# Hydrogen Evolution Reaction and $CO_2$ Reduction Reaction on Customizable Metal Nanostructures on Silicon Electrodes

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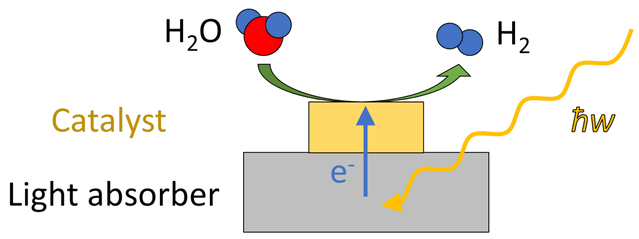
## Motivation

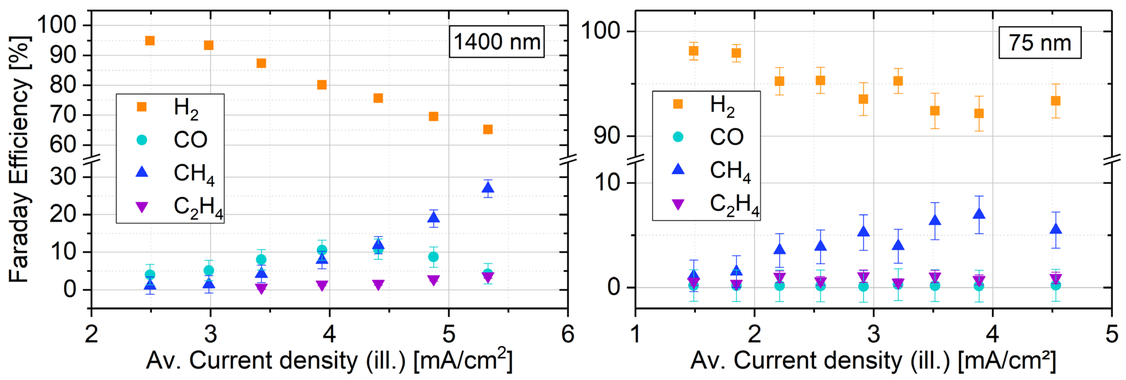
For the production of solar fuels by a photoelectrochemical device a light absorbing part must be combined with an electrocatalytic component. We investigate fundamental properties of the interface between a silicon-based light absorber and a metal-based catalyst.

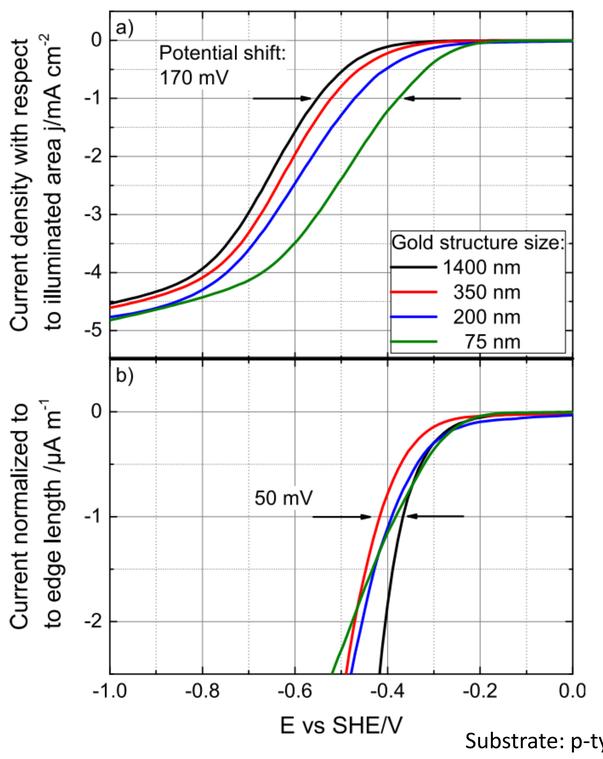



## Electrochemical properties of structured electrodes

We investigate the catalytic behavior of illuminated p-type silicon electrodes with gold islands, which were electrochemically plated with copper, towards $CO_2$ reduction reaction (CRR) and hydrogen evolution reaction (HER) in a $CO_2$ saturated neutral electrolyte (75mM $K_2CO_3$, pH = 6.8) for different gold structure diameters.

It is observed that the smaller the structures are the **higher** is the **share of $H_2$ product gas** compared to C-products. This indicates a preference of HER:




Substrate: p-type silicon

Additionally, it is observed for pure Au structures on p-type silicon substrate that the smaller the structures are, the **lower** is the **overpotential** needed for the onset of reduction reactions.

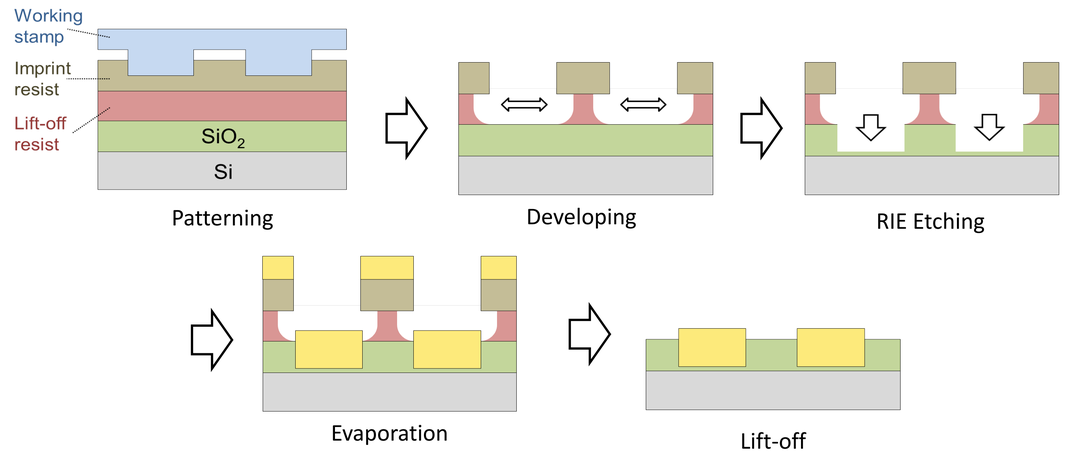
It is shown in [2] that the effect of lowering the overpotential:

(1) Is independent of substrate doping
=> Not caused by a MOS effect or photovoltage but has an electro-chemical origin

(2) Scales with the total boundary length of the $Au/SiO_2$ interface
=> Enhancement due to larger total boundary length

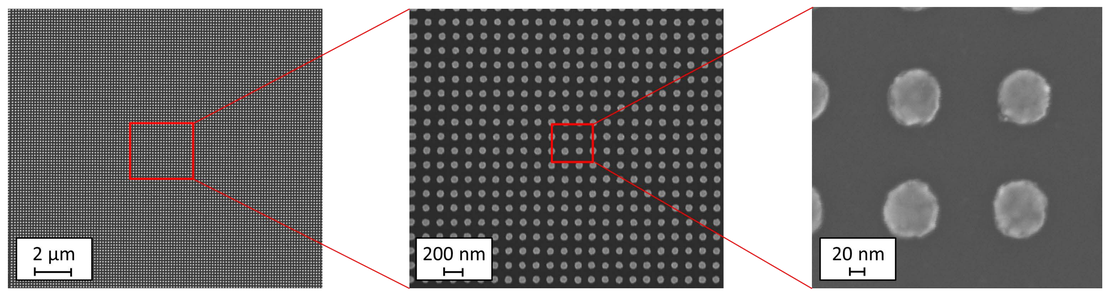
## Electrode fabrication: Lift-off nanoimprint lithography

The investigated electrodes are Metal/Oxide/Semiconductor (MOS) structures. We use mesoscopic metal islands (diameter between 1400nm – 75nm) as catalysts, which are fabricated with the method Lift-off nanoimprint lithography [1]:



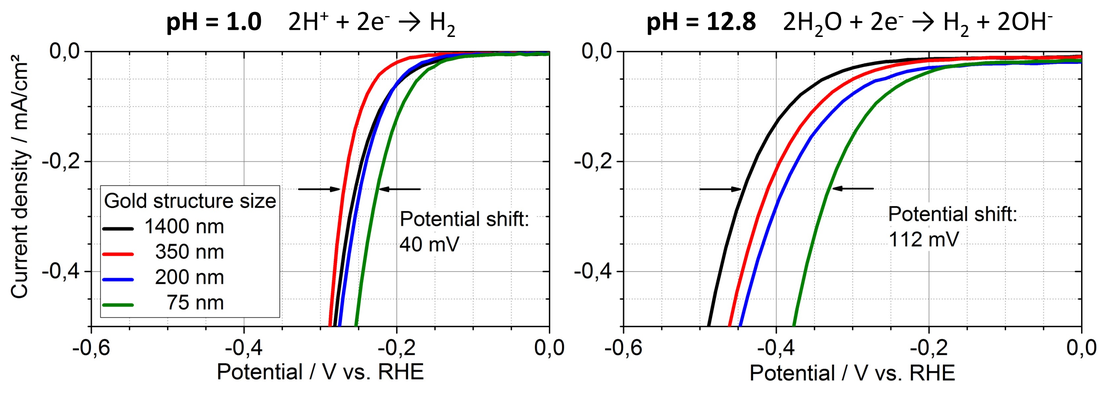

This fabrication technique allows for:

(1) Very homogenous nanopatterning on large scale (currently 5x5mm²)
(2) Tunable geometric properties (diameter, pitch ratio)
(3) Customizable substrate, oxide and catalyst material (e.g. Au, Pt, Cu)

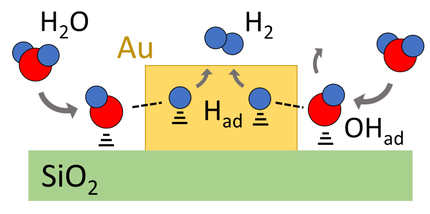



## Enhancing alkaline HER by electrode structuring

A study of gold structures on n-type silicon substrate regarding HER shows that this onset-potential shift (mentioned left) is **more pronounced in alkaline** than in acidic medium. Thus it appears that the effect is sensitive to the reaction mechanism:




Substrate: n-type silicon




**Possible Explanation**: Occurrence of a bicatalytic mechanism taking place at the $Au/SiO_2$ boundary, which enhances the alkaline HER.

## References

[1] R.D. Nagel, S. Filser, T. Zhang, A. Manzi, K. Schönleber, J. Lindsly, J. Zimmermann, T.L. Maier, G. Scarpa, K. Krischer, P. Lugli; *J. Appl. Phys*., **2017**, 121(8), 84305.
[2] S. Filser, T.L. Maier, R.D. Nagel, W. Schindler, P. Lugli, M. Becherer, K. Krischer; *Electrochimica Acta,* **2018**, 268, 546-553

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e-conversion
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