

Full Paper

Evaluation of the Usefulness of an Electrochemical Sensor in Detecting Ascorbic Acid using a Graphite Screen-printed Electrode Modified with NiFe₂O₄ Nanoparticles

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Abstract- In this study, a new modified electrode was proposed to measure ascorbic acid. Graphite screen printed electrode was modified with NiFe₂O₄ nanoparticles (NiFe₂O₄/SPE). Cyclic voltammetry (CV), Chronoamperometry (CHA) and differential pulse voltammetry (DPV) methods were used to analyze the prepared electrode. The catalytic property resulting from the synergistic effect of this modifier not only increased the oxidation current but also reduced the oxidation potential of ascorbic acid. Scan rate and pH effects on the performance of NiFe₂O₄/SPE were also investigated. The linear calibration curve of ascorbic acid was obtained within the linear range of 5.0×10^{-7} – 1.0×10^{-4} M, and the detection limit was calculated as 1.0×10^{-7} M. Finally, the modified electrode was successfully used to measure ascorbic acid in some real samples.

Keywords- Ascorbic acid, NiFe₂O₄ nanoparticles, Voltammetric sensor, Screen printed electrode

1. INTRODUCTION

In recent years, the interdisciplinary applications of the electrochemical method in sciences (such as clinical medicine, environmental protection, and agriculture) have attracted

more attention for the reasons of their recognition properties, simplicity, high sensitivity, good stability, high selectivity, low cost, fast response and real time detection [1-9].

The graphite screen printed electrodes (SPEs) modified with electroactive films have been widely applied for the determination of trace amounts of important analytes and the use of modified materials with large surface area can provide better sensitivity [10-13]. Different type of nanoparticles has attracted much research attention in fabricating modified electrochemical sensors due to its high specific surface area, excellent electrical conductivity, high electrocatalytic activity, and the outstanding electronic property [14-22].

Recently, the electrochemical properties of different binary metal oxides with spinel structures have been studied extensively because of their good electrical conductivity, lower activation energy for electron transportation between cations, good structural stability and relatively higher specific capacitance in comparison to the unitary metal oxides [23,24]. Among various spinel transition metal oxides, NiFe_2O_4 is a promising material for modified electrode due to its high theoretical capacities (914 mA h/g) and low toxicity [25-27].

Ascorbic acid, one of the principal antioxidants present in variable amount in fruits and vegetables, has been widely used in the pharmaceutical, chemical, cosmetic and food sectors [28-30]. The development of sensitive and reproducible procedures for the detection of ascorbic acid is still under study nowadays, which is evidenced by the large scientific publications that can be found [31]. Compared with conventional methods: fluorimetry, chromatography, spectrophotometry and redox titration, electrochemical methods have the obvious advantages of low cost, high sensitivity, short response time and simple operation [32,33]. Although ascorbic acid is an effective reductive compound, it cannot be detected directly by the electrochemical methods using the conventional electrode such as glassy carbon electrode, graphite electrodes and Pt electrode for its high overpotential, low selectivity, low reaction sensitivity and poor reproducibility on these electrodes [34,35]. In order to solve these problems, many kinds of modified electrodes were prepared to replace the conventional electrodes [36-47].

In this work, a screen printed electrode modified with the NiFe_2O_4 nanoparticles was used for sensitive voltammetric determination of ascorbic acid and the modified electrode exhibited excellent electrocatalytic activity to ascorbic acid.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software.

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode and an unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Ascorbic acid and all other reagents were analytical grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

2.2. Synthesis of NiFe₂O₄ nanoparticles

NiFe₂O₄ nanoparticles were synthesized in the presence of urea using a solvothermal method. Solution of urea was dissolved in 100 ml of ethylene glycol (EG). Then 10 mL FeCl₃.6H₂O (16 mmol) and 10 mL NiCl₂.6H₂O (8 mmol) were added into the above solution, respectively. The mixed solutions, with stoichiometric 30 molar ratio of urea/Fe³⁺ (with excess urea that form sufficient precipitating ions for metal oxides formation), were magnetically stirred until all the starting materials were totally dissolved at 25 °C. These solutions were further homogenized in an ultrasonic water bath for 15 min and then respectively transferred into Teflon-lined stainless steel autoclave with a capacity of 200 ml in order to keep them at 200 °C for 24 h in an oven. Subsequently, the autoclaves were air cooled to room temperature. The as-obtained precipitates were centrifuged, and then washed with DI water and absolute ethanol for several times to remove the impurities in the products. The resulting products were dried in a vacuum oven at 100 °C for 12 h.

2.3. Preparation of the electrode

The bare screen-printed electrode was coated with NiFe₂O₄ nanoparticles according to the following simple procedure. 1 mg NiFe₂O₄ nanoparticles were dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

2.4. Preparation of real samples

One milliliter of a vitamin C ampoule (Darou Pakhsh Company, Iran, contained 1 mg/mL of AA) was diluted to 10 mL with 0.1 M PBS (pH 7.0); then, different volume of the diluted solution was transferred into each of a series of 25 mL volumetric flasks and diluted to the mark with PBS. The ascorbic acid content was analyzed by the proposed method using the standard addition method.

Five vitamin C tablets (labeled 250 mg per tablet, Osvah Pharmaceutical Company, Iran) were grinding. Then, the tablet solution was prepared by dissolving 400 mg of the powder in 25 mL water by ultrasonication. Then, different volume of the diluted solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The

ascorbic acid content was analyzed by the proposed method using the standard addition method.

Five vitamin C effervescent tablets (labeled 500 mg per tablet, Hakim Pharmaceutical Company, Iran) were grinding. Then, the tablet solution was prepared by dissolving 1.07 g of the powder in 25 mL water by ultrasonication. Then, different volume of the diluted solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The ascorbic acid content was analyzed by the proposed method using the standard addition method.

3. RESULT AND DISCUSSION

3.2. Electrochemical profile of the ascorbic acid on the NiFe₂O₄/SPE

To study the electrochemical behaviour of ascorbic acid which is pH-dependent, it is necessary to obtain the optimized pH value in order to achieve the accurate results. By performing the experiments by use of modified electrodes at various pH values ranging from 2.0–9.0, it was revealed that the best results for electro-oxidation of ascorbic acid occur at pH=7.0. The obtained cyclic voltammograms in the presence of 100.0 μM ascorbic acid using the NiFe₂O₄/SPE (Curve a) and bare SPE (Curve b) are shown in Fig. 1. According to CV results the maximum oxidation of ascorbic acid on the NiFe₂O₄/SPE occurs at 340 mV which is about 180 mV more negative compared with unmodified SPE.

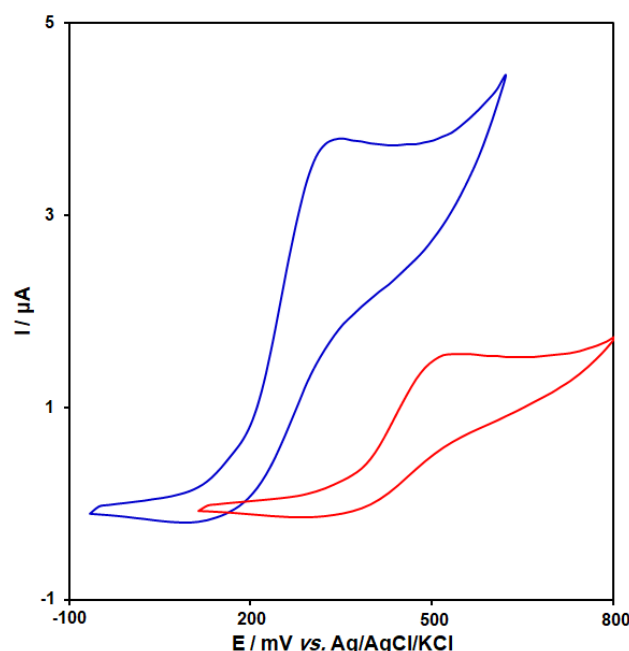


Fig. 1. Cyclic voltammograms of (a) NiFe₂O₄/SPE and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 100.0 μM at the scan rate 50 mVs^{-1}

3.2. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of ascorbic acid, Fig. 2. In addition, there is a linear relationship between I_p and the square root of the potential scan rate ($v^{1/2}$) that demonstrates that the oxidation procedure of analyst is in control of diffusion.

Fig. 3 shows the LSV of a $\text{NiFe}_2\text{O}_4/\text{SPE}$ obtained in 0.1 M PBS (pH 7.0) containing 70.0 μM ascorbic acid, with a sweep rate of 10 mV s^{-1} . The points show the rising part of the voltammogram (known as the Tafel region), which is affected by the electron transfer kinetics between ascorbic acid and $\text{NiFe}_2\text{O}_4/\text{SPE}$. If deprotonation of ascorbic acid is a sufficiently fast step, the number of electrons involved in the rate determining step can be estimated from the slope of the Tafel plot. The inset of Fig. 3 shows a Tafel plot that was drawn from points of the Tafel region of the LSV. The Tafel slope of 0.1293 V obtained in this case agrees well with the involvement of one electron in the rate determining step of the electrode process, assuming a charge transfer coefficient of $\alpha=0.54$ [48].

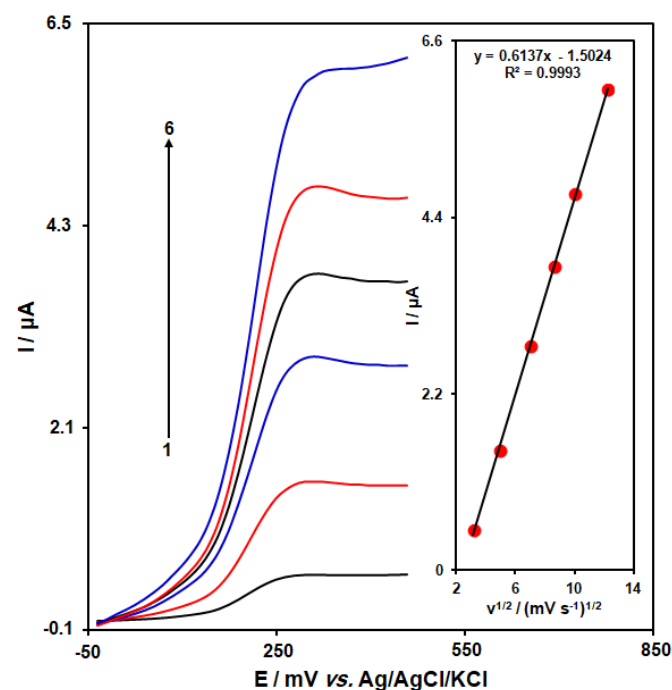


Fig. 2. LSVs of $\text{NiFe}_2\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) containing 70.0 μM ascorbic acid at various scan rates; numbers 1-6 correspond to 10, 25, 50, 75, 100 and 150 mV s^{-1} , respectively. Inset: Variation of anodic peak current vs. $v^{1/2}$

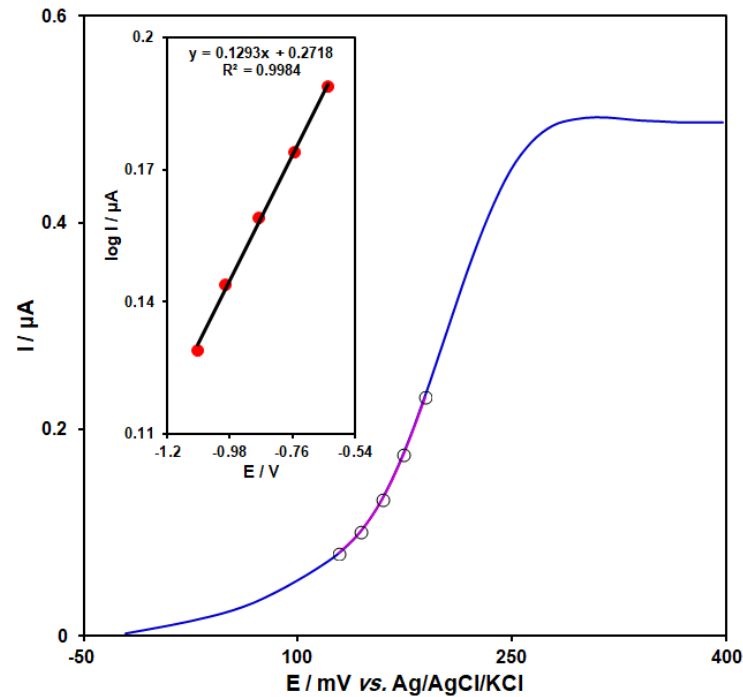


Fig. 3. LSV (at 10 mV s^{-1}) of a $\text{NiFe}_2\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) containing $70.0 \mu\text{M}$ ascorbic acid. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

3.3. Chronoamperometric analysis

The analysis of chronoamperometry for ascorbic acid samples was performed by use of $\text{NiFe}_2\text{O}_4/\text{SPE}$ vs. Ag/AgCl/KCl (3.0 M) at 0.6 V. The Chronoamperometric results of different concentration of ascorbic acid sample in PBS (pH 7.0) are demonstrated in Fig. 4. The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follow [48]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where D represents the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), and C_b is the applied bulk concentration (mol cm^{-3}). Experimental results of I vs. $t^{-1/2}$ were plotted in Fig. 4A, with the best fits for different concentrations of ascorbic acid. The resulted slopes corresponding to straight lines in Fig. 4A, were then plotted against the concentration of ascorbic acid (Fig. 4B). The mean value of D was determined to be $1.4 \times 10^{-6} \text{ cm}^2/\text{s}$ according to the resulting slope and Cottrell equation.

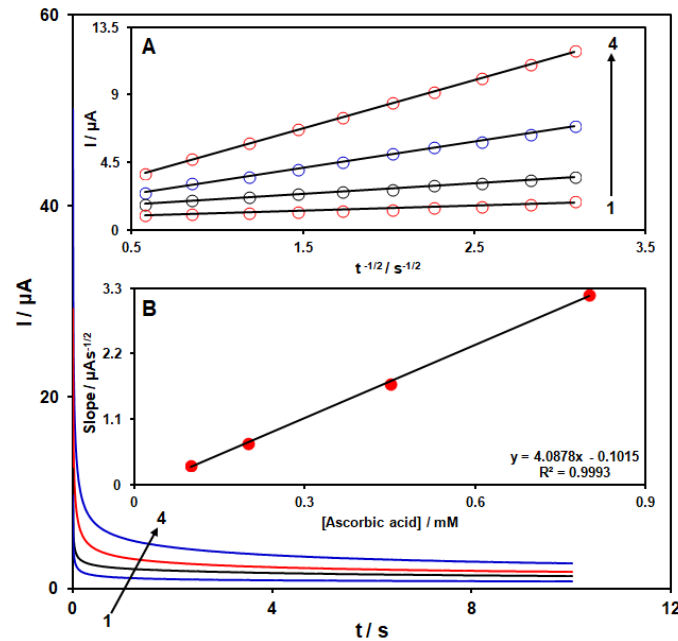


Fig. 4. Chronoamperograms obtained at NiFe₂O₄/SPE in 0.1 M PBS (pH 7.0) for different concentration of ascorbic acid. The numbers 1–4 correspond to 0.1, 0.2, 0.45 and 0.8 mM of ascorbic acid. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against ascorbic acid concentration

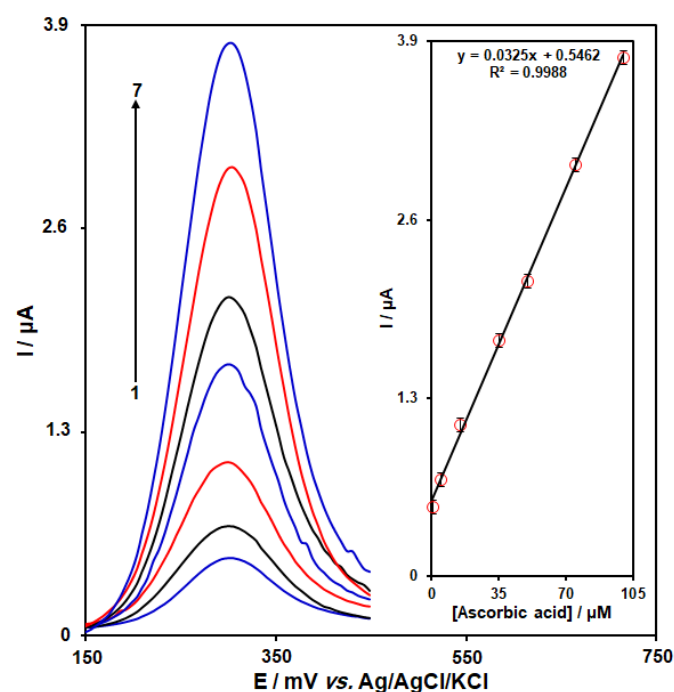


Fig. 5. DPVs of NiFe₂O₄/SPE in 0.1 M (pH 7.0) containing different concentrations of ascorbic acid. Numbers 1–7 correspond to 0.5, 5.0, 15.0, 35.0, 50.0, 75.0 and 100.0 μM of ascorbic acid. Inset: Plot of the electrocatalytic peak current as a function of ascorbic acid concentration in the range of 0.5–100.0 μM

3.4. Calibration curves

Based on the resulting peak currents of ascorbic acid by use of NiFe₂O₄/SPE, the quantitative analysis of two targets were done (Initial potential=0.15 V, End potential=0.45 V, Step potential=0.1 V, Modulation amplitude=0.02505 V) in water solutions. The modified electrode (NiFe₂O₄/SPE) as working electrode in the range of ascorbic acid concentration in 0.1 M PBS was used in differential pulse voltammetry (DPV) due to the advantages of DPV including the improved sensitivity and better performance in analytical applications (Fig. 5). According to the results, a linear relationship exists between the peak currents and concentrations of ascorbic acid within the concentration range of 0.5-100.0 μM with the correlation coefficient of 0.9988. The detection limit was obtained 0.1 μM. Table 1. shows a comparison of the analytical figures of merit of the proposed method with different reported techniques for the determination of ascorbic acid.

Table 1. Comparison of some electrochemical procedures used in the determination of ascorbic acid

Electrode	Linear Range (μM)	Detection Limit (μM)	Ref.
Glassy carbon electrode modified with platinum, gold nanoparticles and L-Cysteine	103.0-1650.0	103.0	[49]
Glassy carbon electrode modified with PdAu/graphene nanocomposites	12.5-700.0	12.5	[50]
Glassy carbon electrode modified with flake hexagonal boron nitride	30.0-1000.0	3.77	[51]
Glassy carbon electrode modified with chrysanthemum-like titanium nitride	50.0-1500.0	1.52	[52]
Glassy carbon electrode modified with poly(3,4-ethylenedioxythiophene)	30.0-500.0	45.0	[53]
Glassy carbon electrode modified with ferrocene hybrid/three dimensional graphene hydrogel	20.0-450.0	0.183	[54]
Glassy carbon electrode modified with carbon nano-onions	0.0-50.0	0.34	[55]
Graphite screen printed electrode modified with NiFe ₂ O ₄ nanoparticles	0.5-100.0	0.1	This Work

3.5. Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of ascorbic acid in vitamin C ampoule, vitamin C tablet and vitamin C effervescent using the described method. In order to perform this analysis, standard addition method was employed and the results are listed in Table 2. Accordingly, the results of ascorbic acid recovery are satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

Table 2. The application of NiFe₂O₄/SPE for determination of ascorbic acid in vitamin C ampoule, vitamin C tablet and vitamin C effervescent (n=5). All concentrations are in μM

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Vitamin C ampoule	0	10.0	-	3.2
	5.0	15.7	104.7	2.7
	10.0	19.6	98.0	2.4
	15.0	25.7	102.8	1.6
Vitamin C tablet	0	5	-	2.6
	10.0	14.4	98.6	1.8
	15.0	20.6	103	3.1
	20.0	24.4	97.6	2.5
Vitamin C effervescent tablet	0	5	-	2.4
	10.0	14.8	98.6	3.7
	15.0	19.7	98.5	3.2
	20.0	24.9	99.6	2.6

4. CONCLUSION

We proposed here a simple and environmental friendly method for the preparation of NiFe₂O₄ nanoparticles by using ethylene glycol. In addition, this NiFe₂O₄ nanoparticles exhibited high electrochemical activity and some attractive analytical features for the determination of ascorbic acid. The linear working range for the quantitation of ascorbic acid was 0.5–100.0 μM ($R^2=0.9988$) with a detection limit of 0.1 μM (3σ of blank). The proposed method was successfully applied to the determination of ascorbic acid in real samples.

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