



# Impedimetric and stripping voltammetric determination of methamphetamine at gold nanoparticles-multiwalled carbon nanotubes modified screen printed electrode



Banafsheh Rafiee<sup>a</sup>, Ali Reza Fakhari<sup>b,\*</sup>, Mohammad Ghaffarzadeh<sup>c</sup>

<sup>a</sup> Department of Chemistry, Shahr-e-Qods Branch, Islamic Azad University, Tehran, Islamic Republic of Iran

<sup>b</sup> Department of Pure Chemistry, Faculty of Chemistry, Shahid Beheshti University, G.C., P.O. Box 19839-4716, Evin, Tehran, 1983969411, Islamic Republic of Iran

<sup>c</sup> Chemistry and Chemical Engineering Research Center of Iran, PO Box 14335-186, Tehran, Islamic Republic of Iran

## ARTICLE INFO

### Article history:

Received 30 December 2014

Received in revised form 26 March 2015

Accepted 30 March 2015

Available online 11 April 2015

### Keywords:

Methamphetamine

Impedimetric sensor

Anodic stripping voltammetry

Gold nanoparticles

Screen printed electrode

MWCNTs

## ABSTRACT

A high performance electrochemical sensor for the detection of methamphetamine (MA) at the gold nanoparticle (GNP)/multiwalled carbon nanotube (MWCNT)-Nafion (Nf) modified screen printed electrode (SPE) is reported. Gold nanoparticles were electrodeposited on the substrate using a constant potential. Energy dispersive X-ray (EDX) spectrum and mapping and also scanning electron microscopy (SEM) results showed that GNPs were deposited and dispersed uniformly on the SPE/MWCNTs-Nf-Nf, respectively. The electrochemical behavior of MA was studied by cyclic voltammetry (CV), and modified electrode was used for the determination of sub-nanomolar amounts of MA in samples using square wave stripping voltammetry (SWSV) and electrochemical impedance spectroscopy (EIS). Under the optimized experimental conditions, the modified SPE revealed broad linear ranges of 0.02–0.1 and 3.0–50  $\mu\text{M}$  (LOD = 6 nM) for SWSV and 1.15–26.9 nM (LOD = 0.3 nM) for EIS. Finally, the SPE/MWCNTs-Nf/GNPs showed stable electrochemical cyclic voltammetry responses. The high performances of the novel MA impedimetric sensor are mainly attributed to high surface area-to-volume ratio, excellent conducting capability and interface-dominated properties of GNPs which in combination with special properties of MWCNTs provide an effective modifier for MA oxidation. Moreover, using sensitive methods like impedimetric and stripping results in excellent responses.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

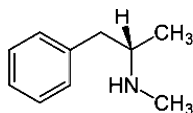
Methamphetamine (MA) (Scheme 1) is a powerful central nervous system stimulant [1] that brings about wakefulness and anorexia [2] and is abused in many countries [3]. It produces a rapid pleasurable feeling, which is followed by feelings of depression and irritability when the drug wears off.

The drug is available as water soluble white crystalline form. Pure methamphetamine, the smokable form of the drug, is called “glass”, “ice”, “crystal” or “quartz” because of its clear, chunky crystals which resemble frozen water. Despite warnings of irreversible damage to the central nervous system due to its consumption (even strokes and death), enhancement the abuse of this drug (especially among the young generation) is causing an increase in cost and crime and finally serious social problems in many countries [4,5]. One reason might be the ease of synthesis from readily available

raw materials, which brings lots of money for sellers and smugglers [6]. Therefore, there is a great interest for the quantitative analysis of such drugs by an inexpensive and powerful method in forensic as well as clinical laboratories. Several methods have been introduced for this purpose like gas chromatography (GC) [7], GC–mass spectrometry (GC–MS) [8], high-performance liquid chromatography (HPLC) [6], HPLC–tandem mass spectrometry (LC/MS/MS) [9], electrochemiluminescence (ECL) [10], immunoassay [11], Ion mobility spectrometry (IMS) [12] and capillary electrophoresis (CE) [13]. Although these methods are accurate but they suffer from problems of time-consuming, laborious operations and expensive apparatuses. Furthermore, they need several preparation steps before main procedure. Therefore, a simple, fast and accurate method is necessary for routine analysis and detecting MA in samples. Electrochemical detection is a simple and inexpensive method and also is attractive as it can provide sensitivity and reduces analysis time to enable continuous real-time measurements compared to the above methodologies. To our knowledge, electrochemical method has scarcely been applied to determine MA. Our findings show that there is just one report for electrochemical study of MA which the

\* Corresponding author. Tel.: +98 21 22431661; fax: +98 21 22431683.

E-mail addresses: [a-zavareh@sbu.ac.ir](mailto:a-zavareh@sbu.ac.ir), [afakhariz@yahoo.com](mailto:afakhariz@yahoo.com) (A.R. Fakhari).



**Scheme 1.** Structural formula of methamphetamine.

authors have investigated the electrochemical behavior of MA at a glassy carbon electrode [14].

In electrochemical analysis, the key component is electrode modification, which requires the selection of suitable material to improve the determination performance [15]. In principle, the electroanalytical detection limit at a nanoelectrode can be much lower than that at an analogous macro-sized electrode because the ratio between the faradic and capacitive currents is higher [16].

Carbon nanotubes (CNTs) have attracted much attention due to their special properties [17–19]. As electrode modifiers, CNTs show negligible surface fouling [20], decreased overpotential and increased voltammetric currents. Indeed, CNT electrode is driving the electron transfer reaction faster than many other carbon electrodes surfaces observed, with very small apparent activation barrier at the electrode surface [21].

Nanosized particles of noble metals, especially gold nanoparticles (GNPs), have received great interests due to their high surface area-to-volume ratio, excellent conducting capability, excellent biocompatibility and their interface-dominated properties.

Anodic stripping voltammetry (ASV) has been recognized as a powerful technique for electrochemical measurements of trace analytes in which a preconcentration step is combined with a stripping step, thereby enhancing the sensitivity [22]. When square-wave voltammetry (SWV) is employed for anodic stripping, the resulting method of square wave anodic stripping voltammetry (SWASV) offers many advantages over the more popular methods like differential-pulse ASV (DPASV) [23–25].

Electrochemical impedance spectroscopy (EIS) is a rapidly developing technique for the study of sensing events at the surface of an electrode [26] and is widely used in different fields' studies [27–33]. Faradic impedimetric systems are based on measuring the charge transfer resistance of a redox probe at an electrode interface. Impedance detection has been found to be sensitive, rapid and can detect at very low concentration reaching a limit of detection of  $10^{-18}$  M in some cases [34]. Moreover, the measurement does not have any specific prerequisites (e.g., labels or electroactive moieties in the molecule) [35].

Screen-printed carbon electrodes (SPEs) represent a widely accessible, disposable electrochemical sensor, simple, inexpensive and non-toxic [36]. Replacement of conventional electrochemical cells by SPEs connected to miniaturized potentiostats is a main trend in the shift of lab electrochemical equipments to hand-held field analyzers [37]. They are also suitable for working with micro-volumes and for decentralized assays (point of care tests), etc.

The main goal of this work is to investigate the electrochemical response of MA on the surface of SPE/MWCNTs-Nf/Nf/GNPs and develop a novel electrochemical sensor for quantitative detection of MA in forensic or clinical samples. For this purpose, MA was determined by SWASV. We have also reported the impedimetric detection to have comprehensive investigation of MA oxidation at this modified electrode. To the best of the author's knowledge, this study presents the first ever electrochemical detection of MA with this type of nano-modified electrodes.

## 2. Experimental

### 2.1. Chemicals and materials

Multiwalled carbon nanotubes with purity 95% (20–40 nm diameter and 1–10  $\mu$ m length) were obtained from Research

Institute of Petroleum Industry (Tehran, Iran). MA, as the hydrochloride salt, was purchased from Dr Ghaffarzadeh (Institute of Chemistry and Chemical Engineering). Nafion 5% solution was purchased from Sigma. All other solvents and reagents were purchased from Aldrich or Merck and were used without further purification. A stock solution of MA (0.10 M) was prepared by dissolving MA in deionized water. MA solutions were prepared by diluting aliquots of the MA stock solutions with a carrier solution and were freshly prepared just prior to use. All other solutions were prepared with doubly distilled water. All experiments were carried out at room temperature.

### 2.2. Instruments

All electrochemical experiments were performed using Autolab potentiostat/galvanostat type 30 (2) (Eco Chemie, Netherlands), equipped with FRA and GPES 4.9 software. Screen-printed carbon electrode (SPE) (3.0 mm in diameter) from Dropsens (Spain) was used as a planar three electrode based on a graphite working electrode, a carbon counter electrode and a silver pseudo-reference electrode. The electrode was rinsed in deionized water and pre-conditioned in 0.10 M HCl solution by potential scanning in  $-0.3$  to  $+1.3$  V at a scan rate of  $100$  mV  $s^{-1}$ . The following parameters were employed for CV and SWASV, respectively: CV: scan rate  $50$  mV  $s^{-1}$  and MA solution of  $5.0$  mM; SWASV: pulse amplitude  $10$  mV, pulse width  $10$  ms and MA solution of  $0.1$  mM. EIS experiments carried out with a dc-offset potential of  $280$  mV and in the frequency range of  $100,000$  to  $0.01$  Hz. Scanning electron microscopy (SEM) images, were obtained using KYKY-EM3200 SEM and energy dispersive X-ray (EDX) spectrum and EDX mapping were obtained using Philips XL-30 ESEM.

### 2.3. Preparation of modified electrode

MWCNTs were stirred in concentrated  $HNO_3$  for 6 h and then refluxed in the mixture of concentrated  $H_2SO_4:HNO_3$  (3:1) for 24 h to obtain the carboxylated multi-walled carbon nanotubes [36]. The MWCNTs were washed with doubly distilled water and dried in vacuum at  $80^\circ C$ . Carboxylated MWCNTs ( $10.0$  mg) and  $5.0$   $\mu$ l of 5% nafion solution were dispersed in  $5.0$  ml water with ultrasonication for 1 h to get a homogenous suspension. The SPE/MWCNTs-Nf was prepared by casting  $10.0$   $\mu$ l of the suspension onto the surface of screen printed electrode and let to evaporate to dryness at room temperature. The electrodeposition of gold nanoparticles on SPE/MWCNTs-Nf was conducted using a constant potential. The characteristic of gold deposition on the electrode surface is strongly influenced by several parameters: the two most important being the  $HAuClO_4$  concentration and the deposition time [38]. Both factors have been optimized and the constant potential of  $-400$  mV versus Ag was applied on these electrodes for a period of 30 s in  $0.10$  M HCl solution containing  $10.0$  mM  $HAuCl_4$  [39].

## 3. Results and discussion

### 3.1. Structures characterization

The surface morphology and nanostructure of the screen printed electrode/carboxylated multiwalled carbon nanotube/gold nanoparticles (SPE/MWCNTs-Nf/GNPs) was characterized by SEM and EDX techniques.

#### 3.1.1. SEM results

Fig. 1 shows the SEM images of the SPE surface modified with MWCNTs-Nf (A) and MWCNTs-Nf/GNPs (B). As shown in this figure, a network-like structure of MWCNTs without aggregation was observed on the SPE surface which suggested that the MWCNTs

Download English Version:

<https://daneshyari.com/en/article/739834>

Download Persian Version:

<https://daneshyari.com/article/739834>

[Daneshyari.com](https://daneshyari.com)