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Synthesis and Characterization of NiO Nanoparticle as a High Sensitive Voltammetric Sensor for Vitamin C Determination in Food Samples

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Production of NiO nanoparticles (NiO/NPs) by chemical precipitation is the approach utilized in this work. Nanopowders properties are identified by TG, FTIR, XRD, SEM, and TEM. The results obtained confirm the presence of nickel oxide nanopowders produced during chemical precipitation. In continuous, a novel NiO/NPs carbon paste electrode (NiO/NPs/CPE) had been fabricated. Electrochemical behavior of vitamin C at the NiO/NPs /CPE had been investigated in pH 7.0 phosphate buffer solution (PBS) by cyclic voltammetry (CV), chronoamperometry (CA) and differential pulse voltammetry (DPV). The experimental results suggested that the modified electrode exhibited an electrocatalytic activity toward the redox of vitamin C. Detection limit of vitamin C was found to be 0.05 µM. The proposed sensor was successfully applied for the determination of vitamin C in food samples.

Keywords: Vitamin C, NiO nanoparticle, Food analysis, Modified electrode

1. INTRODUCTION

Ascorbic acid or vitamin C is distributedwidely in both plant and animal kingdoms. In vegetable cells, it bound to protein as ascorbigen [1]. Among animal organs, the liver, leukocytes and anterior pituitary lobe show the highest concentrations of ascorbic acid. Vitamin C also is present in many other biological systems and multivitamin preparations, which are commonly used to supplement inadequate dietary intake [2]. Nevertheless, it is widely used in foods as an antioxidant for the stabilization of color and aroma with subsequent extension of the storage time of the products [3]. Different methods such as spectrophotometry, high performance liquid chromatography (HPLC), and electrochemical methods have so far been available for the determination of TP [4-7].

Nanotechnology has become one of the most interesting disciplines in science and technology today [8-18]. The intense interest in nanotechnology is being driven by various interesting fields and is leading to a new industrial revolution [19-21]. Nano-materials such as nanoparticles, carbon nanotubes or nanocomposite connected with biomolecules are being used for several bioanalytical applications [22-42]. Electroanalysis is taking advantages from all the possibilities offered by nanomaterials easy to be detected by conventional electrochemical methods [43–70]. Nanoparticle of a variety of shapes, sizes and compositions are changing nowadays the bioanalytical measurement [71].

Electroanalytical applications, which utilize chemically modified electrodes (CMEs), should offer a potentially significant efficiency [72-90]. Recently there has been a considerable effort in the investigation of catalytic function of CMEs on the oxidation of environmentally and biologically important compounds [91-114].

In this study, we proposed NiO/NPs as a mediator for the rapid, sensitive, and highly selective voltammetric determination of vitamin C on the surface of a carbon paste electrode. The results showed that the catalytic current depends on the concentration of vitamin C. The proposed method is selective, sensitive, and fast for the determination of vitamin C in real samples such as fruit juices and vegetables with good reproducibility.

2. EXPERIMETAL

2.1. Chemical and Apparatus

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Morphine sulfate was purchasedfrom Sigma. Doubly distilled water was used throughout.

X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-Ka radiation (k = 1.54 Å). ZnO/NPs was characterized by scanning electron microscopy (SEM) (Seron Tech. AIS 2100).

Cyclic voltammetry, chronoamperometry, and differential pulse voltammetry were performed in an analytical system, μ-Autolab with PGSTAT (Eco Chemie, the Netherlands). The system was run on a PC using NOVA software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an $Ag/AgCl/KCl_{sat}$ electrode as a reference electrode was used. The working electrode was both an unmodified carbon paste electrode (CPE) and NiO/NPs nanopaticle modified carbon paste electrode NiO/NPs/CPE.

1.0×10^{-2} mol L^{-1} AA solution was prepared daily by dissolving 0.176 g ascorbic acid in water and the solution was diluted to 100 mL with water in a 100 mL volumetric flask. The solution was kept in a refrigerator at 4 ^{0}C in the dark. More dilute solutions were prepared by serial dilutions with water.

2.2. Synthesis of ZnO/NPs

To prepare of NiO/NPs, in a typical experiment, a 0.25M aqueous solution of zinc nitrate Ni $(NO_3)_2$ and 0.5 M aqueous solution of sodium hydroxide (NaOH) were prepared in distilled water. Then, the beaker containing NaOH solution was heated at the temperature of about 55°C. The Ni $(NO_3)_2$ solutions were added drop wise (slowly for 1.5 h) to the above-heated solution under high-speed stirring. The beaker was sealed at this condition for 2 h. The precipitated NiO/NPs were cleaned with deionized water and ethanol then calcined at 300 °C for 2 hours.

2.3. Preparation of the electrode for electrochemical investigation

NiO/NPs/CPE was prepared by hand–mixing of 0.90 g of graphite powder and 0.10 g NiO/NPs plus paraffin at a ratio of 70/30 (*w*/*w*) and mixed well for 50 min until a uniformly wetted paste was obtained. 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. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper.

2.4. Preparation of practical samples

Fresh fruit juices were obtained using a mechanical squeezer. The juices obtained were filtered. A 0.5 mL portion of the filtrate juice was added to the supporting electrolyte solution in voltammetric cell. Vegetable juices were obtained using a grater and a centrifuge respectively, a 0.5 mL portion of vegetable juice was subjected for the voltammetric measurement. In all cases the amounts of vitamin C in the samples were evaluated by the standard addition method.

3. RESULTS AND DISCUSSION

3.1. Nanostructures characterization

The XRD patterns of the NiO/NPs showed diffraction peaks absorbed at 2θ values (Fig. 1). The prominent peaks were used to calculate the grain size via the Scherrer equation, expressed as follows:

$$D=K\lambda/(\beta \cos\theta) \qquad (1)$$

Where λ is the wavelength ($\lambda = 1.542$ Å) (CuKα), β is the full width at half maximum (FWHM) of the line, and θ is the diffraction angle. The grain size of the NiO nanostructure was 12 nm, and the peaks were observed at the (11), (200), (220), (311) and (222) planes. These peaks correspond to NiO.

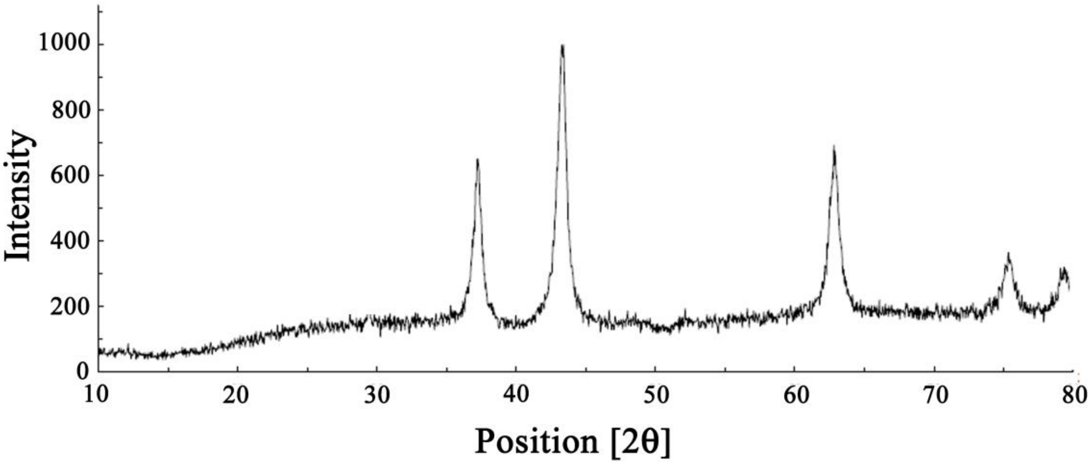


Figure 1. XRD patterns of as-synthesized NiO/NP.

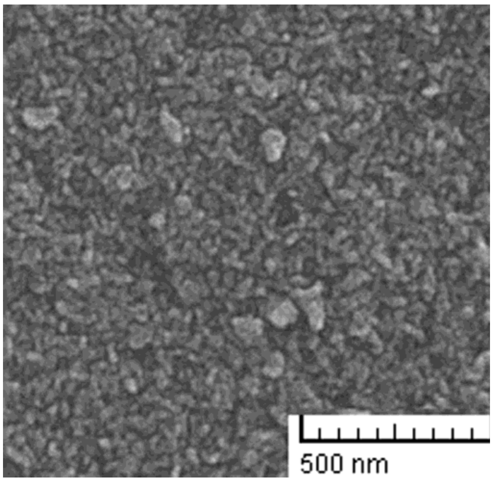
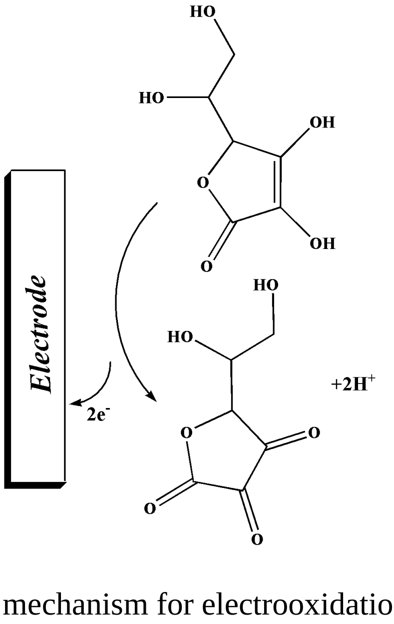


Figure 2. SEM image of NiO/NP.



Scheme 1. The mechanism for electrooxidation of vitamin C

The morphology of the as-grown nanostructures was characterized by SEM technique. Figure 2 shows the SEM images of the product synthesized. It is clear that in this case, NiO/NPs were successfully prepared.

Vitamin C can be oxidized at positive potential depends on the electrode type and solution pH [1-3]. Scheme 1 shows the oxidation reaction of vitamin C [112].

We anticipated that the oxidation of vitamin C would be pH dependent. In order to ascertain this, the voltammetric response of vitamin C at a surface of NiO/NPs/CPE was obtained in solutions with varying pH. Result shows that the peak potential of the redox couple was pH dependent with a slope of −65.2 mV/pH unit at 25 °C which was equal to the anticipated Nernstian value for a two-electron, two-proton electrochemical reaction [112]. It can be seen that the maximum value of the peak current was appeared at pH 7.0, so this value was selected throughout the experiments (Fig. 3).

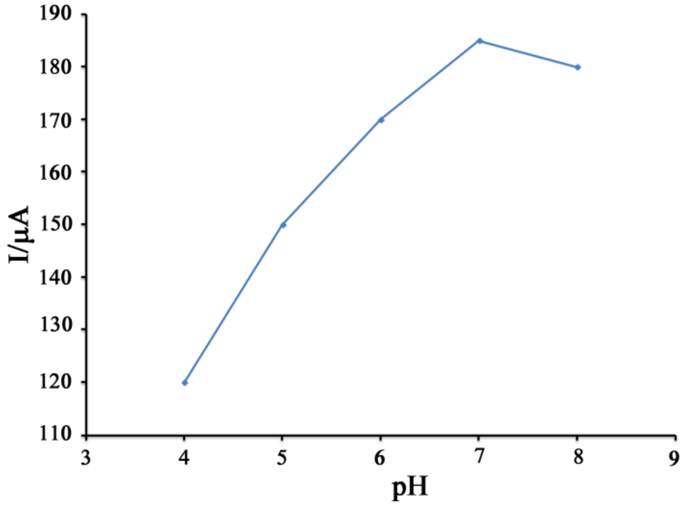


Figure 3. Current–pH curve for electrooxidation of 300.0 µM vitaminC at NiO/NPs/CPE with a scan rate of 50 mV s^{-1}.

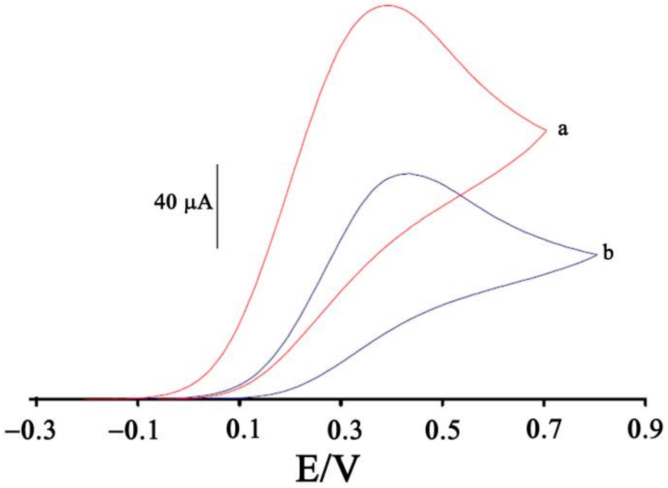


Figure 4 Cyclic voltammograms of a) NiO/NPs/CPE, and b) CPE in presence of 300 µM vitamin C at a pH 7.0, respectively.

Fig. 4 (curves a and b) showed the electrochemical responses of NiO/NPs/CPE and CPE in 300 μM vitamin C in PBS solution (pH 7.0), respectively. Vitamin C showed an irreversible oxidation peak at NiO/NPs/CPE, and CPE, with oxidation peak potential (E_{pa}) of 0.38, and 0.43 V, respectively. However, the peak current of vitamin C at NiO/NPs/CPE was much larger than that at the CPE; it was about 1.6 times larger than CPE (using cyclic voltammetry). Thus, the modified electrode exhibited an electrocatalytic activity toward the oxidation of vitamin C. This further testified the superiority of NiO/NPs/CPE to CPE and indicated that the use of NiO/NPs as modifier facilitated the electron transfer between morphine and electrode.

The effect of scan rate (υ) on the oxidation current of vitamin C was also examined. The results showed that the peaks current increased linearly with increasing the square root of scan rate that ranged from 20 to 150 mV s^{-1} according to regression equation of:

$$I_p = 2.036\, \nu^{1/2} + 0.994\ (r^2 = 0.998,\ I \text{ in } \mu A,\ \nu \text{ in mV s}^{-1}) \qquad (2)$$

The result shows that the electrode process is controlled under the diffusion step [113, 114]. On the other hand, the peak potential shifts in negative direction when the scan rate increases, meaning that the electrochemical reaction is irreversible.

To obtain information about the rate-determining step, the Tafel plot was drawn, as derived from points in the Tafel region of the cyclic voltammogram (Fig. 5). The slope of the Tafel plot was equal 2.3RT /n(1−α)F which comes up to 0.188 V $decade^{-1}$. We obtained α=0.8. In addition, the value of α was calculated for the oxidation of vitamin C at pH 7.0 for both the NiO/NPs/CPE and CPE using the following equation:

$$\alpha n_\alpha = 0.048/(EP - E_{P/2}) \qquad (3)$$

where $E_{P/2}$ is the potential corresponding to $i_{P/2}$. The values for αn_α were found to be 0.8 and 0.6 at the surface of both the NiO/NPs/CPE and the CPE, respectively.

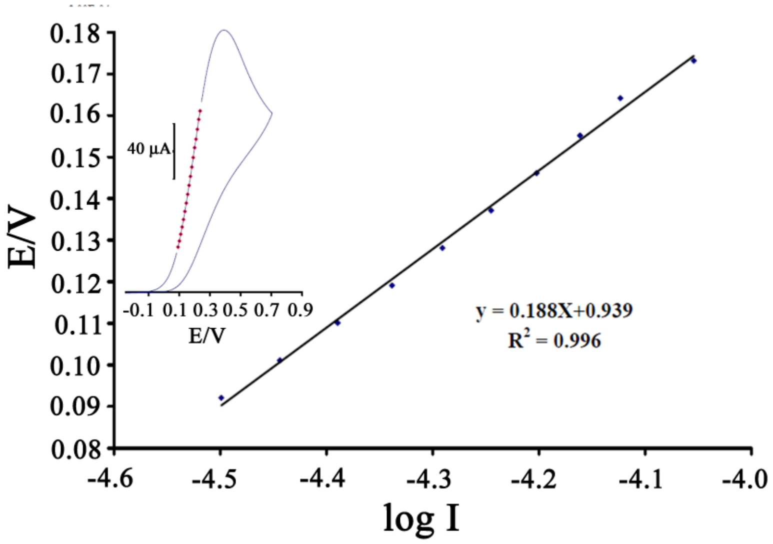


Figure 5. Tafel plot for NiO/NPs/CPE in 0.1 M PBS (pH 7.0) with a scan rate of 50 mV s^{-1} in the presence of 300 μM vitamin C.

These values show that the over-potential of vitamin C oxidation is reduced at the surface of the NiO/NPs/CPE, and also that the rate of the electron transfer process is greatly enhanced. This phenomenon is, thus, confirmed by the larger I_{pa} values recorded during cyclic voltammetry at the NiO/NPs/CPE.

Chronoamperometry results obtained for the various concentrations of vitamin C solution using NiO/NPs/CPE are shown in Fig. 6A. The plot of current (I) versus $t^{-1/2}$ for vitamin C solution at various concentrations using NiO/NPs/CPE (Fig. 6 B) gives straight lines with different slopes. From the slopes we calculated a diffusion coefficient of 2.6×10^{-5} cm^2 s^{-1} (assuming n=1 and the electrode surface area (A) of 0.25 cm^2) for vitamin C using the Cottrell equation [112].

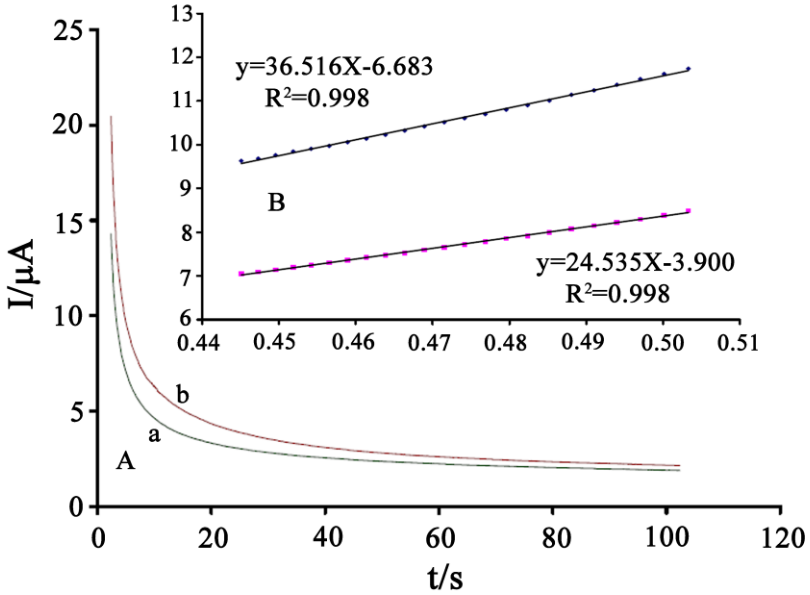


Figure 6 A) Chronoamperograms obtained at the NiO/NPs/CPE in the presence of a) 100; and b) 200 µM vitamin C in the buffer solution (pH 7.0). B) Cottrell's plot for the data from the chronoamperograms.

3.2. Reproducibility and repeatability

The repeatability and stability of NiO/NPs/CPE were investigated using DPV measurements of 10.0 µM vitamin C. The relative standard deviation (RSD%) for seven successive assays of vitamin C was 1.5%. When using four different electrodes, the RSD% for three measurements was 2.1%. When the electrode was stored in our laboratory at room temperature, the modified electrode retained 97% its initial response after a week and 94% after 25 days. These results indicate that NiO/NPs/CPE has good stability and reproducibility, and can be used for vitamin C.

3.3. Calibration plot and limit of detection

The DP voltammograms clearly show that the plot of peak current versus vitamin C concentration is linear for 0.1–700 µmol L^{-1} of vitamin C, the regression equation being I_p(µA) =

(0.0291±0.002)$C_{\text{vitamin C}}$ + (1.740±0.235) ($r^2 = 0.991$), where C is µM concentration of vitamin C and I_p is the peak current. The detection limit was determined at 0.05 µM of according to the definition of $Y_{LOD} = Y_B + 3\sigma$ [115].

3.4. Interferences study

In order to evaluate the selectivity of the proposed method in the determination of vitamin C, the influence of various foreign species on the determination of 10.0 µM vitamin C was investigated. The tolerance limit was taken as the maximum concentration of foreign substances which caused no more than ±5% relative error in the determination. The results are presented in Table 1. Although vitamin C shows interference, its interference can be minimized, if necessary, by using the ascorbic oxidase enzyme, which exhibits high selectivity for the oxidation of vitamin C.

Table 1. Interference study for the determination of 10.0 µM vitamin C under the optimized conditions.

Species	Tolerant limits ($W_{\text{Substance}}/W_{\text{L-cysteine}}$)
Glucose, Sacarose, , Lactose, Feroctose	900
Li^+, Br^-, NO_3^-, ClO_4^-, Mg^{2+}, SO_4^{2-}	700
Folic acid, Galic acid, Tryptophan, Glycine, Methionine, Valine, Histidine	500
Thiouear, Uric acid, Urea	200
Starch	Saturation

3.5. Real sample analysis

Table 2. Determination of AA in real samples (n=3).

Sample	AA Added (µM)	Found (AA) Proposed method (µM)	Found (AA) Published method (µM)	F_{ex}	F_{tab}	t_{ex}	$t_{tab(95\%)}$
Grape	-	50.32±0.76	501.76±0.89	8.5	19.0	2.8	3.8
Orange “	-	145.45±1.02	143.82±1.75	12.5	19.0	3.6	3.8
Kiwi “	-	82.23±1.22	83.05±1.70	8.0	19.0	2.7	3.8
Peach		20.55±0.62	19.33±1.25	7.4	19.0	2.5	3.8
Apple “	-	15.22±0.12	14.85±0.55	6.5	19.0	1.2	3.8
Dill	-	75.55±1.02	74.92±1.21	9.1	19.0	3.5	3.8
Radish	-	35.25±0.38	36.00±0.65	6.0	19.0	1.1	3.8

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of vitamin C in fruit juice and vegetable juice samples. Based on the repeated differential pulse voltammetric responses (*n*=3) of the diluted analyte and the samples that were spiked with specified concentration of vitamin C, measurements were made for determination of vitamin C concentrations in food samples. The results are listed in Table 2. In addition, a published electrochemical method [2] was used for the analysis to confirm the accuracy of the proposed method with a standard procedure (Table 2). The results presented in Table 2 indicate that the modified electrode retained its efficiency for the determination of vitamin C in real samples with satisfactory results.

4. CONCLUSION

In this work, we describe synthesis of NiO/NPs as a high sensitive sensor for voltammetric determination of vitamin C using carbon paste electrode. The synthesized NiO/NPs were characterized with different methods such as SEM and XRD. Compared with its response at CPE, the electrochemical sensitivity of vitamin C at the proposed electrode was improved dramatically, revealing some advantages of NiO/NPs/CPE over CPE such as high conductivity and fast electron transfer. Finally, the propose sensor was successfully used for the determination of vitamin C in food samples.

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