

# ChemCatChem

Supporting Information

## **Aminopolysiloxane as Cu<sub>2</sub>O Photocathode Overlayer: Photocorrosion Inhibitor and Low Overpotential CO<sub>2</sub>-to- formate Selectivity Promoter**

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## Experimental details

Copper(I) oxide electrodes were made using a well-established electrodeposition method. Previously cleaned FTO slits (1.0 x 3.0 cm) were immersed in a 0.4 M Cu(SO<sub>4</sub>)<sub>2</sub> aqueous solution containing 3 M lactic acid. NaOH pellets were added until solution pH reached 11. The electrodeposition bath was heated at 60°C and then the FTO-glass working electrode was polarized at -0.5 V until 3.0 C of charge flowed through the system. Stainless steel sheet and metallic Ag were used as counter-electrode and pseudo-reference electrode, respectively. The resulting thin, homogeneous, reddish film was thoroughly washed with deionized water and let for drying overnight at room temperature.

SEM images were obtained in a JSM-6360-LV equipment (JEOL) operating at 20 kV. XRD analysis were ran in a Shimadzu XRD7000 diffractometer using Cu K $\alpha$  radiation. Samples were probed in the 10-60° range of 2 $\theta$ .

Cyclic voltammetry, Zero-current potential (ZCP) measurements and electrolysis experiments were performed using an Autolab PGSTAT 128N potentiostat and Ag|AgCl|KCl 3 M as reference electrode. For experiments under illumination, a HAL-320 (Asahi Spectra) solar simulator was used as light source, which was calibrated to provide 1 Sun illumination.

Incident photon-to-current conversion efficiency (IPCE) measurements were obtained using a set of LED light sources of different wavelengths (ThorLabs). For each wavelength, electrodes were polarized at -0.3 V versus Ag|AgCl|KCl 3 M for one minute in the dark, then illuminated until stable photocurrent was obtained. After establishing photocurrent value for each wavelength, the electrode was kept polarized at -0.3 V versus Ag|AgCl|KCl 3 M for another minute, to assure that the current density returns to the original value. IPCE value for each wavelength was calculated according to the equation:

$$IPCE(\lambda) = \frac{1240 I(\lambda)}{\lambda P(\lambda)}$$

Where  $\lambda$  is the wavelength,  $I(\lambda)$  is the photocurrent generated by  $\lambda$  light source and  $P(\lambda)$  is the incident irradiance from  $\lambda$  light source, which was previously measured for each LED source using a radiometer.

For all electrochemistry experiments, the potentials presented can be converted to the reversible hydrogen electrode (RHE) scale as a function of pH using Nernst equation,

$$E_{RHE} = E^{\circ}_{Ag|AgCl} + E_{Ag|AgCl} + 0.059 \times \text{pH}$$

Where  $E_{RHE}$  is the potential at RHE scale,  $E^{\circ}_{Ag|AgCl}$  is 0.198 V (the equivalent of 0 V at the hydrogen scale) and  $E_{Ag|AgCl}$  is the measured potential.

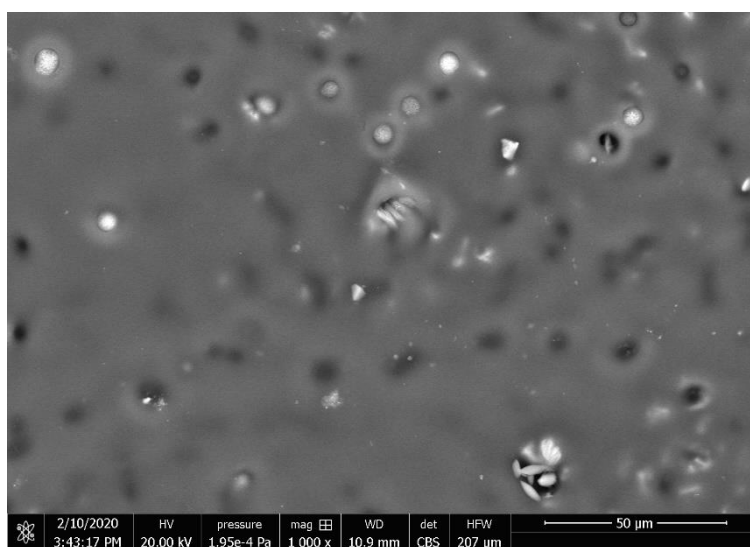
Product quantification by HPLC was performed using a LC-6AD liquid chromatograph (Shimadzu) equipped with ultraviolet detector adjusted for 205 nm wavelength and a Aminex HPX-87 column. 0.5 M H<sub>2</sub>SO<sub>4</sub> was used as mobile phase.

The measurement of FTIR *in situ* were collected with a Shimadzu Prestige-21 spectrometer. As a detector a mercury cadmium telluride (MCT) was used. The spectra were collected in specular reflectance mode, in thin layer configuration, during chronoamperometry measurements from open circuit potential (OCP) to -0.3 V versus Ag|AgCl|KCl 3 M. Thus, a three-electrode electrochemical glass cell coupled to a Ca<sub>2</sub>F window at its bottom was used. The working electrode was then pressed against the window to form the thin layer. The Fourier transform

infrared spectroscopy (FTIR) spectra were composed by 256 interferograms with a resolution of  $4\text{ cm}^{-1}$  in R/Ro were Ro was the background at OPC after 15 minutes of continuous  $\text{CO}_2$  purge in the system. A purge of  $\text{CO}_2$  was kept constant during all the chronoamperometry measurements.

This procedure was done in the presence and in the absence of light. To perform the experiment in the presence of light, an optic fiber was settled in front of the specular reflectance accessory in a way it to do not obstruct the IR beam.

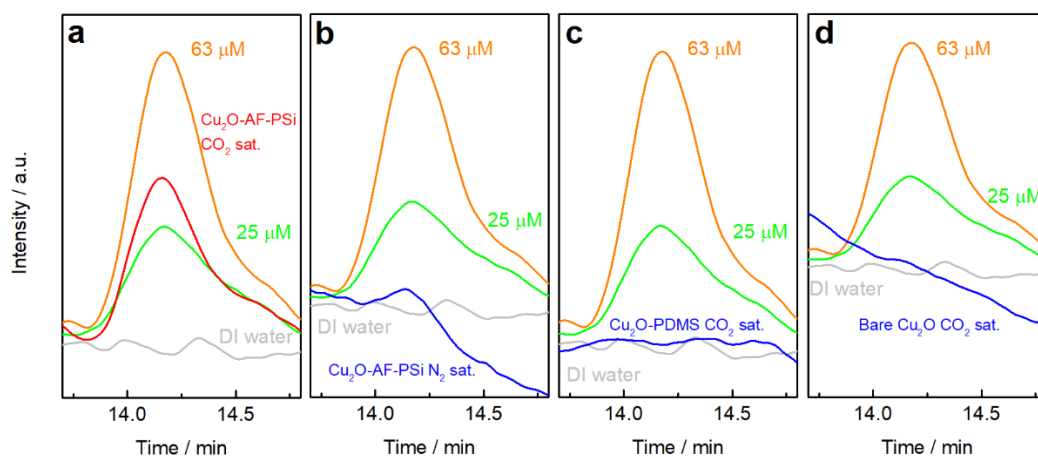
The measurements of ATR of the standard chemicals were done using a ZnSe prism. The spectra were composed by 20 interferograms with a resolution of  $4\text{ cm}^{-1}$  in R/Ro were Ro was the solvent spectra collected as background.



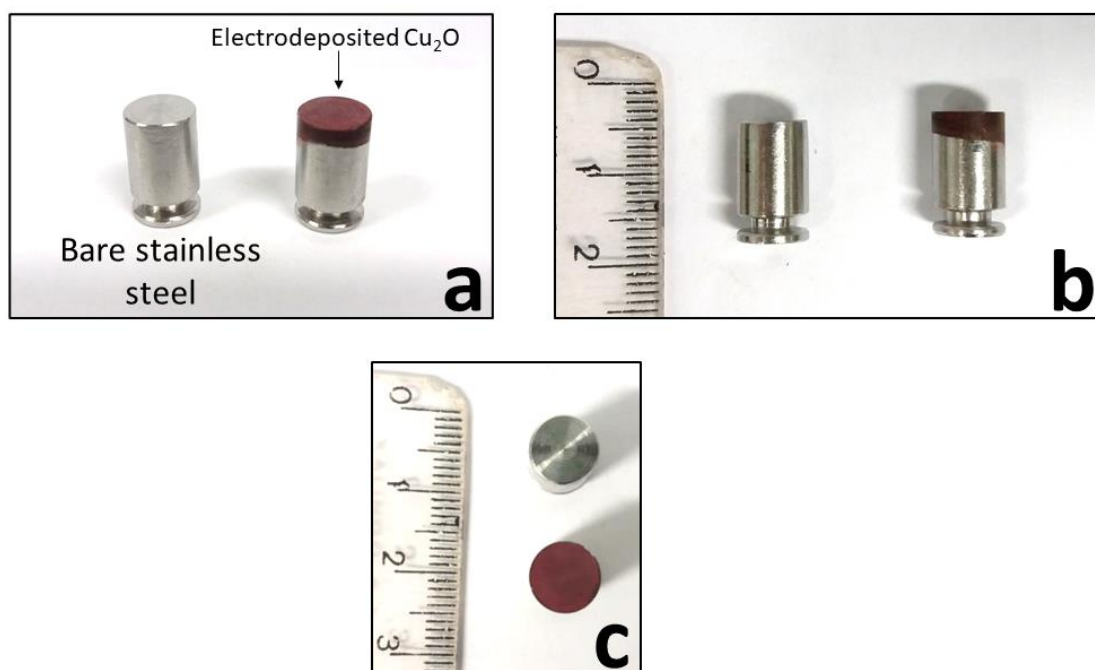
**Figure S1.** SEM image of  $\text{Cu}_2\text{O}$ |AF-PSi electrode surface.

### **Product quantification by HPLC**

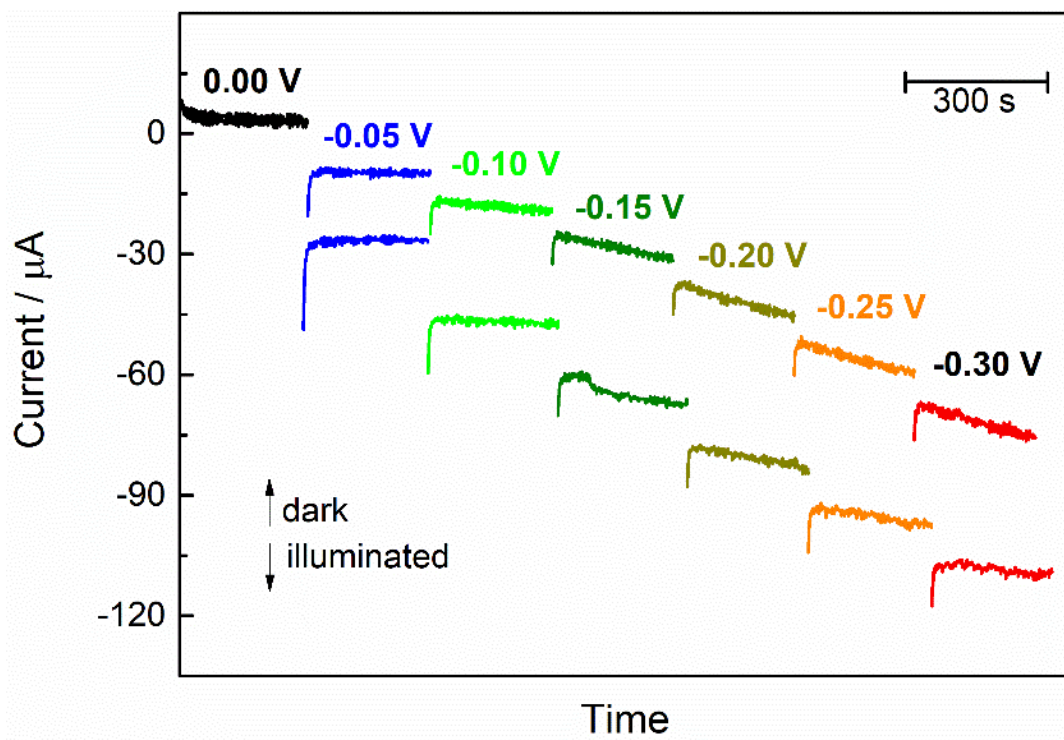
Activity of bare  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_2\text{O}$ |AF-PSi and  $\text{Cu}_2\text{O}$ |PDMS photoelectrodes towards PEC  $\text{CO}_2$ RR were evaluated by 2 h electrolysis performed under potentiostatic control at  $-0.3\text{ V}$  (vs  $\text{Ag}|\text{AgCl}$ ), a potential that assures  $\text{CO}_2$  consumption and minimizes hydrogen evolution reaction in  $0.2\text{ M}$   $\text{Na}_2\text{SO}_4$  aqueous electrolyte. HPLC analysis identified formate as the only product in solution, with 61% faradaic efficiency when AF-PSi is present at  $\text{Cu}_2\text{O}$  photocathode surface (Figure S2a) and it was not observed in  $\text{N}_2$  saturated solution (Figure S2b). Also, no product was detected when  $\text{FTO}|\text{Cu}_2\text{O}|$ PDMS (Figure S2c) or bare  $\text{FTO}|\text{Cu}_2\text{O}$  electrodes (Figure S2d) were used, which further supports the role of N-containing group in activating  $\text{CO}_2$  for PEC  $\text{CO}_2$ RR.



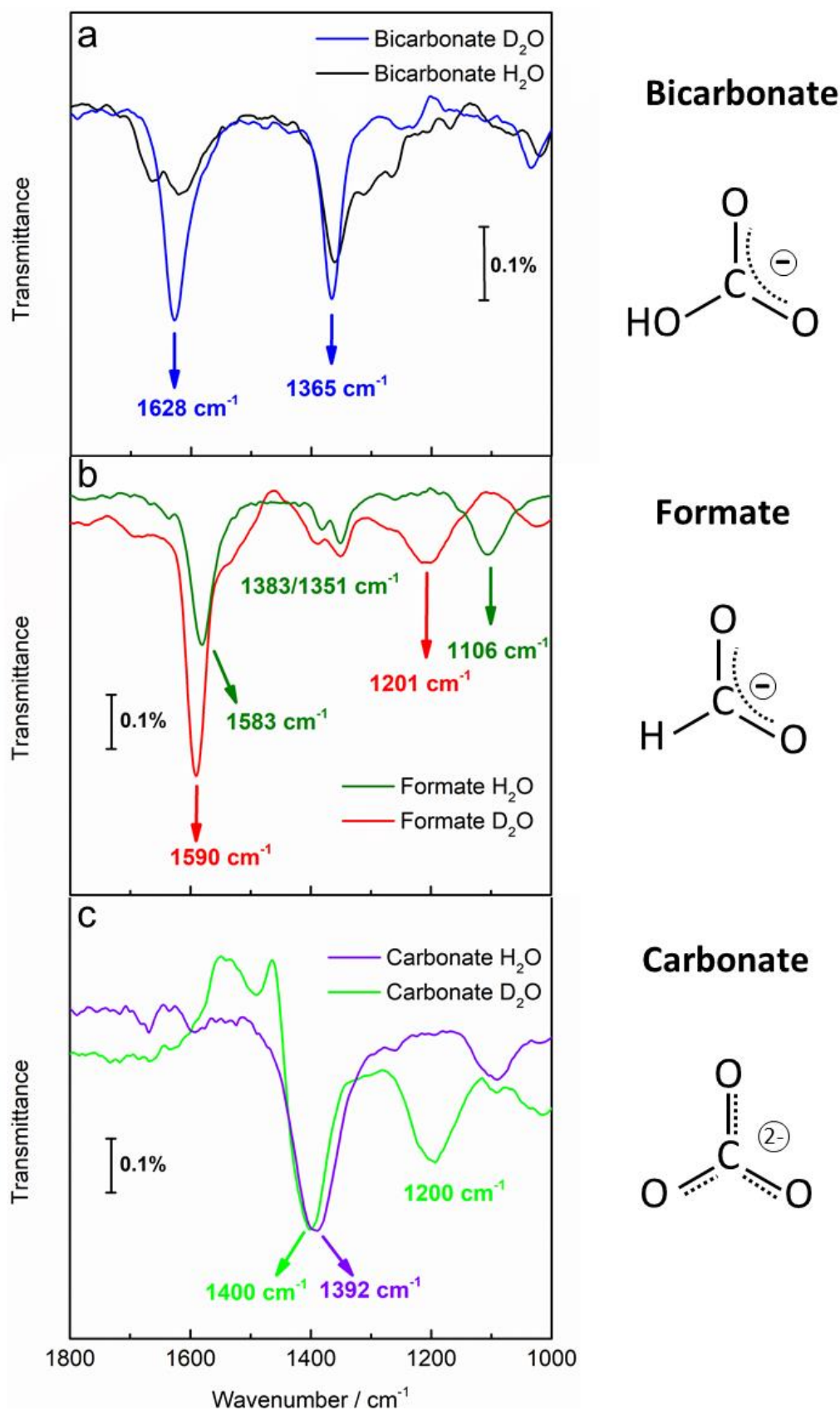
**Figure S2.** HPLC chromatograms obtained from two-hour electrolysis experiments under illumination at different conditions: AF-PSi-modified  $\text{Cu}_2\text{O}$  electrode in  $\text{CO}_2$ -saturated solution (a), AF-PSi-modified  $\text{Cu}_2\text{O}$  electrode in  $\text{N}_2$ -saturated solution (b), PDMS-modified  $\text{Cu}_2\text{O}$  electrode in  $\text{CO}_2$ -saturated solution (c) and bare  $\text{Cu}_2\text{O}$  electrode in  $\text{CO}_2$ -saturated solution (d). Green and orange lines are peaks associated with some of the sodium formate solutions ( $25$  and  $63 \mu\text{mol L}^{-1}$ , respectively) used as standards in calibration.



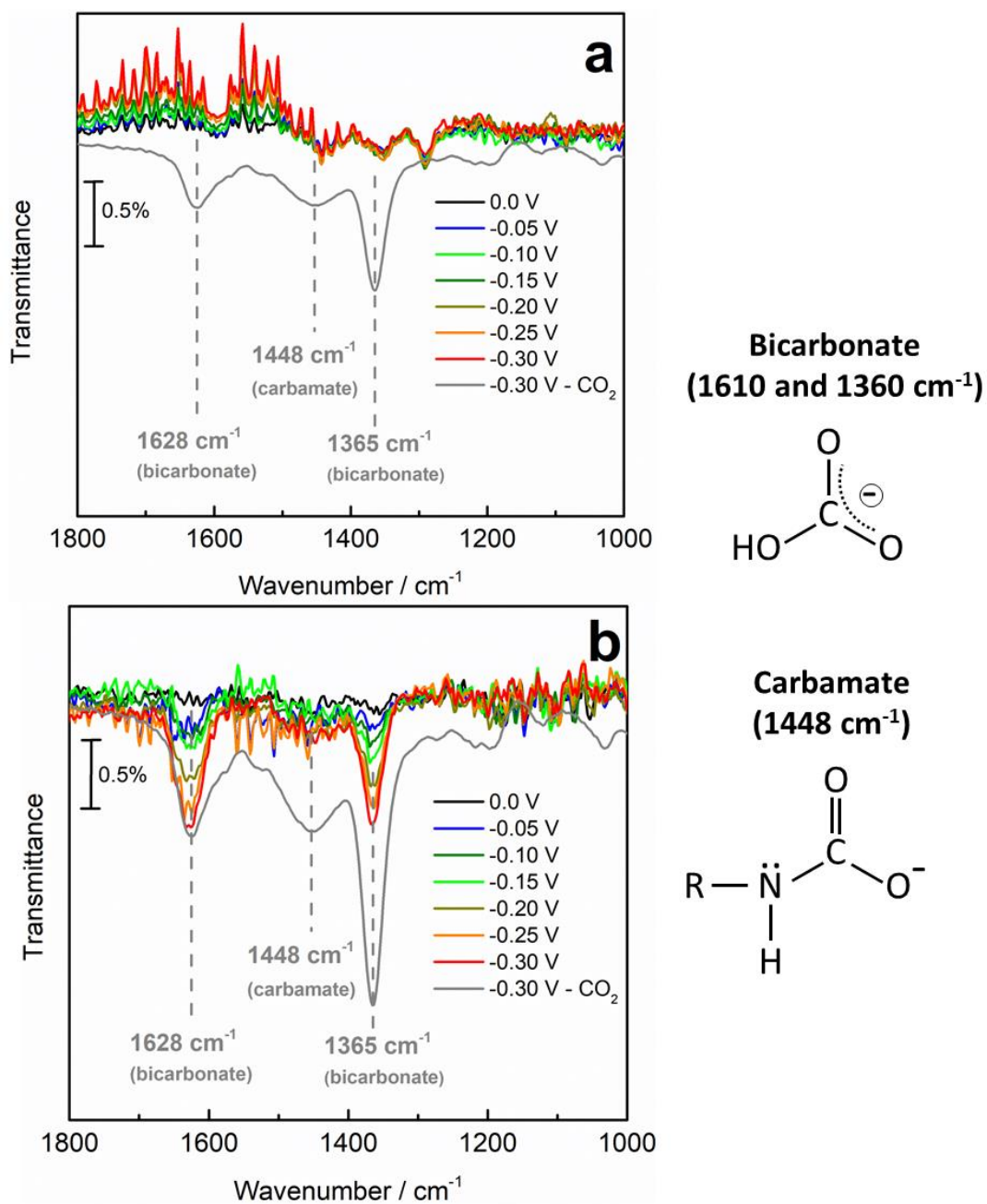
**Figure S3.**  $\text{Cu}_2\text{O}$  electrodes used for in-situ FTIR measurements: full view (a); side view (b); top view (c).



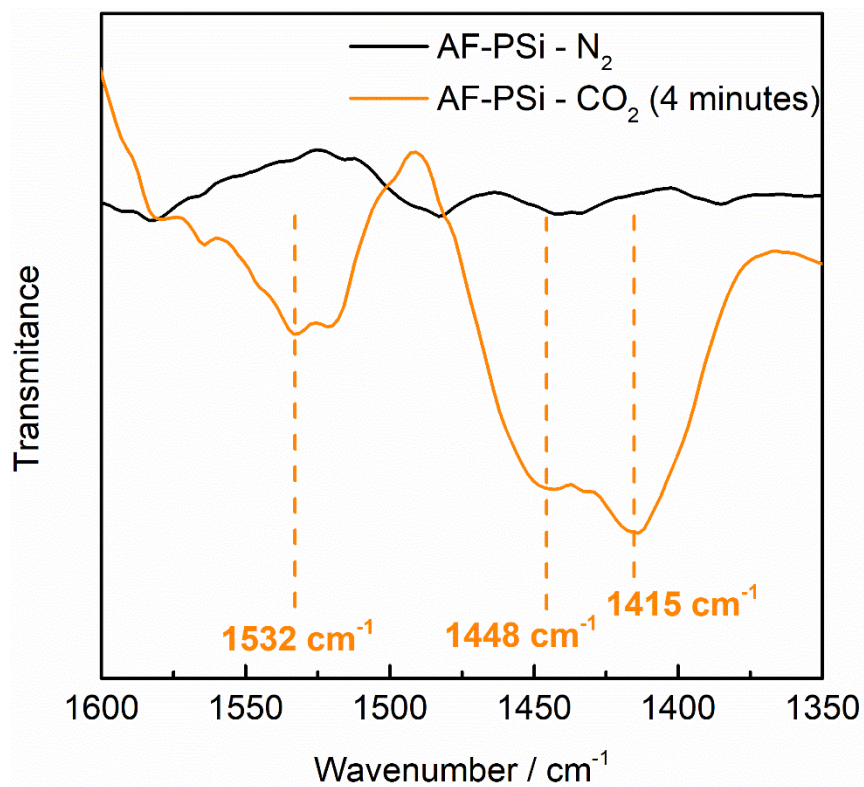
**Figure S4.** Current vs time profiles obtained during each FTIR measurement of  $\text{Cu}_2\text{O}|$ AF-PSi electrodes: dark (upper curves) and illuminated (lower curves) chronoamperometries



**Figure S5.** Reference FTIR spectra obtained from 20 mM solutions prepared in laboratory: sodium bicarbonate (a), sodium formate (b) and sodium carbonate (c). All solutions were prepared using 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution, to reproduce the same conditions observed during in-situ FTIR experiments.

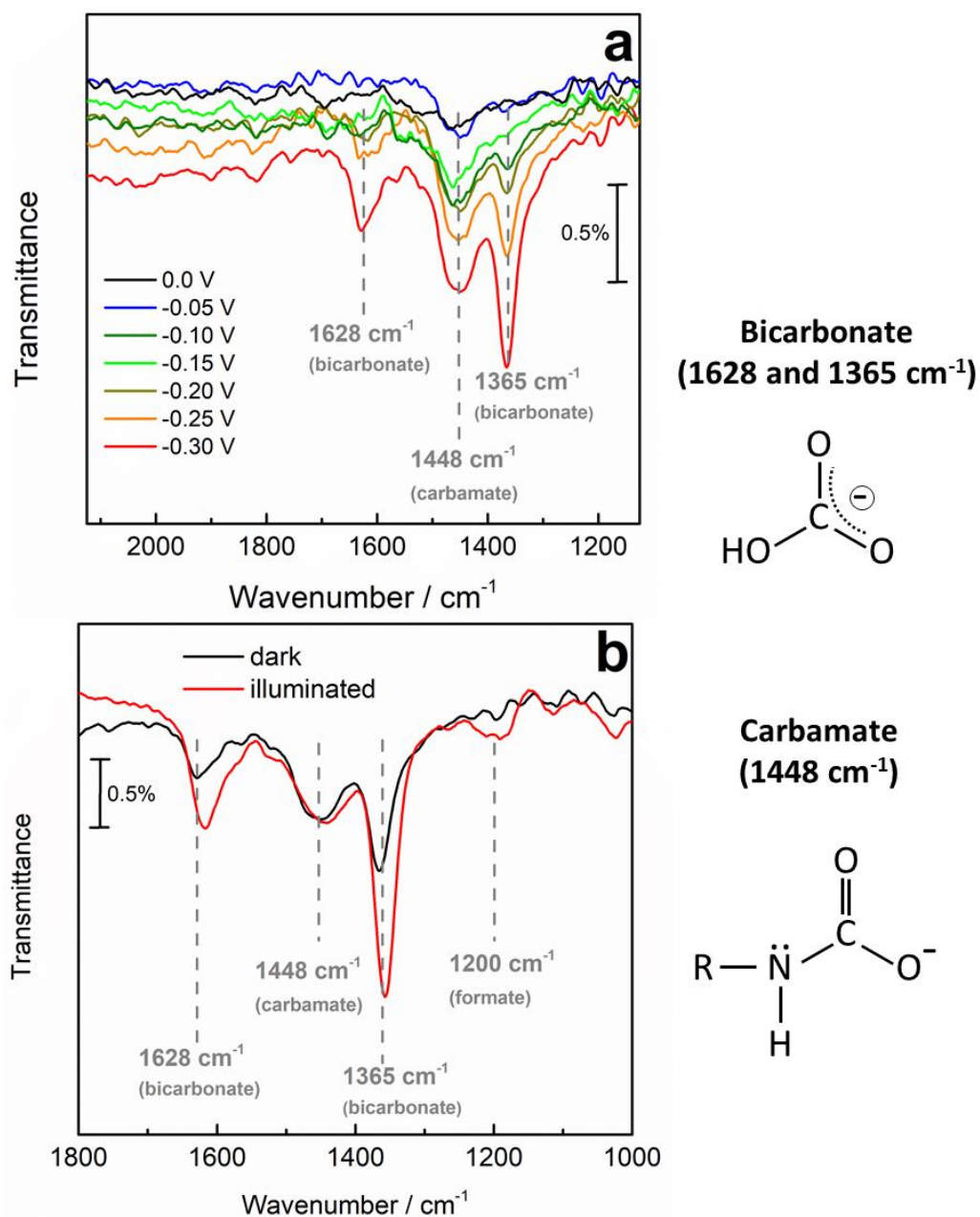


**Figure S6.** In-situ FTIR spectra collected during chronoamperometry experiments at different potentials: a)  $\text{Cu}_2\text{O}$ |AF-PSi electrode, 0.2 M  $\text{Na}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  as electrolyte, saturated with  $\text{N}_2$ . b)  $\text{CuO}$ |PDMS electrode, 0.2 M  $\text{Na}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  as electrolyte, saturated with  $\text{CO}_2$ .

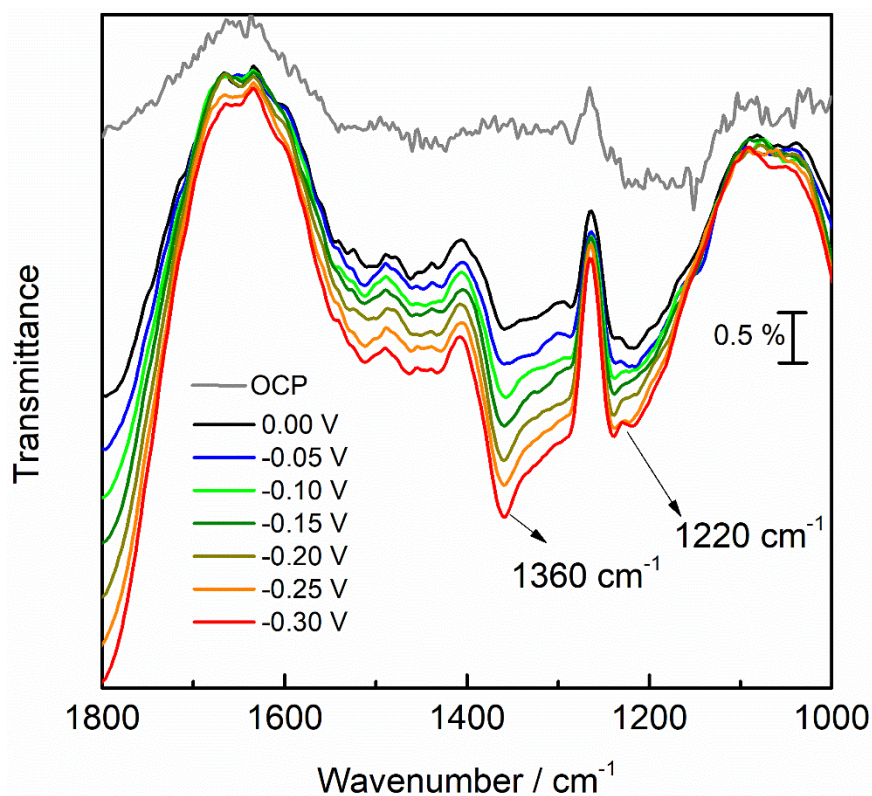


**Figure S7.** FTIR spectra of pure AF-PSi before (black) and after (orange) CO<sub>2</sub> bubbling.

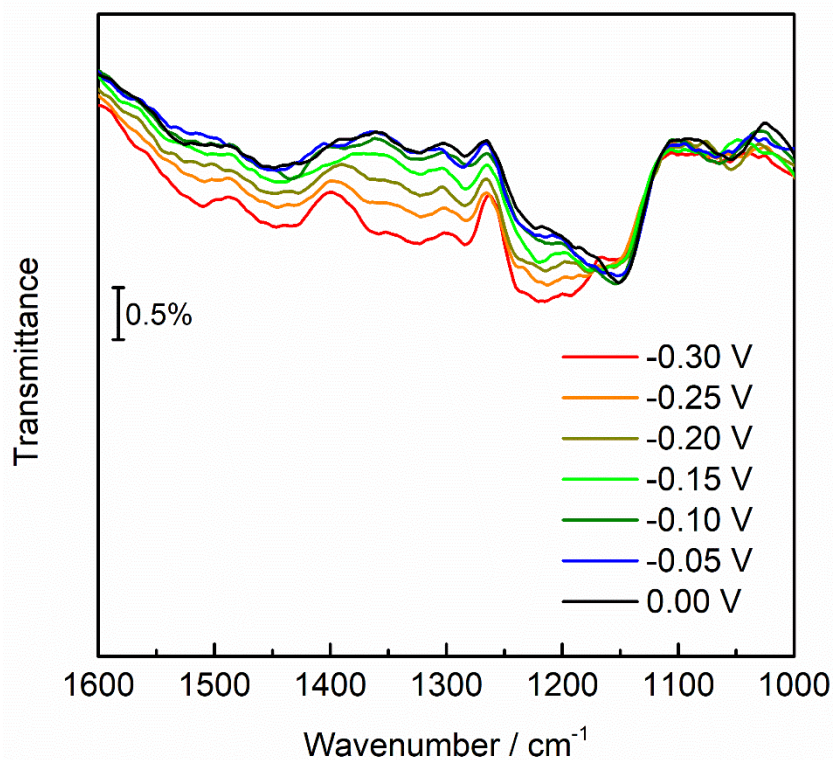




**Figure S8.** In-situ FTIR spectra collected during chronoamperometry experiments at different potentials:  $\text{Cu}_2\text{O}|\text{AF-PSi}$  electrode, 0.2 M  $\text{Na}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  as electrolyte, saturated with  $\text{CO}_2$ . Measurements in the dark (a) and comparison between dark and illuminated at -0.3 V (b).



**Figure S9.** In-situ FTIR spectra collected during chronoamperometry experiments at different potentials:  $\text{Cu}_2\text{O}|\text{AF-PSi}$  electrode, 0.2 M  $\text{Na}_2\text{SO}_4$  in  $\text{H}_2\text{O}$  as electrolyte, saturated with  $\text{CO}_2$ .



**Figure S10.** In-situ FTIR spectra collected during chronoamperometry experiments without illumination at different potentials:  $\text{Cu}_2\text{O}|\text{AF-PSi}$  electrode, 0.2 M  $\text{Na}_2\text{SO}_4$  in  $\text{H}_2\text{O}$  as electrolyte, saturated with  $\text{CO}_2$ .