Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Overview of record Solar-To-Fuel efficiencies (in absence of chemical or electrical bias, without sacrificial reagents, under (simulated) solar illumination)

Year	Notation	Type	Oxidation catalyst	Reduction catalyst	Main reduction product(s)	Photoanode	PV	Photocathode	Electrolyte	STF Efficiency	Reference
1976	TiO_2|1jn-Si|–Pt	PV-PEC	-	Pt	H_2	TiO_2	1jn-Si	-	0.1 M NaOH	0.10%	1
1976	n-TiO_2/p-GaP	PEC	-	-	H_2	TiO_2	-	p-GaP	0.1 M H_2SO_4	0.25%	2
1983	$SrTiO_3$	Photocatalytic	-	-	Formic acid, formaldehyde, methanol	$SrTiO_3$	-	-	0.1 M Li_2CO_3 (CO_2 satd.)	0.011%	3
1984	RuO_2|2jn-Si|Pt	Buried PV	RuO_2	Pt	H_2	-	2jn-Si	-	5 M H_2SO_4	2.6%	4
1987	MnO|n-GaAs|–|p-InP/Pt	PEC	MnO	Pt	H_2	n-GaAs	-	p-InP	6 M KOH	8.2%	5
1988	RuO_2|3jn-Si|Pt	Buried PV	RuO_2	Pt	H_2	-	3jn-Si	-	0.5 M H_2SO_4	2.93%	6
1989	RuO_2|3jn-Si/Pt	Buried PV	RuO_2	Pt	H_2	-	3jn-Si	-	1 M H_2SO_4	5%	7
1998	Co-Mo|3jn-Si|$NiFe_yO_x$	Buried PV	$NiFe_{0.19}O_{0.2}$	$Co_{0.73}Mo_{0.27}$	H_2	-	3jn-Si	-	1 M KOH	7.8%	8
1998	Pt–|1jn-GaAs|p-$GaInP_2$	PV-PEC	Pt	-	H_2	-	1jn-GaAs	p-$GaInP_2$	3 M H_2SO_4	12.4%*	9
2000	TiO_2/NiO_x	Photocatalytic	-	NiO_x	H_2	TiO_2	-	-	2.2 M Na_2CO_3	0.016%	10
2001	$In_xNi_yTaO_4$/NiO_x	Photocatalytic	-	NiO_x	H_2	$In_{0.9}Ni_{0.1}TaO_4$	-	-	H_2O	0.030%	11
2001	Pt|1jn-GaAs|1jn-$GaInP_2$|–Pt	Buried PV	Pt	Pt	H_2	-	1jn-GaAs 1jn-$GaInP_2$	-	2 M KOH	16.5%	12
2001	RuO_2|1jn-AlGaAs|1jn-Si|Pt	Buried PV	RuO_2	Pt	H_2	-	1jn-AlGaAs 1jn-Si	-	1 M $HClO_4$	18.3%	13
2005	WO_3|2jn-Si|–Ni-Mo	PV-PEC	-	Ni-Mo	H_2	WO_3	2jn-Si	-	0.33 M H_3PO_4	0.70%	14
2006	WO_3–(I_3^-/I^-)–1xDSSC|Pt	PV-PEC	-	Pt	H_2	WO_3	1xDSSC	-	0.25 M Na_2SO_4	1.90%	15
2007	WO_3–|2xDSSC|–Pt	PV-PEC	-	Pt	H_2	WO_3	2xDSSC	-		2.50%	16
2008	TiO_2–Cu-Ti-O	PEC	-	-	H_2	TiO_2	-	$Cu_{0.74}Ti_{0.26}O_x$	1 M KOH (anode) 0.1 M Na_2HPO_4 (cathode)	0.30%**	17
2009	N-TiO_2/Cu	Photocatalytic	-	Cu	Methane, H_2	N-TiO_2	-	-	Gaseous CO_2 (H_2O satd.)	0.0148%	18
2009	$BiVO_4$+$SrTiO_3$:Rh/Ru	Photocatalytic	-	Ru	H_2	$BiVO_4$	-	$SrTiO_3$:Rh	Aqueous H_2SO_4 (pH 3.5)	0.12%	19
2010	RuO_2/WO_3|2jn-Si|–Ni-Mo	PV-PEC	RuO_2	Ni-Mo	H_2	WO_3	2jn-Si	-	0.33 M H_3PO_4	3%	20
2011	TiO_2–p-InP/RuCP	PEC	-	Dual Ru polypyridyl complex polymer	Formate	TiO_2	-	p-InP	0.01 M $NaHCO_3$ (CO_2 satd.)	0.04%	21
2011	Co|3jn-Si|NiMoZn	Buried PV	Co-P_i	NiMoZn	H_2	-	3jn-Si	-	0.5 M K-B_i + 1.5 M KNO_3	4.7%	22
2012	WO_3–|1xDSSC|–Pt	PV-PEC	-	Pt	H_2	WO_3	1xDSSC	-	1 M $HClO_4$	3.10%	23
2013	$SrTiO_3$–p-InP/RuCP	PEC	-	Dual Ru polypyridyl complex polymer	Formate	$SrTiO_3$	-	p-InP	0.1 M $NaHCO_3$ + H_3PO_4 (pH 7.7) (CO_2 satd. at the cathode)	0.14%**	24
2013	Co-Pi/W-$BiVO_4$–|2jn-Si|–Pt	PV-PEC	Co-P_i	Pt	H_2	W-$BiVO_4$	2jn-Si	-	0.1 M K-P_i	4.9%	25

*Obtained under concentrated sunlight

**Obtained with a small chemical bias

Notation

The notation is written from the water oxidation side (left) to the reduction side (right). Only photoactive materials and co-catalysts are given. Materials for interconnects, back contacts *etc.* are omitted. The following symbols are used to indicate connections between active materials:

	Buried interface: semiconductor shielded entirely from electrolyte (*e.g.* |1jn-Si| = single junction silicon PV with protective coating on both sides)
/	Non-buried interface: semiconductor in contact with electrolyte (*e.g.* p-InP/Pt = Pt islands deposited on a p-InP photoelectrode)
–	Wired: electrodes are electrically connected through a wire (*e.g.* TiO_2–Pt = TiO_2 photoelectrode externally connected with a Pt counter electrode)
$–(I_3^-/I^-)–$	Redox mediator: electrons are shuttled between electrodes *via* ionic species
+	No connection: different particles are mixed together in a suspension, without wiring or mediator

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