Investigating the effects of pyridine and poly(4-vinylpyridine) on CO_2 reduction electrocatalysis at gold electrodes using *in-situ* surface-enhanced Raman spectroelectrochemistry

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Electronic supplementary information

1 Experimental

Pyridine, poly(4-vinylpyridine) (4-PVP, M_W = 60,000 g.mol^{-1}), methanol (MeOH, 99 %), KCl, $NaHCO_3$ (> 99 %), Na_2CO_3, $LiClO_4$ (electrochemical grade) were purchased from Sigma Aldrich and used as received. All aqueous solutions were made up using Milli-Q water. The methanolic deposition solution for drop-casting of 4-PVP was 10 mg/200 µL (5 % w/v) and 5 µL drops were cast (*ca*. 250 µg of polymer and thus *ca*. 3.2 µmol of py monomer units). CO_2 (N4.0) was purchased from Air Products.

Cyclic and linear sweep voltammetry was performed using a CHInstruments 660 potentiostat with a gold disc working electrode (d = 2 mm, CHInstruments), a Pt coil counter electrode and a Ag/AgCl (sat. KCl) reference electrode, which was calibrated daily vs. a master saturated calomel electrode. The electrolyte used was either 0.1 M $NaHCO_3/H_2O$ or 0.1 M $LiClO_4$/MeOH. All solutions were purged with N_2 or CO_2 for 20 minutes prior to experiments and were kept under a blanket of gas throughout. In all cases two CV cycles were recorded and the data shown are from the second cycle. The pH of the solution was 5.3 (N_2 purged) or 3.9 (CO_2 purged).

Electrocatalytic measurements were performed in a custom-made H-cell using a gold disc working electrode either unmodified or coated with a drop-cast film of 4-PVP. The working electrode compartment was sampled periodically for gas products (H_2 and CO) using gas chromatography. Gas chromatography was performed using a Varian CP-3800 employing N5 helium as the carrier gas (20 ml.min-1) at 60˚C. A 5 Å molecular sieve column (Varian 1041, 3.7 m, 1/8 inch stainless steel) and a pulsed discharge detector (D-3-I-HP, Valco Vici) were employed. CO peak areas were quantified with multiple calibrant gas (200 ppm CO, 200 ppm CH_4, 500 pm H_2 in a helium matrix, Calgaz) injections and were re-calibrated daily.

Surface enhanced Raman spectroscopy (SERS) was performed using a Horiba Jobin Yvon HR800 UV spectrometer. The laser (532 nm) was generated by a Coherent Innova 70c solid state Ar-ion laser (532 nm) and a 20x microscope objective. A 600 grooves/mm diffraction grating was employed. The x-axis was calibrated versus the Rayleigh line (0 nm) and the phonon mode from silicon wafer (520 cm^{-1}). UV/Vis spectroscopy was performed using a Jasco V750 spectrometer with slit

widths of 1 mm, with films of 4-PVP/MeOH drop-cast onto quartz slides and allowed to dry in air prior to spectral recording. Solution FTIR spectra were recorded using a Perkin-Elmer Spectrum 100 (16 scans, 4 cm^{-1} resolution) by placing a drop of solution directly onto a diamond ATR tip. Film thicknesses were measured using a Bruker DektakXT stylus profilometer at a scan speed of 0.1 mm/s.

Surface-enhanced Raman spectroelectrochemistry (SERS SEC) was performed using a CHInstruments 660 potentiostat as described above. The cell was setup in a glass vial for voltammetry (ALS Japan) and a Teflon cap to hold electrodes in position. The cell was purged with N_2 or CO_2 for 20 minutes prior to experiments and were kept under a blanket of gas throughout. An inverted laser (532 nm) was focussed through the bottom of the glass and onto the working electrode/electrolyte interface. Spectral acquisition was averaged over 4 scans of 8 seconds each.

2 pH dependence of films by UV spectral titration and linear sweep voltammetry

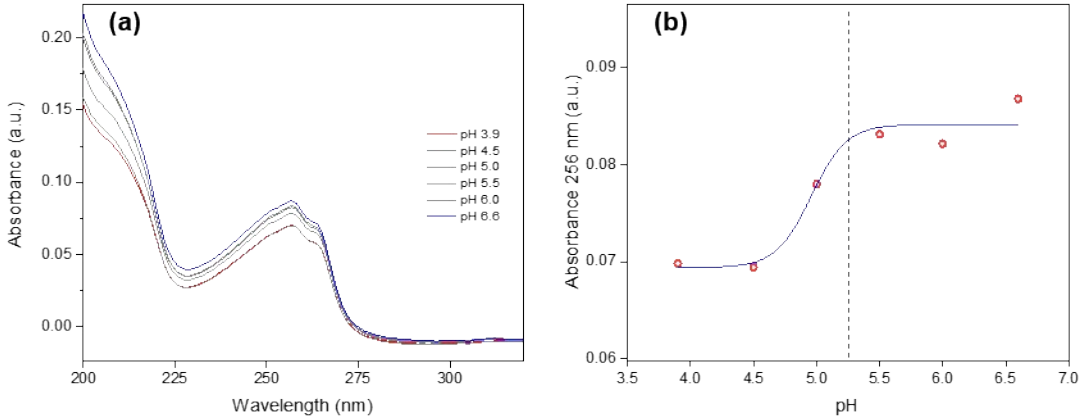

Fig. S1 (a): pH dependence of the UV spectrum of a 4-PVP film drop-cast (5 µL of 5 % w/v solution in MeOH) onto a quartz slide. (b) Plot of $Abs_{256\ nm}$ *vs*. pH of contact solution is non-linear and shows a pK_a of *ca*. 5.0 for 4-PVP, which is similar to the literature value of free pyridine pK_a dissolved in aqueous solution (dashed line in (b)). The blue line in (b) represents the sigmoidal best fit using a Boltzmann function in Origin 2018 64 bit.

In Fig. S1 (a) the changes in absorbance of the π-π* transition centred at 256 nm are most likely due to the differences in UV absorption of the pyridine and pyridinium forms of the species.[S1] The transformation from one form to the other is not quantitative, based on reported molar extinction coefficients for py and pyH^+ monomers,[S1] suggesting that not all py units are protonated to pyH^+. An isosbestic point was not observed, potentially due to physical changes occurring throughout the film; indeed, swelling and contraction of 4-PVP films in contact with solution of pH above and below the pK_a of py has been shown previously.[S2] Additionally, the py and pyH^+ spectra exhibit λ_{max} values that differ by a reported 0.5 nm only,[S1] suggesting overlap of the two spectra at a given wavelength is unlikely. Attempts to conduct equivalent studies into the protonation state of the film as a function of contact solution pH using ^{15}N-NMR spectroscopy were unsuccessful.[S3] In this experiment, a film of 4-PVP was deposited from MeOH on the inner walls of a standard NMR tube and allowed to dry overnight in air. The NMR solvent used was D_2O pD-corrected[S4] using NaOD or DCl to pD values of *ca*. 8 and 3 respectively; however, only spectra of the blank electrolyte in an unmodified tube could be

acquired with the spectrometer unable to lock on the PVP-coated tube. Future experiments will focus on the development of a manual locking protocol to monitor these spectral changes.

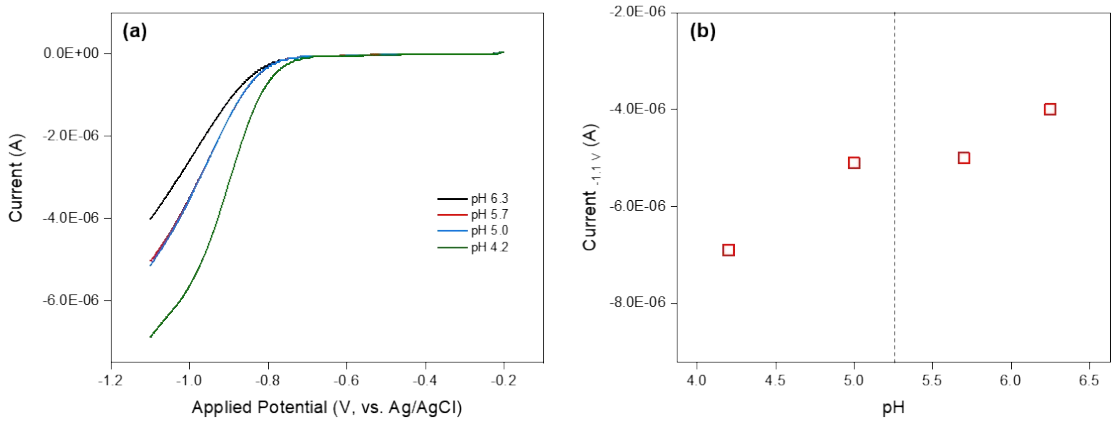

Fig. S2: pH dependence of CVs of a 4-PVP film drop-cast (5 µL of 5 % w/v solution in MeOH) on Au WE under CO_2 in 0.5 M KCl. Current max at -1.1 V *vs*. Ag/AgCl shows pH dependence is non-linear around the literature pK_a value of pyridine dissolved in aqueous solution (dashed line in (b)).

3 Film thickness by profilometry

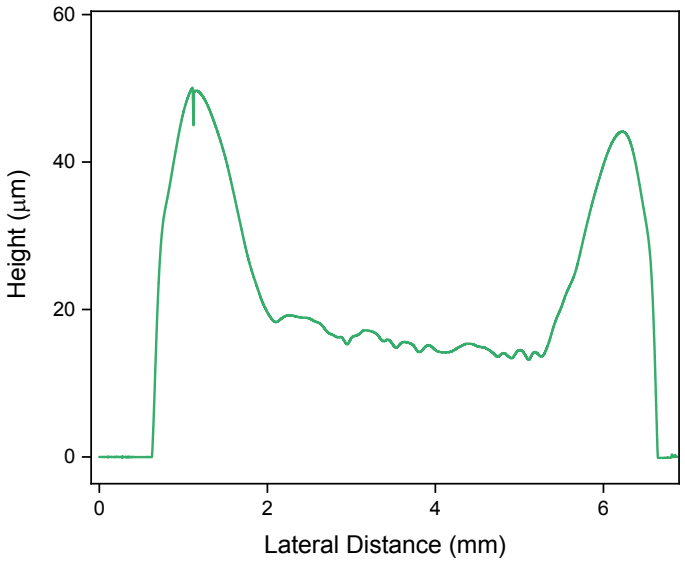

Fig. S3: Profilometry of a 4-PVP film drop-cast (5 µL of 5 % w/v solution in MeOH) onto Au foil.

4 Controlled potential electrolysis

Electrode	V, vs. Ag/AgCl	V, vs. RHE	FE H_2	FE CO	FE Total
Au	-0.9	-0.376	71	0	71
Au/4-PVP	-0.9	-0.376	75	0	75
Au	-1.2	-0.676	25	64	89
Au/4-PVP	-1.2	-0.676	11	68	79

Table S1: CPE data for Au foil electrode (area = 0.7 cm^2 approx.) for unmodified and 4-PVP film-modified electrodes. Electrolysis was conducted in a CO_2-purged H-cell for 30 minutes. No formate was detected in the catholyte post-experiment by ^{1}H-NMR.

5 Raman and FTIR spectroscopy

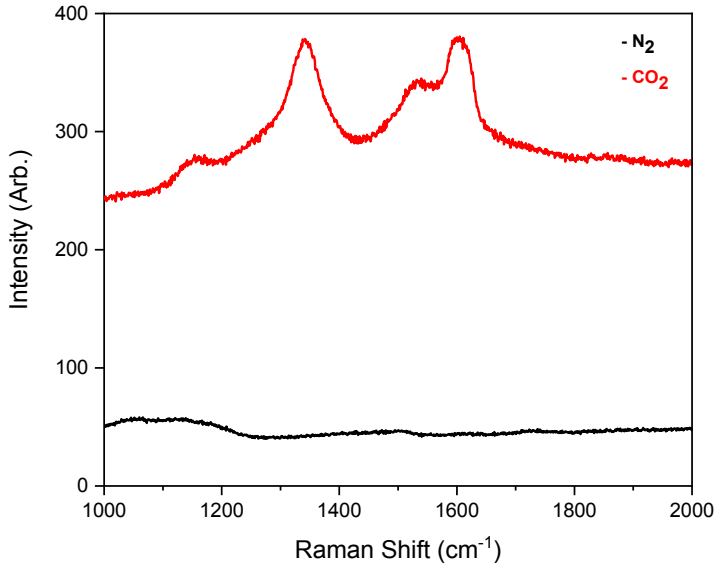

Fig. S4: SERS of a blank, unmodified Au electrode in N_2-purged 0.5 M KCl under a blanket of N_2 (black). After CO_2 purging of the same solution, four intense Raman modes appear (red).

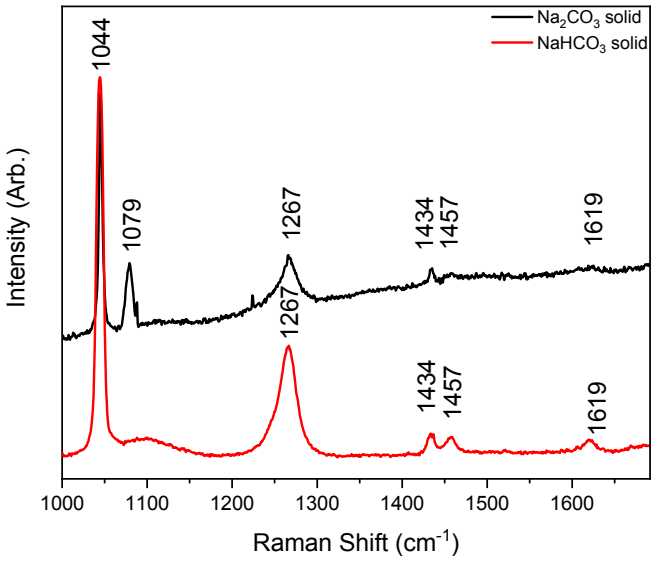

Fig. S5: Raman spectra of solid $NaHCO_3$ and Na_2CO_3 crystals.

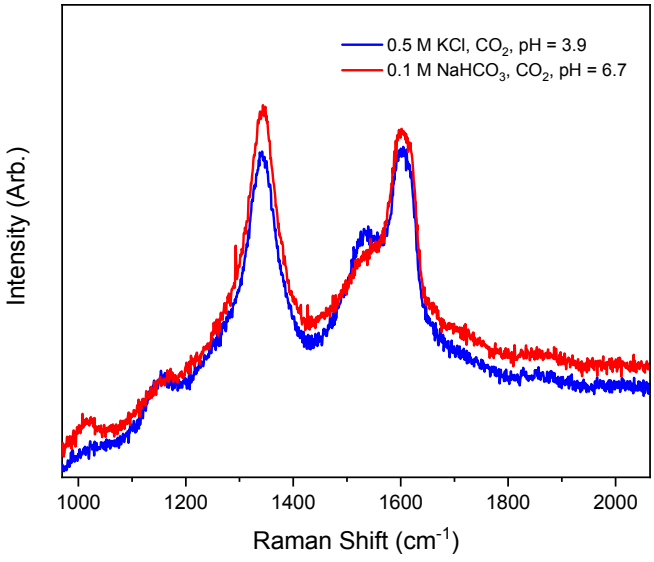

Fig. S6: SERS of Au disc electrode in different electrolytes and at different pH values.

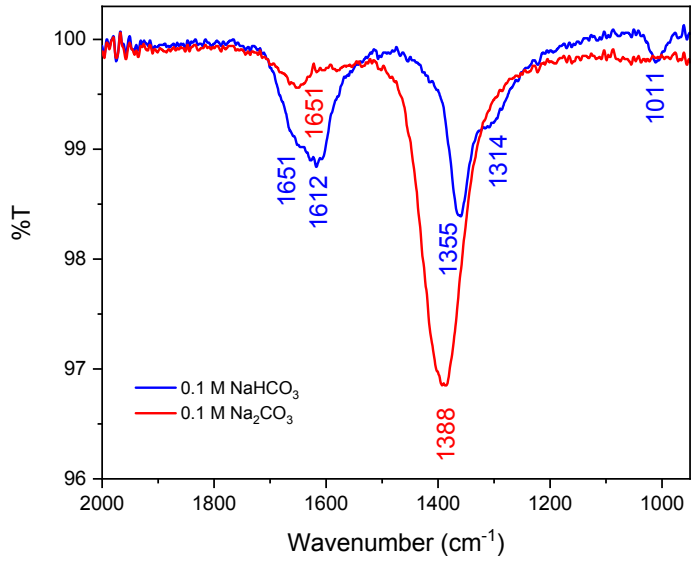

Fig. S7: ATR-FTIR spectra of 0.1 M solutions of $NaHCO_3$ and Na_2CO_3.

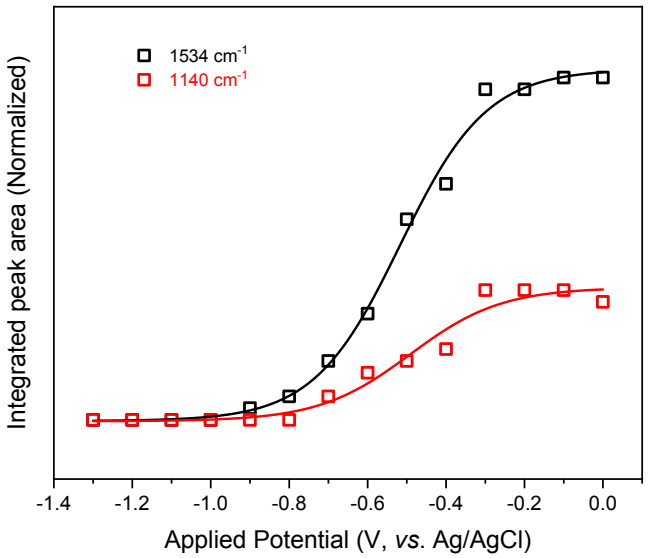

Fig. S8: Integrated areas from peak-fitted SERS spectra of a blank, unmodified Au electrode in CO_2-purged 0.5 M KCl/H_2O electrolyte at all applied potentials showing loss of modes at 1534 and 1140 cm^{-1} occurs simultaneously and are therefore attributed to the same species (adsorbed deprotonated HCO_3^- as CO_3^-). The solid lines represent sigmoidal best fits using a Boltzmann function in Origin 2018 64 bit.

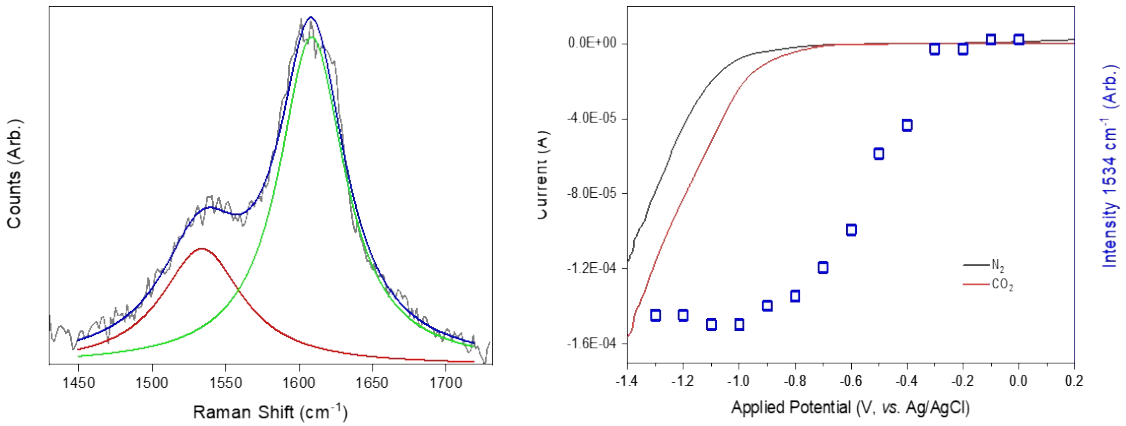

Fig. S9 (a): Peak-fitted SERS of a blank, unmodified Au electrode in CO_2-purged 0.5 M KCl/H_2O electrolyte at - 0.5 V a broad band at 1608 cm^{-1} and a shoulder at 1534 cm^{-1}. The band at 1608 cm^{-1} can itself be peak fit to show two maxima at 1598 and 1620 cm^{-1}, potentially corresponding to the OH bend of interfacial water[S5] in addition to the ν_{as} C-O stretch of chemisorbed deprotonated bicarbonate, but in Fig. S9 (a) the fit has been reduced to two peaks for simplicity. Grey: raw recorded data; green and red: fits to the two maxima; blue: summation of red and green curves. (b) Linear sweep voltammetry of a blank Au electrode in 0.5 M KCl/H_2O electrolyte under N_2 (blank) and CO_2 (red) atmospheres. The blue squares show that the disappearance of the adsorbed bicarbonate mode at 1534 cm^{-1} does not correlate with electrocatalytic potentials for HER or CO_2RR. The data were fit to a series of overlapping Lorentzian peaks using the function y = y0 + (2*A/pi)*(w/(4*(x-xc)^2 + w^2)) in Origin 2018 64 bit.

An excellent fit of the spectrum shown in Fig. S9(a) revealed two modes with maxima at 1540 and 1610 cm^{-1} (broad). There may be some asymmetry in the mode at 1610 cm^{-1} and a reasonable fit could be attained with three maxima at 1540, 1598 and 1620 cm^{-1}. This could correspond to the two modes of physisorbed and chemisorbed bicarbonate, as well as the interfacial bending mode of adsorbed H_2O at 1620 cm^{-1}, consistent with previous studies.[S5] This fit was not as high quality as that shown in Fig. S9(a), however, so the discussion herein is presented in terms of the broad mode at 1610 cm^{-1}. This feature may be more clearly resolved at higher resolution in future studies.

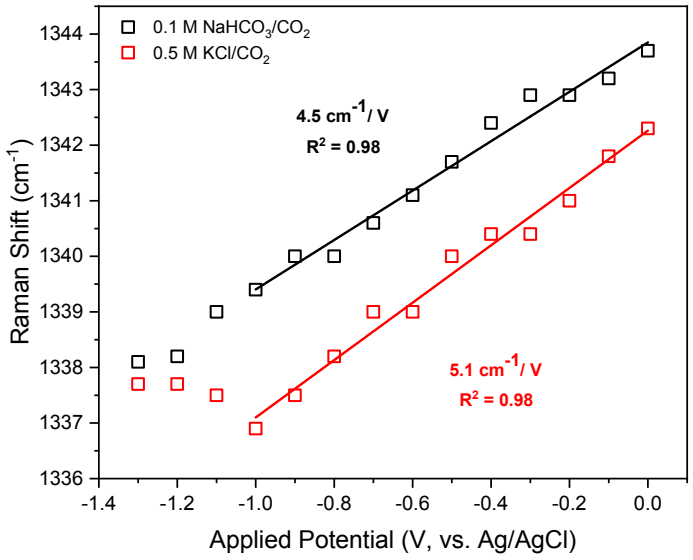

Fig. S10: Plot of peak maxima at *ca*. 1340 cm^{-1} (ν_s C-O stretch of chemisorbed deprotonated bicarbonate) for unmodified Au disc electrodes in the presence of different electrolytes. The Stark shifts of approximately 5 $cm^{-1}.V^{-1}$ for both systems are indicative of chemisorption and the lack of Stark shifting for the modes at 1140 and 1534 cm^{-1} implies that these modes are due to non-chemisorbed (i.e.: physisorbed) species.

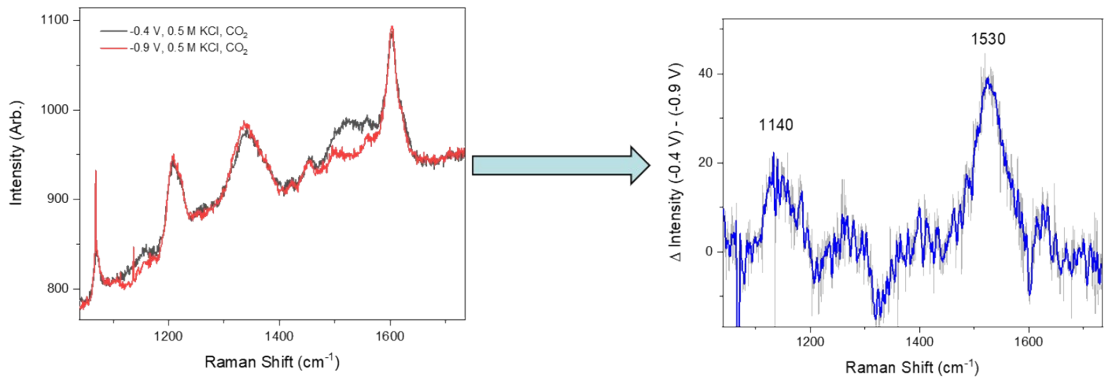

Fig. S11: A difference spectrum shows the changes in intensity between spectra acquired at -0.4 V and -0.9 V for a PVP-coated Au disc WE in CO_2-purged 0.5 M KCl. The greatest changes in intensity are at approximately 1530 and 1140 cm^{-1}, which correlates with the spectral changes in Figs. 3, S8 and S9 and are attributed to the desorption of physisorbed deprotonated bicarbonate through cracks in the thick PVP film. No spectral signal was observed for the chemisorbed bicarbonate, indicative of surface blocking by the PVP layer. Smoothing (blue) was performed using the Savitsky-Golay function with a 2nd order polynomial and a ten data point window.

References

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