

Full Paper

Electrochemical Determination of Tert-butylhydroxyanisole uses Carbon Paste Electrode Modified with Ionic Liquid and CdO Nanoparticle

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Abstract- A square wave voltammetric sensor based on carbon paste electrode modified with CdO nanoparticles (CdO/NPs) and 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (CdO/NPs/BIHF/CPE) was fabricated for tert-butylhydroxyanisole (BHI) analysis. CdO/NPs were characterized with TEM and XRD methods. The CdO/NPs/BIHF/CPE showed good electrocatalytic activity to the electro-oxidation of BHI. The peak currents of square wave voltammograms (SWV) of BHI increased linearly with its concentration in the ranges of 0.08–550 μM . The detection limit for BHI was 0.04 μM . The CdO/NPs/BIHF/CPE was successfully applied for the determination of BHI in food samples.

Keywords- 1-Butyl-3-methylimidazolium hexafluorophosphate, CdO nanoparticles, Voltammetry, Butylhydroxyanisole

1. INTRODUCTION

Antioxidants are essential components for human body that inhibit for the oxidation of other molecules. Tert-butylhydroxyanisole is useful antioxidant in food samples. Butylhydroxyanisole has been found to have an anti-viral effect, so this is available as a

health food supplement and inert ingredient in some medications [1]. Some analytical methods were suggested for determination of BHI in food and pharmaceutical samples such as high performance liquid chromatography [2], micellar electrokinetic capillary chromatography [3] and electrochemical methods [4-6]. In between, electrochemical methods suggest high advantage such as fast response, low cost, high sensitivity and good selectivity for analysis of electroactive compounds [7-15].

Application of carbon paste electrodes as transducer suggests high advantages as sensor such as easy modification and low non faradic response for analysis of electroactive materials [16-25]. Modified carbon paste electrodes showed highly sensitivity with good electrocatalytic activity for pharmaceutical and food compounds [26-30].

Nanomaterials such as metal oxide nanoparticles, graphene based nanomaterials, carbon nanotubes and etc. are good choice for modification of electrodes due to high electrical conductivity [31-37]. On the other hand, room temperature ionic liquid can be replaced to paraffin oil as binder for fabrication of carbon paste electrodes [38-43]. Ionic liquids have more electrical conductivity as binder for modification of solid based electrodes and especially carbon paste electrodes.

In this work we tried for synthesis of CdO/NPs described by chemical precipitation method as a modifier. In continuous, the fabrication of CdO/NPs/BIHF/CPE described as a high performance electrochemical sensor for analysis of BHI. Also, we test application of CdO/NPs/BIHF/CPE for determination of BHI in real samples with satisfactory results.

2. EXPERIMENTAL

2.1. Chemicals and Instrumentation

Cadmium acetate, phosphoric acid, Graphite powders, tert-butylhydroxyanisole, paraffin oil and sodium hydroxide were purchased from Sigma-Aldrich. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-K α radiation ($\lambda=1.54 \text{ \AA}$). 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 NiO/NPs

0.5 M of cadmium acetate and a 1.0 M sodium hydroxide were prepared in distilled water. The beaker containing 1.0 M sodium hydroxide was heated at the temperature of about 30 °C and cadmium acetate solutions were added drop wise to the above heated solution under high-speed stirring. The beaker was sealed at this condition for 3 h. The precipitated

Cd(OH)₂ were cleaned with deionized water and ethanol then calcined at 500 °C for 3.0 h for synthesis of CdO/NPs.

2.3. Preparation of CdO/NPs/BIHF/CPE

The CdO/NPs/BIHF/CPE was prepared by mixing of 0.2 g of CdO/NPs and 0.8 g of graphite powder in the presence of 0.68 g paraffin oil and 0.32 g ionic liquid. 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

Antioxidant-free samples of soybean biodiesel and ketchup were spiked with BHI at different ratios. Each spiked sample was then diluted in ethanol using calibrated flasks to achieve a final concentration of approximately 10% (biodiesel:ethanol, v/v). A suitable amount of previous solution was transferred into the electrochemical cell.

3. RESULT AND DISCUSSION

3.1. CdO nanoparticle characterization

CdO nanopowders were analyzed by X-ray powder diffraction method. The XRD pattern of CdO nano-particle, in the 2θ range of 10–80°, is shown in Fig. 1. Results confirm the synthesis of CdO nano-particle. The mean grain size (D=28 nm) of the particles was determined from the XRD line broadening measurement using Scherrer equation.

The morphology of the as-grown nanostructures was characterized by TEM methods. Typical TEM micrograph of the CdO/NPs nanopowder is shown in Fig. 2. Results confirm the synthesis of CdO/NPs nanopowder.

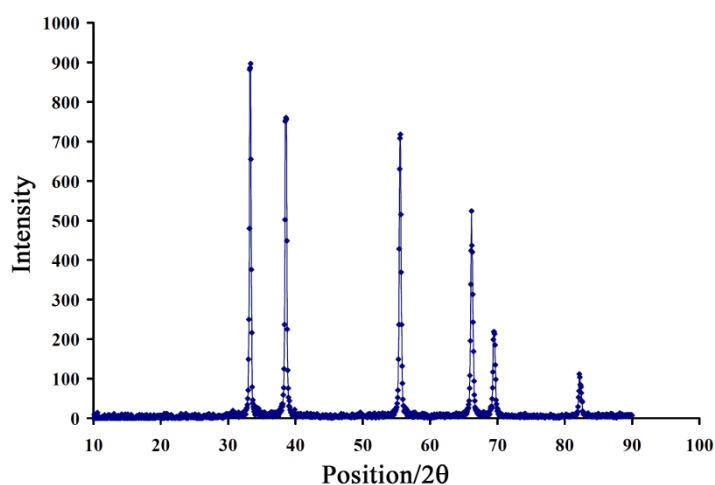


Fig. 1. XRD patterns of CdO nanoparticles

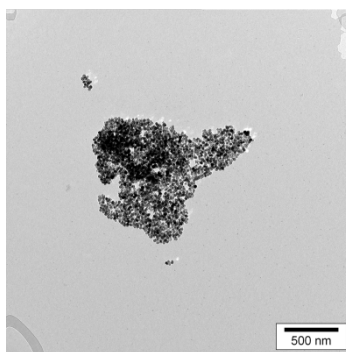


Fig. 2. TEM image of CdO nanoparticles

Since BHI has a hydroquinone moiety, we anticipated that the redox response of BHI would be pH dependent. The voltammetric response of BHI was obtained in solutions with varying pH from 4 to 7 at the surface of CdO/NPs/BIHF/CPE (Fig. 3 insert). The result shows that the formal potential (E^0) of the redox couple was pH dependent (Fig. 3), with a slope of -52.0 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 6.0 (Figure 4), so this value was selected throughout the experiments.

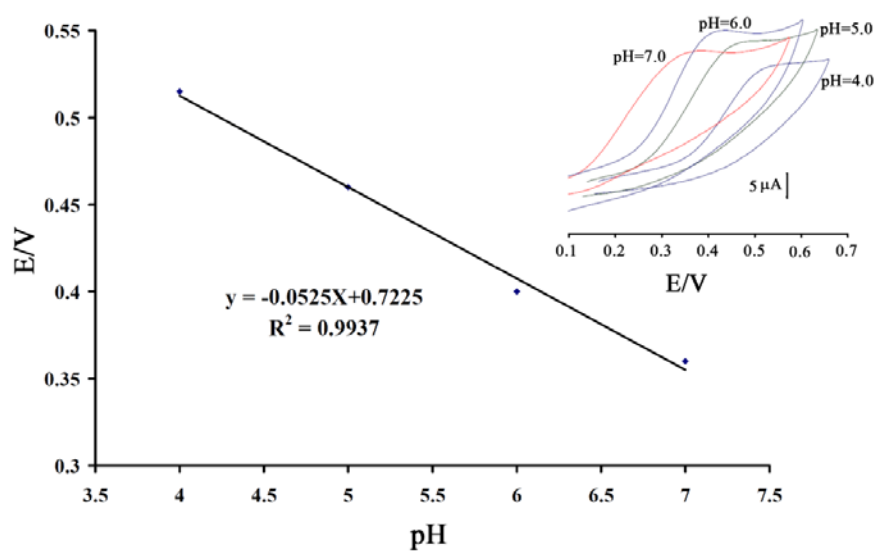


Fig. 3. Plot of potential, E , vs. pH for the electro-oxidation of 350 μ M BHI at a surface of CdO/NPs/BIHF/CPE. Inset: influence of pH on cyclic voltammograms of BHI at a surface of the CdO/NPs/BIHF/CPE

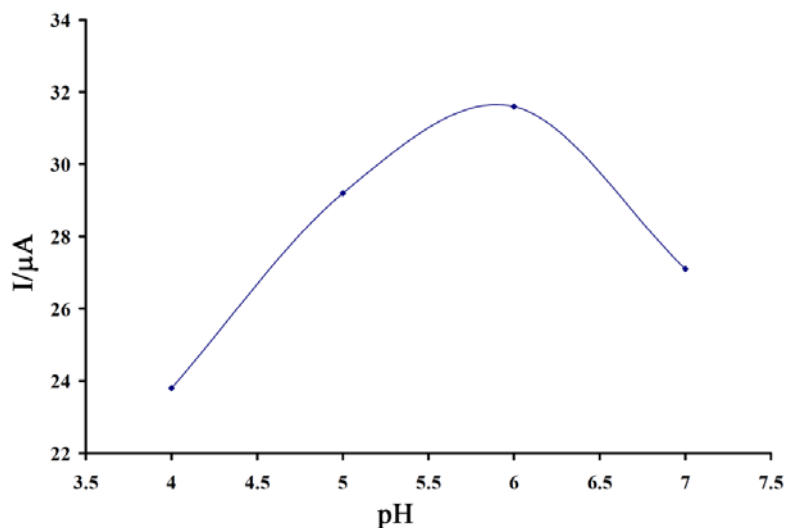


Fig. 4. Current–pH curve for electrooxidation of 350.0 μM BHI at CdO/NPs/BIHF/CPE

Fig. 5 inset shows the current density derived from the cyclic voltammograms of 500 μM BHI at the surface of different electrodes. The obtained results show that the presence of CdO/NPs and BIHF together causes the increase of the electrode surface. The electrochemical oxidation of BHI on the modified electrodes was investigated by cyclic voltammetry method. Fig. 5 shows cyclic voltammograms of 500 μM BHI at pH 6.0 at the surface of different electrodes with a scan rate of 100 mV s^{-1} . CdO/NPs/BIHF/CPE exhibited significant oxidation peak current around 375 mV with the peak current of 51.4 μA (Fig. 5, curve a).

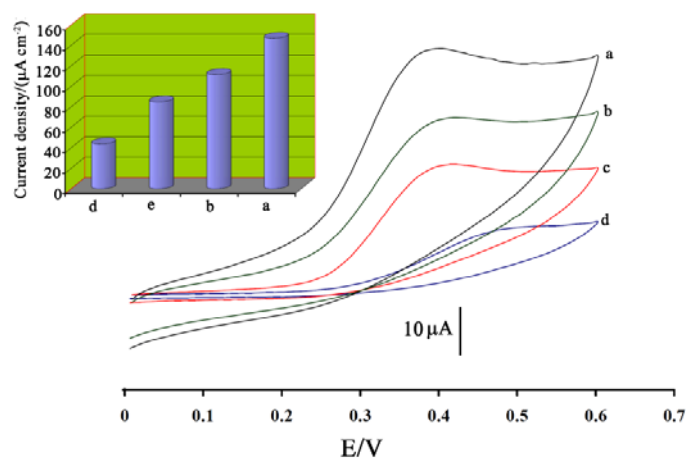


Fig. 5. Cyclic voltammograms of (a) CdO/NPs/BIHF/CPE, (b) BIHF/CPE, (c) CdO/NPs/CPE and CPE in the presence of 500 μM BHI at pH 6.0, respectively. Inset: the current density derived from cyclic voltammetric responses

On the other hand, low oxidation activity peak was observed at CdO/NPs/CPE (Fig. 5, curve c) and at CPE (Fig. 5 curve d) over the same condition. The BHI oxidation peak potential at CdO/NPs/CPE and at CPE observed around 400 and 470 with the oxidation peak current of 27.2 and 14.1 μA , respectively. In addition, at the surface of BIHF/CPE, the oxidation peak which appeared at 390 mV with the peak current was 36.1.3 μA (Fig. 5, curve b), which indicated that the presence of BIHF in CPE could enhance the peak currents and decrease the oxidation potential. A substantial negative shift of the currents starting from oxidation potential for BHI and dramatic increase of oxidation current of BHI indicated the catalytic ability of CdO/NPs/BIHF/CPE to BHI oxidation.

The effect of scan rate (ν) on the electro-oxidation current of BHI was also examined (Fig. 6 inset). The results of this investigation showed that the peak currents increased linearly with the increasing square root of scan rate that ranged from 10 to 130 mV s^{-1} (Fig. 6).

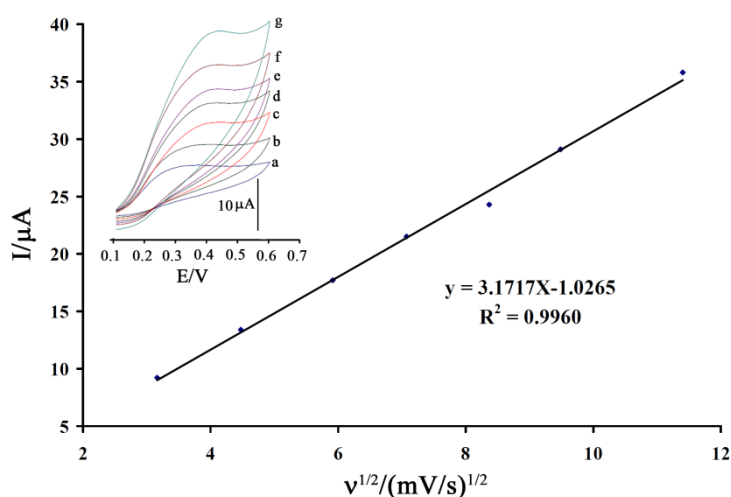


Fig. 6. Plot of I_{pa} vs. $\nu^{1/2}$ for the oxidation of BHI at CdO/NPs/BIHF/CPE. Inset shows cyclic voltammograms of BHA at CdO/NPs/BIHF/CPE at different scan rates of a) 10, b) 20, c) 35, d) 50, e) 70, f) 90 and g) 130 mV s^{-1} in 0.1 M phosphate buffer, pH 6.0

The Tafel plot was used for determination of α for electro-oxidation of BHI at a surface of CdO/NPs/BIHF/CPE (Fig. 7). The slope of the Tafel plot was equal to $2.3 RT/n(1-\alpha)F$, which came up to 0.1253 V decade^{-1} for scan rate 10 mV s^{-1} (Fig. 7). Therefore, we obtained the mean value of $n(1-\alpha)$, which is equal to 0.76.

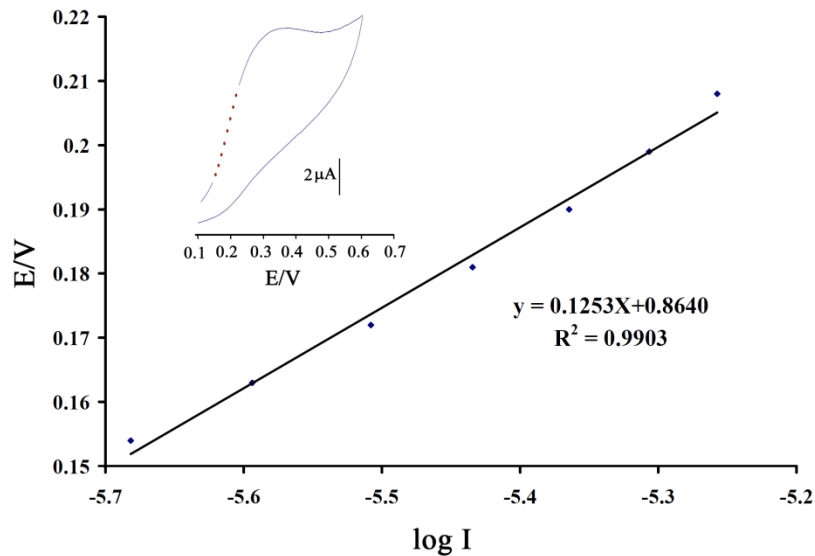


Fig. 7. Tafel plot for CdO/NPs/BIHF/CPE in 0.1 MPBS (pH 7.0) at the scan rate of 10 mV s⁻¹ in the presence of BHI

Chronoamperometry was used with CdO/NPs/BIHF/CPE to determine the diffusion coefficient of BHI (Fig. 8). We have determined the diffusion coefficient, D , of BHI using the Cottrell equation. According to the Cottrell equation, we calculated a diffusion coefficient of 3.57×10^{-5} cm²/s for BHI.

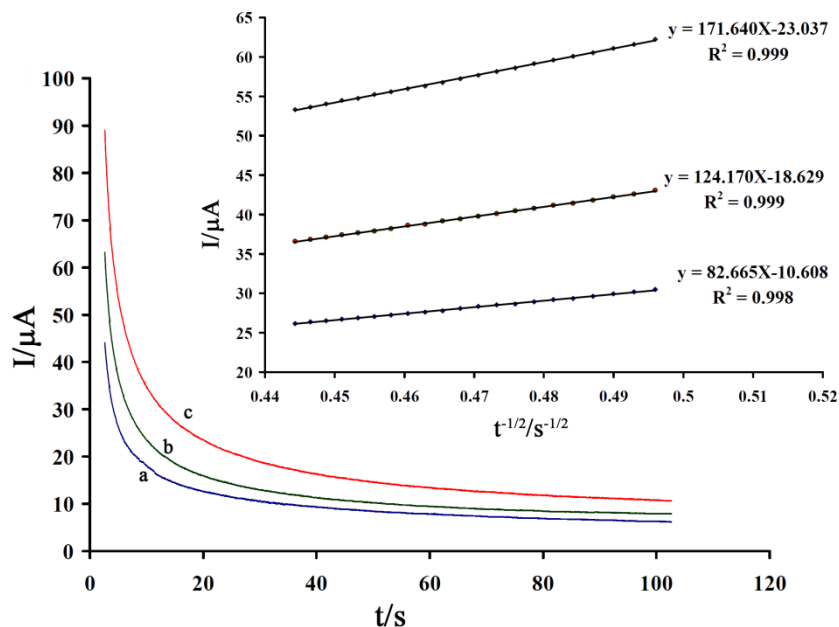


Fig. 8. Chronoamperograms obtained at the CdO/NPs/BIHF/CPE in the presence of a) 350.0, b) 450.0 and c) 550 μM BHI in the buffer solution (pH 7.0). Insert) Cottrell's plot for the data from the chronoamperograms

Since SWV has a much higher current sensitivity and better resolution than cyclic voltammetry, SWV was used for the determination of BHI (Fig. 9). The plot of peak current vs. BHI concentration is linear with slopes of $0.0711 \mu\text{A}/\mu\text{M}$ in the concentration ranges of $0.08\text{--}550 \mu\text{M}$. The detection limit of BHI was determined to be $0.04 \mu\text{M}$.

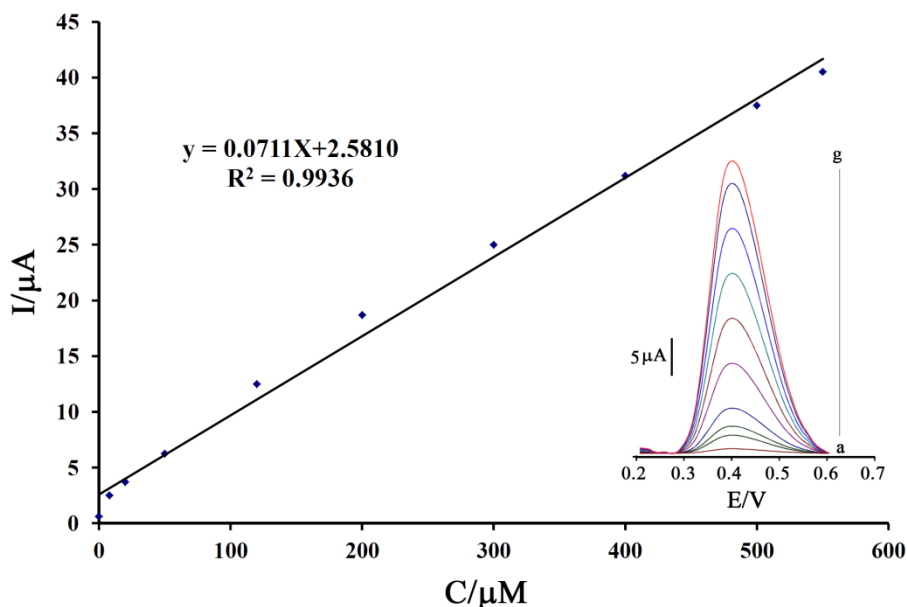


Fig. 9. The plots of the electrooxidation peak current as a function of BHI concentration. Inset; SWVs of CdO/NPs/BIHF/CPE containing different concentrations of BHI μM . (From inner to outer): 0.08, 8.0, 20.0, 50.0, 120.0, 200.0, 300.0, 400.0, 500 and 550 respectively

Table 1. Determination of BHI in food samples

Sample	Added (μM)	Expected (μM)	Founded (μM)	Recovery %
Ketchup	—	—	—	—
	10.00	10.00	9.87 ± 0.63	98.8
Soybean oil	—	—	—	—
	20.00	20.00	20.65 ± 0.73	103.25
Margarine oil	—	—	—	—
	20.00	20.00	19.84 ± 0.55	99.2

The effect of foreign substances to the oxidation peak current and peak potential response of the BHI at a surface of CdO/NPs/BIHF/CPE was tested and no interference was caused until the addition of 1000-fold excess of methionine, alanine, phenylalanine and glucose and 900-fold excess of Br^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Li^+ , Cl^- , SO_4^{2-} in a pH 6.0 buffer containing $15.0 \mu\text{M}$ BHI.

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

4. CONCLUSION

In this work, the 1-butyl-3-methylimidazolium hexafluorophosphate modified CdO/NPs carbon paste electrode was used to investigate the electrochemical behaviors of BHI. The CdO/NPs/BIHF/CPE showed great improvement to the electrode process of BHI compared to the CPE. Under the optimum conditions, the peak current was proportional to the BHI concentration in the range of 0.08–550 μM with the detection limit of 0.04 μM . The suggestion sensor was successfully used for the determination of BHI in food samples.

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