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Silver nanoparticles/multi walled carbon nanotubes nanocomposite modified electrode: Voltammetric determination of clonazepam

Biuck Habibi*, Mojtaba Jahanbakhshi

Electroanalytical Chemistry Laboratory, Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, Tabriz, 53714-161, Iran

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ABSTRACT

In the present study, a new, simple and highly sensitive electrochemical method is developed for the determination of clonazepam (CZP) based on a silver nanoparticles/multi walled carbon nanotubes nanocomposite modified glassy carbon electrode (AgNPs/MWCNTs/GCE). Cyclic voltammetry and differential pulse voltammetry (DPV) methods were used for the electrochemical studies and measurements. The obtained results show that the AgNPs/MWCNTs/GCE exhibits high electrocatalytic activity toward the reduction of CZP. During the electrochemical reduction of CZP, an irreversible cathodic peak appears at about -0.61 V vs. silver/silver chloride electrode. The DPV measurements confirmed that the reduction peak currents increased linearly with CZP concentration in the range of 5.0×10^{-8} - 2.5×10^{-6} M with a detection limit of 6.0×10^{-9} M. The stability, reproducibility and repeatability of the nanocomposite modified electrode were checked and the obtained relative standard deviations showed that the AgNPs/MWCNTs/GCE had excellent stability, reproducibility and repeatability. Finally, the nanocomposite modified electrode was effectively applied for the determination of CZP in some real samples without any interference.

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1. Introduction

Clonazepam (CZP) [5-(2-Chlorophenyl)-1, 3-dihydro-7-nitro-2H-1, 4-benzodiazepin-2-one] is a member of the benzodiazepine series of drugs, having various properties [1] such as anxiolytic, anticonvulsant, sedative, muscle relaxant, and hypnotic. It is classified as a high potency nitro-benzodiazepine and is sometimes used as a second-line treatment of epilepsy to prevent seizures or intravenous infusions in status epilepticus [2] and neonatal convulsions [3] and is useful in various types of attacks in both children and adults [4]. CZP has now become recognized in the area of drug-facilitated sexual assaults [5] and is available in tablets containing 0.5, 1.0, and 2 mg CZP [6]. CZP, like as all benzodiazepines, is also a benzodiazepine receptor agonist [7,8].

One third of individuals treated with CZP or other benzodiazepines for longer times than four weeks develop a dependence on the drug and experience a withdrawal syndrome upon dose reduction [9]. On the other hand, the use of CZP in long term treatment is inhibited by its ability to induce tolerance to the anticonvulsant effects [10]. So that CZP should be quantified in plasma and serum blood in order to monitor compliance in those receiving the drug therapeutically, to confirm the diagnosis in potential poisoning victims and or to assist in the forensic investigation in the case of fatal overdosage. Consequently, because of the healing importance and extensive use of CZP, a rapid, sensitive and selective analytical method is necessary for the biopharmacological, clinical and toxicological studies and determination. Several analytical methods such as spectrophotometry [11–13], liquid chromatography [14–17], gas chromatography [18] and chemiluminescence [19] have been reported for the analysis of CZP. Most of spectrophotometric and chromatographic methods usually suffer from either extensive sample preparation involving extractions [20] and long-time analysis [21] or expensive equipment [22], so they are not suitable for routine works; nevertheless, the electrochemical methods are very simple, highly sensitive, highly selective and less expensive in comparison to the above mentioned methods [23–39]. Hence, it is desirable to develop a simple, sensitive and precise electrochemical method for the determination of CZP. So far, very few literature reports are available for the electrochemical determination of CZP. Vinh et al. [40] reported the determination of CZP in drug formulations by dc polarography. Salem et al. [41] studied the use of solid contact ion-selective electrodes for potentiometric determination of diazepam, bromazepam and CZP. Correia dos Santos et al. [42] reported the square-wave voltammetric techniques for the determination of psychoactive 1, 4- benzodiazepine drugs (CZP, bromazepam, midazolam, diazepam, medazepam, and flurazepam) at hanging mercury drop electrodes. De Carvalho et al. [43] studied the use of a voltammetric method for determination of 1, 4-benzodiazepines (CZP, flurazepam, alprazolam, midazolam, medazepam, chlordiazepoxide, and diazepam) in the presence of

* Corresponding author. Tel.: +98 412 4327541, fax: +98 412 4327541.
E-mail address: B.Habibi@azaruniv.edu (B. Habibi).

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amfepramone by the use of a hanging mercury drop electrode. Reddy et al. [44] reported the electrochemical study and polarographic assay of CZP formulations. It should be noted that, the reduction of CZP at the mercury drop electrode requires high overpotential which consequences poor reproducibility, low selectivity and sensitivity. Recently Doménech-Carbó et al. [45] have studied the use of the voltammetry of microparticles, a solid-state electrochemical technique, for determination of benzozodiazepinic anxiolytics (CZP, flurazepam, alprazolam, midazolam, medazepam, chlordiazepoxide, diazepam) and Deliberto et al. [46] reported the electrochemical behavior of nitro derivative drugs such as the CZP, nitrazepam, and nimesulide on the glassy carbon electrode modified by poly (benzyl viologen).

In the past decades, there has been increasing interest in the use of carbon nanotubes (CNTs) as the heterogeneous catalyst supports. Multi walled carbon nanotubes (MWCNTs) possess unique properties such as high chemical stability, good electrical conductivity, tubular structure, high surface-to-volume ratio, strong adsorptive ability and electrocatalytic properties [47,48]. MWCNTs with metal nanoparticles are particularly attractive due to the special properties of metal nanoparticles. Studies have been shown that metal nanoparticles supported on the MWCNTs may provide much improved electrocatalytic activity [49]. Among the metal nanoparticles, silver nanoparticles (AgNPs) have been attracted considerable interest because they not only have common characteristics of noble metal nanoparticles but also have high catalytic activity [50–52]. Therefore, in order to take full advantage of the two kinds of nanomaterials (MWCNTs and AgNPs), it is desirable to create the AgNPs/MWCNTs nanocomposite, so that the individual properties of each material can be integrated and the interactions between the two components may bring out novel properties. Herein, we used the functionalized MWCNTs as a template to synthesize of the AgNPs/MWCNTs nanocomposite and for the first time we applied the obtained nanocomposite modified electrode, silver nanoparticles/multi walled carbon nanotubes modified glassy carbon electrode (GCE), to the study of the voltammetric behavior and determination of CZP. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods were used to the electrochemical studies and the measurements of CZP. The stability, reproducibility and repeatability of the nanocomposite modified electrode were checked and then it was effectively applied for determination of CZP in some real samples without any interference.

2. Experimental

2.1. Chemicals

MWCNTs with 95% purity (10-20 nm) and 1 μm length were purchased from Nanolab (Brighton, MA, USA). Clonazepam was obtained from Zahravi pharmaceutical Co. (Tabriz, Iran). $AgNO_3$ and other reagents were purchased from Merck and Fluka and used without any further purification. Phosphate buffer solutions (0.1 M) of different pH values were prepared from stock solutions of 0.1 M H_3PO_4, NaH_2PO_4, Na_2HPO_4 and NaOH. Doubly distilled water was used throughout the experiments.

2.2. Apparatus

The electrochemical experiments were performed on an AUTOLAB PGSTAT-100 (potentiostat/galvanostat) (Metrohm Co., Holland). Three-electrode system was used with a silver/silver chloride electrode [Ag/AgCl/KCl (3.0 M)] (Azar Electrode Co., Iran), a platinum wire electrode (Azar Electrode Co., Iran) and the AgNPs/MWCNTs/GCE respectively as reference, counter and working electrode. Scanning electron microscopy (SEM) images were obtained by using JSM-6700F field emission SEM (JEOL Ltd., Japan). X-ray Diffraction (XRD) was studied using a Brucker AXF (D8 Advance) (Brucker Co., Germany) X-ray power diffractometer with a Cu K_α radiation source ($\lambda = 0.154056$ nm) which was generated at 40 kV and 35 mA.

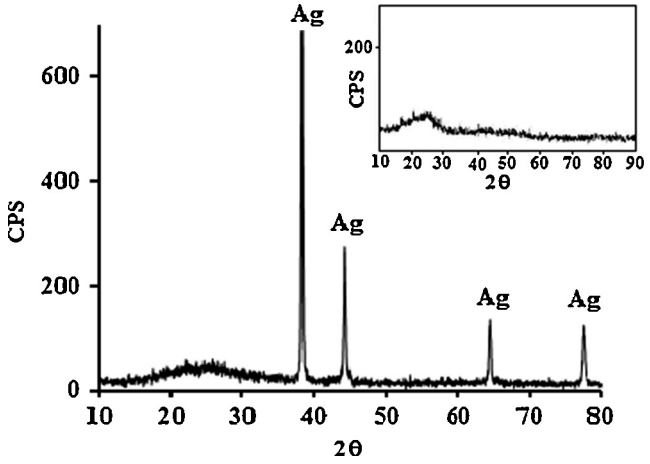

Fig. 1. XRD pattern of the AgNPs/MWCNTs and the MWCNTs (inset).

2.3. Preparation of the nanocomposite modified electrode

2.3.1. Synthesis of AgNPs/MWCNTs nanocomposite

MWCNTs were dissolved in the mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v), and refluxed for about 5 h to obtain carboxylated MWCNTs. The resulted MWCNTs was separated by centrifugation (6000 rpm) and washed with double distilled water until the pH of the resulted MWCNTs solution became neutral. Then the AgNPs/MWCNTs were synthesized by the process which was reported in literature and our previous work [53,54]. In brief, the functionalized MWCNTs (1.0 mg mL^{-1}) in a flask were dispersed in an ultrasonic bath (40 kHz) for about 3 min and then the $AgNO_3$ solution (0.01 M) was added drop wise while the content of the flask was stirred by a magnetic stirrer. After 20 h, the AgNPs/MWCNTs which were synthesized without any additional reducing reagent were collected by centrifuging. The XRD experiment was used to confirm the presence of the AgNPs in the obtained nanocomposite. Fig. 1 shows the XRD results for the MWCNTs and the AgNPs/MWCNTs nanocomposite. In the range of 30-80° (2θ), except for some small noise like peaks and one main peak corresponding to the element carbon, there is no peak appeared in the pattern of the MWCNTs (inset of Fig. 1), whereas four-peaks position at corresponding values of 38.8, 45.1, 64.5 and 78.0° appear for the AgNPs/MWCNTs nanocomposite, in which the diffraction peaks of the metallic AgNPs correspond to the cubic structure Ag (111), (200), (220) and (311) planes, respectively. Thus, it is confirmed that the AgNPs have been decorated onto the surface of MWCNTs and their average crystal size was calculated about 25 nm by using Scherrer's equation. Scheme 1

2.3.2. Preparation of AgNPs/MWCNTs/GCE

First, the GCE was polished by the 0.05 μm alumina slurry on a polishing cloth, rinsed carefully with water and sonicated in water for 3 min. Then 5 μL of AgNPs/MWCNTs nanocomposite suspension was cast on the freshly polished GCE surface and dried in the room temperature to remove solvent. After that the nanocomposite modified electrode was washed and used as the working electrode for the voltammetric study and for the determination of CZP in 0.1 M phosphate buffer solution (PBS) (pH 7.0).