Electronic Supplementary Information

for

A robust ALD-protected silicon-based hybrid photoelectrode for hydrogen evolution under aqueous conditions

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Table S1: Selected silicon photocathodes interfaced with metals/metal sulphide catalysts under one Sun irradiation (100 mW.cm^{-2}) (adapted with modification from reference [1]).

Photocathode construction	**Electrolyte**	**pH**	**j (mA.cm^{-2}) @ (0 V vs. RHE)**	**Onset potential (V vs. RHE)**	**Reference**
p-Si|Ti|NiFe	1 M KOH	14	~ -7	~ 0.3	[2]
p-Si|Al_2O_3|MoS_2	1 M $HClO_4$	0	~ -35.6	~ 0.4	[3]
n^+p-Si|Ti|FTO|TiO_2|Ir	0.1 M KOH	14	~ -35	~ 0.5	[4]
n^+p-Si|Mo|MoS_2	0.5 M H_2SO_4	0	~ -16	~ 0.35	[5]
p-Si|$SrTiO_3$|Ti|Pt	0.5 M H_2SO_4	0	~ -15	~ 0.4	[6]
p-Si|a-$CoMoS_x$	Phosphate buffer	4.25	~ -17.5	~ 0.25	[7]
p-Si|Ti|Ni	Borate buffer	9.2	~ -5	~ 0.2	[8]
Nanostructured p-Si interfaced with metals/metal sulphide catalysts were detailed in our previous report					[9]

Table S2: Semiconductor photocathodes without dyes interfaced with molecular catalysts/enzymes (adapted with modification from reference [10])

Photocathode construction	**Electrolyte**	**pH**	**j ($mA.cm^{-2}$) @ 0 V vs. RHE**	**Onset potential V vs. RHE**	**Illumination Intensity/source**	**References**
p-GaP|Cobaloxime	1 M phosphate buffer	7.0	~ -2.70	~ 0.76	100 $mW.cm^{-2}$	[11]
	0.1 M acetate buffer	4.5	~ -1.10	~ 0.5	100 $mW.cm^{-2}$	[12]
	0.1 M phosphate buffer	7.0	~ -0.92	~ 0.72	100 $mW.cm^{-2}$	[13]
	0.1 M phosphate buffer	7.0	~ -1.3	~ 0.61	100 $mW.cm^{-2}$	[14]
	0.1 M phosphate buffer	7.0	~ -0.89	~ 0.65	100 $mW.cm^{-2}$	[15]
p-GaP|Cobalt-porpyrin	0.1 M phosphate buffer	7.0	~ -1.3	~ 0.55	100 $mW.cm^{-2}$	[16]
p-$InGaP_2$|TiO_2|Cobaloxime| TiO_2	0.1 M NaCl	13	~ -9	0.7	100 $mW.cm^{-2}$	[17]
NiO | CdSe|Cobaloxime	0.1 M Na_2SO_4	6.8	~0.1	n/a	300 W lamp	[18]
Au|InP| $Fe_2S_2(CO)_6$	0.1 M $NaBF_4$	7.0	0.045×10^6	n/a	n/a	[19]
P3HT:PCBM|Cobaloxime	0.1 M acetate	4.5	~ -0.002	n/a	100 $mW.cm^{-2}$	[20]
p-Si|mesoTiO_2|NiP	0.1 M acetate buffer	4.5	~ -0.340	~0.4	100 $mW.cm^{-2}$	[10]
p-Si|TiO_2|hydrogenase	0.05 M MES buffer	6	~ - 0.001	~ 0.25	10 $mW.cm^{-2}$	[21]
p-Si|ALD-TiO_2|SC-TiO_2|**$Co_{C_{11}P}$**|ALD-TiO_2	1 M phosphate buffer	7	~ -1.3	~ 0.47	100 $mW.cm^{-2}$	Our work

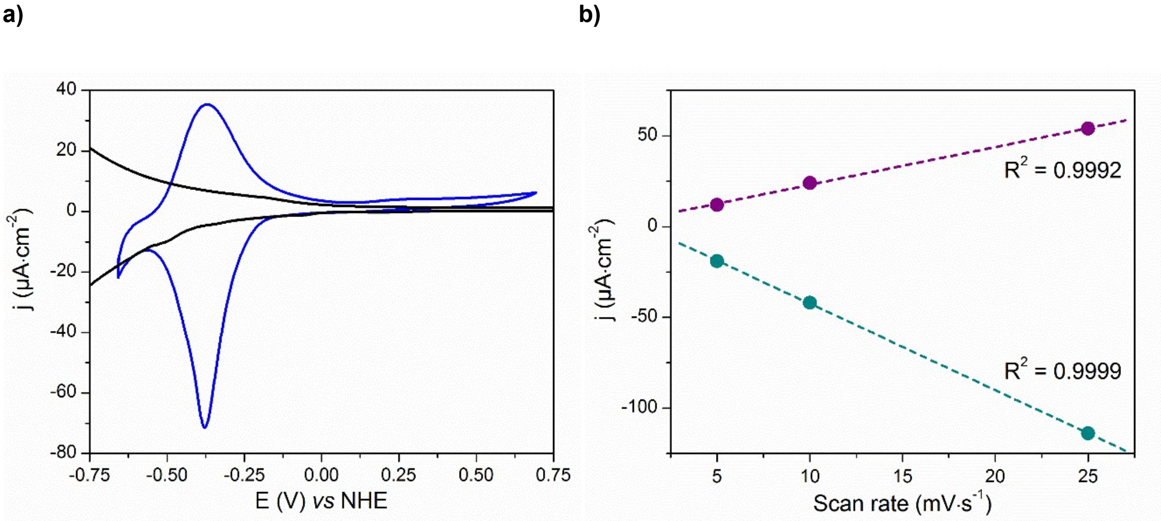

Figure S1. a) CVs at TiO_2/$\mathbf{Co_{C_{11}P}}$ (blue line) and blank TiO_2 (black line) screen printed electrodes on FTO substrate, respectively recorded at 10 mV·s^{-1} in a NaCl 0.1 M aqueous electrolyte and b) anodic (purple) and cathodic (cyan) peak currents (dots) and associated linear fits (dotted lines) versus scan rate for CVs at TiO_2/$\mathbf{Co_{C_{11}P}}$ recorded in a NaCl 0.1 M aqueous electrolyte (pH ≈ 7).

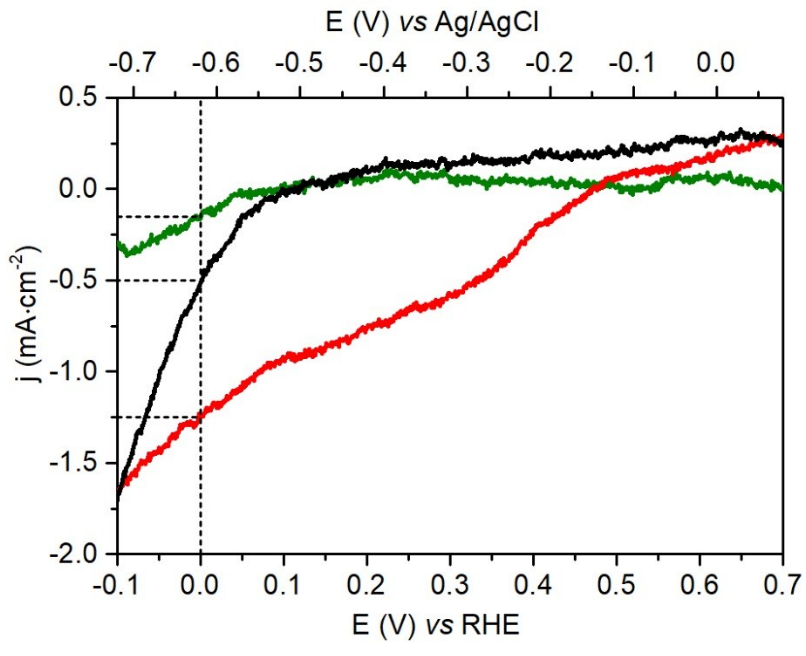

Figure S2. LSV (10 mV.s^{-1}) of p-Si|ALD-TiO_2|SC-TiO_2|$\mathbf{C_{10P}}$|ALD-TiO_2 electrode (green trace), p-Si|ALD-TiO_2|SC-TiO_2|$\mathbf{Co_{C_{11}P}}$ electrode (black trace) and p-Si|ALD-TiO_2|SC-TiO_2|$\mathbf{Co_{C_{11}P}}$|ALD-TiO_2 electrode (red trace) in 1M phosphate buffer (pH 7) under one Sun irradiation.

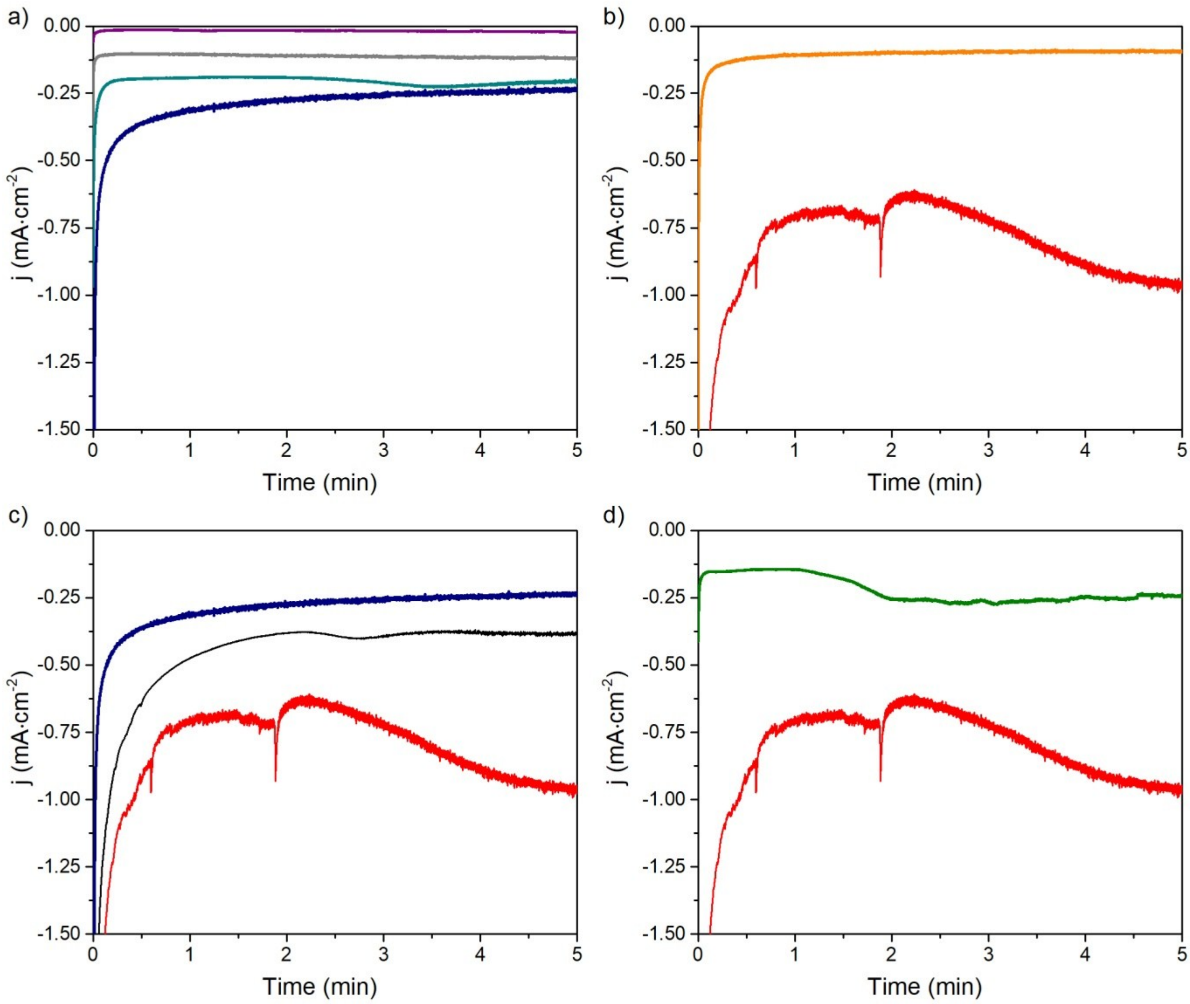

Figure S3: Chronoamperometric profiles recorded at 0 V vs RHE in 1 M phosphate buffer (pH 7) under one sun AM1.5 irradiation, showing effects of: a) TiO_2 layers on p-Si; b) catalyst loading; c) anchorage shielding; d) Co catalytic core. Curves: p-Si (purple), p-Si|ALD-TiO_2 (gray), p-Si|ALD-TiO_2|SC-TiO_2 (cyan), p-Si|ALD-TiO_2|SC-TiO_2|ALD-TiO_2 (blue), p-Si|ALD-TiO_2|$\mathbf{Co_{C_{11}P}}$|ALD-TiO_2 (orange), p-Si|ALD-TiO_2|SC-TiO_2|$\mathbf{Co_{C_{11}P}}$|ALD-TiO_2 (red), p-Si|ALD-TiO_2|SC-TiO_2|$\mathbf{Co_{C_{11}P}}$ (black), p-Si|ALD-TiO_2|SC-TiO_2|$\mathbf{C_{10}P}$|ALD-TiO_2 (green).

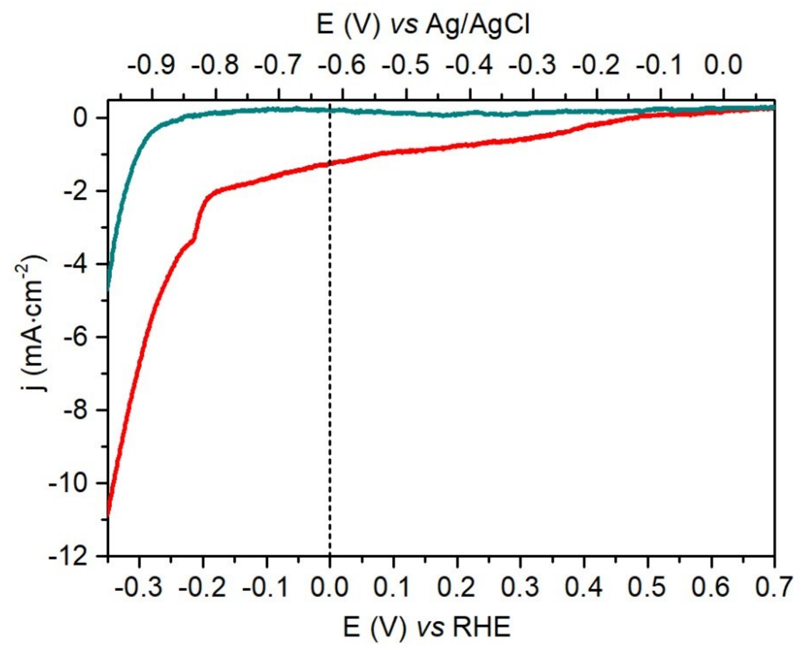

*Figure S4: LSV (10 mV.s^{-1}) of p-Si|ALD-TiO$_2$|SC-TiO$_2$ (cyan trace) and p-Si|ALD-TiO$_2$|SC-TiO$_2$|**Co$_{C_{11}P}$**|ALD-TiO$_2$ electrode (red trace) in 1M phosphate buffer (pH 7) under one Sun irradiation.*

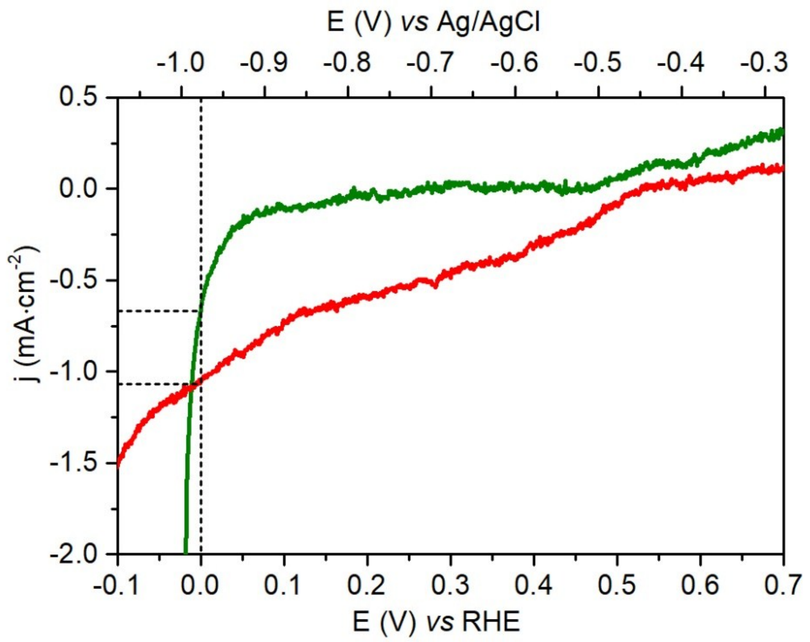

*Figure S5: LSV (10 mV.s^{-1}) of p-Si|ALD-TiO$_2$|SC-TiO$_2$|**C$_{10P}$**|ALD-TiO$_2$ electrode (green trace) and p-Si|ALD-TiO$_2$|SC-TiO$_2$|**Co$_{C_{11}P}$**|ALD-TiO$_2$ electrode (red trace) in 0.1 M NaOH (pH 13) under one Sun irradiation.*

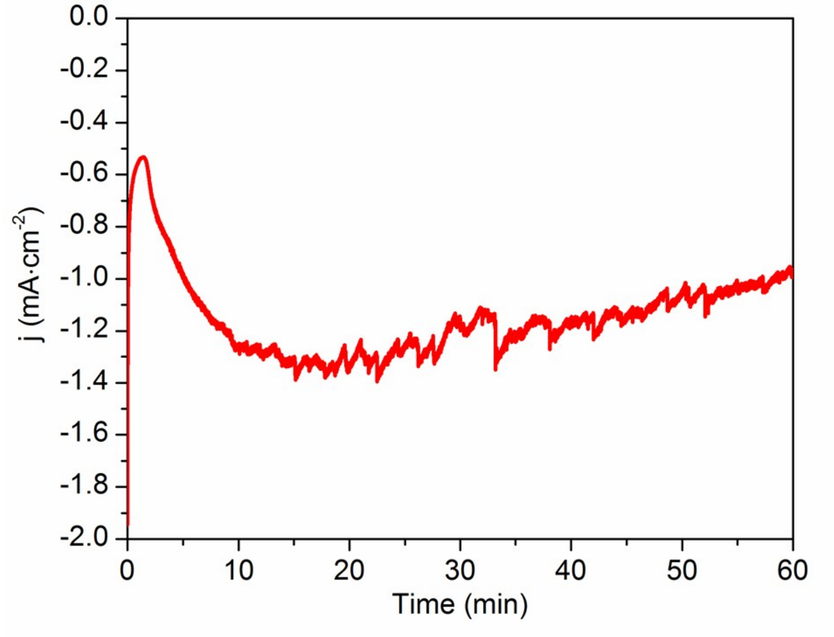

*Figure S6: Chronoamperometic profile of p-Si|ALD-TiO$_2$|SC-TiO$_2$|**Co$_{C11P}$**|ALD-TiO$_2$ electrode recorded at 0 V vs RHE in 0.1 M NaOH (pH 13) for 60 min run under one Sun irradiation***.**

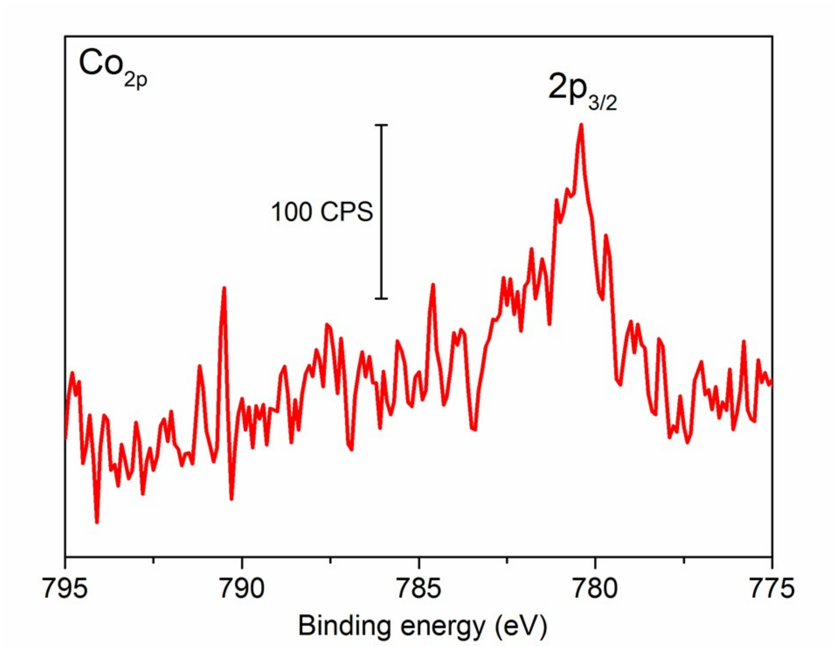

*Figure S7: Co 2p core region XPS spectrum of p-Si|ALD-TiO$_2$|SC-TiO$_2$|**Co$_{C11P}$**|ALD-TiO$_2$ electrode analyzed after one hour of photoelectrolysis (0 V vs RHE) in 0.1 M NaOH.*

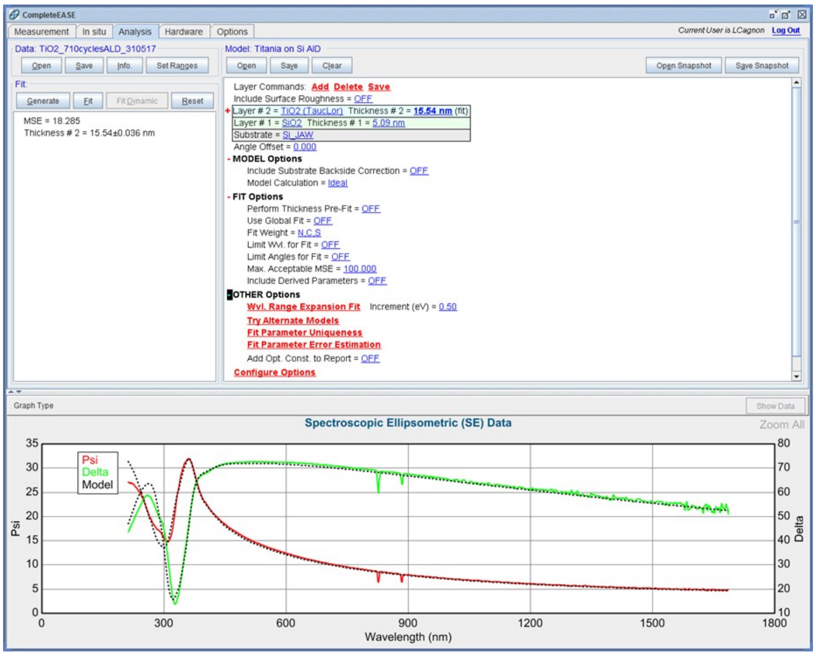

Figure S8: Ellipsometry spectra and corresponding fits for the p-Si|ALD-TiO_2 sample.

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