Electrochemical Detection of Hydrazine Using a Copper oxide Nanoparticle Modified Glassy Carbon Electrode

Jahan Bakhsh Raoof[*], Reza Ojani, Fakhrosadat Jamali, Sayed Reza Hosseini

Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, 3rd Kilometer of Air Force Road, Postal Code: 47416-95447, Babolsar, Iran

[*] Corresponding author: E-mail address: j.raoof@umz.ac.ir

Abstract: Metallic copper nanoparticles modified glassy carbon electrode is fabricated by reduction of $CuSO_4$ in the presence of cetyltrimethylammonium bromide (CTAB) through potentiostatic method. As-prepared nanoparticles are characterized by scanning electron microscopy and electrochemical methods. Copper oxide modified glassy carbon electrode (nano-CuO/MGCE) is prepared using consecutive potential scanning in 0.1 M NaOH solution. The electrochemical properties of hydrazine is studied onto either nano-CuO/MGCE or bare GCE by using cyclic voltammetry and chronoamperometry techniques. The results show that the nano-CuO/MGCE can catalyze the hydrazine oxidation in alkaline medium. The electrocatalytic oxidation peak current shows linear dependency on hydrazine concentration. Linear analytical curves are obtained in the ranges of 0.025-1.66 mM and 0.05-2.5 mM by using differential pulse voltammetry (DPV) and amperometry methods, respectively. The detection limits (3s) are determined as 2×10^{-5} M and 1.2×10^{-5} M by using amperometry and DPV methods, respectively. The Catalytic rate constant is estimated by using chronoamperometry method. Stability of the modified electrode has also been investigated.

Key words: Hydrazine; Electrocatalytic oxidation; Copper oxide nanoparticles; Glassy carbon electrode

1. Introduction

Hydrazine (N_2H_4) is the simplest diamine and the starting material in preparation of several hydrazine derivatives. Hydrazine and derivatives have found various applications such as fuel in fuel cells, catalysts, corrosion inhibitors and antioxidants, initiator of polymerization, emulsifiers, reducing agents, starting material in

the production of some insecticides and herbicides, pesticides, dyes stuffs and explosive, plant growth regulators and in the preparation of several pharmaceutical derivatives [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. Despite the wide use of hydrazine in various areas, it has been known to be harmful for human life and so its detection and determination in low concentrations in various media is highly important. Therefore, the electrooxidation of hydrazine is a reaction with practical importance. Several electrochemical methods based on reducing character were developed [2-4]. Mechanism and kinetics of hydrazine oxidation have been studied at various electrodes such as silver [5], nickel [6], mercury [5,7,8] and platinum [7,8]. These investigations showed that the overpotentials of hydrazine oxidation at Pt, Au and Ag electrodes are smaller than those other metallic electrodes. However, the noble metals being expensive are not suitable in practice and the use of carbon electrodes is not common because of the large overpotential of oxidation at these electrodes. In order to overcome these difficulties, chemically modified electrodes (CMEs) with various mediators were used as hydrazine oxidation beds [9,10]. 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.

Nanoparticles have unique features attracted much research interest [11-13], and the great attention has also been paid to the electrochemistry of chemically nanoparticles modified electrodes [14,15]. Because of the significant properties such as magnetic, electrical, optical, and chemical features that can not be achieved by their bulk counterparts, inorganic nanoparticles are very proper candidates for electrochemical studies owing to their outstanding activity and catalytic power [16-18]. In other hand, nanoparticles can promote mass transport, have high catalytic activity, large effective area and control the microenvironment of electrode [19]. A lot of metal nanoparticles were used for electrochemical detection [20]. Copper or its oxides modified electrode can catalyze the oxidation reaction of some bio-substances such as carbohydrates, amino acids and peptides [21].

Despite so much modified electrodes, a literature survey confirms that effort about the preparation of new patterns for electrocatalytic oxidation of hydrazine is still in progress. In this study, the nano-CuO/MGCE is prepared which is able to catalyze the hydrazine oxidation in alkaline medium.

2. Experimental

2.1. Apparatus and materials

Electrochemical experiments were performed using a potentiostat/galvanostat (Sama 500-c electrochemical analysis system, Iran) coupled with a Pentium IV personal computer to acquire gain the data. A conventional three electrode cell was used with Ag|AgCl|KCl (3M) as reference electrode, platinum wire as auxiliary electrode and GCE (geometric surface area = 0.03 cm^2) (from Azar Electrode Co., Iran) as working electrode substrate. All experiments were carried out at ambient temperature.

The surface morphologies of the deposits were confirmed by scanning electron microscope (SEM) (Leo1455VP, Oxford Instrument, Institute for Colorants, Paints & Coatings (ICPC)). All potentials reported referenced to the reference electrode. Sodium hydroxide and sulfuric acid used in this work were analytical grade of Merck origin and used without further purification. Hydrazine, CTAB and $CuSO_4$ were purchased from Fluka.

2.2. Preparation of the nano-CuO/MGCE

Modification of GCE was performed according to the procedure proposed by Ding Hai-Yun and et. al. [22]. Briefly; the GCE was carefully polished with alumina slurries on a polishing cloth. Then, the electrode was placed in ethanol and sonicated to remove adsorbed particles. Cyclic voltammetry was performed in 0.1 M NaOH solution between -256 and 744 mV at υ=0.1 Vs^{-1}. Copper nanoparticles was initially deposited through constant potential process in an electrolyte composed of 6 ml 5.0×10^{-3} M $CuSO_4$ + 2 ml 1.0×10^{-2} M CTAB + 2 ml 2.5×10^{-2} M H_2SO_4. After this, the electrode was removed, rinsed with distilled water and the sides wiped with soft tissue paper. Figure 1 shows the SEM image of the nano-Cu/MGCE.
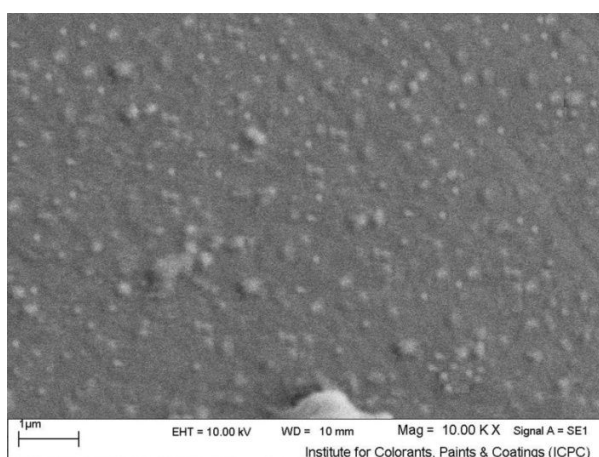

Figure 1: Typical SEM image of the nano-Cu/MGCE.

As can be seen, Cu nanoparticles uniformly dispersed on the GC electrode surface with diameter of approximately 70 nm. The polarization behavior was examined in 0.1 M NaOH solution by using CV technique. This technique allows the oxide (hydroxide) film formation in parallel to inspecting the electrochemical reactivity of the surface.

3. Results and discussion

3.1. Electrocatalytic oxidation of hydrazine onto the nano-CuO/MGCE

The electrocatalytic oxidation of hydrazine was investigated in 0.1 M NaOH solution onto the nano-CuO/MGCE by using CV method and cyclic voltammograms were shown in Fig. 2. The Cyclic voltammograms show that modified electrode can catalyze the hydrazine oxidation. Cyclic voltammetry process in alkaline solution produces Cu^{III} species which is investigated an effective component that catalyzes the hydrazine oxidation [23-33]. Curves (a) and (b) in this figure show the CVs of bare GCE in the absence and presence of 0.48 mM hydrazine, respectively. As can be seen, there is no obvious peak corresponding to the hydrazine oxidation at the surface of bare GCE. Curves (c) and (d) are the electrochemical behavior of the nano-CuO/MGCE in the absence and presence of hydrazine, respectively. As shown in this figure, the oxidation current of hydrazine onto the modified electrode is significantly increased and its oxidation potential is shifted towards less positive values. This behavior is typical of that expected for electrocatalysis at CMEs.
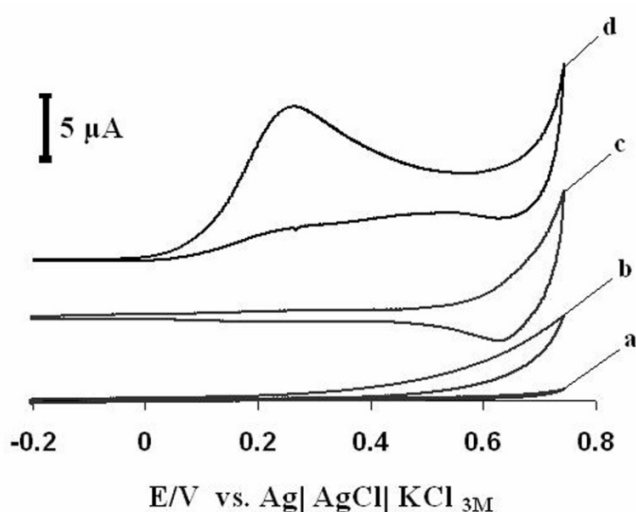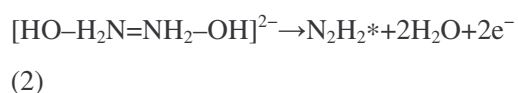

Figure 2: Cyclic voltammograms of a bare GCE **a, b** and nano-CuO/MGCE **c, d** in 0.1 M NaOH solution **a** and **c** in the absence of hydrazine; **b** and **d** in the presence of 0.48 mM hydrazine at v= 50 mVs^{-1}.

Although the exact mechanism of hydrazine oxidation is hard to confirm, the first intermediate in alkaline media seems to be [HO–$H_2N=NH_2$–OH]$^{2-}$. Based on the studies reported in the relevance literature [23] the following mechanism can be proposed for the hydrazine oxidation:

$$N_2H_4 + 2OH^- \rightarrow [HO–H_2N=NH_2–OH]^{2-} \quad (1)$$
$$[HO–H_2N=NH_2–OH]^{2-} \rightarrow N_2H_2* + 2H_2O + 2e^- \quad (2)$$
$$N_2H_2* + 2OH^- \rightarrow N_2 + * + 2H_2O + 2e^- \quad (3)$$

The star (∗) designates an adsorbed species or a free adsorption site. For confirmation of the above mechanism, the effect of NaOH concentration on the hydrazine oxidation was investigated. Figure 3 shows the CVs of the nano-CuO/MGCE in the presence of 0.48 mM hydrazine at NaOH solutions with various concentrations.

It was shown that the peak potential shifted towards negative direction with increasing of NaOH concentration indicating that the formation of [HO–$H_2N=NH_2$–OH]$^{2-}$ ion is rate-determining step. In higher concentrations, NaOH has no limitations on hydrazine oxidation process. Figure 4 shows Tafelic curves with different slopes indicating that the mechanism of the hydrazine oxidation at the nano-CuO/MGCE changes with NaOH concentration in the range of 0.1–0.01 M.
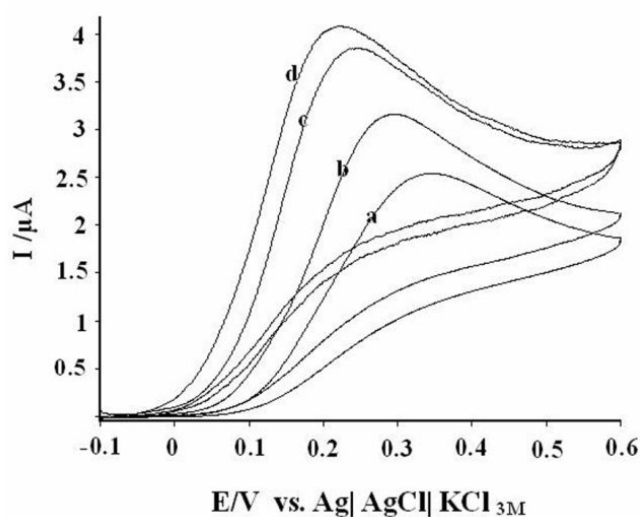

Figure 3: Cyclic voltammograms of 0.48 mM hydrazine at the nano-CuO/MGCE in the presence of **a** 0.01 M, **b** 0.025 M, **c** 0.05 M and **d** 0.1 M NaOH solution at v=10 mVs^{-1}.
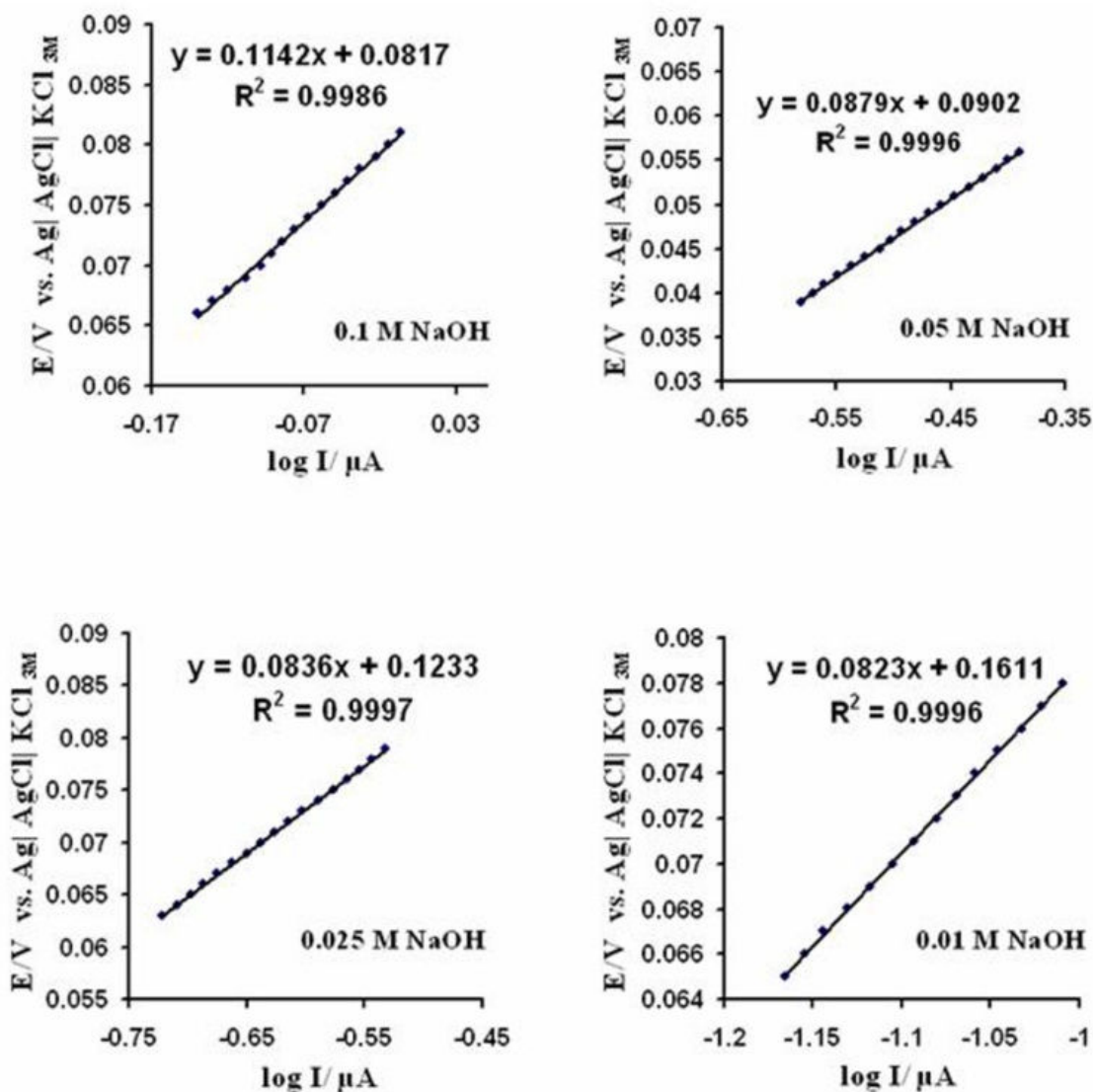
Figure 4: Tafel plots for electrocatalytic oxidation of hydrazine at the nano-CuO/MGCE at different NaOH concentrations.

For 0.1 M NaOH solution, the slope is 0.1142 V decade^{-1} indicating a first electron transfer depending on the applied potential as the rate determining step, whereas at NaOH concentrations of 0.05, 0.025 and 0.01 M, the slopes are 0.0879, 0.0836 and 0.0823 V decade^{-1}, respectively and indicating the presence of two different mechanisms which operates simultaneously. On the other hand, the slope does not change in 0.1 M NaOH solution

for different hydrazine concentrations and it has a unique value. This means that a unique mechanism not depending on the hydrazine concentration operates at 0.1 M NaOH solution, where the rate-determining step is the first electron transfer.

3.2. Effect of scan rate on the anodic peak height

Figure 5A shows CVs of the modified electrode in 0.1 M NaOH solution containing 0.48 mM hydrazine at various potential scan rates. It can be noted from this figure that with increasing of scan rate, the peak potential for both catalytic oxidation of hydrazine and Cu^{II} oxidation shifts to more positive values, suggesting a kinetic limitation in the reaction between the redox sites of the nano-CuO and hydrazine. When peak current values are plotted against $\upsilon^{1/2}$ (Fig. 5B), the linear relationship (I_p=-2.7941 + 1.6609 $\upsilon^{1/2}$) is obtained. This behavior indicates that the oxidation process of hydrazine is controlled by diffusion. A similar behavior was observed in the relevance literature [34].
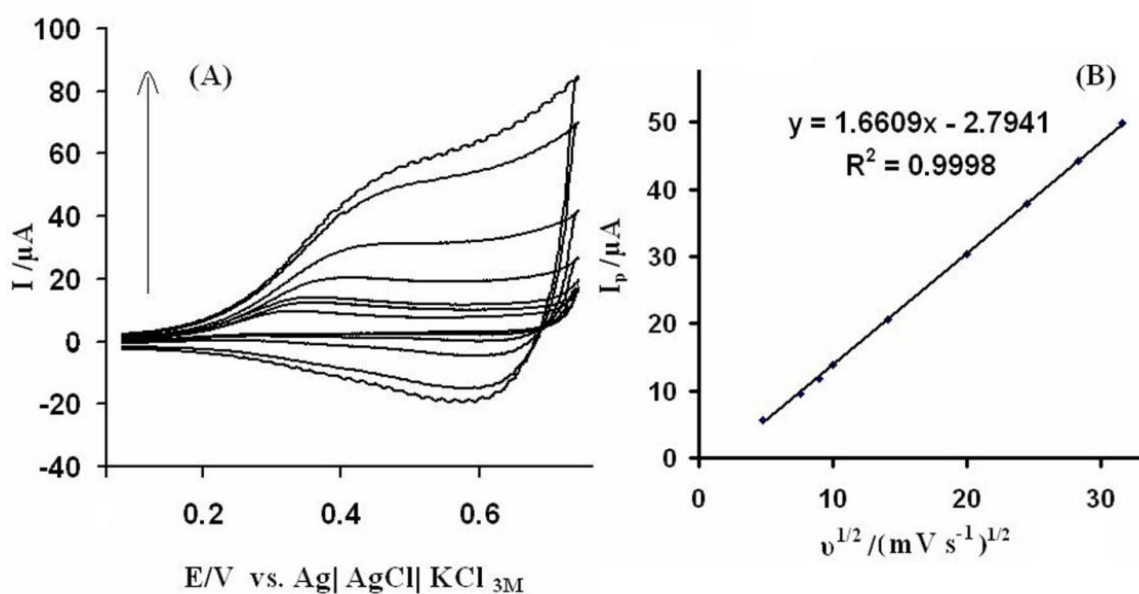

Figure 5: A Cyclic voltammograms of the nano-CuO/MGCE at various potential sweep rates in 0.1 M NaOH solution containing 0.48 mM hydrazine. The υ from inner to outer are: 5, 10, 20, 50, 80, 100, 200, 400, 600, 800 and 1000 mVs^{-1}, respectively. **B** Dependency of the anodic peak current with $\upsilon^{1/2}$.

3.3. Effect of hydrazine concentration

Figure 6A shows the effect of hydrazine concentration on the CVs of the nano-CuO/MGCE. As can be seen, the height of anodic peak increases with increasing of hydrazine concentrations. Figure 6B shows that the plot of I_p versus hydrazine concentration

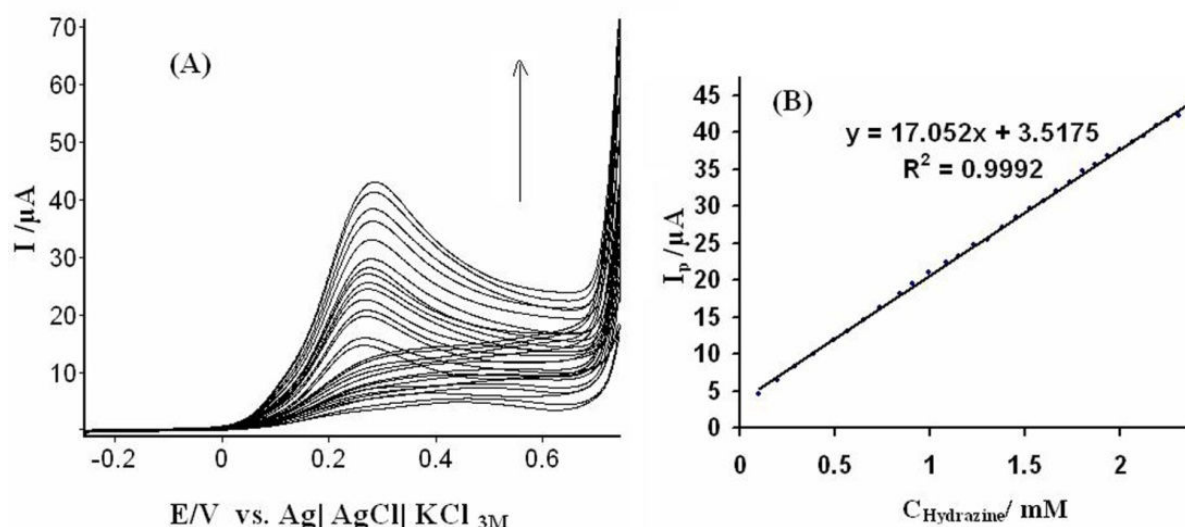between 0.099 and 2.366 mM which consists of one linear segment.

Figure 6: A Cyclic voltammograms of the nano-CuO/MGCE in 0.1 M NaOH solution containing increasing concentrations of hydrazine from 0.099 to 2.366 mM (from inner to outer) at v=50 mVs^{-1}. **B** The corresponding calibration curve.

3.4. Chronoamperometric studies

Chronoamperometry as well as other electrochemical methods may be used for investigation of the electrode processes at CMEs. The chronoamperograms obtained for hydrazine with various concentrations as illustrated in Fig. 7A.

An increment in hydrazine concentration was accompanied by an increment in anodic currents obtained for a potential step of 0.3 to 0.0 V. As can be seen in figure 7B (a′), the forward and

backward potential step chronoamperometry of the modified electrode in the blank solution shows an almost equal charge consumed for the oxidation/reduction of the surface-confined sites. However, in the presence of hydrazine, the charge value associated with the forward chronoamperometry is greater than that backward (Fig. 7B (b′)).

The current is negligible when potential is stepped down to 0.3 V, indicating that the electrooxidation of hydrazine is irreversible

process. Chronoamperometry can also be used for evaluation of the chemical reaction between the hydrazine and catalyst layer (catalytic rate constant, k) according to [35]:

$$I_C/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kct)^{1/2} \qquad (4)$$

Where I_L, I_C, k, c and t are the currents in the absence and presence of hydrazine, the catalytic rate constant, the bulk concentration of hydrazine and the elapsed time, respectively. From the slope of the I_C/I_L vs. $t^{1/2}$ plot, presented in Fig. 7(C), the mean value of k for hydrazine concentration ranging from 0.196 to 2.42 mM is estimated about 2×10^7 cm^3 mol^{-1} s^{-1}.
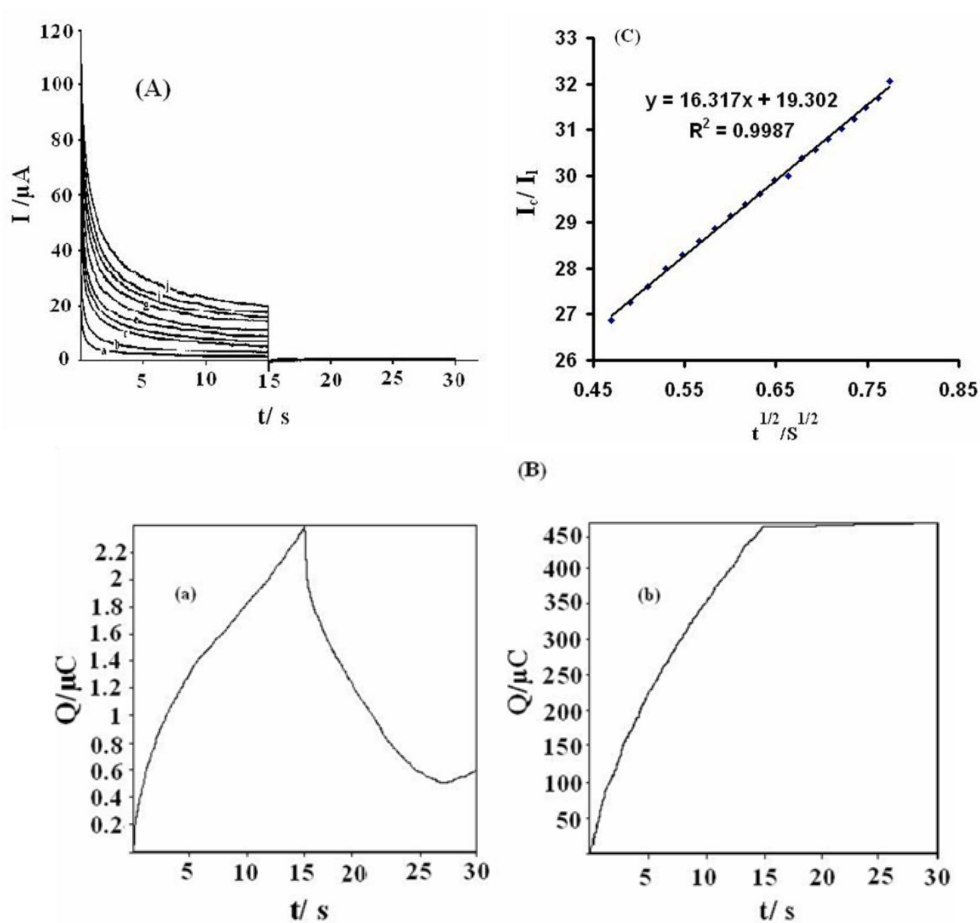

Figure 7: A Chronoamperograms of the nano-CuO/GCE in 0.1 M NaOH solution in the absence **a** and the presence **b–j** at various hydrazine concentrations: 0.196, 0.385, 0.566, 0.741, 0.909, 1.07, 1.23, 1.67 and 1.87 mM, respectively. **B** The dependency of charge Q vs. t derived from the data of chronoamperograms **a** and **f**. **C** The dependency of I_C/I_L on $t^{1/2}$ derived from the data of chronoamperograms **a** and **f** in the main panel.

3.5. Amperometric studies

Chronoamperometry was also used to test the applicability of the nano-CuO/MGCE for determination of hydrazine. Figure 8(A) shows a typical current-time curve of the modified electrode at applied potential of 0.3 V by successive additions of hydrazine. The oxidation current increases sharply to reach a steady-state value and achieves 95% the steady-state current within 2s. The current response and the hydrazine concentration have a linear relationship with a concentration range from 0.05 mM to 2.5 mM (Fig. 8B) and the detection limit is estimated to be 2×10^{-5} M (S/N=3).
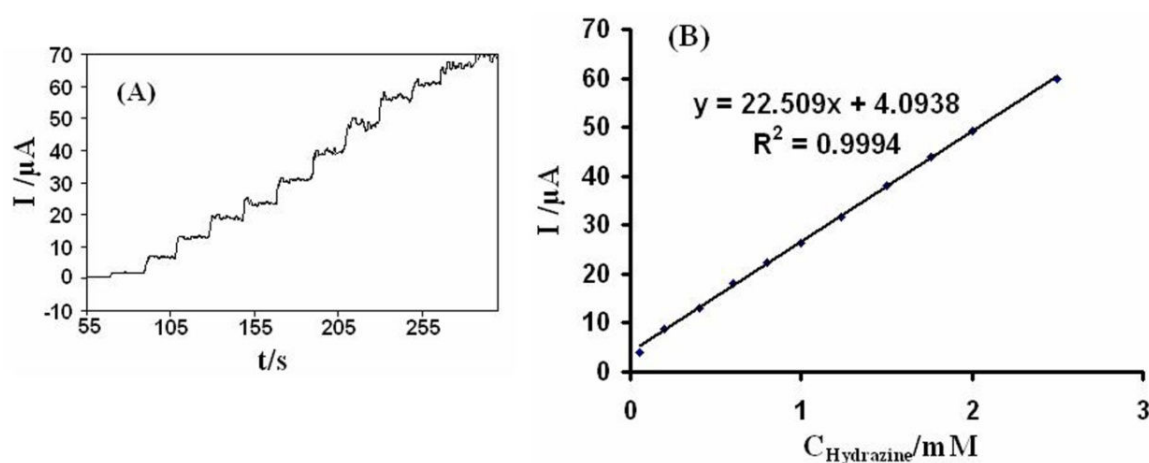

Figure 8: A Current-time responses for hydrazine oxidation at the nano-CuO/MGCE in 0.1 M NaOH solution after subsequent spiking of 0.05 mM hydrazine. **B** Calibration plot for hydrazine at an applied potential of 0.3 V vs. reference electrode.

3.6. Differential pulse voltammetric studies

The determination of hydrazine concentration onto the nano-CuO/MGCE was also performed with DPV method (Fig. 9A). The oxidation peak currents of hydrazine were measured in optimum conditions and plotted against the bulk concentration of hydrazine (Fig. 9B).

The dependency of peak currents on hydrazine concentration is a linear relationship in the range of 0.025 to 1.66 mM. The linear regression equation is expressed as: Ip (mA) = 8.3605C (mM) + 0.593. The detection limit (3s) is 1.2×10^{-5} M.

Table 1 shows a comparison between previously reported some modified electrodes for determination of hydrazine and the proposed electrode which shows comparability of the nano-CuO/MGCE for hydrazine determination. At the end of this work, long-term stability of the modified electrode was investigated and

results showed that it is stable for three weeks in
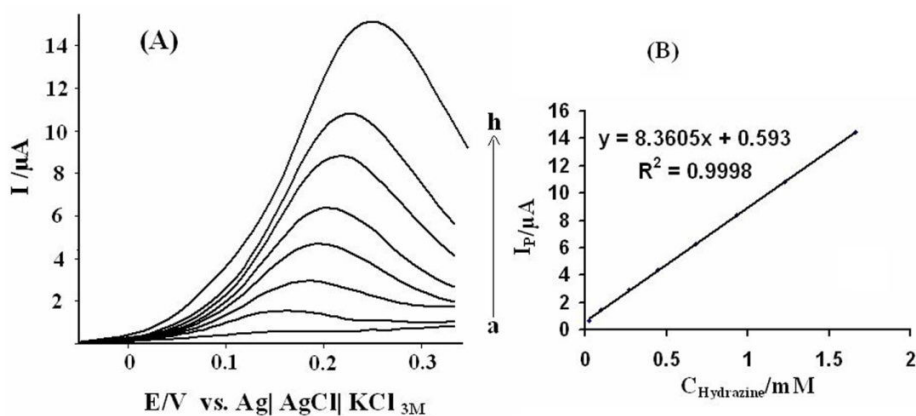
dry conditions after repetitive measurements.

Figure 9: **A** Differential pulse voltammograms of the nano-CuO/MGCE in the presence of different hydrazine concentrations: a 0.025, b 0.099, c 0.268, d 0.452, e 0.659, f 0.909, g 1.228 and h 1.666 mM. **B** The plot of electrocatalytic oxidation peak current vs. hydrazine concentration.

Table 1: literatures for electrocatalytic detection of hydrazine at some modified electrodes.

Modified electrode	pH	LOD/μM	Reference
Pd nanoparticle modified BDD	7.0	2.6	[9]
Pd nanowires modified CILE	7.0	0.82	[10]
Tetrabromo-p-benzoquinone modified carbon paste electrode	10.0	5.2	[36]
Pd nanoparticle decorated bamboo MWCNTs	7.0	10	[37]
Cobalt phthalocyanine (CoPc) modified carbon paste electrode	13.0	100	[38]
Mixed-valent CoOx/cyanocobaltate film electrode	4.0	150	[39]
Chlorogenic acid/carbon ceramic composite electrode	8.0	20	[40]
Carbon nanotube modified microelectrode	7.0	1.0	[41]
Pd/CNT/4-aminobenzene monolayer grafted GCE	4.0	1.0	[42]
Nano-CuO modified GCE	13.0	12	This work

4. Conclusion

The present work demonstrates an application of the nano-CuO/MGCE for electrocatalytic oxidation of hydrazine in 0.1 M NaOH solution. The electrochemical behavior of hydrazine at the nano-CuO/MGCE has been studied by cyclic voltammetry and chronoamperometry.

The electrocatalytic oxidation peak current of hydrazine showed a linear dependency on concentration and linear analytical curves were

obtained in the concentration ranges of 0.05-2.5 mM and 0.025-1.66 mM with amperometry and DPV methods, respectively.

 The detection limits (3s) were determined as 2×10^{-5} M and 1.2×10^{-5} M by using amperometry and DPV methods, respectively. The proposed voltammetric method is a rapid and simple.

The k value indicates that the modified electrode can overcome the kinetic limitations of hydrazine oxidation by a catalytic process and can decreases the overpotential of its oxidation reaction.

5. References

[1] H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaborg, Kirk-Othmer Encyclopedia Chemical Technology, 5th ed., Wiley, New York, 2005.

[2] C. Zhao, J. Song, J. Zhang, Anal. Lett. 34 (2001) 2111.

[3] S.H. Wu, D.H. Chen, J. Coll. Inter. Sci. 259 (2003) 282.

[4] S.D. Holmstrom, Z.D. Sandlin, W.H. Steinecker, J.A. Cox, Electroanalysis 12 (2000) 262.

[5] K. Korinek, J. Korita, M. Nusiloua, J. Electroanal. Chem. 21 (1969) 319.

[6] M. Fleischmann, K. Korinek, D. Piewner, J. Electroanal. Chem. 34 (1972) 499.

[7] S. Karr, L. Meites, J. Am. Chem. Soc. 84 (1962) 906.

[8] J.A. Harrison, Z.A. Khan, J. Electroanal. Chem. 26 (1970) 1.

[9] C. Batchelor-McAuley, C.E. Banks, A.O. Simm, T.G. J. Jones, R.G. Compton, Analyst 131 (2006) 106.

[10] N. Maleki, A. Safavi, E. Farjami, F. Tajabadi, Anal. Chim. Acta 611 (2008) 151.

[11] S. Vaucher, M. Li, S. Mann, Angew. Chem. Int. 39 (2000) 1793.

[12] P.A. Hassan, S.N. Sawant, N.C. Bagkar, J.V. Yakhmi, Langmuir 20 (2004) 4874.

[13] L. Wang, Y. Sunb, G. Chea, Z. Li, Appl. Surf. Sci. 257 (2011) 7150.

[14] H.J. Kima, H.J. Sohna, S. Kim, S.N. Yi, D.H. Ha, Sens. Act B 156 (2011) 990.

[15] P. Taknistov, Biosens. Bioelectron. 19 (2004) 441.

[16] J.M. Domynguez-Vera, E. Colacio, Inorg. Chem. 42 (2003) 6983.

[17] E.C. Cho, C. Glaus, J. Chen, M. J. Welch, Y. Xia, Trend Mol. Med. 16 (2010) 561.

[18] P. Setua, R. Pramanik, S. Sarkar, C. Ghatak, V.G. Rao, N. Sarkar, S.K. Das, J. Mol. Liq. 162 (2011) 33.

[19] C.M. Welch, R.G. Compton, Anal. Bioanal. Chem. 384 (2006) 601.

[20] B. Ijukic, R. Baron, C. Salter, A. Crossley, R.G. Compton, Anal. Chim. Acta 590 (2007) 67.

[21] S.A. Brazill, P. Singhal, W.G. Kuhr, Anal. Chem. 72 (2000) 5542.

[22] H.Y. Ding, Y. Zhou, S.J. Zhang, X.B. Yin, Y.J. Li, X.W. He, Chin. J. Anal. Chem. 36 (2008) 839.

[23] V. Rosca, M.T.M. Koper, Electrochim. Acta 53 (2008) 5199.

[24] J.M. Marioli, T. Kuwana, Electrochim. Acta 37 (1992) 1187.

[25] A.M. Shamseldin, F.M. Abdel Wahab, Electrochim. Acta 9 (1964) 113.

[26] J.M. Brisard, J.D. Rudnicki, F. Molarnon, E.J. Cairns, Electrochim. Acta 40 (1995) 859.

[27] S.T. Farrell, C.B. Breslin, Electrochim. Acta 49 (2004) 4497.

[28] N. Torto, T. Ruzgas, L. Gorton, J. Electroanal. Chem. 464 (1999) 252.

[29] L.D. Burke, K.J.O. Dwyer, Electrochim. Acta 36 (1991) 1937.

[30] S.M. Abdel Haleem, B.D. Ateya, J. Electroanal. Chem. 117 (1981) 309.

[31] C.H. Pyun, S.M. Park, J. Electrochem. Soc. 132 (1986) 2024.

[32] S.V. Prabhu, R.P. Baldwin, Anal. Chem. 61 (1989) 852.

[33] I.G. Casella, M. Gatta, J. Electroanal. Chem. 494 (2000) 12.

[34] G. Karim-Nezhad, R. Jafarloo, P. Seyed Dorraji, Electrochim. Acta 54 (2009) 5721.

[35] A.J. Bard, L.R. Faulkner, Electrochemical methods, 2nd ed., Wiley, New York, 2001.

[36] J.B. Raoof, R. Ojani, M. Ramine, Electroanalysis 19 (2007) 597.

[37] X. Ji, C.E. Banks, A.F. Holloway, K. Jurkschat, C.A. Thorogood, G.G. Wildgoose, R.G. Compton, Electroanalysis 18 (2006) 2481.

[38] K.M. Korfhage, K. Ravichandran, R.P. Baldwin, Anal. Chem. 56 (1984)1514.

[39] J. Zhou, E. Wang, Talanta 40 (1993) 943.

[40] A. Salimi, R. Hallaj, Electroanalysis 16 (2004) 1964.

[41] W.D. Zhang, H. Chen, Q.M. Luo, Talanta 58 (2002) 529.

[42] D.J. Guo, H.L. Li, Electrochem. Commun. 6 (2004) 999.