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Complete List of Authors:	<p>Ait Ahmed, Nadia; Laboratoire d'Electrochimie, de Corrosion et de Valorisation Energétique(LECVE), Université de Bejaia, 06000 Bejaia, Algérie.</p> <p>Hammache, Houa; Laboratoire d'Electrochimie, de Corrosion et de Valorisation Energétique(LECVE), Université de Bejaia, 06000 Bejaia, Algérie.</p> <p>Eyraud, Marielle; Aix-Marseille Univ, CNRS, MADIREL UMR 7246, équipe Electrochimie des Matériaux, 13397 Marseille Cedex 20, France.</p> <p>Makhloufi, Laid; Laboratoire d'Electrochimie, de Corrosion et de Valorisation Energétique(LECVE), Université de Bejaia, 06000 Bejaia, Algérie.</p> <p>Gabouze, Noureddine; Centre de Recherche en Technologie des Semiconducteurs pour l'Energétique (CRTSE), 2, bvd. Frantz Fanon, B.P. 140 Alger 7 Merveilles, Alger, Algérie.</p>
Keywords:	ZnO, Electrodeposition, Copper, Electrocatalysis, Nitrate reduction

Synthesis of nanostructured ZnO/copper electrodes for nitrate electroreduction

N. Ait Ahmed¹, H. Hammache¹, M. Eyraud², L. Makhloufi¹, N. Gabouze³

¹Laboratoire d'Electrochimie, de Corrosion et de Valorisation Energétique(LECVE), Université de Bejaia, 06000 Bejaia, Algérie.

²Aix-Marseille Univ, CNRS, MADIREL UMR 7246, équipe Electrochimie des Matériaux, 13397 Marseille Cedex 20, France.

³Centre de Recherche en Technologie des Semiconducteurs pour l'Energétique (CRTSE), 2, bvd. Frantz Fanon, B.P. 140 Alger 7 Merveilles, Alger, Algérie.

Abstract

In this work, ZnO thin films were synthesized on the surface of copper electrodes by an electrochemical method at different deposition potentials -0.6, -0.8, -1 and -1,2 V versus SCE. The as-prepared ZnO modified Cu electrodes (ZnO/Cu) have been employed for electrocatalytic nitrate reduction under neutral pH (pH =6.8) condition in 0.1 M KNO₃ using cyclic voltammetry and amperometry techniques. The electrode surface and structure were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The effects of the electrodeposition potential and time on the morphology, structure and electrocatalytic properties were studied. The results show that under optimized ZnO electrodeposition conditions, the ZnO/Cu electrode exhibits interesting electrocatalytic performance in nitrate reduction. A well defined and reproducible peak with maximum current density was obtained for ZnO/Cu electrode elaborated at -1V for 20 min electrodeposition time. Kinetic study by chronoamperometry is indicative of ammonia formation.

Keywords: ZnO; Electrodeposition; Copper; Electrocatalysis; Nitrate reduction

1. INTRODUCTION

Nitrate reduction and determination is extremely important for environment and public health issues. The development of specific analytical methods for the detection and destruction of nitrate is of great importance to limit pollution of the natural environment. Many methods are used to remove NO₃⁻ ions from contaminated water, such as reverse osmosis, photocatalytic, biochemical, chemical and electrochemical reduction [1-4]. Most of them involving complicated and time-consuming procedures. In contrast, electrochemical nitrate treatment

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3 can offer a promising and attractive solution due to its advantages regarding low cost
4 effectiveness, convenience, ability to treat highly concentrated nitrate effluents and
5 environmental friendliness [5, 6].
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8 As the products of the nitrate electroreduction are critically dependent on the nature of the
9 cathode material [7, 8], several simple metal electrodes (Nickel, Platinum, Graphite, Glassy
10 carbon, Copper, etc.) have been widely used for the reduction of nitrate [9-14]. Compared to
11 other materials, Cu metal has shown good catalytic character for nitrate reduction [15-17].
12 However, the use of bare electrodes for the reduction of nitrate requires high potentials [18,
13 19] and these electrodes tend to be poisoned by the species formed during the electrochemical
14 process [20]. This considerable drawback limits their use for large scale applications. A good
15 way of lowering the reduction potential and limiting surface poisoning is the use of modified
16 electrodes and their application has received considerable attention in recent years due to
17 many advantages, such as wider operational potential window, easy manufacture, low price,
18 renewable surface and longer life time [21-23]. In the other hand, ZnO are the object of
19 quickly growing in the last few years, due to its number of exciting properties [24-26]. It is a
20 wide band gap semiconductor material with $E_g \approx 3.3$ eV and large excitonic binding energy
21 of ~ 60 meV [27]. Also, it's an environmentally friendly material that does not form toxic
22 byproducts [28], with low price, high chemical and thermal stability. Due to these excellent
23 properties, ZnO nanomaterials have been used as efficient electron mediators for the
24 fabrication of electrochemical sensors. The electrochemical reduction of nitrate ions has been
25 investigated over a large number of modified electrodes, for example, metals modified
26 electrode [29, 30] and polymer modified electrode [31]. To our knowledge, fewer research
27 articles have been published on electrocatalytic activity of ZnO toward nitrate reduction.
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30 The main objective of the present study is to elaborate ZnO modified copper electrode by
31 electrodeposition method and we have reported the applicability of a ZnO/Cu electrode for the
32 selective reduction of NO_3^- under neutral pH condition. The electrocatalytic activity of the as-
33 prepared Cu-ZnO electrode is compared with that of a pure Cu surface.
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35
36 The electrocatalytic ability of ZnO/Cu was thoroughly investigated by cyclic voltammetry
37 (CV) and chronoamperometry.
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2. Materials and methods

2.1. Reagents and solutions

All chemicals were of analytical-reagent grade from Merck or Fluka and were used directly without further purification. All aqueous solutions were prepared with bi-distilled water

(presenting high resistance $\sim 18 \text{ M}\Omega$). The supporting electrolyte used in all the experiments was 0.1 M KNO_3 or 0.1 M phosphate buffer solutions.

2.2. Apparatus

All the electrochemical experiments were carried out using a potentiostat/galvanostat (Autolab PGSTAT30) coupled with HP computer under "Voltmaster logiciel". The electrochemical cell was assembled with a conventional three-electrode system: a bare Cu or ZnO /Cu were employed as working electrodes. Platinum wire is used as auxiliary electrode and a saturated calomel electrode (SCE) as reference.

The surface morphology of the modified electrode was investigated by a scanning electron microscope (SEM) (Hitachi, S-570). The Si-Li electrode was used for light elements with a 133 eV resolution at low counting rate and beam parameters of 20 keV and 160 pA . X-ray diffraction (XRD) analyses were performed on a Siemens D5000 diffractometer using filtered $\text{CuK}\alpha$ ($\lambda = 0.15406 \text{ nm}$) as a radiation source. The diffractometer was operated at 40 kV , room temperature, with a scanning rate of 10 min^{-1} .

2.3. Preparation of the synthesized ZnO/Cu electrode

A wet electrochemical method was employed for the synthesis of ZnO thin film. ZnO thin films were deposited from an electrolyte containing $5 \cdot 10^{-3} \text{ M Zn (NO}_3)_2$, $6 \text{ H}_2\text{O}$ and 0.1 M KNO_3 at 70°C using a different potentials -0.6 , -0.8 , -1 and -1.2 V/SCE and at different deposition times 5 , 10 , 15 , 20 , 25 and 30 min . The pH of solution is fixed at 6 .

Before the electrodeposition process, the massive Cu were polished using emery paper with 1200 grit , degreased with acetone, cleaned with twice distilled water and dried with a soft tissue paper. This Cu electrode was then used as the working electrode in the electrodeposition of ZnO on a copper electrode.

3. RESULTS AND DISCUSSION

3.1. Electrochemical study by cyclic voltamperometry and chronoamperometry

Prior to the development of ZnO by chronoamperometry, we found it useful to consider the voltammetric behavior of ZnO deposit. The cyclic voltammetry study was performed in a potential range of -0.5 to -1.6 V versus SCE onto copper substrate. The potential scan was initiated in the negative direction from the open circuit potential (OCP) at a scan rate of 8 mVs^{-1} (Fig. 1). As stated in our previous works [25], the ZnO reaction formation is initiated by the nitrate reduction reaction. We can see in Fig. 1 that the current begins to increase for a potential of -0.2 V indicating that the reaction of nitrate reduction on the copper substrate is

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3 very active leading to ZnO deposit at very low cathodic potentials. Below -0.6 V, the cathode
4 current increases faster with the potential increase indicating the activation of the ZnO
5 formation process. However, the rapid increase in intensity at -1.25 V corresponds to the
6 water reduction reaction. No anodic peak appears in the return sweep, indicating that no zinc
7 metal is codeposited with ZnO.
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11 Accordingly to the voltammetric study, ZnO may be deposited at low cathodic potential as -
12 0.2 V and high deposition rate will be reached for a potential values more cathodic than -0.6
13 V; thus a large potential window from -0.6 V to -1.2 V versus SCE was chosen to deposit
14 ZnO thin films on Cu substrate using chronoamperometry, in solution containing 5 mM of Zn
15 $(\text{NO}_3)_2$ and 0.1 M KNO_3 . The applied potentials correspond to the maximum peak for ZnO
16 deposit, readings from the previous figure. The obtained current transients curves are
17 illustrated in **Fig.2**. We can see that after an initial sharp peak the current decreases rapidly in
18 the first few seconds due to the charge of the double layer which can be accompanied by the
19 adsorption of ZnO at the interface. After this, the current stabilize to form a plateau
20 corresponding to the stability of ZnO. Also, we can see that an increase in cathodic potential
21 was accompanied by an increase in cathodic plateau. It is worth noting that increasing applied
22 potential leads to the increase in zinc oxide deposition current densities.
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31 **3.2. Morphological and structural properties of the synthesized ZnO thin films**

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33 The SEM micrographs and the XRD spectra for a selected ZnO/Cu electrodes synthesized at
34 20 min electrodeposition time are shown in Fig. 3 and 4. It can be noted that, the morphology
35 of the surface of ZnO deposited at -0.6 V (**Fig.3 (a)**) reveals the grains structure, with an
36 inhomogeneous distribution. Increasing the potential at -0.8 V (**Fig.3 (b)**), the deposit
37 becomes more compact, homogeneous and the surface is made from hexagonal shapes stems.
38 For more cathodic potentials as -1V and -1.2V (**Fig. 3(c and d)**), the morphology of the ZnO
39 modified electrode is in the form of flowers oriented on the substrates surface and each flower
40 consists of petals. ZnO nanoflowers will offer large surface area and expected to enhance
41 electrocatalytic activity.
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48 The XRD measurements confirm the formation of ZnO thin films on Cu substrate (**Fig. 4**).
49 Three pronounced peaks are observed in the as-prepared samples, which can be indexed to the
50 (100), (002), and (101) reflections of ZnO at 2θ value of 31.7° , 34.4° and 36.3° , respectively.
51 No other diffraction peaks were detected excluding the peaks originating from ZnO. Although
52 all ZnO diffraction peaks are in good agreement with the JCPDS card (36-1451) for a
53 wurtzite-type ZnO crystal. It can be seen that, for the ZnO thin film electrodeposited at -1V
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3 for 20 min, a significantly higher intensity of (002) diffraction peak is obtained indicating that
4 ZnO flowers were preferentially oriented along the c-axis direction crystallographic face.

6 **3.3. Electrochemical behavior of nitrate ions at bare Cu and ZnO/Cu modified** 7 **electrode**

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10 In order to evaluate the electrocatalytic behavior of the ZnO/Cu modified electrode towards
11 nitrate reduction, we performed voltammograms in absence of NO_3^- ions at Cu electrode
12 (**Fig.5 (a)**) and in 0.01M KNO_3 at bare Cu (**Fig.5 (b)**) and at ZnO/Cu (**Fig.5 (c)**) electrodes.

13
14 It can be seen that, in the presence of NO_3^- , a very broad reductive wave was observed on the
15 voltammogram recorded at Cu bare electrode, corresponding to the reduction of nitrates, in
16 agreement with the results of literature [16]. For the voltammogram recorded at the ZnO
17 modified electrode obtained by chronoamperometry at -1V for 20 min, a one single, sharp and
18 intense reduction peak appears at around -0.7 V/SCE (**Fig.5(c)**). This is the sign of increasing
19 electrocatalytic activity on the ZnO/Cu modified electrode. Compared to the bare Cu
20 electrode, in KNO_3 solution with a less intense peak reduction, we can conclude that the ZnO
21 promoted the nitrates reduction. The increase in the peak current of the analytes at the surface
22 of the ZnO/Cu (about 2.0 times) can be explained by the increase in electronic transfer due to
23 the increase in the surface area or to the synergic effect between ZnO and Cu. Also, of one
24 single, reduction peak is indicative a one step reduction reaction. To -0.8 V the current
25 intensity increases and this area corresponds to the reduction of proton.

35 **3.4. Electrocatalytic reduction of nitrate onto ZnO/Cu modified electrode**

36 It has already shown that the operating conditions have a directly effect on the morphology
37 and properties of the deposits [24, 13].

38
39 In our study, we investigated the effects of electrodeposition time, bath temperature and
40 deposition potential on the morphology and structure of the ZnO deposits and their possible
41 effects on the electrocatalytic nitrate reduction.

45 **3.4.1. Effect of electrodeposition time and potential**

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47 **Fig.6 (a, b, c and d)** shows the effect of both electrodeposition potential and time on the
48 electrocatalytic activity of ZnO/Cu towards nitrate reduction. Peak current of the CVs was
49 increased with increasing electrodeposition time and potential, suggesting that the
50 morphology and structure of the deposit have great influence on the electrocatalytic activity of
51 ZnO/Cu modified electrodes towards nitrate reduction. It can be observed that, ZnO/Cu
52 electrode obtained at 20 min electrodeposition time shows sharper reduction peak and higher
53 current intensity for nitrate reduction for all potentials.
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3 **Figure 6 (e)** summarizes the effects of potential on the electrocatalytic activity of ZnO/Cu
4 electrode at 20 min electrodeposition time. These results indicated that the electrocatalytic
5 action was more pronounced with the ZnO/Cu fabricated at -1 V. So these potential and time
6 values were chosen as the optimums giving the best results. This increased electrocatalytic
7 activity is probably due to the specific morphology shown by SEM analysis. In this case the
8 ZnO deposit in the form of flowers is denser and covers the Cu substrate entirely leading to
9 the increase in the surface area and improved mass transport. As electrodeposition time
10 increases over 20 min the electrocatalytic nitrate reduction decreases probably due to the
11 decrease of the synergetic effect between ZnO and Cu because Cu will be covered by more
12 compact ZnO deposit. Also, the electrocatalytic nitrate reduction decreases for ZnO deposited
13 at -1.2 V due to poor morphology and structure because of hydrogen competing reaction.

21 **3.4.2. Effect of temperature**

22 **Fig.7** shows the cyclic voltammetry of ZnO modified electrode deposited at -1V for 20 min
23 obtained at different temperatures. As can be seen from **Fig. 7**, an increase in the temperature
24 results in an increase in the intensity of the peak of nitrate reduction. The increase in the
25 intensity of the nitrate reduction corresponds to well-ordered ZnO deposit. This process can
26 be explained by more efficient conversion of Zn (OH)₂ to ZnO in an ultimate step due to the
27 temperature effect. For the rest of our study we chose a temperature of 70°C to make deposits.

33 **3.4.3. Effect of nitrate concentration**

34 **Fig. 8** shows the voltammograms of nitrate reduction in the concentration range of 0.03 -10
35 mM KNO₃ recorded using the ZnO/Cu electrode at a potential sweep rate of 8 mV s⁻¹. We
36 can see that the nitrate reduction peak current increases with increasing NO₃⁻ concentration
37 and has a linear relationship with the concentration of NO₃⁻ in the considered range of
38 concentration with a correlation coefficient of 0.9987. The regression equations is $y=0.1374$
39 $C_{\text{NO}_3^-} - .60.3676$ with $R^2= 0.99815$. From these results, we can conclude that the ZnO/Cu
40 electrode can be used for nitrate electroreduction and detection.

47 **3.4.4. Chronoamperometric measurements on ZnO/Cu modified electrode in the** 48 **presence of nitrate.**

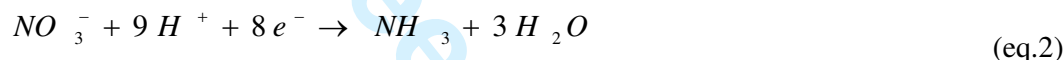
49 **Figure 9 (a)** illustrates the current versus time transients at a cathodic potential of -0.68V/
50 SCE, onto ZnO/ Cu electrode in 10 mM of nitrate ions. This applied potential corresponds to
51 the maximum peak for nitrate reduction (**Fig.6.e**). It is verified that, the variation of current i
52 versus $t^{-1/2}$ is linear with a correlation coefficient of 0.9984 (**Fig. 9(b)**).

From the slope of the line $i = f(t^{-1/2})$ (**Fig.9 (b)**) we can estimate the total number of electrons transferred during the reaction of nitrate reduction using the Cottrell equation (eq.1).

$$i = n.F.A.D^{1/2}.C_{NO_3^-}.\pi^{-1/2}.t^{-1/2} \quad (\text{eq.1})$$

where C is the bulk concentration (mol. cm⁻³), D the diffusion coefficient, n the number of electron transferred, F the Faraday constant, A the electrode area, i is the current density controlled by the diffusion of NO₃⁻ ions from the bulk solution to the electrode/solution interface.

To a concentration C (NO₃⁻) = 0.01M, D = 2.10⁻⁵ cm².s⁻¹[5], n is equal to 7.901 (n = 8) corresponding to the number of electrons exchanged in the reaction in accordance with nitrate reduction into ammonia (**eq. 2**).



The one step reduction reaction was indicative of rapid NO₃⁻ reduction process occurring at the ZnO/Cu modified electrode. These results indicate that the reaction proceeds in one step and might be used for ammonia synthesis, a useful product from the industrial point of view.

3.4.5. Effect of sweep rate

Figure 10(a) shows the CV responses of ZnO/Cu electrode at different scan rates (8, 20, 40, 60, 100 and 200 mV/s). We can see that the nitrate reduction current increases with the increase of sweep rate and was proportional to the square root sweep rate (**Fig. 10(b)**), implying that the reduction process is diffusion controlled

Conclusion

The development of specific analytical methods for the detection and destruction of nitrate is of great importance to limit pollution of the natural environment.

In this study, the reduction of nitrate ions on copper electrodes modified by electrodeposition of ZnO thin films was investigated. The influence of both electrodeposition potential and time on the morphology and structure of ZnO was studied.

The obtained results showed that, these electrodeposition parameters have a great influence on the structure and morphology of the deposit. The structural analysis of ZnO obtained at -1 V versus SCE for 20min, by XRD shows a polycrystalline structure with a preferential

orientation along the c axis perpendicular to the substrate. SEM characterization shows a ZnO deposit in the form of flowers oriented on the substrate surface.

The results of the electrocatalytic study have shown that the copper electrode modified by ZnO thin films, at -1V for 20 min electrodeposition time exhibits excellent electrocatalytic activity towards the reduction of nitrate ions. The results are reproducible over a nitrate concentration range of [0.03 mM to 10 mM]. The number of electrons exchanged in the nitrate reduction reaction was determined by chronoamperometry study which is equal to 8. These results indicate that the reaction proceeds in one step and leads to ammonia a useful product from the industrial point of view. We can conclude that ZnO/Cu electrode might be used for ammonia synthesis as well as NO_3^- detection.

References

- [1] Kim YH, Hwang ED, Shin WS, Choi JH, Ha TW, Choi SJ. Treatments of stainless steel wastewater containing a high concentration of nitrate using reverse osmosis and nanomembranes. *Desalination* 2007; 202: 286-292.
- [2] Elmidaoui A, Elhannouni F, Sahli M, Chay L, Elabbassi H, Hafsi M, Largeteau D. Pollution of nitrate in Moroccan ground water: removal by electrodialysis. *Desalination* 2001; 136: 325–332.
- [3] Molinari R, Argurio P, Romeo L. Studies on interactions between membranes (RO and NF) and pollutants (SiO_2 , NO_3^- , Mn^{++} and humic acid) in water. *Desalination* 2001; 138: 271–281.
- [4] Aslan I, Turkman AE. Combined biological removal of nitrate and pesticides using wheat straw as substrates *Process Biochem* 2005; 40: 935–943.
- [5] Reyter D, Chamoulaud G, Bélanger D, Roué L. Electrocatalytic reduction of nitrate on copper electrodes prepared by high-energy ball milling. *J Electroanal Chem* 2006; 596: 13-24.
- [6] Durivault L, Brylev O, Reyter D, Sarrazin M, Bélanger D, Roué L. Cu–Ni materials prepared by mechanical milling: Their properties and electrocatalytic activity towards nitrate reduction in alkaline medium, *J Alloys Compd* 2007; 432: 323.
- [7] Shimazu K, Goto R, Tada K. Electrochemical reduction of nitrate ions on tin-modified platinum and palladium electrodes. *Chem Lett* 2002; 31: 204–205.
- [8] Peel JW, Reddy KJ, Sullivan BP, Bowen JM. Electrocatalytic reduction of nitrate in Water. *Water Res* 2003; 37: 2512–2519.
- [9] Santos L A L, Denier LJ, Varela H. The effect of ultra-low proton concentration on the electrocatalytic reduction of nitrate over platinum. *Catal. Commun* 2008; 9: 269-272.

- 1
2
3 [10] Taguchi S, Feliu J M, Electrochemical reduction of nitrate on Pt (S) [n (1 1 1) × (1 1 1)]
4 electrodes in perchloric acid solution. *Electrochim Acta* 2007; 52: 6023-6033.
5
6 [11] Groot M T, Koper M T. The influence of nitrate concentration and acidity on the
7 electrocatalytic reduction of nitrate on platinum. *J Electroanal Chem* 2004; 562: 81.
8
9 [12] Taguchi S, Feliu JM. Kinetic study of nitrate reduction on Pt (1 1 0) electrode in
10 perchloric acid solution. *Electrochim Acta* 2008; 53: 3626-3634.
11
12 [13] Keita B, Abdeljalil E, Nadjio L, Contant R, Belgiche R. First examples of efficient
13 participation of selected metal-ion-substituted heteropolyanions in electrocatalytic nitrate
14 reduction. *Electrochem Commun* 2001; 3: 56-62.
15
16 [14] Reyter D, Belanger D, Roue L. Study of the electroreduction of nitrate on
17 copper in alkaline solution. *Electrochimica Acta* 2008; 53: 5977–5984.
18
19 [15] Bouzek Paidar K, Sadilkova M A, Bergmann H. Electrochemical reduction of
20 nitrate in weakly alkaline solutions. *Journal of Applied Electrochemistry* 2001; 31: 1185.
21
22 [16] Aouina N, Cachet H, Debiemme-Chouvy C, Mai Tran T T. Insight into the
23 electroreduction of nitrate ions at a copper electrode, in neutral solution, after determination
24 of their diffusion coefficient by electrochemical impedance spectroscopy. *Electrochim. Acta*
25 2010; 55: 7341–7345.
26
27 [17] Pérez-Gallent E, Marta C, Katsounaros I, Marc T, Koper M. .Electrocatalytic reduction
28 of Nitrate on Copper single crystals in acidic and alkaline solutions. *Electrochimica Acta*
29 2017; 22: 777-84.
30
31 [18] Newbry J E, de Haddad MPL. Amperometric determination of nitrite by oxidation at a
32 glassy carbon electrode. *Analyst* 1985; 110: 81-82.
33
34 [19] Chamdi AY, Fogg AG. Oxidative flow injection amperometric determination of nitrite at
35 an electrochemically pre-treated glassy carbon electrode. *Analyst* 1998; 113: 1723-1727.
36
37 [20] Barisci J N, Wallace GG. Development of an improved on-line chromatographic monitor
38 with new methods for environmental and process control. *Analytica Chimica Acta* 1995; 310:
39 79-92.
40
41 [21] Kalcher K, Kauffmann JM, Wang J, Svancara I, Vytras K, Neuhold C and al. Sensors
42 based on carbon paste in electrochemical analysis: a review with particular emphasis on the
43 period 1990-1993. *Electroanalysis* 1995; 7: 5-22.
44
45 [22] Svancara I, Vytras K, Zima J, Barek J. Carbon paste electrodes in modern electroanalysis
46 (a review). *Crit Rev Anal Chem* 2001; 31: 311-345.
47
48
49
50
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52
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54
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60

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2
3 [23] Hamam A, Oukil D, Hammache H, Makhloufi L, Saidani B. Polypyrrole coated
4 cellulosic substrate modified by copper oxide as electrode for nitrate electroreduction, Surf
5 Rev and Lett, 2015; 22(5): 1550065.

6
7 [24] Ait Ahmed N, Hammache H, Makhloufi L, Sam S, Keffous A, Gabouze N. Effect of
8 electrodeposition duration on the morphological and structural modification of the flower-like
9 nanostructured ZnO. Vacuum 2015; 120: 100-106.

10
11 [25] Ait Ahmed N, Eyraud M, Hammache H, Vacandio F, Sam S, Gabouze N and al. New
12 insight into the mechanism of cathodic electrodeposition of zinc oxide thin films onto vitreous
13 carbon. Electrochim Acta 2013; 94: 238– 244.

14
15 [26] Ait Ahmed N, Fortas G, Hammache H, Sam S, Keffous A, Manseri A and al. Structural
16 and morphological study of ZnO thin films electrodeposited on n-type silicon. Appl Surf Sci
17 2010; 256: 7442-7445.

18
19 [27] Pearton SJ, Norton DP, Ip K, Heo YW, Steiner T. Recent advances in processing of ZnO.
20 J Vac Sci Technol B 2004; 22: 932–948.

21
22 [28] Wang Y, Yang J, Jia H, Yu M, Jin H. Self-assembled urchin-like ZnO nanostructures
23 fabricated by electrodeposition-hydrothermal method. J of Alloys and Compounds 2016; 665:
24 62-68.

25
26 [29] Hasnat MA, Amirul Islam M, Borhanuddin SM, Ullah Chowdhury MR, Machida M.
27 Influence of Rh on electrocatalytic reduction of NO_3^- and NO_2^- over Pt and Pd films, J of
28 Molecular Catalysis A: Chemical 2010; 317: 61–67.

29
30 [30] Hasnat M A, Ahamad N, Nizam Uddin S M. Silver modified platinum surface/ H^+
31 conducting Nafion membrane for cathodic reduction of nitrate ions. Appl Surf Sci 2012; 258:
32 3309–3314.

33
34 [31] Zhang X, Wang J, Wang Z, Wang Sh. Electrocatalytic reduction of nitrate at polypyrrole
35 modified electrode. Synthetic Metals 2005; 155: 95–99

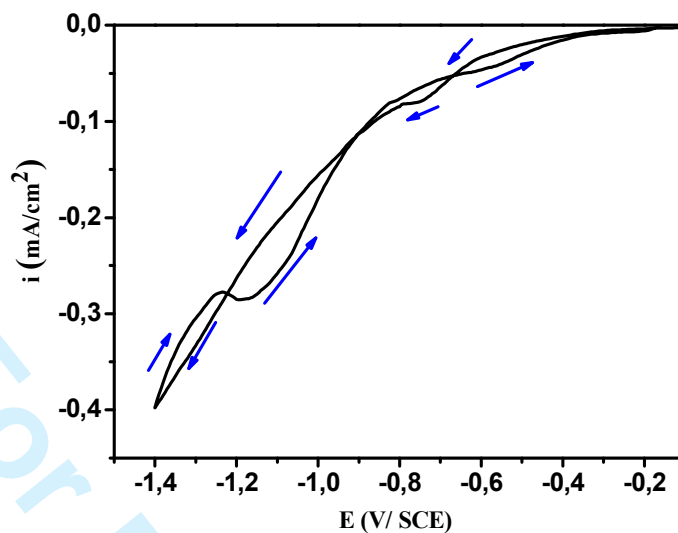


Fig.1: Cyclic voltammogram of 5mM $\text{Zn}(\text{NO}_3)_2$ + 0.1 M KNO_3 solutions recorded using Cu electrode, $\text{pH}=6.8$, $T=70^\circ\text{C}$, $V_b=8\text{mV/s}$.

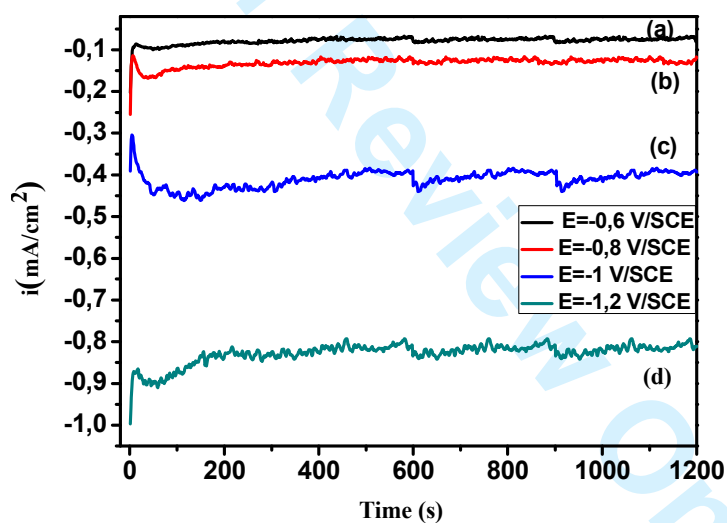


Fig.2: Chronoamperometric response of Cu electrode in solution containing: $[\text{Zn}(\text{NO}_3)_2]=5\text{mM}$ and $[\text{KNO}_3]=0.1\text{M}$ at different potentials (a) -0.6; (b) -0.8; (c) -1 and (d) -1.2V/SCE. $\text{pH}=6.8$, $T=70^\circ\text{C}$, $V_b=8\text{mV/s}$.

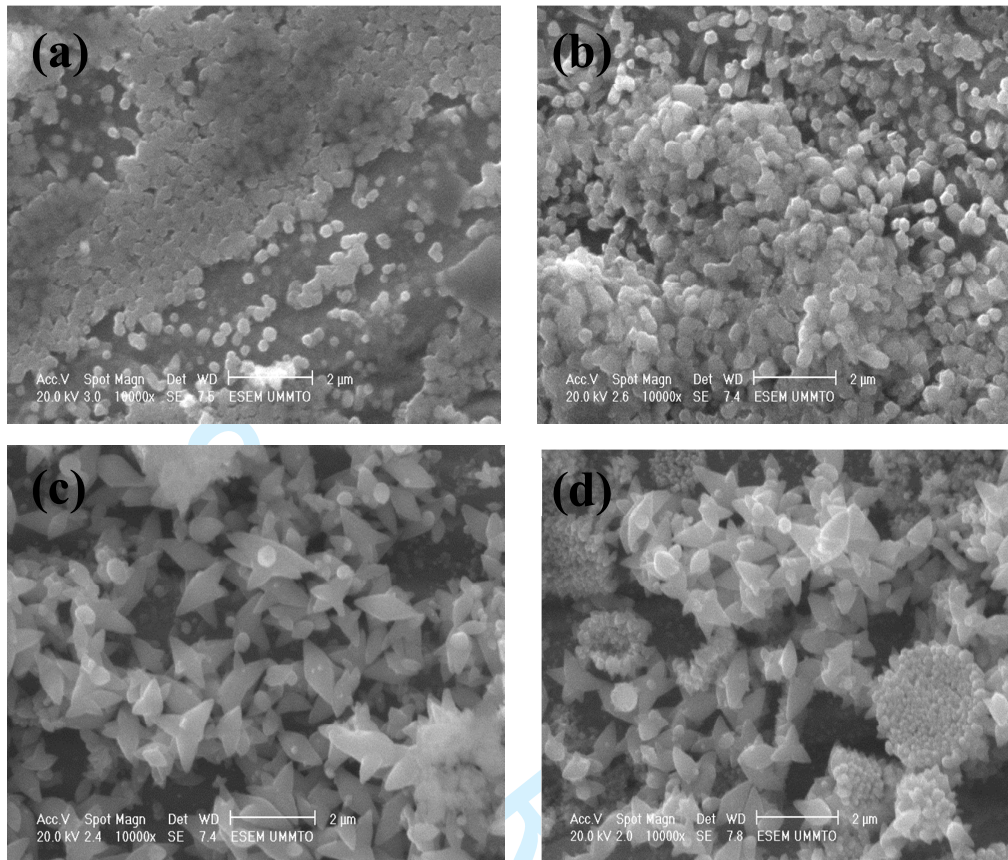


Fig.3: SEM images of ZnO thin films obtained at different deposition voltages: (a): -0.6V, (b): -0.8V, (c): -1V and (d): -1.2V.

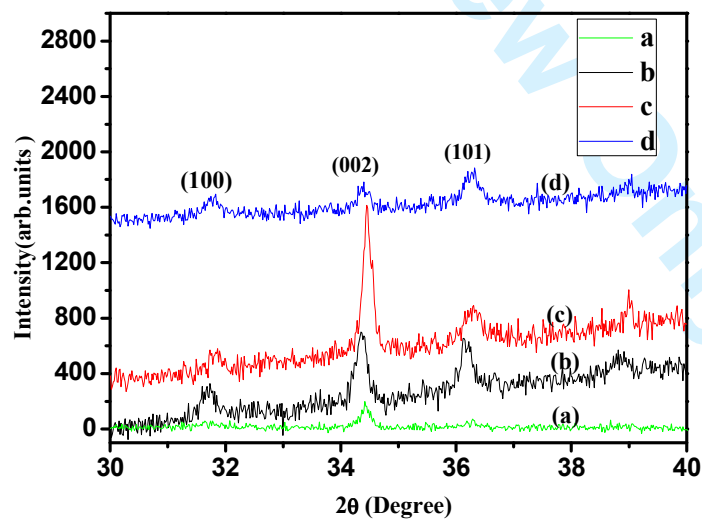


Fig.4: XRD patterns of ZnO thin films obtained at different deposition voltages: (a): -0.6V, (b): -0.8V, (c): -1V and (d): -1.2V.

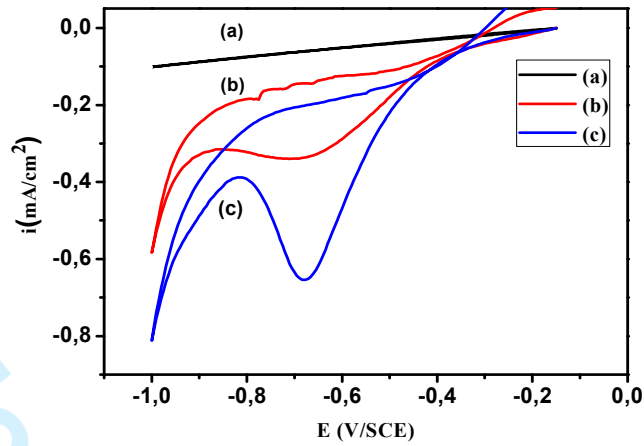
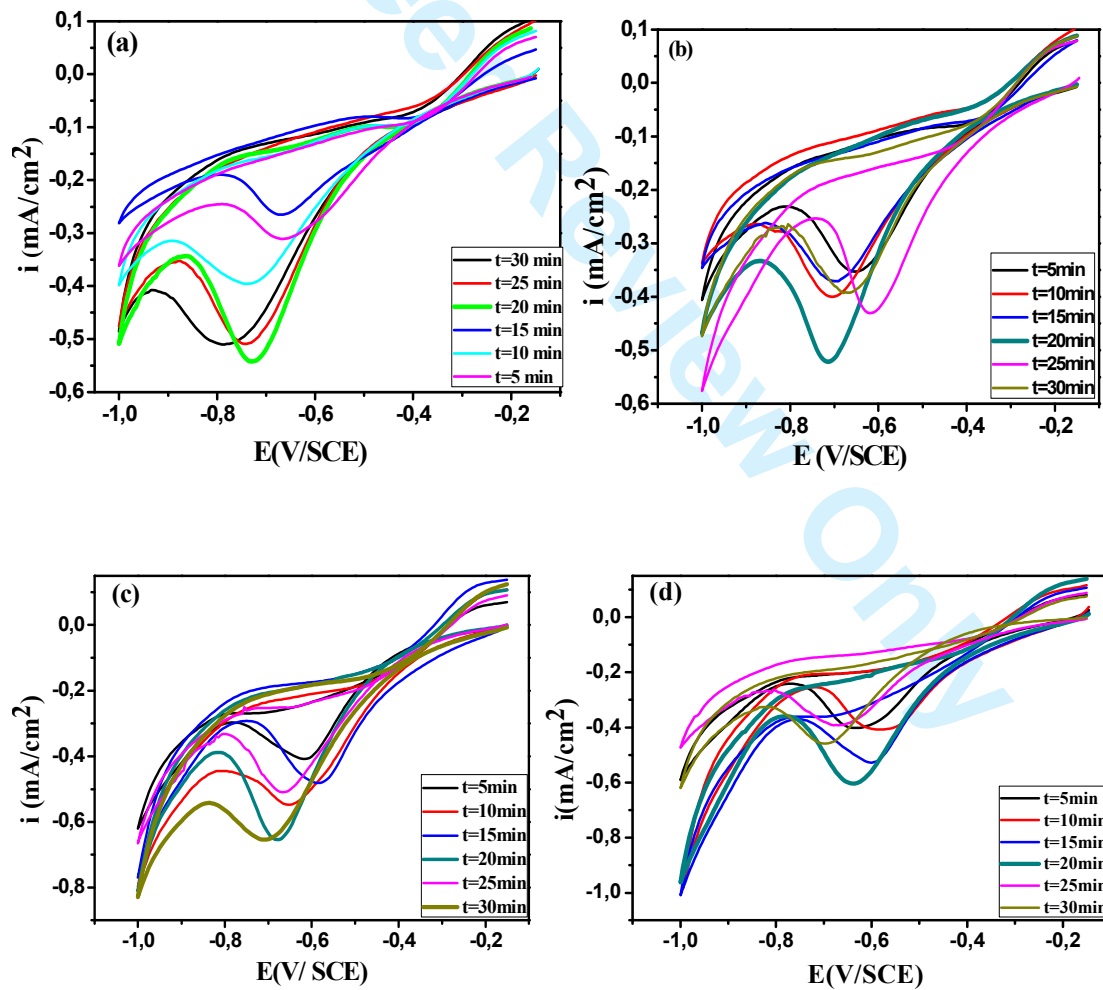


Fig.5: Cyclic voltammograms obtained at bare/Cu (a) in $[KCl] = 0.1M$ and (b) in $[KNO_3] = 0.01M$, $pH=6.9$), (c) ZnO/Cu deposited at $[E=-1V, t=20 \text{ min}, T=70^\circ C, pH=6.8]$ in $[KNO_3] = 0.01M$, $pH=6.9$), $V_b=8mV/s$.



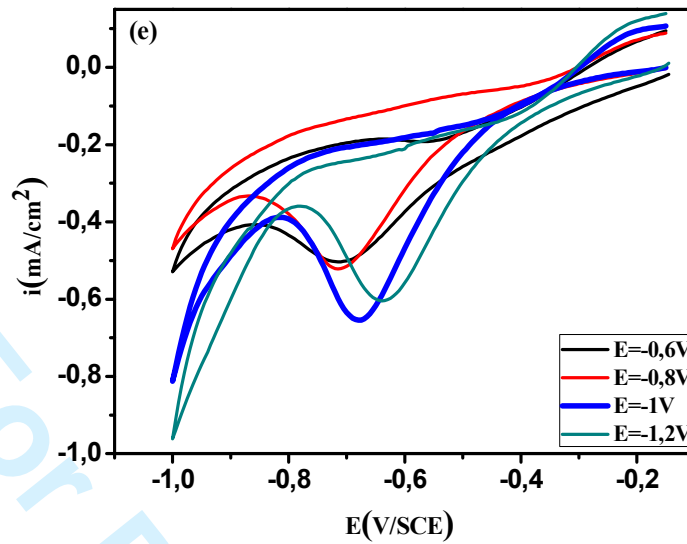


Fig. 6 : Cyclic voltammograms of ZnO modified Cu electrode in 0.01M KNO₃, (pH=6.9) at different potentials ; (a)-0.6, (b)-0.8, (c)-1, (d)-1.2 V/SCE and different deposition times ; 5,10, 15, 20, 25 and 30 min, $V_b=8$ mV/s. (e): Cyclic voltammograms of ZnO modified Cu electrode in ([KNO₃]=0.01M, pH=6.9) at different potentials ($E=-0.6$, -0.8, -1, -1.2 V/SCE) for 20 min, $V_b=8$ mV/s.

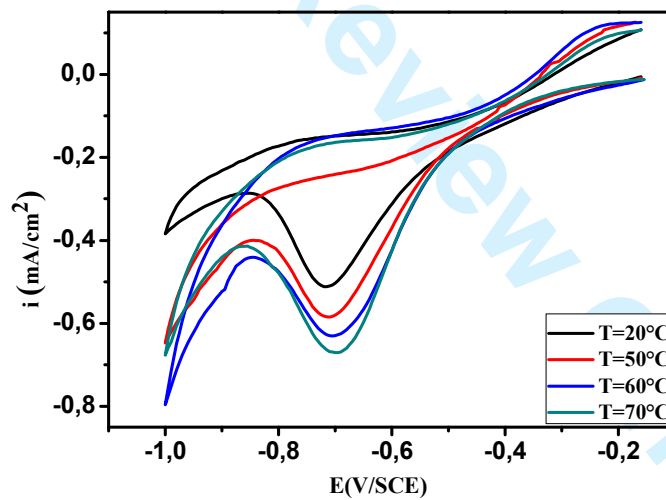


Fig.7: Cyclic voltammograms of ZnO modified Cu electrode in 0.01M KNO₃, (pH=6.9) deposited at -1V for 20 min with different temperatures, $V_b=8$ mV/s.

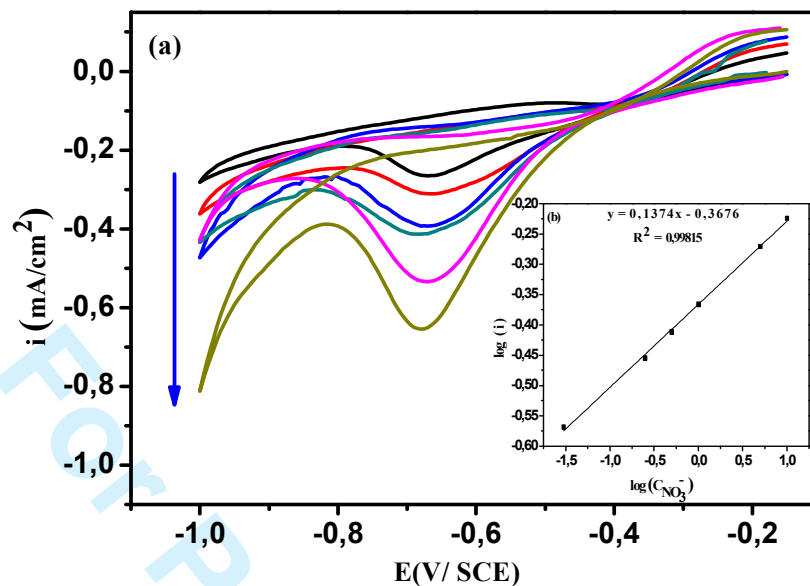


Fig.8: (a) Cyclic voltammograms of ZnO modified Cu electrode in 0.01M KNO₃, (pH=6.9) containing different nitrate concentration:0.03, 0.25, 0.5, 1, 5 and 10 mM. (b) The insert shows the log of peak current variation with log of nitrate concentrations. Scan rate 8 mV s⁻¹.

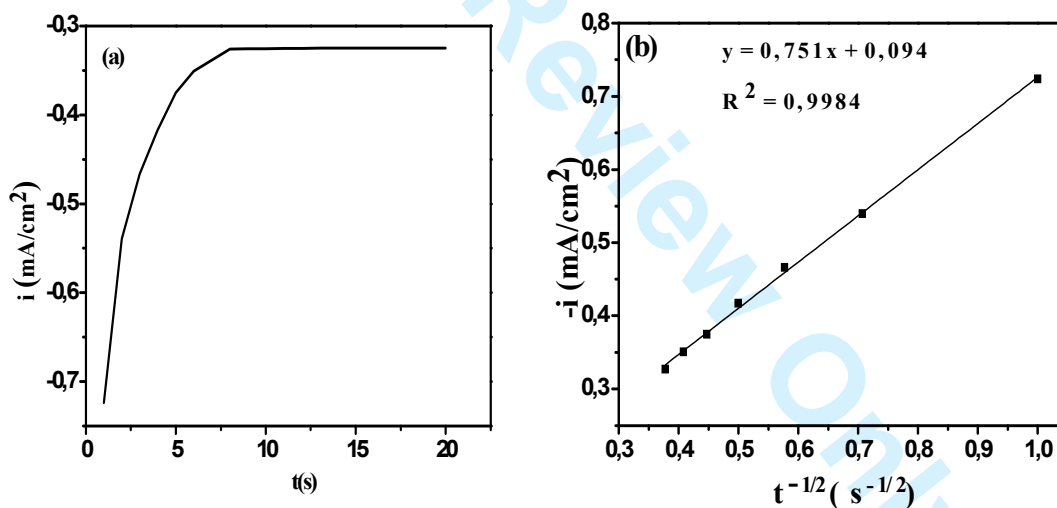


Fig.9: (a) Chronoamperometric response of ZnO modified Cu electrode in solution containing 10 mM of nitrate at imposed potential of -0.68 V/SCE (peak potential of Fig. 8). (b) Dependence of the peak current with $t^{1/2}$.

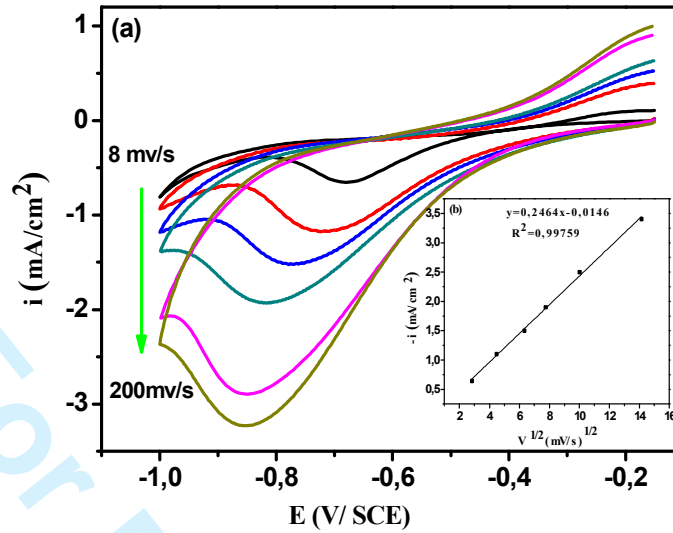


Fig.10 (a):Cyclic voltammetry sweep curve for ZnO modified Cu electrode at various scan rates from 8 to 200 mV/s in 0.01M KNO₃ (pH=6.9) and (b) the insert figure is the plot between cathodic current versus the square root of the scan rate.

Figures Captions:

Fig.1: Cyclic voltammogram of 5mM Zn (NO₃)₂ + 0.1 M KNO₃ solutions recorded using Cu electrode, pH=6.8, T=70°C, Vb=8mV/s.

Fig.2: Chronoamperometric response of Cu electrode in solution containing: [Zn (NO₃)₂] =5mM and [KNO₃] =0.1M at different potentials (a) -0.6; (b) -0.8; (c) -1 and (d) -1.2V/SCE. pH= 6.8, T=70°C, Vb=8mV/s.

Fig.3: SEM images of ZnO thin films obtained at different deposition voltages: (A): -0.6V, (B): -0.8V, (C):-1V and (D): -1.2V.

Fig.4: XRD patterns of ZnO thin films obtained at different deposition voltages: (a): -0.6V, (b): -0.8V, (c):-1V and (d): -1.2V.

Fig.5: Cyclic voltammograms obtained at bare/Cu (a) in [KCl] =0.1M and (b) in ([KNO₃] =0.01M, pH=6.9), (c) ZnO/Cu deposited at [E=-1V, t=20 min, T=70°C, pH=6.8] in ([KNO₃] =0.01M, pH=6.9), Vb=8mV/s.

Fig. 6 : Cyclic voltammograms of ZnO modified Cu electrode in 0.01M KNO₃, (pH=6.9) at different potentials ; (a)-0.6, (b)-0.8, (c)-1, (d)-1.2 V/SCE and different deposition times ; 5,10, 15,20, 25 and 30 min, Vb=8mV/s. (e): Cyclic voltammograms of ZnO modified Cu electrode in ([KNO₃] =0.01M, pH=6.9) at different potentials (E=-0.6, -0.8, -1, -1.2 V/SCE) for 20 min, Vb=8mV/s.

Fig.7: Cyclic voltammograms of ZnO modified Cu electrode in 0.01M KNO₃, (pH=6.9) deposited at -1V for 20 min at different temperatures, Vb=8mV/s.

Fig.8: (a) Cyclic voltammograms of ZnO modified Cu electrode in 0.01M KNO₃, (pH=6.9) containing different nitrate concentration:0.03, 0.25, 0.5, 1, 5 and 10 mM. (b)The insert shows the log of peak current variation with log of nitrate concentrations. Scan rate 8 mV s⁻¹.

Fig.9: (a) Chronoamperometric response of ZnO modified Cu electrode in solution containing 10 mM of nitrate at imposed potential of -0.68 V/SCE (peak potential of Fig. 9). (b) Dependence of the peak current with t^{1/2}.

Fig.10 (a):Cyclic voltammetry sweep curve for ZnO modified Cu electrode at various scan rates from 8 to 200 mV/s in 0.01M KNO₃ (pH=6.9)and (b) the insert figure is the plot between cathodic current versus the square root of the scan rate.