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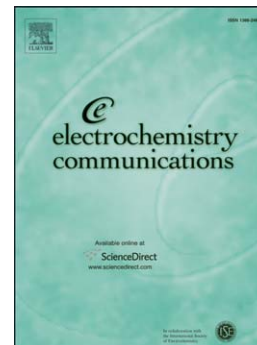
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**Electrochemical reduction of CO<sub>2</sub> in water-acetonitrile mixtures on nanostructured Cu electrode**

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**Abstract**

This communication studies the CO<sub>2</sub> reduction reaction in H<sub>2</sub>O/CH<sub>3</sub>CN mixtures on nanostructured copper. It was found that nanostructured copper electrode presents a well-defined voltammogram in acetonitrile, where it can be seen three signals related to adsorbed or surface attached (thin films) species. Also, it was found that the current density of CO<sub>2</sub> reduction in mixtures H<sub>2</sub>O/CH<sub>3</sub>CN on nanostructured copper electrodes with a molar fraction around 0.25 is higher than those observed with molar fractions lower than 0.15 or higher than 0.35. Finally, nanostructured Cu electrodes show higher catalytic activity towards the CO<sub>2</sub> reduction than copper electrode.

**Keywords:** nanostructured copper, Au electrode, CO<sub>2</sub> reduction, electrocatalysis, water-acetonitrile mixtures

## Introduction

There is an urgent need for the development of catalysts capable to reduce  $\text{CO}_2$  at low overpotentials, as an alternative to storage energy in fuels and to avoid the consequences of global warming, caused by the continuous increasing of atmospheric  $\text{CO}_2$  levels [1]. The most extensively electrode employed in the electrochemical reduction of  $\text{CO}_2$  is metallic copper [2-4]. On this electrode  $\text{CO}_2$  is reduced to form hydrocarbons, aldehydes and alcohols in an aqueous media, but in nonaqueous supporting electrolytes CO is the main product. One of the drawbacks in using Cu electrodes is its fast deactivation, usually observed after 30 minutes of the electrolysis [5]. The presence of Cu-complexing agents in the supporting electrolyte, such as ammonia or pyridine, enhanced the efficiency of the electrochemical reduction [6]. Another way to tune the mechanism of  $\text{CO}_2$  reduction is to change the chemical environment around copper nanoparticles. For example, when Cu is supported on a cation-exchange membrane, the main product is ethane, while Cu on an anion-exchange membrane is selective to the formation of formaldehyde [6].

Many reports have shown that the  $\text{CO}_2$  reduction is a surface sensitive reaction on Cu electrodes [7,8]. In this sense many protocols have been proposed to synthesize copper electrodes with altered surface structures, as the electrochemically reduction of thin film of metal oxides [9-12] or the electro-deposition of copper at high overpotentials [13]. Density functional theory (DFT) calculations [2,3] have suggested that the key step in the formation of hydrocarbons from  $\text{CO}_2$  is the protonation of adsorbed  $\text{CO}^*$  to form adsorbed  $\text{CHO}^*$ . Durand *et al.* [13] found by DFT calculations that the most active surface to achieve the

electro-reduction process is the Cu(211) facet. Also, it has been shown that nanostructured Cu electrode and nanoparticles have many advantages as electrocatalysts for CO<sub>2</sub> reduction. The enhanced electrocatalysis is usually explained taken into account changes on the surface area and morphology of the material [14].

It is well known that the reduction of CO<sub>2</sub> in water is not very efficient due to the low solubility of CO<sub>2</sub> and the high H<sub>2</sub> production. Acetonitrile is often used in electrochemistry due to its high dielectric constant and potential window, but a proton source, like water, has to be added in order to obtain better products, like methane or methanol, at low overpotentials [15-16].

This communication is focused on the study of a suitable catalyst based on nanostructured Cu electrodes for the electrochemical reduction of CO<sub>2</sub> towards compounds that can be used as alternative fuels (like alcohols or methane). Taken into account that water has a high dielectric constant, it is a weak acid and miscible with acetonitrile, we decided to study the CO<sub>2</sub> reduction in mixtures of H<sub>2</sub>O/CH<sub>3</sub>CN by cyclic voltammetry.

## **Materials and methods**

Electrodeposition of copper was done using a two-electrode cell. A copper disk (99,9 %) was used as working electrode. It was polished with 3 μm alumina powder, and rinsed with deionized water prior to use. A copper foil polished with 600-grade sandpaper was used as counter electrode. Nanostructured Cu deposits were prepared using reported methods [17-19]. The electrodes were immersed in a 0.2 M CuSO<sub>4</sub> (99,99%, Aldrich) and 1.5 M H<sub>2</sub>SO<sub>4</sub>

(95-97%, Merck) and a reduction potential of -4 V was applied to the working electrode for 15 s.

For the electrochemical experiments, a Pt wire counter electrode and an Ag/AgCl reference electrode in a Luggin capillar were used. The working electrodes used were copper, nanostructured Cu deposited on a Cu disk, Glassy Carbon (GC) and an Au disk. They were mechanically polished with 3  $\mu\text{m}$  alumina powder prior to use. The Au electrode was activated in 0.5 M  $\text{H}_2\text{SO}_4$  by cyclic voltammetry for 1 hour in 0.5 M  $\text{H}_2\text{SO}_4$ . The cell was deoxygenated with  $\text{N}_2$  (Grade 5, Cryogas) for 10 minutes prior to each experiment. The projected surface areas of the electrodes were determined using a Stemi DV4 stereomicroscope (Zeiss).

The 0.1 M  $\text{NaClO}_4$  (99,99%, Aldrich) solution was prepared with acetonitrile (HPLC grade, Merck), previously dried with molecular sieve (5 $\text{\AA}$ ) when it was necessary, and Milli-Q water (18.2M $\Omega$  cm). The  $\text{CO}_2$  reduction was studied by bubbling  $\text{CO}_2$  (Anaerobic, Cryogas) for 10 minutes in  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  mixtures (Molar Fractions  $X=0.15, 0.25, 0.35, 0.45$ ). During the voltammetric measurements the potential range was shifted according to the water concentration in order to ensure that the potential scan was inside the potential window.

## Results and discussion

Figure 1a shows the voltammograms of nanostructured Cu electrodeposited on a Cu electrode. A characteristic profile is obtained in these experimental conditions, where it can be seen three signals related to adsorbed or surface attached species. Also, the data shown

in the figure 1a allow the calculation of the electrode capacitance at -1.050 V and, therefore, a relation between the areas of the nanostructured Cu and the polycrystalline electrodes. The capacitance for the nanostructured Cu was 120  $\mu\text{F}$ , while the capacitance measured for a polycrystalline Cu was 9.03  $\mu\text{F}$ , meaning that the ratio between areas is almost 13. Figure 1b shows the voltammograms as a function of the current density.

The characteristic voltammetric profiles of crystalline electrodes have been extensively studied in different experimental conditions. On noble metals, hydrogen and oxygen species are electroadsorbed at underpotential conditions, but to the best of the author's knowledge, there is no report of characteristic reversible voltammetric profiles of Cu, primarily because of the strong adsorption of water, the low oxidation potential of Cu and surface reconstruction [20]. Moreover, it is not easy to measure the specific adsorption of anion on electrodes like Cu, which have low potential of zero charge, because the hydrogen evolution reaction (HER) can take place at a potential near the adsorption of anions [21]. In this case is very difficult discriminate the adsorption of anions and hydrogen.

<Figure 1 here>

**Figure 1.** a) Cyclic voltammetry of Cu (black line) and nanostructured Cu (red line) electrodes, b) same as figure 1a after area correction and c) voltammogram of Pt(111) between -0.30 and -1.60 V. Supporting electrolyte 0.1 M  $\text{NaClO}_4$  in  $\text{CH}_3\text{CN}$ . The scan rate was 100  $\text{mV s}^{-1}$ .

However, the voltammetric profiles of nanostructured Cu electrodes obtained in acetonitrile are very similar to those reported by Suárez-Herrera *et al.* [22] on Pt(111) in the same electrolyte (figure 1c). The authors reported that the voltammetry of low-index single-crystal platinum electrodes in acetonitrile is similar to that obtained in aqueous alkaline media, where it can be clearly seen the signals associated with hydrogen and hydroxyl adsorption. Taken into account that perchlorate anions [21] and acetonitrile are not specifically adsorbed on Cu electrode at room temperatures, the signals observed in figure 1a can be assigned as follow: hydrogen electroadsorption between -1.4 V and -1.25V, hydroxyl adsorption between -1.25V and -1.1V and, finally, the formation of a thin layer of copper oxides between -1V and -0.8V [23].

Maurice *et al.* [20], using in situ scanning tunnelling microscopy measurements of Cu(111) in 0.1M NaOH in the underpotential range of Cu<sub>2</sub>O formation, suggested that the adsorbed species present in this potential range are hydroxide ions or hydroxyl groups rather than adsorbed oxygen. Protopopoff and Markus [24] predicted the potential domain of hydrogen electroadsorption on Cu using the thermochemical data obtained for hydrogen chemisorption on Cu in gas phase. The authors suggested that below the H<sup>+</sup>/H<sub>2</sub> standard potential, hydrogen is adsorbed on copper, but as a reaction intermediate in the HER. It seems that the low polarity of wet acetonitrile strongly suppresses the hydrogen evolution. Thus, the specific adsorption–desorption of hydroxyl and hydrogen appears to be clearly separated from the hydrogen evolution reaction.

The surface coverage of OH<sub>ad</sub> on Cu(*hkl*) are largely lacking in the literature. From the data shown in figure 1 it can be obtained the total charge of the OH<sub>ad</sub> peak, which is 45 μC



$\text{cm}^{-2}$ . This value is much lower than that expected for one monolayer of OHad coverage on Pt(111) ( $241 \mu\text{C cm}^{-2}$  for 1 electron per atom on Pt(111)-(1 × 1)).

Figure 2 shows the effect of the amount of water on the voltammetric profile of the nanostructured Cu electrode and on  $\text{CO}_2$  reduction. As the water concentration is higher, the signals of solvent reduction and hydroxyl adsorption-desorption peaks are shifted to more positive potentials. Also, the height of hydroxyl and copper oxide signals, and the capacitive currents decrease. This behaviour is due to the strong adsorption of water and the increase of the hydrogen concentration in the electrochemical cell at higher water concentrations.

<Figure 2 here>

**Figure 2.** Cyclic voltammetry of  $\text{CO}_2$  reduction on nanostructured Cu electrodes in 0.1 M  $\text{NaClO}_4$  in mixtures  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  at a) 0, b) 0.15, c) 0.25, d) 0.35 and d) 0.45 molar fraction of water. The black line is the first scan and the red line is the 10<sup>th</sup> scan. Dashed line corresponds to the voltammograms in the absence of  $\text{CO}_2$ . The scan rate was  $100 \text{ mV s}^{-1}$ .

The cyclic voltammetry of nanostructured Cu electrode in the presence of  $\text{CO}_2$  using different mixtures of  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  shows that the highest reduction currents were obtained when a mixture of 0.25 molar fraction of water was used. The increasing currents when an amount of water is added to the cell can be explained because protons play an important

role in CO<sub>2</sub> electroreduction as it was suggested by Zhang and Sethuraman [25]. They proposed that CO protonation is the limiting step in CO<sub>2</sub> electroreduction. The enhanced kinetics for CO<sub>2</sub> reduction in the X<sub>H<sub>2</sub>O</sub> 0.25 mixture can be due to the following facts: (i) low hydrogen evolution but the presence of enough sources of protons for the proton coupled electron transfer reactions, (ii) the solvation of CO<sub>2</sub> is not so strong as it happens in pure water and (iii) the electrode is less passivated in this mixture.

Besides, Williams *et al.* [26] have proposed that CO<sub>2</sub> and acetonitrile can form stable complexes. Therefore, it is expected that the structure and energy state of CO<sub>2</sub> molecule change according to the solvent polarity, or water concentration. Moreau *et al.* [27] found that, in H<sub>2</sub>O/CH<sub>3</sub>CN mixtures, there are three different structure regions. In acetonitrile rich region, the water molecules are solvated by acetonitrile via dipole-dipole interactions, whereas in a middle region ( $0.5 \leq X_{CH_3CN} \leq 0.7$ ) water and acetonitrile molecules form aggregates. It seems that in this case low concentrations of water not only act as a source of protons, but also provide a unique solvent structure where the charge transfer kinetics is improved.

In order to verify if the X<sub>H<sub>2</sub>O</sub> 0.25 mixture is more convenient for CO<sub>2</sub> reduction on other electrodes, additional experiments were carried out on different polycrystalline electrodes (Figure 3). In the first place, the reduction signal of CO<sub>2</sub> on Au increases upon potential cycling, figure 3a. In second place, the GC electrode shows no activity towards the CO<sub>2</sub> reduction, figure 3b, as expected.

In the case of Au electrode, mixtures of H<sub>2</sub>O/CH<sub>3</sub>CN with molar fractions of water lower than 0.15 or higher than 0.35 for CO<sub>2</sub> reduction show a decrease of the cathodic signals

upon potential cycling (data not shown), which means that the  $X_{\text{H}_2\text{O}}$  0.25 mixture is the best solvent for  $\text{CO}_2$  reduction on both polycrystalline gold and nanostructured Cu electrodes. As the most common product of  $\text{CO}_2$  reduction on Au surfaces is CO [28], the produced CO can be adsorbed on the electrode and further react electrochemically at the interface or chemically with hydrogen, which is likely to be present at high reductive potentials, thus increasing on time the chemical species that can be reduced. Comparing the nanostructured Cu and Au electrodes, it is clear that the  $\text{CO}_2$  reaction happens at lower overpotentials on nanostructured Cu than on Au.

<Figure 3 here>

**Figure 3.** Comparison of  $\text{CO}_2$  reduction on different electrodes in 0.1 M  $\text{NaClO}_4$  in  $\text{CH}_3\text{CN}$  with 0.25 molar fraction of water: in presence (red line) and absence (black line) of  $\text{CO}_2$ . It shows the 10<sup>th</sup> scan. The scan rate was 100 mV s<sup>-1</sup>.

Figure 3d shows that onset potential of the  $\text{CO}_2$  reduction on nanostructured Cu electrode (-1.01 V) in the  $X_{\text{H}_2\text{O}}$  0.25 mixture is much higher than the one observed for polycrystalline Cu (-1.10 V), which means that the former electrode is a better electrocatalyst for this reaction, agreeing with the work of Fan *et al.* [29], and Tang *et al.* [30]. The higher activity for the  $\text{CO}_2$  reduction reaction of nanostructured copper electrode can be explained not only

by the increasing actual surface area but also by differences on the surface structure, as it is clear in figure 1.

Finally, it is important to state that the proposed interpretation of the voltammograms shown in figure 1 is preliminary and based on the information available, but it is clear that further studies are needed in order to find out the real nature of the adsorbed species at the different applied potentials. On the other hand, it is imperative to characterize the nature of the reduction products formed during the CO<sub>2</sub> reduction on both nanostructured Cu and Au electrodes in mixtures acetonitrile/water.

## Conclusions

The elucidation of the surface structures of the Cu electrodes formed by reducing thick Cu<sub>2</sub>O layers or electrochemically deposited is very important in order to find insights about the structural requirements for preferential CO<sub>2</sub> reduction. This work shows that these electrodes can be characterized in acetonitrile where well-defined electrochemical signals are obtained. On the other hand, the present study has provided new light on the electrocatalytic activity of nanostructured copper and the effect of solvent on the kinetics of CO<sub>2</sub> reduction. Particularly, it was found that the current density of CO<sub>2</sub> reduction in mixtures H<sub>2</sub>O/CH<sub>3</sub>CN with a water molar fraction around 0.25 is higher than those observed with other mixtures and that the nanostructured Cu electrode is a better electrocatalyst for the CO<sub>2</sub> reduction reaction than the polycrystalline Cu or Au electrodes in this media.

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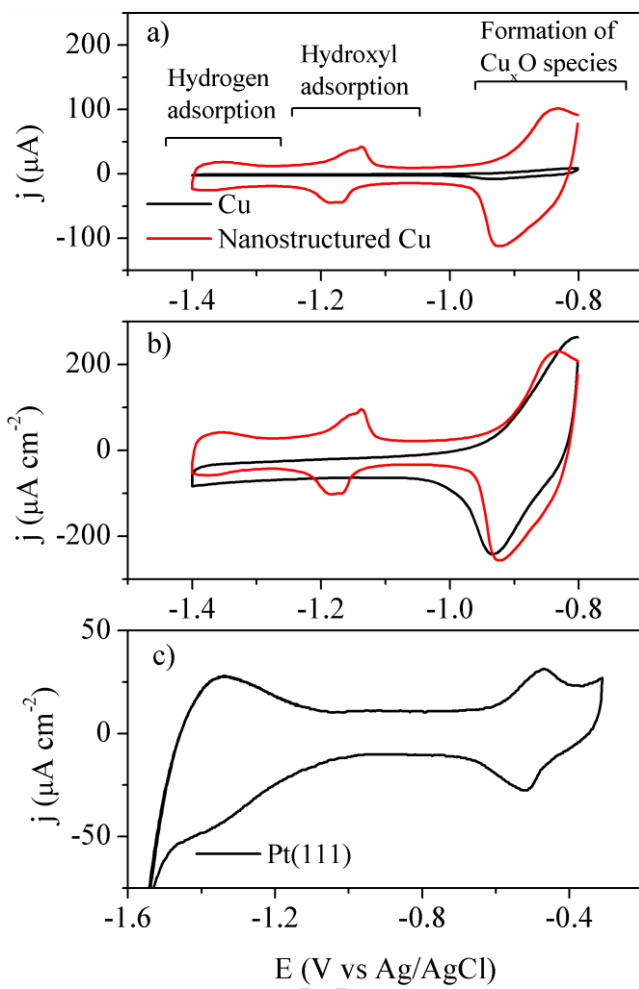


Figure 1

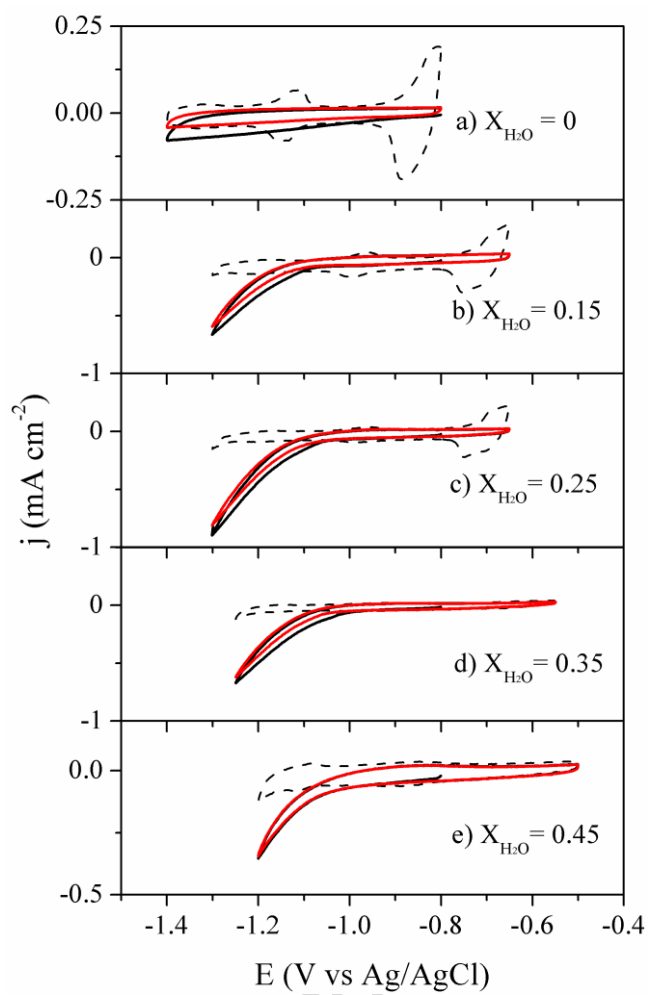


Figure 2

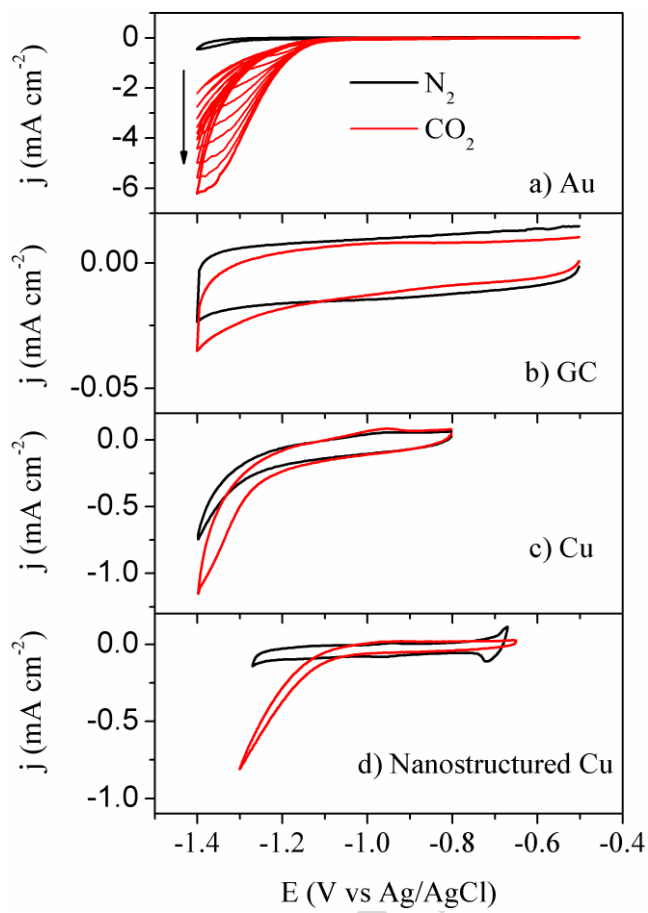


Figure 3

**Highlights**

- Nanostructured Cu electrodes shows well-defined electrochemical signals in acetonitrile.
- High CO<sub>2</sub> reduction currents are obtained in H<sub>2</sub>O/CH<sub>3</sub>CN mixture of 0.25 water molar fraction.
- Nanostructured Cu electrode is a better electrocatalyst for CO<sub>2</sub> reduction than Cu or Au electrodes.