

Voltammetric Determination of Hydroxylamine Using a Ferrocene Derivative and NiO/CNTs Nanocomposite Modified Carbon Paste Electrode

Fereshteh Golestanifar¹, Hassan Karimi-Maleh^{1,*}, Necip Atar^{2,*}, Ercan Aydoğdu³, Bengü Ertan³, Mehdi Taghavi⁴, Mehmet Lütfi Yola⁵, Mousa Ghaemy⁶

¹ Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran

² Department of Chemical Engineering, Pamukkale University, Denizli, Turkey

³ Department of Chemistry, Dumlupınar University, Kütahya, Turkey

⁴ Polymer Chemistry Research Laboratory, Faculty of Science, Shahid Chamran University, Ahvaz, 61357-43337, Iran

⁵ Department of Metallurgical and Materials Engineering, Sinop University, Sinop, Turkey

⁶ Polymer Chemistry Research Laboratory, Department of Chemistry, University of Mazandaran, Babolsar 47416-95447, Iran

*E-mail: h.karimi.maleh@gmail.com; necipatar@gmail.com

Received: 24 March 2015 / Accepted: 12 May 2015 / Published: 27 May 2015

The electrochemical activities of hydroxylamine (HX) as a pollutant compound at a 1,1-bis(phenylacetyl)ferrocene/NiO/CNTs modified carbon paste electrode (1,1-BPF/NiO/CNTs/CPE) has been studied. 1,1-BPF was used as a suitable mediator for electrocatalytic interaction with HX. The voltammetric properties of HX at the 1,1-BPF/NiO/CNTs/CPE was investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronoamperometry, and square wave voltammetry (SWV) methods. The oxidation peak current increases linearly with HX concentration in the range 0.5–250.0 μM and the detection limit for HX was 0.2 μM . The sensor was applied to wastewater samples with excellent performance.

Keywords: NiO/CNTs nanocomposite, Ferrocene-derivative, Hydroxylamine analysis, Carbon paste electrode

1. INTRODUCTION

The quantification of pollutant compounds such as HX, hydrazine, sulfite, phenol and etc is very important for industrial purposes [1-5]. HX was used as a kind of reducing reagent in important processes. In addition, it is harmful mutagen and interferes with biological systems [6]. Therefore,

determination of HX is very important and many scientists suggest analytical sensors for this goal [7-10]. In between of analytical methods for biological, pharmaceutical and environmental compounds analysis, electrochemical based methods is gaining significance in kind of industrial process [11-20].

Modification of electrodes is good and powerful strategy for overcoming of unmodified electrodes limitation such as low selectivity, poor sensitivity, low stability and the blockage of electron transfer [20-30]. A wide variety of electro-active compounds have been utilized for the modification of surface [31-35]. The nano-materials such as quantum dots, nanosheet and carbon nanotubes are utilized for modification of electrodes in the recent years [36-45].

In this study, the high sensitive and selective electrochemical surface was applied to the determination of submicromolar amounts of HX in waste water samples. In the first step, we describe synthesis of NiO/CNTs nanocomposite using direct chemical precipitation methods. The synthesized nanocomposite was characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD). After that, the performance and application of a 1,1-BPF/NiO/CNTs/CPE as sensor was investigated in an aqueous solution and real samples.

2. EXPERIMENTAL

2.1. Materials and reagents

Nickel nitrate, sodium hydroxide, graphite powder and paraffin oil were supplied from Sigma-Aldrich.

Stock solution (1.0×10^{-2} mol L⁻¹) of HX was prepared in double distilled water. Phosphate buffer solutions (PBS) with different pH values were utilized.

2.2. Preparation of modified electrodes

1,1-BPF/CPE was made by dissolving CA (10 mg) in diethyl ether then mixing with graphite powder (990 mg) in a mortar and pestle. After the evaporation of the solvent, paraffin was added to the previous mixture using a syringe and the mixture was mixed for 60 min. The paste was transported into glass tube. A carbon paste electrode (CPE) without mediator was prepared according to the above procedure without 1,1-BPF addition. For more investigation, we also prepare 1,1-BPF/NiO/CNTs/CPE by adding NiO/CNTs and complete the procedures used to prepare 1,1-BPF/CPE.

2.3. Apparatus

The experiments of CV, EIS, chronoamperometry and SWV were carried out with PGSTAT 302N (Eco Chemie, the Netherlands). A platinum wire as an auxiliary electrode and an Ag/AgCl (KCl_{sat}) electrode as a reference electrode were utilized. The working electrode was unmodified or modified carbon paste electrode. The studies of XRD were performed with STOE diffractometer with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$).

3. RESULTS AND DISCUSSION

3.1. Nanostructures characterization

The XRD patterns of NiO/CNTs showed that diameter of NiO nanoparticle was calculated from the broadness peak of $2\theta=43.5$ by using Scherrer equation ($D=K\lambda/(\beta \cos\theta)$), and it is about 15.0 nm. (Fig. 1).

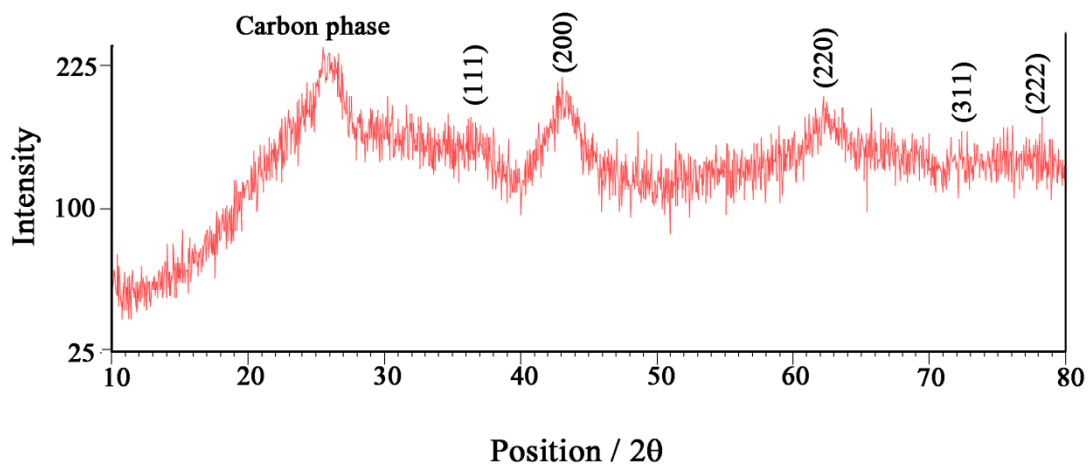


Figure 1. XRD patterns of as-synthesized NiO/CNTs nanocomposite.

The surface of NiO/CNTs was characterized by SEM. Fig. 2 shows a typical SEM micrograph of the NiO/CNTs. According to the results, the presence of NiO was shown on CNTs.

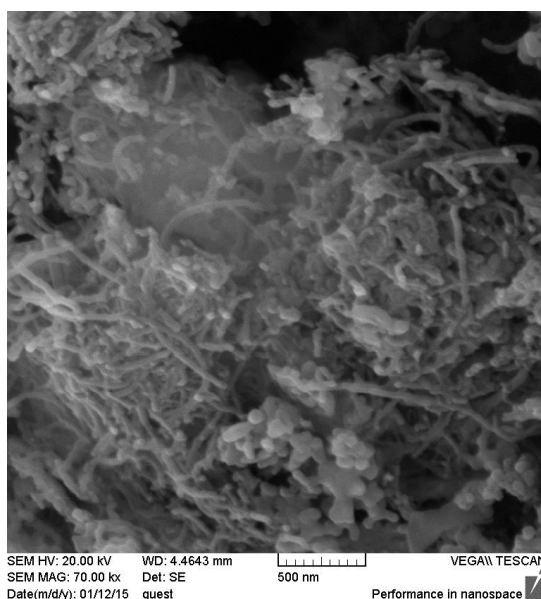


Figure 2. SEM image of NiO/CNTs.

3.2. Electrochemical investigation

The cyclic voltammetric responses of 800 μM of HX at 1,1-BPF/NiO/CNTs/CPE (Fig. 3 curve c), 1,1-BPF/CPE modified carbon paste electrode (Fig. 3 curve b), NiO/CNTs/CPE (Fig. 3 curve d), and CPE (Fig. 3 curve e) were shown in 0.1 mol L⁻¹ PBS (pH 5.0) and scan rate of 20 mV s⁻¹.

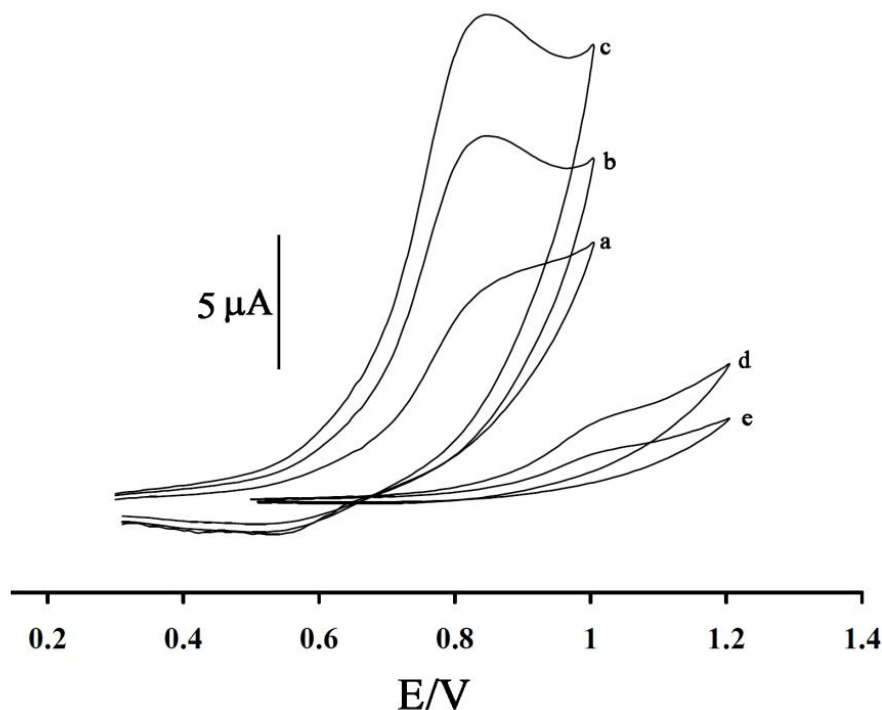


Figure 3. Cyclic voltammograms of (a) the buffer solution at 1,1-BPF/NiO/CNTs/CPE; (b) 800 μM HX at 1,1-BPF/CPE; (c) 800 μM HX at 1,1-BPF/NiO/CNTs/CPE; (d) 800 μM HX at NiO/CNTs/CPE; (e) 800 μM HX at CPE.

The oxidation peaks of HX at 1,1-BPF/NiO/CNTs/CPE (curve c) and NiO/CNTs/CPE (curve d) are about 840 and 1150 mV, respectively. In addition, the voltammetric peaks are about 840 and 1200 mV at 1,1-BPF/CPE (curve b) and CPE (curve e), respectively. Hence, the oxidation of HX at 1,1-BPF/NiO/CNTs/CPE (curve c) shifted to less values, in comparison to the NiO/CNTs/CPE (curve d) and unmodified surface (curve e), respectively. In addition, the oxidation signals of HX at the surface of 1,1-BPF/NiO/CNTs/CPE (curve c) are better than those at 1,1-BPF/CPE. The results show that the NiO/CNTs nanomaterial improves the analytical performance of HX.

In addition, the inset of Fig.4 shows a positive shift of the oxidation potential and an increase of current for HX. The relation between the peak current and the square root of the scan rate indicates a diffusion-controlled behavior at the 1,1-BPF/NiO/CNTs/CPE (Fig.4) [46-50].

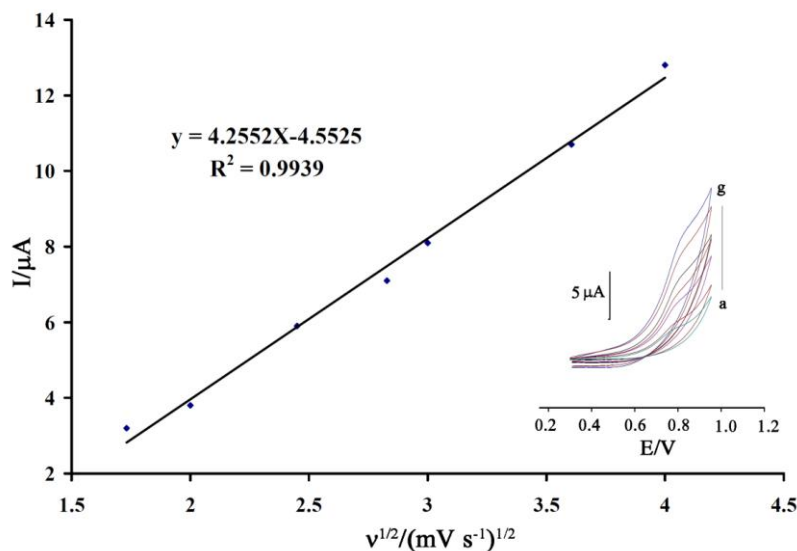


Figure 4. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of HX at 1,1-BPF/NiO/CNTs/CPE. Inset shows cyclic voltammograms of HX at 1,1-BPF/NiO/CNTs/CPE at different scan rates of a) 3; b) 4; c) 6, d) 8, e) 9, f) 13 and g) 16 mV s^{-1} in 0.1 M phosphate buffer, pH 5.0.

A Tafel plot (Fig. 5, inset) was developed for 1,1-BPF/NiO/CNTs/CPE by using the data from the current–voltage curve (Fig. 5). The slope of the Tafel plot is $n(1-\alpha)F/2.3RT$, which rises to $0.2682 \text{ V decade}^{-1}$. The n_a is equal to 0.53 with $n = 1$, then $\alpha = 0.78$.

The chronoamperometric measurements of HX at 1,1-BPF/NiO/CNTs/CPE were performed at 600 mV for 950 μM HX solution (Fig. 6A). The plots of I versus $t^{-1/2}$ with various concentrations of HX were carried out. The slopes of the lines were plotted versus the concentrations of HX (Fig. 6B) by using the Cottrell equation [51]:

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

A diffusion coefficient (D) is calculated as $5.47 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ for HX.

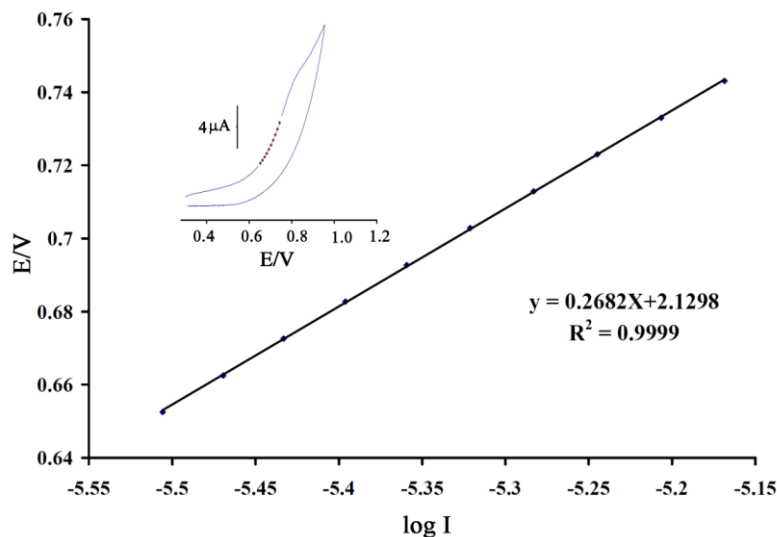


Figure 5. Tafel plot for 1,1-BPF/NiO/CNTs/CPE in the presence of HX in 0.1 M phosphate buffer solution (pH 5.0) at a scan rate of 14 mV/s .

Also, the experiment of chronoamperometry was performed to calculate the catalytic rate constant, k , for the reaction between HX and the 1,1-BPF/NiO/CNTs/CPE [52]:

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

where t is the time elapsed and C_b is the bulk concentration of HX. The equation based on the slope of the I_C/I_L versus $t^{1/2}$ finds the rate constant of the catalytic process (k). (Fig. 6C). Hence, an average value of k was calculated to be as $1.81 \times 10^3 \mu\text{mol}^{-1} \text{L s}^{-1}$.

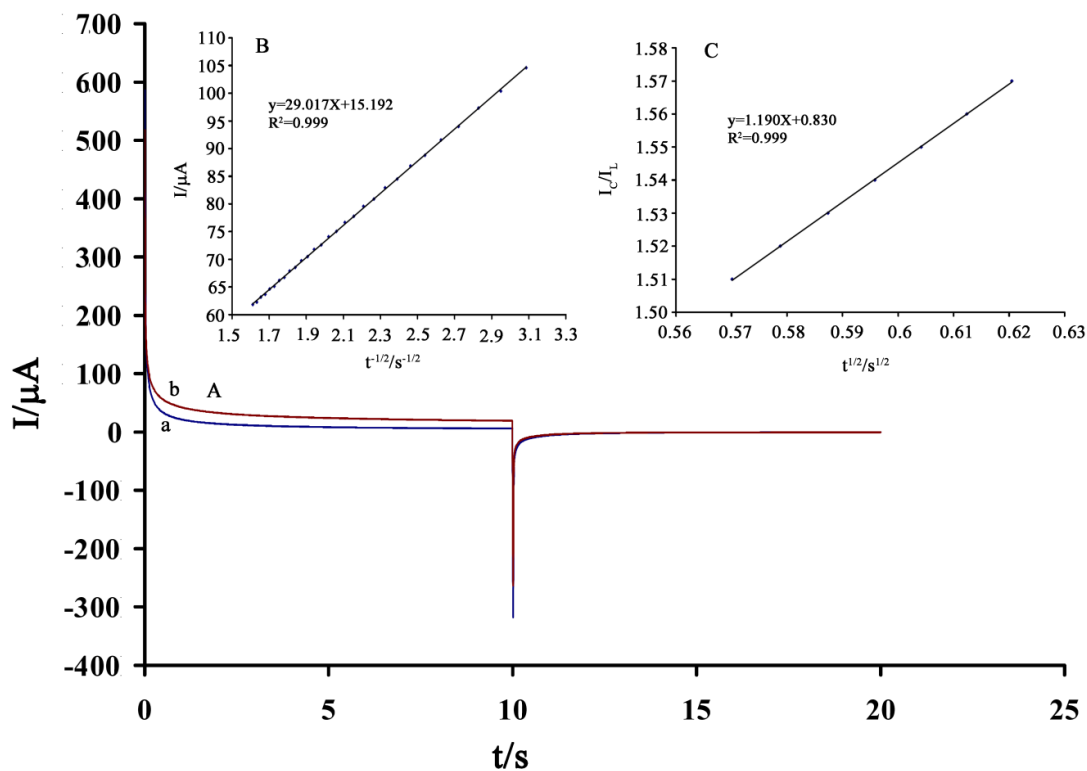


Figure 6. A) Chronoamperograms obtained at 1,1-BPF/NiO/CNTs/CPE (a) in the absence, and in the presence of (b) 250.0 μM at pH 5.0, respectively. (B) Cottrell's plot for the data from the chronoamperogram. (C) Dependence of I_C/I_L on the $t^{1/2}$ derived from the chronoamperogram data.

3.3. Calibration plot and limit of detection

The limits of detection and quantification are two important parameters for analytical sensors that suggested for new sensors [53-68]. Therefore, the peak currents were linear with HX concentrations (0.5-250 μM) and a current sensitivity of 0.0991 $\mu\text{A}/\mu\text{M}$. The detection limit (3σ) was 0.2 μM .

3.4. Determination of HX real samples and interference study

The proposed sensor was applied to water and waste water samples. The samples tested were found to be free from HX and, thus, synthetic samples were prepared by adding known amounts of HX

to the water samples. The results are given in Table 1. In continuous, the influence of different substances as potential interfering compounds on the sensor selectivity were studied using 20 μM HX at pH 5.0. The tolerance limit was taken as the maximum concentration of the foreign substances, which caused an approximately $\pm 3\%$ relative error in the determination. The obtained results are shown in Table 2.

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

Species	Tolerance limits (W/W)
Ethanol, Methanol	950
F ⁻ , Al ⁺³ , Li ⁺ , Zn ⁺² , Pb ⁺² , Mg ⁺² , Na ⁺ , K ⁺ , ClO ₄ ⁻ , Ni ⁺² , CN ⁻ , Ca ⁺² , Br ⁻ , Ag ⁺ , Mn ⁺² , and SCN ⁻	700
Urea, Thiourea,	600

Table 2. Ability of propose sensor in determination of HX in water samples (n=3).

Sample	Added (μM)	Expected (μM)	Founded (μM)	Published Method (M) [1]	F _{ex}	F _{tab}	t _{ex}	t _{tab}
Tap water	5.00	5.00	4.85 \pm 0.35	5.22 \pm 0.45	6.5	19.0	1.3	3.8
Well water	15.0	15.0	15.44 \pm 0.55	15.65 \pm 0.76	8.9	19.0	1.9	3.8
River water ^a	20.0	20.0	20.89 \pm 0.94	19.75 \pm 1.01	11.6	19.0	2.8	3.8
Waste water	50.0	50.0	50.55 \pm 0.65	50.65 \pm 0.86	9.5	19.0	3.2	3.8

^a Syahrood, Qaemshahr, Iran; F_{ex} is calculated F-value; F_{tab} is the F value obtained from one-tailed table of F-test; t_{exp} is calculated value of t-student test; t_{tab} is the t-value obtained from the table of student t-test.

4. CONCLUSION

In this study a carbon paste electrode modified with 1,1-BPF and NiO/CNTs has been utilized for voltammetric determination of HX in water samples. The results confirmed that the electrooxidation of HX at the surface of 1,1-BPF/NiO/CNTs/CPE occurs at a potential of about 360 mV less positive than unmodified CPE. As a final point, this sensor is useful for the determination of HX in water and waste water samples using the standard addition method.

ACKNOWLEDGEMENT

We are grateful to the Kerman Graduate University of Advanced Technology and the Iranian Nanotechnology Initiative Council for their support.

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