# Supporting information

# Origin of photoelectrochemical CO<sub>2</sub> reduction on bare Cu(In,Ga)S<sub>2</sub> (CIGS) thin films in aqueous media without co-catalysts

Rajiv Ramanujam Prabhakar<sup>1,5†</sup>, Sudhanshu Shukla<sup>2,3,4†\*</sup>, Haoyi Li<sup>1,5</sup>, R. Soyoung Kim<sup>5</sup>, Wei Chen<sup>6</sup>, Jérôme Beaudelot<sup>3,7</sup>, Jan D'Haen<sup>4</sup>, Daniely Reis Santos<sup>2,3,4</sup>, Philippe M. Vereecken<sup>3,7,8</sup>, Gian-Marco Rignanese<sup>6,9</sup>, Ethan J. Crumlin<sup>5,10</sup>, Junko Yano<sup>1,11</sup>, Bart Vermang<sup>2,3,4</sup>, and Joel W. Ager III<sup>1,5,12,13\*</sup>

<sup>1</sup> Liquid Sunlight Alliance, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

<sup>2</sup> Imec, Imo-imomec, Thor Park 8320, 3600 Genk, Belgium

<sup>3</sup> EnergyVille, Thor Park 8320, 3600 Genk, Belgium

<sup>4</sup>Hasselt University, Imo-imomec, Martelarenlaan 42, 3500 Hasselt, Belgium

<sup>5</sup> Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

<sup>6</sup> UCLouvain, Institut de la Matiere Condensée et des Nanosciences (IMCN), Louvain-la-Neuve 1348, Belgium

<sup>7</sup> Imec Leuven Kapeldreef 75, 3001 Leuven, Belgium

<sup>8</sup> KU Leuven, M<sup>2</sup>S, cMACS, Celestijnenlaan 200F, 3001 Leuven, Belgium

<sup>9</sup> WEL Research Institute, 1300 Wavre, Belgium

<sup>10</sup> Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, United States

<sup>11</sup> Molecular Biophysics and Integrated Bioimaging Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, United States

<sup>12</sup> Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, CA 94720, USA

<sup>13</sup> Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California94720, United States

<sup>†</sup>Equal contribution

#### **Experimental details**

# Cu(In,Ga)S<sub>2</sub> CIGS Synthesis

CIGS films were fabricated by  $H_2S$  sulfurization of the pre-sputtered CuGa and In multistack films. First, 500 nm of back contact Mo was deposited by sputtering on a soda lime glass substrate. Subsequently, a 10x stack of CuGa/In was deposited on the Mo back contact by sputtering. Sulfurization was performed in an Annealsys AS-ONE rapid thermal processing (RTP) system to complete the CIGS layers. The procedure consists of a temperature stabilizing stage at 150 °C. Afterwards  $H_2S$  and  $N_2$  gases were introduced until the pressure of 600 mbar is reached. The system is then ramped to the sulfurization temperature of 580 °C at ramping rate of 2.4 °C/s. After 30 mins of annealing, the system is cooled down in a controlled manner to 150 °C, before the termination of the process and cooling to room temperature. Before sulfurization, the stack was annealed in  $N_2$ atmosphere at 300 °C.

# CuInGa(S,Se)<sub>2</sub> CIGSSe Synthesis

The Cu(In,Ga)(S,Se) on Mo/glass samples were prepared in a two-step process using selenization and sulfurization of a metallic precursor stack. First, 500 nm of back contact Mo was deposited by sputtering on a soda lime glass substrate. Subsequently, a 10x stack of CuGa/In was deposited on the Mo back contact by sputtering. Finally, a 2  $\mu$ m thick Se layer was evaporated on top of the precursor stack.

This glass/Mo/(CuGa/In)x10/Se stack was then put inside a closed graphite box into a rapid thermal anneal chamber. In this chamber the sample was rapidly heated at a rate of  $10^{\circ}$ C/s to a temperature of 580°C in an atmosphere of 700 mbar N<sub>2</sub> and 30 mbar H<sub>2</sub>S. Then the sample was annealed for 10 minutes at a temperature of 580°C before the heating was stopped and the sample cooled down naturally over a timeframe of about 10 minutes in the same atmosphere until 250°C. Then the annealing chamber is pumped, and further cooling happens before the sample is removed from the annealing chamber and the graphite box.

# X-ray diffraction (XRD)

Thin film XRD were carried out with a Bruker D8 Advance equipped with a Lynxeye detector and operated with Cu-K<sub> $\alpha$ </sub> X-ray ( $\lambda = 1.5418$  Å) radiation.

#### **Operando** Raman spectroscopy

Operando Raman measurements were carried out in a  $3.5 \text{ cm}^2$ , 4.5 mL electrochemical flow cell (redox.me Raman ECFC) with a Renishaw Virsa<sup>TM</sup> analyser. A film-covered Leica water immersion objective (HC APO, L x63/0.90 NA, 2.2 mm WD) was used to acquire high-resolution spectra during electrochemical operation in CO<sub>2</sub>-purged, 0.1 M potassium bicarbonate electrolyte (pH 6.8), using a platinum wire counter electrode and an eDAQ ET072-1 Leakless Miniature Ag/AgCl reference electrode. A VSP/VMP3 Biologic multichannel potentiostat was used to control the potential of the working electrode *vs* the reference electrode. The selected potential was applied for 30 s before initiating the Raman acquisition and kept the same during the whole measurement time. A laser excitation of 532 nm with a power of 10 mW and spot size of 1  $\mu$ m was used for the measurements. The signal was recorded using 20 s acquisition time and 30 accumulations and then averaged and baseline-subtracted using Renishaw Wire 5 software. Raman measurements on the bare sample were measured in the same set-up, using Olympus 50X long working distance objective.

# Photoluminescence (PL) spectroscopy

The PL measurements were performed in a photospectrometer from PicoQuant FluoTime 300 system with excitation wavelength of 532 nm.

Wide scan PL measurements were performed by global hyperspectral imager (IMA; Photon etc., Canada). The samples were homogeneously excited with a 532 nm laser, and the PL was acquired with a deep cooled Zephir 1.7x InGaAs detector coupled to IMA hyperspectral microscope. The scan was collected from 600 nm - 1647 nm spectral range with spatial resolution of 3 nm. The exposure time was set to 15 sec.

# Secondary -ion mass spectrometry (SIMS)

Time of flight (ToF)-SIMS measurements were performed using ION.TOF NCS instrument (IONTOF GmBH, Muenster, Germany). Sputtering was carried out with a 2 keV  $O_2$  ion beam. The sputter area of 350x350  $\mu$ m<sup>2</sup>, and an analysis area of 100x100  $\mu$ m<sup>2</sup> was used for the depth profiles, with a raster of 128x128 pixels. 15 keV Bi<sup>+</sup> was used as analysis beam.

#### X-ray photoelectron spectroscopy (XPS) characterization

The synchrotron radiation-based XPS experiments in Figure 5 were performed at beamline 9.3.1 at Advanced Light Source (BL 9.3.1 at ALS), Lawrence Berkeley National Laboratory. The photon energy was used as 3.0 keV and the pass energy of the Scienta analyzer (R4000 HiPP-2) was set as 100 eV. The sample holder was electrically connected to a multi-axis manipulator of the end-station. The sample surface and the analyzer nozzle were grounded in the XPS system. The incident angle between the incoming photons and sample surface was kept as 15°. All the spectra were collected at high vacuum (named as HV, 10<sup>-4</sup> Torr). A clean Au foil was utilized to optimize the photon energy intensity at the focal point (0.35 mm away from the front cone) and Au 4f spectrum was collected for binding energy calibration (Binding energy = 84.0 eV as reference). The Spectra deconvolution was conducted by CasaXPS version 2.3.19PR1.0 (Casa Software Ltd, Teignmouth, UK). A symmetrical Voigt function (Gaussian/Lorentzian ratio ranging from 90/10 to 70/30) was used to fit Ga 2p, S 2p, In 3d and Cu 2p photoelectron peaks with Shirley background subtraction.

#### X-ray absorption spectroscopy (XAS) characterization

Soft X-ray absorption spectra were recorded in Total Electron Yield (TEY) mode at beamline 7.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). The TEY signal was obtained by measuring the drain current to ground and normalized by the beam intensity measured with a gold mesh upstream of the sample. The X-ray energy was calibrated with the first peak in the Ti L<sub>3</sub>-edge XAS of TiO<sub>2</sub> (458 eV) for the In  $M_{5,4}$ -edges and the first peak of Ga<sub>2</sub>O<sub>3</sub> (1120 eV) for the Ga L<sub>3</sub>-edge.<sup>1</sup> A linear background fitted to the flat pre-edge region was subtracted from the raw spectra.

#### Photoelectrochemical testing of CO<sub>2</sub>R photocathodes

All photoelectrochemical measurements were performed using a Biologic SP-300 potentiostat under simulated AM 1.5 G illumination, calibrated using a silicon diode. Details about the polyetheretherketone (PEEK) cell employed for  $CO_2R$  can be found in our prior work. The PEEK cell was cleaned in nitric acid and DI water before every measurement.<sup>2</sup> The working electrode (Mo/CIGS) was connected to a Cu tape with In-Ga eutectic. The counter electrode used was graphite wire and a leak free Ag/AgCl reference electrode was used. After the assembly of the cell, the electrolyte (0.05M K<sub>2</sub>CO<sub>3</sub>) was bubbled with CO<sub>2</sub> at a flow rate of 5 sccm and the volume of the electrolyte employed in both the cathode and anode chamber was 2 ml. Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) in the dark was performed to measure the resistance of the solution. PEIS was performed from 1 MHz to 100 Hz to obtain the correct frequency in determining Rs (10 kHz). The VSP-300 potentiostat's IR compensation function only compensates 85% of Rs, thus the remaining 15% of Rs was corrected manually. Final voltage calculation after 100% IR compensation is as below:

V100%IR<sub>s</sub> (RHE) = V85% IR (RHE) + 15% average R<sub>s</sub> (Ohms) \* average I (A).

#### Gas products characterization by gas chromatography (GC)

A SRI 8610C Gas chromatograph is used to detect and quantify gas products. The gas phase  $CO_2R$  products (CO and H<sub>2</sub>) were quantified using the calibration curves by injected known concentrations of gaseous products. Briefly in GC, the  $CO_2$  was continuously flowing through the PEC cell; a portion of the exiting gas is directed into the sampling loops of the gas chromatograph. Two channels were used. Channel 1 comprises a 6' Heysep-D and a 6' Molsieve 13x column, a 1 ml sampling loop, Ar carrier gas and H<sub>2</sub> for flame ignition. This channel is S12 equipped with a flame ionization (FID) detector and a methanizer for CO to CH<sub>4</sub> conversion. Channel 1 has capability to detect the CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. Channel 2 has a 6' Heysep-D column, a 2 ml sampling loop, and N<sub>2</sub> carrier gas. This is equipped with a TCD detector for H<sub>2</sub> detection.

The Faradaic efficiency of the  $CO_2$  reduction gaseous products is estimated using the equation below –

$$FE(\%) = \frac{F \times n \times x \times F_{CO2}}{I}$$

where *F* is the Faraday constant (96485 C mol<sup>-1</sup>), *n* is the number of the electrons required for a particular  $CO_2$  reduction product, *x* is the mole fraction of the gaseous product obtained from the GC,  $F_{CO2}$  is the molar flow rate of  $CO_2$  through the cell, and *I* is the average current during the run. The number of electrons required are 2 for CO and H<sub>2</sub>. In this work, we observed only CO and H<sub>2</sub> as the gaseous products of  $CO_2R$  for CIGS photocathodes.

#### Liquid products characterization by nuclear magnetic resonance spectroscopy (NMR)

The quantification of liquid products was performed using 1D <sup>1</sup>H NMR (Bruker 500 MHz) using 50 mM phenol and 10 mM dimethyl sulfoxide (DMSO) as the internal standards. The water peak was suppressed by a presaturation sequence. 400  $\mu$ L of electrolyte after CO<sub>2</sub> photoelectrolysis was

added to 50  $\mu$ L of D<sub>2</sub>O and 50  $\mu$ L of internal standard solution. To determine the concentration of each CO<sub>2</sub>R product, the area of their corresponding peak should be compared with the area of the standards. For all peaks on the left side of the water peak (> 4.7 ppm), the phenol is the calibration standard. For all peaks on the right side of the water peak (< 4.7 ppm), DMSO is the calibration standard. The products were identified using the work of Robert and co-workers.<sup>3</sup> The concentration of each product C<sub>product tube</sub> in the tube can be computed using the following equation.

$$C_{product} = C_{standard\ tube} \times \frac{\frac{A_{Product}}{H_{product}}}{\frac{A_{standard}}{H_{standard}}}$$

A corresponds to the area of the peak and **H** corresponds to the number of protons corresponding to this peak. Finally, the Faradaic efficiency of the liquid product can be computed using the following equation.

$$FE = \frac{C_{product} \times V_e \times n \times F}{I \times t}$$

 $V_E$  corresponds to the volume of the electrolyte; *n* is the number of the electrons required for a particular CO<sub>2</sub>R product, *t* corresponds to the duration of the electrochemical test [s] and  $C_{product}$  corresponds to the concentration of product in the electrolyte. In this work, we observed only HCOO<sup>-</sup> as the liquid product of CO<sub>2</sub>R for CIGS photocathodes.

#### **Computational Studies**

Spin-polarized density functional theory (DFT) calculations are carried out with the PBE0 hybrid functional incorporating 25% of Fock exchange using the VASP code. The van der Waals dispersion interactions are taken into account through the DFT-D3 method. The sole  $\Gamma$ -point is used for the 192-atom supercell. Following the computational hydrogen electrode (CHE) method, the Gibbs free energy difference corresponding to a proton-coupled electron transfer reaction  $A \rightarrow B + H_{aq}^+ + e^-$  can be expressed as

$$\Delta G = \mu(B) - \mu(A) - \frac{1}{2}\mu(H_{2(g)}),$$

where the chemical potential of a given species is obtained by

$$\mu = E_{DFT}(T = 0 K) + ZPE - TS + \Delta U^{0 \to T}$$

 $E_{DFT}$  is the total energy from DFT calculations. ZPE is the zero-point energy of the species (either free or adsorbed) calculated in the harmonic approximation. The entropy S includes the vibrational, rotational, and translational contributions obtained within the ideal gas approximation for the free species. In the case of adsorbates, only the vibrational entropy is considered by accounting for the degree of freedom pertaining to the adsorbed species in the harmonic approximation.  $\Delta U$  is the change in the internal energy due to the finite temperature T. Specifically, the Gibbs free energy difference for the HER and the two CO<sub>2</sub>Rs can be expressed as

$$\Delta G_{1} = \mu(H^{*}) - \mu(slab) - \frac{1}{2}\mu(H_{2(g)}),$$
  

$$\Delta G_{2} = \mu(COOH^{*}) - \mu(slab) - \mu(CO_{2(g)}) - \frac{1}{2}\mu(H_{2(g)}),$$
  

$$\Delta G_{3} = \mu(HCOO^{*}) - \mu(slab) - \mu(CO_{2(g)}) - \frac{1}{2}\mu(H_{2(g)}).$$

**Table S1.** Surface composition of a CIGS thin film determined from EDX.

Cu (atomic %)	In (atomic %)	Ga (atomic %)	S (atomic %)
18.9	20.1	6.3	54.5

Elemental ratios -

[Cu]/[Ga]+[In] (CGI) = 0.71

[Ga]/[Ga]+[In] (GGI) = 0.24



**Figure S1**. (a) XRD peak shift (112) (determined from XRD data Figure 1) compared to reference  $CuInS_2$  and  $CuGaS_2$  peak position<sup>4</sup> (shown in blue dots) and (b) bandgap as a function of Ga/Ga + In ratio; dotted line represents the linear function predicted by Vegard's law for  $Cu(In,Ga)S_2$ . Data point (red) for the synthesized film is determined from XRD data and photoluminescence for (a) and (b) respectively.



Figure S2. Cross-section backscattered electron micrograph of the CIGS thin film.

**Table S2.** Summary of the reported values observed for typical wide bandgap CIGS or related photocathodes for PEC HER and  $CO_2R$  in the literature.

Photocathode stack/absorber Composition	Bandgap	Maximum Photocurrent	Reaction Targeted	Faradaic Efficiency	Reference
ITO/Cu <sub>0.8</sub> Ag <sub>0.2</sub> S <sub>2</sub> /Ru	2.35 eV	$\sim 3 \text{ mA/cm}^2$	HER	-	J. Mater. Chem. A,, 3, 21815– 21823 (2015)
$Au/CuIn(S_{0.4}Se_{0.6})_2$	1.09 eV	~ 1.5 mA/cm <sup>2</sup>	HER	90 % (H <sub>2</sub> )	Chem. Mater., 30, 4422–4431 (2018)
Mo/CuIn <sub>0.3</sub> Ga <sub>0.7</sub> S <sub>2</sub>	2.0 eV	$\sim 7 \text{ mA/cm}^2$	HER	97 % (H <sub>2</sub> )	Angew. Chem. Int. Ed., 60, 23651 – 23655 (2021)
Mo/CuInS <sub>2</sub>	1.5 eV	$\sim 4.5 \text{ mA/cm}^2$	HER	Close to 100 % (H <sub>2</sub> )	Adv. Energy Mater., 6, 1501949 (2016)
Mo/CuInS <sub>2</sub> /CdS/ TiO <sub>2</sub> /Pt	1.5 eV	$\sim 8 \text{ mA/cm}^2$	HER	Close to 100 % (H <sub>2</sub> )	Adv. Energy Mater., 6, 1501949 (2016)
Mo/CuInGaS <sub>2</sub>	2.1 eV	$\sim 3 \text{ mA/cm}^2$	HER	Close to 100 % (H <sub>2</sub> )	Adv. Energy Mater., 6, 1501949 (2016)

Mo/CuGaS <sub>2</sub>	2.4 eV	$\sim 2 \text{ mA/cm}^2$	HER	Close to 100 % (H <sub>2</sub> )	Adv. Energy Mater., 6, 1501949 (2016)
FTO/CuInGaS <sub>2</sub>	2.05 eV	$\sim 5 \text{ mA/cm}^2$	HER	_	ACS Appl. Energy Mater., 2, 8, 5515– 5524 (2019)
Mo/CuGa <sub>3</sub> Se <sub>5</sub> / CdS/molecular coating	1.8 eV	~ 1.2 mA/cm <sup>2</sup>	CO <sub>2</sub> R	80 % (CO)	ACS Energy Lett., 7, 3, 1195–1201 (2022)
Mo/Cu(In,Ga)Se <sub>2</sub> / CdS/ZnO/ZnO:Al/ZnO  CoPcTA	1.2 eV	$\sim$ 7 mA/cm <sup>2</sup>	CO <sub>2</sub> R	93 % (CO)	ACS Energy Lett., 8, 8, 3488–3493 (2023)
Mo/CuIn <sub>0.1</sub> Ga <sub>0.9</sub> Se <sub>2</sub> / CdS/ZnO(AZO)/TiO <sub>2</sub> / molecular catalyst	1.6 eV	$\sim 3 \text{ mA/cm}^2$	CO <sub>2</sub> R	97 % (CO)	Nat Commun 11, 3499 (2020)
Mo/Cu(In,Ga)Se <sub>2</sub> / CdS/ZnO/AZO	1.1-1.2 eV	~ 4.8 mA/cm <sup>2</sup>	CO <sub>2</sub> R	99.3 % (CO)	J. Catal., 384, 88-95 (2020)
Mo/CuIn <sub>0.3</sub> Ga <sub>0.7</sub> S <sub>2</sub>	2.0 eV	$\sim 3 \text{ mA/cm}^2$	CO <sub>2</sub> R (non- aqueous media)	68.6 % (CO)	ACS Energy Lett., 8, 4, 1645–1651 (2023)
Mo/CuIn <sub>0.7</sub> Ga <sub>0.3</sub> S <sub>2</sub>	1.77 eV	~ <b>2.8</b> mA/cm <sup>2</sup>	CO <sub>2</sub> R (aqueous	30 % (CO) 14 %	This Work

	media)	(HCOO <sup>-</sup> )	



(b)



Figure S3. (a) Morphology of CIGS film (SM top view) before and after  $CO_2R$  photoelectrolysis and, (b) Cross-section SEM of the representative CIGS film on Mo substrate after PEC  $CO_2$  operation in 0.1 M KHCO<sub>3</sub> at -0.4 V vs RHE under 1 sun illumination for 80 mins.



**Figure S4.** *Operando* Raman spectrum of  $Cu_{0.84}InGa_{0.26}(S,Se)_2$  (CIGSSe) thin films at open-circuit voltage (OCV) and time evolution (10 – 30 min) Raman spectra in 0.1 M KHCO<sub>3</sub> under 1 sun illumination at -0.4 V vs RHE.



**Figure S5.** Soft X-ray absorption spectra (XAS) of CIGS before and after 80 mins of PEC operation at the (a) Ga  $L_3$ -edge and the (b) In  $M_{5,4}$ -edge.



**Figure S6.** (a) Slab model of the pristine CIGS (112) surface. (b) Top view of the (112) surface in the presence of a Cu vacancy. The neighboring sites subject to adsorption of  $CO_2R$  intermediates are indicated.

**Table S3.** Gibbs free energy of change for adsorption of COOH\* and HCOO\* on NaInS<sub>2</sub> (003) surfaces terminated with either indium (denoted by In-X) or sodium atoms (Na-X).

	In-X	Na-X
COOH*	-3.06	-1.34
HCOO*	-5.85	-3.37

# **Supplemental References**

- 1. K.-i. Shimizu, M. Takamatsu, K. Nishi, H. Yoshida, A. Satsuma and T. Hattori, *Chemical Communications*, 1996, 1827-1828.
- 2. P. Lobaccaro, M. R. Singh, E. L. Clark, Y. Kwon, A. T. Bell and J. W. Ager, *Physical Chemistry Chemical Physics*, 2016, **18**, 26777-26785.
- 3. T. Chatterjee, E. Boutin and M. Robert, *Dalton Transactions*, 2020, **49**, 4257-4265.
- 4. S. Shukla, D. Adeleye, M. Sood, F. Ehre, A. Lomuscio, T. P. Weiss, D. Siopa, M. Melchiorre and S. Siebentritt, *Physical Review Materials*, 2021, **5**, 055403.