

Electronic Supplementary Information

CoOOH/CdIn₂S₄ Film Photoanodes Driving Unbiased Tandem Cells towards Simultaneously Efficient Oxidation of Benzyl Alcohol and Selective Generation of Ethanol from CO₂ Reduction

Yiqing Wei,^a Huichao He,^{b*} Shuyuan Yang,^c Yongcai Zhang,^d Xin Zhou,^{c*} Zhigang Zou^{a, e} and Yong Zhou^{a, e, f*}

^aNational Laboratory of Solid-State Microstructures, Collaborative Innovation Center of Advanced Microstructures, School of Physics, Jiangsu Key Laboratory of Nanotechnology, Eco-materials and Renewable Energy Research Center (ERERC), Nanjing University, Nanjing, 210093, Jiangsu, P. R. China.

^bSchool of Metallurgy and Materials Engineering, Chongqing University of Science and Technology, Chongqing 401331, P. R. China.

^cCollege of Environment and Chemical Engineering, Dalian University, Dalian, 116622, Liaoning, P. R. China.

^dSchool of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225009, P. R. China.

^eSchool of Science and Engineering, The Chinese University of Hongkong (Shenzhen), Shenzhen, Guangdong 518172, P. R. China.

^fSchool of Chemical and Environmental Engineering, Anhui Polytechnic University, Wuhu 241000, P. R. China.

*Corresponding authors.

zhouyong1999@nju.edu.cn (Y. Zhou)

hehuichao@cqust.edu.cn (H. Chao)

zhouxin@dlu.edu.cn (X. Zhou)

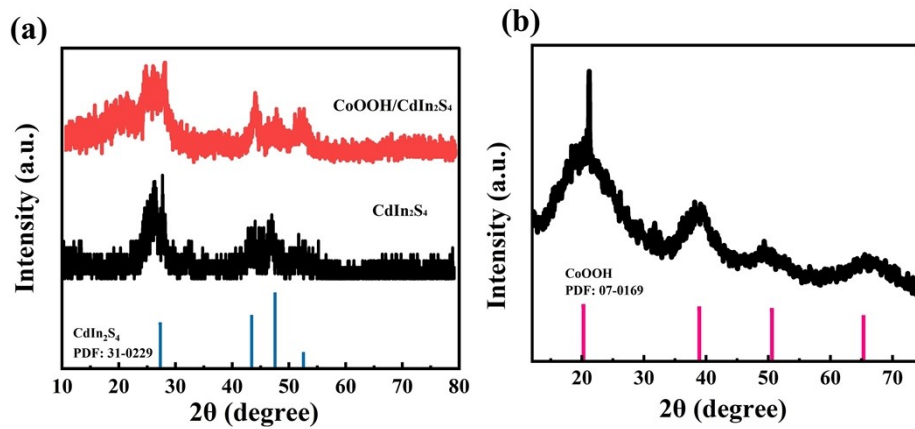


Fig. S1 The XRD patterns of (a) CdIn₂S₄ and CoOOH/CdIn₂S₄, (b) CoOOH.

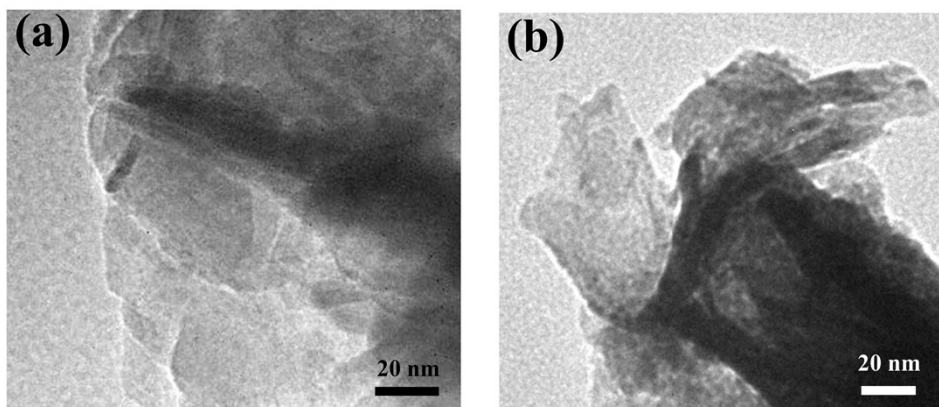


Fig. S2 TEM image of CdIn₂S₄ and CoOOH/CdIn₂S₄.

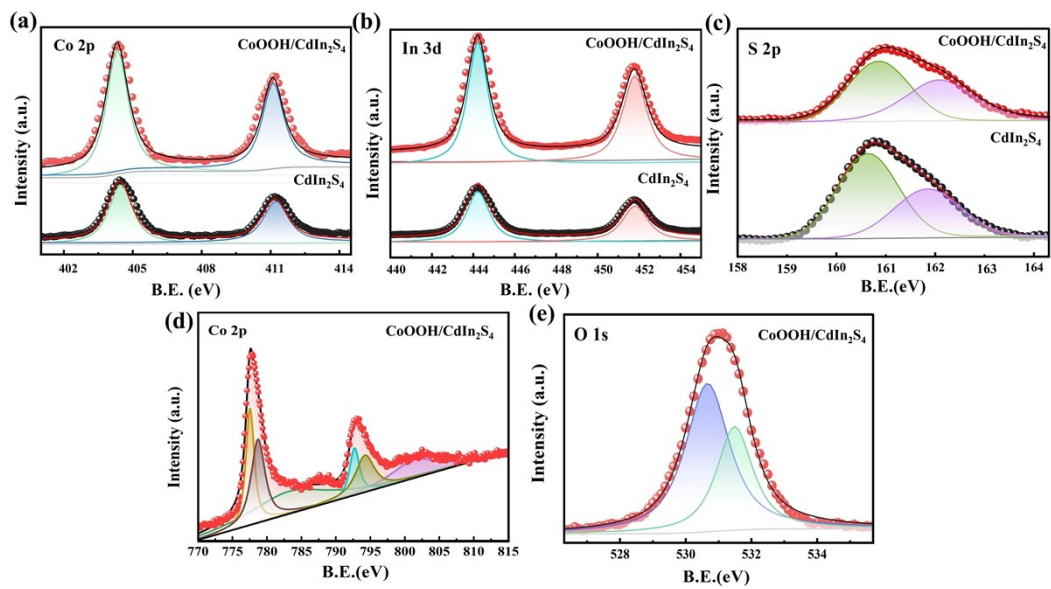


Fig. S3 XPS data collected from the CoOOH/CdIn₂S₄ sample.

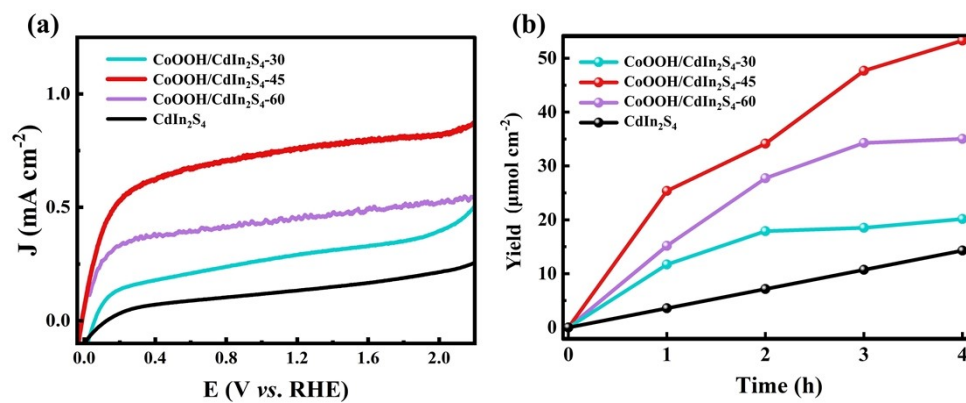


Fig. S4 (a) LSV curves of CdIn₂S₄, CoOOH/CdIn₂S₄-30, CoOOH/CdIn₂S₄-45 and CoOOH/CdIn₂S₄-60 photoanode in benzyl alcohol aqueous electrolyte under AM 1.5 G irradiation; (b) Yield plots of CdIn₂S₄, CoOOH/CdIn₂S₄-30, CoOOH/CdIn₂S₄-45 and CoOOH/CdIn₂S₄-60 photoanode for the production of benzaldehyde in benzyl alcohol aqueous electrolyte.

Table S1 Yield and selectivity of photoanodes for the production of benzaldehyde and benzoic acid in benzyl alcohol aqueous electrolyte during 4 h of reaction.

Photoanode	Benzaldehyde ($\mu\text{mol cm}^{-2}$)	Benzoic acid ($\mu\text{mol cm}^{-2}$)	Selectivity for benzaldehyde
CdIn ₂ S ₄	14.28	7.49	65.59%
CoOOH/CdIn ₂ S ₄ -30	20.14	9.87	67.11%
CoOOH/CdIn ₂ S ₄ -45	53.28	0.46	99.14%
CoOOH/CdIn ₂ S ₄ -60	34.04	11.18	75.28%

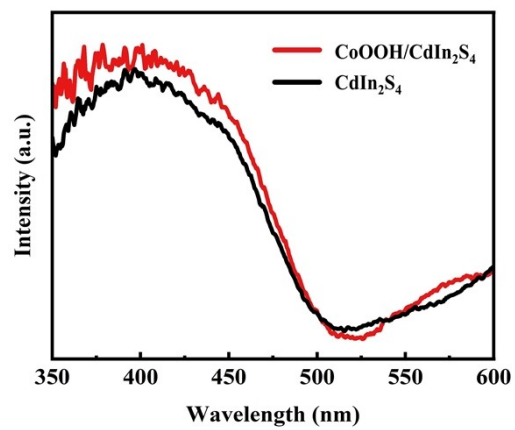
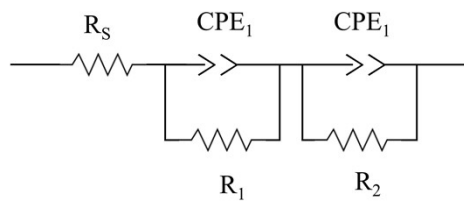


Fig. S5 UV-vis light absorption spectra of CdIn₂S₄ and CoOOH/CdIn₂S₄ film.

Table S2 The fitted results for the EIS shown in **Fig. 3c**.

Sample	$R_s(\Omega)$	CPE_1-T	CPE_1-P	$R_1(\Omega)$	CPE_2-T	CPE_2-P	$R_2(\Omega)$
$CdIn_2S_4$	24.39	1.47×10^{-4}	0.51	538.10	2.56×10^{-5}	0.91	8259
$CoOOH/Cd_2In_2S_4$	23.11	1.53×10^{-4}	0.52	125.50	3.50×10^{-5}	0.72	1929

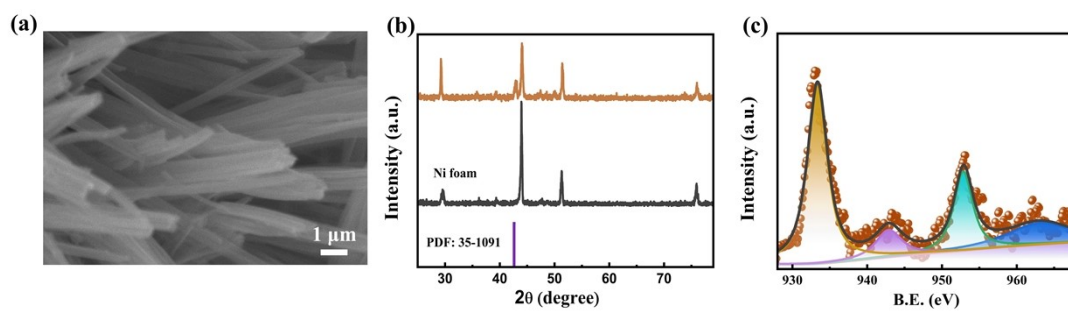


Fig. S6 SEM, XRD and XPS for Cu₂O film on Ni foam.

Table S3 The products in reported tandem PEC cells with Cu₂O cathode for CO₂ reduction.

Product	Photoanode	Photocathode	External bias or not	Reference
C₂H₅OH	CoOOH/CdIn₂S₄	Cu₂O	no	This work
HCOOH	Ti/NtTiO ₂ /CuO	Cu ₂ O/GDL	no	<i>ChemSusChem.</i> , 2019, 12, 4274.
CO	Si	Ag	yes	<i>Nat Commun.</i> , 2022, 13, 7111.
CO, H ₂	IrO _x /a-Si	CoPc/CNT-C-CsFAPb(I _{Br}) ₃	no	<i>Adv. Energy Mater.</i> , 2020, 10, 2002105.
CO, H ₂	CH ₃ NH ₃ PbI ₃	ZnO@ZnTe@CdTe-Au	no	<i>ACS Nano.</i> , 2016, 10, 6980.
HCOOH	NiOOH/ α -Fe ₂ O ₃	Bi/GaN/Si	yes	<i>Nat Commun.</i> , 2023, 14, 1013.
HCOOH	mTiO ₂	mITO	no	<i>Nat Synth.</i> , 2022, 1, 77.
HCOOH	PVK IOTiO ₂ FDH	BiVO ₄	no	<i>Joule.</i> , 2021, 5, 2771.
CO, HCOOH	BiVO ₄	Cu-In	yes	<i>Chem. Eng. J.</i> , 2019, 355, 1.
C ₂ H ₅ OH, C ₂ H ₄	Si	Cu	yes	<i>Nat Commun.</i> , 2022, 13, 7111.
CH ₃ OH, CH ₃ OH, C ₂ H ₅ OH, CH ₃ COOH,	TNT	Pt/GA/CF	yes	<i>Chem. Eng. J.</i> , 2017, 322, 22.

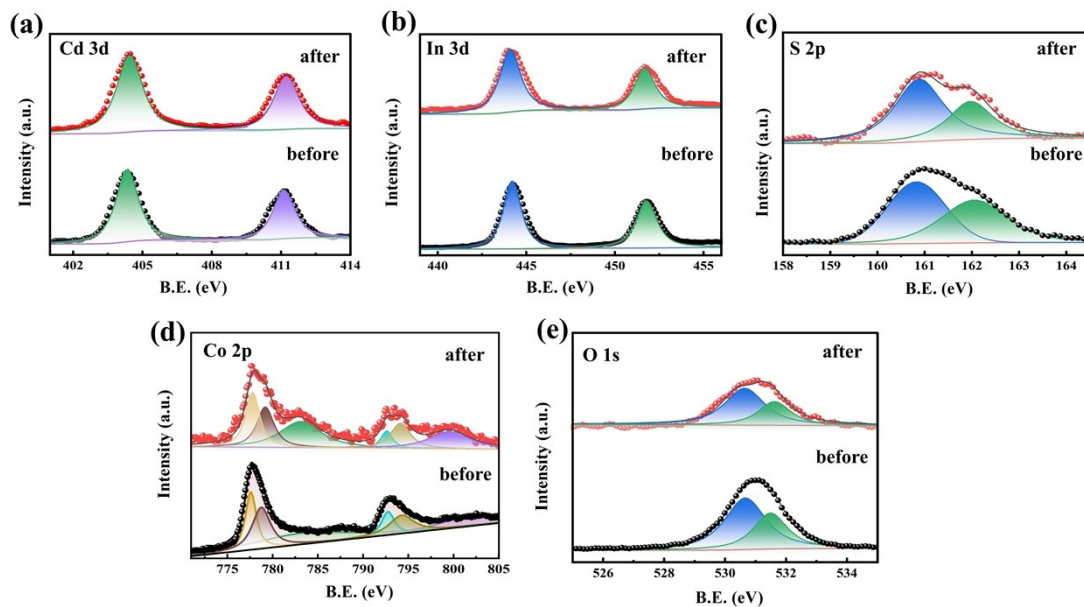


Fig. S7 XPS spectra of CoOOH/CdIn₂S₄ photoanode before and after 4 h of testing.