air dry at room temperature for 30 min and the electrode was named as CHI/SPE. In second step, CHI/SPE was immersed in deoxygenated precursor solution of 0.2 mM gold containing 0.5 M H_2SO_4. AuNPs were electrochemically deposited [51–53] by performing five successive voltammetric cycles between −1.5 and 0.5 V at 30 mV s^{-1} scan rate. Bright red electrode surface was noticed after electrodeposition confirming the deposition of AuNPs. Finally, AuNP/CHI/SPE was washed with distilled water and subjected for five CV cycles (0.4–1.2 V) in phosphate buffer (pH 5.5) to obtain constant peak response. AuNP/SPE was also prepared for comparison using same method. The whole process of sensor fabrication is depicted in Scheme 1.