Supplementary Information

Efficiency and Stability of Narrow-Gap Semiconductor-Based Photoelectrodes

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Table S1. Reported photoelectrochemical (PEC) performances of the photocathodes by surface modification, and their detailed working conditions. The photocurrent at 0 V *vs* RHE is simplified as $J_{ph,ca}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Treatment method	pH	$J_{ph,ca}$	Stability	J_{in}	J_{de}/J_{in}	Remark	Ref.
2018	p-InP	Repeated surface oxidation/reduction	0	-24				500 W Hg/Xe lamp	82
2018	Cu(In, Ga)(S, Se)$_2$	Different S, Ga composition	0.6	-6	1	-18	80	100 mW cm^{-2}, -0.2 V *vs* RHE	101
2017	SnS	Fast annealing	1	-0.7	3	-7	41	100 mW cm^{-2}, -0.3 V *vs* RHE	107
2018	p-Si	Nanowire	0	0	1	-52	2	100 mW cm^{-2}, -0.75 V *vs* RHE	108
2017	Cu_2O	High-index facet	7	-0.75	0.25	-0.75	40	100 mW cm^{-2}, -0 V *vs* RHE	109
2018	CuIn(S$_{1-x}$Se$_x$)$_2$	Different S, Se composition	14	-1.2	12	-0.5	10	100 mW cm^{-2}, NA	110
2017	p-Si	Micro-pillar array	0	-15	0.058	-18.5	0	100 mW cm^{-2}, -0.07 V *vs* RHE	111
2018	WSe_2	Intraflake and edge defects	0	-1.63	0.129	-1.63	0	100 mW cm^{-2}, 0 V *vs* RHE	112
2018	Cu_2O	Eu doping	4.9	-3.2				35 mW cm^{-2}	113
2018	Sb_2Se_3	Compositing Graphene	3	-0.65	0.167	-0.65	94	100 mW cm^{-2}, 0 V *vs* RHE	114
2018	Cu_2O	Nanowires	7	-5.45				100 mW cm^{-2}	115
2018	CuGaSe	Different Cu, Ga composition	0	-2	408	-12	0	100 mW cm^{-2}, -1 V *vs* RHE	116
2018	p-CuInS	Different Cu composition	3	-0.05	0.05	-0.015	0	100 mW cm^{-2}, no applied bias	117
2018	CuGa(S,Se)$_2$	Different Cu composition	13	-0.8				100 mW cm^{-2}	118
2019	ReS_2	Different phase interface	7	0	12	-10	0	100 mW cm^{-2}, -0.25 V *vs* RHE	119
2019	WSe_2	Surface oxidation	4.3	-10.6				100 mW cm^{-2}	120

Table S2. Reported photoelectrochemical (PEC) performances of the photoanodes by surface modification, and their detailed working conditions. The photocurrent at 1.23 V *vs* RHE is simplified as $J_{ph,an}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Treatment method	pH	$J_{ph,an}$	Stability	J_{in}	J_{de}/J_{in}	Remark	Ref.
2018	n-Si	Porous, nanowire	8	1.1	0.33	1.1	32	100 mW cm^{-2}, 1.23 V *vs* RHE	102
2018	CdS	Gradient oxygen doping	11	6	42	6	0	100 mW cm^{-2}, 0.4 V *vs* RHE	105
2018	n-CuInS	Different Cu composition	3	0.61	0.05	0.015	0	100 mW cm^{-2}, no applied bias	117
2016	$Zn_{1.7}Si_{0.3}GeO_4$	Substitution of Si atom	7	0.006	0.153	0.006	0	300 W Xe lamp 1.6 V *vs* SCE	122
2018	Ag_2ZnSnS_4	Different Ag, Zn composition	7	0.31	0.278	0.44	0	100 mW cm^{-2}, 1 V *vs* RHE	123
2017	CdS	Surface oxidation	7	0.2	1.333	0.15	33	5 mW cm^{-2}, 470 nm light, 0.99 V *vs* RHE	124
2019	InGaN	H_3PO_4 treatment	0	18				100 mW cm^{-2}	125

Table S3. Reported photoelectrochemical (PEC) performances of the photocathodes with conductor/semiconductor structure, and their detailed working conditions. The photocurrent at 0 V *vs* RHE is simplified as $J_{ph,ca}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Surface materials	pH	$J_{ph,ca}$	Stability	J_{in}	J_{de}/J_{in}	Remark	Ref.
2016	Si nanowire	Au_3Cu nanoparticle	6.8	-0.95	18	-4.8	33	20 mW cm^{-2}, 740 nm light, -0.26 V *vs* RHE	23
2017	p-Si	Pt CoP	7	-7 -5.5				100 mW cm^{-2}	98
2017	p-Si	Stoichiometric MoS_2	0.3	-22.2	24	-31	6	100 mW cm^{-2}, -0.29 V *vs* RHE	126
2018	p-Si nanowire	Co_2P	0.3	-21.9	20	-18.4	3	100 mW cm^{-2}, 0 V *vs* RHE	127
2014	p-Si	1T-MoS_2	0.3	-17.6	3	-17.6	23	100 mW cm^{-2}, 0 V *vs* RHE	128
2018	Si	Carbon nanosheet	0	-13	1	-13	79	100 mW cm^{-2}, 0 V *vs* RHE	129
2012	p-Si nanowire	Pt nanoparticle	1	-28.2			0	100 mW cm^{-2}	130
2018	Cu_2O	Reduced graphene oxide	6.5	-2.4	0.278	-2.4	23	85 mW cm^{-2}, 0 V *vs* RHE	131
2015	p-Si	Marcasite-type $CoSe_2$	0	-9	0.833	-9	0	100 mW cm^{-2}, 0 V *vs* RHE	132
2017	p-Si wire	NiMoZn particle	0	-1.45	3.5	-1.45	4	100 mW cm^{-2}, 0 V *vs* RHE	133
2018	p-Si micropyramid	$WS_{2-x}P_x$ nanosheet	0	-19.11	8	-19.11	14	110 mW cm^{-2}, 0 V *vs* RHE	134
2013	p-WSe_2	Pt-Ru	4.2 2 10	> -24	 2 2	 -15.5 -14	 3 11	100 mW cm^{-2}, -0.65 V *vs* SCE -0.6 V *vs* SCE	135
2018	3D structured p-Si	Co-P nanoparticle	0	-24.8	30	-24.8	20	100 mW cm^{-2}, 0 V *vs* RHE	136
1982	p-Si	Pt(0)	4	-3.25	0.5	-3.25	25	100 mW cm^{-2}, 0 V *vs* RHE	137
2017	p-Si	Nanoporous Au thin film	8.5	-1.25	4.5	1.8	20	100 mW cm^{-2}, -0.59 V *vs* RHE	138
2015	Si nanowire	N-doped graphene quantum	0	-34				100 mW cm^{-2}	139
2018	p-Si	$Ni(TEOA)_2Cl_2$	0.3	-5.57	24	-26	4	100 mW cm^{-2}, not shown	140
2018	Si nanowire	Ultrathin MoS_2 layer	0.5	-16.5	48	-15	7	100 mW cm^{-2}, 0 V *vs* RHE	141
2017	Sb_2Se_3	MoS_x-S MoS_x	0 0	-16 -5	20 20	-16 -5	100 28	100 mW cm^{-2}, 0 V *vs* RHE	142

2018	Black n^+p-Si	Pd nanoparticle	0	-13.8				100 mW cm^{-2}	143
2018	Cu_2O	Oligoaniline layer	5.5	-0.8	2	-0.7	72	100 mW cm^{-2}, 0.1 V *vs* RHE	144
2018	$CuGaS_2$	Au nanoparticle	7	-1.5	0.0625	-2	37	300 W Xe lamp, 0 V *vs* RHE	145
2018	Cu_2O	Thin MoS_2 layer	6.7	-3.5	0.167	-3	7	100 mW cm^{-2}, 0 V *vs* RHE	146
2017	Macroporous p-Si	H-$Co_{0.85}Se$|P	7	-1	2	-8	6	100 mW cm^{-2}, -0.6 V *vs* RHE	147
2018	Cu_2O nanowire	Ag	7.4	-0.24	0.056	-0.24	0	Xe lamp 0 V *vs* RHE	148
2016	p-Si p-InP p-GaP	2H-MoS_2 layer	1.1	-24.6 -6.8 -2.25	0.583	-40	0	100 mW cm^{-2}, from 0.4 to -1 V *vs* RHE	149
2015	n^+-p-p^+-Si	CoPS	0	-35				100 mW cm^{-2}	150
2019	p-Si	Metallic Bi	7.4	0	7	-4	12.5	50 mW cm^{-2}, -0.32 V *vs* RHE	151
2019	p-Si	ReS_2 nanosheets	0	-18.5				100 mW cm^{-2}	152
2019	Black Si	Pt	0.7	-19.5	90	-23	28	100 mW cm^{-2}, no applied bias	153

Table S4. Reported photoelectrochemical (PEC) performances of the photoanodes with conductor/semiconductor structure, and their detailed working conditions. The photocurrent at 1.23 V *vs* RHE is simplified as $J_{ph,an}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Surface materials	pH	$J_{ph,an}$	Stability	J_{in}	J_{de}/J_{in}	Remark	Ref.
2018	p^+n-Si	$MoSe_2$	0	30	14	2	15	100 mW cm^{-2}, 0.38 V *vs* RHE	154
2018	CdS nanowire	1T-MoS_2	7	16.8				300 W Xe lamp	155
2018	Nanostructured CdS	PANI-PPY	6	0.77	8	0.77	9	80 mW cm^{-2}, 1.23 V *vs* RHE	156
2017	n-Si	Thin Ni layer	9.5	31				100 mW cm^{-2}	157
2013	n-Si	Single layer graphene	7.6	5.5	>0.278	11	0	100 mW cm^{-2}, 0 V *vs* solution	158
2013	n-Si nanowire	PEDOT layer	13.6	3				100 mW cm^{-2}	159
2016	n-Si	PEDOT:PSS	0	28.8	17	10	8	100 mW cm^{-2}, 0.3 V *vs* RHE	160
2016	Porous CdS	Nafion molecule	12	7.2	1.39	5.68	8	100 mW cm^{-2}, 0 V *vs* RHE	161
2018	3D CdS	Au	7	1.04	2.78	1.04	23	100 mW cm^{-2}, not shown	162
2019	SnS_2	Pt	7	0.112	0.55	0.112	40	100 mW cm^{-2}, 1.23 V *vs* RHE	163

Table S5. Reported photoelectrochemical (PEC) performances of the photocathodes with semiconductor (insulator)/semiconductor structure, and their detailed working conditions. The photocurrent at 0 V *vs* RHE is simplified as $J_{ph,ca}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Surface materials	pH	$J_{ph,ca}$	Stability	J_{in}	J_{de}/J_{in}	Remark	Ref.
2011	p-Si pillar	Mo_3S_4	0	-9.5	24	-2.15	5	100 mW cm^{-2}, 0 V *vs* RHE 620 nm light, 28.3 mW cm^{-2}	39
2017	Cu_2O nanowire	C	7	-1.5	0.167	-1.5	0	100 mW cm^{-2}, no applied bias	164
2016	a-Si:H/a-SiGe:H	Hydrogen doped TiO_2 layer	13.6	-5.51	5	-6	8	100 mW cm^{-2}, 0 V *vs* RHE	165
2017	p-Si micropillar	α-Fe_2O_3 layer	7	-0.36	0.011	-0.2	5	100 mW cm^{-2}, -0.52 V *vs* SCE	166
2018	Cu_2O nanowire	TiO_2-Cu^+	6.8	-2.3	0.5	-0.47	72	100 mW cm^{-2}, 0.3 V *vs* RHE	167
2016	Cu_2O	NiFe-LDH	7	-2.42	40	-0.45	5	100 mW cm^{-2}, -0.2 V *vs* Ag/AgCl	168
2017	Zn:Cu_2O	Cu_2O	4.25	-2				100 mW cm^{-2}	169
2017	Cu_2O nanowire	ZnO nanoparticle	7	-3.4				100 mW cm^{-2}	170
2017	Cu_2O	NiFeSP	13.7	-12.1				100 mW cm^{-2}	171
2018	p-Si	ReS_2	0	-9	3	-9	0	100 mW cm^{-2}, 0 V *vs* RHE	172
2014	p-Si nanowire	$Ni_{12}P_5$ nanoparticle	0	-21	1	-13	3	100 mW cm^{-2}, 0.2 V *vs* RHE	173
2013	p-GaP	Cobaloxime	7	-2.7	0.083	-1.3	17	100 mW cm^{-2}, 0.17 V *vs* RHE	174
2017	p-Si	GaN nanowire	14	-0	5	-40	30	100 mW cm^{-2}, not shown	175
2017	n^+p-GaAs	$SrTiO_3$ layer	7	-6	24	-6	10	100 mW cm^{-2}, 0 V *vs* RHE	176
2017	Cu_2O	RuO_x	5	-0.8				100 mW cm^{-2}	177
2018	Cu_2O	CuO	6	-0.3	21	-0.3	77	300 W Xe lamp, > 420 nm light 0 V *vs* RHE	178
2018	Cu_2O nanowire	Cu_2S layer	4.9	-5.05	5	-5.05	50	100 mW cm^{-2}, 0 V *vs* RHE	179
2017	Nanoporous Si	HfO_2	0	0	12	-12.5	11	100 mW cm^{-2}, -0.8 V *vs* Ag/AgCl	180
2016	p-Si	Al_2O_3	0	0	20	-25	0	100 mW cm^{-2}, -0.55 V *vs* RHE	181
2019	Cu_2O	$Cd(OH)_2$	4.9	-6.9	0.44	-6.9	45	100 mW cm^{-2}, 0.4 V *vs* RHE	182

Table S6. Reported photoelectrochemical (PEC) performances of the photoanodes with semiconductor (insulator)/semiconductor structure, and their detailed working conditions. The photocurrent at 1.23 V *vs* RHE is simplified as $J_{ph,an}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Surface materials	pH	$J_{ph,an}$	Stability	J_{in}	J_{de}/J_{in}	Remark	Ref.
2012	n-Si	NiO_x	7.2	0.1	4	6.5	85	100 mW cm^{-2}, not shown	73
2016	n-Si	CoO_x thin layer	13.6	20.88	2500	30.2	14	100 mW cm^{-2}, 1.63 V *vs* RHE	186
2018	In_2S_3 nanosheet	ZnO	5.97	0.351	0.111	0.287	70	100 mW cm^{-2}, 1.2 V *vs* RHE	187
2018	n-Si	TiO_x	6	1.6	0.111	0.8	21	100 mW cm^{-2}, 0 V *vs* SCE	188
2018	ZnS yolk	CdS multi-shell	12.9	4.8				100 mW cm^{-2}	189
2018	CdS nanorod	Cu_2O nanoparticle	12	4.7	2	4	7	100 mW cm^{-2}, not shown	190
2018	CdSe core	$Pb_xCd_{1-x}S$ gradient layer	13	10.2	2	8	5	100 mW cm^{-2}, 0.2 V *vs* RHE	191
2012	n-Si wire	Fe_2O_3	13.8	17.27				100 mW cm^{-2}	192
2018	In_2S_3 nanosheet	ZnO shell	7	0.6	0.111	0.48	0	100 mW cm^{-2}, 1.23 V *vs* RHE	193
2018	CdS microbox	MoS_2	7		0.083	0.25	10	Not shown	194
2018	g-C_3N_4 nanosheet	$Zn_{0.1}Cd_{0.9}S$	7.4	0.04	0.111	12.2	0	150 mW cm^{-2}, not shown	195
2013	Nanotextured n-Si	$NiRuO_x$	7.2	1.34	1.5	7	15	100 mW cm^{-2}, 2.25 V *vs* RHE	196
2018	CdS nanorod	SnS_x nanosheet	7	1.59	0.5	1.59	50	100 mW cm^{-2}, 1.23 V *vs* RHE	197
2013	n-Si	MnO	13.6	5	0.5	22	16	100 mW cm^{-2}, 0 V *vs* solution	198
2016	Porous Si	TiO_2 layer	13.6	0.03	1	0.35	0	Solar simulator, 1 V *vs* SCE	199
2018	Si nanowire	Cu_2O nanocube	13.6	2				100 mW cm^{-2}	200
2018	InGaN nanowire	IrO_x nanoparticle	0	11	0.5	8	100	100 mW cm^{-2}, 0.8 V *vs* RHE	201
2018	Ag_8SnS_6	ZnSe	7	4.4	0.833	5.5	0	100 mW cm^{-2}, 0 V *vs* RHE	202
2015	p^+n-Si	NiO_x	13.6	30	1200	32	6	100 mW cm^{-2}, 1.73 V *vs* RHE	203
2018	$Cu_2ZnSn(S_{1-x},Se_x)_4$	ZnO nanoarray	10.9	2.5				100 mW cm^{-2}	204
2018	n-Si	GeAs nanosheet	13	3.3	1	3	73	100 mW cm^{-2}, 0.9 V *vs* RHE	205
2018	WS_2 nanosheet	CdS quantum dot	7.4	0.024	0.078	0.012	4	Not shown	206

2019	Ag_2ZnSnS_4	TiO_2 layer	12.8	2.75	1	2.5	40	100 mW cm^{-2}, 0.4 V *vs* RHE	207
2019	Ta_3N_5	$NiFeO_x$	13	6.3	0.25	6.3	21	100 mW cm^{-2}, no applied bias	208

Table S7. Reported photoelectrochemical (PEC) performances of the photocathodes with conductor/semiconductor (insulator or conductor)/semiconductor structure, and their detailed working conditions. The photocurrent at 0 V *vs* RHE is simplified as $J_{ph,ca}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Middle layer	Surface materials	pH	$J_{ph,ca}$	Stability	J_{in}	J_{de}/ J_{in}	Remark	Ref.
2018	Black p-Si	Black TiO_2	Pd nanoparticle	14	-8.3	100	-10	0	100 mW cm^{-2}, -0.012 V *vs* RHE	17
2018	n$^+$p-Si microwire	SiO_2	Ni-Mo nanoparticle	1	-34	72	-34	0	100 mW cm^{-2}, 0 V *vs* RHE	41
2013	a-Si	TiO_2	Ni-Mo alloy	4	-11.6	12	-10.8	5	100 mW cm^{-2}, 0 V *vs* RHE	72
2015	n$^+$p-Si	TiO_2	Pt	0	-19.34	48	-0.39	0	100 mW cm^{-2}, no applied bias	81
2018	1D Sb_2Se_3	TiO_2	Pt	0.5	-12.5	4.5	-7.8	87	100 mW cm^{-2}, 0 V *vs* RHE	210
2013	p-Si nanowire	TiO_2	Pt	0	-21	1	-26	2	100 mW cm^{-2}, -1.67 V *vs* RHE	211
2018	Sb_2Se_3	TiO_2	a-MoS_x	0	-4.8	1	-11	0	100 mW cm^{-2}, -0.2 V *vs* RHE	212
2018	p-Si	TiO_2	3D MoS_2 layer	0	-27.5	108	-27.5	3	100 mW cm^{-2}, 0 V *vs* RHE	213
2016	Cu(In,Ga)(Se,S)$_2$, (CIGS)	ZnS	Pt nanoparticle	0.91	-16	10	-24	67	100 mW cm^{-2}, -0.5 V *vs* RHE	214
2018	Cu_2O	TiO_{2-x}	Nafion	6.4	-1.2	2	-1.2	30	100 mW cm^{-2}, 0 V *vs* RHE	215
2018	p-Si	TiO_2	Pt nanoparticle	0	0	5	-25	0	100 mW cm^{-2}, -0.9 V *vs* SCE	216
2016	InP nanowire	TiO_2	Pt nanoparticle	0	-15.2	10	-10	20	100 mW cm^{-2}, not shown	217
2018	p-Si	WS_2	Au	0		0.833	-0.4	0	300 W Xe lamp, -1 V *vs* Ag/AgCl	218
2012	n$^+$p-Si	TiO_x	MoS_x	0	-16.2	1	-16.2	4	38.6 mW cm^{-2}, $>$ 635 nm light 0 V *vs* RHE	219
2015	a-Si	SiO_x	Ni-Mo	4.5	-6	25	-6	0	100 mW cm^{-2}, 0 V *vs* RHE	220
2014	p-Si	Al_2O_3	Pt	6	0	12	-28	0	100 mW cm^{-2}, -0.9 V *vs* RHE	221
2013	n$^+$p-Si	Mo	MoS_2	0	-12	120	-8	0	1 sun red light, not shown	222
2015	p-Si	Ti	Ni	14	-20	12	-10	75	225 mW cm^{-2}, -0.8 V *vs* Ag/AgCl	223
2018	Cu_2O	CuO	Ni_xP_y	7	-3.19	0.111	-1.45	7	100 mW cm^{-2}, 0.05 V *vs* RHE	224

2016	p-Si	TiO_2	Pt	14	-17.5	24	-17.5	4	38.6 mW cm^{-2}, red light, 0 V *vs* RHE	225
2012	Nanotextured p-InP	TiO_2	Ru	0.51	-37	4	-36	3	100 mW cm^{-2}, 0.23 V *vs* NHE	226
2013	Si nanowire	SiO_2	Pt nanoparticle	1	-9.1	5	-9.1	0	100 mW cm^{-2}, 0 V *vs* RHE	227
2016	$CuSbS_2$	CdS	Pt	6.5	-4.2	1	-4.2	17	100 mW cm^{-2}, 0 V *vs* RHE	228
2015	p-Cu_2O nanowire	Graphene	Au-Cu nanoalloy	5	-4.5	30	-4.5	8	100 mW cm^{-2}, 0 V *vs* RHE	229
2018	n^+p-Si	TiO_2	Pt	7	-7.5				100 mW cm^{-2}	230
2019	n^+p-Si	TiN	Cubic-NiP_2	0	-18	125	-18	8	100 mW cm^{-2}, 0 V *vs* RHE	231
2019	$(CuInS_2)_{0.81}(ZnS)_{0.19}$	CdS	Pt	7	-16.7	1	-16.7	28	100 mW cm^{-2}, 0 V *vs* RHE	232
2019	p-Si nanowire	α-Fe_2O_3 layer	C layer	7	0	2	-27	11	100 mW cm^{-2}, -1.9 V *vs* RHE	233
2019	Pyramid n^+p-Si	Amorphous Ti layer	Ni layer	14	-38.7	8	-10	7	100 mW cm^{-2}, 0.375 V *vs* RHE	234
2019	$CuInS_2$ nanosheet	SnS_2	C_{60}	7	0	3	-4.51	0	100 mW cm^{-2}, -0.45 V *vs* RHE	235
2019	Amorphous Si	TiO_2	Au	6.8	-3.6	10.5	-4.85	0	100 mW cm^{-2}, -0.1 V *vs* RHE	236
2019	p-Si	SiO_x	Ag-Pt	0	-28	24	-32.5	18	100 mW cm^{-2}, -0.2 V *vs* RHE	237
2019	n^+np^+-Si	Ni	Ni-Mo	13.6	-36.3	105	-7.97	0	100 mW cm^{-2}, no applied bias	238

Table S8. Reported photoelectrochemical (PEC) performances of the photoanodes with conductor/semiconductor (insulator or conductor)/semiconductor structure, and their detailed working conditions. The photocurrent at 1.23 V *vs* RHE is simplified as $J_{ph,an}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Middle layer	Surface materials	pH	$J_{ph,an}$	Stability	J_{in}	J_{de}/ J_{in}	Remark	Ref.
2017	n-Si	ZrO_2	Pt	14	25	13.3	25	10	100 mW cm^{-2}, from 0.4 to -0.2 V *vs* Ag/AgCl	240
2017	p$^+$n-Si	SiO_2	Ni-Fe inverse opal	14	31.2	10.4	32.5	9	100 mW cm^{-2}, 1.5 V *vs* RHE	241
2015	n-Si	P(VDF-TrFE)	Ni	14	12.4				100 mW cm^{-2},	242
2017	n-Si	SiO_x	Ni nanoparticle	14	3.5	40	30	2	100 mW cm^{-2}, 1 V *vs* SCE	243
2018	n-Si	Porous SiO_2	Ni	14	8	24	9	33	100 mW cm^{-2}, not shown	244
2018	n-Si	TiO_2	NiAu	14	18.8	20	10.8	7	100 mW cm^{-2}, not shown	245
2018	n-Si	ZrO_2	NiFe nanoparticle	14	34.4	13.33	34.4	5	100 mW cm^{-2}, from 0.4 to -0.2 V *vs* Ag/AgCl	246
2017	n-Si	TiO_2	$Ni_xFe_{(1-x)}$ nanoflake	14	21.5	20	10	28	100 mW cm^{-2}, 1.16 V *vs* RHE	247
2017	Si	TiO_2	Ni	14	11	24	11	27	100 mW cm^{-2}, 1.23 V *vs* RHE	248
2016	p$^+$n-Si	Fluorinated graphene	Pt	0	25.2	28	31.25	5	100 mW cm^{-2}, 0 V *vs* solution	249
2017	p$^+$n-Si	SiO_x	NiFe	13.7 9.5	30.7 12.1	14 100	28.5 30	25 0	100 mW cm^{-2}, 1.85 V *vs* RHE, 1.8 V *vs* RHE	250
2015	n-Si n-InP	$NiCo_2O_4$	NiFe nanoparticle	14	26 0	72 4	31 17	6 20	100 mW cm^{-2}, 1.4 V *vs* RHE, 1.624 V *vs* RHE	251
2015	n-Si	TiO_2	Ni	14	2	60	35	14	100 mW cm^{-2}, 1.85 V *vs* RHE	252
2018	n-Si microwire	SiO_x	Ni nanoparticle	14	4.5	6	10	10	100 mW cm^{-2}, not shown	253
2019	p$^+$pn$^+$-Si	Ni	Ni-Mo	13.6	34.5	105	7.97	0	100 mW cm^{-2}, no applied bias	238

Table S9. Reported photoelectrochemical (PEC) performances of the photocathodes with semiconductor/semiconductor (insulator or conductor)/semiconductor structure, and their detailed working conditions. The photocurrent at 0 V *vs* RHE is simplified as $J_{ph,ca}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Middle layer	Surface materials	pH	$J_{ph,ca}$	Stability	J_{in}	J_{de}/J_{in}	Remark	Ref.
2017	p-Si	TiO_2	NiFe LDH	14	-7	24	-10	9	100 mW cm^{-2}, not shown	239
2018	n^+n^+p-Si	Pt nanoparticle	TiO_2	0	-35.1	168	-20	12	100 mW cm^{-2}, 0.4 V *vs* RHE	254
2018	p-Si	SiO_2	NiO_x	14	-30.6	8	-10	50	100 mW cm^{-2}, not shown	255
2018	a-SiC:H	n-SiO_x:H	TiO_2	4	-5.5	1	-5.5	18	Not shown, 0 V *vs* RHE	256
2015	p-Si nanowire	Pt nanoparticle	TiO_2	0	-7.5	2	-27	0	100 mW cm^{-2}, -0.5 V *vs* RHE	257
2015	a-Si	TiO_2	Mo_2C	14	-11.2	1	-10.5	14	100 mW cm^{-2}, 0 V *vs* RHE	258
2018	p-Si	Inverse opal TiO_2	Hydrogenases	6	-0.7	5	-0.7	86	100 mW cm^{-2}, > 420 nm light 0 V *vs* RHE	259
2018	$(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$	CdS	Ru_2O	13	-9.1	17	-2.9	3	100 mW cm^{-2}, 0.6 V *vs* RHE	260
2019	p-Si	SiO_2	Porous NiO_x	14	-21	1	-10	0	100 mW cm^{-2}, 0.6 V *vs* RHE	261
2019	n^+p-Si	Ti	NiS_xO_y	14	-26	6	-10	0	100 mW cm^{-2}, 0.05 V *vs* RHE	262
2019	Cu_2O	CuO	$Ni(OH)_2$	6	-7.25	24	-7.25	15.7	100 mW cm^{-2}, 0 V *vs* RHE	263

Table S10. Reported photoelectrochemical (PEC) performances of the photoanodes with semiconductor/semiconductor (insulator or conductor)/semiconductor structure, and their detailed working conditions. The photocurrent at 1.23 V *vs* RHE is simplified as $J_{ph,an}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Middle layer	Surface materials	pH	$J_{ph,an}$	Stability	J_{in}	J_{de}/ J_{in}	Remark	Ref.
2011	Triple junction, amorphous Si	ITO layer	Cobalt|borate	9.2	4.4	0.2	1.1	0	100 mW cm^{-2}, -0.26 V *vs* RHE	12
2018	Black n-Si	Ni	Nb-doped NiO_x	14	5.1	24	15.3	0	100 mW cm^{-2}, 1.43 V *vs* RHE	14
2014	p^+n-Si	Ni	Fe-treated NiO	14	17.3	300	18.5	20	100 mW cm^{-2}, > 635 nm light 1.3 V *vs* RHE	40
2015	n-Si	CoO_x	NiO_x	14	28	1700	30	0	100 mW cm^{-2}, 1.63 V *vs* RHE	42
2015	p^+n-Si	FTO	WO_3	0	1.24	20	1.24	0	100 mW cm^{-2}, no applied bias	81
2017	n-Si	ZnO	SiO_2	7	0.28	1	0.21	0	100 mW cm^{-2}, 0.3 V *vs* Ag/AgCl	85
2016	p^+n-Si	SiO_2	CoO_x	14	30.8	72	10	0	100 mW cm^{-2}, not shown	264
2016	Porous n-Si	TiO_2	ZnO	7	8.2	50	11.5	22	100 mW cm^{-2}, not shown	265
2017	μc-Si:H	ITO	NiO_x	14	7.64	1.33	7.5	1	100 mW cm^{-2}, 0.62 V *vs* Ag/AgCl	266
2017	Black Si	TiO_2	$Co(OH)_2$	14	7.8	4	31	17	100 mW cm^{-2}, 1.65 V *vs* RHE	267
2013	n-Si	Ni	NiO_x	14 9.5	12.5 0	12 80	10 10	0 0	225 mW cm^{-2}, 0.15-0.3 V *vs* RHE, 0.6-0.65 V *vs* RHE	268
2017	Si	TiO_2 nanorod	MOFs-derived Porous Co_3O_4	14	2.71	2	2.68	0	100 mW cm^{-2}, 1.2 V *vs* RHE	269
2016	n-Si	Al_2O_3	NiO_x	14	3.36	20	9.3	0	100 mW cm^{-2}, 1.33 V *vs* RHE	270
2014	p^+n-Si	Ir	IrO_x	0	21	18	21	40	38.6 mW cm^{-2}, 1.23 V *vs* RHE	271
2016	Ta_5N_3 nanotube	TaO_x	$Co(OH)_x$	14	6.3	2	7	86	100 mW cm^{-2}, 0.23 V *vs* Ag/AgCl	272
2019	p^+n-Si	Ni	Ni-O	13.6	39.7	100	10	0	100 mW cm^{-2}, 1.02 V *vs* RHE	273

Table S11. Reported photoelectrochemical (PEC) performances of the photocathodes with multi-layered (n > 3) structure, and their detailed working conditions. The photocurrent at 0 V *vs* RHE is simplified as $J_{ph,ca}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Middle layers	Surface materials	pH	$J_{ph,ca}$	Stability	J_{in}	J_{de}/ J_{in}	Remark	Ref.
2017	p-Si	SiO_2/Ti	Pt	0	-4.5	40	-8	7	100 mW cm^{-2}, not shown	184
2017	Cu_2O	AZO/TiO_2	RuO_x	5	-5.25	5	-3.6	0	100 mW cm^{-2}, 0 V *vs* RHE	274
2017	$GaInP_2$	TiO_2/MoO_x/	Graded MoS_x	0.3	-11	20	-11.2	18	100 mW cm^{-2}, 0 V *vs* RHE	275
2017	Cu_2O	AZO/TiO_2	Pt	4.15	-2.74	2	-2.74	85	100 mW cm^{-2}, 0 V *vs* RHE	276
2016	$(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$	CdS/Ti/Mo	Pt	7	-7.1	0.5	-0.9	20	100 mW cm^{-2}, no applied bias	277
2017	$(ZnSe)_{0.85}(CuIn_{0.7}Ga_{0.3}Se_2)_{0.15}$	CdS/ZnS	Pt	7	-4.3	1	-4.3	7	100 mW cm^{-2}, 0 V *vs* RHE	278
2018	$CH_3NH_3PbI_3$	PCBM/Ag/Ti	Pt nanoparticle	0 7 14	-18	12	-17.5 -16 -17.5	36 25 36	100 mW cm^{-2}, 0 V *vs* RHE	279
2014	p-Si	$SrTiO_3$/Ti	Pt	0	-23.4	35	-31	3	100 mW cm^{-2}, 0.6 V *vs* Ag/AgCl	280
2017	p-Si	Ti/TiO_x/TiO_2	Pt	0	-20.5	300	-17.2	9	100 mW cm^{-2}, 0.3 V *vs* RHE	281
2016	Cu_2O	AZO/TiO_2	Re(bipy)	7.8	0	0.25	-2.5	50	100 mW cm^{-2}, -1.9 V *vs* Fc^+/Fc	282
2014	n^+p-Si	Mo_xSi/Mo	MoS_2	0	-17	100	-17	6	100 mW cm^{-2}, 0 V *vs* RHE	283
2018	p-SnS nanoplatelet	CdS/TiO_2	Pt	0	-3	1.67	-3	0	80 mW cm^{-2}, 0 V *vs* RHE	284
2017	GaInAs	GaInP/AlInP	GaInP	0	-13.2				100 mW cm^{-2}	285
2015	GaInP	$Al_xIn_{1-x}P$/$AlInPO_x$	Rh	0	-14.5	40	-12.3	50	100 mW cm^{-2}, 0.6 V *vs* RHE	286
2016	a-SiC	nc-SiO_x/TiO_2/Ni	Ni-Mo	14	-14	1	-13.6	61	100 mW cm^{-2}, 0 V *vs* RHE	287
2016	p-Si	SiO_2/Pt	SiO_x	0	-27.8	12	-10	0	100 mW cm^{-2}, 0.05 V *vs* RHE	288
2017	p-Si	SiO_2/SiF_x/Ti/TiO_2	Au	0	-28	1	-32.5	0	Not shown, -0.8 V *vs* NHE	289
2014	Porous p-$CuInS_2$	CdS/TiO_2	Pt	10	-13	1	-13	0	100 mW cm^{-2}, 0 V *vs* RHE	290
2013	p-Si	SiO_x/Ti	Pt	0	-18	2.5	-8.13	0	100 mW cm^{-2}, -0.04 V *vs* RHE	291
2015	n^+p-Si	n-GaN/ n^{++}-GaN	p-InGaN	0	-31.2	3	-20.5	0	130 mW cm^{-2},	292

		InGaN/p^{++}-GaN							-0.006 V *vs* NHE	
2011	Cu_2O	AZO/TiO_2	Pt	4.9	-7.6	1.33	-0.8	87	100 mW cm^{-2}, not shown	293
2017	n$^+$p-Si	SiO_2/Mo_xSi/Mo_xO	MoS_2	0	-13	1488	-13	31	100 mW cm^{-2}, 0 V *vs* RHE	294
2014	Cu_2O	n-AZO/TiO_2	MoS_{2+x}	1	-5.7	10	-5.7	0	100 mW cm^{-2}, 0 V *vs* RHE	295
2017	Porous Si	Graphene/Ni_3Se_2	Co_9S_8	14	0	10	-10	0	100 mW cm^{-2}, not shown	296
2016	$CH_3NH_3PbI_3$	PCBM/PEIE-Ag	Pt	8.5	-7.7	2	-7.7	87	100 mW cm^{-2}, 0 V *vs* RHE	297
2018	p-Cu_2O nanorod	p-Cu_2O/n-Cu_2O	Pt	7	-10	0.167	-10	50	100 mW cm^{-2}, 0 V *vs* RHE	298
2015	Cu_2O	Ga_2O_3/TiO_2	Pt	4.26	-2.95	2	-2.95	0	100 mW cm^{-2}, 0 V *vs* RHE	299
2018	n$^+$p-Si	GaN/TiO_2	Pt	7.5	-68	10	-21	17	800 mW cm^{-2}, 0.27 V *vs* RHE	300
2015	Cu_2O	AZO/TiO_2/MoS_2	NiMo	14	-6.3	10	-6.3	76	100 mW cm^{-2}, 0 V *vs* RHE	301
2017	p-GaAs	n-GaAs/n-AlGaAs/ n$^+$-GaAs/Pt/Ti/Pt	Au	0	-23.1	192	-23.1	9	100 mW cm^{-2}, 0 V *vs* RHE	302
2018	Cu(In,Ga)Se_2	CdS/rGO	Pt	6.8	-22.2	7	-22.4	0	100 mW cm^{-2}, 0 V *vs* RHE	303
2017	Se-annealed Sb_2Se_3	CdS/TiO_2	Pt	6.5	-8.6	10	-8.6	16	100 mW cm^{-2}, 0 V *vs* RHE	304
2014	n$^+$p-Si	Ti/FTO/TiO_2	Ir	14	-39	48	-31.2	0	Not shown, 0.3 V *vs* RHE	305
2018	Cu_2S	CdS/TiO_2	RuO_x	5	-5.95	3.33	-3.55	15	100 mW cm^{-2}, 0 V *vs* RHE	306
2018	c-Si	TaO_x/Ti	Pt	0	-37.1	2	-37.1	0	100 mW cm^{-2}, 0 V *vs* RHE	307
2018	a-Si	ZnOB/Ti	CoS	7 13.6	-6.34	10	-6.34	5	100 mW cm^{-2}, 0 V *vs* RHE	308
2012	Cu_2O	AZO/TiO_2	Pt	1	-3.8	10	-3.8	38	100 mW cm^{-2}, 0 V *vs* RHE	309
2013	n$^+$p-Si	Ti/TiO_2	Pt	0	-23.8	72	-19.8	0	100 mW cm^{-2}, > 635 nm light 0.3 V *vs* RHE	310
2015	p-$GaInP_2$	TiO_2/Cobaloxime	TiO_2	13	-11.5	0.333	-9	11	100 mW cm^{-2}, 0 V *vs* RHE	311
2019	Cu(In, Ga)SSe	CdS/ZnO	CoS	7	-3.1				100 mW cm^{-2}	312
2019	CuGaSe	CdS/TiO_2	MoS_2	0	-6.5	24	-6.5	69	100 mW cm^{-2}, 0 V *vs* RHE	313

Table S12. Reported photoelectrochemical (PEC) performances of the photoanodes with multi-layered (n > 3) structure, and their detailed working conditions. The photocurrent at 1.23 V *vs* RHE is simplified as $J_{ph,an}$ (mA cm^{-2}), the operation time Stability (h), the initial photocurrent during stability measurements J_{in} (mA cm^{-2}), and the degradation rate J_{de}/J_{in} (%). The Remark grid is used to illustrate the testing light source and the potentials during stability measurements.

Year	Light absorber	Middle layers	Surface materials	pH	$J_{ph,an}$	Stability	J_{in}	J_{de}/ J_{in}	Remark	Ref.
2017	n-GaAs	Al_2O_3/SiO_2	NiFe	14	5				100 mW cm^{-2}	184
2015	n-Si	SiO_x/Co	CoOOH	14 9	35	5 120	10 8	100 0	100 mW cm^{-2}, 1 V *vs* Ag/AgCl 1.3 V *vs* Ag/ AgCl	314
2011	n-Si	SiO_2/TiO_2	Ir	14	7	24	3	0	100 mW cm^{-2}, 1.7 V *vs* NHE	315
2017	CdS	CdTe/MoO_x/Ti	$Co(OH)_x$	8	3.8	0.5	2.18	68	100 mW cm^{-2}, no applied bias	316
2017	Black p^+n-Si	$SnO_2/BiVO_4$	CoPi	7	2	1	0.6	58	100 mW cm^{-2}, not shown	317
2017	n-Si	SiO_x/ITO	a-NiOOH	14	27.4	30	27.4	0	100 mW cm^{-2}, 1.23 V *vs* RHE	318
2015	p^+n-Si	SiO_2/TiO_2	Ir	0	5.1				100 mW cm^{-2}	319
2016	GaAs	GaInP/TiO_2	Ni	9.3	8.7	110	8.7	0	100 mW cm^{-2}, -0.016 V *vs* RHE	320
2016	Ta_3N_5	TiO_2/Ferrhydrite	$Ni(OH)_x$	13.6	12.1				100 mW cm^{-2}	321
2016	n-Si	SiO_2/TiO_2	Ir	0	0	8	3	66	Not shown	322
2018	n^+p-Si	SiO_x/Ni/NiO_x	NiFe LDH	14	37	68	10	10	225 mW cm^{-2}, not shown	323
2018	n-Si	SiO_2/Al_2O_3/Pt	Ni	14	24				100 mW cm^{-2}	324
2015	$CH_3NH_3PbI_3$	Spiro-MeOTAD/Au	Ni	12.8	13	0.278	13	84	100 mW cm^{-2}, not shown	325
2017	n-Si	SiO_x/Al_2O_3/Pt	Ni	14	19.2	200	25	4	100 mW cm^{-2}, 1.7 V *vs* RHE	326
2016	Si	SiO_2/TiO_2-RuO_2	Ir	0	12.5				100 mW cm^{-2}	327
2016	n-Si	GO/SWCNT/ Graphene	Ni	14	0	0.25	2.45	28	100 mW cm^{-2}, 1.73 V *vs* RHE	328
2017	p^+n-Si	TiO_2/C/CNT	Ru^{IV}(tda)(py-pyr)$_2$O	7	0.35	3.33	0.35	0	100 mW cm^{-2}, 1.23 V *vs* RHE	329
2014	p^+n-Si	ITO/Au/ITO	NiO_x-triton-X	13.8	3.88	0.444	1.96	5	100 mW cm^{-2}, From 1 to -0.05 V *vs* RHE	330
2017	n-Si	SiO_x/Ni	$Ni(OH)_2$	14 9	13.5	300	8	0	100 mW cm^{-2}, 1.73 V *vs* RHE	331
2016	GaAs	InGaP/TiO_2	Ni	13.7	0	3	8	0	100 mW cm^{-2}, no applied bias	332
2016	p^+n-Si	SiO_2/TiO_2	Ir	14	2.9				100 mW cm^{-2}	333

2019	Si heterojunction	ITO/graphdiyne	NiO_x	14	5	0.11	15	7	100 mW cm^{-2}, 1.4 V *vs* RHE	334
2019	n-Si	SiO_2/NiFe	NiFe(OOH)	13.6	25.4	52	32	0	100 mW cm^{-2}, 1.5 V *vs* RHE	335