

Formaldehyde measurement based on its electrocatalytic oxidation by Ni-TiO₂ nanoparticles/chitosan modified carbon paste electrode as an effective method

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ABSTRACT

In this work, for the first time, a new and effective bulk modified carbon paste electrode (CPE) was prepared by TiO₂ nanoparticles and chitosan and then Ni²⁺ ions were incorporated to this electrode by immersion of the modified electrode in nickel chloride solution. The values of electron transfer coefficient, charge-transfer rate constant and electrode surface coverage for Ni(II)/Ni(III) redox couple of the TiO₂/chitosan modified carbon paste electrode (Ni-TiO₂/CHIT/CPE) were found to be 0.66, $3.28 \times 10^{-1} \text{ s}^{-1}$ and $5.14 \times 10^{-8} \text{ mol cm}^{-2}$, respectively. The prepared Ni-TiO₂/CHIT/CPE material was characterized by scanning electron microscopy and X-ray diffractometry. The electrochemical behaviour of the Ni-TiO₂/CHIT/CPE towards oxidation of formaldehyde was evaluated and proved. The effects of various factors on the efficiency of electrocatalytic oxidation of formaldehyde were optimized. Under the optimized condition, a calibration curve was obtained in the linear dynamic range of 2.80×10^{-4} to $2.50 \times 10^{-2} \text{ mol L}^{-1}$ with detection limit of $7.14 \times 10^{-5} \text{ mol L}^{-1}$ ($3\sigma/\text{slope}$) for formaldehyde determination. Also, the method was successfully applied for formaldehyde measurement in the real sample.

Keywords: TiO₂ nanoparticles, Chitosan, Modified carbon paste electrode, Formaldehyde, Electrocatalytic oxidation, Measurement.

1. Introduction

Chitosan (CHIT) has been defined as a promising material for modification of the electrode surface due to its attractive properties such as good stability, high permeability and strong adherence to the electrode surface, non-toxicity, and low cost material. Recently, much attention has been paid to the study of the application of chitosan in electroanalytical chemistry [1,2]. The chitosan structure contains free hydroxyl and amino functional groups, which can form chemical bonds of other biomolecules and can act as a sorbent of Ni(II) or other cations. Several electrochemical sensors have been fabricated based on the interaction between chitosan and analytes [3,4].

Nanomaterials, specifically nanoparticles because of their small size (1-100 nm), present unique chemical, physical, and electronic properties. Therefore, considering these behaviours, nanoparticles are found to have broad applications in electrochemistry [5-7].

A major problem of the solid electrodes, however, was the contamination and fouling of the electrode surface due to the product(s) of these electro-oxidations. The CPE overcomes these problems due to its easily renewed surface. Furthermore, the CPE exhibits a low residual background current, reproducibility of successive voltammetric scans, applications to both oxidations and reductions and low costs [8]. The application of the carbon paste electrodes modified with nanostructured substances remarkably increases electrochemical property of many important compounds [9,10]. The comparison of a nanoparticle modified electrode with a macroelectrode shows that the first nanoparticle has the great advantages such as high effective surface area, mass transport, catalysis, and control over local microenvironment [11,12]. There is a remarkable interest in using TiO₂ nanoparticles as an electrode modifier in sensors. Also, Sonogel carbon electrode modified with nanostructured TiO₂ for catechol detection [13], nano-TiO₂ film/nafion-modified glassy carbon electrode for the investigation of dopamine [14], TiO₂ nanoparticle-modified carbon

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paste electrode for buzepide methiodide determination [15], and carbon-Pt nanoparticles modified with TiO₂ nanoparticles for the detection of dopamine [16] have been reported.

Formaldehyde is one of the toxic pollutants (as a carcinogen) [17]. Also, this material was applied as an extremely important industrial raw material for the production of phenol-, urea- and melamine-formaldehyde resins and manufacturing of building plates, plywood and lacquer materials [18,19]. Formaldehyde is also used in chemical synthesis as an intermediate for the production of consumer goods as detergents, soaps, shampoos, and as a sterilizing agent in pharmacology and medicine. On the other hand, formaldehyde is a natural metabolite of living organisms. It can be found in fruits, vegetables, flesh [20] and biological fluids of human origin [18]. Therefore, simple and sensitive methods for determination of formaldehyde are needed for specific biotechnological processes, environmental control, medicine and even for drinking water and food analysis. Compared with spectral and chromatographic analysis, electroanalytical method has been considered as a good alternative to formaldehyde detection due to its high sensitivity, selectivity and its potential for providing real-time measurements. Achmann et al. studied the sensor electrode with multi walled carbon nanotube films modified with the graft percentage of amino-groups modified electrode to detect the concentration of formaldehyde [21]. The result illustrated that the sensor displayed high chemical selectivity, fast response and good reproducibility to low concentration formaldehyde. Amperometric sensors in the potentiostatic mode using noble metals as electrode nanomaterials are also used for formaldehyde detection [22]. Metal nanomaterials have high effective surface areas and extraordinary electron-transport properties. Their uses as the electrochemical interface provides a rapid current response and high-detection sensitivity. Consequently, the electron transfer between the electrode and the probe molecules is accelerated. Zhang et al. introduced the electrodeposition of a nanostructured palladium in the aluminum oxide membrane coated glassy carbon electrode [23]. The proposed sensor not only possesses a broad linear range, good reproducibility and high sensitivity, but also exhibits a synergistic effect that minimizes poison formation. Yi et al. reported a novel formaldehyde detection method based on the nanoporous palladium modified TiO₂ electrode in alkaline solutions [24].

In respect of literature survey, no TiO₂/chitosan modified carbon paste electrode was employed hitherto for electrocatalytic oxidation of formaldehyde. The aim

of this work is to develop a new TiO₂/chitosan modified carbon paste electrode to form complex with Ni²⁺, which provided a simple, sensitive, rapid and low-cost sensor for electrocatalytic oxidation of formaldehyde in the alkaline medium.

2. Experimental

2.1. Reagents and chemicals

TiO₂ powder (Degussa P25) with the particle size of 30 nm and surface area of 50 m² g⁻¹ was obtained from Degussa Corp. Graphite powder and high-purity paraffin oil from Fluka were used for fabrication of the carbon paste electrode. Sodium hydroxide, formaldehyde, NiCl₂.6H₂O, potassium hexacyano ferrate (K₄Fe(CN)₆) and potassium chloride were purchased from Merck company; they were of analytical reagent grade. Chitosan (molecular weight 100000-300000 g mol⁻¹) was prepared from Acros Company (USA). All materials were used without any further purification. Also, all solutions were prepared with double distilled water. All other reagents were of analytical grade. Phosphate buffer (pH 1-9) was used as supporting electrolyte and adjusting pH. The retailer of all chemicals from different companies was KimiaExir.

2.2. Apparatus

Voltammetric measurements were performed at a Metrohm Computrace Voltammetric Analyzer Model 797 VA with a conventional three-electrode cell. The bare CPE, chitosan modified CPE (CHIT/CPE) and TiO₂/chitosan modified CPE (TiO₂/CHIT/CPE) were used as working electrodes. Also, the auxiliary electrode was a platinum rode, and an Ag|AgCl|KCl (3 M) was applied as a reference electrode. During the measurements, the solution in the cell was neither stirred nor aerated. Measurements of pH were made with a Denver Instrument Model 827 pH meter equipped with a Metrohm glass electrode. Scanning electron microscopy (SEM) (Philips Corp., XL30 model) was used for seeing of the surface morphology of the modified electrodes. X-ray diffraction (XRD) was conducted on a an X-ray diffractometer (XRD, GBC MMA Instrument) with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.3. Preparation of TiO₂ nanoparticles/chitosan modified CPE

The unmodified CPE was constructed by hand mixing of graphite powder with paraffin oil at a ratio 18:7 (w/w) in an agate mortar. The TiO₂/CHIT/CPE was fabricated with 0.90 g graphite powder, 0.35 g paraffin, and certain values of TiO₂ and chitosan. The steps of preparation of the TiO₂/CHIT/CPE are shown in Fig. 1. The amount of TiO₂ and chitosan was changed to prepare the modified

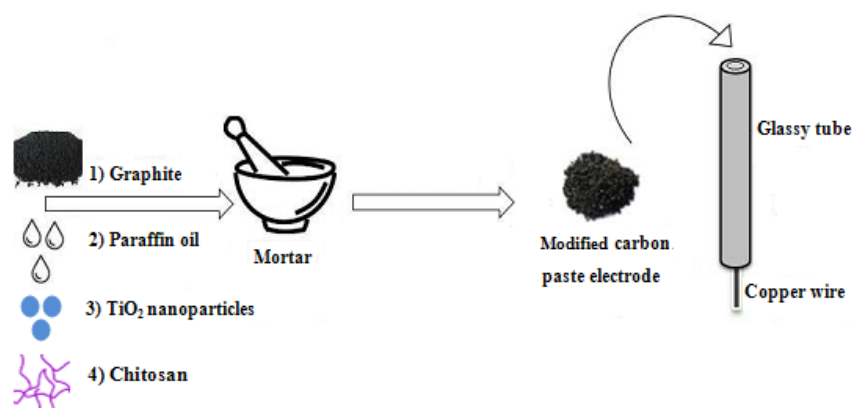


Fig. 1. Schematic procedure of the TiO₂/CHIT/CPE preparation.

electrode with different percentages. TiO₂ powder and graphite were dissolved in diethyl ether then the solvent was evaporated by stirring. The resulting mixture and paraffin were blended by hand-mixing until a uniform paste was obtained. The resulting paste was inserted at the bottom of a tube (internal radius 3 mm) and smoothed on a weighing paper. Electrical connection was implemented by a copper wire lead fitted into the tube. A fresh electrode surface was obtained by squeezing out a small portion of the paste and polishing it with filter paper until a smooth surface was obtained. For comparison, the CHIT/CPE was also prepared in the same mentioned method in the absence of TiO₂.

2.4. Sample analysis

100 μ L of formalin was diluted in 10 mL of water and then, an aliquot (400 μ L) was added to 25 mL of 0.1 M NaOH solution and recorded by the cyclic voltammetry under optimized experimental conditions. The concentration of formaldehyde was evaluated from calibration curve. All experiments were performed in triplicate.

3. Results and Discussion

3.1. Electrochemistry of the fabricated electrodes

Cyclic voltammetry was used to investigate electrochemical properties of fabricated bare CPE, CHIT/CPE and TiO₂/CHIT/CPE in K₄Fe(CN)₆ solution. Fig. 2 illustrates the cyclic voltammograms of the electrochemical oxidation of K₄Fe(CN)₆ at the surface of the bare CPE (a) CHIT/CPE (b) and TiO₂/CHIT/CPE (c) in the 10 mM of K₄Fe(CN)₆ solution. As can be seen in Fig. 2, the anodic and cathodic peak currents for the CHIT/CPE were higher than that at the bare CPE and peak currents for the TiO₂/CHIT/CPE are greater than that of the CHIT/CPE. The experimental results show reproducible anodic and cathodic peaks ascribed to Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ redox couple at slow scan rates on

the surface of CHIT/CPE. This is a quasi-reversible system because the peak separation potential, ΔE_p ($E_{pa} - E_{pc}$), is equal to 172.6 mV (244-71.4) and is greater than 59 mV which is expected for a reversible system. The ΔE_p of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ redox couple on the surface of the bare CPE was obtained to be 303.5 mV (as a quasi-reversible system) [25] and is greater than that of the CHIT/CPE and TiO₂/CHIT/CPE. The anodic peak potential, E_{pa} , for the coupled Fe(II/III) of the Fe(CN)₆⁴⁻ adsorbed on the polymer is 244 mV, and the potential for the free Fe(CN)₆⁴⁻ is 369 mV; both were measured against the reference electrode. The interaction between the cyanides of the complex and the hydroxyls of chitosan by hydrogen bonding reduced the donor ability of the cyanides, increased the effective nuclear charge of the metallic centre and shift the oxidation potential to more positive values [26].

3.1. Surface morphology of the fabricated electrodes

The surface morphology of the fabricated electrodes was characterized by SEM. As shown in Fig. 3, unmodified CPE exhibited a microstructure with a heterogeneous grain growth (Fig. 3A).

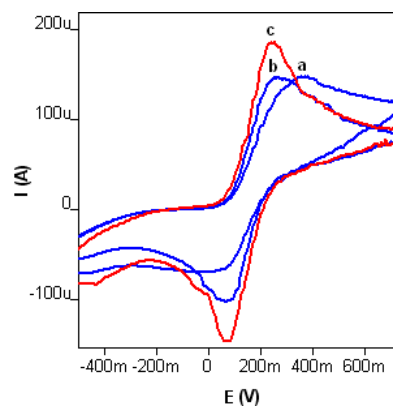


Fig. 2. The cyclic voltammograms of 10 mM K₄Fe(CN)₆ at the surface of (a) bare CPE, (b) CHIT/CPE and (c) TiO₂/CHIT/CPE in the phosphate buffer solution (pH 7.0) at a scan rate of 20 mV s⁻¹.

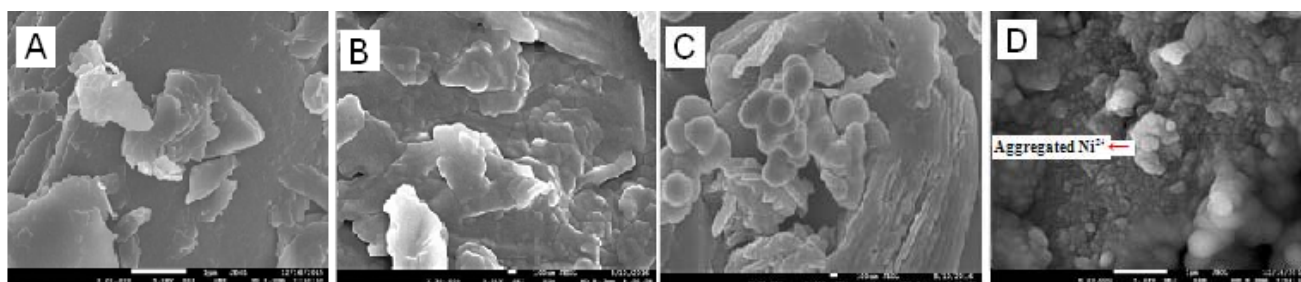


Fig. 3. SEM images of A) unmodified CPE, B) CHIT/CPE, C) $\text{TiO}_2/\text{CHIT}/\text{CPE}$ D) $\text{Ni-TiO}_2/\text{CHIT}/\text{CPE}$ (before immersion in 0.1 M NaOH).

After introduction of CHIT, the surface became rough and uneven compared to that of unmodified CPE (Fig. 3B). In the case of $\text{TiO}_2/\text{CHIT}/\text{CPE}$, it can be shown from the micrograph that the TiO_2 particle aggregates were dispersed on the surface of carbon, (Fig. 3C). The obtained three-dimensional porous structure in $\text{TiO}_2/\text{CHIT}/\text{CPE}$ is effective to exhibit the electroactivity of $\text{TiO}_2/\text{CHIT}/\text{CPE}$ and improve the performance of the electrochemical sensor.

To incorporate Ni(II) ions on the surface of the CPE, CHIT/CPE and $\text{TiO}_2/\text{CHIT}/\text{CPE}$, these electrodes were placed in a well-stirred aqueous solution of 0.5 M NiCl_2 in an open circuit for 15 min at 150 rpm and then washed completely with double distilled water to remove the surface adsorbed species. Interaction between ions and different sorbents take place via several single or mixed interactions including chelation or coordination, electrostatic attraction or ion exchange and formation of ion pair [27]. The type of chitosan-Ni(II) interaction depends on the Ni(II) chemistry, solution pH, chemical and physical nature of chitosan. Apparently, in this case, because the solution is alkaline the mechanism of the adsorption is heterogeneous and may follow the chelation binding mechanism, in which metal-chelate complexes with composition of (1:2) are formed between Ni(II) ions and amine or hydroxyl groups of chitosan as shown in Fig. 4. Also, apparently, the metal-chelate complexes type (b) is more stable than type (a)

and the metal-chelate complexes type of the surface adsorbed Ni^{2+} ions may be (b). Also, Fig. 3D is related to the nickel ions dispersed into the $\text{TiO}_2/\text{CHIT}/\text{CPE}$ and shows that the nickel ion aggregated on the surface of fabricated electrode. Comparison of the SEM images of three electrodes demonstrates that the surface of $\text{TiO}_2/\text{CHIT}/\text{CPE}$ was completely covered with spherical nickel particles

3.2. Electrochemical behaviour of Ni^{2+} ions incorporated at the fabricated electrodes surface

Fig. 5A illustrates cyclic voltammograms of the (a) CPE, (b) CHIT/CPE and (c) $\text{TiO}_2/\text{CHIT}/\text{CPE}$ in 0.1 M NaOH solution at the potential range from 0.2 to 0.7 V vs. $\text{Ag}|\text{AgCl}|\text{KCl}$ (3 M) and potential sweep rate of 10 mV s^{-1} . Also, Fig. 5B shows (a) Ni-CPE, (b) Ni-CHIT/CPE and (c) Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ (CPE, CHIT/CPE and $\text{TiO}_2/\text{CHIT}/\text{CPE}$ were immersed in the 0.5 M NiCl_2) in the similar conditions of Fig. 5A. It can be concluded that the electrochemical behaviour of Ni-CHIT/CPE and Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ as modified electrodes in alkaline solution is similar to that of Ni anode [28,29].

These redox waves are ascribed to the oxidation of $\text{Ni}(\text{OH})_2$ at the chitosan/electrolyte interface to NiOOH and reduction and change of NiOOH to $\text{Ni}(\text{OH})_2$ with a peak potential of 0.43 and 0.30 V vs. $\text{Ag}|\text{AgCl}|\text{KCl}$ (3 M), respectively [30-34].

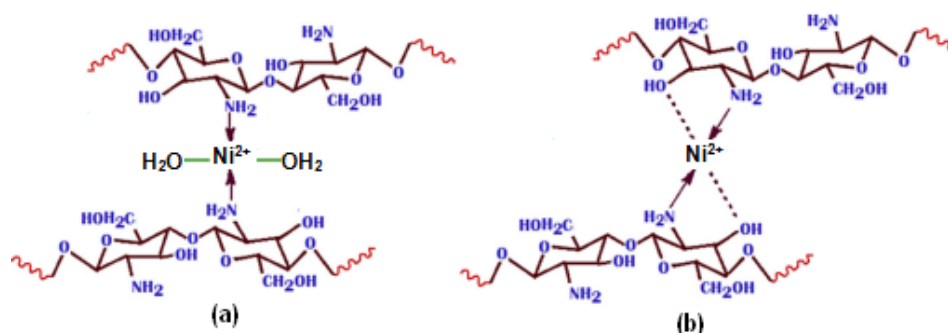


Fig. 4. Scheme of the proposed sorption mechanism of complex formation of chitosan and Ni(II) (a) interaction between Ni(II) ions and amino group from chitosan moiety and hydroxyl group from water and/or peptidoglycan moiety in chitosan (b) interaction between Ni(II) ions and both amino and hydroxyl groups from chitosan moiety.

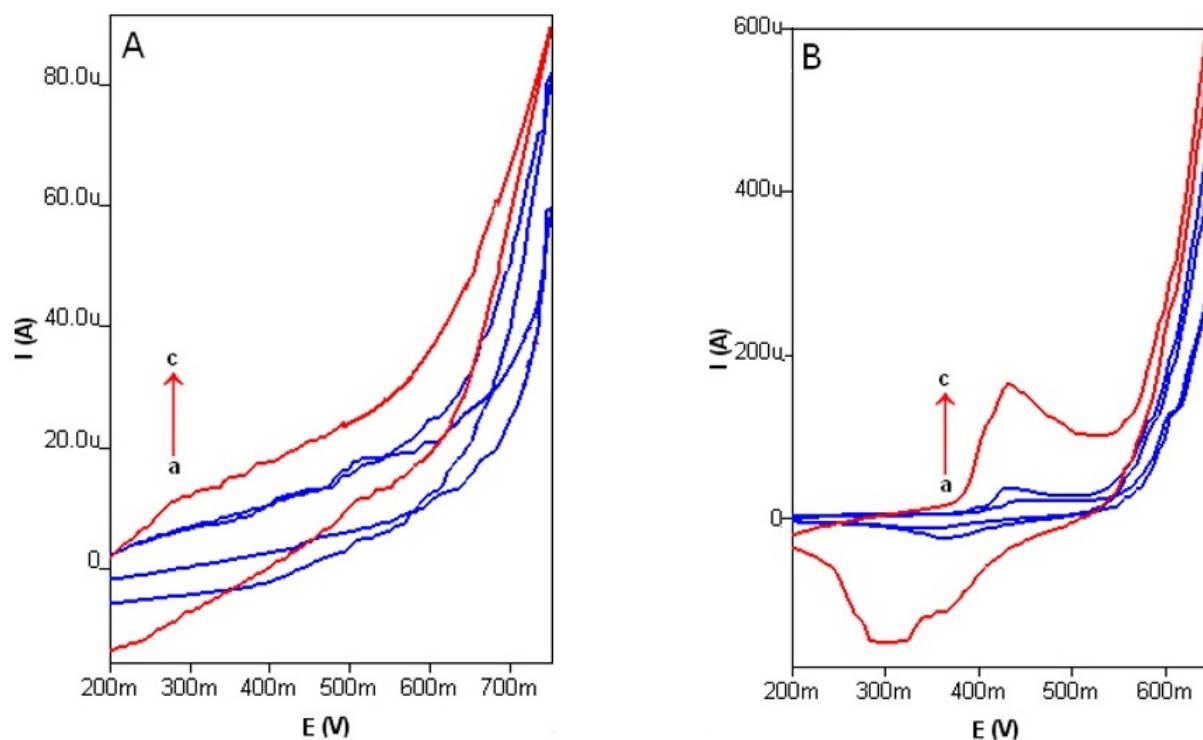


Fig. 5. The cyclic voltammograms of (A): (a) CPE, (b) CHIT/CPE and (c) $\text{TiO}_2/\text{CHIT}/\text{CPE}$ and (B): (a) Ni-CPE, (b) Ni-CHIT/CPE and (c) Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ in 0.1 M NaOH at a scan rate of 10 mV s^{-1} .

Comparison of Fig. 5a, b and c indicated that the presence of chitosan and TiO_2 in the electrode construction had a significant effect on accumulation of nickel species on the surface of electrode. Because the chitosan structure contains free hydroxyl and amino functional groups, it can act as a sorbent of Ni^{2+} cation [35,36]. On the other hand, the TiO_2 nanoparticles greatly increase the effective surface area and three dimensional porous structures and consequently, enhance the electron transfer rate between the electrode surface and $\text{Ni}(\text{OH})_2$ [37]. As can be seen in Fig. 6, the electrochemical responses of Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ obtained in an acidic solution show a complete loss of electrode activity in the potential range from -0.15 to 0.90 V in the absence and presence of formaldehyde. However, the Ni^{2+} ions adsorbed into the electrode was not removed under these experimental conditions, and its response was recovered when the electrode was immersed in an alkaline solution. XRD patterns of the $\text{TiO}_2/\text{CHIT}/\text{CPE}$ (a) and Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ (b) (after immersing in 0.1 M NaOH, recording cyclic voltammograms as above mentioned and then washing completely with double distilled water) have been presented in Fig. 7. This Fig. indicates the formation of $\text{Ni}(\text{OH})_2$ at the surface of $\text{TiO}_2/\text{CHIT}/\text{CPE}$.

In this work, the oxidation of formaldehyde was first studied on the surface of $\text{TiO}_2/\text{CHIT}/\text{CPE}$ (without the incorporation of nickel ions) by cyclic voltammetric

experiments in 0.1 M NaOH solution. Typical results obtained for a potential range from 0.2 to 0.9 V vs. $\text{Ag}|\text{AgCl}|\text{KCl}$ (3 M) at the potential scan rate of 10 mV s^{-1} are shown in the Fig. 8A.

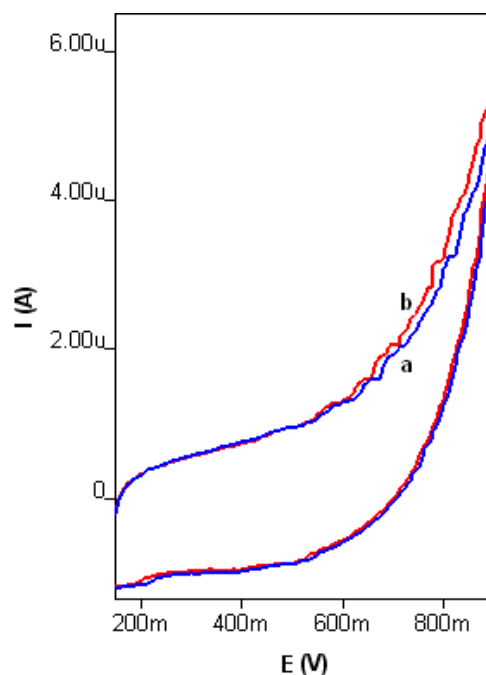


Fig. 6. The electrochemical responses of Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ (a) in 0.1 M H_2SO_4 , (b) in 0.1 M H_2SO_4 consisting of 4.0 mM formaldehyde at a scan rate of 10 mV s^{-1} .

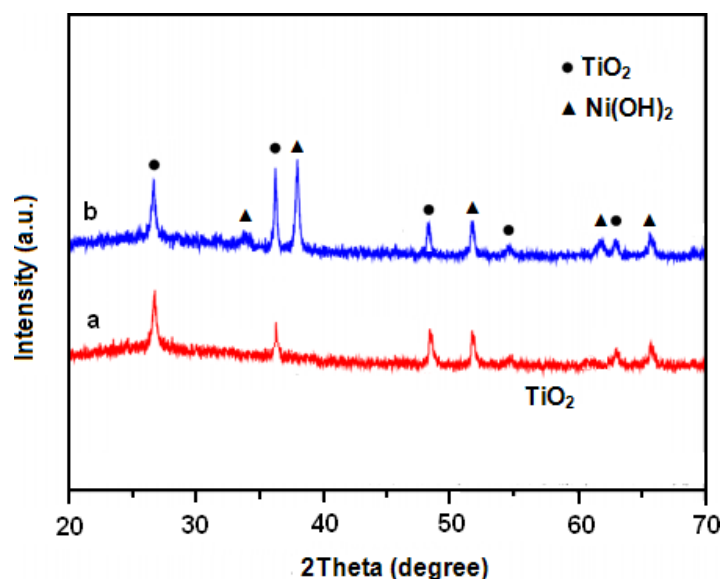


Fig. 7. XRD pattern of the (a) TiO₂/CHIT/CPE and (b) Ni-TiO₂/CHIT/CPE (after immersion in 0.1 M NaOH).

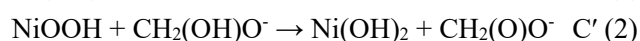
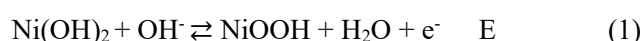
The response of the TiO₂/CHIT/CPE in the absence of formaldehyde, is shown in Fig. 8A (a). The addition of the 4.0 mM formaldehyde to the alkaline solution causes no effect on the electrochemical response of the TiO₂/CHIT/CPE (Fig. 8A (b)).

On the other hand, the electrochemical oxidation of formaldehyde was investigated on the surface of Ni-TiO₂/CHIT/CPE in 0.1 M NaOH solution (Fig. 8B). Curve (b) in this Fig. displays the cyclic voltammogram of electrocatalytic oxidation of 4.0 mM formaldehyde on the surface of Ni-TiO₂/CHIT/CPE in 0.1 M NaOH at scan rate of 10 mV s⁻¹. In the presence of formaldehyde, an increase in current was observed on the surface of Ni-TiO₂/CHIT/CPE (Fig. 8B (b)). Comparison of curves (a) and (b) in Fig. 8B demonstrates that incorporation of chitosan and TiO₂ onto a carbon paste electrode enhances the electrochemical signal of formaldehyde oxidation. It can be observed in Fig. 8B(b) that the oxidation of formaldehyde raises a typical electrocatalytic response, with an increase in the anodic peak current and a decrease in the cathodic peak current. The oxidation potential of Ni(OH)₂ in the presence of formaldehyde is observed at ca. 497 mV which is more positive than the potential observed for Ni²⁺ to Ni³⁺ transition on the surface of Ni-TiO₂/CHIT/CPE in the absence of formaldehyde (i.e. 432 mV). Also, Fig. 8C shows typical cyclic voltammograms of 4.0 mM formaldehyde in 0.1 M NaOH on the surface of CPE (a), Ni-CPE (b), Ni-CHIT/CPE (c) and Ni-TiO₂/CHIT/CPE (d). As can be seen in this figure, the peak current of electrocatalytic oxidation of formaldehyde on the surface of Ni-TiO₂/CHIT/CPE is greater than that on surfaces of the CPE, Ni-CPE and Ni-CHIT/CPE and also the Ni-CHIT/CPE is greater than that of the

Ni-CPE. These observations can explain clearly the role of the chitosan and TiO₂ on enhancement of the electrocatalytic oxidation currents of formaldehyde at the Ni-TiO₂/CHIT/CPE. Furthermore, the effect of TiO₂ particles size on the electrocatalytic behaviour of Ni-TiO₂/CHIT/CPE toward formaldehyde oxidation was studied (Fig. 8D). The larger formaldehyde response at the Ni-TiO₂/CHIT/CPE (b) (with nanometer sized TiO₂ particles) with respect to Ni-TiO₂/CHIT/CPE (a) (with micrometer sized TiO₂ particles) is proposed to be the nanostructure effect which enhances the catalytic properties of Ni(OH)₂ through fine dispersion of the catalyst particles into the electrode matrix. It results in a drastic increase in the surface area.

It can be specified that the formaldehyde molecule is completely hydrated and converted to the methylene glycol (CH₂(OH)₂) with an equilibrium constant on the order of 10³ in an aqueous solution [38]. The methylene glycol exists predominantly in its ionized form (CH₂(OH)O⁻) in 0.1 M NaOH solution due to its pK_a of ca. 12.8. CH₂(OH)O⁻ diffuses from the bulk solution to the electrode surface and is quickly oxidized to CH₂(O)O⁻ by the NiOOH species on the surface of Ni-TiO₂/CHIT/CPE. Therefore, the amount of NiOOH species decreases due to its chemical reaction with CH₂(OH)O⁻. In the overall reaction, formaldehyde can be converted to the CH₂(O)O⁻ and generated one electron (see Fig. 9) [39,40].

Simply, this behaviour is a typical observation expected from the mediated oxidation (EC' mechanism), illustrated in the following equations:



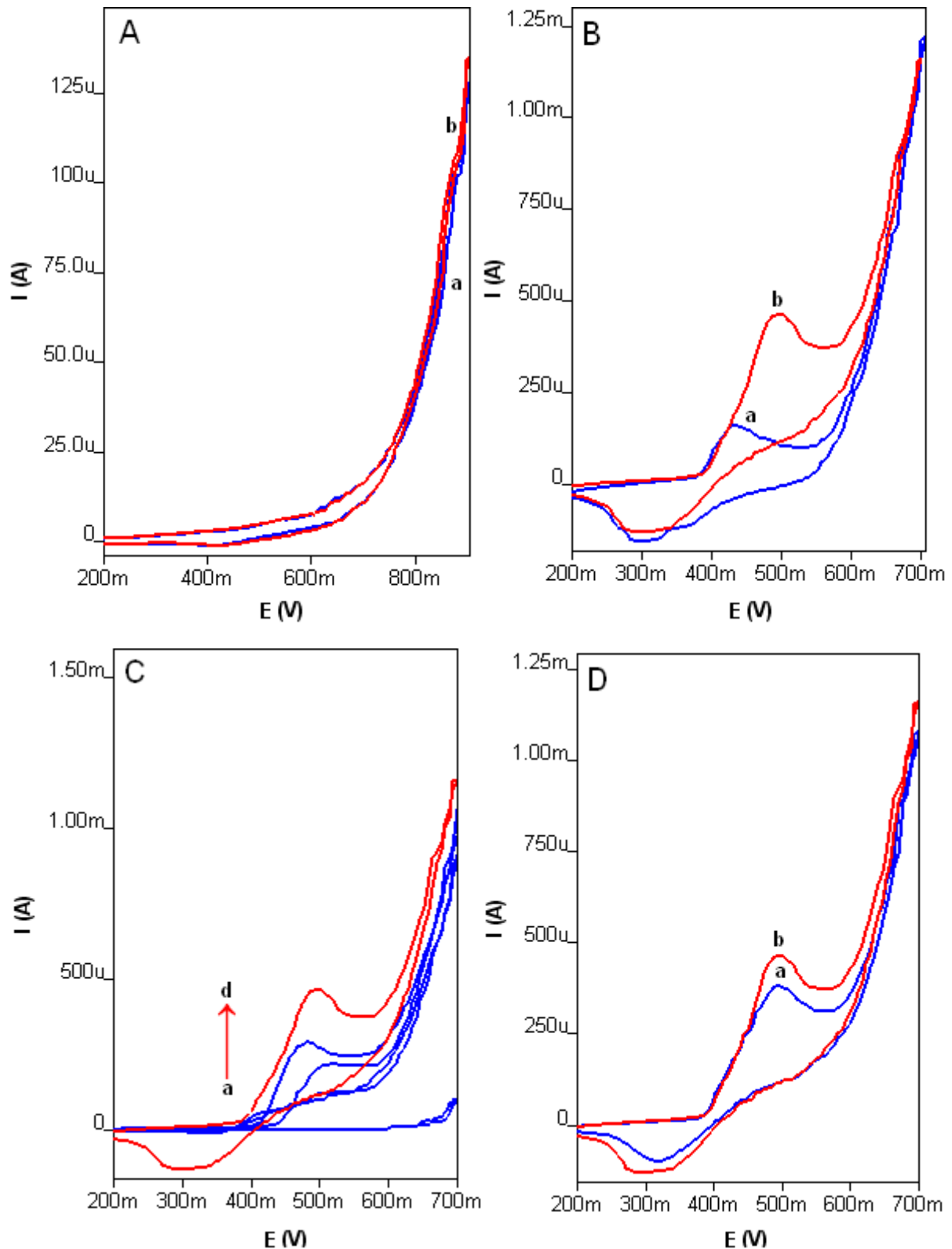


Fig. 8. The cyclic voltammograms of (A) $\text{TiO}_2/\text{CHIT}/\text{CPE}$ and (B) $\text{Ni-TiO}_2/\text{CHIT}/\text{CPE}$ in the absence (a) and presence (b) of 4.0 mM formaldehyde in 0.1 M NaOH at scan rate of 10 mV s^{-1} . (C) The cyclic voltammograms of (a) CPE, (b) Ni-CPE, (c) Ni-CHIT/CPE and (d) Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ in 0.1 M NaOH containing 4.0 mM formaldehyde at scan rate of 10 mV s^{-1} . (D) The cyclic voltammograms of Ni- $\text{TiO}_2/\text{CHIT}/\text{CPE}$ with (a) micrometer-sized TiO_2 and (b) nanometer-sized TiO_2 particles in 0.1 M NaOH containing 4.0 mM formaldehyde at scan rate of 10 mV s^{-1}

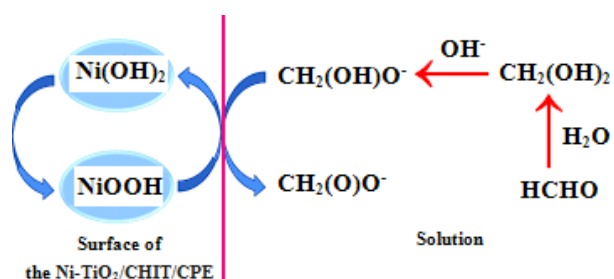


Fig. 9. Representative schematic for mechanism of formaldehyde electrooxidation at the surface of Ni-TiO₂/CHIT/CPE.

The electrochemical behaviour of Ni-TiO₂/CHIT/CPE was investigated in 0.1 M NaOH at various scan rates. Fig. 10A shows the cyclic voltammograms of Ni-TiO₂/CHIT/CPE in 0.1 M NaOH solution at different potential sweep rates. As can be seen, the anodic and cathodic currents were enhanced when scan rate

increased and a potential moved to positive values. The positive shift may be due to the kinetic limitation in diffusion layer which was created at the high current density. The ΔE_p was increased with the scan rate, this indicated a limitation in the charge transfer kinetics. Obviously, the anodic and cathodic peak currents are linearly proportional to the potential sweep rate at low values from 10 to 50 mV s⁻¹ (Fig. 10B). The electrode surface coverage (Γ^*) can be calculated from the linear part of the plot and using the following equation which corresponds to reversible process with adsorbed species [41].

$$I_p = (n^2F^2/4RT)vA \Gamma^* \quad (3)$$

where I_p , n , Γ^* and A are the peak current, the number of electrons involved in the reaction ($n = 1$), the surface coverage of the redox species and the surface area of the electrode (0.28 cm²), respectively.

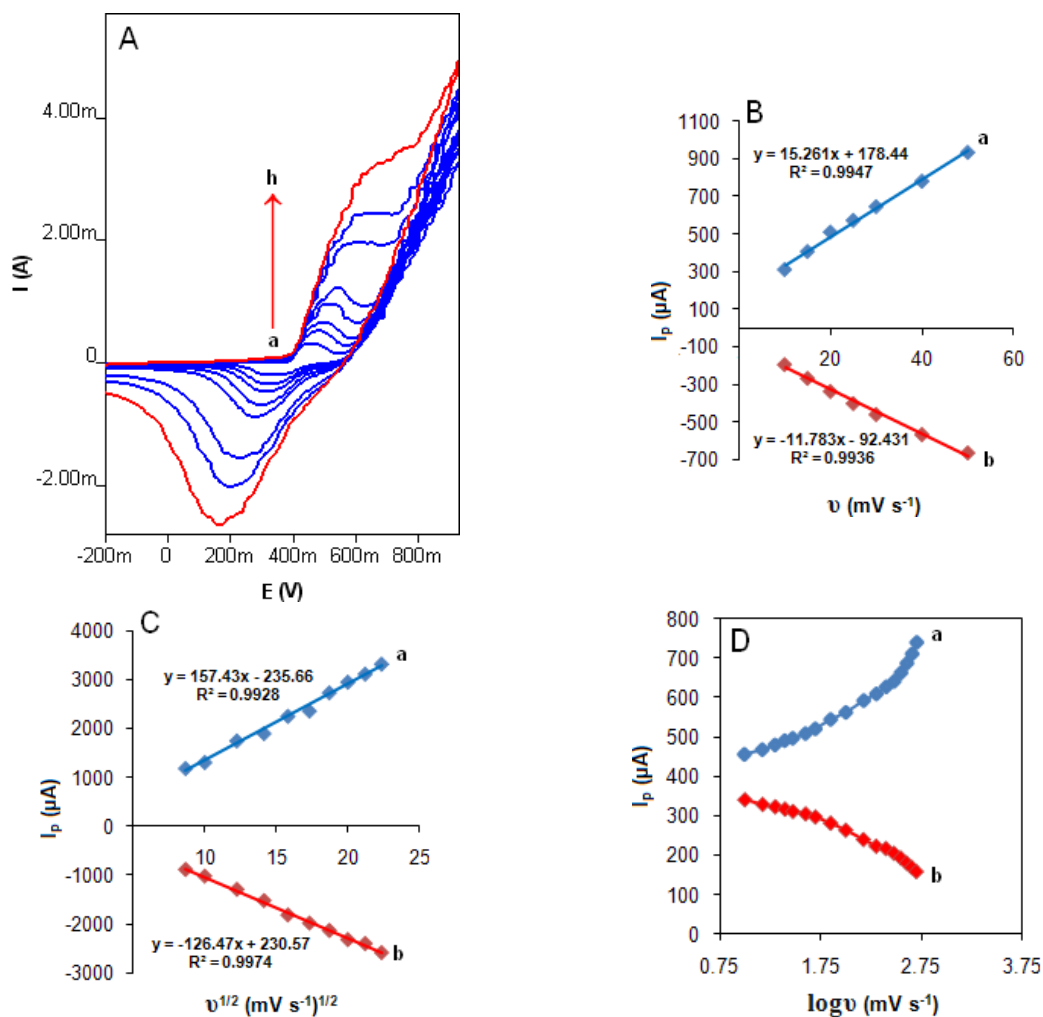


Fig. 10. (A) The cyclic voltammograms of Ni-TiO₂/CHIT/CPE in 0.1 M NaOH at some scan rates from (a) to (h): 10, 20, 30, 50, 75, 200, 300 and 500 mV s⁻¹. (B) The dependency of I_{pa} (a) and I_{pc} (b) on v at lower values of v (10-50 mV s⁻¹), and (C) the plot of I_{pa} (a) and I_{pc} (b) on $v^{1/2}$ at higher values of v ($v > 75$ mV s⁻¹). (D) Plot of E_p vs. $\log v$ for cyclic voltammograms recorded at the surface of Ni-TiO₂/CHIT/CPE in 0.1 M NaOH solution; (a) for anodic peaks and (b) for cathodic peaks.

The total surface coverage of the immobilized active species [Ni (II)] is found to be about 5.14×10^{-8} mol cm^{-2} , considering the mean of both anodic and cathodic currents. At scan rates higher than 75 mV s^{-1} , both the anodic and cathodic peak currents depend on the root mean square of the scan rate ($v^{1/2}$); this expresses that a diffusion controlled process is dominated by increasing the scan rates (see Fig. 10C). This limiting-diffusion process can be related to the charge neutralization of the electrode surface during the oxidation/reduction process [42].

The effect of v on peak potential was also investigated by voltammetry. When v , increases, the oxidation peak potential is positively shifted, and the reduction peak potential is negatively shifted; this indicates that the redox reversibility of nickel oxide film was impaired. Under the surface controlled redox process, the electron transfer kinetics of nickel oxide film on the surface of the Ni-TiO₂/CHIT/CPE can be obtained using the approach developed by Laviron [43]; when peak to peak separation is higher than 200 mV/n , the relationship between the peak potential, E_p , and the scan rate can be expressed in Eq. 4:

$$E_p = f(\log v) \quad (4)$$

Fig. 10D provided the variations of peak potentials with the logarithm of the scan rate in the ranges of $10\text{-}500 \text{ mV s}^{-1}$ for both anodic and cathodic peaks in which data were extracted from cyclic voltammograms of the Ni-CHIT/CPE in 0.1 M NaOH solution. It can be observed that E_p is proportional to $\log v$ at $v > 50 \text{ mV s}^{-1}$. The electron transfer coefficient (α) of nickel oxide film was calculated based on the slope of the oblique asymptotes,

where for cathodic peak, the slope value is $-2.3RT/\alpha nF$, and for anodic peak, $2.3RT/(1-\alpha)nF$. Furthermore, the standard rate constant of reaction, k_s , is expressed in Eq. 5 [43]:

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nFv) - [\alpha(1-\alpha)nF\Delta E_p]/(2.3RT) \quad (5)$$

where ΔE_p is the peak to peak potential separation. The resulting values of α and k_s were obtained 0.66 and $3.28 \times 10^{-1} \text{ cm s}^{-1}$, respectively.

Fig. 11A displays the cyclic voltammograms of Ni-TiO₂/CHIT/CPE in 0.1 M NaOH solution containing 4.0 mM formaldehyde at different potential sweep rates. Also, Fig. 9B presents a plot of scan rate normalized current ($I_{pa}/v^{1/2}$) vs. logarithm scan rate ($\log v$) obtained based on data of Fig. 11A. Fig. 11B shows the characteristic shape of an EC' process which expresses that the electrode reaction is coupled with an irreversible follow up chemical step [44-46].

3.3. Effect of experimental parameters on the Ni-TiO₂/CHIT/CPE performance

3.3.1. Effect of accumulation time

To study this factor, voltammetric responses of the Ni-TiO₂/CHIT/CPE at the five different accumulation times $2.5, 5.0, 10.0, 15.0$ and 20.0 min were performed by cyclic voltammetry technique at 0.1 M NaOH solution containing 4.0 mM formaldehyde. The value of ΔI_p increased gradually with increasing of accumulation times. The maximum value was at 10 min then leveled off, so 10 min was chosen as the optimum time; this indicated that saturated accumulation on the Ni-TiO₂/CHIT/CPE had been achieved (Fig. 12).

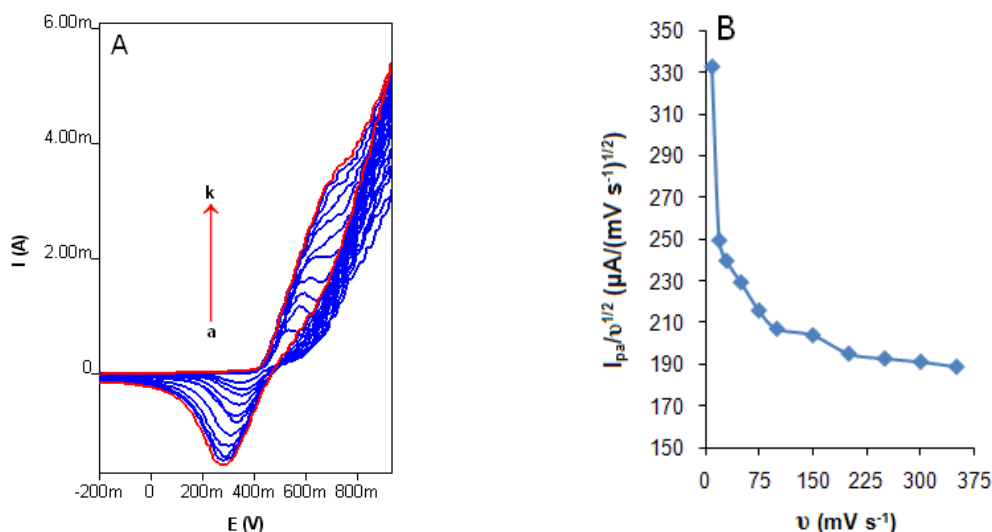


Fig. 11. (A) The cyclic voltammograms of Ni-TiO₂/CHIT/CPE in 0.1 M NaOH consisting of 4.0 mM formaldehyde at some scan rates from (a) to (h): $10, 20, 30, 50, 75, 100, 150, 200, 250, 300$ and 350 mV s^{-1} . (B) The plot of the normalized anodic peak currents ($I_{pa}/v^{1/2}$) of cyclic voltammograms of the (A) vs. scan rate in the presence of 4.0 mM formaldehyde at the mentioned scan rates.

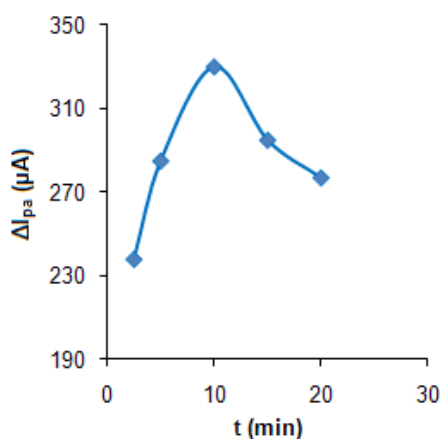


Fig. 12. Effect of accumulation time on difference between anodic peak currents (ΔI_{pa}) of the Ni-TiO₂/CHIT/CPE (chitosan percentage 4%, TiO₂ percentage 10% and immersed in 0.5 M NiCl₂ solution) in the absence and the presence of 4.0 mM formaldehyde in 0.1 M NaOH at scan rate of 10 mV s⁻¹.

3.3.2. Effect of nickel concentration

The effect of the amount of nickel on response of the Ni-TiO₂/CHIT/CPE with chitosan percentage of 4% and TiO₂ percentage of 10% was studied at the accumulation time of 10.0 min by varying the concentration of nickel chloride (0.25, 0.50, 1.0 and 1.5 M) in the deposition bath in 0.1 M NaOH solution containing 4.0 mM formaldehyde. It was observed that as the concentration of Ni in the bath increased, the formaldehyde oxidation currents also increased up to 1.0 M; after which, it remained almost constant (Fig. 13). This may probably be due to the fact that surface active sites of modified electrode get saturated at this concentration; this hinders further deposition of Ni.

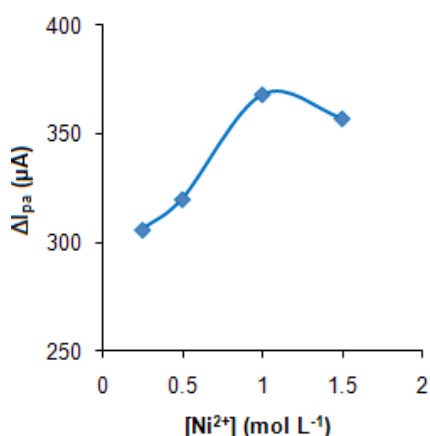


Fig. 13. Effect of nickel concentration on difference between anodic peak currents (ΔI_{pa}) of the Ni-TiO₂/CHIT/CPE (chitosan percentage 4%, TiO₂ percentage 10% and accumulation time 10 min) in the absence and the presence of 4.0 mM formaldehyde in 0.1 M NaOH at scan rate of 10 mV s⁻¹.

3.3.3. Effect of chitosan percentage

For this purpose, the experiments were carried out with the five different modified electrodes containing chitosan ratio of 4, 8, 12, 12, 16 and 20% (w/w) with respect to the graphite powder.

The cyclic voltammograms of Ni(OH)₂/NiOOH oxidation on different modified electrodes showed that higher anodic current is obtained in 8% of chitosan with respect to the graphite powder (Fig. 14). It is suggested that at the low ratio of chitosan, the amount of chitosan is so low on the surface of modified electrodes in way that the available site for Ni²⁺ insertion can be decreased. Also, with increasing the chitosan over than 8% in the modified electrodes, the anodic peak currents difference of the Ni-TiO₂/CHIT/CPE in the absence and presence of formaldehyde decreases. It may be due to Ni²⁺ ions saturation on the surface of modified electrode and also the excessive presence of chitosan on the electrode surface decreases the electrode conductivity.

3.3.4. Effect of TiO₂ percentage

A set of experiments was carried out to study the effect of TiO₂ percentage. According to Fig. 15, in order to investigate the effect of the TiO₂ percentage on the electrocatalytic oxidation of formaldehyde using the Ni-TiO₂/CHIT/CPE, the experiments were carried out in 0.1 M NaOH solution in presence of 4.0 mM formaldehyde with the four different modified electrodes containing TiO₂ percentage of 2.5, 5.0, 7.5 and 10.0% (w/w). The electrode response was decreased with the increase of TiO₂ percentage. This happens because the increase of TiO₂ percentage in the modified electrode increases the sites for adsorption.

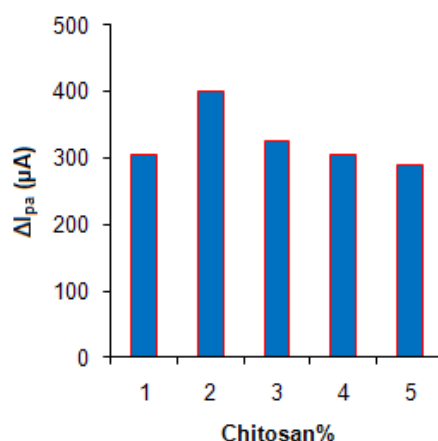


Fig. 14. Influence of chitosan percentage on difference between anodic peak currents (ΔI_{pa}) of the Ni-TiO₂/CHIT/CPE (TiO₂ percentage 10%, accumulation time 10 min and immersed in 1.0 M NiCl₂ solution) in the absence and the presence of 4.0 mM formaldehyde in 0.1 M NaOH at scan rate of 10 mV s⁻¹.

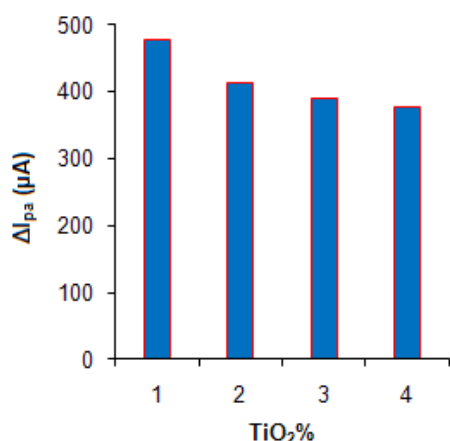


Fig. 15. Influence of TiO₂ percentage on difference between anodic peak currents (ΔI_{pa}) of the Ni-TiO₂/CHIT/CPE (chitosan percentage 8%, accumulation time 10 min and immersed in 1.0 M NiCl₂ solution) in the absence and the presence of 4.0 mM formaldehyde in 0.1 M NaOH at scan rate of 10 mV s⁻¹.

As can be seen in Fig. 2c, the presence of TiO₂ increases the sites for formaldehyde adsorption similar to K₄Fe(CN)₆, subsequently, the oxidation peak current increases. However, the excess of TiO₂ increases the resistance of the electrode and the anodic peak currents difference of the Ni-TiO₂/CHIT/CPE in the absence and

presence of formaldehyde decreases. Hence, a TiO₂ (2.5%, w/w)-modified carbon paste electrode was used as an optimum condition.

3.4. Calibration curve

The cyclic voltammograms were recorded for calibration graph construction on the Ni-TiO₂/CHIT/CPE under the optimum conditions described above using a standard addition method as presented in Fig. 16A. Under all the optimized experiment conditions, the anodic peak current was proportional to the concentration of formaldehyde and linear dynamic range (LDR) was obtained in a range from 2.80×10^{-4} to 2.50×10^{-2} mol L⁻¹ as shown in Fig. 16B. The limit of detection (LOD) was estimated to be 7.14×10^{-5} mol L⁻¹ (3σ). Since the acceptable detection limit according to the standards of Occupation Safety and Health Administration (OSHA), varies from 0.1 to 1 mM formaldehyde [20], therefore, this sensor offers a suitable low detection limit of the quantification of formaldehyde. Also, the simplicity of the electrode preparation is a main advantage of this method to determine formaldehyde. The comparison of several parameters of formaldehyde at some modified electrodes is listed in Table 1.

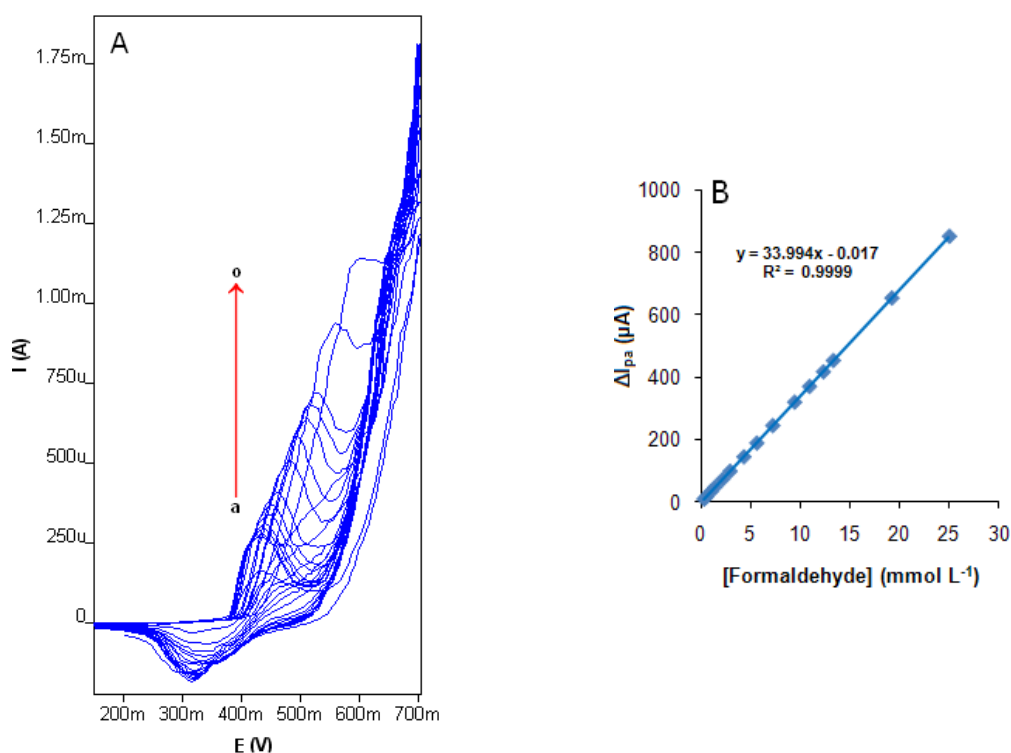


Fig. 16. (A) The cyclic voltammograms for different concentrations of formaldehyde, (a) 0.28 (b) 0.52, (c) 0.98, (d) 1.38, (e) 2.15, (f) 2.90, (g) 4.30, (h) 5.60, (i) 7.20, (j) 9.40, (k) 10.90, (l) 12.30, (m) 13.30, (n) 19.20 and (o) 25.00 mM in 0.1 M NaOH on the Ni-TiO₂/CHIT/CPE at optimized cyclic voltammetry parameters (chitosan percentage 8%, TiO₂ percentage 2.5%, accumulation time 10 min and immersed in 1.0 M NiCl₂ solution). (B) Calibration curve for the determination of formaldehyde.

Table 1. Comparison some of the analytical parameters of the different modified electrodes for formaldehyde determination.

Electrode	Method	LDR (mM)	LOD (mM)	Ref.
AOXISFET ^a	Potentiometry	5-200	-	[47]
CNFGNPGE ^b	Amperometry	0.01-1	-	[48]
PTOE ^c	Chronoamperometry	2.5-17.7	0.015	[49]
Ni-TiO ₂ /CHIT/CPE	Cyclic voltammetry	0.28-25.0	0.0714	This study

^aHighly or partially purified alcohol oxidase immobilized on the ion sensitive field effect transistor.

^bCathodic electrode position paints modified with Os(bpy)₂Cl complexes-NAD⁺-formaldehyde dehydrogenase-glutathione-nafion architecture modified platinumized graphite electrode.

^cPalladium modified TiO₂ electrode.

It can be seen from the Table 1 that the detection limit and linear range obtained in this study are comparable with values reported by other research groups for the electrocatalytic oxidation of formaldehyde on the surface of chemically modified electrodes by other mediators [47-49].

3.5. Repeatability and stability of the Ni-TiO₂/CHIT/CPE

To evaluate and confirm the repeatability of Ni-TiO₂/CHIT/CPE, five-repeatedly-cyclic voltammetry was performed under the optimized conditions. The anodic peak currents of Ni-TiO₂/CHIT/CPE for electrocatalytic oxidation of 4.0 mM formaldehyde were tested and the relative standard deviation (RSD) was 5.6% for five measurements. This result showed that the repeatability of the electrode is suitable. The stability of the electrode was estimated by monitoring of the electrode response to electrocatalytic oxidation of 4.0 mM formaldehyde after being stored at room temperature for 20 days. It was observed that the current response preserved almost 89% of its initial amounts.

3.6. Real sample analysis

In order to demonstrate the capability of the Ni-TiO₂/CHIT/CPE to determine formaldehyde in a real sample, this modified electrode was used in voltammetric determination of formaldehyde in formalin. The determination of formaldehyde was carried out by the standard addition method. The data obtained for analysis of formaldehyde by this method have been illustrated for several times in Table 2. Also, in order to investigate the proposed method, the same sample was analyzed using the iodometric titration

method in an acidic solution [50]. The results have been summarized in Table 2. As it can be seen, the results obtained from the two methods are in good agreement and confirm the reliability of the proposed method. A statistical test (F-test) was used to confirm the precision of the proposed method. As it can be seen, F-test results bear a noticeable difference in the critical value (19.00 in four degrees of freedom and 95% of confidence). Moreover, a statistical t-test was performed to evaluate the accuracy of the proposed method. The results suggested that there is no evidence of systematic difference between the results obtained by either of the methods. Four degrees of freedom and 95% of confidence as well as the critical t-value (2.78) were used to support the conclusions of this test.

4. Conclusions

In this paper, it was firstly described that TiO₂ nanoparticles, chitosan and Ni²⁺ ions together have been used for bulk modified CPE fabrication. Scanning electron microscopy and X-ray diffractometry were used for the characterization of Ni-TiO₂/CHIT/CPE. The Ni-TiO₂/CHIT/CPE showed a reasonable catalytic performance for the electrocatalytic oxidation of formaldehyde. Electrocatalysis of formaldehyde oxidation is sensitive to various parameters such as accumulation time, nickel concentration, chitosan and TiO₂ percentages. This new and simple sensor showed promising determination of formaldehyde with good detection limit and it is comparable with values reported by other researchers. The Ni-TiO₂/CHIT/CPE can be successfully used as a voltammetric sensor for formaldehyde determination in the real sample with suitable precision and accuracy.

Table 2. Comparison of results for the Ni-TiO₂/CHIT/CPE sensor with those from titration official method for formaldehyde determination in formalin sample.

Labeled ^a	Proposed method		Official method		t _{exp}	F _{exp}
	Found ^{a,b}	Recovery (%)	Found ^{a,b}	Recovery (%)		
13.32	12.57	94.37	12.64	94.89	0.43	2.44

^aUnit based on mol L⁻¹.

^bAverage of three replicate measurements.

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