

## Application of copper oxide nanoparticles modified glassy carbon electrode for electrocatalytic oxidation of methanol

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### ABSTRACT

Copper nanoparticles were fabricated by electro-reduction of  $\text{CuSO}_4$  solution in the presence of cetyltrimethylammonium bromide (CTAB) cationic surfactant as an additive through potentiostatic method. The prepared copper nanoparticles were characterized by scanning electron microscopy (SEM) and electrochemical methods. The SEM images reveal that the nanoparticles with diameters at about 70 nm were uniformly dispersed on the electrode surface. Copper oxide nanoparticles modified glassy carbon electrode (nano CuO/MGCE) was prepared by using consecutive potential cycling between -1.0 to 1.0V at  $100\text{mVs}^{-1}$  in 0.1 M NaOH solution. The electrochemical techniques such as cyclic voltammetry and chronoamperometry showed that the nano CuO/MGCE can catalyze the methanol oxidation in 0.1 M NaOH solution. It has been found that in the course of an anodic potential sweep, the methanol oxidation follows the formation of  $\text{Cu}^{\text{III}}$  and is catalyzed by this species through a mediated electron transfer. Also, the modified electrode was stable for three weeks in dry conditions after repetitive measurements.

**Keywords:** Copper oxide nanoparticles, Electrocatalytic oxidation, Methanol, Cyclic voltammetry

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### 1. INTRODUCTION

In the past decades, much attention has been paid to fuel cells because they offer highly efficient and environmentally friendly technology for energy conversion. However, the use of hydrogen is limited by problems of production, purification, storage and distribution. Compared with other fuel cells, direct methanol fuel cell (DMFC) has several advantages such as high efficiency, very low polluting emis-

sions, a potentially renewable fuel source and convenient refueling. The low operation temperature of a DMFC (typically  $<95\text{ }^\circ\text{C}$ ) allows for easy start up and rapid response to changes in load or operating conditions [1]. On the other hand, slow kinetic of the methanol oxidation on several electrode materials is one of the unsolved problems in development of DMFCs and represents a serious impediment in the use of electro-

chemical methods, based on the direct oxidation of this molecule on the electrode [2]. Thus, a number of investigations have been carried out to decrease the typically large over-voltages encountered in the direct oxidation of methanol at most unmodified electrode surfaces [3, 4]. The mechanism and kinetics of methanol oxidation have been studied under a wide range of conditions and on a variety of electrodes including Pt [5], binary and ternary alloys [6] and nanocomposites [7]. Although noble metals such as Pt and its alloys exhibit fairly good activities in the methanol oxidation, they are too expensive to afford practical applications. Thus, the possibility of methanol electrooxidation on non-noble metals is sought. One approach to the development of DMFC is to use alkaline electrolyte which is based on the assumption that electrocatalysis is generally more facile in this medium. In recent years, multi-electron oxidation processes, C–C bond cleavage and generation of lower molecular weight products from organic substrates on copper-based electrodes in alkaline solutions have received considerable attention [8, 9]. To our best knowledge, there is no report on the application of the nano-CuO/MGCE for electrocatalytic oxidation of methanol in literature. The general objective of the present work is to obtain an application for the nano-CuO/MGCE in the electrocatalysis of methanol oxidation in an alkaline medium.

## 2. EXPERIMENTAL

### 2.1 Apparatus and materials

The electrochemical experiments were performed using a potentiostat/galvanostat (Sama 500-c electro-chemical analysis system, Iran) coupled with a Pentium IV personal computer to acquire gain the data. A conventional

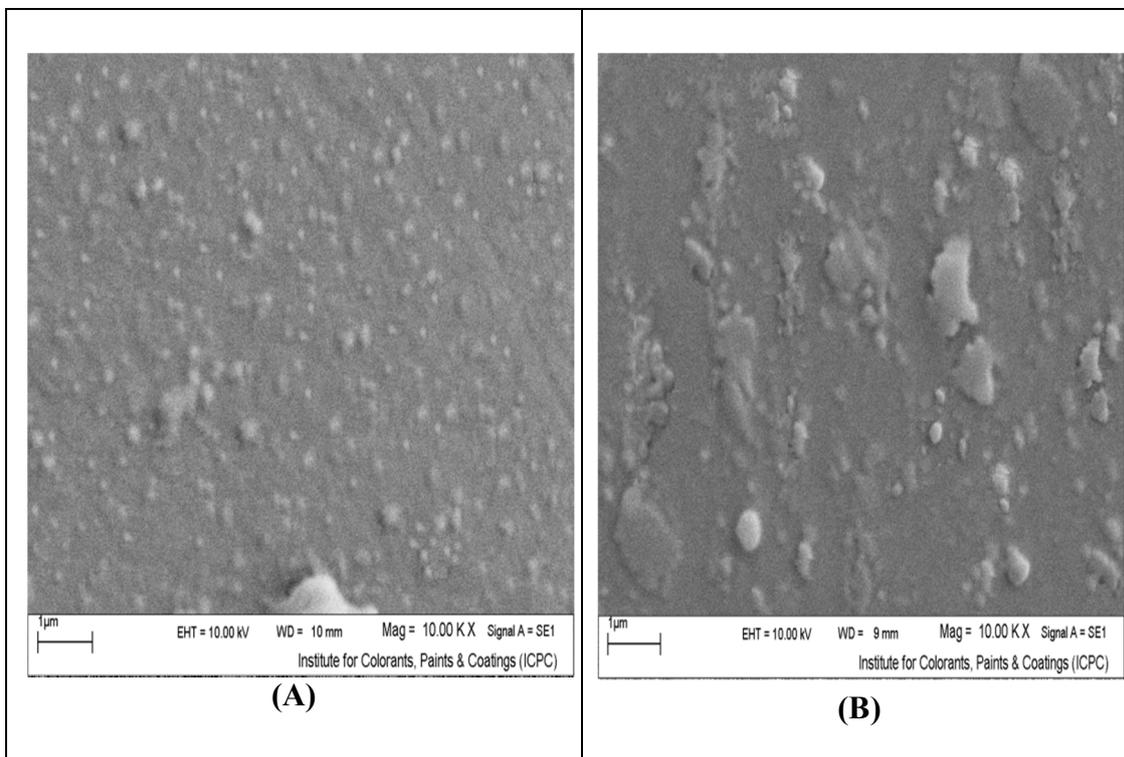
three electrode cell was used with Ag|AgCl|KCl(3M) as reference electrode, platinum wire as auxiliary electrode and Glassy carbon (geometric surface area=0.03 cm<sup>2</sup>) (Azar Electrode Co., Iran) as working electrode. All experiments were carried out at ambient temperature. The surface morphologies of the deposits were confirmed by scanning electron microscopy (SEM) (Leo1455VP, Oxford Instrument, Institute for Colorants, Paints & Coating (ICPC)). Sodium hydroxide, methanol and sulfuric acid used in this work were analytical grade of Merck origin and used without further purification. CTAB and CuSO<sub>4</sub> were purchased from Fluka.

### 2.2. The fabrication of the nano-CuO/MGCE

Modification of the GCE was performed according to the procedure proposed by Ding Hai-Yun et al [10]. Briefly; the GCE was carefully polished with alumina slurries on a polishing cloth. Then, the electrode was placed in absolute ethanol and sonicated to remove adsorbed particles. Cyclic voltammetry was performed in 0.1 M NaOH solution between -0.256 and +0.744 V vs. Ag|AgCl|KCl (3 M) at  $v = 100 \text{ mV s}^{-1}$ . Cu nanoparticles was initially deposited through constant potential process (-0.056 V for 480 s) in an electrolyte composed of 6 mL  $5.0 \times 10^{-3} \text{ M CuSO}_4 + 2 \text{ mL } 1.0 \times 10^{-2} \text{ M CTAB} + 2 \text{ mL } 2.5 \times 10^{-2} \text{ M H}_2\text{SO}_4$ . Then, the electrode was removed, rinsed with water and the sides wiped with soft tissue paper. Figure 1 shows the SEM image of the copper nanoparticles modified GCE. As can be seen, the Cu nanoparticles were uniformly dispersed on the GCE surface with diameter of approximately 70 nm. When the electrolyte did not contain CTAB, conjugated Cu particles with diameter of about 0.7  $\mu\text{m}$  were

deposited. After this, the polarization behavior was examined by using consecutive potential cycling between -1.0 to +1.0 V at  $v = 100 \text{ mV s}^{-1}$  in 0.1 M NaOH solution. This technique

allows the oxide (hydroxide) formation in parallel to inspecting the electrochemical reactivity of the electrode surface.



**Fig. 1.** Typical SEM images of the (A) copper nanoparticles prepared in the presence of CTAB and (B) copper microparticles prepared in the absence of CTAB.

### 3. RESULTS AND DISCUSSION

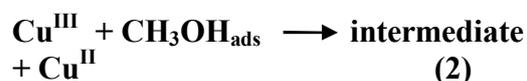
#### 3.1. Electrocatalytic oxidation of methanol on the nano CuO/MGCE

The electrocatalytic oxidation of methanol was investigated in 0.1 M NaOH solution onto the nano CuO/MGCE by using cyclic voltammetry method and the CVs were shown in Fig. 2. Trace (a) in this figure shows the background current of a bare GCE in 0.1 M NaOH solution and trace (b) shows the cyclic voltammogram of the bare GCE in the same solution containing 0.116 M methanol. There is no obvious peak corresponding to the methanol oxidation at bare GCE surface in potential range between 0.25 and 1.0 V. Curve (c) is the

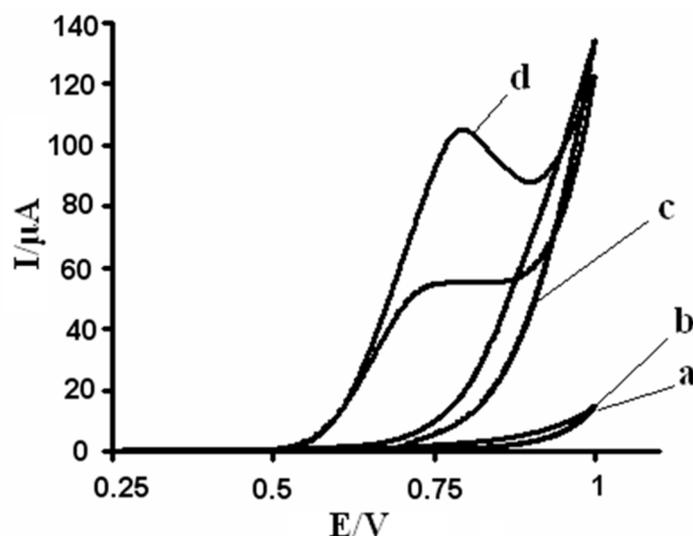
electrochemical response of the nano CuO/MGCE in the absence of methanol and curve (d) is the voltammetric response in the presence of the same methanol concentration. As can be seen, the oxidation current related to methanol at the modified electrode surface is significantly increased. This behavior is typical of that expected for electrocatalysis at chemically modified electrodes. The results indicate that the nano CuO/MGCE can catalyze the methanol oxidation. Voltammetry process of the copper nanoparticles in 0.1 M NaOH solution produces  $\text{Cu}^{\text{III}}$  which is an effective component that catalyzes the oxidation of methanol in this medium

[11-17]. It should be mentioned that methanol is inactive at copper electrode at low potentials and it must dissociate prior to oxidation and group IB metals are not well capable of dissociatively adsorbing methanol. So, it seems that methanol initially chemisorbs on the lower valence state copper oxides and further oxidizes through reactive species. Moreover, the peak due to methanol oxidation is reproducible with no evidence of film formation or electrode passivity. There is ample evidence in literature regarding the role of  $\text{Cu}^{\text{III}}$  species in the oxidation of organic substrates [18]. This species that is generated at positive potentials has a vital role of redox mediator. The electrode reaction may take place with a mechanism involving a rate limiting step where an intermediate is formed upon a chemical reaction with  $\text{Cu}^{\text{III}}$  species. Without going into the details

of the surface structure of  $\text{Cu}^{\text{III}}$  species, we simply assume that it originates from the  $\text{Cu}^{\text{II}}$  species of one kind or another and goes on to propose the following mechanism for the electro-oxidation of methanol in alkaline solutions [13]:



Where the intermediate is further oxidized to the product, formate or carbonate, through a similar oxidation process:



**Fig. 2.** Cyclic voltammograms of a bare GCE (a) and the nano CuO/MGCE (c) in 0.1 M NaOH solution in the absence of methanol, (b) as (a) and (d) as (c) in the presence of 0.116 M methanol at  $\nu=20 \text{ mV s}^{-1}$ .

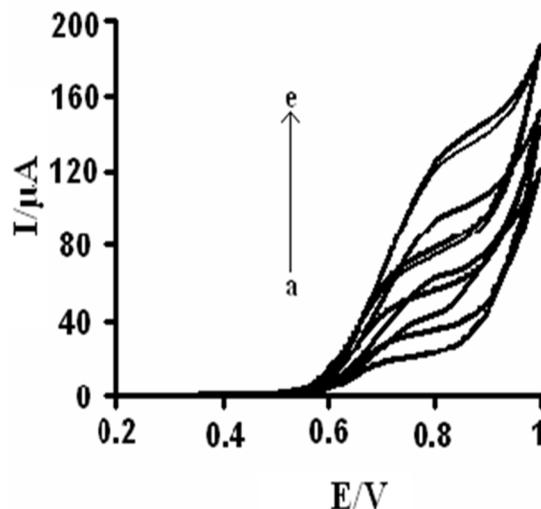
### 3.2. The effect of methanol concentration

Figure 3 shows the effect of methanol concentration on the cyclic voltammograms of the nano CuO/MGCE. It

shows that upon increasing of methanol concentration, its irreversible oxidation develops in the region of the electrochemical formation of  $\text{Cu}^{\text{III}}$ .

Thus, it is likely that the electro-generated  $\text{Cu}^{\text{III}}$  species is the active moiety, which efficiently speeds up the methanol oxidation. Any increasing in methanol concentration causes an enhancement of the anodic peak. It

appears that at the excess methanol concentrations, adsorption sites are saturated and no fresh Cu sites will be available for further adsorption.



**Fig. 3.** Current-potential curves of the nano CuO/MGCE in 0.1 M NaOH solution in the presence of different methanol concentrations: (a) 0.019, (b) 0.039, (c) 0.078, (d) 0.116 and (e) 0.154 M at  $\nu=20 \text{ mV s}^{-1}$ .

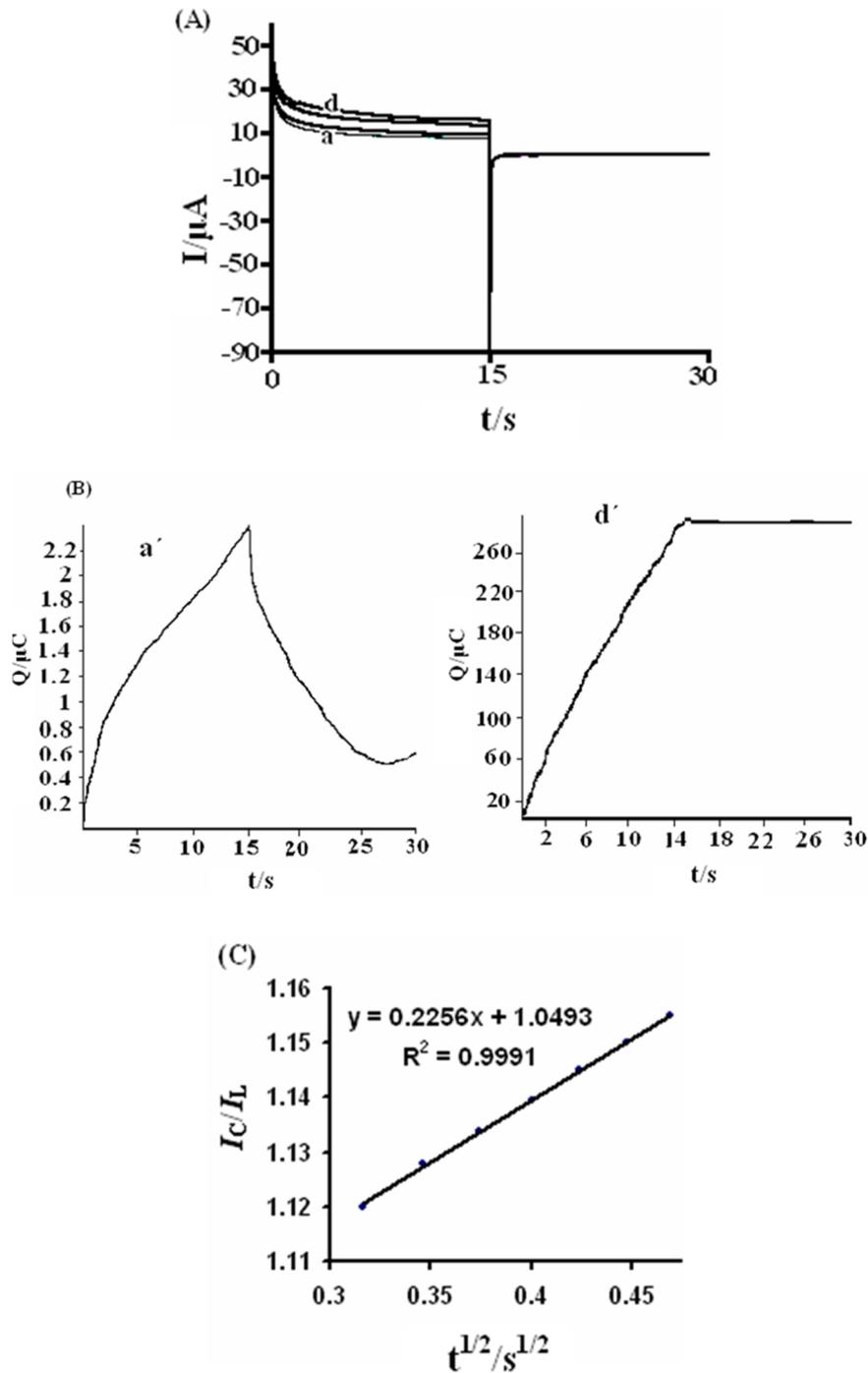
### 3.3. Chronoamperometric studies

Chronoamperometry was used to investigate of electrochemical processes at the modified electrode. Figure 4A represents the chronoamperograms in the absence and presence of methanol at various concentrations in 0.1 M NaOH solution. The transient current is due to catalytic oxidation of methanol and varies correspondingly and also the current increases as the methanol concentrations are raised. No cathodic current is observed when the electrode potential is stepped to 0.0 V, indicating the irreversible nature of methanol oxidation. As can be seen in Figure 4B (a'), the forward and backward potential step chronoamperometry of the modified electrode in the blank solution show an almost

equal charges consumed for the oxidation/reduction process of the surface-confined sites. However, in the presence of methanol, the charge value associated with the forward chronoamperometry is greater than that of backward (Figure 4B (d')). Chronoamperometry can also be used for evaluation of the chemical reaction between methanol and the catalyst layer (catalytic rate constant,  $k$ ) according to equation 4 [19]:

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

where,  $I_L$ ,  $I_C$ ,  $k$ ,  $c$  and  $t$  are currents in the absence and presence of methanol, the catalytic rate constant, the bulk concentration of methanol and the



**Fig. 4:** (A) Double potential step chronoamperograms of the nano CuO/MGCE in 0.1 M NaOH solution containing different methanol concentrations: (a) 0.00, (b) 0.078, (c) 0.10 and (d) 0.161 M. (B) The dependency of charge  $Q$  vs.  $t$  derived from the data of chronoamperograms of (a) and (d). (C) The dependency of  $I_C/I_L$  on  $t^{1/2}$  derived from the data of chronoamperograms (a) and (d) in the main panel.

elapsed time, respectively. From the slope of the  $I_C/I_L$  vs.  $t^{1/2}$ , presented in Figure 4C, the mean value of the  $k$  for methanol concentration ranging from 0.078 to 0.161 M is calculated to be

about  $4.2 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . At the end of this work, stability of the modified electrode was investigated and results show that it is stable for

three weeks in dry conditions after repetitive measurements.

#### 4. CONCLUSION

The present work demonstrates an application of the nano CuO/MGCE for electrocatalytic oxidation of methanol in 0.1 M NaOH solution. The electrochemical behavior of methanol at bare GCE in basic medium is poor and methanol does not undergo oxidation prior to discharge of the supporting electrolyte. The copper nanoparticles modifying the electrode surface have played a mediate role on the heterogeneous catalytic oxidation of methanol. The oxidation process commences at a potential where the oxidizing Cu<sup>III</sup> species are generated. The *k* value indicates that the modified electrode can overcome the kinetic limitation of methanol oxidation by a catalytic process and can decrease the overpotential of methanol oxidation reaction.

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## کاربرد الکتروکاتالیزور کربن اصلاح شده با نانوذرات مس (II) اکسید در اکسایش الکتروکاتالیزوری متانول

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### چکیده:

نانوذرات مس با کاهش الکتروشیمیایی محلول مس (II) سولفات در حضور سورفکتانت کاتیونی CTAB به عنوان ماده افزودنی از طریق روش پتانسیو استاتیک تهیه شد. نانو ذرات تهیه شده توسط میکروسکوپ الکترونی روبشی (SEM) و روش های الکتروشیمیایی مشخصه یابی شدند. تصاویر SEM نشان داد که نانو ذرات با اندازه ذرات ۷۰ نانومتر بطور یکنواخت بر روی سطح الکتروکاتالیزور پخش شده است. الکتروکاتالیزور کربن اصلاح شده با نانوذرات مس (II) اکسید (CuO/MGCE) به کمک چرخه زنی پتانسیلی متوالی بین -۱ تا +۱ در ۱۰۰ میلی ولت بر ثانیه در محلول ۰/۱ مولار سدیم هیدروکسید تهیه شد. تکنیک های الکتروشیمیایی مانند ولتامتری چرخه ای و کرومیاپرومتری نشان داد که الکتروکاتالیزور (CuO/MGCE) قادر به کاتالیز کردن واکنش اکسایش متانول در محلول ۰/۱ مولار سدیم هیدروکسید است. مشخص شد که در طی روبش پتانسیل آندی، واکنش اکسایش متانول از تشکیل گونه Cu(III) پیروی کرده و واکنش توسط این گونه از طریق انتقال الکترون کاتالیز شده است.

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