Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting information

"Efficient and selective carbon dioxide reduction on low cost protected Cu_2O photocathodes using a molecular catalyst"

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Experimental

Protected Cu_2O photocathodes were prepared as previously described [1] with the exception that the ALD deposition of aluminum-doped zinc oxide (AZO) was modified. The deposition of AZO was carried out in pulse mode instead of exposure mode. While constantly under vacuum, diethylzinc was pulsed for 15 ms, followed by a 10 second wait time. Subsequently, H_2O was pulsed for 15 ms, also followed by a 10 second wait time. After every 20th cycle, trimethylaluminum was pulsed for 15 ms, followed by 10 seconds wait time, and subsequently H_2O was pulsed for 15 ms, followed by 10 seconds wait time as well. 5 x (20 + 1) cycles were carried out in this manner, leading to 20 nm of aluminium-doped zinc oxide.

Re(tBu-bipy)$(CO)_3$Cl was prepared as follows: Re$(CO)_5$Cl (0.8 g, 2.21 mmol) was dissolved in 150 mL of toluene which was then heated to 60°C until the suspension fully dissolved. An equimolar amount of 4,4'-di-tert-butyl-2,2'-bipyridine (0.594 g, 2.21 mmol) was added to the hot solution, and the reaction mixture was stirred under reflux for 2 h. The reaction mixture changed color from colorless, to yellow, and finally to orange. After 2 h of reflux the reaction mixture was removed from heat and cooled in a freezer. A shiny needle-shaped yellow solid precipitated from cold toluene over 24 h. The solid product was isolated by filtration and dried overnight under high vacuum at room temperature. Spectroscopically pure product was obtained from the reaction with an overall yield of 95%. ^{1}H NMR (acetonitrile-d^3): δ 1.46 (s, 18H, tBu), 7.65 (dd, 2H, 5 and 5' H's), 8.42 (d, 2H, 6 and 6' H's), 8.89 (d, 2H, 3 and 3' H's).

Photoelectrochemical experiments were carried out in a custom gastight photoelectrochemical cell. A Gamry Interface 1000 was used as potentiostat. The counter electrode was a Pt wire, separated by a gastight diaphragm (Metrohm, Switzerland). An Ag/AgCl wire, separated by a similar diaphragm, was used as reference electrode, and ferrocene, measured at a secondary Pt working electrode, was used as an internal standard. All compartments were filled with the same electrolyte. For tests with 1.0 M MeOH, 630 µL of MeOH (Sigma Aldrich, >99.8%) were added to 15 mL of cell content. A 450 W Xe arc lamp (Lot Oriel) with a KG3 filter was used to simulate the AM 1.5 G solar spectrum in the absorption range of Cu_2O, and the intensity was calibrated with a silicon photodiode. For long term stability tests, a collimated LED light source (MCWHL5, Thorlabs, USA) was used, which had previously been calibrated to match the photocurrents that were obtained on Cu_2O photocathodes measured using the simulated AM 1.5 G illumination. This LED light source was interrupted for 2 seconds every 2 minutes in order to verify the absence of dark current. CV experiments were carried out at 100 mV sec^{-1} between 0 and -2.0 V vs. the Ag/AgCl wire, which translates to -0.4 and -2.4 V vs. Fc/Fc$^+$, whereas linear sweeps were carried out in the same potential range at 50 mV/sec. Chopped light experiments were performed at 10 mV/sec with a chopping frequency of 1 Hz. Experiments at glassy carbon electrodes were performed in an electrochemical cell (Metrohm, Switzerland) using a commercial 3 mm dia. glassy carbon electrode (Metrohm, Switzerland), which had been polished with a slurry of Al_2O_3 powder (Buehler, USA) of subsequently finer particle size down to 0.05 µm. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Sigma Aldrich) in anhydrous MeCN (Sigma Aldrich, < 0.001% H_2O). CO_2 (99.998 %) and Ar (99.998 %) were obtained from Carbagas, Switzerland. Before each experiment, the cell was sparged for at least 30 min in order to saturate the liquid with CO_2. For measurements with Ar, the cell was purged for at least 45 min. Gas analysis was carried out using a Thermo Trace Ultra gas chromatograph, equipped with a Pulse Discharge Detector (Vici) and a Shincarbon column (Restek) using He (Carbagas, 99.99990 %) as carrier gas. CO_2 was passed through the headspace of the cell at 7.5 mL/min using a mass flow controller (Bronkhorst, Netherlands), directly transported into the sample loop of the gas chromatograph, and periodically injected onto the column. The resulting data were smoothed using adjacent averaging over 5 points. The gas measurements were corrected for the volume that is added to the effluent stream by the evaporation of the solvent. This error was determined by measuring the drop of concentration in CO when flowing a 500 ppm CO standard through the cell at 7.5 mL/min using a 100 mL/min CH_4 mass flow controller, which was scaled to the standard in He using the gas conversion factors supplied by Bronkhorst. We estimate an error of 10% on the measurement of the faradaic efficiency. XRD Data was recorded using an X'Pert MPD PRO (Panalytical) equipped with a ceramic tube (Cu anode, λ=1.54060 Å), a secondary graphite (002) monochromator and a RTMS X'Celerator (Panalytical). The measurements were done in the Bragg-Brentano geometry. The samples were mounted without further modification and the automatic divergence slit and beam mask were adjusted to the dimension of the films. A step size of 0.008° was chosen for an acquisition time of 7.5 min deg^{-1}. The data were adjusted for a small angular shift (~0.6°) by aligning the most prominent Cu_2O peak (36.42°) to the standard JCPDS card No. 05-0667. SEM micrographs were taken using a Zeiss Merlin high resolution microscope. Crystalline anatase TiO_2 layers were deposited from a solution of 0.4 mL acetylacetone, 0.6 mL titanium diisopropoxide bis(acetylacetonate) and 9 mL of ethanol which was sprayed onto FTO substrates at 450°C using oxygen as carrier gas. UV-Vis spectra were acquired using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu, Japan). XPS measurements were carried out on a ESCA KRATOS AXIS ULTRA system (Kratos, UK).

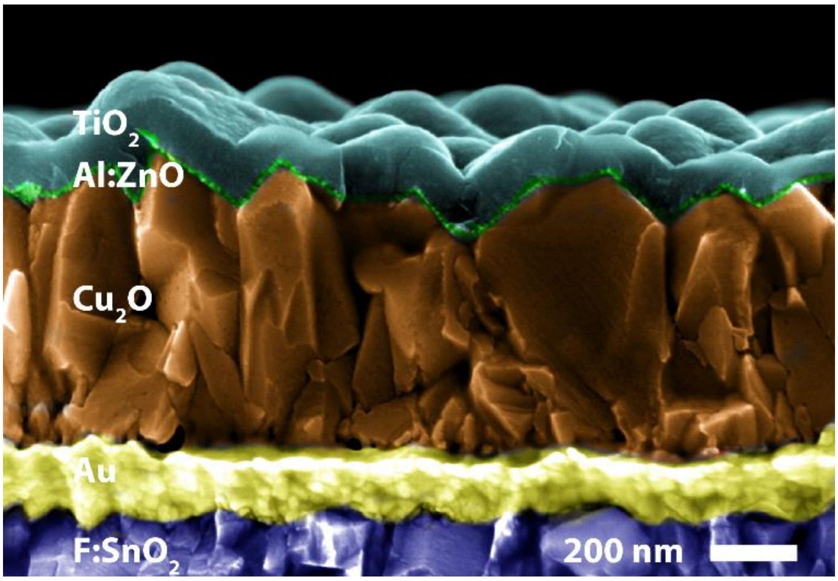

Fig. S1: SEM cross-section of a protected Cu₂O photocathode. The conformal nature of the protective ALD layers is evident

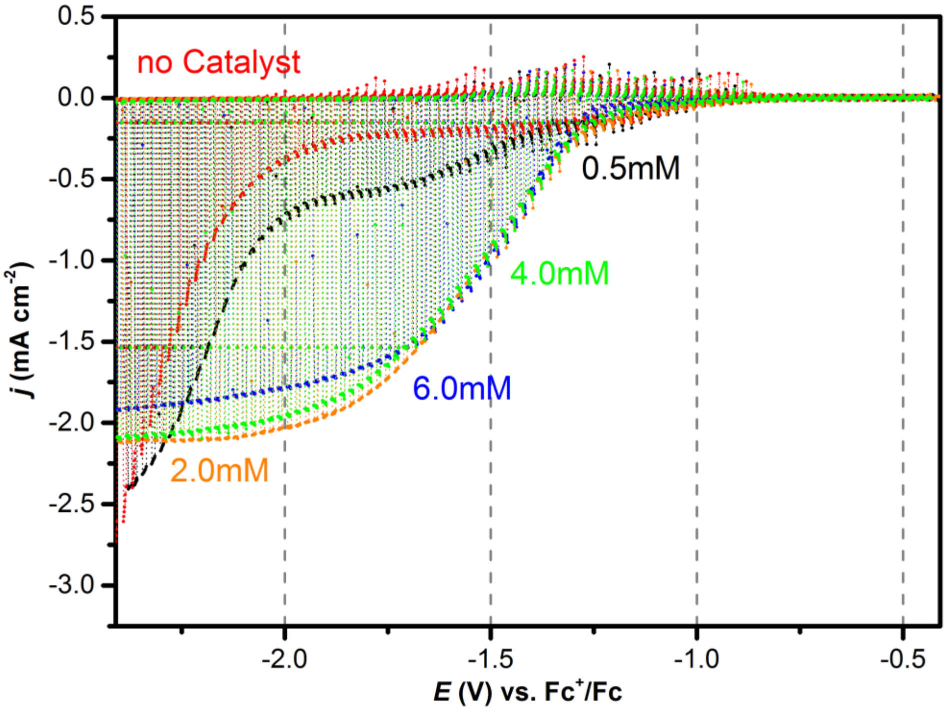

Fig. S2: Chopped light linear sweeps on the Cu₂O photocathode at different catalyst concentrations in the presence of MeOH. Increasing the catalyst concentration beyond 2.0 mM leads to a decrease in photocurrent due to increased light absorption.

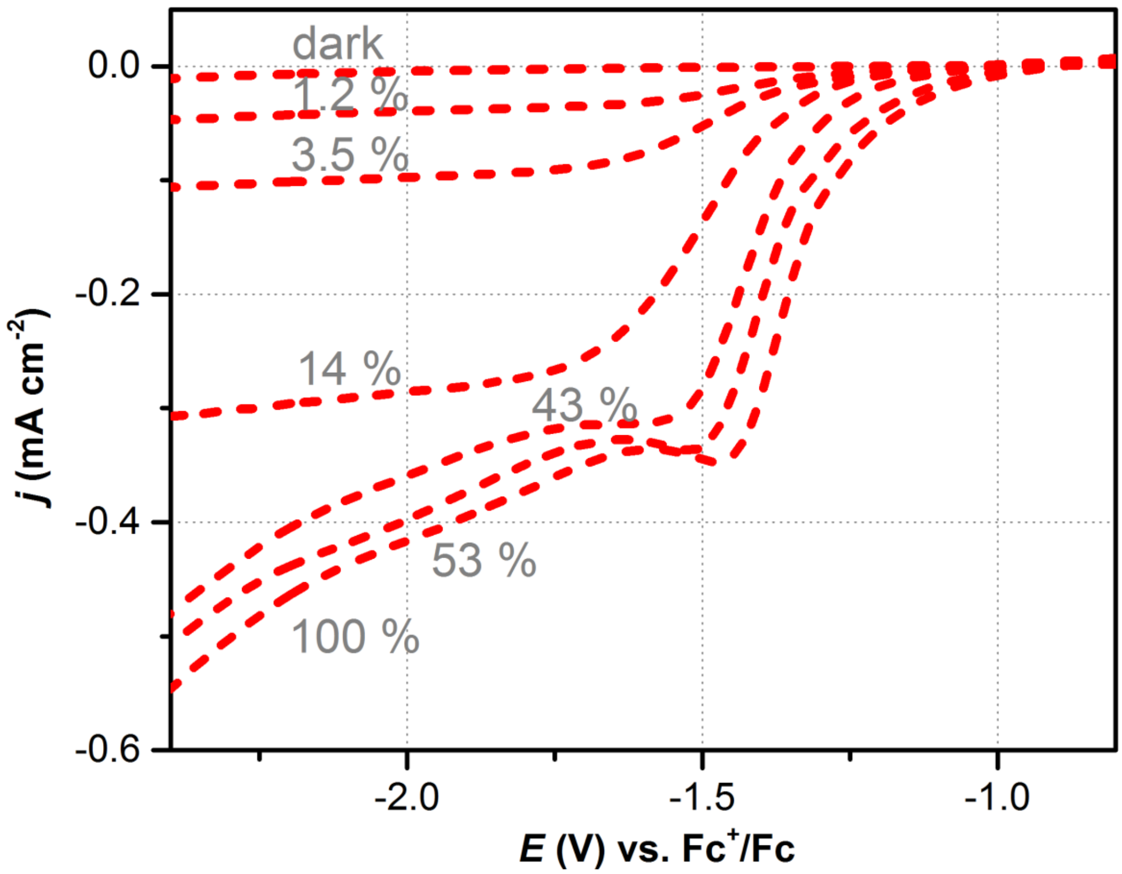

Fig. S3: Linear sweep scans at different light intensities (% of AM 1.5G indicated by grey labels). 2 mM Re(tBu-bipy)(CO)$_3$Cl in the absence of a protic additive. It becomes obvious that while the quasi-fermi level increases with increasing light intensity, the photocurrent saturates above 14% AM 1.5G irradiation.

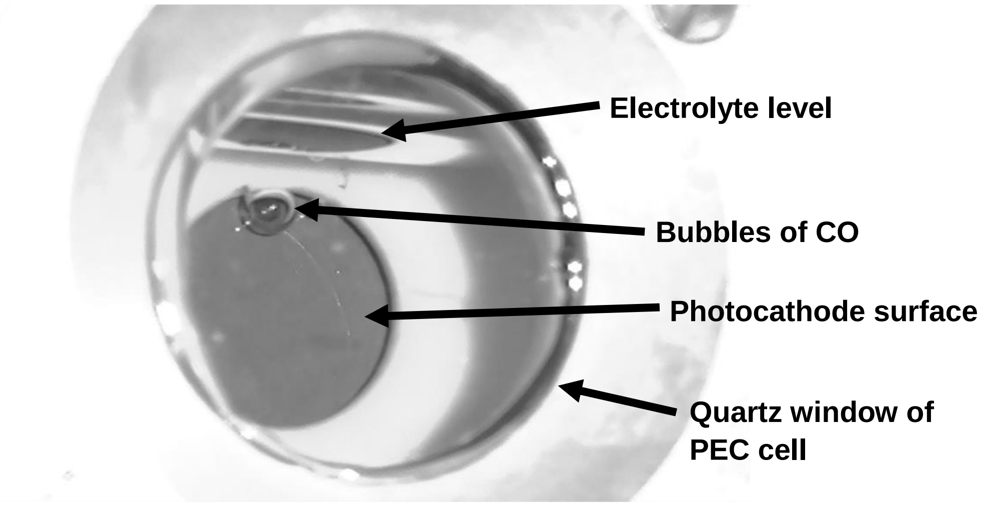

Fig. S4: Picture of the electrode during the stability test. Once the electrolyte is saturated with carbon monoxide, CO bubble formation is observed on the electrode.

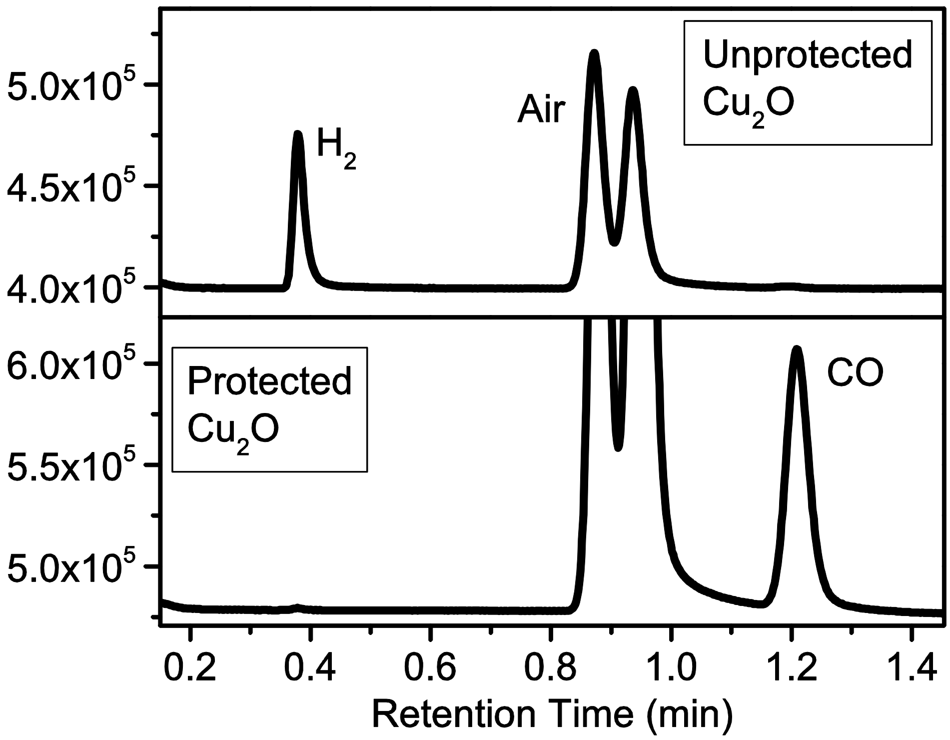

Fig. S5 : Representative GC traces from protected and unprotected Cu_2O electrodes. On unprotected Cu_2O only hydrogen is formed.

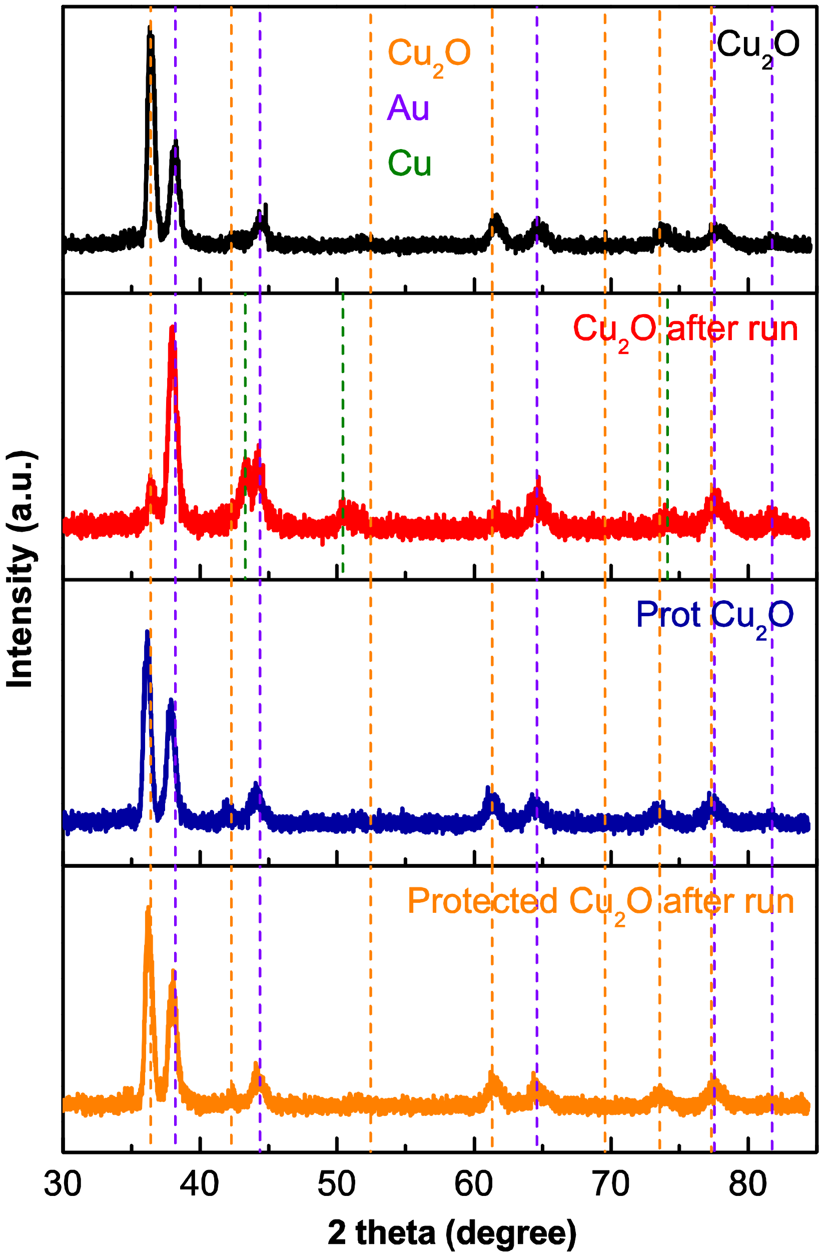

Fig. S6 : XRD Analysis of Cu_2O electrodes before and after CO_2 reduction experiments.

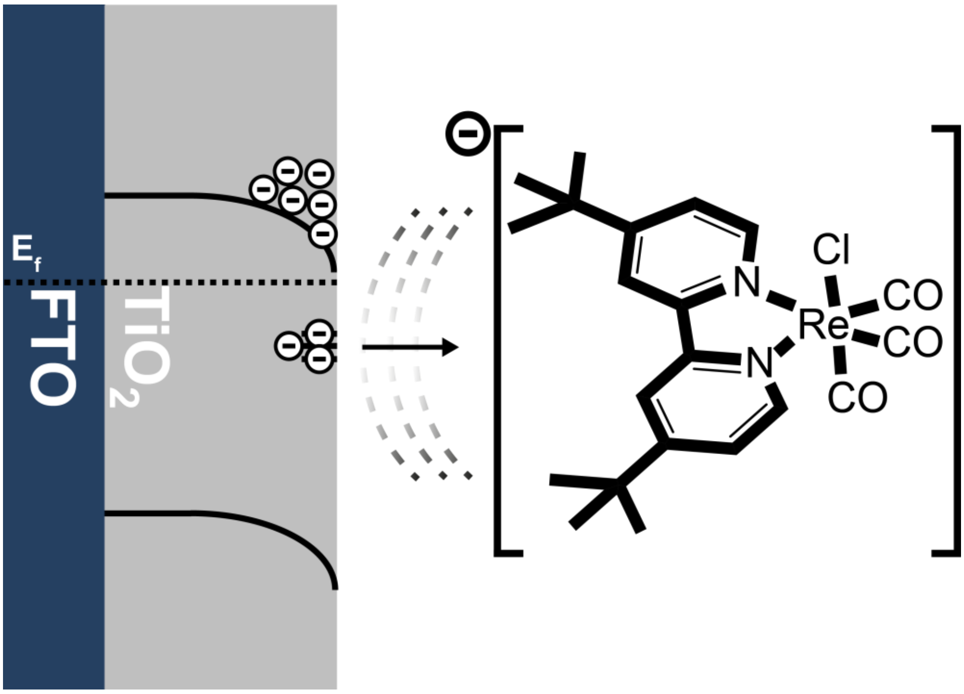

Fig. S7 : Sketch showing the coulombic repulsion of the negatively charged singly reduced catalyst molecule by a TiO$_2$ surface in accumulation.

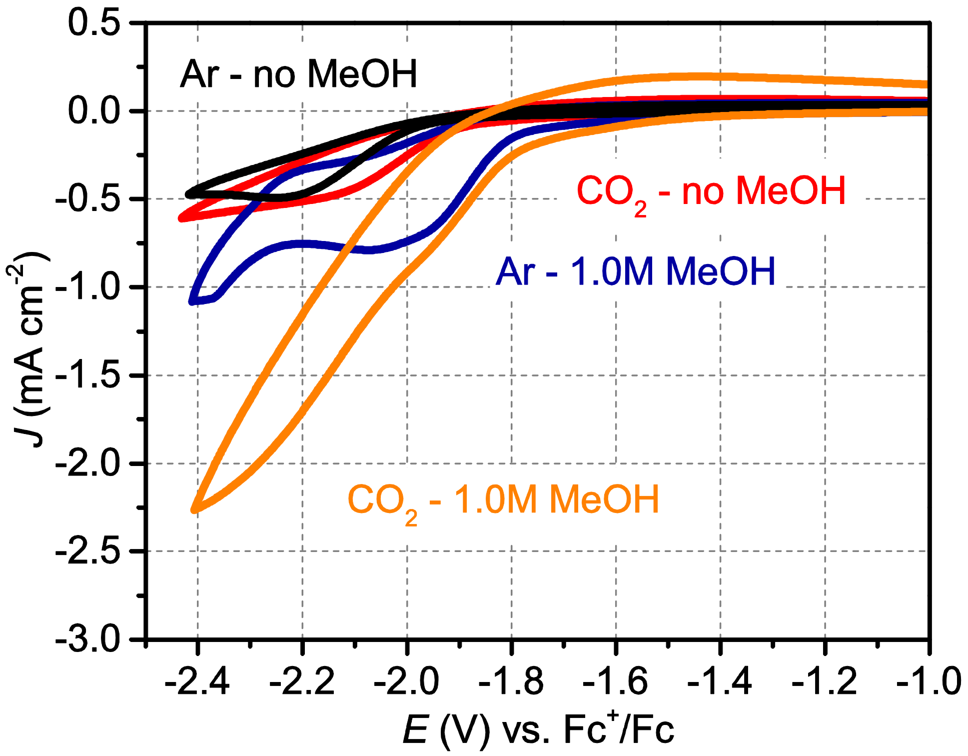

Fig. S8 : 2 mM Re(tBu-bipy)(CO)$_3$Cl on TiO$_2$-coated FTO (100 nm TiO$_2$)

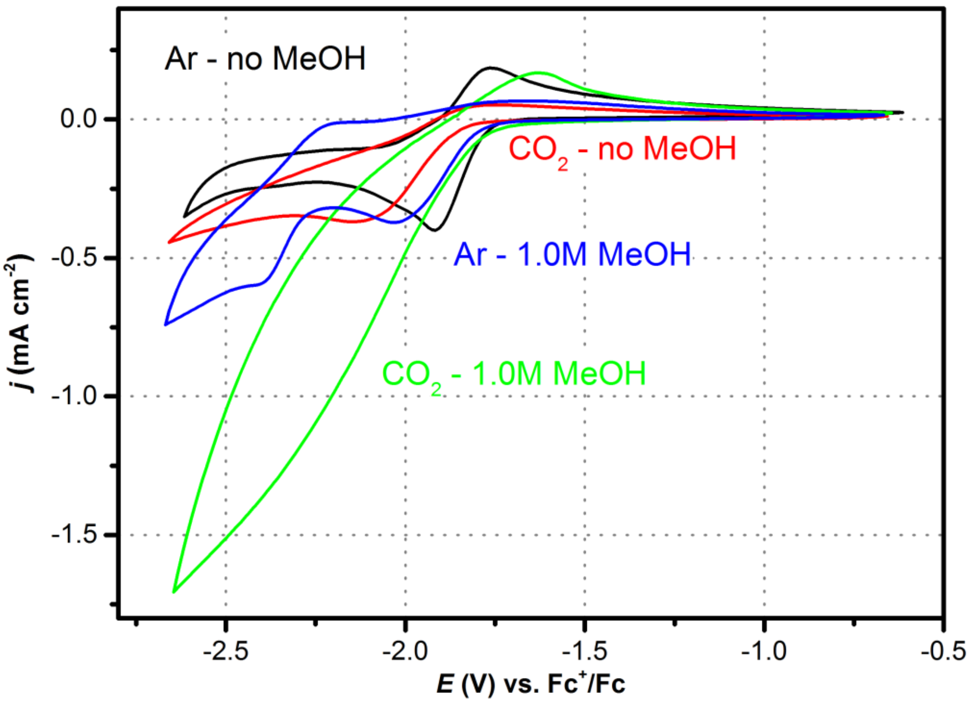

Fig. S9 : CV experiments on a crystalline anatase film in the presence of 2 mM Re(tBu-bipy)(CO)$_3$Cl with and without MeOH additive. The same behavior as on the ALD films can be observed.

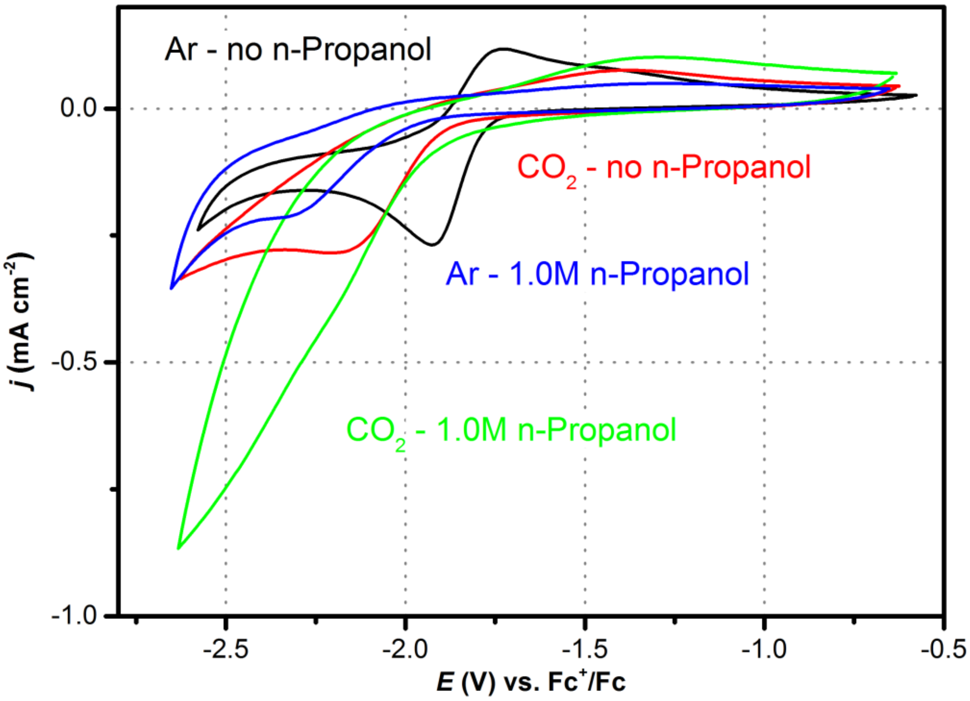

Fig. S10 : 2 mM Re(tBu-bipy)(CO)$_3$Cl on TiO$_2$-coated FTO (100 nm TiO$_2$) with and without 1-Propanol as protic additive.

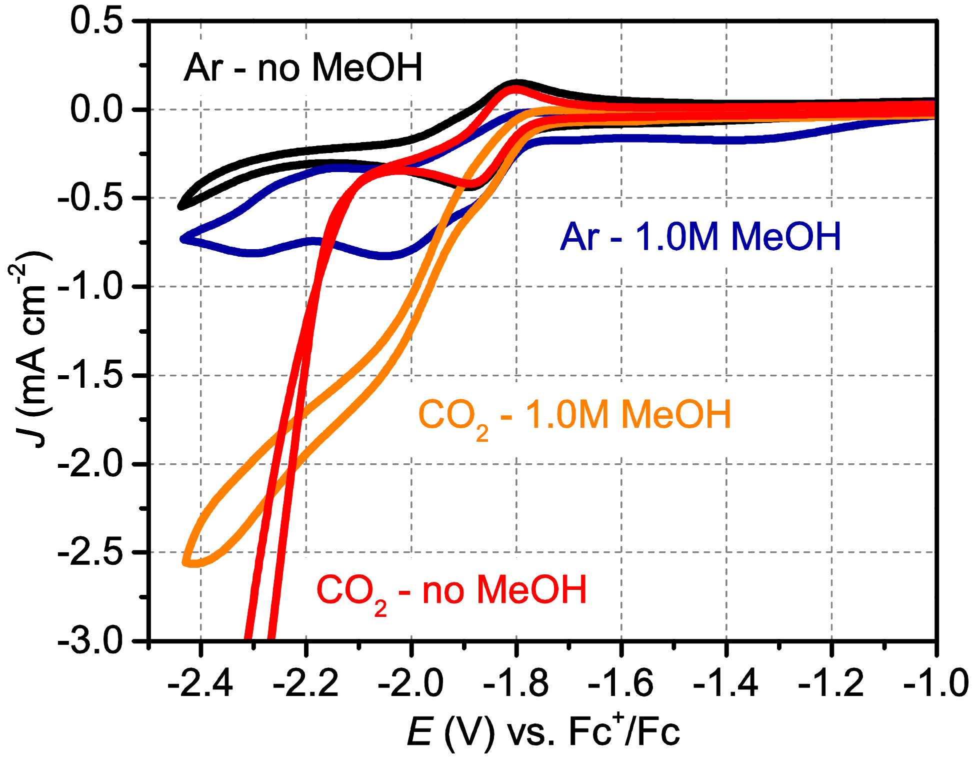

Fig. S11 : 2 mM Re(tBu-bipy)(CO)$_3$Cl on Glassy Carbon

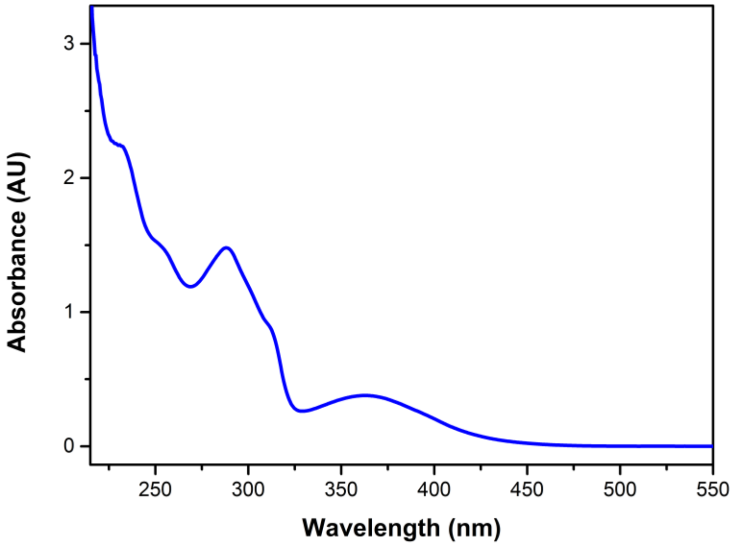

Fig. S12 : Absorbance spectrum of Re(tBu-bipy)(CO)$_3$Cl molecular catalyst solution, 0.13 mM in acetonitrile

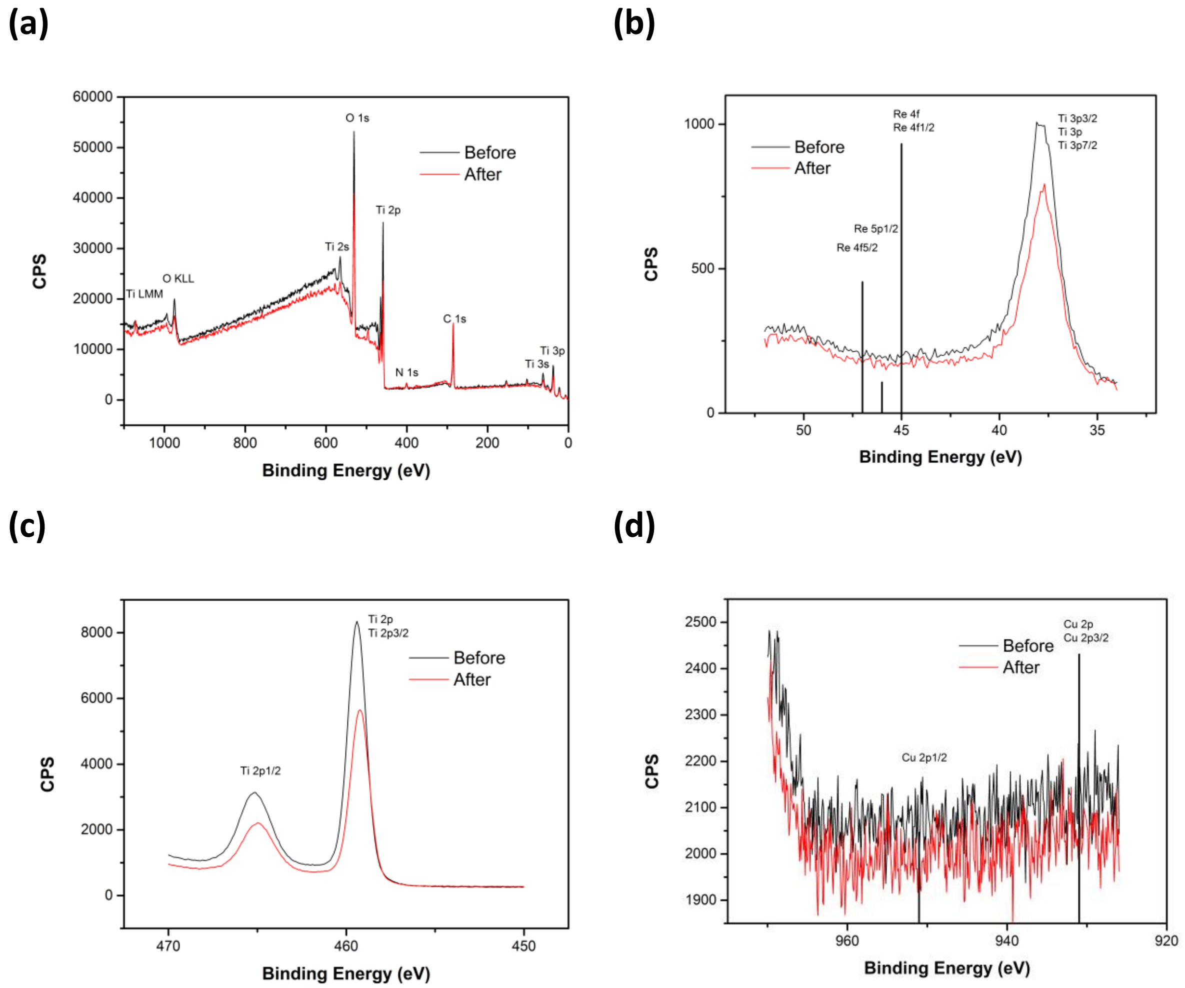

Fig. S13 : X-ray photoelectron spectroscopy of photocathode device before and after extended photoelectrochemical testing. (a) Survey scan, (b) Re detail, (c) Ti detail, (d) Cu detail. No trace of Re is observed on the device after testing, supporting that the catalyst remained in solution in its molecular state and did not yield deposited by-products. The Ti peaks look essentially identical before and after testing the photocathode, showing the chemical stability of the TiO_2 overlayer. No signal from Cu was observed either before or after testing, also showing the effectiveness of the stabilizing overlayer.

[1] S. D. Tilley, M. Schreier, J. Azevedo, M. Stefik, and M. Graetzel, *Adv. Funct. Mater*., 2014, **24**, 303–311.