PECSYS Virtual Workshop
5th November 2020

WP 3: Results of the CIGS based integrated PV-EC device approach

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J. Oscarsson (SRAB), P. Neretnieks (SRAB), J. Mathiasson (SRAB), K. Theelen (SRAB), L. Stolt (SRAB)

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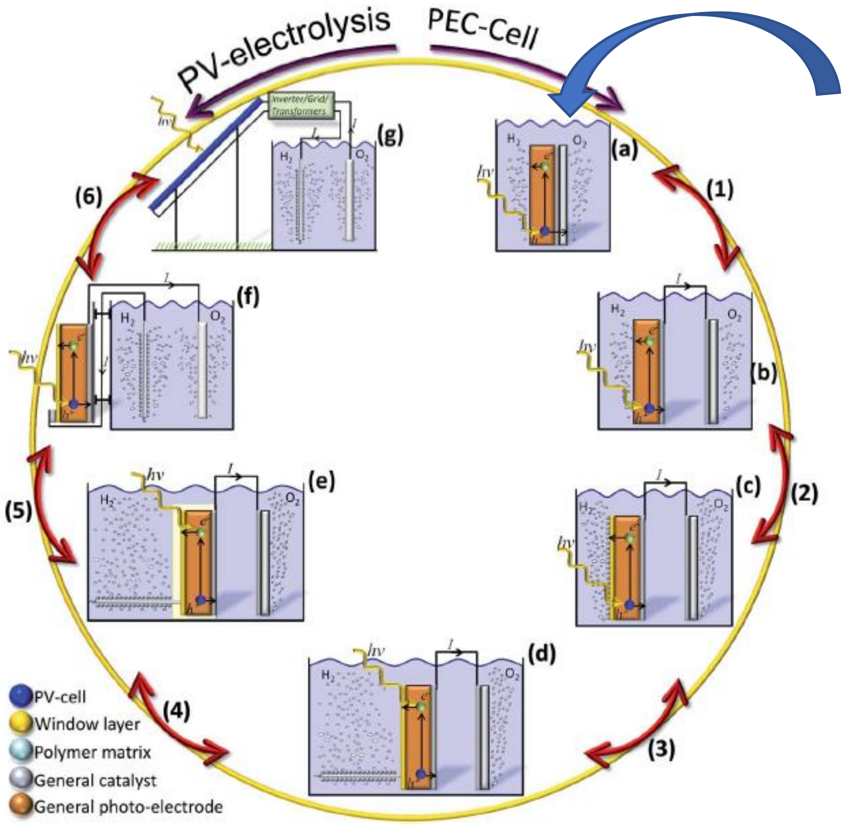
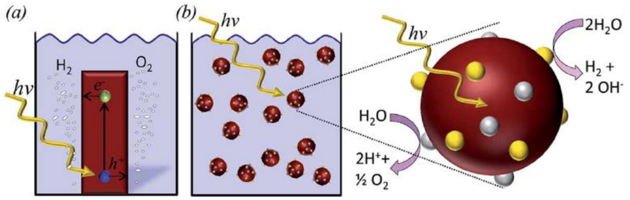
Workpackage objectives and main tasks

Objective: Development of higher voltage CIGS materials, development of catalyst modules and upscaling of the CIGS based approach with non-precious HER and OER catalysts

Task description	
T 3.1	Improved photo-voltage in CIGS and catalyst development
T 3.2	Development of CIGS lab-scale PEC/PV and PEC-EC devices
T 3.3	10 – 30 cm^2 Alkaline water splitting modules

Explanation of the concept: From PEC to PV-electrolysis





Jacobsson, T. J.; Fjällström, V.; Edoff, M.; **Edvinsson, T.,**
Energy & Environmental Science, **2014**, 2014, 7, 2056

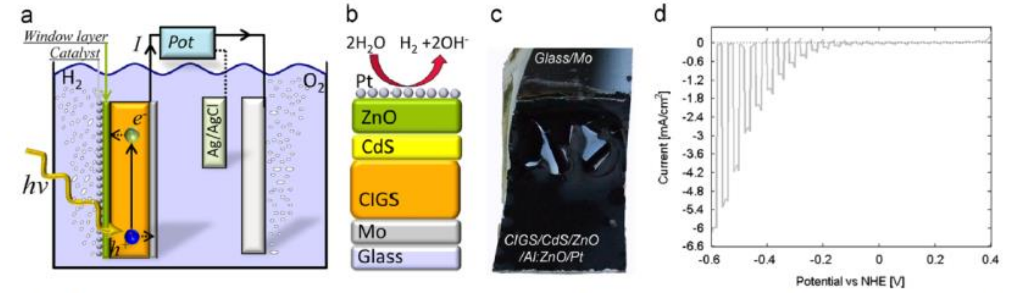
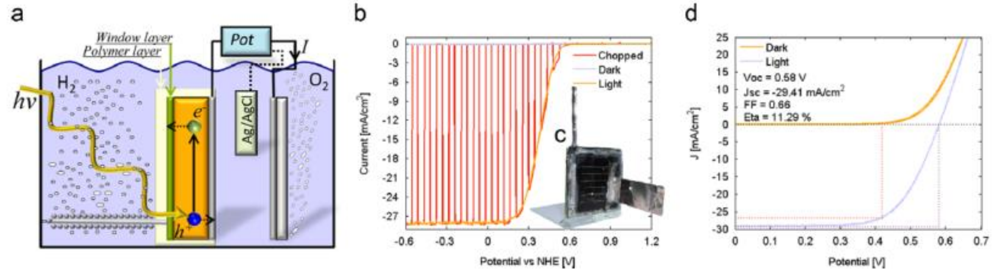


Fig. 4. (a) Experimental configuration for a CIGS with a solid state pn-junction consisting of CdS and ZnO and with platinum nanoparticles as a catalyst. A type (c) configuration. (b) Principal configuration of the electrode. (c) Photo illustrating the macroscopic degradation of the films under operation. (d) Photocurrent as a function of potential under chopped illumination corresponding to AM 1.5 G CIGS/CdS/ZnO/Pt.



Jacobsson, T. J.; Fjällström, V.; Edoff, M.; **Edvinsson, T.,**
Solar Energy Materials & Solar Cells, **2015**, 134, 185–193

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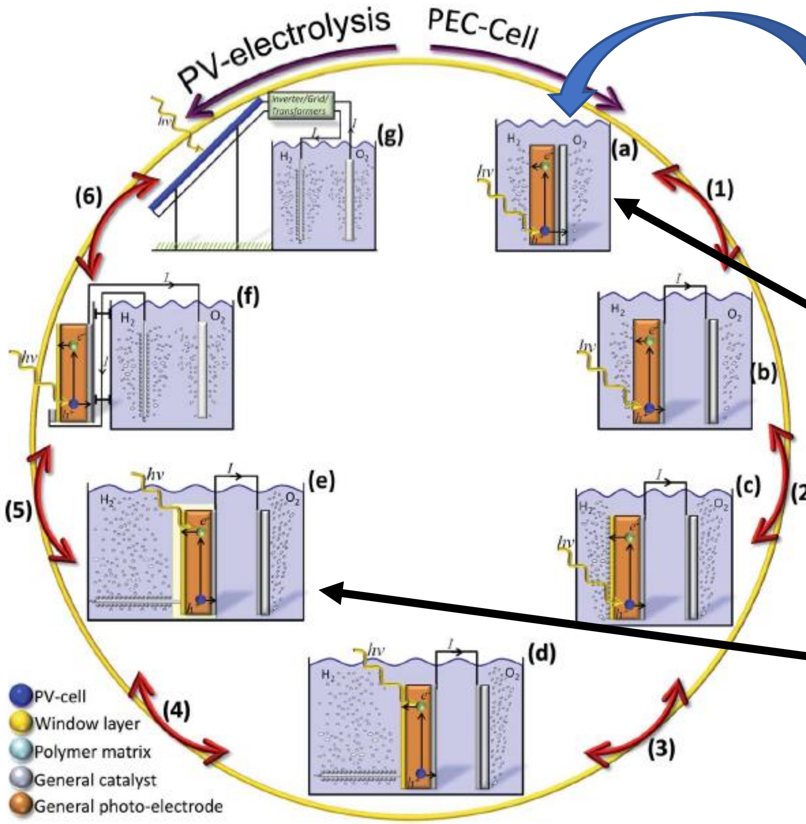

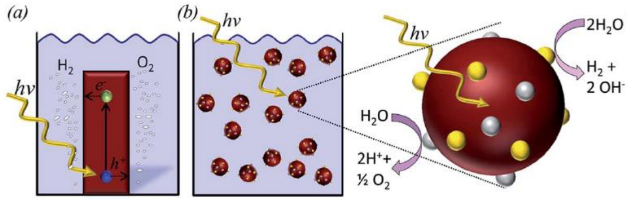

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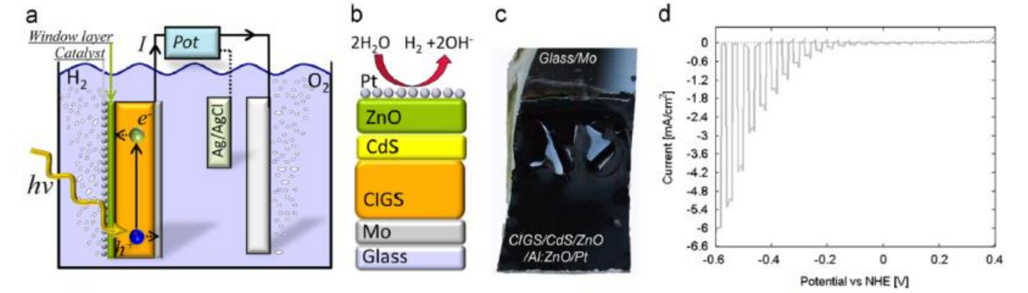

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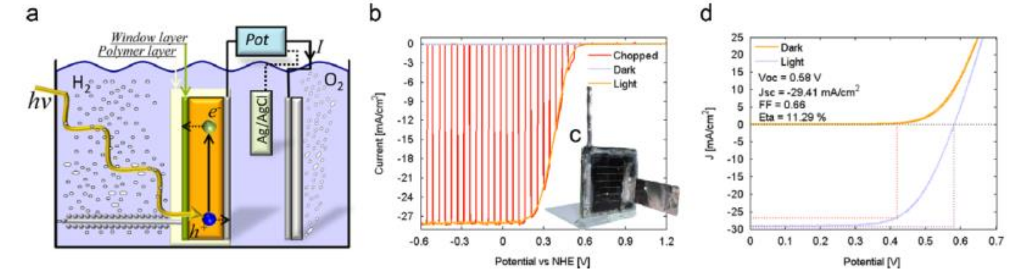
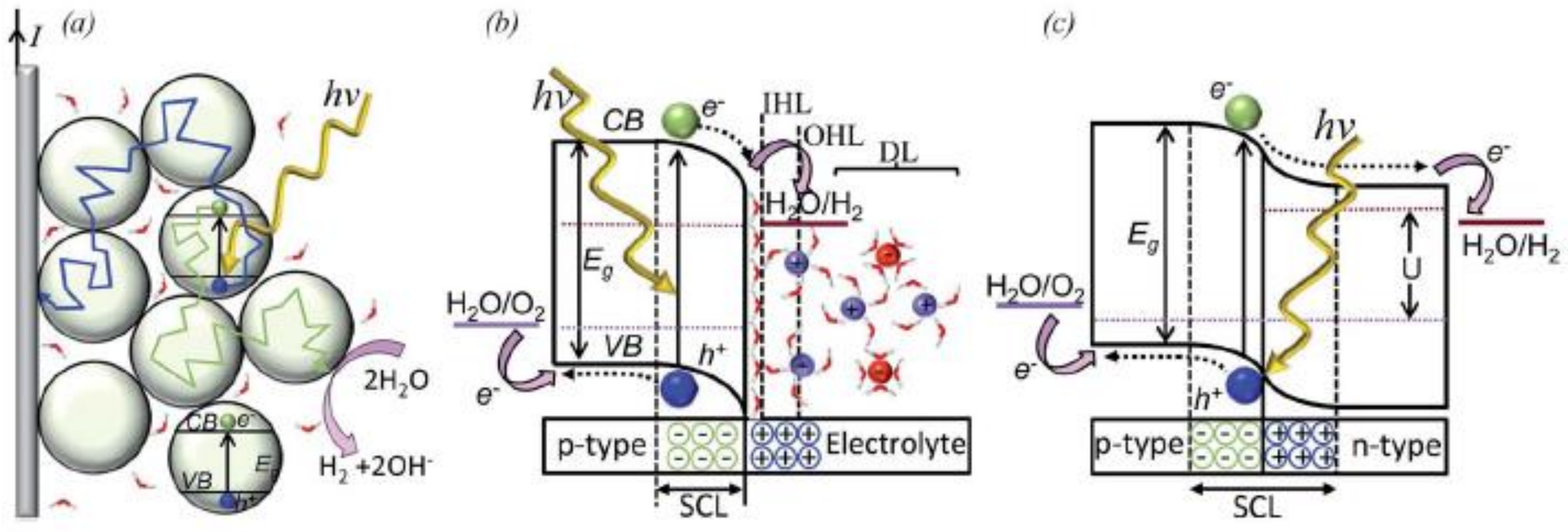


Jacobsson, V. Fjällström, M. Sahlberg,
M. Edoff and **T. Edvinsson**
Energy & Environmental Science, **2013**, 6, 3676–3683

Jacobsson, T. J.; Fjällström, V.; Edoff, M.; **Edvinsson, T.,**
Solar Energy Materials & Solar Cells, **2015**, 134, 185–193

Mechanisms of charge separation and transport



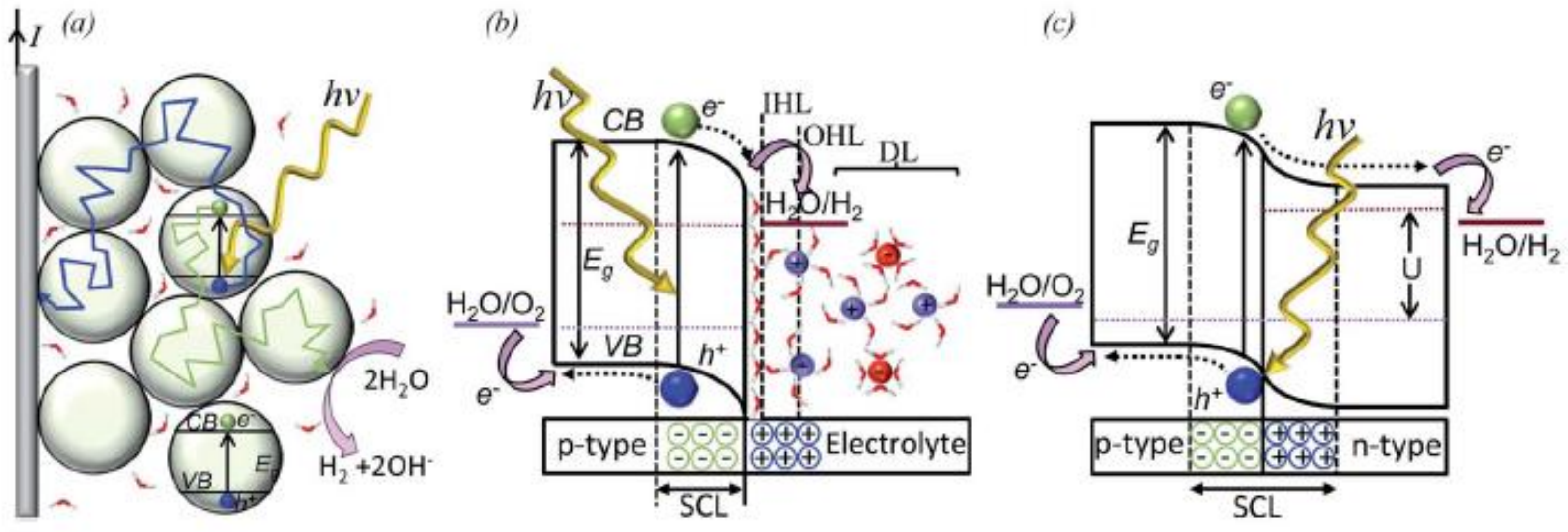
No fields
Diffusion dominates

Local fields
Diffusion + migration

Macrosopic fields
Migration dominates

Jacobsson, Fjällström, Edoff, and **Edvinsson**
Energy & Environmental Science., **2014**, 7, 2056-2070

Mechanisms of charge separation and transport



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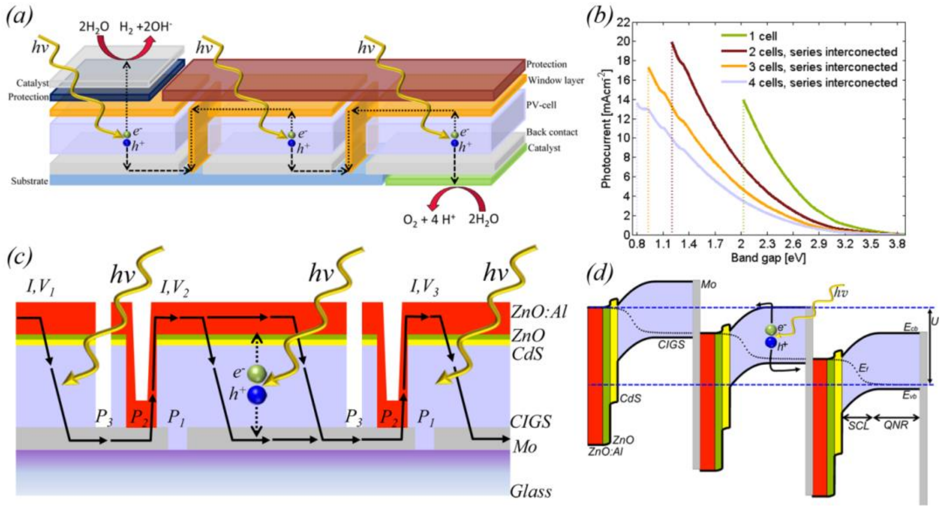
Jacobsson, Fjällström, Edoff, and **Edvinsson**
Energy & Environmental Science., **2014**, 7, 2056-2070

As long as there is an effective charge separation and transport in a material heterojunction as in PVs, there is **no need to place the photoabsorbing materials in water**

Serial interconnected devices

The band gap problem: To absorb more photons in the solar spectrum and transform them into higher chemical potential, several absorber units can be connected in series side by side as an alternative to tandem.



$$J_{ph} = \frac{1}{n}\int_0^{hc/E_g} E(\lambda)EQE(\lambda)d\lambda$$

$$V_{photo} = n\left(V_{photo,single}\right)$$

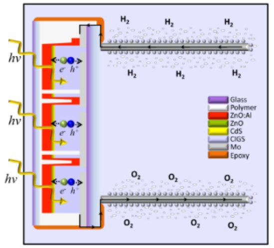
The photocurrent density will decrease by a factor equal to the number of connected cells, but the voltage difference between the cathode and the anode will increase by the same factor, keeping the efficiency per area the same. It is a very simple solution, previously largely overlooked in the literature !

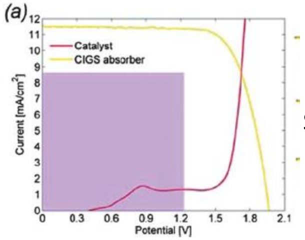
Jacobsson, V. Fjällström, M. Sahlberg, M. Edoff and **T. Edvinsson**
Energy & Environmental Science, **2013**, 6, 3676–3683

Serial interconnected devices

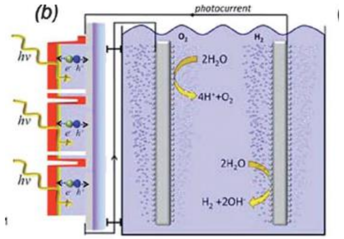
10% STH
3-CIGS
precious catalysts

CIGS





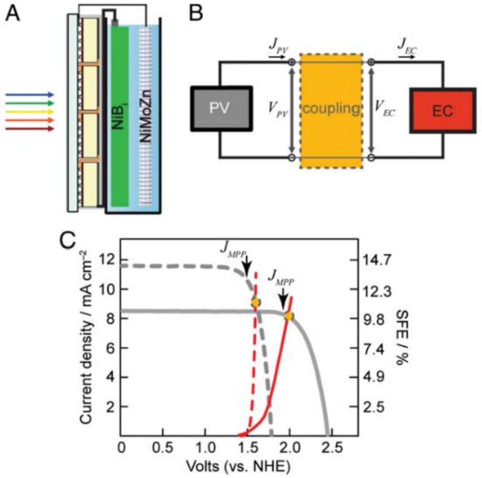
10-10.5%
Solar-to-hydrogen



Jacobsson, Fjällström, Sahlberg, Edoff, **Edvinsson**,
Energy Environ. Sci., **2013**, 6, 3676

Si

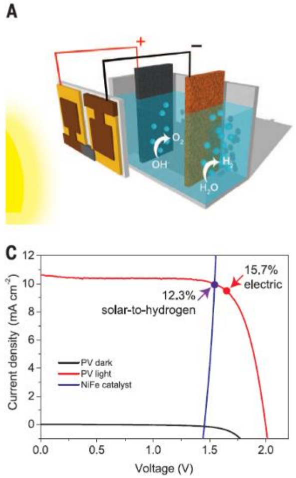
10% STH
4-Si
nonprecious catalysts
(NiBi anode and NiMoZn cathode)



Cox,Lee, Nocera, Buonassisi,
PNAS, **2014**, 111, 14057-14061

Hybrid perovskites

12.3% STH
2-cell perovskite
nonprecious catalysts
(NiFe LDH as anode and $Ni(OH)_2$)



Luo, Im, Mayer, Schreier, Nazeeruddin, Park, Tilley, Fan, Grätzel,
Science, **2014**, 345, 1593-1594

Advantages and disadvantages with integrated PV-electrolysis

Advantages

- Stores and accumulated the solar energy in a fuel, avoiding grid-transmission losses from PV-to-grid, grid transport losses, and grid-to-electrolyzer losses
- Avoids losses from dc-dc conversion and cost of power electronics
- Enables heat transfer from PV to electrolyzer
- Potential savings in material costs and area occupation if sharing the same substrate/framing and footprint.

Advantages and disadvantages with integrated PV-electrolysis

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Disadvantages

- Potential increase in maintance cost in comparison to a non-integrated system
- Lower flexibility in applying routes towards pressurized electrolysis
- Building integration more challanging
- Challenging outdoor-utilization in parts of the world having colder climate (freezing of electrolyte, viscosity/mass transport changes)

Photovoltage requirements for water splitting: V_{mp} > 1.23 V + free energy driving force

$$\eta = \frac{J_{sc} \cdot V_{oc} \cdot ff}{P_{light}}$$

$$qV_{oc} = E_g - \eta_{sep} = E_g - k_B T \ln\left[\frac{8\pi (k_B T)^2}{c^2 h^3}\frac{n^2 E_g}{j_{gen}}\alpha L \Phi_{rec}\right]$$

where E_g is the bandgap, k_B is Boltzmann's constant, *T* is the temperature, *h* is Planck's constant, *c* is the speed of light in vacuum, n is the refractive index, j_{gen} is the rate of photon absorption in the AM1.5 spectra, Φ_{rec} is the ratio between the non-radiative and radiative recombination rates, *α* is the absorption coefficient, and *L* is the minority carrier diffusion length and should be replaced with the material thickness, *d*, if $d < L$.

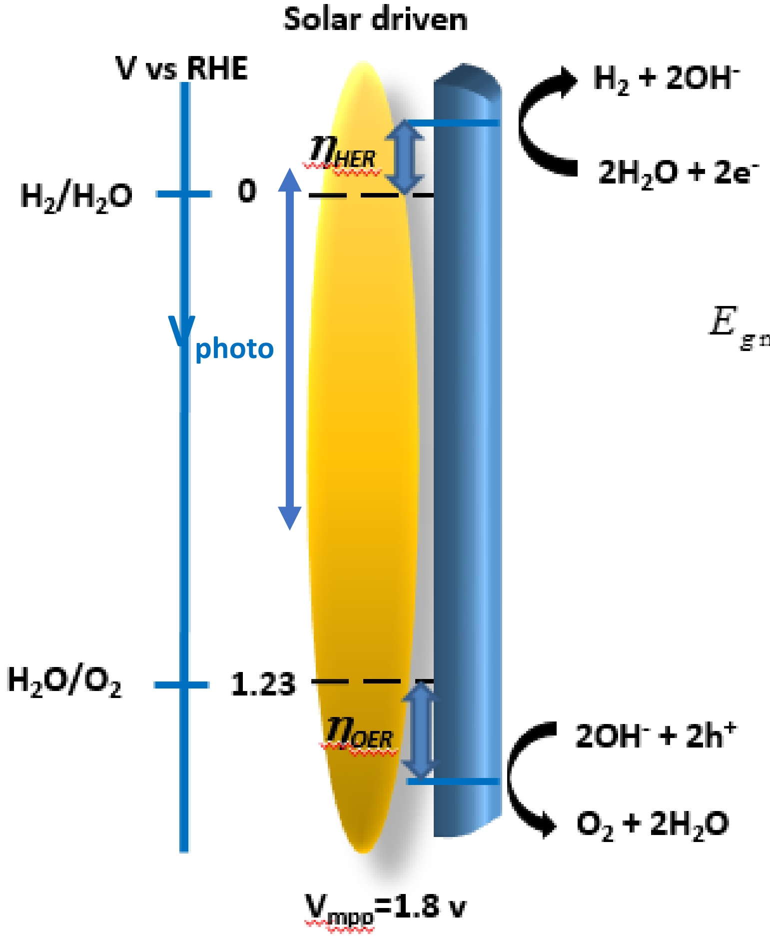
W.Shockley,H.J.Queisser,
J.Appl.Phys. **1961**, 32, 510–519.

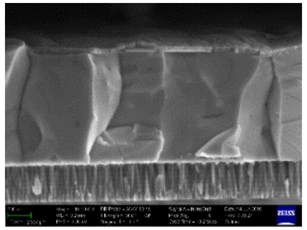
Jacobsson, T. J.; Fjällström, V.; Edoff, M.; Edvinsson, T.,
Solar Energy Materials & Solar Cells, **2015**, 138, 85-95

Typical experimental values for η_{sep} in state-of-the-art materials in solar cells are:

0.3 eV in GaAs
0.36 eV in silicon (0.61 in a-silicon)
0.4 eV in MA-lead iodide Perovskites (V_{oc}=1.15 V, Eg=1.55 eV)
0.4 eV in InP
0.41 eV in CIGS (V_{oc}=0.76 V, Eg=1.17 eV)
0.6 eV in CdTe (0.4 in single crystals)
> 0.6 eV in organic solar cells

Work on optimized photovoltage and lowering of the overpotential for the catalysts



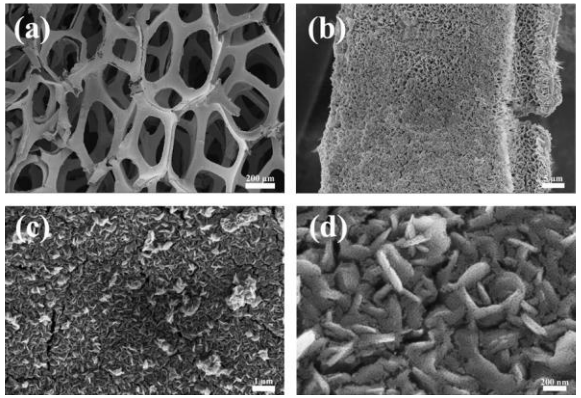


CIGS

$$E_{g\,min} = 1.23 + \eta_{sep} + \eta_{trans} + \eta_{cat}$$

Catalysts

$$\eta_{cat} = \eta_{HER} + \eta_{OER}$$



Solar fuel generation and electrolysis

Energy & Environmental Science **2013**, 6, 3676
Energy & Environmental Science **2014**, 7, 2056
Energy & Environmental Science **2017**, 10 , 1372
Energy & Environmental Science **2019**, 12, 572
Nano Energy **2018**, 49, 40
Energies, **2019**, 12, 4064.
Nature Energy **2019**, 4, 354
Nano Energy **2019**, 66, 104118
Angewandte Chemie Int Ed **2020**, 59, 2

Main Results

D3.1	Determination of optimal amount of Ga and synthesis condition to adapt the photovoltage in CIGS with maximum current density.

Only 0.41 eV loss i CIGS (V_{oc}=0.76 V, Eg=1.17 eV)
Ga/(Ga+In) ratio 0.3 and 20% of Cu replaced with silver

From: Edoff *et al*, High Voc in (Cu,Ag)(In,Ga)Se_2 solar cells, 44th IEEE Photovolt. Spec. Conf. Proc. (UU, Solibro AB), **2017**, 7, 1789-1794

For comparison: **0.46 eV loss in planar MA-lead halide perovskite solar cells (V_{oc}=1.15 V, Eg=1.61 eV**)
(Edvinsson, Boschloo and co-workers, *Energy Environ. Sci.,* **2016**, 9, 3770-3782)

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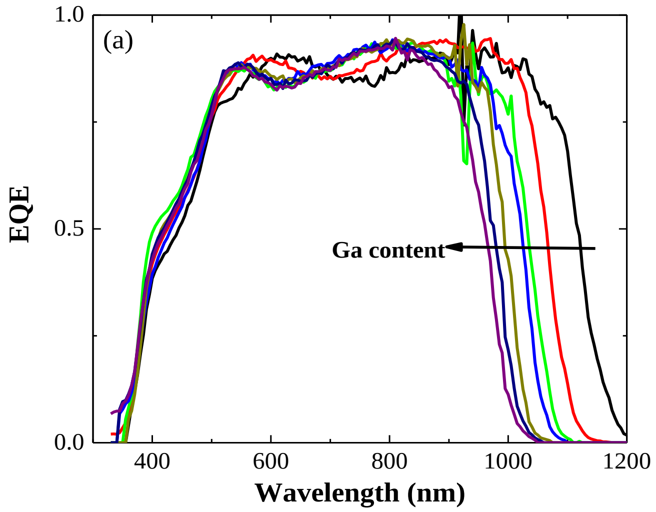
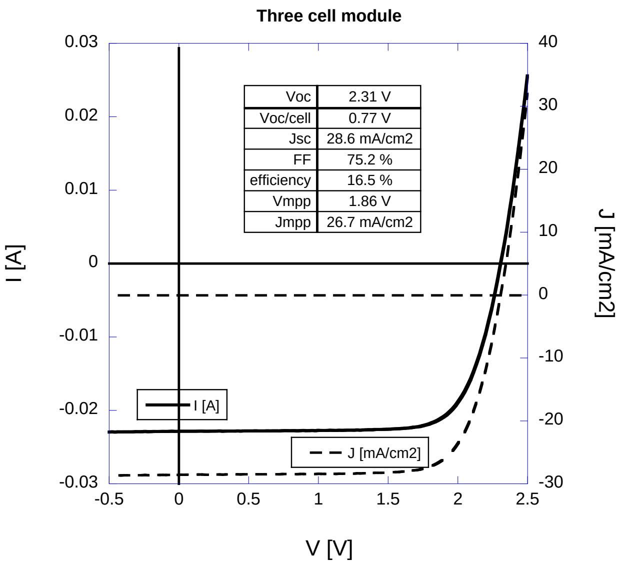
Main Results

Ga contents between 32% and 42% as defined from Ga/(Ga+In) where photocurrent on-sets from 1000 nm to 1200 nm (Figure) and photo voltages between 1.8 V to 2.45 V for 3-cell modules of CIGS.

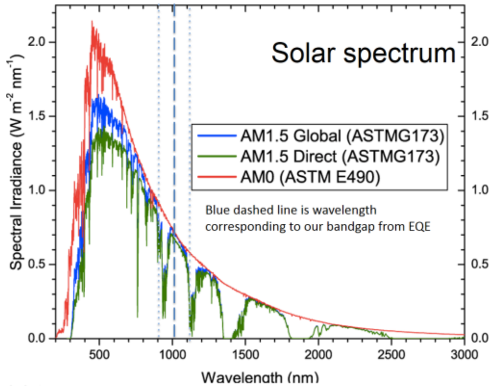




E_g =1.24 eV

V_{oc}=0.77 V (loss 0.47)

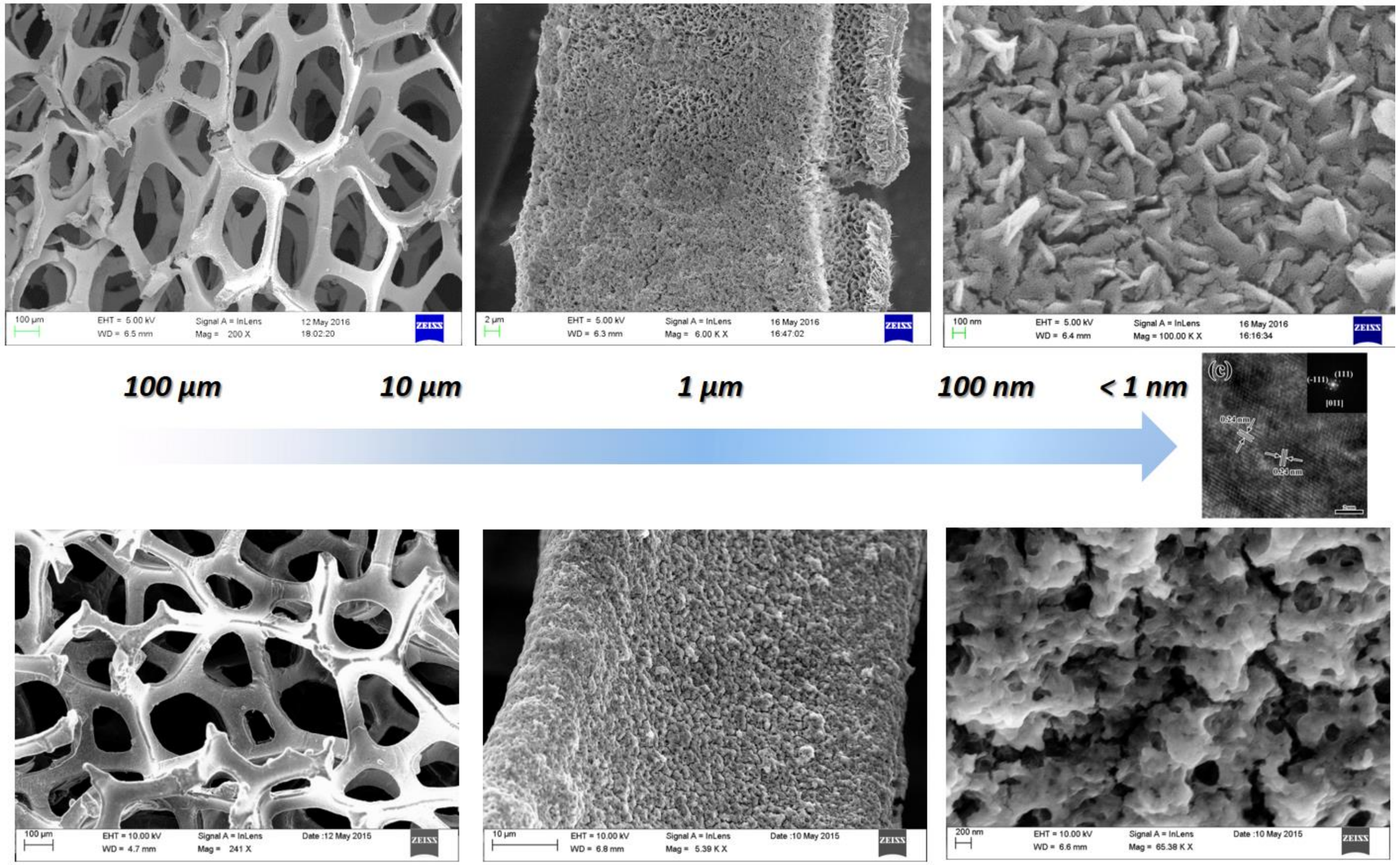
1.86 V at the MPP



For the non-precious and earth-abundant catalyst, >1.8 V at the maximum power point (MPP) is targeted.
Modules with 1.86 V at MPP developed.

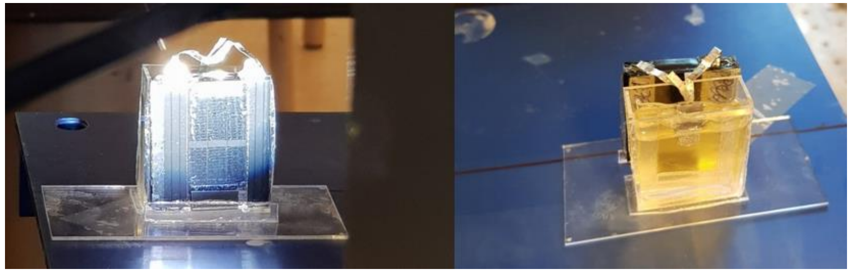
Catalyst development: From micro to nanostructuring.

NiO nanosheets/Ni foam



Fe-NiO nanosheets/Ni foam

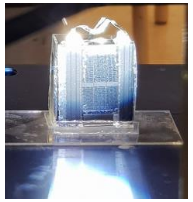
1st generation integrated device assembly



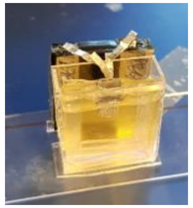
Water splitting set-ups using CIGS/NiO/membrane/NiMoW4 with sputtered catalysts (left) and CIGS/FeNiO/membrane/NiMo with hydrothermally grown catalysts (right).

The distance between the electrodes are 1 mm and the CIGS is attached on the container to provide a thermal contact ***enabling heat exchange with the electrolyte*.**

PV	EC	PV-Area(cm^2)	EC-Area(cm^2)	I measured (mA)	STH (%)
CIGS-3	NiO/NiMoW4	0.27	0.25	2.8	12.78



PV	EC	PV-Area(cm^2)	EC-Area(cm^2)	I measured (mA)	STH (%)
CIGS-2	FeNiO/NiMo	0.9	0.25	9.22	12.60



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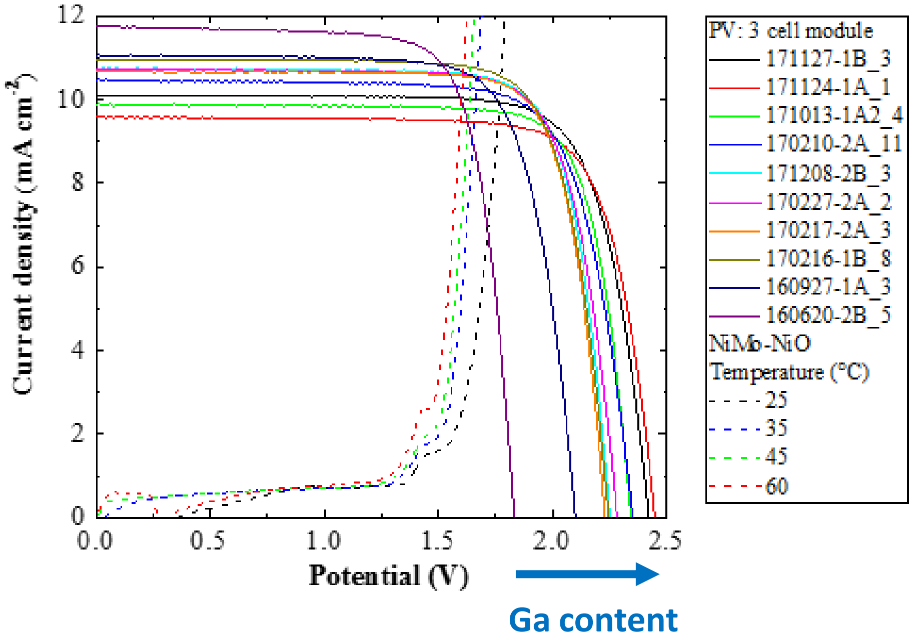
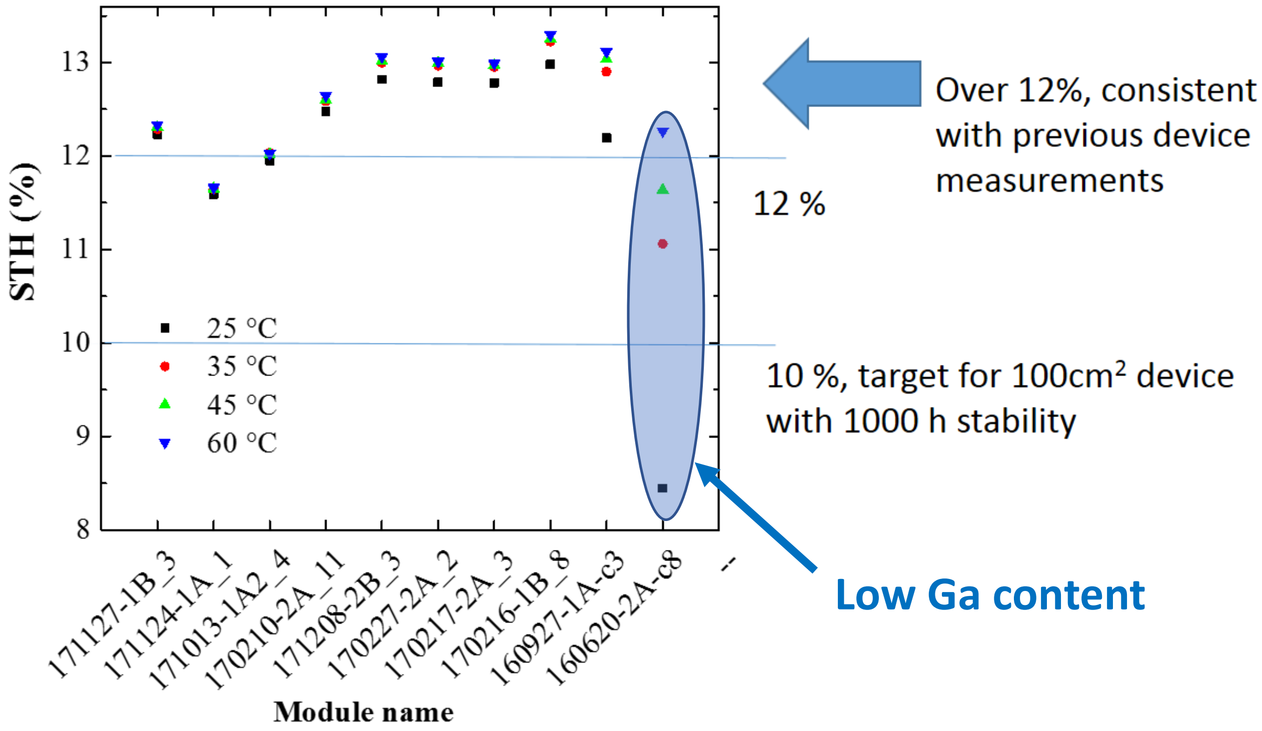
Sensitivity to Ga content and electrolyte temperature





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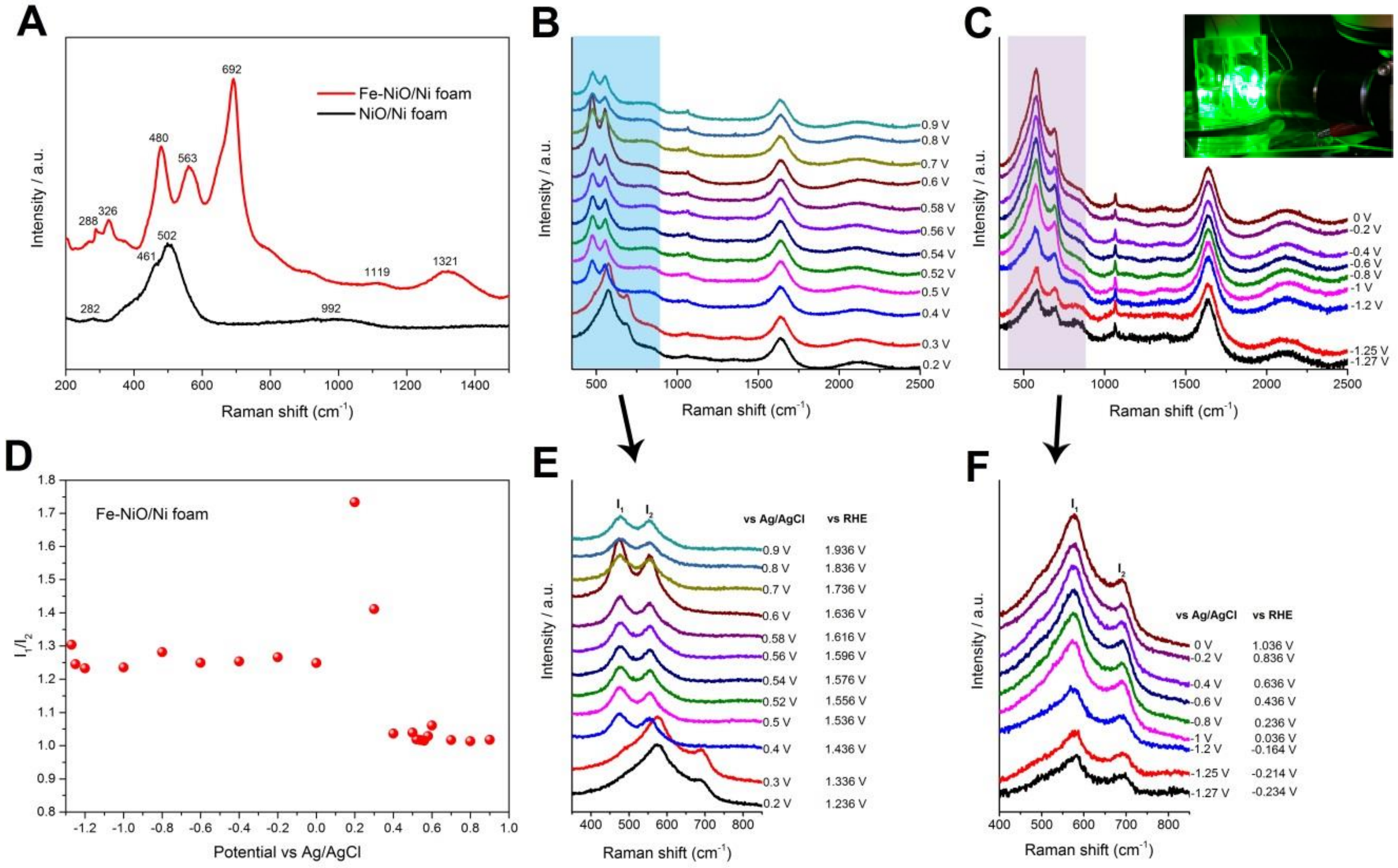
In-operando Raman spectroscopy lifted in from other projects



Vetenskapsrådet

Swedish research council

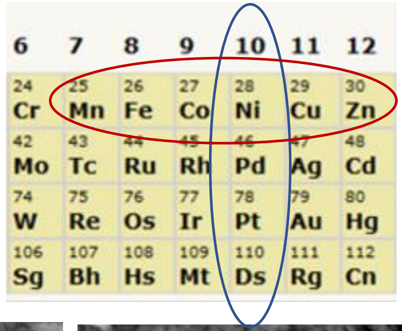
Energy & Environmental Science **2019**, 12, 572
Nano Energy **2019**, 66, 104118

Investigations of scalability of hydrothermally grown catalysts vs sputtered catalysts

Pt electronic configuration

[Xe]$4f^{14}5d^{9}6s^{1}$

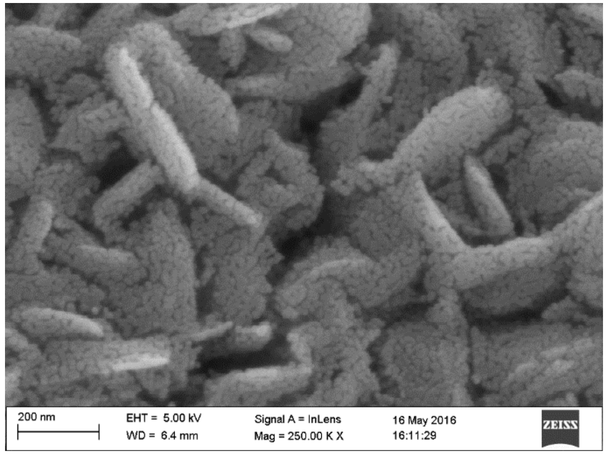
Work function: 5.12 – 5.93 eV

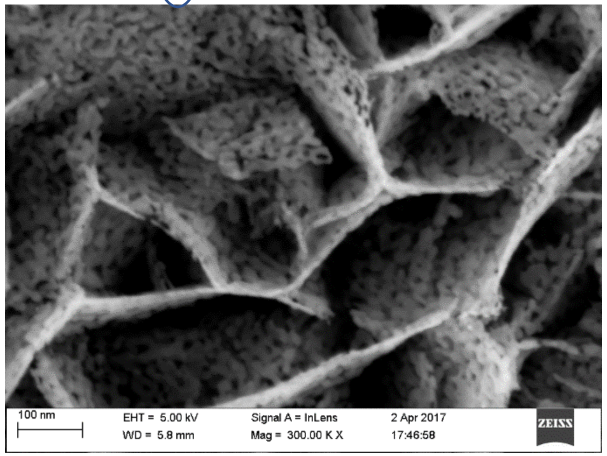


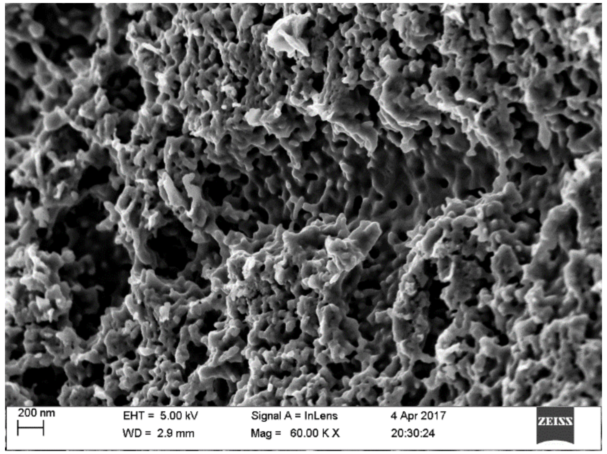
Ni electronic configuration

[Ar]$4s^{2}3d^{8}$

Work function: 5.04 – 5.35eV







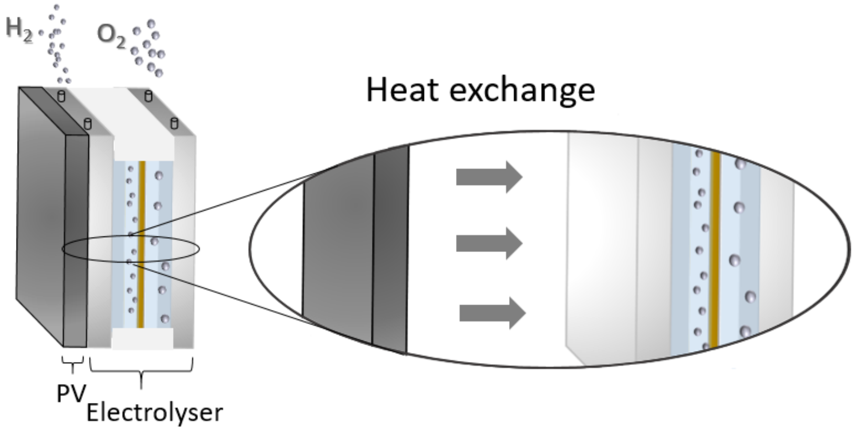
Non-precious HER and OER catalysts

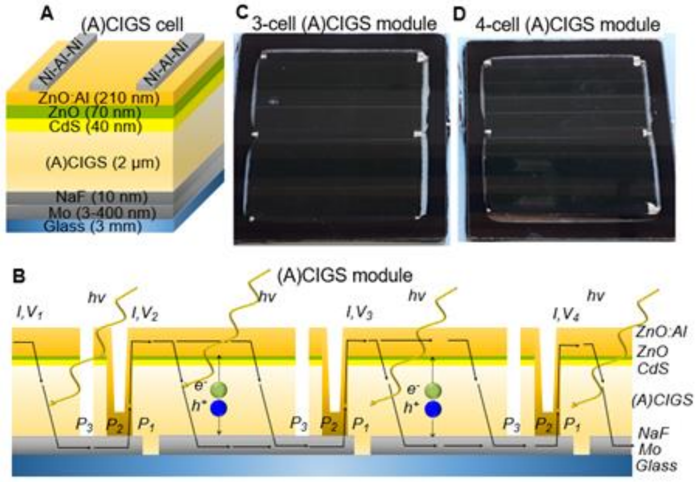
η_{HER}= 59 mV @ 10mA/cm^{-2}

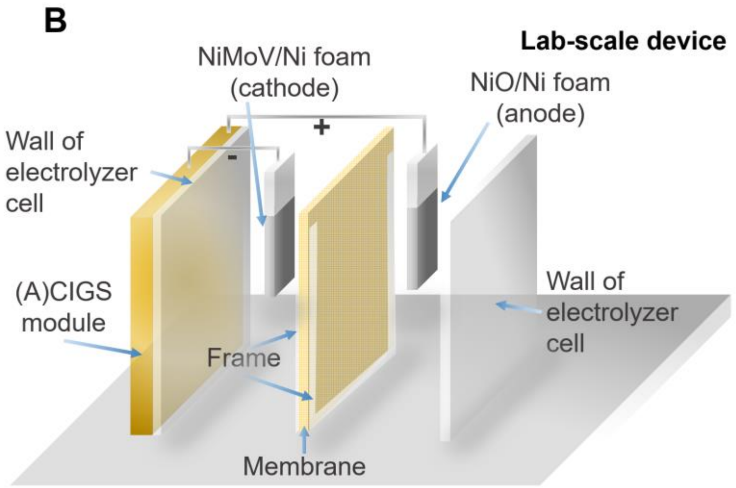
Best combination of HER and OER => **1.48 V @ 10 mAcm^{-2}**

83% electricity-to-fuel efficiency @ 10 mAcm^{-2} **(*95%* @ 1 mAcm^{-2})**

2nd and 3rd generation integrated device



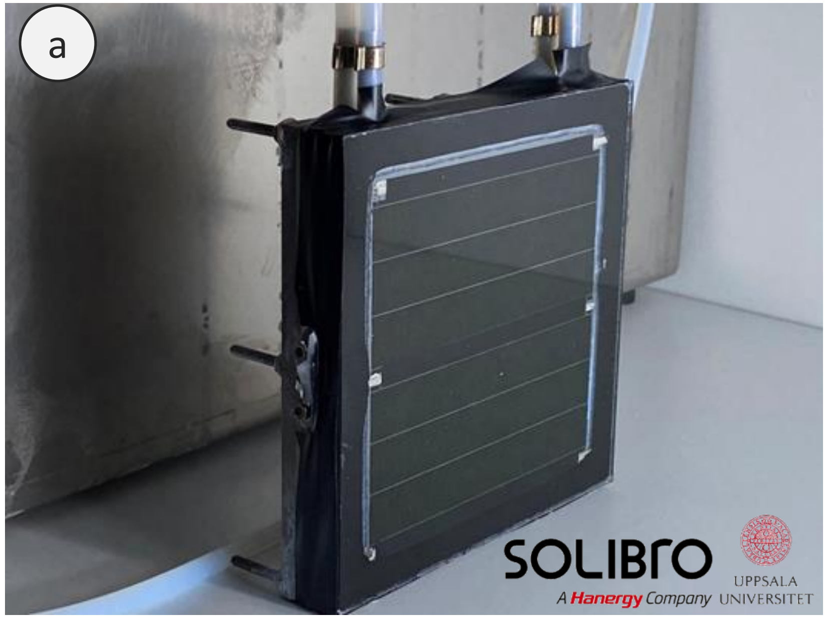


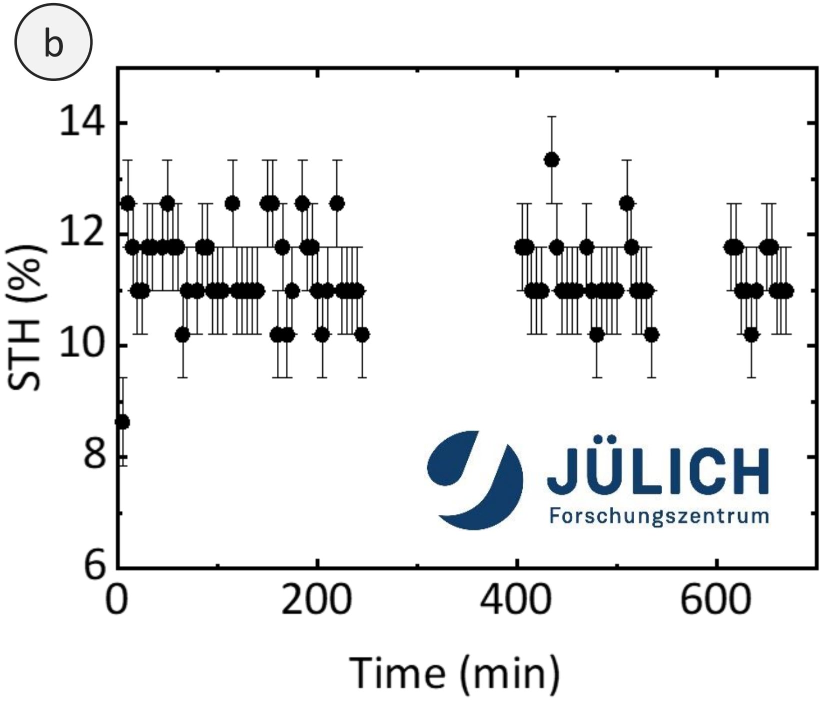


STH from 9% to 13%
(2nd to 3rd generation)

Bayrak Pehlivan, Oscarsson, Qiu,Stolt, Edoff, Edvinsson (manuscript under revision in iScience)

The 3rd generation integrated device





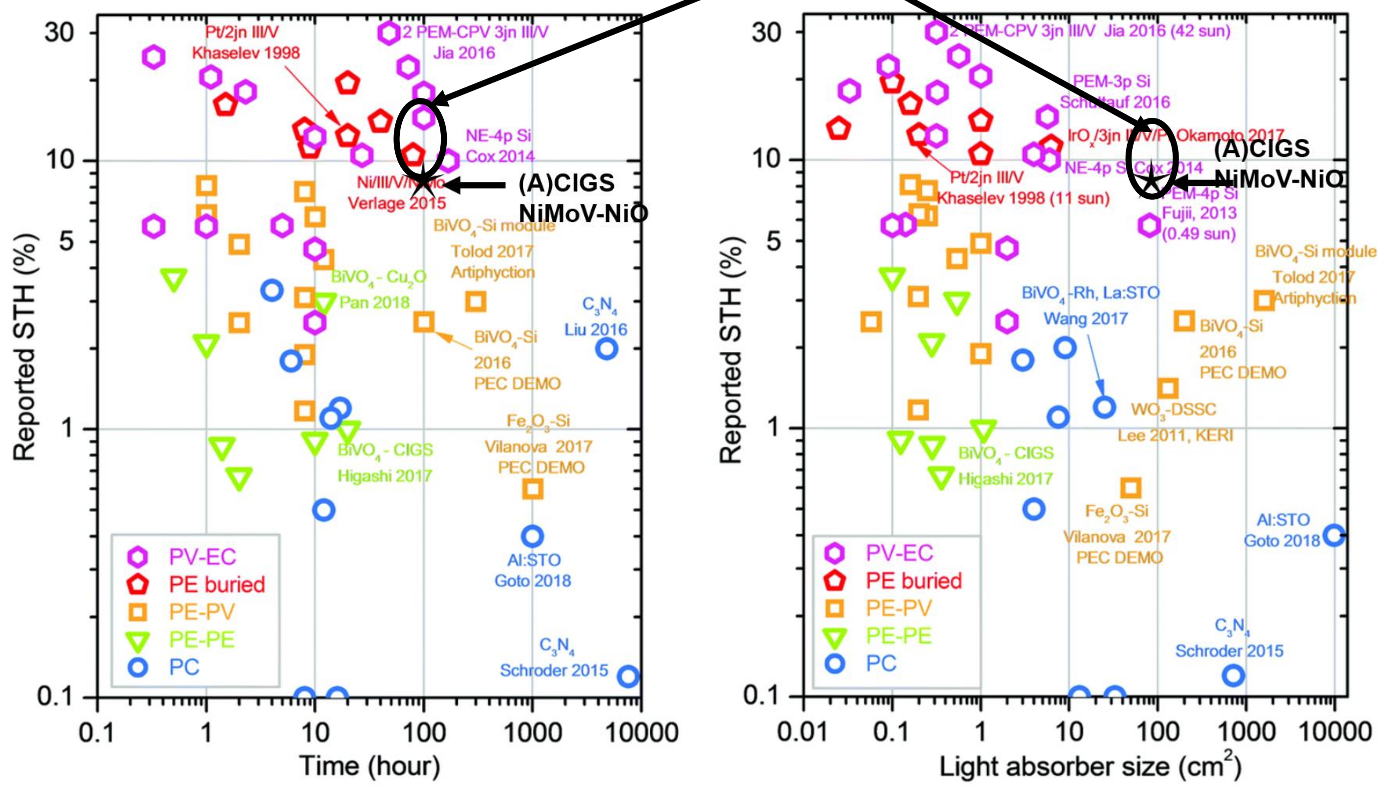
A thermally integrated device constructed with a 2×3-cell CIGS photovoltaic module (active area ~ 82.3 cm²) and a FeNiOH (cathode)-FeNiOH (anode)-based alkaline electrolyser with an electrode area of 100 cm²

3rd generation integrated device: The Movie

Progress beyond state of the art and impact

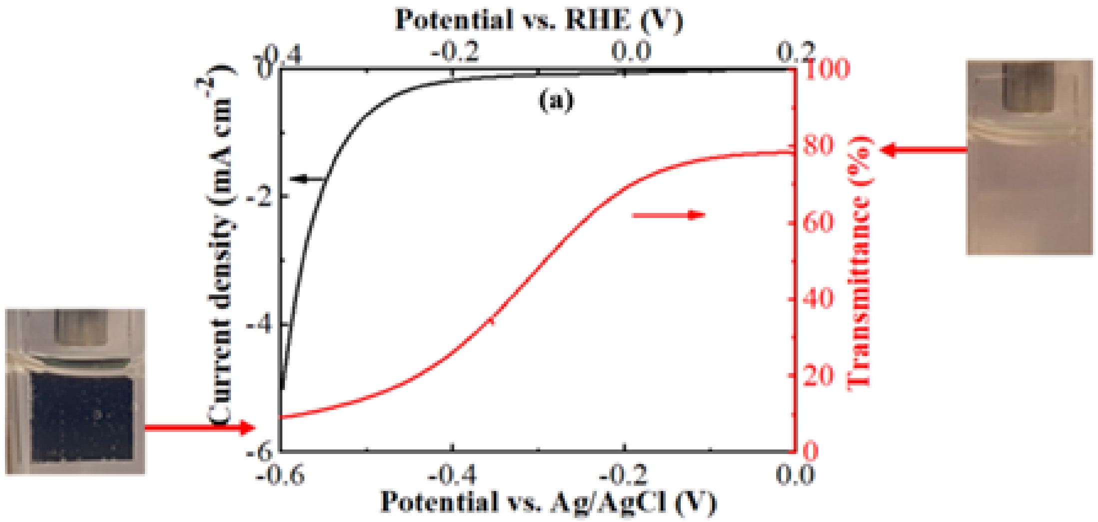
- Progress close to, and in some cases beyond state of the art

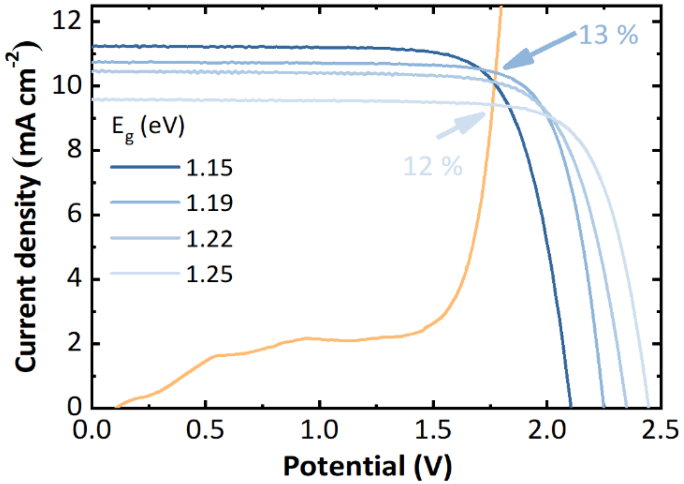
ACIGS + nano catalysts (3rd generation, STH 13%)



Data from Kim et al *Chemical Society Reviews*, 2019, 48: 1908-71.

Electrochromic water splitting using WO_3





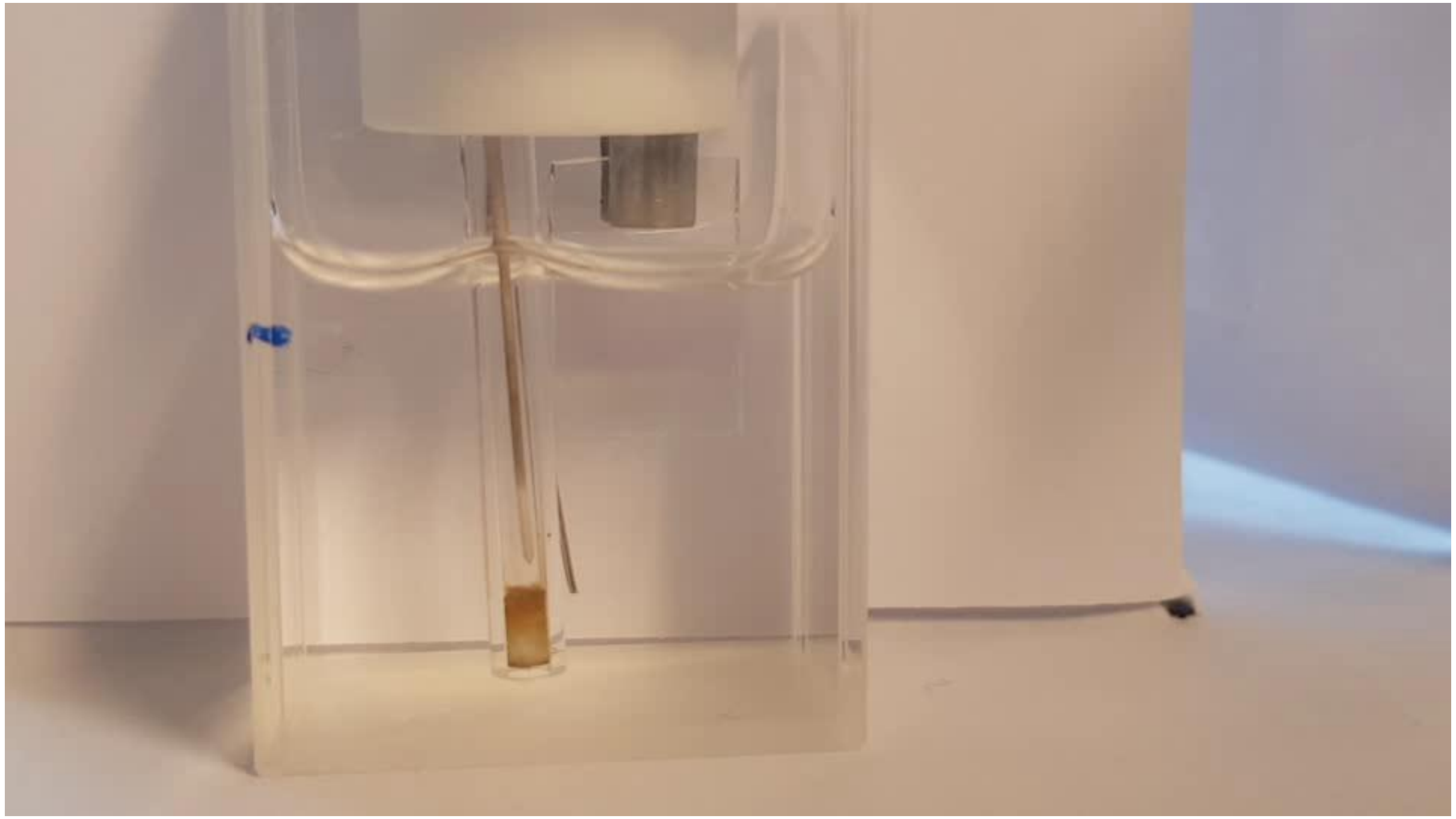
The coloration of WO_3 is attributed to intervalence electron transfer between W^{6+} and W^{5+} valence states during intercalation of H^+ during water splitting.

STH = 13% using WO_3 on Ni-foam and about half of that if using flat TCOs.

Bayrak Pehlivan, Atak, Niklasson, Stolt, Edoff, Tomas Edvinsson (manuscript under revision).

Erno.kemppainen@helmholtz-berlin.de

Electrochromic water splitting: The Movie



Conclusions and Outlook

Conclusions

- CIGS allow band gap modification to match a specific catalyst system
- Optimum Ga-content and targeted photovoltages achieved
- Sol-gel and sputtered non-precious catalyst were developed with good performance
- Final device generation allow heat exchange in-between the PV and electrolyzer and STH of 10-13% can be achieved even for CIGS modules with modest efficiency.

Outlook

- Further electrolyzer engineering
- Electrolyte development to include additives/freeze point depressors
- Development of high photovoltage 2-cell ACIGS modules

Thank you for your kind attention!

Acknowledgements: All members of the Consortium and

CIGS, Watersplitting
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Lars Stolt (Solibro AB)
Zhen Qiu (UU)
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Low dimensional semiconductors and catalysis
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