Full Paper

ZnO Nanoparticle Modified Carbon Paste Electrode as a Sensor for Electrochemical Determination of Tert-Butylhydroquinone in Food Samples

Mahbobe S. Rahmanpour and Mohammad A. Khalilzadeh*

Department of Food Science, Sari Branch, Islamic Azad University, Sari, Iran

*Corresponding Author, Tel.:+98-911-1130400; Fax: +98-11- 42155117

E-Mail: khalilzadeh73@gmail.com

Abstract- A fast response voltammetric sensor based on ZnO nanoparticles (ZnO/NPs) carbon paste electrode (ZnO/NPs/CPE) is suggested for the determination of tert-butylhydroquinone in the aqueous buffer solution. ZnO nanoparticles synthesized by direct chemical precipitation method and characterized with X-ray diffraction (XRD) method. In the second step, application of the ZnO/NPs for the preparation of modified carbon paste electrode was investigated. At the optimum condition (pH 7.0), the oxidation signals of tert-butylhydroquinone increased linearly with its concentration in the ranges of 1.0–750 μM. The detection limit for tert-butylhydroquinone was 0.7 μM. The ZnO/NPs/CPE was used for the determination of tert-butylhydroquinone in food samples such as sesame and soybean oil.

Keywords- Tert-butylhydroquinone; ZnO nanoparticles, Food sample analysis, Modified electrode

1. INTRODUCTION

Tert-butylhydroquinone is an important antioxidant and it is used as a preservative for unsaturated vegetable oils and many edible animal fats. It does not cause discoloration even in the presence of iron, and does not change flavor or odor of the material to which it is added [1]. Tert-butylhydroquinone can be combined with other preservatives such as butylated

hydroxyanisole (BHA). According to the United States Food and Drug Administration (FDA) reported application of tert-butylhydroquinone is safe to consume in foods. It is used industrially as a stabilizer to inhibit autopolymerization of organic peroxides. According to the above points, it is very important for determination of tert-butylhydroquinone in food samples. Capillary electrophoresis [2], high-performance liquid chromatography [3] and electrochemical methods were suggested for determination of tert-butylhydroquinone in food samples [4,5].

Nanotechnology and nanoscience represent new and enabling platforms that promise to provide a broad range of novel uses and improved technologies for environmental, biological and other scientific applications [6]. Recently, nanostructured materials have also been incorporated into electrochemical sensors for biological and pharmaceutical analyses [7–15]. While they have many properties similar to other types of bulk materials, they offer unique advantages including enhanced electron transfer, large edge plane/basal plane ratios and rapid kinetics of the electrode processes [16–26].

In this project, we describe the synthesis and application of a novel ZnO/NPs modified carbon paste electrode. The electrochemical behavior of tert-butylhydroquinone at ZnO/NPs/CPE and unmodified electrodes was investigated. The obtained results show the advantage of ZnO/NPs/CPE to the bare carbon paste electrode in terms of better reversibility and higher sensitivity.

2. EXPERIMENTAL

2.1. Chemicals and Instrumentation

Zinc acetate, phosphoric acid and sodium hydroxide were purchased from Sigma-Aldrich. Tert-Butylhydroquinone, graphite powders, and paraffin oil, were purchased from Merck. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu–Ka radiation (l=1.54 Å). Voltammetric investigation was performed in an electroanalytical system, μ-Autolab PGSTAT 12, potentiostat/galvanostat connected to a three-electrode cell, Metrohm Model 663 VA stand linked with a computer (Pentium IV) and with Autolab software. The system was run on a PC using NOVA software.

2.2. Synthesis of ZnO/NPs

To prepare ZnO/NPs in a typical experiment, a 0.25 M aqueous solution of zinc acetate and a 0.5 M aqueous solution of sodium hydroxide were prepared in distilled water. The zinc acetate solution was added dropwise to the above-heated solution under high-speed stirring. The beaker was sealed at this condition for 2 h. The precipitated ZnO/NPs were cleaned with deionised water and ethanol, and then calcined at 300 °C for 2 h.

2.3. Preparation of Sensor

The suggestion sensor was prepared by mixing of 0.05 g of ZnO/NPs and 0.95 g of graphite powder in the presence of suitable amount of paraffin. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture.

2.4. Preparation of real samples

10.0 gr edible oil sample input into 200 mL Erlenmeyer flask in the presence of 10.0 mL methanol as a solvent. In continuous, the samples were shaken for 50 min and then centrifuged at 2000 rpm for 20 min. The obtained extracts were transferred into a 50 mL volumetric flask and diluted to methanol.

3. RESULTS AND DISCUSSION

ZnO nanopowders were analyzed by XRD method. The XRD pattern of ZnO nanopowder, in the 2θ range of 20–80°, is shown in Fig. 1. Results confirm the synthesis of ZnO nanopowder. The mean grain size (D=29 nm) of the particles was determined from the XRD line broadening measurement using Scherrer equation.
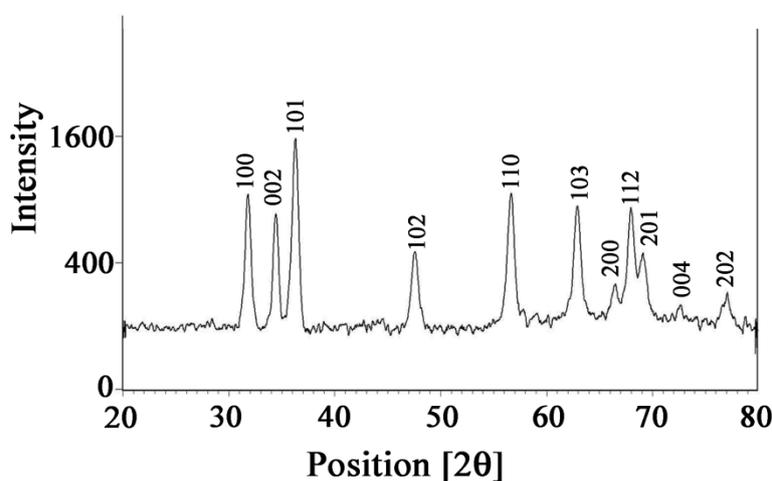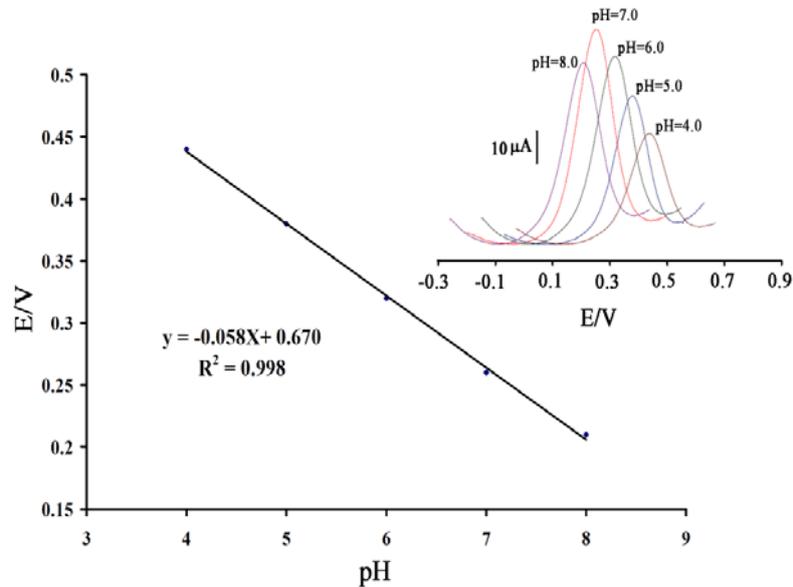

Fig. 1. XRD patterns of ZnO nanoparticles

Since tert-butylhydroquinone has a hydroquinone moiety, we anticipated that the redox response of tert-butylhydroquinone would be pH dependent. In order to ascertain this, the voltammetric response of tert-butylhydroquinone was obtained in solutions with varying pH from 4 to 8 at the surface of ZnO/NPs/CPE (Fig. 2 insert).

Fig. 2. Plot of potential, E, *vs*. pH for the electro-oxidation of 50 μM tert-butylhydroquinone at a surface of ZnO/NPs/CPE. Inset: influence of pH on square wave voltammograms of tert-butylhydroquinone at a surface of the modified electrode (pH 4–8, respectively)

The result shows that the formal potential (E^0) of the redox couple was pH dependent (Fig. 2), with a slope of −58.0 mV/pH unit at 25 °C, which was equal to the anticipated Nernstian value for a two electron, two-proton electrochemical reaction. It can be seen that the maximum value of the peak current appeared at pH 7.0 (Fig. 3), so this value was selected throughout the experiments.
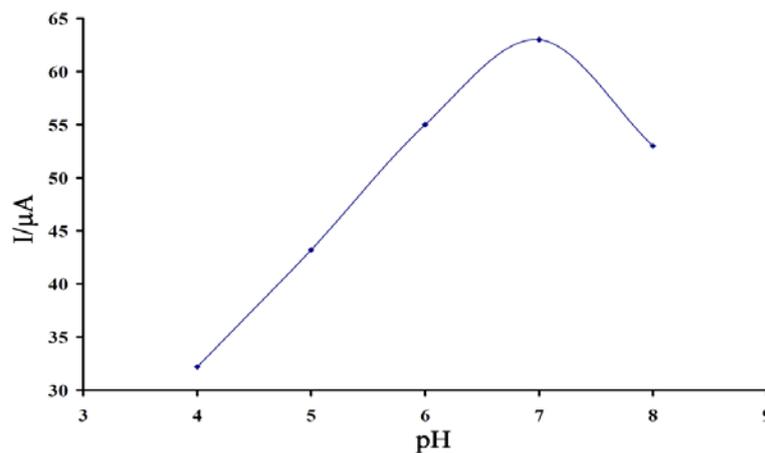

Fig. 3. Current–pH curve for electrooxidation of 50.0 μM tert-butylhydroquinone at ZnO/NP/CPE

Using Randles–Sevcik equation and in the presence of known concentration of $K_4Fe(CN)_6$, the active surface areas of the ZnO/NPs/CPE and CPE are estimated. The

microscopic areas were calculated 0.284 and 0.32 cm^2 for CPE and ZnO/NPs/CPE, respectively.

Fig. 4 inset shows the current density derived from the square wave voltammograms of 50 μM tert-butylhydroquinone at the surface of different electrodes. The obtained results show that the presence of ZnO/NPs causes the increase of the electrode surface. Fig. 4 (curves a&b) showed the square wave voltammetric signals of ZnO/NPs/CPE and CPE in 50 μM tert-butylhydroquinone in PBS solution (pH 7.0), respectively. At ZnO/NPs/CPE, and CPE, tert-butylhydroquinone showed an oxidation peak, with oxidation peak potential (E$_{pa}$) of 0.244 V, and 0.339 V, respectively. However, the peak current of tert-butylhydroquinone at ZnO/NPs/CPE was much larger than that at the CPE; it was about 1.96 times larger than CPE by square wave voltammetry. Thus, the ZnO/NPs/CPE exhibited a catalytic activity toward the oxidation of tert-butylhydroquinone. This further testified the superiority of ZnO/NPs/CPE to CPE and indicated that the use of ZnO/NPs as modifier facilitated the electron transfer between tert-butylhydroquinone and electrode.
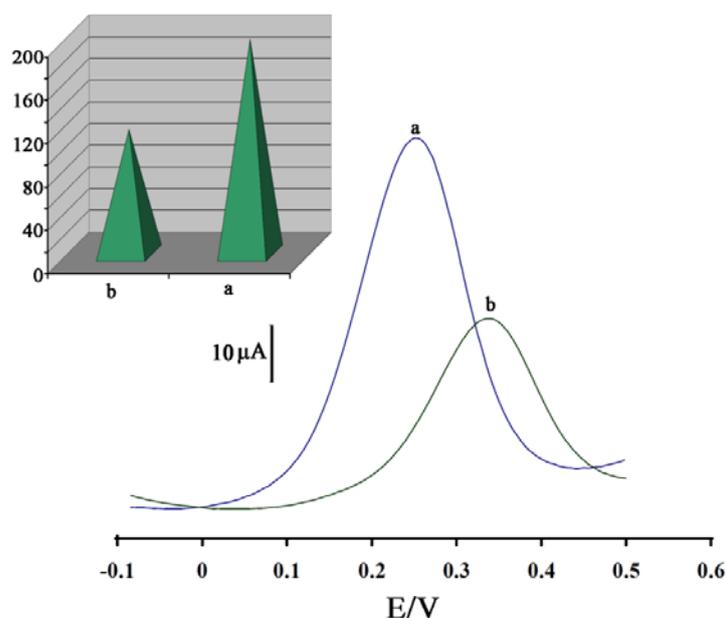

Fig. 4. Square wave voltammograms of (a) ZnO/NPs/CPE, and (b) CPE in the presence of 50 μM tert-butylhydroquinone at pH 7.0, respectively. Inset: the current density derived from Square wave responses

The Tafel plot was used for determination of α for electro-oxidation of tert-butylhydroquinone at a surface of modified electrode (Fig. 5). The slope of the Tafel plot was equal to 2.3 RT/n(1−α)F , which came up to 0.1642 V decade^{-1} for scan rate 20 mV s^{-1} (Fig. 5). Therefore, we obtained the mean value of n(1-α), which is equal to 0.82.
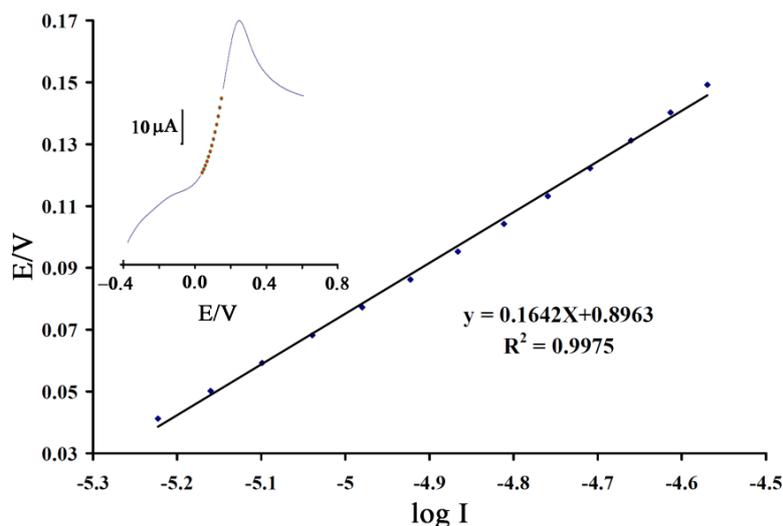
Fig. 5. Tafel plot for ZnO/NPs/CPE in 0.1 MPBS (pH 7.0) at the scan rate of 20 mV s^{-1} in the presence of 500.0 µM tert-butylhydroquinone

Chronoamperometry was used with ZnO/NPs/CPE to determine the diffusion coefficient of tert-butylhydroquinone (Fig. 6). We have determined the diffusion coefficient, D, of tert-butylhydroquinone using the cottrell equation. According to the cottrell equation, we calculated a diffusion coefficient of 2.5×10^{-5} cm^2/s for tert-butylhydroquinone.
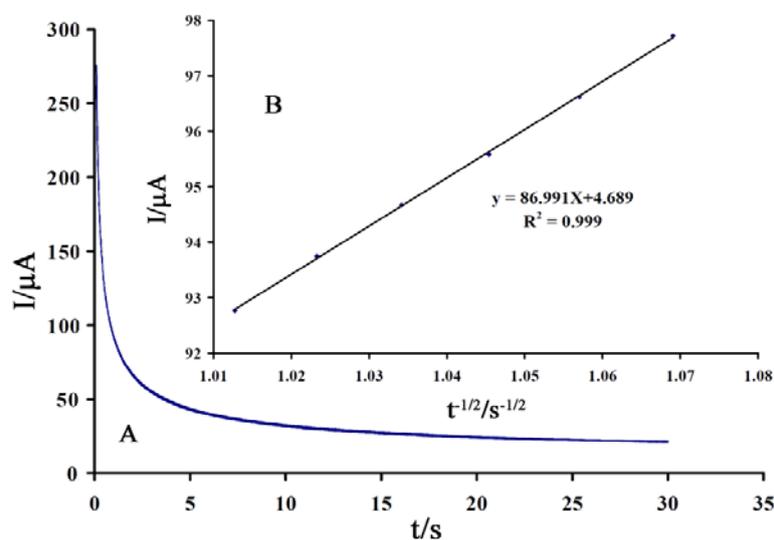

Fig. 6. A) Chronoamperograms obtained at the ZnO/NPs/CPE in the presence of 500 µM tert-butylhydroquinone in the buffer solution (pH 7.0); B) Cottrell's plot for the data from the chronoamperograms

The stability of ZnO/NPs/CPE was investigated by SWV measurements of 50.0 µM tert-butylhydroquinone. When the electrode stored in the laboratory, the ZnO/NPs/CPE retains

96% of its initial response after two week and 91% after 40 days. These results indicate that ZnO/NPs/CPE has good stability, and could be used for tert-butylhydroquinone.

Since SWV has a much higher current sensitivity and better resolution than cyclic voltammetry, SWV was used for the determination of tert-butylhydroquinone (Fig. 7). The plot of peak current *vs.* tert-butylhydroquinone concentration is linear with slopes of 0.6923 μM in the concentration ranges of 1.0–750 μM. The detection limit of tert-butylhydroquinone was determined to be 0.7 μM.
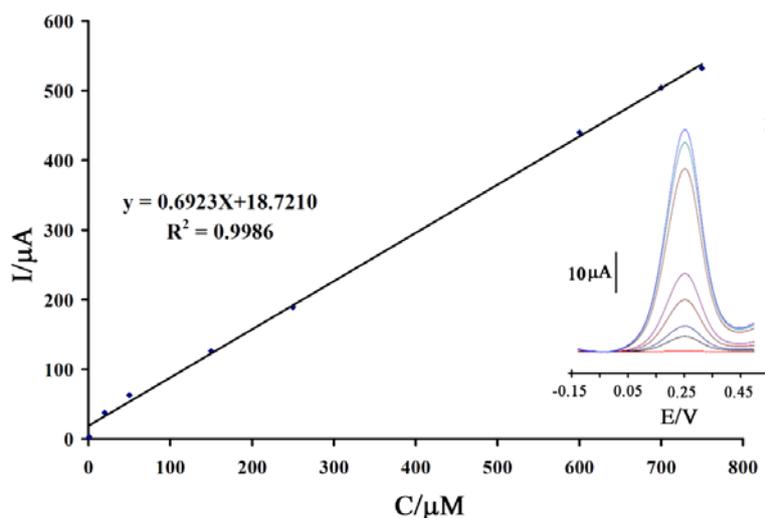
Fig. 7. The plots of the electrooxidation peak current as a function of tert-butylhydroquinone concentration. Inset; SWVs of ZnO/NPs/CPE containing different concentrations of tert-butylhydroquinone μM. (from inner to outer): 1.0, 20.0, 50.0, 150.0, 250.0, 600.0, 700 and 750 respectively

Table 1. Determination of tert-butylhydroquinone in food samples

Sample	Added (μM)	Expected (μM)	Founded (μM)	Recovery %
Sesame oil	—	—	7.55±0.62	—
	10.00	17.55	17.98±0.77	102.45
Soybean oil	—	—	7.05±0.44	—
	10.00	17.05	16.98±0.52	99.58

The effect of foreign substances to the oxidation peak current and peak potential response of the tert-butylhydroquinone at a surface of ZnO/NPs/CPE was tested and no interference was caused until the addition of 1000-fold excess of glucose, Na^+, K^+, SO_4^{2-}, Al^{3+}, NH_4^+ and

F^- and 800-fold excess of tryptophan, glutamic acid and alanine in a pH 7.0 buffer containing 50.0 μM tert-butylhydroquinone.

In order to find out the applicability of the ZnO/NPs/CPE for determination of tert-butylhydroquinone in the real samples, the electrode was used in food samples analysis. The obtained results in Table 1, confirm that the ZnO/NPs/CPE has a good efficiency for the determination of tert-butylhydroquinone in real samples.

4. CONCLUSION

Zinc oxide nanoparticles were incorporated onto the surface of a carbon paste electrode and were assessed using XRD procedures. The direct electrochemistry of tert-butylhydroquinone at the surface of ZnO/NPs/CPE was assessed by chronoamperometry and SWV methods. The presence of ZnO nanoparticles helped tert-butylhydroquinone have a favoured orientation and reduce the effective electron transfer distance.

Acknowledgement

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