Suplementary information to:

Palladium-gold catalyst for the electrochemical reduction of CO_2 to C_1 - C_5 hydrocarbons

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S1. Materials

Cylindrical polycrystalline gold and palladium electrodes (99.995% Au and 99.9% Pd, purchased at Mateck GmbH) with a diameter of 4.5 mm and 5 mm, respectively, embedded in Teflon were used as working electrodes in the standard electrochemical measurements. For faradaic efficiency measurements a polycrystalline gold plate (99.995% Au, Mateck GmbH) was used a working electrode. Prior to every experiment the working electrode was polished mechanically to a mirror-like finish using alumina pastes. Afterwards, the electrode was sonicated in ultra-pure water.

Electrolytes were made from ultra-pure water (Millipore MilliQ gradient A10 system, 18 m Ω cm) and high purity reagents (Sigma Aldrich TraceSelect). Before each experiment the electrolytes were first purged with Argon (Air Products, 5.7) for 15 minutes to remove air from the solution. In the case of CO₂ reduction experiments the electrolyte was subsequently purged with CO₂ (Linde, 4.5) for at least 30 minutes to saturate the solution.

S2. Electrochemical measurements

Cyclic voltammetry measurements were carried out in a standard electrochemical cell using a three-electrode assembly at room temperature. The cell and all other glassware were first cleaned by boiling in a 1:1 mixture of concentrated sulfuric and nitric acid and were cleaned before every experiment by boiling in ultra-pure water. Either a gold electrode with a diameter of 4.5 mm or a palladium electrode with a diameter of 5 mm was used as working electrode. A coiled gold wire was used as counter electrode. All potentials are reported versus the reversible hydrogen electrode (RHE) as a reference electrode in a separate compartment filled with the same electrolyte, at the same pH as the electrolyte in the electrochemical cell. The voltammograms were recorded on an Ivium A06075 potentiostat at a scan rate of 50 mV s⁻¹ unless stated otherwise.

Faradaic efficiency measurements were performed in a custom-made Teflon flow cell, consisting of two compartments separated with a Nafion 115 membrane. Both compartments had a volume of 12 ml which was filled with 10 ml electrolyte, leaving 2 ml gas headspace. Prior to use the flow cell was cleaned in a similar way as the cell used for cyclic voltammetry. A gold plate was used as a counter electrode, which was cleaned by flame annealing before experiments, and a Ag/AgCl reference electrode was used. All potentials were converted to the RHE scale using $V_{vs. RHE} = V_{vs. Ag/AgCl} + 0.197 + 0.059 \times 6.7$ (pH of the electrolyte). The resistance of the cell was determined before every experiment by electrochemical impedance spectroscopy (EIS) on an Ivium A06075 potentiostat. For the chronoamperometry measurements a Biologic VSP multichannel potentiostat was used, which compensated for 85% of the ohmic drop that was measured with EIS.

Palladium overlayers on a gold polycrystalline electrode (Pd-Au) were made by electrodepositing palladium onto gold from a $0.1 \text{ M H}_2\text{SO}_4 + 1.0 \text{ mM PdCl}_2$ solution at 0.27 V vs. SCE for 60 seconds, using a procedure earlier used for the deposition of palladium on platinum.¹⁹

In order to deposit palladium monolayers, a monolayer of copper was first deposited on a polycrystalline gold electrode from a 0.1 M H₂SO₄ electrolyte containing 1 mM CuSO₄ using under potential deposition (UPD).²⁰ After determining the UPD region for copper on gold using cyclic voltammetry the polycrystalline gold electrode was held at -0.05 V vs. Ag/AgCl for 3 minutes, which should correspond to a complete copper monolayer, after which the electrode was rinsed with ultra-pure water. The copper layer was subsequently displaced by palladium using of galvanic displacement. Therefore, the electrode was placed in a 0.1 M H₂SO₄ electrolyte containing 0.1 mM PdCl₂ at open circuit potential for 10 minutes.

S3. SEM Images Pd overlayers on Au

Scanning electron microscopy (SEM) images were acquired using a FEI Nova NanoSEM 200 microscope.



Figure S1. Scanning electron microscopy (SEM) images of palladium overlayers electrodeposited on a gold electode at different magnifications; **a**) overview of the deposition layer , **b**) scale-like structure, **c**) triangular structure.

S4. XPS spectra

X-ray photoelectron spectroscopy (XPS) spectra were collected on a Quantera SXM (scanning XPS microprobe) spectrometer equipped with a monochromatic Al K α x-ray source (1486.6 eV). The source was operated with a 25 W emission power, beam size of 200 μ m and pass energy of 224 eV. The resolution of the spectrometer was 0.2eV and 0.8 eV for high resolution element scan and survey spectra, respectively.

S4.1 XPS data for an Au electrode



Figure S2. XPS survey spectrum from -5 eV to 1345 eV of a gold electrode. Pass energy is 224 eV and δE is 0.4 eV.



Figure S3. Au 4*f* spectral region in XPS for a gold electrode.

S4.2 XPS data for a Pd-Au electrode



Figure S4. XPS survey spectrum from -5 eV to 1345 eV of a Pd-Au electrode. Pass energy is 224 eV and δE is 0.4 eV.



Figure S5. Pd 3d spectral region in XPS for a Pd-Au electrode.



Figure S6. Pd 4s and Au 4f spectral region in XPS for a Pd-Au electrode.



S4.3 XPS data for a Pd-Au electrode after electrolysis

Figure S7. XPS survey spectrum from -5 eV to 1345 eV of a Pd-Au electrode after 30 minutes of electrolysis at -1.2 V vs. RHE. Pass energy is 224 eV and δE is 0.4 eV.



Figure S8. Pd 3*d* spectral region in XPS for a Pd-Au electrode after 30 minutes of electrolysis at -1.2 V vs. RHE.



Figure S9. Pd 4*s* and Au 4*f* spectral region in XPS for a Pd-Au electrode after 30 minutes of electrolysis at -1.2 V vs. RHE.





Figure S10. XPS survey spectrum from -5 eV to 1345 eV of an Au electrode covered with 4 Pd MLs. Pass energy is 224 eV and δE is 0.4 eV.



Figure S11. Pd 3*d* spectral region in XPS of an Au electrode covered with 4 Pd MLs.



Figure S12. Au 4*f* spectral region in XPS of an Au electrode covered with 4 Pd MLs.



Figure S13. Cu 2*p* spectral region in XPS of an Au electrode covered with 4 Pd MLs.



S4.5 XPS data for an Au electrode with 4 Pd MLs after electrolysis

Figure S14. XPS survey spectrum from -5 eV to 1345 eV of an Au electrode covered with 4 Pd MLs after 30 minutes of electrolysis at -1.2 V vs. RHE. Pass energy is 224 eV and δE is 0.4 eV.



Figure S15. Pd 3*d* spectral region in XPS of an Au electrode covered with 4 Pd MLs after 30 minutes of electrolysis at -1.2 V vs. RHE.



Figure S16. Au 4*f* spectral region in XPS of an Au electrode covered with 4 Pd MLs after 30 minutes of electrolysis at -1.2 V vs. RHE.



Figure S17. Cu 2p spectral region in XPS of an Au electrode covered with 4 Pd MLs after 30 minutes of electrolysis at -1.2 V vs. RHE.

S5. Additional OLEMS data

Online Electrochemical Mass Spectrometry (OLEMS) was used to detect gaseous products of the reactions.^[24] The products were collected with a small hydrophobic tip which was positioned close (about 10 μ m) to the electrode with the aid of a camera. The tip was constructed as a porous Teflon cylinder with a diameter of 0.5 mm and an average pore size of 10-14 μ m in a Kel-F holder. The tip is connected to a mass spectrometer with a PEEK capillary. Before use the tip was cleaned in a solution of 0.2 M K₂Cr₂O₇ in 2 M H₂SO₄ and rinsed thoroughly with Millipore water. A secondary electron multiplier (SEM) voltage of 2400 V was used for detection in a Balzers Quadrupole mass spectrometer, except for hydrogen (m/z = 2) where a SEM voltage of 1200 V was used. The products were measured while changing the potential of the electrode from 0.0 V to -1.5 V, and back at 1 mV s⁻¹.



Figure S18. Formation of hydrogen (m/z = 2), methane (m/z = 15) and ethylene (m/z = 26) from CO₂ reduction on a polycrystalline palladium electrode followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).



Figure S19. Formation of hydrogen (m/z = 2), methane (m/z = 15) and ethylene (m/z = 26) from CO₂ reduction on a polycrystalline gold electrode followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).



Figure S20. Formation of hydrogen (m/z = 2), methane (m/z = 15) ethylene (m/z = 26), C₃ hydrocarbons (m/z = 39 and 42) and C₄ hydrocarbons (m/z = 56) from CO reduction on a Pd-Au electrode followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).



Figure S21. Formation of hydrogen (m/z = 2), methane (m/z = 15) ethylene (m/z = 26), C₃ hydrocarbons (m/z = 39 and 42) and C₄ hydrocarbons (m/z = 56) from CO₂ reduction on a polycrystalline gold electrode covered with 1 palladium ML followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).



Figure S22. Formation of hydrogen (m/z = 2), methane (m/z = 15) ethylene (m/z = 26), C₃ hydrocarbons (m/z = 39 and 42) and C₄ hydrocarbons (m/z = 56) from CO₂ reduction on a polycrystalline gold electrode covered with 2 palladium MLs followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).



Figure S23. Formation of hydrogen (m/z = 2), methane (m/z = 15) ethylene (m/z = 26), C₃ hydrocarbons (m/z = 39 and 42) and C₄ hydrocarbons (m/z = 56) from CO₂ reduction on a polycrystalline gold electrode covered with 3 palladium MLs followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).



Figure S24. Formation of hydrogen (m/z = 2), methane (m/z = 15) ethylene (m/z = 26), C₃ hydrocarbons (m/z = 39 and 42) and C₄ hydrocarbons (m/z = 56) from CO reduction on a polycrystalline gold electrode covered with 4 MLs palladium followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).



Figure S25. Formation of hydrogen (m/z = 2), methane (m/z = 15) ethylene (m/z = 26), C₃ hydrocarbons (m/z = 39 and 42) and C₄ hydrocarbons (m/z = 56) from CO₂ reduction on a PdAg followed with OLEMS in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).

S6. Online HPLC

For online detection of products dissolved in the electrolyte as a function of applied potential online High Performance Liquid Chromatography (HPLC) was used. While changing the potential from 0.0 V to the required potential, samples were collected with an open tip positioned close (~10 μ m) to the electrode. Sampling was done at a rate of 60 μ L min⁻¹ and each sample had a volume of 60 μ L. Since the potential was changed at 1 mV s⁻¹, each sample contained the products averaged over a potential change of 60 mV. After voltammetry, these samples were analyzed by HPLC (Prominence HPLC, Shimadzu; Aminex HPX 87-H column, Biorad).



Figure S26. Formation of formic acid during CO₂ reduction on a Pd-Au electrode followed with online HPLC in a pH 6.7 phosphate buffer electrolyte (0.1 M $KH_2PO_4/$ 0.1 M K_2HPO_4).



Figure S27. Formation of formic acid on a polycrystalline palladium electrode detected with online HPLC using a phosphate buffer at pH 6.7 ($0.1 \text{ M KH}_2\text{PO}_4/0.1 \text{ M K}_2\text{HPO}_4$).



Figure S28. Formation of formic acid from CO reduction on a polycrystalline gold electrode covered with 1-4 MLs palladiummonolayers (a-d) followed with online HPLC in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).

S7. NMR spectroscopy identification of products

Liquid products formed during electrolysis were identified with 1D and 2D ¹H-NMR. First, an electrolysis experiment was conducted using the same two-compartment flow cell used for the GC experiment. A potential of -1.2 V vs. RHE, corrected for the resistance of the cell, was applied for 15 hours. Afterwards, samples were taken from the catholyte and prepared for NMR analysis by addition of D₂O (sample to D₂O ratio = 9:1). The NMR experiments were performed on a Bruker AV-III 600 MHz NMR spectrometer, using a presaturation sequence to suppress the water signal.

Table S1. Liquid products identified with ¹H-NMR spectroscopy after 15 hours of CO_2 reduction at -1.2 V vs. RHE with a Pd-Au electrode in a 0.1 M KH₂PO₄/0.1 M K₂HPO₄ electrolyte (pH 6.7).

Assignment	Probed nucleus	Chemical shift (δ)	Multiplicity	J-coupling (Hz)	COSY cross
rissignment	110000 indefedas	(0)		(112)	peaks
Formate	HCOO-	8.41	S		
Methanol	CH ₃ OH	3.31	S		
Ethanol	CH ₃ CH ₂ OH	3.61	q	6.4	1.13
Ethanol	CH ₃ CH ₂ OH	1.13	t	9.6	3.61
Acetate	CH ₃ COO ⁻	2.18	S		



Figure S29. ¹H-NMR spectrum of a sample (sample to D_2O ratio = 9:1) of the catholyte compartment (0.1 M KH₂PO₄ / 0.1 M K₂HPO₄ electrolyte (pH 6.7)) after 15 hours of electrolysis with a Pd-Au electrode at -1.2 V vs. RHE.



Figure S30. COSY spectrum of a sample (sample to D_2O ratio = 9:1) of the catholyte compartment (0.1 M KH₂PO₄ / 0.1 M K₂HPO₄ electrolyte (pH 6.7)) after 15 hours of electrolysis with a Pd-Au electrode at -1.2 V vs. RHE.

S8. IR compensation

Electrochemical impedance measurements were carried out prior to the long term electrolysis experiments to determine the resistance of the H-cell (see section S3). The impedance measurements were carried out using an Ivium A06075 potentiostat, at frequencies ranging from 10 kHz to 0.1 to measure the solution resistance. Since the resistance of the cell can vary for each experiment, it is important to correct for the resistance of the cell so that the applied potential during the electrolysis experiment corresponds to the intended electrode potential. A Nyquist plot was plotted as shown in Figure S10 and in the high-frequency part a linear fit was performed and the axis intersection was calculated. The value of this intersection represents the ohmic resistance of the cell. An average of 3 measurements was taken to calculate the value of R. Typically, very small resistances were measured, ranging from 4 to 12 Ω . This measured resistance was compensated for during the electrolysis experiments.



Figure S31. Typical Nyquist plot used to calculate the resictance of the cell prior to electrolysis experiments.

S9. Faradaic efficiencies on Pd-Au and 4MLs Pd on Au

Quantitative faradaic efficiency measurements of the gas products were carried out using Gas Chromatography (GC).^[25] At atmospheric pressure, CO₂ was continuously purged through a two-compartment flow cell at a rate of 5 mL/min for 20 min to saturate the electrolyte. The flow rate was decreased to 2 mL/min while a constant potential was applied for 30 minutes. The cell effluent was sampled via GC once every 6 minutes. CO, CO_2 , H_2 and hydrocarbons were simultaneously separated using two series columns (ShinCarbon 2 m micropacked column and Rtx-1). The quantitative analysis of the gas products was performed using a thermal conductivity detector (TCD) and flame ionization detector (FID).

E (V)		CH ₄	C_2H_4	C_2H_6	ΣC_2	C ₃ H ₆	C ₃ H ₈	ΣC_3
vs. RHE	CO (%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
-0.4	19.62							
-0.5	24.07							
-0.6	30.92							
-0.7	18.26							
-0.8	9.62	0.92	0.08	0.23	0.31			
-0.9	9.00	1.26	0.10	0.28	0.38	0.09	0.03	0.12
-1.0	7.49	1.36	0.09	0.27	0.35	0.10	0.03	0.13
-1.1	6.77	1.54	0.10	0.35	0.45	0.10	0.03	0.14
-1.2	1.44	1.25	0.10	0.34	0.44	0.15	0.05	0.21
-1.3	1.75	1.49	0.14	0.40	0.53	0.19	0.06	0.25
-1.4	3.02	2.03	0.13	0.54	0.67	0.22	0.07	0.29
-1.5	6.70	1.16	0.13	0.42	0.55	0.21	0.07	0.28

Table S2. Faradaic efficiencies toward C_1 - C_3 hydrocarbons produced during CO_2 reduction on Pd-Au in a pH 6.7 phosphate buffer (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).

E (V) vs. RHE	Isobutane (%)	1-butene (%)	Butane (%)	ΣC ₄ (%)	2-methyl- butane (%)	Pentene (%)	Pentane (%)	ΣC ₅ (%)
-0.4								
-0.5								
-0.6								
-0.7								
-0.8								
-0.9								
-1	0.03	0.07	0.04	0.14				
-1.1	0.02	0.06	0.03	0.12				
-1.2	0.02	0.08	0.04	0.14	0.02	0.04	0.01	0.06
-1.3	0.03	0.09	0.04	0.16	0.01	0.02	0.00	0.04
-1.4	0.02	0.09	0.04	0.15	0.02	0.04	0.01	0.07
-1.5	0.02	0.08	0.04	0.14	0.01	0.04	0.01	0.06

Table S3. Faradaic efficiencies toward C_4 - C_5 hydrocarbons produced during CO_2 reduction on Pd-Au in a pH 6.7 phosphate buffer (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄).

Table S4. Faradaic efficiencies toward C_1 - C_3 hydrocarbons produced during CO_2 reduction on 4 Pd MLs on Au in a pH 6.7 phosphate buffer (0.1 M KH₂PO₄ / 0.1 M K₂HPO₄).

E (V) vs. RHE	CO (%)	CH ₄ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	ΣC ₂ (%)	C ₃ H ₆ (%)	C ₃ H ₈ (%)	ΣC ₃ (%)
-0.4	80.86		. ,	, , , , , , , , , , , , , , , , , , ,	`, ,		`,	. , ,
-0.5	81.43							
-0.6	73.77							
-0.7	60.63							
-0.8	27.23	4.48	0.38	1.16	1.54			
-0.9	14.17	2.82	0.33	1.00	1.33			
-1	5.34	2.90	0.21	0.74	0.95	0.11	0.28	0.39
-1.1	5.93	3.19	0.19	0.80	0.99	0.12	0.32	0.45
-1.2	8.47	3.30	0.18	0.77	0.95	0.12	0.32	0.44
-1.3	6.35	1.78	0.15	0.50	0.65	0.08	0.20	0.28
-1.4	4.33	1.07	0.10	0.31	0.41	0.05	0.12	0.17
-1.5	2.22	0.72	0.07	0.21	0.27	0.03	0.08	0.11

Table S5. Faradaic efficiencies toward C_4 - C_5 hydrocarbons produced during CO_2 reduction on 4 Pd MLs on Au in a pH 6.7 phosphate buffer (0.1 M KH₂PO₄ / 0.1 M K₂HPO₄).



Figure 32. Faradaic efficiencies for the reduction of CO_2 on an Au electrode covered with 4 Pd MLs in a pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄) toward different C₁-C₅ hydrocarbon products.



Figure 33. a) Cyclic voltammograms of a polycrystalline gold electrode recorded in a 0.1 M $KH_2PO_4 / 0.1 M K_2HPO_4$ electrolyte (pH 6.7) at a scan rate of 50 mV/s purged with either argon (green) or CO₂ (blue); **b)** Cyclic voltammograms of a polycrystalline palladium electrode recorded in a 0.1 M $KH_2PO_4 / 0.1 M K_2HPO_4$ electrolyte (pH 6.7) at a scan rate of 50 mV/s purged with either argon (green) or CO₂ (blue).



Figure S34. Cyclic voltammograms of a polycrystalline Au electrode covered with 1 monolayer Pd (green line), 2 Pd monolayers (purple dashed line), 3 Pd monolayers (blue dashed line) and 4 Pd monolayers (red dashed line) in a $0.5 \text{ M H}_2\text{SO}_4$ electrolyte purged with argon at a scan rate of 20 mV/s.



Figure S35. Cyclic voltammograms of a polycrystalline Au electrode with diffent amounts of Pd monolayers recorded in a 0.1 M KH₂PO₄ / 0.1 M K₂HPO₄ electrolyte (pH 6.7) at a scan rate of 50 mV/s purged with either argon (green) or CO₂ (blue); **a)** 1 Pd monolayer; **b)** 2 Pd monolayers; **c)** 3 Pd monolayers; **d)** 4 Pd monolayers.

S11. Additional Flory-Schulz distributions



Figure S36. Flory-Schulz product distribution of the hydrocarbon products produced at -1.4 V vs. RHE on a Pd-Au electrode in a pH pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄). w_n : weight fraction, n : carbon number.



Figure S37. Flory-Schulz product distribution of the hydrocarbon products produced at -1.3 V vs. RHE on a Pd-Au electrode in a pH pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄). w_n : weight fraction, n : carbon number.



Figure S38. Flory-Schulz product distribution of the hydrocarbon products produced at -1.2 V vs. RHE on a Pd-Au electrode in a pH pH 6.7 phosphate buffer electrolyte (0.1 M KH₂PO₄/ 0.1 M K₂HPO₄). w_n : weight fraction, n : carbon number.