



Gold nanoparticle/multi-walled carbon nanotube modified glassy carbon electrode as a sensitive voltammetric sensor for the determination of diclofenac sodium



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ABSTRACT

A simple and highly sensitive sensor for the determination of diclofenac sodium based on gold nanoparticle/multi-walled carbon nanotube modified glassy carbon electrode is reported. Scanning electron microscopy along with energy dispersive X-ray spectroscopy, electrochemical impedance spectroscopy, cyclic voltammetry and square wave voltammetry was used to characterize the nanostructure and performance of the sensor and the results were compared with those obtained at the multi-walled carbon nanotube modified glassy carbon electrode and bare glassy carbon electrode. Under the optimized experimental conditions diclofenac sodium gave linear response over the range of 0.03–200 $\mu\text{mol L}^{-1}$. The lower detection limits were found to be 0.02 $\mu\text{mol L}^{-1}$. The effect of common interferences on the current response of DS was investigated. The practical application of the modified electrode was demonstrated by measuring the concentration of diclofenac sodium in urine and pharmaceutical samples. This revealed that the gold nanoparticle/multiwalled carbon nanotube modified glassy carbon electrode shows excellent analytical performance for the determination of diclofenac sodium in terms of a very low detection limit, high sensitivity, very good accuracy, repeatability and reproducibility.

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1. Introduction

Diclofenac sodium (sodium [*o*-(2,6-dichloroanilino) phenyl] acetate, DS) is a non-steroidal anti-inflammatory drug (NSAID) with strong antipyretic, analgesic and anti-inflammatory properties (Fig. 1). DS is well absorbed after oral administration with extensive hepatic metabolism. This compound exhibits a terminal half-life of 1–2 h, volume of distribution of 0.17 l/kg, and 99% protein binding and enters the synovial fluid. The determination of small amounts of DS in pharmaceutical preparations is very important for medical and pharmaceutical needs where it is used for the treatment of various diseases. Therefore it is vital to develop a simple, fast, selective and cost-effective method for the determination of the trace amounts of DS in different pharmaceutical formulations [1–3].

In recent years, chemically modified electrodes have attracted large interest due to their potential applications in various analyses [4–7]. Carbon-based nanostructures such as carbon nanofibers, carbon nanotubes (CNTs), and mesoporous carbons have been extensively used in fabrication of modified electrodes for applications in both analytical electrochemistry and industrial electrochemistry, because in addition to their low price, they exhibit suitable electrocatalytic activity for a

variety of redox reactions, a broad potential window, and relatively inert electrochemistry [8]. One of the most important applications of these materials is the early electrochemical detection of cancer by effective and applicable biosensors in clinical diagnostics and public health protection [9]. Carbon nanotubes (CNTs) have become the subject of intense investigation since their discovery. Such considerable interest reflects the unique behavior of CNTs, including their remarkable electrical, chemical, mechanical and structural properties. CNT can display metallic, semiconducting and superconducting electron transport, possess a hollow core suitable for storing guest molecules and have the largest elastic modulus of any known material. The unique properties of carbon nanotubes make them extremely attractive for the task of chemical sensors, in general and electrochemical detection, in particular [10–13].

Gold nanoparticles (AuNPs), with large surface area, stability, good biocompatibility, high conductivity and electro-catalysis characteristics, have been used to improve the sensitivity and the detection limit in electrochemical studies. They are also suitable for many surface immobilization mechanisms and can act as tiny conduction centers and can facilitate the transfer of the electrons [14–18].

In view of the prominence of DS in clinical applications, various efforts have been made for the determination of DS, including gas chromatography–mass spectrometry [19,20], liquid chromatography [21–23], liquid chromatography–tandem mass spectrometry [24], spectrophotometry [25–29], colorimetry [30], spectrofluorimetry [31], and voltammetry [32–43] in biological fluids.

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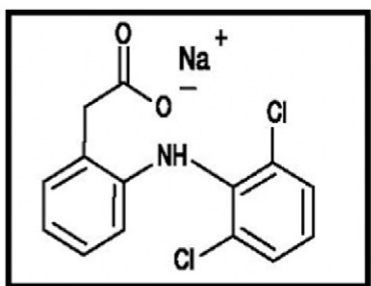


Fig. 1. Chemical structure of diclofenac sodium.

Spectrophotometry entails extensive sample preparation by chemical reaction or extraction. Gas chromatography demands extraction and derivatization prior to separation and detection [41]. These methods are time consuming and/or expensive and often need the pretreatment step. Also, some of them suffer from low sensitivity and selectivity in the corresponding determinations. To overcome these defects, electrochemical methods are used extensively for the elegant and sensitive properties such as selectivity, reproducibility, low cost and simplicity of this approach [4,44–46].

Electrochemical methods have confirmed to be highly sensitive for the analysis of drugs in pharmaceutical formulations and also in human body fluids. On the other hand, electrochemical techniques are simple and versatile due to their advantages such as cheap instrumentation, quick response time, high sensitivity and wide linearity [41,43].

In the current study, gold nanoparticle/multiwalled carbon nanotube modified glassy carbon electrode (AuNP/MWCNT/GCE) was used for the determination of DS. The electrochemical behaviors of DS at the AuNP/MWCNT/GCE were investigated using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. The experimental results indicated that AuNP/MWCNT hybrid exhibits remarkable ability to increase the electroactive surface area and enhances the electron-transfer between the electrode and the analyte. Finally, to evaluate the utility of the modified electrode for analytical applications, it was used for the voltammetric determination of DS in real samples such as commercial tablets and urine samples. We developed a method that is simple, rapid, selective, and sensitive for the determination of DS in real samples.

2. Experimental

2.1. Chemicals

DS, acidic solution of HAuCl_4 and the other reagents were obtained from Merck Company (Darmstadt, Germany) and used as received. Multiwalled carbon nanotubes (10–20 nm in diameter, length of 30 μm , purity of 95%) were purchased from Neutrino Company (Iran). All the chemical reagents used were of analytical grade. A $1.0 \times 10^{-3} \text{ mol L}^{-1}$ DS solution was prepared daily by dissolving 0.0318 g DS in water and the solution was diluted to 100 mL with water in a 100-mL volumetric flask. The solution was kept in a refrigerator at 4 °C and in the dark. More dilute solutions were prepared by serial dilution with water. A phosphate buffer solution (PBS) of pH 4.0 served as the supporting electrolyte solution. The pharmaceutical sample, DS tablet (25.0 mg, Rouz Darou Company, Iran), was obtained from local drug stores. All the solutions were prepared with double distilled water (DDW).

2.2. Apparatus

Voltammetric systems were conducted using a Metrohm model 797 VA Computrac polarograph. All the reagents used were of analytical grade. Three-electrode cell systems were used to monitor the cyclic

and square-wave voltammograms. An Ag/AgCl/KCl (3.0 mol L^{-1}) electrode, a platinum wire and an AuNP/MWCNT/GCE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm Model 827 pH lab (Herisau, Switzerland) pH-meter with a combined glass electrode was used for pH measurements. Double distilled water (DDW) was used throughout. The electrode prepared was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

2.3. Electrode preparation

A bare GCE was polished successively with 0.3 μm Al_2O_3 water slurry using a polishing cloth and it was rinsed with doubly distilled water, sonicated subsequently in a 1:1 aqueous HNO_3 solution, acetone, and doubly distilled water each for 10 min. The freshly cleaned GCE was electrochemically activated in a $1.0 \mu\text{mol L}^{-1}$ H_2SO_4 solution at a scan rate of 100 mV s^{-1} using 20 times cyclic potential sweeps in the range of -0.6 to 2.0 V . The fabrication of MWCNT is described as follows. The MWCNT suspension was prepared by dispersing 1.0 mg MWCNTs in 5.0 mL 3:1:1 (v/v) mixture of DDW, ethanol and sodium dodecyl sulfate (SDS) under sonication for 30 min. A 10.0 μL aliquot of black suspension was dropped directly onto the clean GCE surface and dried at room temperature to form a MWCNT film at the GCE surface and prepare a MWCNT-modified GCE (MWCNT/GCE) [4]. The formation of AuNPs on the MWCNT/GCE was carried out by cyclic voltammetry scanning from 0.7 V to 0.0 V, vs. Ag/AgCl, in 0.1 mol L^{-1} KCl and 2.0 mol L^{-1} HCl solution containing 250 mg L^{-1} HAuCl_4 at a scan rate of 50 mV s^{-1} for 15 cycles. The obtained electrode was marked as AuNP/MWCNT/GCE. The modified electrode was taken out and rinsed with water. Through changing the cycle number in the electrodeposition process, the amount and the size of the deposited AuNPs can be controlled. Because the size of the nanoparticles significantly influenced the catalytic efficiency [47], 15 cycles was chosen as the optimum cycle number in the gold electrodeposition process.

2.4. Pharmaceutical sample solution preparation

Five tablets of the DS were finely powdered in a mortar with pestle. Calculated amounts of the tablets required for DS were separately transferred into a 50 mL volumetric flask and were dissolved in PBS of pH 4.0. The content of the flask was sonicated for 5 min to affect complete dissolution. Finally the solutions were filtered and suitable aliquot of the clear filtrate was collected and stored in the refrigerator for further uses.

2.5. Urine sample preparation

Urine sample was obtained from apparently healthy volunteer and then stored in a refrigerator at 4 °C immediately after collection. A 25.0 mL of sample was centrifuged for 15 min at 2500 rpm. The supernatant was filtered twice using a filter and then diluted with PBS (pH 4.0) in 100 mL volumetric flask. The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment.

3. Results and discussion

3.1. Characterization of AuNP/MWCNT/GCE

For the characterization of surface morphology of AuNP/MWCNT/GCE a scanning electron microscope was employed. Fig. 2 shows the SEM images for MWCNT (Fig. 2A (a)) and AuNPs at the MWCNT film surface (Fig. 2A (b)). Fig. 2A (a) shows that MWCNTs were dispersed on the electrode without aggregation with special three dimensional structures and smooth surface. The SEM image for AuNPs (Fig. 2A (b)) shows a network-like structure of MWCNTs that metallic gold nanoparticles are located over the surface of it. The AuNPs were homogeneously distributed with an average size of about below 50 nm. Moreover, the

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