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# Photoelectrochemical reduction of $CO_2$ on $Cu/Cu_2O$ films: Product distribution and pH effects

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## HIGHLIGHTS

- Photoelectrochemical $CO_2$ reduction at a $Cu/Cu_2O$ electrode.
- Formation of methanol, ethanol, formaldehyde, acetaldehyde, and acetone.
- A reaction scheme is presented to account for the product evolution.
- The medium pH was identified as a key variable in the product distribution.

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## ABSTRACT

This work focuses on photoelectrochemical $CO_2$ reduction at a $Cu/Cu_2O$ electrode ($1 \times 1$ cm$^2$). The formation of methanol, ethanol, formaldehyde, acetaldehyde, and acetone was monitored during UV–visible radiation for 3 h at +0.20 V (vs. Ag/AgCl reference); 80% of the initial $CO_2$ was removed. In this process, the photogenerated electrons in the *p*-type $Cu_2O$ semiconductor reduced $CO_2$ ($CO_2 + e^- \rightarrow CO_2^{\cdot-}$). Subsequent reaction involved radical species that originated during photolysis and dictated the product distribution observed. Methanol formation prevailed for a short period (<30 min); acetaldehyde and acetone were the main products after a longer accumulation period (>120 min). A reaction scheme is presented to account for the product evolution and reactions with the $H^{\cdot}$, $CH_3^{\cdot}$, and $OH^{\cdot}$ radical species generated in situ. The medium pH was identified as a key variable in the selectivity of the methanol formation.

## 1. Introduction

The development of methods to convert $CO_2$ into value added products and/or high-energy content fuel has received much attention [1,2]. The main methods are based on use of biomass [2,3], thermochemical [4,5], electrochemical [6–8], photocatalytic [9–12] and photoelectrocatalytic processes [13–17]. The challenge of converting $CO_2$ into fuels by electrochemical methods has been pursued by several researchers since long time [7,18–20]. There is a large consensus that the electrode reaction and products generated are strongly dependent of pH, $CO_2$ concentration, nature of the supporting electrolyte, catalyst and mainly of the electrocatalytic activity of the electrode material. Among them, copper and copper oxide-based electrodes has been widely applied in electrocatalytic $CO_2$ reduction, and they have shown a good performance [1,21–26]. Recently copper oxide electrodes were also applied in photoelectrocatalytic $CO_2$ reduction presenting a good yield for methanol and ethanol formation [14,27,28]. These studies present the potentiality of the copper and copper oxide for the $CO_2$ reduction.

Among prominent methods, photoelectrochemical $CO_2$ reduction in an aqueous medium is attractive, especially relative to the (dark) electrochemical process counterpart. It is relatively inexpensive and resembles the artificial photosynthesis process that employs semiconductors such as ZnO, CdSe, $ZrO_2$, $Ga_2O_3$, and $TiO_2$ doped with different metals as photocatalyst [29]. The first study about $CO_2$ reduction applying photoelectrocatalysis technique was performed by Halmman in 1978 [30] obtaining formic acid, methanol and formaldehyde as products. This precursor study showed the advantages of applying his technique for the $CO_2$ reduction comparing to electrocatalysis and photocatalysis [14,15,31].

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Since this first research on photoelectrocatalytic $CO_2$ reduction, other researchers had applied the technique with the same aim [32–34]. However, the number of researches using photoelectrocatalysis for $CO_2$ reduction has been increasing in the last two years [14–16,27,28,35]. This happened because the photoelectrocatalytic $CO_2$ reduction produces pure or oxygenated hydrocarbons with high energetic content [36]. Besides, it minimizes the recombination of photogenerated electron–hole pairs accelerating the electron–hole transfer to their respective acceptors and maximizing the yield [14].

The photoelectrochemical process consists of photoirradiating the semiconductor surface to generate $e^-/h^+$ pairs. The inertness of the $CO_2$ molecule requires considerable overpotentials and/or a co-catalyst to drive the reduction despite the energy efficiency and cost-effectiveness of the dark electrochemical conversion process. On the other hand, the photoelectrochemical approach utilizes the photovoltage gained at the semiconductor/solution interface to generate an underpotential. In many respects, this process resembles artificial photosynthesis but employs inorganic semiconductors such as CdSe, GaAs, GaP, ZnS, SiC or $TiO_2$ [30,37–39] instead. Thus the photogenerated electrons at the semiconductor/solution interface reduce $CO_2$ to organic products such as $CH_4$, $CH_3OH$, and HCOOH. Numerous studies have investigated $CO_2$ reduction in this manner [10,12,27,29,30,37,39–42]. However, the rather low $CO_2$ photoreduction efficiency and limited knowledge of the photoreduction mechanism (especially, the product distribution and its sensitivity to process variables such as solution pH) call for further studies.

For these reasons, this work describes the facile preparation of small copper electrodes ($1 \times 1\ cm^2$) coated with copper oxide nanoparticles ($Cu/Cu_2O$) by electrochemical deposition. It differentiates itself from the existing body of work on this topic [10,12,27,29,30,37,39–42] in mapping the product distribution profiles; specifically, methanol ($CH_3OH$), ethanol ($C_2H_5OH$), formaldehyde ($CH_2O$), acetaldehyde ($C_2H_4O$), and acetone ($CH_3COCH_3$). The sensitivity of these profiles to process variables such pH, applied bias potential, and the electrolyte composition is presented. A self-consistent reaction scheme is presented to account for the products observed.

## 2. Experimental

### 2.1. Electrochemical preparation of the $Cu/Cu_2O$ electrode

$Cu/Cu_2O$ electrodes measuring 1 cm × 1 cm were prepared according to a previously described method [43,44]. Sanded and cleaned copper plates (99.95%, Alfa Aesar, 0.80 mm thick and area of $1\ cm^2$) were polished to mirror quality and smooth finished using silicon carbide sandpaper of successively finer roughness (220, 320, 400, 800, 1200, and 1500 grit). After polished, the copper plates were submitted to surface treatment with hydrogen peroxide/ammonium hydroxide (1:1) solution to improve $Cu_2O$ film adhesion to the copper plate surface. Afterwards, the substrate was immersed in a 0.4 mol $L^{-1}$ cupric sulfate solution containing 3.0 mol $L^{-1}$ lactic acid. The pH solution was adjusted to 12.0 with 12.0 mol $L^{-1}$ NaOH and the substrate submitted to a potential of −0.40 V (vs. Ag/AgCl reference; all potentials below quoted on this scale) during 30 min kept temperature at 60 °C. An AUTOLAB Model PGSTAT 302 potentiostat/galvanostat was used to control the potential using an electrochemical cell containing a three-electrode electrochemical cell arrangement containing the copper foil as working electrode, a platinum foil measuring 1 cm × 1 cm as counter electrode and an Ag/AgCl, KCl(sat)) reference electrode. Afterwards, the electrode was dried at room temperature.

### 2.2. Characterization of the $Cu/Cu_2O$ electrode

X-ray diffractograms of the $Cu/Cu_2O$ electrode were recorded on a Siemens Model D 5000 diffractometer; radiation in the $2\theta$ 4–70° range was used. The structures and morphologies were analyzed by field emission scanning electron microscopy (FE-SEM) on a Zeiss model Supra 35 equipped with an energy dispersive X-ray (EDX) spectrometer. Linear sweep voltammetry was carried out at a scan rate of 0.01 V $s^{-1}$, in the presence and absence of UV–vis radiation, in 0.1 mol $L^{-1}$ sodium carbonate/bicarbonate buffer solution, 0.1 mol $L^{-1}$ sodium carbonate solution, or 0.1 mol $L^{-1}$ sodium bicarbonate solution as supporting electrolyte.

### 2.3. Apparatus and procedure for photoelectrochemical $CO_2$ reduction

The photoelectrochemical experiments were performed in a 250 mL cylindrical one-compartment glass reactor equipped with a cooling system. The $Cu/Cu_2O$ working electrode ($1 \times 1\ cm^2$) was irradiated with UV–vis light (125-W high pressure mercury lamp from Oriel) vertically inserted in a central quartz glass bulb. A saturated Ag/AgCl (KCl sat) electrode was used as reference, and the counterelectrode consisted of Pt gauze.

$CO_2$ reduction was accomplished under controlled-potential electrolysis and UV–vis radiation. The reaction was carried out in 150 mL supporting electrolyte containing dissolved $CO_2$ by bubbling $CO_2$ gas (OXI-MEDIN) through it. Quantification of dissolved $CO_2$ was done by dissolved inorganic carbon analysis; a total organic carbon analyzer Shimadzu model TOC-$V_{CPN}$ was employed for this purpose.

### 2.4. Product profiles in photoelectrochemical $CO_2$ reduction

Formaldehyde ($CH_2O$), acetaldehyde ($C_2H_4O$), and acetone ($CH_3COCH_3$) were detected and quantified by liquid chromatography coupled to a diode-array detector [45] after derivatization with 2,4-dinitrophenylhydrazine (DNPH) [46]. Chromatographic analysis of the derivatized products was carried out in the isocratic mode. A Model 10AVP Shimadzu HPLC chromatograph equipped with C18 (3 μm, 250 mm × 4.6 mm) Phenomenex column was employed; the mobile phase was methanol/1.0 mmol $L^{-1}$ lithium perchlorate 80:20 (v/v) at a flow rate of 0.7 mL $min^{-1}$ after filtration in a 0.45-μm membrane (Millipore). $CH_2O$-DNPH, $C_2H_4O$-DNPH, and $CH_3COCH_3$-DNPH stock solutions were prepared by dilution with acetonitrile. Analytical curves were constructed for each standard based on triplicate measurements, and good linearity between 0.6 and 100 mg $L^{-1}$ was established. The determination coefficients were 0.995, 0.999, and 0.996 for $CH_2O$, $C_2H_4O$, and $CH_3COCH_3$ respectively. The detection limits for these products were 0.93, 0.01, and 0.12 ppm, respectively.

Methanol ($CH_3OH$) and ethanol ($C_2H_5OH$) were analyzed by gas chromatography on a Model CP-3800 Varian instrument fitted with a flame ionization detector; a solid-phase micro-extraction technique (SPME) was employed. The SPME technique relies on the use of a fiber covered with a thin, selective layer that extracts organic compounds directly from aqueous samples for gas chromatography analyses [47]. For this purpose, a 0.5-mL aliquot of the photoelectrolyzed solution was transferred to a properly closed container (1.5 mL) and subjected to heating in a bath for 7 min. Then, the fiber was exposed to the vapors for 5 min and injected into the gas chromatograph. The chromatographic column was Stabilvax RESTEC with a length of 30 m, internal diameter of 0.25 mm, and film thickness of 25 μm. The carrier gas was nitrogen at a flow rate of 1.0 mL $min^{-1}$. The injector and detector were maintained at 250 °C. The heating ramp was as follows: 35 °C for 4 min, heating