Electrochemical determination of thiosemicarbazide using the glassy carbon electrode modified with multi-walled carbon nanotubes

Neda Faizbakhsh [1], Zhila Safari *[,2]

[1] Department of Chemistry, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran
[2] Department of Chemistry, Dezful Branch, Islamic Azad University, Dezful, Iran

Abstract

According to the advantages of electrochemical analysis like high selectivity, high sensitivity, low analyte concentration, cost-effective, portable and easy-to-use setup, this method has attracted a great amount of attention among scientists for determination of different compounds. in this work, a simple, inexpensive, and rapid electrochemical method for the determination of thiosemicarbazide (TSC) was developed by using the modified glassy carbon electrode with multi-walled carbon nanotubes (MWCNT/GCE). Cyclic voltammetry (CV) studies indicated that TSC had a sensitive irreversible oxidative peak at 0.7 V. Compared to the untreated electrode, the modified electrode showed a negative shift in the oxidation peak of TSC. Differential pulse voltammetry on MWCNT/GCE showed a linear dependence on the concentration of TSC in the range of 1×10^{-6}-100×10^{-6} M with a limit of detection (LOD) of 0.6×10^{-6} M. The proposed method was successfully applied to the determination of TSC in city water samples.

Keywords: Thiosemicarbazide, Electrochemical determination, Glassy carbon electrode, Multi-walled carbon nanotube.
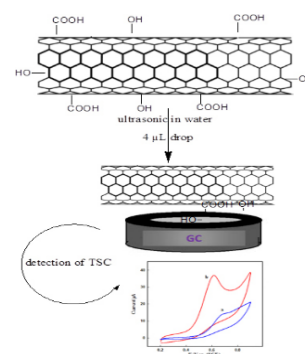
Introduction

Thiosemicarbazide (TSC) derived from thiourea is the main structural component of a set of TSC derivatives.[1] This compound and its derivatives have widely used as metal complexing agents in the various fields such as the characterization of aliphatic or aromatic aldehydes, ketones, and polysaccharides.[2-4] Their biological activity against certain kinds of tumor, protozoa, influenza, pesticides, and fungicides come from their ability to chelate trace metals. Because of the toxicity of TSC in environmental samples determination of its values is essential. Until now, various methods have been reported for determination of TSC, such as potentiometry,[5,6] titrimetry,[7,8] spectrophotometry,[9,10] stripping voltammetry techniques, particularly anodic, adsorptive cathodic stripping voltammetry (ACSV), and HPLC.[11-14] Most of the spectrophotometric and chromatographic methods are usually difficult to apply because of the vast sample preparation, treatment involving extractions, long-time analysis, and expensive equipment.[15] Also, due to mercury's toxicity, the application of polarography technique is now limited and may be prohibited in the electro-chemical analysis. Therefore, they are not suitable for routine tasks; so, it is significant to find a new method with high sensitivity, simplicity, and efficiency for the detection of this TSC. Due to measurable electrochemical behavior of drugs and biomolecules and simplicity of them in comparison to the above-mentioned methods, the application of electrochemical sensors for environmental, medicinal pharmaceutical, food and agricultural analyzes are rapidly increasing.[16-18] After the discovery of MWCNT,

this material has been used by many scientists in various fields among electrochemical sensor and biosensor because of their unique properties such as electrical conductivity, stability, and high surface area.[19,20] Also recent studies show that carbon nanotubes can increase the electrochemical reactivity and electron transfer rate of types of the compounds. Glassy carbon electrodes (GCEs) are simple to make and offer an easily renewable surface for electron exchange and are widely used for electrochemical measurements. To our knowledge, this is the first study in which electrochemical behavior and voltammetric determination of TSC has been performed by using modified GCE. In this paper, the electrochemical behavior of TSC was carefully investigated in MWCNT/GCE which may be a new idea for determination of TSC.

Experimental

Reagents

Multi-walled carbon nanotubes (diameter: 10–20 nm, length: 1–2μm, purity: ≥95%), was obtained from Nanolab Inc. KCl, $K_3[Fe(CN)_6]$, TSC, were obtained from Merck. All reagents were of analytical grade and used without further purification. In all experiments, a stock Britton–Robinson (BR) buffer solution (containing 0.04 M of glacial acetic acid, orthophosphoric acid, and boric acid) was used as the supporting electrolyte. Buffer solutions of varying pH were then prepared by the addition of 0.2 mol L^{-1} sodium hydroxide. All aqueous solutions were prepared with analytical grade chemicals and deionized water.

Corresponding author:
Zhila Safari, Email: Zhila.safari@gmail.com

The scanning electron microscopy (SEM) images were obtained using a scanning electron microscope (Vega©Tescan SEM operated at 30 kV). The electrochemical studies were performed with a µAutolab Type III/FRA2 computer-controlled potentiostat/galvanostat three-electrode system. The utilized three-electrode system was composed of an Ag/AgCl electrode as the reference electrode, the platinum wire as auxiliary electrode, and GCE as the working electrode.

MWCNT purification

The MWCNTs were purified according to the following procedure: 0.5 g of MWCNT dispersed in the mixture of the concentrated nitric and sulfuric acids with a ratio of 4/1 (v/v) for 6 h at room temperature with the aid of ultrasonic agitation, then washed with distilled water to neutrality and dried in an oven at 100 °C. 5 mg MWCNT were dispersed in 1 mL water using an ultrasonic to give homogeneous black suspensions. The GCE was coated by casting 4 µL of MWCNTsuspension in water and dried in the air.

Results and discussion

Studying the morphology of the MWCNT/GCE

Determination of the structure and the size of electrocatalytic particles deposited on different surfaces is very important for their applications in various fields. It has been found that the electrocatalytic properties of these particles depend on their size and structure. At the same time with the development of such electrocatalysts, many studies have been performed on the relationship between their electrocatalytic properties and the structure and size of particles. One of the conventional methods for studying the structure and size of such electrocatalysts is the use of SEM. Therefore, the SEM has been used to study the morphology of the particles on the electrode surface. Figure 1A shows the SEM images of the GCE. As seen in this image, the surface of the carbon electrode is smooth and uniform, and there is no pore in it. In Figure 1B, the glassy carbon electrode surface is uniformly covered by the carbon nanotubes.
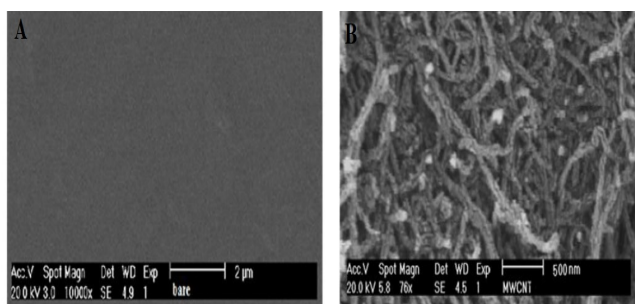

Figure 1. The SEM images of (A) GCE and (B) MWCNT/GCE.

The electroactive surface area of the MWCNT/GCE

The effective surface area of MWCNT/GCE was evaluated by CV using 5 mM $K_3[Fe(CN)_6]$ as a probe at various scan rates. According to the Randles-Sevcik equation[21]:

$$I_{pa} = (2.69 \times 10^5)\, n^{2/3}\, A\, D^{1/2}\, \nu^{1/2}\, C$$

where I_{pa} refers to the peak current, n is the electron number, A

denotes the surface area of the electrode, D and C are the diffusion coefficient and concentration of $K_3[Fe(CN)_6]$ respectively, and ν is the scan rate. For a 5 mM $K_3[Fe(CN)_6]$, n = 1, D=7.6×10⁻⁶ cm² s⁻¹,[21] it was calculated that the effective surface area of GC-MWCNT modified electrode is 0.081 cm², which was about 3 times larger than that of the bare GCE (0.0314 cm²).

Electrochemical behavior of TSC on the MWCNT/ GCE electrode surface

To find out the electrocatalytic activity of the modified MWCNT/GCE, its CV responses in the presence of TSC solution (100 µM) were investigated in a BR buffer solution with pH=2 at the scan rate of 100 mV/s (Figure 2). The curves drawn in this diagram show the response of single GCE and MWCNT/GCE. From the analysis of these voltammograms, it can be concluded that with the addition of MWCNTs to the GCE, the position of the oxidation potential of TSC is slightly shifted to the lower potentials. Reduction of overvoltage is one characteristic of the electrocatalytic reaction at the modified electrode surface. Therefore, it can be concluded that the modification of GCE by MWCNTs, in addition to the reduction of overvoltage, increases the sensitivity of the sensing due to the increase in anodic current intensity. The above results are summarized in Table 1.

Table 1. *Comparison of the anodic current intensity and position of oxidation potential for TSC in the CV of the 100 µM solution at the GCE and MWCNT/GCE in a BR buffer solution with pH=2.*

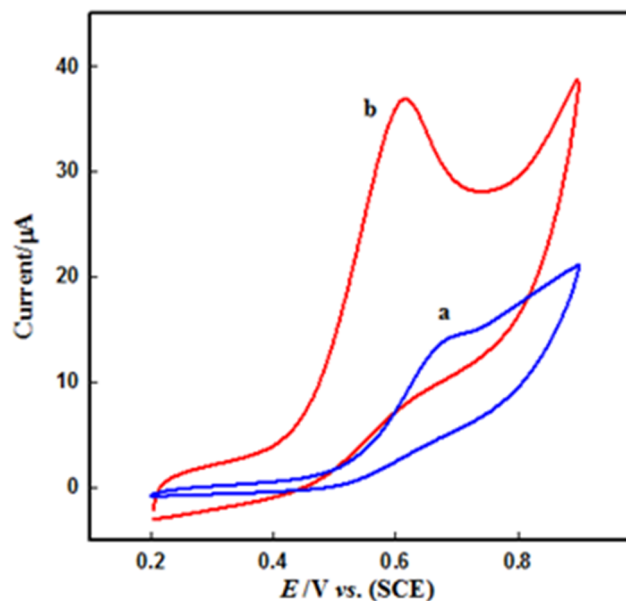| Electrode	E_a (V)	I_a (µA)
GCE	0.7	13.9
MWCNT/GCE	0.6	36.8

Figure 2. *The plot of CV for 0.1 mM TSC in BR solution with pH=2 at the surface of (a) GCE and (b) MWCNT/GCE at the scan rate of 100 mV/s.*

Accumulation behavior of TSC solution

Cyclic voltammograms of the modified electrode in 0.1 mM TSC BR buffer solution were obtained at pH=2 after a specified accumulation time (first scan). As observed in Figure 3, significant changes have been occured in the peak current for the second and third Scan, which indicates the instability of this electrode under the continuous scanning conditions.
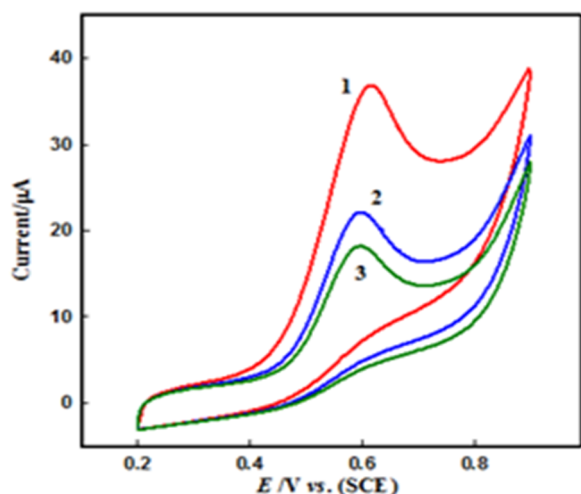
Figure 3. *The plot of three continuous CVs in 0.1 mM TSC solution at the MWCNT/GCE surface with the scan rate of 100 mV/s.*

The effect of pH

The pH effect of the BR buffer solution on the electrochemical behavior of TSC was studied by the CV method in the pH range of 2 to 8. In this study, the highest sensitivity was observed at pH=2 (Figure 4A). By increasing the pH of the buffer solution, the negative shift in the anodic peak potential is observed according to Figure 4 and the $E_{p,a}$ (mV)= -35.393 pH + 689.25 (R^2=0.99).

The plot of the anodic peak potential versus pH shows the linear relationship with the slope of about 35.39 mV. Therfore, the participation of two electrons and the transfer of one proton in the oxidation process of TSC is resulted. Based on the structure of TSC, it can be concluded that in the acidic media, amine moiety (NH_2 attached to the carbon dioxide) is protonated, and the anodic current is obtained from the oxidation of this group.
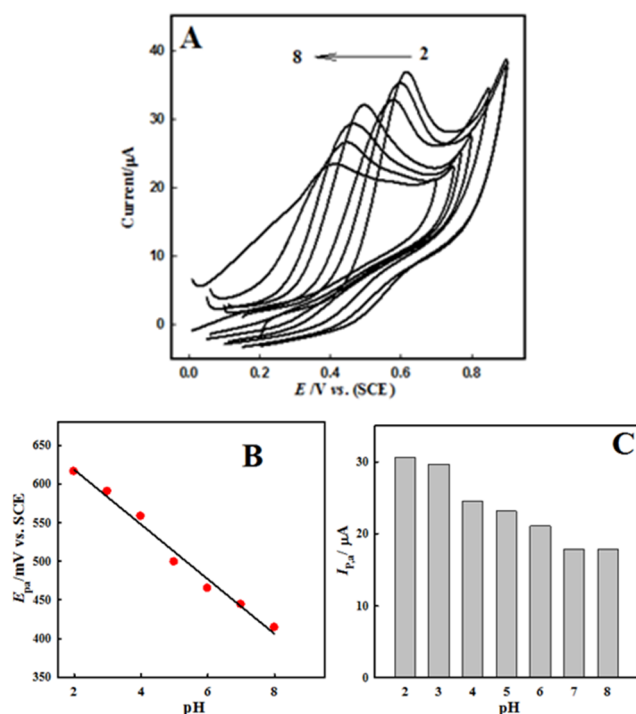
Figure 4. *(A) The CV plots of the 0.1 mM TSC oxidation at the CNT/GCE surface to check the effect of pH, (B) the plot of E_{pa} against the pH and (C) the plot of I_{pa} against the pH.*

The effect of potential scan rate on the electrochemical behavior of TSC

Considering the effect of potential scan rate on the CVs of TSC, the diffusion or absorption nature of these species on the modified electrode surface can be investigated. Therefore, the effect of the changes in the potential scan rate on the modified electrode response of TSC solution (100 μM) was investigated by voltammetric technique (Figure 5A). The existence of dependence between the peak current and square root of scan rate indicating the diffusion behavior at the electrode surface (Figure 5B).
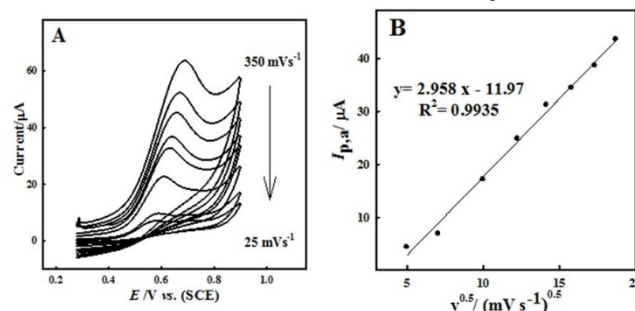
Figure 5. *(A) CVs of the solution of TSC 0.1 mM in a BR buffer solution with pH=2 at the MWCNT/GEC surface at different potential scan rates and (B) The plot of anodic current versus root square of potential scan rate.*

The Tafel curve was used to obtain the information about the rate-determining step, which was plotted using the plot of current-potential data, and its slope was calculated. In Tafel curves, by plotting the logarithmic current versus potential in the rising portion of the voltammogram the straight line is obtained which the slope of curve for anodic oxidation reaction is equal Slope=2.303RT/(1-α)nF.[21] In this equation, R is universal gas constant (R= 8.314 J mol^{-1} K^{-1}), F is Faraday constant (F= 96500 C mol^{-1}), and the temperature is T (K). Based on the Figure 6, the slope value of the plot log I_P versus E_p is obtained. Thus, the electron transfer coefficient α for TSC is equal to 0.34.
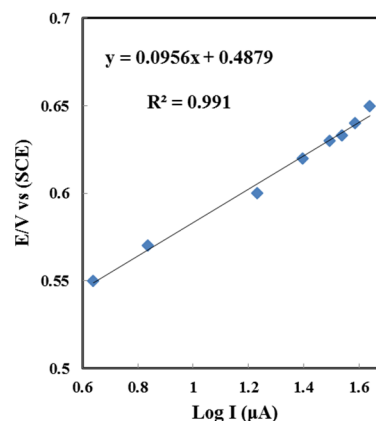
Figure 6. *The plot of Tafel obtained from the recorded current-potential curve at the scan rate of 25- 350 mV s^{-1}.*

Analytical measurements of TSC

MWCNT/GCE was used as an acceptable electrochemical sensor with high sensitivity and low detection limit to measure the small amounts of TSC. Differential pulse voltammograms (DPV) for different concentrations of TSC were prepared in two optimal condition range 10-100 μm (Figure 7A) and the range of 1 to 10 μm (Figure 7B). The oxidation current is linearly dependent on the concentration of TSC. The calibration curve shown in Figure 7C is in the range of 1 to 100 μm.
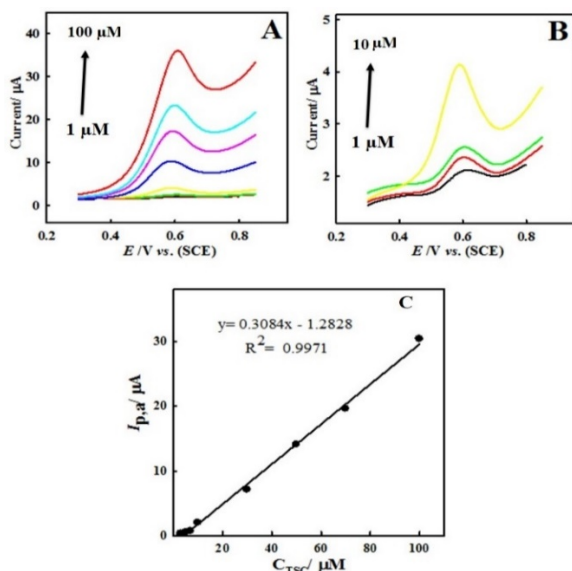
Figure 7. (A) DPVs of different concentrations of TSC in the low to high range (1 to 100 µM) of the BR buffer with pH=2 at the MWCNT/GCE surface and (B) DPVs for different concentrations of TSC in the low to high range (1 to 10 µM).C) The plot of the linear calibration curve for peak current $I_{p,a}$ versus the TSC concentration.

One of the parameters that distinguish an analytic method from different analytical methods for measuring a sample is detection limit of the method obtained from the relation (LOD=3S/m). The electrochemical response of MWCNT/GCE is compared with other electrochemical methods regarding the detection limit and dynamic range, and the results are presented in Table 2. The present work and detection limit and has acceptable performance in determining the TSC using the differential pulse volumetric method.

Table 2. The comparison of the electrochemical methods for TSC determination.

Electrode	Background electrolyte	Method	Dynamic range (µM)	LOD (µM)	Ref.
Carbon	pH=7	CV	75-100	75	11
CGMDE	pH=1	ACSV	0.0015-0.015	0.0015	12
HMDE	PH=9.5	ACSV	0.015-15	0.003	13
CNT/GCE	pH=2	DPV	3-100	0.6	This work

Investigation of the real sample

The recovery efficiency test was performed on the urban water samples. The amount of the resulting efficiency was evaluated to increase the standard solution of sample analyte into the sample of urban water which its pH was adjusted according to the optimum conditions of quantitative measurement. The results are shown in Table 3.

Conclusion

In this research, the simple and effective method was used to prepare the carbon nanotube-modified electrode. The properties like the intrinsic conductivity, catalytic behavior, high selectivity, and appropriate sensitivity of carbon nanotubes reduce the peak potential and increase the peak current. DPV can be selected as a suitable method for measuring the TSC, because of its fast response, high sensitivity, and acceptable stability of the modified

electrode. The parameters such as the effect of pH and scan rate were optimized, and the kinetic parameter α was calculated to evaluate the applicability of the electrode.

Table 3. The output of recovery test of an added sample using the TSC standard solution in the urben water sample.

No.	Added value (µM)	Obtained value (µM)	Recovery%
1	7	6.66	95.1
2	10	9.8	98.34
3	30	28.3	94.39
4	70	65.09	92.98

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