Full Paper

Thiourea Modified Copper Electrode: Application to Electrocatalytic Oxidation of Hydrazine

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Abstract- In this work the copper electrode modified with thiourea was used for electrocatalytic oxidation of hydrazine in 0.1 M NaOH. The Modified electrode showed excellent character for electrocatalytic oxidation of hydrazine with decrease in overpotential and increase in the anodic current. The kinetic parameters such as the electron transfer coefficient (α_a) and the catalytic rate constant (K_{cat}) for the oxidation of hydrazine were determined. The diffusion coefficient (D) of hydrazine in the solution was also calculated by chronoamperometry. The detection limit (3σ) was determined as 7.6 µmol L^{-1}.

Keywords- Modified electrode, Thiourea, Electrocatalytic oxidation, Hydrazine

1. INTRODUCTION

Hydrazine and its derivatives are commonly known fuels in explosives, antioxidants, rocket propellants, blowing agents, photographic chemical, corrosion inhibitor, insecticides, and plant growth regulators [1]. Also, hydrazine is very important in pharmacology because it has been recognized as a carcinogenic and hepatotoxic substance, which affects liver and brain glutathione. Consequently, drug regulatory authorities are becoming increasingly aware

of the need to control the levels of hydrazones in isoniazid and other hydrazide drugs and in their formulations. Despite the wide use of hydrazine in various areas, it has been known to be harmful for human life. Therefore, a highly sensitive method is necessary for the reliable measurement of hydrazine concentration and the electrooxidation of hydrazine is a reaction of practical importance. The mechanism and kinetics of hydrazine oxidation have been studied under a wide range of conditions [2] and by several techniques, such as coulometry [3], spectrophotometry [4] and titrimetry [5] and by different electrode materials including the ion selective electrodes [6], mercury [7,8] and nickel [9]. Metals such as silver, gold [10] and platinum [11-13] are very active for the oxidation of hydrazine, but are too expensive to be used in practical applications and the use of carbon electrodes is not common because of the large overpotential of hydrazine oxidation at these electrodes. Electrochemical measurement techniques have been shown to provide a sensitive and selective approach for the detection of numerous compounds. Although electroanalytical techniques generally offer high selectivity in the detection of hydrazine at the conventional electrodes, they have high overvoltage and low sensitivity for quantitative work. In order to overcome these difficulties, chemically modified electrodes with various mediators were used as hydrazine oxidation beds. Chemically modified electrodes (CMEs) have attracted considerable interest over the chemical nature of an electrode. It is well documented that functionalization of an electrode surface can offer significant analytical advantages in voltammetric experiments.

Copper is second only to silver in its ability to conduct electricity [14]. Many attentions are focused on the modifying of the copper surface for two goals: 1) formation of a stable layer on the surfaces of copper to protect the electrode from corrosion and 2) formation of an electrocatalytic layer on the surfaces of copper to enhance the electrochemical properties of the electrode [15-21]. It seems reasonable if a layer of thiourea film is formed on the surface of the copper; it can be protect the electrode from corrosion and effectively enhances the electrochemical properties of it for hydrazine. The modified electrode was examined for electrocatalytic oxidation of hydrazine and very promising results were obtained. The results of the present work showed that in comparison to bare copper electrode, electrochemical behavior of hydrazine have been greatly improved at thiourea modified copper electrode, indicating that the anodic oxidation of hydrazine could be catalyzed at thiourea modified copper electrode.

2. EXPERIMENTAL

2.1. Chemical and Solutions

All solvents and reagent were purchased from Merck (Darmstat, Germany)) and were used without further purification. All solutions were prepared with double distilled water.

2.2. Apparatus

All electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system with PGSTAT-12 boards (ECO Chemie, Utrecht, The Netherlands). The system was run by a PC using the GPES 4.9 software. The three electrode cell consisted of an Ag/AgCl as the reference electrode, a platinum wire as the counter electrode and a bare copper electrode with a diameter of 4 mm (modified and unmodified) as working electrode. All of the employed electrodes were purchased from Azar electrode (I.R. Iran). The surface morphology of modified copper electrode was examined using scanning electron microscopy (SEM) taken on a KYKY (EM 3200).

2.3. Electrode Modification Procedure

The thiourea film was electrochemically deposited on the copper electrode in the following manner: the base copper electrode surface was polished with a slurry 0.05 μm alumina powder until a mirror-like surface was obtained. The electrode was then washed thoroughly with acetone and distilled water. The polished electrode was modified by 16 cycles of the potential sweep between -250 and 100 mV (at scan rate of 100 mVs^{-1}) in a fresh solution containing 0.1 M NaOH, 0.04 M thiourea. After 16 cycles, copper electrode was taken out and rinsed thoroughly with water. The modified copper electrode was pretread by cycling the potential several times (16 cycles) between -250 and 800 mV *vs*. Ag/AgCl (at scan rate of 50 mVs^{-1}) until a low and steady background was obtained.

3. RESULTS AND DISCUSSION

3.1. Morphological characterization

The surface morphology of thiourea modified copper electrode was examined by scanning electron microscopy (SEM). SEM image of bare copper electrode (Fig. 1A), copper electrode loaded by thiourea (Fig. 1B) and the thiourea modified copper electrode pretread by cycling the potential (16 times) between -250 and 800 mV *vs*. Ag/AgCl (Fig. 1C) have been shown in Fig. 1. The results show that a good coverage of thiourea catalyst particles has been formed on the surface of the copper electrode during the modification.

3.2. Effect of NaOH concentration on electrocatalytic oxidation of hydrazin

The oxidation of hydrazine shows a strong dependence to NaOH concentration. The electrochemical response for hydrazine was investigated over the concentration range of 0.01-0.1 M. Fig. 2 shows the cyclic voltammograms for 2 mM hydrazine at the thiourea modified copper electrode under different NaOH concentration condition.
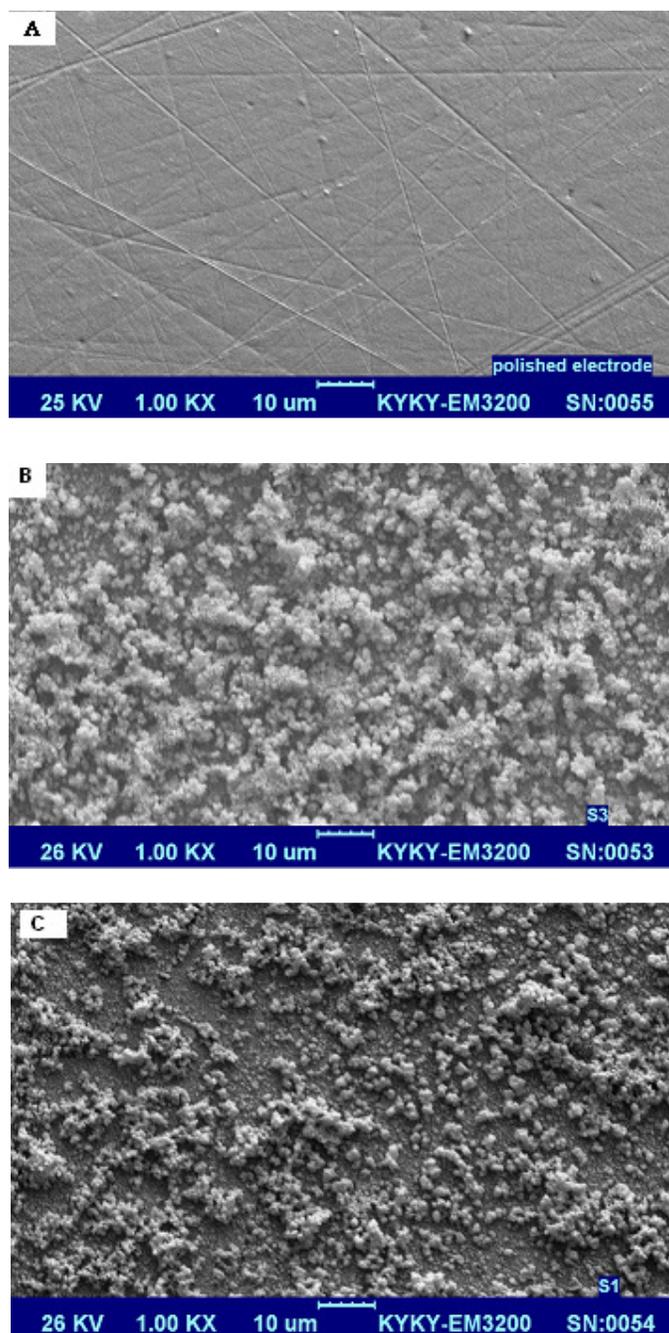
Fig. 1. Scanning electron micrographs (SEM) of electrodes types **A** (bare copper electrode), **B** (copper electrode loaded by thiourea) and **C** (thiourea modified copper electrode pretread by cycling the potential (16 times) between -250 and 800 mV)

Inset shows the dependence of hydrazine oxidation peak potential versus NaOH concentration and its peak current versus NaOH concentration. As shown in the figures, when NaOH concentration is increased from 0.01 to 0.1, the peak current increases and the

oxidation peak potential shifts to negative values. From this results can be concluded that the catalytic oxidation is more favoured at 0.1 M NaOH.
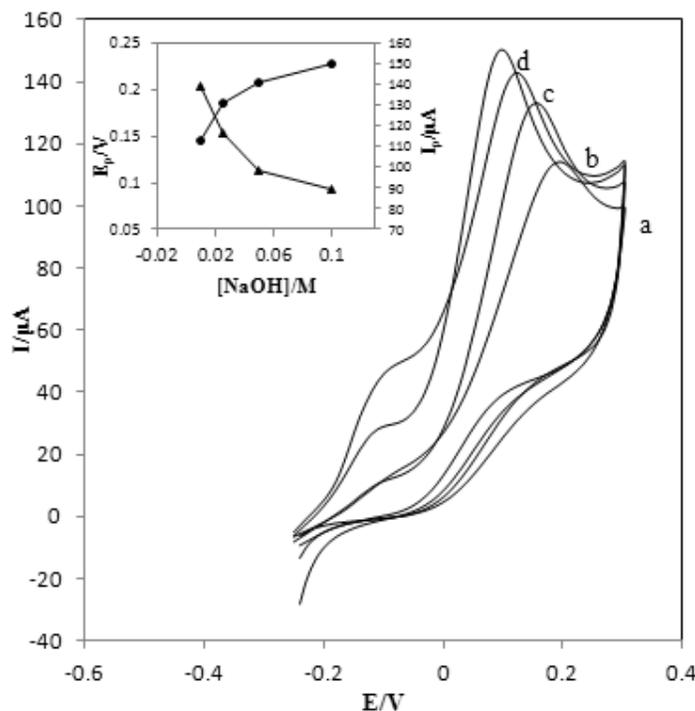

Fig. 2. Cyclic voltammograms of the thiourea modified copper electrode of 2 mM hydrazine in different concentration of NaOH (a) 0.01, (b) 0.025, (c) 0.05, and (d) 0.1 M at a scan rate of 50 mVs^{-1}. Inset: Dependence of the oxidation peak current (circle) and peak potential (triangles) of 2 mM hydrazine in different concentration of NaOH

3.3. Electrocatalysis of hydrazine oxidation

The cyclic voltammetric responses of a bare copper electrode in 0.1 M NaOH solution, without and with hydrazine in solution, are shown in Fig. 3 (curves c and d respectively). A small anodic current by the oxidation of hydrazine is observed but no cathodic peak is found, indicating an irreversible heterogeneous charge transfer in this system. If the electrode is modified with thiourea and then placed into the same hydrazine-containing electrochemical cell, a large anodic peak is observed without a cathodic counterpart (curve 3b). That the current observed is associated with hydrazine oxidation and not the oxidation of surface-attached copper electrode, is demonstrated by comparing the current in curve 3b with those in curve 3a, which shows the cyclic voltammetric behavior of an electrode modified with thiourea in a hydrazine free electrolyte (0.1 M NaOH). It is apparent that the anodic current associated with the surface attached material is significantly less than that obtained in the

solution containing hydrazine. The anodic peak potential for oxidation of hydrazine at the thiourea modified copper electrode is about 120 mV (curve 3b), while hydrazine starts to oxidize at about 340 mV (curve 3d) at an unmodified electrode under identical conditions. So, a 220 mV decrease in overpotential is observed.
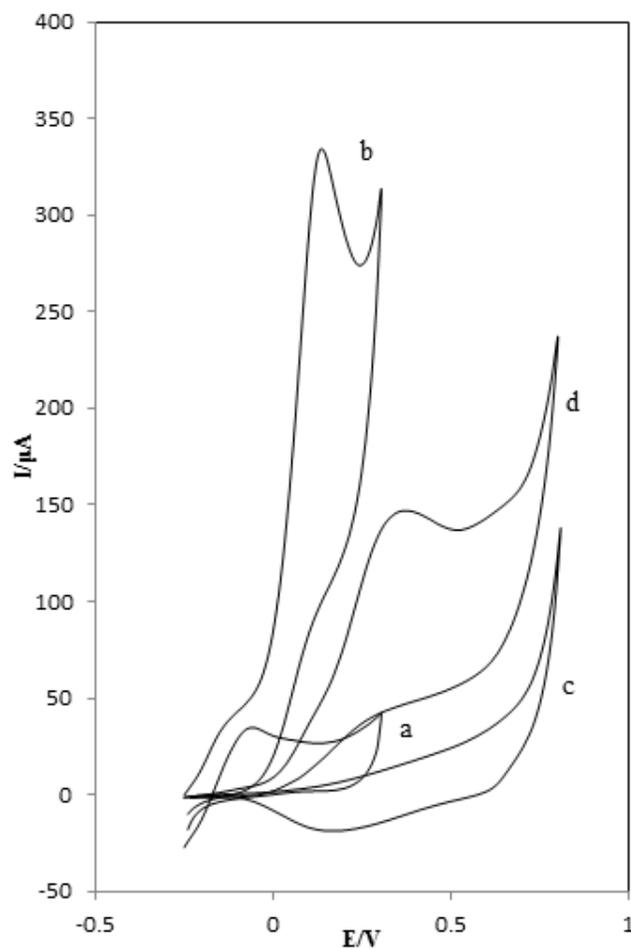

Fig. 3. Cyclic voltammograms of thiourea modified copper electrode at 50 mVs^{-1} in 0.1 M NaOH. (a) In the absent; (b) in the presence of 5 mM hydrazine; (c) as (a) and (d) as (b) for bare copper electrode

Under the optimum conditions, peak currents of cyclic voltammograms linearly depended on hydrazine concentrations. The cyclic voltammograms at different concentration of hydrazine are shown in Fig. 4A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 0.13 to 5 mM hydrazine (see Fig. 4B). The detection limit calculated of hydrazine was obtained 7.6 μM based on signal-to-noise method with considering S/N=3.
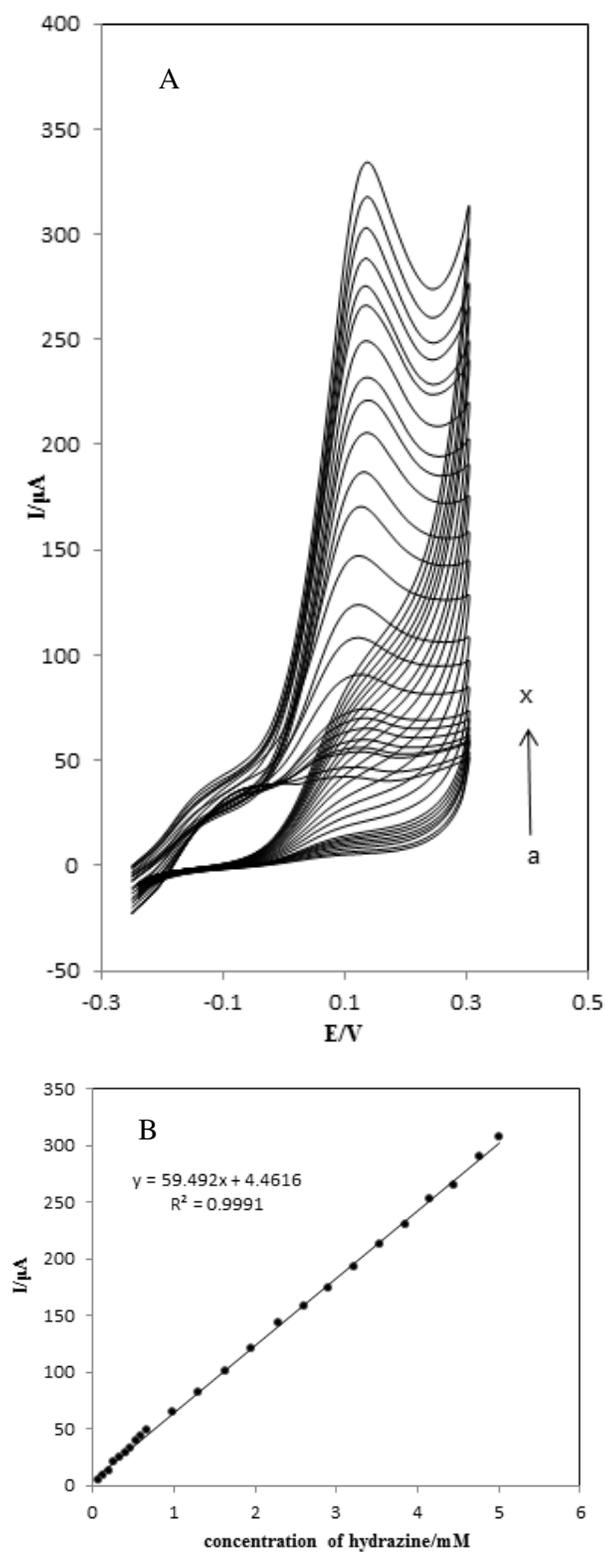
Fig. 4. (A) Cyclic voltammograms for increasing concentrations of hydrazine from (a) 0.13 to (x) 5 mM at 50 mVs^{-1} in 0.1 M NaOH solution on thiourea modified copper electrode. (B) Calibration plot for concentration of hydrazine from cyclic voltammograms

The nature of the oxidation process was found to be diffusion controlled in the alkaline system studied, as evidenced from the linear plots of the peak current I_p versus square root of the scan rate $v^{1/2}$ for hydrazine. Fig. 5A shows the cyclic voltammograms of thiourea modified copper electrode in 0.1 M NaOH containing 2.2 mM hydrazine at scan rates: 3, 5, 9, 12, 15, 20, 25, 30, 40, 50 and 60 mVs^{-1}. It can be noted from Fig. 5A that the anodic currents increase and the peak potential shifts as the scan rate increases. When peak current values were plotted against $v^{1/2}$ (Fig. 5B) the following linear relationship was obtained:

$$I_P = 1.4584 + 16.031v^{1/2}(\text{mV}^{1/2}\text{ s}^{-1/2}), \qquad R^2 = 0.9966 \tag{1}$$

This behavior suggests that the oxidation process is controlled by diffusion. For determination of the transfer coefficient (α) and the number of electrons involved in the rate-determining (n_α), Tafel plot was drawn (not shown here) using the data from the rising part of the current voltage curve at scan rate 5 mVs^{-1}. The Tafel slope was 103 mVdecade^{-1} and by considering that α equals 0.42, the results indeed suggest one-electron ($n_\alpha = 1.14 \cong 1$) transfer process in the rate- determining step for the electrocatalytic oxidation of hydrazine. The Tafel slope could be calculated by another method, i.e. it can be determined from the following equation [22]:

$$E_p = \frac{b}{2}\log v + constant \tag{2}$$

Where b is the Tafel slope and k is a constant value. Fig. 5C Shows the plot of E_P versus Log(v). The slope of this plot is 60.452 mV, therefore, the slope becomes120.9 mVdecade^{-1}. This result is close to that obtained from the rising part of voltammogram recorded at the 5 mVs^{-1}. If α was assumed equal to 0.51, n_α is 1. Total number of electrons (n) in oxidation process was calculated according to the following equation for a totally irreversible diffusive process [23]:

$$I_P = 3.01 \times 10^5\, n[(1-\alpha)\, n_\alpha]^{1/2}\, ACD^{1/2}\, v^{1/2} \tag{3}$$

With considering $[(1-\alpha)\, n_\alpha] = 0.49$, $D = 4.12 \times 10^{-6}$ cm^{2}s^{-1}(see chronoamperometric studies) and A=0.1256 cm^2, it is estimated that the total number of the electrons involved in the anodic oxidation of hydrazine is n=4.2 $\cong$4. Based on the above results the following mechanism can be proposed for the oxidation of hydrazine:

$\text{N}_2\text{H}_4 + \text{OH}^- \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O} + e^-$ (slow)   (1)
$\text{N}_2\text{H}_3 + 3\text{OH}^- \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3e^-$ (fast)   (2)

The rate-determining step is a single electron transfer followed by a three-electron process to give N_2 as a final product.
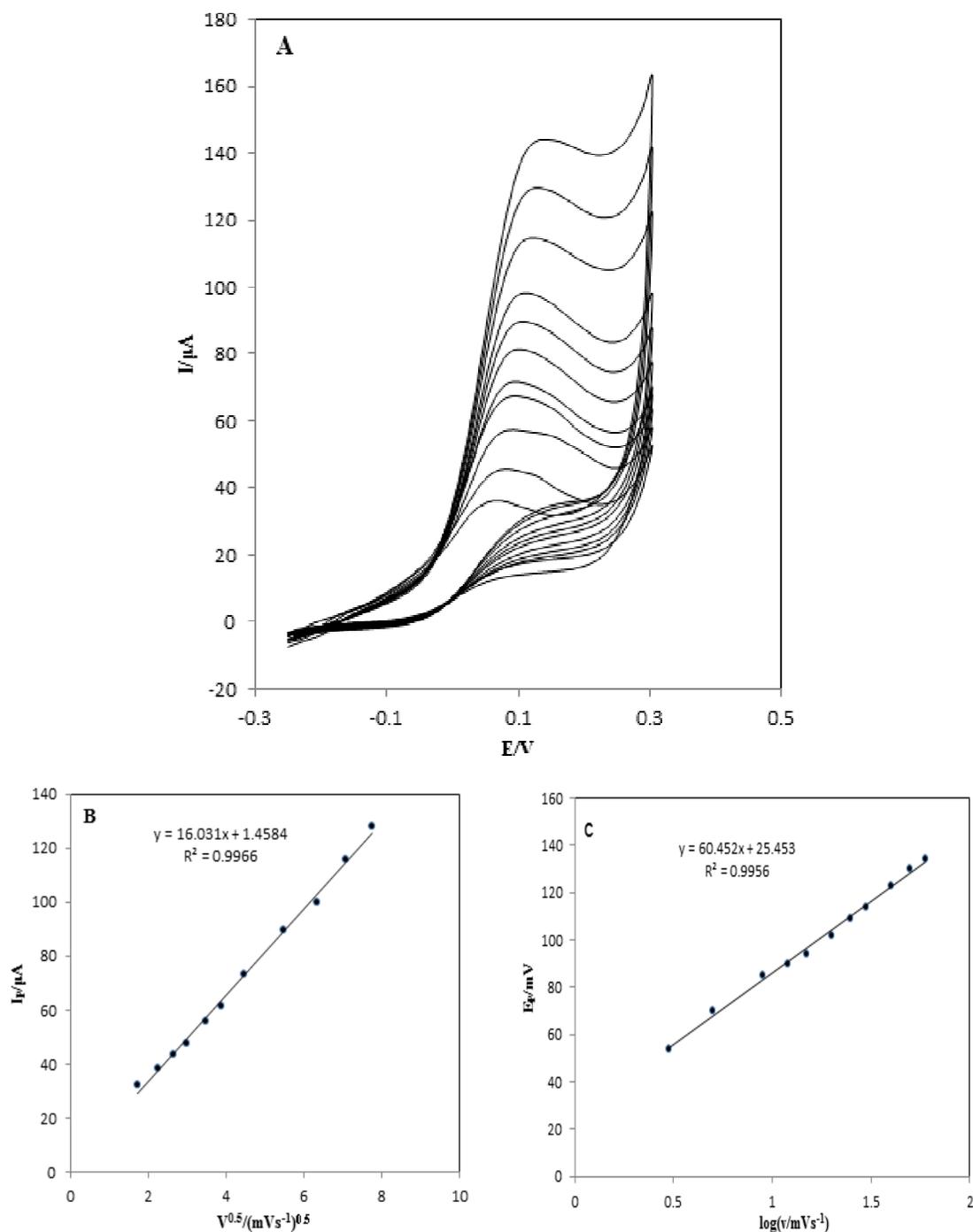
Fig. 5. (A) Cyclic voltammograms of thiourea modified copper electrode in 0.1 M NaOH containing 2.2 mM hydrazine at scan rate (a) 3;(b) 5;(c) 9; (d)12; (e) 15;(f) 20; (g) 25; (h) 30; (i) 40; (j) 50 and 60 mVs^{-1}. (B) dependence of the peak current with square root of the scan rate in 0.1 M NaOH containing 2.2 mM hydrazine.(C) The plot of E_P *vs.* log v

3.4. Choronoamperometry

Chronoamperometry as well as other electrochemical methods may be used for the investigation of electrode processes at modified electrodes. The chronoamperograms obtained for a series of hydrazine solutions with various concentrations as illustrated in Fig. 6. An increase in concentration of hydrazine was accompanied by an increase in anodic currents obtained for a potential step of 103 mV. The inset of Fig. 6 shows plots of currents sampled at fixed time as a function of hydrazine concentration. The response is linearly proportional to the concentration of hydrazine in the range of 1300–5000 μM.

Chronoamperometry can be used for the estimation of the diffusion coefficient of hydrazine in the solution. For an electroactive material with a diffusion coefficient D, the current corresponding to the electrochemical reaction (under diffusional control) is described by Cottrell equation [22]:

$$I = nFAD^{1/2}C^*(\pi t)^{-1/2} \tag{4}$$

Where D and C are the diffusion coefficient (cm^2 s^{-1}) and bulk concentration (molcm^{-3}), respectively. Under diffusion control, a plot of I *vs.* t$^{-1/2}$ will be linear, and the value of D can be determined from the slope.
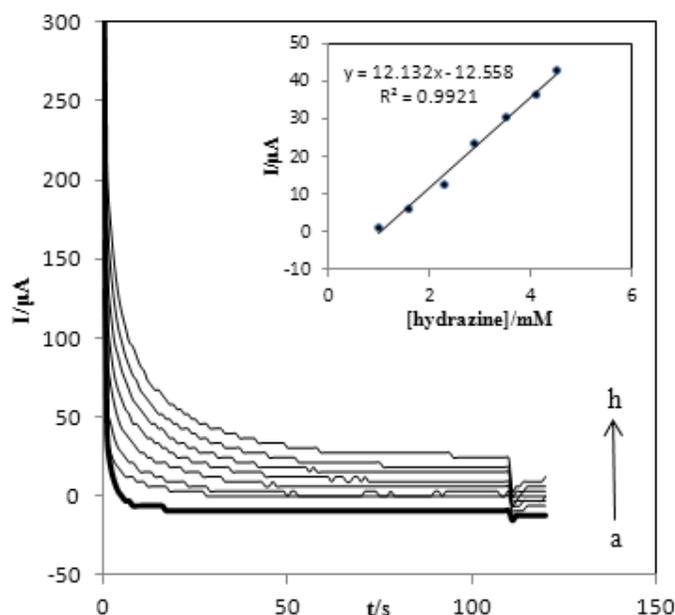

Fig. 6. Chronoamperograms of thiourea modified copper electrode in 0.1 M NaOH solution in the absence (a) and presence (b-h) of various concentrations of hydrazine: 1.3, 1.96, 2.6, 3.22, 3.85, 4.45, 5 mM, respectively. Insets: variation of chronoamperometric currents at *t* =30 s *vs.* concentration of hydrazine

Fig. 7 shows the fitted experimental plots of I verses $t^{-1/2}$ for different concentration of hydrazine. The inset of Fig 7 shows slopes of the resulting straight line were then plotted versus the hydrazine concentration, from its slope diffusion coefficient has been obtained $4.12\times10^{-6}cm^2s^{-1}$ for hydrazine. The calculated value of diffusion coefficient is in a good agreement with 4.15×10^{-6} cm^2 s^{-1} [24], and 4.5×10^{-6} cm^2s^{-1} [25] which were previously reported for hydrazine in literature.

Chronoamperometry can be used for the evaluation of the catalytic rate constant. The rate constant for the chemical reaction between hydrazine and modified copper electrode is determined according to the method described in the literature [26].

$$\frac{I_{catal}}{I_d} = \lambda^{1/2}\pi^{1/2}(kCt)^{1/2}$$

(5)

Where k, C and t are the catalytic rate constant, catalyst concentration and time elapsed. I_{cat} and I_L are the currents of the modified copper electrode in the presence and absence of hydrazine, respectively. From the slope of the I_{cat}/I_L- *vs.* $t^{1/2}$ plot (Fig. 8), the value of k for 2.6 mM hydrazine was calculated to be 1.32×10^3 cm^3 mol^{-1} s^{-1}. Table 1, compares some of the results of this work with those reported by others.
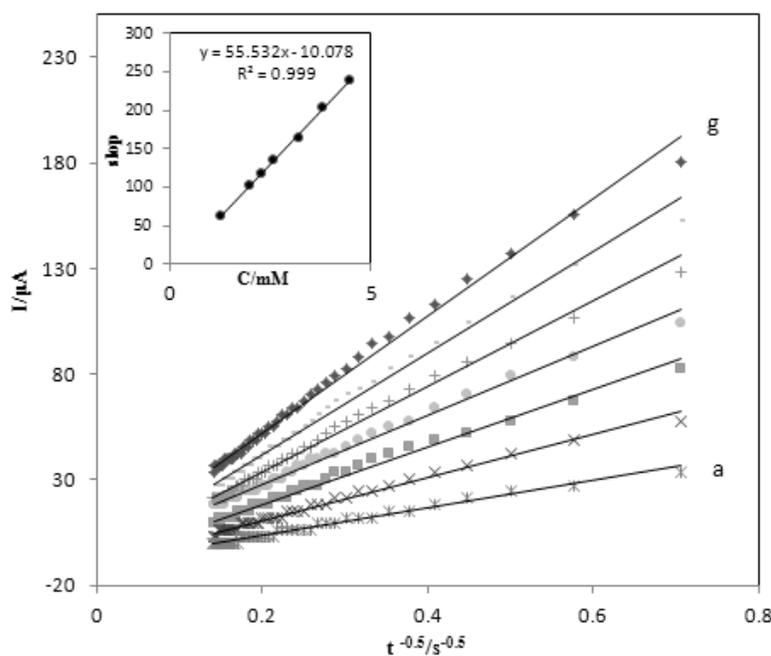

Fig. 7. Plot of *I vs.* $t^{-1/2}$ obtained from chronoamprometric experiments for the thiourea modified copper electrode in 0.1 M NaOH solution containing hydrazine concentrations of (a) 1.3, (b) 1.96, (c) 2.6, (d) 3.22, (e) 3.85, (f) 4.45 and (g) 5 mM. Inset shows the relationship between the slop of the linear segments and the hydrazine concentration
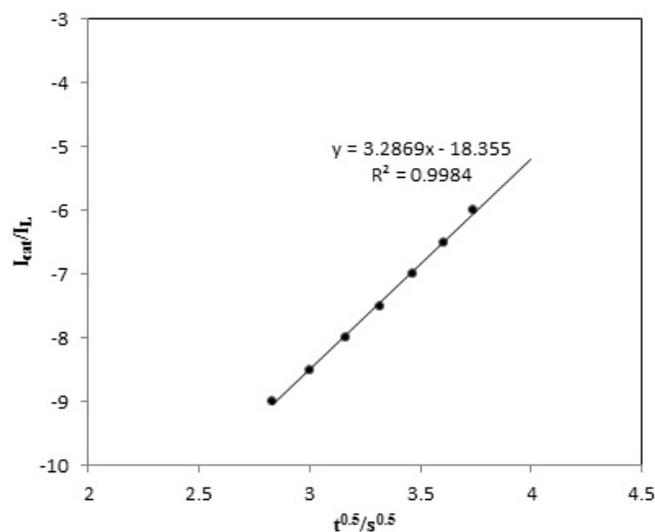
Fig. 8. Plot of I_{cat}/I_L *vs.* $t^{1/2}$ for hydrazine

Table 1. Comparison of some analytical parameters of different modified electrodes for hydrazine determination

Electrode	Modifier	Electrochemical method	Linear range/μM	Detection limit/μM	Ref.
Glassy carbon	ethylenediamine cellulose immobilized palladium nanoparticles.	differential pulse voltammetry	5–150	1.5	[24]
copper	copper (hydr)oxide	chronoamperometry	100–1800	—	[27]
glassy carbon	overoxidized polypyrrole	amperometry	13-2000	3.6	[28]
titanium	gold nanoparticles	cyclic voltammetry	5000–40000	42	[29]
carbon ceramic	nickel hexacyanoferrate nanoparticles	cyclic voltammetry	20–2000	8	[30]
glassy carbon	hydroquinone salophen derivatives	cyclic voltammetry	10–400	1.6	[31]
glassy carbon	Pyrogallol red	linear sweep voltammetry	5–600	2.0	[32]
Carbon paste	cobalt phthalocyanine	cyclic voltammetry	125–980	73.5	[33]
graphite	nickel hexacyanoferrate	cyclic voltammetry	2.4–8200	1.0	[34]
aluminum	Palladium hexacyanoferrate	Amperometry	390–10000 and 20000- 7500	4.6	[35]
copper	Thiourea	Cyclic voltammetry	130-5000	7.6	This work

4. CONCLUSIONS

Thiourea modified copper electrode can be used for electrocatalytic oxidation of hydrazine. The modified electrode decrease anodic overpotential for oxidation of hydrazine with respect to unmodified electrode and increases the anodic peak current in CV. The charge transfer coefficient, the number of electrons involve in the rate- determining step, the overall number of electrons in the oxidation of hydrazine and electron transfer coefficient of hydrazine were obtained using electrochemical approaches which is comparable with those reported in the literature.

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