



A carbon paste electrode modified with a nickel titanate nanoceramic for simultaneous voltammetric determination of *ortho*- and *para*-hydroxybenzoic acids

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Abstract

An electrochemical sensor is described for the simultaneous determination of *ortho*-hydroxybenzoic acid (OHB) and *para*-hydroxybenzoic acid (PHB). The sensor consists of a carbon paste electrode modified with nickel titanate nanoceramics (NiTiO₃/CPE). The NiTiO₃ nanoceramics and the nanostructured modified CPE were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, electrochemical impedance spectroscopy and cyclic voltammetry. Differential pulse voltammetry indicates that the response to OHB (best measured at 0.90 V vs. Ag/AgCl) and PHB (measured at 0.80 V vs. Ag/AgCl) is significantly improved at the modified CPE compared to a bare CPE. The limits of detection (at S/N = 3) are 0.38 and 0.10 μM for OHB and PHB, respectively. The method was applied to the determination of the two isomers in peeling skin lotion and during the Kolbe-Schmitt reaction.

Keywords Nanostructured sensor · Interference-free determination · Monohydroxy benzoic acid isomers · Salicylic acid · Microscopic and electrochemical techniques

Introduction

The antioxidant activity of phenolic carboxy acids has been considered to be a very important cause of many biological capabilities, including antiviral, anti-inflammatory, antibacterial, antiatherogenic, and anticancer effects [1–7].

Some existing analytical procedures are available in literature for the detection of *ortho*-hydroxybenzoic acid (OHB) or salicylic acid and *para*-hydroxybenzoic acid (PHB), either alone or in combination with other drugs by high performance capillary electrophoresis [8], magnetic molecularly imprinted polymers [9], titrimetric method [10] and

high-performance liquid chromatography (HPLC) [11–16]. Such methods are important as there seem to be an increasing trend in using combinations of preservatives, not only in pharmaceutical formulations, but also in food industry, cosmetic, and senselle lubricant products. In addition, PHB is the product of hydrolysis of many parabens and therefore is often found in wastewaters. Furthermore, many of the methods use complex and labor-intensive pre-treatment procedures such as steam distillation multiple-steps, gradient elution, and solid phase extractions. Therefore, the purpose of the present study was to develop and validate a novel, simple, sensitive and accurate one-step method for simultaneous determination of OHB and PHB based on electrochemical techniques. The major difficulty of the electrochemical method is that the oxidation/reduction peaks of these two isomers are highly overlapped with each other. Furthermore, the rivalry of the isomers with electrode surface causes the non-linear relationship between the voltammetric peaks and the isomers concentrations. The key factor to overcome the problems is optimization of the effective parameters and selection of the appropriate electrode material which has excellent electrocatalytic activity. The increasing demand for it has led to the development of a rapid, simple and non-separation method for the simultaneous determination of the isomers where the

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concept of chemically modified electrodes (CMEs). CMEs have emerged as an efficient and versatile approach, and have attracted considerable attention over the past decades due to its advantages in terms of reduced costs, automatic and fast analysis, high sensitivity and selectivity [17].

In this study, nickel titanate/carbon paste electrode (NiTiO₃/CPE) was established as a sensitive sensor for the electrochemical determination of *ortho*- and *para*-hydroxy benzoic acids. Characterization of the nanostructured modified electrode was performed by different techniques [18]. The pH value which is an important factor in the separation of the oxidation peaks of the two isomers has been optimized. The performance of the sensor, such as the linear range and detection limit, was evaluated and discussed. Then the suggested method was used in real samples with satisfactory results.

Experimental

Materials and synthesis

Phenol, OHB and PHB were purchased from Merck with a purity of 99%. Britton–Robinson buffer (B-R, 0.2 M, in the pH range of 2.0–6.0) was used as a supporting electrolyte. To prepare the buffer the following reagents were used: 0.2 M CH₃COOH, H₃BO₃ and H₃PO₄ (Merck, <http://www.merck.com/>). The pH was adjusted using suitable amounts of NaOH. All solutions were prepared using deionized water and dilutions were prepared from the stock solutions. A fresh solution of 1.0×10^{-3} M OHB and PHB was prepared in deionized water as a stock solution. For preparation the mixture of OHB and PHB, appropriate volume of each stock solution was mixed and diluted by B-R buffer to obtain a solution containing appropriate concentration of OHB and PHB. Paraffin oil (DC 350, density = 0.88 g cm⁻³) and graphite powder (particle size <100 μm) used for constructing electrodes were purchased from Merck. The B-R buffer containing 5.0 mM [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] (Merck) was used to electrochemically characterize the modified nanostructured electrode.

Apparatus

All electrochemical measurements were carried out using a Sama 500 potentiostat electrochemical workstation (Isfahan, Iran) with a usual three-electrode system with a platinum wire as an auxiliary electrode, a silver/silver chloride (Ag/AgCl/KCl 3.0 M) as the reference electrode, and a modified carbon paste electrode as the working electrode. All potential values have been measured versus Ag/AgCl/KCl 3.0 M reference electrode. The impedance measurements were taken with a PGSTAT 35 (Eco Chemie Utrecht, Netherlands) potentiostat/galvanostat, coupled to a computer using the NOVA software

(version 1.6) for data acquisition. pH measurements were performed on a Metrohm pH (model 691) meter with a combined pH glass electrode calibrated against standard phosphate buffer pH 4.0 and 7.0. The crystal structures of the nanopowders were obtained by X-ray diffraction (XRD) analysis. The XRD spectra of the nanoparticles were recorded with a Model PTS 3003 of SEIFERT diffractometer within a range of 10° to 80° by Cu K_α radiation (λ = 1.5418 Å). The morphology of the nanopowders was examined by scanning electron microscopy (SEM) equipped with a KYKY-EM3200 instrument. The fine powders were dispersed in amyl acetate on a carbon coated transmission electron microscopy (TEM) copper grid. Ultrapure water was obtained from an ultrapure water system (smart 2 pure, TKA, Germany).

Choice of materials

Wide attention has been paid to electrochemical studies on metal nanoparticle modified electrodes. Titanium based oxides (MTiO₃) containing metals such as M: Ni, Pb, Co, Fe, Cu and Zn are generally known as inorganic functional materials with wide applications. For instance, the materials have been used in solid oxide fuel cell electrodes, industries, metal-air barriers, gas sensors and high performance catalysts [19, 20]. Among them NiTiO₃ has been investigated as a photocatalysts, tribiological coating to reduce friction and wear at high temperature applications without using liquid lubricants [21, 22]. Because of NiTiO₃ has been shown excellent properties in the previous literatures, it was seemed the properties of the compound in nano scale can be improved significantly. Therefore, NiTiO₃ nanostructures can be create an appropriate sensor for the analytes with overlapping peaks. Therefore, NiTiO₃ nanopowders were selected for simultaneous determination of OHB and PHB with overlapping voltammetric peaks.

Synthesis of NiTiO₃ nanoparticles

In this research, NiTiO₃ nanopowders were prepared by the sol-gel method [23]. Therefore, 0.006 mol Ni(NO₃)₂·6H₂O were dissolved into 30 mL of distilled deionized water. Then an appropriate amount of stearic acid (C₁₈H₃₆O₂) was added to the above solution under magnetic stirring, and it was heated at 70 °C. At this temperature, the stearic acid was melted and two organic and aqueous phases were formed in the reaction vessel. So, heating was continued until complete removal of the aqueous phase. Afterward, tetra butyl titanate with a custom stoichiometric ratio (C₁₆H₃₆O₄Ti, purity of 99.5%) was added to the solution, stirred to form a homogeneous solution, cooled to room temperature and drying in an oven for 12 h to achieve dried gel. Finally, the gel was calcined at 750 °C in air to eliminate organic impurities and form nano-crystallites of NiTiO₃.

Preparation of the NiTiO₃/CPE

The modified carbon paste electrode is made in the following steps: Firstly, 0.05 g (optimal amount) of purified NiTiO₃ nanopowders were added to a beaker containing 5.0 mL de-ionized water and then sonicated for about 30 min to give a homogeneous and stable suspension. Secondly, this suspension was mixed with 0.5 g graphite powder. After evaporation of water, the final paste obtained by addition of paraffin oil to the mixture and mixed for 30 min in a small mortar. The prepared paste was accumulated into the hole of the electrode body. A Teflon tube (10 cm in length) with a hole at one end (inside diameter of 2.0 mm) for the carbon paste filling served as the electrode body. Electrical contact was created by a copper wire placed into the opposite end of the tube. When renewal of the electrode surface is needed, the surface of the NiTiO₃/CPE was polished with a weighing paper.

Preparation of the real samples

One of the major properties of OHB is its ability to remove skin cells of the most upper layer of the skin that makes it a useful peeling agent for patients with acne. On the other hand, PHB appears frequently as antimicrobial preservatives in cosmetic products. Therefore, to investigate the ability of the suggested sensor for determination of OHB in the presence of its isomer, a peeling skin lotion was also selected. For this purpose, 5.0 mL of this lotion moved to 25.0 mL volumetric flask and the volume was brought. Then 0.5 mL of this solution in volume brought to 50.0 mL. Finally, a certain amount of this solution was transferred to the electrochemical cell for determination of intended compounds by the method.

Results and discussions

Characterization of the NiTiO₃ nanoceramics and NiTiO₃/CPE

SEM and TEM analysis of NiTiO₃ nanopowders

A scanning electron microscope provides details surface information about nanoparticle including morphological characterization, homogeneity and the size of the particles. Figure 1a indicates the SEM micrograph of NiTiO₃ nanoparticles. As can be observed the NiTiO₃ nanoparticles present homogeneous morphology with spherical form and the average diameter of the nanoparticles is about 38.0 nm.

Also, Fig. 1b shows the TEM micrograph of NiTiO₃ nanopowders calcined at 750 °C for 2 h [21]. Using the technique, the particle size of NiTiO₃ nanoparticles was obtained in the range of 30–65 nm.

Characterization of the NiTiO₃/CPE by EIS

In this study, EIS technique was used to indicate the additional effect of nickel titanate nanoparticles on the modified carbon paste electrode. EIS graphs of the modified and unmodified electrodes in [Fe(CN)₆]^{3-/4-} (Fe²⁺/Fe³⁺) as negatively charged redox probe is shown in Fig. 2. The value of the electron transfer resistance (R_{ct} , semicircle diameter) depends on the dielectric and insulating features at the electrode/electrolyte interface [24]. The results were approximated by an equivalent circuit. As can be observed the presence of NiTiO₃ nanoparticles on the surface of the carbon paste electrode increases the electron transfer at the surface of the modified electrode. By the other hand, the modified electrode compared to a bare electrode, had lower charge transfer resistance.

Voltammetric studies of the modified carbon paste electrode

Kinetic parameters of the NiTiO₃/CPE were investigated by cyclic voltammetry (CV) method. Cyclic voltammograms of the modified electrode on Fe²⁺/Fe³⁺ probe solution in the range of scan rates from 10.0 to 70.0 mV s⁻¹ are shown in Fig. 3. It can be seen in Fig. 3c for scan rate values higher than 300.0 mV s⁻¹, the anodic potential is directly proportional to the logarithm of scan rate. Afterward, electron transfer rate constant (k_s , s⁻¹) and charge transfer coefficient (α) can be calculated by the Laviron's equation (Eq. 1) [25].

$$\text{Log } k_s = \alpha \log(1-\alpha) + (1-\alpha) \log \alpha - \log(RT/nFv) - \alpha(1-\alpha) n_\alpha F \Delta E_p / 2.3RT \quad (1)$$

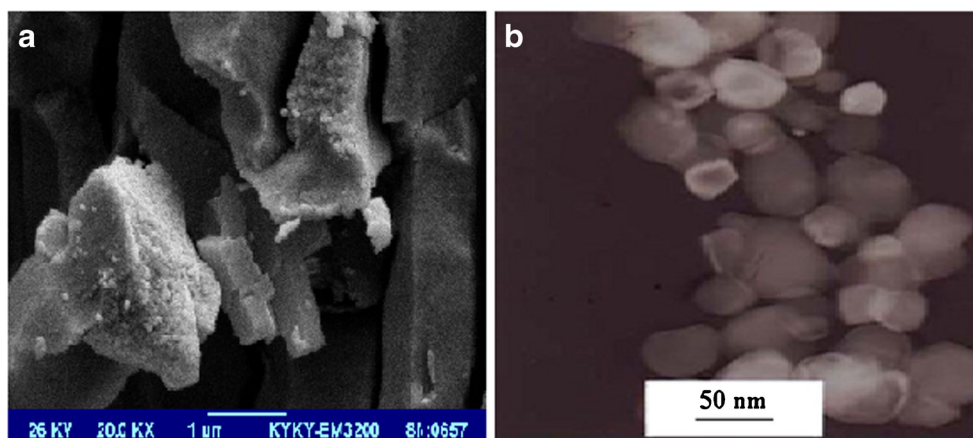
Where v is different scan rate values and n is the number of electrons involved in the redox reaction. From these expressions, α can be determined by measuring the variation of the peak potential with respect to the scan rate, and k_s can be determined by measuring the ΔE_p values. According to these results, the value of α and k_s were obtained to be 0.32 and 0.14 s⁻¹, respectively. Also, the surface area of the modified electrode can be calculated from the Randles-Sevcik equation [25]. Based on the equation, surface area of the NiTiO₃/CPE was obtained 0.56 cm².

Application to electrochemical studies of monohydroxy benzoic acid isomers

Oxidation of OHB and PHB on the unmodified and modified electrodes

The electrochemical behaviors of OHB and PHB have been investigated by DPV. Figure 4 shows differential

Fig. 1 **a** SEM and **b** TEM micrographs of NiTiO₃ nanopowders



pulse voltammograms of the CPE and NiTiO₃/CPE in B-R buffer (pH 5.0) containing 50.0 μM PHB and 50.0 μM OHB. Based on Fig. 4 a significant enhancement in voltammetric response of NiTiO₃/CPE is observed in compared with the bare CPE. The effect proves the presence of nickel titanate nanoparticles on the modified electrode. So, the modified electrode was used for simultaneous determination of OHB and PHB with high sensitivity and suitable detection limit.

pH dependence study

The electrochemical behavior of OHB and PHB at NiTiO₃/CPE were studied in the presence of B-R buffer with different pHs (2.0 to 6.0) using differential pulse voltammetry (DPV). Differential pulse voltammograms of the modified electrode toward OHB and PHB are shown in Figs. S3 A and S4 A, respectively. As can be seen, the anodic peak potentials of OHB and PHB shift to negative values with increasing of pH. So, protons participate in the OHB and PHB

oxidation reaction and acidity of the electrolyte has a significant effect on the oxidation. Moreover, it indicates that the optimum pH 2.0 can be used for the determination of OHB and PHB individually (Figs. S3 B and S4 B). But when OHB and PHB determine simultaneously at pH 2.0, both of them have only one peak in DPV about 1.05 V (Fig. S5). Therefore, we used another pH value to resolve the two isomers peaks from each other. Based on Fig. S6, in pH 5.0 there are two separate peaks with good sensitivity for two isomers. In pH = 5.0 PHB shows an oxidation peak at about 0.8 V whereas oxidation peak of OHB observed at about 0.9 V. Therefore, pH = 5.0 was selected for simultaneous determination of these isomers.

Interferences studies

The ability of the nanostructured sensor for determination of OHB and PHB in the presence of common interfering substances was investigated by DPV technique. The experiments were carried out by analyzing a standard solution containing 50.0 μM OHB and PHB using an increasing amount of interfering species. The tolerance limit was defined as the concentrations which give an error less than ±5.0% in the oxidation peak current of OHB and PHB [26]. Some common cations and anions such as Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺, Cl⁻, CO₃²⁻, NO₃⁻ and I⁻ were studied for its interference with detection of OHB and PHB. The results demonstrate that these ions virtually have no obvious interference to the DPV signals of the targets at the NiTiO₃/CPE. Some organic compounds such as gallic acid, uric acid and dopamine have been considered to have no influence on the signals of OHB and PHB with deviations below 5%. These results have been reported in Table S1. However, some compounds with similar structures with OHB and PHB can be effect on the determination. For example,

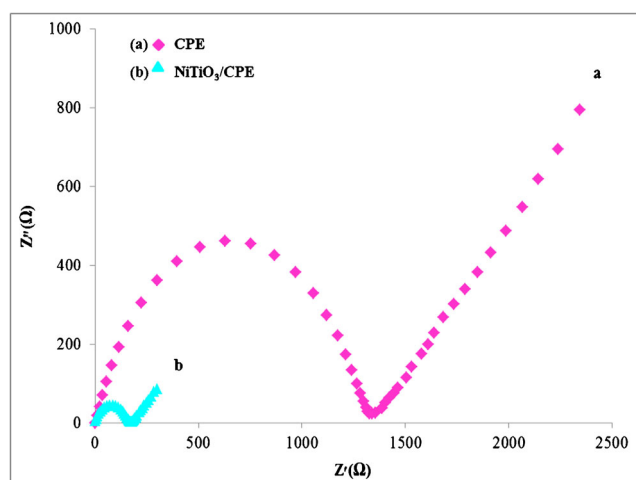
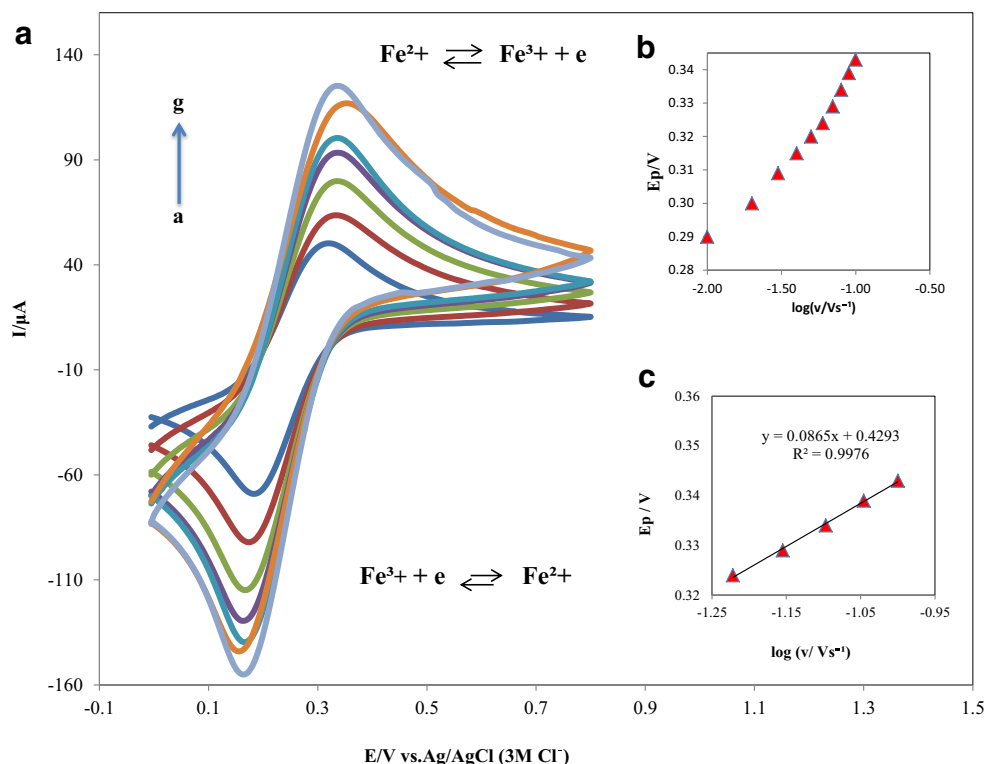


Fig. 2 The Nyquist plot of the CPE and NiTiO₃/CPE in 5.0×10^{-3} M [Fe(CN)₆]^{3-/4-}

Fig. 3 **a** Cyclic voltammograms of 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at the surface of $\text{NiTiO}_3/\text{CPE}$ in various scan rates containing 20.0, 30.0, 40.0, 50.0 and 60.0 mVs^{-1} (from inner to outer); **b** and **c** ΔE_p vs. $\log(v/\text{Vs}^{-1})$



methylparaben and propylparaben showed interference for voltammetric determination of PHB.

Stability and repeatability of $\text{NiTiO}_3/\text{CPE}$

The ability to generate a modified electrode with a stable surface was investigated in optimized experimental conditions, using continuous DPV determination of OHB and PHB. Successive measurements of oxidation currents of

50.0 μM OHB and PHB at the same $\text{NiTiO}_3/\text{CPE}$ for 15 days period were performed. The relative standard deviation (RSD) for the current signal was obtained at 4.2%. The results demonstrate $\text{NiTiO}_3/\text{CPE}$ has an excellent long-time stability for the determination of OHB and PHB without any fouling.

Moreover, for repeatability investigation, five parallel modified electrodes were fabricated in the same way, and their electrochemical responses (peak current density) toward 50.0 μM OHB and PHB were recorded. The RSD of the measurements was estimated to be 4.5% and 3.4% for OHB and PHB, respectively, confirming that the modified electrode is highly reproducible. According to these results, $\text{NiTiO}_3/\text{CPE}$ is a repeatable and stable electrode for determination of OHB and PHB.

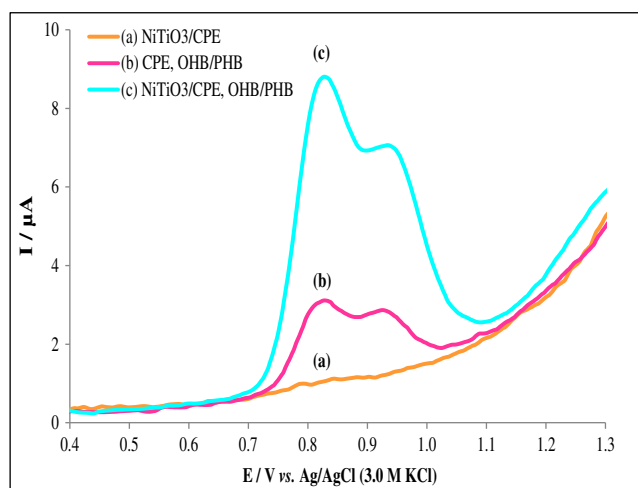


Fig. 4 (a) Differential pulse voltammograms of B-R buffer (pH 5.0), (a): at $\text{NiTiO}_3/\text{CPE}$, (b) and (c) in the presence of 50.0 μM OHB and 50.0 μM PHB at CPE and $\text{NiTiO}_3/\text{CPE}$, respectively

Interference-free determination of OHB and PHB

Since DPV has low detection limit and insignificant charging current contribution to the background current than CV, it was chosen for simultaneous determination and evaluation of the detection limit of OHB and PHB. The differential pulse voltammograms of OHB and PHB with different concentrations in 0.2 M B-R buffer (pH 5.0) at the surface of $\text{NiTiO}_3/\text{CPE}$ are shown in Fig. 5. The oxidation peak at about 0.8 V and 0.9 V is attributed to PHB and OHP, respectively. Under the optimized conditions, two linear dynamic ranges were observed for OHB and PHB. Fig. 5b indicates the oxidation peak current

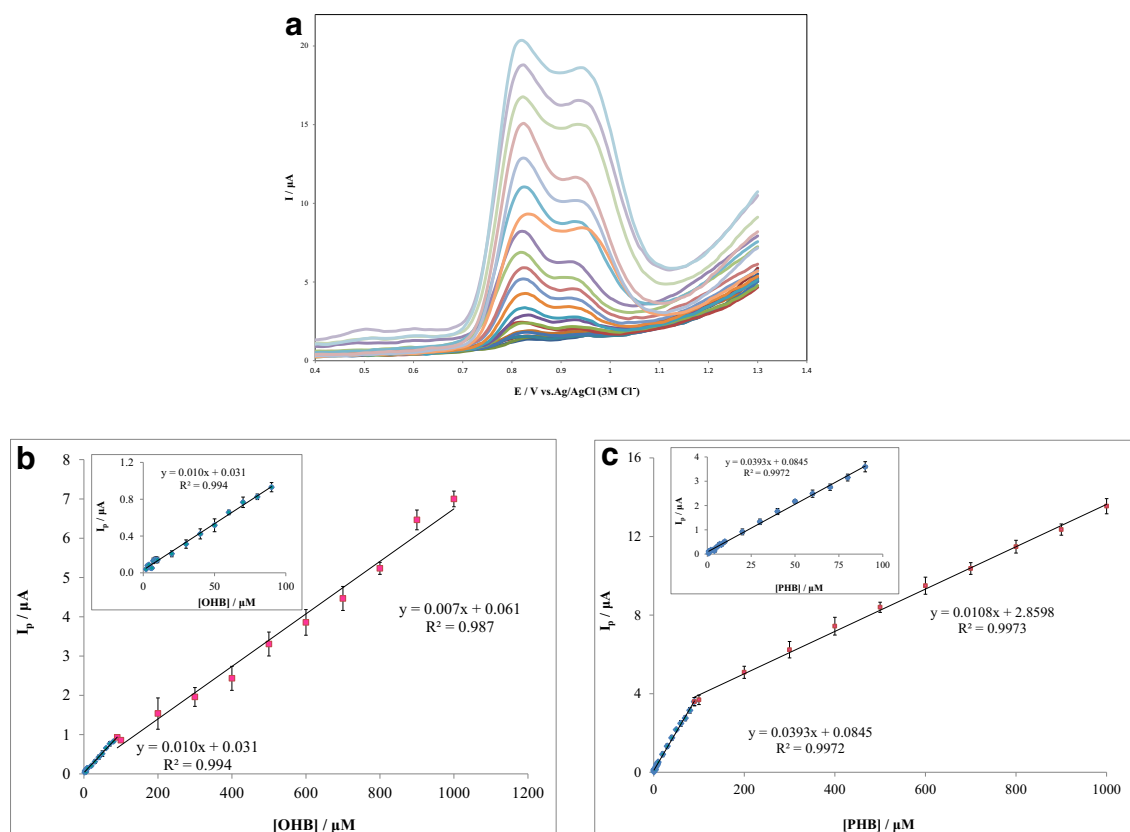


Fig. 5 DPV of NiTiO₃/CPE in a 0.2 M B-R buffer (pH = 5.0), containing different concentrations of OHB and PHB. a-z correspond to: 3.0–100.0 μM of OHB and 3.0–100.0 μM PHB (a), Plots of the

electrocatalytic peak current as a function of OHB and PHB concentration (b); E_{pa} (PHB) ≈ 0.8 V, E_{pa} (OHB) ≈ 0.9 V, scan rate, 110.0 mVs⁻¹

of OHB has two linear calibration ranges of 10.0–90.0 μM and 90.0–1000.0 μM. The specific calibration equations for these concentration ranges are:

$$I_{pa} = 0.010 C + 0.031$$

$$I_{pa} = 0.007 C + 0.061$$

$$R^2 = 0.994$$

$$R^2 = 0.987$$

The linear regression equations for PHB (ranges of 10.0–90.0 μM and 90.0–1000.0 μM) were also obtained to be (Fig. 5c):

$$I_{pa} = 0.039 C + 0.085$$

$$I_{pa} = 0.011 C + 2.860$$

$$R^2 = 0.997$$

$$R^2 = 0.997$$

Table 1 An overview on previously reported nanomaterial-based electrochemical methods for determination of OHB and PHB

Method applied	Method applied	Detection limit (OHB) (μg/mL)	Detection limit (PHB) (μg/mL)	Reference
RP-HPLC-DAD ^a	C ₁₈ ODS ^b	—	3.5	[15]
RP-HPLC-DAD	C ₁₈	—	2.5	[28]
Fluorescence Spectroscopy	α- and β-cyclodextrin	—	0.04	[30]
Electrochemistry	Screen-printed electrode	0.77	—	[31]
GC-MS ^c	GCB ^d	0.24	—	[32]
Electrochemistry	CFE ^e	0.23	—	[33]
Electrochemistry	NiTiO ₃ /CPE	0.05	0.01	This work

^a Reverse phase-high performance liquid chromatography photo diode array detector

^b C₁₈ ChromSpher polymeric octadecylsilane

^c Gas chromatography-mass spectrometry

^d Graphitized carbon blacks

^e Carbon-fiber electrode

Detection limit is defined as the lowest concentration that can be distinguished from the noise level [27]. According to the slope of the above equations, the detection limits were calculated, which were 0.38 μM and 0.10 μM for OHB and PHB, respectively. Also, the sensitivity were obtained 0.18 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ and 0.70 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ for OHB and PHB, respectively. In Table 1, some of the analytical parameters achieved in the present study are compared with those previously reported by others [11, 28–32]. These data show that the responses of the method are superior to the previously reported literatures.

Real sample analysis

In order to estimate the validity of the above method in a cosmetic product, the $\text{NiTiO}_3/\text{CPE}$ was applied to measure the OHB and PHB concentration simultaneously in a commercial peeling skin lotion using standard addition method. Table S2 indicates the analytical results.

Also, the nanostructured modified electrode was used for the analysis in the resulting solution of the Kolbe-Schmitt reaction. The standard addition method was applied for testing recovery. The results of the spiked samples are acceptable and are shown in Table S3. This result reveals that simultaneous or independent measurements of the two products are possible without much interference and also demonstrates the applicability of the modified CPEs in organic chemistry. Therefore, the NiTiO_3 nanostructured modified electrode was applied for the determination of OHB and PHB in real samples with satisfactory results.

Conclusions

NiTiO_3 nanoparticles are introduced as a novel CPE modifier for simultaneously electrochemical detection of OHB and PHB without any interference. Because of similar physico-chemical properties, the two isomers interfere with each other during their identification. Moreover, these isomers are formed in Kolbe-Schmitt reaction at the same time and simultaneous determination of them has particular importance. The present method enables sensing of OHB without interference by PHB. Under optimal conditions, the sensor represents excellent performance for detecting OHB and PHB with a detection limit of 0.38 μM and 0.1 μM , respectively. The desirable selectivity and sensitivity of the modified electrode are ascribed to the excellent conductivity and electrocatalytic ability of NiTiO_3 nanoparticles. This modified electrode is a promising approach to the simultaneous voltammetric determination of the isomers in real samples without any separation with satisfactory results.

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