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Strategies for stable water splitting via protected photoelectrodes

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Supplementary Information

Table S1. Reported stabilities of photocathodes for hydrogen evolution reaction, and detailed working conditions.

Year	Photoelectrodes	Protection layer	Method	Catalyst	Carrier transport	Thickness	pH	Stability	Degradation	$J_{int.}$	Remark	Ref.
1977	p-Si	TiO_2	CVD	NA	band bending	NA	7	0.42	0	NA	Recorded data not shown	39
1981	p-InP	Surface oxide	Chemical oxidation	Ru	Tunneling	NA	0	0.014	0	NA	Recorded data not shown	52
1982	p-InP	Surface oxide	Chemical oxidation	Rh	Tunneling	NA	-0.6	1	30	60	2-3 suns	53
1996	p-Si	No	NA	Pt	NA	NA	0	60	0	4	33 mW cm^{-2}, @ 0V vs. SCE	54
1999	GaAs/p-GaInP_2	No	NA	Pt	NA	NA	-0.3	0.42	3.5	8.5	3.8 suns, @ 0V vs. SCE	83
2008	p-CuGaSe_2	No	NA	NA	NA	NA	0.3	0.33	0	13	@ -0.9V vs. SCE	55
2010	P-Cu(In,Ga)Se_2/n-CdS	No	NA	Pt	band bending	50	9.5	0.67	20	11.2	λ = 350–800 nm	56
2011	p-Cu_2O/n-AZO	TiO_2	ALD	Pt	band bending	10	5	0.014	22	5.7	@ 0V vs. RHE	40
2011	p-Si	No	Drop cast	Mo_3S_4	NA	NA	0	1.08	6	14.4	Light/Dark, 28.3 mW cm^{-2}	57
2012	pn^+-Si	Ti	Sputtering	MoS_X	Ohmic	9	0	0.042	7	14	38.6 mW cm^{-2}, @ 0V vs. RHE	38
2012	p-InP	TiO_2	ALD	Ru	band bending	5	0	0.17	0	35	@ 0.23 V vs. NHE	41
2012	p-Cu_2O/n-AZO	TiO_2	ALD	Pt	band bending	20	5	0.042	38	4.2	@ 0V vs. RHE	58
2012	pn^+-Si	No	NA	Ni-Mo	NA	NA	4.5	0.042	9	10.1	@ 0V vs. RHE	59
2012	p-$CuGa_3Se_5$/ZnS	No	NA	Pt	NA	NA	9.5	1.042	0	2.8	Measured @ 0.1V vs. RHE	60
2012	p-Cu_2O	NiO_X	Spin coating	NiO_X	band bending	10	6	0.014	28	0.42	26 mW cm^{-2}, @ 0.1V vs. NHE	65
2013	pn^+-Si	TiO_2	ALD	Pt	band bending	100	0	30	14	21.5	@ 0.3V vs. RHE, 38.6 mW cm^{-2}	42
2013	pn^+-Si	TiO_2	Sputtering	Pt	band bending	100	0	3	0	20	@ 0.3V vs. RHE, 38.6 mW cm^{-2}	43
2013	P3HT/PCBM	TiO_2:MoS_3	Spin coating	MoS_X	NA	90	0.3	0.0313	8	0.05	λ > 400 nm, @ 0.16 V vs. RHE	61
2013	p-Cu_2O	Carbon	Glucose decomposition	NA	NA	20	7	0.042	19.3	4	@ 0V vs. RHE	62
2013	pn^+-Si	MoS_2	Sputtering	MoS_2	NA	10	0	5	0	7	38.6 mW cm^{-2}, @ 0V vs. RHE	63
2013	n-i-p Si	TiO_2	Sputtering	Pt	band bending	80	4	0.5	5	10.8	@ 0V vs. RHE	64
2013	p-WSe_2	Ru/Pt	Photodeposition	Pt	Schottky junction	NA	2	0.0833	0	15.8	@ 0V vs. RHE	84
2013	p-WSe_2	Ru/Pt	Photodeposition	Pt	Schottky junction	NA	10	0.0833	9	14	@ 0V vs. RHE	84
2014	pn^+-Si	TiO_2	Spin casting	Ir	band bending	50	14	3	19	30	@ 0.3V vs. RHE	13
2014	p-Cu_2O/n-AZO	TiO_2/MoS_{2+x}	ALD/Photodeposition	MoS_{2+x}	band bending	100	4	0.42	6	4.5	@ 0V vs. RHE	16
2014	p-Cu_2O/n-AZO	TiO_2/MoS_{2+x}	ALD/Photodeposition	MoS_{2+x}	band bending	100	9	0.42	40	2	@ 0V vs. RHE	16
2014	p-Cu_2O/n-AZO	TiO_2/MoS_{2+x}	ALD/Photodeposition	MoS_{2+x}	band bending	100	1	0.25	77	5.7	@ 0V vs. RHE	16
2014	p-Cu_2O/n-AZO	TiO_2	Electrodeposition	Pt	band bending	100	1	0.1	29	7	@ 0V vs. RHE	16
2014	p-Cu_2O/n-AZO	TiO_2	ALD	RuO_2	band bending	100	5	8	6	5	@ 0V vs. RHE	46

2014	p-Si	$SrTiO_3$	MBE	Pt	band bending	1.6	0.3	1.46	6	31	@ 0V versus Ag/AgCl	48
2014	pn^+-Si	MoS_2	CVD	MoS_2	band bending	40-80	0.3	0.125	30	17.5	@ 0V vs. RHE	66
2014	p-Si	Al_2O_3	ALD	Pt	Tunneling	2.3	0.3	0.5	0	30	@ -0.9V vs. RHE	67
2014	p-(Ag,Cu)$GaSe_2$/CdS	No	NA	Pt	NA	NA	10	2.3	0	7	@ 0V vs. RHE, Ag 5.9%	68
2014	pn^+-Si	MoS_2	Sputtering/Sulfidation	MoS_2	NA	3.6	0.3	4.17	0	17.5	@ 0V vs. RHE	69
2014	p-GaP	No	NA	Pt	NA	NA	0	1	97	0.78	@ 0V vs. RHE, 38.6 mW cm^{-2}	85
2014	p-GaP	TiO_2	Sputtering	Pt	band bending	100	0	1	8	1.04	@ 0V vs. RHE, 38.6 mW cm-2	85
2014	p-GaP	Nb_2O_5	Sputtering	Pt	band bending	100	0	1	90	0.66	@ 0V vs. RHE, 38.6 mW cm^{-2}	85
2015	p-(Ag,Cu)$GaSe_2$/CdS	No	NA	Pt	NA	NA	7	20	0	7.9	@ 0V vs. RHE	18
2015	p-GaP	Surface oxide	Chemical oxidation	Pt	Tunneling	NA	0	0.271	7.8	9.1	@ 0V vs. RHE	19
2015	p-InP	TiO_2	ALD	Pt	band bending	10	0	0.083	0	25	@ 0V vs. RHE	23
2015	p-Si	Ti/Ni	Evaporation	Ni	Schottky junction	15/5	14	0.5	50	10	CP @ 10mA cm-2, 2.25 suns	71
2015	p-Si	Ti/Ni	Evaporation	Ni	Schottky junction	15/5	9.5	0.5	30	10	CP @ 10mA cm-2, 2.25 suns	71
2015	p-Cu(In,Ga)Se_2	TiO_2:Pt	CVD	Pt	band bending	100	0.3	1.042	0	9	@ 0V vs. RHE	72
2015	pn^+ mc-Si	Al_2O_3	ALD	NA	Tunneling	4.5	1	4.17	0	27.5	@ -0.8V vs. RHE	73
2015	p-Cu(In,Ga)Se_2/CdS	Ti/Mo	Sputtering	Pt	NA	3/3	6.8	10	30	24	@ 0V vs. RHE	74
2016	pn^+-Si	TiO_2	Sputtering	Pt	band bending	100	14	1	3	17.5	@ 0.3V vs. RHE 38.6 mW cm^{-2}	34
2016	p-Cu(In,Ga)Se_2/CdS/i-ZnO/AZO	TiO_2	ALD	Pt	band bending	100	0.3	0.417	33	28.6	@ 0V vs. RHE	70
2016	a-SiC	TiO_2/Ni	ALD	Ni-Mo	band bending	25	14	0.042	65	13.6	@ 0V vs. RHE	75
2016	PEDOT:PSS/$CH_3NH_3PbI_3$/PCBM	Ag/InBiSn	Evaporation/Melting	Pt	NA	100/NA	8.5	0.0625	20	7.7	@ 0V vs. RHE, Back-illuminated	76
2016	p-InP	Ti/MoS_X	Sputtering/Photodeposition	MoS_X	Schottky junction	10/35	0	0.083	11	15.8	@ 0V vs. RHE	77
2016	a-Si:H/a-Si:H/uc-Si:H/uc-Si:H/AZO/Ag	Ni	Evaporation	Ni	Ohmic	150	13	0.17	0	6.1	@ 0V vs. RHE	78
2016	a-Si:H/uc-Si:H/uc-Si:H/AZO/Ag	Pt	Evaporation	Pt	Ohmic	150	13	0.17	7	7	@ 0V vs. RHE	78
2016	a-Si:H/a-SiGe:H	TiO_2:H	Sputtering	NA	band bending	80	13.6	0.21	8	6	@ 0V vs. RHE	79
2016	p-Cu_2O	SnO_2	ALD	RuO_2	band bending	50	5	2.34	10	3.9	@ 0V vs. RHE	80
2016	p-$GaInP_2$	MoS_2	Sputtering/Sulfidation	MoS_2	NA	3	-0.48	2.92	18	6.2	@ -0.025V vs. RHE	81
2016	nc-Si/SiO_2/p-Si/SiO_2/nc-Si	TiO_2:H	Sputtering	Pt	band bending	100	0	41	13	20.5	@ 0.4V vs. RHE	82
2016	a-Si:H/uc-Si:H/uc-Si:H/AZO/Ag	Pt	Evaporation	Pt	Ohmic	150	14	0.0035	35	7.7	@ 0V vs. RHE	78

Note that units for thickness, stability, $J_{int.}$ and degradation are nm, days, mA cm^{-2} and %, respectively.

Table S2. Reported stabilities of photoanodes for oxygen evolution reaction, and detailed working conditions.

Year	Photoelectrodes	Protection layer	Method	Catalyst	Carrier transport	Thickness	pH	Stability	Degradation	$J_{int.}$	Remark	Ref.
1984	n-Si	SiO_2	Chemical oxidation	Pt	Tunneling	10	0.3	4.2	30	0.9	40 mW cm^{-2}, @ 2.02V vs. NHE	36
1986	n-Si	Pd/Mn_2O_3	CBD	Mn_2O_3	NA	20	4.7	25	21	1.4	@1.3V vs. NHE	100
1987	np^+-Si	Pt/Ni	Sputtering	Ni	Ohmic	3	14	0.33	0	15	@1.0V vs. Hg/HgO, 80 mW cm^{-2}	37
1987	np^+-Si	Pt/Ni-W	Sputtering/Electrodeposition	Ni-W	Ohmic	3	14	0.17	0	14	@1.0V vs. Hg/HgO, 80 mW cm^{-2}	37
1987	n-GaAs	Pt/Mn_2O_3	CBD	Mn_2O_3	NA	20	13.7	0.056	0	11	Unknown fixed potential	101
2011	n-Si	TiO_2/Ir	ALD	Ir	Tunneling	2	7	0.75	0	5.1	@1.5V vs. Ag/AgCl	44
2011	n-Si	TiO_2/Ir	ALD	Ir	Tunneling	2	0	0.33	0	1	@1.0 mA cm^{-2} in CP	44
2011	n-Si	TiO_2/Ir	ALD	Ir	Tunneling	2	13.6	0.33	0	1	@1.0 mA cm^{-2} in CP	44
2011	3J a-Si	FTO/CoO_X	Unknown/Photodeposition	CoO_X	NA	70	9.2	1.33	0	4.5	@1.3V vs. RHE	102
2012	Ta_3N_5	Co_3O_4	Calcination of $Co(OH)_X$	Co_3O_4	NA	10	13.6	0.83	27	1.1	@1.2V vs. RHE	103
2012	n-Si	NiO_X	Spin coating	NiO_X	band bending	37.4	7.2	3	84	6.4	@1.92V vs. RHE	104
2013	n-Fe_2O_3:Pt	No	NA	Co-Pi	NA	NA	7	0.125	7	4.3	@1.23 V vs. RHE	27
2013	n-Si	Ni	Evaporation	NiO_X	band bending	2	9.5	3.33	0	10	@10 mA cm^{-2} in CP, 2.25 suns	105
2013	n-Si	Ni	Evaporation	NiO_X	band bending	2	14	0.5	0	10	@10 mA cm^{-2} in CP, 2.25 suns	105
2013	n-$BiVO_4$	CoO_X	ALD	CoO_X	NA	1	13	0.069	7	1.35	@1.23 V vs. RHE	106
2013	n-Si	MnO_X	ALD	MnO_X	State-mediated	10	14	0.0208	0	22.5	@1.62 V vs. RHE	107
2013	$BaTaO_2N$:H	No	NA	RhO_X w/ CoO_X	NA	NA	8	0.042	14	14	@1.07 V vs. RHE	108
2013	n-Si	$NiRuO_X$	Sputtering	$NiRuO_X$	Shottky junction	NA	7.2	0.0625	15	7	CV 500 cycles	109
2013	$CaFe_2O_4$/TaON	No	NA	Co-Pi	NA	NA	11	0.125	50	1	@1.23 V vs. RHE	133
2014	np^+-Si	TiO_2	ALD	Ni	State-mediated	44	14	4.58	10	40	@2 V vs. RHE, 1.25 Suns	14
2014	np^+-GaAs	TiO_2	ALD	Ni	State-mediated	118	14	1.042	8	14	@ 1.26 V vs. RHE	14
2014	n-GaP	TiO_2	ALD	Ni	State-mediated	118	14	0.23	18	1.1	@ 1.26 V vs. RHE	14
2014	WO_3	No	NA	NA	NA	NA	-1.2	0.5	53	2.35	@ 0.87V vs. RHE	15
2014	n-$BiVO_4$	FeOOH/NiOOH	Photodeposition	FeOOH/NiOOH	NA	NA	7	2	0	2.6	@ 0.6V vs. RHE	17
2014	np^+-Si	NiO_X:Fe	Sputtering	NiO_X:Fe	band bending	50	14	12.5	17	17.5	@1.3V vs. RHE, 38.6 mW cm^{-2}	110
2014	np^+-Si	CoO_X	ALD	CoO_X	NA	2	13.6	1	0	10	@10 mA cm^{-2} in CP	111
2014	n-CdTe	TiO_2	ALD	Ni	band bending	140	14	4.17	14	22	@2.07V vs. RHE	112
2014	n-Ta_3N_5	Ferrihydrite	CBD	Co_3O_4	NA	NA	13.6	0.25	6	5	@1.23V vs. RHE	113
2014	n-$BiVO_4$	TiO_2/Ni	ALD/Sputtering	Ni	NA	1	13	0.17	0	1.35	@1.23V vs. RHE, 1.35 suns	114

2014	np^+-Si	ITO/Au/ITO	Sputtering	NiO_X	band bending	100/5/100	13.6	0.042	5	11.7	CV 360 cycles, 51.2 mW cm^{-2}	115
2014	n-$CaFe_2O_4$/n-$BiVO_4$	No	NA	Co-Pi	NA	> 300	7	0.083	60	4.3	@ 1.3V vs. RHE	116
2014	np^+-Si	IrOx	Sputtering	IrO_X	Ohmic	4	0	0.75	0	12.5	@1.23V vs. RHE, 38.6 mW cm^{-2}	117
2014	n-WO_3/n-$BiVO_4$:(W,Mo)	FeOOH/NiOOH	Photodeposition	FeOOH/NiOOH	NA	NA	7	7	8.7	3.1	@0.6V vs. RHE	118
2015	np^+-InP	NiO_X	Sputtering	NiO_X	Ohmic	75	14	2	21	24	@1.73V vs. RHE	21
2015	n-$BiVO_4$:N	FeOOH/NiOOH	Photodeposition	FeOOH/NiOOH	NA	NA	7.2	2.21	46	3.2	@0.6V vs. RHE	22
2015	np^+-Si	TiO_2/$NiCrO_X$	ALD/Sputtering	$NiCrO_X$	NA	94	14	91.67	0	4.7	@1.59V vs. RHE	45
2015	np^+-Si	TiO_2	Sputtering	Pt	Ohmic	100	0	2.5	0	22	@1.68V vs. RHE, 38.6 mW cm^{-2}	50
2015	np^+-Si	NiO_X	Sputtering	NiO_X	NA	75	14	50	6	33.6	@1.73V vs. RHE	119
2015	n-CdTe/NiO_X	NiO_X	Sputtering	NiO_X	NA	75	14	41.67	0	22.5	@1.73V vs. RHE	120
2015	HTJ-Si	NiO_X	Sputtering	NiO_X	NA	75	14	8.3	0	35	@1.73V vs. RHE	120
2015	n-a-Si:H/NiO_X	NiO_X	Sputtering	NiO_X	NA	75	14	4.2	0	5	@1.73V vs. RHE	120
2015	n-Si	TiO_2	ALD	Ni	State-mediated	100	14	2.5	10	35	@1.85V vs. RHE	121
2015	n-Si/SiO_X/CoO_X	NiO_X	Sputtering	NiO_X	band bending	85	14	70.83	0	30	@1.63V vs. RHE	122
2015	np^+-Si	$NiCoO_X$	Sputtering	(Ni,Fe)OOH	band bending	40	14	3	0	30	@1.4 V vs RHE	123
2015	n-ZnO	Ta_2O_5	ALD	No	Tunneling	1.5	13	0.21	0	0.82	@1.23V vs. RHE	124
2015	n-$BiVO_4$:CoO_X	NiOOH	ALD	CoO_X/NiOOH	band bending	6	7	0.67	18	2.8	@0.8V vs. RHE	125
2015	n-Fe_2O_3	IrO_X	Electrodeposition	Metal oxide	NA	1	1.01	0.208	5	0.65	@1.23V vs. RHE	126
2015	n-$BiVO_4$:Mo,H	Co-Ci	Photodeposition	Co-Ci	NA	4-10	7	2.5	0	3.2	@1.03V vs. RHE	127
2015	n-$BiVO_4$:Mo,H	Co-Ci	Photodeposition	Co-Ci	NA	4-10	9	2.5	0	3.1	@1.03V vs. RHE	127
2016	p^+nn^+-Si	$NiCoO_X$	Sputtering	$NiCoO_X$	band bending	100	14	6	0	21.3	@1.2V vs. RHE	24
2016	n-Si/n-Ta_3N_5	No	NA	$NiFeO_X$	NA	NA	13	1	40	1.6	@1.23V vs. RHE, λ < 590 nm	128
2016	n-WO_3:Na	No	NA	WO_3:Na	NA	NA	-1.2	0.83	10	3	@1.2V vs. RHE	129
2016	n-$LaTiO_2N$	No	NA	CoO_X	NA	NA	13	0.083	80	1.6	@1.0V vs. RHE	130
2016	n-WO_3	FeOOH	Electrodeposition	FeOOH	NA	NA	6.6	0.083	36	1.4	@1.23V vs. RHE	131
2016	n-Si	TiO_X/ITO/NiOOH	ALD/Sputtering/Photodeposition	NiOOH	band bending	3/15/140	12	0.285	54	13	@1.23V vs. RHE	132

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