

## **Fabrication of Nanostructured Copper Thin Films at Disposable Pencil Graphite Electrode and its Application to Electrochemical Reduction of Nitrate**

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In this work, a galvanostatic double-pulse technique was presented for fabrication of nanostructured copper thin films. Multi-layer structure was obtained for copper deposits. The thickness of copper nanolayers was observed to be 60-70 nm using scanning electron microscopy (SEM). The resulting electrode exhibits an excellent electrocatalytic activity for the reduction of nitrate. Cyclic voltammetry (CV) shows that the nitrate ions were reduced at -0.65 V vs SCE. From kinetic order of reduction reaction of nitrate (0.95) and Tafel slope at a constant surface coverage (-1.98 V decade<sup>-1</sup>), it is concluded that the rate-determining step is the reduction of nitrate to nitrite. The reduction of nitrate is controlled by diffusion and diffusion coefficient of nitrate was calculated.

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**Keywords:** Copper, nanostructure, nitrate, electroreduction

### **1. INTRODUCTION**

Studies of nanostructured thin films have been attracting considerable attention from the researches [1-3]. The synthesis of nanomaterials requires an atomistic deposition process and extreme control over the deposition. The fact that electrochemical deposition (ED), also being an atomic deposition process, can be used to synthesize nanostructures has generated a great deal of interest in recent years [4-6]. Recently using of nanostructures in electrocatalyze application was developed [7-9]. Modulation potential techniques were developed to prepare of copper nanostructures [10, 11]. In some cases, including reversible, quasi reversible and electrochemical systems with board anodic and cathodic peaks, modulation potential techniques would not be suitable for the preparation of nanostructures. In these cases, deposited copper nuclei in nucleation pulse dissolves completely in the growth pulse. Hence, in the above mentioned electrochemical systems, galvanostatic double-pulse

technique should be applied. In this method, first an appropriate reductive pulse current was applied to the surface of substrate for a short time, as a result of which, potential of electrode was set on the diffusion plateau of  $\text{Cu}^{2+}$  ions. In this nucleation pulse, copper nuclei were produced on the surface of substrate. After a short relaxation time for the recovery of the copper /solution interface boundary, a much smaller reductive current pulse was applied to the surface of substrate for an appropriate time, which led to obtaining copper nanostructures. On the other hand, the electrochemical reduction of nitrate has a long history since 1834, when the first attempt was made by Faraday [12]. The electrochemical reduction of nitrate at different electrodic surfaces such as copper [13–15], nickel [16], copper–nickel alloys [17], copper–cadmium alloys [18], copper–palladium alloys [19], platinum [20], lead [21], silver [22], rhenium [23], boron-doped diamond [24] and gold [25] have been reported. As Copper exhibits the best electrocatalytic activity for the nitrate reduction compared to other materials [26], using of copper nanostructures for this purpose could be interest. Nucleation mechanisms and electrodeposition of copper at surface of disposable pencil graphite electrode were studied in our previous work [27]. In this work fabrication of nanostructured copper thin films and their application to electrocatalytic reduction of nitrate were investigated by electrochemical techniques.

## 2. EXPERIMENTAL PART

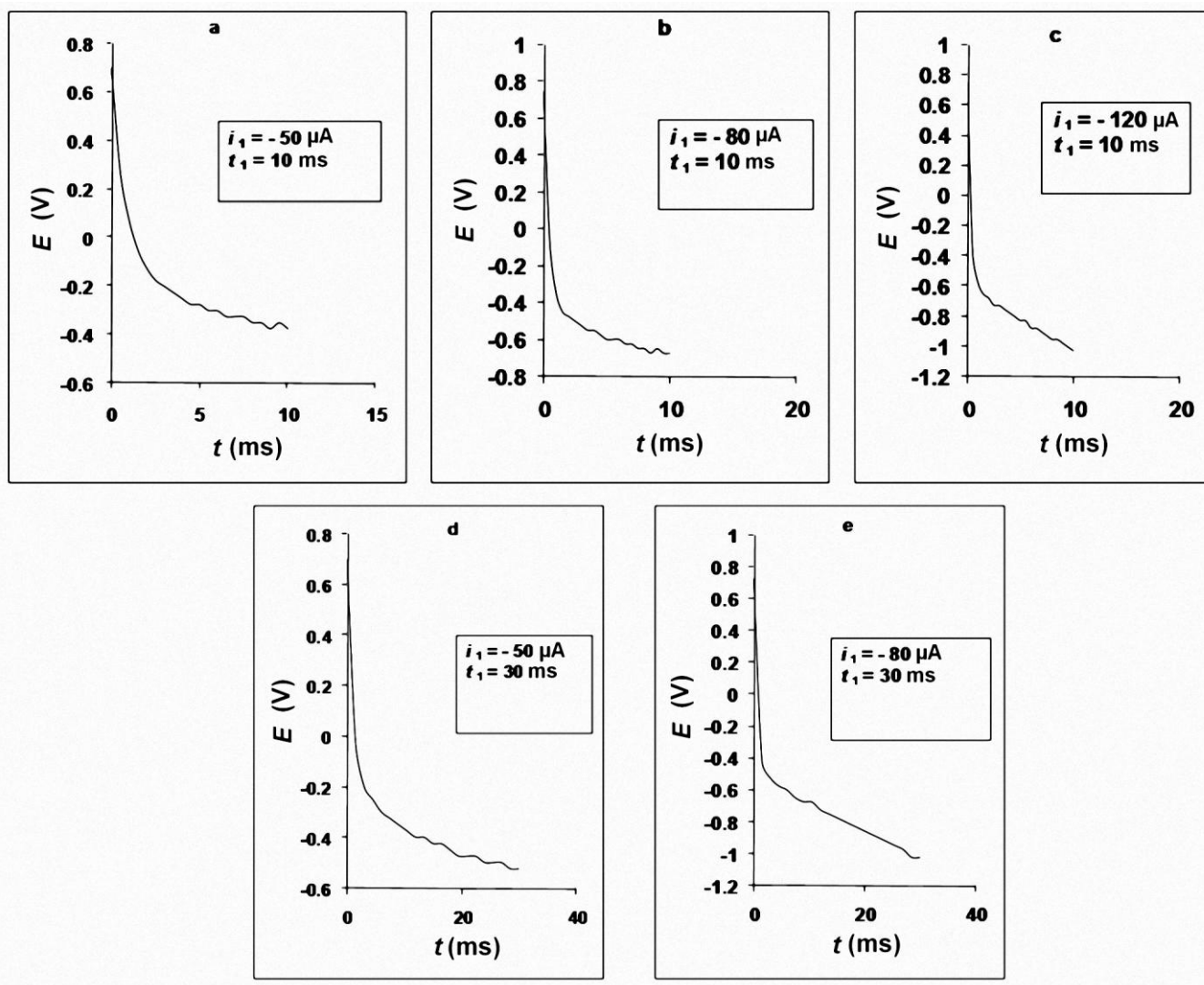
All solutions were freshly prepared from analytical-reagent grade chemicals used without further purification. All chemical reagents were purchased from Merck Chemical Co. Double-distilled water was used throughout. The electrochemical setup was a conventional three-electrode cell with a platinum wire as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials are quoted with respect to the SCE. Reference and counter electrodes were obtained from Azar Electrode Co., Urmia, Iran. The working electrode (2mm diameter) was a PGE purchased from Rotring (Germany). Electrochemical experimental conditions were adjusted by a potentiostat–galvanostat (PerkinElmer, EG&G 273 A) with computerized control (M 270 software). All experiments were performed under room temperature. Surface micrographs were obtained with a scanning electron microscope (OXFORD 7059).

## 3. RESULTS AND DISCUSSION

### 3.1. Fabrication and characterization of copper nanostructures

For the nucleation of copper at the surface of PGE an appropriate reductive pulse current must be applied so as to set potential of electrode on the diffusion plateau of  $\text{Cu}^{2+}$  ions. The duration,  $t_1$ , and the current,  $i_1$ , of the nucleation pulse must possess certain minimum values to force nucleation. On the other hand, care should be taken so that these parameters would not exceed certain maximum threshold levels. If potential of electrode is set at negative side of diffusion plateau of  $\text{Cu}^{2+}$  ions, side reduction reactions would affect the nucleation process. Fig.1a-e shows the effect of  $t_1$  and  $i_1$  on the

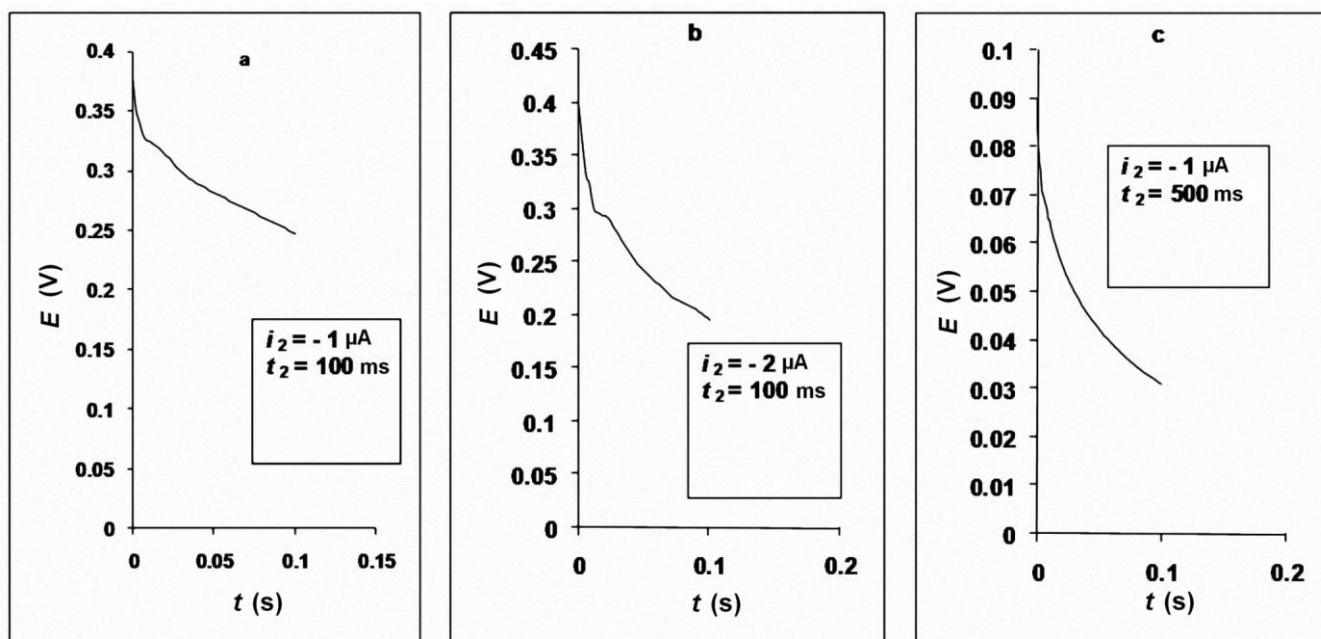
experimentally observed potential transients. It is clear that increase of  $i_1$  leads to more negative potentials (Fig.1a-c).



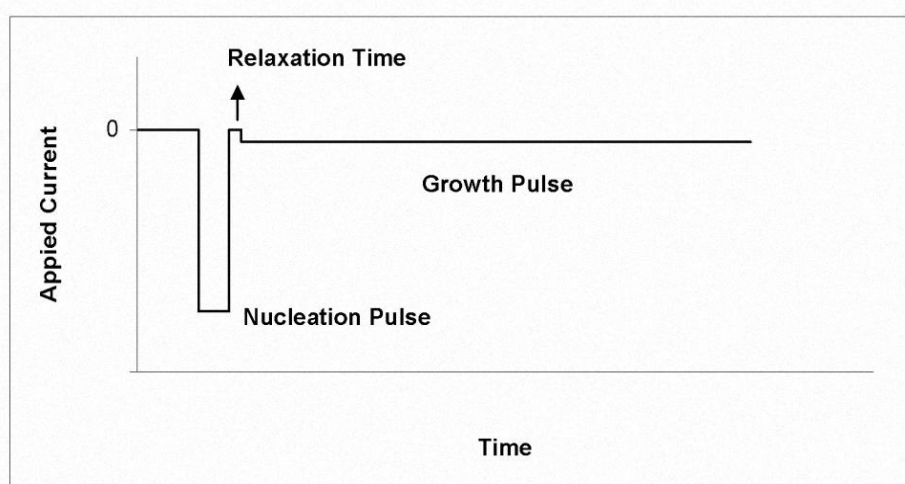
**Figure 1.** Galvanostatic potential transients for electrodeposition of  $\text{Cu}^{+2}$  (0.001 M), in presence of 0.1M  $\text{K}_2\text{SO}_4$  on PGE at different  $i_1$ ,  $t_1$  (a-e)

Also, when  $t_1$  was increased, final potential shifted to more negative values (Fig.1a, d and Fig.1b, e). It seems that the expected nucleation pulse can be achieved through controlling  $t_1$  and  $i_1$  (Fig.1b, d). In these cases, potential of the electrode was set at the values corresponding to the diffusion plateau and the appropriate duration prevents substantial growth during the nucleation pulse. It seems that applying an accumulative potential to the surface of PGE for a period of time (about 100 s) before nucleation pulse can cause the  $\text{Cu}^{2+}$  ions to be accumulated in the electrode/solution boundary layer. Therefore, when the nucleation pulse was applied, potential of the electrode reached the expected values quickly. As  $\text{Cu}^{2+}$  ions were reduced in nucleation pulse, a relaxation period was necessary for the recovery of electrode/solution boundary layer. Growth pulse has a critical role in the

preparation of nanostructures. During the growth pulse, the crystal growth has to be conducted at a slow rate, i.e. at low overvoltage.



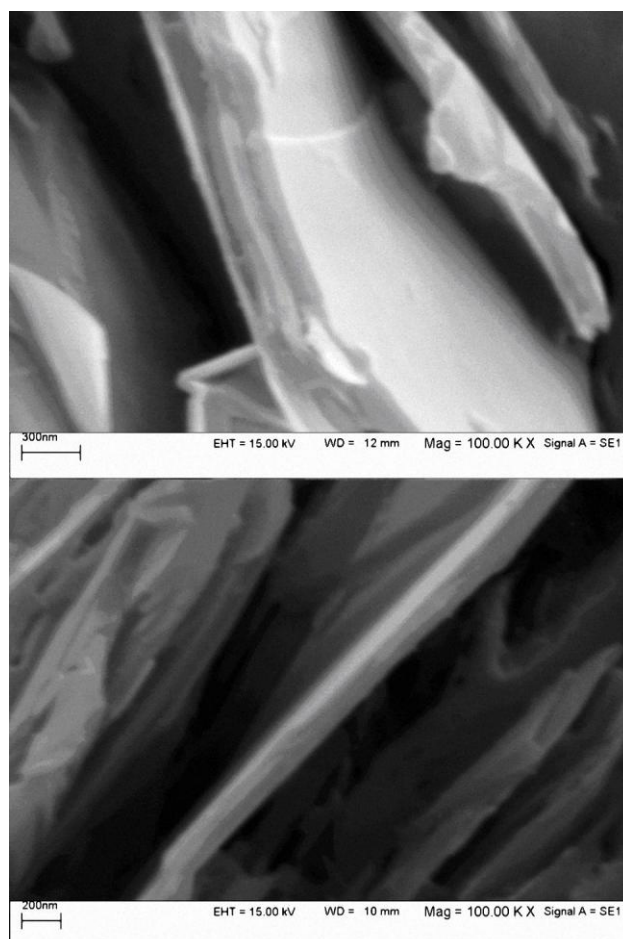
**Figure 2.** Galvanostatic potential transients for electrodeposition of  $\text{Cu}^{+2}$  (0.001 M), in presence of 0.1M  $\text{K}_2\text{SO}_4$  on PGE at different  $i_2$ ,  $t_2$  (after the proper nucleation pulse i.e. Fig.3b or Fig.3d)



**Figure 3.** Schematic representation of the galvanostatic double-pulse technique.

Therefore, the pulse current applied in the growth pulse must set the potential of electrode at potentials at which electrodeposition of copper should not be observed. For a suitable growth pulse, the effect of the two parameters  $t_2$  and  $i_2$  should be considered. The effect of  $t_2$  and  $i_2$  on the obtained potentials was presented in Fig.2 a-c. Increasing  $t_2$  or  $i_2$  caused the potential of electrode to shift to less

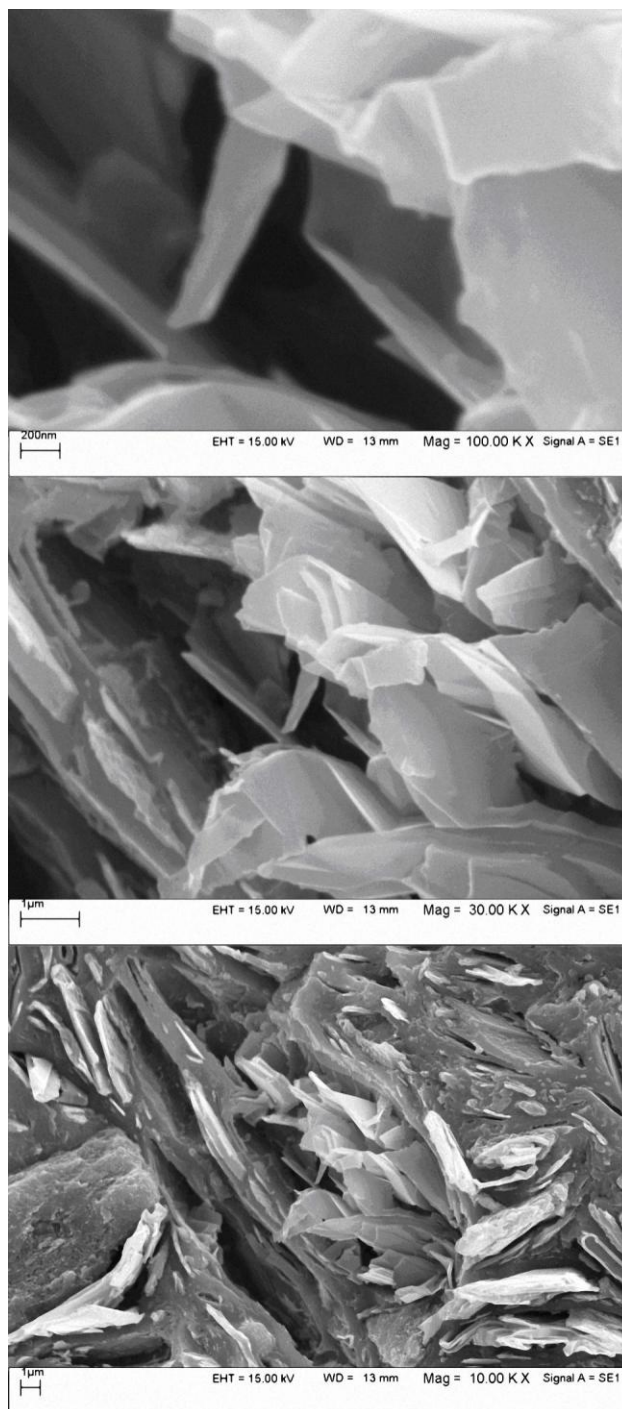
positive values. However, it should be considered that this shift to less positive potentials must not be carried out to the extent resulting in the electrodeposition of copper at the surface of PGE.



**Figure 4.** SEM images for two different PGE surfaces following the electrodeposition of  $\text{Cu}^{+2}$  (0.001 M) in presence of 0.1 M  $\text{K}_2\text{SO}_4$  using nucleation pulse ( $i_1 = -50\mu\text{A}$ ,  $t_1 = 30$  ms) and growth pulse ( $i_2 = -1\mu\text{A}$ ,  $t_2 = 100$  ms)

In this case, the growth of electrodeposited copper proceeds on the produced nuclei in the nucleation pulse. Although the potential of electrode was shifted to more positive values during switching nucleation pulse to the growth pulse, it is important to say that applying a very small reductive current in growth pulse can reduce  $\text{Cu}^{2+}$  ions on the initial copper nuclei. Fig. 3 shows the schematic representation of the galvanostatic double-pulse technique. SEM analyses have been reported of the in-plane morphology of nanoelectrodeposits [2]. Fig. 4 illustrates the SEM images for two PGE surfaces, following the electrodeposition of copper using  $i_1 = -50\mu\text{A}$ ,  $t_1 = 30$  ms in nucleation pulse, and  $i_2 = -1\mu\text{A}$ ,  $t_2 = 100$  ms in growth pulse. It has been revealed that the copper sheets had multilayer structure with thickness about 200-300 nm which thickness of each monolayer was 60-70 nm. The density of active sites at the surface of PGE is higher than those obtained at the surface of glassy carbon and highly oriented pyrolytic graphite electrodes due to its relatively large

surface area [27]; therefore, while applying a very short nucleation pulse, the initially produced copper nuclei are located above the mentioned substrate and have higher surface area than the substrates.



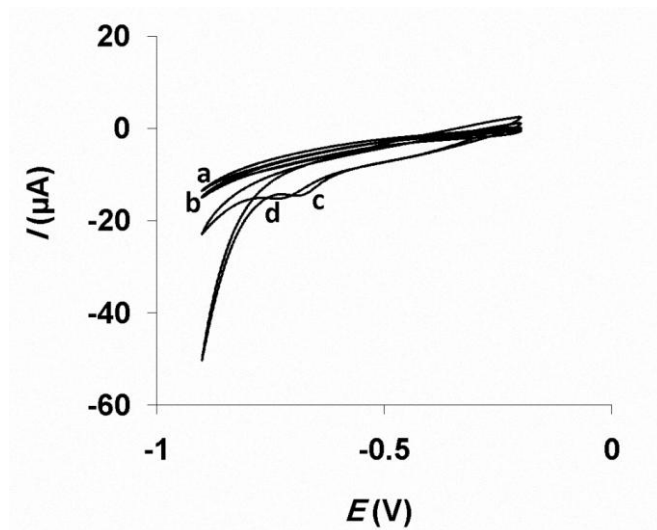
**Figure 5.** SEM images with different magnifications for a PGE surface following the electrodeposition of  $\text{Cu}^{+2}$  (0.001 M) in presence of 0.1 M  $\text{K}_2\text{SO}_4$  using nucleation pulse ( $i_1 = -50 \mu\text{A}$ ,  $t_1 = 30 \text{ ms}$ ) and growth pulse ( $i_2 = -2 \mu\text{A}$ ,  $t_2 = 100 \text{ ms}$ )

In this case, a relatively large surface area of electrodeposited copper with a thickness in nano-scale range might induce a high electrocatalytic activity for the copper deposits. The structure of

copper nanolayers was affected by the growth pulse parameters. For this purpose,  $i_2$  was increased and  $t_2$  was constant. Resulting SEM images for a PGE surfaces with different magnifications, following the electrodeposition of copper using  $i_1 = -50\mu\text{A}$ ,  $t_1 = 30\text{ ms}$  in nucleation pulse, and  $i_2 = -2\mu\text{A}$ ,  $t_2 = 100\text{ ms}$  in growth pulse were presented in Fig.5. An increase in  $i_2$  produced copper nanolayers with relatively large surface area. As discussed above, the reductive pulse current in growth pulse must not be able to reduce  $\text{Cu}^{2+}$  ions; therefore, when the duration of growth was constant, the thickness of nanolayer of electrodeposited copper was not affected (Fig.5a-c) and the surface of copper deposits may have increased as a result of the applied pulse current passing from all of the surface in the short duration of growth pulse.

### 3.2. Electrocatalytic reduction of nitrate ions

Fig.6 shows the electrocatalytic reduction of nitrate ions at surface of copper modified pencil graphite electrodes. Electroreduction of nitrate ions were studied at surface of PGEs modified with copper nano and bulk structures.



**Figure 6.** Cyclic voltammetry of pencil graphite electrode in  $0.05\text{ M K}_2\text{SO}_4 + 0.01\text{ M H}_2\text{SO}_4$  at scan rate of  $20\text{ mVs}^{-1}$  (a) bare, (b) modified with Cu nanostructure in absence of  $\text{KNO}_3$ , (c) modified with Cu nanostructure in presence of  $2\text{mM KNO}_3$ , (d) modified with Cu bulk structure in presence of  $2\text{mM KNO}_3$

The nano-scale structure of copper thin films caused that the reduction potential of nitrate ions shifted to less negative values than when copper bulk structures were used. A linear relation between electrode potential and the logarithm of the reduction current density (Tafel line) holds in the potential range between  $-0.5$  and  $-0.63\text{ V}$  with a slope of  $-1.98\text{ V decade}^{-1}$  and independent of the nitrate concentration. Obtained slope indicates that two electron ( $\alpha=0.75$ ) is exchanged in the rate-determining step. The kinetic order of reduction reaction of nitrate ( $0.95$ ) can be obtained from the slope of linear

relation between the logarithm of reduction current density and the logarithm of concentration (related figures were not shown). From these results, it is concluded that one nitrate ion exchanges two electron at the surface of modified electrode. In acidic media nitrite can be produced therefore this mechanism is proposed:

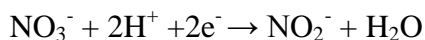
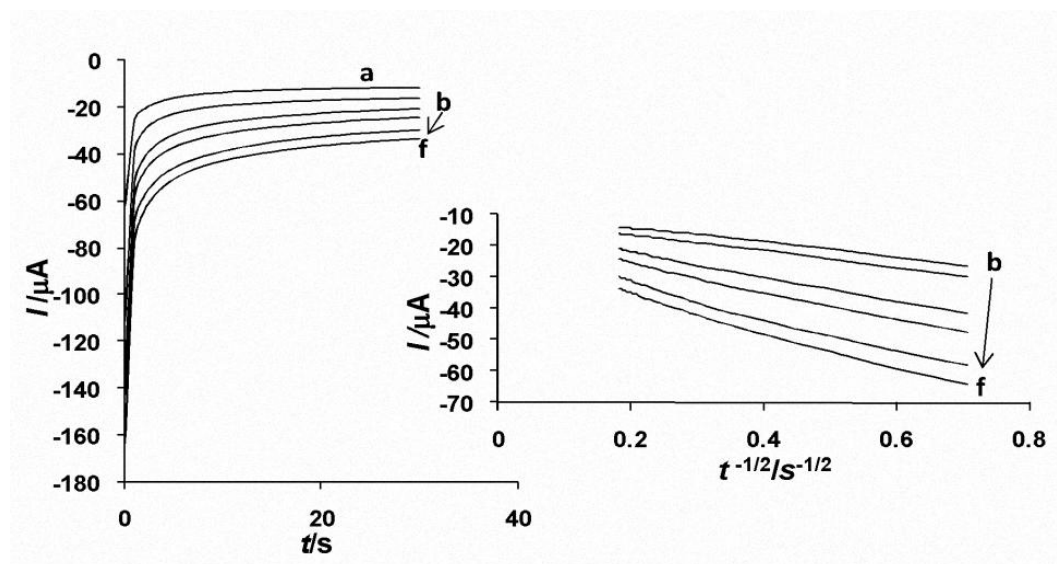


Fig.7 shows the chronoamperometric response of nanostructure modified electrode with and without of nitrate ions, and steady state conditions. Diffusion coefficient of nitrate can be calculated from the slope of the curve plotted between current and  $t^{-1/2}$  (inset in Fig.7). Diffusion coefficient of nitrate in mentioned media is calculated  $0.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  using of chronoamperometry technique.



**Figure 7.** Chronoamperometric response of Cu nanostructure modified electrode in 0.05M  $\text{K}_2\text{SO}_4$ , pH = 2, step voltage: -0.7V, (a) in absence of  $\text{KNO}_3$ , (b→f) in presence of different concentration of  $\text{KNO}_3$ .

#### 4. CONCLUSIONS

Copper nanostructures were fabricated using galvanostatic double-pulse technique and their ability to electrocatalytic reduction of nitrate ions was evaluated by electrochemical techniques. The following conclusions can be made.

1. Copper nanostructures were prepared in multi-layer form where thickness of each mono layer was about 60-70 nm.
2. Structure of nanolayers of copper deposits was affected by parameters of nucleation and growth pulses.
3. Electrocatalytic reduction of nitrate ions was affected by structure of electrocatalyst.



4. At surface of modified electrode nitrate was reduced to nitrite by exchanging two-electron in rate-determining step.

#### ACKNOWLEDGMENTS

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