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Efficient Determination of Butylated Hydroxyanisole Using an Electrochemical Sensor Based on Cobalt Oxide Nanoparticles Modified Electrode

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A simple and reliable electrochemical sensor based on cobalt oxide nanoparticles modified glassy carbon electrode (GCE/CoOxNPs) for determination of butylated hydroxyanisole is presented here. The nanoparticles were fabricated by electrodeposition method. The modified electrode shows excellent catalytic activity toward butylated hydroxyanisole oxidation in pH 12.0 phosphate buffer solution (PBS). The detection limit ($S/N = 3$), sensitivity and catalytic rate constant (k_{cat}) of the modified electrode toward butylated hydroxyanisole were $2.9 \mu\text{M}$, $5.1 \text{ nA } \mu\text{M}^{-1}$ and $1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at linear concentration rang up to $1350 \mu\text{M}$. The capability of the modified electrode for direct butylated hydroxyanisole quantification in real samples is also discussed. This modified electrode shows many advantages such as good catalytic activity, good reproducibility, simple preparation procedure and long-term stability of signal response during butylated hydroxyanisole oxidation. In this report, compared with most cases previously reported, the detection potential of the BHA occurs at a lower potential.

Keywords: Butylated hydroxyanisole, Cobalt oxide nanoparticles, Electrodeposition, Electrocatalytic oxidation

INTRODUCTION

Butylated hydroxyanisole (BHA) is a synthetic phenolic antioxidant that is commonly used in many food formulations as food preservatives for their antioxidant properties. BHA is added into food, pharmaceutical and other commercial products as a common additive to retard the autooxidation that leads to rancidity [1,2]. It is also used in cooked or fried foods in animal oils, because of its high thermal stability and its ability to remain active in baked and fried foods [3,4]. Recently, it has been found that the artificial phenolic antioxidants may cause a loss of nourishment, and even produce toxic effects [5]. In most countries, the amount of BHA in foodstuffs is limited by legislation [6,7]. Thus, it is necessary to develop a fast, simple, reliable and reproducible method for the

determination of BHA in food or other products to ensure our health.

Several analytical methods have been reported for the determination of BHA. These included gas chromatographic [8,9], spectrophotometry [10], high-performance liquid chromatography (HPLC) [11], micellar electrokinetic chromatography and flow injection analysis and so on [12,13]. These reported methods for determination of BHA usually require complex pretreatment steps, long response time, expensive instrumental equipment and nonsuitability in field use. Therefore, easy and fast analytical tools are prerequisite to effectively determine BHA in different samples.

Electrochemical methods with their unique properties such as functional simplicity, inexpensiveness, and their fast and selective response are valuable approaches which worth for further investigation [14-17].

The application of nanometal or metal oxide particles has emerged as an attractive investigation in recent years

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[18-21]. Metal nanoparticles, represent excellent electronic conductivity and electrocatalytic properties which cause acceleration of electron transfer rate between electrode surface and redox species [22]. Therefore, modification of the electrochemical interface with nanosized metal and metal oxide nanostructures is one of the recent approaches used extensively in the development of sensing platforms [23].

Among the metal oxide materials, cobalt oxide-based materials have been widely used for electrochromic thin films [24,25], energy storage system [26], magnetoresistive devices [27] and heterogeneous catalysis [28] and electrocatalysis [29]. Choosing an electrodeposition technique for preparation of thin oxide films or their alloys offers a number of unique advantages in comparison with other procedures [30]. Thin films with specific composition, morphology and good adhesion between the deposited film and the substrate can be easily prepared by electrochemical techniques.

Antifouling properties, and excellent electrocatalytic activity of cobalt oxide redox couples have made these nanomaterial-based modified electrodes promising sensors for the detection of different molecules and biomolecules [31].

In this paper, cobalt oxide film is electrodeposited on the surface of GC electrode using cyclic voltammetry. In our research, for the first time, the electrochemical oxidation of BHA at cobalt oxide nanoparticles modified GC electrode is investigated. The response of BHA on CoOx nanoparticles modified glassy carbon electrode is also compared with cyclic voltammetry and hydrodynamic amperometry, using rotating modified electrode. The fabricated sensor was used for the detection ultra-trace amount of BHA concentrations and linear concentration rang at pH = 12, using hydrodynamic amperometry.

Since the higher detection potentials is followed by interferences of the other electro-active species that might change the contribution of response signal, detection potential of the analytes would be one of the important aspects in determining the selectivity of the sensor. In this report, compared with most cases previously reported, the detection potential of BHA occurs at a lower potential. In

addition, wide linear concentration range was remarkable compared with the results reported by the other researchers (Table 1).

EXPERIMENTAL

Materials and Reagents

3-Tert-butyl-4-hydroxyanisole, $\text{CoCl}_2 \cdot x\text{H}_2\text{O}$, KCl and other reagents were purchased from Merck and used without purification. The phosphate buffer solutions (0.1 M) were prepared from Na_3PO_4 , NaH_2PO_4 and Na_2HPO_4 . The pH of buffer solutions was adjusted with HCl and NaOH solutions. All the solutions were prepared with double distilled water.

Apparatus

The pH was measured by a Metrohm model 780 pH/mV meters. All the electrochemical experiments were conducted by a μ -AUTOLAB type III and FRA2 board computer controlled Potentiostat/Galvanostat (Eco-Chemie, The Switzerland) driven by NOVA software. A conventional three-electrode system comprising of an Ag/AgCl/(sat. KCl) reference electrode, a Pt wire as the counter electrode and a GC disk (modified and unmodified) as the working electrode were used for the measurements. All experiments were carried out at ambient temperature of 25 ± 1 °C. The scanning electron microscopy (SEM) imaging of the electrode surface was obtained by scanning electron microscopy (Philips Company, The Netherlands) at an acceleration voltage of 30 kV.

Modification of GC Electrode with Electrodeposited CoOx Nanoparticles

Cyclic voltammetry was used for the modification of GCE/CoOxNPs based on the reported procedure [32]. The bare GC electrode (2 mm in diameter) was carefully polished with alumina on a polishing cloth and then cleaned by brief ultrasonic. The freshly polished GC electrode was immersed in the 0.1 M KCl solution containing 1 mM CoCl_2 and repetitive potential cycling (30 cycles at scan rate 100 mV s^{-1}) between 1.1 V and -1.1 V was used for electrodeposition cobalt oxihydroxide film on the surface of

Table 1. Analytical Parameters for BHA at Several Modified Electrodes

Modified electrode	Methodolog	Working point	Linear range (μM)	Ability to simultaneous measurement	Ref.
GCE ^a	FIA ^b	0.8 V	0.55-55.4	BHT ^c	[7]
Pt/PPy/NiPcTs ^d	CV ^e , DPV ^f	0.571 V	200-1000	TBHQ ^g	[3]
CoHCF/GPWCE ^h	Amp ⁱ	0.5 V	0.79-190	-	[1]
AgHCF/GWCE ^j	Amp	0.7 V	7.4-830	-	[37]
MnHCF/GWCE ^k	Amp	0.45 V	0.49-1429	-	[38]
NAPCFE ^l	Amp	0.5 V	0.624-219	-	[39]
GR-PB/GCE ^m	Amp	0.45 V	0.09-70	-	[36]
SPE-MWCNT ⁿ	DPV,LSV ^o	0.33 V	0.5-10	TBHQ	[40]
AuNPs/GCE ^p	LSV ^q	0.502 V	0.45-6.8	BHT,TBHQ	[41]
IrOx NPs/GC ^r	Amp	0.58 V	1-280	-	[19]
CoOx NPs/GC ^s	Amp	0.45 V	30-1350	-	This work

^aGlassy carbon electrode. ^bFlow injection with amperometric detection. ^cTert-butylhydroxytoluene. ^dNickel(II) phthalocyanine tetrasulfonate modified polypyrrole electrode. ^eCyclic voltammetry. ^fDifferential pulse voltammetry. ^gTert-butylhydroquinone. ^hCobalt hexacyanoferrate-modified graphite paraffin wax composite electrode. ⁱAmperometry. ^jGraphite-wax composite electrode chemically modified with silver hexacyanoferrate. ^kManganese(II) hexacyanoferrate modified graphite-wax composite electrode. ^lNickel aquapentacyanoferrate modified electrode. ^mGraphene-prussian blue composites modified glassy carbon electrode. ⁿMulti-walled carbon nanotube screen-printed electrodes. ^oLinear sweep voltammetry. ^pGlassy carbon electrode modified with gold nanoparticles. ^qLinear sweep voltammetry. ^rGlassy carbon electrode modified by iridium oxide nanoparticles. ^sGlassy carbon electrode modified by Cobalt oxide nanoparticles.

glassy carbon electrode. The resulted GCE/CoOxNPs was thoroughly rinsed with doubly distilled water and used for other applications as detailed below.

RESULTS AND DISCUSSION

Characterization of Cobalt Oxide Nanoparticles and Electrochemical Properties of the Modified Electrode

The formation of cobalt oxide layer on the electrode

surface was checked by recording cyclic voltammograms of the modified electrode in alkaline solution (pH 12) without cobalt ions (not shown). We observed a voltammogram same as others reported in the literature [30,33]. To investigate the formation and growth of the cobalt oxide nanoparticles SEM images of an electrodeposited CoOx film on glassy carbon electrode are shown. Figure 1 shows the scanning electron microscope (SEM) image for the surface of modified electrode. As shown, small particles

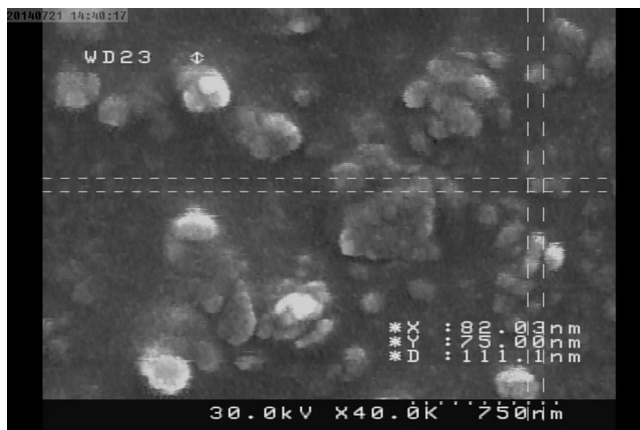


Fig. 1. SEM image of the electrodeposited CoOxNPs on GCE, scale bar is 750 nm.

with an average diameter ranging from 50-100 nm are almost uniformly distributed on the GCE surface.

To obtain the kinetic parameters of CoOx film, the scan rate effect was investigated. The effect of potential scan rate on the cyclic voltammograms was examined in the range of 10-100 mV s^{-1} (Fig. 2). As seen, the ratio of cathodic to anodic peak currents is about unity and the cathodic and anodic peak currents are directly proportional to the scan rate of potential. The peak currents vs. scan rates plots shown in the inset exhibit a linear relationship ($R^2 = 0.9986$), as expected for surface confined redox process. In addition, the shift in peak potential is negligible at scan rates 10-100 mV s^{-1} (Fig. 2), suggesting a facile charge transfer kinetics over this range of scan rate.

According to the slope of I_p versus scan rate curve and the following equation, the surface coverage (Γ) of CoOx films was estimated [34].

$$I_p = n^2 F^2 v A \Gamma / 4RT \quad (1)$$

where v is the sweep rate, A is the surface area (0.11 cm^2) of the modified electrode and the other symbols have their usual meaning. The surface coverage value for the GCE/CoOxNPs was $2.6 \times 10^{-9} \text{ mol cm}^{-2}$.

pH Response of the GCE/CoOxNPs

Past research showed that cobalt oxide electrodes can be

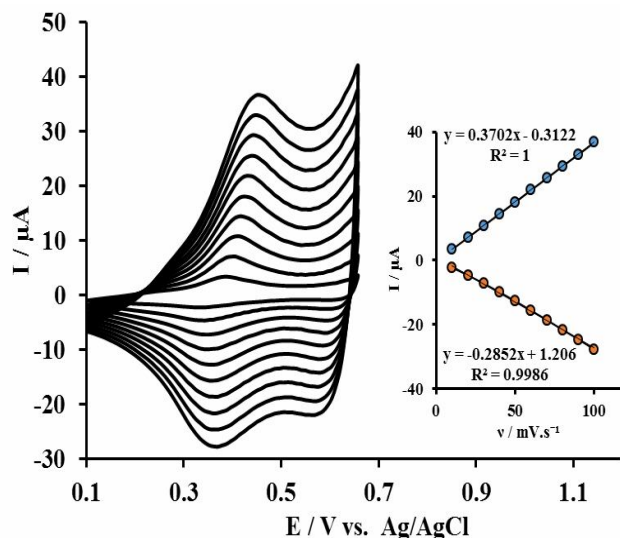


Fig. 2. (A) Cyclic voltammetric responses of a GCE/CoOxNPs in PBS (pH 12) at scan rates (inner to outer) of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s^{-1} . (B) Plots of peak currents vs. the scan rate.

used for electroanalytical or other applications [32]. This modified electrode as can be seen well defined cyclic voltammograms were observed at alkaline pH range. To investigate the effect of pH on the electrochemical behavior of the GC electrodes modified with cobalt oxide films, the cyclic voltammograms of the modified electrode were recorded in electrolyte solutions over the pH range 7-13. Anodic and cathodic peak potentials of the GCE/CoOxNPs electrode were shifted to less positive values with increasing of pH, the results are presented in Fig. 1S at a scan rate 20 mV s^{-1} .

Electrocatalytic Oxidation of BHA at GCE/CoOxNPs

An objective of the present study was to fabricate a modified electrode capable of electrocatalytic oxidation of BHA. Thus, to verify the electrocatalytic activity of the modified electrode for BHA oxidation, the cyclic voltammograms were obtained in the presence and absence of BHA at both bare GCE and GCE/CoOxNPs. Figure 3 compares the recorded typical cyclic voltammograms for the oxidation of BHA at the bare and modified GCEs. At the bare electrode, BHA is not electroactive at potential

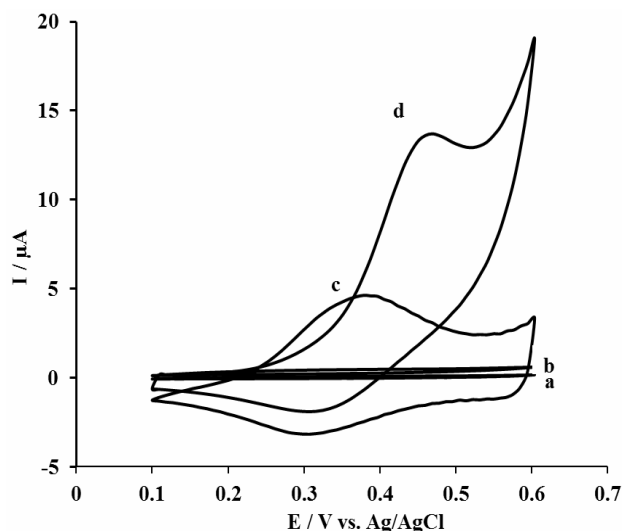


Fig. 3. Measured cyclic voltammograms of (a) GCE in 0.1 M PBS pH 12.0 at scan rate of 20 mV s^{-1} and (b) in the presence of 1.7 mM BHA (c) and (d) similar to (a) and (b) for CoOxNPs/GCE.

range of 0.1-0.6 V, suggesting a very slow electron transfer of BHA at bare GCE. However, at the GCE/CoOxNPs, the oxidation process commencing from 0.45 V was largely facilitated at GCE/CoOxNPs (Fig. 3). The decreased overvoltage and increased peak current of BHA oxidation confirm that cobalt oxide nanoparticles have high catalytic ability for BHA oxidation.

The effect of pH on the electrocatalytic activity of modified electrode toward BHA oxidation was investigated. Figure 4 illustrates the cyclic voltammograms of modified electrode in different pH solutions in the presence of 0.2 mM of BHA. As shown, the modified electrode has excellent electrocatalytic activity toward BHA oxidation at alkaline pH range (7-13). The anodic peak potential has shifted negatively along with the increase of pH. This is a consequence of the deprotonation involved in the oxidation process, which is facilitated at higher pH values. Based on the more reproducible results and high catalytic activity of the modified electrode observed at pH 12, it was selected as an optimal value for BHA measurements.

To evaluate the electrocatalytic activity of cobalt oxide film, the cyclic voltammograms of the modified electrode in the presence of different concentrations of BHA were

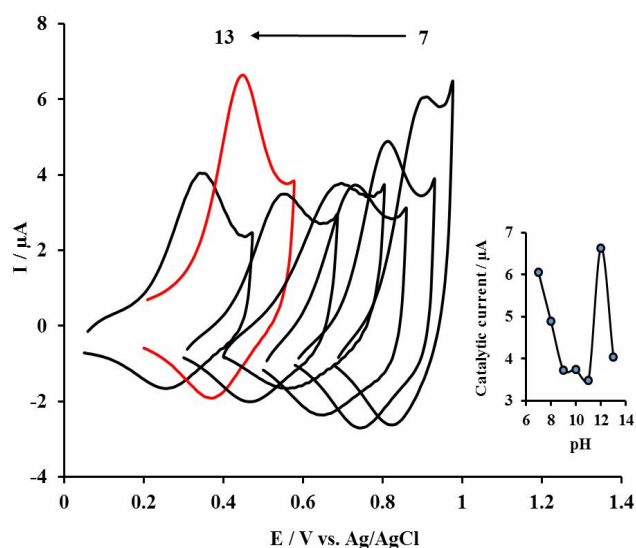


Fig. 4. Cyclic voltammograms of the GCE/CoOxNPs in different pH solutions, from right to left, 7 to 13, in the presence of 0.2 mM of BHA and scan rate of 20 mV s^{-1} . Inset, plot of peak current vs. pH values.

recorded (Fig. 5). As shown, with increasing BHA concentration the anodic peak currents increase and cathodic peaks are disappeared. Inset of Fig. 5 shows the plot of catalytic current (at potential 0.45 V) versus BHA concentration. The catalytic currents increase linearly with BHA concentration in the range of 0.25-1.35 mM, and are fitted to the equation $I (\mu\text{A}) = 5.0087 [\text{BHA}] (\text{mM}) - 0.0878$ and $R^2 = 0.997$.

To investigate the electrocatalytic mechanism of the modified electrode toward BHA oxidation, cyclic voltammograms of 0.7 mM BHA at different scan rates were recorded (not shown). The peak current for the anodic oxidation of BHA is proportional to the square root of the scan rate, suggesting that the process is controlled by diffusion of the analyte, as expected for a catalytic system. Also, a plot of the scan rate-normalized current ($I_p/v^{1/2}$) vs. scan rate exhibited the characteristic shape of a typical EC' catalytic process. During the anodic scan, Co(II) present in the mediator is electrochemically oxidized to Co(III), which in turn chemically oxidizes BHA (reduced form) present in the solution to BHA (oxidized form) and getting itself reduced to Co(II). Co(II) is again reoxidized to Co(III), at the electrode surface, which again oxidizes BHA (reduced

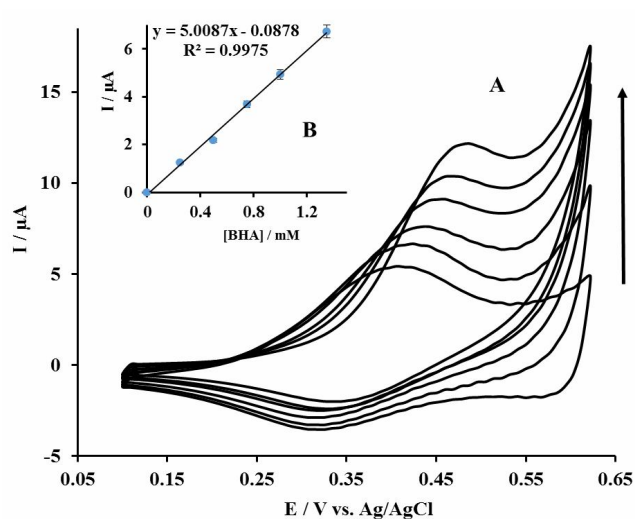


Fig. 5. Cyclic voltammograms of GCE/CoOxNPs in PBS pH 12 at scan rate 20 mV s^{-1} with increasing BHA concentration (from inner to outer) 0.25, 0.50, 0.75, 1 and 1.35 mM. Inset, plot of peak current vs. BHA concentrations.

form) chemically, and this process is repeated a number of times, resulting in electrocatalytic oxidation of BHA by the mediator present in the modified electrode.

Based on the observed results, the following catalytic scheme describes the reaction sequence in the oxidation of BHA by a CoOx redox couple:

For an EC' mechanism, the Andrieux and Saveant theoretical model [35] can be used to calculate the catalytic

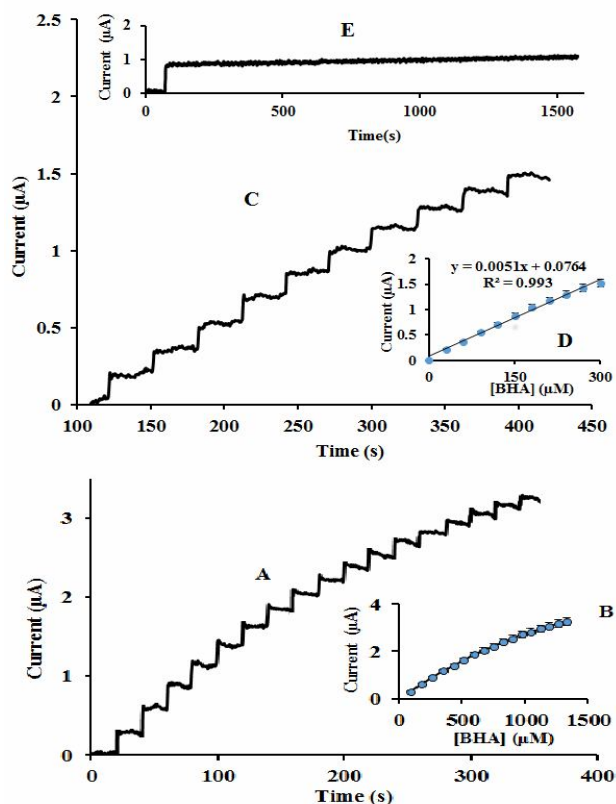
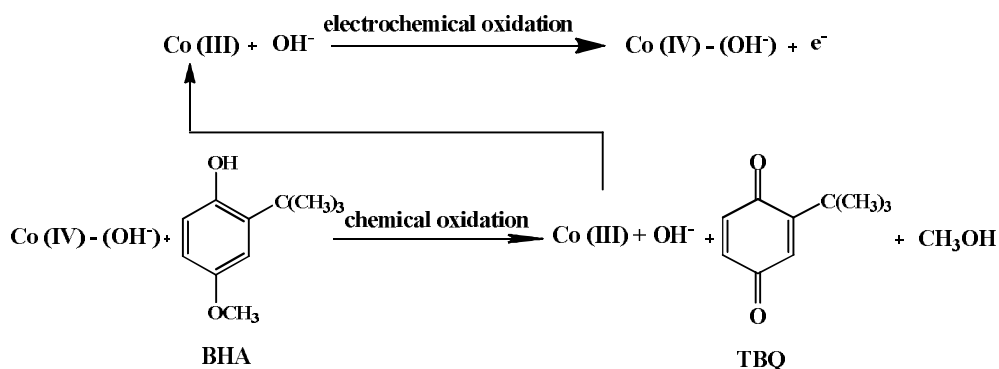


Fig. 6. Amperometric response at the rotating GCE/CoOxNPs (rotation speed 1500 rpm) held at 0.45 V in PBS (pH 12) for successive additions of (A) 90 μM and (C) 30 μM BHA (B) and (D) Plots of chronoamperometric currents vs. BHA concentrations. (E) The recorded chronoamperogram for 90 μM BHA during long period time (26 min).



rate constant. Based on this theory, there exists a relation between the peak current and the concentration of substrate for slow scan rates and large catalytic rate constant

$$I_p = 0.44nFAD^{\frac{1}{2}} \left(\frac{\nu F}{RT} \right)^{\frac{1}{2}} C_s \quad (3)$$

where D and C_s are the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and the bulk concentration (mol cm^{-3}) of substrate (BHA), respectively, and other symbols have their usual meanings. Low values of K_{cat} result in values of the coefficient lower than 0.496. For low scan rates ($5\text{--}20 \text{ mV s}^{-1}$), the average coefficient value (α) in equation 3 is found to be 0.319 for a GCE/CoOxNPs, with a surface coverage of $2.6 \times 10^{-9} \text{ mol cm}^{-2}$ and geometric area of 0.11 cm^2 in 0.7 mM BHA at pH 12. According to the approach of Andrieux and Saveant, and using Fig. 1 in Ref. [35], the average values of the calculated K_{cat} are $1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for modified electrode. The high K_{cat} obtained for GCE/CoOxNPs implies that this system can be efficiently used as an electrochemical sensor for BHA detection.

Amperometric Detection of BHA on the Modified Electrode

As discussed above, the modified CoOx/GC electrodes have excellent and strong mediation properties and facilitate the low potential amperometric measurement of BHA. Hydrodynamic amperometric method was used to examine the sensitivity of a modified electrode towards the detection of BHA. Figure 6 shows the amperometric $i\text{-}t$ curve obtained for BHA at rotating modified electrode (rotation speed 1500 rpm), under the conditions that the potential was maintained at the constant value of 0.45 V (*vs.* Ag/AgCl) in phosphate buffer solution (pH 12). As shown during the successive additions of $30 \mu\text{M}$ and $90 \mu\text{M}$ of BHA, a well-defined response was observed which quickly reached a stable value within 3 s.

The calibration plot of current response *vs.* BHA concentration is shown in Figs. 6B and D. The amperometric current response was increased linearly with increasing BHA concentration in the wide concentration range ($30\text{--}1350 \mu\text{M}$), while for a high concentration of BHA the plot of current *vs.* analyte concentration deviates from linearity (Fig. 6B). The linear least square calibration curve

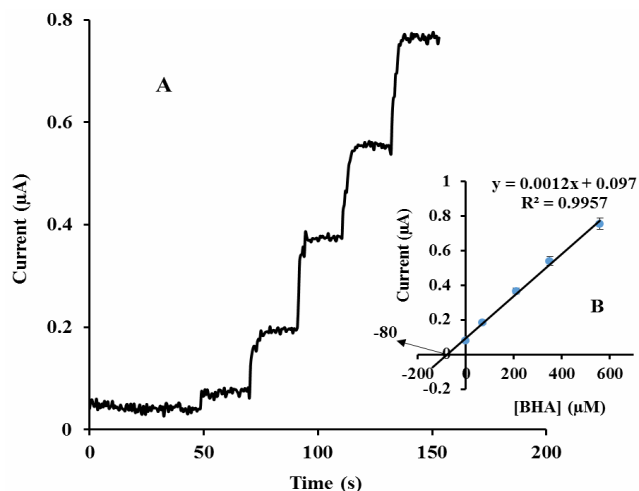


Fig. 7. (A) Amperometric response of GCE/CoOxNPs (rotation speed 1500 rpm) held at 0.45 V in buffer solution (pH 12), and in real sample pH 12 in the presence of different concentrations of BHA ($0, 70, 210, 350$ and $560 \mu\text{M}$) (B) Plot of currents (I_a) *vs.* BHA concentration.

over the range of $30\text{--}300 \mu\text{M}$ (10 points) is $I (\mu\text{A}) = 0.0051 [\text{BHA}] \mu\text{M} + 0.0764 \mu\text{A}$ with a correlation coefficient of 0.993, indicating that the regression line is fitted very well with the experimental data and the regression equation can be applied in the unknown sample determination. The detection limit (signal to noise of 3) and sensitivity were found to be $2.9 \mu\text{M}$ and $5.1 \text{ nA } \mu\text{M}^{-1}$, respectively. In addition, cobalt oxide nanoparticles showed higher stability for amperometric measurements of BHA. Figure 6E shows the amperometric response of $90 \mu\text{M}$ solution of BHA, recorded over a continuous period of 26 min. As seen, the response remains stable throughout the experiment, indicating no inhibition effect of BHA and its oxidation products for the modified electrode. Therefore, the GCE/CoOxNPs has imparted higher stability for amperometric measurements of BHA. The results above demonstrate that the modified electrode has satisfactory analytical performance and it can be a feasible sensor for BHA.

Application of the Modified Electrode for BHA Detection in Spiked Potato Chips Samples

For studying the applicability of the proposed sensor, it

was used for BHA detection in the real samples. The standard addition method was used for BHA detection in potato chips samples. The samples were treated according to the reported method [36]. Different concentrations of BHA standard solutions were added into samples. The recorded amperometric response of the modified electrode in this specimen for different concentration of BHA is shown in Fig. 7A. The calibration curve (as shown in Fig. 7B) is obtained as $I_p (\mu\text{A}) = 0.0012 [\text{BHA}] (\mu\text{M}) + 0.097 (\mu\text{A})$ with a correlation coefficient of 0.9957. Using the intercept point of this equation with the concentration axis, the concentration of BHA in the real sample is obtained as $80 \pm 0.02 \mu\text{M}$ which is very close to the real concentration of initial BHA ($75 \mu\text{M}$) in the solution, confirming the capability of our sensor for determination of BHA in the real specimens.

Selectivity

The effects of common interfering species on the amperometric responses at the GCE/CoOxNPs modified electrode at 0.45 V were studied. The selectivity of the GCE/CoOxNPs electrode was studied toward determination of $70 \mu\text{M}$ BHA in the presence of common interfering species such as, 10-fold of glucose, citric acid, Na^+ , glycine, acetate and alanine. Figure 8 shows amperometric response of the rotated modified electrode for BHA in the presence of several interference in buffer solution, pH 12. As seen, no response is observed for the modified electrode in the presence of different interfering substances. Furthermore, the electrode response for BHA has not changed after adding interfering substances. These results confirm the acceptable selectivity of the proposed modified electrode.

Working point, and linear calibration range of the proposed modified electrode were compared with those previously reported, and the results are summarized in Table 1. The results above demonstrate that GCE/CoOxNPs has a satisfactory analytical performance and it can be a feasible sensor for BHA.

To check the reproducibility of the GCE/CoOxNPs, a series of four electrodes fabricated in a same manner were employed for the detection of $90 \mu\text{M}$ in 0.1 M PBS (pH 12). A relative standard deviation (RSD) of the peak current values obtained at the four electrodes was 2.1%, suggesting

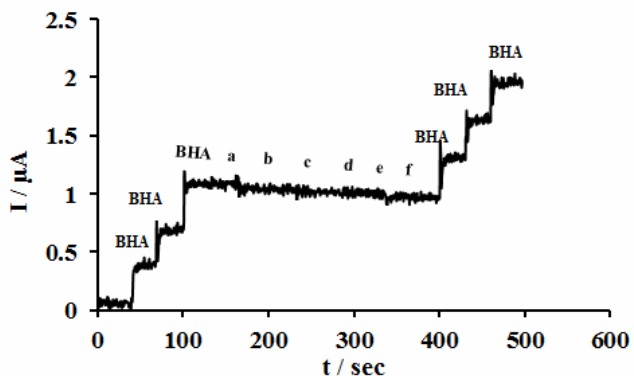


Fig. 8. Amperometric response of GCE/CoOxNPs (rotation speed 1500 rpm) at an applied potential of 0.45 V in PBS (pH 12) for the successive addition of $70 \mu\text{M}$ of BHA and 0.7 mM glucose (a), citric acid (b), Na^+ (c), L-glycine (d), acetate (e), L- alanine (f).

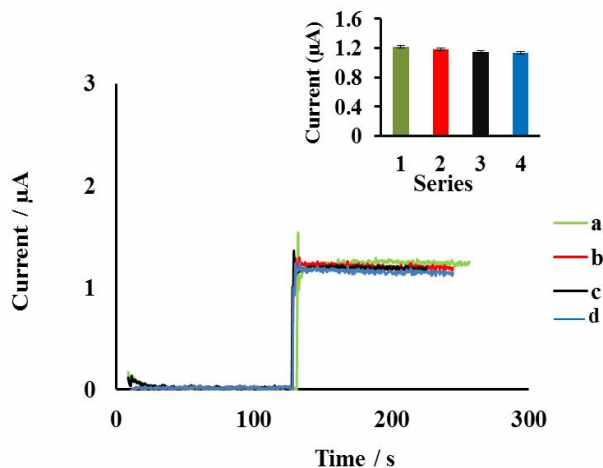


Fig. 9. Amperometric response for four series of GCE/CoOxNPs (rotation speed 1500 rpm) at an applied potential of 0.45 V in PBS (pH 12) containing $90 \mu\text{M}$ of BHA. Inset: plot of currents (I_a) vs. series.

good reproducibility of the proposed electrode (Fig. 9).

CONCLUSIONS

In summary, we have demonstrated a novel, yet simple electrochemical sensor for the detection of BHA. Potential

cycling was used for electrodeposition of cobalt oxide nanoparticles on the surface of glassy carbon electrode. The modified electrode can be used for micromolar concentration range of BHA, using hydrodynamic amperometric technique in a wide linear concentration range. The method is simple, inexpensive, fast and sensitive, and it was applied successfully to determine BHA in real samples. Furthermore, in this report, compared with most cases previously reported, the detection potential of the BHA occurred at a lower potential.

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