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Fabrication of Amplified Nanostructure Based Sensor for Analysis of *N*-Acetylcysteine in Presence of High Concentration Folic Acid

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A high selective sensor based on carbon paste electrode chemically modified with MgO nanoparticles (MgO/NPs) and acetylferrocene (AF) was used for the simultaneous determination of N-acetylcysteine (NAC) and folic acid (FA) in aqueous solution. Electrochemical methods such as cyclic voltammetry (CV), chronoamperometry (CHA), and differential pulse voltammetry (DPV) were used to study the ability of proposed sensor for the electrocatalytic oxidation of NAC. On the best condition in voltammetric analysis, the DPV peak current of NAC increased linearly with its concentration in the ranges of 0.005–0.5 µmol L^{-1} and 1.0–50.0 µmol L^{-1}. The detection limit (S/N = 3) was 1.0 nmol L^{-1} for NAC. The prepared sensor exhibits good resolution between NAC and FA signals for simulations determination of these compounds.

Keywords: Electrocatalysis, Chemically modified electrodes, Folic acid, Carbon paste electrode, MgO nanoparticle, N-acetylcysteine

1. INTRODUCTION

Cysteine and its derivative NAC are two important compounds with crucial roles in biological system and human body [1]. NAC has good ability for treatment of acetaminophen overdose [2]. Some of the scientist have even reported that NAC can be used for complexation with heavy metals and remove them from the human body. Finally, NAC can be suggested as anticancer drug due to its antioxidant activity and glutathione precursor ability [3].

The analysis of NAC in biological and pharmaceutical samples has received considerable attention due to its biological and pharmaceutical significance. Some of the scientists reported determined of NAC by chromatographic [4], spectrophotometric [5], fluorimetric [6], flow injection [7], potentiometric [8] and electrochemical sensors [9-12]. In comparison, application of electrochemical methods proposed fast and sensitive analysis methods due to the acceptable results [13-22]. According to previous report, electro-oxidation of NAC has a high overpotential and weak signal at a surface of bare electrodes and application of modified electrodes for analysis of NAC is very important [12, 23-25].

Folic acid is one of most important members the water-soluble vitamin B groups that have a high performance with a range of pharmaceutical and food fortification application [26]. On the other hand, FA is vital for cell growth in human body. Many countries mandated fertilization with folic acid in food samples to reduce birth defects in pregnant women [26]. Owing to the wide use of folic acid, some published papers based on analysis systems such as HPLC [27,28] , HPLC–MS [29] , colorimetry [30], spectrophotometry [31], chemiluminescence [32], flouorimetric [33] and microbial methods [34] have been reported for the trace analysis of folic acid.

Modified carbon paste electrode (MCPE) has been widely used in trace analysis of important electroactive compounds such as drugs, pollutant, biological compounds, vitamins and other species [35-41]. MCPEs have high specific properties such as easy preparation and wider potential window compare to other usual electrode such as glassy carbon electrodes [42-46]. Nanomaterials and electroactive mediators are most of the important compounds for modification of the electrodes to improve the electrochemical behaviors [47-58].

This work proposed acetylferrocene as suitable mediator and MgO nanoparticle as a high conductive modifier for the selective voltammetric determination of NAC. AF/MgO/NPs/CPE shows good ability for quantification of NAC in the presence of high concentration of folic acid. In the final step, AF/MgO/NPs/CPE was used for determination of NAC and FA in real samples.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical analysis performed with an Autolab type III. A three-electrode system including an AF/MgO/NPs/CPE as working electrode, an Ag/AgCl electrode as reference electrode and a Pt rod as auxiliary electrode was used to obtain the electrochemical data. Analytical-grade diethyl ether, graphite powder, was obtained from Merck (Darmstadt, Germany). N-acetylcysteine, folic acid and $Mg(NO_3)_2.6H_2O$ were procured from Sigma-Aldrich. MgO nanoparticle synthesized by our previous published paper [59].

2.2. Preparation of the modified electrode

The AF/MgO/NPs/CPE was prepared by mixing 0.01 mg AF and 0.1 g MgO nanoparticles in 0.89 g graphite powder with a mortar and pestle. Then, 0.8 mL of paraffin oil were added to the above mixture and mixed for 30 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a glass tube with an inner diameter of 0.30 cm. A copper wire inserted into the carbon paste provided the electrical contact. A new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

2.3. Real samples preparation

Eleven NAC tablets were grinded and then dissolving suitable of them in 100 mL water/ethanol solution. The solution was diluted with phosphate buffer solution (PBS) (pH 7.0).

Also, ten folic acid tablets was used for preparation of real samples. The above procedure was used for preparation of folic acid solution from tablet samples. The NAC and folic acid content were analyzed by the proposed method using the standard addition method.

Urine samples were stored in a refrigerator (at 4 °C) immediately after collection. Ten milliliters of the sample was centrifuged for 30 min at 2000 rpm. The supernatant was filtered using a 0.45 μm filter and then it was diluted 5 times with the phosphate buffer of pH 7.0.

3. RESULTS AND DISCUSSION

3.1. Characterization of MgO nanoparticles

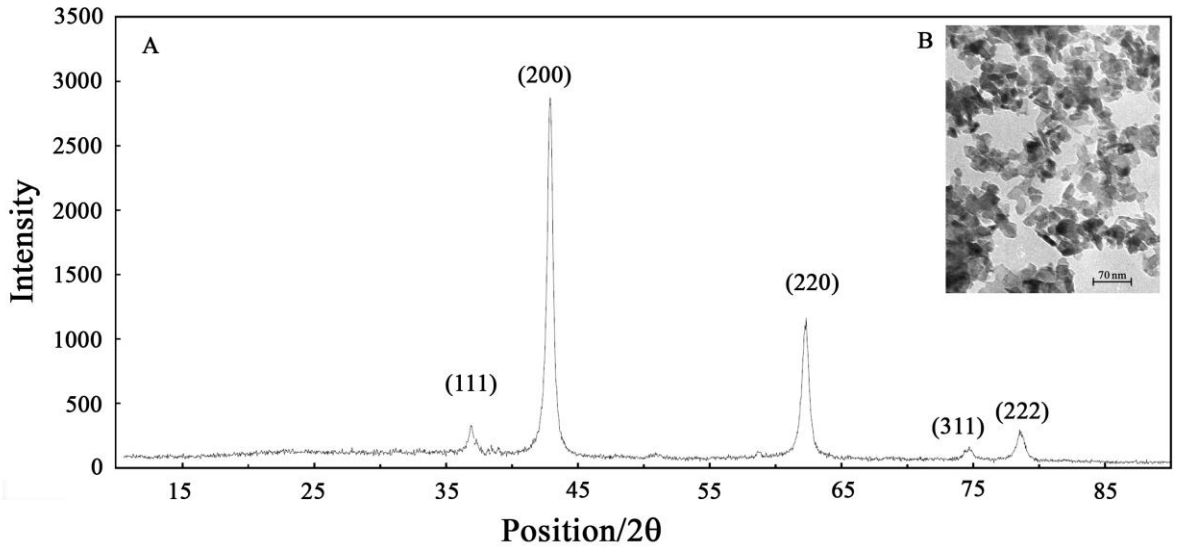

Figure 1. A) A typical XRD for MgO nanoparticles synthesized in this work. B) TEM image of MgO/NPs.

Figure 1A represents the XRD pattern of MgO nano-powder. A definite line broadening of the XRD peaks indicates that the prepared powders consist of particles in nano scale size. The diffraction peaks located at the peak observed at 2θ = 38.105°, 42.915°, 62.310°, 74.770°, and 78.565 correspondence to the planes: (111), (200), (220), (311) and (222), respectively (JCPDS 01-1235). The synthesized MgO nano-powder diameter (~ 27 nm) was calculated using Debye-Scherrer equation ($D=K\lambda/(\beta \cos\theta)$). Where λ is the wavelength (λ = 1.542 Å) (CuKα), β is the full width at half maximum (FWHM) of the line, and θ is the diffraction angle.

In continuous, the TEM method was used for investigation MgO/NPs morphology. Figure 1B shows the TEM images of the product synthesized. The dark spots correspond to MgO/NPs, which were only synthesis in my synthesis condition.

3.2. Electrochemical characterization of the modified electrode

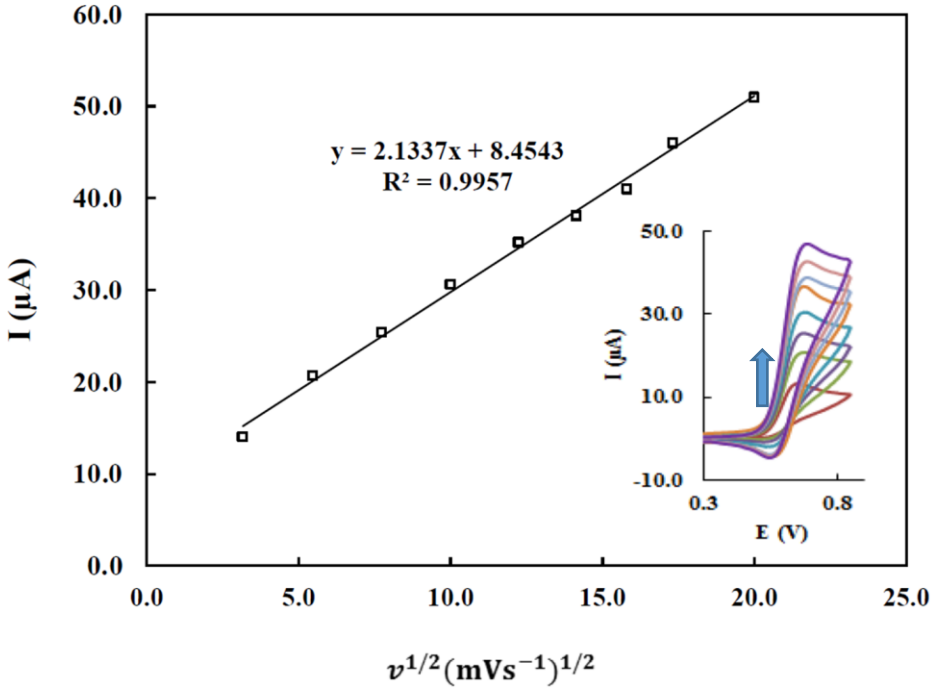

Figure 2. Plot of I_p vs. $v^{1/2}$ for the oxidation of AF/MgO/NPs/CPE. Inset: cyclic voltammograms at various scan rates: from inner to outer, 10, 30, 60, 100, 150, 200, 300 and 400 mV s^{-1}, respectively, in 0.1 mol L^{-1} PBS (pH 7.0).

Cyclic voltammetry was employed for study of the electrochemical properties of AF/MgO/NPs/CPE (pH 7.0). Fig. 2 insert shows the cyclic voltammograms obtained for AF/MgO/NPs/CPE at various scan rates. The cyclic voltammogram exhibits anodic and corresponding cathodic peaks with E_{pa}=0.65 V and E_{pc}=0.58V vs. Ag/AgCl as a references electrode. The

experimental results show well-defined and reproducible anodic and cathodic peaks related to Fc/Fc^{+} redox couple with a quasi-reversible behavior and a peak separation potential ($\Delta E_p = E_{pa} - E_{pc}$) of 70 mV. Also the plot of the anodic peak current was linearly dependent on $v^{1/2}$ with a correlation coefficient of 0.995 at all scan rates (Fig. 2). This behavior shows that redox process is diffusion-controlled.

3.3. Electrocatalytic investigation

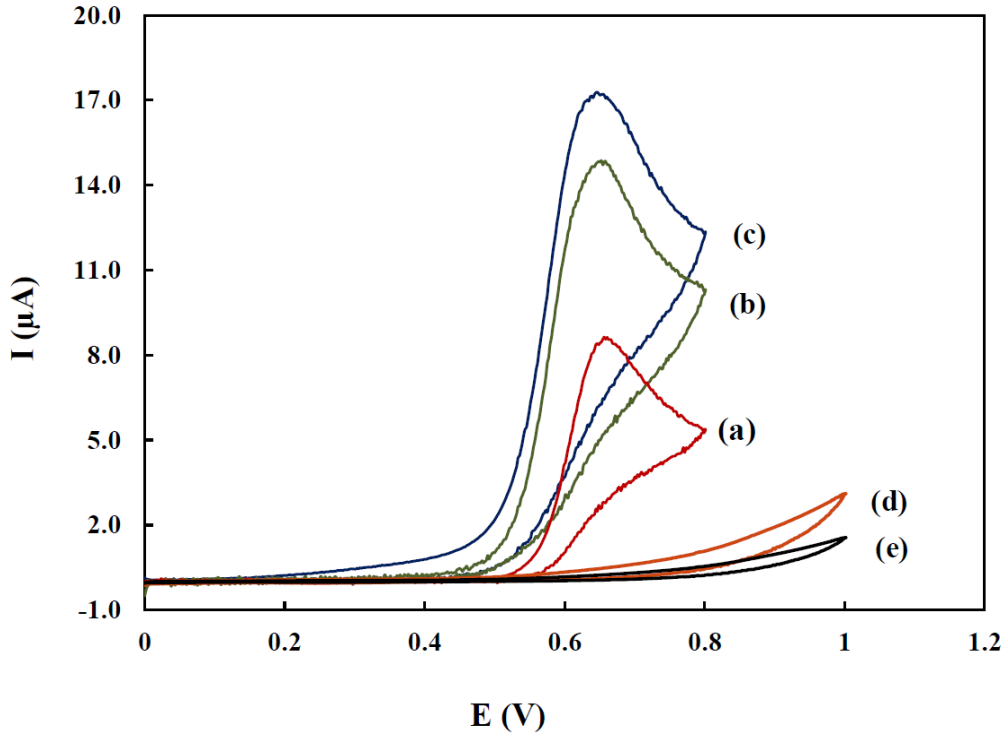

Figure 3. Cyclic voltammograms of (a) the buffer solution at AF/MgO/NPs/CPE; (b) 300 µmol L^{-1} NAC at AF/CPE; (c) 300 µmol L^{-1} NAC at AF/MgO/NPs/CPE; (d) 300 µmol L^{-1} NAC at MgO/NPs/CPE and (e) 300 µmol L^{-1} NAC at CPE. Conditions: 0.1 mol L^{-1} PBS (pH7.0), scan rate of 10 mVs^{-1}.

In continuous, we investigated the catalytic interaction between mediator and NAC at pH=7.0 as optimum condition. Fig. 3 depicts the cyclic voltammetric responses from the electrochemical oxidation of 300 µmol L^{-1} NAC at AF/MgO/NPs/CPE (curve c), at AF/CPE (curve b), at MgO/NPs/CPE (curve d) and at bare CPE (curve e). As can be seen, the anodic peak potentials for the oxidation of NAC at the AF/MgO/NPs/CPE (curve c) and the AF/CPE (curve b) was about 650 mV, while at MgO/NPs/CPE (curve d), the peak potential was about 880 mV. At the unmodified CPE, the peak potential was about 900 mV of NAC (curve e). According to the above results, it was established that the best electrocatalytic effect for NAC oxidation was observed at the AF/MgO/NPs/CPE (curve

c). The obtained data showed that the combination of MgO nanoparticles and AF improve the characteristics of NAC oxidation. The AF/MgO/NPs/CPE in 0.1 mol L^{-1} phosphate buffer (pH 7.0) without NAC in the solution exhibited a well-behaved redox reaction (curve a) upon the addition of 300.0 µmol L^{-1} NAC, the anodic peak current of mediator was increased. This behavior is typical of that expected for electrocatalysis at chemically modified electrodes [60-63].

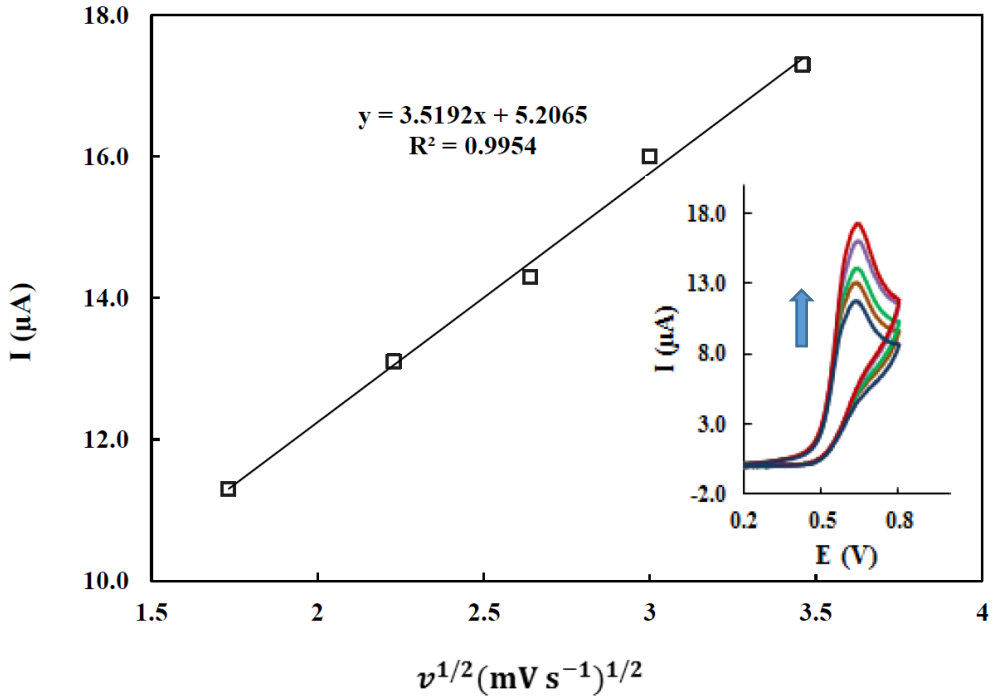

Figure 4. Plot of I_{pa} vs. $\nu^{1/2}$ for the oxidation of NAC at AF/MgO/NPs/CPE. Inset: cyclic voltammograms of 300 µmol L^{-1} NAC at various scan rates from inner to outer; 3.0, 5.0, 7.0, 9.0 and 12.0 mVs^{-1}, in 0.1 mol L^{-1} PBS (pH 7.0).

The effect of scan rate (ν) on peak potential (E_p) and peak current (I_p) of 300 µmol L^{-1} NAC in pH=7.0 PBS was studied in the range of 3.0–12.0 mV s^{-1} at AF/MgO/NPs/CPE (Fig. 4, inset). The oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. However, the oxidation currents change linearly with the $\nu^{1/2}$(Fig. 4), suggesting that the process is diffusion rather than surface controlled.

In order to obtain information about the rate-determining step, Tafel plot (plots of log I vs. potential) was drawn (Fig. 5) which were derived from points of the Tafel region of the cyclic voltammogram in Fig. 5 (insert). The slope of the Tafel plot is equal to $2.3RT/(1-\alpha)\ n_\alpha F$ which comes up to 0.106 $Vdecade^{-1}$. We obtained nα equal to 0.45. Assuming n=1, then α=0.44.

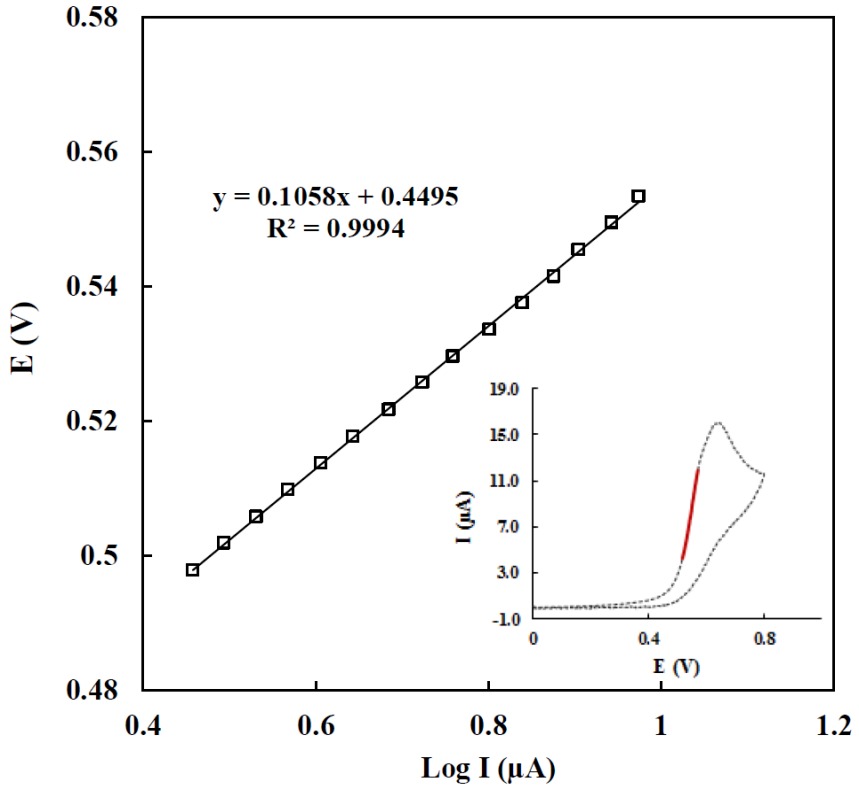

Figure 5. Tafel plot for AF/MgO/NPs/CPE in 0.1 mol L^{-1} PBS (pH 7.0) at the scan rate of 10 mVs^{-1} in the presence of 300.0 µmol L^{-1} NAC.

3.4. Chronoamperometric measurements

The electro-catalytic oxidation of NAC by AF/MgO/NPs/CPE was also studied by chronoamperometry method (Fig. 6). Chronoamperometric measurements of different concentrations of NAC at AF/MgO/NPs/CPE were done by setting the working electrode potential at 200 and 800 mV as first and second potential condition. In chronoamperometric studies, we have determined the diffusion coefficient (Fig.6 insert B), D, of NAC using the Cottrell equation [64]:

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

We calculated a diffusion coefficient of 9.6×10^{-4} cm^2 s^{-1} for NAC.

Chronoamperometry can also be employed to evaluate the catalytic rate constant, k_h, for the reaction between NAC and mediatpr according to the method of Galus [65]:

$$I_C/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}\,(k_h C_b t)^{1/2} \quad (2)$$

The above equation can be used to calculate the rate constant of the catalytic process k_h. Based on the slope of I_C/I_L vs. $t^{1/2}$ plot, k_h can be obtained for a given NAC concentration (Fig. 6. insert C).

From the values of the slopes, an average value of k_h was found to be $k_h=2.14\times10^3$ mol^{-1} L s^{-1}. The value of k_h explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of NAC at the surface of AF/MgO/NPs/CPE.

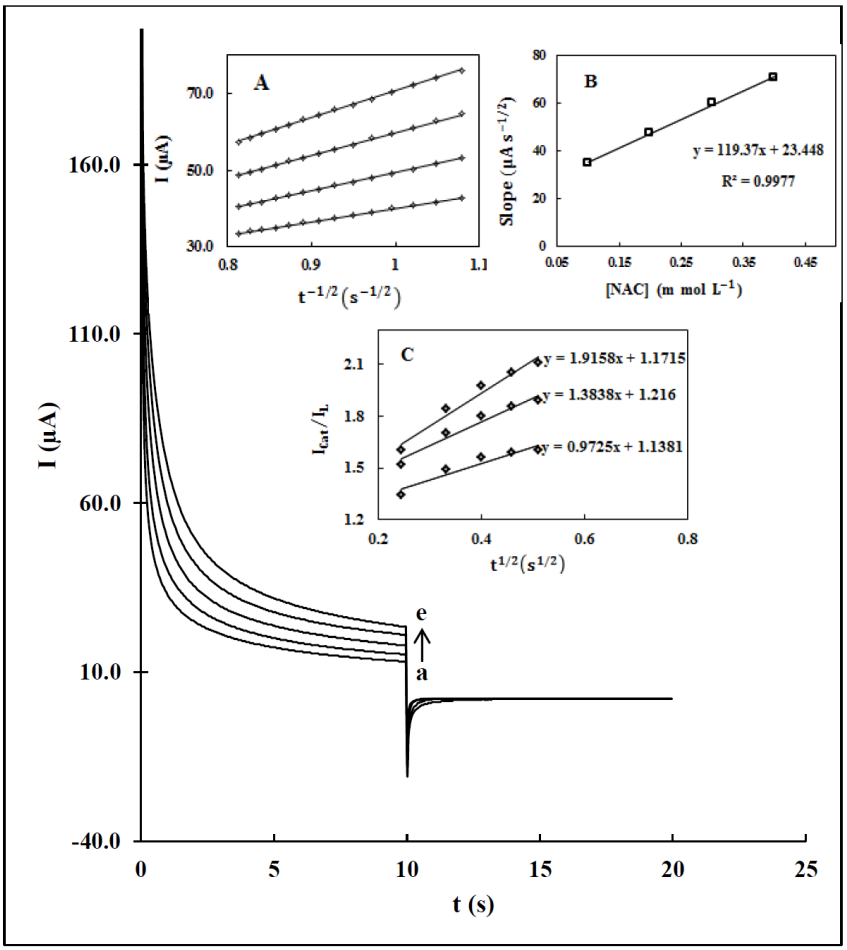

Figure 6. Chronoamperograms obtained at the AF/MgO/NPs/CPE (a) in the absence, and in the presence of (b) 100, (c) 200, (d) 300, and (d) 400 µmolL^{-1} NAC at pH 7.0. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms b–e. (B) Plot of the slope of the straight lines against N-acetylcysteine concentration. (C) Dependence of I_C/I_L on $t^{1/2}$ derived from the chronoamperogram data.

3.5. Analytical application of AF/MgO/NPs/CPE

The DPV method was applied to determine the linear dynamic range of NAC at a surface of AF/MgO/NPs/CPE (Not shown). The plot of peak current *vs.* NAC concentration consisted of two linear segments with slopes of 2.72 and 0.070 µA µmol^{-1} L in the concentration ranges of 0.005–0.5 µmol L^{-1} and 1.0–50.0 µmol L^{-1}, respectively. The detection limit of NAC was found to be 1.0 nmol

L^{-1}. The limit of detection and linear dynamic range for analysis of NAC at a surface of AF/MgO/NPs/CPE compare to with previous published papers (Table 1)

Table 1. The analytical data reported by some different electrochemical sensors for NAC analysis

Electrode	pH	Dynamic range (μM)	Limit of detection (μM)	Reference
Carbon paste	9.0	1.0-400	0.6	[11]
Carbon paste	7.0	0.1-600	0.07	[66]
Carbon paste	7.0	0.25-400	0.08	[67]
Carbon paste	7.0	0.5-200	0.2	[68]
Carbon paste	7.0	0.1-662	0.09	[69]
Carbon paste	7.0	0.2-400	0.08	[70]
Carbon paste	7.0	0.47-500	0.21	[71]
Carbon paste	7.0	0.005-50.0	0.001	This work

3.6. Simultaneous determination of N-acetylcysteine and folic acid

Simultaneous determination of NAC and FA is one of the main objectives of proposed sensor. The effective application of the AF/MgO/NPs/CPE for this goal was demonstrated by simultaneously changing above analytes concentrations. Fig. 7 shows typical DPV for the simultaneous changing of NAC and FA in optimum condition. The insert A and B show the dependence of DPV peak currents on the concentration of NAC and FA respectively.

The DP voltammetric results showed that simultaneous determination of NAC and FA with two well-distinguished anodic peaks at 650 and 810 mV potentials, corresponding to the oxidation of NAC and FA is possible at the modified electrode. The presence data confirm ability of proposed sensor for simultaneous determination of NAC and FA.

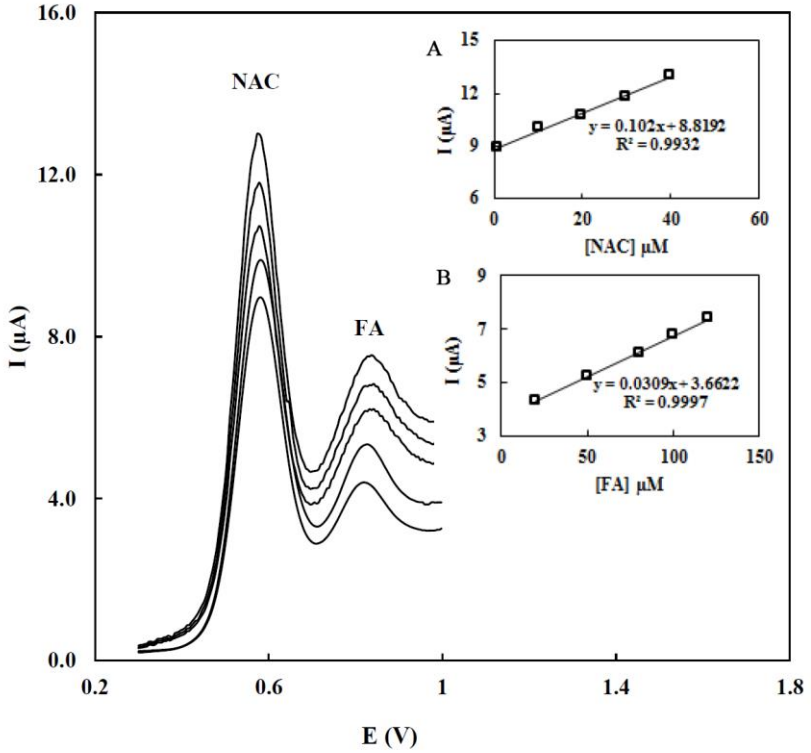

Figure 7. DPVs of AF/MgO/NPs/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of N-acetylcysteine and folic acid in μmol L^{-1}, from inner to outer: 1.0 + 20.0, 10.0 + 50.0, 20.0 + 80.0, 30.0 + 100.0, and 40.0 + 120.0 respectively. Insets (A) plots of I_p vs. N-acetylcysteine concentration and (B) plot of I_p vs. folic acid concentrations.

3.7. Interference study

In order we check the selectivity of AF/MgO/NPs/CPE in the presence of 10.0 μmol L^{-1} NAC at pH 7.0. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than ±5% for the determination of NAC. The results showed that 1000- fold of glucose, lactose and fructose; 550-fold of Ca^{2+}, Mg^{2+}, Li^{+}, Cl^{-}, SO_4^{2-}, Al^{3+},NH_4^{+}, and F^{-}; 300-fold of urea; 350-fold of methionine and alanine, phenylalanine, glycine; and 10-fold of cysteine did not affect the selectivity.

3.9. Application of AF/MgO/NPs/CPE in real sample analysis

In order the ability of AF/MgO/NPs/CPE was check for the determination of NAC and FA in their tablets. The obtained data for real samples analysis of NAC and FA by AF/MgO/NPs/CPE are listed in table 1. As can be seen, the AF/MgO/NPs/CPE showed high selectivity and good ability for analysis of NAC and FA in real samples.

Table 1. Determination of N-AC in real sample

Sample	Added (μM)		Found (μM)		Recovery (%)	
	NAC	FA	NAC	FA	NAC	FA
NAC tablet	0	0	5	----		
	10.0	50	14.8	48.8	98	97.6
	15.0	100	19.9	99.3	102	101
	20.0	150	24.8	150.7	98	102.8
FA tablet	0	0	----	50		
	10.0	20.0	9.8	69.7	98	98.5
	15.0	40.0	14.6	90.6	97.3	104
	20.0	60.0	19.7	111.2	98.5	103

4. CONCLUSION

In the present study, a high performance nanostructure voltammetric sensor based on carbon paste electrode modified with AF and MgO nanoparticles was used for the determination of NAC in aqueous solution. The AF/MgO/NPs/CPE successfully resolves the overlapped voltammetric peaks of NAC and folic acid, so that the AF/MgO/NPs/CPE displays high selectivity in the DPV measurement of NAC and folic acid in their mixture solutions. This proposed sensor was also suggested for the determination of NAC and FA in drug samples.

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