

Full Paper

Analysis of Nitrite using a Voltammetric Sensors Employing NiO Nanoparticle Modified Carbon paste Electrode

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Abstract- A carbon paste electrode modified with NiO nanoparticles (CPE-M-NiO/NPs) was fabricated and used as a high performance sensor for nitrite (NT). CPE-M-NiO/NPs was prepared by mixing NiO/NPs, graphite powder and liquid paraffin together. The CPE-M-NiO/NPs showed electrocatalytic activity to the electro-oxidation of NT, and an irreversible oxidation peak appeared at 0.90 V with improved peak current. The linear response range was found to be 0.8–1100 μM . Detection limit (3σ) of NT was found to be 0.3 μM by square wave voltammetry (SWV) method. The CPE-M-NiO/NPs was successfully applied for the determination of NT in food samples.

Keywords- Nitrite analysis, Modified electrode, NiO nanoparticles, Voltammetry

1. INTRODUCTION

Sodium nitrite is a most widely used substance in food industrial and specially in curing of meat due to its effect on prevents bacterial growth. On the other hand, the high level of NT can be harmful for human body. Therefore, determination of NT dose in food samples in very important in standard food laboratories. High performance liquid chromatography [1,2], spectrophotometry [3,4], and electrochemical [5,6] techniques were reported for determination of NT in food samples. In between, electrochemical methods have more

attention due to high selectivity, good sensitivity, low cost for analysis and fast response in determination of electroactive compounds [7-11].

Nanostructured materials such as graphene, metal nanoparticles, nanowire, carbon nanotubes, and nanocomposite have been used in to electrochemical sensors for electroactive compounds in the recent years [12-15]. Nano-materials with high surface area and good conductivity are best choice for modification of working electrodes in electroanalysis systems [16-20]. In between, NiO nanoparticles are an important multifunctional material with applications such as gas sensors and catalysts. The various applications of NiO are due to the specific chemical, surface and microstructural properties of this material.

In this paper we synthesized NiO/NPs by direct chemical precipitation method and used this nanoparticle for the fabrication of a novel electrochemical voltammetric sensor. This novel sensor shows good electrocatalytic effect on NT electro-oxidation. This approach shows advantages in terms of sensitivity, reproducibility, and selectivity. Also, we test application of modified electrode for determination of NT in real samples with satisfactory results. The kinetic and thermodynamic parameters were obtained by electrochemical investigation for proposed sensor in NT analysis.

2. EXPERIMENTAL

2.1. Chemicals and Instrumentation

Sodium nitrite, Nickel(II) nitrate hexahydrate, phosphoric acid and sodium hydroxide were purchased from Sigma-Aldrich. Graphite powders, diethyl ether and paraffin oil, were purchased from Merck.

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 aqueous solution of Ni (NO₃)₂.6H₂O and a 1.0 M aqueous solution of NaOH were prepared in distilled water. The beaker containing NaOH solution was heated at the temperature of about 60 °C and Ni (NO₃)₂ solutions were added drop wise to the above heated solution under high-speed stirring. The beaker was sealed at this condition for 2 h. The precipitated Ni(OH)₂ were cleaned with deionized water and ethanol then calcined at 450 °C for 2.0 h for synthesis of NiO/NPs.

2.3. Preparation of Sensor

The suggestion sensor was prepared by mixing of 0.1 g of NiO/NPs and 0.9 g of graphite powder in the presence of suitable amount of paraffin. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture.

2.4. Preparation of real samples

For real sample analysis, sausage and pickled vegetables were purchased at local stores. In the first step, 10 g of the food sample was crushed into mash and mixed with 25.0 ml saturated borax solution. In continuous, 600 ml of 80 °C water were added and the mixture was heated at boiling for 30 min. To remove of the proteins, 10 ml of 20% zinc acetate was introduced. After being cooled to room temperature, the mixture was diluted to 1000 ml with water solution and then filtered. The obtained sample solution was stored at 4 °C in a refrigerator. Standard addition method was used for determination of nitrite concentration in food samples. The obtained data compare to Griess assay method.

3. RESULTS AND DISCUSSION

Fig. 1A shows the X-ray diffraction (XRD) data for synthesis NiO/NPs in this work. The mean grain size ($D=17$ nm) of the particles was determined from the XRD line broadening measurement using Scherrer equation.

The size and morphology for the NiO/NPs was characterized using TEM studies. Fig. 1B shows the TEM image morphology of NiO/NPs. The TEM image clearly indicates that nano particle shape of NiO in this work.

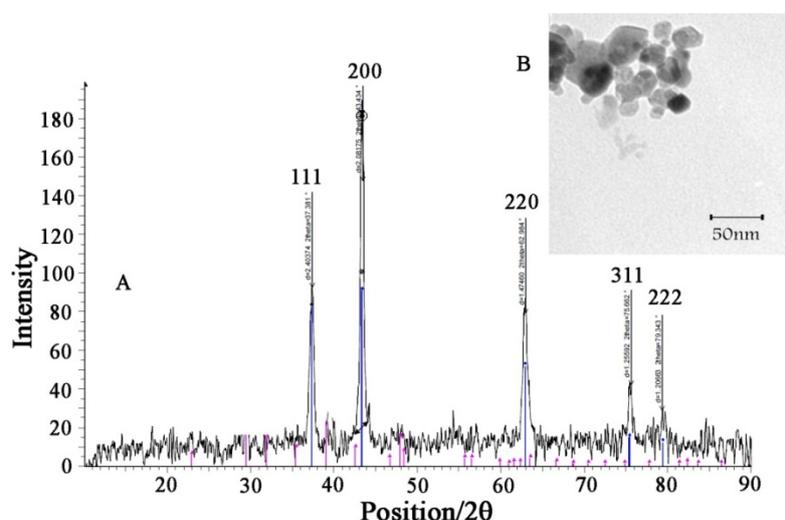


Fig. 1. A) XRD patterns of as-synthesized NiO nanoparticle; B) TEM image of NiO/NPs

The active surface areas of the CPE-M-NiO/NPs and CPE are estimated according to the slope of the I_P versus $v^{1/2}$ plot for a known concentration of $K_4Fe(CN)_6$, based on the Randles–Sevcik equation. The microscopic areas were calculated 0.284 and 0.32 cm^2 for CPE and CPE-M-NiO/NPs, respectively.

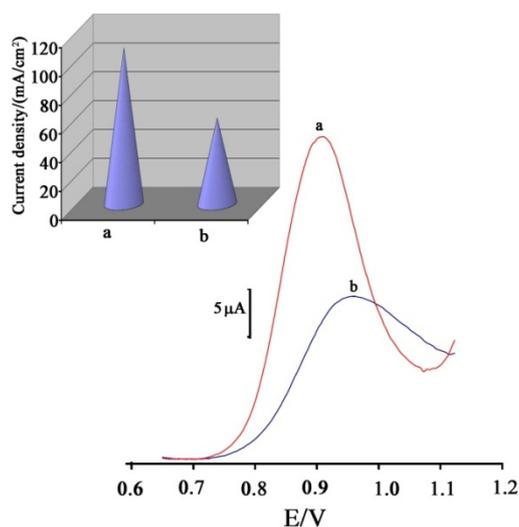


Fig. 2. Square wave voltammograms of (a) CPE-M-NiO/NPs, and (b) CPE in the presence of 300 μM NT at pH 7.0, respectively. Inset: the current density derived from Square wave responses

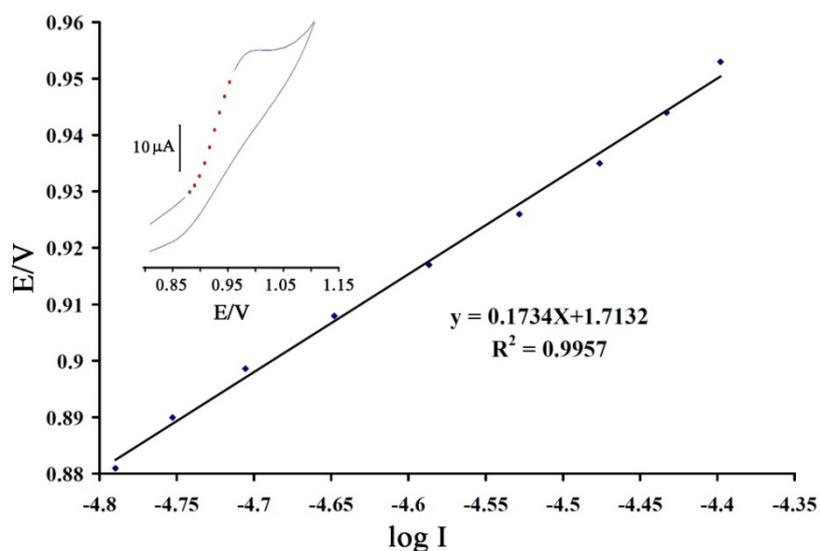


Fig. 3. Tafel plot for CPE-M-NiO/NPs in 0.1 MPBS (pH 7.0) at the scan rate of 50 $mV s^{-1}$ in the presence of 300.0 μM NT

Fig. 2 (curves a&b) showed the voltammetric signals of CPE-M-NiO/NPs and CPE in 300 μM NT in PBS solution (pH 7.0), respectively. At CPE-M-NiO/NPs, and CPE, NT showed an oxidation peak, with oxidation peak potential (E_{pa}) of 0.90 V, and 0.96 V, respectively. However, the peak current of NT at CPE-M-NiO/NPs was much larger than that at the CPE; it was about 2.0 times larger than CPE by square wave voltammetry. Thus, the CPE-M-NiO/NPs exhibited a catalytic activity toward the oxidation of NT. This further testified the superiority of CPE-M-NiO/NPs to CPE and indicated that the use of NiO/NPs as modifier facilitated the electron transfer between NT and electrode. The Tafel plot was used for determination of α for electro-oxidation of NT at a surface of modified electrode (Fig. 3).

The slope of the Tafel plot was equal to $2.3 RT/n(1-\alpha)F$, which came up to $0.1734 \text{ V decade}^{-1}$ for scan rate 50 mV s^{-1} (Fig. 3). Therefore, we obtained the mean value of $n(1-\alpha)$, which is equal to 0.34.

Chronoamperometric measurements of NT at CPE-M-NiO/NPs were carried out by setting the working electrode potential at 1.0 V for the various concentrations of NT in PBS (Fig. 4A).

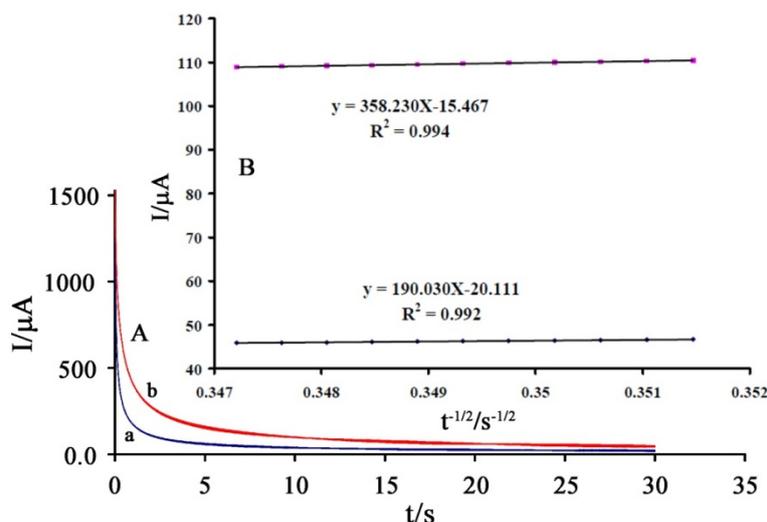


Fig. 4. (A) Chronoamperograms obtained at CPE-M-NiO/NPs in the presence of (a) 0.8 and (b) 1.0 mM NT in the buffer solution (pH 7.0); (B) Cottrell's plot for the data from the chronoamperograms

Experimental plots of I vs. $t^{1/2}$ were employed, with the best fits for different concentrations of nitrite. The slopes of the resulting straight lines were then plotted vs. nitrite concentration (Fig. 4B). Using the obtained slopes and Cottrell equation the mean value of the D was found to be $7.38 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The repeatability and stability of CPE-M-NiO/NPs was investigated by SWV measurements of $30.0 \mu\text{M}$ NT. The relative standard deviation (RSD%) for seven successive assays was 1.6%. When using four different electrodes, the RSD% for ten measurements was

2.4%. When the electrode stored in the laboratory, the CPE-M-NiO/NPs retains 98% of its initial response after a week and 93% after 20 days. These results indicate that CPE-M-NiO/NPs has good stability and reproducibility, and could be used for NT.

The square wave voltammetry was used for determination of analytical parameters for proposed sensor. The SW voltammograms clearly show that the plot of peak current vs. NT concentration is linear for 0.8–1100 μM of NT (Figure 6).

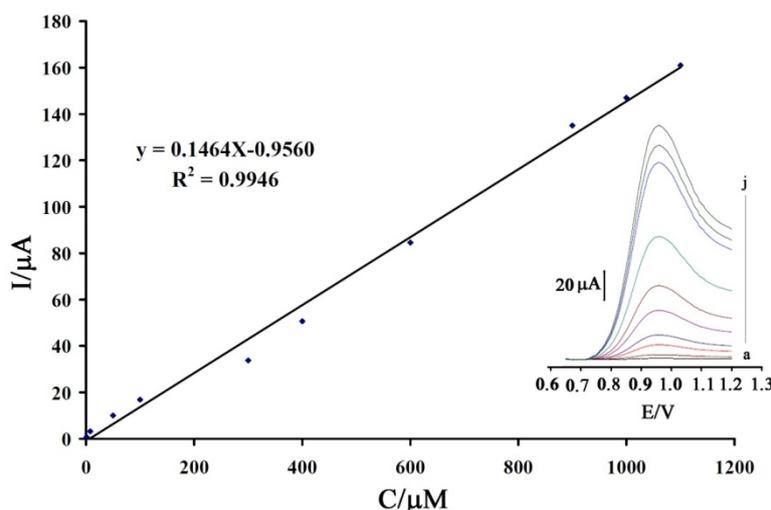


Fig. 6. The plots of the electrooxidation peak current as a function of NT concentration. Inset; SWVs of CPE-M-NiO/NPs containing different concentrations of NT. μM . (from inner to outer): 0.8, 8.0, 50.0, 100.0, 300.0, 400.0 600, 900, 1000 and 1100, respectively

The detection limit was determined at 0.3 μM nitrite by square wave voltammetry (SWV) method. Selectivity is an important factor for a new sensor for analytical application. To evaluate the selectivity of the designed sensor, the interference effect of biological and other interference compounds were examined in the presence of 20.0 μM NT. The results are shown in Table 1.

Table 1. Interference study for the determination of 20.0 μM NT under optimized conditions

Species	Tolerance limits ($W_{\text{species}}/W_{\text{analyte}}$)
Glucose	1000
Glutamic acid, Alanine, Phenylalanine, Histidine, Na^+ , SO_4^{2-} , K^+ , Cl^- , Br^- , CO_3^{2-} and Li^+	800
Starch	500
Ascorbic acid*	Saturation
	600

*After addition of 1.0 mM ascorbic oxidase

In order to find out the applicability of the CPE-M-NiO/NPs for determination of NT in the real samples, the electrode was used in food samples analysis. The obtained results in Table 2, confirm that the CPE-M-NiO/NPs has a good efficiency for the determination of NT in real samples

Table 2. Ability of propose sensor for determination of NT in real samples

Samples	Detected by Griess assay (mg kg ⁻¹)	Detected by this Method (mg kg ⁻¹)
Sausage	13.08±(0.03)	13.05±(0.04)
Pickled vegetable	4.06±(0.022)	4.16±(0.05)

4. CONCLUSION

In this study, the NiO/NPs modified carbon paste electrode was used to investigate the electrochemical behaviors of NT. The NiO/NPs synthesized by chemical precipitation method and characterized with XRD and TEM methods. The novel sensor showed great improvement to the electrode process of NT compared to the bare carbon paste electrode. In addition, the modified electrode exhibited a distinct advantage of simple preparation, surface renewal, good reproducibility and good stability.

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REFERENCES

- [1] H. Lia, C. J. Meiningerb, and G. Wu, *J. Chromatogr. B* 746 (2000) 199.
- [2] S. B. Butt, M. Riaz, and M. Z. Iqbal, *Talanta* 55 (2001) 789.
- [3] A. Kazemzadeh, and A. A. Ensafi, *Anal. Chim. Acta* 442 (2001) 319.
- [4] A. Syty, and R. A. Simmons, *Anal. Chim. Acta* 120 (1980) 163.
- [5] W. J. R. Santos, P. R. Lima, A. A. Tanaka, S. M. C. N. Tanaka, and L. T. Kubota, *Food Chem.* 113 (2009) 1206.
- [6] L. Guanghan, J. Hong, and S. Dandan, *Food Chem.* 59 (1997) 583.
- [7] M. Baghayeri, M. Namadchian, H. Karimi-Maleh, and H. Beitollahi, *J. Electroanal. Chem.* 697 (2013) 53.
- [8] H. Karimi-Maleh, F. Tahernejad-Javazmi, M. Daryanavard, H. Hadadzadeh, A. A. Ensafi, and M. Abbasghorbani, *Electroanalysis*, 26 (2014) 962.
- [9] A. A. Ensafi, M. Izadi, and H. Karimi-Maleh, *Ionics* 19 (2013) 137.

- [10] A. A. Ensafi, H. Karimi-Maleh, and S. Mallakpour, *Electroanalysis* 23 (2011) 1478.
- [11] A. A. Ensafi, S. Dadkhah-Tehrani, and H. Karimi-Maleh, *Anal. Sci.* 27 (2011) 409.
- [12] B. J. Sanghavi, and A. K. Srivastava, *Electrochim. Acta* 55 (2010) 8638.
- [13] B. J. Sanghavi, and A. K. Srivastava, *Electrochim. Acta* 56 (2011) 4188.
- [14] V. Arabali, M. Ebrahimi, M. Abbasghorbani, V. K. Gupta, M. Farsi, M. R. Ganjali, and F. Karimi, *J. Mol. Liq.* 213 (2016) 312.
- [15] R. Sadeghi, H. Karimi-Maleh, A. Bahari, and M. Taghavi, *Phys. Chem. Liq.* 51 (2013) 704.
- [16] M. L. Yola, and N. Atar, *Electrochim. Acta* 119 (2014) 24.
- [17] M.L. Yola, N. Atar, M.S. Qureshi, Z. Üstündağ, A.O. Solak. *Sens Actuators B* 171–172 (2012) 1207.
- [18] N. F. Atta, A. Galal, A. A. Wassel, and A. H. Ibrahim, *Int. J. Electrochem. Sci.*, 7 (2012) 10501.
- [19] N. F. Atta, A. Galal, S. M. Azab, *Int. J. Electrochem. Sci.* 6 (2011) 5082.
- [20] A. A. Ensafi, H. Karimi-Maleh, S. Mallakpour, and M. Hatami, *Sens. Actuators B* 155 (2011) 464.