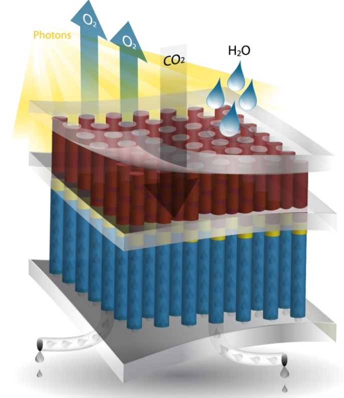

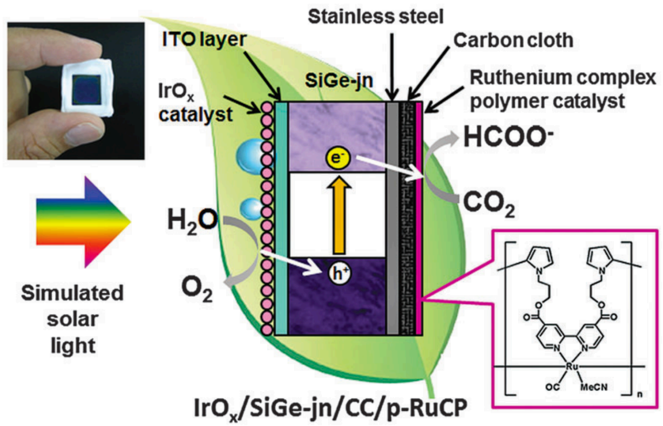

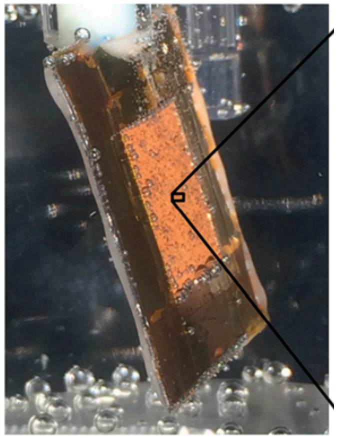

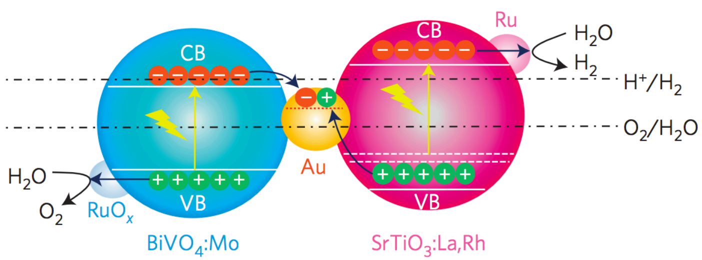

OVERVIEW OF PHOTOELECTROCHEMICAL DEVICES FOR CONVERSION OF CO_2 AND WATER TO OXYGEN AND FUELS

Chengxiang ("CX") Xiang
Joint Center for Artificial Photosynthesis (JCAP)
California Institute of Technology

Addressing the Mars ISRU Challenge Workshop
Keck Institute for Space Studies
June 28 - July 1, 2016

OUTLINE

- The Basic Operating Principles of a Photoelectrochemical (PEC) CO_2 Reduction Reaction (CO_2RR) System.
- Materials and Components.
- Device Designs and Demonstration.

What is a Photoelectrochemical CO_2 Reduction System

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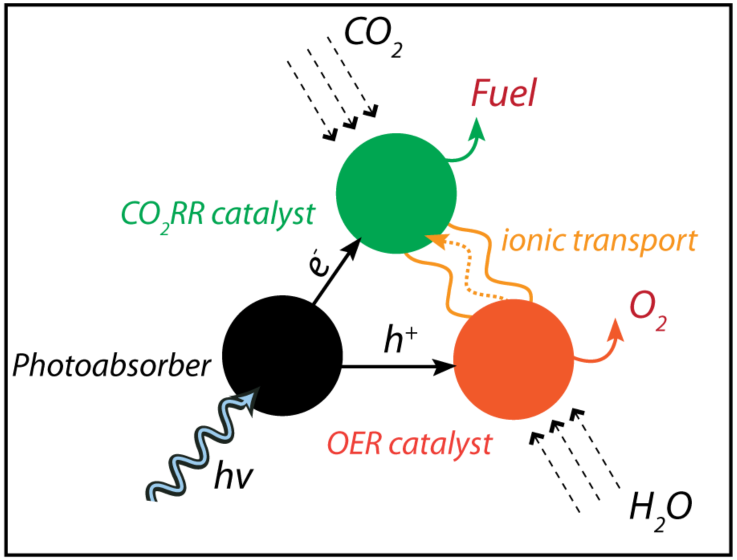

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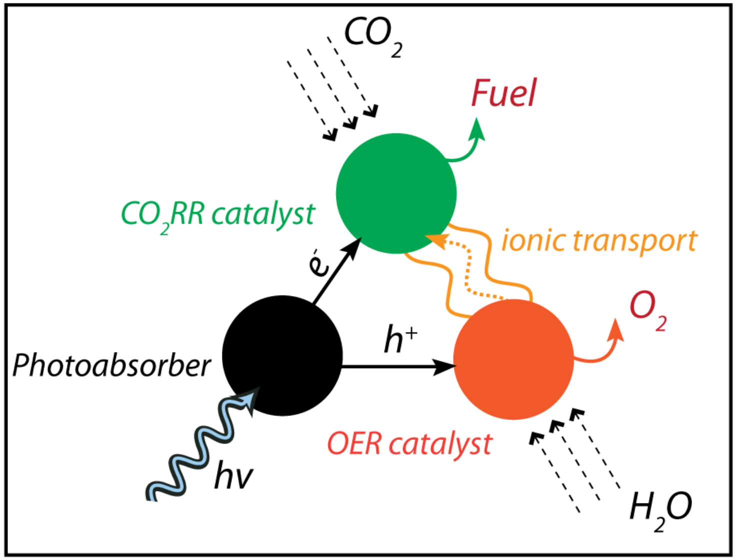

Oxygen evolution reaction (OER)

$$H_2O \longrightarrow \tfrac{1}{2}O_2\,(g) + 2H^+ + 2e^-$$

CO_2 Reduction reaction (CO_2RR)

$$CO_2 + 2e^- + 2\,H^+ \longrightarrow CO + H_2O$$
$$CO_2 + 2e^- + 2\,H^+ \longrightarrow HCOOH$$
$$CO_2 + 6e^- + 6\,H^+ \longrightarrow CH_3OH + H_2O$$
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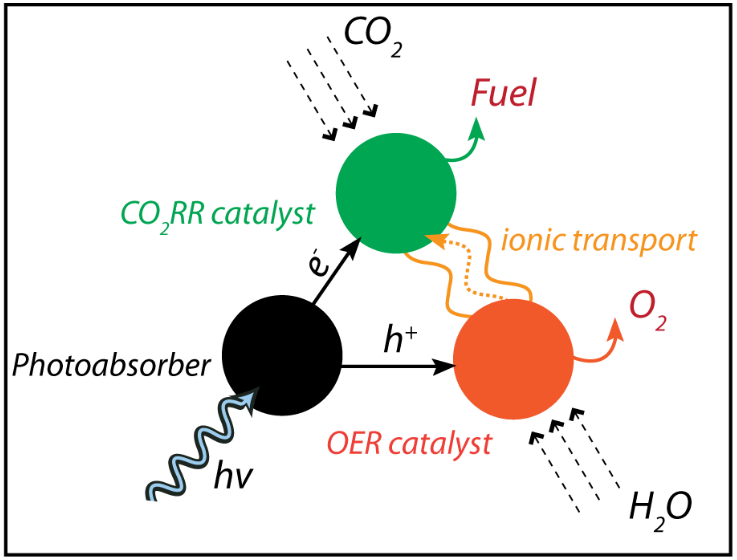

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- OER catalyst

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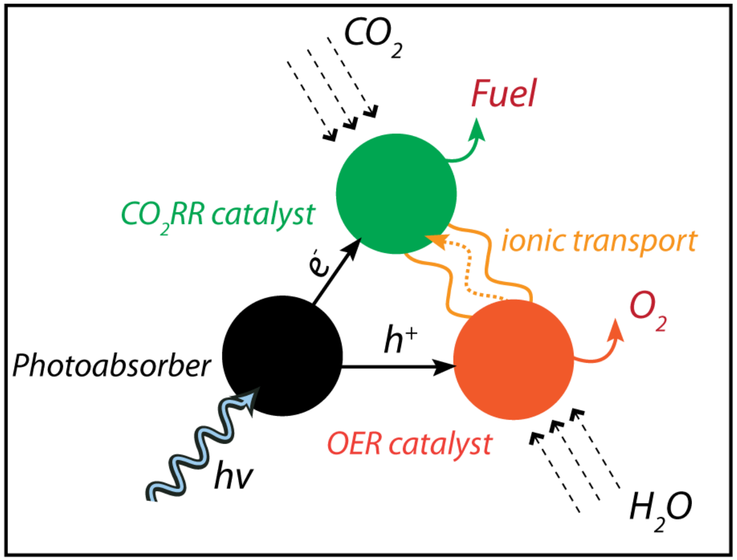

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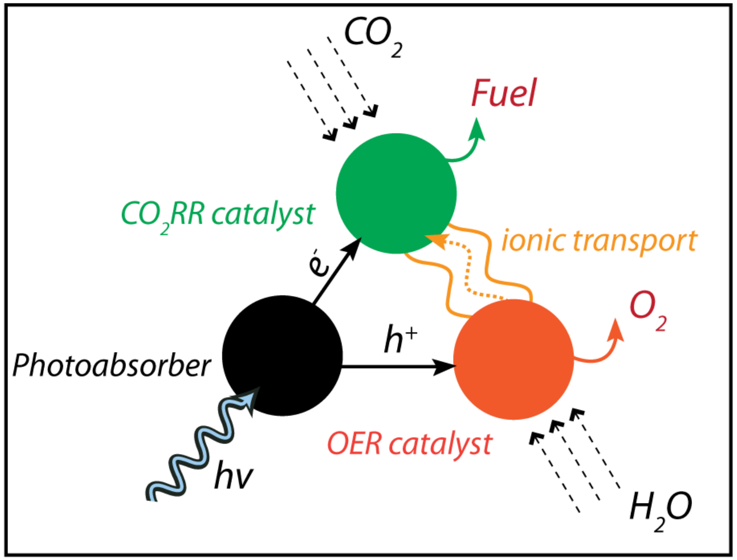

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Key components:
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Key performance metrics:
- Conversion efficiency
- Selectivity
- Stability
- Scalability

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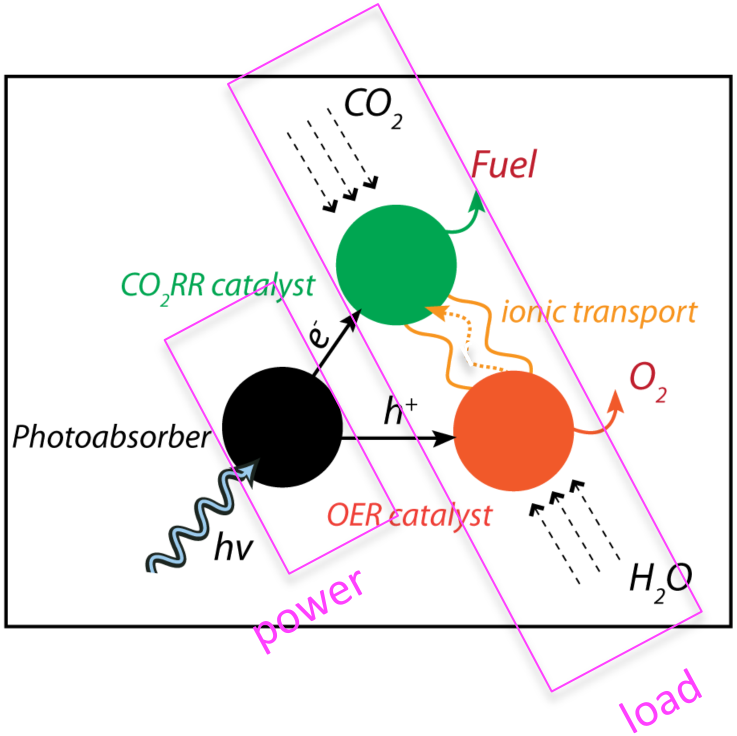

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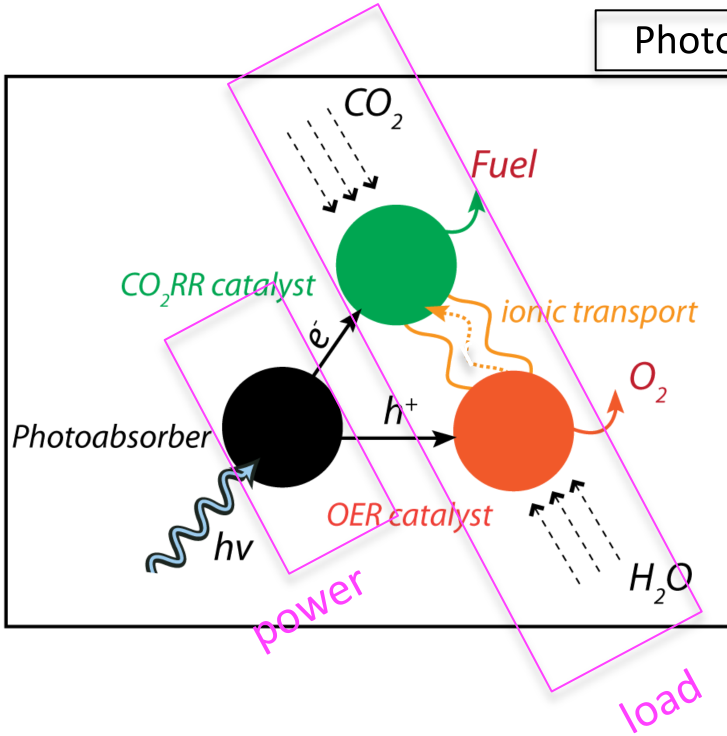

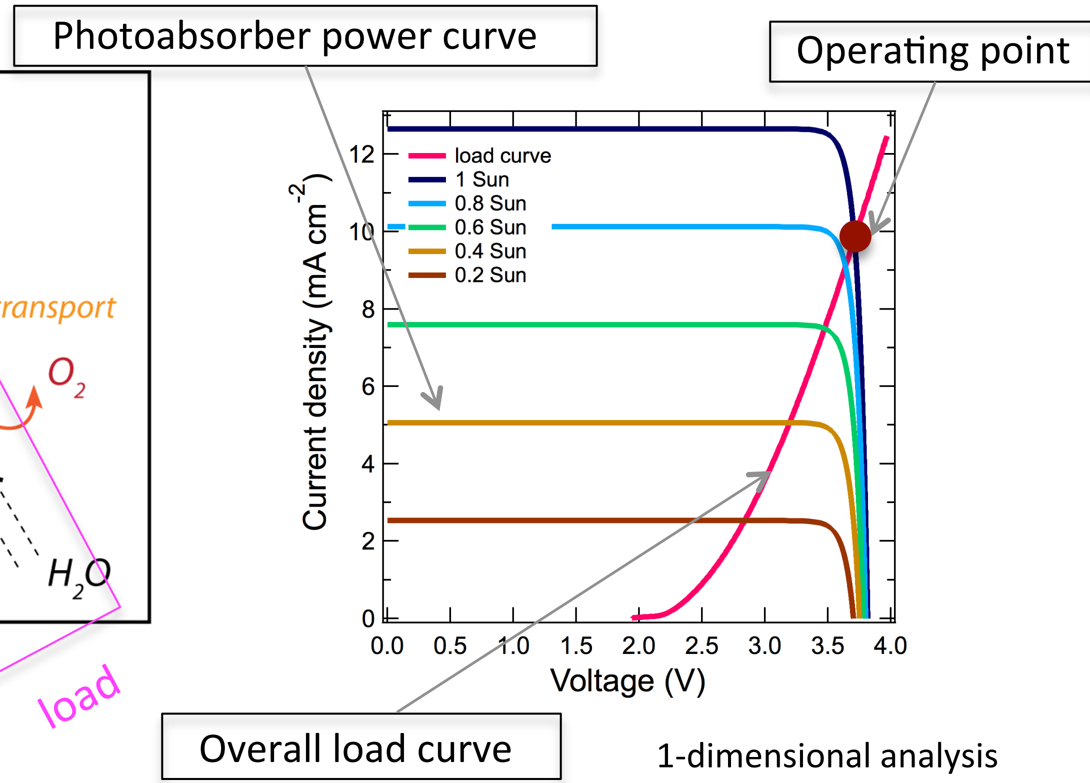

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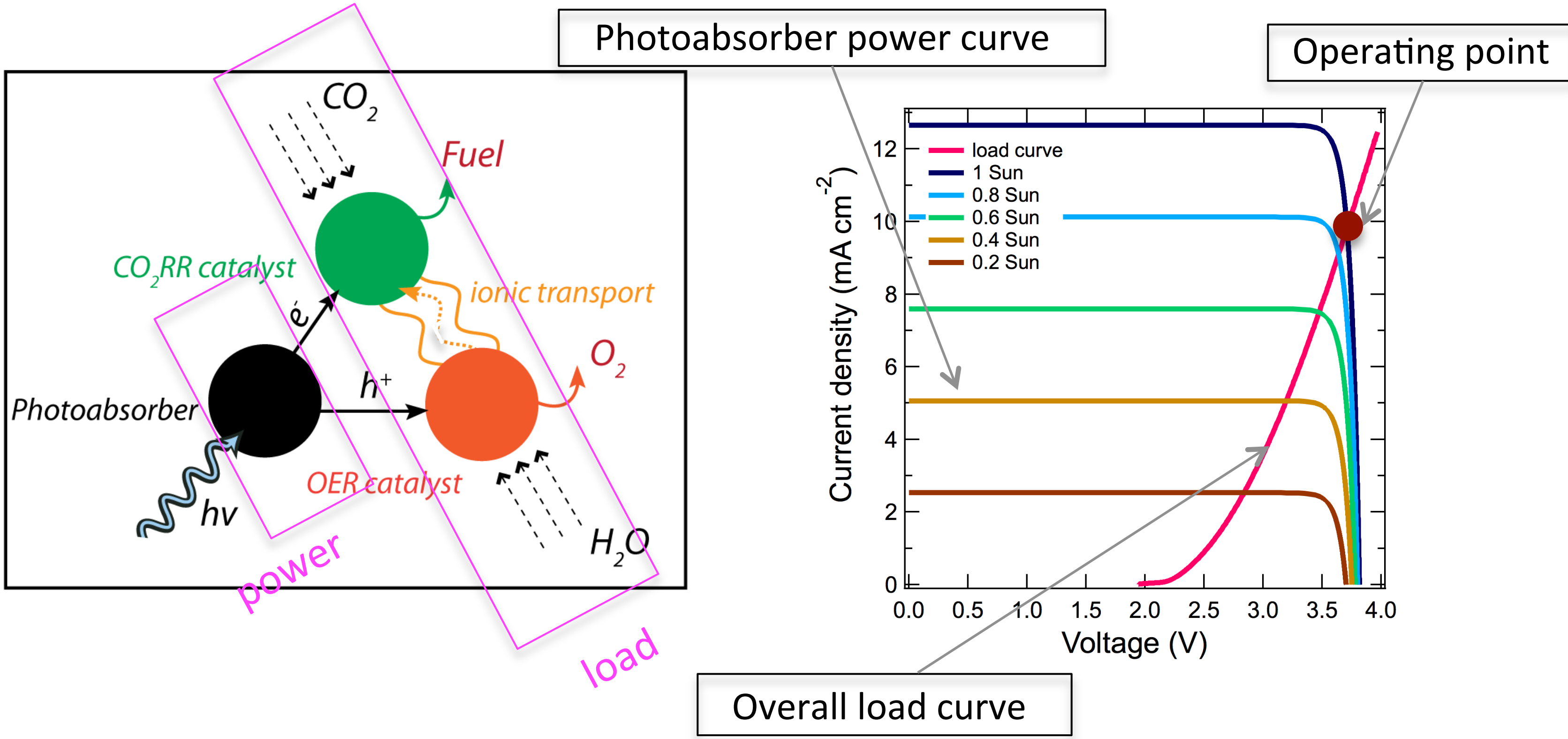

The overall load curve includes:

- Thermodynamic voltage window.
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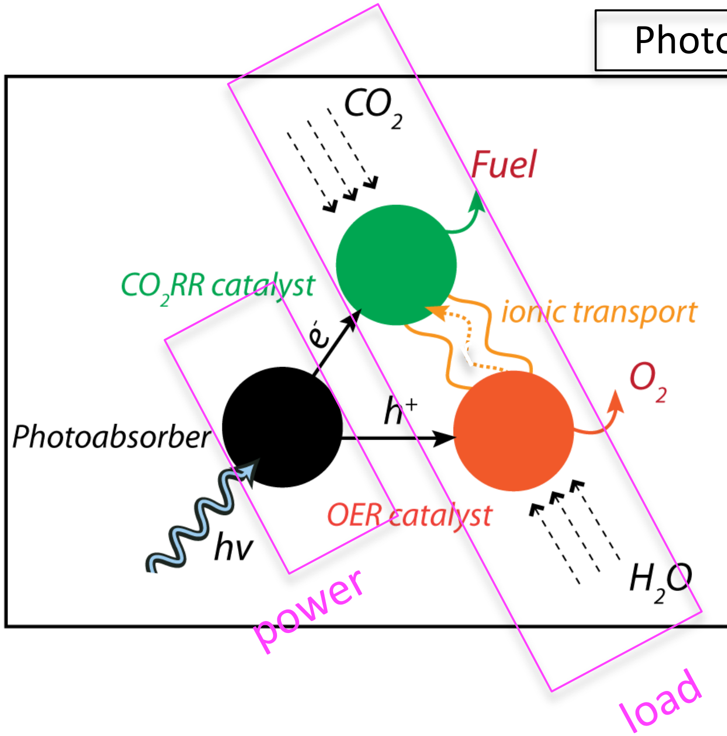

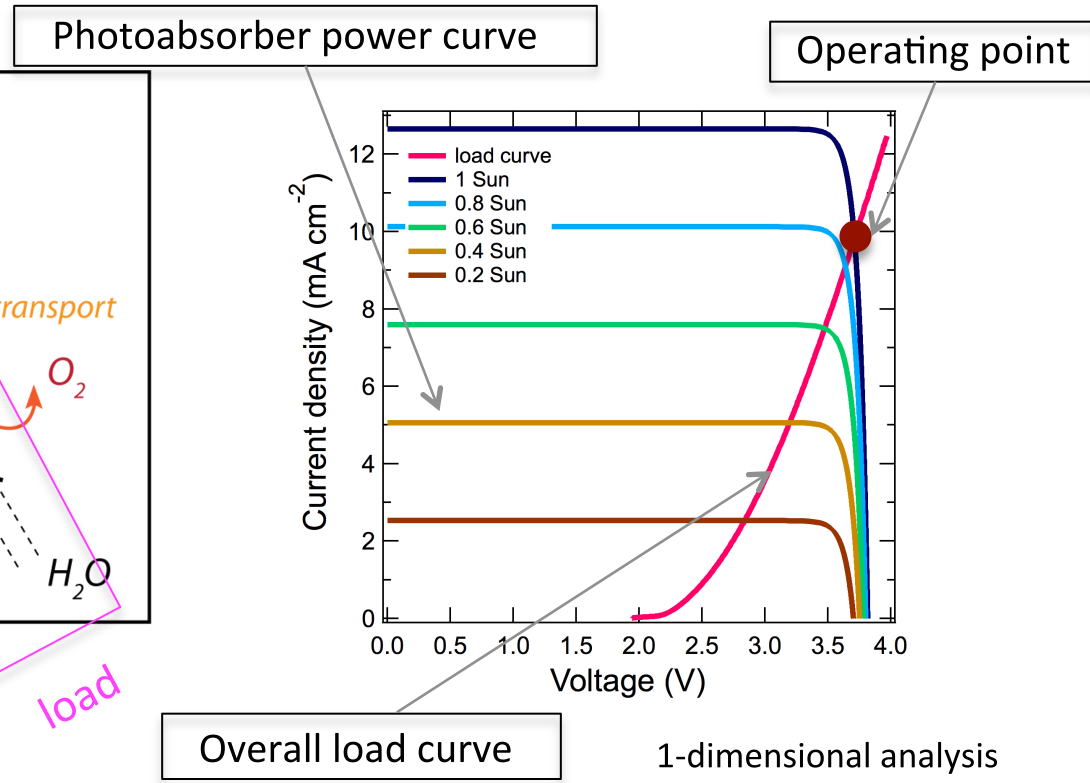

1-dimensional analysis

The overall load curve includes:

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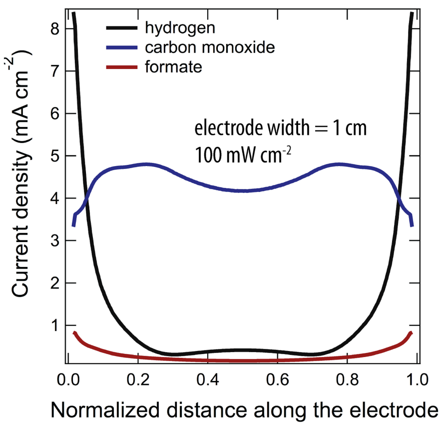
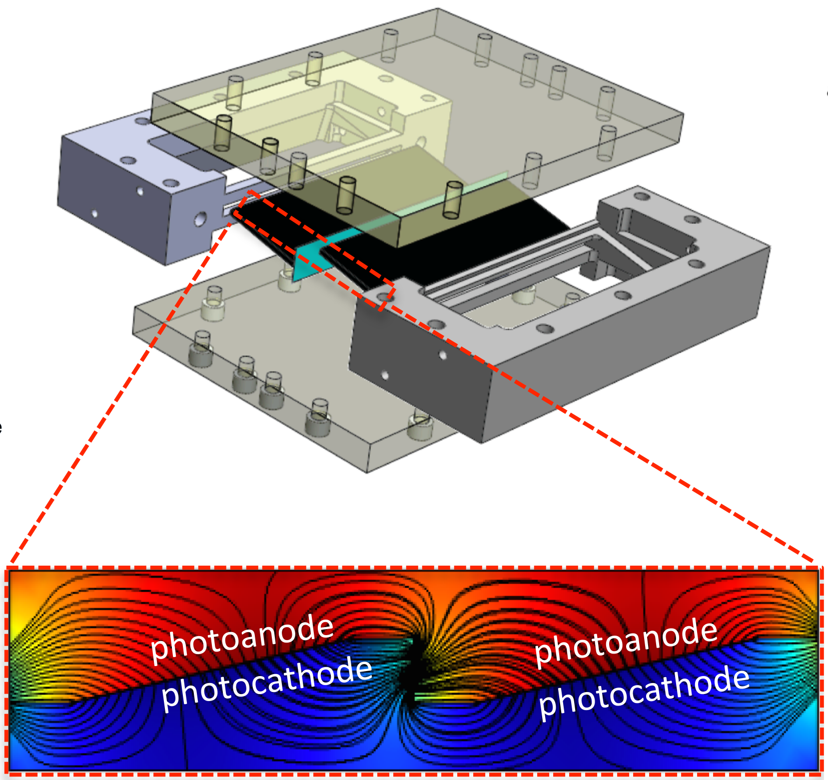
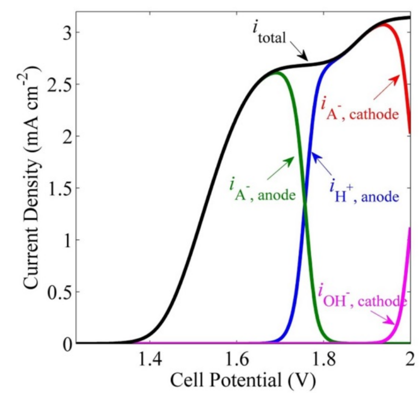
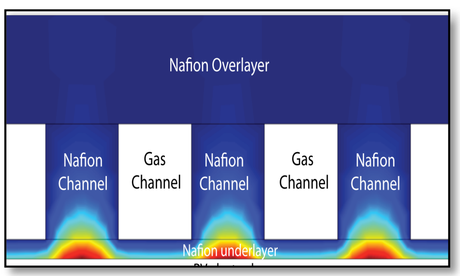
What is a Photoelectrochemical CO_2 Reduction System

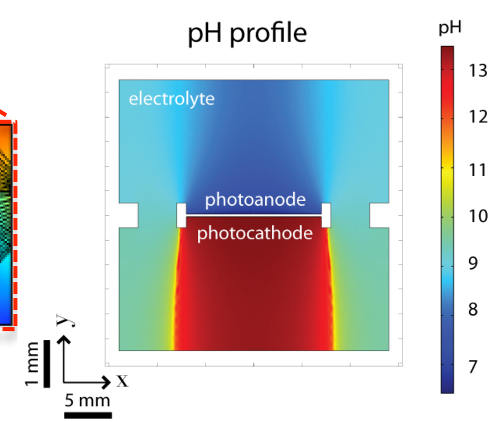
Modeling and simulation of multi-dimensional prototype performances











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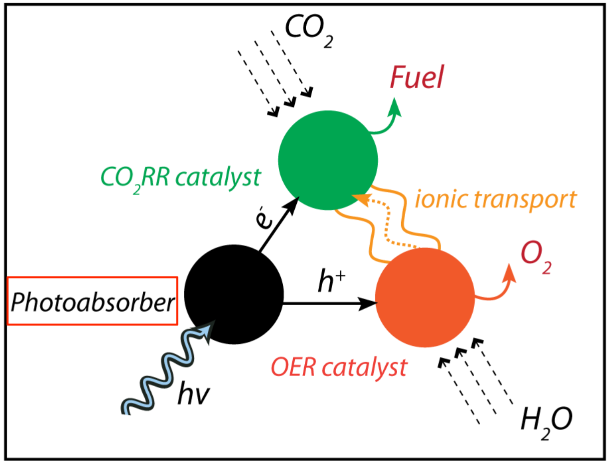

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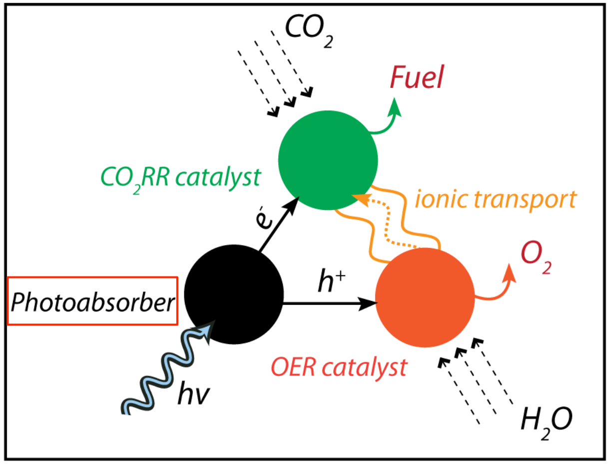
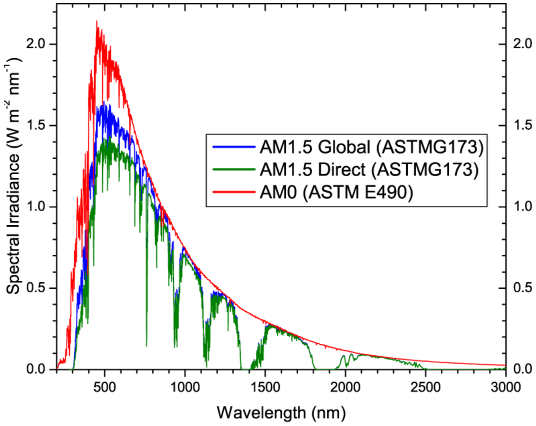
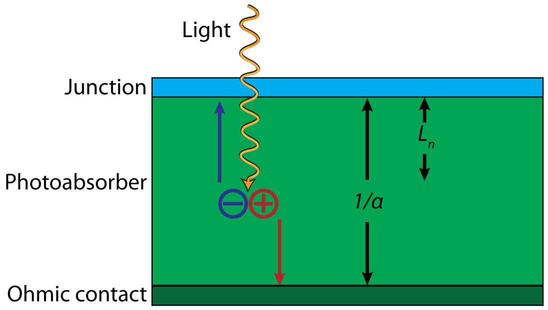


Solar spectrum



Photoabsorber charge-separation



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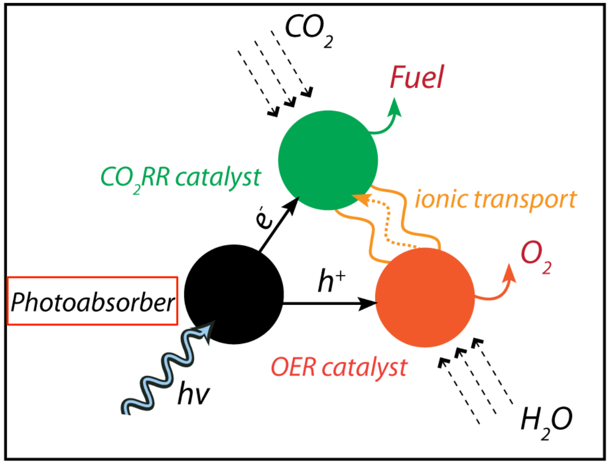

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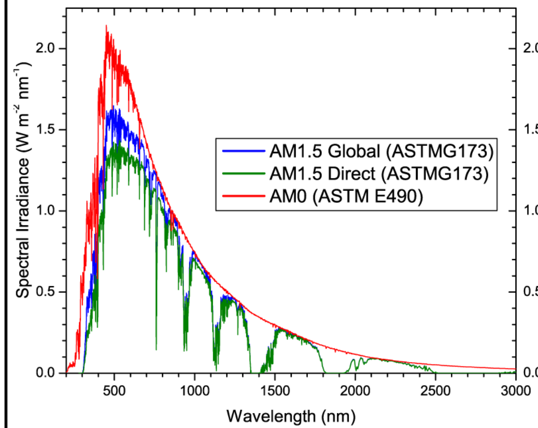

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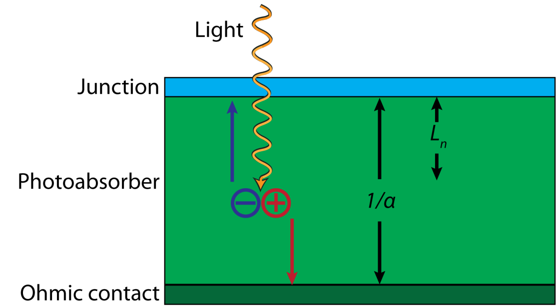
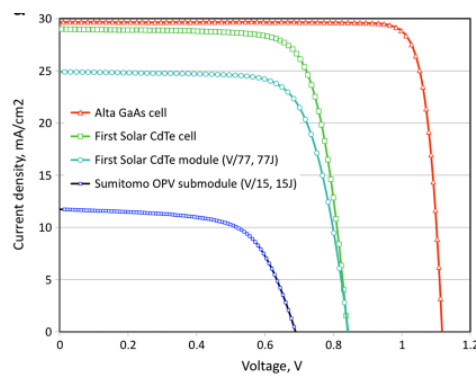


Single junction photoabsorber



http://www.nrel.gov/solar_radiation/

Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D., Solar cell efficiency tables (version 40). *Progress in Photovoltaics* **2012,** 20, (5), 606-614.

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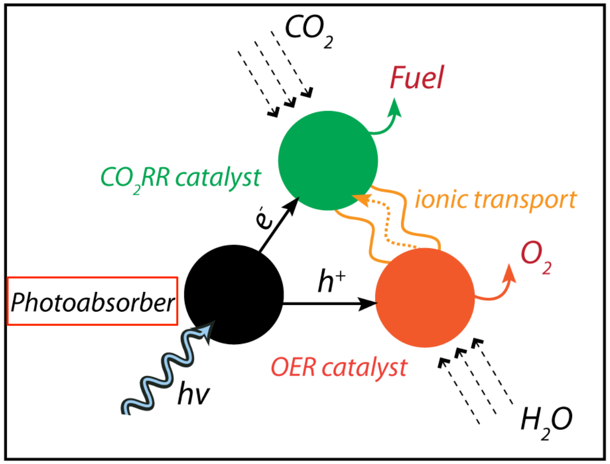

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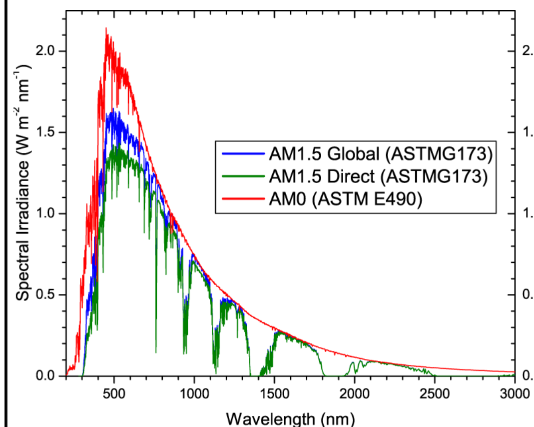

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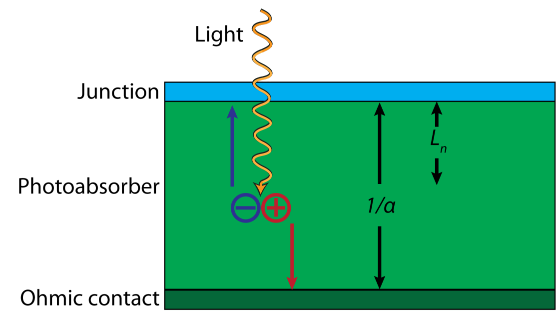

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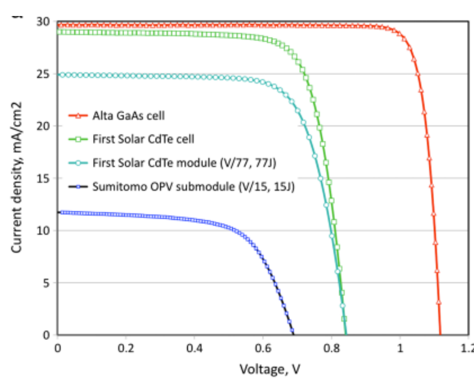
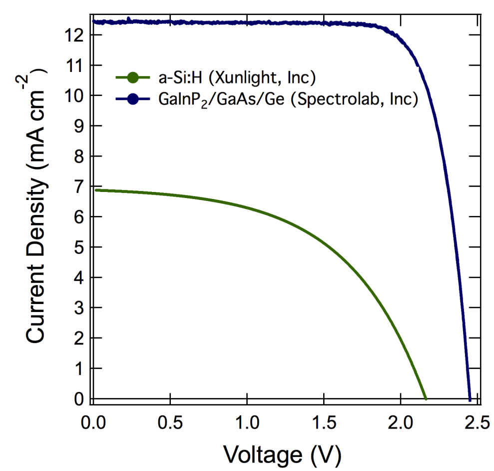


Triple junction photodiode curves



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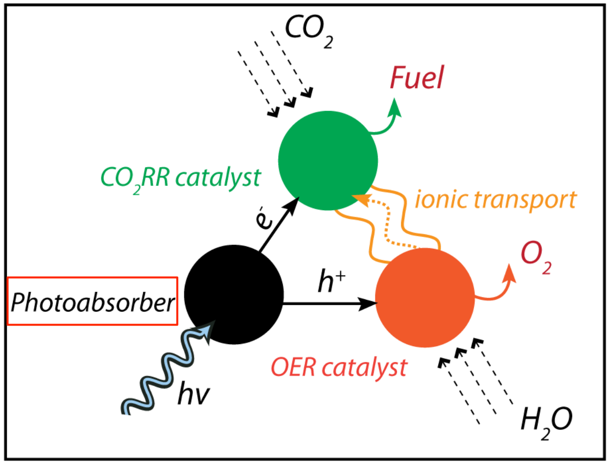

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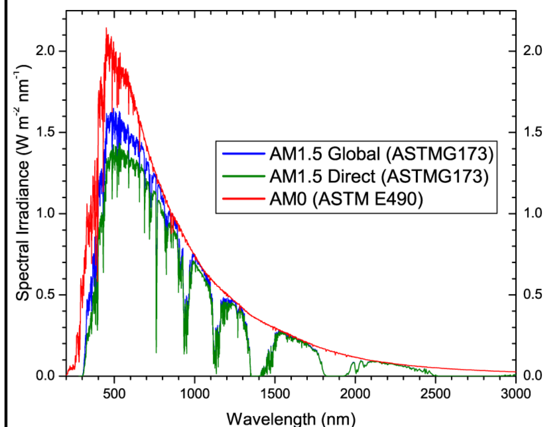

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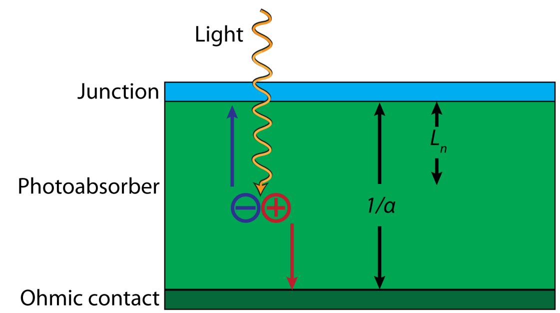

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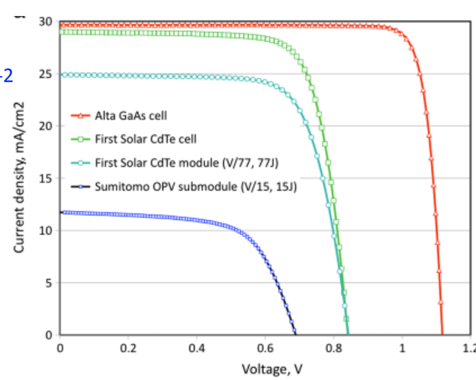

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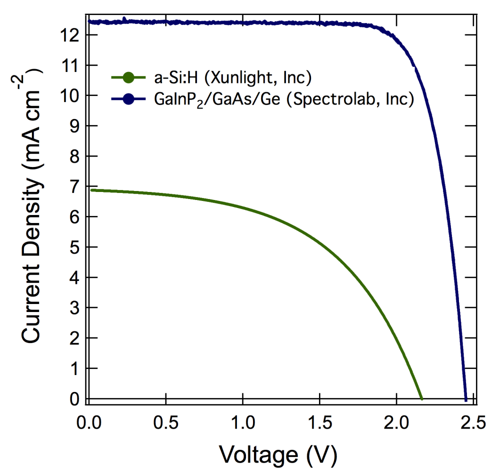

Electrochemical conversion of CO_2 to CO at 10 mA cm^{-2}

- Thermodynamic voltage window: 1.33 V
- Kinetic overpotential for OER: ~300 mV
- Kinetic overpotential for CO_2RR ~200 mV
- Concentration overpotentials: ~100 mV
- Ionic transport losses: ~100 mV

Total voltage needed at 10 mA cm^{-2} = ~2.03 V

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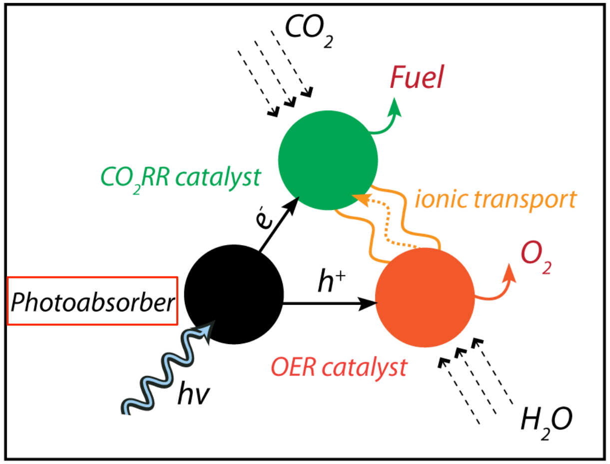
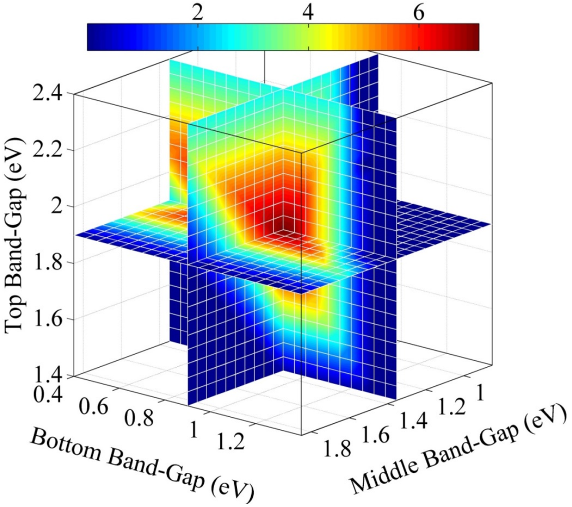


Electrochemical conversion of CO_2 to CH_4 at 10 mA cm^{-2}

- Thermodynamic voltage window: 1.33 V
- Kinetic overpotential for OER: ~300 mV
- Kinetic overpotential for CO_2RR **~1.4 V**
- Concentration overpotentials: ~100 mV
- Ionic transport losses: ~100 mV

Total voltage needed at 10 mA cm^{-2} = **~3.23 V**

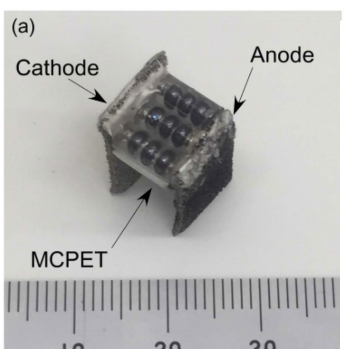
STF efficiency for CH_4

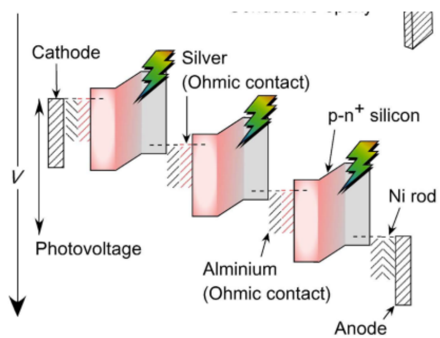


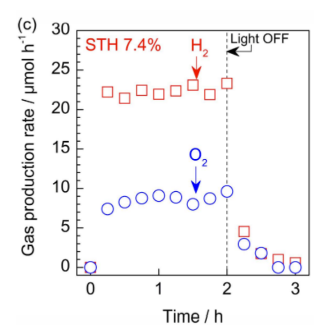
Max Efficiency- 6.95% at optimal band-gap combination

For high operating voltages

- Current-voltage optimization by coupling various PV modules in series and/or in parallel and by adjusting area ratios of the catalyst to PV area.







Kageshima, Y.; Shinagawa, T.; Kuwata, T.; Nakata, J.; Minegishi, T.; Takanabe, K.; Domen, K., A miniature solar device for overall water splitting consisting of series-connected spherical silicon solar cells. *Scientific Reports* **2016,** 6.

Singh, M. R.; Clark, E. L.; Bell, A. T., Thermodynamic and achievable efficiencies for solar-driven electrochemical reduction of carbon dioxide to transportation fuels. *Proceedings of the National Academy of Sciences of the United States of America* **2015,** 112, (45), E6111-E6118.

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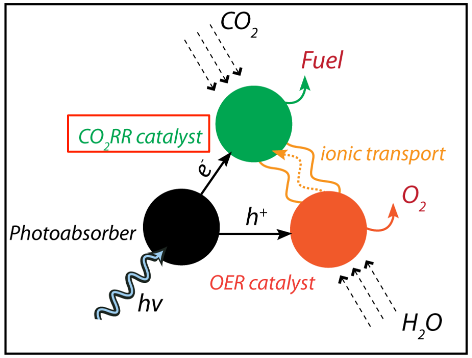
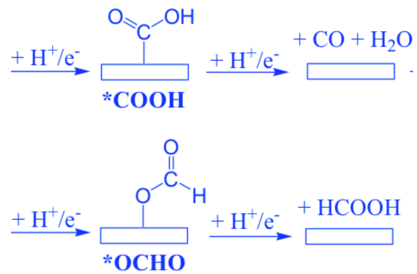
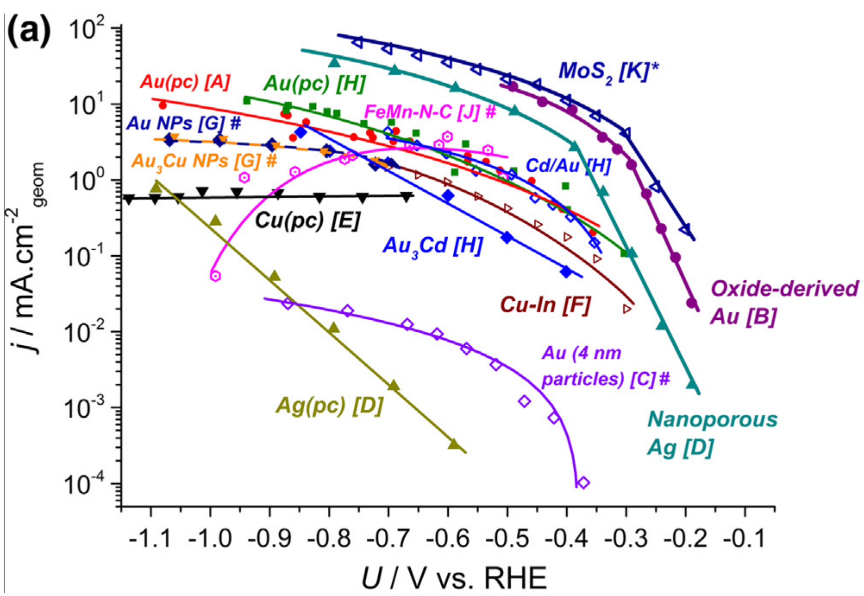
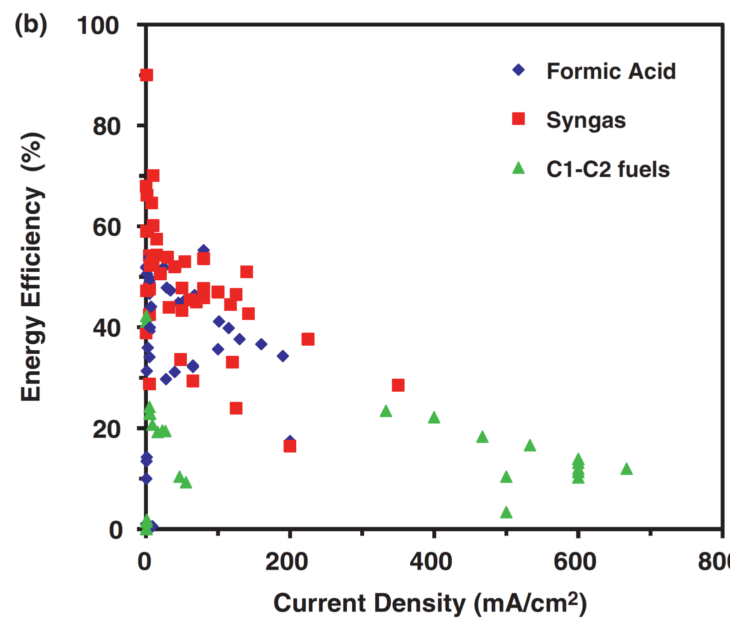
CO_2 Reduction Reaction (CO2RR) Catalyst





We can perform CO_2 reduction to CO or formic acid quite well!





Kortlever, R.; Shen, J.; Schouten, K. J. P.; Calle-Vallejo, F.; Koper, M. T. M., Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J Phys Chem Lett* **2015,** *6*, 4073-4082

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Jhong, H. R.; Ma, S. C.; Kenis, P. J. A., Electrochemical conversion of CO2 to useful chemicals: current status, remaining challenges, and future opportunities. *Curr Opin Chem Eng* **2013,** *2*, 191-199

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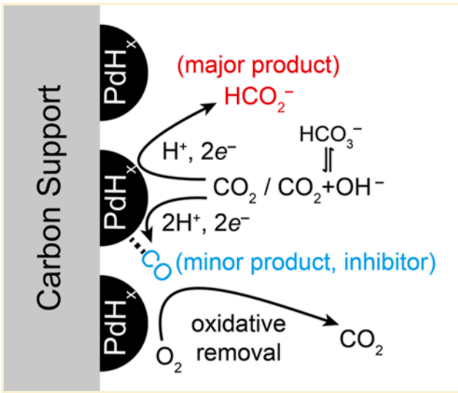

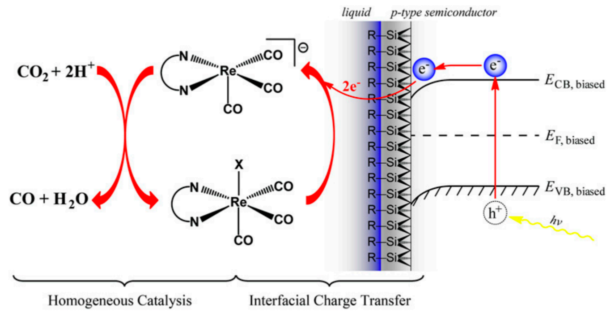

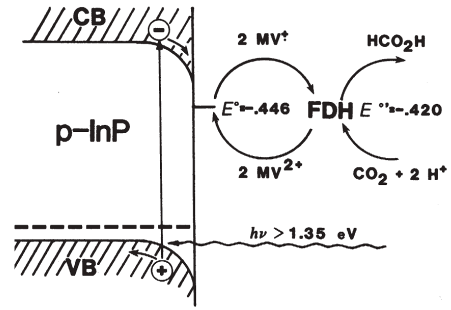

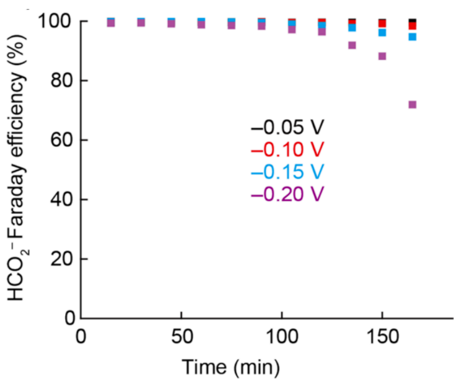

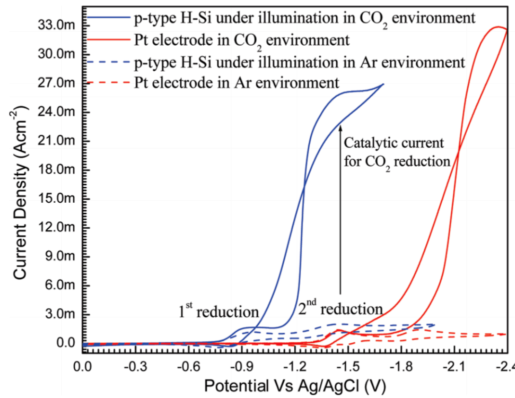

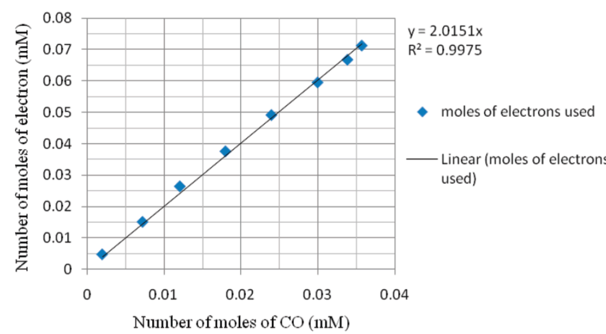

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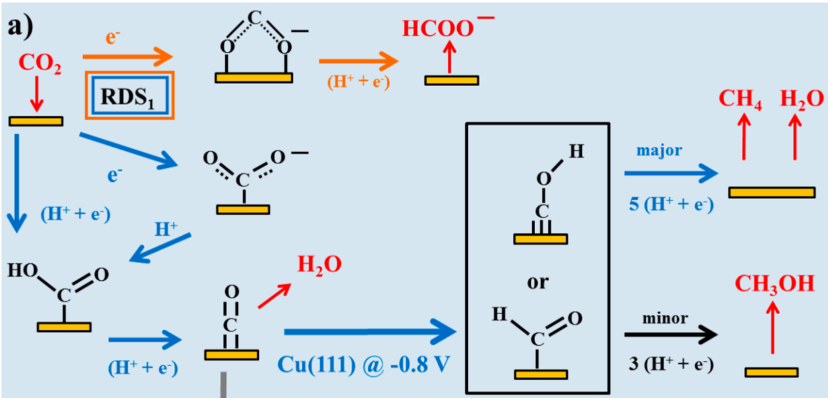
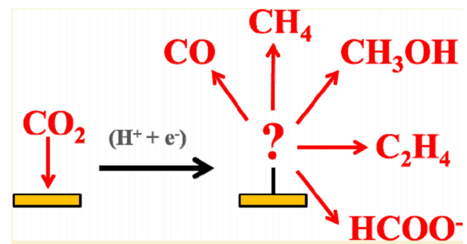
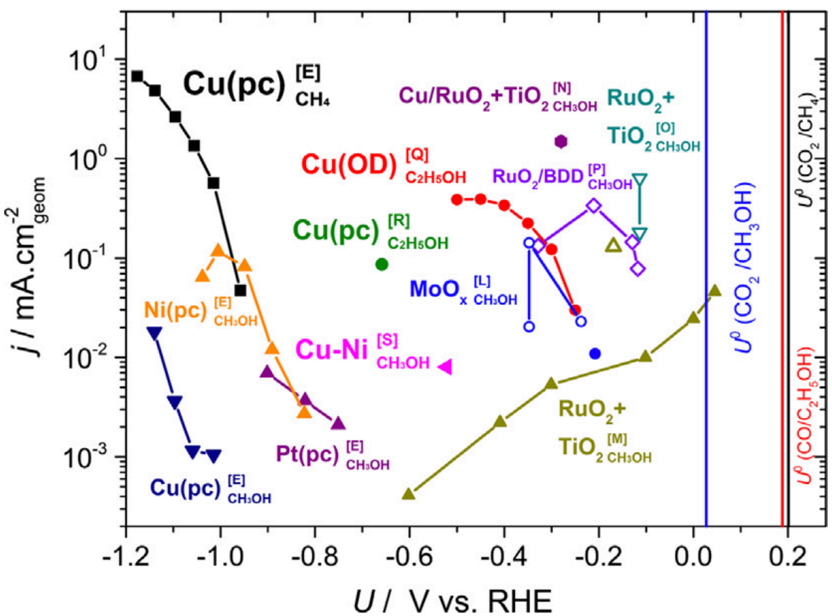
CO2 Reduction Reaction (CO2RR) Catalyst

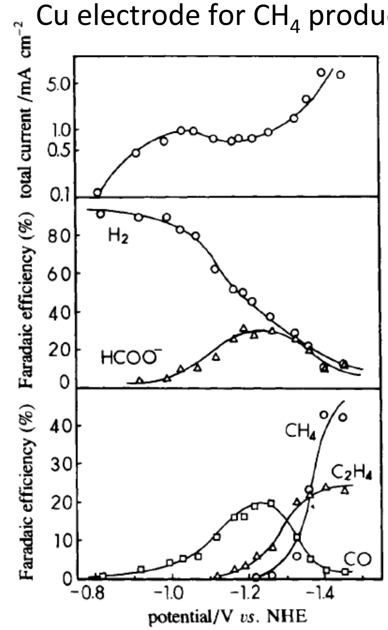


What about everything else?





Cu electrode for CH_4 production



Kortlever, R.; Shen, J.; Schouten, K. J. P.; Calle-Vallejo, F.; Koper, M. T. M., Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J Phys Chem Lett* **2015,** *6*, 4073-4082
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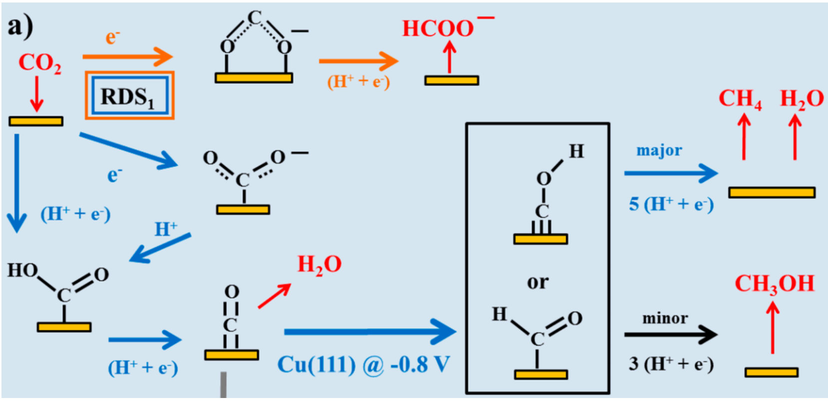
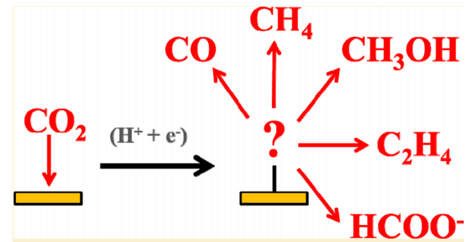
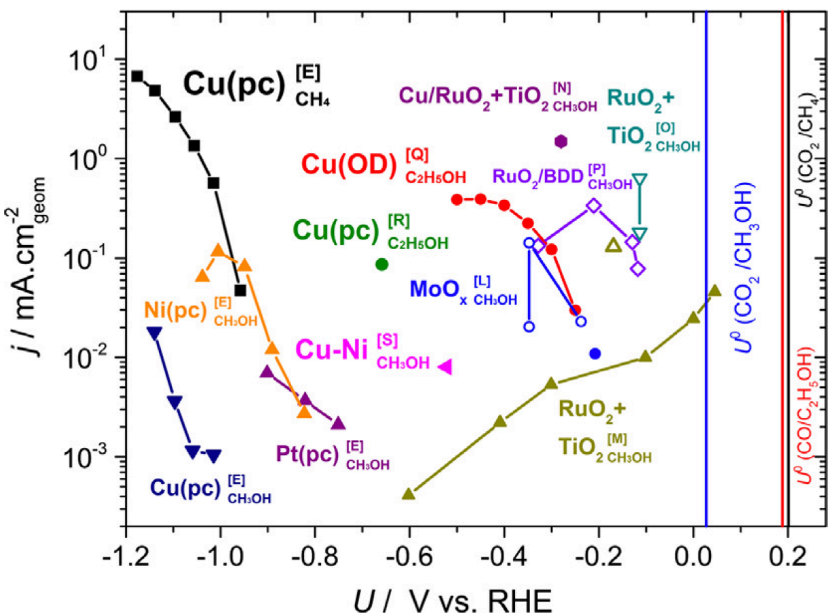
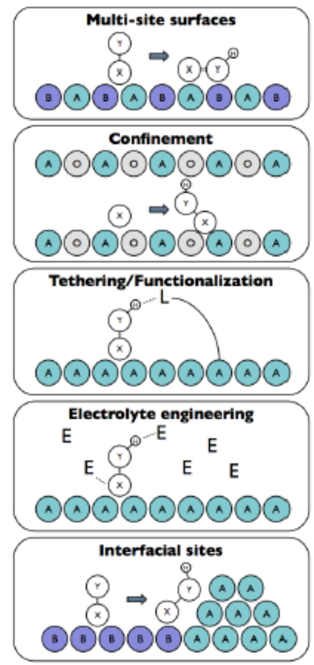
CO2 Reduction Reaction (CO2RR) Catalyst



What about everything else?







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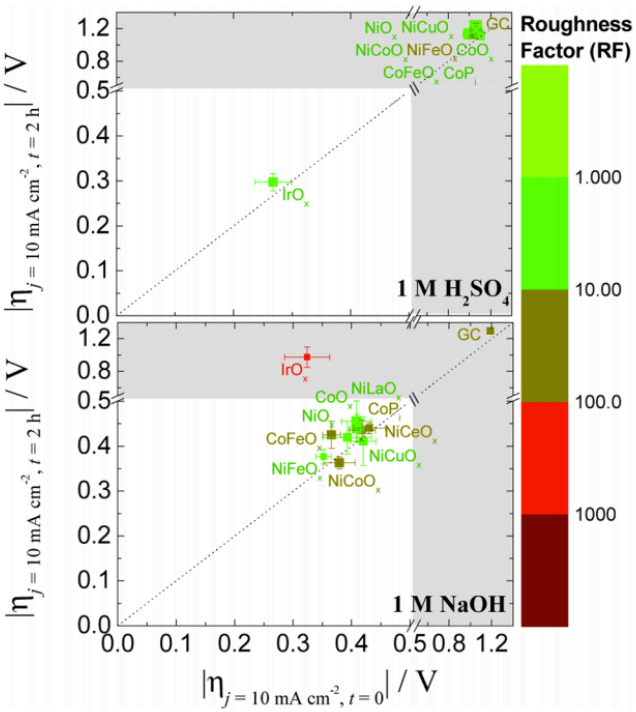
Kortlever, R.; Shen, J.; Schouten, K. J. P.; Calle-Vallejo, F.; Koper, M. T. M., Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J Phys Chem Lett* **2015,** *6*, 4073-4082
Jovanov, Hansen, Varela, Malacrida, Peterson, Nørskov. Stephens, Chorkendorff , J. Catal. (2016)
Jhong, H. R.; Ma, S. C.; Kenis, P. J. A., Electrochemical conversion of CO2 to useful chemicals: current status, remaining challenges, and future opportunities. *Curr Opin Chem Eng* **2013,** *2*, 191-199
Hori, Y.; Murata, A.; Takahashi, R., Formation of Hydrocarbons in the Electrochemical Reduction of Carbon-Dioxide at a Copper Electrode in Aqueous-Solution. *Journal of the Chemical Society-Faraday Transactions I* **1989,** 85, 2309-2326.

OXYGEN EVOLUTION REACTION (OER) CATALYST

Bench mark OER catalyst performance



The-state-of-the-art OER catalysts

Table 1. Comparison of catalytic parameters of gelled FeCoW and controls.

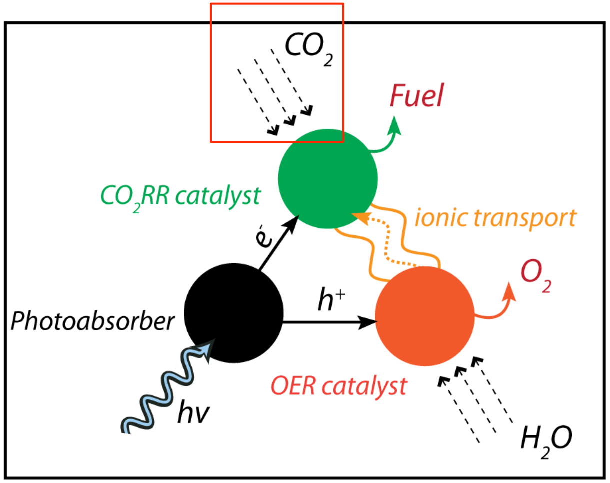
Samples	On gold foam Overpotential* (mV)	On glass carbon Overpotential* (mV)	TOF† (s^{-1})	On Au(111) Overpotential* (mV)	*ΔH* (kJ mol^{-1}) at η=300 mV	Reference
LDH FeCo	279 (-/+8)	331 (-/+3)	0.0085	429 (-/+4)	81	This work
Gelled-FeCo	215 (-/+6)	277 (-/+3)	0.043	346 (-/+4)	60	This work
Gelled-FeCoW	191 (-/+3)	223 (-/+2)	0.46 (-/+0.08)	315 (-/+5)	49	This work
Annealed-FeCoW	232 (-/+4)	301 (-/+4)	0.17	405 (-/+2)	80	This work
Amorphous-$FeCoO_x$‡	–	300	–	–	–	*(4)*
LDH NiFe	–	300	0.07	–	–	*(25)*
CoOOH	–	–	–	550	–	*(23)*
IrO_2	–	260	0.05	–	–	*(25)*
NiFeOOH	–	340	–	–	66 (-/+5)	*(27)*
$Ni_{60}Co_{40}$ oxides	–	263	–	–	72.6§	*(29)*
NiFe LDH/ GO	–	210	0.1	–	–	*(22)*

*Obtained at the current density of 10 mA cm^{-2}, without *iR*-correction.
†Obtained at 95% *iR*-corrected overpotential = 300 mV, assuming all loaded 3d-metal atoms as active sites.
‡Obtained from the LSV plots at the current density of 4 mA cm^{-2} in 0.1 M KOH aqueous solution.
§Obtained at 280 mV in 1M NaOH aqueous solution.

Zhang, B.; Zheng, X. L.; Voznyy, O.; Comin, R.; Bajdich, M.; Garcia-Melchor, M.; Han, L. L.; Xu, J. X.; Liu, M.; Zheng, L. R.; de Arquer, F. P. G.; Dinh, C. T.; Fan, F. J.; Yuan, M. J.; Yassitepe, E.; Chen, N.; Regier, T.; Liu, P. F.; Li, Y. H.; De Luna, P.; Janmohamed, A.; Xin, H. L. L.; Yang, H. G.; Vojvodic, A.; Sargent, E. H., Homogeneously dispersed multimetal oxygen-evolving catalysts. *Science* **2016,** *352*, 333-337

McCrory, C. C. L.; Jung, S. H.; Peters, J. C.; Jaramillo, T. F., Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J Am Chem Soc* **2013,** *135*, 16977-16987

CO_2 Delivery to the Electrode Surface



Key materials:

- Photoabsorber
- CO_2RR catalyst
- OER catalyst

Key components:

- Reactant delivery
- Ionic transport
- Product separation

CO_2 DELIVERY TO THE ELECTRODE SURFACE

- Elevated pressure

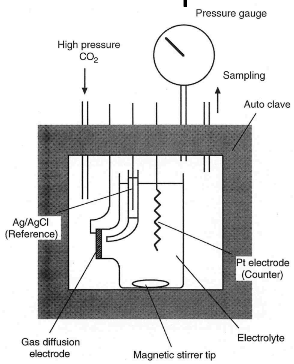
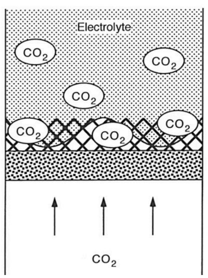


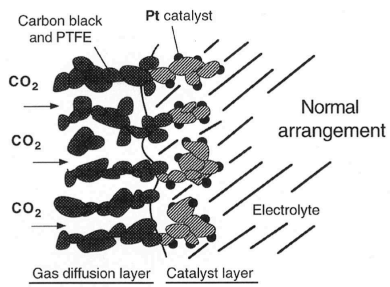
Table II. Effects of CO_2 pressure on the electrochemical reduction of CO_2 using a Pt-GDE.

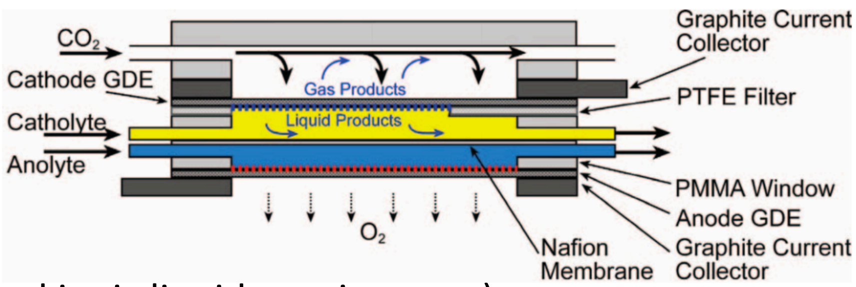
CO_2 pressure (atm)	E^a (V)	Faradaic efficiency (%)						
		CH_4	C_2H_4	C_2H_5OH	CO	$HCOO^-$	H_2	Total
1	−1.89	0.9	0.03	0.2	N	N	96.8	98.0
5	−1.89	31.2	0.59	2.9	3.1	2.8	60.9	101.8
10	−1.90	36.3	0.78	2.8	2.9	4.4	45.6	92.9
20	−1.93	38.8	0.57	2.6	3.8	6.3	42.2	94.4
30	−1.93	33.4	0.67	2.3	3.3	10.5	28.8	79.1
50	−1.90	28.3	0.66	2.3	N	6.7	27.8	65.9

Cathode, Pt-DGE (apparent surface, area, 1 cm^2); reaction temperature, 25°C; current density, 600 mA cm^{-2}; passed charge, 150 C; electrolyte, 0.5 mol dm^{-3} $KHCO_3$.
[a] Corrected with an IR compensation instrument (*vs.* Ag/AgCl).

- Gas diffusion electrodes



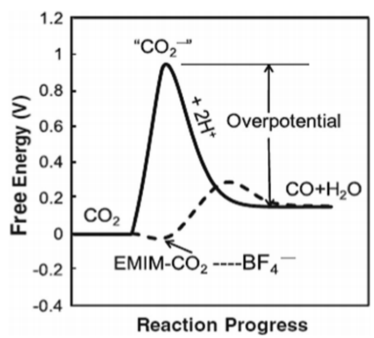


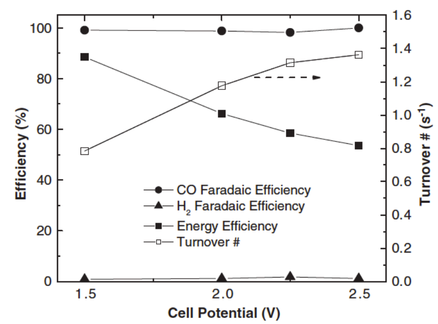


- Non-aqueous solvent (imidazolium-based ionic liquids, amines, etc)

CO_2 Solubility (25°C, 1 atm):

- 0.034 M in water
- 0.28 M in acetonitrile
- ~ 1 M in imidazolium-based ionic liquids

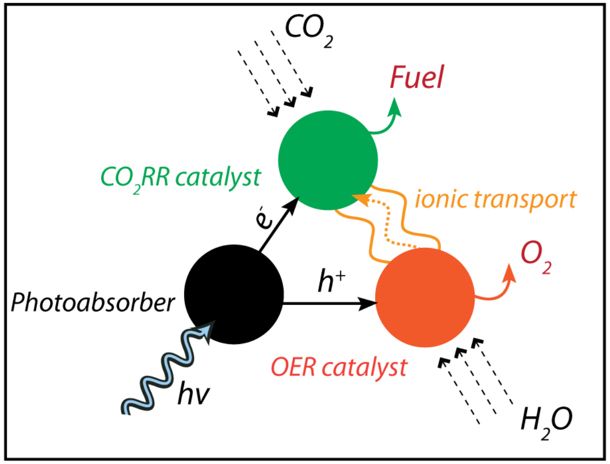




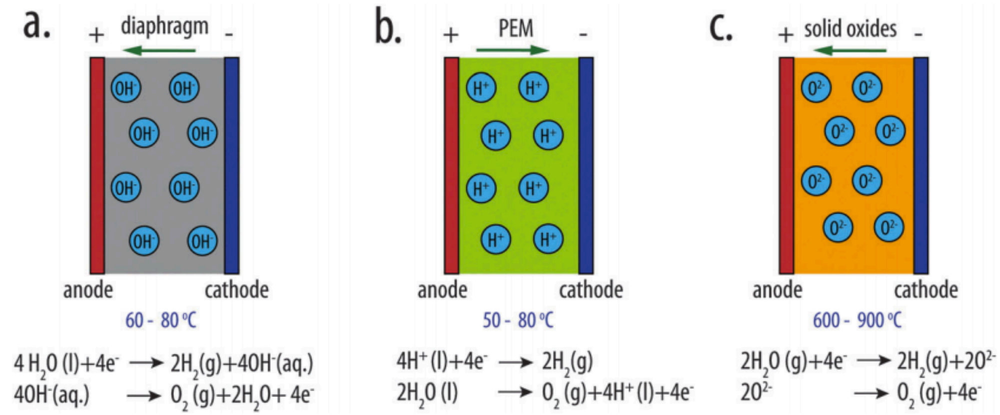
Hara, K., et al., *High-Efficiency Electrochemical Reduction of Carbon-Dioxide under High-Pressure on a Gas-Diffusion Electrode Containing Pt Catalysts.* Journal of the Electrochemical Society, 1995. **142**(4): p. L57-L59.
Hara, K. and T. Sakata, *Electrocatalytic formation of CH4 from CO2 on a Pt gas diffusion electrode.* Journal of the Electrochemical Society, 1997. **144**(2): p. 539-545.
Thorson, M.R., K.I. Siil, and P.J.A. Kenis, *Effect of Cations on the Electrochemical Conversion of CO2 to CO.* Journal of the Electrochemical Society, 2013. **160**(1): p. F69-F74.
Alvarez-Guerra, M.; Albo, J.; Alvarez-Guerra, E.; Irabien, A., Ionic liquids in the electrochemical valorisation of CO2. *Energy & Environmental Science* **2015,** 8, (9), 2574-2599.
Rosen, B. A.; Salehi-Khojin, A.; Thorson, M. R.; Zhu, W.; Whipple, D. T.; Kenis, P. J. A.; Masel, R. I., Ionic Liquid-Mediated Selective Conversion of CO2 to CO at Low Overpotentials. *Science* **2011,** 334, (6056), 643-644.

Ionic Transport and Product Separation

At extreme pHs



Schematic illustration of an alkaline electrolyzer, PEM electrolyzer and a solid oxide electrolyter



Gas-tight diaphragm: ceramic and micro-porous materials

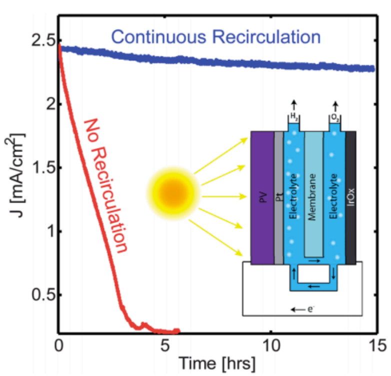
Solid polymer electrolyte: Nafions, Felmions, or Aciplexs.

Solid oxide electrolyte: yttrium zirconium oxides (YSZ)

Xiang, C. X.; Papadantonakis, K. M.; Lewis, N. S., Principles and implementations of electrolysis systems for water splitting. *Materials Horizons* **2016,** 3, (3), 169-173.

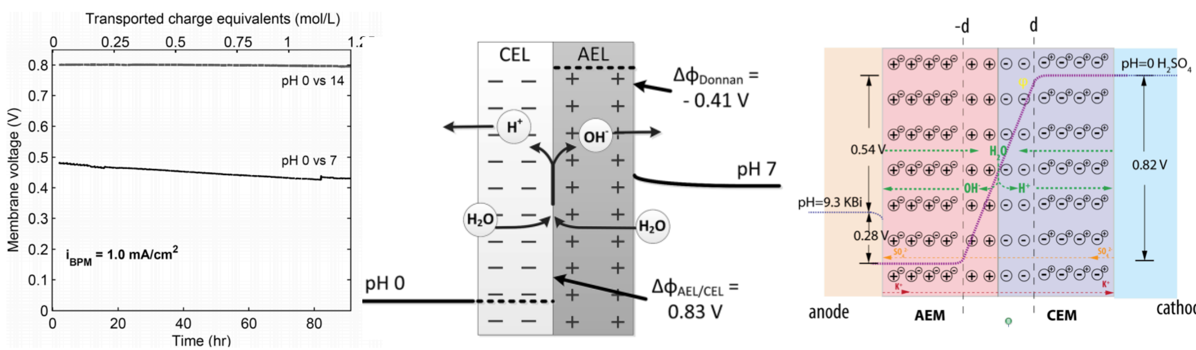
At near neutral pHs

Re-circulation with other cations as the ionic current carriers



Modestino, M. A.; et.al., Robust production of purified H-2 in a stable, self-regulating, and continuously operating solar fuel generator. *Energy & Environmental Science* **2014,** 7, (1), 297-301.

Bipolar membrane for sustainable electrolysis at near neutral pH.



Vermaas, D. A.et. al., Photo-assisted water splitting with bipolar membrane induced pH gradients for practical solar fuel devices. *Journal of Materials Chemistry A* **2015,** 3, (38), 19556-19562.

Sun, K. et.al., A Stabilized, Intrinsically Safe, 10% Efficient, SolarDriven Water-Splitting Cell Incorporating Earth-Abundant Electrocatalysts with Steady-State pH Gradients and Product Separation Enabled by a Bipolar Membrane, Advanced Energy Materials, 2016, 1600379.

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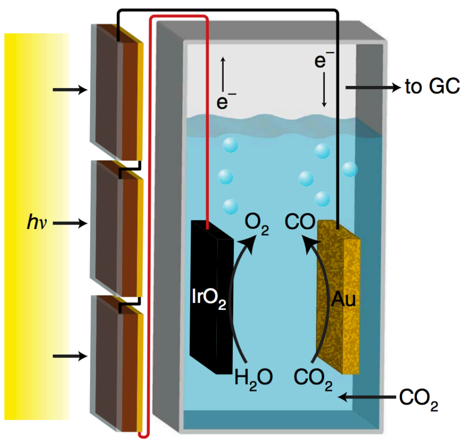
OUTLINE

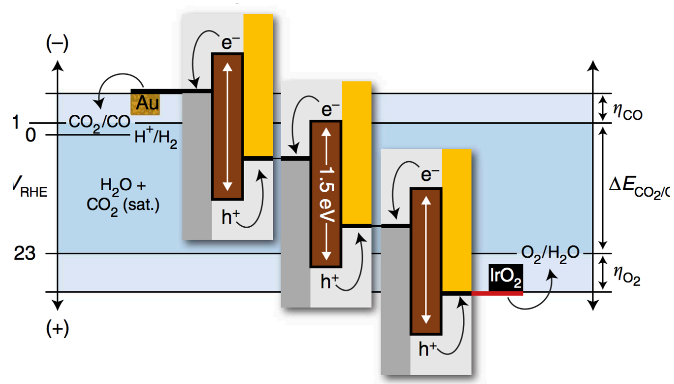
- The Basic Operating Principles of a Photoelectrochemical (PEC) CO_2 Reduction Reaction (CO_2RR) System.
- Materials and Components.
- Device Designs and Demonstration.

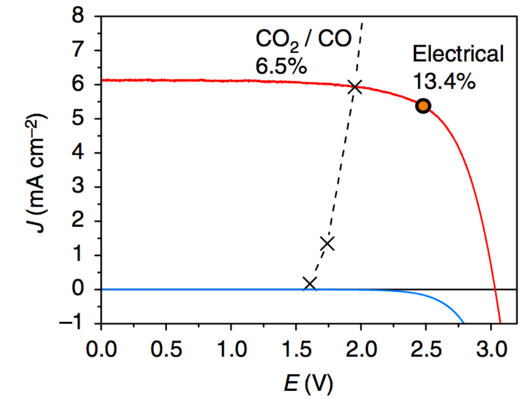
STAND-ALONE PV+MEA DESIGN

1. Series connected PV+MEA design

6.5% to CO

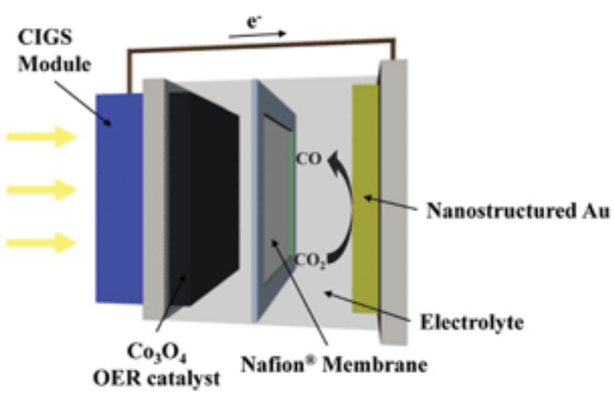


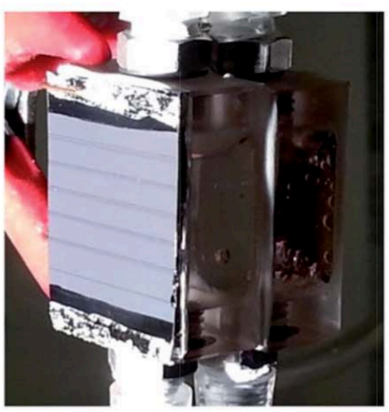


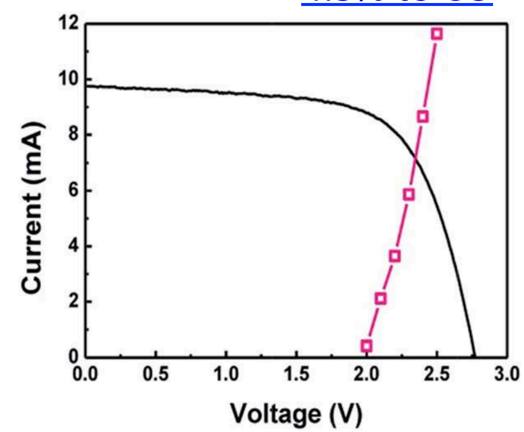


Jeon, H. S.; Koh, J. H.; Park, S. J.; Jee, M. S.; Ko, D. H.; Hwang, Y. J.; Min, B. K., A monolithic and standalone solar-fuel device having comparable efficiency to photosynthesis in nature. *Journal of Materials Chemistry A* **2015,** *3*, 5835-5842

4.5% to CO







Jeon, H. S.; Koh, J. H.; Park, S. J.; Jee, M. S.; Ko, D. H.; Hwang, Y. J.; Min, B. K., A monolithic and standalone solar-fuel device having comparable efficiency to photosynthesis in nature. *Journal of Materials Chemistry A* **2015,** *3*, 5835-5842

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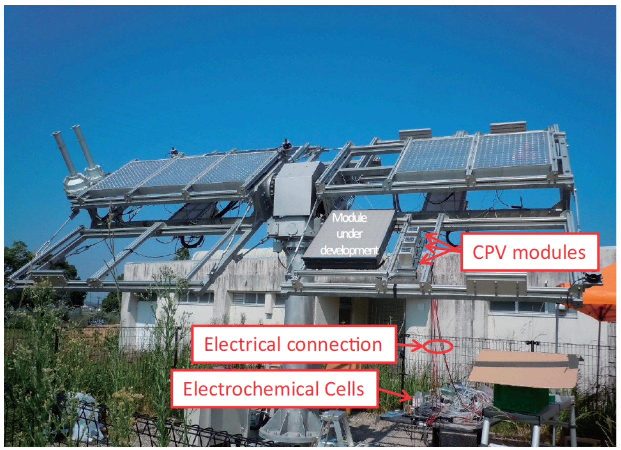
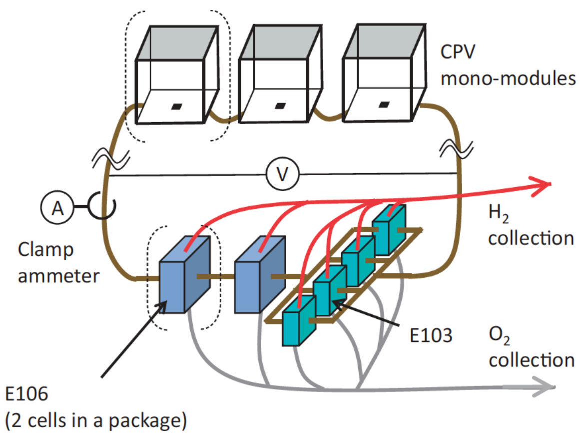
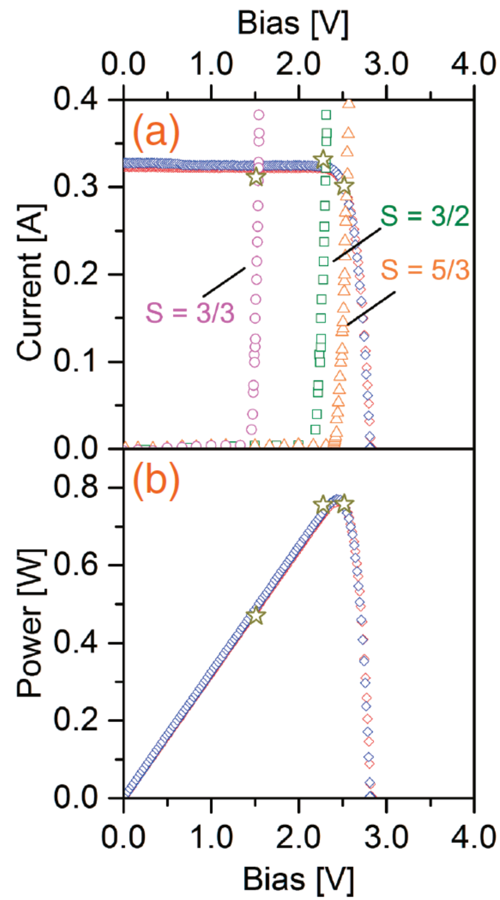
Stand-alone PV+MEA Design

Some inspiration from PEC water-splitting system:

1. Series connected PV+MEA design coupled with solar concentrator







24.4% solar to hydrogen conversion efficiency

Nakamura, A.; Ota, Y.; Koike, K.; Hidaka, Y.; Nishioka, K.; Sugiyama, M.; Fujii, K., A 24.4% solar to hydrogen energy conversion efficiency by combining concentrator photovoltaic modules and electrochemical cells. *Appl Phys Express* **2015,** *8*

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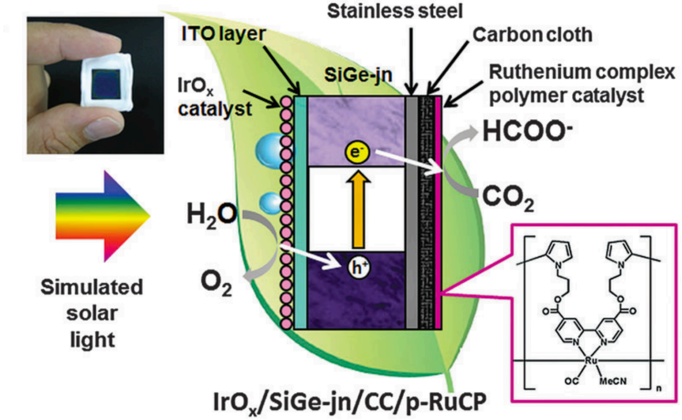
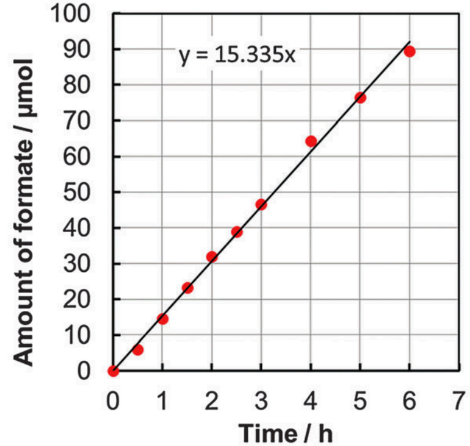
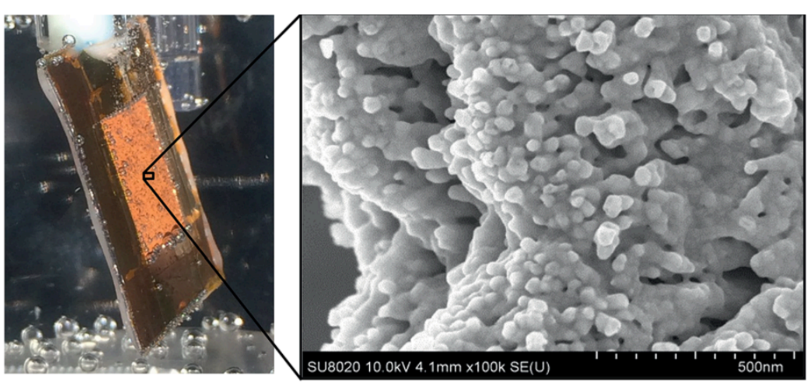
2. Integrated macroscopic planar devices



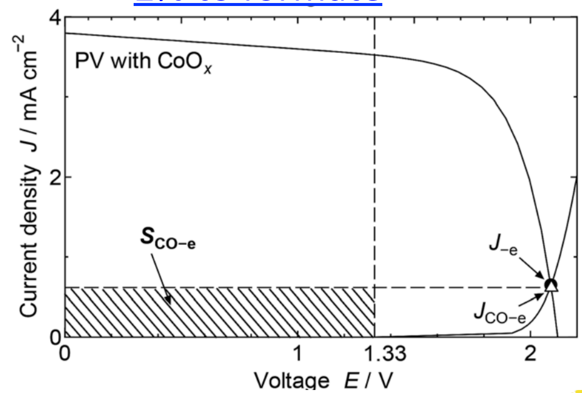
4.6% to formate



Arai, T.; Sato, S.; Morikawa, T., A monolithic device for CO2 photoreduction to generate liquid organic substances in a single-compartment reactor. *Energ Environ Sci* **2015,** *8*, 1998-2002



2% to formate



Sugano, Y.; Ono, A.; Kitagawa, R.; Tamura, J.; Yamagiwa, M.; Kudo, Y.; Tsutsumi, E.; Mikoshiba, S., Crucial role of sustainable liquid junction potential for solar-to-carbon monoxide conversion by a photovoltaic photoelectrochemical system. *Rsc Adv* **2015,** *5*, 54246-54252

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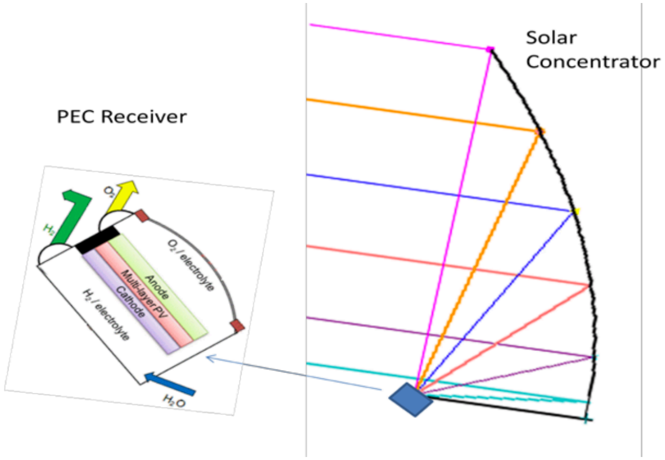
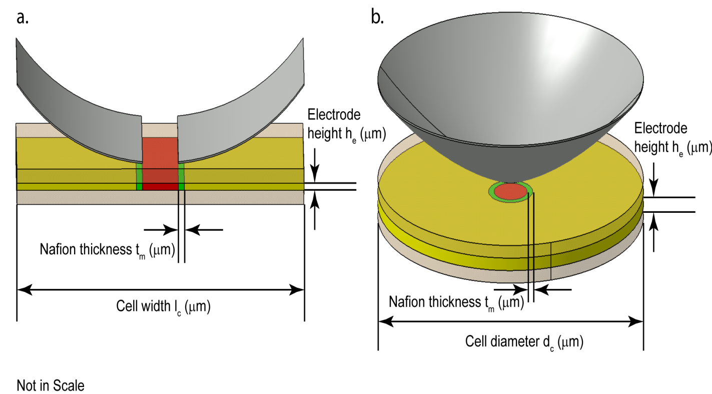
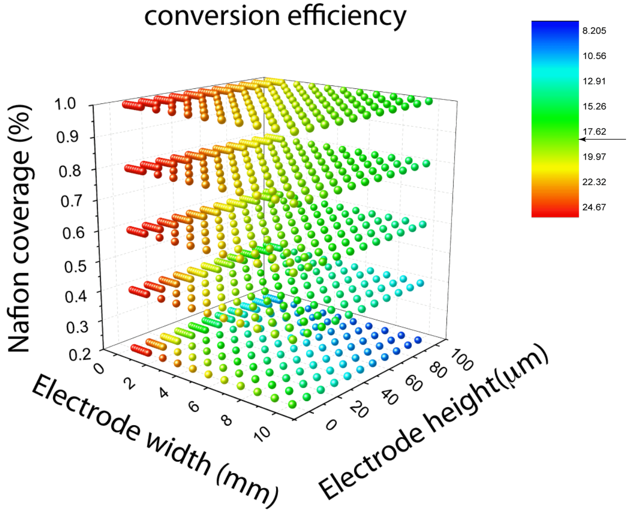
INTEGRATED PEC CO2RR SYSTEM

2. Integrated macroscopic planar devices coupled with solar concentrator

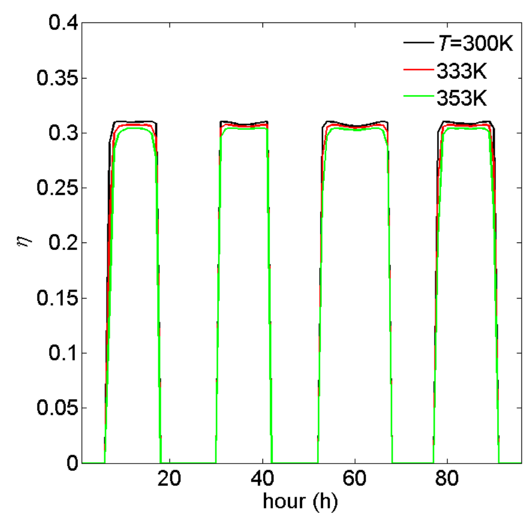




Solar to hydrogen conversion efficiency



Optimal bandgap combination for the integrated system: 1.6 eV/1.0 eV



James, B. D.; Baum, G. N.; Perez, J.; Baum, K. N. *Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production*; Directed Technologies: 2009

Haussener, S.; Hu, S.; Xiang, C. X.; Weber, A. Z.; Lewis, N. S., Simulations of the irradiation and temperature dependence of the efficiency of tandem photoelectrochemical water-splitting systems. *Energy & Environmental Science* **2013,** 6, (12), 3605-3618

Chen, Y. K.; Xiang, C. X.; Hu, S.; Lewis, N. S., Modeling the Performance of an Integrated Photoelectrolysis System with 10 x Solar Concentrators. *Journal of the Electrochemical Society* **2014,** 161, (10), F1101-F1110

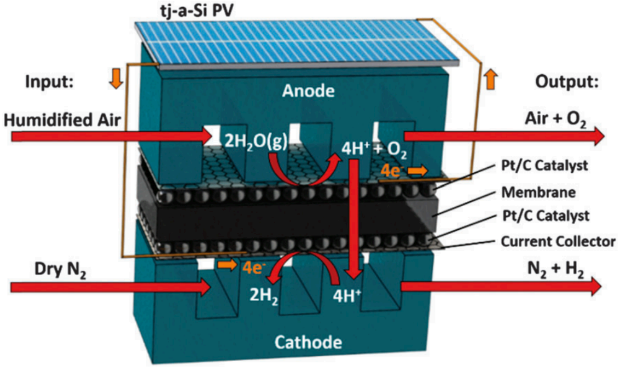
JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

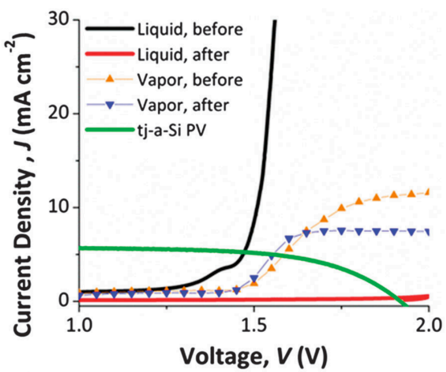
WHAT A PEC CO2RR SYSTEM MIGHT LOOK LIKE?

Some inspiration from PEC water-splitting system:

3. Vapor feed cell design

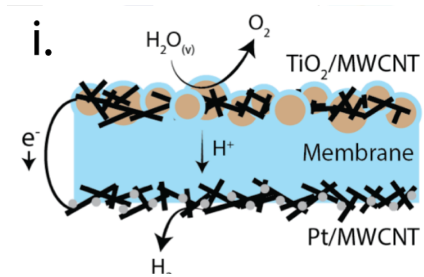
Seawater vapor electrolysis at 6% STH conversion efficiency.

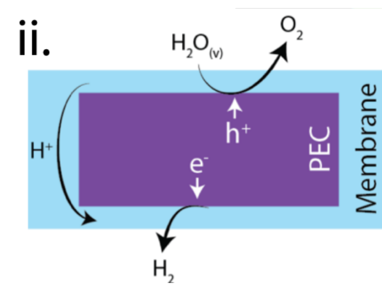


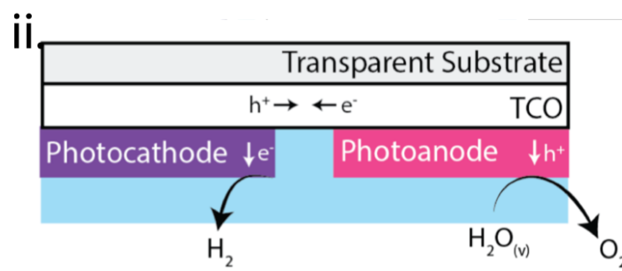


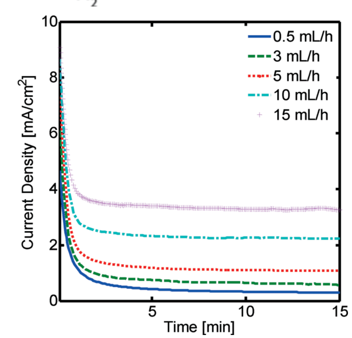
- Eliminate the use of strong base and strong acid as the system input feedstock.
- Mitigate the deleterious effects associated with bubble formation.
- Potential advantage in product separation for liquid fuel devices

Various water vapor device designs









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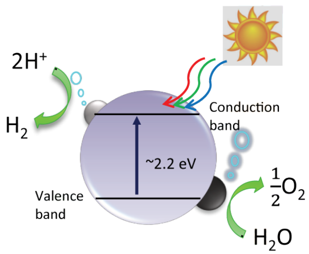
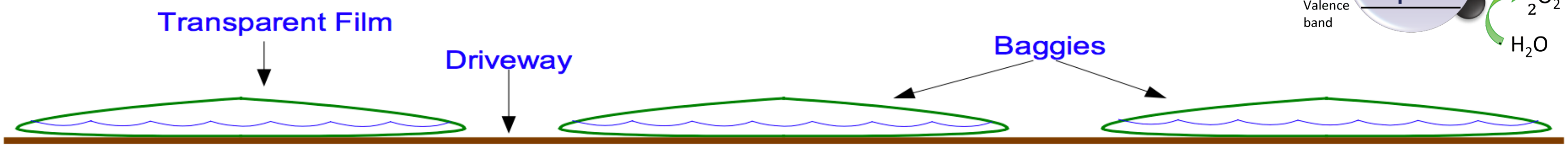
“BAGGIE” DESIGN

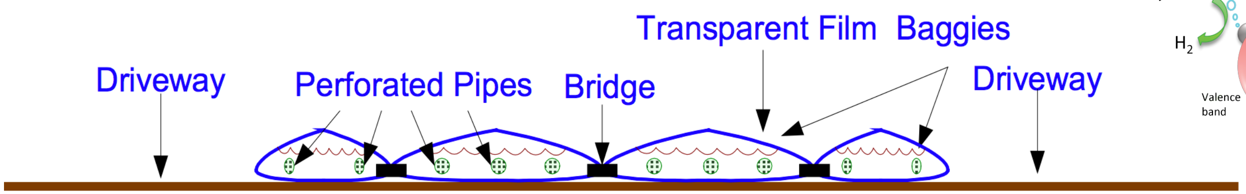
Some inspiration from PEC water-splitting system:

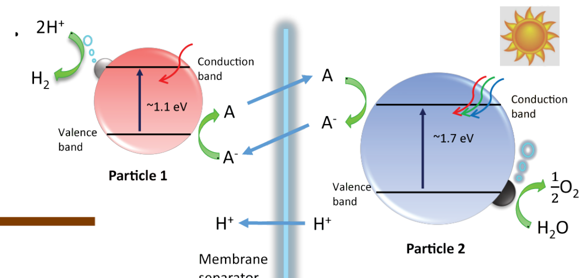
4. Nanoparticle-based “baggie” design

i.









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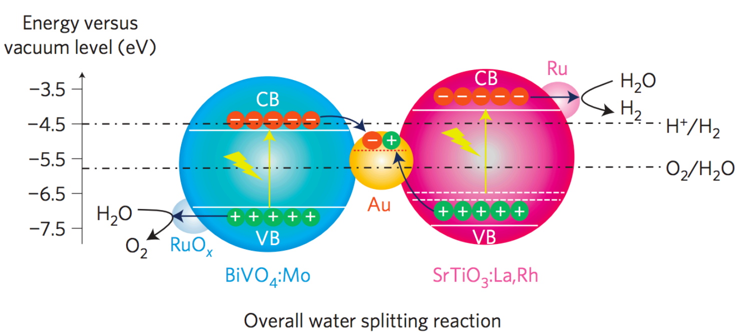
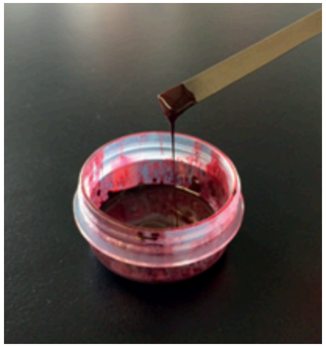
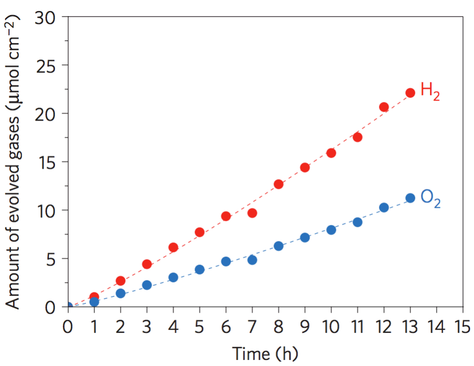




~1% STH conversion efficiency



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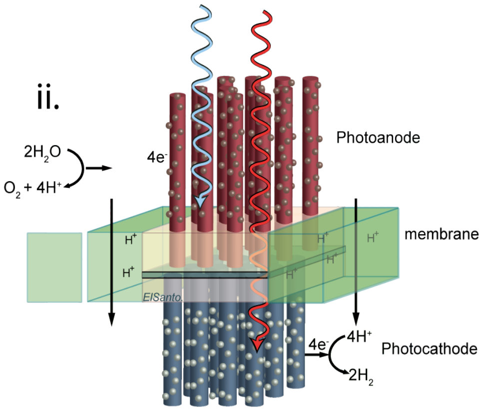
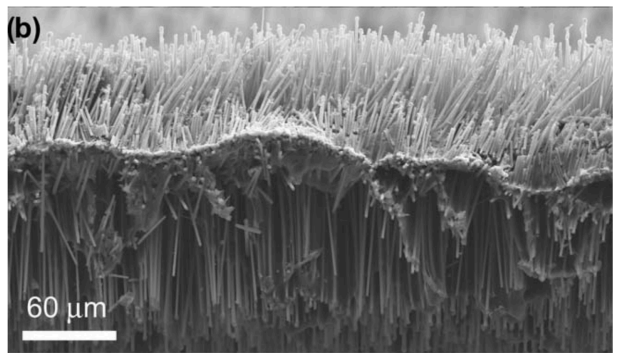
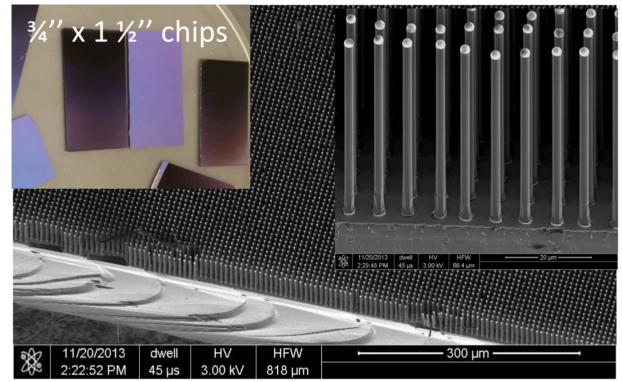
What a PEC CO2RR System Might Look Like?

Some inspiration from PEC water-splitting system:

5. Integrated microwire-based PEC devices







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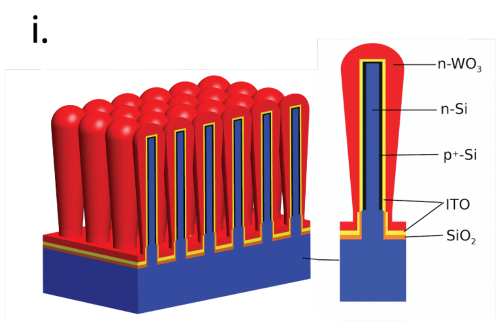
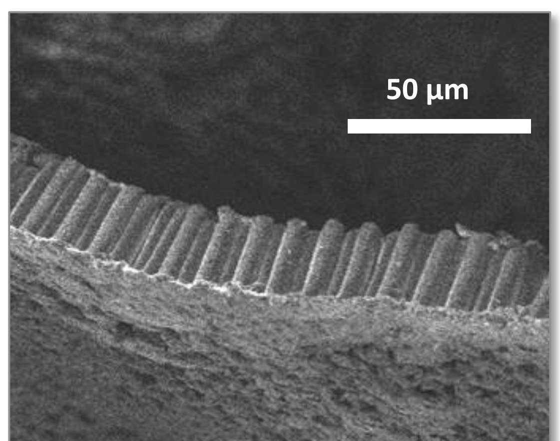
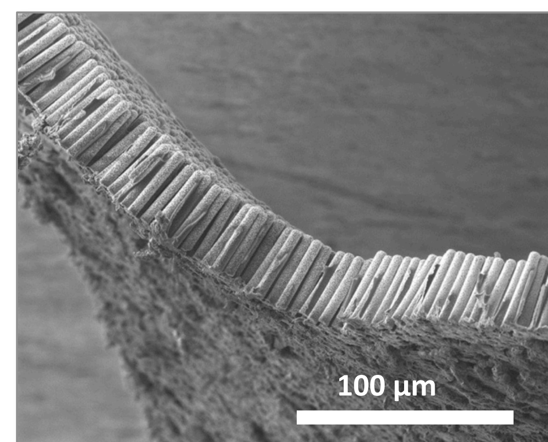
- 





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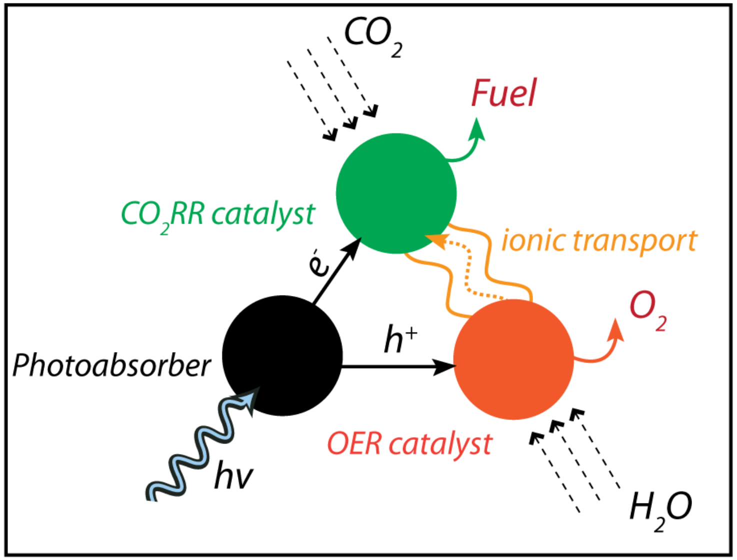
SUMMARY

The system takes the sunlight, carbon dioxide and water and converts them into fuels and oxygen.



Oxygen evolution reaction (OER)

$H_2O \longrightarrow \frac{1}{2}O_2\,(g) + 2H^+ + 2e^-$

CO_2 Reduction reaction (CO_2RR)

$CO_2 + 2e^- + 2\,H^+ \longrightarrow CO + H_2O$

$CO_2 + 2e^- + 2\,H^+ \longrightarrow HCOOH$

$CO_2 + 6e^- + 6\,H^+ \longrightarrow CH_3OH + H_2O$

$CO_2 + 8e^- + 8\,H^+ \longrightarrow CH_4 + 2\,H_2O$

Key materials:
- Photoabsorber
- CO_2RR catalyst
- OER catalyst

Key components:
- Reactant delivery
- Ionic transport
- Product separation

Key performance metrics:
- Conversion efficiency
- Selectivity
- Stability
- Scalability

The Joint Center for Artificial Photosynthesis (JCAP) is the nation's largest research program dedicated to the development of an artificial solar-fuel generation technology. Established in 2010 as a U.S. Department of Energy (DOE) Energy Innovation Hub, JCAP aims to find a cost-effective method to produce fuels using only sunlight, water, and carbon-dioxide as inputs. JCAP is led by a team from the California Institute of Technology (Caltech) and brings together more than 140 world-class scientists and engineers from Caltech and its lead partner, Lawrence Berkeley National Laboratory. JCAP also draws on the expertise and capabilities of key partners from the University of California campuses at Irvine (UCI) and San Diego (UCSD), and the Stanford Linear Accelerator (SLAC). In addition, JCAP serves as a central hub for other solar fuels research teams across the United States, including 20 DOE Energy Frontier Research Center.

For more information, visit http://www.solarfuelshub.org.

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