MIS Photocathodes for Solar Fuel Generation

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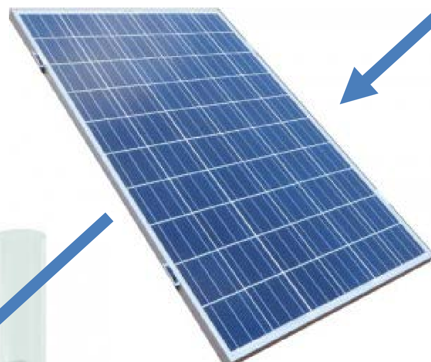
TU München

Solar to Chemical Energy

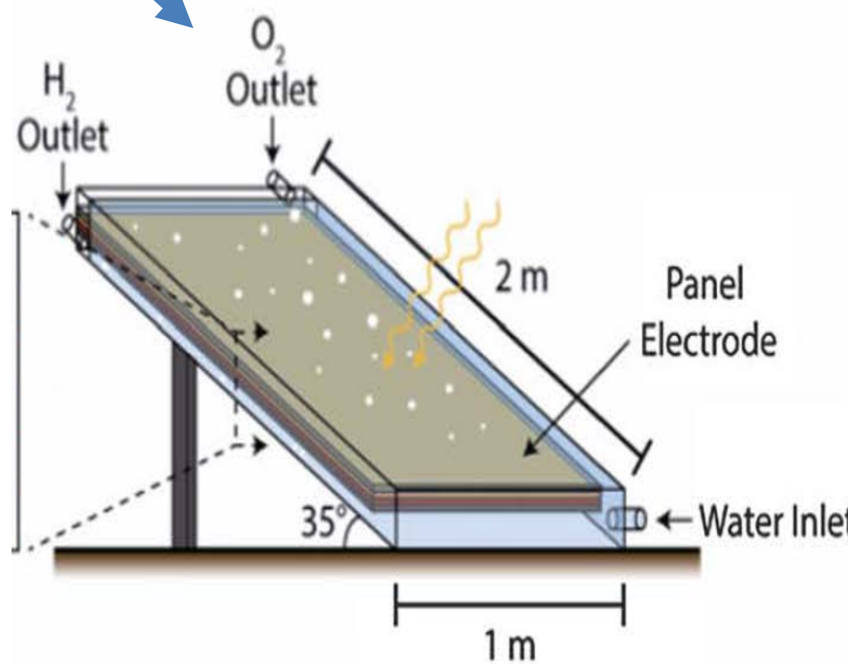
PV – E

Photovoltaic + Electrolyzer



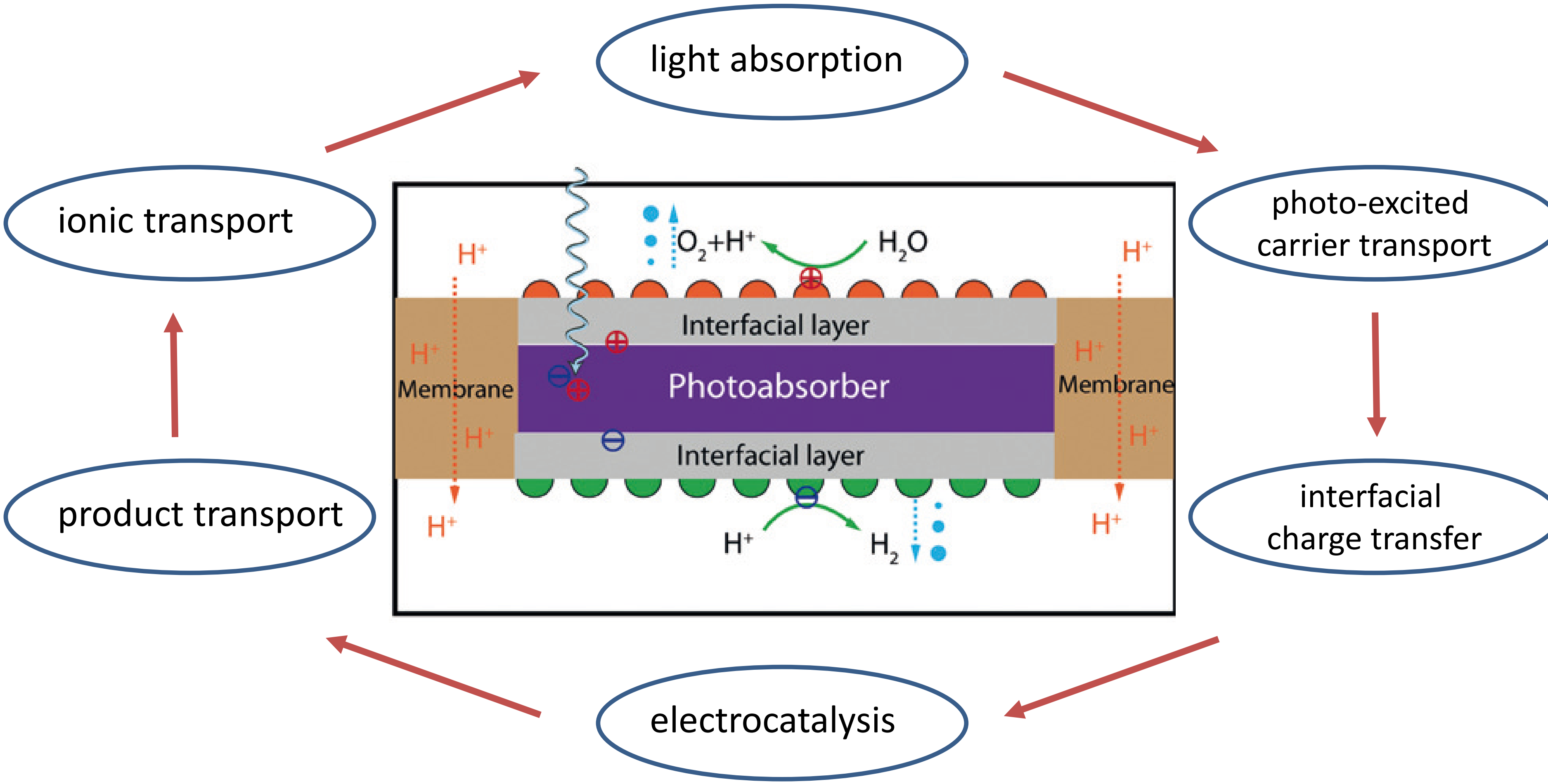
PEC

Integrated photoelectrolysis system



Pinaud et al., *Energy Environ. Sci.*, 2013, **6**, 1983

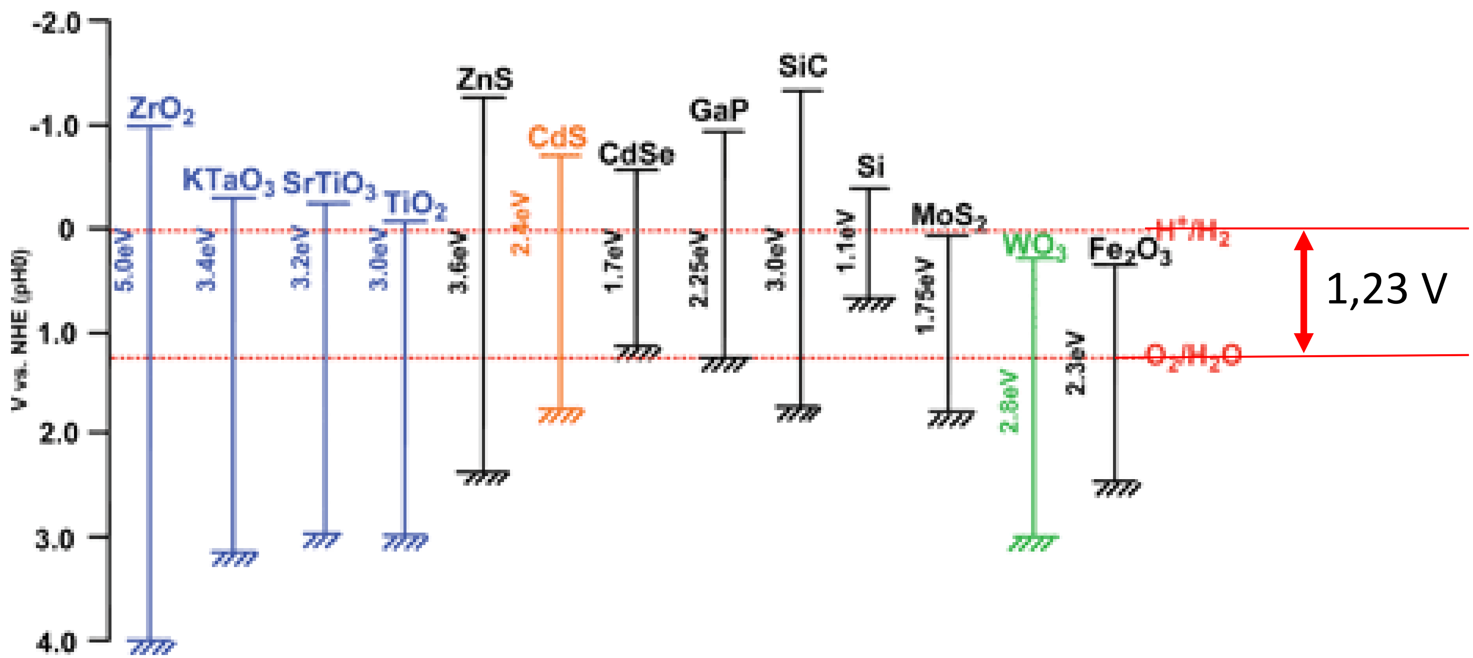
Coupled elementary processes in a PEC



Xiang et al., *Angew. Chem. Int. Ed.*, 2016, **55**, 12974

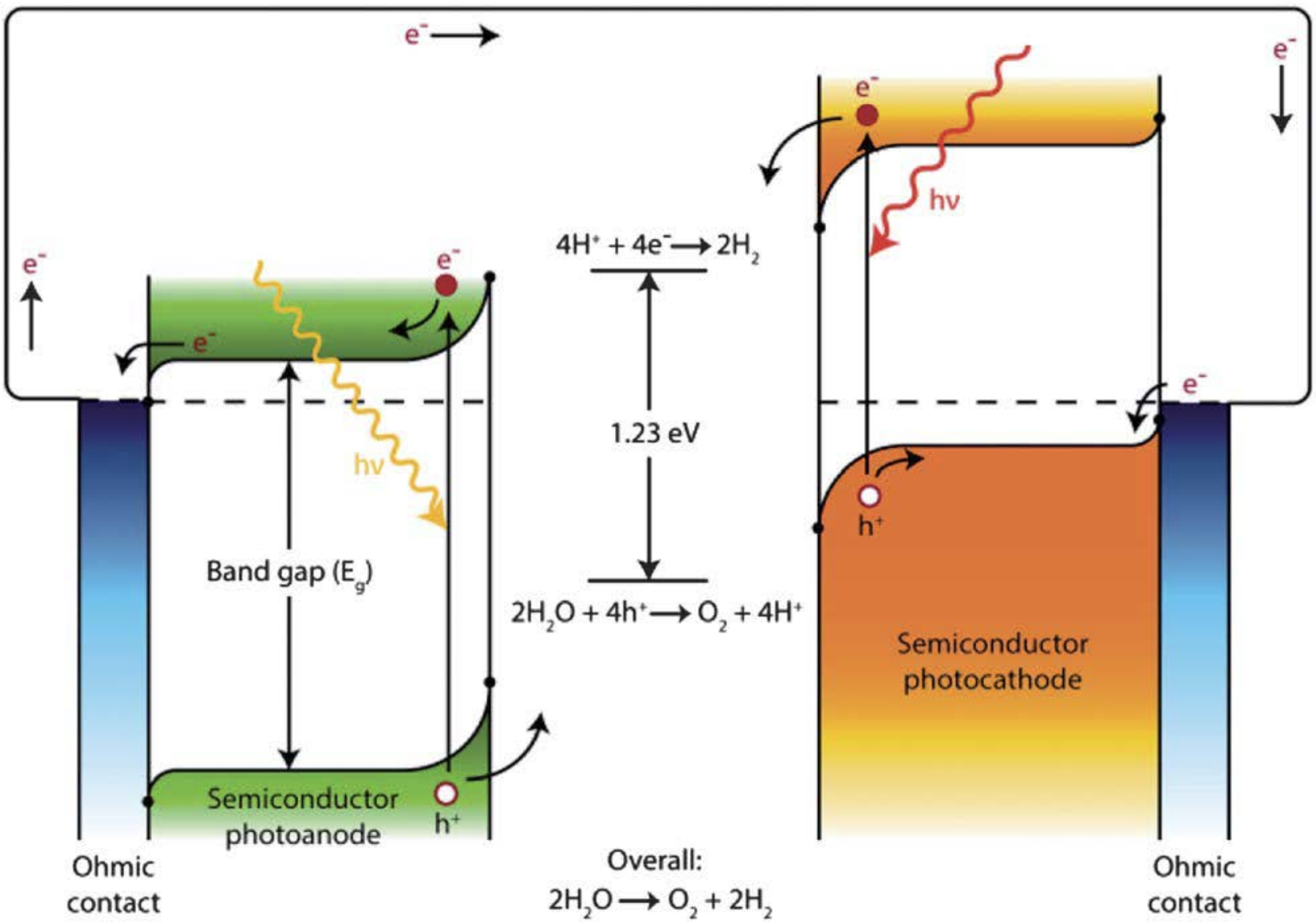
Energetics

To drive water splitting: U >> 1,23 V → Dual junction cells



Kudo and Miseki, *Chem. Soc. Rev.,* 2009, **38**, 253-278

Band Diagram



Pinaud et al., *Energy Environ. Sci.*, 2013, **6**, 1983

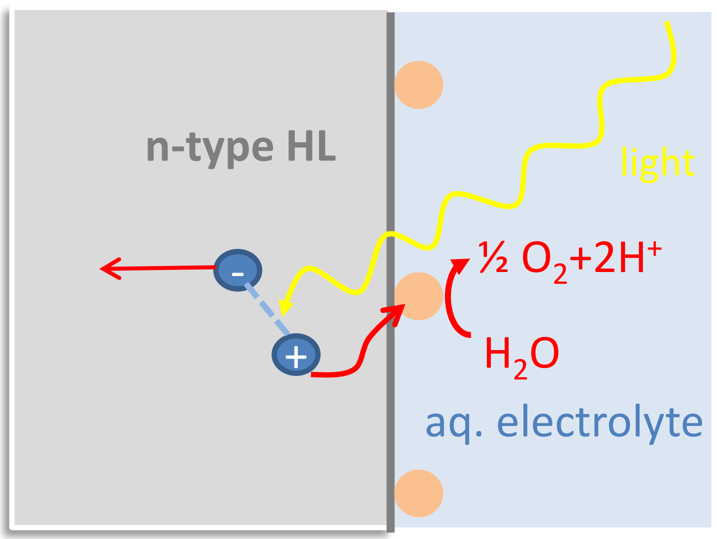
Alternative solar fuels from CO_2 reduction

Reaction		E_0 [V]
$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\rightleftharpoons 2\,H_2O(l)$	1.23
$2\,H^+(aq) + 2\,e^-$	$\rightleftharpoons H_2(g)$	0.00
$CO_2(g) + 2\,H^+(aq) + 2\,e^-$	$\rightleftharpoons CO(g) + H_2O(l)$	-0.11
$CO_2(g) + 8\,H^+(aq) + 8\,e^-$	$\rightleftharpoons CH_4(g) + 2\,H_2O(l)$	0.17
$CO_2(g) + 2\,H^+(aq) + 2\,e^-$	$\rightleftharpoons HCOOH(l)$	-0.25
$2\,CO_2(g) + 12\,H^+(aq) + 12\,e^-$	$\rightleftharpoons C_2H_4(g) + 4\,H_2O(l)$	0.08

- Suppresion of H_2 evolution
- Selectivity

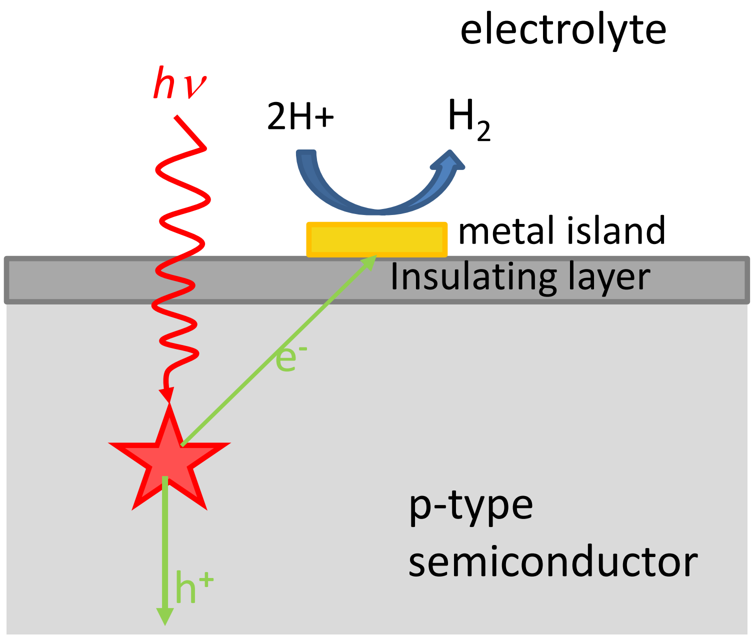
Optimization of the Semiconductor- Electrolyte Interface

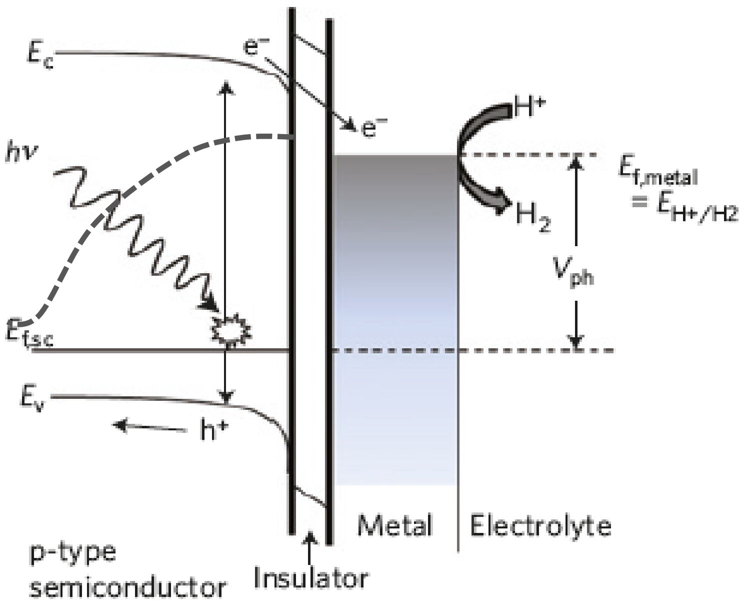
Requirements for high efficiency



- High catalytic activity of the interface
- Sufficient passivation of the surface (low rate of electron-hole recombination)
- Adjustment of energy levels of catalyst and reaction
- No further parasitic energy levels in the electrolyte

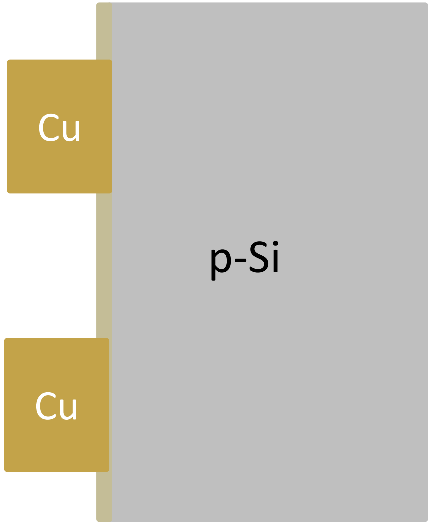
Metal/Insulator/Semiconductor Photoelectrode





Cu particle decorated SiO_2/p-Si electrodes

Combining two well studied subsystems



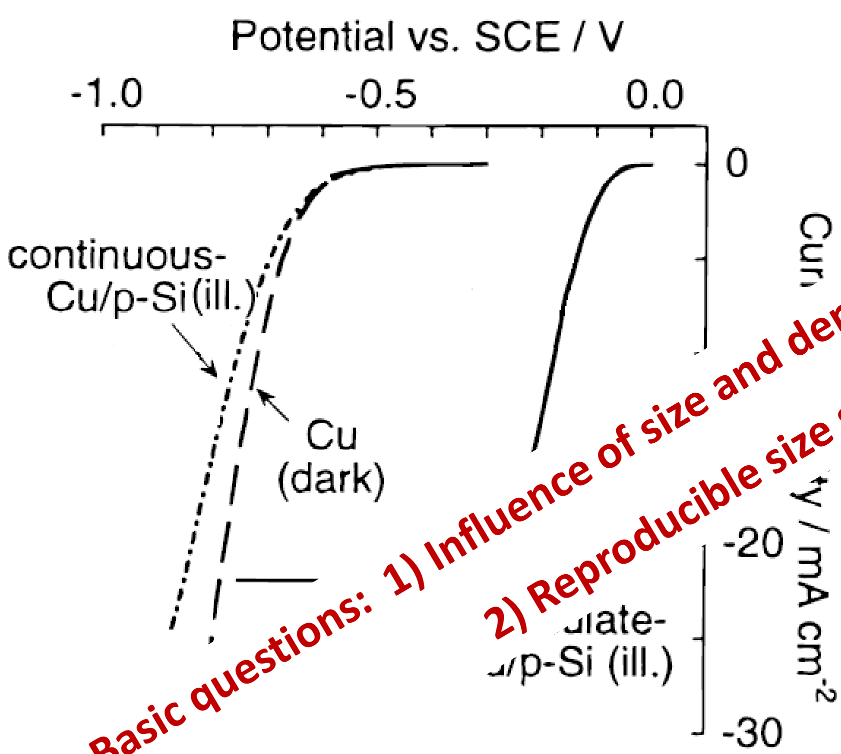
Advantages Si:

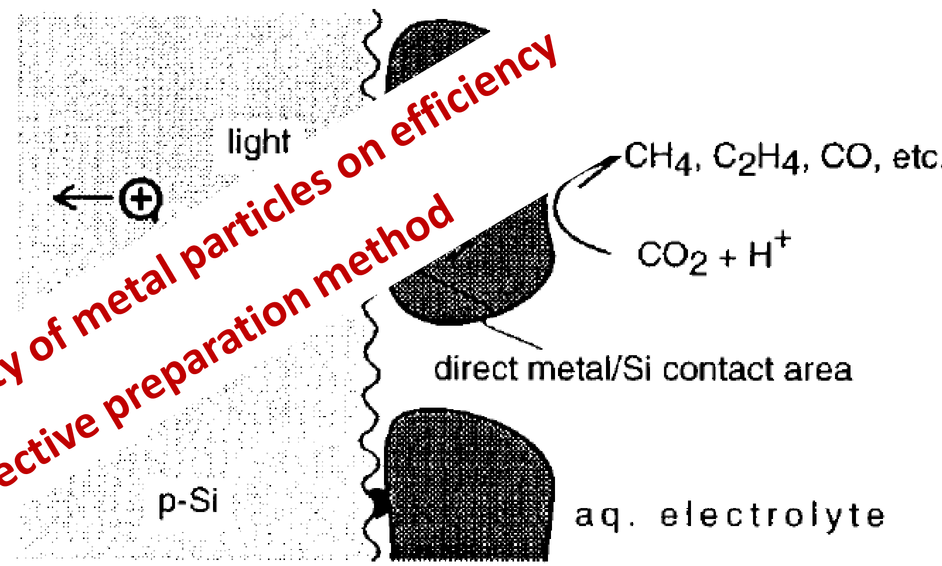
- abundant, sustainable
- band gap well matched to solar spectrum
- widely used in photovoltaics → technology available, low cost material
- SiO_2 insulating layer stable over wide pH and potential ranges

Advantages Cu:

- Electrochemically active for reduction of CO_2 to methane or ethylene
- Electrochemistry well studied

Current understanding: CO_2 reduction on p-Si/Cu photoelectrodes



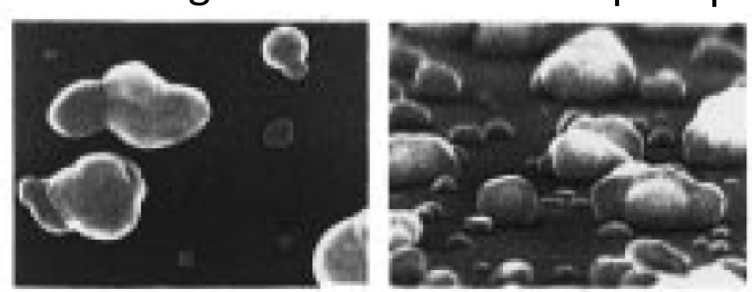


Basic questions: 1) Influence of size and density of metal particles on efficiency

2) Reproducible size selective preparation method

SEM image:

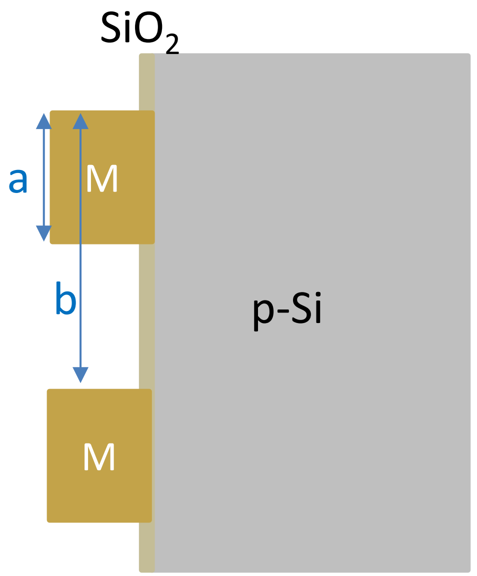
200 nm



R. Hinogami, Y. Nakamura, S. Yae, and Y. Nakato: J. Phys. Chem. B, 1998

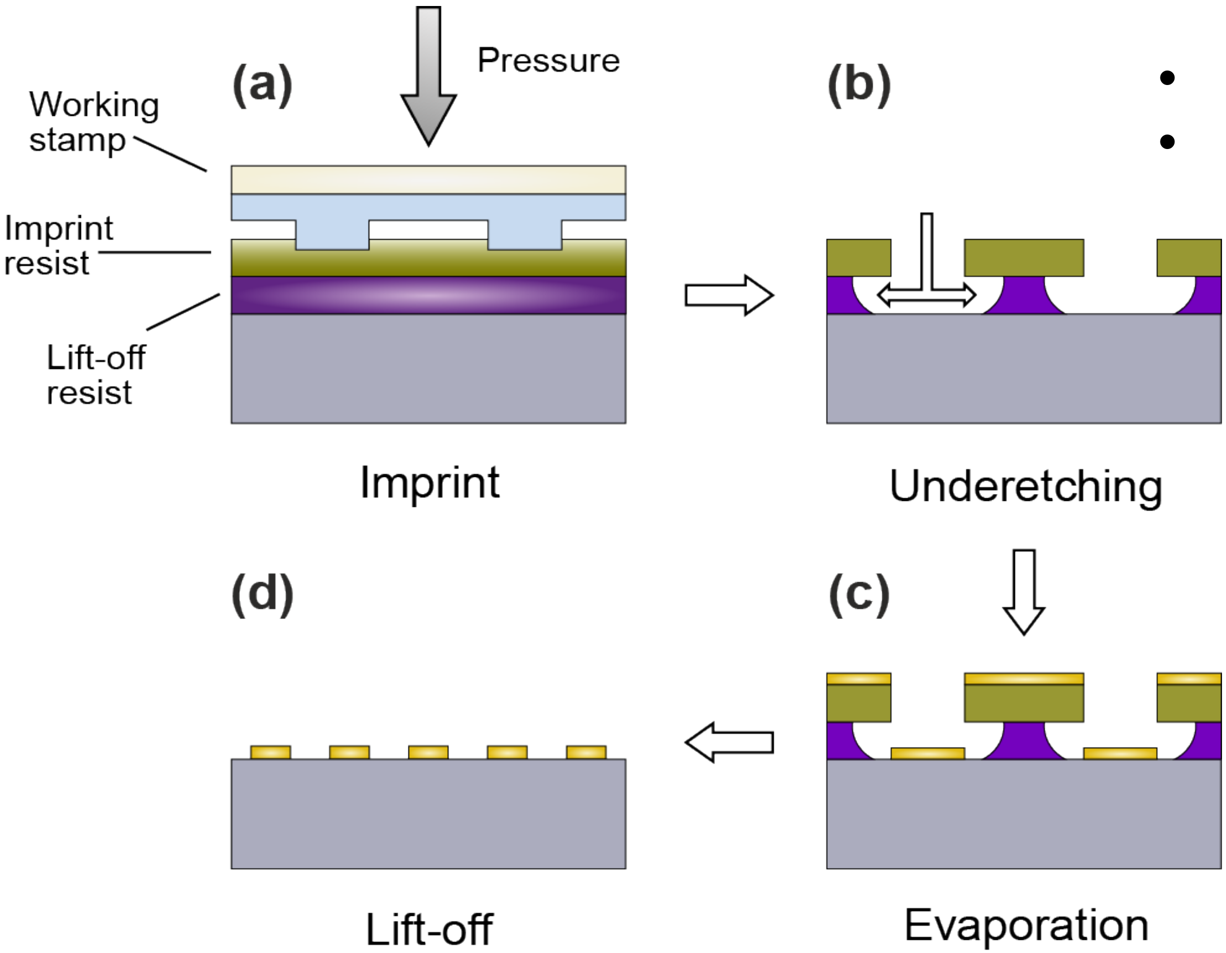
Ideal design of the Si/SiO_x/metal interface?

- Ideal strucutre size *a*
- Ratio of structure size *a* to pitch size *b*
- Influence on structure size on energetics and catalytic activity



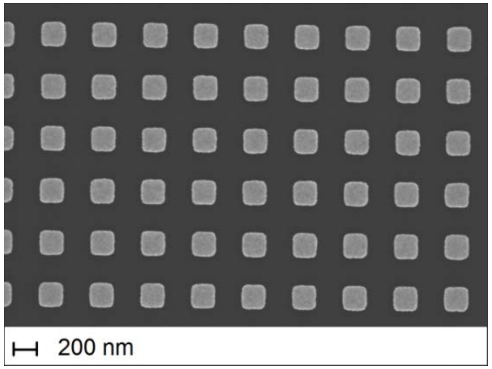
Lift-off nanoimprint lithography

large-scale deposition of metal structures (cm^2 range)

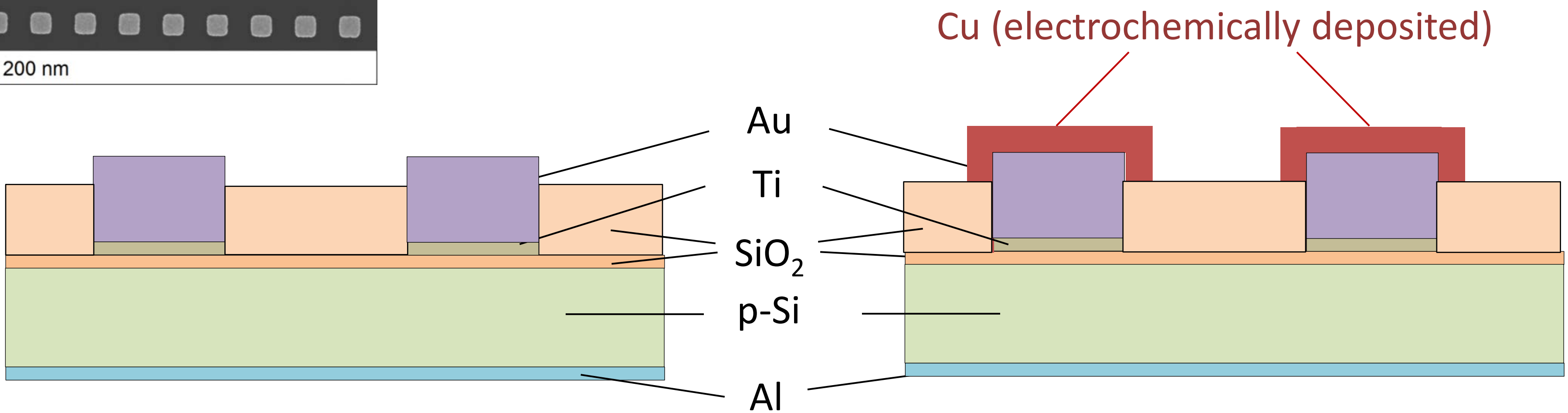


- Feature size down to 45nm
- Feature size tuning

R. D. Nagel. S. Filser, T. Zhang, A. Manzi, K. Schönleber, J. Lindsly, J. Zimmermann, T. L. Maier, G. Scarpa, K. Krischer, and P. Lugli, *J. Appl. Phys*., **2017**, 121(8), 84305.



Final Electrode Design



- SiO_2 (~ 1nm): diffusion barrier layer
- Ti (~ 0.5 nm): adhesion layer
- Thermal oxide (~ 15nm): passivating layer
- Au (Cu): electrochemically active area

R. D. Nagel. S. Filser, T. Zhang, A. Manzi, K. Schönleber, J. Lindsly, J. Zimmermann, T. L. Maier, G. Scarpa, K. Krischer, and P. Lugli, *J. Appl. Phys*., **2017**, 121(8), 84305.

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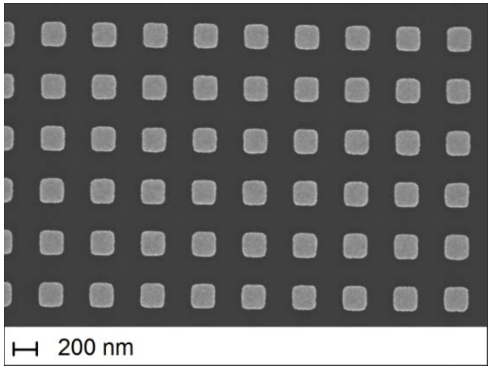
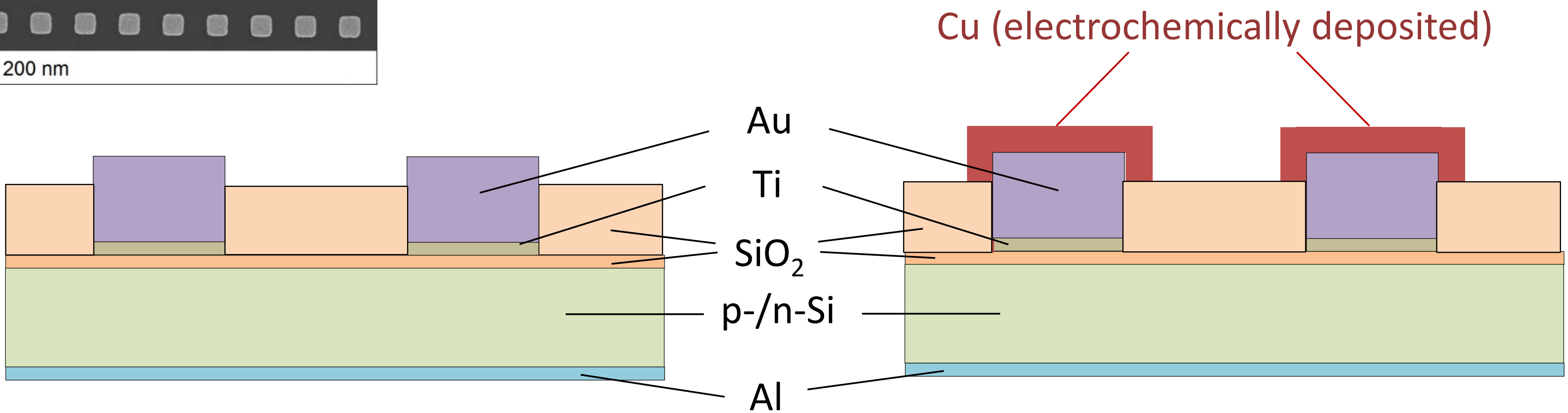


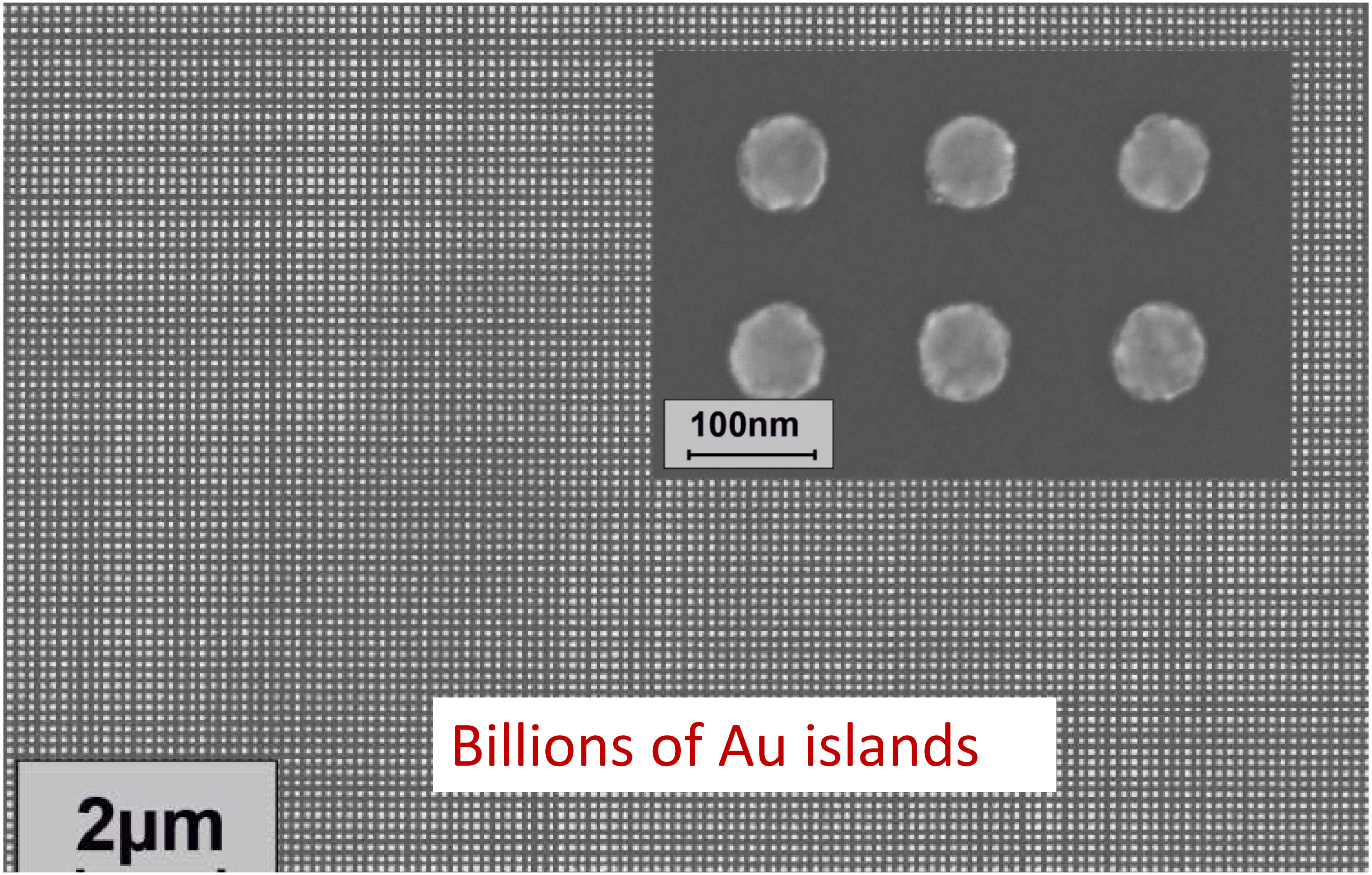


- SiO_2 (~ 1nm): diffusion barrier layer
- Ti (~ 0.5 nm): adhesion layer
- Thermal oxide (~ 15nm): passivating layer
- Au (Cu): electrochemcally active area

- Electrochemically stable
- Homogeneously distributed and well defined
- Tunable in size (down to 45 nm diameter possible)

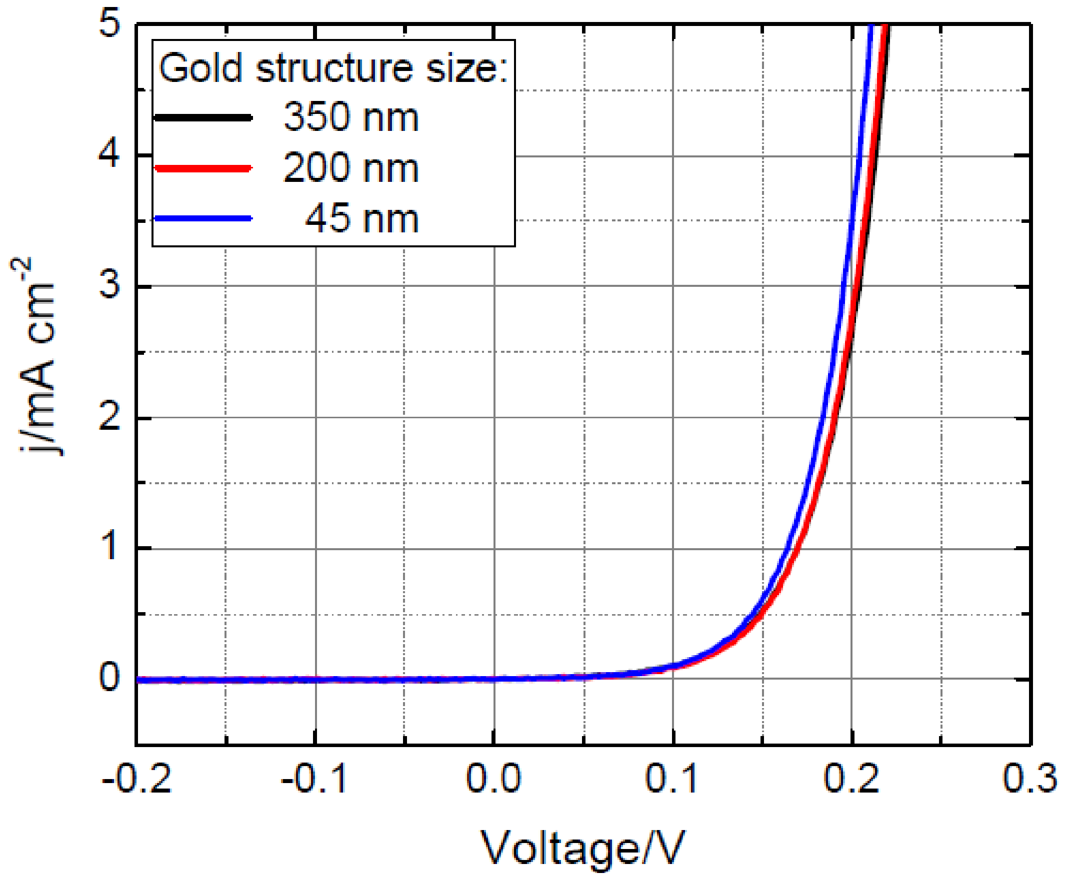
R. D. Nagel. S. Filser, T. Zhang, A. Manzi, K. Schönleber, J. Lindsly, J. Zimmermann, T. L. Maier, G. Scarpa, K. Krischer, and P. Lugli, *J. Appl. Phys*., **2017**, 121(8), 84305.

Lift-off nanoimprint lithography



R. D. Nagel. S. Filser, T. Zhang, A. Manzi, K. Schönleber, J. Lindsly, J. Zimmermann, T. L. Maier, G. Scarpa, K. Krischer, and P. Lugli, *J. Appl. Phys*., **2017**, 121(8), 84305.

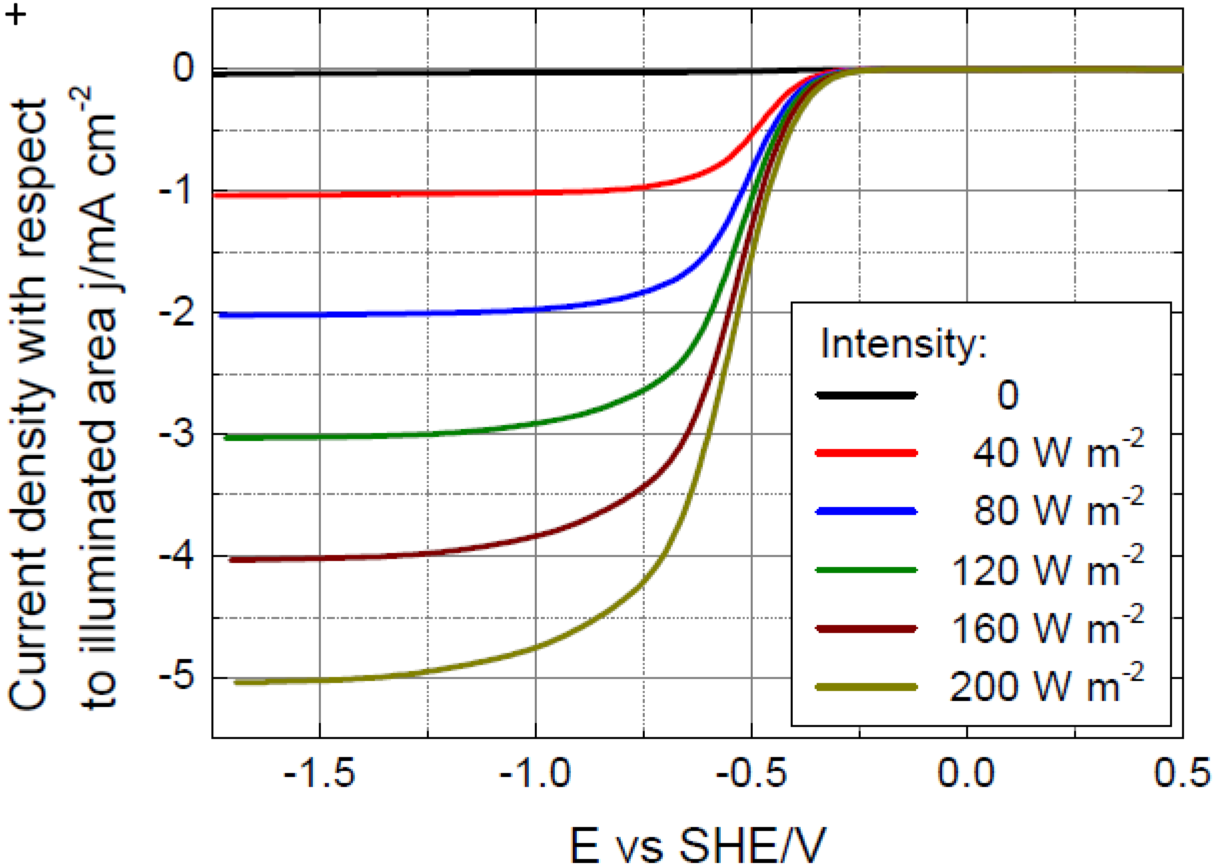
‚Dry' *I*-*U* curves of p-Si/SiO_2/Ti/Au nanostructure



Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochim. Acta (2018)

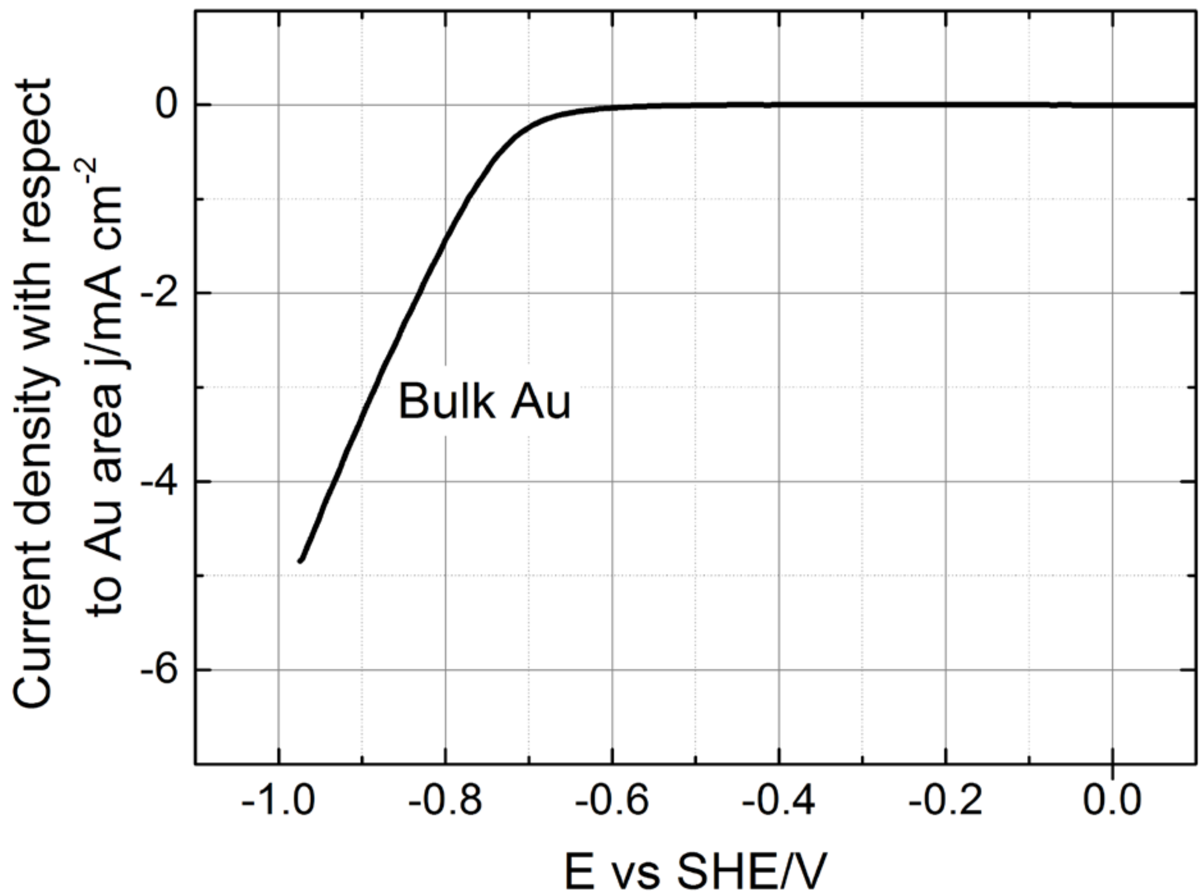
I-U curves of the Au/Ti/SiO_2/p-Si/electrolyte interface for different illumination intensities

- WE: 200 nm Au squares
- Electrolyte: 75 mM K_2CO_3 + 100 mM H_3PO_4 purged with CO_2



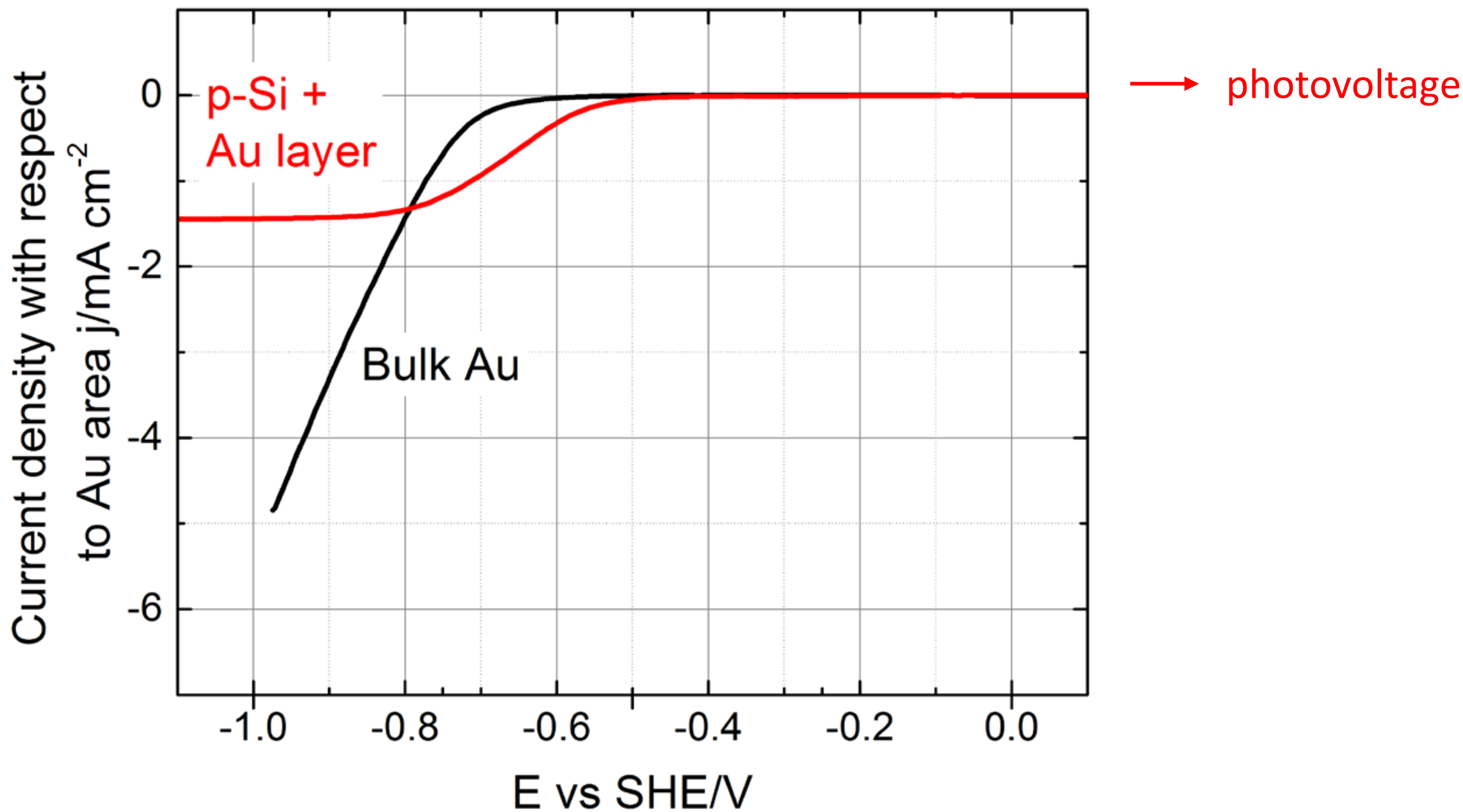
Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochim. Acta (2018)

Comparison of continuous Au layer and nanostructured Au on p-Si/SiO_2



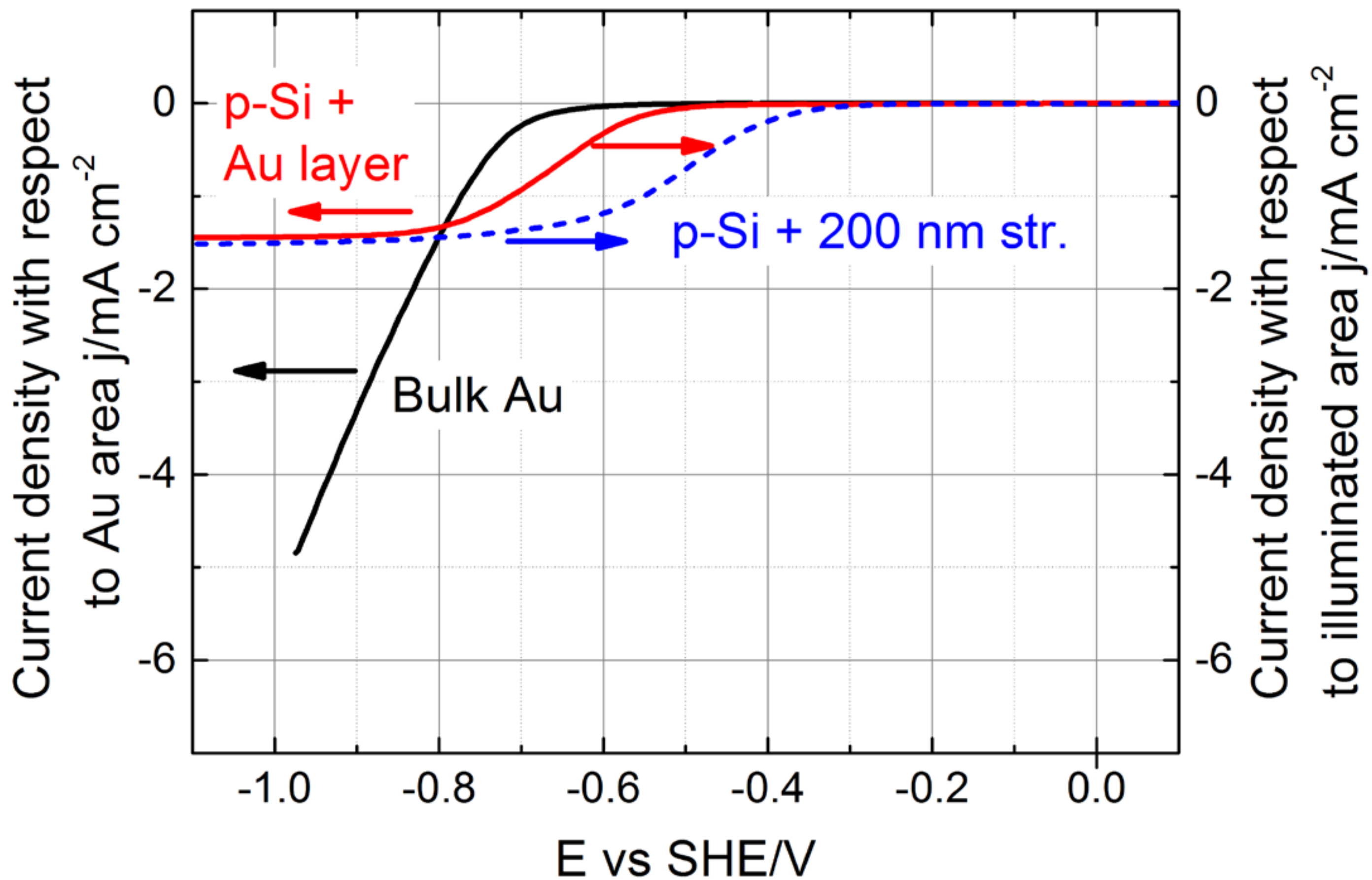
Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

Comparison of bulk Au, continuous Au layer and nanostructured Au on SiO_2/p-Si



Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

Comparison of bulk Au, continuous Au layer and nanostructured Au on p-Si/SiO$_2$



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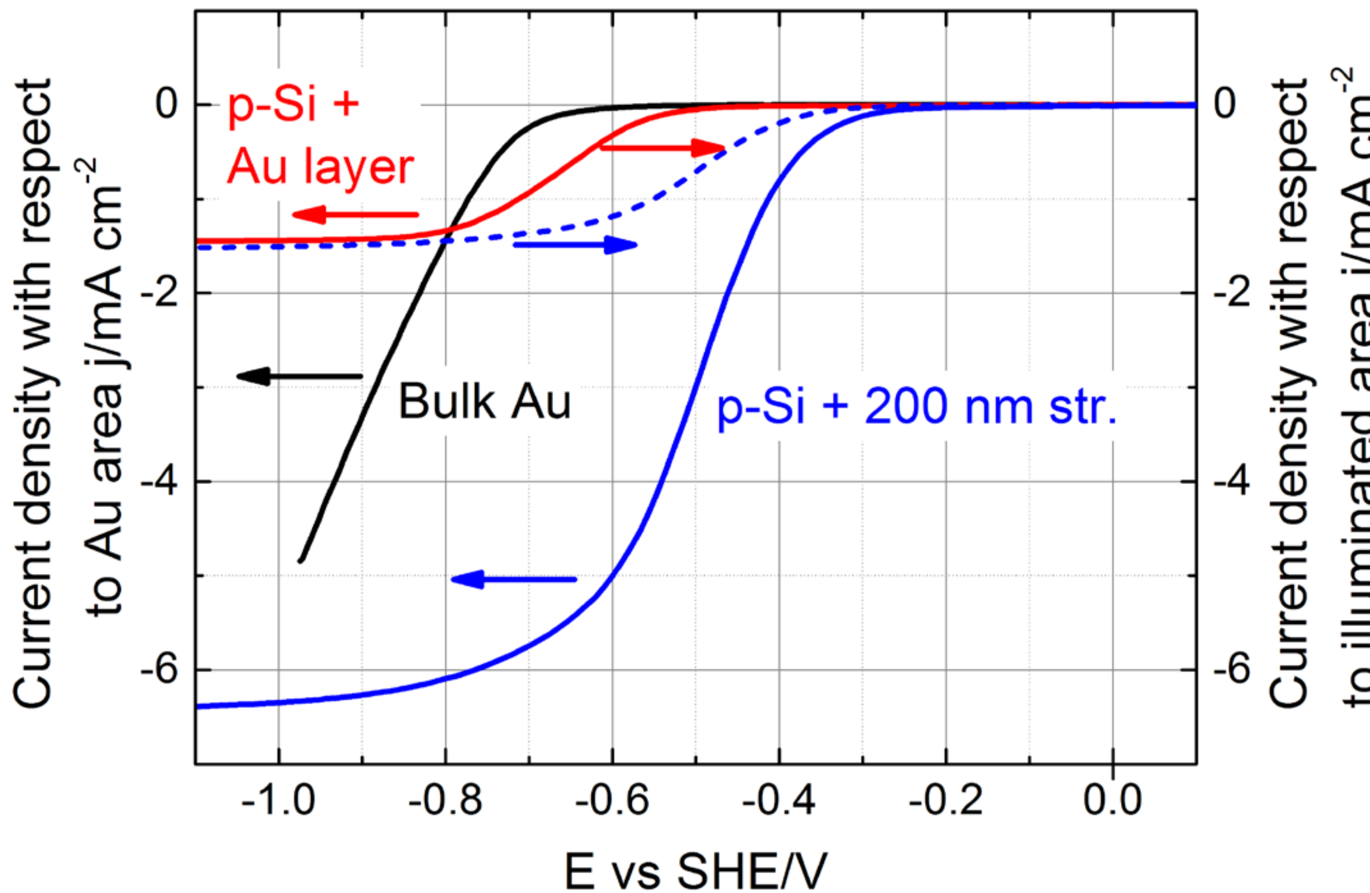
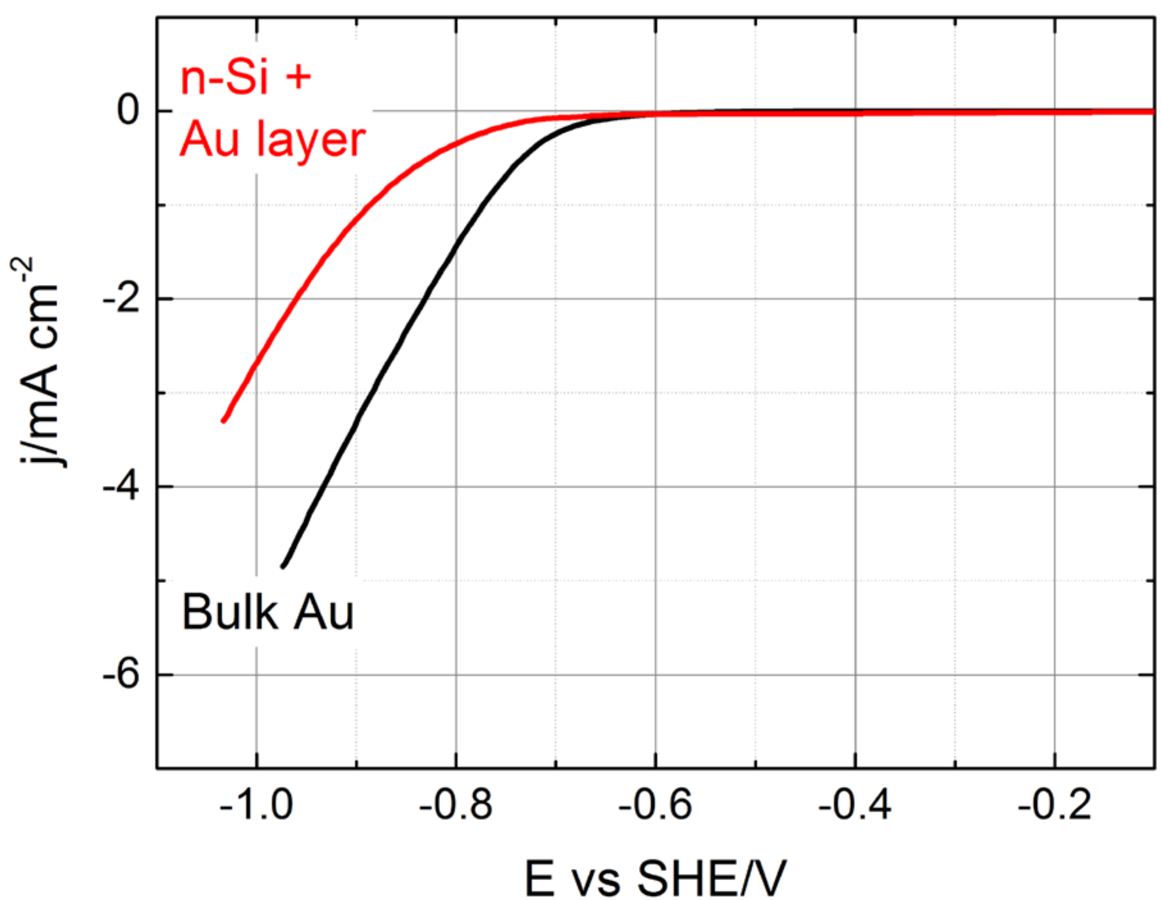


Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

Comparison of bulk Au and n-Si and p-Si based MIS electrodes



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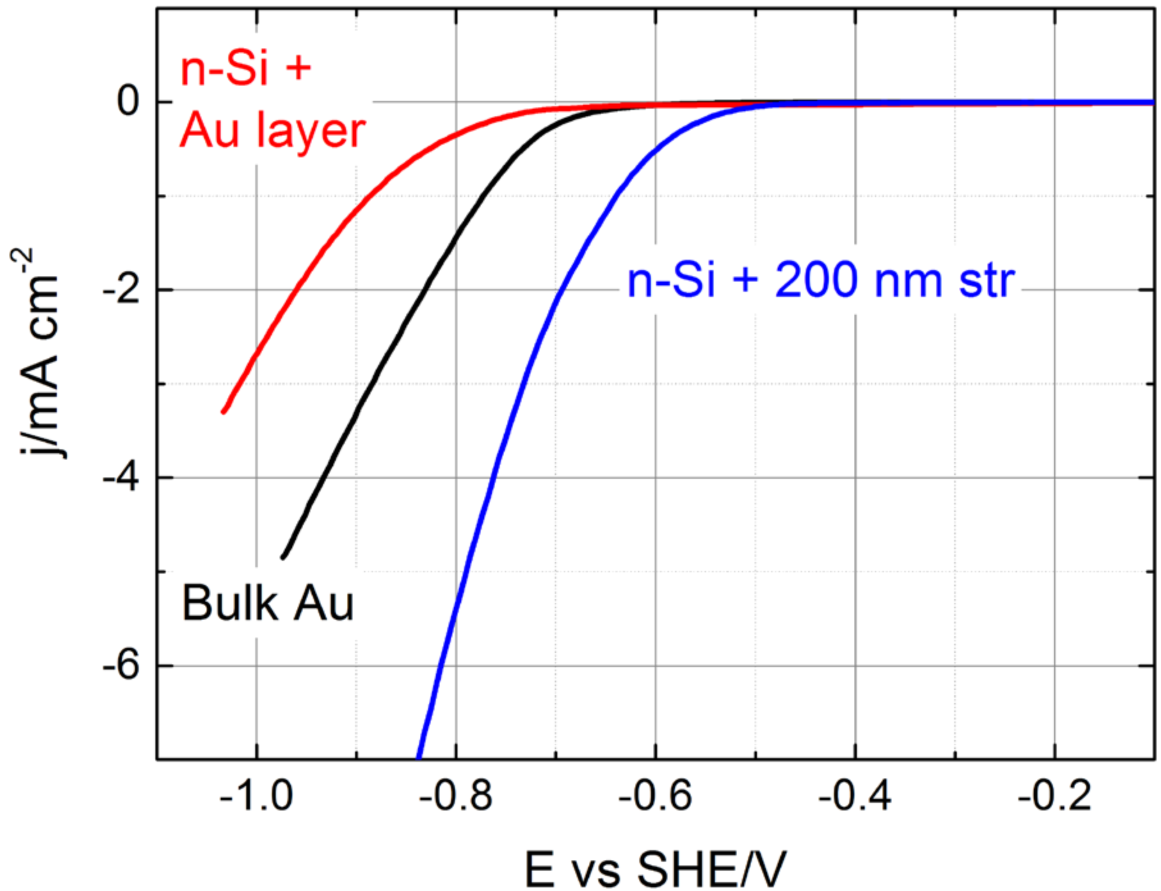

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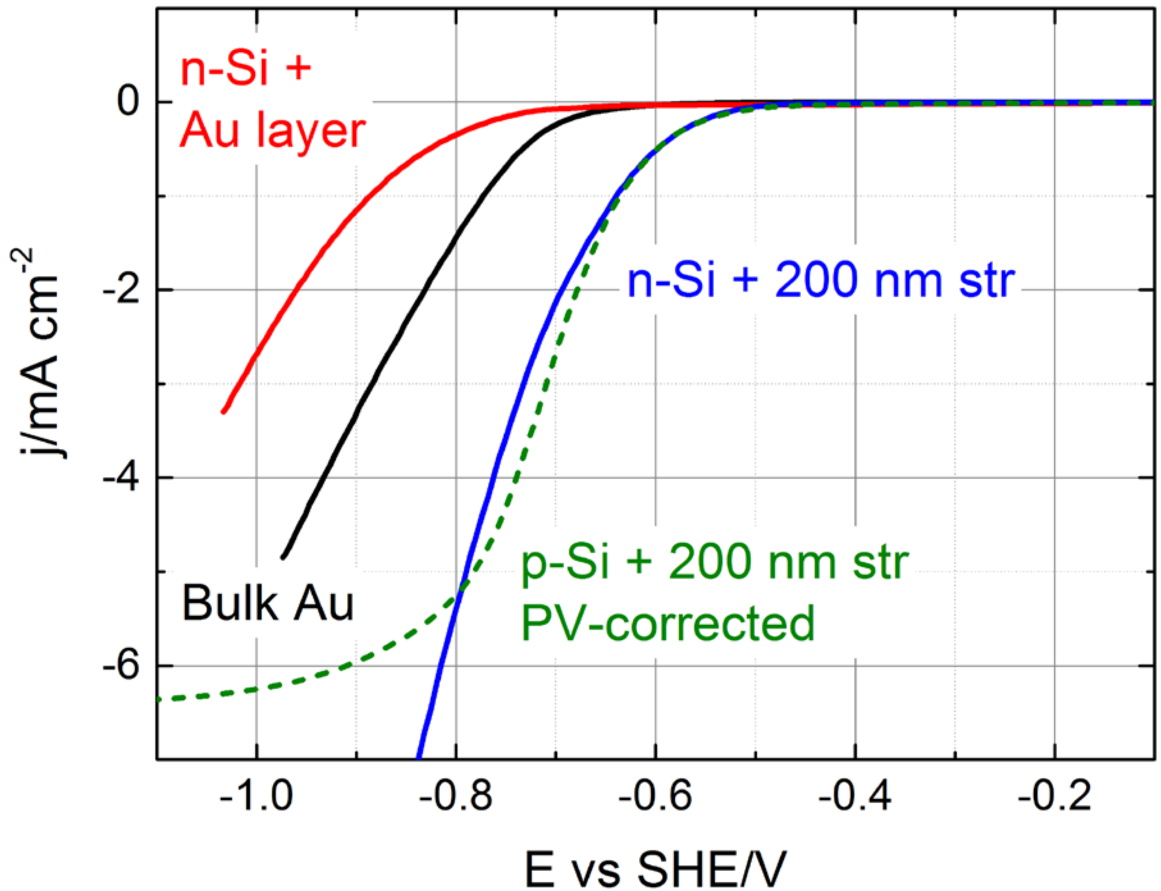
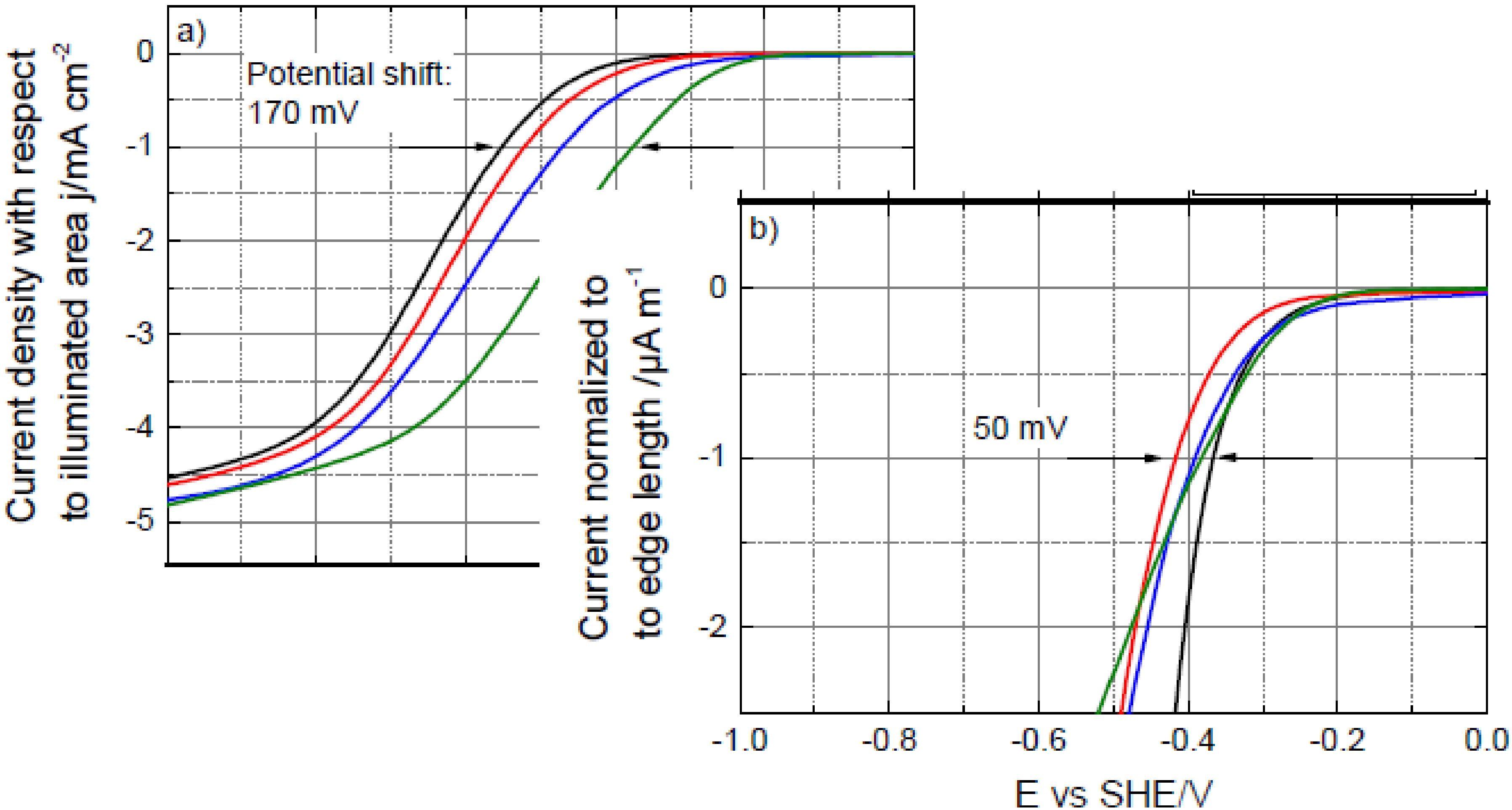


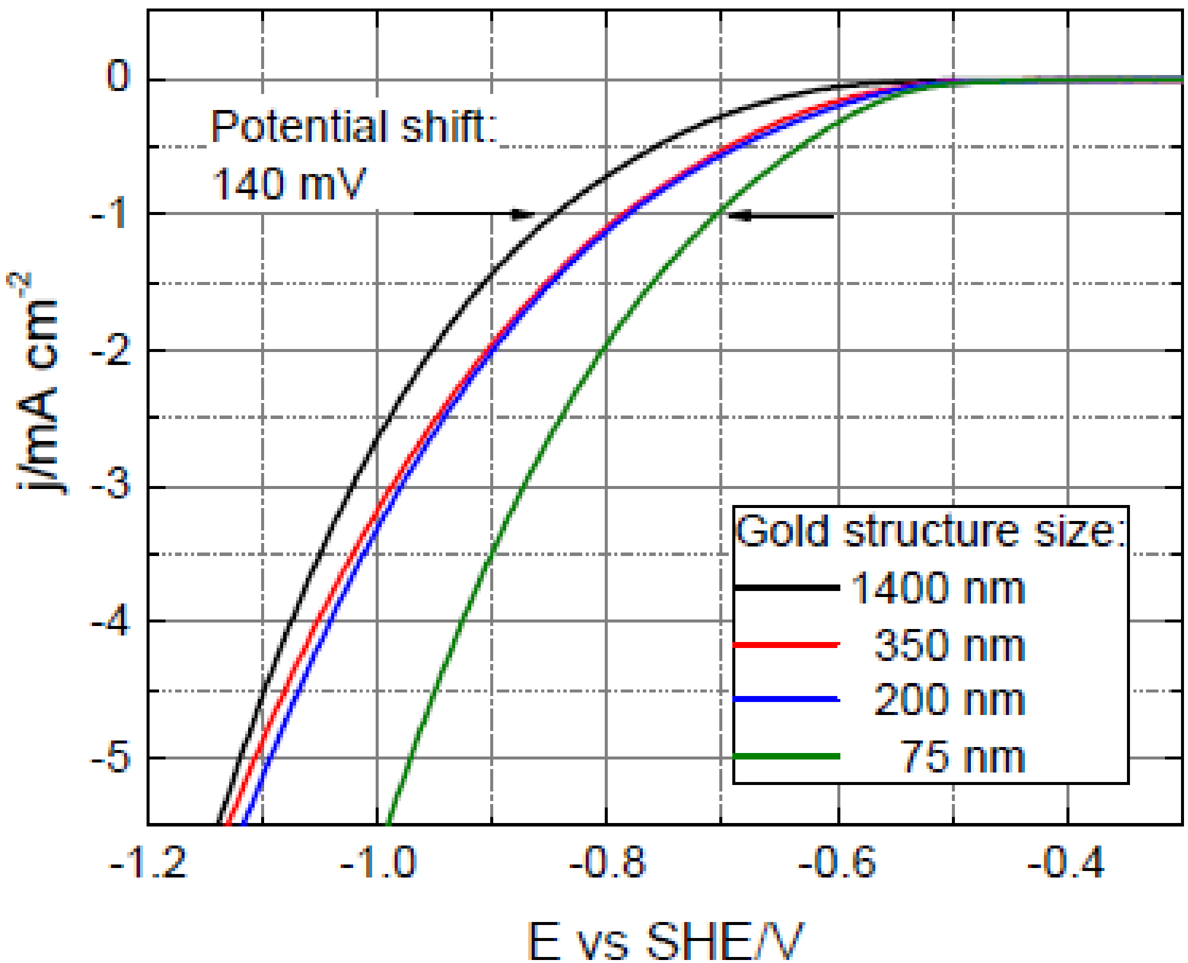
Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

p-Si/SiO_2/Au: Influence of structure size



Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

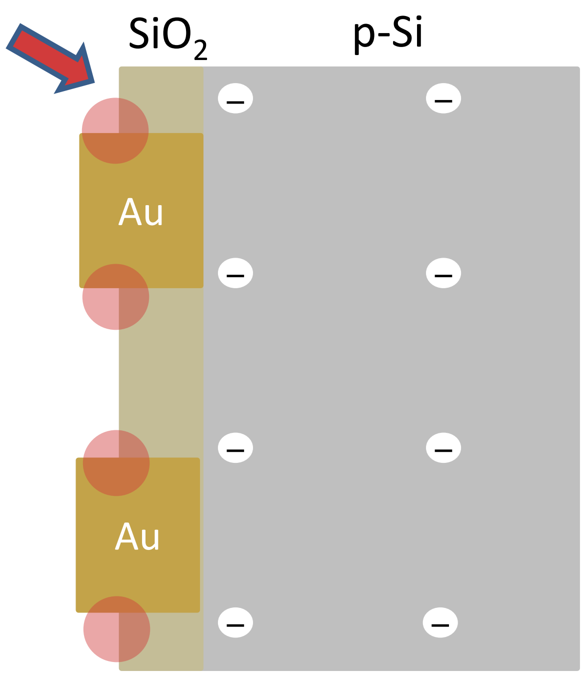
Degenerately doped p^{++}-Si/SiO_2/Au: Influence of structure size

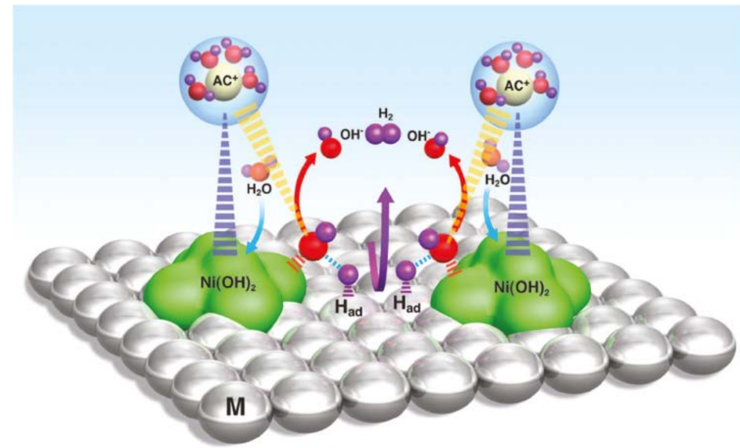


Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

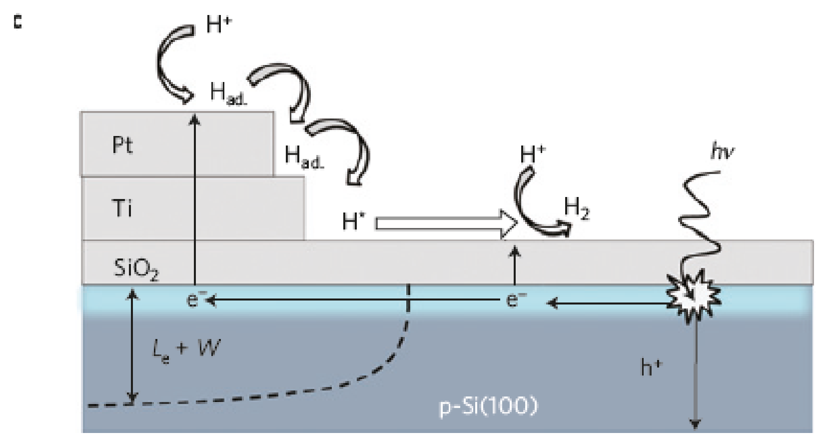
Enhanced reactivity at edges → bifunctional mechanism?

Chemical modification of reactivity along the rime





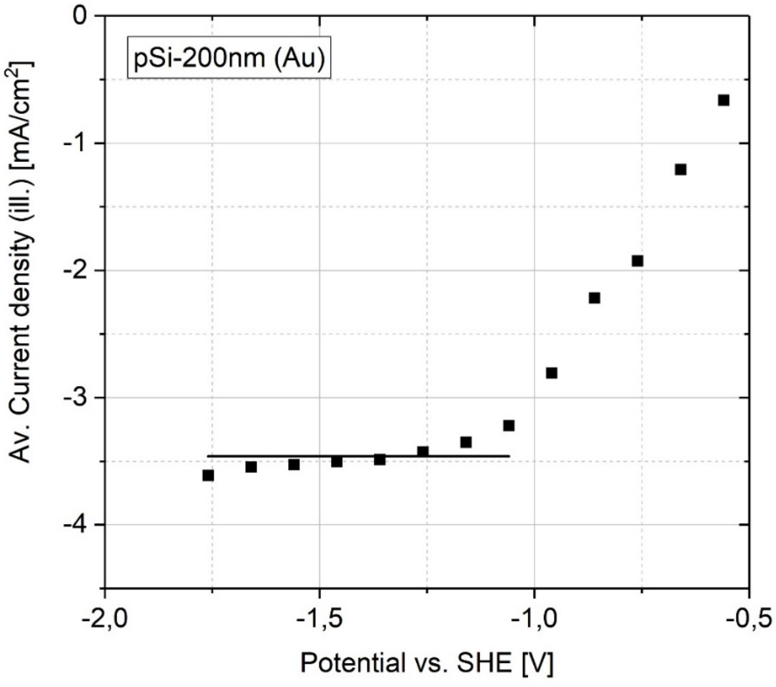
Subbaraman et al., Science (2011)



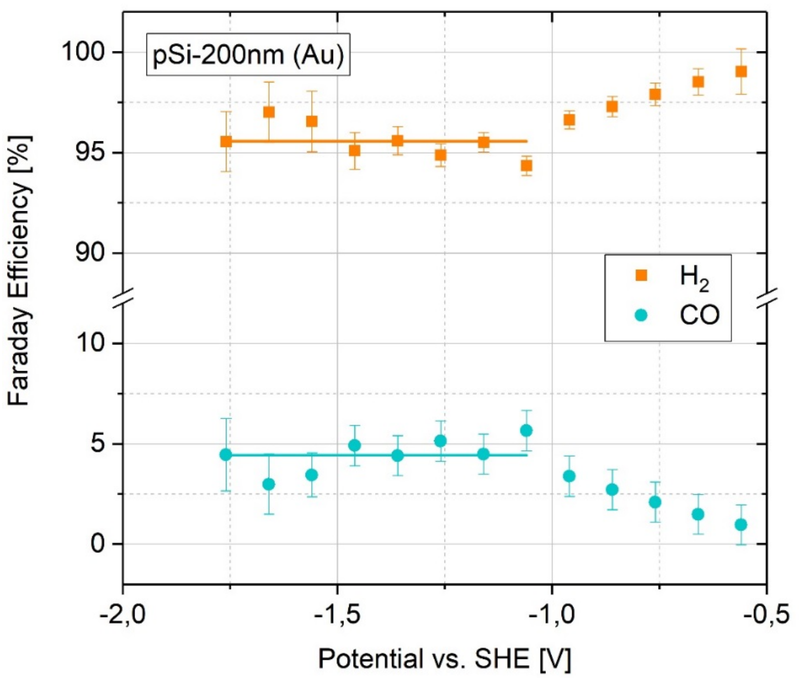
Esposito et al., Nature Materials (2013)

Electrolysis measurements: Au arrays

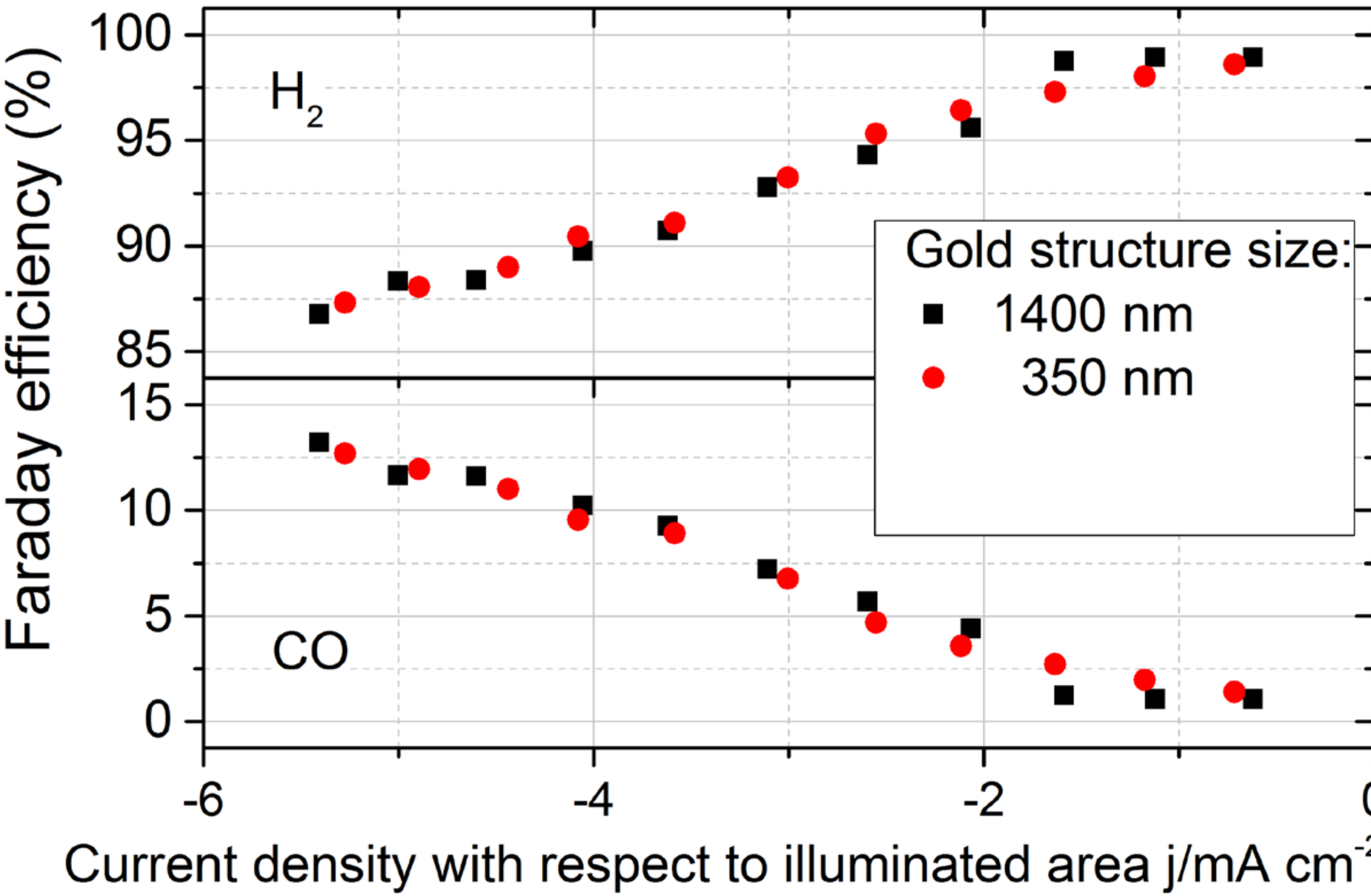
Av. Current vs. Potential



Product distribution vs. Potential

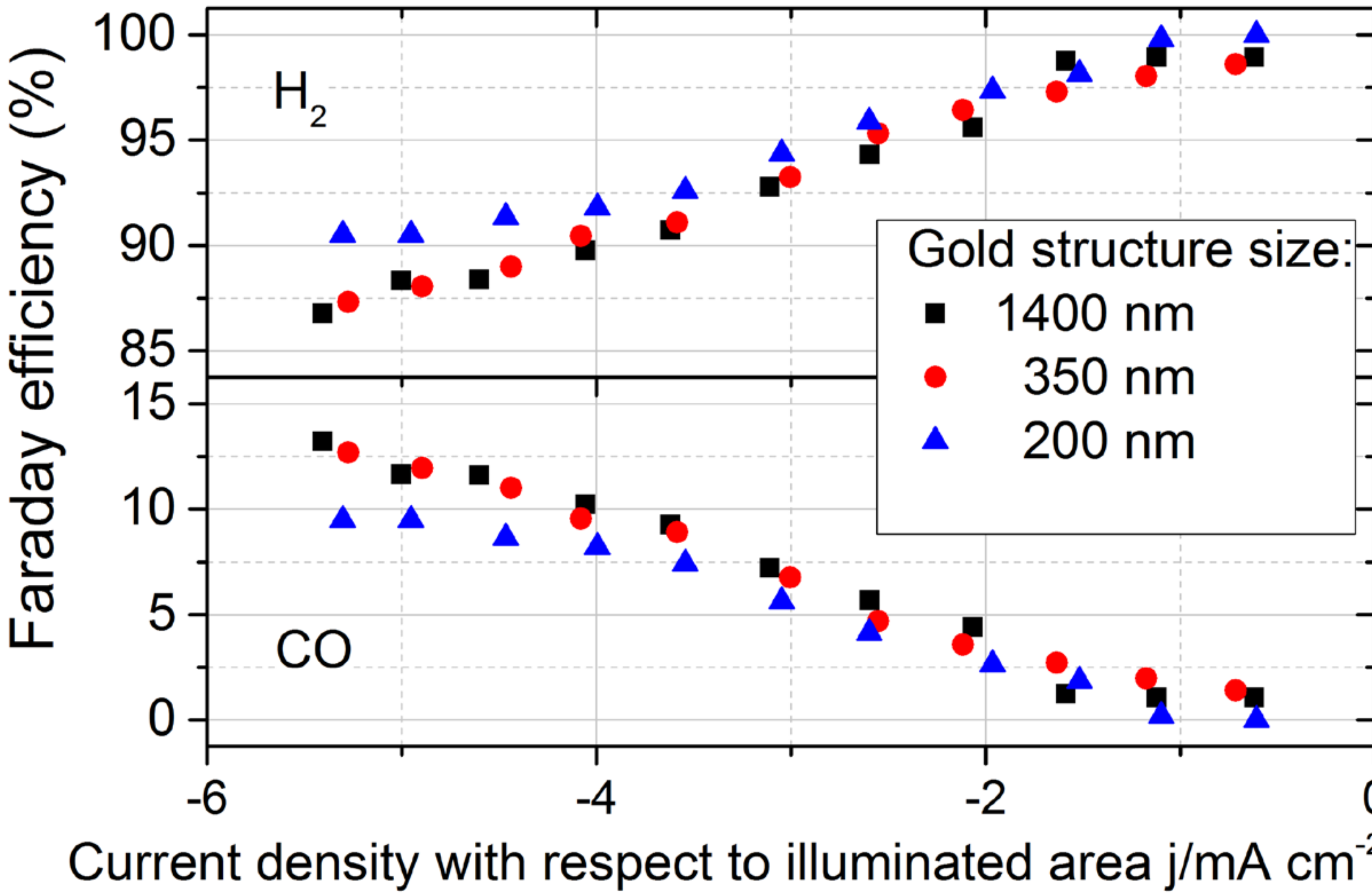


Product distribution



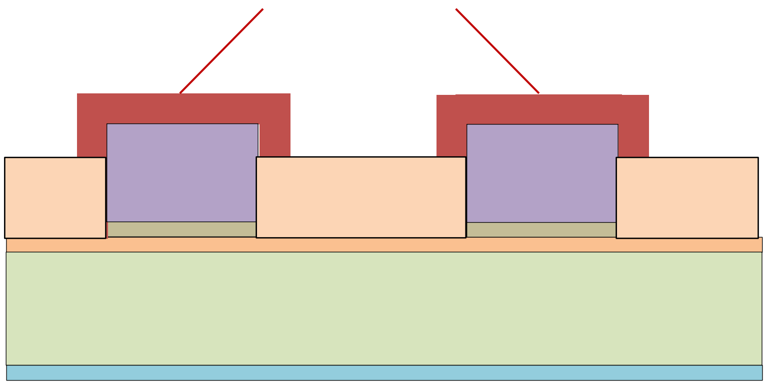
Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

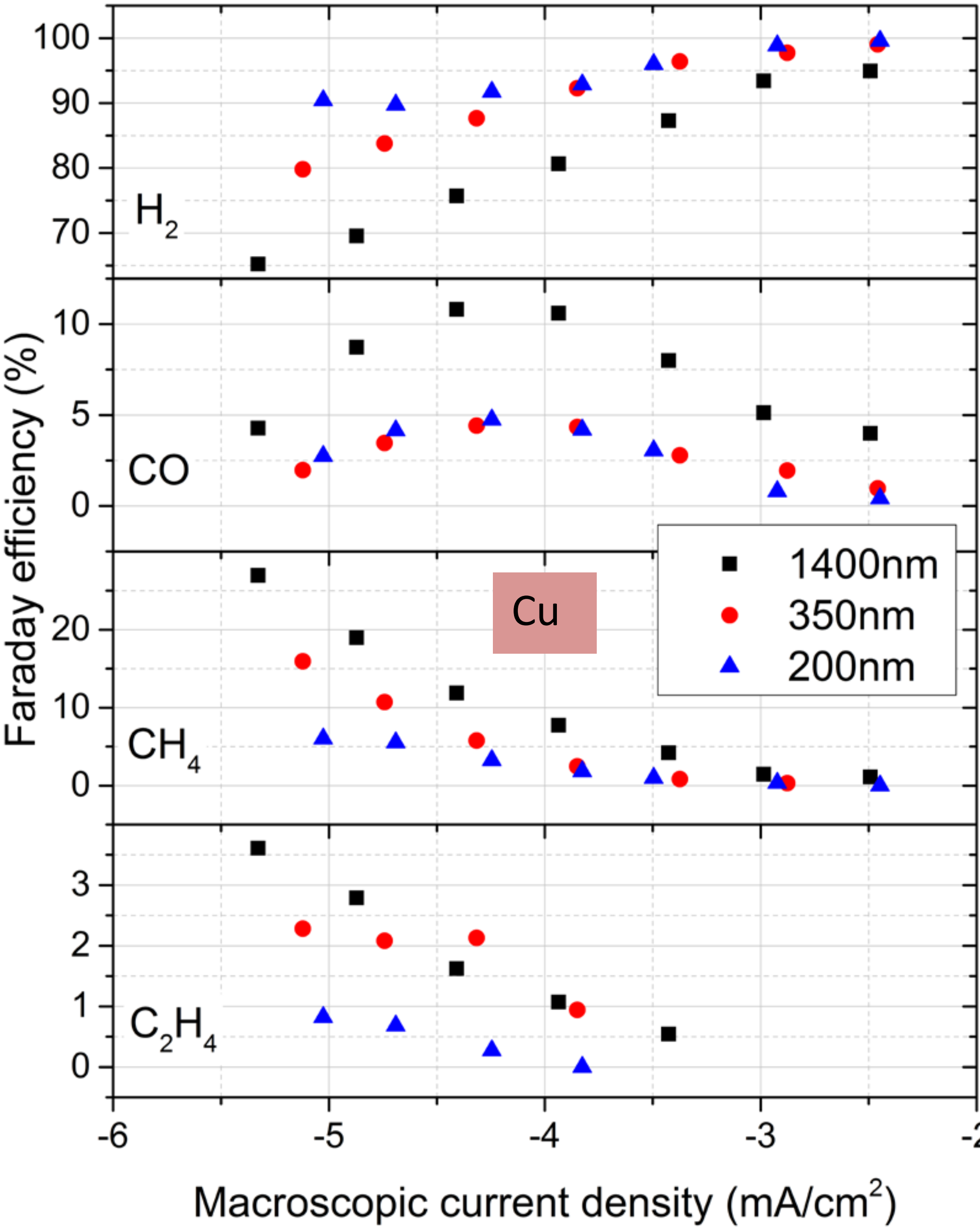
Product distribution



Filser, Maier, Nagel, Schindler, Becherer, Lugli, Krischer, Electrochimica Acta (2018)

Cu-coated Au arrays

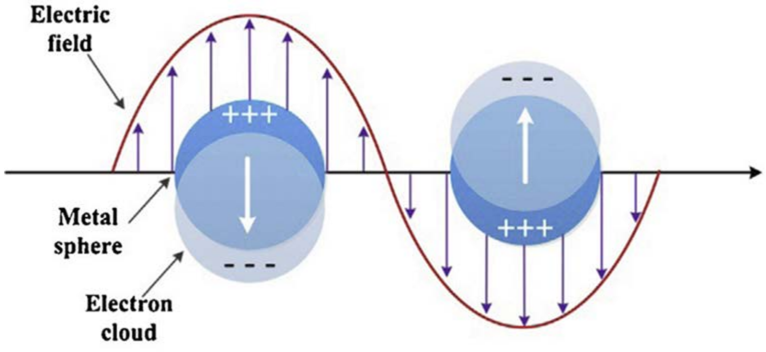




With decreasing size: reduced hydrocarbon efficiency

Localized surface plasmon (LSP)

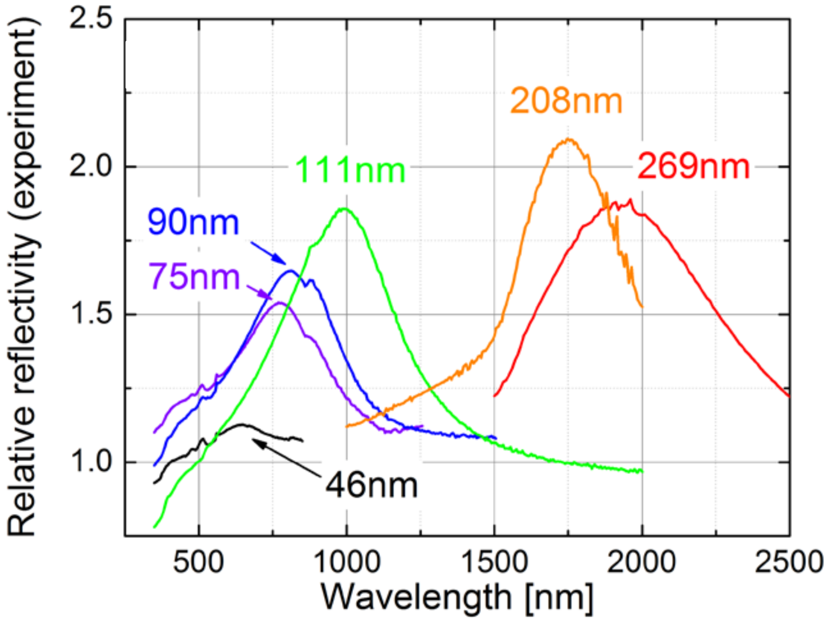
LSP: Surface plasmon confined in a nanoparticle of size comparable to or smaller than the wavelength of light used to excite the plasmon.



Sun, Chen and Lin, DOI: 10.5772/64380

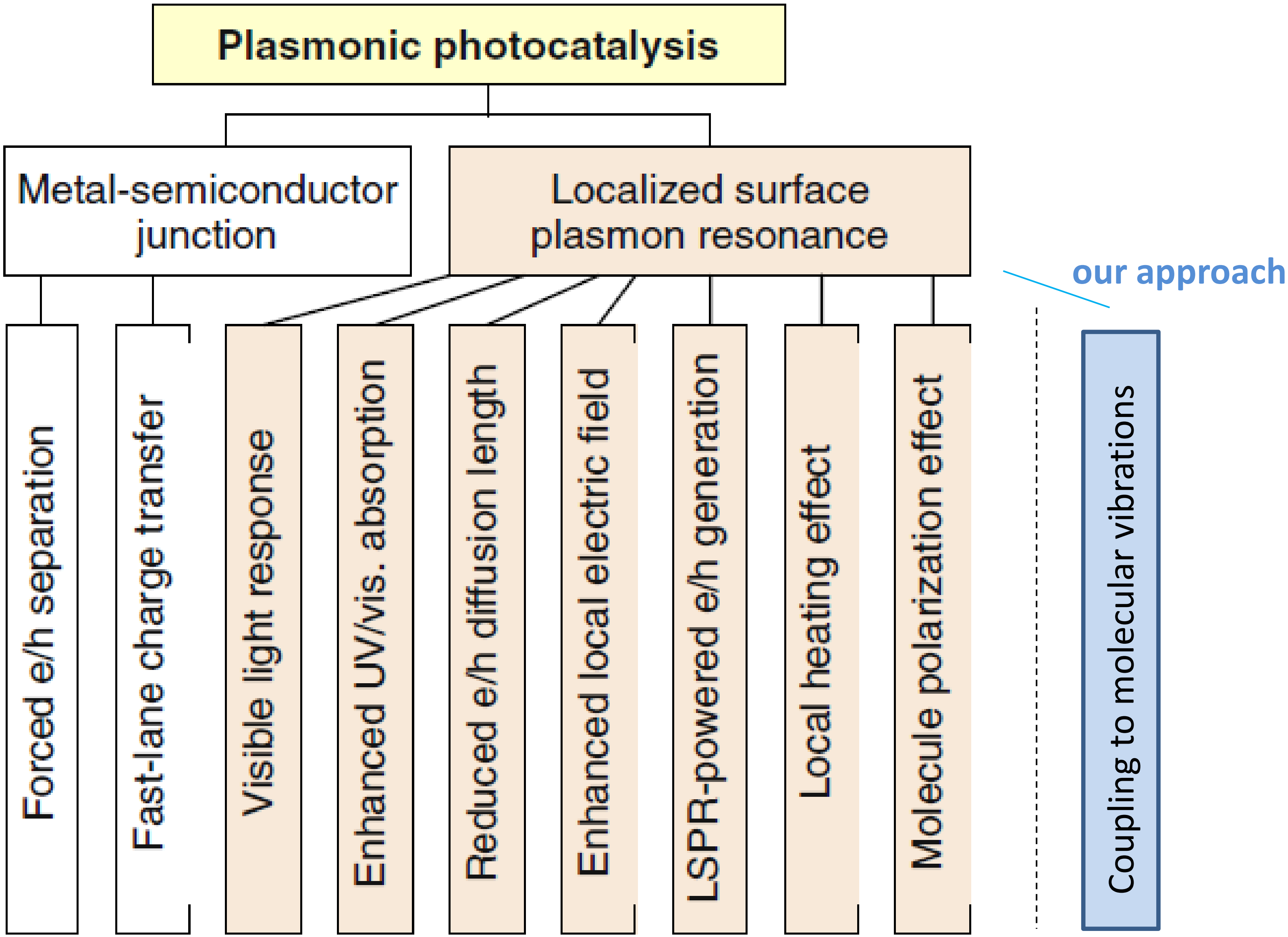
- strongly enhanced electric fields near the particle's surface
- Strong absorption around the plasmon resonance frequency

Tunable plasmonic resonances



- UV-Vis spectra and simulations of differently sized gold structures in good agreement

R. D. Nagel. S. Filser, T. Zhang, A. Manzi, K. Schönleber, J. Lindsly, J. Zimmermann, T. L. Maier, G. Scarpa, K. Krischer, and P. Lugli, *J. Appl. Phys*., **2017**, 121(8), 84305.



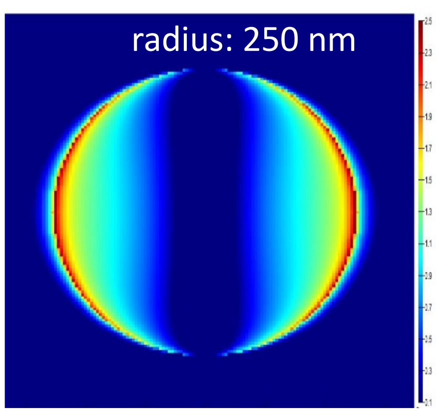
Zhang et al., *Rep. Prog. Phys*. **76** (2013) 046401

Coupling of LSPs to molecular vibrations

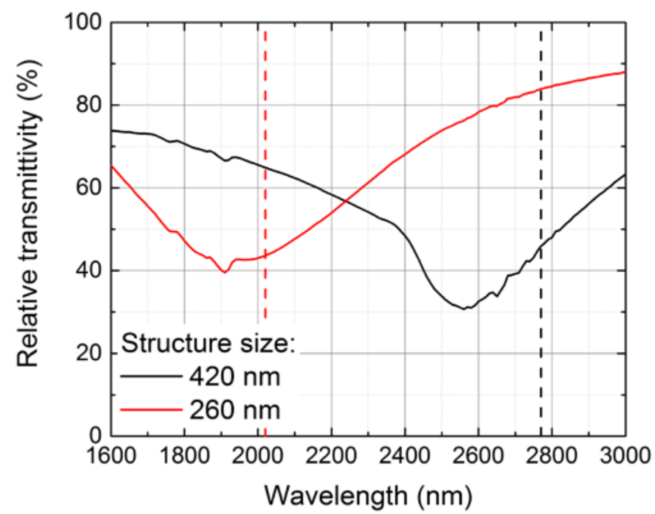
- Reduction of activation energy of a reaction → Plasmonic catalysis
- Selectively influence a certain reaction pathway → Higher selectivity

<u>CO_2 reduction on Au in aqueous electrolyte:</u>

CO_2 overtone @ 2,8 μm

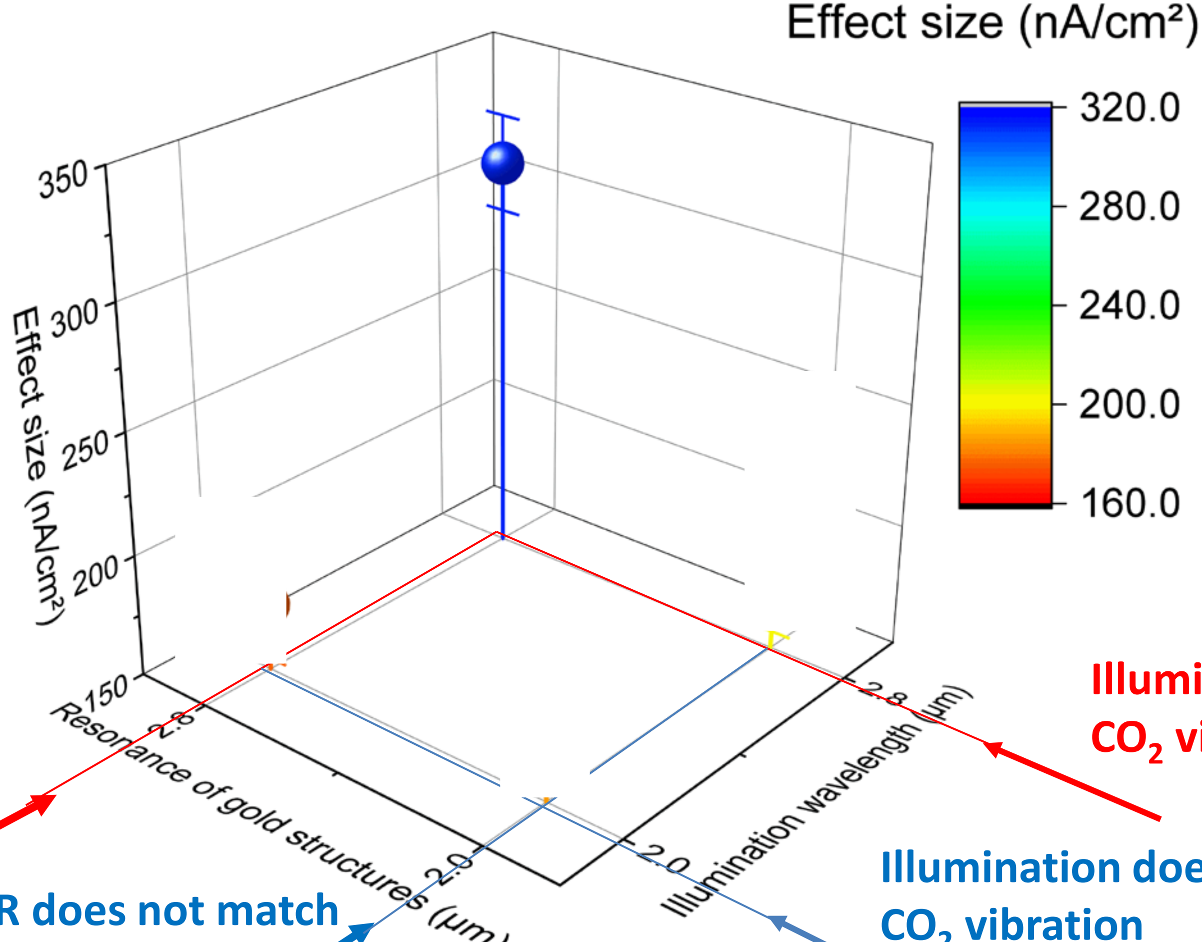


Simulation of Au nanodisks on SiO_2/Si



Transmission spectra of Au arrays on SiO_2/Si

LSPR enhanced reactivity



LSPR matches CO_2 vibration

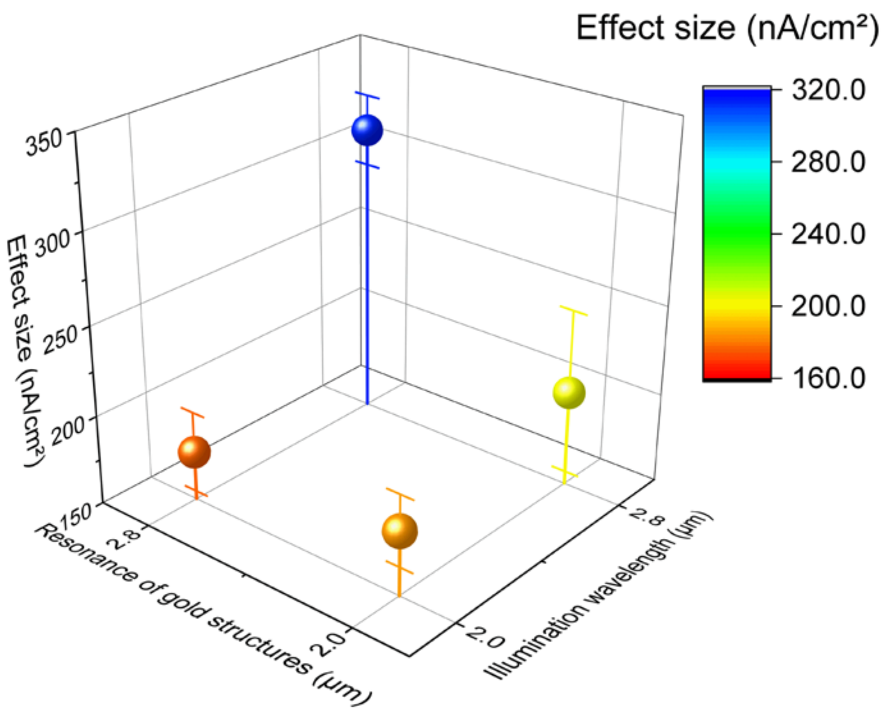
LSPR does not match CO_2 vibration

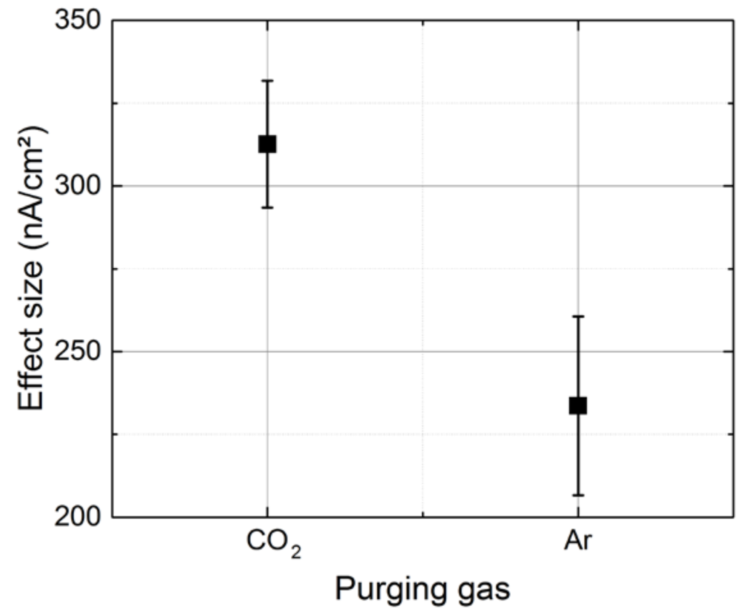
Illumination matches CO_2 vibration

Illumination does not match CO_2 vibration

Filser, Maier, Zimmermann, Nagel, Schindler, Becherer, Krischer, preprint (2018)

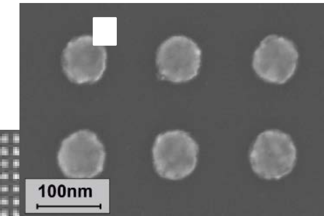
LSPR enhanced reactivity and selectivity





Filser, Maier, Zimmermann, Nagel, Schindler, Becherer, Krischer, preprint (2018)

Summary

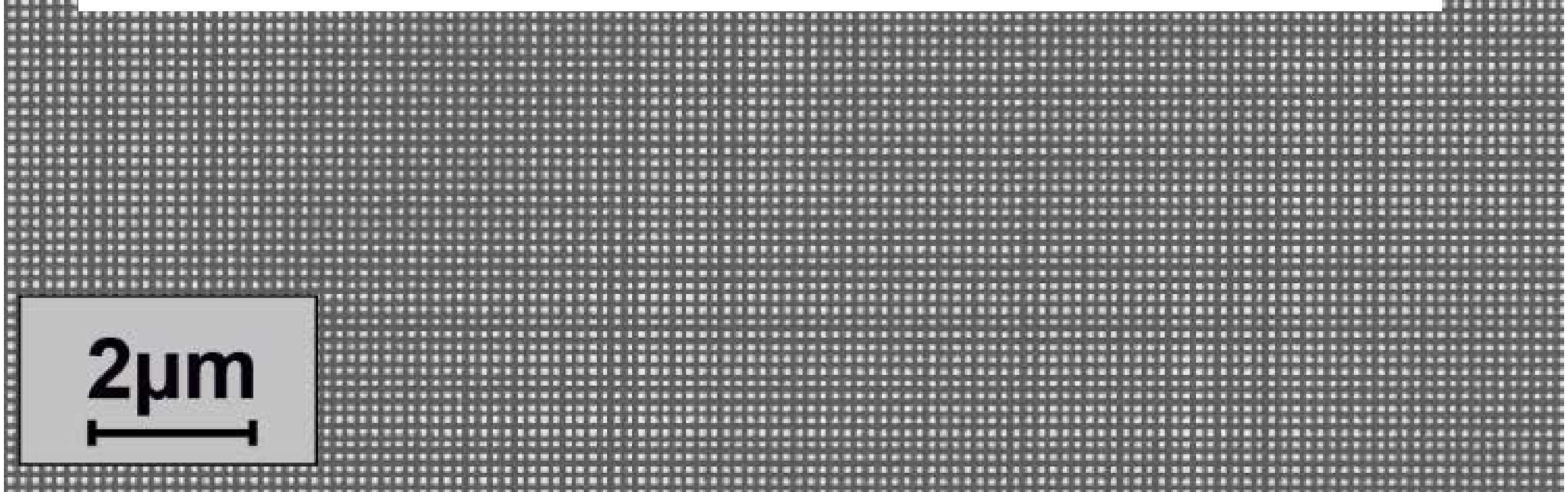


- Au(Cu)/SiO_2 /p-Si MIS structures exhibit enhanced catalytic activity towards H_2 evolution

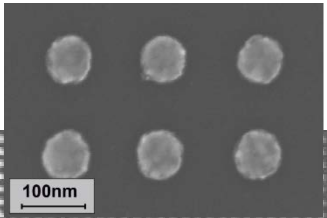
➡ *bifunctional mechanism / strong metal support interaction*

or

energetics (ϕ distribution at the 3 phase interface?)



Acknowledgements



Simon Filser
Robin Nagel (TUM EI)
Thomas Maier
Dr. Werner Schindler
Josef Zimmermann
Prof. Andreas Ulrich
Prof. Paolo Lugli (TUM EI)
Prof. Markus Becherer (TUM EI)

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DFG

Frequency dependence of enhancement effect