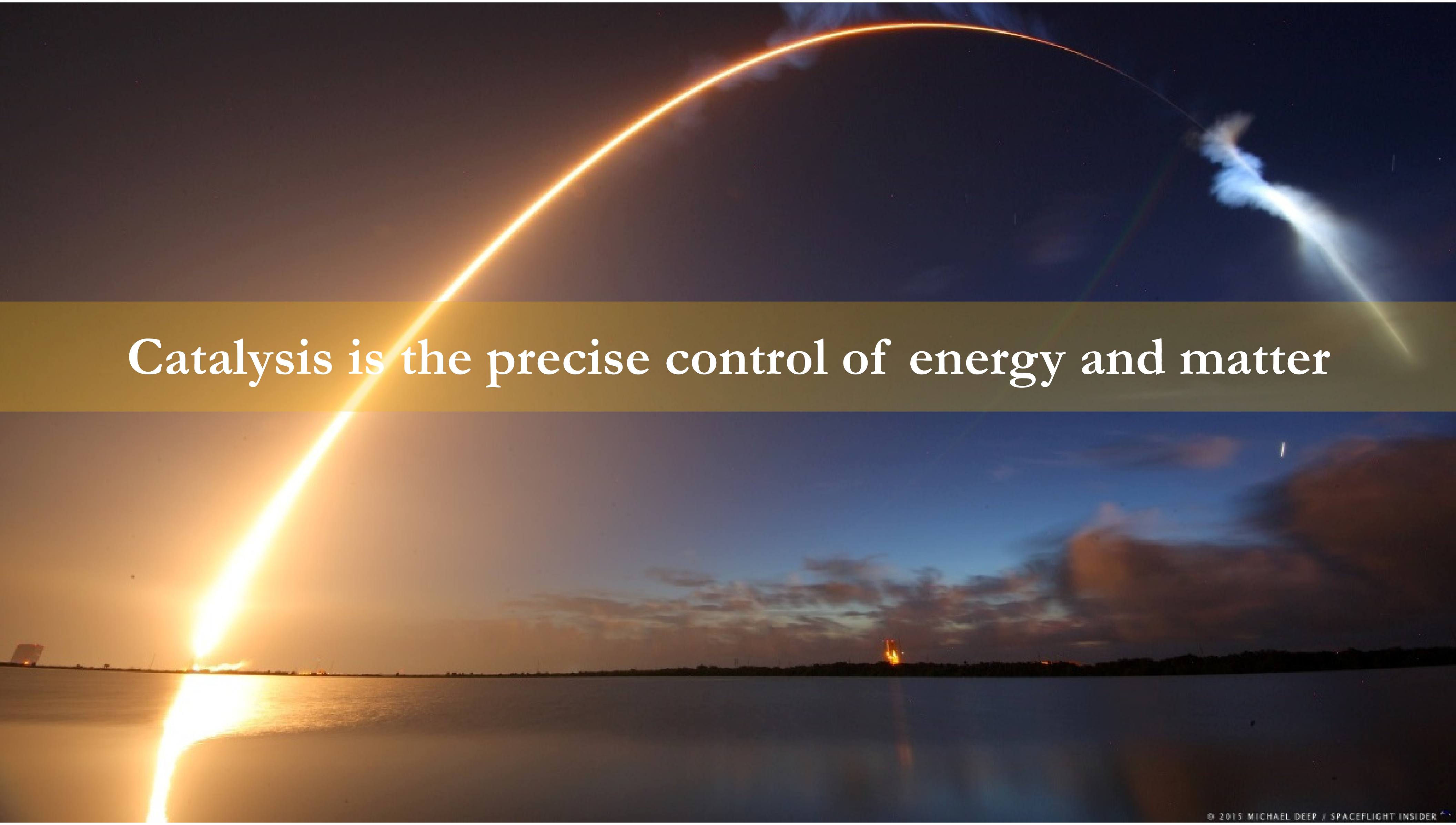
Advances in Nanoscale Control of Catalysts

NATIONAL ENERGY TECHNOLOGY LABORATORY

Douglas R. Kauffman

Sept. 6th, 2018

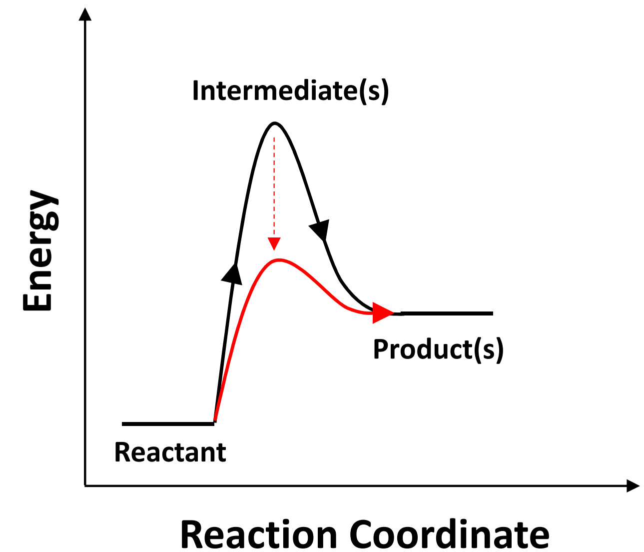

Catalysis is the precise control of energy and matter
© 2015 MICHAEL DEEP / SPACEFLIGHT INSIDER

Catalysis enables the modern world

What is a catalyst?

- Material that increases reaction rates, lowers activation barriers, improves selectivity, reduces cost

- **A *few* examples**
  - Nitrogen → ammonia (fertilizers & food)
  - Plastics and polymer production
  - Chemicals & fuels
  - Flavors and fragrances



Problems for catalysis

Processes with large carbon and energy foot-prints

Fossil fuel-derived electricity

CO_2

Fossil-fuel derived hydrogen

$CH_4 \rightarrow 2H_2 + CO_2$

Coal/hydrocarbons $\rightarrow nH_2 + CO_2$

~10 tonnes CO_2 per tonne H_2

Ammonia

Extremely large energy requirements

Consumes ~50% of all H_2

Carbon footprint (420 Mt CO_2)

Creating new processes with catalysts

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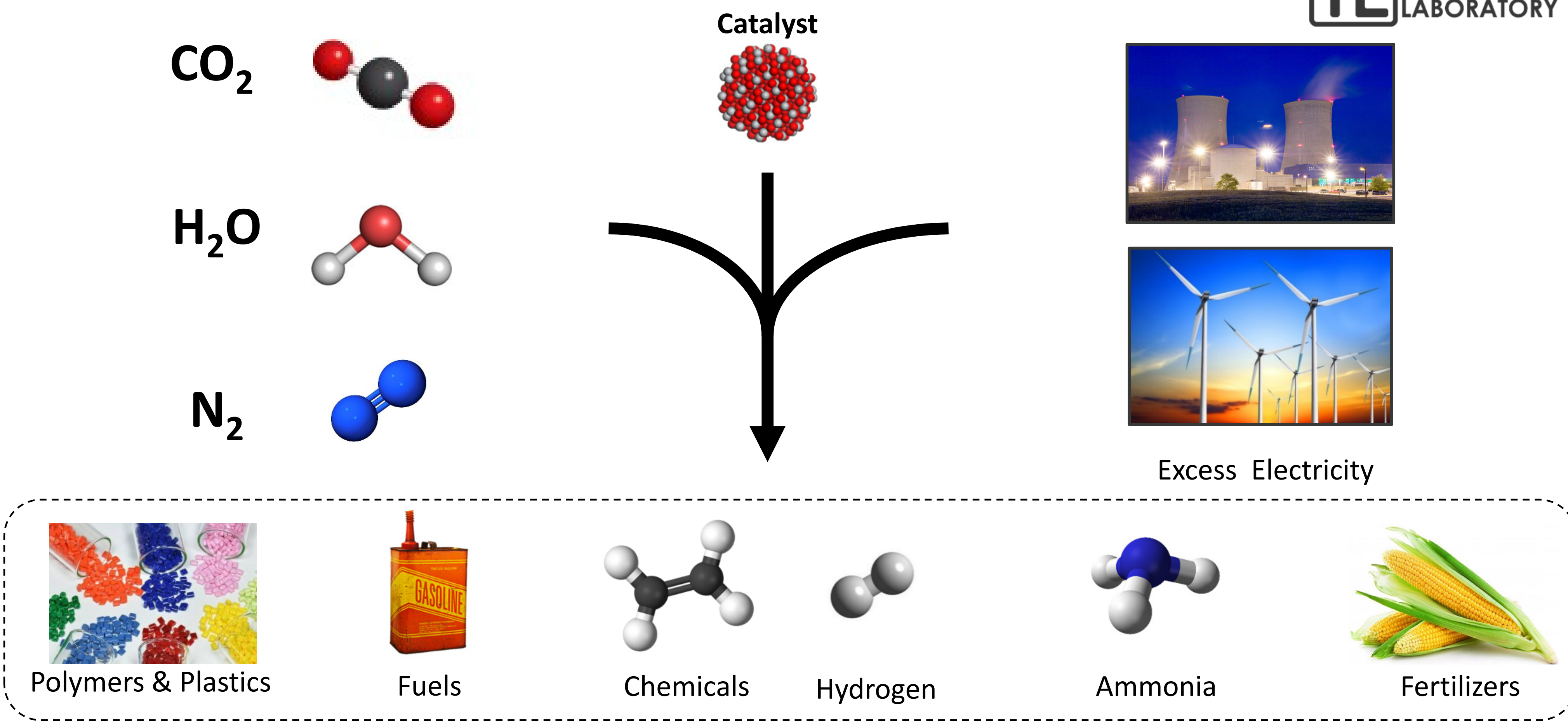
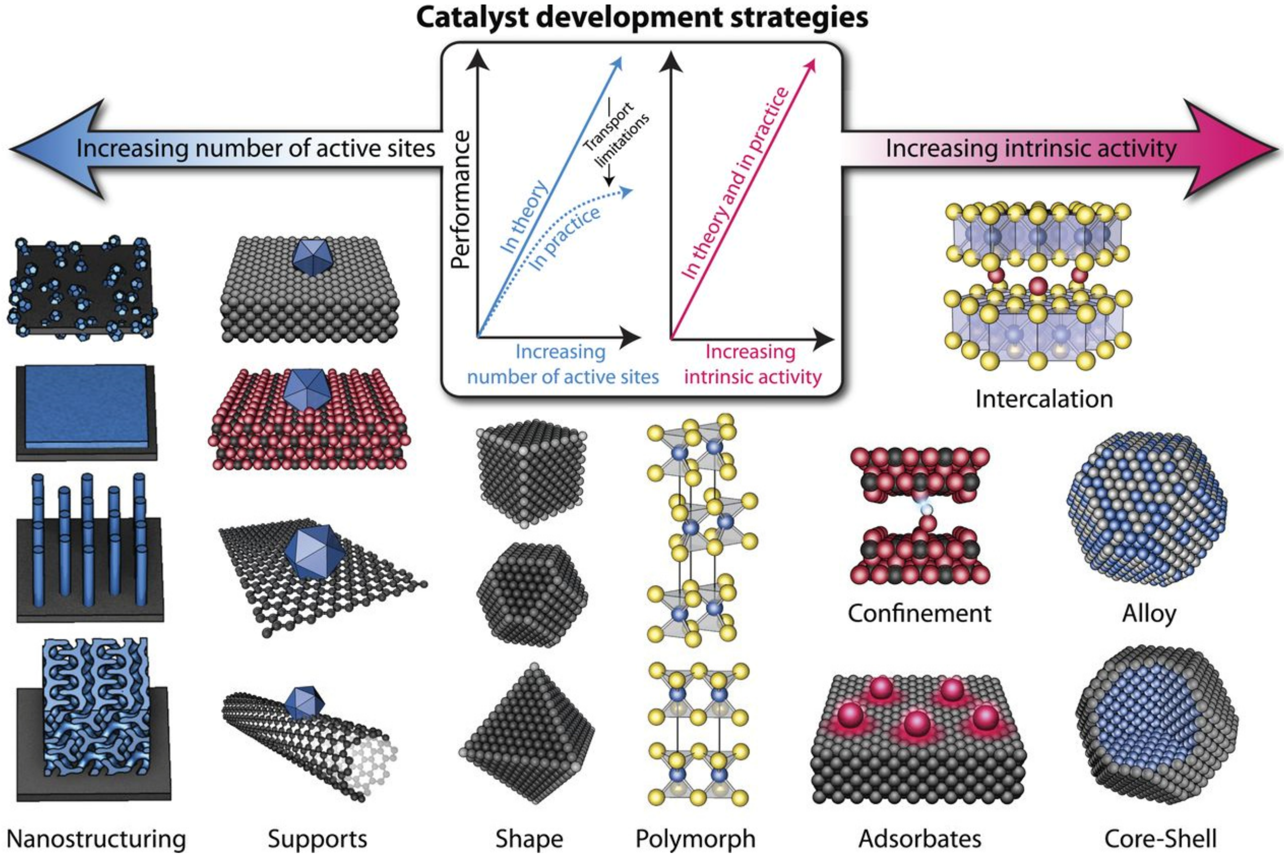


Design flexibility



Science **2017**, *355*, article eaad4998

Why nanomaterials?

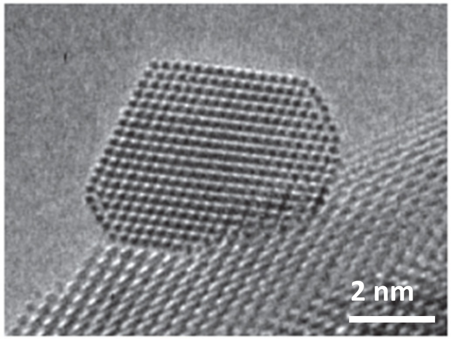
Ordinary materials can develop extraordinary properties in the nanoscale regime

Bulk gold: Inert, shiny, and valuable

Nano-scale size control

Gold Nanoparticles in Solution

nanocomposix.com



Gold Nanoparticle on CeO_2 Support

Adapted from *Science* 2012, 335, 317.

"Accidental" ancient nanotechnology

Nanoparticles have been around for a while…

The **Lycurgus Cup:** 4th-century Roman glassware containing gold and silver nanoparticles

https://www.britishcouncil.org/voices-magazine/nanotechnology-tiny-tech-massive-impact

"Medieval artisans discovered through alchemical experimentation that adding *gold chloride** to molten glass resulted in a red tint, and adding silver nitrate turned the glass yellow." -- https://www.sciencehistory.org/distillations/magazine/from-nanotech-to-nanoscience

***Gold chloride is still the most common route for nanoparticles**

Investigating ancient scientific curiosities

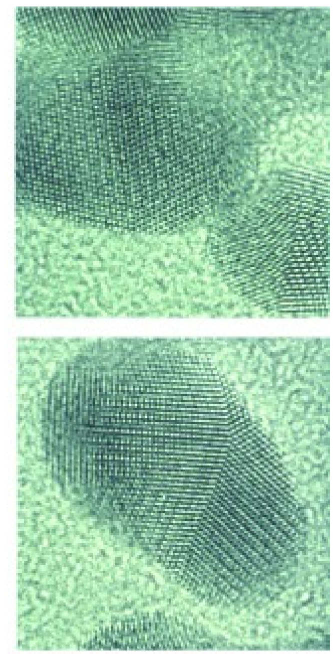
- **Michael Faraday systematically investigated gold chloride chemistry**

- **1857**: "… gold is reduced in exceedingly fine particles, which become diffused, produce a beautiful ruby fluid"

Philosophical Transactions of the Royal Society of London, **1857**, 147, 145-181

Faraday's "Beautiful Ruby Fluid"

Gold Bulletin, **2007**, 40, 267-269

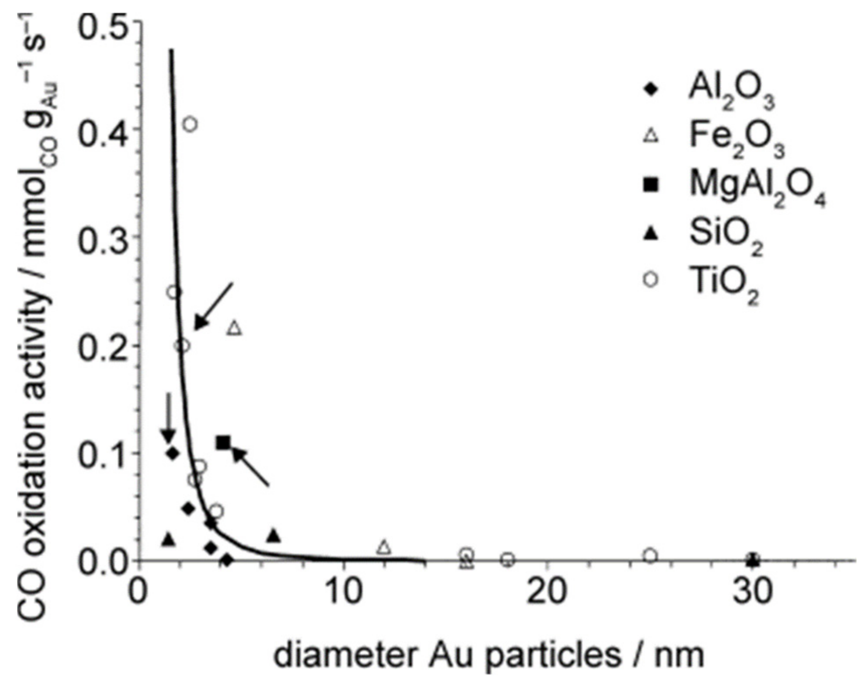


Colloidal gold - $10^7\times$

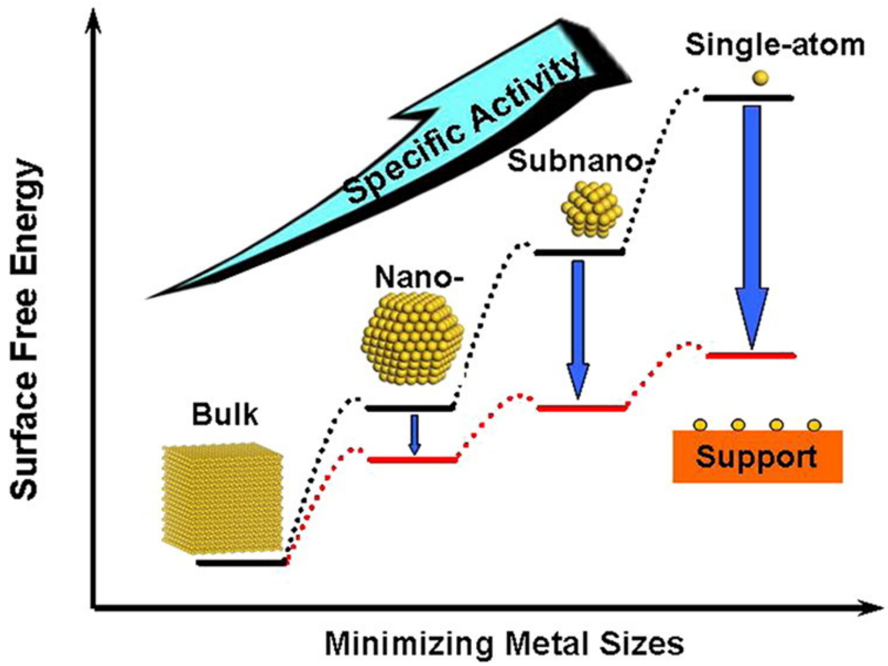
Angew. Chem. Int. Ed. **2007**, 46, 5480-5486

Reactivity

- **Gold particles had traditionally shown low reactivity.**
- **<u>1987</u>: Haruta first showed small supported gold nanoparticles were extremely reactive for CO oxidation[1]**
  - X-ray diffraction estimated ~5nm particles
  - Larger particles were not as reactive

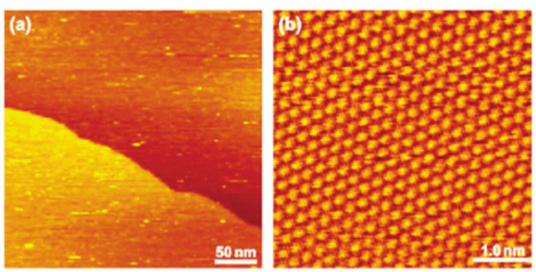


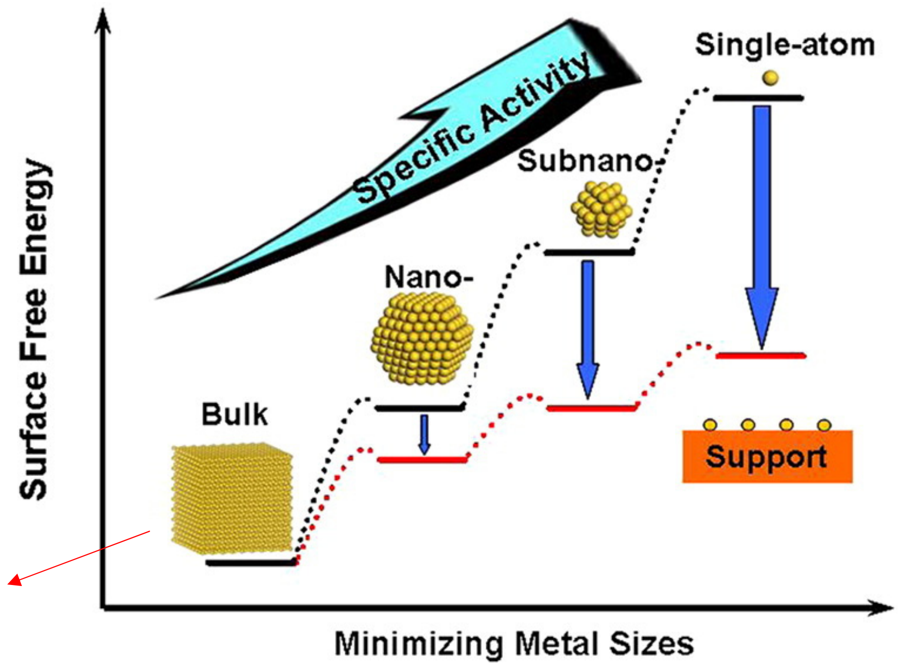
Size Dependent Reactivity



Acc. Chem. Res. **2013,** 46, 1740-1748

Size Dependent Reactivity





Au (111) surface is featureless and smooth

Phys. Chem. Chem. Phys. **2012**, *14*, 2286-2291

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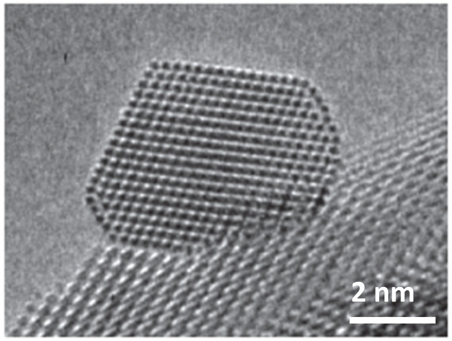

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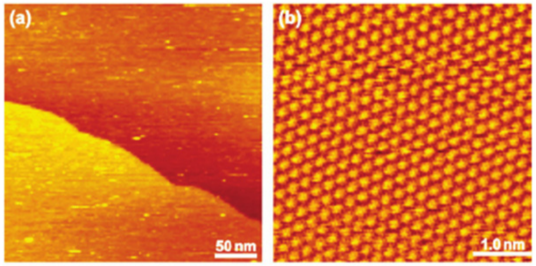
Science 2012, 335, 317.



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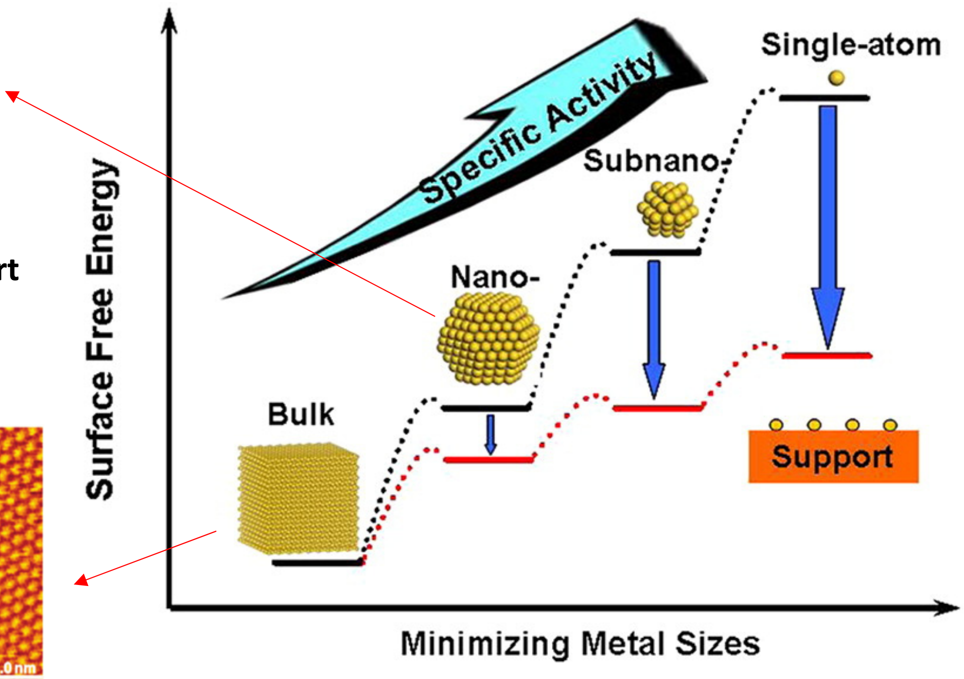

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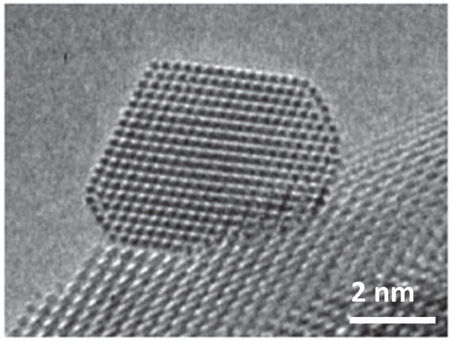

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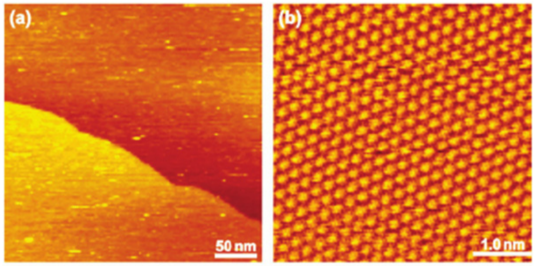

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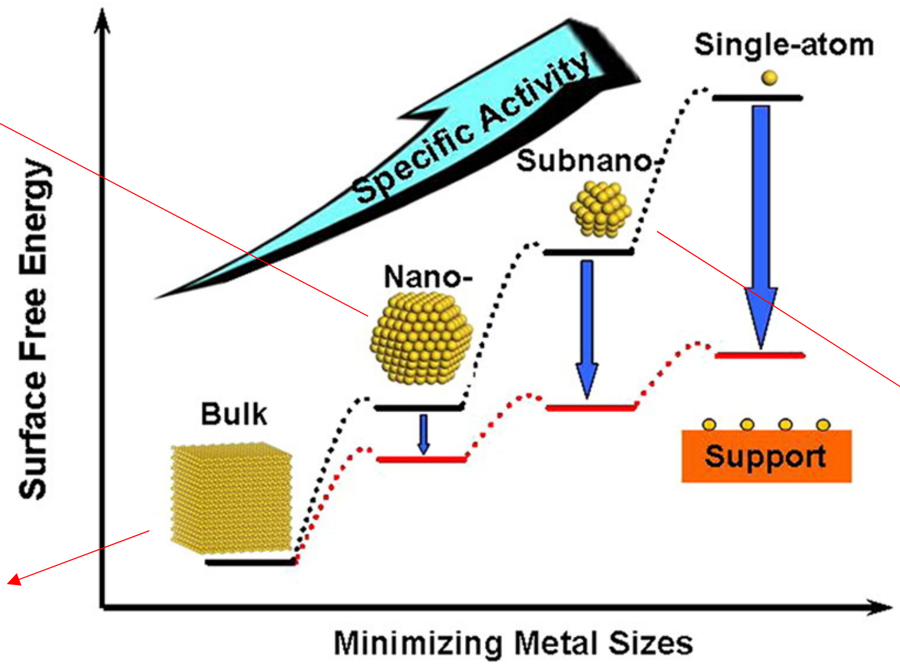

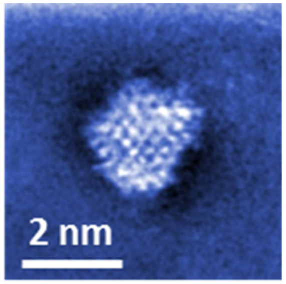

Sub-2nm Au and alloy nanoparticles

Kauffman *et al. J. Phys. Chem. C.* **2018**, *in press*

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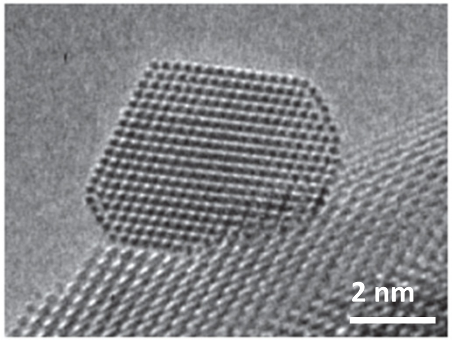

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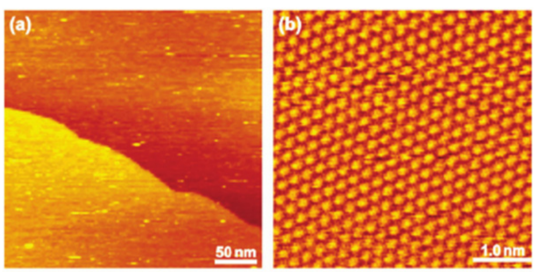

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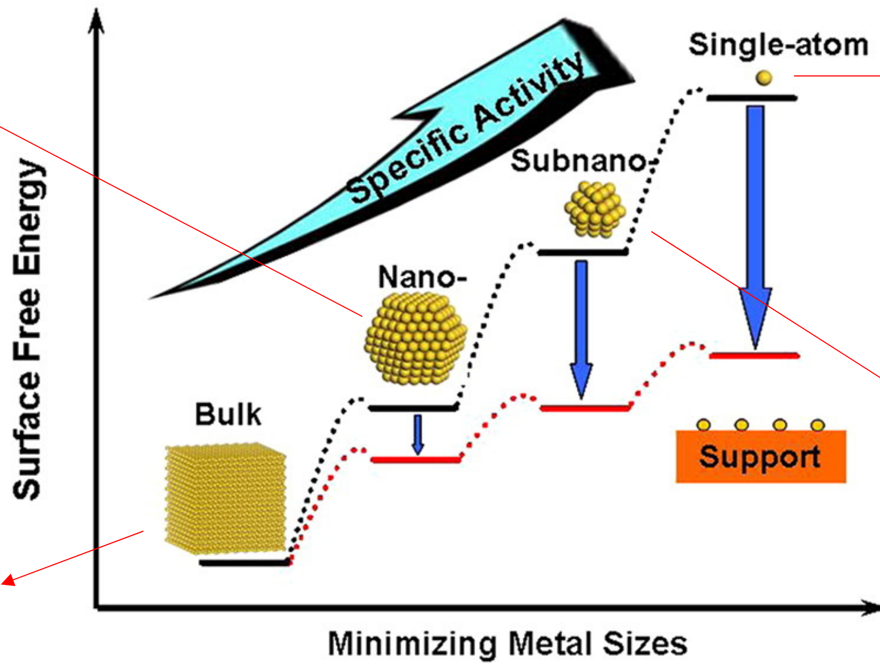
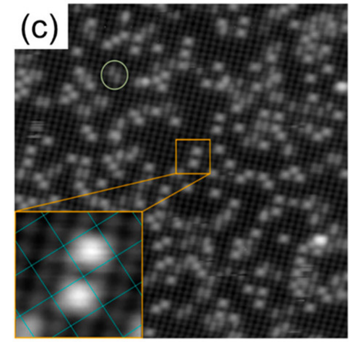
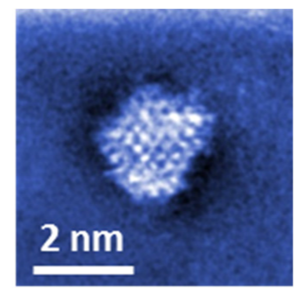




Single Au atom catalysts

Phys. Rev. Lett. **2012, 108, 216103.**



Sub-2nm Au and alloy nanoparticles

Kauffman *et al. J. Phys. Chem. C.* **2018**, *in press*

General outline

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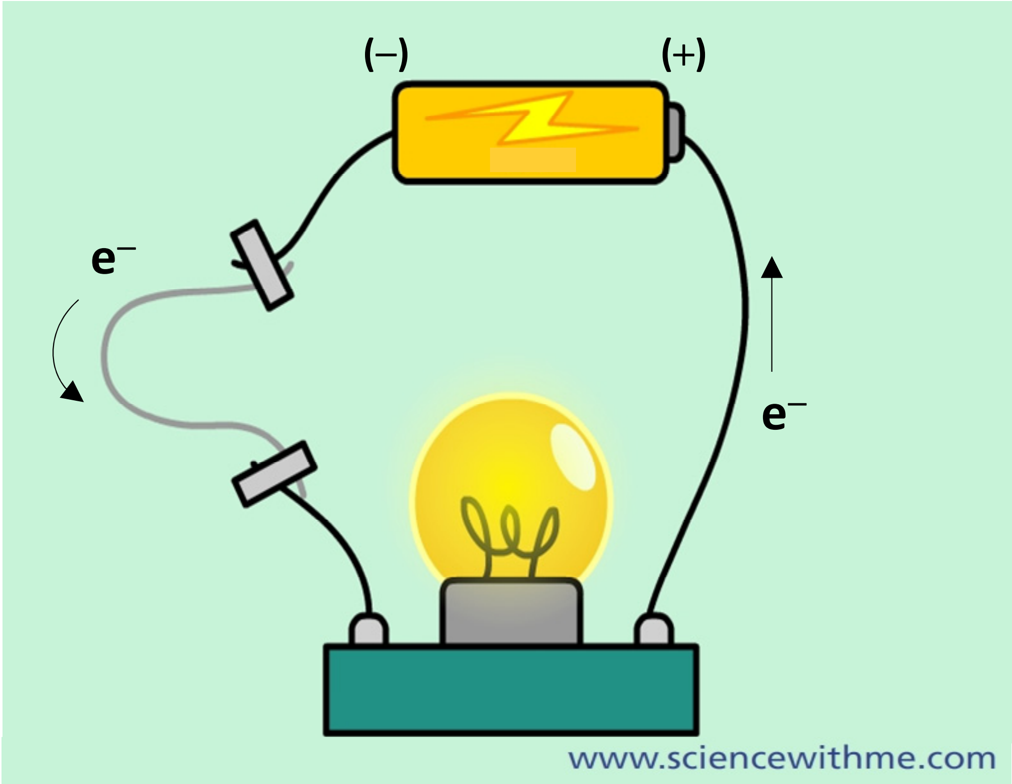
- **CO_2 nanocatalysis**
  - Gold and copper

- **Water splitting for carbon-free hydrogen and oxygen**
  - Moving away from precious metals

- **NH_3 synthesis: the next big thing?**
  - Emerging examples and challenges

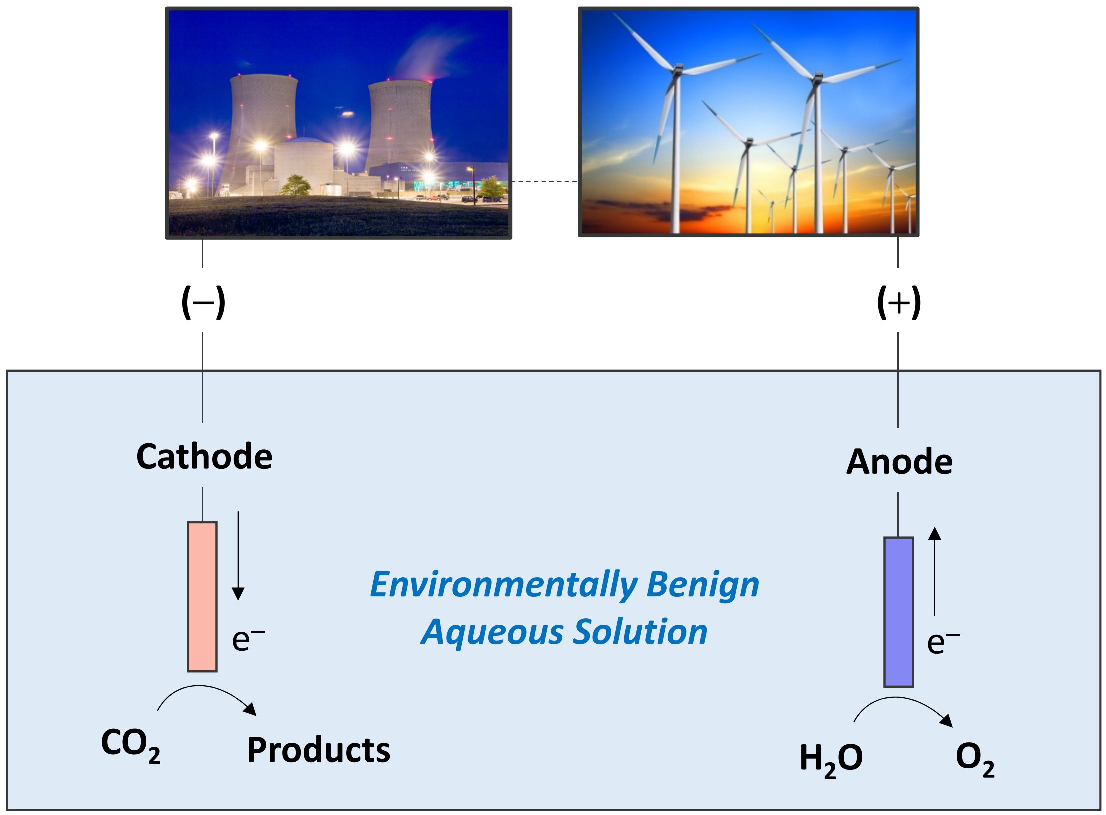
General approach: electrochemical CO_2 conversion

Electrochemistry moves electrons



General approach: electrochemical CO_2 conversion

Use excess electrons to convert CO_2



Exemplary products

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Approximate market price and global demand

Product	# e-	Market Price ($/kg)	Global Production/ demand (Mtonne)
Carbon Monoxide (synthesis gas)	2	0.06-0.60	150
Methane	8	0.18	250
Ethylene	12	0.5-1.5[a]	140
Methanol	6	0.58	110
Ethanol	12	1.00	77
Formic Acid	2	0.74	0.6

Ind. Eng. Chem. Res. **2018**, *57*, 2165−2177

a) https://www.icis.com/resources/news/2018/03/20/10204214/us-ethylene-spot-prices-fall-to-nine-year-low/

Exemplary products

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Approximate market price and global demand

	Product	# e-	Market Price ($/kg)	Global Production/ demand (Mtonne)
Crowd Favorites	* Carbon Monoxide (synthesis gas)	2	0.06-0.60	150
	Methane	8	0.18	250
	* Ethylene	12	0.5-1.5[a]	140
Big news!	* Methanol	6	0.58	110
	* Ethanol	12	1.00	77
	Formic Acid	2	0.74	0.6

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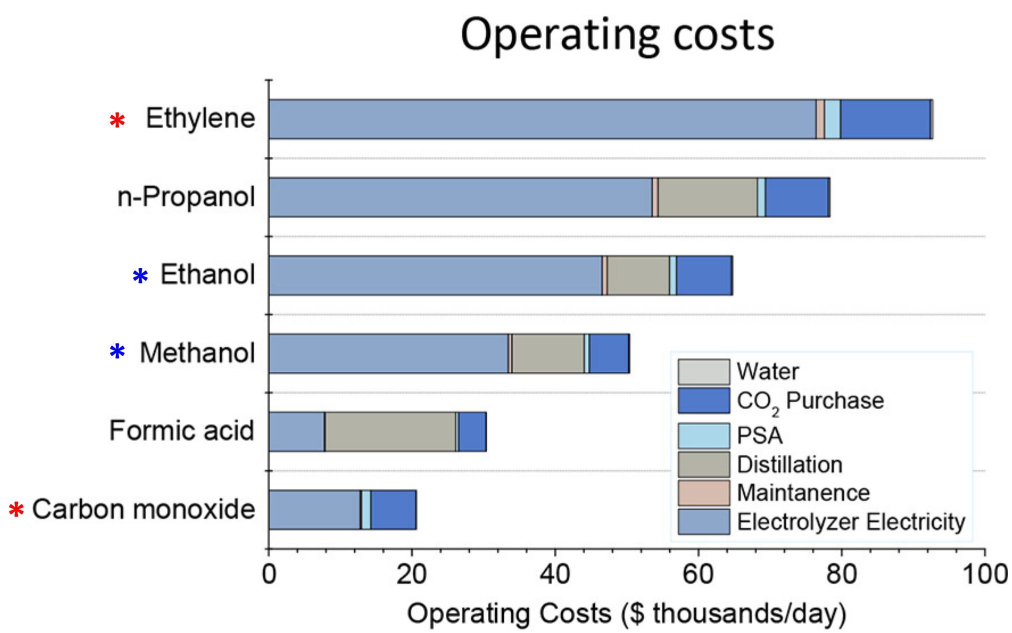
Exemplary products



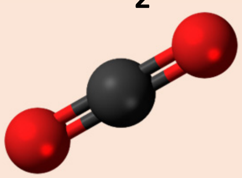
*under optimistic case assumptions.

Table 3. Process Assumptions for CO_2 Electrolyzer Model

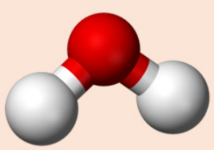
parameter	base case	optimistic case
production rate (ton/day)	100	100
lifetime (years)	20	20
operating time (days/year)	350	350
electricity price ($/kWh)	0.05	0.03
current density (mA/cm^2)	200	300
cell voltage (V)	2.3	2
product selectivity (%)	90	90
conversion (%)	50	50
CO_2 price ($/ton)	70	40
interest rate (%)	10	10
electrolyzer cost ($/m^2)	1840	920

“Coinage” Metal Catalysts

CO_2



Water



Gold

Synthesis gas
($CO + H_2$)

Industrial Chemicals

Fuels

Polymers and Plastics

Copper

$H_2 + CO$
formic acid
methane
C_2+ hydrocarbons
alcohols

Purified product

Rough timeline of CO_2 electrochemistry

- **Late 1980s through early 1990**
  - Most common metals were tested
  - Au and Ag were selective for CO and H_2 (synthesis gas)
  - Cu produced a variety of products, but not selective
  - No metals were very active (bulk)

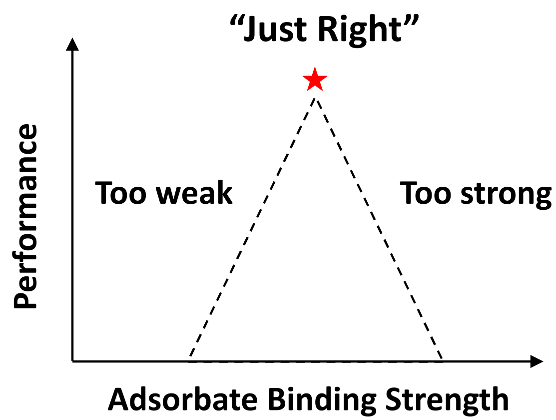
- **For ~20 years CO_2 electrochemistry was "niche" topic in specialized journals**

- **2008-present: NETL and the rest of the world started thinking about CO_2 nanocatalysis**
  - I started at NETL in 2010 as a post-doc with the idea of using nanoparticles for CO_2 electrochemistry

Can we control structure and function?

★ **Molecular Binding Impacts: energy input, reaction rates, efficiency, selectivity and stability** ★

Sabatier Principle

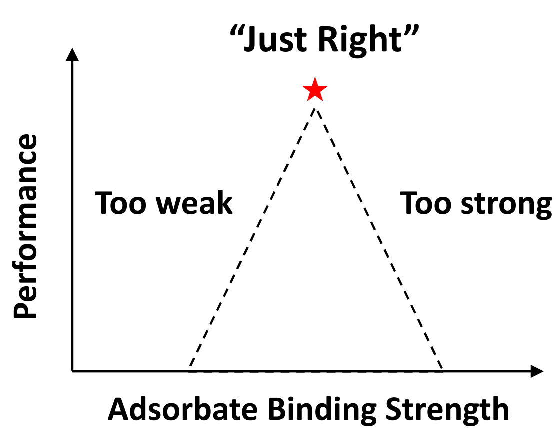


Typical materials contain a mixture of shapes, sizes and "colors". Hard to identify which "piece" is doing what.

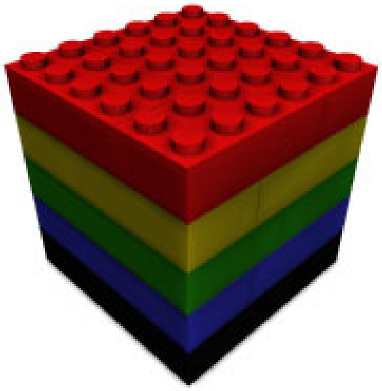
Can we control structure and function?

★ **Molecular Binding Impacts: energy input, reaction rates, efficiency, selectivity and stability** ★

Sabatier Principle

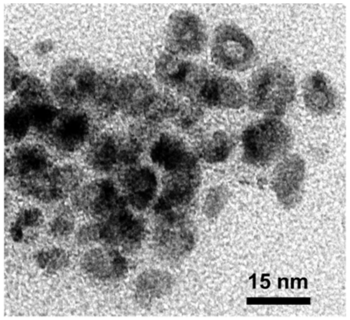


Can we build well-defined nanocatalysts to understand and eventually *control* chemistry?

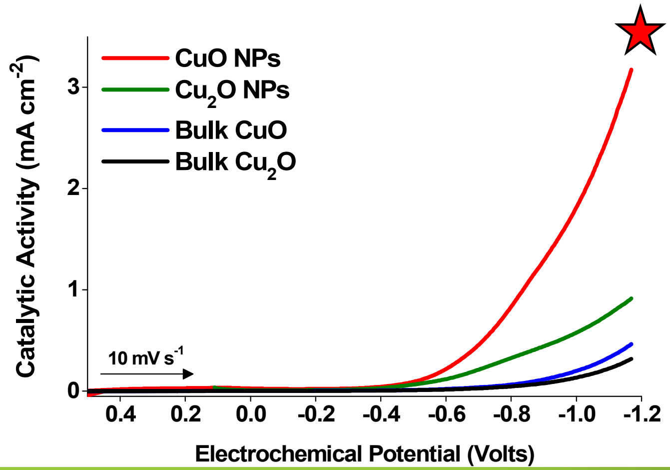


Controlling function through structure

- **Copper oxide nanocatalysts with organic surface groups**
  - Controlled size and retained surface oxides
- **Improved activity and selectivity – more "gold-like" than copper!**
- **Surface groups sustained oxides and directed CO_2 to CO conversion**



~10 nm CuO NPs



Kauffman *et al.* *J. Phys. Chem. Lett.* **2011**, *2*, 2038–2043

Atomic-level control of gold nanocatalysts

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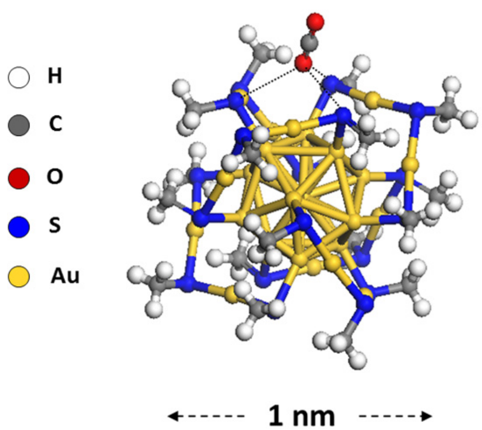
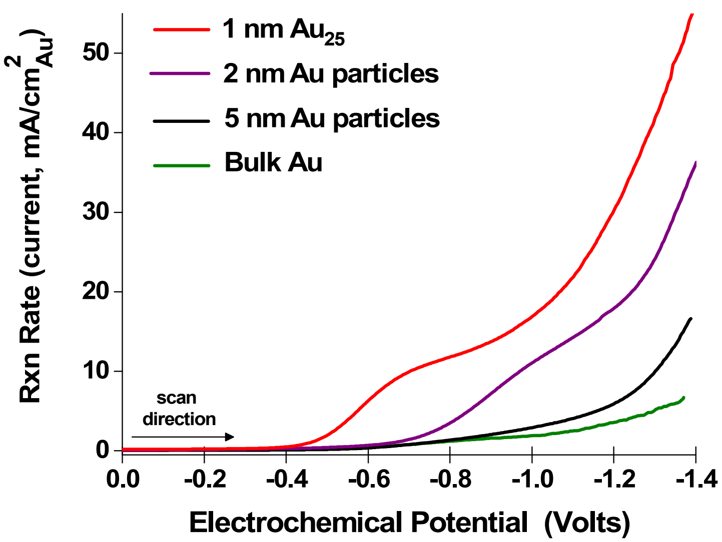
Surface organothiol groups create precise atomic structure and influence chemistry

$Au_{25}(SR)_{18}$ Nanocluster



Extremely active for $CO_2 \rightarrow CO$



J. Am. Chem. Soc. 2012; J. Phys. Chem. Lett. 2013; Chemical Science 2014; ACS Applied Materials and Interfaces 2015; J. Chem. Phys. 2016; ACS Catalysis 2016; MRS Commun. 2017, J. Phys. Chem. C. 2018, US Patent 9,139,920.

Atomically engineered nano-alloys

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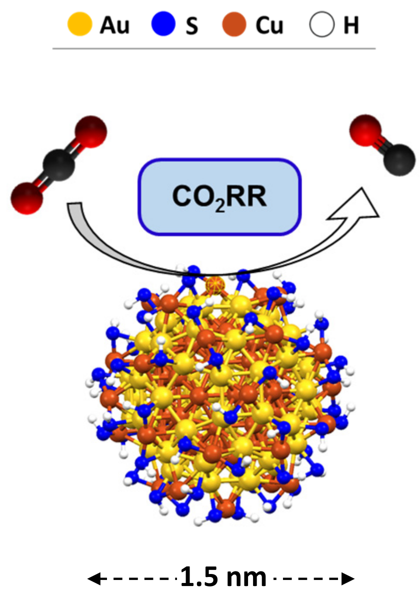
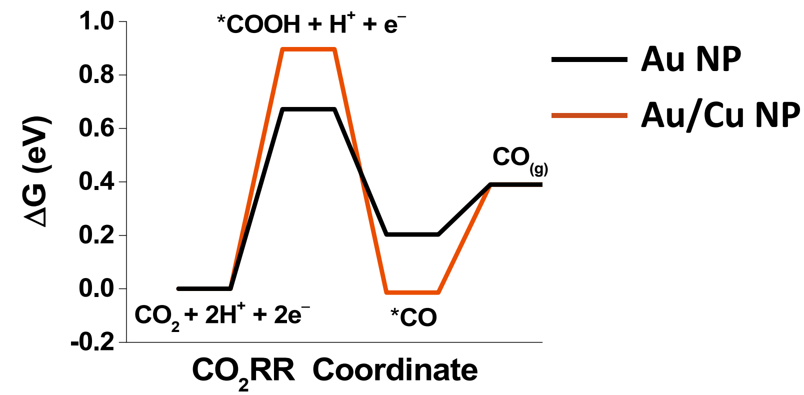
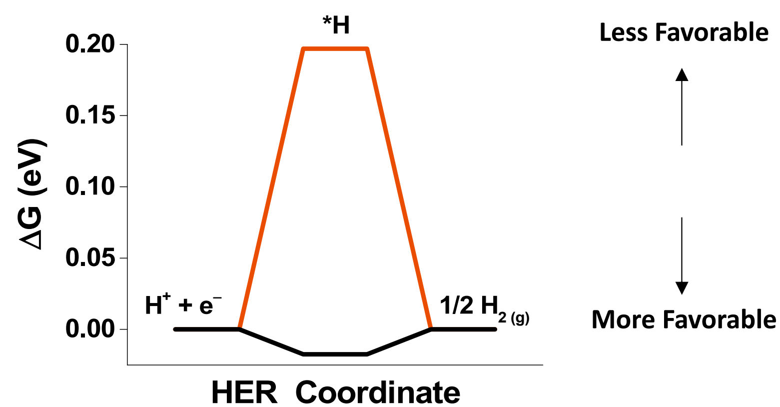
Gold-Copper Nanocatalysts





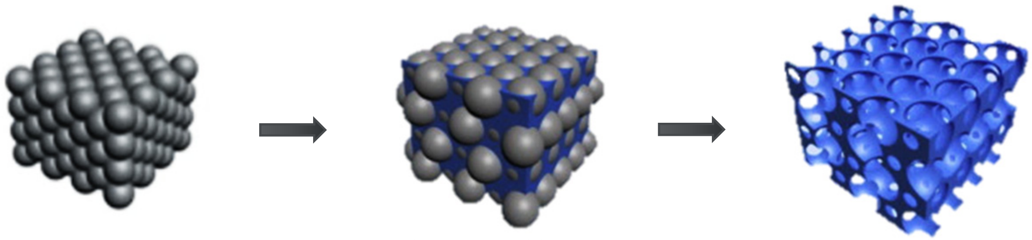


Improved performance with ~50% reduction in gold

**** Just accepted and chosen for JPCC Cover! ****

Kauffman et al. J. Phys. Chem. C, 2018, online ahead of print: DOI: 10.1021/acs.jpcc.8b06234

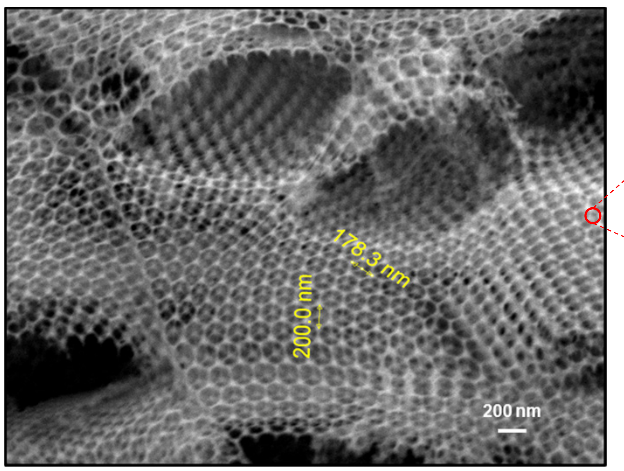
Coming full circle: Back to copper

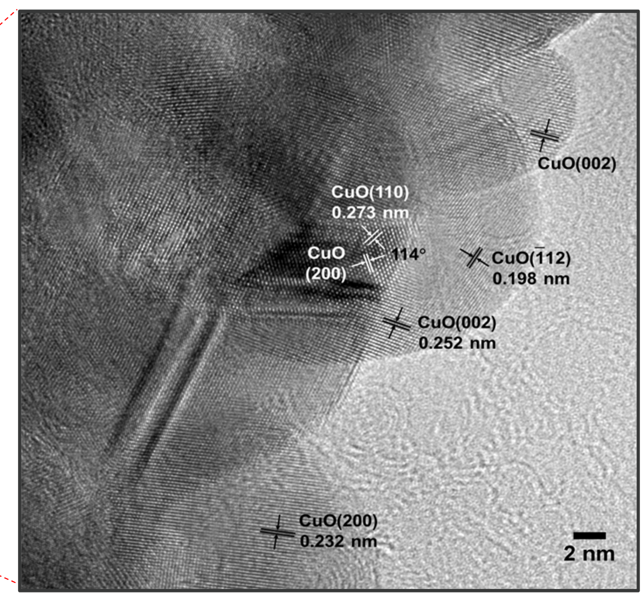


3D opal template
(200 nm PMMA colloids on substrate)

Precursor@opal
heterostructure

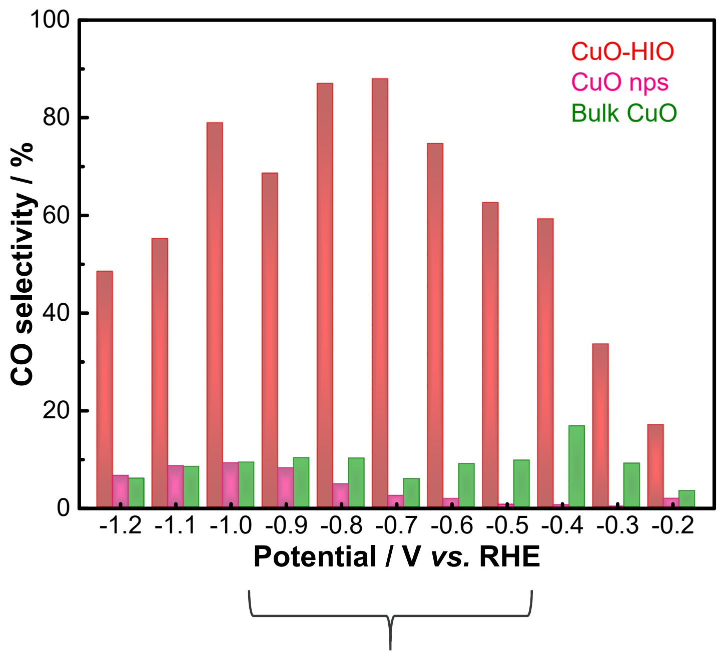
Inverse opal

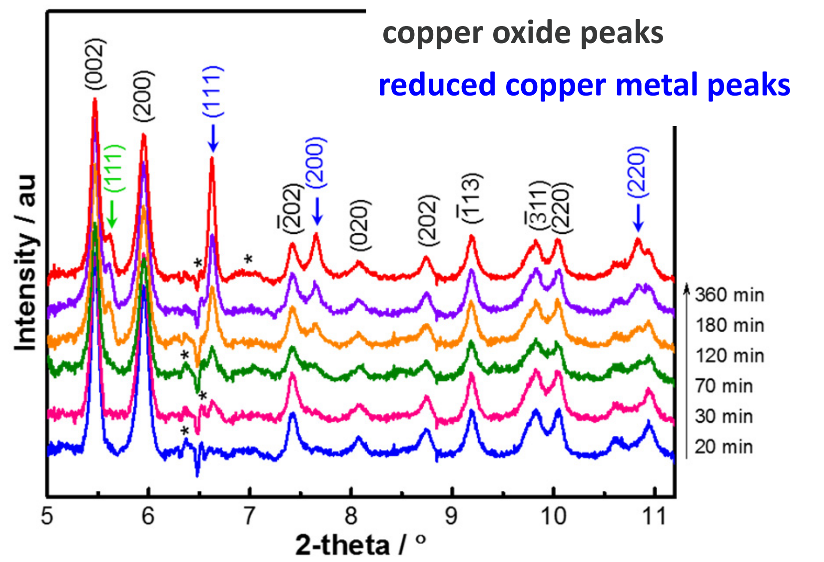




Selectivity and activity rivaling gold

Almost no H_2 below -1V , minor CH_4 and HCOOH, trace C_2





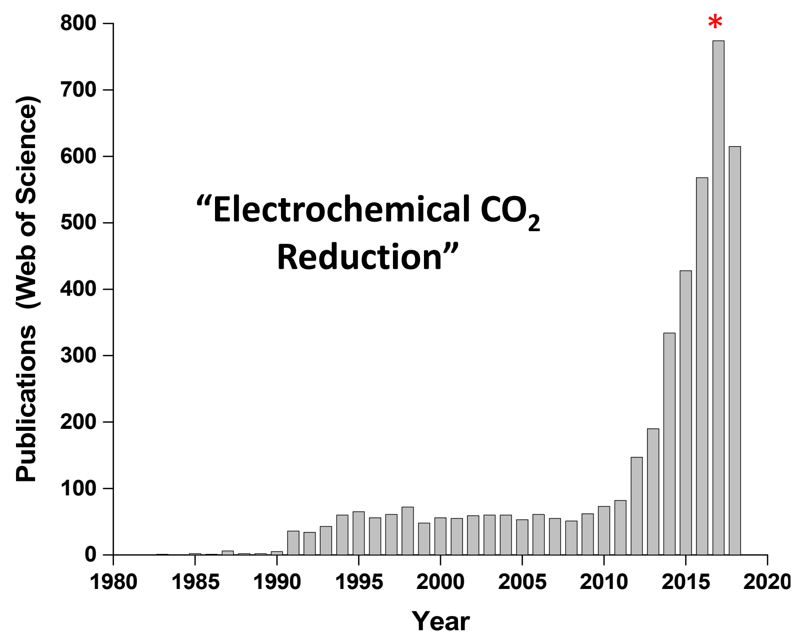
- ~8x more selective than commercially available CuO powder
- ~10-60x more selective than commercially available CuO nanoparticles

The field has exploded!

Invited topical review in 2017

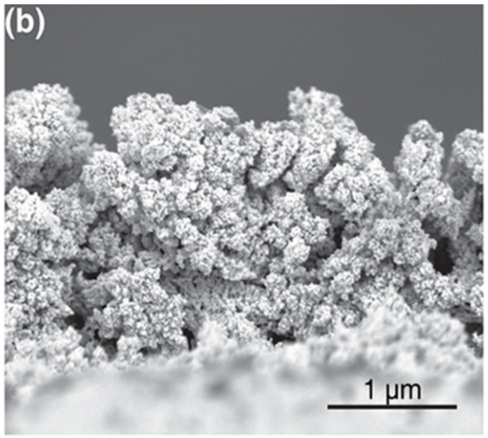
“Electrochemical Carbon Dioxide Reduction at Nanostructured Gold, Copper, and Alloy Materials”

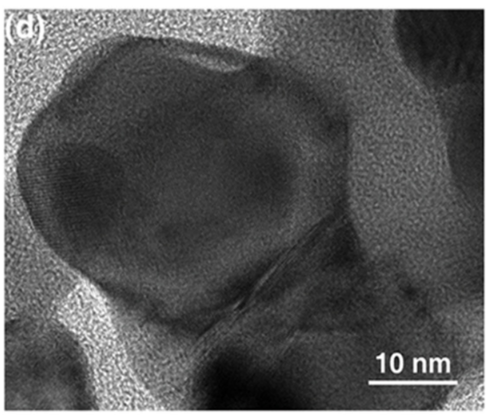
Named "Best of 2017“ in *Energy and Technology*

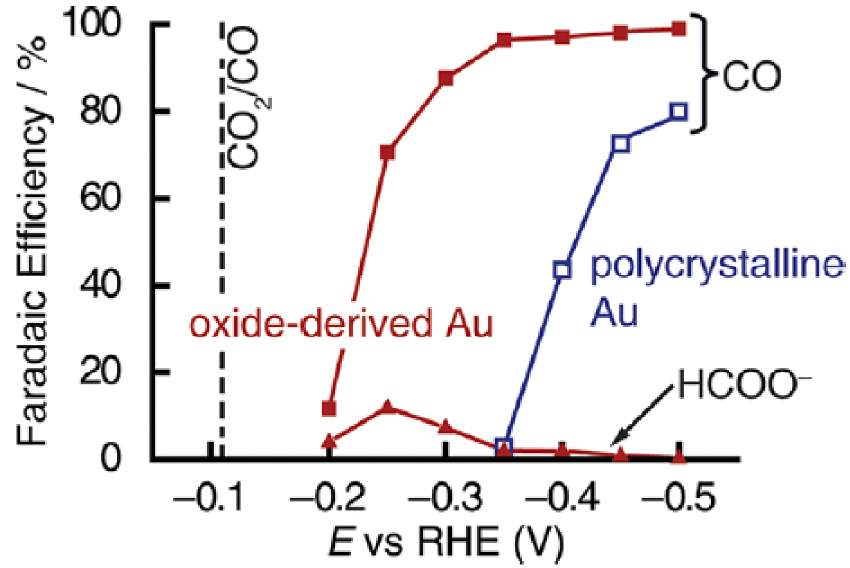


Vickers, Alfonso and Kauffman, *Energy Technology*, **2017**, *5*, 775-795

Other studies in gold vs surface structure

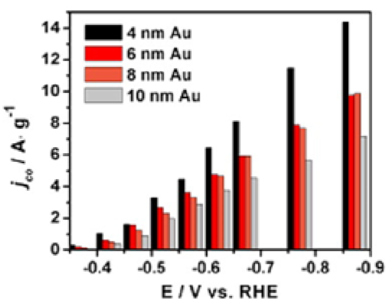


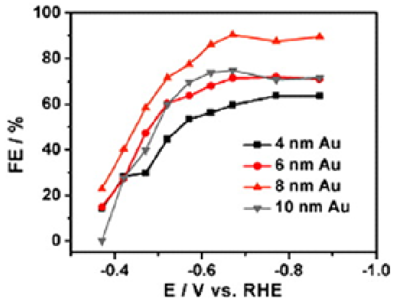


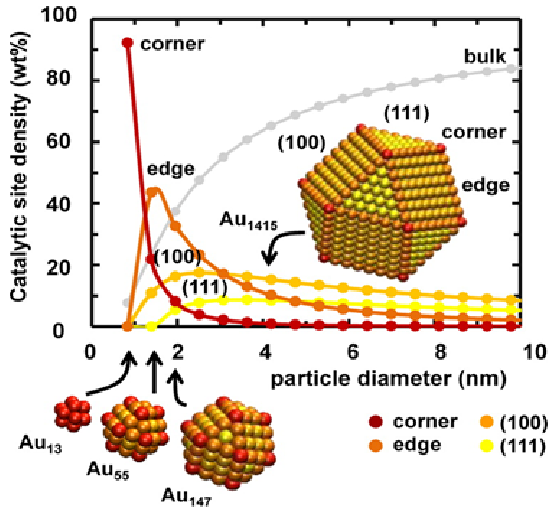


Kanan and coworkers: *J. Am. Chem. Soc*. **2012**, 134, 19969−19972

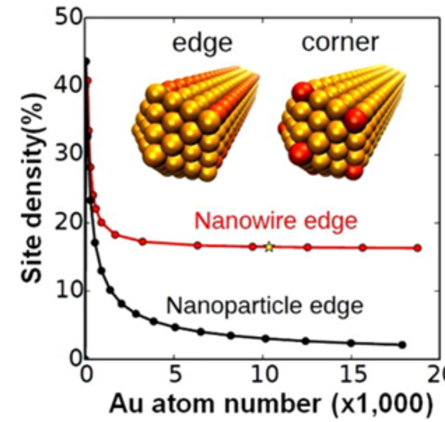
Gold Nanocatalysts of all shapes and sizes

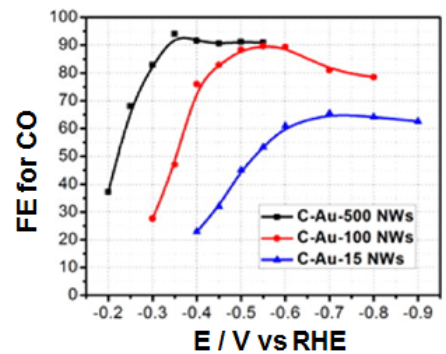






Size and shape drastically impact reactivity



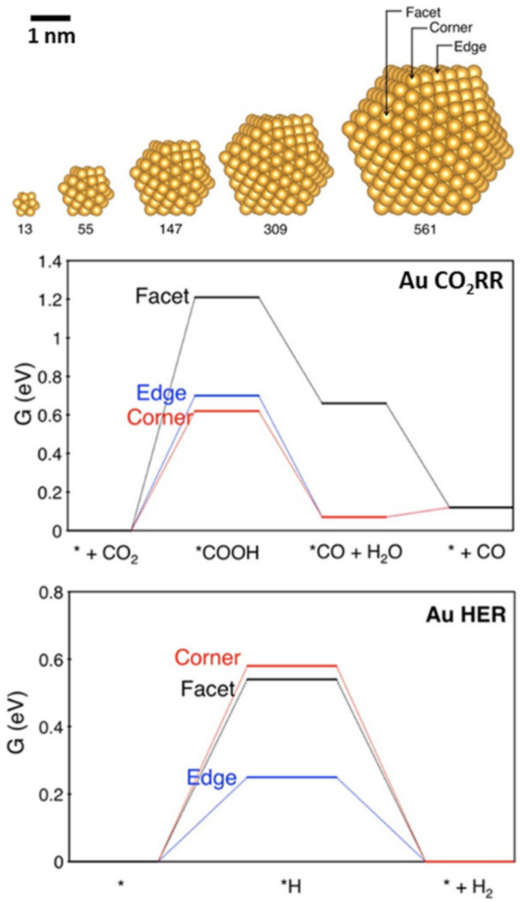


J. Am. Chem. Soc. **2013**, *135*, 16833-16836

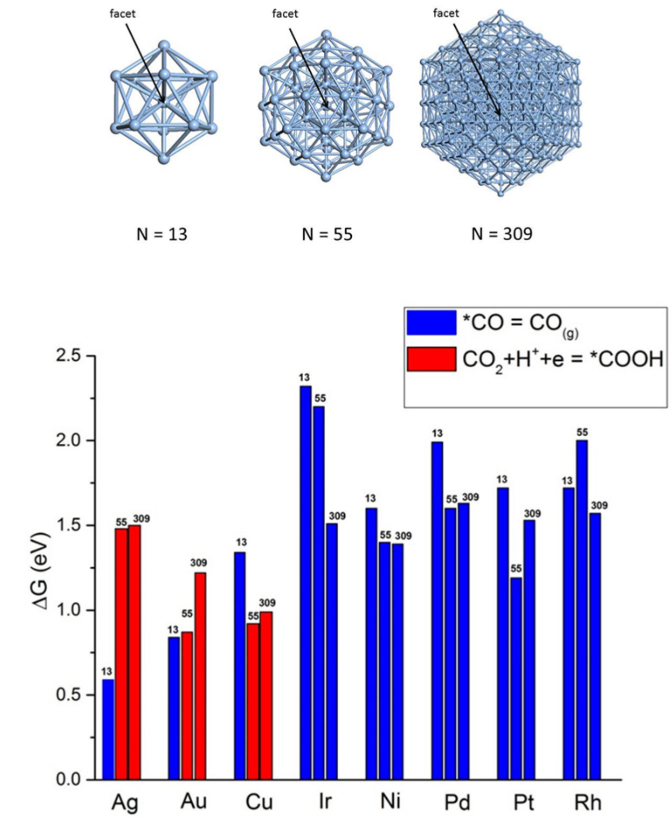
J. Am. Chem. Soc. **2014,** 136, 16132-16135

Theory catches up

NATIONAL ENERGY TECHNOLOGY LABORATORY



Approaching computationally-lead *predictive* catalyst design

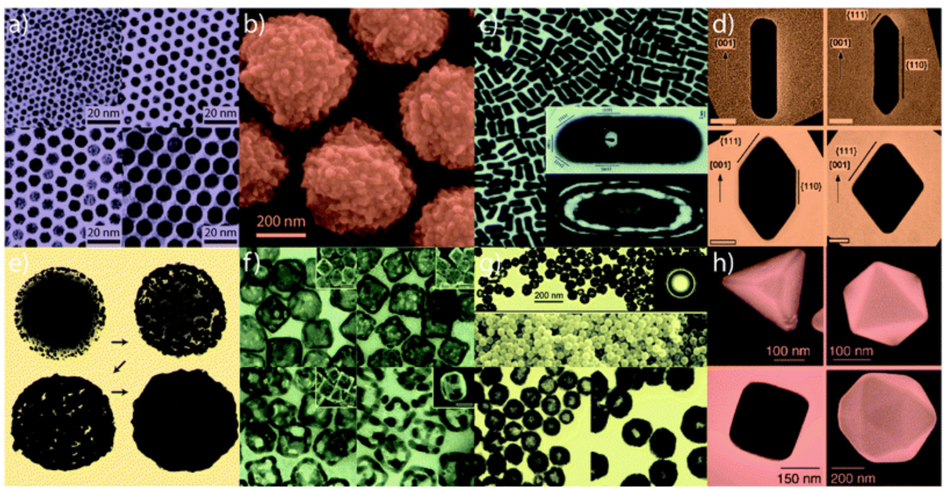


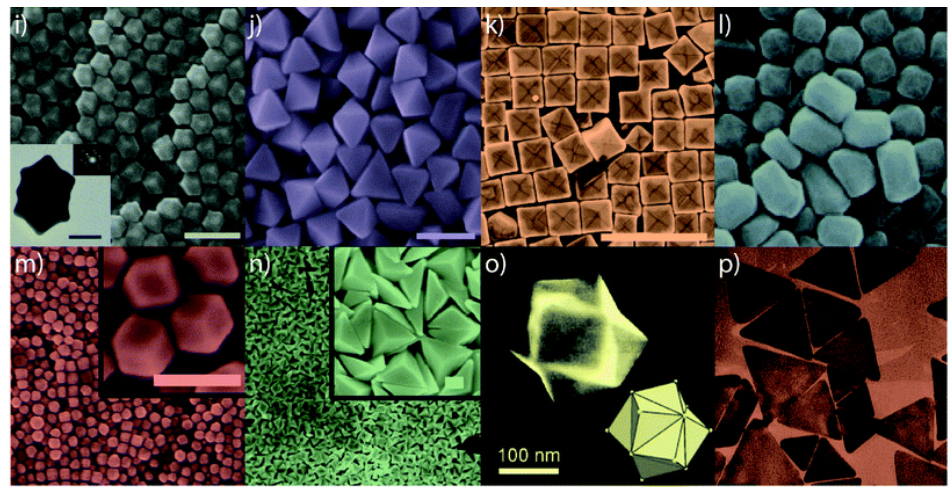
ACS Catal. **2015**, *5*, 5089-5096

Alfonso & Kauffman, *MRS. Commun*. **2017**, *7*, 601–606

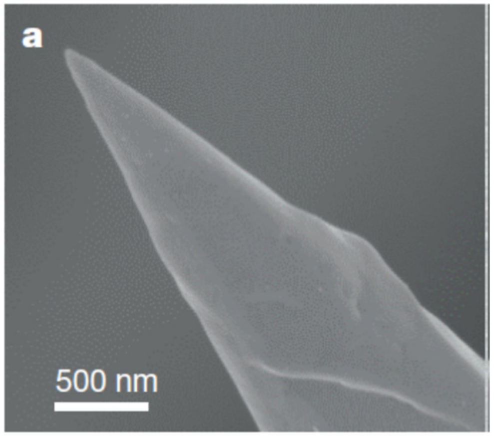
“Endless” possibilities in structural control

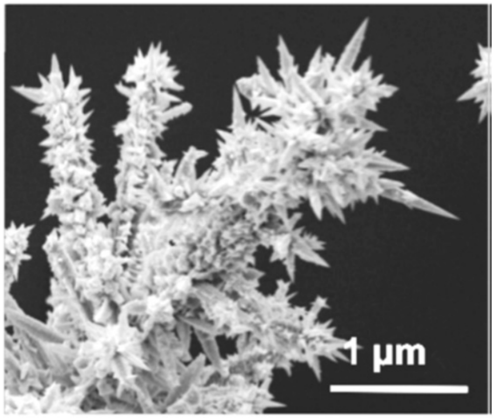
Nanoparticles can be synthesized in a dizzying array of shapes, sizes, crystallographic orientations, *etc*.

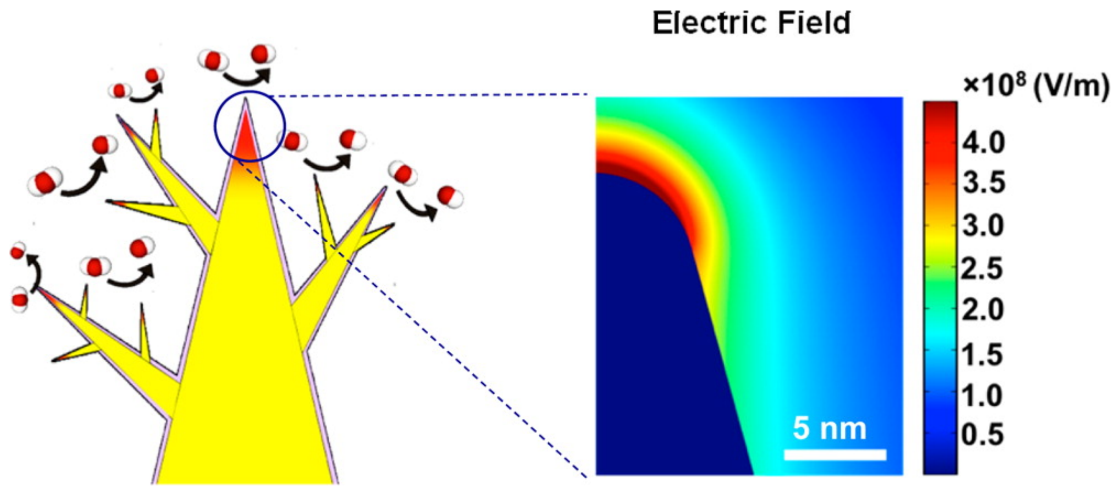




Emerging Nano-needles







Gold Nanoneedles: excellent CO selectivity and activity

Copper Nanoneedles: improved ethylene selectivity and activity

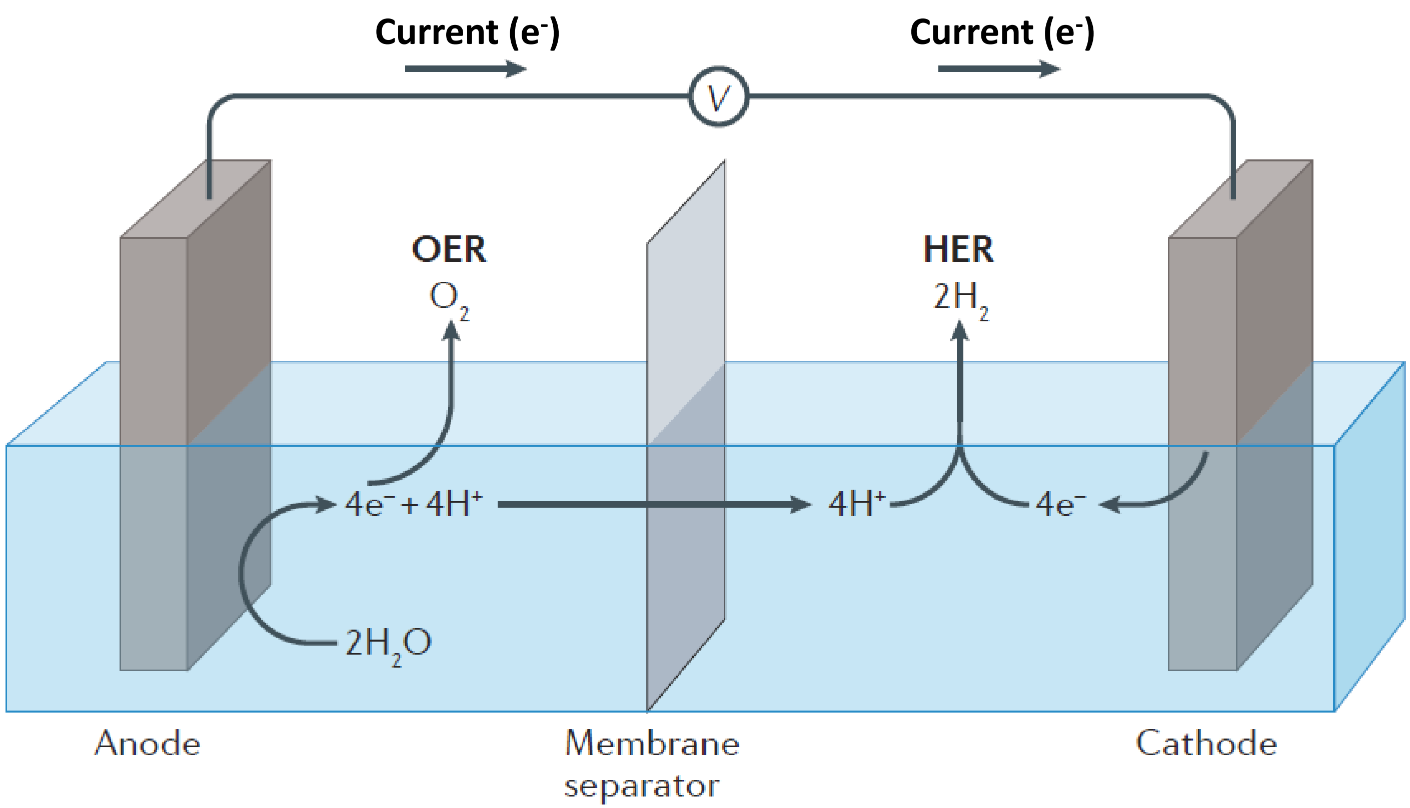
Sargent & Coworkers. Nature **2016***,* 537*, 382-386; Nano Lett.* **2016,** 16, 7224-7228; *Nature Catalysis* **2018**, *1*, 103-110

Remaining CO_2 challenges

NATIONAL ENERGY TECHNOLOGY LABORATORY

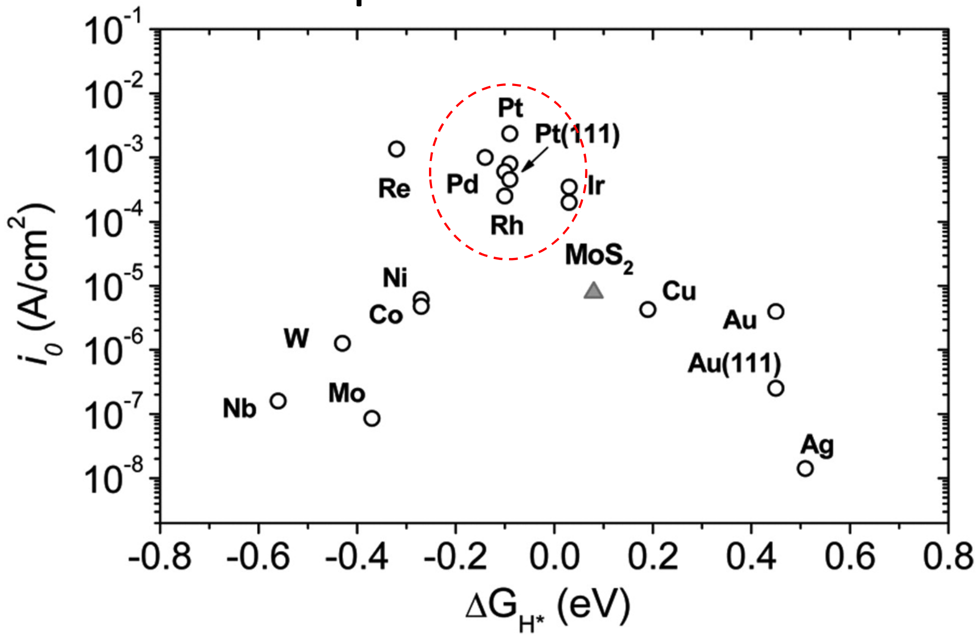
- Activity (still less than water electrolyzers)
- Selectivity (H_2 evolution still a problem)
- Reduced precious metals
- Longevity

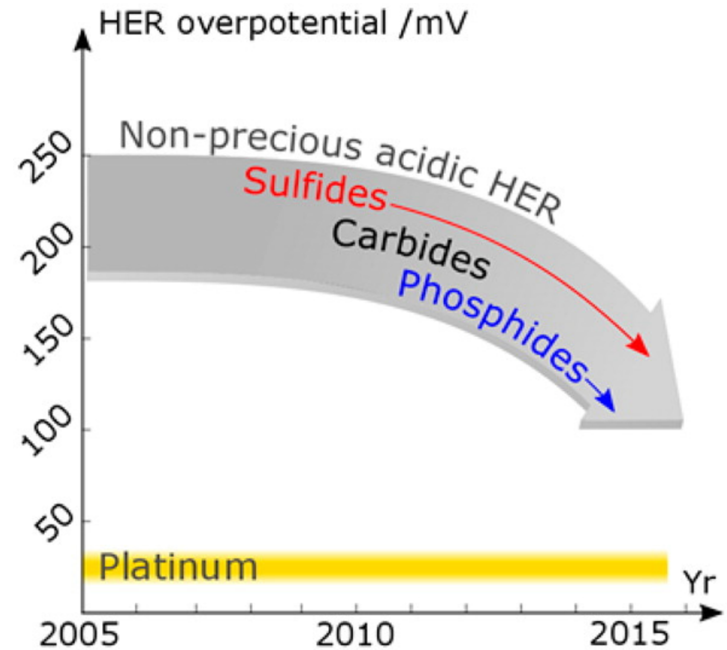
Water splitting for H_2 and O_2 production



Water splitting for H_2 production

Expensive metals are best



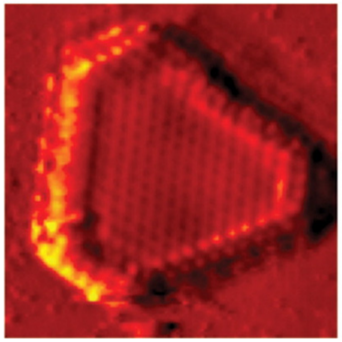


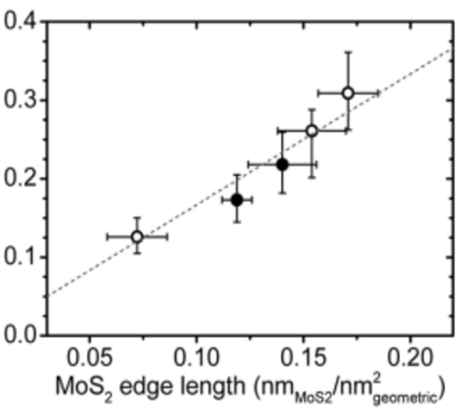
Science **2007**, *317*, 100-102

J. Phys. Chem. Lett., **2015**, *6*, 951–957

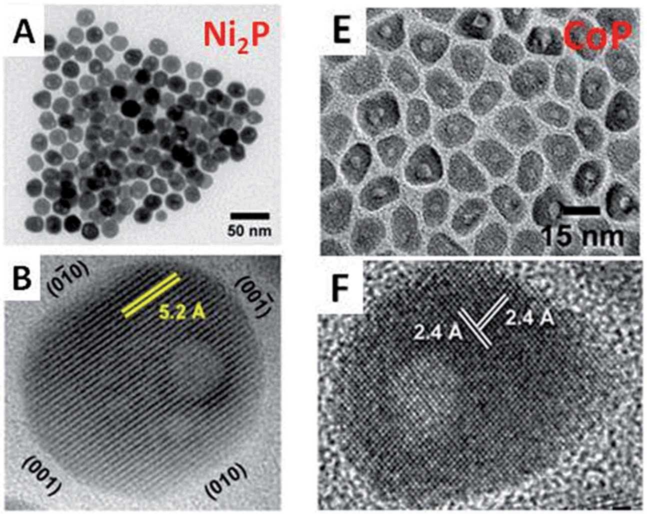
Nanostructured nonprecious catalysts

MoS_2

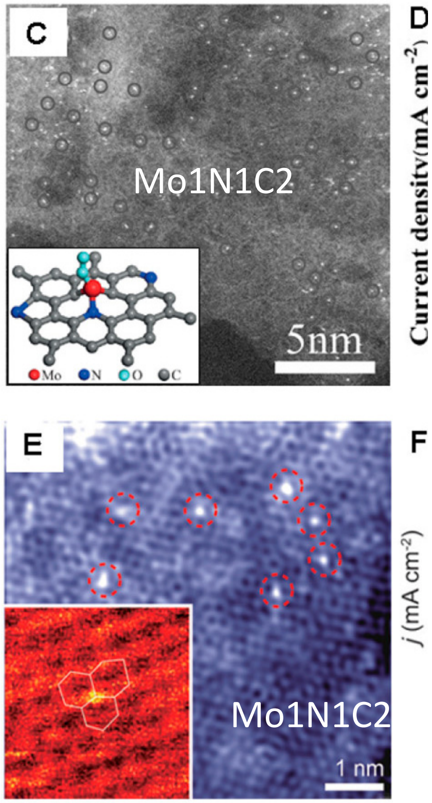




Metal phosphides

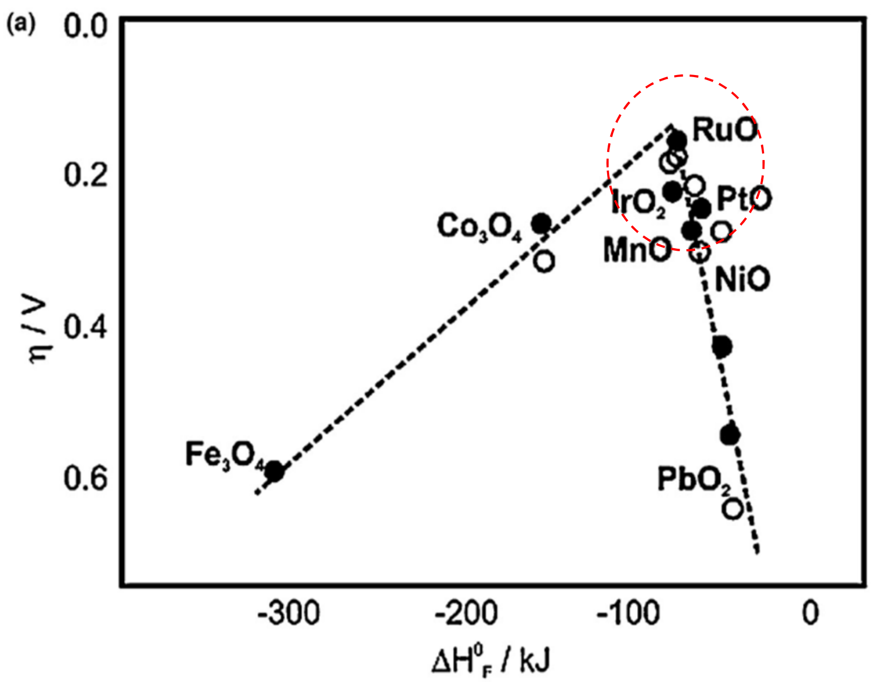


Single-site catalysts

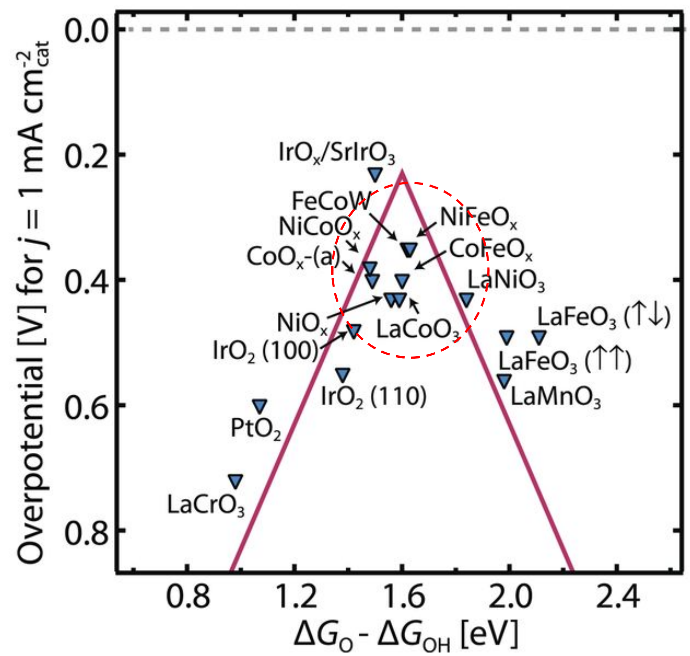


Water splitting for O_2 production

Expensive metals are still best



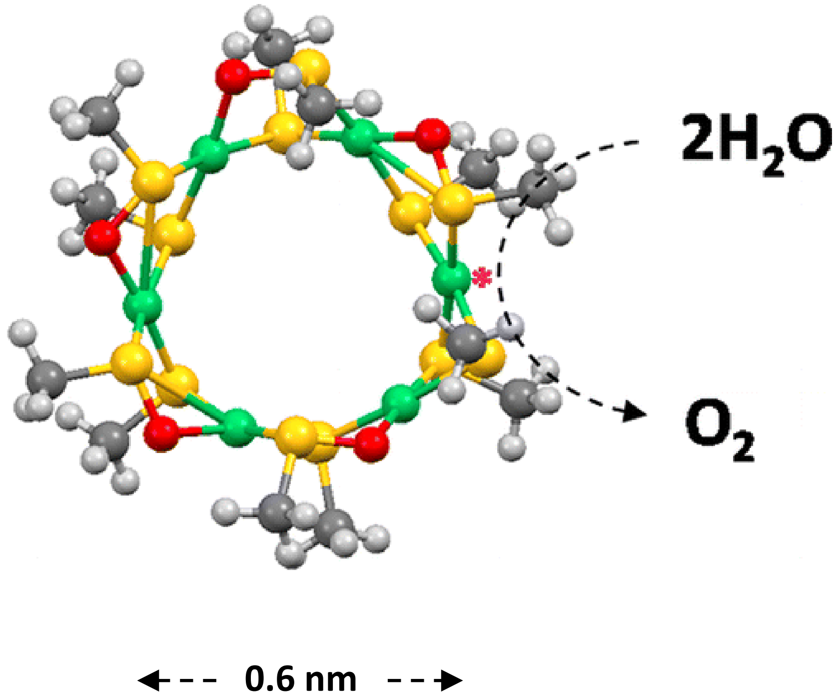
Emerging trends in mixed transition metals

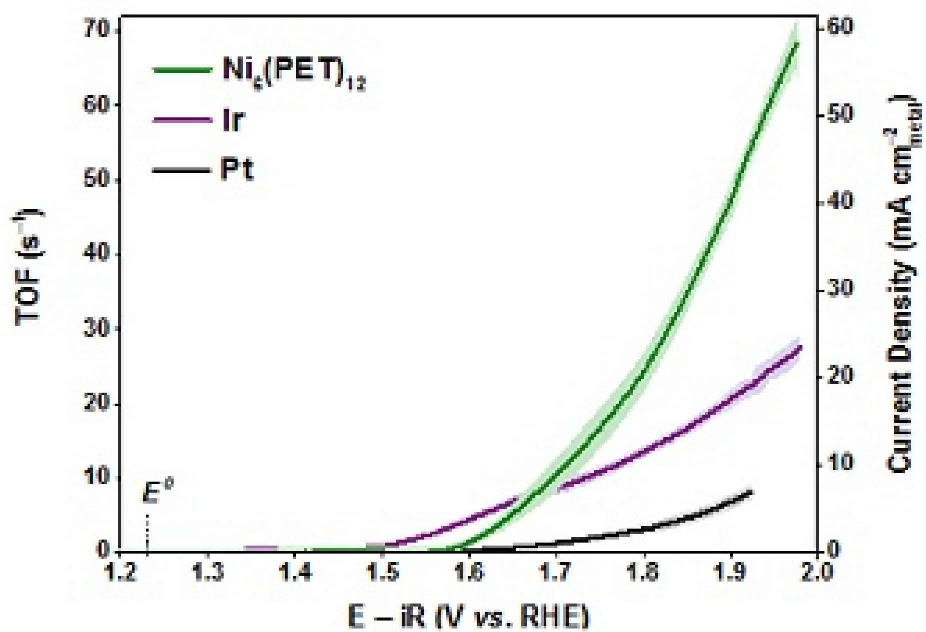


Electrochimica Acta **1984**, *29*, 1503-1512

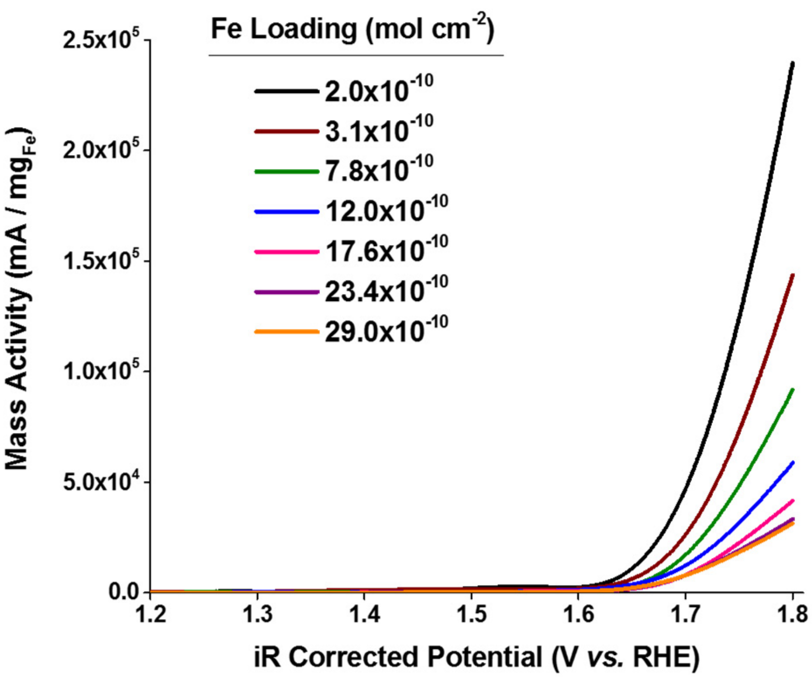
Science, **2017**, *355*, article: eaad4998

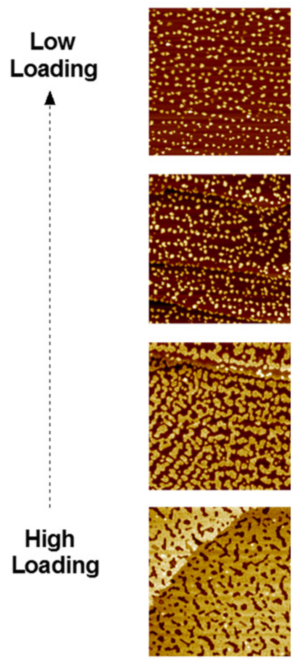
“Atomically Precise” O_2 evolution



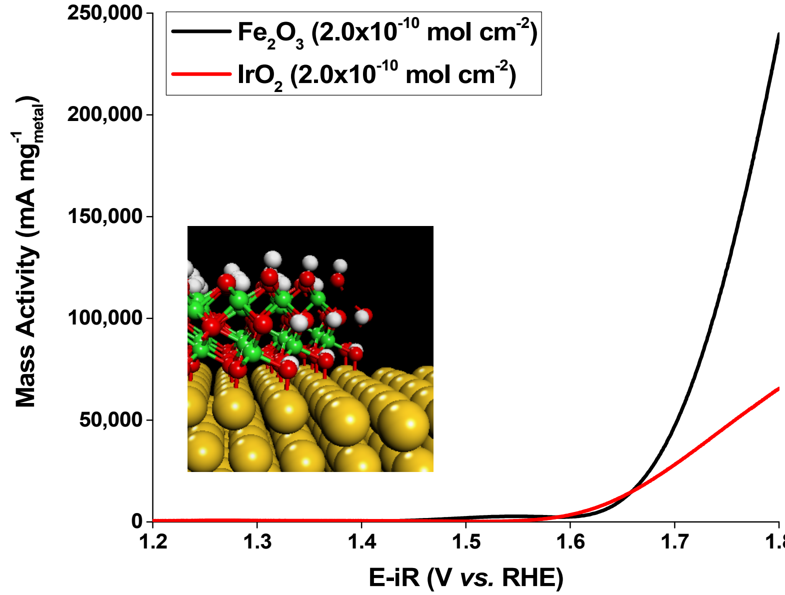


Combining Electrochemistry and Surface Science





Nanostructured iron outperforms iridium

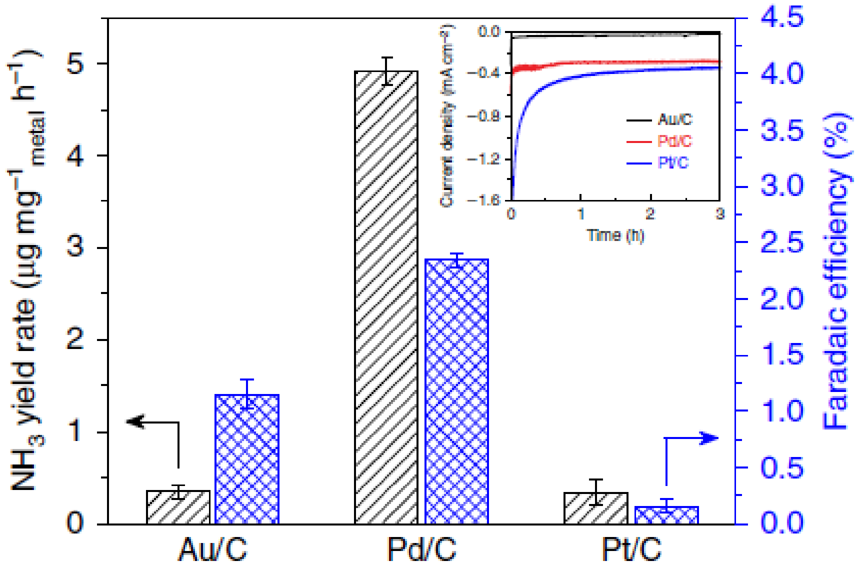


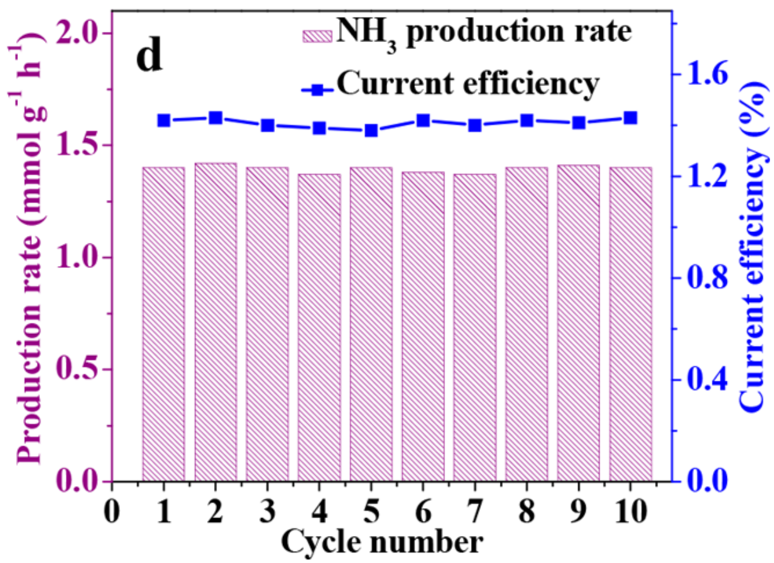
Ammonia: the next BIG thing?

- **Fertilizer**
  - Huge market, huge energy requirements, huge carbon foot print
- **Energy storage**
  - Use NH_3 directly as fuel
  - Convert into H_2 for end use application
- **Air separation**
  - Can we remove N_2 from air streams *via* catalysis?
- **Modular**
  - Can electrochemistry reduce the energy requirements and size?

Recent Ammonia Progress

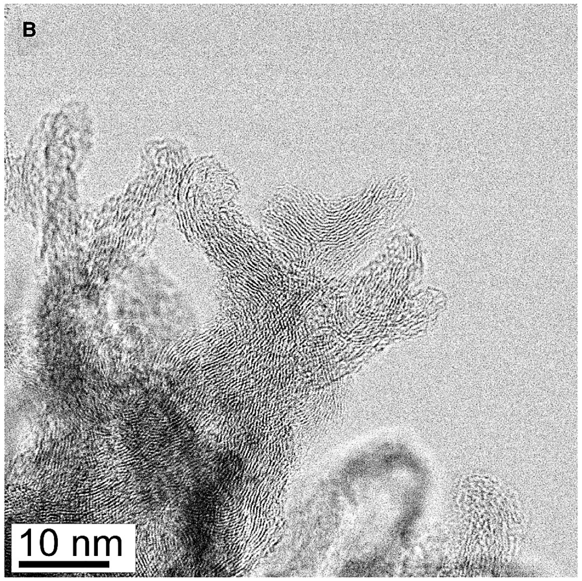
Metal nanoparticles and nitrogen-doped carbons show some activity, but very low efficiency



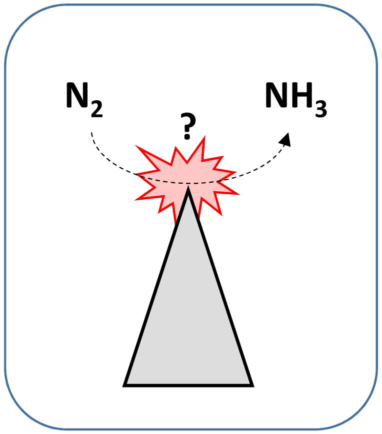


Recent Ammonia Progress

- Carbon nano-needles electrochemically convert N_2 into NH_3
- <u>Currently</u>: Small scale, Low activity , Faradaic Efficiency < 12%; Energy Efficiency less than 5%
- Haber Bosh ~55% Energy Efficiency at industrial scale; high pressure, large infastructure

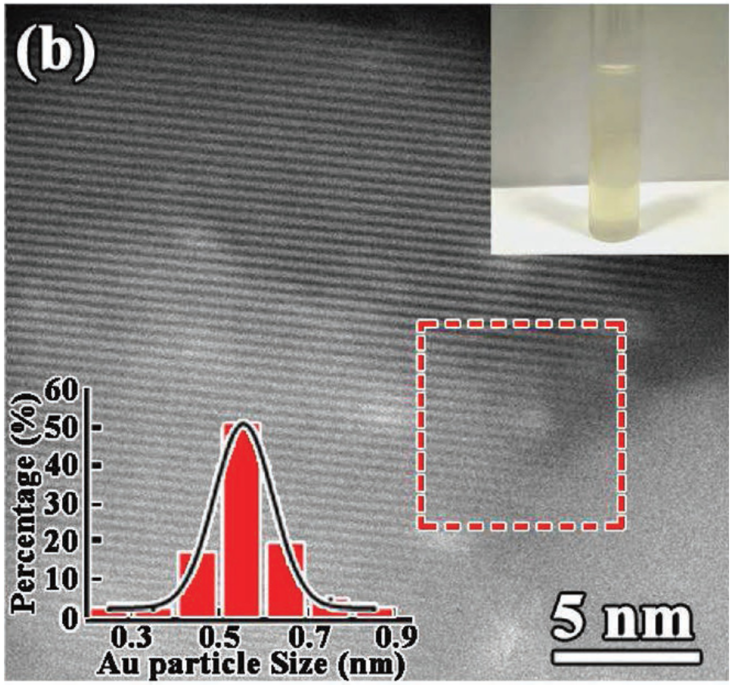


Sharp tips seem to help

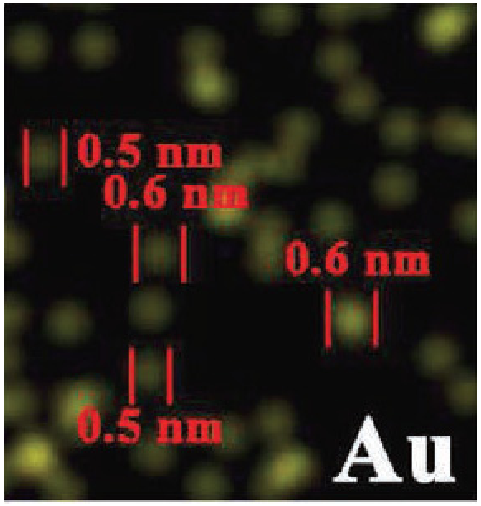


Recent Ammonia Progress

"Single-site" Au catalysts on TiO_2



8% Electron Efficiency; 0.4 mA/cm² current density



Adv. Mater. **2017**, *29*, 1606550

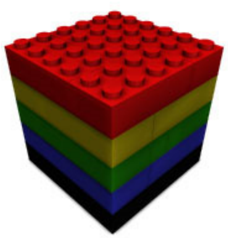
Ammonia: the challenges

- **Challenges with electrochemical ammonia synthesis**
  (1) Selectivity

  (2) Efficiency

  (3) Reaction rates (current density)

- **<u>Fundamental</u> studies to address structure *vs.* function**



Concluding thoughts

- **We've learned a lot about controlling nanoscale structuring and function**

- **Direct these lessons towards challenging energy-related problems**

- **Still much to learn and accomplish**
  - fundamental studies linking structure and performance
  - improve activity, efficiency, stability, *etc*.
  - modular reactors, intermittent operation

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Thank you for your attention!

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