

Electronic Supplementary Information

Scalable and thermally-integrated solar water-splitting modules using Ag-doped Cu(In,Ga)Se₂ and NiFe layered double hydroxide nanocatalysts

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Methods

PV preparation and characterization methods

The ACIGS material and subsequent solar cell modules were fabricated on soda-lime glass substrates with the Mo layer deposited on the glass substrates by DC magnetron sputtering in an industrial in-line sputter with cylindrical targets. The thickness of the Mo films was about 0.3 μm and the corresponding sheet resistance was 0.6 ohm. The 10 nm NaF layer was deposited by evaporation in a large area in-line evaporation system using effusion cells. The deposition rate was determined by a profilometer measurement after the designated times in order to enable optimal process control in the final manufacturing process.

The ACIGS layer was deposited by means of vacuum co-evaporation at a substrate temperature of 530 °C, with the compositions and thicknesses of the as-deposited films being monitored by XRF calibrated to thickness standards made of the material. The samples were fabricated with an Ag/(Ag+Cu) ratio of 0.2, providing an optical bandgap in the ACIGS films of 1.15 eV as calculated from the absorption edge in external quantum efficiency measurements. A post deposition process with RbF, intended to reduce interface recombination losses, was performed immediately after the ACIGS deposition in a separate vacuum chamber on the same cluster tool. During the RbF deposition, the substrate temperature was 300 °C and no Se was simultaneously evaporated. RbF deposited with a thickness of about 5–8 nm does not form a layer, but appears as an impurity. Fluorine ebbs away and some Rb is present throughout the chalcopyrite film, especially at both interfaces to the Mo and CdS. The CdS

layer was deposited via wet chemical bath deposition using a mixture of solutions of Cd-sulphate, thiourea, and ammonia.¹

A double layer of un-doped ZnO and a layer of Al-doped ZnO were deposited by means of rf magnetron sputtering and DC magnetron sputtering, respectively. The targets used were a planar ceramic target for un-doped ZnO and a cylindrical ZnO/1 wt % Al₂O₃ for ZnO:Al. In this case, an in-line tool with a coating width of 63 cm was used. The ratio of the Ar:O₂ plasma gas mixture was about 1:2000 for the un-doped ZnO and 1:200 for the ZnO:Al. The ZnO:Al films were grown at 170 °C and the resulting sheet resistance was 50 ohm. No intentional heating was applied to the un-doped ZnO. An Al grid was evaporated from resistively-heated, wire-fed sources and defined by photolithography.

Series interconnected cells on one monolithic substrate were obtained using a laser-scribing step for the Mo layer. P1 was used for the back-contact, forming the stripe-shaped molybdenum back contacts. Mechanical scribing was used for the subsequent scribing steps; P2 was utilized for the series interconnect formation between the adjacent cells (contact vias); P3 was employed for the neighboring cell isolation following the top-contact deposition. In the P3 step, the ACIGS layer, the ZnO layers, and the grid were simultaneously removed. The processes follow commercially-applied deposition and scribing utilized in CIGS thin film manufacturing, and are thus scalable and expected to be of similar cost-performance as the commercial CIGS counterparts, apart from the addition of Ag as a dopant. The amount of silver added, however, was very low and did not approach the high amount presently used in contacts for commercial Si-solar cells, which accounts for about 15% of the annual global consumption of Ag, which can even constitute a constraint for conventional Si-technology.²

Catalyst preparation and characterization methods

A 5 × 5 cm² piece of Ni foam (MTI Corp, purity: 99.99%) with ≥ 95% porosity and a thickness of 1.6 mm was initially ultrasonicated in 3 M HCl (37%, Sigma-Aldrich) for 5 min to remove the surface oxide layer. The substrate was Ni foam and rinsed in ethanol (VWR Chemicals) and deionized (DI) water for 8 min to clean it from possible residues. The foams were left to air dry for the time necessary to prepare the reaction solution and then finished off with a final drying process in a jet of N₂. In a typical synthesis, 0.290 g of nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma-Aldrich, purity ≥97.0%), 0.404 g of iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Sigma-Aldrich, purity ≥ 98%), and 0.600 g of urea (Sigma-Aldrich, ≥ 99.5%) were dissolved in 80 mL of DI water under magnetic stirring for at least 10 min in order to form a clear solution, and then transferred to a 100 mL autoclave Teflon liner. Prior to immersing the pre-treated Ni foam in the reaction solution, two edges of the foam were covered with Kapton tape (one face only) in order to limit the deposition of the nanostructures and ensure good electrical contact in the region. The substrate was then adapted to fit the liner by gentle bending, and the inserting of it vertically into an autoclave. The autoclave was then sealed, placed in a furnace and heated from room temperature to 120 °C with a ramp of 5 °C min⁻¹ and held for 12 h to allow the growth of the nanostructure. Upon completion, the autoclave was left to cool naturally (closed furnace) and removed once the temperature registered was between 40 and 50 °C. The coated Ni foam was then extracted and washed via ultrasonication in DI water for 3 × 8 min to remove any loosely bound product. The foam was then reshaped to a flat surface and dried at 80 °C for about 15 h.

The surface morphology and homogeneity of the catalysts were analyzed with a Zeiss 1530 scanning electron microscope (SEM) operated with a 5 kV electron accelerating voltage. The grazing incidence X-ray diffraction (GIXRD) measurements were performed on the NiFe LDH catalyst using a Siemens D5000 system with Cu Kα1 radiation ($\lambda = 1.54 \text{ \AA}$). The incidence angle was set to 1° and scans were performed between 20° and 65° with a 0.02° step.

Raman spectroscopy measurements on the as-prepared samples were conducted on an RM 1000 confocal Raman microscope (Renishaw) using a 532 nm frequency doubled Nd:YAG diode laser (100 mW), 1800 line mm⁻¹ of grating, and a 20× objective. The laser intensity is decreased throughout the mirrors and lenses in the Raman system, and was additionally filtered to 1% using neutral-density filters during the measurement in order to avoid laser heating effects. To acquire enough of a signal-to-noise ratio, each sample spot was subjected to 45 accumulations of 10 s measurements, each in an extended mode intended to capture a wider wavenumber range. The Raman spectrometer was calibrated to the 520.5 cm⁻¹ Si signal.

Electrochemical measurements were carried out on a CHI 760C potentiostat in 1 M KOH at room temperature. The catalyst was investigated independently for both the HER and OER in a three-electrode setup. For these measurements, a Pt mesh (2 × 1 cm²) was used as a counter-electrode (CE), whereas the working electrode (WE) was cut from the catalyst-loaded foam into a 1 × 1 cm² size, with Ag/AgCl (sat. KCl) being used as a reference (RE). LSV was performed with a scan rate of 5 mV s⁻¹ and shown to be without iR compensation. A stability test was then conducted in a two-electrode setup and monitored *vi* current versus the time curve for 100 h at a constant potential (yielding an initial current of 10 mA). Both the cathode and anode consisted of a 1 × 1 cm² loaded Ni foam cut-out. Currents were reported and normalized to the WE's geometrical area and potentials reported vs. the RHE in pH = 14 according to equation 1:

$$E_{\text{RHE}} (\text{V}) = E_{\text{measured}} + 0.059 \times \text{pH} + 0.197 (\text{V}) \quad (1)$$

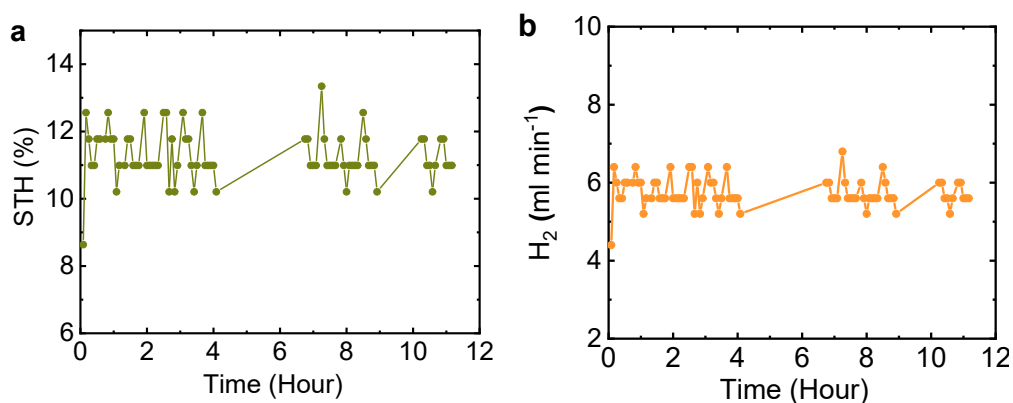
A three-compartment cell with CE and WE divided by a glass frit was used for all of the measurements in order to minimize any influence of Pt contamination from the CE.

PV-electrolysis device formation

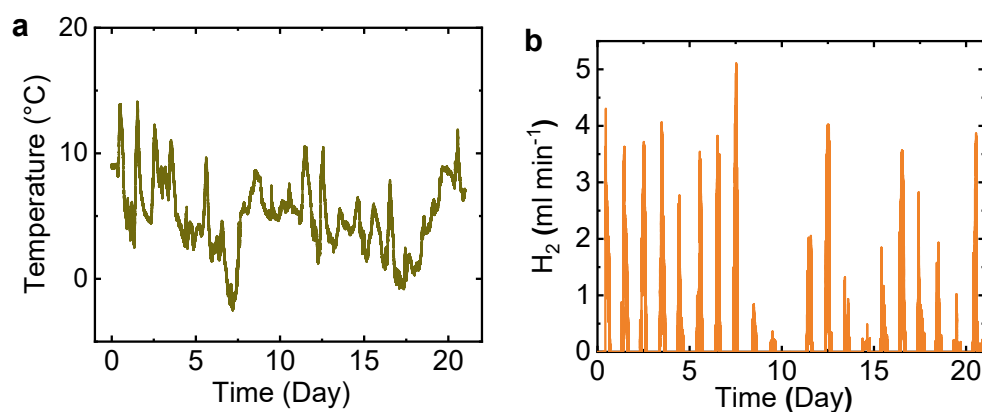
The electrolyzer consisted of two 130 × 130 × 5 mm Ni plates (Ni 201, 99% Ni) as cases, NiFe LDH on Ni foam (100 cm² active geometric area) as catalysts for both the cathodic and anodic sides, two 2 mm-thick ethylene propylene diene monomer (EPDM) rubber gaskets to create space for gases to escape from the catalyst surfaces, and an anion exchange membrane (Fumasep FAA-3-PK-130 Fuelcellstore) at the center. Screws in the insulating bushings were used to hold the Ni plates together and compress the gaskets so as to ensure no leakage of the electrolyzer. The PV module and electrolyzer were combined using a boron nitride thermal paste.

Supplementary Table 1. Raman peak assignments of the pristine NiFe LDH catalyst.

Assignment	Raman peak ^{17,18} (cm ⁻¹)	Raman peak [this work] (cm ⁻¹)
Symmetrical bending of the metal–oxygen bond	332	331
F _{2g} (b) vibrations, asymmetric stretching of Fe–O and Ni–O bonds	487	483
F _{2g} (c) vibrations, asymmetric bending of metal–oxygen bond	570	572
A _{1g} vibration, the symmetric stretching of Fe–O and Ni–O bond	691	699
C–H bending	1341	1341



Supplementary Fig. 1. Performance of the integrated 2 × 3 cell ACIGS-2 module with a total area of 82.3 cm²-alkaline electrolyzer NiFe LDH (cathode)-NiFe LDH (anode) with a 100 cm² catalyst area under a 100 mW cm⁻² illumination for an eleven-hour gas volume measurement: (a) STH efficiency; and (b) hydrogen production rate. The electrolyte was 1 M KOH.



Supplementary Fig. 2. Performance of the integrated 82.3 cm² ACIGS-2 module and NiFe LDH (cathode)-NiFe LDH (anode) electrolyzer with 100 cm² areas measured for 21 days (500 hours): (a) Ambient temperature; and (b) hydrogen production.

References

- 1 İ. Bayrak Pehlivan, M. Edoff, L. Stolt and T. Edvinsson, *Energies*, 2019, **12**, 4064.
- 2 S. Lo Piano, A. Saltelli and J. P. van der Sluijs, *Frontiers in Energy Research*, 2019, **7**, 56.