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Supplementary Information

Photogenerated Carrier-assisted Electrocatalysis: Mechanistic Perspectives and Catalytic Advances

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Table S1. Timeline of major developments in PCAE.

Year	Development	Ref.
1972	First photo-assisted water splitting	20
1984	First photo-assisted CO_2 reduction	22
2005	First photo-assisted methanol oxidation	23
2014	First photo-assisted formic acid oxidation	24
2014	First light-assisted Li-O_2 battery	25
2018	First photo-assisted rechargeable Zn-air batteries	26
2021	First photo-driven urea-assisted hydrogen generation	27
2023	First light field-enhanced nitrogen reduction reaction	28

Table S2. The strategy and performance of PCAE.

No.	Catalyst	Strategy	Dark condition				Light condition				Stability	Reaction type	Ref.
			Overpotential (mV)	Tafel (mV dec^{-1})	Mass activity (mA mg^{-1})	Others	Overpotential (mV)	Tafel (mV dec^{-1})	Mass activity (mA mg^{-1})	Others			
			Note: unless stated otherwise, measurements were performed in in 1 M KOH at 10 mA cm^{-2}										
1	BP QDs/MoS_2	Heterojunction	320/470/670/770 [1/0.5/0.2/0.1 M KOH]	108/141/245/264 [1/0.5/0.2/0.1 M KOH]	-	-	170/400/650/720 [1/0.5/0.2/0.1 M KOH]	95/135/231/247 [1/0.5/0.2/0.1 M KOH]	-	-	CA: 10000 s [1.4 V, 7.5 mA cm^{-2}]	OER	42
2	CoFe PBA/CoS_2 CNBs	Heterojunction	301	79.6	-	-	275 mV	59.2	-	-	CA: 45 h [1.5 V]	OER	43
3	CoS_2/MoS_2/Ni_3S_2	Heterojunction	195/341 [10/100 mA cm^{-2}]	56.2	-	-	166/282 [10/100 mA cm^{-2}]	-	-	-	CA: 12 h [0.4 V]	OER	44
4	SnS_2/NiO	Heterojunction	388	215	-	-	310	190	-	-	CA: 10 h [87.8%, normalized current]	OER	45
5	CF/WS/CNTs	Heterojunction	224	47	-	-	291	78	-	-	CA: 10 h [0.291 V]	OER	39
6	Pt-BiOBr	Schottky junction	-	-	26.5/155.4[MOR/EOR]	-	-	-	751.7/929.8[MOR/EOR]	-	CA: 3000 s [30.9/16.9 mA mg^{-1} MOR/EOR]	MOR/EOR	46
7	Pt/$BiVO_4$/Bi_2O_3	Heterojunction	-	-	506.6	-	-	-	281.4	-	CA: 425 s [0.751 V, light chopping mode]	MOR	47
8	WO/CN-Ni@CF	Heterojunction	Potential: 1.48 V [100 mA cm^{-2}]	-	-	-	Potential: 1.34 V [100 mA cm^{-2}]	-	-	-	CP: 18 h [1.18 V]	UOR	48
9	TiO_2-Fe_2O_3	Heterojunction	-	-	-	Power density: 22 mW m^{-2}	-	-	-	Power density: 28 mW m^{-2}	-	UOR	49
10	$Ni_3(VO_4)_2$	Morphological regulation	122	82	-	-	90	50	-	-	CV: 1000 cycle	HER	50
11	CdSe/WS_2	Quantum dots sensitized	-1030	132	-	-	-400	56	-	-	CA: 24 h [-0.4 V]	HER	51
12	Ti_3C_2@P-WO_3	Heterojunction	162	102	-	-	44	41	-	-	CV: 5000 cycle	HER	52
13	STO/A-R TNTAs	Heterojunction	-	-	-	HCOOH: 68.24 μmol cm^{-2} h^{-1}; H_2: 1.77 μmol h^{-1}	-	-	-	-	CA: 24 h	CO_2RR	53

14	$IrO_2 \cdot nH_2O$	Dye 1 as sensitizer and a molecular bridge	-	-	-	Current density: 12.7 μA cm^{-2}	-	-	-	-	-	Water Splitting	54
15	$CdS@Co_9S_8/Ni_3S_2$	Morphological regulation	-	91.3 [OER]	-	-	69.6/285 [HER/OER, -10/ 20 mA cm^{-2}]	121/87.2 [HER/OER]	-	-	CP: 40 h [1.15 V]	Water Splitting	55
16	$CdS@Ni_3S_2/Ni_3P$	Heterojunction	-	-	-	-	-130/300 [HER/OER]	103.0/108.7[HER/OER]	-	-	CA: 12 h [1.54 V]	Water Splitting	56
17	NiFe-ZAIS	Heterojunction	151/242 [HER/OER]	111.7/71.6 [HER/OER]	-	-	129/220 [HER/OER]	105.0/54.6 [HER/OER]	-	-	CV: 1000 cycle	Water Splitting	33
18	PDTB TiO_2	Double cathode	-	-	-	Discharge: 1.20 V; Charge:1.8 V	-	-	-	Discharge: 1.90 V; Charge: 0.59 V	Discharge/charge after cycle: 1.18/0.86 V	ORR/OER	57
19	$CeVO_4$@CNT	Heterojunction	-	-	-	-	-	-	-	Discharge: 2.59 V; Charge:3.48 V	50 cycle specific capacity limit of 0.15 mAh cm^{-2} for each cycle at 0.15 mA cm^{-2}	ORR/OER	58
20	Cu_2O/β-Bi_2O_3	Heterojunction	-	-	-	Current density: 30.1 mA cm^{-2}	-	-	-	Current density: 40.4 mA cm^{-2}	CA: 9 h	CO_2RR	63
21	S-$NiFeO_xH_y$/CC	Doping	265	78	-	Cdl: 1.58 mF cm^{-2}	250	63	-	Cdl: 10.93 mF cm^{-2}	CP: 24 h [20 mA cm^{-2}]	OER	64
22	Pt-Fe_2O_3	Schottky junction	-	-	167.8	-	-	-	389.1/218.7 [Solar/visible light]	-	CV: 300cycle	MOR	65
23	Pd/hollow TiO_2 sphere (PHTG)	Morphological regulation	-	-	2657	-	-	-	3687 [UV]	-	CA: 10000 s [1627 mA cm^{-2}]	MOR	66
24	$CdS@Ni_3S_2$	Heterojunction	330	85.5	-	-	260	75	-	-	CA: 6 h [8.6 mA cm^{-2}]	Water Splitting	69
25	CeO_2/MnO_2-CFP	Heterojunction	-	-	-	Capacitance: 303.0 F·g^{-1} at 0.25 A·g^{-1}	-	-	-	Capacitance: 169.7 F·g^{-1} at 0.25 A·g^{-1}	CV: 100 cycle	Supercapacitors	70
26	$CdS@Ni_3S_2/Cu_2S$	Heterojunction	223/347 [HER/OER 20 mA cm^{-2}]	151.7 [OER]	-	-	334 [OER, 20 mA cm^{-2}]	133.7 [OER]	-	-	CA: 40 h [15 mA cm^{-2}]	Water Splitting	71
27	In_2O_3@InP	Heterojunction	-44	121.2	-	Photocurrent density: 0.3 mA cm^{-2}	-164	106.9	-	Photocurrent density: 0.9 mA cm^{-2}	CA: 80 h [-10/-20/-50/-100 mA cm^{-2}]	HER	72
28	Ni- or Co-doped CeO_2	Schottky junction	330 320	98 112	-	-	266 285	86 78	-	-	-	OER	73

29	CoMo-LDH@$Ti_3C_2T_x$	Heterojunction	-	-	-	NO_3^- yield of 125.9 μg h^{-1} mg_{cat}^{-1}; EF: 43.7%	-	-	-	NO_3^- yield of 198.55 μg h^{-1} mg_{cat}^{-1}; EF: 46.22%	CA: 6000 s	NOR	74
30	Ru NPs/SAs@N-TC	Schottky junction	150	75	-	-	90	58	-	-	CA: 50000 s	HER	75
31	Rh/SnO_2	Schottky junction	-	127.6	-	Current density: 11.89 mA cm^{-2}	247.05	92.6	-	-	Current density: 13.19 mA cm^{-2}	FAOR	76
32	Pd/CeO_2	Schottky junction	-	322	2409.31	-	-	285	4161.72	-	-	FAOR	77
33	PdSn/WO_3	Schottky junction	-	188	1339.5	-	-	203	2262.3	-	CA: 20000 s	FAOR	78
34	CoCr-LDH/CFP	Morphological regulation	445 [100 mA cm^{-2}]	85	-	-	417 [100 mA cm^{-2}]	74	-	-	CA: 15 h [1.57 V, 15 mA cm^{-2}]	Water Splitting	81
35	CCN@FFC	Heterojunction	137/271 [HER/OER]	97/53 [HER/OER]	-	Cdl: 1.53 mF cm^{-2}	68/182 [HER/OER]	38/44 [HER/OER]	-	Cdl: 4.87 mF cm^{-2}	CA: 18 h [10 mA cm^{-2}]	Water Splitting	82
36	CdS-CdSe/MoS_2/NiFe-LDH	Heterojunction	-	177	-	Cdl: 15.9 mF cm^{-2}	-	78	-	Cdl: 22.2 mF cm^{-2}	CV: 500 cycle	HER	83
37	$LaCoO_3$/NiFe LDH	Heterojunction	310	100	-	-	260	95	-	-	CA: 60 h [1.8 V, 460 mA cm^{-2}]	OER	84
38	Pt/g-C_3N_4	Schottky junction	-	-	56	-	-	-	132	-	CA: 2000 s	MOR	85
39	Pt/g-C_3N_4/MoS_2	Heterojunction	-	-	76.9	-	-	-	165.5	-	CA: 3000 s [-0.2 V]	EOR	86
40	Pt-Bi_2WO_6/MoS_2	Heterojunction	-	-	1781	-	-	-	2743	-	CA: 1500 s [-0.2 V]	MOR	87
41	Cd-CoS_x	Doping	-	-	10.4 [0.6 V]	-	-	-	14.5 [0.6 V]		CA: 8 h [0.6 V]	MOR	89
42	N-doped CoNiOOH	Doping	-	-	-	95 μmol h^{-1} cm^{-2} [1.5 V]	-	-	-	160 μmol h^{-1} cm^{-2} [1.5V]	CA: 48 h [2.5 V]	Water Splitting	90
43	AB-OV/CC	Defect Engineering	-	-	-	Discharge: 2.76 V; Charge: 3.94 V	-	-	-	Discharge: 3.05 V; Charge:3.25 V	Charge voltage retention of 70% [500 h]	Li–O_2 Batteries	91
44	Au-N_v-C_3N_4	Defect Engineering	-	-	-	Discharge: 1.18 V; Charge: 3.52 V	-	-	-	Discharge: 1.60 V; Charge:3.05 V	Cycle stability [500 h]	Li-N_2 batteries	92
46	$LaFe_{1-x}O_3$-Fe_v	Defect Engineering	450	73.0	-	-	634	65.7	-	-	CA: 30 h [1.8 V, 12 mA cm^{-2}]	Water Splitting	93
47	$NiCo_2S_4$	Doping	-	-	-	-	80/243 [HER/OER]	58.5/54.9 [HER/OER]	-	-	CA: 24 h [1.60 V, 80 mA cm^{-2}]	Water Splitting	96

48	$MnWO_4$/FeCoNi	Schottky junction	104/234 [HER/OER]	60.6/67.4 [HER/OER]	-	-	64/204 [HER/OER]	53.1/56.1 [HER/OER]	-	-	CA: 720 h [500/1000 mA cm^{-2}]	Water Splitting	97
49	CuO/ZnO/graphene	Heterojunction	-	-	-	-	-	-	-	H_2 production: 37.2 mmol g^{-1} h^{-1}	H_2 production rate: 208 mmol g^{-1}	Water Splitting	98
50	PtNi/C-TiO_2NTs	Doping	-	-	108 mA cm^{-2}	-	-	-	123 mA cm^{-2}	-	CA: 1800 s [51%, 61 mA cm^{-2}]	MOR	103
51	TiO_2	Defect Engineering	-	-	-	Power density: 5.8 μW cm^{-2}	-	-	-	Power density: 22.2 μW cm^{-2}	CP: 15 min [0.54 V, 90 μA cm^{-2}]	MOR	104
52	ZnO, TiO_2, Fe_2O_3	1D semiconductor	-	-	-	-	-	-	-	1.12/1.34/1.14 ZnO/TiO_2/Fe_2O_3	-	MOR	105
53	Si NWs@ZnO	Heterojunction	-	-	-	Short circuit current: 67.0 μA cm^{-2}; OCP: 0.4 V	-	-	-	Short circuit current: 100.5 μA cm^{-2};	CA: 20000 s [97.4%]	MOR	106
54	pTTh	Polymer semiconductor	-	-	-	Onset Potential: 0.66 V; current density: 1.2 mA cm^{-2}	-	-	-	Onset Potential: 1.34 V; current density: 52.8 mA cm^{-2}	CA: 10 h [0.8 V]	ORR	107
55	W-$BiVO_4$/V_2O_5 photoanode/ Cu_2O/CuO photocathode	Heterojunction	-	-	-	R_{ct}: 161,000 Ω; J_{sc}: 0 mA cm^{-2}; OCP: 0.03 V	-	-	-	R_{ct}: 241 Ω; J_{sc}: 8.05 mA cm^{-2}; OCP: 0.41 V	-	ORR	108
56	Nickel foam/TiO_2	Semiconductor coating	-	-	-	R_{ct}: 3,822.25 Ω	-	-	-	R_{ct}: 2497.75 Ω; Photocurrent density: 0.025 mA cm^{-2}	CA: 1200 s [0.5 M NaOH with 0.05/0.07/0.2/0.3/0.5 M Urea]	UOR	109
57	TiO_2-Fe_2O_3/CC	Heterojunction	-	-	-	Discharge plateaus: 2.9 V [0.01 mA cm^{-2}]; Charge plateaus: 4.2 V [0.01 mA cm^{-2}]	-	-	-	Discharge plateaus: 3.2/2.5 V [0.01/1 mA cm^{-2}]; Charge plateaus: 3.2 V [0.01 mA cm^{-2}]	3.0/3.2 V[Discharge/charge potential after 100 cycle]	Li-O_2 Battery	114
58	Co-TABQ	Semiconducting Metal/Organic Polymer	-	-	-	Discharge voltage: 2.63 V; charge voltage: 4.31 V [0.10 mA cm^{-2}]	-	-	-	Discharge voltage: 3.13/3.06/2.96/2.83 V; charge voltage: 3.33/3.41/3.50/3.61 V [0.10/0.20/0.30/0.50 mA cm^{-2}]	50 cycle	Li-O_2 Battery	115
59	In_2S_3@CNT/SS	Structural Design	-	-	-	Discharge voltage: 2.73 V; charge voltage: 3.86 V; Round Trip Efficiency: 70.7%	-	-	-	Discharge voltage: 3.14 V; charge voltage: 3.20 V； Round Trip Efficiency: 98.1%	25 cycle/Flexibility Test 10 cycle [0°, 45°, 180°]	Li-CO_2 Battery	116

60	TiO_2/CC	Semiconductor	407/505 [CO_2RR/CO_2ER]	-	-	Discharge voltage: 2.67 V; charge voltage: 3.97 V; Energy Efficiency: 67.3%	-	-	289/373 [CO_2RR/CO_2ER]	Discharge voltage: 2.82 V; charge voltage: 2.88 V; Energy Efficiency: 97.9%	Stable Cycling: 60 h [0.01 mA cm^{-2}]	Li-CO_2 Battery	117
61	$BiVO_4$ or α-Fe_2O_3	Semiconductor	-	-	-	Charge voltage: 2.0/2.0 V [$BiVO_4$/α-Fe_2O_3]	-	-	-	Charge voltage: 1.20/1.43 V [$BiVO_4$/α-Fe_2O_3];	CA: $BiVO_4$ [10 min, 84.6%] α-Fe_2O_3 [5 h, 100%]	Zn-air battery	121
62	VLS-RZAB	Semiconductor	-	-	-	Charge voltage: 1.72 V; Energy Efficiency: 75.64%	-	-	-	Charge voltage: 1.35/1.28 V; Energy Efficiency: 97.78/101.64% [Visible light/UV]	50 cycle [1.65 V, 100 mW cm^{-2}]	Zn-air battery	122
63	Ru@TS@C	Semiconductor	-	-	-	295 mV at 0.2 mA cm-2	-	-	-	218 mV at 0.2 mA cm-2	76% round-trip efficiency retention after 300 h under light	Zn-air battery	123