



Amperometric sensing of anti-HIV drug zidovudine on Ag nanofilm-multiwalled carbon nanotubes modified glassy carbon electrode

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ABSTRACT

The zidovudine (ZDV) is the first drug approved for the treatment of HIV virus infection. The detection and determination of this drug are very importance in human serum because of its undesirable effects. A new ZDV sensor was fabricated on the basis of nanocomposite of silver nanofilm (Ag-NF) and multiwalled carbon nanotubes (MWCNTs) immobilized on glassy carbon electrode (GCE). The modified electrodes were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), cyclic voltammetry (CV), and linear sweep voltammetry (LSV) techniques. Results showed that the electrodeposited silver has a nanofilm structure and further electrochemical studies showed that the prepared nanocomposite has high electrocatalytic activity and is appropriate for using in sensors. The amperometric technique under optimal conditions is used for the determination of ZDV ranging from 0.1 to 400 ppm (0.37 μM –1.5 mM) with a low detection limit of 0.04 ppm (0.15 μM) ($S/N = 3$) and good sensitivity. The prepared sensor possessed accurate and rapid response to ZDV and shows an average recovery of 98.6% in real samples.

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1. Introduction

The properties of sensors and biosensors can be improved by using nano dimension materials [1–4]. Carbon nanotubes, a new class of nanomaterial which has been discovered in 1991 by Iijima [5], have been widely employed in sensors and biosensors due to its unique mechanical, chemical and electrical properties [6,7]. Nonetheless, the MWCNTs tend to bundle up due to strong van der Waals interactions between tubes and hydrophobic interactions in aqueous solutions [8]. Consequently usage of these materials in electrochemical applications is confined because: 1) imperfect interface with electrolytes in aqueous solutions and 2) defective interaction between the MWCNTs as substrate and the deposited metals as catalysts. Therefore, it is necessary to convert hydrophobic nature of the MWCNTs in to hydrophilic nature and separate MWCNTs from the tight bundles to get a homogeneous mixture and take advantage of their unique properties. The hydrophilicity of MWCNTs can be improved by using surfactants [9] or acid treatment methods [10,11]. These methods have some disadvantages such as increase impurity of MWCNTs due to adsorption of surfactants on the surface of MWCNTs and consequently decrease their conductivity. Also, the improvement of the hydrophilicity of MWCNTs with acid treatment typically involves the use of a strong oxidizing agent along

with a high temperature and a long time that significantly increase cost of modification process [12]. As a new method, the hydrophobic nature of the MWCNTs can be converted into hydrophilic nature by a simple solid-phase mechanochemical reaction at room temperature [13–15]. This method produces modified MWCNTs with multiple hydroxyl groups that not only improve water solubility of MWCNTs but also provide active surfaces for depositions of metals onto MWCNT surfaces.

The large surface area and high electric conductivity of MWCNT made it possible to load metallic nanostructures with high catalytic activity as a new application of MWCNTs in sensors and biosensors [16,17]. Fabricating MWCNT-supported nanostructures is desirable not only because the MWCNTs can improve the electrical and mechanical properties of composites but also because the composites possess the properties of individual components with a synergistic effect [4] that may be helpful in widening the applications. During recent years, silver nanostructures have received much attention in electrochemical sensors due to their good biocompatibility and excellent chemical, electrical and electrocatalytic properties [18–23]. These properties and large surface-to-volume ratio will be used in generating an intense signal when analyte molecules interact with silver nanostructures [15]. Several approaches including physical deposition [24], chemical reduction [2], colloidal method [1], and electrochemical reduction [25] have been used to prepare MWCNT–metal nanocomposite. Among them, electrochemical methods are simple, fast, and effective techniques for depositing desired metal nanostructures on the MWCNTs without

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using protecting agents, reducing agents, or precursor complexes, which may decrease catalytic performance of deposited nanostructures.

Zidovudine ([1-[(2*R*,4*S*,5*S*)-4-azido-5-(hydroxymethyl)oxolan-2-yl]-5-methylpyrimidine-2,4-dione], Fig. 1 shows the structure of ZDV) is the first drug approved for the treatment of HIV virus infection [26,27]. However, the detection and determination of ZDV are of outstanding importance because of its undesirable effects above 10 μ M serum concentrations in human [28]. Many methods have been developed for the determination of ZDV, including chromatography [29], fluorescence polarization immunoassay [30], fluorescence spectroscopy [31] and voltammetry [32,33]. Among these methods, electrochemical techniques are considerably interesting due to their fast response, inexpensive cost, and high sensitivity.

To our knowledge, the utilization of electrodeposition technique for deposition of Ag nanofilm on MWCNT modified GCE and their electrocatalytic behavior toward ZDV has never been reported. Therefore, in this paper we utilized an electrodeposition technique as a suitable method for controlling electrodeposition of Ag nanofilm on MWCNT/GCE surface by adjusting the electrodeposition parameters, which exhibited well-defined electrocatalytic activity toward ZDV detection and determination.

2. Experimental

2.1. Materials

Zidovudine was purchased from Bakhtar Bioshimi (www.bbpharmaco.com, Iran). MWCNTs were purchased from Neutrino (www.neunano.com, Iran). All other reagents were of analytical grade from Merck (Germany). Phosphate buffer solutions (PBS) (0.1 M) were prepared from H_3PO_4 , KH_2PO_4 and K_2HPO_4 and pH values were adjusted with HCl and KOH solutions. The solutions were prepared with deionized water and deoxygenated by bubbling high purity (99.99%) nitrogen gas through them for 15 min prior to the experiments. All experiments were carried out at room temperature (25 ± 0.1 °C).

2.2. Apparatus and procedures

Electrochemical experiments were performed with a computer-controlled μ -Autolab modular electrochemical system (PGSTAT101, the Netherlands, www.ecochemie.nl/), driven with NOVA Software (upgrade 1.7). A conventional three-electrode cell was used with an Ag/AgCl, sat. KCl as reference electrode, a platinum plate as counter electrode and GC (2 mm diameter, Azar electrode Co., Iran) as working electrode (all from Azar Electrode Co., Iran). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) images were obtained using a VEGA TESCAN SEM. X-ray powder diffraction

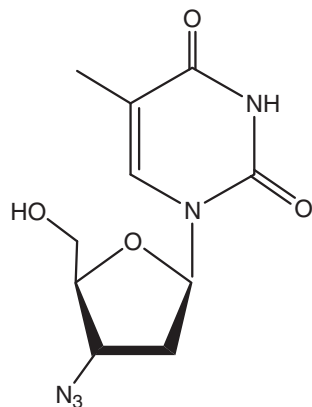


Fig. 1. Chemical structure of ZDV.

pattern of the samples was collected by an X-ray diffractometer Itai Structures model APD2000 with applying Cu K α radiation wavelength ($\lambda = 0.15405$ nm).

2.3. Dispersion and modification of MWCNTs

Based on a solid-state mechanochemical reaction [15], the hydrophobic nature of the MWCNTs converted into hydrophilic nature and MWCNTs separate from the tight bundles to get a homogeneous mixture and take advantage of their unique properties. Typically, 5 mg of MWCNTs and 100 mg of potassium hydroxide were ground together for 1.5 h into a ruby mortar. The mixture was dissolved in 10 mL deionized water, centrifuged, and dried in an oven for 1 h at 60 °C. Then, the dried mixture was ground again with 100 mg of KOH into a ruby mortar for 1.5 extra hours. Finally, the reaction mixture was dissolved in 10 mL of deionized water and precipitated many times into methanol for complete removal of potassium hydroxide. The obtained MWCNTs were redispersed in 10 mL absolute ethanol and ultrasonicated for 3 h to get a homogeneously solution (0.5 mg/mL) with multiple hydroxyl groups modified MWCNTs (M-MWCNTs) that is stable over 1 months.

2.4. Modification of GCE with MWCNTs

The GCE was carefully polished with alumina powder (0.05 μ m) on a polishing cloth placed in ethanol and sonicated to remove adsorbed particles. Coating of MWCNTs on the electrode surface was done (with optimal condition we obtained previously [15]) by carefully dropping 35 μ L of homogeneously dispersed MWCNT-ethanol solution (0.5 mg/mL) on the electrode surface from the microsyringe. Then, the electrode was dried in air to form a MWCNT film on the electrode surface. The GC electrode modified by pure MWCNT and M-MWCNT solutions called MWCNT/GCE and M-MWCNT/GCE, respectively.

2.5. Electrodeposition of silver nanofilm on M-MWCNT/GCE

The potentiostatic technique was used for electrodeposition of Ag-NF on the M-MWCNT/GC electrode from a deaerated KNO_3 solution (0.1 M) containing 0.2 mM $AgNO_3$. The electrodeposition was done in stirring solution at a potential of -0.2 V (vs. Ag/AgCl sat. KCl) for 60 s. For comparison, a film of silver with bulk structure (Ag-bulk) by the same method electrodeposited on the M-MWCNT/GC electrode from 5.0 mM $AgNO_3$ solution, at a potential of -0.25 V for 120 s. The prepared electrodes were thoroughly washed with deionized water and dried before use.

3. Results and discussion

3.1. Properties of modified MWCNTs (M-MWCNTs)

The hydrophilic nature of modified MWCNTs was studied in Fig. 2. For comparison, pure MWCNTs were dispersed in various solvents such as ethanol, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) with 3 h ultrasonication (0.5 mg/mL). Then the solutions were centrifuged at 3500 rpm for 15 min, and after 24 h imaging of samples was performed. Result showed that the dispersed MWCNTs in THF (Fig. 2c) and DMSO (Fig. 2d) were completely separated from the solutions after centrifuge. For pure MWCNTs immersed in ethanol, centrifuge causes most of the solids to be deposited and only leaving a very small amount in the supernatant. Furthermore, the solids remaining in the supernatant eventually agglomerate if allowed standing for a longer time (Fig. 2b, 24 h after centrifuge). The most stable and uniformly dispersed suspension was obtained when the MWCNTs were modified with hydroxyl groups by mechanochemical reaction and dispersed in ethanol. For this solution when the suspension was centrifuged, a very large amount of finely dispersed MWCNTs was still remained in the

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