Electronic Supplementary Information:

Ionic liquids enhance the electrochemical CO_2 reduction catalyzed by MoO_2

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Experimental Methods

Materials

All electrochemical measurements were performed using a Gamry Instruments Reference 3000. All of the experiments described below were conducted in a double layered glass cell with five-necks and the temperature was controlled by a cooling machine which makes a flow of toluene on the surface of the cell. The picture of the double layered glass cell is shown in Figure S5. Gasses used for electrochemistry including Nitrogen, Carbon dioxide (99.998%) and Carbon monoxide were purchased from Carbagas and used as delivered.

The ionic liquids in this study were purchased from two different companies. 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6, ≥ 98%) and 1-Ethyl-3-methylimidazolium hexafluorophosphate ([EMIM]PF_6, ≥ 98%) were purchased from TCI. 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl, ≥ 98%) , 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4, ≥ 97%) and 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4, ≥ 98%) were purchased from Sigma Aldrich. Acetonitrile (99.999%, electronic grade) was obtained from Sigma Aldrich. Molybdenum (IV) Oxide (> 99%), platinum wire (0.5 mm, 99.99%) and silver wire (0.5 mm, 99.9%) were purchased from Sigma Aldrich. Lead (powder type, > 97%) was purchased from Fluka. All water used in either experimentation or cleaning, came from a Millipore Milli-Q® Integral water purification system (18.2 MΩ cm resistivity).

Preparation of the Working Electrode

Pb pellet has been chosen as a substrate for the working electrode. The surface of bulk Pb was cleaned by chemical etching in 50% acetic acid then ultrasonically washed in deionized water before use. Pb was first pelletized by the pressure of 5 bar and then a thin layer of powdered catalyst (MoO_2 : Pb = 8 : 2 weight ratio) was spread on one side of the pellet. The whole set was pelletized under 10 bar to make a contact between the powdered catalyst and Pb substrate. This modified-pellet was used as a working electrode and a copper wire was connected on the back of the pellet by soldering to make an electrical contact. The contact area of the copper wire with the soldering site was isolated from the solution using molten polypropylene.

Preparation of the Auxiliary (Counter) and Reference Electrodes

A platinum wire was used as an auxiliary electrode and an Ag/Ag^+ ($AgNO_3$ (10 mM) in 0.1 M $TBAPF_6$-MeCN) electrode was used as a reference electrode. The Ag/Ag^+ reference electrode was assembled first by sealing a porous Vycor tip or silica gel to the tip of the glass capillary using a piece of heat shrink. The capillary was then filled with the silver nitrate solution described above and sealed at the top by a Teflon cap. And a Pt wire counter electrode was separated by a glass frit. Ferrocene (Fc, ABCR, ≥ 99.0%) was used as an internal standard in order to calibrate our non-aqueous reference electrode. The Ag/Ag^+ reference electrode had a potential of -0.11 V *vs.* Fc/Fc^+ couple.[1, 2] All potentials reported here vs. Fc/Fc^+ were converted by adding -0.11 V to the potentials measured vs. the Ag/Ag^+ electrode.

The Electrochemical Cell Assembly

The electrochemical cell was made of a double-layered glass with five-necks on the top. Figure S5 shows a picture of the gas tight cell used for the all electrochemical measurements in this chapter. The joints that make up the working, counter and reference electrodes are secured to the each neck of the cell. The other two necks were connected to the inlet and outlet of the gas in the headspace of the cell. All the three electrodes were submerged into the electrolyte solution and the Pt counter electrode was separated by a glass frit.

Polarization Measurements (Linear Sweep Voltammetry)

In order to monitor the reduction of CO_2 dissolved in the electrolyte solution, linear sweep voltammograms were taken before and after the addition of CO_2 into the electrolyte solution. Initially the electrolyte solution was sparged with N_2 (gas) for 60 min to remove any residual moisture and oxygen. Linear sweep voltammetry measurements of this control experiment were taken at a scan rate of 50 mV/s with IR compensation. After the control experiment, the solution was sparged with CO_2 for 60 min (CO_2 saturated MeCN) and the electrocatalytic CO_2 reduction was measured. The measurements for the CO_2 saturated experiments followed the same specifications as the blank, except for the gas of the headspace.

Potentiostatic Electrolysis

The potentiostatic measurements were carried out at room temperature (RT) and -20 °C. 70 mL of the electrolyte solution was used in the electrolysis experiments. When the internal temperature of the solution was verified with the aid of a thermometer, CO_2 gas was purged for 60 min prior to the electrolysis. The electrode setup was identical to that of the polarization measurements as described above. After the electrolysis, a small fraction of the cell's headspace (2 mL) was sampled by gas tight syringe and analyzed by gas chromatography.

Gas Chromatography, Ion Chromatography and the Calculation of Current Efficiency

Gas chromatography measurements were conducted on a home-built GC with a TCD detector (Valco Instruments CO. Inc.) and a HayeSep DB 100/120 mesh packed column (Agilent) with Helium (He) as a carrier gas. Calibration with different CO volume in the fixed volume of the headspace was done. Since the amount of CO dissolved in ILs/MeCN is not known, calibration was performed with the same cell assembly as for the actual experiments. First CO_2 gas was purged for 30 min through the solution and the pressure of the headspace in the cell was maintained at 1 atm. When the solution was saturated with CO_2, a 1 mL aliquot of CO gas was injected into the headspace, which was then allowed to stir for 30 min to equilibrate the system. After the addition of each aliquot, a small fraction of the cell's headspace (2 mL) was analyzed by GC. Hence the area of the CO peak in the gas chromatogram was determined after the injection of 0.1, 0.3, 0.5, 1, 1.5 and 2 mL of CO. This procedure was repeated more than 3 times for each aliquot of CO and between these results only the most 3 reliable data without O_2 detection were chosen for the calibration. Detected O_2 indicates a gas leak in the cell. The mean values of the respective CO area were plotted against the injected CO volumes and the points were fitted linearly. The obtained calibration curve is shown in Figure S6 with its linear equation.

$$y = 0.06803\ x + 0.0142$$

With the transformed equation;

$$V_{co}\ (\mathrm{mL}) = \frac{\text{Area of detected CO - 0.0142}}{0.06803}$$

the amount of produced CO during an electrolysis experiment can be directly determined with the detected area of CO peak from GC analysis. After the electrolysis, the current efficiency of an electrolysis experiment was calculated as follows. The total transferred charge (C) was divided by the Faraday constant (96485 C/mol) as well as by the factor of two, because two electrons are needed to form one CO molecule from CO_2. This gave the theoretical numbers of CO moles, considering 100% of yield. The number of moles of produced CO (derived from GC analysis) was then divided by the number of CO theoretically obtained. Multiplication of this result by 100% expressed the current efficiency as a percentage. The yield of H_2 was calculated in the same method. The liquid-phase products were analyzed and quantified by ion chromatography (Metrohm IC, Switzerland) at the end of the electrolysis. All samples were diluted 10 fold into water. The calibration for quantification of the liquid product and the calculation of current efficiency were performed in the same method as gas chromatography. The chromatograms of a gas mixture and CO calibration peaks are shown below in Figure S7.

Scanning Electron Microscopy (SEM) and Powder X-ray Diffraction (PXRD)

SEM secondary electron (SE) images were taken in a Phillips (FEI) XLF-30 FEG scanning electron microscope (Figure S8). PXRD measurements were carried out on an X'Pert Philips diffractometer using a Cu Kα radiation source (0.1540 nm). Figure S9 shows a PXRD pattern for the MoO_2 bulk powder in the 2θ range of 20°–65°. The diffraction peaks at 26.1°, 37.1°, 53.6° and 60.1° correspond respectively to the (0 1 1), (2 1 1), (0 2 2) and (0 3 1) lattice planes of the monoclinic MoO_2 crystal with lattice constants a = 0.5620(0) nm, b = 0.4860(0) nm, c = 0.5630(0) nm and β = 120.94.[3] Peak of Mo of body centric cubic (bcc) structure is also observed. No peaks of any other phases or impurities were observed from the PXRD patterns, indicating the high purity of monoclinic MoO_2.

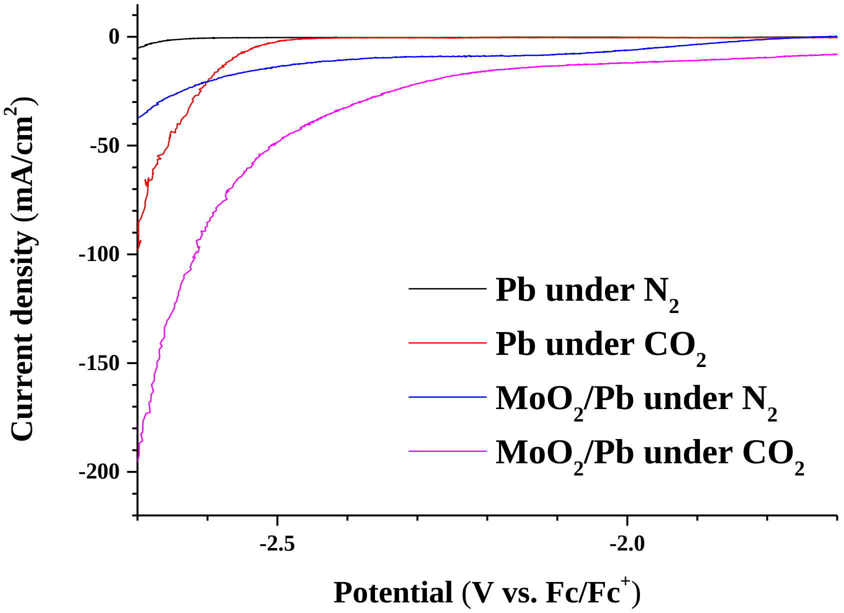


Figure S1. Linear sweep voltammograms (LSVs) of Pb and MoO_2/Pb electrodes in N_2 and CO_2-saturated MeCN at RT. Electrolyte: 0.3 M [BMIM]PF_6; scan rate: 50 mV/s .

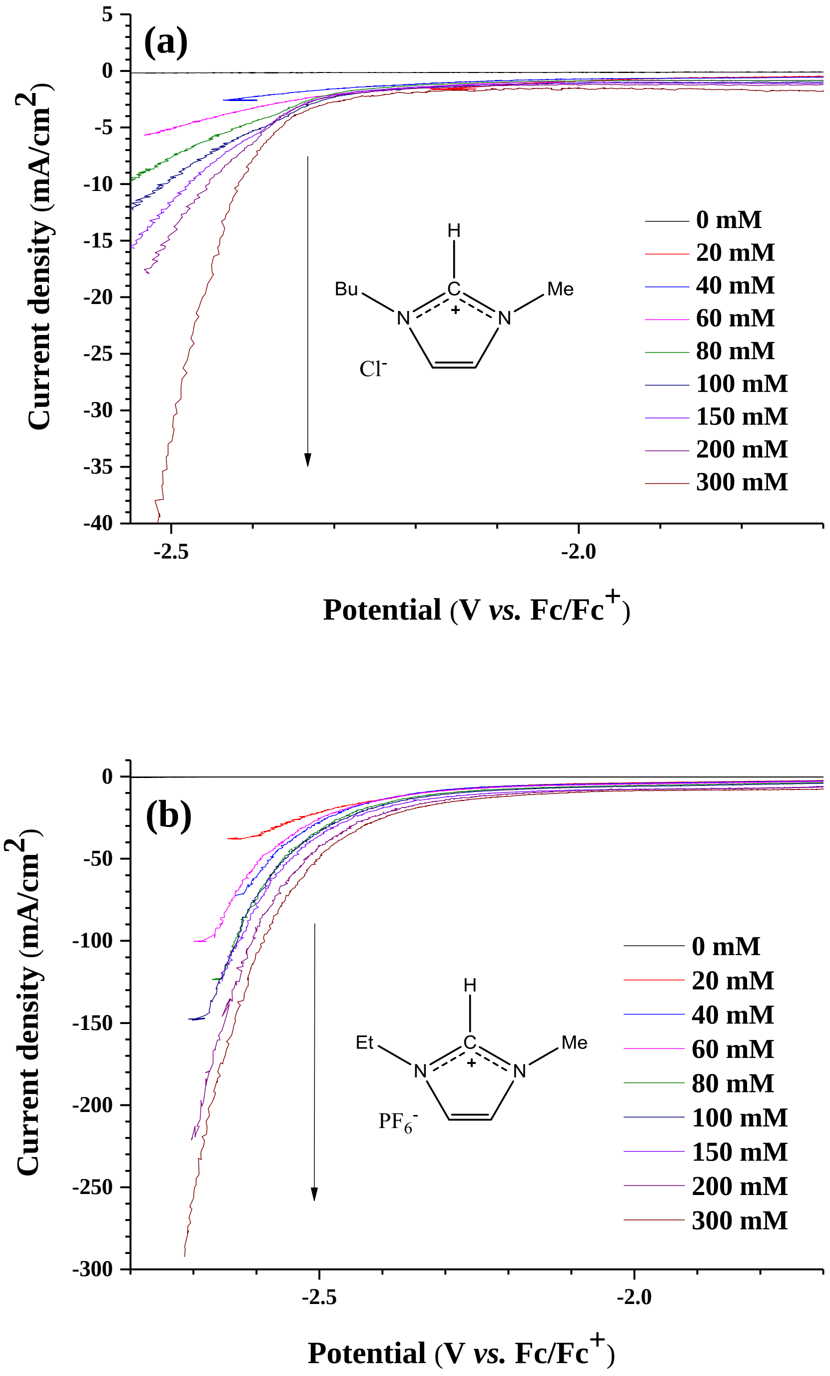


Figure S2. Linear sweep voltammograms (LSVs) using MoO_2/Pb electrodes in CO_2 saturated MeCN containing varying amounts of (a) [BMIM]Cl and (b) [EMIM]PF_6, at RT. Scan rate: 50 mV/s.

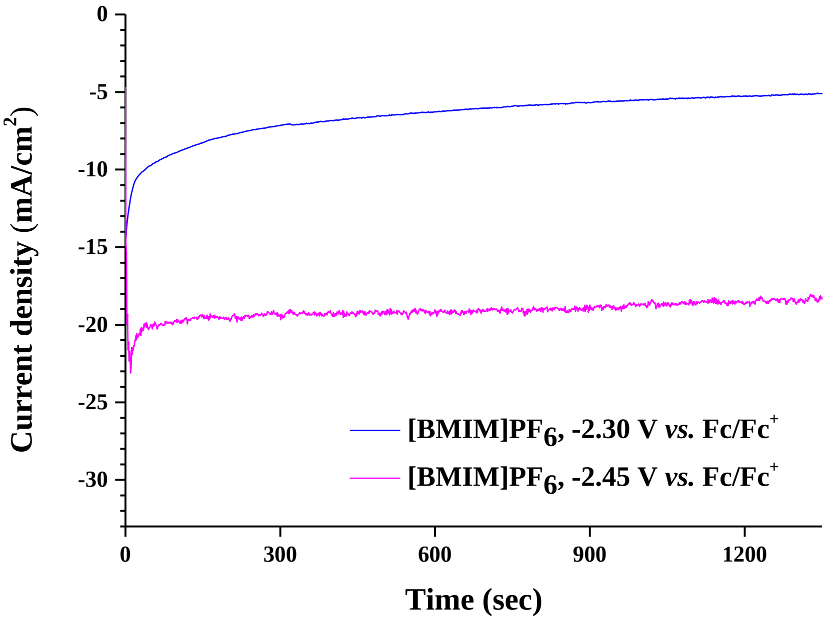


Figure S3. Potentiostatic electrolysis for CO_2 reduction by the MoO_2/Pb electrode in 0.3 M BMIM PF_6/MeCN at RT.

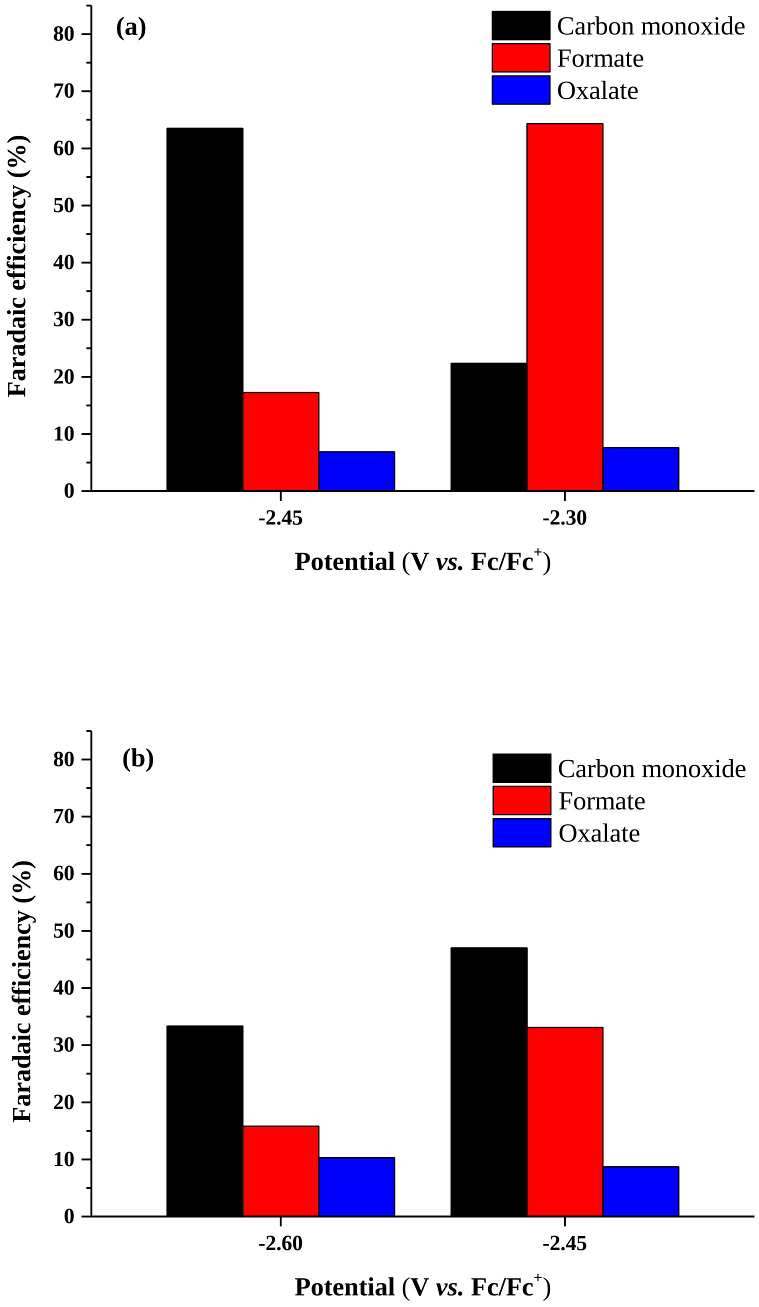


Figure S4. Potential-dependent Faradaic efficiency of the formation of CO, formate and oxalate from electrocatalytic CO_2 reduction. Data were obtained on a MoO_2/Pb electrode (a) in 0.3 M [BMIM]Cl/MeCN solution and (b) in 0.3 M [EMIM]PF_6/MeCN solution.

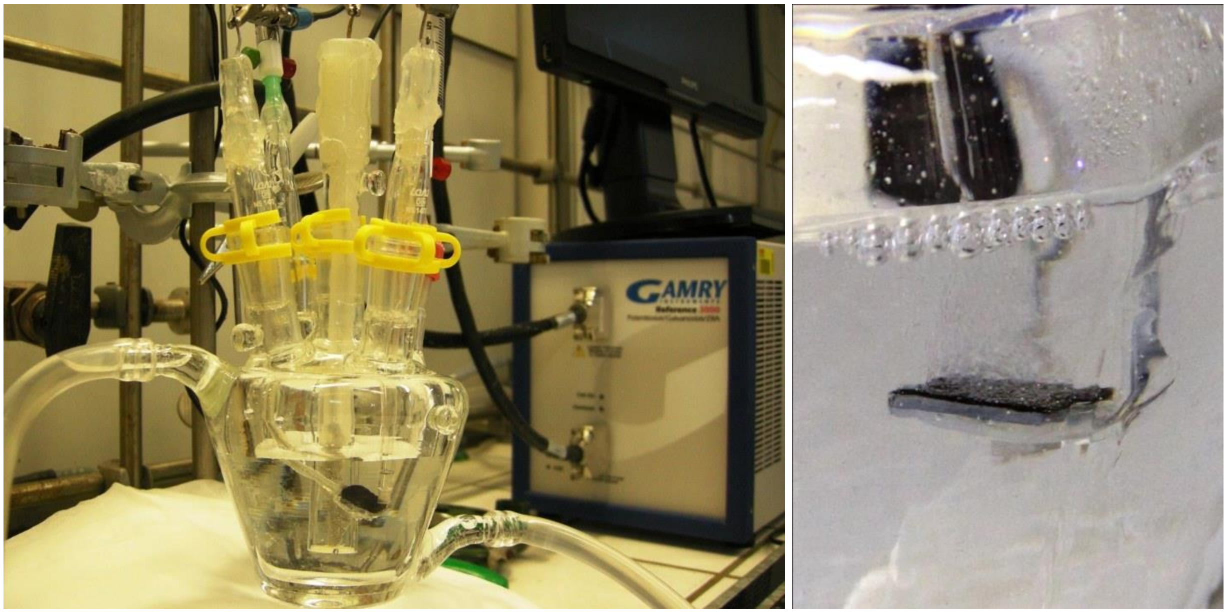
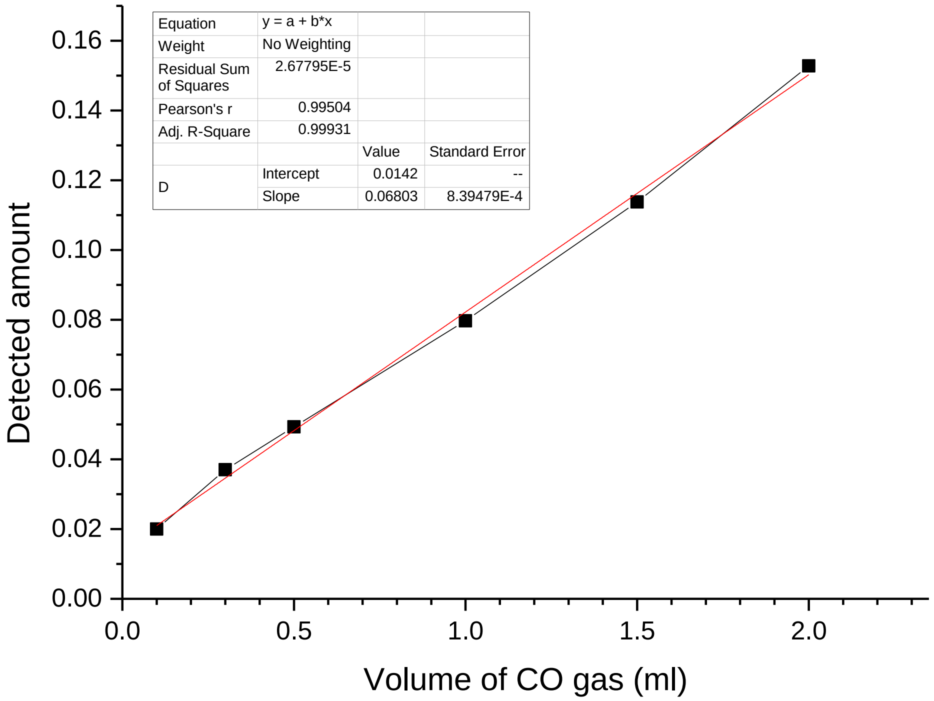


Figure S5. Picture of (left) the gas tight cell used for the electrolysis and (right) the gas formation from the working electrode during the electrolysis.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2.67795E-5		
Pearson's r	0.99504		
Adj. R-Square	0.99931		
		Value	Standard Error
D	Intercept	0.0142	--
	Slope	0.06803	8.39479E-4

Figure S6. Calibration curve for the total amount of CO in the electrolysis cell.

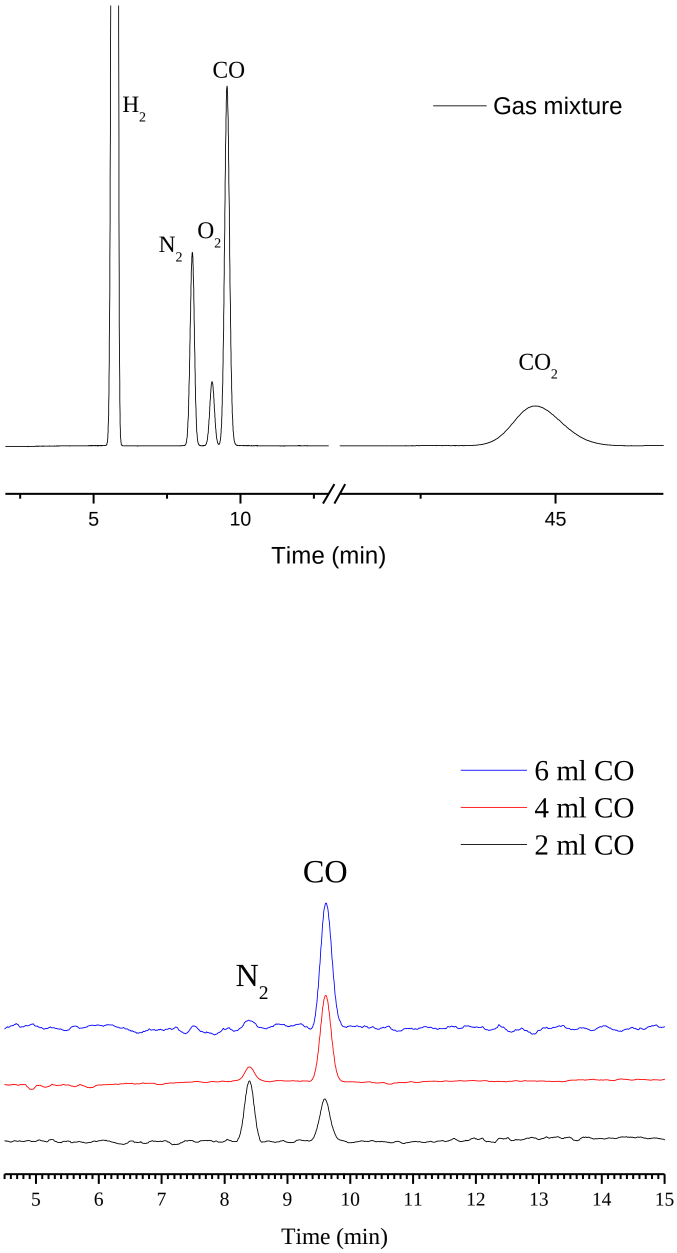


Figure S7. Gas chromatograms of (left) the gas mixture and (right) CO calibration data.

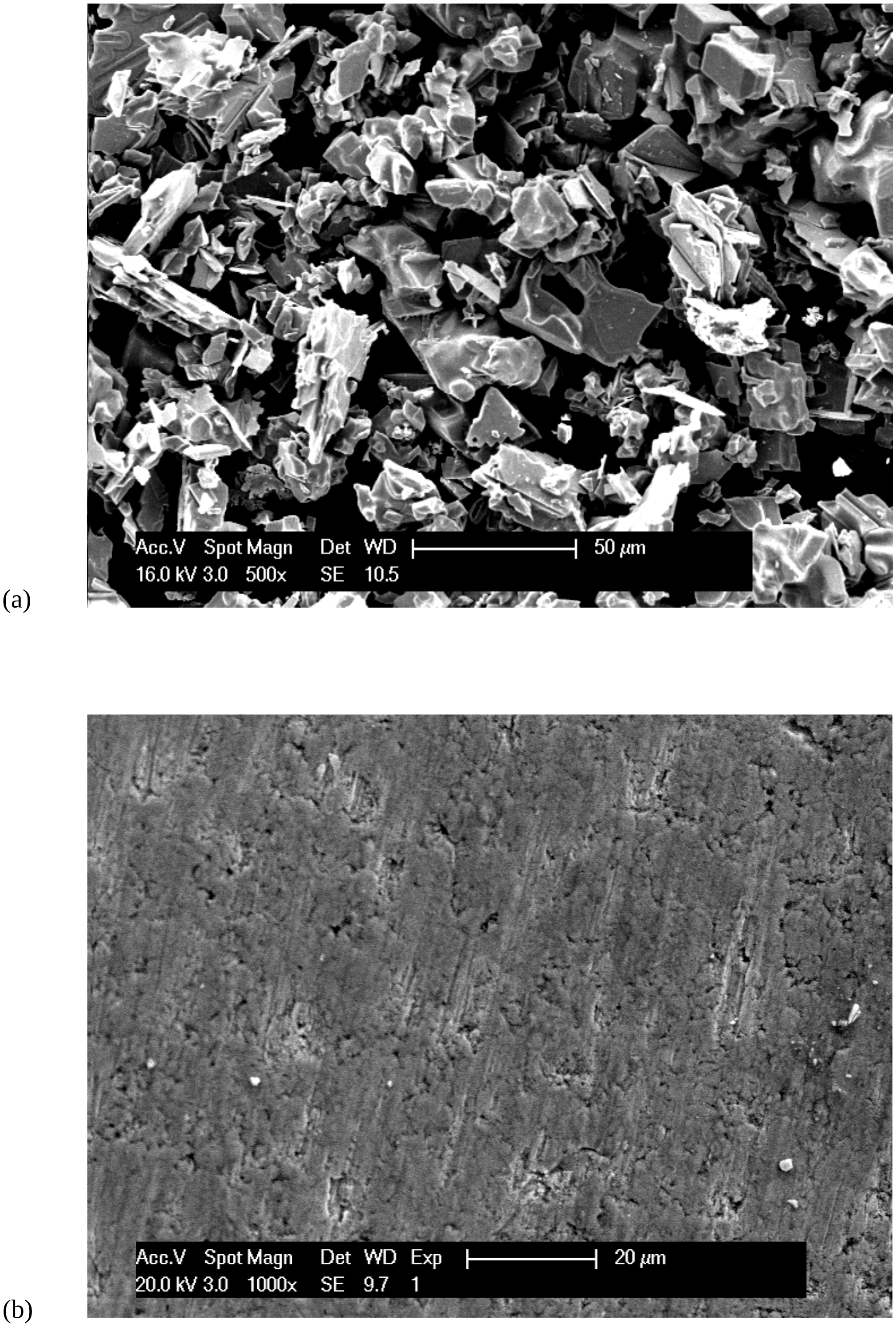


Figure S8. SEM image of (a) the MoO_2 particles and (b) pure Pb electrode (used as a substrate).

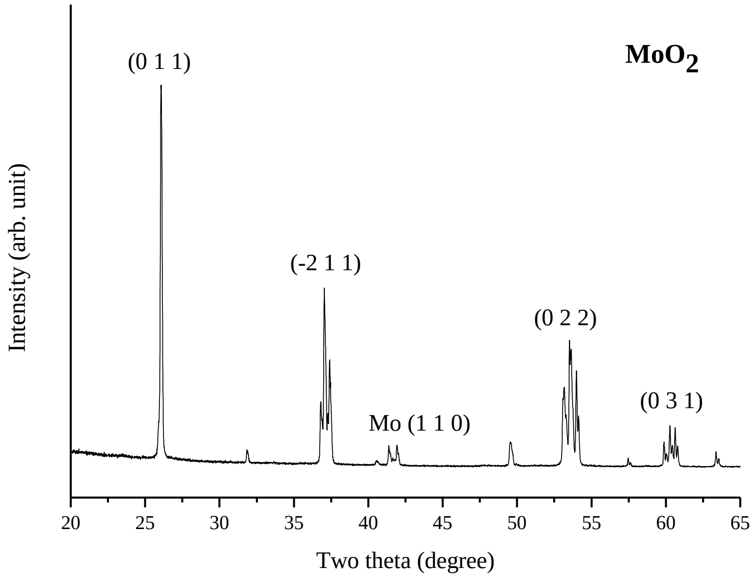


Figure S9. Powder X-ray diffraction pattern of the MoO$_2$ particles.

References

1. R. R. Gagne and D. M. Ingle, *J. Am. Chem. Soc.*, 1980, **102**, 1444-1446.
2. G. Gritzner and J. Kuta, *Pure Appl Chem*, 1984, **56**, 461-466.
3. J. Zhou, N. S. Xu, S. Z. Deng, J. Chen and J. C. She, *Chem Phys Lett*, 2003, **382**, 443-446.