

Mechanistic Study of plasmon assisted *in situ* photoelectrochemical CO₂ reduction to acetate with a Ag/Cu₂O nanodendrite electrode

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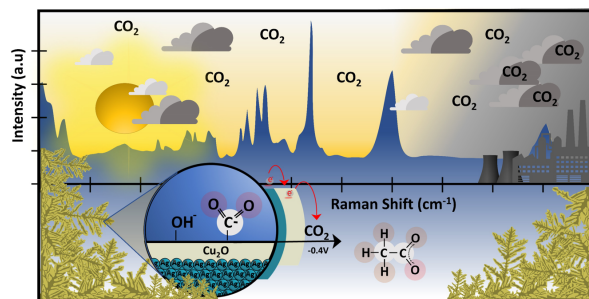
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Abstract

Electrochemical and more recently, photoelectrochemical CO₂ reduction have been widely investigated to convert atmospheric CO₂ into other useful chemicals. However, understanding the mechanism and selectivity of materials capable of reducing CO₂ remains a challenge. Using plasmonic dendritic electrodes of silver and cuprous oxide (Ag/Cu₂O) and employing Raman spectro-electrochemistry (Raman E-CHEM) detection we observe the selective photoelectroreduction mechanism from CO₂ to acetate as a value-added compound instead of the more commonly reported products like methanol, ethylene, or ethane. The selectivity, efficiency and low overpotential (-0.4V vs Ag/AgCl) in the CO₂ reduction is favored by the basic microenvironment, the semiconductor properties of the Cu₂O and the accumulation of hot electrons from the Localized Surface Plasmon Resonance (LSPR) of the Ag nanostructure. Lateral surface interactions between adsorbed CO species are key to the formation of acetate. The rate-determining step of the reaction is the single transfer of an electron from the electrode to the CO₂ molecule to reduce it to the *CO₂⁻ radical anion and subsequently forms adsorbed CO, which is a key intermediate in the formation of the carbon-carbon bond during the reduction process.



Keywords: CO₂ reduction, plasmonics, heterogeneous catalysis, photo- electrocatalysis, nanomaterials.

Introduction

The reduction of CO₂ into added value compounds remains a topic of high interest. In the last decades CO₂ emission has increased over 400 ppm and is considered the main cause of climate change, above other greenhouse gases such as methane, nitrous oxides, water and organofluorocarbons.¹

CO₂ reduction to C₁, C₂ and C₂₊ compounds is a very important issue due to the fact that these compounds can be useful as fuels, chemical products or chemical precursors.² Industrial synthesis of C₂ and C₂₊ products is more complicated than for C₁ compounds as the development of electrode materials with high selectivity toward these products has been a challenge³ and, in addition to being complex, has not been studied as in-depth as the formation of C₁ compounds.

Among the metals used for CO₂ reduction, Cu has shown the capability to electrochemically reduce CO₂ toward hydrocarbons and oxygenates.⁴ In the early 1980s, Hori and coworkers,^{5,6} using a polycrystalline Cu electrode detected mostly CH₄, C₂H₄ and HCOO⁻. More recently, Jaramillo et al detected at least 16 reduction products including methane, ethanol, acetate and carbon monoxide among others⁷. These products highlight the complexity of this reaction. Interestingly, derived copper oxides have shown improvements in selectivity towards C₂ and oxygenates with the detection of methane, acetylene, and ethanol as the main products.^{8,9} It has been further shown with these products that the selectivity towards the C-C coupling is strongly influenced

by the formation of *CO (asterisk (*) denotes an adsorbed species) adsorbed on the electrode,¹⁰ since the adsorbed CO decreases the available sites for HER increasing efficiency towards the reduction of CO₂.¹¹

In a recent work,¹² we designed a high surface area silver nanodendrite electrode covered with a copper oxide thin film that can reduce CO₂ photoelectrochemically at low overpotential (-0.4V versus Ag/AgCl) in a 0.1M Na₂SO₄ solution. With the Silver/Copper oxide nanodendrite electrode, we detected a C₂ oxygenated compound (Acetate) with a high faradaic efficiency (54%) and interestingly, we detected CO in low quantities with an efficiency of less than 1% giving us a first indication of the pathways by which CO₂ is reduced to acetate. Our system showed, not only the C-C coupling at a low overpotential, but also the suppression of the formation of other compounds such as ethylene, ethane, and ethanol. The selectivity and high efficiency at a low overpotential are the result of the plasmonic and semiconductor properties of the Ag/Cu₂O nanodendrites which helps the electron transfer from the silver nanodendrite to the surface of the electrode to be injected into the LUMO of CO₂. This plasmonic effect has been highly studied¹³⁻¹⁵ and, demonstrated in catalytic processes such as hydrogen electroreduction or oxygen evolution reaction where the necessary overpotential decreases dramatically when the processes occur on a plasmonic material that leads to locally enhanced negative electric fields.^{16,17}

On the other hand, the role of the Cu₂O toward the CO₂ reduction has been well described in the literature. Under visible light illumination the band-gap excitation and

formation of free charge carriers is followed by several pathways of de-excitation where, in the best case, the successful donation of the electron to the CO₂ at the surface will lead to the desired reduction reaction.¹⁸ In the case of the Silver-cuprous oxide material, the Fermi level moves upwards, with its potential becoming more negative and then discharging the electrons into the CO₂ more easily than on the Cu₂O by itself.

Understanding of the CO₂ reduction mechanism is multistep. In addition to the injection of electrons from the electrode, the chemical pathways involve electrons, protons, the cleavage of C-O bonds, and the formation of C-H bonds; all of which are difficult to track while the reaction is ongoing. In recent years, *in situ* Raman Spectroscopy has offered insight into the nature of the chemical species formed, improving the spectroscopic task of identifying reactants and intermediates while the reaction is ongoing.¹⁹ In these experiments, metal nanomaterials such as Ag, Au and Cu are most commonly used due to the Surface-Enhanced Raman Scattering (SERS) phenomenon. In SERS, when these materials are struck by incident light that matches the localized plasmon resonance of the material, the Raman intensity is enhanced by several orders of magnitude.²⁰ The SERS signal from silver nanodendrites has provided *in situ* information from both the electrode and the adsorbates present at the catalytic site.^{21,22}

The challenge to studying the formation of C₂ products is understanding the formation of the C-C bond as well as the identification of the intermediates that give rise to the final products. In the overall reaction for the reduction of CO₂ to acetate, 8 electrons must be transferred to the CO₂ molecule as shown in equation 1:



Considering that the transfer of these 8 electrons is a complex reaction, the combination of *in situ* SERS and electrochemical measurements is an effective approach to evaluate the chemical species involved and the rate-determining step (RDS) of the reaction mechanism.²³ Thus, in this work we use this approach to elucidate the mechanism of selective photoelectrochemical CO₂ reduction to acetate at low overpotential. The *in situ* Raman, electrochemical and supporting experiments illuminate the identity of key species and identify reaction steps that can be controlled to uniquely alter the products obtained.

Experimental

Materials and reagents

Silver nitrate (Sigma Aldrich, >99.0 %), Sodium citrate tribasic dihydrate (Sigma Aldrich, > 99.0%), Copper (II) sulfate pentahydrate (Sigma Aldrich, >98.0%), Sodium Hydroxide (Sigma Aldrich, 97.0 %), and 4-mercaptobenzonitrile (Sigma Aldrich, 95%) were used as received. Ultrapure water (resistivity of 18.2 MΩ-cm) was used for all aqueous solutions.

Electrode modification

The Ag/Cu₂O electrode was prepared by a double step electrodeposition method (Figure S1). First, the silver nanodendrites electrodeposition was performed using an aluminum foil as working electrode and applying -1.6 V in a

0.05M AgNO₃ solution and then the electrode was dried for 24 hrs. Afterwards, the Cu₂O was electrodeposited by a multipotential step method in a copper-citrate solution with 0.05 M CuSO₄·5H₂O and 0.1 M C₆H₅Na₃O₇·2H₂O (Na₃Cit) to then rinsed with ultrapure water as previously described.²⁴

Electrochemical measurements

Electrochemical and spectroelectrochemical experiments were performed with a CHI 660D potentiostat (CH Instruments, Austin, TX) using a Ag/AgCl (KCl 1M) as a reference electrode and a platinum wire as auxiliary electrode.

To detect products, electrolysis was performed for 1-hour under continuous illumination using a white light LED (Thorlabs) light source (100 Wcm⁻²) and applying -0.4V. While aqueous products were detected by NMR.

Tafel analysis was performed at a scan rate of 10 mVs⁻¹ in a potential range between +0.2 and -0.3 vs Ag/AgCl (KCl 1M) in a CO₂ saturated 0.1M Na₂SO₄ solution.

Raman spectroelectrochemical measurements

Raman spectroelectrochemical experiments were performed with a Renishaw InVia Microscope equipped with a 632.8 nm HeNe laser and a homemade spectroelectrochemical cell. A Leica 40X (NA =0.80) water immersion objective was used for illumination and collection in these measurements. The photoexcitation of the plasmon was achieved using a 455 nm LED (Thorlabs) as light source. Unlike electrochemical experiments, the use of a 455 LED instead of a white light LED was done to avoid interference with the detected Raman scattering, while exciting the LSPR of the underlying Ag nanostructures. The LED illumination was filtered from the Raman scattering by the 633 edge filter in the Raman microscope used to reject Rayleigh scattering. The LED could be turned on or off to assess photo-induced processes that were analyzed from the data acquired from the surface in the Raman shift range between 110 and 3200 cm⁻¹.

MBN monolayer experiments

A 4-mercaptobenzonitrile (MBN) monolayer was adsorbed to the surface of the Ag/Cu₂O nanodendrites to generate a SERS signal. Clean electrodes were soaked in a 0.01 M ethanolic solution of MBN for 24 hours to create the monolayer.

The Raman spectroelectrochemical experiments with Ag/Cu₂O/MBN were performed using a potential stepped from open circuit potential (OCP) (≈0.0V) to -0.6V in 50 mV increments, holding the potential constant while the Raman spectra were collected by mapping 10 μm x10 μm area with 1 μm steps, acquiring 121 spectra at each applied potential.

Results and Discussion

In situ spectroelectrochemistry experiments were performed to monitor the chemical conversion of CO₂ on the Ag/Cu₂O electrode previously characterized spectroscopically and morphologically (Figures S2 and S3). In 0.1M Na₂SO₄ solution, -0.4V vs Ag/AgCl was applied for 30 minutes under continuous 455 nm LED illumination. The 455 nm LED avoids interference with the Raman scattering from the 632.8 nm laser. Figure 1a shows spectra recorded from a CO₂-saturated solution under LED illumination as a function of time. New peaks are observed that are not detected in the control experiments performed in a N₂-saturated solution or from a CO₂-saturated solution without LED illumination (Figure S4). In Figure 1a, these new bands are assigned to

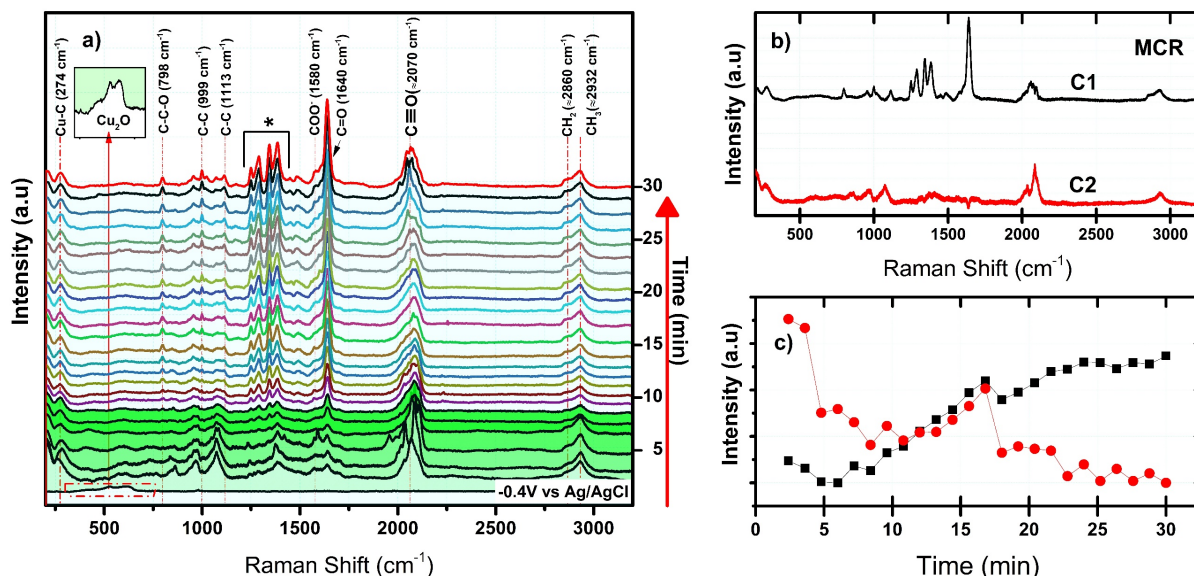


Figure 1: a) Raman spectra of Ag/Cu₂O electrodes for CO₂ reduction carried out under 455 nm LED illumination and applying -0.4V vs Ag/AgCl for 30 minutes. b) MCR analysis of the spectra collected decomposed into the 2 main components. c) Intensity vs time is shown for the MCR components. The two MCR components account for > 99% of the variance in the data.

various, C-C, C-O, and C-H containing functional groups. Other bands are difficult to identify due to the close proximity between the peak frequencies, as can be seen in the region between 1200-1400 cm⁻¹ where at least 4 peaks (see * in the figure 1a) are observed that could correspond to stretching, bending or deformation of COO⁻, CH₂ and O-CH₃ bonds²⁵⁻²⁷. These bands are consistent with our previous report of photoreduction of CO₂ to acetate on this surface.¹²

The time resolved spectra indicate two different reaction regimes over the course of the electrolysis. At the beginning, the bands assigned to Cu₂O surface species disappear when the -0.4 V potential is applied, which suggests the rapid activation of the surface with the adsorption of CO₂ molecules. These bands are accompanied by broad bands in regions characteristic of C-H, C=O and CO that start to appear. At approximately 8 minutes into the electrolysis reaction, the spectrum changes and the new peaks persist until the end of the reaction, while the peaks observed in the initial reaction diminish. To clarify the changing spectral patterns, multivariate curve resolution (MCR) analysis was used to deconvolute the components of the SERS data. A two component model accounted for essentially all the variance in

the data, with component 1 (C1) contributing 74.5% and component 2 (C2) accounting for 25.5% (Figure 1b). Component 1 and component 2 show different time dependent contributions to the overall signal (Figure 1c). Component 2 is dominant initially; however, component 2 diminishes and component 1 is observed to grow in intensity during the reaction. The SERS signals in Figure 1a, from the CO₂-saturated solution, shows changes in peak frequency and intensity that can be used to identify reaction intermediates and to evaluate its behavior over time, enabling us to propose a reduction mechanism. The identification of these intermediates is presented below.

Anion radical *CO₂⁻: The carboxylate radical anion (*CO₂⁻) has previously been detected on metallic surfaces of copper and silver. Vibrational modes at 700 and 1540 cm⁻¹ have been identified for in-plane deformation and asymmetric stretching, respectively^{19,26-28}. These peaks are consistent with our SERS spectra (Figure. 1a), where a small peak at 698 cm⁻¹ is visible during the electrolysis time while a shoulder at 1580 cm⁻¹ can be assigned to the asymmetric stretching of *CO₂⁻. Contrary to what might be expected regarding the intensity of these bands, they are both weak. The SERS signals suggest that this radical anion, once adsorbed on the surface of the electrode, is rapidly reduced to form new C-C, C-O and C-H bonds. The formation of this reaction intermediate is further supported by electrochemical studies analyzing the behavior of the Tafel slope. Figure 2 shows the Tafel behavior of the Ag/Cu₂O nanodendrites under white light illumination (100 mWcm⁻²) in the electrochemical window from +0.2V to -0.3V vs Ag/AgCl. The cathodic Tafel slope is 119 mV dec⁻¹, which is consistent with a rate determining step being the initial one-electron reduction of CO₂ forming the carboxylate radical anion *CO₂⁻.²⁹ The agreement between the spectroscopy and Tafel plot enables us to discard others possible steps, such as the formation of carboxyl or formyloxyl species through Proton-coupled electron transfer (PCET) or through hydride transfer mechanisms.²⁶

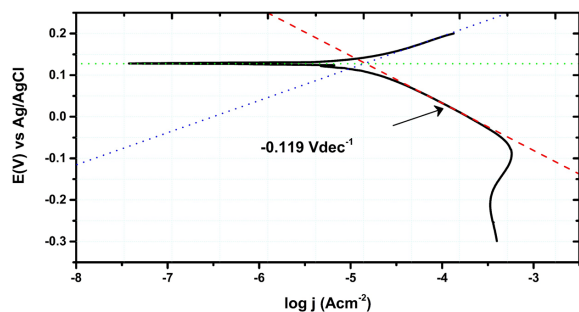


Figure 2: Tafel plot recorded for the photoelectrochemical reduction of CO₂ to acetate using Ag/Cu₂O electrodes.

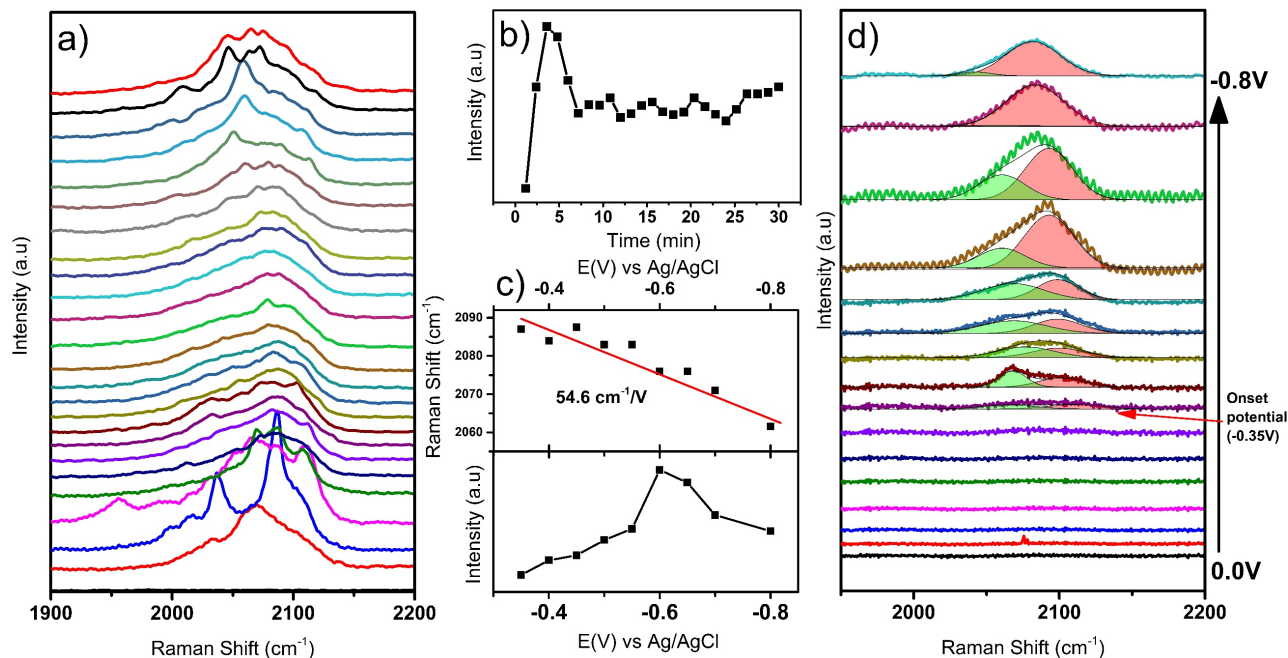


Figure 3: a) SERS spectra for the CO stretching and b) CO frequency intensity during an electrolysis of 30 minutes at -0.4V in a CO₂-saturated 0.1M Na₂SO₄ solution. c) Raman shift and CO intensity of the CO peak d) potential dependence of the CO frequency in an experiment carried out from open circuit potential (~0.0V) to -0.8V

Carbon monoxide: Using copper and oxide-derived copper electrodes, various publications have proposed that the formation and adsorption of CO is key for the formation of the C-C bond, through a dimerization reaction. This coincides with publications reporting the formation of the C₂ compounds CH₃COO⁻, CH₃CH₂OH, and C₂H₄ as products.^{30–33} Our results show that during CO₂ reduction, *C≡O appears throughout the process with an intense broad SERS band at ~2070 cm⁻¹ (Figure. 1a). Our prior report detected trace amounts of CO (g) during electrolysis.¹² The band at 2070 cm⁻¹ has been uniquely assigned to CO stretching, which, depending on the degree of adsorption, shifts to a lower frequency than for the free molecule. The adsorbed *CO assignment is further supported by the Raman band at 280 cm⁻¹ assigned to Cu-CO frustrated rotation in our data.

Analysis of the CO band intensity over the course of the reaction (figure 3a and b) indicate that the concentration of CO on the surface increases rapidly during the first minutes of the reaction, reaching a maximum at about 5 minutes, and then decreases and to a steady state until the end of the reaction, which agrees with the MCR analysis in Figure 1, suggesting component 2 and the behavior of the spectra during the first minutes of the electrolysis reaction arise from CO₂ reduction to adsorbed CO on the surface. This adsorption and reduction to CO is in accordance with prior literature where of C₂ and C₂₊ compounds are formed.^{10,34,35}

The potential dependence (Figure 3c) of the CO peak indicates that this intermediate is chemisorbed onto our nanodendrite surface at a considerably higher rate than reported for metallic copper electrodes,²⁶ which we believe is a key factor in the high selectivity towards the formation of acetate. It has been reported that the selectivity in CO₂ reduction is highly dependent on the adsorption strength of key intermediates^{36,37}. Deconvolution of the *CO peak (figure

3d) shows at least two different interactions are detected on our electrode. The intensity and frequency of peaks associated with the *CO changes as the applied potential becomes more negative. At the onset potential of -0.35 V, the *CO band is weighted toward a low frequency component, and as the applied potential becomes increasingly negative, the intensity in the *CO manifold shifts to higher frequency, and the low frequency component disappears. The disappearance of the low frequency *CO band is consistent with reduction of Cu₂O to Cu, and possibly the desorption of CO from the metal surface. The prevalence of this low energy peak at less negative potentials indicates the importance of Cu⁺ in the selectivity of the reaction. The importance of stabilizing Cu⁺ for selective CO₂ reduction has been previously reported.³⁸ For example Chu et al³⁸ used a CuO-CeO₂ interface to stabilize Cu⁺ and produce ethylene with a faradaic efficiency (FE) as high as 50.0% at -1.1 V vs RHE.

Carbonate: The SERS spectra show intense peaks at ~1070 cm⁻¹ (Figure 1a), previously assigned to adsorbed carbonate. This peak is almost unaffected by potential indicating that the CO₃²⁻ anion is physisorbed to the surface of the nanodendrite as shown in (Figure S5). The onset potential for the appearance of the peak is -0.2V, where the surface is expected to be negatively charged. The peak position of CO₃²⁻ at -0.4V is close to the peak position of dissolved CO₃²⁻,²⁶ indicating the adsorption strength is relatively weak. Detecting CO₃²⁻ instead of HCO₃⁻, which is the main species in solution, indicates the local pH on the surface of the electrode is highly basic compared to the pH of the solution (pH=4.2). The combination of identifying the *CO₂⁻ radical anion as the RDS of the reduction, accompanied by the weak adsorption of CO₃²⁻, suggests CO₃²⁻ does not participate in the CO₂ reduction observed.

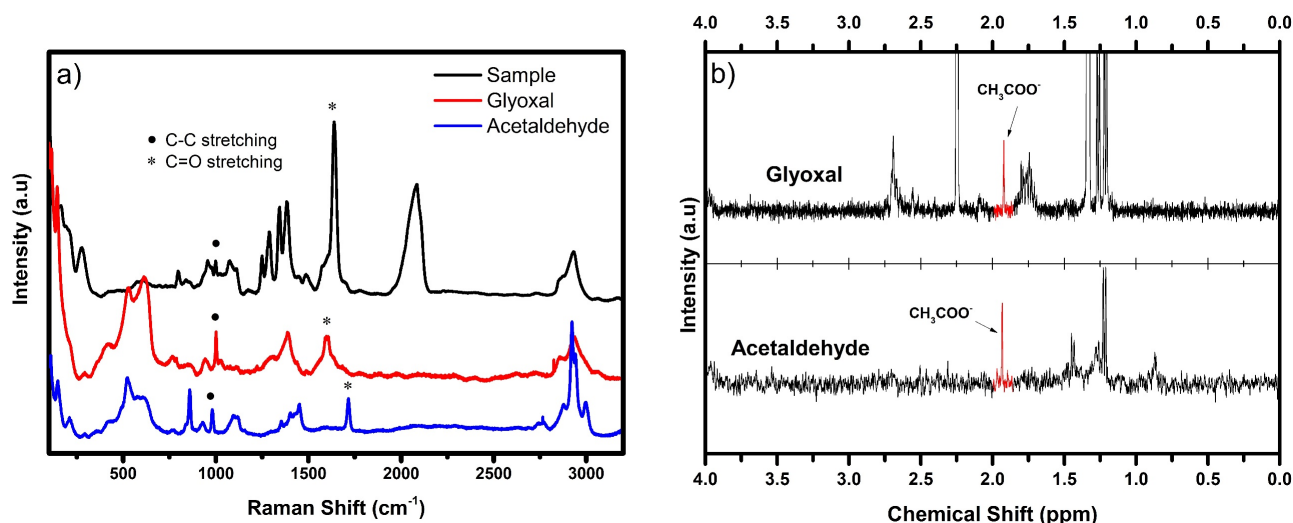


Figure 4: a) Average SERS spectrum of CO₂ reduction for 30 minutes compared with the spectra of glyoxal and acetaldehyde in 0.1M Na₂SO₄. b) ¹H NMR of glyoxal and acetaldehyde solution after electrolysis carried out at -0.4V and under light illumination. The peak assigned to acetate is highlighted in red.

C₂ intermediates: Prior literature of CO₂ reduction to C₂ compounds on copper surfaces has implicated glyoxal, oxalate and, acetaldehyde as possible intermediates that end up forming ethylene, ethanol, ethylene glycol, glycolaldehyde or acetate as reduction products.³⁹ In addition to *CO₂, *CO or *CO₃²⁻, our data shows *C=O, CH and C-C bonds that may correspond to any of these compounds. In Figure 4a, the reference spectra of glyoxal and acetaldehyde standards show features consistent with our data. To corroborate the possible role of these intermediates, we performed the electrolysis of glyoxal and acetaldehyde containing solutions under the same conditions used for the reduction of CO₂ and detected acetate as a reaction product by ¹H NMR from both compounds (Figure 4b).

Light and overpotential effects on the LSPR

To further explore the relationship between the LSPR and the low overpotential to reduce CO₂ we performed Raman

spectroelectrochemical measurements with the Ag/Cu₂O nanodendrites analyzing the vibrational Stark shift from the MBN nitrile mode under light (455 nm LED) and dark conditions (Raman laser only). The stretch mode from MBN (~2230 cm⁻¹) provides a probe of the local surface potential which can be affected by potential, light or both⁴⁰.

Figure 5a shows the observed CN stretching frequency as a function of applied electrochemical potential from MBN adsorbed to the Ag/Cu₂O nanodendrites. In dark and light conditions, as the potential becomes more negative, the CN stretch frequency is observed to decrease to lower Raman shifts with a Stark tuning coefficient of 8.1 and 2.8 cm⁻¹/V respectively, showing the increase of the negative charge on the electrode surface which will favor electron transfer from the plasmonic material to the analyte for reduction.

Interestingly, at open circuit potential with LED illumination, the observed CN stretch is lower than in the dark

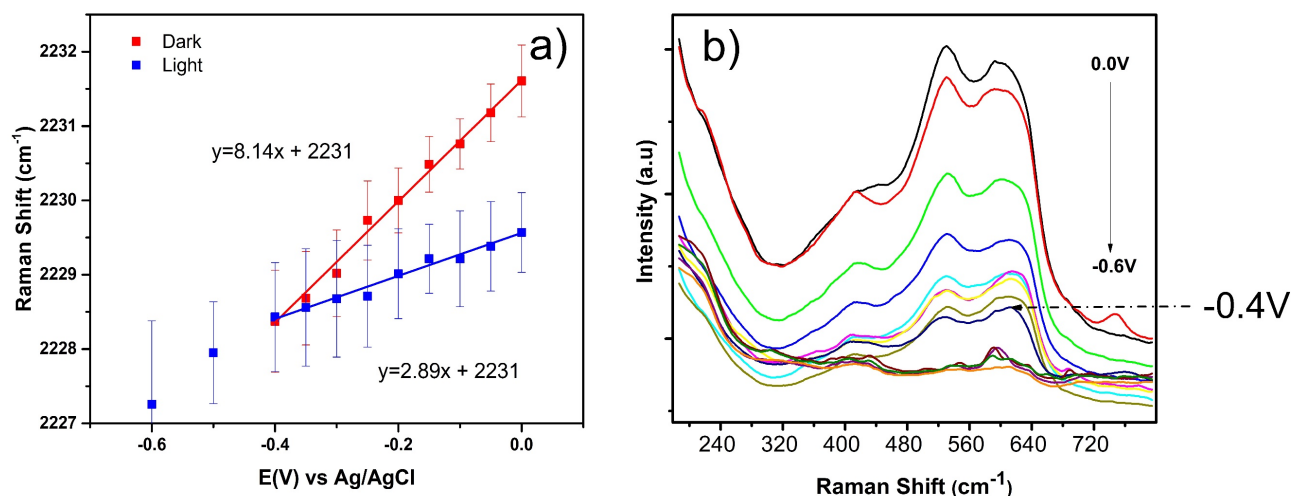


Figure 5: a) CN stretch frequency as a function of applied electrochemical potential under dark and continuous 455 nm LED illumination. b) Potential dependence of the Ag/Cu₂O electrode during the photoelectrochemical CO₂ reduction

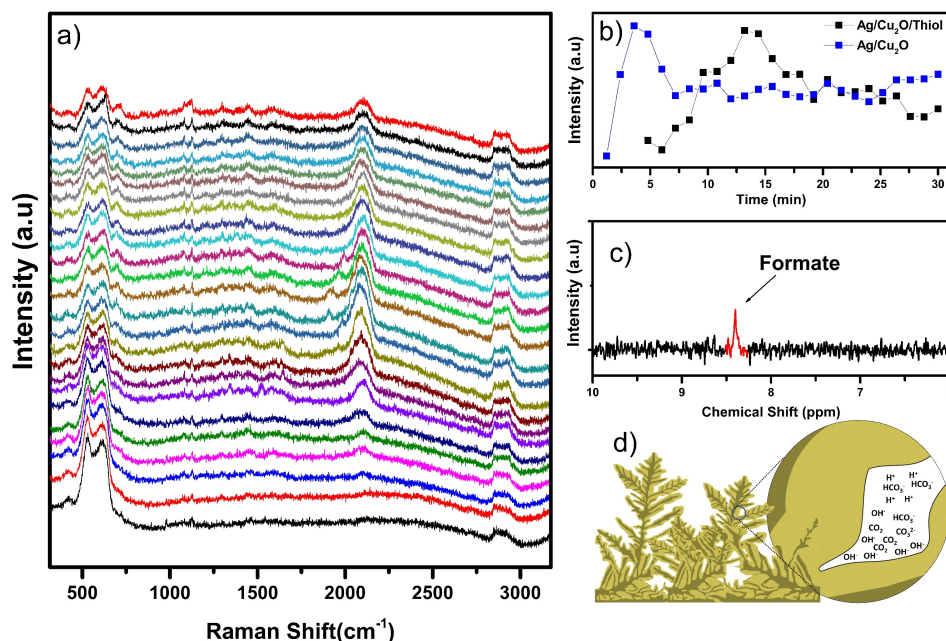


Figure 6: a) Raman spectra of Ag/Cu₂O/pentanethiol electrodes for CO₂ reduction carried out under 455 LED illumination and applying -0.4V vs Ag/AgCl for 30 minutes. b) CO intensity comparison of Ag/Cu₂O with Ag/Cu₂O/Pentanethiol. c) H NMR of formate peak when a Ag/Cu₂O/pentanethiol electrodes was used. d) Representative scheme of microenvironment of Ag/Cu₂O during the CO₂ reduction process.

condition, indicating that the surface potential is strongly affected by LED illumination. A linear extrapolation of the nitrile frequency with applied potential with and without illumination shows an intercept near -0.4 V. After -0.4 V, the change in the nitrile frequency is the same for both light and dark conditions. Interestingly, the behavior of the stretch mode from MBN seems to be related to the CO₂ reduction potential where at -0.4V acetate was detected and yet at higher potentials, the electrode is reduced to something more consistent with Cu⁰ as shown in Figure 5b. The stability of our material is limited to a small electrochemical window that goes from open circuit potential to -0.4V. At potentials more positive than OCP, the silver nanodendrites are oxidized while at potentials more negative than -0.4V the reduction of Cu₂O takes place. However, -0.4V seems to be the ideal potential for CO₂ reduction.

We believe that at -0.4V the Cu₂O surface is partially reduced to Cu, which improves CO adsorption facilitating electronic transfer from the excited plasmon resonance. Ren et al. observed that in aqueous solution and using Cu₂O that CO₂ reduction improves when the Cu₂O is reduced to Cu⁰ at negative potentials.⁴¹ In a similar work Kas et al. investigated Cu₂O with different orientation and thickness and concluded that the selectivity depends on the initial Cu₂O thickness and not on the orientation⁴² and, in agreement with Ren et al., concluded that CO₂ reduction begins only after Cu₂O is reduced to Cu⁰. In contrast to what was stated by Ren and Kas, our results indicate that Cu₂O is an important material during the CO₂ reduction and changes in Stark tuning rate of the CN stretch under light illumination support this role of Cu₂O. Another report by Kim et al indicated the importance of Cu₂O for reducing CO₂ using branched copper oxide activated to cuprous oxide to obtain highly selective ethylene production⁴³.

Our results indicate that at -0.4V the efficiency in reducing CO₂ is higher compared to other applied potentials. In addition to the presence of Cu₂O on the plasmonic surface of silver, it is possible that at this -0.4 V reduction potential part of the Cu₂O is reduced to copper metal in a proportion such that the material retains its initial nature but that with the presence of Cu⁰, the CO₂ adsorption is favored improving its reduction.

We note that electrolysis was performed with a white light LED, while the Raman measurements used a 455 nm LED. However, the correlation between species evident by NMR (white light) and Raman (455 nm) indicate the illumination conditions do not have a significant impact on the observed products. It was previously reported that H₂ photoreduction on a Cu-ternary composite material that blue LED illumination⁴⁴ increased the H₂ yield by focusing energy into the appropriate band. Further experiments may show a wavelength dependence to further improve the acetate yield.

SERS detection of C-O, C-H and C-C bonds as well as the presence of adsorbed functional groups such as *COO⁻, *CO and *CO₃²⁻, OH⁻, aid in deducing and understanding the reduction mechanism by providing chemical information about the species present at the catalytic site and hence the selectivity of the reaction. The selectivity has been correlated to the local environment of the active sites, appropriate adsorption strength³⁷ of the key intermediates, and LSPR excitation at interstitials or sharp edges⁴⁵. Wagner et al identified three aspects of the local environment that can affect reactivity: surface effects, solution interactions and three-dimensional materials,⁴⁶ which we will evaluate further.

Surface effects: It is well known that the nature of the species adsorbed on the surface of the electrode can affect the selectivity and efficiency of CO₂ reduction. Thus, the early

detection of *CO is a key compound in the selectivity of the reaction. Its adsorption not only directs the reduction towards C_{2+} compounds, but also suppresses the hydrogen evolution reaction. In our results we do not detect hydrogen by Gas Chromatography (GC) or Linear Sweep Voltammetry (LSV) experiments. The current density observed in LSV with N_2 is lower than in a CO_2 saturated solution (Figure S6) indicating poor H_2 production at the working potential.

Electrode functionalization can alter the reaction selectivity by modifying the physicochemical nature of the surface. Our SERS results in Figure 3 suggest a buildup of adsorbed CO prior to the production of C_2 products. To better understand the role of the *CO adsorbed, we functionalized the Ag/ Cu_2O electrode with pentanethiol to restrict lateral surface interactions, and we carried out electrolysis and Raman photoelectrochemical experiments to see the effect on the selectivity. Wakerley et al showed electrochemical CO_2 reduction to C_2/C_3 products by functionalizing Cu dendrites with 1-octadecanethiol, attaining attained a 56% Faradaic efficiency for ethylene and 17% for ethanol.⁴⁷ In a similar work, Baker et al showed dodecanethiol on Au nanoparticles affects the activity, selectivity, and stability of the Au nanoparticles for electrochemical carbon dioxide reduction. In particular, they showed in the presence of this surface ligand, the yield of CO increased more than 100 times compared to the polycrystalline gold electrode at an identical potential⁴⁸. Figure 6a shows the Raman spectra for an Ag/ Cu_2O /pentanethiol modified electrode at -0.4V and under continuous light illumination where unlike unmodified electrodes, only the 2070 cm^{-1} peak, attributed to CO stretching, changes over time, which indicates that there is reduction from CO_2 to CO, but this intermediate does not react further to a C_2 or C_{2+} compound. Figure 6b shows the CO intensity when the Ag/ Cu_2O /pentanethiol and Ag/ Cu_2O electrodes are compared. For the Ag/ Cu_2O /pentanethiol electrodes the maximum CO intensity occurs at least 10 minutes later than the Ag/ Cu_2O electrodes which shows that the functionalization of the electrodes with pentanethiol affects the CO_2 reduction.

Electrolysis at controlled potential on the pentanethiol covered surface shows a change in the detected product. Formate is produced in solution on the pentanethiol covered surface, as detected by 1H NMR in Figure 6c. Formate is considered a dead end pathway in the reduction of CO_2 . Using a silver catalyst surface, Bohra et al. reported the adsorbed formate intermediate (*OCHO) may react with adsorbed protons (*H) along the reaction pathway towards CO.⁴⁹ In our Raman spectroelectrochemical experiments, a maximum intensity for the CO stretching is observed at ~13 minutes, after which the intensity begins to decrease (Figure 6b). The SERS detection of CO on the Ag/ Cu_2O /pentanethiol electrodes suggests the functionalization with thiols affects the surface diffusion of CO molecules, blocking dimerization reactions by increasing the distance between adsorbed CO moieties, and thus preventing the formation of the C-C bond that results in the formation of acetate. However, the functionalization does not seem to affect the nature of the Ag/ Cu_2O electrode with bands corresponding to Cu_2O (figure 6a) are present throughout the electrolysis as well as the CO stretch bands

whose SERS intensity is not affected by the presence of pentanethiol. Also, the detection of formate as well as the formation of acetate with non-functionalized electrodes at low overpotential (-0.4V) is evidence that the photoelectrocatalytic activity is not interrupted, and the hot electrons generated by LSPR are still reaching the Cu_2O surface to promote the reduction the CO_2 .

Solution interactions: In addition to the adsorbed species, the species in solution, mainly Na^+ , CO_3^{2-} , HCO_3^- , H_2CO_3 and OH^- ions create a unique microenvironment for the selective reduction of CO_2 . Na^+ and SO_4^{2-} ions are present due to their use as the supporting electrolyte, while CO_3^{2-} , HCO_3^- and H_2CO_3 arise from the acid-base equilibrium established when CO_2 is dissolved in water. The detection of CO_3^{2-} over HCO_3^- and H_2CO_3 is an indicator of a highly basic microenvironment which impacts pH-sensitive reactions on the surface, but the low adsorption energy indicates the presence of CO_3^{2-} does not affect the CO_2 reduction. The OH^- ions arise from the CO_2 reduction process or water splitting. Acetate production generates 7 OH^- anions for every 2 CO_2 molecules reduced, while water splitting forms 2 OH^- for every 2 H_2O molecules increasing the local alkalinity. The effect of pH on selectivity towards C_2 and C_{2+} compounds is a widely discussed issue. Lijima et al⁵⁰ reported the local pH affects the catalytic activity, indicating that the OH layer attracts *CO molecules closer to each other while reducing them to C_2 and C_{2+} products. This observation agrees with Liu et al who reported C_2 products are favored from CO_2 reduction under alkaline conditions on Cu electrodes.⁵¹

Three-dimensional materials: The morphology of the Ag/ Cu_2O nanodendrite shows a complex branching with surface roughness forming diffusion gradients that can impact the local alkalinity and the acetate selectively as is shown in the scheme of the Figure 6d. The branched structure may promote a basic microenvironment that differs from the bulk of the solution. In this microenvironment, the production of acetate is thermodynamically favored with respect to ethanol, ethylene, or ethane, whose corresponding standard redox potentials vs RHE are -0.65, -0.74, -0.74 and -0.68, respectively.⁹ Most of the prior research using copper or copper derivatives report good efficiencies for the production of ethanol, ethylene, or ethane over acetate, indicating that the CO_2 reduction to acetate is kinetically unfavorable with copper electrodes. However, as we have previously described, our material reduces CO_2 to acetate with high efficiency at a very low overpotential. We believe the branch structure not only generates the LSPR and energetic charge carriers, but also favors an ideal microenvironment for the formation of acetate. Other dendritic materials have been explored for CO_2 reduction. Scholten et al fabricated dendritic Cu electrocatalysts improving the selectivity toward ethylene and ethanol establishing a strong structure/chemical state-selectivity correlation in CO_2 reduction.⁴⁹ Similarly Urbain et al fabricated a highly selective silver dendrite catalyst to reduce CO_2 to CO and attributed the activity to the large surface area of the nanodendrites⁵².

Effect of the isotope exchange on SERS spectra

To further validate the observed intermediates, we made SERS measurements substituting the CO_2 and the solvent for

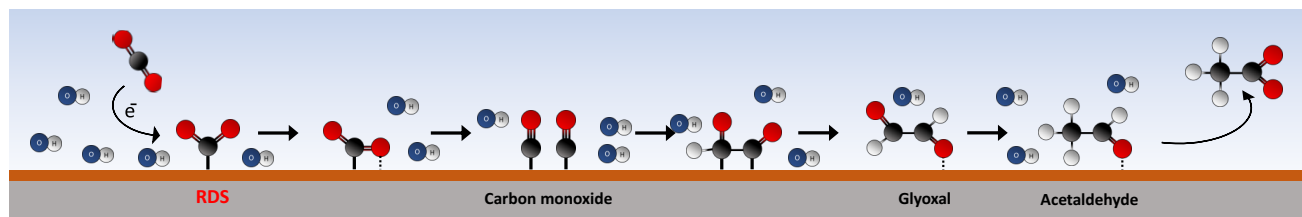


Figure 7: Proposed mechanism for the reduction of CO₂ to Acetate on Ag/Cu₂O electrodes

¹³CO₂ and D₂O respectively. For D₂O/H₂O isotope exchange experiments the peaks at 1250, 1343 and 1487 cm⁻¹ were red-shifted (Figure S7a), which corroborates that the chemical bonds involve at least one C-H bond that affects the observed vibrational mode. These peaks correspond to C-H bond coming from CH deformation and CH₂, CH₃ asymmetric stretching, respectively, based on prior reports.²⁷ ¹³C isotopic substitution resulted in the peaks at 1640 and 2086 cm⁻¹ being red-shifted to 1593 and 2073 cm⁻¹, respectively (Figure S7b). The Stark shift observed from these peaks with applied potential showed the same trend (Figure 3d), which is evidence that the chemical bond is related to a carbon atom from the carbonyl (C=O) and CO (C≡O) group. ¹³C/¹²C isotope exchange effect also allowed us to eliminate possible organic contamination coming from the electrode preparation or the electrochemical cell.

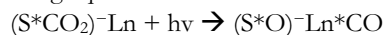
Mechanism and discussion

The photoelectrocatalytic activity of Ag/Cu₂O nanodendrites generates acetate as the major product and small concentrations of CO. These products, the *in situ* Raman spectroelectrochemistry studies, and Tafel analysis support the mechanism for the photoelectrochemical reduction of CO₂ to acetate shown in Figure 7.

First, the Tafel slope values indicate the dissolved CO₂ is adsorbed on the electrode and reduced to the radical anion *CO₂⁻ through a single electron transfer from the electrode to the CO₂. The activation of CO₂ is an energetically unfavorable process with a thermodynamic reduction potential of -1.9V vs NHE,¹⁸ though well within the energy range expected for a hot electron generated by the LED illumination. The partial reduction to *CO₂⁻ on the dendritic cuprous oxide surface is improved by the generation of hot-electrons from the underlying silver that increase the available electrons on the conduction band of the semiconductor which decreases the reduction potential to -0.4V vs Ag/AgCl. The specific -0.4 V appears to be related to the oxidation state of the Cu, where the reaction occurs. The stark-shift and Raman data in Figure 5 indicate plasmon modulation of the Cu₂O and Cu composition at this potential; however, the reaction is not observed on Cu surfaces without plasmonic assistance, indicating Cu₂O is the important surface species. We infer that Cu may promote adsorption of the initial CO₂ species. In the next step, this radical is reduced to *CO adsorbed to the surface to be further reduced to C₂⁺ products through C-C coupling.

The *CO₂ to *CO pathway has been studied extensively and various stabilization mechanisms have been proposed, for example some works have shown that the *CO₂⁻ is stabilized by a single proton transfer from water, and then through a proton-electron transfer is reduced to *CO.^{53,54} Another

pathway proposed by Sheng and collaborators,⁵⁵ the *CO₂⁻ is reduced to *CO through a single electron transfer of a *CO₂⁻ dimer radical anion to convert it to *CO and CO₃²⁻. Other works indicate that the pathway from CO₂ towards the intermediate *CO strongly depends on the excitation wavelength and the nature of the catalyst, where recent research⁵⁶ suggests that the activation and division of the CO₂ molecule depends on hot electrons produced from the decay of and that the strong reduction of this molecule from these hot electrons is accompanied by its stabilization through the surface (S) and solvent molecules (Ln) as shown in the following equation:



Where the *CO₂⁻ dissociation takes place on the excited state potential energy surface, which may yield an adsorbed *CO molecule. The formation of adsorbed *CO agrees with our *in situ* time-resolved experiments, where we observe a rapid increase in *CO during the first minutes of electrolysis that then persists during the entire time the experiment is carried out. It has been well documented that the increase of CO on the surface of the electrode favors the dimerization,^{3,50,57} giving way to the formation of C₂ compounds. Interestingly, in our *in situ* experiments when CO intensity remain stable, the peaks at 1640 and 1384 cm⁻¹ begins to raise. Then 2 *CO molecules dimerize to form a C-C coupling favored by an increased local pH due to CO₂ or H₂O reduction as previously discussed. This coupling gives rise to oxygenated intermediaries through proton-electron transfer. The existence of these new intermediates is clearly detected by the identification of new Raman peaks at 797 cm⁻¹ assigned to C-CO stretching, and two peaks at 997 and 1112 cm⁻¹ both assigned for C-C stretching (figure 1a). Glyoxal and acetaldehyde appear to be possible oxygenated intermediates supported by the *in situ* SERS spectra and H NMR experiments. We detect acetate using glyoxal and acetaldehyde as starting compounds instead of CO₂, indicating that glyoxal and acetaldehyde are intermediates along pathway to form acetate as the majority product. It has been shown that glyoxal can be reduced to acetaldehyde at low overpotential, and at higher overpotential that the acetaldehyde can be reduced to ethanol.³⁹ Our results show no evidence of ethanol, likely due to the low overpotential necessary for the reduction and the rapid e⁻/h⁺ transfer from the bulk electrode to the surface to react with the CO₂ molecule. The change in observed products with the functionalization of the electrode with pentanethiol supports lateral interactions on the copper surface are important to enable *CO molecules to dimerize and be reduced to acetate. When these active sites are blocked, the selectivity changes toward the formation of C₁ products. The physical and nature of the electrode does not change despite the formation of

formate instead of acetate. It is worth noting that the overpotential is still low for the CO₂ reduction toward formate, which could extend the use of this type of electrodes for the reduction of CO₂ towards other products.

In summary, the increased efficiency on our electrode arises from the synergistic properties of silver dendrites (hot electron generation) while presenting a thin layer of copper oxide to mediate adsorption and reactivity of the adsorbed CO. The high efficiency (54%), low overpotential (-0.4V vs Ag/AgCl) and selectivity towards acetate formation derives from the physical-chemical nature of our electrodes that create the ideal microenvironment for efficient and selective CO₂ reduction. Importantly, prior reports of acetate production efficiency do not exceed 15% with copper electrodes or copper derivatives.⁵⁸

Conclusions

In conclusion, electrochemical and spectroelectrochemical methods enable the mechanism by which CO₂ is photoelectrochemically reduced to acetate on dendritic nanomaterials with plasmonic and semiconductor properties to be elucidated. The SERS signal produced by our material allowed us to identify possible intermediates to deduce the mechanism by which CO₂ was transformed into acetate, or formate if pentanethiol is incorporated. The mechanism proposes *CO₂⁻ as the slowest step in the reduction process. The fast CO increase and the strong adsorption on the electrode surface is evidence that acetate production depends on the formation of this intermediate, whose increase is favored by the basic microenvironment of the surface. The preference for acetate over ethanol is explained by several aspects: the nature of the electrode (plasmonic and semiconductor material) modulating adsorption and reactivity, a highly basic local microenvironment, and the large area provided by the nanodendrites. The basic pH of the local microenvironment arises from either CO₂ or H₂O reduction on the electrode surface. This highly basic condition is favored by the branched structure of the nanodendrite which allows the accumulation of OH⁻ ions in the corners and edges of the nanodendrites, decreasing the thickness of the diffusion layer, and favoring mass transport for CO₂ electrolysis. We believe this basic microenvironment favors the lateral interaction between CO molecules to form acetate as the final product. These all contribute to the selectivity for acetate when an overpotential, as low as the thermodynamic reduction potential, is applied and the plasmon resonance is photoexcited (-0.4V vs Ag / AgCl). Our studies on this photocatalyst show an efficient and selective system towards the reduction of CO₂ to acetate and suggest that lateral interactions on the electrode surface are important for the formation of C₂₊ products. Our results illuminate the identity of key intermediates that may impact the formation of other products; either by controlling the dendrites and Cu₂O, or by controlling the applied potential and illumination to activate the material. This understanding may enable not only acetate production but also the selective reduction towards CO or more complex CO₂ reduction products. This improved mechanistic understanding of CO₂ photoelectroreduction with plasmonic and semiconductor materials enables efficient and

selective production of high added value compounds such as acetate from CO₂ under low cost and environmentally friendly environmental conditions.

Supporting Information

Figures S1-S7 providing characterization, additional control experiments, and additional details are provided.

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