

Photoelectrochemical CO₂-to-fuel conversion with simultaneous plastic reforming

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Supplementary Information

Photoelectrochemical CO₂-to-fuel conversion with simultaneous plastic reforming

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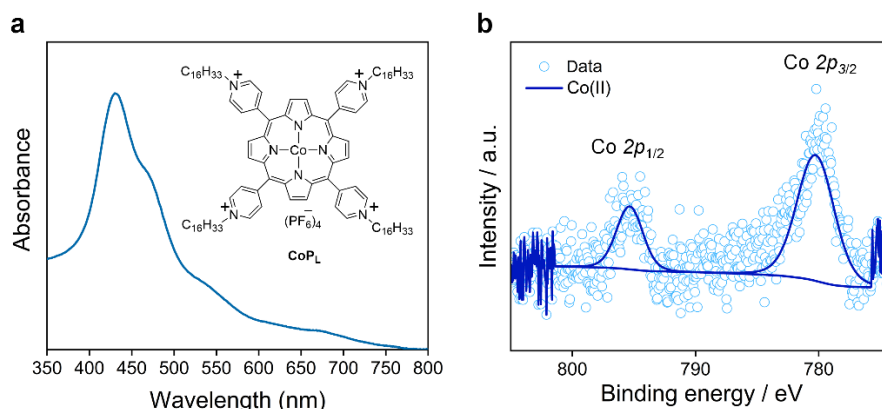
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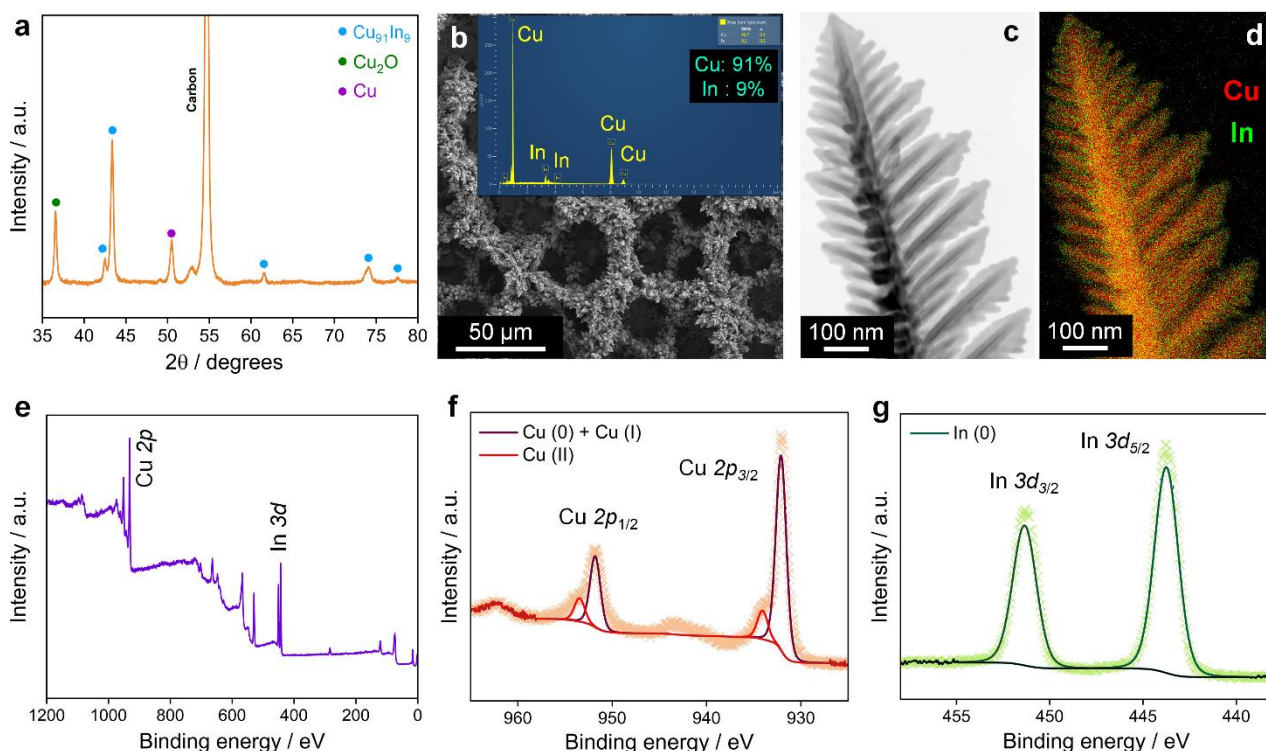
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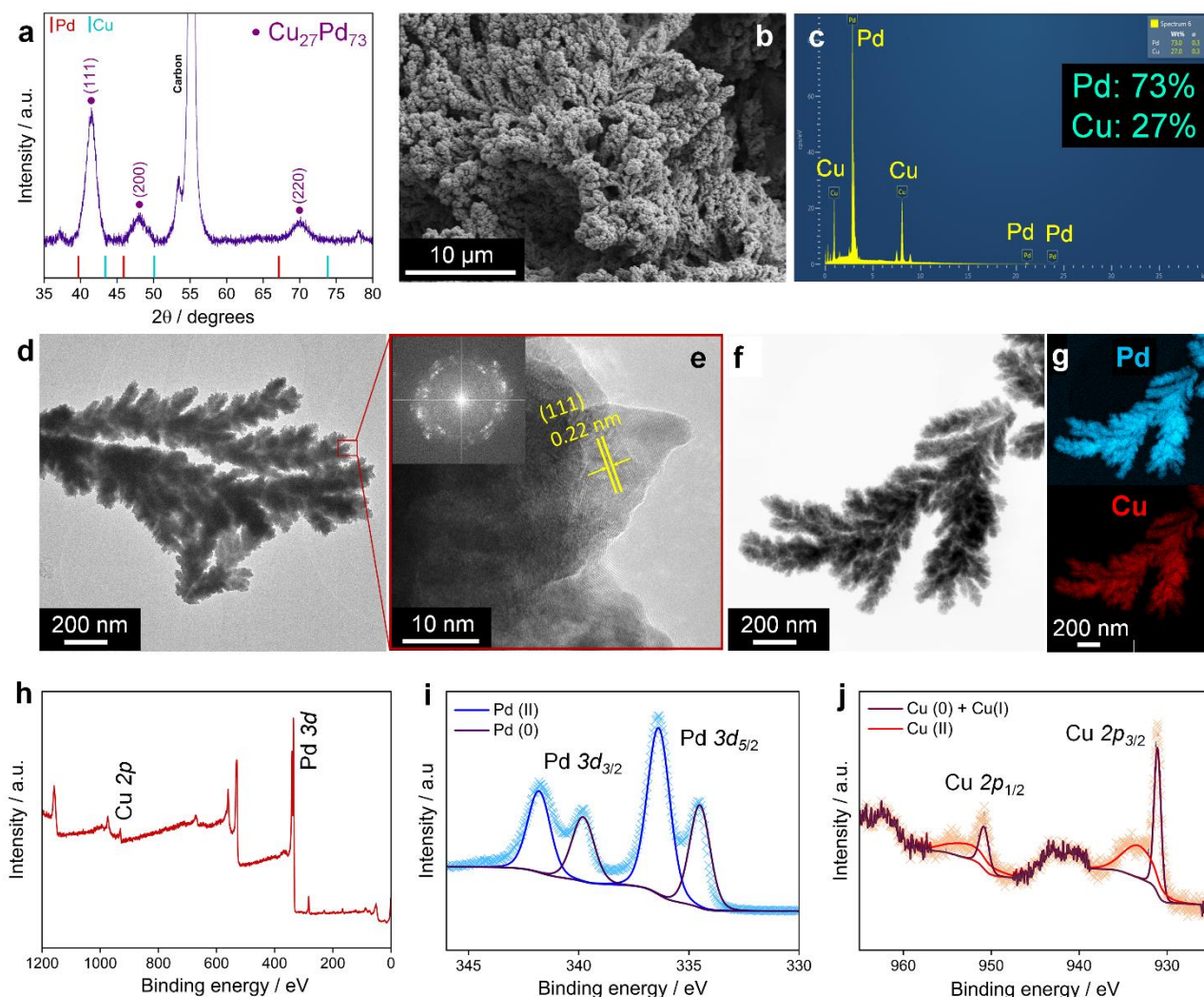
Supplementary Figures



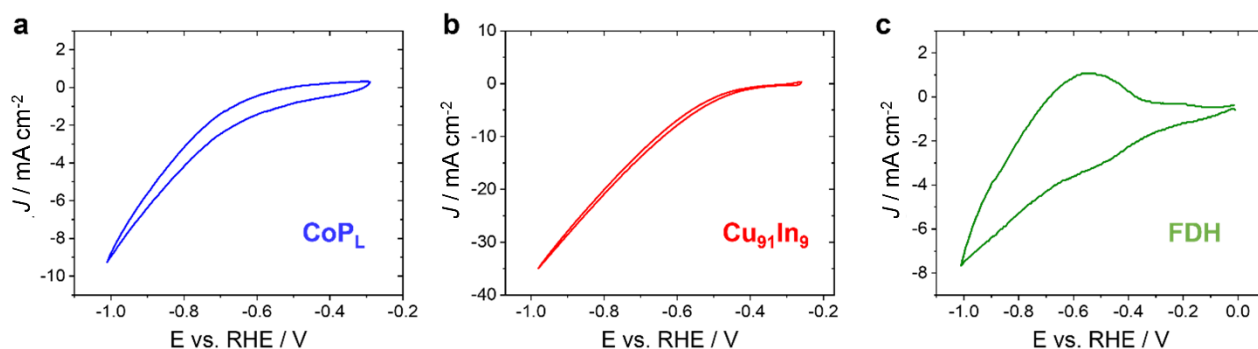
Supplementary Fig. 1 | Characterization of the CoPL catalyst. **a**, UV-vis spectra of CoPL (in DMF) showing an absorption peak at ~430 nm. Inset shows the structure of the CoPL catalyst. **b**, The deconvoluted XPS spectra of CoPL in the Co 2p region.



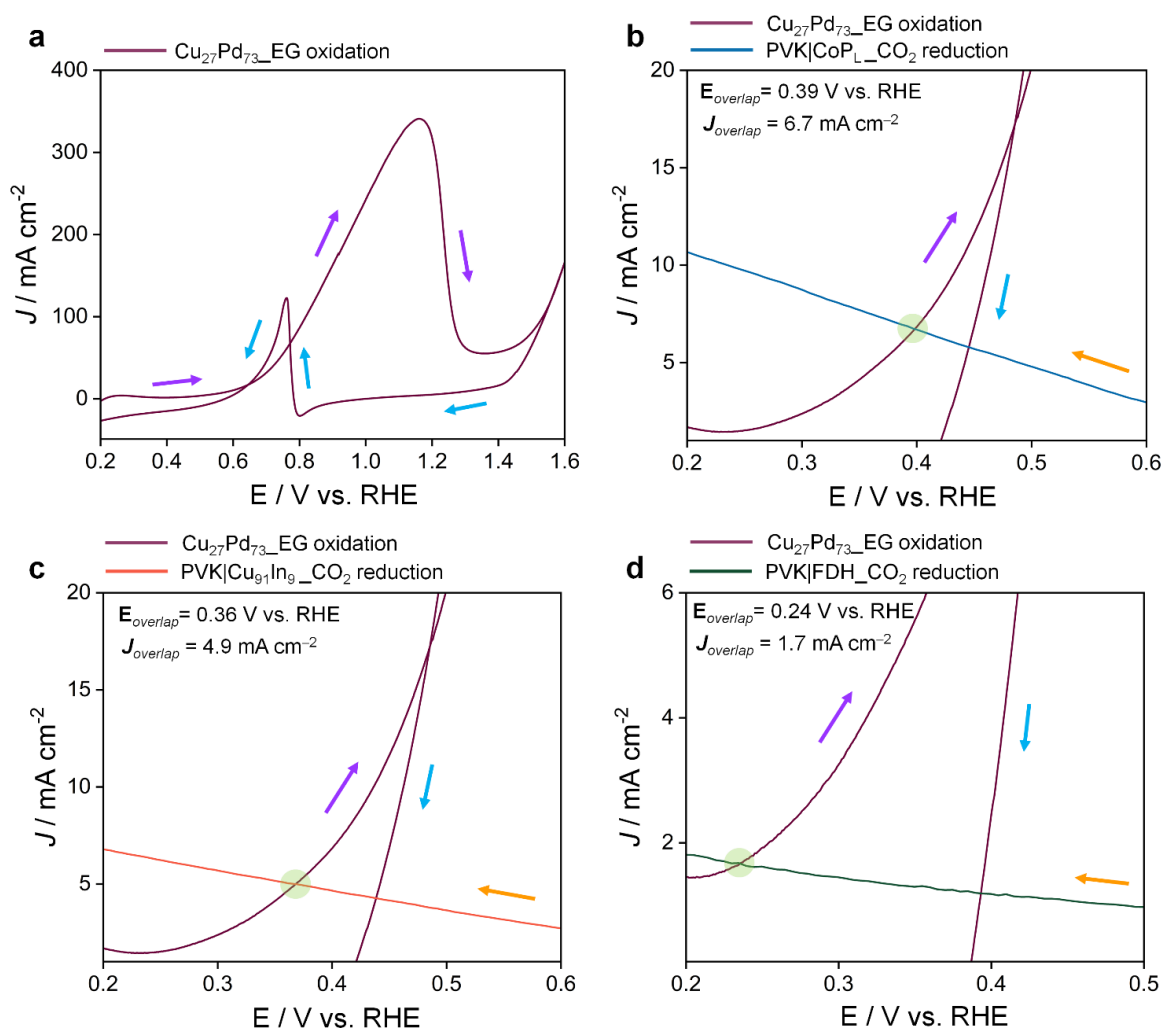
Supplementary Fig. 2 | Characterization of the Cu₉₁In₉ catalyst. **a**, PXRD pattern of the Cu₉₁In₉ catalyst (Cu₉₁In₉, Cu₂O and Cu phases are according to the JCPDS No. 35-1150, 75-1531, and 85-1326, respectively). **b**, FESEM image of Cu₉₁In₉ with corresponding EDX spectra (inset) showing the composition. **c**, **d**, STEM-BF image (**c**) and corresponding elemental map (**d**) showing homogenous distribution of Cu and In on a single dendrite. **e**, Survey XPS spectra of Cu₉₁In₉. **f**, **g**, The deconvoluted XPS spectra of Cu₉₁In₉ in the Cu 2p (**f**) and In 3d (**g**) regions.



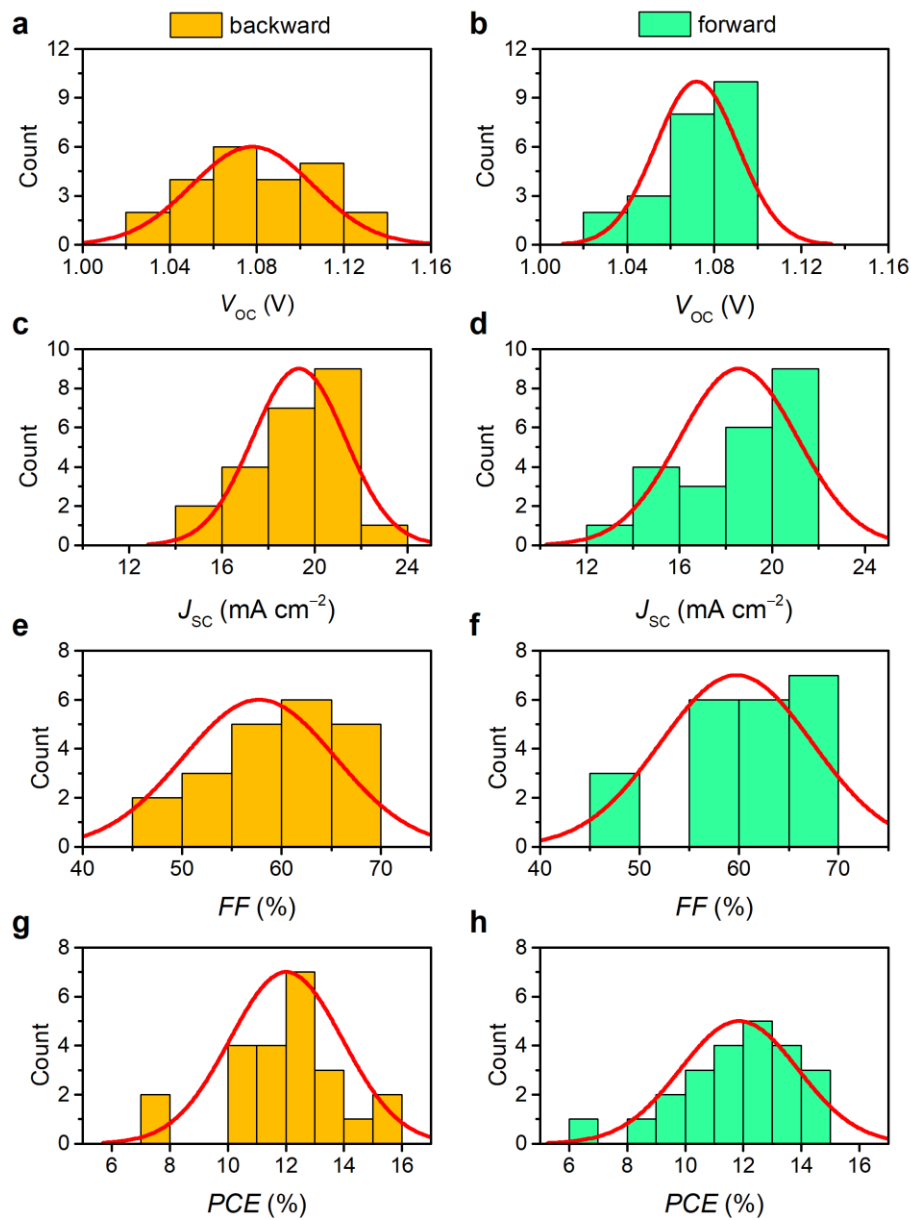
Supplementary Fig. 3 | Characterization of the $\text{Cu}_{27}\text{Pd}_{73}$ oxidation catalyst. **a**, PXRD pattern of the $\text{Cu}_{27}\text{Pd}_{73}$ catalyst showing the alloy phases. FESEM image of $\text{Cu}_{27}\text{Pd}_{73}$ (**b**) with corresponding EDX spectra (**c**). **d**, TEM image of $\text{Cu}_{27}\text{Pd}_{73}$. **e**, HRTEM image of $\text{Cu}_{27}\text{Pd}_{73}$ showing the lattice fringes corresponding to (111) reflection. The inset shows the corresponding Fast Fourier Transform (FFT) pattern. **f**, **g**, STEM-BF image of $\text{Cu}_{27}\text{Pd}_{73}$ (**f**) with corresponding elemental maps (**g**) showing Pd (blue) and Cu (red) indicating homogeneous distribution of Cu and Pd on a single dendrite. **h**, Survey XPS spectra of $\text{Cu}_{27}\text{Pd}_{73}$. **i**, **j**, The deconvoluted XPS spectra of $\text{Cu}_{27}\text{Pd}_{73}$ in the Pd 3d (**i**) and Cu 2p (**j**) regions.



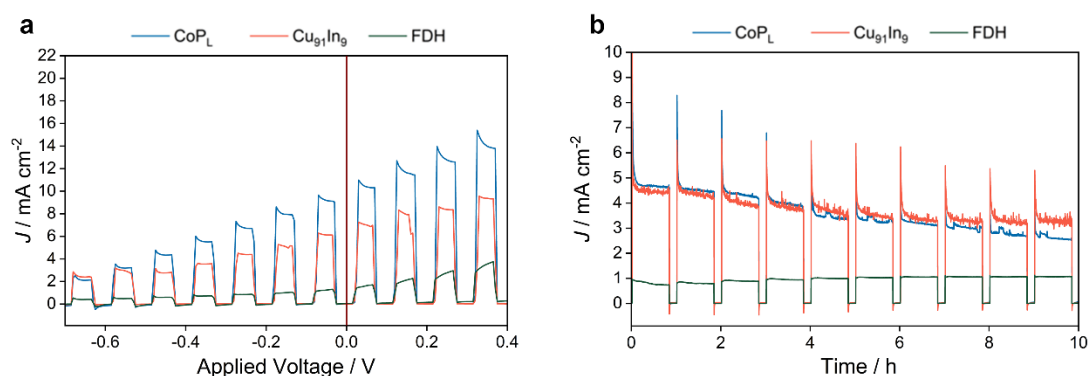
Supplementary Fig. 4 | Cyclic voltammetry (CV) scans recorded with different CO_2R catalysts under electrochemical conditions. a-c, CVs of CoP_L molecular catalyst (a), $\text{Cu}_{91}\text{In}_9$ bimetallic catalyst (b), and FDH biocatalyst (c). The CVs were recorded at room temperature with 25 mV s^{-1} scan rate. CO_2 -saturated 0.5 M KHCO_3 buffer (pH 7.2) was used as an electrolyte for both CoP_L and $\text{Cu}_{91}\text{In}_9$ catalysts and CO_2 -saturated MOPS buffer (pH 6.4) was used as an electrolyte for FDH biocatalyst.



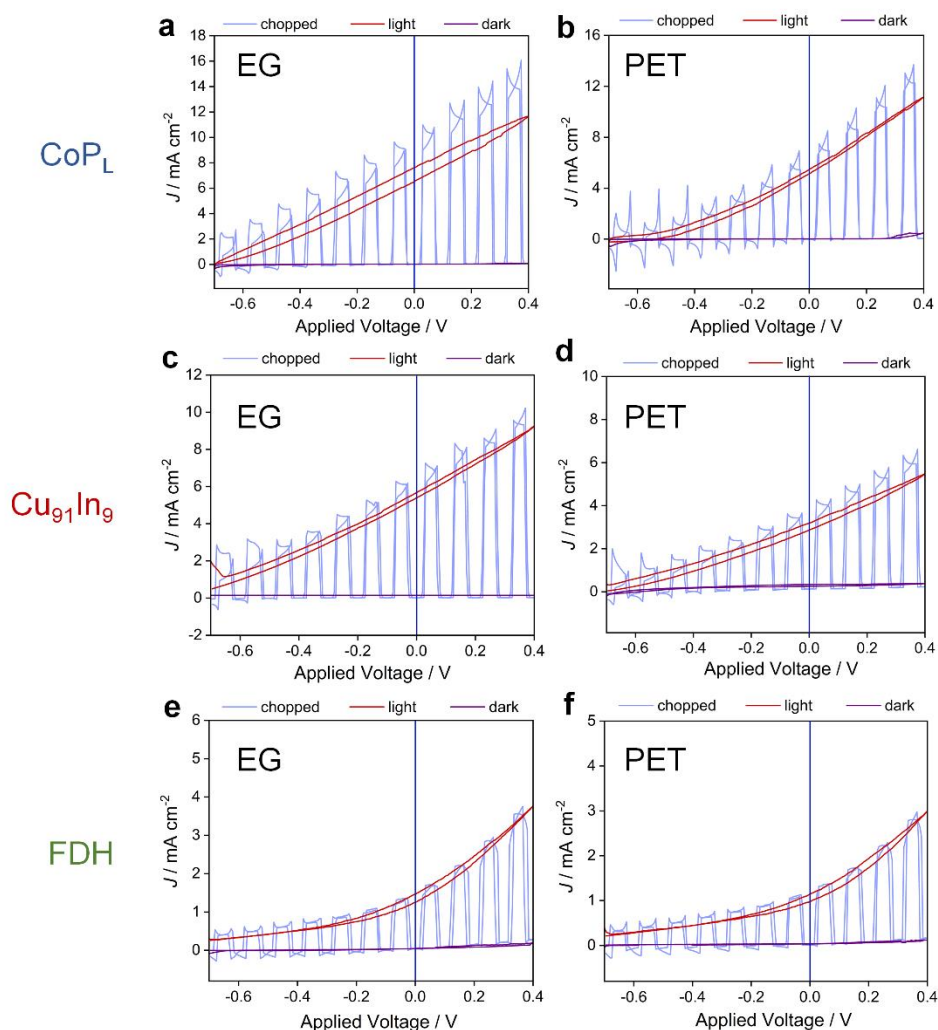
Supplementary Fig. 5 | Determination of overlap potential and anticipated steady-state photocurrent densities at zero applied voltage. a, CV scan with $\text{Cu}_{27}\text{Pd}_{73}$ catalyst and EG substrate (0.5 M in 1 M aqueous KOH) in a two-compartment, three-electrode setup with 25 mV s^{-1} scan rate at room temperature with stirring. During both the forward and reverse scans, two anodic peaks are observed. The peak during the forward scan (purple arrows) corresponds to the primary oxidation peak of EG, after which the current drastically decreases (after $\sim 1.2 \text{ V vs. RHE}$) owing to the formation of PdO species rendering the surface inactive.^{1,2} During the reverse scan (blue arrows), the surface PdO species are reduced, exposing fresh (reactivated) Pd sites for the oxidation of EG resulting in the additional anodic peak.²⁻⁴ The overlap of Ni foam| $\text{Cu}_{27}\text{Pd}_{73}$ oxidation curve (forward scan corresponding to the primary curve) with the reduction curve of PVK|CO₂R_{cat} under continuous illumination (incorporating chemical bias) for the different CO₂R_{cat} systems: **b**, CoP_L, **c**, Cu₉₁In₉ and **d**, FDH is shown to identify the active potential range and anticipated steady-state photocurrent density during PEC operation at zero applied voltage. The cathodic current density is flipped to positive scale to facilitate interpretation. It is observed that for CoP_L and Cu₉₁In₉, the overlap potentials are $\sim 0.39 \text{ V}$ and $\sim 0.36 \text{ V vs. RHE}$, whereas the FDH catalyst shows a lower overlap potential of $\sim 0.24 \text{ V vs. RHE}$. The corresponding anticipated steady-state photocurrent densities at zero applied voltage are 6.7, 4.9 and 1.7 mA cm^{-2} for CoP_L, Cu₉₁In₉ and FDH, respectively.



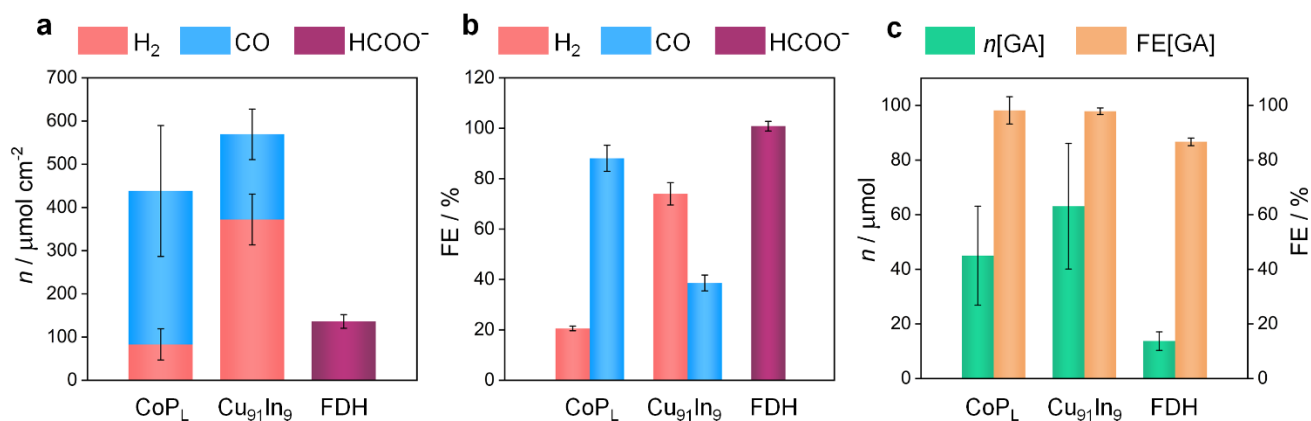
Supplementary Fig. 6 | Photovoltaic parameters of the devices used in this study. **a-h**, The histograms are depicted in orange for the backward scans (**a**, **c**, **e**, **g**) and green for the forward scans (**b**, **d**, **f**, **h**). Open circuit voltage (V_{oc}) (**a**, **b**), short circuit current density (J_{sc}) (**c**, **d**), fill factor (FF) (**e**, **f**), and photovoltaic cell efficiency (PCE) (**g**, **h**). The normal distribution curves are indicated by the red lines.



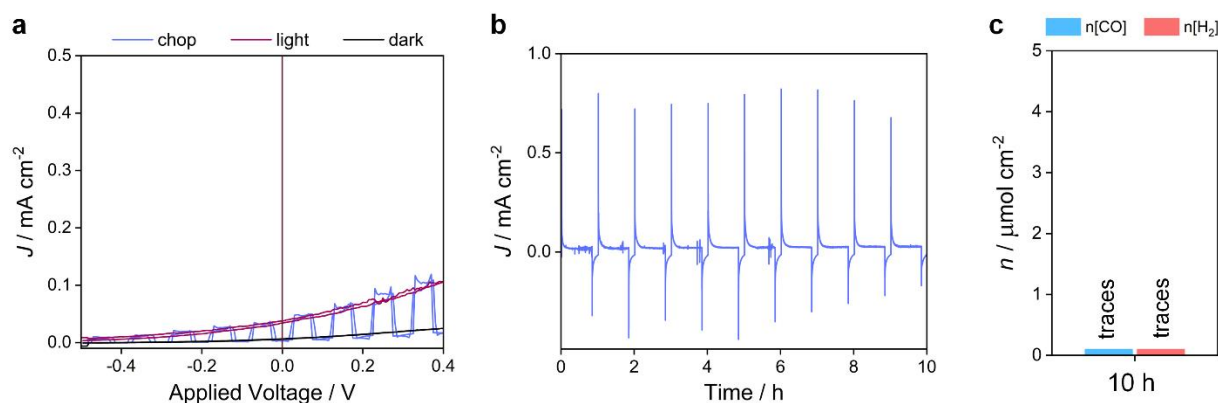
Supplementary Fig. 7 | PEC responses for EG model substrate. PEC responses in two-compartment, two-electrode configuration PEC system separated by bipolar membrane (Cu₂₇Pd₇₃||PVK|CO₂R_{cat}; CO₂R_{cat}: CoP_L, Cu₉₁In₉ and FDH) using EG model substrate (0.5 M) recorded at room temperature and stirring in both compartments. The catholyte consisted of CO₂-saturated 0.5 M KHCO₃ (pH 7.2) for CoP_L and Cu₉₁In₉ systems, and CO₂-saturated MOPS buffer (pH 6.4) for the biological FDH system. The anolyte was N₂-purged 1 M aqueous KOH (pH 14). **a**, Representative forward CV scans (scan rate 5 mV s⁻¹) recorded under chopped simulated solar light irradiation (AM 1.5G) for the different CO₂R_{cat} systems with EG as substrate at the anode. **b**, Corresponding photocurrent transients for 10 h operation (at zero applied voltage) under 1 sun irradiation (50 min on, 10 min off) for the different systems. The average steady-state photocurrent density obtained for CoP_L, Cu₉₁In₉ and FDH are 3.8±0.6, 3.7±0.4, 1.0±0.1 mA cm⁻², respectively which is consistent with the current (J_{overlap}) anticipated from the overlap of the CVs of PVK|CO₂R_{cat} under continuous illumination and that of Ni foam|Cu₂₇Pd₇₃ under dark conditions (Supplementary Fig. 5b-d).



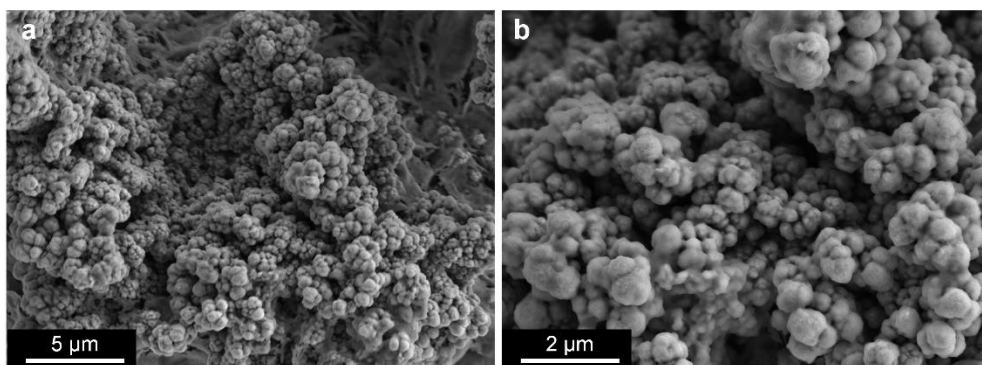
Supplementary Fig. 8 | CVs for the different catalyst systems. **a, b**, Chopped, light and dark CV scans recorded with $\text{Cu}_{27}\text{Pd}_{73}||\text{PVK}|\text{CoP}_\text{L}$ for EG (0.5 M) model substrate (**a**) and pre-treated PET (**b**) at the anode. Chopped, light and dark CV scans recorded with $\text{Cu}_{27}\text{Pd}_{73}||\text{PVK}|\text{CoP}_\text{L}$ for EG model substrate (**c**) and pre-treated PET (**d**) at the anode. Chopped, light and dark CV scans recorded with $\text{Cu}_{27}\text{Pd}_{73}||\text{PVK}|\text{FDH}$ for EG model substrate (**e**) and pre-treated PET (**f**) at the anode. Conditions: AM 1.5G; catholyte: CO_2 -saturated 0.5 M KHCO_3 (pH 7.2) for CoP_L and $\text{Cu}_{91}\text{In}_9$ systems, and CO_2 -saturated MOPS buffer (pH 6.4) for the biological FDH system; anolyte: N_2 -purged 1 M aqueous KOH (pH 14); bipolar membrane; room temperature, stirring in both compartments. The onset voltages for all the cases are in the range of -0.8 to -0.6 V.



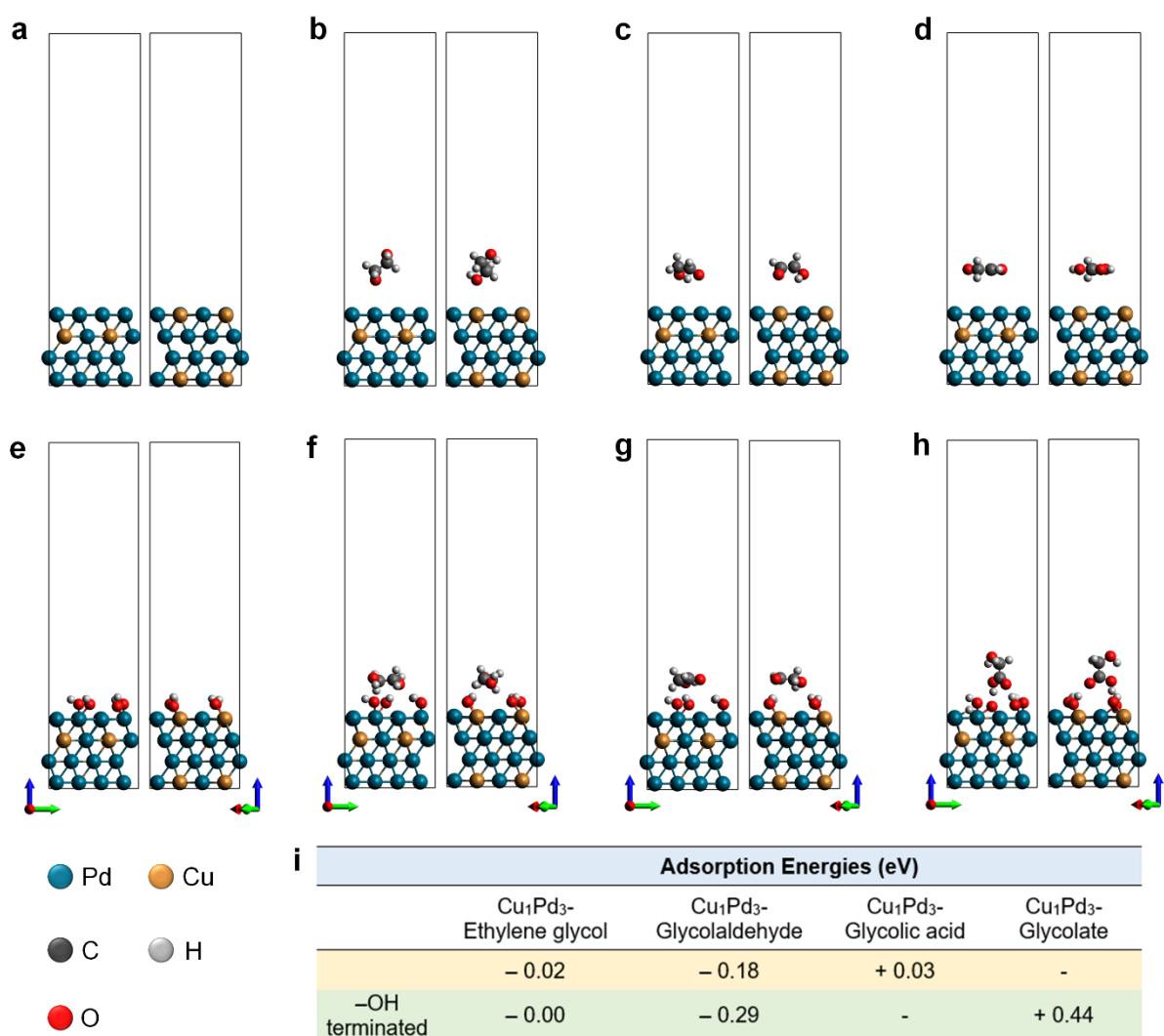
Supplementary Fig. 9 | Product distribution: PEC CO₂-to-fuel conversion coupled to EG (model substrate) conversion. **a, b**, The CO₂R product formation (**a**) and corresponding FEs (**b**) for the different systems at the photocathode with EG model substrate at the anode after 10 h. **c**, The amount of oxidation product (GA indicates glycolic acid) formed at the anode and corresponding FEs with EG model substrate after 10 h. Experimental Conditions: PEC responses in two-compartment, two-electrode configuration PEC system separated by bipolar membrane ($\text{Cu}_{27}\text{Pd}_{73}||\text{PVK}|\text{CO}_2\text{R}_{\text{cat}}$; $\text{CO}_2\text{R}_{\text{cat}}$: CoP_L , $\text{Cu}_{91}\text{In}_9$ and FDH) using EG model substrate (0.5 M) recorded at room temperature and stirring in both compartments. The catholyte consisted of CO₂-saturated 0.5 M KHCO₃ (pH 7.2) for CoP_L and $\text{Cu}_{91}\text{In}_9$ systems, and CO₂-saturated MOPS (pH 6.4) buffer for the biological FDH system. The anolyte was N₂-purged 1 M aq. KOH.



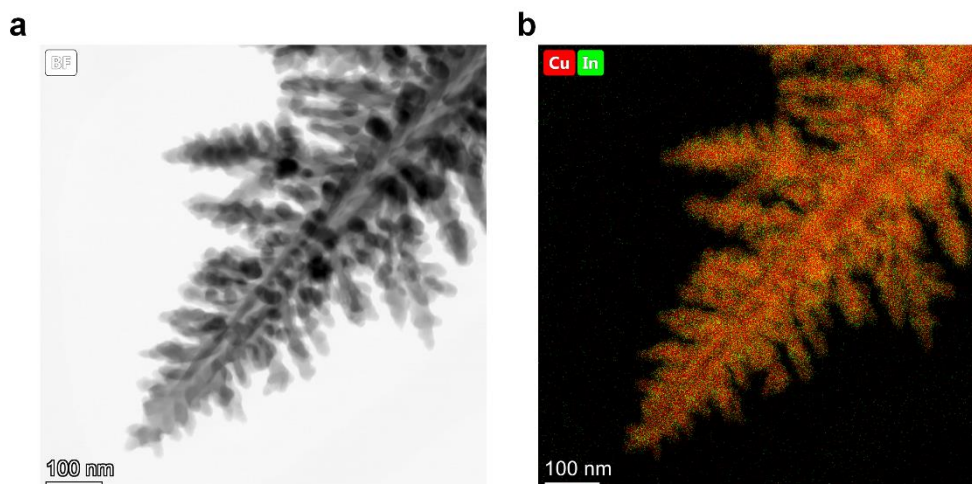
Supplementary Fig. 10 | Control PEC experiments with only TPA as substrate at the anode. **a**, Chopped, light and dark CV scans recorded with $\text{Cu}_{27}\text{Pd}_{73}||\text{PVK}|\text{CoP}_L$ for TPA (0.5 M) substrate at the anode. **b**, Corresponding photocurrent transients for 10 h operation (at zero applied voltage) under 1 sun irradiation (AM 1.5G, 50 min on, 10 min off) and **c**, bar plots showing negligible product formation after 10 h. Conditions: Catholyte: CO₂-saturated 0.5 M KHCO₃; anolyte: N₂-purged 1 M aq. KOH containing 0.5 M TPA; room temperature, stirring in both compartments.



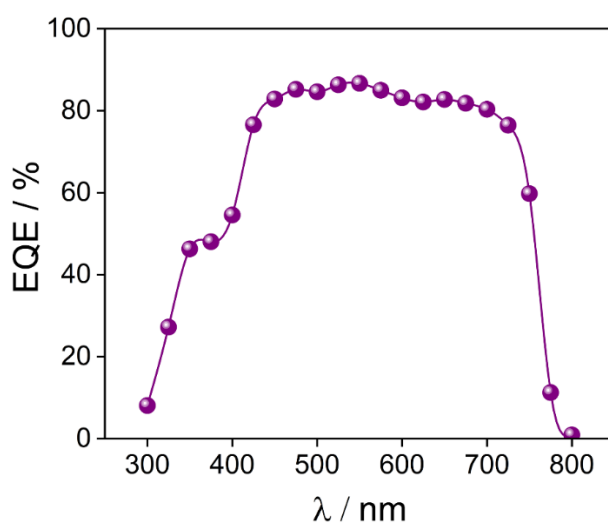
Supplementary Fig. 11 | Post-experiment characterizations with Cu₂₇Pd₇₃. **a, b**, Post-catalytic (after 10 h PEC measurement at zero applied voltage) FESEM images of Cu₂₇Pd₇₃ alloy oxidation catalyst showing retention of flower-like morphology.



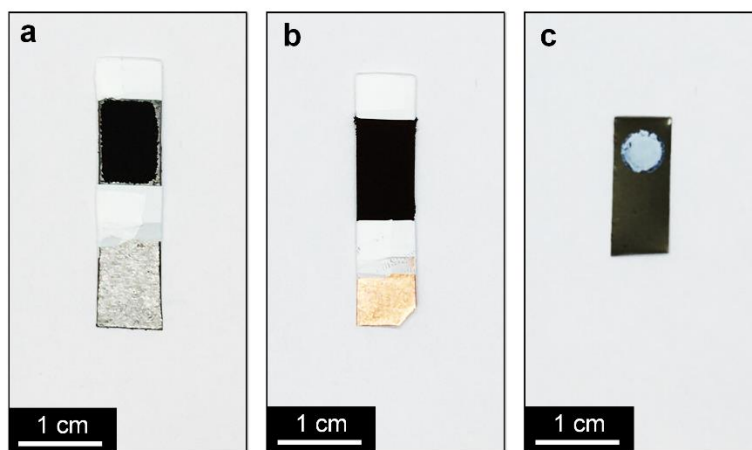
Supplementary Fig. 12 | DFT calculations. **a-d**, Optimized slab models for Cu₁Pd₃ surface (**a**) with different adsorbates: EG (**b**), glycolaldehyde (**c**) and glycolic acid (**d**). **e-h**, Optimized slab models for -OH terminated Cu₁Pd₃ surface (**e**) with different adsorbates: EG (**f**), glycolaldehyde (**g**) and glycolic acid (**h**). **i**, Table showing the corresponding adsorption energies obtained from DFT calculations. DFT calculations were performed to probe the adsorption energies of intermediates on the surface of Cu₂₇Pd₇₃ alloy (modelled through the (111) surface termination of Cu₁Pd₃, denoted as Cu₁Pd₃(111); see computational details for further information; main text). The adsorption energies of EG, glycolaldehyde and glycolic acid on the bare Cu₁Pd₃(111) surface were calculated showing lower adsorption energies for EG (-0.02 eV), and glycolaldehyde (-0.18 eV), while glycolic acid shows the highest adsorption energy (0.03 eV). When the surface copper atoms of Cu₁Pd₃(111) are terminated by -OH groups to simulate a more likely surface structure under alkaline conditions a similar trend is observed, namely a higher adsorption energy for glycolic acid. The higher adsorption energy of glycolic acid is consistent with its preferred formation as it would more likely desorb from the metal-alloy surface before further oxidation, competing with the binding of EG and glycolaldehyde.



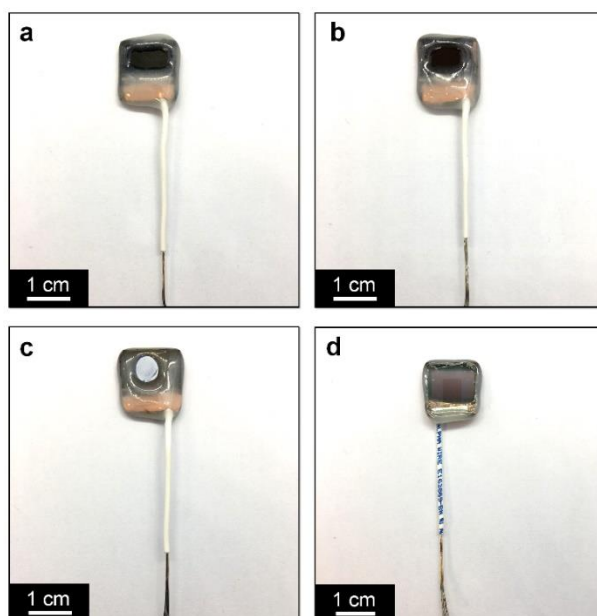
Supplementary Fig. 13 | Post-catalysis analysis of Cu₉₁In₉. **a, b**, STEM-BF image (**a**) and corresponding elemental map (**b**) of a Cu₉₁In₉ dendrite after 10 h PEC measurement at zero applied voltage. Minor phase-separation is observed after experiment as In phase migrated towards the periphery.



Supplementary Fig. 14 | Representative action spectrum (wavelength dependent EQE spectrum) recorded for Cu₂₇Pd₇₃||PVK|Cu₉₁In₉ at zero applied voltage and pre-treated PET substrate at the anode.



Supplementary Fig. 15 | Optical images of the CO₂R_{cat} systems. Photographs of the different CO₂R_{cat} systems: **a**, CoP_L (on activated graphite foil), **b**, Cu₉₁In₉ (on Cu foil) and **c**, FDH (on Ti|IO-TiO₂) prior to integration with the PVK light absorber.



Supplementary Fig. 16 | Optical images of PVK|CO₂R_{cat} photocathodes. Photographs of the photocathodes: **a**, PVK|CoP_L, **b**, PVK|Cu₉₁In₉ and **c**, PVK|FDH. **d**, Back side of a typical photocathode. The CoP_L, Cu₉₁In₉, and FDH are attached/immobilized on activated graphite foil, Cu foil and Ti|IO-TiO₂ scaffolds, respectively prior to integration with the PVK light absorber.

Supplementary Tables

Supplementary Table 1 | Numerical data for PEC CO₂R with EG model substrate. Amount of the CO₂R products obtained at the cathode from the different systems and the corresponding faradaic efficiencies (FE) at different time intervals for zero applied voltage, solar-driven, two-compartment PEC processes using soluble model substrate **ethylene glycol** (0.5 M) in the anodic chamber (N₂ purged). Conditions: *catholyte*: 0.5 M aqueous KHCO₃ (CO₂ purged) for PVK|CoP_L and PVK|Cu₉₁In₉ systems and MOPS buffer (CO₂ purged) for PVK|FDH system; *anolyte*: 0.1 M aqueous KOH with 0.5 M ethylene glycol (N₂ purged); bipolar membrane; room temperature; AM 1.5G; stirring. ‘TON’ indicates “turn-over number”, ‘TOF’ indicates “turn-over frequency”. The numerical data is represented as average ± standard deviation of the measurements.

System	Time (h)	<i>n</i> [H ₂] (μmol cm ⁻²)	<i>n</i> [CO] (μmol cm ⁻²)	<i>n</i> [H ₂ +CO] (μmol cm ⁻²)	FE[H ₂] (%)	FE[CO] (%)	FE[H ₂ +CO] (%)	TON _{CO}	TOF _{CO} (s ⁻¹)
Cu₂₇Pd₇₃ PVK CoP_L	2	14.4 ± 7.8	84.0 ± 45.1	98.4 ± 52.8	14.9 ± 0.9	86.8 ± 8.0	101.8 ± 7.9	0.4 × 10 ⁴	0.48
	5	36.1 ± 17.2	199.2 ± 101.0	235.3 ± 118.0	16.1 ± 0.8	87.5 ± 7.2	103.6 ± 7.1	0.8 × 10 ⁴	0.46
	10	82.9 ± 36.0	355.2 ± 151.6	438.1 ± 187.6	20.5 ± 0.9	88.1 ± 5.2	108.6 ± 5.9	1.5 × 10 ⁴	0.41
Cu₂₇Pd₇₃ PVK Cu₉₁In₉	2	55.8 ± 23.9	60.5 ± 14.1	116.4 ± 38.0	48.1 ± 6.7	53.8 ± 3.5	101.9 ± 3.2	-	-
	5	157.4 ± 49.7	121.0 ± 29.6	278.5 ± 79.3	59.2 ± 1.3	46.0 ± 2.4	105.3 ± 1.2	-	-
	10	372.1 ± 59.0	197.2 ± 58.5	569.3 ± 117.5	73.9 ± 4.4	38.6 ± 3.1	112.6 ± 1.3	-	-
		<i>n</i> [HCOO ⁻] (μmol cm ⁻²)		FE[HCOO ⁻] (%)		TON _{HCOO⁻}		TOF _{HCOO⁻} (s ⁻¹)	
Cu₂₇Pd₇₃ PVK FDH	10	136.2 ± 15.8		100.8 ± 2.0		3.8 × 10 ⁵		10.6	

Supplementary Table 2 | Numerical data for PEC reforming of EG. Amount of oxidation product obtained, product ratio and FE after 10 h of solar-driven, two-compartment PEC processes at zero applied voltage from the different systems using soluble model substrate **ethylene glycol** (0.5 M) in the anodic chamber (N₂ purged). Conditions: *catholyte*: 0.5 M aqueous KHCO₃ (CO₂ purged) for PVK|CoP_L and PVK|Cu₉₁In₉ systems and MOPS buffer (CO₂ purged) for PVK|FDH system; *anolyte*: 0.1 M aqueous KOH with 0.5 M ethylene glycol (N₂ purged); bipolar membrane; room temperature; AM 1.5G; stirring. ‘GA’ indicates “glycolic acid”, ‘TR’ indicates “total reduction products”, ‘#N’ indicates “no. of electrons involved”. The numerical data is represented as average ± standard deviation of the measurements.

System	<i>n</i> [GA] (μmol)	<i>n</i> [TR] (μmol)	#N	Expected <i>n</i> [GA] (μmol)	<i>n</i> [GA]: <i>n</i> [TR]	Expected <i>n</i> [GA]: <i>n</i> [TR]	FE[GA] (%)
Cu₂₇Pd₇₃ PVK CoP_L	45.0 ± 18.1	98.5 ± 42.2	4	49.3 ± 21.1	0.45 ± 0.02	0.5	98.2 ± 5.0
Cu₂₇Pd₇₃ PVK Cu₉₁In₉	63.1 ± 23.0	144.4 ± 49.5	4	72.2 ± 24.7	0.43 ± 0.01	0.5	97.9 ± 1.2
Cu₂₇Pd₇₃ PVK FDH	13.7 ± 3.4	31.1 ± 8.1	4	15.5 ± 4.1	0.44 ± 0.01	0.5	86.7 ± 1.4

Supplementary Table 3 | Numerical data for CO₂R with pre-treated PET substrate. Amount of the CO₂R products obtained at the cathode from the different systems and the corresponding FE at different time intervals for zero applied voltage, solar-driven, two-compartment PEC processes using **pre-treated PET bottle** in the anodic chamber (N₂ purged). Conditions: *catholyte*: 0.5 M aqueous KHCO₃ (CO₂ purged) for PVK|CoP_L and PVK|Cu₉₁In₉ systems and MOPS buffer (CO₂ purged) for PVK|FDH system; *anolyte*: 0.1 M aqueous KOH with pre-treated PET bottle (N₂ purged); bipolar membrane; room temperature; AM 1.5G; stirring.

System	Time (h)	$n[\text{H}_2]$ ($\mu\text{mol cm}^{-2}$)	$n[\text{CO}]$ ($\mu\text{mol cm}^{-2}$)	$n[\text{H}_2+\text{CO}]$ ($\mu\text{mol cm}^{-2}$)	FE[H ₂] (%)	FE[CO] (%)	FE[H ₂ +CO] (%)	TON _{CO}	TOF _{CO} (s ⁻¹)
Cu₂₇Pd₇₃ PVK CoP_L	2	8.3 ± 2.3	66.1 ± 16.9	74.4 ± 19.2	11.6 ± 0.2	93.0 ± 4.2	104.7 ± 4.4	0.3 × 10 ⁴	0.38
	5	21.7 ± 6.6	147.8 ± 45.6	169.4 ± 52.2	13.6 ± 1.1	92.8 ± 7.2	106.4 ± 8.3	0.6 × 10 ⁴	0.34
	10	46.2 ± 16.4	262.6 ± 98.5	308.9 ± 114.9	16.9 ± 1.7	95.6 ± 7.7	112.5 ± 9.4	1.1 × 10 ⁴	0.30
Cu₂₇Pd₇₃ PVK Cu₉₁In₉	2	36.5 ± 11.9	58.5 ± 25.6	94.9 ± 37.5	35.2 ± 0.5	55.2 ± 5.9	90.4 ± 5.4	-	-
	5	106.6 ± 7.7	123.8 ± 66.8	230.4 ± 59.0	45.0 ± 16.7	47.6 ± 12.4	92.6 ± 4.3	-	-
	10	240.4 ± 74.6	212.4 ± 148.3	452.7 ± 73.6	48.6 ± 18.2	42.8 ± 23.5	91.4 ± 10.7	-	-
		$n[\text{HCOO}^-]$ ($\mu\text{mol cm}^{-2}$)			FE[HCOO ⁻] (%)		TON _{HCOO⁻}		TOF _{HCOO⁻} (s ⁻¹)
Cu₂₇Pd₇₃ PVK FDH	10	121.0 ± 86.8			96.4 ± 3.5		3.4 × 10 ⁵		9.4

Supplementary Table 4 | Numerical data for PEC reforming of pre-treated PET. Amount of oxidation product obtained, product ratio and FE after 10 h of solar-driven, two-compartment PEC processes at zero applied voltage from the different systems using **pre-treated PET bottle** in the anodic chamber (N₂ purged). Conditions: *catholyte*: 0.5 M aqueous KHCO₃ (CO₂ purged) for PVK|CoP_L and PVK|Cu₉₁In₉ systems and MOPS buffer (CO₂ purged) for PVK|FDH system; *anolyte*: 0.1 M aqueous KOH with pre-treated PET bottle (N₂ purged); bipolar membrane; room temperature; AM 1.5G; stirring.

System	$n[\text{GA}]$ (μmol)	$n[\text{TR}]$ (μmol)	#N	Expected $n[\text{GA}]$ (μmol)	$n[\text{GA}]:n[\text{TR}]$	Expected $n[\text{GA}]:n[\text{TR}]$	FE[GA] (%)
Cu₂₇Pd₇₃ PVK CoP_L	30.7 ± 7.0	67.6 ± 15.9	4	33.8 ± 8.0	0.45 ± 0.003	0.5	97.5 ± 2.6
Cu₂₇Pd₇₃ PVK Cu₉₁In₉	52.4 ± 17.8	114.5 ± 34.4	4	57.2 ± 17.2	0.45 ± 0.02	0.5	95.8 ± 9.1
Cu₂₇Pd₇₃ PVK FDH	14.2 ± 8.4	32.5 ± 18.4	4	16.3 ± 9.2	0.43 ± 0.01	0.5	96.1 ± 14.0

Supplementary Table 5 | Comparison with representative systems. Comparison of some existing photocatalytic (PC) systems and PEC towards CO₂R with our new Cu₂₇Pd₇₃||PVK|CO₂R_{cat} device. The experiments were conducted in room temperature unless otherwise stated. ‘TEOA’ indicates “triethanolamine”, ‘OER’ indicates “oxygen evolution reaction”, ‘AA’ indicates “ascorbic acid”, ‘HMF’ indicates “hydroxymethylfurfural”.

#	Catalyst/Process	Process	Anode/ Oxidation reaction	Irradiation area / conditions	<i>n</i> [CO]	<i>n</i> [H ₂]	<i>n</i> [HCOO ⁻]	Ref.
1	mpg-CN _x -CoPP _c (0.67 mg mL ⁻¹) (MeCN/TEOA media)	PC	TEOA oxidation	*2.94 cm ² AM 1.5G, 100 mW cm ⁻²	0.014 μmol cm ⁻² h ⁻¹	0.003 μmol cm ⁻² h ⁻¹	-	5
2	RuO ₂ -BiVO ₄ :Mo Au SrTiO ₃ :La,Rh- CotpyP photo-sheet	PC	OER	1 cm ² AM 1.5G, 100 mW cm ⁻²	-	-	1.2 μmol cm ⁻² h ⁻¹	6
3	CdS-Ni(terpyS) ₂ (MeCN/H ₂ O media)	PC	TEOA oxidation	*1.96 cm ² AM 1.5G, 100 mW cm ⁻²	0.16 μmol cm ⁻² h ⁻¹	0.009 μmol cm ⁻² h ⁻¹	-	7
4	TiO ₂ CotpyP (1.67 mg mL ⁻¹) (MeCN/H ₂ O media)	PC	Glucose oxidation	*2.94 cm ² AM 1.5G, 100 mW cm ⁻²	0.1 μmol cm ⁻² h ⁻¹	0.04 μmol cm ⁻² h ⁻¹	-	8
5	ZnSe NiCycP	PC	AA oxidation	*1.96 cm ² AM 1.5G, 100 mW cm ⁻²	0.14 μmol cm ⁻² h ⁻¹	0.3 μmol cm ⁻² h ⁻¹	-	9
6	RGO-CoO _x BiVO ₄ CuGaS ₂	PC	OER	300 W Xe lamp (λ > 420 nm)	6 μmol g ⁻¹ h ⁻¹	-	-	10
7	Cobalt porphyrin cathode PVK-BiVO ₄ tandem (0 applied voltage; dual light absorber)	PEC	OER	~ 0.25 cm ² AM 1.5G, 100 mW cm ⁻²	0.18 μmol cm ⁻² h ⁻¹	0.58 μmol cm ⁻² h ⁻¹	-	11
8	Cu ₉₆ In ₄ cathode PVK-BiVO ₄ tandem (0 applied voltage; dual light absorber)	PEC	OER	~ 0.25 cm ² AM 1.5G, 100 mW cm ⁻²	2.1 μmol cm ⁻² h ⁻¹	0.72 μmol cm ⁻² h ⁻¹	-	12
9	Formate dehydrogenase cathode PVK-BiVO ₄ tandem (0 applied voltage; dual light absorber)	PEC	OER	~ 0.25 cm ² AM 1.5G, 100 mW cm ⁻²	-	-	7.1 μmol cm ⁻² h ⁻¹	13
10	mTiO ₂ STEMPO/DPP-CA mITO FDH (0 applied voltage; dual light absorber)	PEC	HMF oxidation	~0.19 cm ² AM 1.5G, 100 mW cm ⁻²	-	-	0.16 μmol cm ⁻² h ⁻¹	14

11	BiVO ₄ perovskite 3D TiN-CIFDH (0 applied voltage; dual light absorber)	PEC	OER	$\sim 1 \text{ cm}^2$ 100 mW cm ⁻²	-	-	0.78 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	15
12	Au coupled ZnO@ZnTe@CdTe- perovskite tandem (Co-Ci anode) (0 applied voltage; dual light absorber)	PEC	OER	AM 1.5G, 100 mW cm ⁻²	4.9 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	1.4 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	-	16
13	Cr ₂ O ₃ N,Zn-Fe ₂ O ₃ TiO ₂ Ru complex – SrTiO _{3-x} (0 applied voltage; dual light absorber)	PEC	OER	AM 1.5G, 100 mW cm ⁻²	0.31 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	0.12 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	1.55 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	17
14	FeOOH BiVO ₄ CIGS meso-ITO enzyme cascade (0 applied voltage; dual light absorber)	PEC	OER	Xenon Lamp 100 mW cm ⁻²	-	-	0.1 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	18
15	WO ₃ DSSC-Pt Cu _x O (0 applied voltage; dual light absorber)	PEC	OER	0.5 cm ² AM 1.5G, 100 mW cm ⁻²	24 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	4 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	1.1 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	19
16	CoP _c CNT-C CsFAPb(IBr) ₃ a-Si IrO _x (0 applied voltage; dual light absorber)	PEC	OER	$\sim 0.5 \text{ cm}^2$ AM 1.5G, 100 mW cm ⁻²	$J = \sim -3 \text{ mA cm}^{-2}$			20
17	NiO RuRe-CoO _x TaON tandem –0.7 V vs. Ag/AgCl	PEC	OER	-	0.03 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	0.003 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	-	21
18	Cu/CuO/Cu ₂ O –0.4 V vs. SCE	PEC	OER	$\sim 1 \text{ cm}^2$ visible light	-	-	0.6 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	22
19	CuBi ₂ O ₄ –0 V vs. Ag/AgCl	PEC	OER	1000 W m ⁻²	0.004 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	-	-	23
20	Si–meso TiO ₂ -CotpyP –1 V vs. Fc ⁺ /Fc	PEC	OER	100 mW cm ⁻²	0.75 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	-	0.18 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	24
21	TiO ₂ dpp P _{Os} -PSII IO-TiO ₂ FDH Applied voltage: 0.3 V	PEC	OER	AM 1.5G, 100 mW cm ⁻²	-	-	0.19 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	25
22	ZnO@ZnSe photocathode (Pt anode) –0.4 V vs. RHE	PEC	OER	AM 1.5G, 100 mW cm ⁻²	$\sim 1.6 \mu\text{mol cm}^{-2} \text{ h}^{-1}$	$\sim 0.15 \mu\text{mol cm}^{-2} \text{ h}^{-1}$	-	26
23	TiO ₂ photoanode (ZnO@CuO _x cathode) 0.6 V vs. Ag/AgCl	PEC	OER	4 cm ² 300 W Xe lamp	-	-	18.9 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	27
24	Mo-glass CZGS ZnS Pt –0.2 V vs. RHE	PEC	OER	0.35 cm ² AM 1.5G, 100 mW cm ⁻²	0.4 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	9.7 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$	-	28

25	Cu ₂ O SnO _x 50NW Pt –0.35 V vs. RHE	PEC	OER	300 W Xe lamp; 200 mW cm ^{–2}	~60 μmol cm ^{–2} h ^{–1}	~15 μmol cm ^{–2} h ^{–1}	-	29
26	BiVO ₄ -CoF photoanode; cc-CoFPc 0.8 V vs. RHE	PEC	OER	1 cm ² AM 1.5G, 100 mW cm ^{–2}	7.34 μmol cm ^{–2} h ^{–1}	~2 μmol cm ^{–2} h ^{–1}	-	30
27	Si meso TiO ₂ CoPcP –0.53 V vs. SHE	PEC	OER	0.36 cm ² AM 1.5G, 100 mW cm ^{–2}	1.8 μmol cm ^{–2} h ^{–1}	1 μmol cm ^{–2} h ^{–1}	-	31
28	Pd/N-TiO ₂ /Ti ₃ C ₂ –160 BiVO ₄ Applied voltage: –0.6 V	PEC	OER	300 W Xe lamp	-	-	~1.3 μmol cm ^{–2} h ^{–1}	32
29	GaInP GaInAs Ge PV Cathode: GDE Ag Anode: Ti IrO _x	P-EC	OER	0.92 cm ² Concentrated light 450 suns (450 kW m ^{–2})	$J = \sim 150 \text{ mA cm}^{-2}$; η (solar-to-CO) = 17%; η (solar-to-fuel) = 19%		-	33
30	Cu ₂₇ Pd ₇₃ PVK CoP _L (single light absorber; 0 applied voltage)	PEC	PET plastic reforming	~ 0.25 cm ² AM 1.5G, 100 mW cm ^{–2}	26.3 μmol cm ^{–2} h ^{–1}	4.6 μmol cm ^{–2} h ^{–1}	-	This Work
31	Cu ₂₇ Pd ₇₃ PVK Cu ₉₁ In ₉ (single light absorber; 0 applied voltage)	PEC	PET plastic reforming	~ 0.25 cm ² AM 1.5G, 100 mW cm ^{–2}	21.3 μmol cm ^{–2} h ^{–1}	24 μmol cm ^{–2} h ^{–1}	-	This Work
32	Cu ₂₇ Pd ₇₃ PVK FDH (single light absorber; 0 applied voltage)	PEC	PET plastic reforming	~ 0.25 cm ² AM 1.5G, 100 mW cm ^{–2}	-	-	12.1 μmol cm ^{–2} h ^{–1}	This Work

* The irradiation area is calculated as the curved surface area of the light vial (length equivalent to solution height) that is exposed to the incident light.

Supplementary Table 6 | Estimation of solar-to-fuel (STF) efficiencies. The standard thermodynamic potentials were taken from literature³⁴⁻³⁶ for the calculation of the STF efficiencies for each system with the respective catalysts individually using eq. 3 (main text) according to previous reports.^{12, 13, 37-39} Note that STF efficiency is not a decisive metric for comparison in this case as the ΔG° values are very low compared to water oxidation processes (see main text). The chemical bias in the system is not taken into account to avoid inaccurate estimation of the values.³⁷

System	Substrate (at Anode)	Reduction (E° / V)	Oxidation (E° / V)	ΔE° (V)	STF (%)
Cu₂₇Pd₇₃ PVK CoP_L	EG model substrate	CO ₂ /CO : -0.11 2H ⁺ /H ₂ : 0	EG/GA : 0.14	-0.25 -0.14	STF _{CO} : ~0.8 STF _{H₂} : ~0.1
Cu₂₇Pd₇₃ PVK CoP_L	PET solution	CO ₂ /CO : -0.11 2H ⁺ /H ₂ : 0	EG/GA : 0.14	-0.25 -0.14	STF _{CO} : ~0.6 STF _{H₂} : ~0.1
Cu₂₇Pd₇₃ PVK Cu₉₁In₉	EG model substrate	CO ₂ /CO : -0.11 2H ⁺ /H ₂ : 0	EG/GA : 0.14	-0.25 -0.14	STF _{CO} : ~0.4 STF _{H₂} : ~0.4
Cu₂₇Pd₇₃ PVK Cu₉₁In₉	PET solution	CO ₂ /CO : -0.11 2H ⁺ /H ₂ : 0	EG/GA : 0.14	-0.25 -0.14	STF _{CO} : ~0.3 STF _{H₂} : ~0.2
Cu₂₇Pd₇₃ PVK FDH	EG model substrate	CO ₂ /HCOO ⁻ : -0.02	EG/GA : 0.14	-0.16	STF _{HCOO⁻} : ~0.2
Cu₂₇Pd₇₃ PVK FDH	PET solution	CO ₂ /HCOO ⁻ : -0.02	EG/GA : 0.14	-0.16	STF _{HCOO⁻} : ~0.14

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End of Supplementary Information