NATIONAL ENERGY TECHNOLOGY LABORATORY

Catalytic Conversion of CO_2 to C1 Chemicals

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Catalytic CO_2 Utilization Team Members & Collaborators:
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James Lewis (WVU), Rongchao Jin (CMU), Ken Jordan (PITT), Sittichai Natesakhawat (PITT)

CO_2 Conversion to C1 Industrial Chemicals

CO_2

H_2

and/or

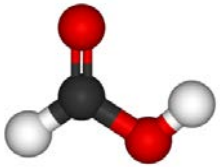
H_2O

Catalyst

Geothermal Heat

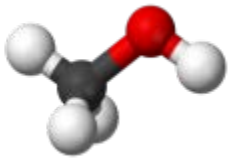
Solar-Heating Or Photo-driven

Wind-Electric

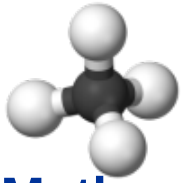


Formic Acid

Formaldehyde



Methanol



Methane

	Formic Acid	Formaldehyde	Methanol	Methane
Approx Yearly Market	25 K Ton[1] ($25 M)	3 M ton ($720 M)	3.6 M ton ($1440 M)	484 M ton ($210,000 M)
Uses	Leather, Pulp	Urea Resins Phenol Resins	Fuel/MTG Formaldehyde	Fuel Acetic Acid

[1] Global Formic Acid Market: 0.5 M Ton ($750 M)

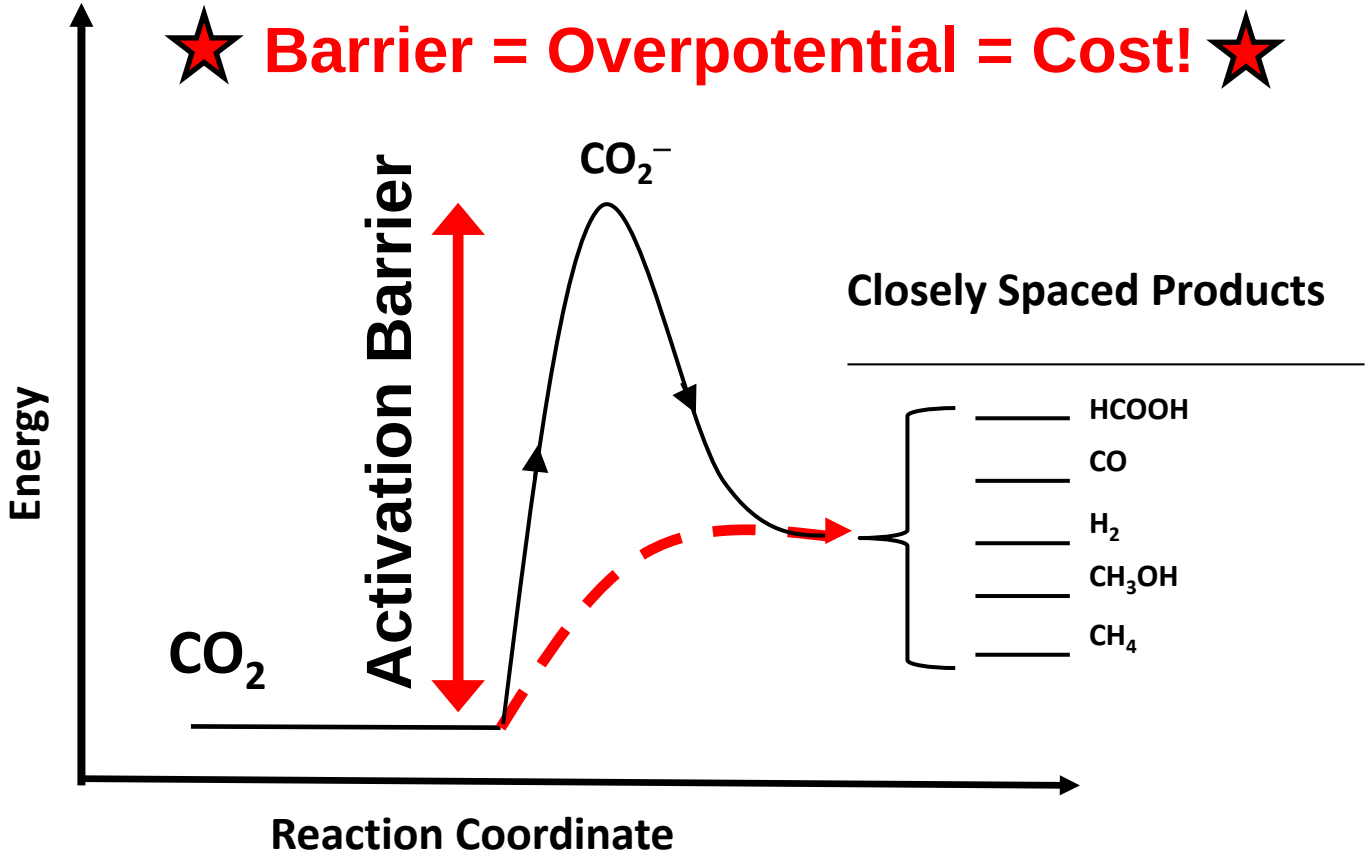
Project Structure

- **Photocatalytic Systems**
  - **Heterostructured Photocatalysts for CO_2 Reduction**
  - **Symmetry Breaking and High Throughput Computational Screening of Delafossites for the Photocatalytic Reduction of CO_2**
  - **Scanning Tunneling Microscopy and Dispersion-corrected Density Functional Theory Studies of TiO_2 Surfaces**

- **Electrocatalytic Systems**
  - **Electronic Structure and Catalytic Activity of Au_{25} Clusters**

- **Thermal Catalytic Systems**
  - **Atomic Structure and Catalytic Activity of Cu/ZnO-Based Materials**

Electroreduction of CO_2: An Uphill Run!

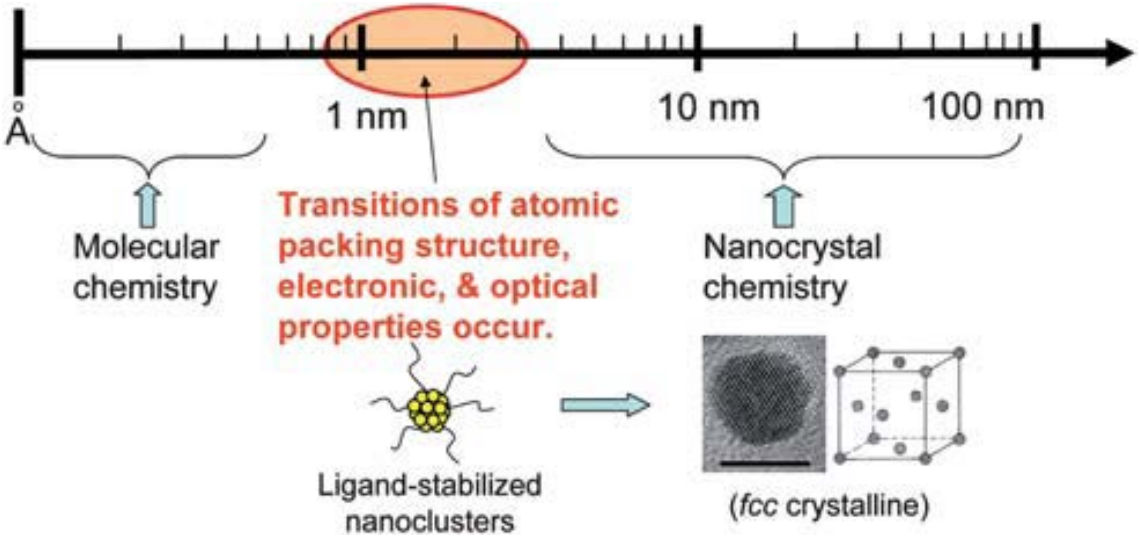


Challenge

Develop high efficiency catalyst with low overpotential and good product selectivity

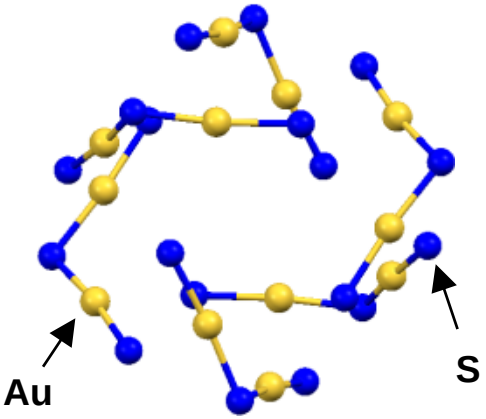
NETL Catalyst Accomplishes This!

Atomically Precise Au_n clusters (n < ~200) for CO_2 Conversion

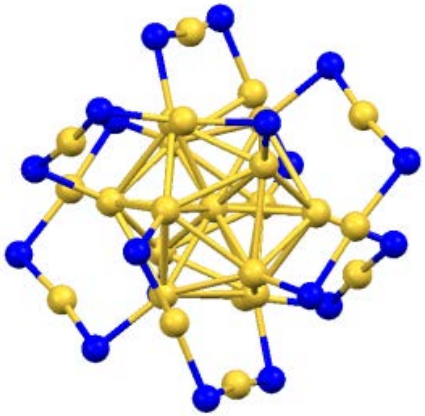


$(–S–Au–S–Au–S–)_6$ "shell"

Au_{13} "core"



Au_{25} cluster



1 nm

-ground state anion

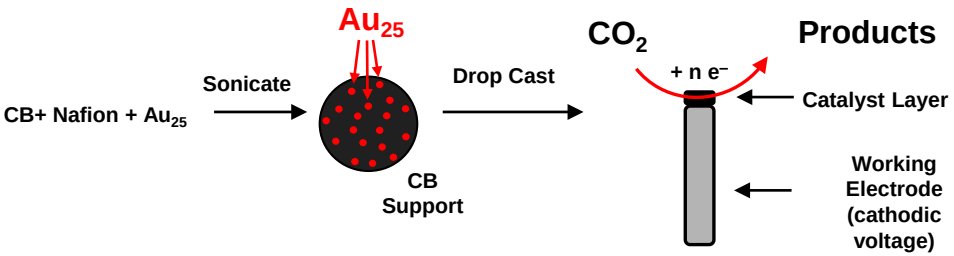
-molecule like electronic structure

-nearly all atoms are "surface"

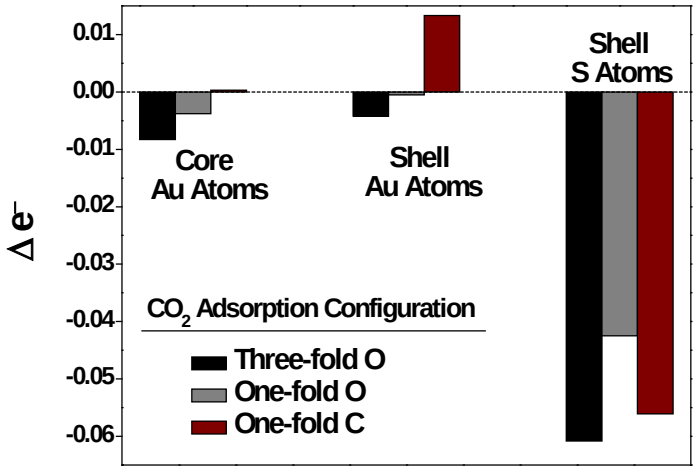
* Figures From R. Jin, *Nanoscale, 2010, 2, 343–362 & JACS 2008*

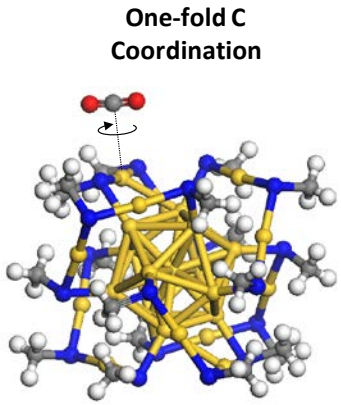
Unprecented Catalytic Efficiency

$CO_2 + 2H^+ 2e^- \rightarrow CO + H_2O$ $\quad E^0 = -0.103$ V (RHE)

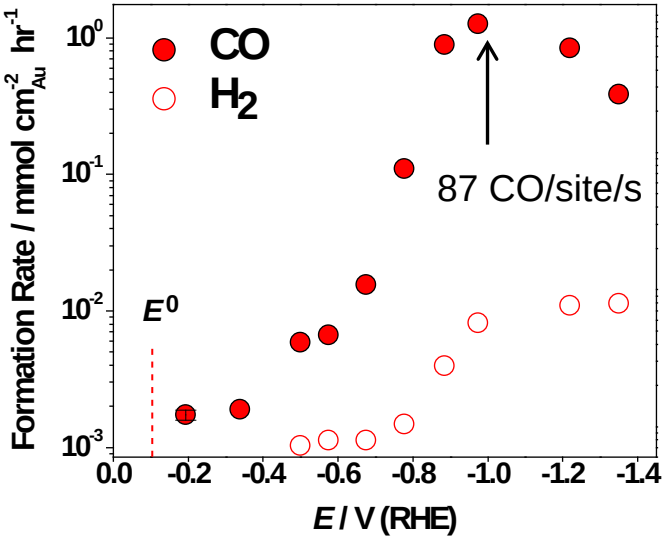


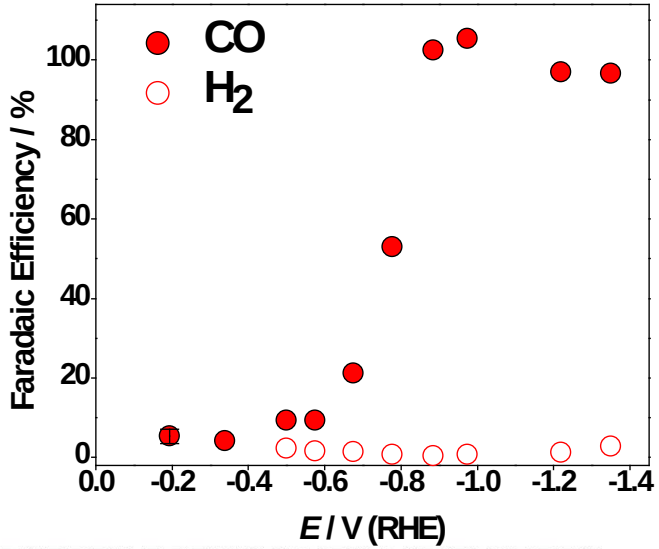
Ab Initio DFT Calculations





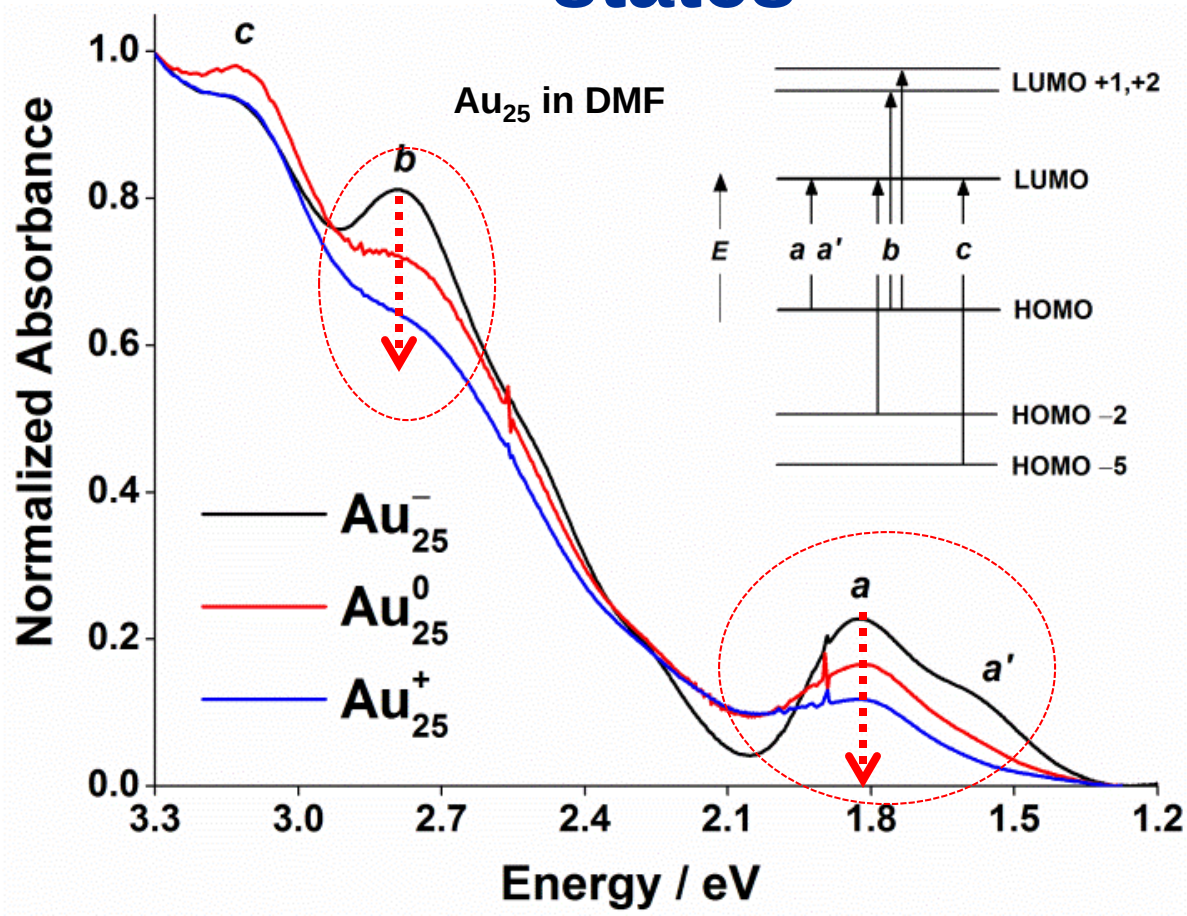
Experiments





Kauffman, et, al. J. Am. Chem. Soc. 2012, 134 (24), 10237-10243.

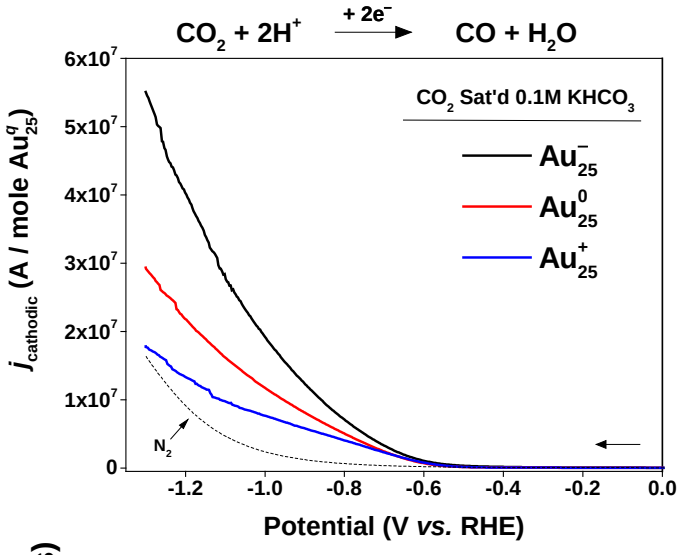
Optical Spectra of Isolated Au_{25}^{q} charge states

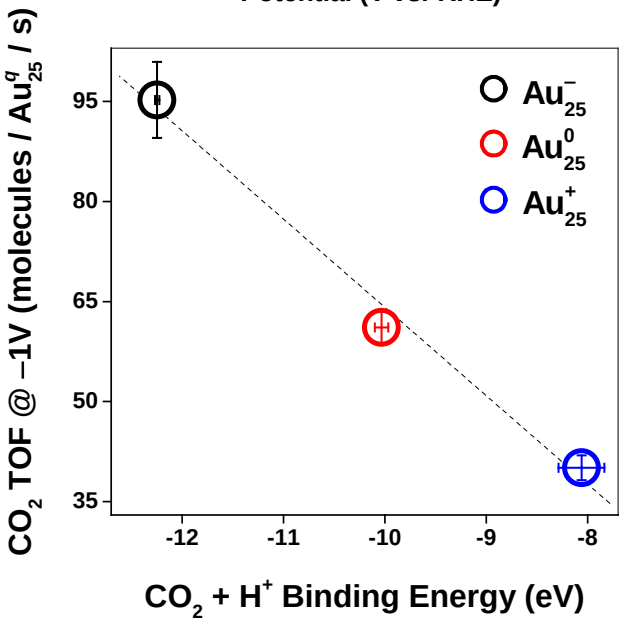


- Crystal structure analysis and XPS show absence of oxides on Au_{25}^{0} and Au_{25}^{+}
- Cluster's structure and charge state retained on CB support and during reactions

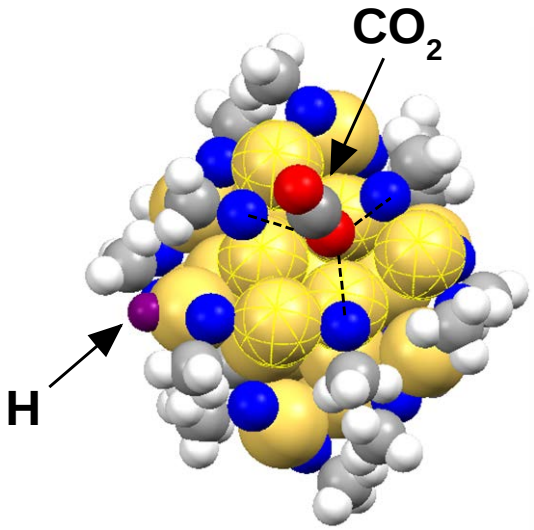
Kauffman, *et al. J. Phys. Chem. Lett.* **2013**, *4*, 195-202 ; Kauffman *et al. Chemical Science,* **2014**, *in press.*

Charge State-Dependent CO_2 Reduction





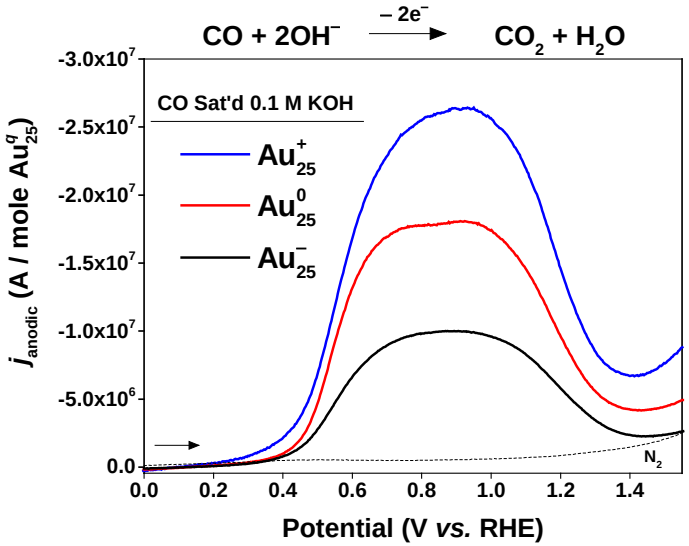
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$

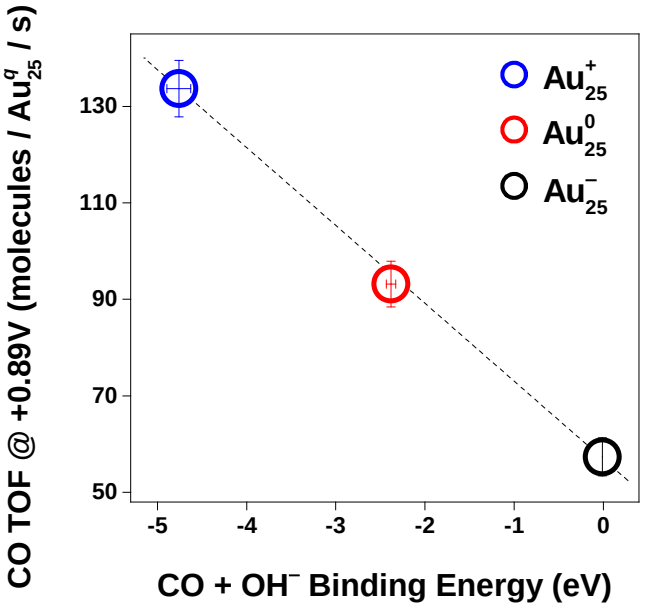


- Negative clusters enhance CO_2 reduction
- Proton adsorption is enhanced on negative clusters
- TOF (exp) correlates with ab initio (DFT) binding energies

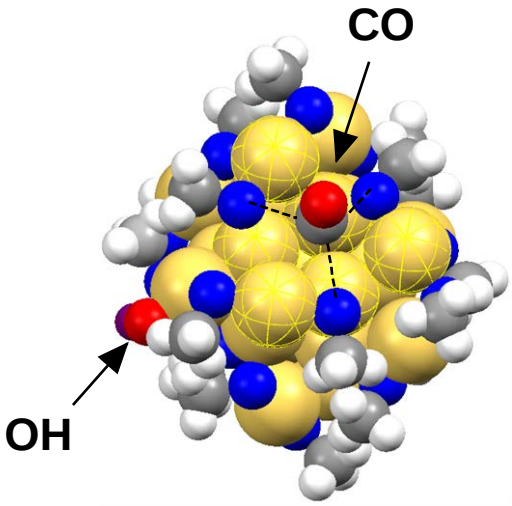
Kauffman *et al Chemical Science*, 2014.

Charge State-Dependent CO Oxidation





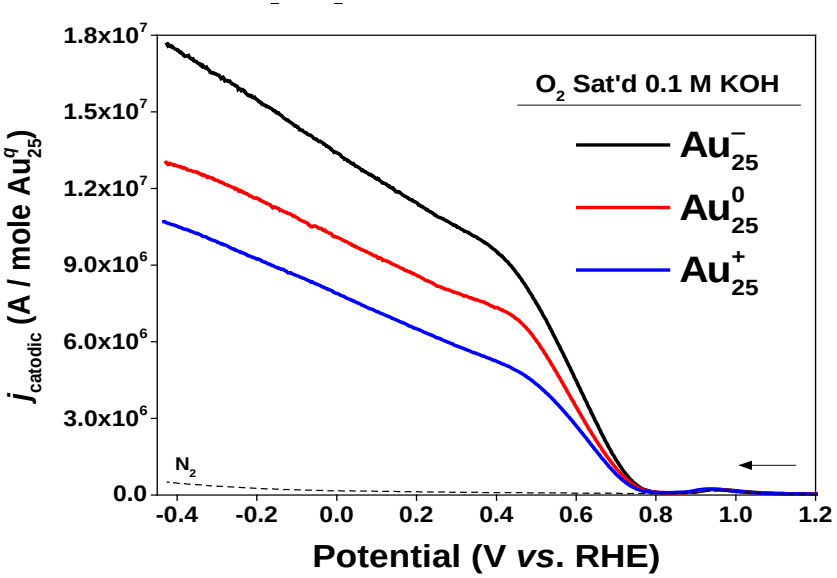
$$CO + 2OH^- \rightarrow CO_2 + H_2O + 2e^-$$



- Positive clusters enhance CO oxidation
- Hydroxl adsorption is enhanced on positive clusters
- TOF (exp) correlates with ab initio (DFT) binding energies

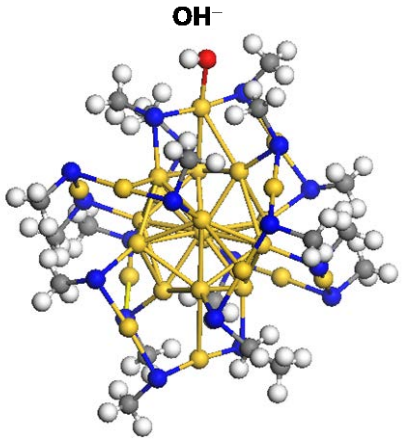
Kauffman *et al Chemical Science*, 2014, in press.

Charge State Dependent O_2 Reduction

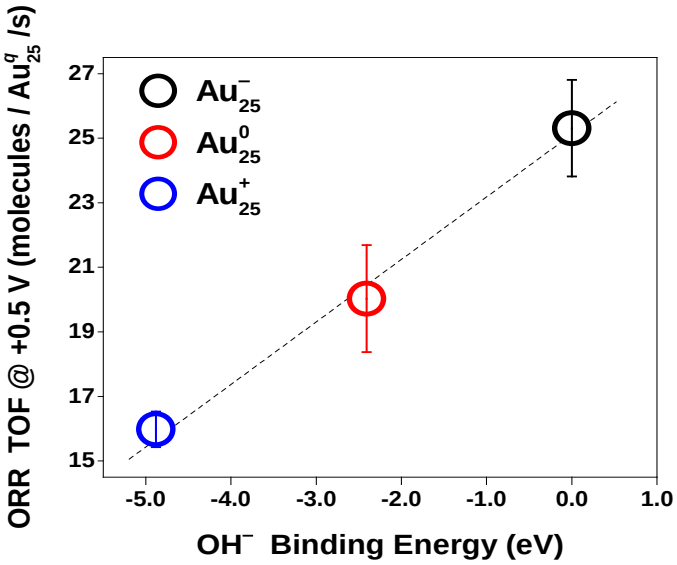


$$O_2 + 2\,H_2O + + 4e^- \rightarrow 4\,OH^-$$

$$O_2 + H_2O + + 2e^- \rightarrow OH^- + OOH^-$$



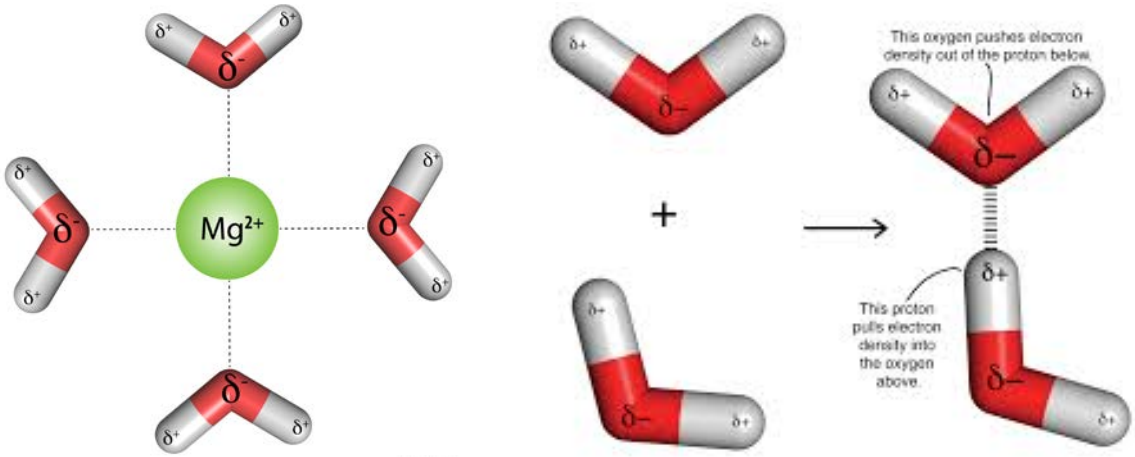
(b)



- Negative clusters enhance O_2 reduction
- Hydroxl adsorption is enhanced on positive clusters & blocks active sites (no desorption)
- TOF (exp) correlates with ab initio (DFT) binding energies

Charged Reactants, Intermediates, & Products are Ubiquitous in Chemistry

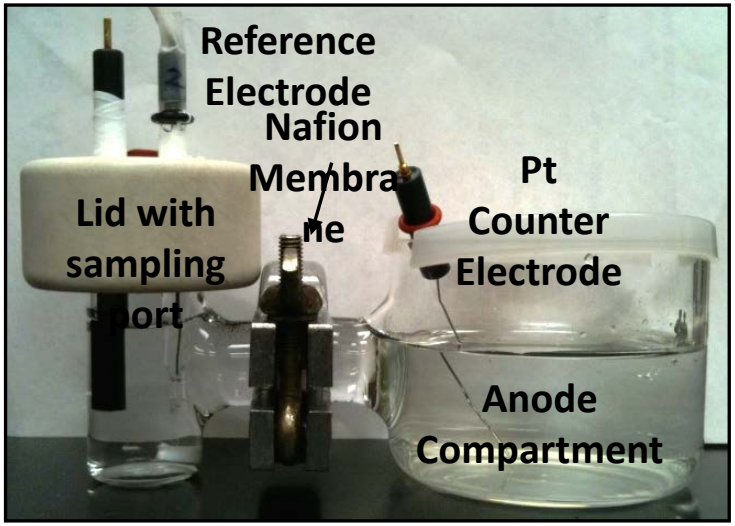
- **OH^-, H^+ and M^{n+} are *UBIQUITOUS* in electrochemical and photochemical reactions**
- **Potential Applications:**
  - **PEM Fuel Cells**
  - **Energy Storage & Battery Chemistry**
  - **General Catalysis**



Reaction	Potential, V
$2H^+ + 2e \rightleftarrows H_2$	0.0000
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828
$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	1.763
$2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$	0.9110
$Hg_2^{2+} + 2e \rightleftarrows 2Hg$	0.7960
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$ (sat'd. KCl)	0.2415
$HgO + H_2O + 2e \rightleftarrows Hg + 2OH^-$	0.0977
$Hg_2SO_4 + 2e \rightleftarrows 2Hg + SO_4^{2-}$	0.613
$I_2 + 2e \rightleftarrows 2I^-$	0.5355
$I_3^- + 2e \rightleftarrows 3I^-$	0.536
$K^+ + e \rightleftarrows K$	−2.925
$Li^+ + e \rightleftarrows Li$	−3.045
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.356
$Mn^{2+} + 2e \rightleftarrows Mn$	−1.18
$Mn^{3+} + e \rightleftarrows Mn^{2+}$	1.5
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$	1.23
$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	1.51
$Na^+ + e \rightleftarrows Na$	−2.714
$Ni^{2+} + 2e \rightleftarrows Ni$	−0.257
$Ni(OH)_2 + 2e \rightleftarrows Ni + 2OH^-$	−0.72
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.695
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$O_3 + 2H^+ + 2e \rightleftarrows O_2 + H_2O$	2.075
$Pb^{2+} + 2e \rightleftarrows Pb$	−0.1251
$Pb^{2+} + 2e \rightleftarrows Pb(Hg)$	−0.1205
$PbO_2 + 4H^+ + 2e \rightleftarrows Pb^{2+} + 2H_2O$	1.468
$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightleftarrows PbSO_4 + 2H_2O$	1.698
$PbSO_4 + 2e \rightleftarrows Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e \rightleftarrows Pd$	0.915
$Pt^{2+} + 2e \rightleftarrows Pt$	1.188
$PtCl_4^{2-} + 2e \rightleftarrows Pt + 4Cl^-$	0.758
$PtCl_6^{2-} + 2e \rightleftarrows PtCl_4^{2-} + 2Cl^-$	0.726
$Ru(NH_3)_6^{3+} + e \rightleftarrows Ru(NH_3)_6^{2+}$	0.10
$S + 2e \rightleftarrows S^{2-}$	−0.447
$Sn^{2+} + 2e \rightleftarrows Sn$	−0.1375
$Sn^{4+} + 2e \rightleftarrows Sn^{2+}$	0.15
$Tl^+ + e \rightleftarrows Tl$	−0.3363

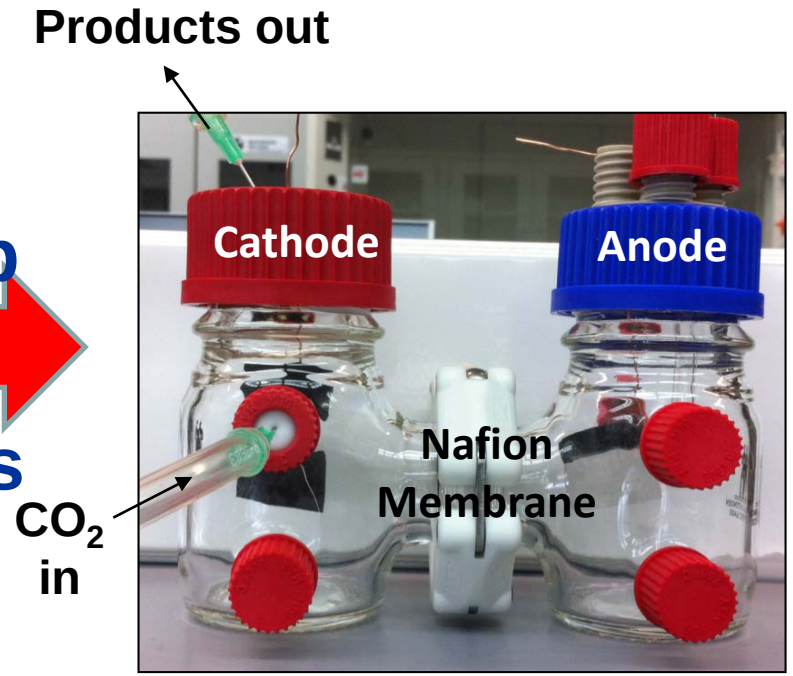
Bigger is Better!

- Catalyst, Reactor, & Electrode Scaled by Over 100 X in 3 months
- CO yields of ~15,000 L g^{-1} h^{-1}



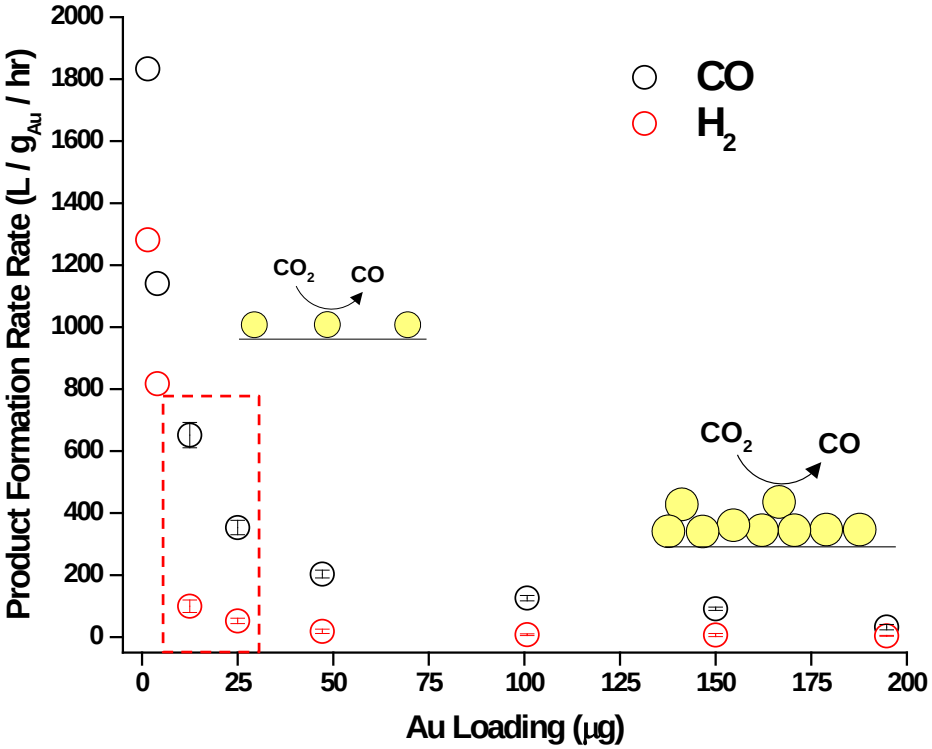
100 Fold Scale Up

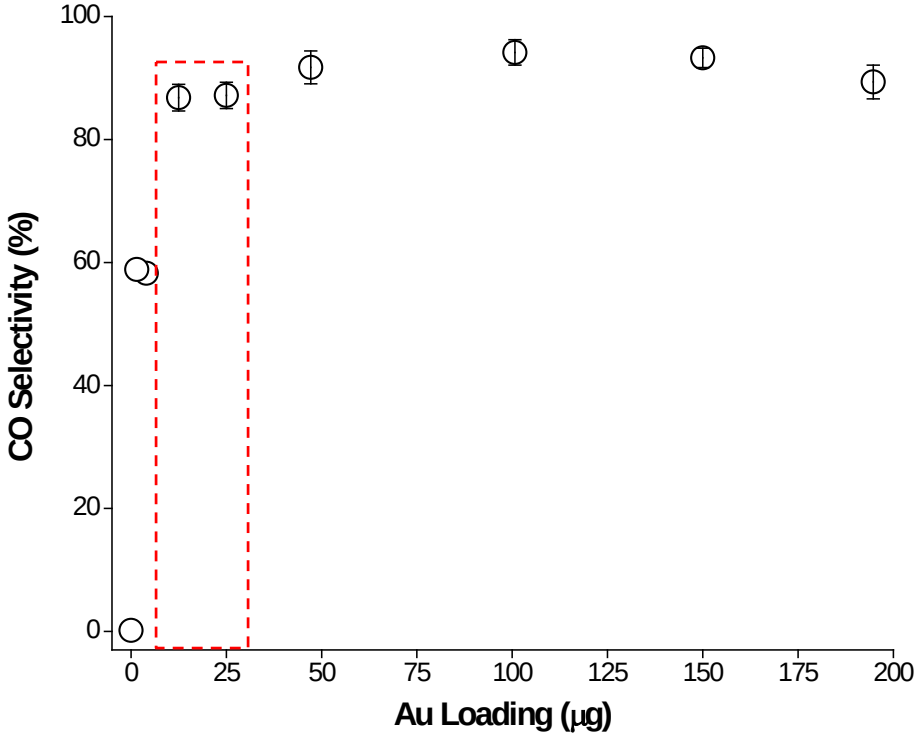
3 months



Electrode Optimization

- Lower reaction rates at high catalyst loading ... Eliminate “catalyst crowding”
- H_2 evolution from catalyst support at extremely low catalyst loading

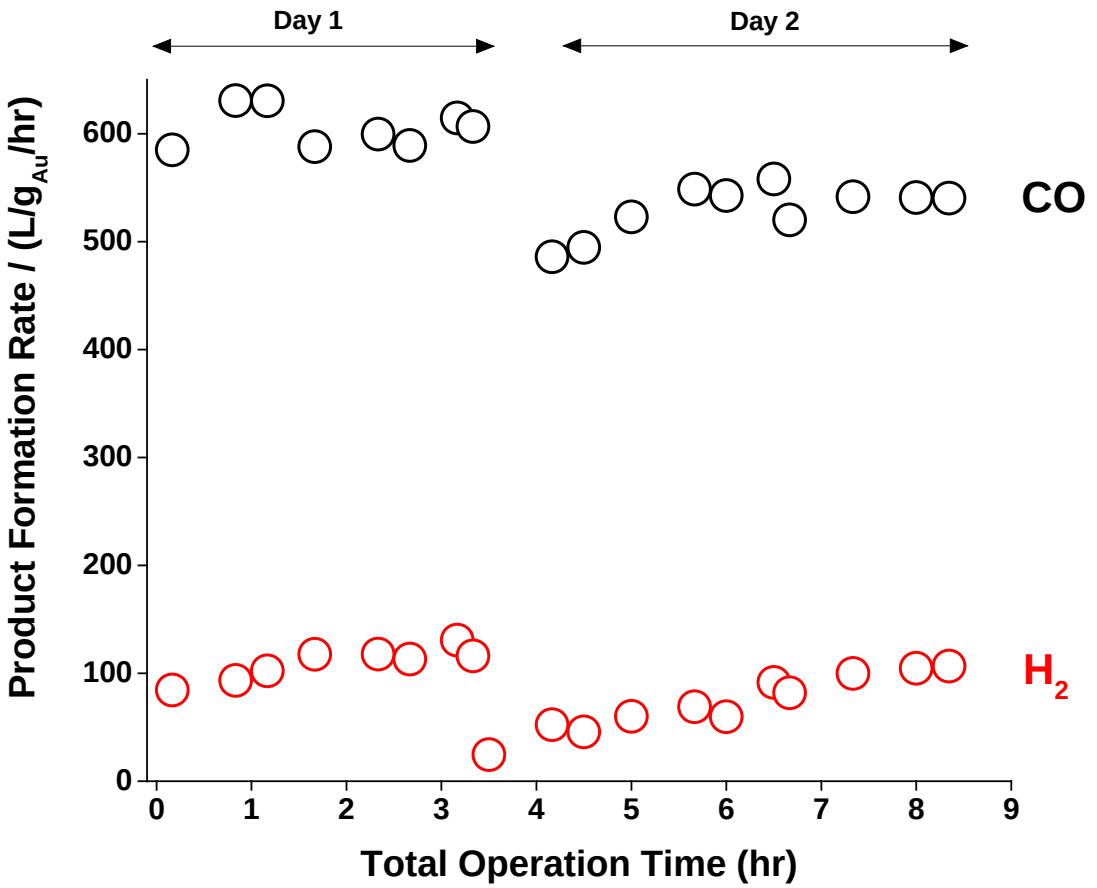




★ Must optimize catalyst loading for high product formation rates and good selectivity

Initial Long-Term Testing

Connected to potentiostat and tested over two days at -1V

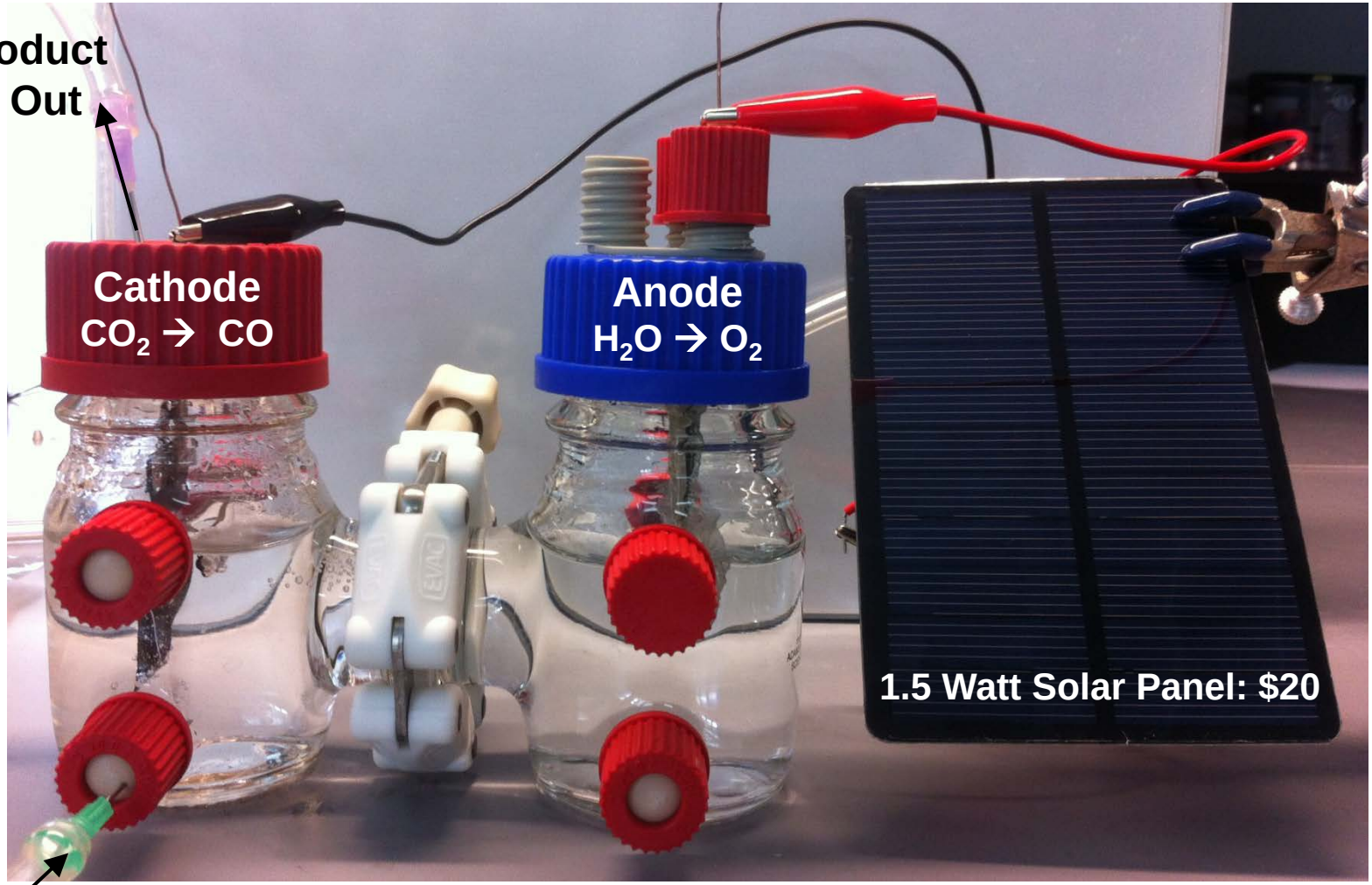


563 ± 44 L CO/g$_{Au}$/hr with 89 ± 3% selectivity

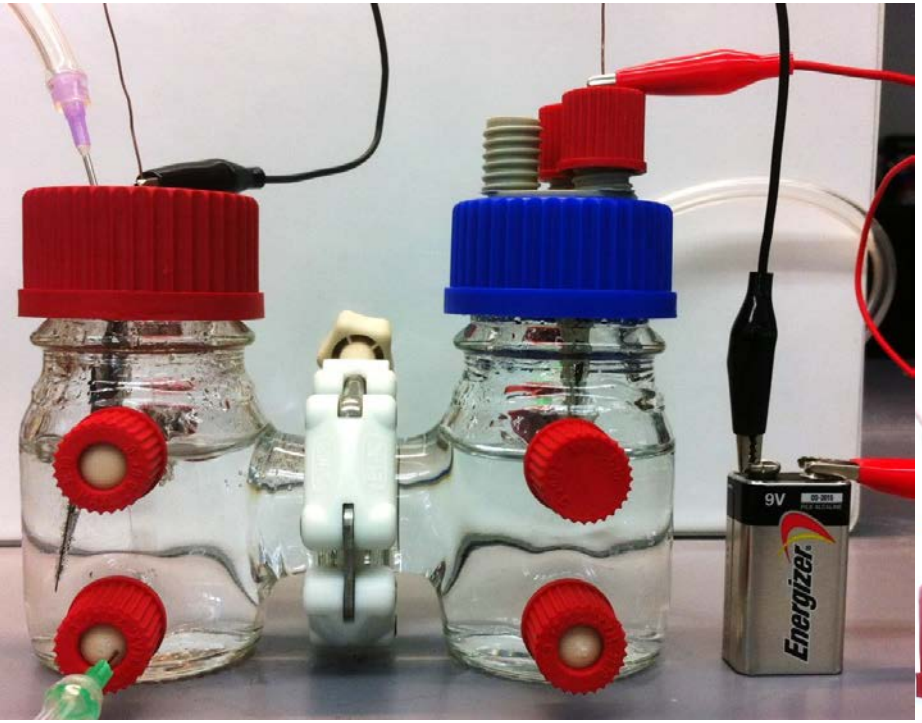
★ **1.1 kg CO_2 converted per gram catalyst per hour** ★

Carbon Negative CO_2 mitigation technology

Cheap Consumer/Hobby Grade Solar Panel Runs Au_{25} E-chem Reactor

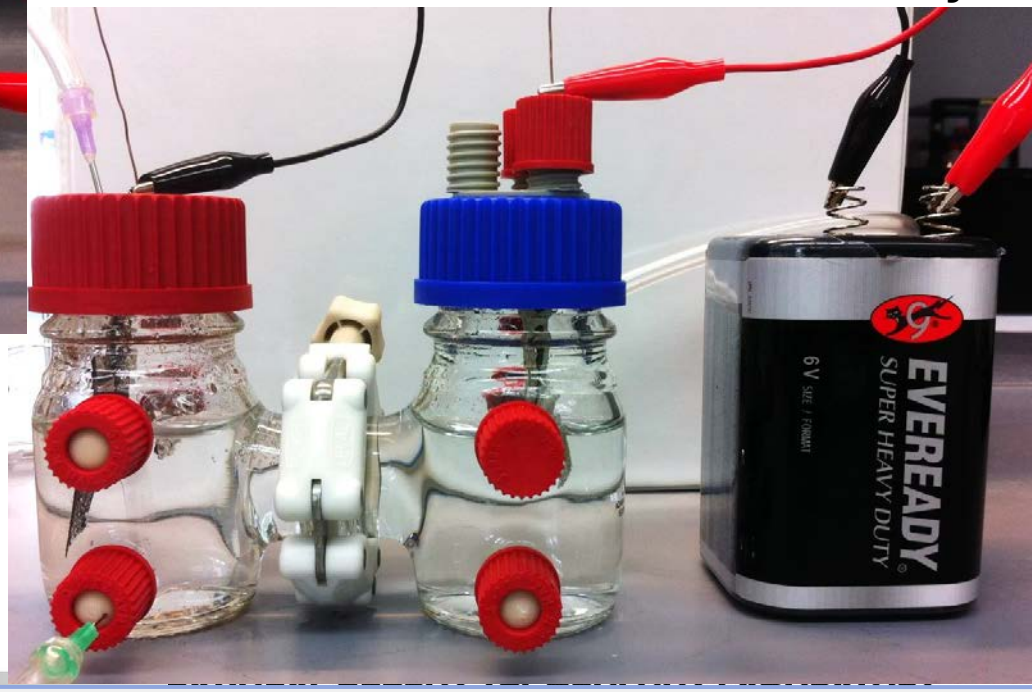


(Solar) rechargeable batteries can also power reactor during night time hours or cloudy days



9 V battery

6 V battery



Summary

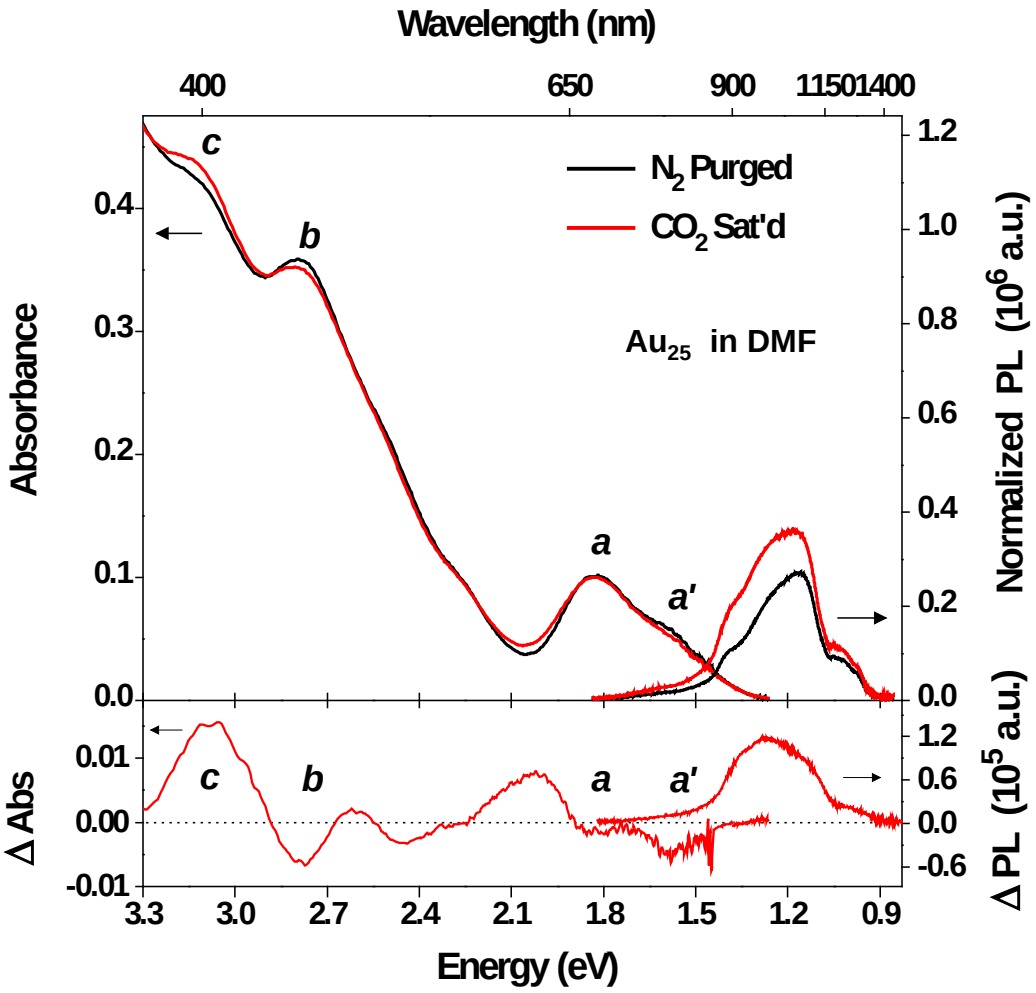
- Au_{25} is one of the most efficient CO_2 catalysts ever reported
- Charged clusters (Au_{25}^-, Au_{25}^0, Au_{25}^+) have been isolated & shown to enhance catalytic activity
- Scalable electrochemical reactor with Au_{25} has been developed
- Carbon negative E-chem reactor demonstrated to run off cheap consumer/hobby grade solar panels & small solar-charged batteries

Appendix

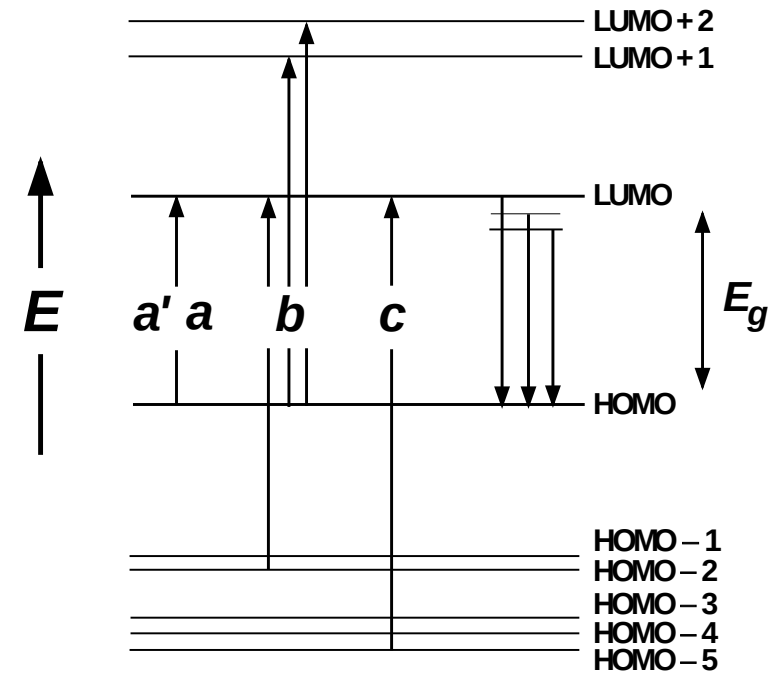
- **Publications**
  1. D. Kauffman, D. Alfonso, C. Matranga, P. Ohodnicki, X. Deng,ab R. Siva, C. Zeng and R. Jin, "Probing active site chemistry with differently charged Au_{25}^{q} nanoclusters (q = -1, 0, +1)", Chemical Science, Vol. 5, 3151-3157, (2014).
  2. J. Lekse, B. Haycock, J. Lewis, D. Kauffman, C. Matranga, "The effect of electronic structure changes in $NaInO_2$ and $NaIn_{0.9}Fe_{0.1}O_2$ on the photoreduction of methylene blue", Journal of Materials Chemistry A, Vol. 2, pgs 9331-9337 (2014).
  3. Haycock, B.J., Underwood, M.K., Lekse, J.W., Matranga, C., and Lewis, J.P., "High-Throughput Approach to Calculate Properties of CuGa1-xFexO_2 Delafossite Oxides," *Journal of Computational Physics*, Volume: 86 Pages:155-164, 2014.
  4. (Invited Paper): Natesakhawat, S., Ohodnicki, P.R., Howard, B.H., Lekse, J.W., Baltrus, J.P., and Matranga, C., "Adsorption and Deactivation Characteristics of Cu/ZnO-Based Catalysts for Methanol Synthesis from Carbon Dioxide," Topics in Catalysis, 2013, 56, 1752–1763, online DOI: 10.1007/s11244-013-0111-5.
  5. Sorescu, D.C., Civiš, S., and Jordan, K.D., "Mechanism of Oxygen Exchange Between CO_2 and TiO_2(101) Anatase," *The Journal of Physical Chemistry C*, Volume: 118 Issue: 3 Pages: 1628-1639 DOI: 10.1021/jp410420e.
  6. Tafen, D.N., Long, R., and Prezhdo, O., "Dimensionality of Nanoscale TiO_2 Determines the Mechanism of Photoinduced Electron Injection from a CdSe Nanoparticle," *Nano Letters*, Volume: 14 Issue: 4 Pages: 1790-1796.
- **Patents**
  1. "Method of Conducting a Thermally Driven Reaction Using Plasmonic Heating" C. Matranga, C. Wang, P. Ohodnicki, Non-provisional patent filing S-134,097, April 2014.
  2. "Controlling Au_{25} Charge State for Improved Catalytic Activity" D. Kauffman, C. Matranga, D. Alfonso, P. Ohodnicki, R. Jin, X. Deng, R. Siva, C. Zeng, Nonprovisional patent filing, (with DOE Chicago Field Office for Fiing)
  3. "Efficient Electrocatalytic Conversion of CO2 into CO using Ligand-Protected Au25". D. Kauffman, C. Matranga, D. Alfonso, P. Ohodnicki, R. Jin U.S. Non-Provisional Patent Application Number S-131,026, Oct 2013.
- **Presentations**
  1. "Gold-based Nanomaterials for Catalytic CO_2 Conversion Applications", Christopher Matranga, University of Pittsburgh and PPG Innovations in Materials Chemistry Symposium, Pittsburgh, May 2014.
  2. "Nanocatalyst Systems for Fossil Energy Applications", Christopher Matranga, Council for Chemical Research Symposium on The Role of Nanotechnology in a Sustainable Future, Pittsburgh, October 2013.
  3. Kauffman, D.R., Alfonso, D., Matranga, C., Deng, X., Ohodnicki, P., Siva, R.C., and Jin, R., "Using Charged Au_{25}q Nanoclusters (q = -1, 0, +1) to Probe the Active Site Chemistry of Supported Gold Catalysts," abstract accepted for presentation at the 225th Meeting of the Electrochemical Society (ECS), Orlando, FL, May 11–15, 2014.
  4. Kauffman, D.R., Alfonso, D., Matranga, C., Ohodnicki, P., Siva, R.C., and Jin, R., "Atomically Precise Au_{25} Nanoclusters for Efficient Electrochemical CO_2 Conversion," abstract accepted for presentation at the 225th Meeting of the Electrochemical Society (ECS), Orlando, FL, May 11–15, 2014.

Reversible Optical Bleaching in Presence of CO_2

Experimental



Electronic Structure



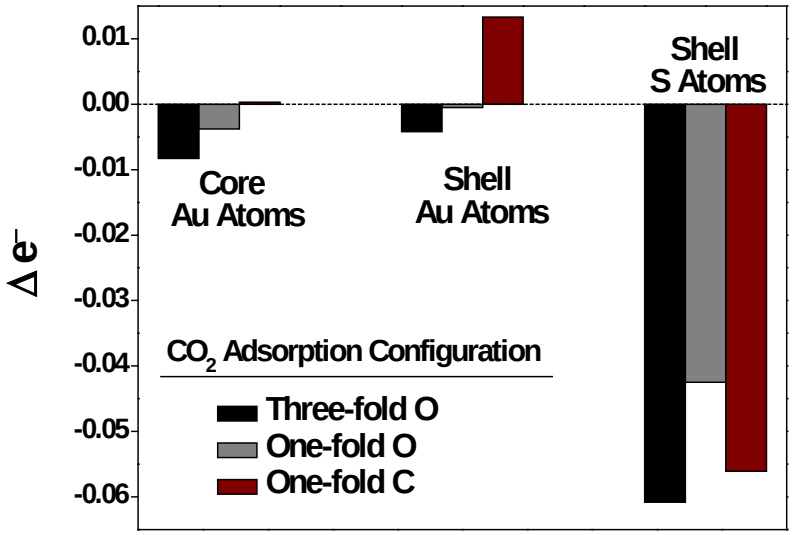
***Reversible* bleaching due to charge redistribution**

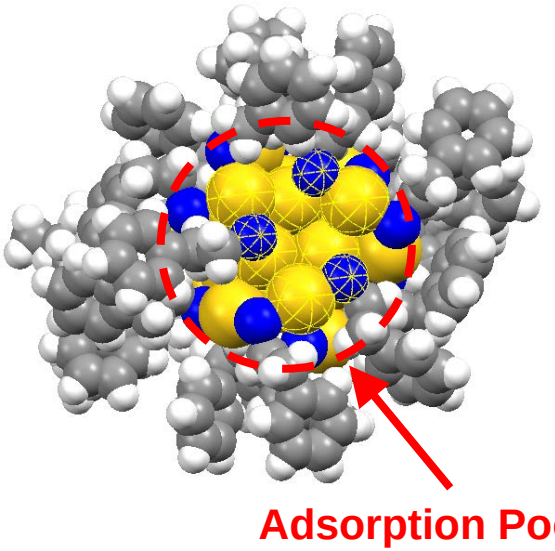
Energy level diagram from Schatz & Jin et. al. JACS 2008, 130 (18), pp 5883–5885

Kauffman, et, al. J. Am. Chem. Soc. 2012, *134*, 10237−10243.

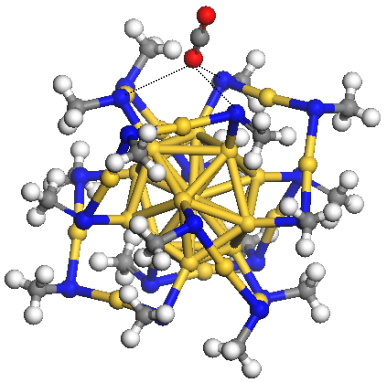
CO_2 Physisorption Reversibly Perturbs Electronic Structure

Optical Bleaching Results from Reversible Charge ***Redistribution***

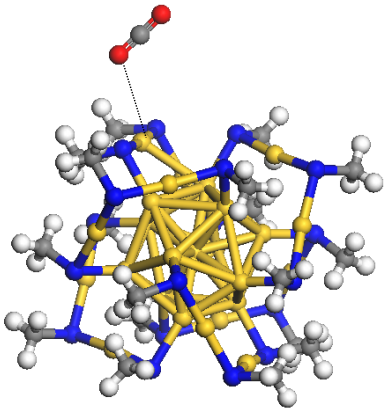




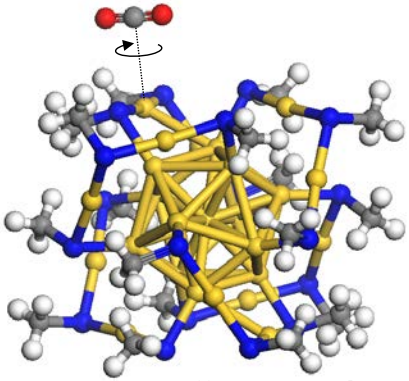
Three-fold O Coordination



One-fold O Coordination



One-fold C Coordination

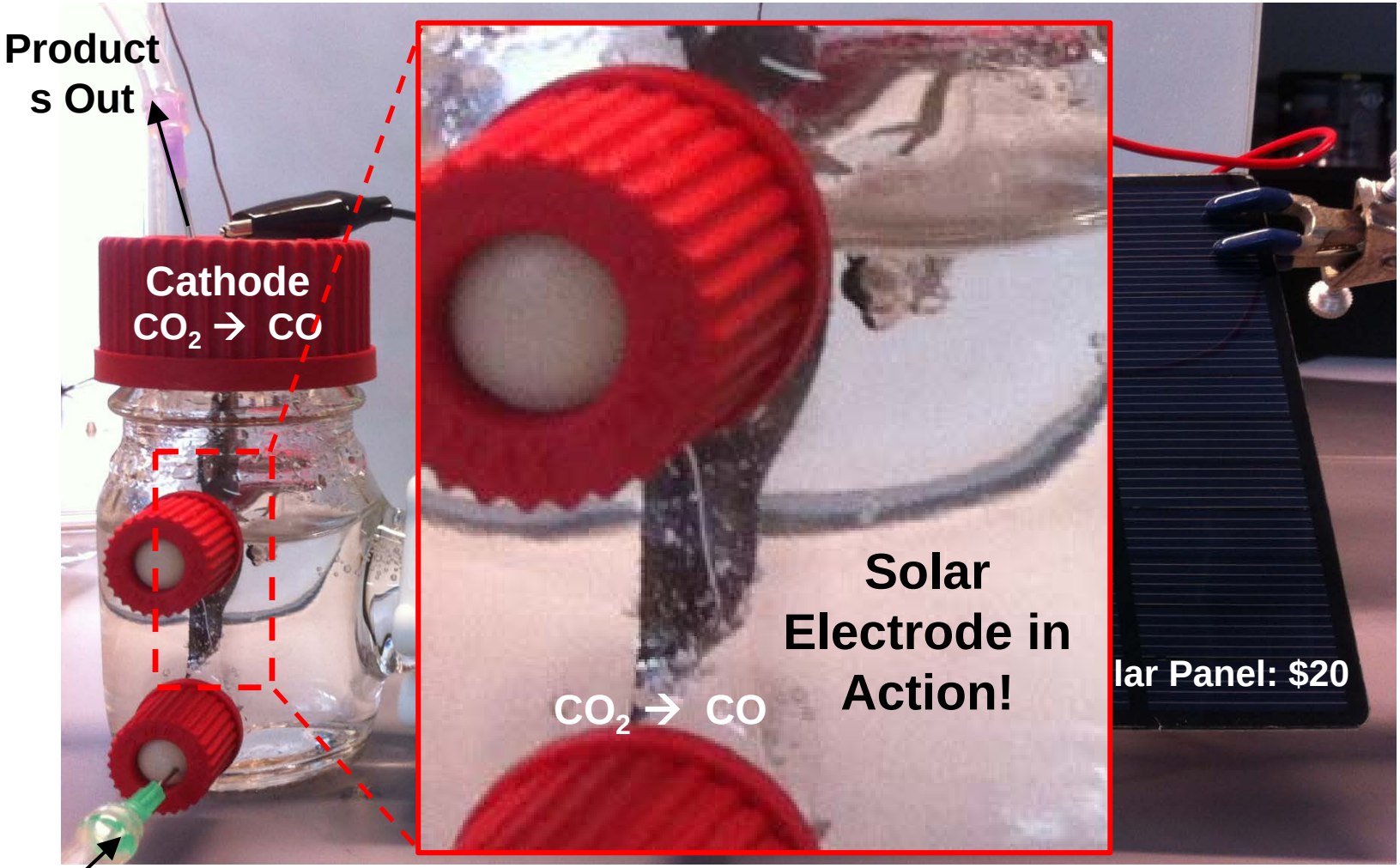


Binding Energies

~ 80 – 140 meV

Kauffman, et, al. J. Am. Chem. Soc. 2008, *130*, 5883-5885.

Carbon Negative CO_2 mitigation technology



(Solar) rechargeable batteries can also power reactor during night time hours or cloudy days

9 V battery

6 V battery