

Electronic Supplementary Information

Earth-abundant Cu-based metal oxide photocathodes for photoelectrochemical water splitting

Changli Li^{a*}, Jingfu He^{a*}, Yequan Xiao^b, Yanbo Li^{b*}, Jean-Jacques Delaunay^{c*}

^aSchool of Materials, Sun Yat-sen University, Guangzhou 510275, China

^bInstitute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China

^cSchool of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

*Corresponding authors, emails: lichli5@mail.sysu.edu.cn (C. Li), hejf27@mail.sysu.edu.cn (J. He), yanboli@uestc.edu.cn (Y. Li), jean@mech.t.u-tokyo.ac.jp (J. J. Delaunay).

Table S1. Selected representative results of Cu₂O based solar cells

Device structure	Modification	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	Ref.
Cu/Cu₂O	Cu ₂ O: thermal oxidation	8.33	0.36	-	1.76 (AM 1)	60
p-Cu₂O/n-Cu₂O	Cu ₂ O: electrodeposition	4.07	0.62	42	1.06	73
Cu₂O/ZnO/ITO/MgF₂	Cu ₂ O: thermal oxidation ZnO: ion beam sputtering	6.78	0.60	50	2.01	68
Cu₂O/AZO	Cu ₂ O: thermal oxidation AZO: PLD	~8	~0.5	~55	2.2	83
Cu₂O/ZnO/AZO	Cu ₂ O: thermal oxidation ZnO, AZO: PLD	9.69	0.71	60	4.13	84
Cu₂O/a-ZTO/AZO	Cu ₂ O: electrodeposition; a-ZTO (amorphous zinc-tin oxide) and ZnO: Al: ALD	7.25	0.62	63.1	2.85	90
Cu₂O/Ga₂O₃/AZO	Cu ₂ O: thermal oxidation Ga ₂ O ₃ : PLD	9.99	0.80	67	5.38	84
Cu₂O: Na/Ga₂O₃/AZO	Cu ₂ O: Na: thermal oxidation Ga ₂ O ₃ : PLD	10.18	0.81	67	5.53	85
Cu₂O/Ga₂O₃/ZnO: Al	Cu ₂ O: electrodeposition; Ga ₂ O ₃ and ZnO: Al: ALD	7.37	1.20	44.7	3.97	90
Cu₂O/Ga₂O₃/AZO	Cu ₂ O: CVD; Ga ₂ O ₃ and ZnO: Al: ALD	2	1.78	-	2.36	94
Cu₂O/Zn_{0.91}Mg_{0.09}O/AZO	Cu ₂ O: thermal oxidation Zn _{1-x} Mg _x O: PLD	9.38	0.73	63	4.31	86

p-Cu₂O:Na/ Cu₂O:Mn/AZO	Cu ₂ O:Na: thermal oxidation Cu ₂ O:Mn: electrodeposition	~9	0.78	60	4.21	74
p-Cu₂O:Na/Cu₂O: Mn/Zn-Ge-O/AZO	Cu ₂ O:Na: thermal oxidation Cu ₂ O:Mn: electrodeposition Zn-Ge-O: PLD	10.1	0.84	56	4.74	75
Cu₂O:Na/Al_{0.025}Ga_{0.975}O /AZO/MgF₂	Cu ₂ O:Na: thermal oxidation Al _{1-x} Ga _x -O: PLD	10.95	0.84	66	6.1	87
Cu₂O:Na/Zn_{0.38}Ge_{0.62}O/ AZO/MgF₂	Cu ₂ O:Na: thermal oxidation Zn _{1-x} Ge _x -O: PLD	~11	~1.2	60	8.1	88

Table S2. Selected representative reports of Cu-based metal oxide photocathodes in PEC cells

Device structure	Photocurrent (mA/cm ²); applied bias	Onset potential (V vs. RHE)	Stability (<i>J</i> / <i>J</i> ₀); time; applied bias (V vs. RHE)	Maximum STH or IPCE (%)	Faradaic efficiency	Electrolyte; light source	Ref
Cu₂O/TiO₂	-0.7; -1 V vs. Ag/AgCl	~0 V vs. Ag/AgCl	-	-	-	0.1 M sodium acetate solution; Xe lamp (700 mW/cm ²)	102
Cu₂O/carbon	-3.95; 0 V vs. RHE	~0.6	~80 %; ~20 min; 0	0.56	-	1 M NaSO ₄ solution; AM 1.5G (100 mW/ cm ²)	96
FTO/Au/Cu₂O/ AZO/TiO₂/Pt	-7.6; 0 V vs. RHE	0.35	~33%; ~20 min; 0	~0.78	~100%	1 M NaSO ₄ -0.1 M potassium phosphate (pH = 4.9); AM 1.5G (100 mW/ cm ²)	13
FTO/Au/Cu₂O/ AZO/TiO₂/Pt	-4.5; 0 V vs. RHE	~0.4	100%; 1 h; 0	~0.66	-	1 M NaSO ₄ -0.1 M potassium phosphate (pH = 4.9); AM 1.5G (100 mW/ cm ²)	67
FTO/Au/Cu₂O/ AZO/TiO₂/Pt	-6.0; 0 V vs. RHE	0.55	-	~1.5	~100%	0.5 M NaSO ₄ - 0.1 M potassium phosphate (pH = 5); AM 1.5G (100 mW/cm ²)	97

FTO/Au/Cu₂O/ AZO/TiO₂/ RuO_x	-5.0; 0 V vs. RHE	0.5	~100%; 4 h; 0	~1.1	~100%	0.5 M NaSO ₄ - 0.1 M potassium phosphate (pH = 5); AM 1.5G (100 mW/cm ²)	97
FTO/Au/Cu₂O/ AZO/TiO₂/ RuO_x	-5.2; 0 V vs. RHE	0.55	~100%; 25 h; 0	-	-	1 M NaSO ₄ -0.1 M potassium phosphate (pH = 4.9); AM 1.5G (100 mW/ cm ²)	103
FTO/Au/Cu₂O/ AZO/TiO₂/ MoS_x	-4.8; 0 V vs. RHE	0.45	~100%; 10 h; 0	-	~100%	0.5 M NaSO ₄ - 0.2 M potassium phosphate (pH = 4); AM 1.5G (100 mW/cm ²)	104
FTO/Au/Cu₂O/ AZO/TiO₂/ Ni-Mo	-6.3; 0 V vs. RHE	0.53	~25%; 10 h; 0	-	~100%	1 M KOH (pH = 13.6); AM 1.5G (100 mW/ cm ²)	105
FTO/Au/Cu₂O/ AZO/TiO₂/ RuO_x	-5.5; 0 V vs. RHE	0.5	--	2.5 for Cu ₂ O- perovskite solar cell tandem device	~100%	0.5 M Na ₂ SO ₄ - 0.1 M KH ₂ PO ₄ solution (pH = 5); AM 1.5G (100 mW/cm ²)	124
FTO/Cu/Cu₂O nanowires/AZ O/TiO₂/RuO_x	-8.0; 0 V vs. RHE	0.48	75%; 55 h; 0	0.88	~100%	0.5 M Na ₂ SO ₄ - 0.1 M KH ₂ PO ₄ solution (pH = 5); AM 1.5G (100 mW/cm ²)	118
FTO/CuO:NiO /Cu₂O/AZO/Ti O₂/RuO_x	-5.2; 0 V vs. RHE	~0.55	~100%; 5 h; 0	~1.1	~100%	0.5 M Na ₂ SO ₄ - 0.1 M KH ₂ PO ₄ solution (pH = 5); AM 1.5G (100 mW/cm ²)	120
FTO/NiO/p-n Cu₂O/AZO/Ti O₂/Pt	-2.74; 0 V vs. RHE	0.61	18%; 2 h; 0	0.46	-	0.5 M Na ₂ SO ₄ - 0.1 M KH ₂ PO ₄ solution(pH=4.1 5); AM 1.5G (100 mW/cm ²)	121
FTO/Au/Cu₂O/ SnO₂/RuO_x	-4; 0 V vs. RHE	~0.35	90%; 57 h; 0	~0.4	~100%	0.5 M NaSO ₄ - 0.1 M KH ₂ PO ₄ solution (pH = 5); AM 1.5G (100 mW/cm ²)	108
FTO/Au/Cu₂O/ ZnS/TiO₂/Pt	-2; 0 V vs. RHE	0.72	-	~0.6	~100%	KH ₂ PO ₄ buffer solution (pH = 7); AM 1.5G (100 mW/cm ²)	109

Cu/Cu₂O/ Ga₂O₃/TiO₂/Pt	-3; 0 V vs. RHE	-1.02	~60%; 2 h; 0	0.78	-	0.5 M Na ₂ SO ₄ - 0.1 M KH ₂ PO ₄ solution (pH = 4.3); AM 1.5G (100 mW/cm ²)	14
Cu₂O/Ga₂O₃/ AZO/TiO₂	-6.5; 0 V vs. RHE	~1	~100%; 20 min; 0	~1.6	-	0.5 M NaSO ₄ - 0.1 M KH ₂ PO ₄ (pH = 5); AM 1.5G (100 mW/cm ²)	111
Dual Cu₂O/Ga₂O₃/ TiO₂/RuO_x photocathode	~7; 0 V vs. RHE	0.9	~100%; 2 h; 0	1.9	~100%	0.5 M NaSO ₄ - 0.1 M KH ₂ PO ₄ - 2 M KOH (pH = 5.1); AM 1.5G (100 mW/cm ²)	112
FTO/Au/Cu₂O nanowires/ Ga₂O₃/TiO₂/Ru O_x	~10; 0 V vs. RHE	~1	~100%; 100 h; 0.5	~3 for Cu ₂ O- BiVO ₄ tandem device	~100%	0.5 M Na ₂ SO ₄ , 0.1 M sodium phosphate (pH = 5); AM 1.5G (100 mW/cm ²)	28
FTO/Au/CuSC N/Cu₂O/Ga₂O₃/ TiO₂/RuO_x	-6.4; 0 V vs. RHE	~1	~94%; 60 h; 0.5	4.55 for Cu ₂ O- perovskite solar cell tandem device	~100%	0.5 M Na ₂ SO ₄ , 0.1 M sodium phosphate (pH = 5); AM 1.5G (100 mW/cm ²)	15
p-n Si microwires/Cu ₂O/Ga₂O₃/TiO₂ /RuO_x tandem structure	-10; 0 V vs. RHE	1.35	100%; 200h; 1	5.51	-	0.5 M Na ₂ SO ₄ and 0.1 M phosphate solution (pH=5) ; AM 1.5G (100 mW/cm ²)	113
FTO/Au/CuO/ CdS/TiO₂/Pt	-1.68; 0 V vs. RHE	0.45	100%; 30 min; 0	~0.24	~100%	1 M phosphate buffer (pH=7); AM 1.5G (100 mW/cm ²)	16
FTO/CuO/AZ O/TiO₂/Au-Pd	-5.3; 0 V vs. RHE	0.53	87%; 5 h; 0	~0.8	98%	0.1 M Na ₂ SO ₄ (pH=5.84); AM 1.5G (100 mW/cm ²)	170
FTO/CuBi₂O₄/ Pt	-0.5; 0.4 V vs. RHE	~1	~10%; 3 min; 0.6	IPCE: ~10% @ 400 nm, 0.6 V vs. RHE	-	Ar-purged 0.3 M K ₂ SO ₄ and 0.2 M phosphate buffer (pH=6.65); AM 1.5G (100 mW/cm ²)	18

FTO/CuBi ₂ O ₄	-0.3; 0.6 V vs. RHE	~0.8	20%; 15 min; 0.6	IPCE: ~14% @ 550 nm, 0.6 V vs. RHE, O ₂ reduction reaction	-	Ar-purged 0.3 M K ₂ SO ₄ and 0.2 M phosphate buffer (pH=6.65); AM 1.5G (100 mW/cm ²)	180
FTO/Cu:NiO/CuBi ₂ O ₄	-1; 0.4 V vs. RHE	~0.8-0.9	~50%; 15 min; 0.6	APCE: ~9% @ 550 nm, 0.6 V vs. RHE	-	Ar-purged 0.3 M K ₂ SO ₄ and 0.2 M phosphate buffer (pH=6.65); AM 1.5G (100 mW/cm ²)	183
FTO/CuBi ₂ O ₄ /CdS/TiO ₂ /Pt	-1; 0 V vs. RHE	~0.6	~60%; 3 h; 0	~0.13	~91%	Ar-purged 0.3 M K ₂ SO ₄ and 0.2 M phosphate buffer (pH=6.65); AM 1.5G (100 mW/cm ²)	181
FTO/CuBi ₂ O ₄ /CdS/TiO ₂ /RuO _x behind BiVO ₄	-0.2; 0.4 V vs. RHE	~0.73	~80%; 1 h; 0	IPCE: ~6% @ 450 nm, 0.6 V vs. RHE	~100%	Ar-purged 0.3 M K ₂ SO ₄ and 0.2 M phosphate buffer (pH=6.8); AM 1.5G (100 mW/cm ²)	20
FTO/NiO/CuBi ₂ O ₄	-0.5; 0.4 V vs. RHE	~1	~50%; 3 h; 0.4	-	-	Ar-purged 0.1 M potassium phosphate (KPi) buffered solution (pH=8.55); AM 1.5G (100 mW/cm ²)	189
FTO/CuO/CuBi ₂ O ₄ /Pt	~0.3; 0.6 V vs. RHE	~1	60%; 20 min; 0.6	IPCE: ~15% @ 600 nm, 0 V vs. RHE	-	Ar-purged 0.3 M K ₂ SO ₄ , 0.1 M phosphate (pH=6.8); AM 1.5G (100 mW/cm ² ; λ>420 nm)	187

FTO/ Bi-Ag-Cu oxide/Pt (Bi:Ag:Cu=22:3:11)	-0.06; 0.6 V vs. RHE	~1	~100%; 45 min; 0.6	-	-	Ar-purged 0.1 M Na ₂ SO ₄ and 0.1 M phosphate buffer (pH=6.8); AM 1.5G (100 mW/cm ²)	194
FTO/CuBi₂O₄/Ag-CuBi₂O₄/Pt	-0.6; 0.5 V vs. RHE	~1.1	~50%; 30 min; 0.6	IPCE: ~3% @ 450 nm, 0.6 V vs. RHE	-	Ar-purged 0.1 M NaOH solution (pH=12.8); AM 1.5G (100 mW/cm ²)	178
FTO/porous CuBi₂O₄	-0.9; 0 V vs. RHE	1	~34%; 2 h; 0.6	-	-	Ar-purged 0.3 M K ₂ SO ₄ and 0.2 M phosphate buffer (pH=6.65); AM 1.5G (100 mW/cm ²)	182
FTO/IO CuFeO₂/C₆₀/CoFe LDH	-4.86; 0 V vs. RHE	0.65	~60%; 1 h; 0.25	IPCE: 17.5% @ 600 nm, 0 V vs. RHE	85-100%	Ar-purged 1 M NaOH (pH = 13.5); AM 1.5G (100 mW/cm ²)	25
FTO/CuFeO₂	-0.085; 0.6 V vs. RHE	0.98	~19%; 20 min; 0.6	IPCE: 2.2% @ 350 nm, 0.6 V vs. RHE	-	Ar-purged 1 M NaOH; AM 1.5 G (100 mW/cm ²)	23
FTO/CuFeO₂/CdS/ TiO₂/ Pt	-0.4; 0 V vs. RHE	0.40	~100%; 50 min; -0.2		~100%	Ar-purged 0.5 M Na ₂ SO ₄ (6.1); AM 1.5G (100 mW/cm ²)	24
FTO/CuAlO₂-CuFeO₂ host-guest	-2.4; 0.4 V vs. RHE	0.75	-	IPCE: 9% @ 600 nm, 0.4 V vs. RHE	-	O ₂ -purged 1 M NaOH (O ₂ reduction); AM 1.5G (100 mW/cm ²)	240
FTO/Oxygen-intercalated CuFeO₂/RGO/ NiFe LDH	-2.4; 0.4 V vs. RHE	~0.8	~100%; 20 min; 0.4	IPCE: 7.5% @ 600 nm, 0.4 V vs. RHE	94%	Ar-purged 1M NaOH; AM 1.5G (100 mW/cm ²)	226
FTO/CuFeO₂ decorated on SiO₂ microspheres	-0.2; 0.6 V vs. RHE	~0.9	-	-	-	O ₂ -purged 1M NaOH; AM 1.5G (100 mW/cm ²)	241

FTO/CuFeO₂/						O ₂ -purged 1 M	
CuAlO₂				IPCE: 2% @		NaOH (O ₂	
decorated on	-1.09; 0.6 V	~0.85	-	600 nm, 0.6	-	reduction); AM	242
PE-SiO₂	vs. RHE			V vs. RHE		1.5G (100	
microspheres						mW/cm ²)	

Maximum STH: Maximum solar-to-hydrogen efficiency; IPCE: Incident photon-to-current conversion efficiency; APCE: Absorbed photon-to-current efficiency