# **Supporting information**

# A Monolithic Device for Solar Water Splitting Based on Series Interconnected Thin Film Absorbers Reaching Over 10 % Solar-To-Hydrogen Efficiency

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### **1. Experimental procedures**

#### **Production of CIGS**

The molybdenum back contact was deposited with sputtering onto 2 mm thick soda lime glass, SLG, in a bilayer structure, using a deposition chamber with a base pressure of less than  $3 \cdot 10^{-6}$  mbar. For both layers, the sputtering power was 1500 W. The first layer (~25 nm) was deposited at relatively high pressure, 15 mTorr of argon atmosphere, while the second layer (~325 nm) was deposited at 6 mTorr. The CIGS absorber layer was grown on the SLG substrates in a batch system, providing metal rates controlled by a quadrupole mass spectrometer and a feedback loop. The CIGS process used in this work was a simulation of a three-source in-line system, described elsewhere(*1*). Selenium was evaporated in excess from a closed crucible during the process and the maximum substrate temperature was 540°C. The pn-junction was created by using a ~50 nm CdS layer deposited by electroless plating using Cd(OAc)<sub>2</sub>, thiourea and ammonia in water solution. A front contact consisting of a bilayer of sputtered non-intentionally doped ZnO and aluminum doped ZnO (ZnO:Al) finalized the photoelectrode stack. For detailed description of these processes, see reference from Lindahl et. al(*1*).

#### Series interconnections

The principal configuration of the series interconnection is given in figure 2.b, and was constructed by doing three scribe lines during different steps in the synthesis. The first one,  $P_1$ , through the Mo-layer separates the back contact for the individual cells. The second one,  $P_2$ , was done after the i-ZnO and before the deposition of the ZnO:Al window layer down to the Mo back contact, allowing the subsequent cell interconnection of front and back contact with ZnO:Al. Finally,  $P_3$ , was done after the deposition of the window layer, isolating the front contacts and forcing the current to go through the Mo-layer. The  $P_1$  scribe was made with a pulsed 10 ns laser, providing a wavelength of 532 nm. The laser beam is incident from the backside of the soda lime glass, ablating the Mo in 50 µm wide lines. The following  $P_2$  and  $P_3$  are patterned with a metal stylus.

#### Encapsulation and design of PEC device

Standard encapsulation procedure was carried out to protect the module surface. An ethylene vinyl acetate, EVA, sheet was placed between the CIGS module and the 2 mm SLG front glass. The structure was then placed in the laminator which was programmed with a total lamination cycle time of roughly 30 minutes, consisting of several heating and low vacuum stages. The resulting device is a CIGS solar module between two 2 mm glasses, fixed together with the cross-linked EVA.

To finalize the PEC device the platinum catalyst modules was placed at the back side of the absorber module oriented perpendicular from the backside. The current transport between the catalyst and the absorber is performed in a tin stripe connected to the molybdenum back contact with an indium solder and to the platinum by silver glue. All seals and contacts were covered by epoxy resins.

#### Catalyst deposition

The surface area of the platinum working electrodes was enhanced by deposition of platinum black. The platinum foils were before deposition cleaned in 50 % aqua regia, (HNO<sub>3</sub> and HCl in the proportion 3:1), rinsed in water, cleaned in concentrated HNO<sub>3</sub>, and rinsed in water. They were also cycled between -0.2 and -1.2 V vs Ag/AgCl in 0.1 M H<sub>2</sub>SO<sub>4</sub> with a sweep rate of 0.1 V/s. The deposition of platinum black was performed at 30 mA/cm<sup>2</sup> for five minutes under stirring from a solution of 0.05 M H<sub>2</sub>PtCl<sub>6</sub> and 0.13 mM Pb(OAc)<sub>2</sub>. The platinum foil was during the deposition well separated from the counter electrode to prevent contamination by chlorine gas.

#### Electrochemical characterization

All electrochemical measurements were performed with a CH Instrument model 760 C. For three electrode measurements potentials were measured with respect to an Ag/AgCl reference electrode, shifted 0.197 V with respect to the standard hydrogen electrode, SHE, and with a platinum wire as counter electrode. The electrolyte used was  $3M H_2SO_4$ . For the two electrode measurements the potentiostat was connected in series with the cell with the reference and the counter electrode to one electrode and the working electrode to the other.

An Oriel solar simulator xenon arc lamp equipped with a global AM 1.5G air mass filter was used to simulate solar irradiance for the water splitting measurements. The intensity at the position of the device was calibrated to  $1000 \text{ W/m}^2$  with a reference Si-diode.

#### Measurement of hydrogen

The gas flow from the working device was measured volumetrically by measuring the volume of electrolyte expelled by the evolving gas. The composition of the produced gas was analyzed in an ultra high vacuum system, equipped with a dynamic sampling mass spectrometer. The base pressure of the system is in the  $10^{-10}$  mbar region and the produced gas was released into the system using a leak valve. Prior to all measurements the system was calibrated by measuring both the system background and by leaking in a known gas (Ar, H<sub>2</sub>). During the measurement, the system pressure was  $1 \cdot 10^{-7}$  mbar, and the H<sub>2</sub> and O<sub>2</sub> signals was at least 2 orders of magnitude above the background signal. The partial pressures of the investigated gases were recorded every 10 s, and the measurements were repeated at least three times to ensure the stability of the gas composition.

### 2. Additional data and figures

The performance of the series interconnected CIGS absorber while used as a solar cell is given in figure S1.a. During the first ten minutes of operation the bubble formation in the highly effective device gives a lowering of the initial solar-to-hydrogen efficiency. This is usually not considered in the literature but here result in a lowering of the initial 11.2 % STH to a steady state-value of slightly above 10 % STH as seen in figure S1.b-c. Stirring or optimizations of the electrode microstructure decrease the bubble formation on the electrode and decreases this initial lowering.



Figure S.1(a) IV characteristics of the series interconnected CIGS-module referred to in the article. (b) STH against time under chopped AM 1.5 illumination for the setup given in figure 3.b in the main article. (c) A close up of the initial lowering of (b)

Table S.1. K	Lev data relate	ed to figure S.1	l and figure 3 in	the main article
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Parameter	Abbreviation	Value
Potential at open circuit	V <sub>oc</sub>	1.97 V
Potential at the maximum power point	V <sub>mp</sub>	1.54 V
Potential at the intercept between CIGS module and catalyst	Vintersept	1.726
Current density at short circuit	J <sub>sc</sub>	11.68 mA/cm <sup>2</sup>
Current density at the maximum power point	J <sub>mp</sub>	11.01 mA/cm <sup>2</sup>
Current density at the intercept between CIGS module and catalyst	J <sub>intersept</sub>	8.586 mA/cm <sup>2</sup>
Fill factor	FF	0.74
Efficiency for CIGS module	η <sub>module</sub>	17.0 %
Efficiency for PEC device	$\eta_{device}$	10.5 %
Ideal efficiency for PEC device	$\eta_{max}$	13.5 %

To better resolve the current response after switching on and of the light source a zoomed version of figure 3.c are given in figure S.2.a. To illustrate the stability of the monolithic device in figure 4 a measurement of the gas flow in a longer time interval is given in figure S.2.b. After approximately a day of uninterrupted operation the gas flow decreased somewhat due to a mechanical failure in one of the polymer seals.



Figure S.2 (a) A zoomed version of figure 3.c in the main article. (b) Gas flow over a longer time period for de device in figure 4 in the main article

## 3. Movie of the monolithic device under working condition

In the supporting material a film of the monolithic structure under working condition is applied. The movie shows the following things in sequence a-i.

- (a) An overview of the experimental setup in the dark
- (b) The device in the dark from the side
- (c) The device in the dark from the front side
- (d) The light is switched on
- (e) From the side view it is seen how gas is evolved at the catalysts
- (f) Top view of the device under illumination showing two distinct columns of gas rising
- (g) The device under illumination from the side
- (h) The device under illumination from the back side
- (i) An overview of the experimental setup under illumination

(1) J. Lindahl *et al.*, Inline Cu(In,Ga)Se2 Co-evaporation for High-Efficiency Solar Cells and Modules. *Photovoltaics, IEEE Journal of* **3**, 1100 (2013).