

Full Paper

Electrocatalytic Oxidation of Hydrazine on a Gold Electrode Modified by new Cd(II) (terpyridine) Complex by Sol-Gel Technique

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Abstract- A novel chemically modified electrode containing Cd(II) (tpy) Complex was achieved on the surface of gold electrode by sol-gel technique. The electrochemical behavior of modified electrode was characterized by cyclic voltammetry in detail. The film electrode obtained was very stable and exhibited electrocatalytic response for oxidation of hydrazine. Results showed at bare Au electrode, a small oxidation peak current was observed at about 0.26 V, And a well- formed sharp catalytic oxidation peak at about 0.154 V was observed at Cd(II) complex modified electrode. The transfer coefficient (α) for electrocatalytic oxidation of hydrazine and the diffusion coefficient of this substance under the experimental conditions were also investigated .

Keywords- Cd(II)(tpy), Sol-Gel Technique, Cyclic Voltammetry, Hydrazine, Electrocatalytic Oxidation

1. INTRODUCTION

The electrocatalysis of slow electron transfer reactions is perhaps the most important feature of chemically modified electrodes (CMEs). Such electrodes enhance the rate of electron transfer by reducing the overpotential associated with a reaction. Therefore, such

electrocatalysis enables a high current density (i.e. increased sensitivity) to be obtained for a poor kinetic reaction at a potential close to the equilibrium potential. In the past years, various CMEs have been prepared and applied in the determination of hydrazine, including cobalt phthalocyanine [1], cobalt proto porphyrine dimethyl ester [2] poly(4-vinyl) pyridine [3], nafion/ruthenium (III) [4], coumestan modified carbon paste electrode [5], 4-pyridil hydroquinone self-assembled platinum electrode [6], nickel hexacyanoferrate modified carbon ceramic electrode [7], hydroquinone salophen derivatives [8], 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy [TEMPO] [9], catechin [10] and metal hexacyanoferrates [11-13] modified glassy carbon electrode, palladium hexacyanoferrate modified aluminum electrode [14], platinum [15] and rhodium [16] modified carbon fibr microelectrode. Hydrazine is widely used in industrial applications. Such as corrosion inhibitors, antioxidants, catalysts, emulsifiers, and reducing agent; as starting material in the production of some insecticides, herbicides, pesticides, dyestuffs, and explosive; and in the preparation of several pharmaceutical derivatives [17]. Hydrazine is also an ideal fuel for a direct fuel cell system because its fuel electrooxidation process does not suffer any poisoning effects [18, 19]. However hydrazine is a toxic material that must be treated with care. Due to the reasons above, it is highly desirable to fabricate a reliable and sensitive analytical tool for the effective detection of hydrazine [20]. One promising approach is the use of chemically modified electrodes (CMEs) containing specifically selected redox mediators immobilized on conventional electrode surface. The sol-gel process is very well adopted for coating of thin films on complex shapes. The porosity and pore size of these films can be controlled to maximize the specific surface area and to ensure that permeability of the film remain high. Furthermore, the sol-gel process involves low-temperature hydrolysis and condensation of appropriate monomeric precursors and is suitable inclusion of organic moieties that cannot withstand high temperatures [21]. To our knowledge, several groups studied the voltammetric response of film coated electrodes that were fabricated by sol-gel technique [22-25] and several groups used terpyridine derivatives for modification of electrodes [26-28]. But up to now, the chemically modified electrodes containing [Cd(tpy)₂] Complex that were fabricated by sol-gel technique have not been reported. In this paper, we used an electrode for electrocatalytic oxidation of hydrazine that was developed via an easy and effective sol-gel immobilization method. This electrode comprises silicon dioxide gel films doped with [Cd(tpy)₂], which retains its structure, electrochemical activity and electrocatalytic properties to a large extent.

2. EXPERIMENTAL

2.1. Reagents and solutions

Hydrazine, Methyltrimethoxysilane (MTMOS), methanol and HCl were of analytical grade supplied by Merck. Deionized water was used for the preparation of all solutions. The background electrolyte solution was prepared from potassium chloride. The pH of solutions was adjusted to 7 with phosphate buffer. The ligand of $[\text{Cd}(\text{tppy})\text{I}_2]$ (Fig.1) was synthesized, purified and characterized as reported [29,30].

2.2. Instrumentation

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands) and a system was run on a pc using GPES 4.9 software. An Au electrode was used as working electrode. A platinum wire was employed as counter electrode and a saturated Ag/AgCl (saturated KCl) served as the reference electrode and all potentials in the text refer to it (all electrode obtained from Azar Electrode Co., Urmia, Iran).

2.3. Preparation of cadmium complex

4'-(4-methylphenyl)-2,2':6',2''-terpyridine (0.323 g, 1 mmol) was placed in one arm of a branched tube and Cd(II) nitrate (0.308 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, the tube was then sealed and the ligand-containing arm immersed in a bath at 60°C while the other remained at ambient temperature. After three days, the crystals that had deposited in the cooler arm were filtered off, washed with solvent, and air dried.

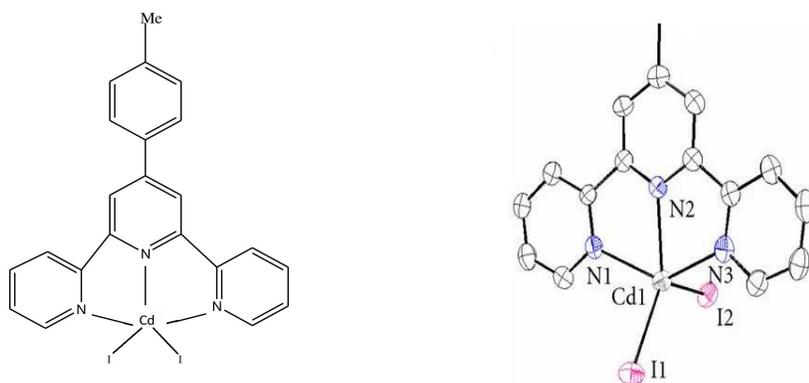


Fig. 1. Molecular structure of $[\text{Cd}(\text{tppy})\text{I}_2]$

2.4. Preparation of modified electrode

The method of immobilizing $[\text{Cd}(\text{tppy})\text{I}_2]$ on Au electrode is described briefly as follows. The Au electrode was polished with emery paper (p 2000) and then by $0.05\ \mu\text{m}$ alumina powder. Then electrode was rinsed by distilled water and sonicated in water and absolute ethanol, respectively (each for 5 min), and then allowed to dry at room temperature. At the first 5 mg $[\text{Cd}(\text{tppy})\text{I}_2]$ was dissolved in 1ml Methanol and homogenized thoroughly by sonication for 5 min until a clear solution was obtained. Then, 0.9 ml of this solution was mixed with 0.6 ml (MTMOS), and 0.1 ml hydrochloric acid (0.1 M) and stirred for 5 min until a homogeneous gel solution resulted. The resulting clear solution was aged for 30 min, and then $10\ \mu\text{l}$ of the freshly prepared mixed solution was pipetted onto the surface of Au electrode. The gel films were dried in an air for 24 h and were ready for use. A few I-E runs were needed at the beginning to stabilize the electrode and obtain reproducible results.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of the modified electrode

The electrochemical properties of the $[\text{Cd}(\text{tppy})\text{I}_2]$ modified Au electrode with sol-gel technique were studied, using cyclic voltammetry. Fig. 2 shows typical cyclic voltammograms of the bare and $[\text{Cd}(\text{tppy})\text{I}_2]$ modified Au electrodes by sol-gel techniques in 0.1M KCl solutions in phosphate buffer electrolyte solution (pH=7) at scan rate $50\ \text{mV s}^{-1}$. It shows that the oxidation and reduction peak areas of $[\text{Cd}(\text{tppy})\text{I}_2]$ modified Au electrodes are much larger than the bare gold electrode.

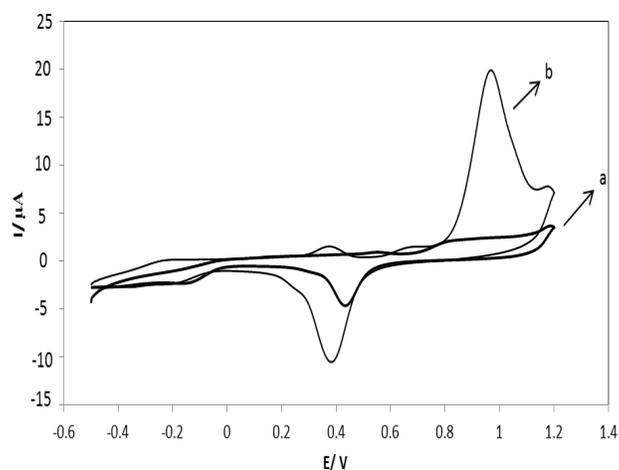


Fig. 2. Cyclic voltammograms of the (a) bare Au electrode and (b) $[\text{Cd}(\text{tppy})\text{I}_2]$ modified Au electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH=7) at scan rate $50\ \text{mV s}^{-1}$

3.2. Electrocatalytic oxidation of hydrazine at the Cd(II)-complex modified Au electrode

In order to evaluate the electrocatalytic activity of the Cd(II) complex modified electrode toward oxidation of hydrazine, voltammograms were obtained in comparison with bare Au electrode in the presence of 1 mM hydrazine, as shown in Fig. 3. At bare Au electrode, a small oxidation peak current was observed at about 0.26 V (a). And a well- formed sharp catalytic oxidation peak at about 0.195 V was observed at Cd(II) complex modified electrode. Thus in comparison with the bare Au electrode, an increase in peak current and a decrease in the overpotential of hydrazine were observed at the Cd(II) complex modified electrode.

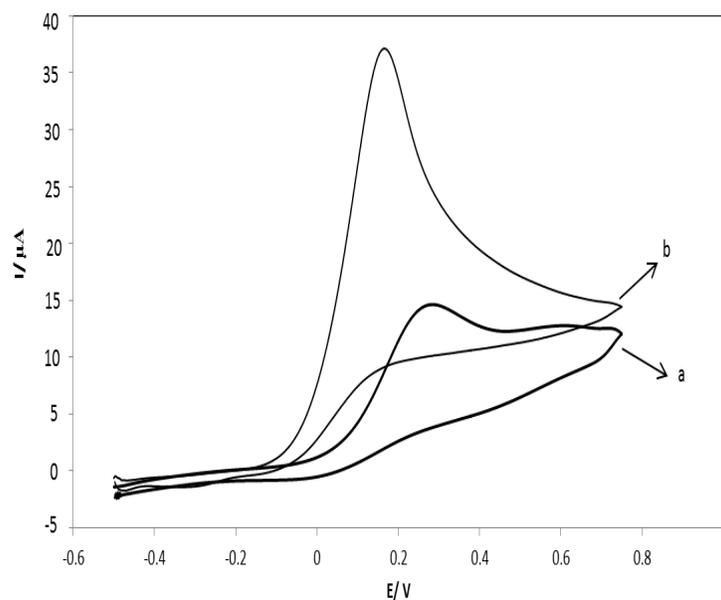


Fig. 3. Cyclic voltammograms of 1 mM hydrazine at (a) bare Au electrode and (b) [Cd(tpy)I₂] modified Au electrodes by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH=7) at scan rate 50 mV s⁻¹

The nature of the oxidation process was found to be diffusion controlled in the buffer system studied, as evidenced from the linear plots of the peak current (i_p) vs. square root of the scan rate ($v^{1/2}$) for hydrazine. Fig. 4A shows the cyclic voltammograms of Cd (II) terpy modified Au electrode in 0.1 M phosphate buffer (pH 7.0) containing 1 mM hydrazine at scan rates: 10, 15, 20, 25, 30, 35, 45, 55, 60, 70, 80 and 100 mV s⁻¹.

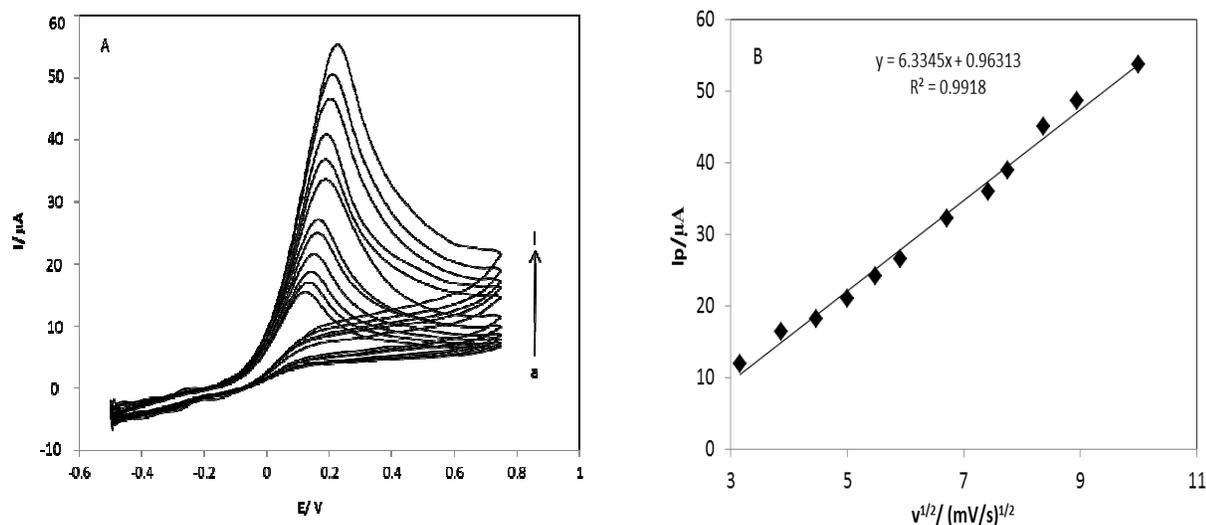


Fig. 4. (A) Cyclic voltammograms of $[\text{Cd}(\text{ttpy})\text{I}_2]$ modified Au electrodes in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH=7) containing 1 mM hydrazine at scan rates of (a) 10, (b) 15, (c) 20, (d) 25, (e) 30, (f) 35, (g) 45, (h) 55, (i) 60, (j) 70, (k) 80 and (l) 100 mV s^{-1} (B) dependence of the peak current with square root of the scan rate.

It can be noted from Fig. 4B 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. 3B), the following linear relationship was obtained:

$$I_p = -9.6313 + 6.3345 v^{1/2} (\text{mV}^{1/2} \text{ s}^{1/2}), \quad R^2 = 0.9918 \quad (1)$$

This behavior suggests that the oxidation process is controlled by diffusion. Thus, according to the following equation for a totally irreversible diffusive process:

$$I_p = 3.01 \times 10^5 n [(1-\alpha) n_a]^{1/2} A c D^{1/2} v^{1/2} \quad (2)$$

And considering $(1-\alpha)n_a=0.28$ (see below), $D=5.02 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (see chronoamperometric studies), $A=0.125 \text{ cm}^2$, it is estimated that the total number of electrons involved in the anodic oxidation of hydrazine is $n \approx 4$.

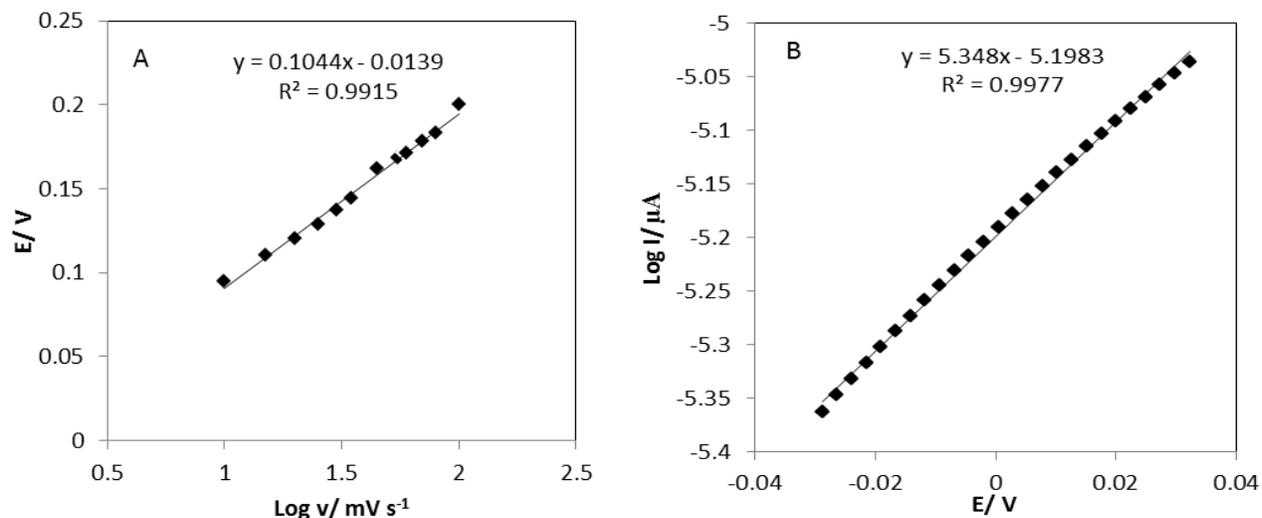


Fig. 5. (A) Plot of E_p vs. $\log v$. (B) Tafel plot Derived from data of the rising part of the current-voltage curve at a scan rate of 10 mV s^{-1}

In order to get information on the rate determining step, The peak potential, E_p , is proportional to $\log v$ as can be seen in Fig. 4A. The slope of E_p vs. $\log v$ is 104 mV . The tafel slope may be estimated according to the equation for the totally irreversible diffusion-controlled process:

$$E_p = (b \log v)/2 + \text{constant} \quad (3)$$

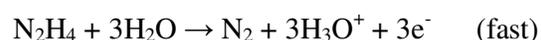
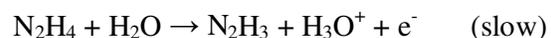
So, $b=0.208 \text{ V}$. this result is close to that obtained from polarization measurement [31].

This slope indicates a one electron transfer to be rate limiting assuming a transfer coefficient of $\alpha=0.72$

The tafel slope, b , can be obtained by another method. A tafel plot was drawn (Fig.5B). Derived from data of the rising part of the current-voltage curve at a scan rate of 10 mV s^{-1} , A slope of 5.35 V^{-1} is obtained which indicates that the rate limiting step is one electron transfer (assuming a transfer coefficient of $\alpha=0.7$) using the following equation:

$$\text{Slope} = (1-\alpha)n_e F/2.3RT \quad (4)$$

Accordingly, the following mechanism can be proposed for the oxidation of hydrazine on a $[\text{Cd}(\text{ttpy})\text{I}_2]$ modified Au electrode in neutral solution:



In other words the rate-determining step is a one electron transfer followed by a three-electron process to give N_2 as a final product [32]

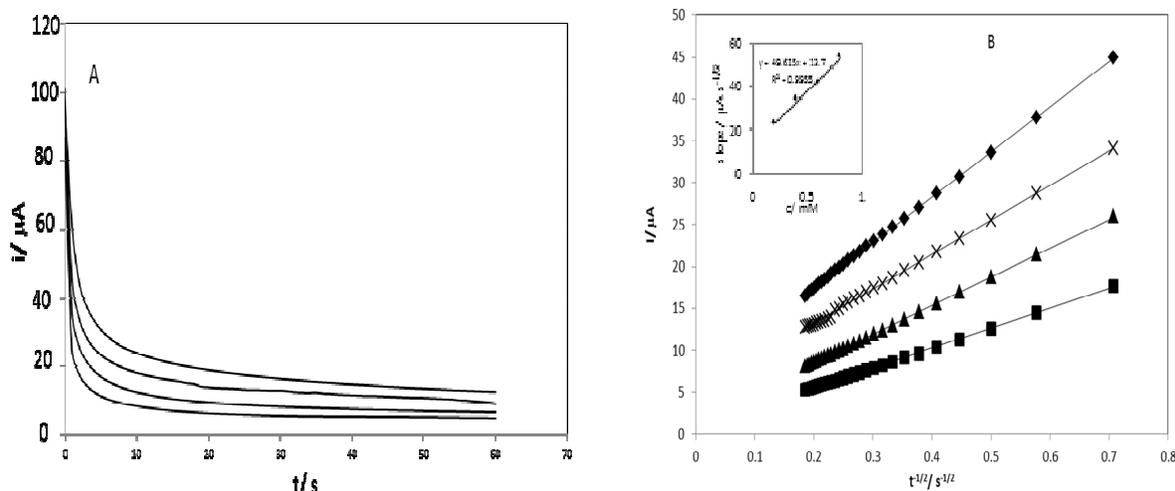


Fig. 6. (A) Chronoamperometric response of a $[Cd(tpy)_2]$ modified electrode in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of hydrazine for a potential step of 400 mV vs. SCE in the range of 0.2, 0.4, 0.6 and 0.8 mM. (B) Plot of plot of I vs. $t^{1/2}$ obtained from chronoamperometric experiments. Inset shows the relationship between the slope of the linear segments and the hydrazine concentration

The electrocatalytic oxidation of hydrazine at the $[Cd(tpy)_2]$ modified electrode was studied by chronoamperometry. 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 400 mV versus SCE. In addition, the level of the Cottrell current, which was measured for 60s, increase with increasing concentration of hydrazine in the range of 0.2–0.8 mM. In chronoamperometric studies, the diffusion coefficient of hydrazine the modified electrode can be determined. The relationship between current and time can be described by the Cottrell equation [33]:

$$I = n F A D^{1/2} c / \pi^{1/2} t^{1/2} \quad (5)$$

Where D is the diffusion coefficient ($cm^2 s^{-1}$) and c is the bulk concentration ($mol cm^{-3}$). The plot of I vs. $t^{1/2}$ will be linear, and from the slope, the value of D can be obtained. Fig. 6B shows the experimental plots of the resulting straight line were then plotted vs. the

concentration of hydrazine (Fig. 6B, inset), from which we calculated a diffusion coefficient of $9.49 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for hydrazine.

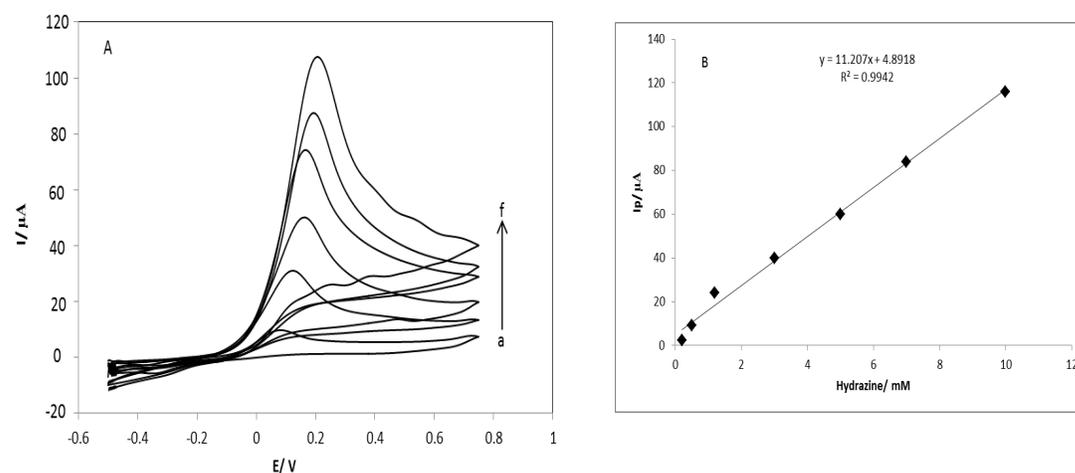


Fig.7. (A) Cyclic voltammograms for increasing concentrations of hydrazine from 0.2 to 10 (a to f) mM (1–6) in buffer solution (pH 7.0) containing 0.1 M KCl solutions on $[\text{Cd}(\text{tpy})\text{I}_2]$ modified electrode. Scan rate was 50 mV s^{-1} . (B) Calibration plot for concentrations of hydrazine from cyclic voltammograms

The cyclic voltammograms at different concentrations of hydrazine are shown in Fig. 7A. A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 0.2–10 mM hydrazine.

4. CONCLUSIONS

Au electrode coated with a thin film of sol-gel doped with $[\text{Cd}(\text{tpy})\text{I}_2]$, act as an electrocatalyst for oxidation of hydrazine. This film exhibits excellent electrocatalytic behavior toward hydrazine oxidation in aqueous phosphate buffer solution containing KCl as supporting electrolyte. The overall number of electrons involved in the oxidation of hydrazine, the number of electrons involved in the rate-determining step and the diffusion coefficient of hydrazine were calculated. Thus, the results obtained for hydrazine shows that terpyridine complex can be used for determination of other compounds.

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