Multi-layered photocathodes based on Cu₂ZnSnSe₄ absorber and MoS₂ catalyst for the Hydrogen Evolution Reaction

Sergi Grau,^a Sergio Giraldo,^b Edgardo Saucedo,^b Joan Ramón Morante,^b Antoni Llobet^{*a,c} and Carolina Gimbert-Suriñach^{*a}

^a Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain. Email: <u>cgimbert@icig.cat</u>; <u>allobet@icig.cat</u>

^{b.}Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 08930 Sant Adrià de Besòs, Spain.
^{c.} Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, Spain.

Supporting information

Outline

Absorber characterization	
Optical band gap determination	
Figure S1. Tauc Plot and EQE of CZTSe photoelectrode.	Page S2
Table S1. Collected optical band gaps and EQE together with reference	Dago S2
values.	Fage 33
Spectroscopic, morphological and compositional characterization	
Figure S2. rRaman, SEM and XRF.	Page S3
Study of MoS ₂ loading on ITO	
Figure S3. Performance of ITO-MoS2 electrodes versus loading of	Page S3
electrocatalyst.	Tage 00
Figure S4. LSV of ITO-MoS ₂ in pH 2 with different loading of electrocatalyst.	Page S3
Figure S5. Transmittance spectra of ITO-MoS ₂ electrodes with different	Page S4
loading of electrocatalyst.	r ugo o r
Study of stability of ITO-MoS ₂ eletrodes	
Figure S6. LSV of ITO-MoS ₂ electrodes in different pHs.	Page S4
Figure S7. Long term CP experiments of ITO-MoS ₂ electrodes in pH 2 and	Page S4
associated LSV before and after the CP.	i ago o i
Figure S8-S10. SEM images of ITO-MoS ₂ electrodes before and after CP	Page S5
experiments.	g
Additional information of ITO-MoS ₂ electrodes and CZTSe-MoS ₂	
photoelectrodes	
Figure S11. E-t profiles for electrodeposition and photoelectrodeposition of	Page S6
MoS ₂ .	ge e e
Figure S12. LSV of CZTSe-MoS ₂ in pH 2 to see transformation of MoS ₃ to	Page S6
MoS ₂ .	g
Figure S13. LSV of CZTSe-MoS ₂ in pH 2 before and after 1h CP.	Page S7
Figure S14. J-V curve of an equivalent Mo/CZTSe/CdS/ZnO/ITO PV device.	Page S7
Calculation of Faradaic Efficiency (FE)	Page S8
Figure S15. Hydrogen evolution profile of a CP of CZTSe-MoS ₂ in pH 2.	Page S9
Figure S16. Calibration plots of the Clark sensors.	Page S9
Figure S17. Long term CP of CZTSe-MoS ₂ in pH 2.	Page S10
Figure S18. LSV of CZTSe-MoS ₂ before and after 5h soaking in pH 2.	Page S10
Table S2. Selected relevant photocathodes for the HER reported in the	Dago Q11
literature.	Faye STI
References	Page S12

Optical band gap determination

Optical band gaps of CZTSe/CdS/ZnO/ITO were measured using the diffuse reflectance UV-VIS spectra of the sample. Kubelka-Munk equation (eq 1) can be used to extract the absorption coefficient (α) from the diffuse reflectance spectrum:¹

$$f(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{s}$$
 (eq. 1)

Where R is diffuse reflectance values at a given wavelength and s is the scattering coefficient.

Assuming that *s* is wavelength independent, we can consider that f(R) is directly proportional to α , and f(R) can be used in place of α to make the Tauc plot (eq 2):

$$\alpha h \nu \propto (h \nu - E_a)^{\frac{1}{n}}$$
 (eq. 2)

Where E_g is band gap energy (in eV) and *n* can take a value of $\frac{1}{2}$ for the direct and allowed transition.

Plotting $(\alpha h\nu)^2$ vs $h\nu$ (Tauc plot) E_g value can be calculated extrapolating the linear region to the baseline (Figure S1, left). The values obtained using this method gives an E_g value of 0.96-1.3 eV for CZTSe, 2.1 eV for CdS, 2.9 eV for ITO and 3.4 eV for ZnO, that is in good agreement with the reported values in the literature.^{2,3}

The band gap was also estimated from EQE measurements by derivative way. Since most of the photons with energy higher than band gap will be absorbed by the absorber, EQE should show an abrupt change at the position of the band gap, so at that position the change rate of EQE should be the largest. Thus, differentiate the EQE curve and then fit the corresponding valley with Gauss mode in ORIGIN software to get the center position X_c , known as the inflection point. Finally use the following equation to calculate the E_g :

$$E_g(eV) = \frac{1239.84}{X_c}$$
 (eq. 3)

With a X_c=1172.81 nm, the estimated value for E_g is 1.05 eV (see Figure S1, right).



Figure S1. Left) Tauc plot of Mo/CZTSe/CdS/ZnO/ITO for direct and allowed transitions. *Right)* First derivative of EQE of Mo/CZTSe/CdS/ZnO/ITO used to estimate *E*_g.

Table S1. Band gap values obtained from DRS and EQE compared to data from the literature.

Method	CZTSe (eV)	CdS (eV)	ZnO (eV)	ITO (eV)
DRS (this work)	0.94-1.35	2.0-2.1	3.0-3.4	2.9
EQE (this work)	1.05			
Literature ^{2,3}	0.95	2.4	3.3	2.8



Figure S2. Structural, morphological and compositional characterization of the CZTSe absorber, including Raman spectroscopy with two different excitation wavelengths, 532 nm and 785 nm (A), cross-sectional SEM analysis (B), and XRF thickness and compositional measurements (C).



Figure S3. Potential required to reach -1 mA/cm² (red dots, left y axis) and j reached at -0.3 V (blue dots, right y axis) versus MoS₂ loading.



Figure S4. LSV of ITO covered with different amounts of MoS_2 in pH 2. Counter electrode: Pt mesh. Reference electrode: SCE. Scan rate: 5mV/s. iR drop corrected at 85%.



Figure S5. Transmittance spectra of ITO coated with different amounts of amorphous MoS₂.



Figure S6. LSV of ITO-MoS₂ in different pHs. Scan rate 5mV/s.



Figure S7. Left) CP of ITO-MoS₂ in pH 2 under stirring conditions. *Right)* LSV before and after 11h of CP in pH 2. iR drop corrected at 85%.



Figure S8. SEM images of ITO-MoS₂ after electrodeposition (Top view) with different magnification.



Figure S9. SEM images of the most damaged areas of $ITO-MoS_2$ after 5h of CP, suggesting hydrogen bubbles as responsible for the peeling of the MoS_2 layers.



Figure S10. SEM images of non-damaged areas of ITO-MoS₂ after 1h of CP (A and B) and after 10h (C and D).



Figure S11. E-t curve (photo)electrodeposition of MoS₂ on ITO and Mo/CZTSe/CdS/ZnO/ITO (photo)cathodes. Dashed gray line indicates redox potential for HER at pH 4.5 (electrodeposition conditions).



Figure S12. 1st LSV of CZTSe-MoS₂ in pH 2. Counter electrode: Pt mesh. Reference electrode: SCE. Scan Rate: 5mV/s. Stirring Conditions. iR drop corrected at 85%.



Figure S13. LSV of CZTSe-MoS₂ in pH 2 under 1 sun ilumination (red line), in dark conditions (black dashed line) and after 1 h of CP at -10mA/cm² (blue line). Counter electrode: Pt mesh. Reference electrode: AgCl/Ag. Scan rate: 5mV/s. LSV recorded under stirring conditions. iR drop corrected at 85%.



Figure S14. Left) Photovoltaic J-V curve of Mo/CZTSe/CdS/ZnO/ITO device used in this work.

Calculation of Faradaic efficiency (FE)

The FE of the CP is calculated using the following formula:⁴

$$FE (\%) = \frac{n_{H2 \ detected}}{n_{H2 \ theoretical}} \cdot 100 \tag{eq. 4}$$

Where $n_{H2 \ detected}$ is the number of mols of molecular hydrogen that Clark Electrode have detected and $n_{H2 \ theoretical}$ is the number of theoretical mols of H₂ calculated from the charge that pass through the electrode.

Clark electrode measures partial pressure of H_2 in the headspace of the electrochemical cell. Calibration slope is required to correlate the signal of the Clark Electrode and the amount of H_2 contained in the headspace.

After the CP, the cell is degased with N₂ for 30 min, and different known amounts of H₂ gas were injected in the head space using a Hamilton syringe. By plotting the reponse of the Clark sensor versus the hygrogen volume added it is possible to obatin a calibration line (Figure S15). With the slope of the calibration, we can convert the Clark's values (mV) in volume of H₂. Using the perfect gases equation, we can obtain the number of moles of hydrogen gas produced by the electrode and measured in the headspace:

$$P \cdot V = n \cdot R \cdot T \qquad (eq. 5)$$

Where P is the pressure of the headspace (1atm), R is the gas constant $(0.082 \frac{atm \cdot L}{K \cdot mol})$ and T the temperature (298K).

To calculate the theoretical number of moles from the electrical charge transferred to the electrode:

$$2H^+ + 2e^- \rightarrow H_2$$

$$n_{H2 \ theoretical} = \frac{c}{F \cdot n} \qquad (eq. 6)$$

Where C is the charge (in C) passed through the electrode, F is the faraday constant (96485C) and n the number of electrons involved to form one molecule of hydrogen (2).



Figure S15. Amount of molecular hydrogen evolved (red line) and the calculated from the charge transferred (black dashed line) associated to the CP experiment in Figure 6 of the main manuscript: CP of CZTSe-MoS₂ in pH 2 at -10 mA/cm² in a two-compartment photoelectrochemical cell.



Figure S16. Calibration slope for calculating the FE of the CP experiments in a two-compartment (photo)electrochemical cell for the ITO-MoS₂ electrodes related to CP in Figure 3 of the main manuscript (Left) and CZTSe-MoS₂ photoelectrodes related to CP in Figure 6 of the main manuscript (Right).



Figure S17. CP of CZTSe-MoS₂ in pH 2 at -10 mA/cm² in a two-compartment photoelectrochemical cell.



Figure S18. Polarization curve of CZTSe-MoS₂ (red line) and the same photocathode after 5h soaked in pH 2 (dashed black line).

Table S2. Relevant works on photocathodes using CZTS/Se as absorber, CIS/CIGS and photocathodes with MoS₂ as HER electrocatalyst.

Material	Catalyst	рΗ	j ov	j @10mA/cm2	E onset	Stability	Year	Ref
			(mA⋅cm⁻²)	(V)	(V)			
Mo/CZTS/CdS/TiO ₂	Pt	9.5	-9.0		+0.60		2010	5
Mo/CZTS/CdS/AZO/TiO ₂	Pt	7	-0.80		+0.4	900 s	2013	6
Mo/CZTS/CdS/ In ₂ S ₃	Pt	6.5	-9.3		+0.64	2 h	2015	7
Mo/Ge-CZTS/CdS/In ₂ S ₃	Pt	6.5	-11.1	+0.10	+0.60	2 h	2017	8
Mo/CZTSe/CdS/ZnO/ITO/TiO2	Pt	0	-37.0	+0.27	+0.45	1 h	2018	9
Mo/CZTS/CdS/ZnS	Pt	6.5	-8.0		+0.65	2 h	2019	10
Mo/CuInS ₂ /In ₂ S ₃	Pt	6.5	-15.0	+0.26	+0.72	3 h	2014	11
Mo/CuInS ₂ /TiO ₂	Pt	10	-13.0	+0.15	+0.60	1 h	2014	12
Mo/ (Ag,Cu)GaSe₂/CuGa₃Se₅/CdS	Pt	10	-8.8		+1.0	20 days	2015	13
Mo/Cu(In,Ga)Se₂/Ti/Mo	Pt	6.8	-30.0	+0.42	+0.63	10 days	2015	14
Ti/p-Si	1T-MoS ₂	0	-17.6		+0.25	3 h	2014	15
Cu ₂ O/AZO/TiO ₂	MoS ₂	14	-6.3		+0.48	10 h	2015	16
p-Si	MoS ₂	0	-24.6	+0.082	+0.17	2.8 h	2016	17
Si/SiO ₂ /Mo _x Si/Mo _x O	MoS_2	0	-15.7	+0.09	+0.31	64 days	2017	18
Mo/CZTSe/CdS/ZnO/ITO	MoS ₂	2	-18.1	+0.100	+0.30	3.5h	2019	This work

References

- D. L. Wood and J. Tauc, Weak Absorption Tails in Amorphous Semiconductors, *Phys. Rev. B*, 1972, **5**, 3144–3151.
- 2 K. Kaur, N. Kumar and M. Kumar, Strategic review of interface carrier recombination in earth abundant Cu-Zn-Sn-S-Se solar cells: current challenges and future prospects, *J. Mater. Chem. A*, 2017, **5**, 3069–3090.
- S. Li, C. Ghinea, T. J. M. Bayer, M. Motzko, R. Schafranek and A. Klein, Electrical properties of (Ba, Sr)TiO₃ thin films with Pt and ITO electrodes: Dielectric and rectifying behaviour, *J. Phys. Condens. Matter*, , DOI:10.1088/0953-8984/23/33/334202.
- 4 A. J. Bard and L. R. Faulkner, *Electrochemical methods, fundamentals and applications*, Wiley, 2nd edn., 2001, vol. 60.
- 5 D. Yokoyama, T. Minegishi, K. Jimbo, T. Hisatomi, G. Ma, M. Katayama, J. Kubota, H. Katagiri and K. Domen, H₂ evolution from water on modified Cu₂ZnSnS₄ photoelectrode under solar light, *Appl. Phys. Express*, 2010, **3**, 2–4.
- 6 L. Rovelli, S. D. Tilley and K. Sivula, Optimization and stabilization of electrodeposited Cu2ZnSnS 4 photocathodes for solar water reduction, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8018–8024.
- 7 T. Minegishi, T. Harada, Y. Kuang, F. Jiang, S. Ikeda, Gunawan and K. Domen, Pt/In₂S₃/CdS/Cu₂ZnSnS₄ Thin Film as an Efficient and Stable Photocathode for Water Reduction under Sunlight Radiation, *J. Am. Chem. Soc.*, 2015, **137**, 13691–13697.
- 8 X. Wen, W. Luo, Z. Guan, W. Huang and Z. Zou, Boosting efficiency and stability of a Cu₂ZnSnS₄ photocathode by alloying Ge and increasing sulfur pressure simultaneously, *Nano Energy*, 2017, **41**, 18–26.
- 9 C. Ros, T. Andreu, S. Giraldo, V. Izquierdo-Roca, E. Saucedo and J. R. Morante, Turning Earth Abundant Kesterite-Based Solar Cells into Efficient Protected Water-Splitting Photocathodes, *ACS Appl. Mater. Interfaces*, 2018, **10**, 13425–13433.
- 10 K. Wang, D. Huang, L. Yu, H. Gu, S. Ikeda and F. Jiang, Environmentally friendly Cu₂ZnSnS₄-based photocathode modified with a ZnS protection layer for efficient solar water splitting, *J. Colloid Interface Sci.*, 2019, **536**, 9–16.
- 11 Gunawan, W. Septina, T. Harada, Y. Nose and S. Ikeda, Investigation of the Electric Structures of Heterointerfaces in Pt- and In₂S₃-Modified CuInS₂ Photocathodes Used for Sunlight-Induced Hydrogen Evolution, ACS Appl. Mater. Interfaces, 2015, 7, 16086–16092.
- 12 T. Yamada, T. Hisatomi, M. Nakabayashi, T. Minegishi, G. Ma, J. Zhao, Gunawan, N. Shibata, M. Katayama, M. Zhong, L. Zhang, S. Ikeda and K. Domen, Enhancement of Solar Hydrogen Evolution from Water by Surface Modification with CdS and TiO₂ on Porous CuInS₂ Photocathodes Prepared by an Electrodeposition-Sulfurization Method, *Angew. Chemie Int. Ed.*, 2014, **53**, 11808–11812.
- 13 L. Zhang, T. Minegishi, M. Nakabayashi, Y. Suzuki, K. Seki, N. Shibata, J. Kubota and K. Domen, Durable hydrogen evolution from water driven by sunlight using (Ag,Cu)GaSe₂ photocathodes modified with CdS and CuGa₃Se₅, *Chem. Sci.*, 2015, **6**, 894–901.
- 14 H. Kumagai, T. Minegishi, N. Sato, T. Yamada, J. Kubota and K. Domen, Efficient solar hydrogen production from neutral electrolytes using surface-modified Cu(In,Ga)Se₂ photocathodes, *J. Mater. Chem. A*, 2015, **3**, 8300– 8307.
- 15 M. J. Shearer, S. Jin, Q. Ding, D. Liang, M. Cabán-Acevedo, A. S. Daniel, C. R. English, F. Meng and R. J. Hamers, Efficient Photoelectrochemical Hydrogen Generation Using Heterostructures of Si and Chemically Exfoliated Metallic MoS₂, J. Am. Chem. Soc., 2014, **136**, 8504–8507.
- 16 C. G. Morales-Guio, L. Liardet, M. T. Mayer, S. D. Tilley, M. Grätzel and X. Hu, Photoelectrochemical hydrogen production in alkaline solutions using Cu₂O coated with earth-abundant hydrogen evolution catalysts, *Angew. Chemie Int. Ed.*, 2015, **54**, 664–667.
- 17 K. C. Kwon, S. Choi, K. Hong, C. W. Moon, Y. S. Shim, D. H. Kim, T. Kim, W. Sohn, J. M. Jeon, C. H. Lee, K. T. Nam, S. Han, S. Y. Kim and H. W. Jang, Wafer-scale transferable molybdenum disulfide thin-film catalysts for photoelectrochemical hydrogen production, *Energy Environ. Sci.*, 2016, 9, 2240–2248.

18 L. A. King, T. R. Hellstern, J. Park, R. Sinclair and T. F. Jaramillo, Highly Stable Molybdenum Disulfide Protected Silicon Photocathodes for Photoelectrochemical Water Splitting, ACS Appl. Mater. Interfaces, 2017, 9, 36792– 36798.