# NEW CATALYSTS FOR PRODUCTION OF SOLAR FUELS

Summer School on '*Materials for the hydrogen economy*',
*Iceland, 17-21 August,2010*

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WWW. CINF. DTU.DK

&

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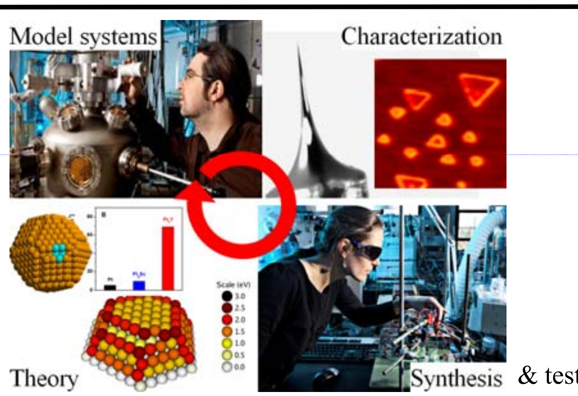
Center for Atomic-scale Materials Design **(CAMD)**
Department of Physics, DTU

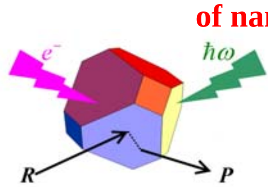
&

K. Herbst
Haldor Topsøe A/S

# CINF Approach

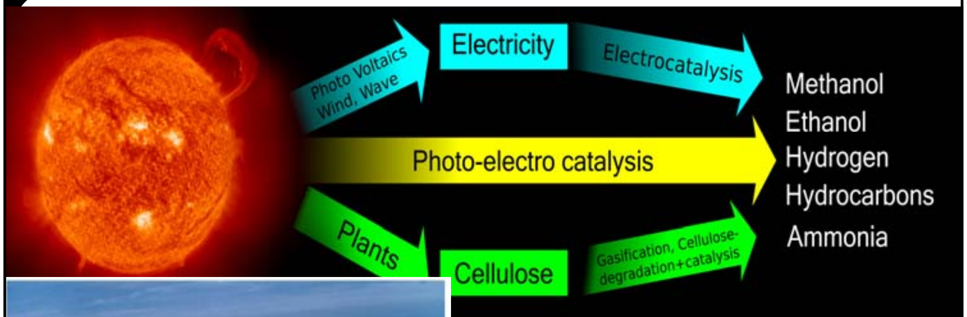



**The common denominator is surface science where the functionality of nanoparticles plays an essential role.**



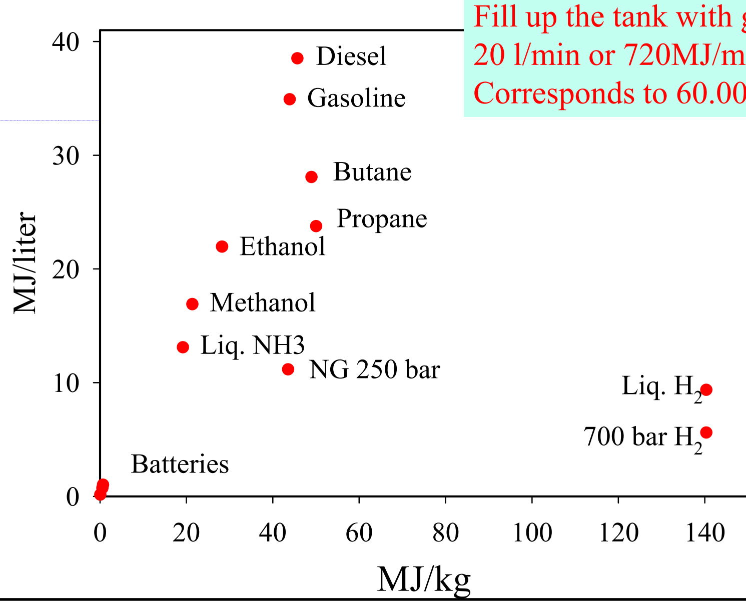

- Heterogeneous Catalysis
- Electrocatalysis
- Photocatalysis

## Catalysis for sustainable Energy (CASE)



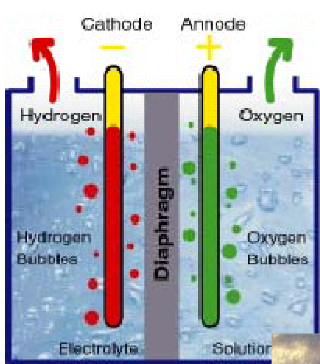

WWW. CASE. DTU.DK

## Energy content of fuels




Fill up the tank with gasoline!
20 l/min or 720MJ/min
Corresponds to 60.000A @ 200V

## Averaging renewal energy sources




Cathode: $2(H^{+}+e^{-}) \rightarrow H_2$

Anode: $H_2O \rightarrow \frac{1}{2} O_2 + 2 H^{+}$

Total: $H_2O \rightarrow \frac{1}{2} O_2 + H_2$

$\Delta G^0 = 2.46$ eV (1.23 eV/electron)

Could be a route for averaging out sustainable energy production i.e. from wind and PV

In DK ~ 21% power from wind alone

~3 % of total energy consumption


## $H_2$-production from wind

Poul la Cour, Askov school for popular education for adults (Denmark) ~1891-1908

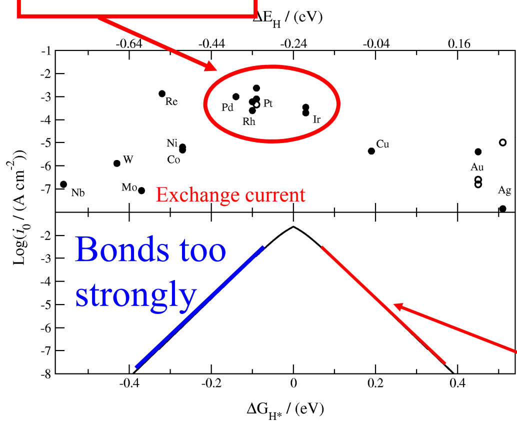
1000 l/h $H_2$ ~1.3kW www.poullacour.dk

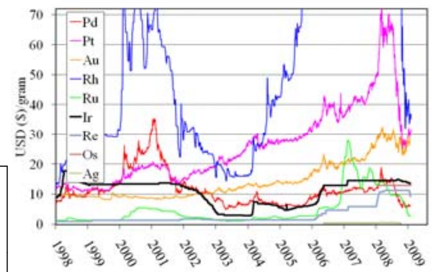
Electricity

$H_2O \rightarrow \frac{1}{2}O_2 + H_2$

## Trends for Hydrogen Production

Expensive and scarce



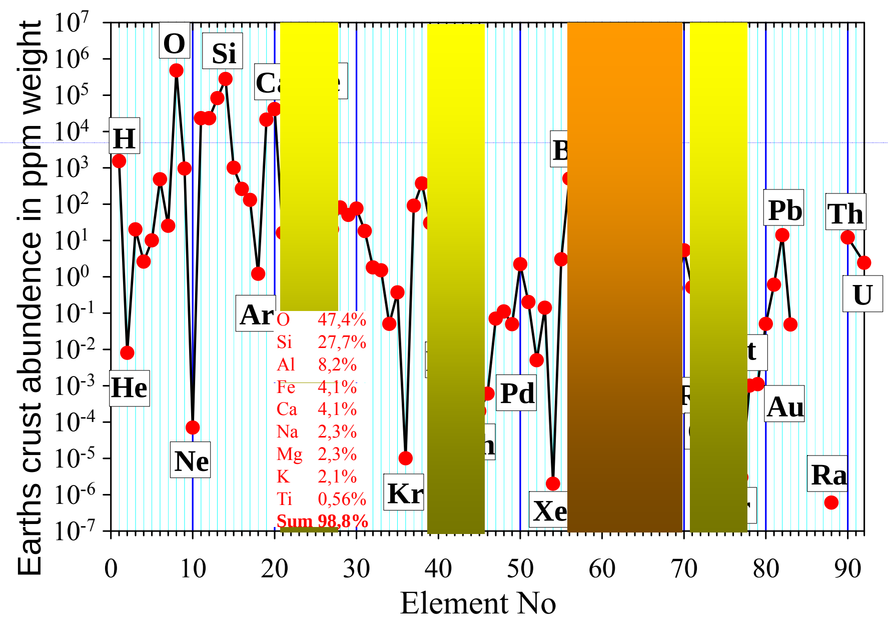

Some 200 Ton Pt a year
Today: 1g Pt per kW or
4 million cars per year!

Barrier for dissociation

*J.K. Nørskov, T. Bligaard, Á. Logadóttir, J.R. Kitchin, J.G. Chen, Pandelov, and U. Stimming: J. Electrochem. Soc. 152, J23, (2005)*

R. Parson 1957

## Composition of Earths Crust



# The Solar spectrum

Ideally: $H_2O + 2h\upsilon \rightarrow 1H_2 + 1/2O_2$

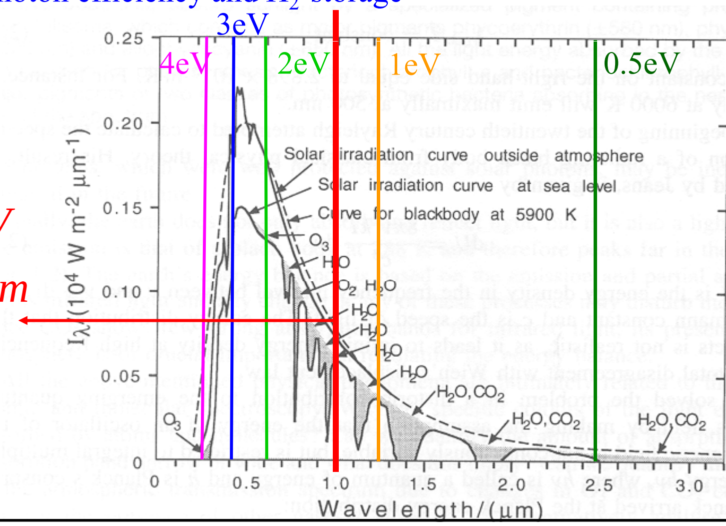
A strongly activated process

Problem: Photon efficiency and $H_2$ storage

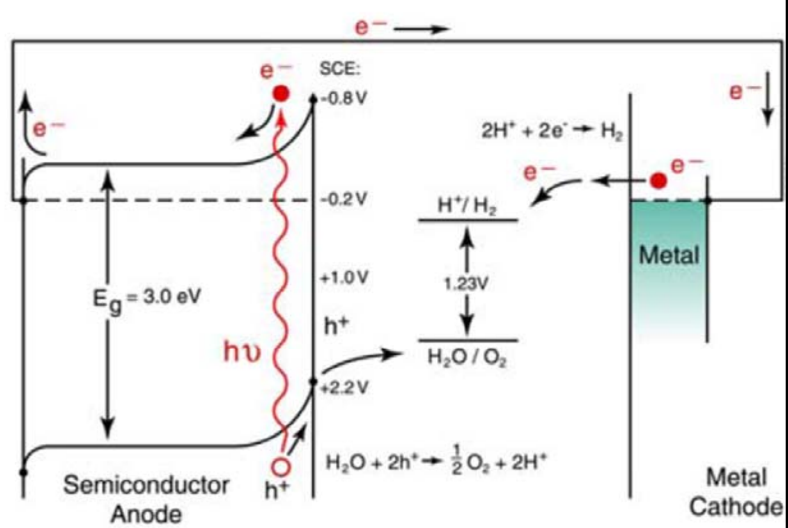
$$h\nu > \frac{\Delta G}{2}$$

$$h\nu > 1{,}23eV$$

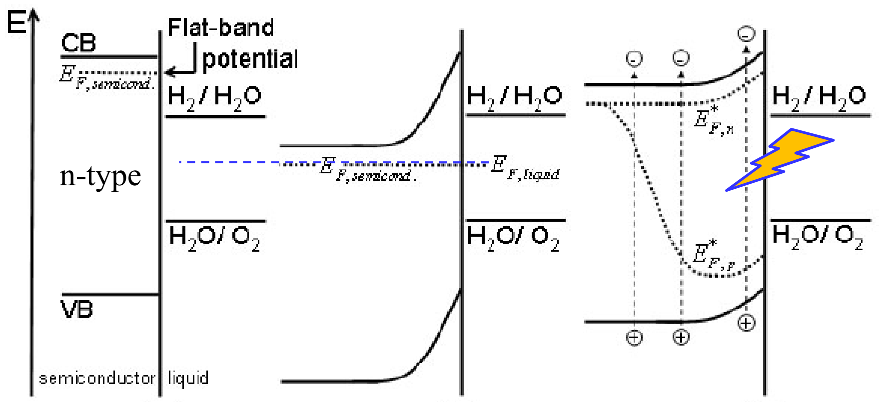
$$h\nu < 1000nm$$




# Basic principle



## Photoelectrocatalysis: Lots of good Physics




(a) not connected (b) connected (c) Light on

All a matter of getting a sufficient bandgap matching the redox potentials for oxidizing water



## Some important definitions:

- Anode: The electrode where oxidation occurs i.e. $A^x \rightarrow A^{x+1}$
- Cathode: The electrode where reduction occurs i.e. $A^x \rightarrow A^{x-1}$

- Going anodic means going positive potential
- Going cathodic means going negative potential

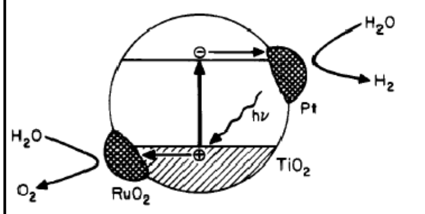
- An anion is, however, negative $A^-$
- While a Cations are positive $A^+$

Confused ? Learn more about electrochemistry and you will get your plate full.

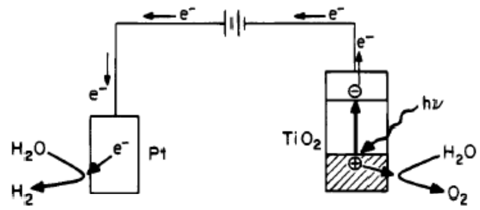
## Setups for water splitting

- Nanoparticles
- Self contained
- Simple - cheap
- Very hard to separate $H_2$ from $O_2$ explosive gas (900kg TNT /Ha*hour)

- Macroscopic electrodes
- Can have complex nanostructures
- More expensive
- Trivial $H_2$ separation




$$H_2O \xrightarrow[RuO_2-TiO_2-Pt]{h\nu} H_2 + \frac{1}{2}O_2$$



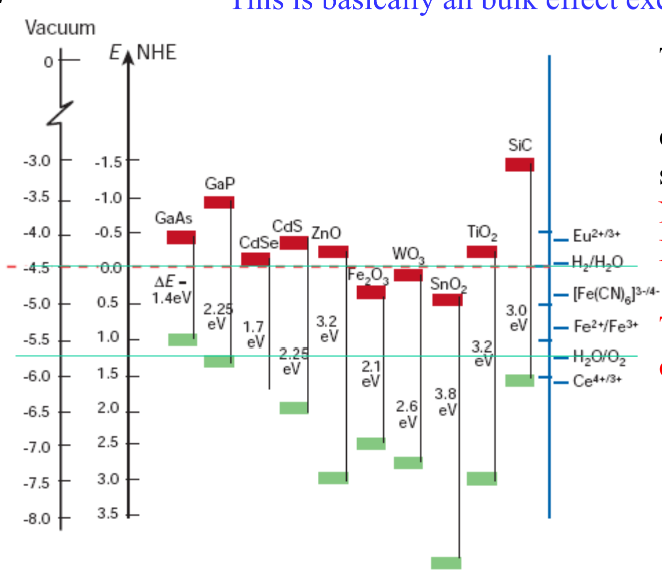

$$H_2O \xrightarrow[Pt-TiO_2]{h\nu} H_2 + \frac{1}{2}O_2$$

Yates et al *Chem. Rev.* 1995



## Band gap Engineering

This is basically an bulk effect except for nano particles




$TiO_2$ was found in 1972 but is not efficient for Water splitting

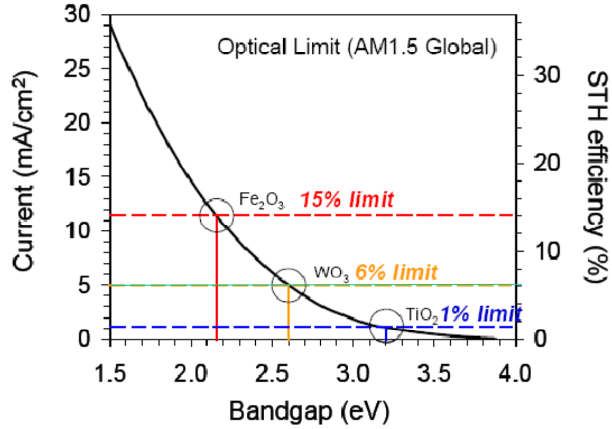
Needs a potential for $H_2$evolution.

Though good for self-cleaning surfaces

## The band gap limitations

Ideally: $H_2O + 2h\upsilon \longrightarrow 1H_2 + 1/2O_2$

$$STH \equiv \frac{F_{H_2}[Mol\ s^{-1}]*237\,[kJ\ /\ Mol]}{P_{Total}[Wcm^{-2}]*Area[cm^{-2}]} @1.5 Air\ Mass 1.5G$$




http://hydrogen.energy.gov/pdfs/review06/pd_6_miller.pdf

## Stability: Splitting water

- Stability is a major issue for many materials - eg $Cu_2O$
- Electrochemical corrosion, photo-corrosion, dissolution
- Criteria:

All surface effects

$$AB + ze^- \rightarrow B^{-z} + A + \Delta G_c$$

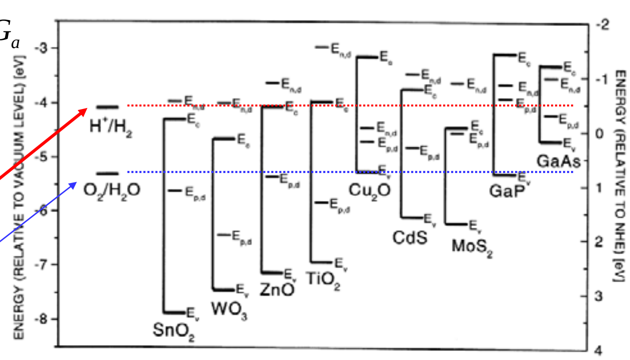
$$AB + zh^+ \rightarrow A^{+z} + B + \Delta G_a$$

$$E_{n,d} = \frac{\Delta G_c}{zN_A}$$

$$E_{p,d} = \frac{\Delta G_a}{zN_A}$$

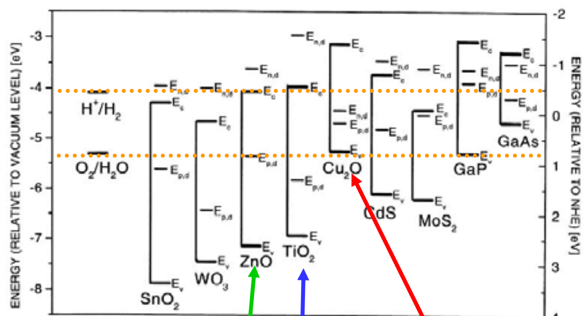
$$E(H^+/H_2) > E_{n,d}$$

$$E(O_2/H_2O) < E_{p,d}$$




Bak et al, 2002, *Intl. J. Hyd. Energy*, **27**

## Some potential photocatalysts




ZnO: (1) bandgap too wide (3 eV)
(2) good $O_2$ energetics
(3) “fair” $H_2$ energetics
(4) photoanodic corrosion

TiO$_2$: (1) bandgap too wide (3 eV)
(2) good $O_2$ energetics
(3) “fair” $H_2$ energetics
(4) stable under illumination

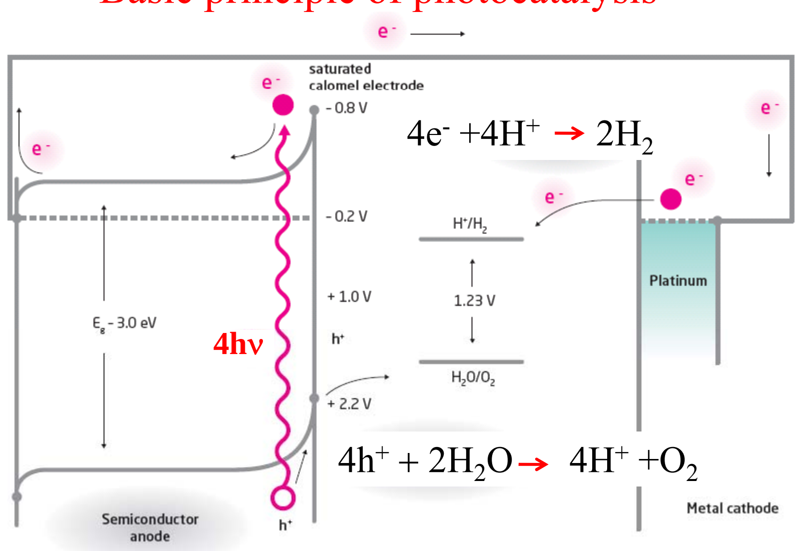
Cu$_2$O: (1) narrower bandgap (2 eV)
(2) “fair” $O_2$ energetics
(3) good $H_2$ energetics
(4) photoanodic AND photocathodic corrosion

Bak et. al., *Int. J. Hydrogen Energy*, vol 27 (2002) 991-1022



## How can we get alleviate this over potential ?

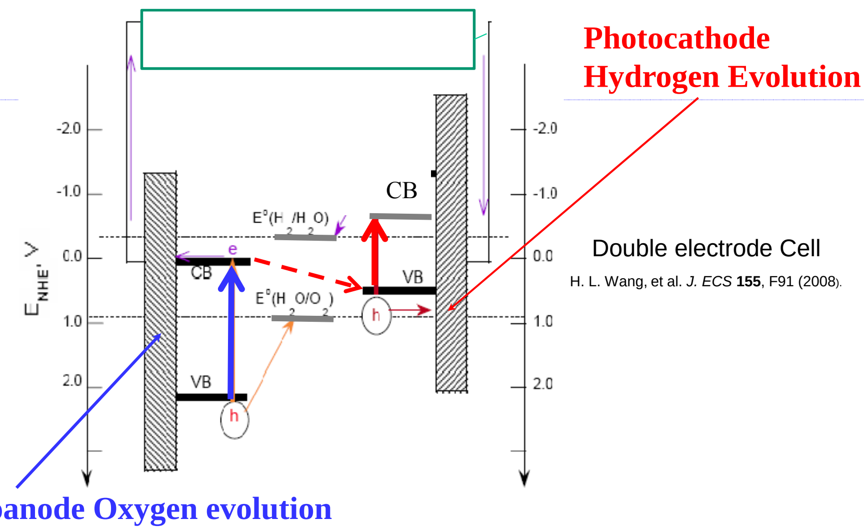
### Basic principle of photocatalysis




$4e^- + 4H^+ \rightarrow 2H_2$

$4h^+ + 2H_2O \rightarrow 4H^+ + O_2$

## What are the Alternatives – Tandem cells?

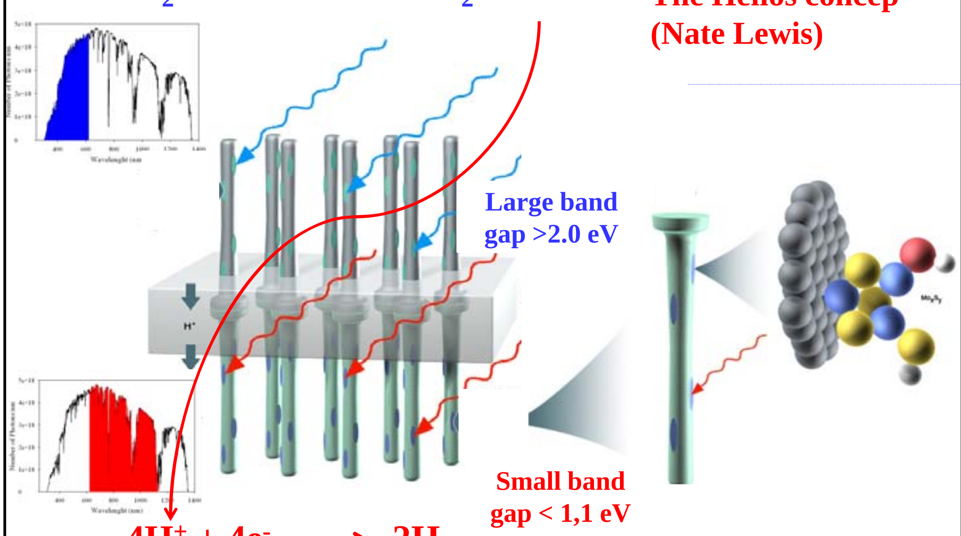



- Choose different materials with optimized properties for each half reaction

## The dream device

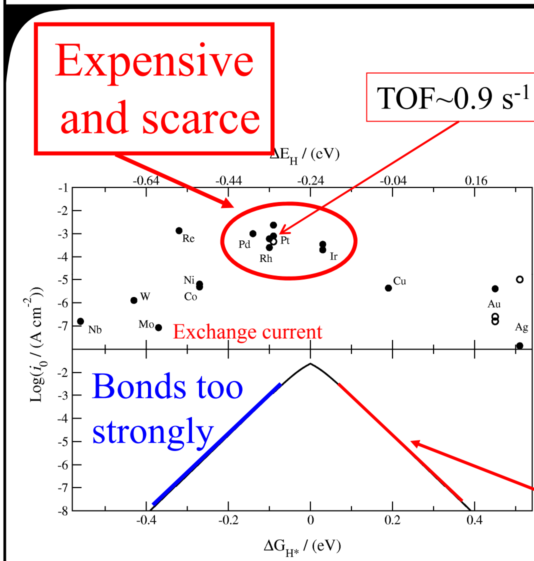
$H_2O + 4h^+ \longrightarrow O_2 + 4H^+$

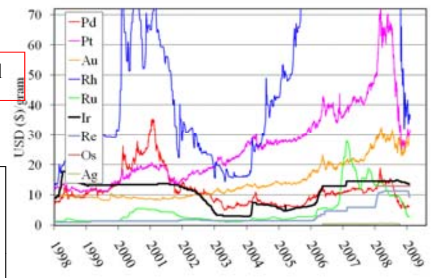
The Helios concep
(Nate Lewis)




$4H^+ + 4e^- \longrightarrow 2H_2$

# Trends for Hydrogen Production




Some 200 Ton Pt a year
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Barrier for dissociation

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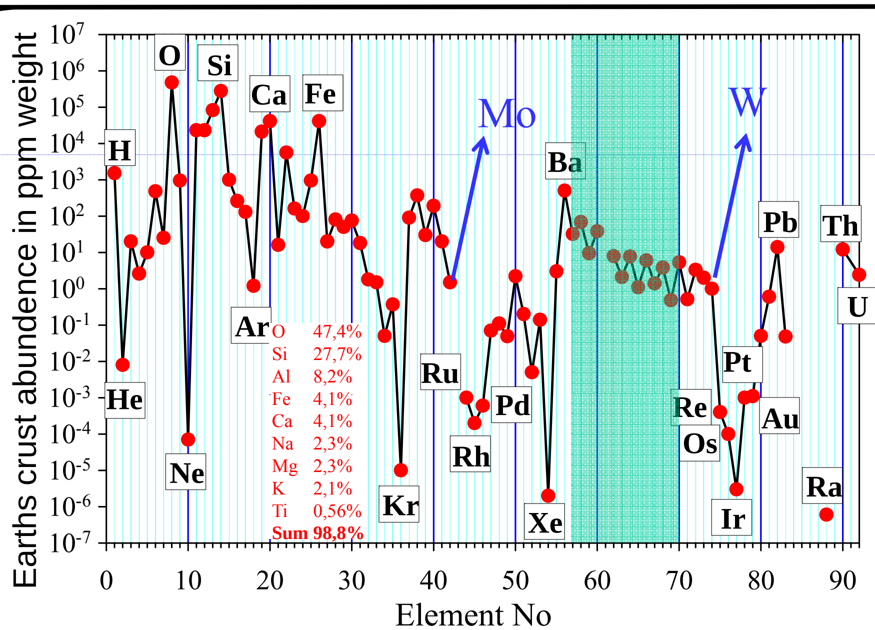
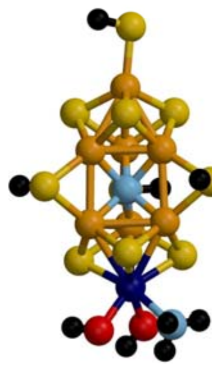
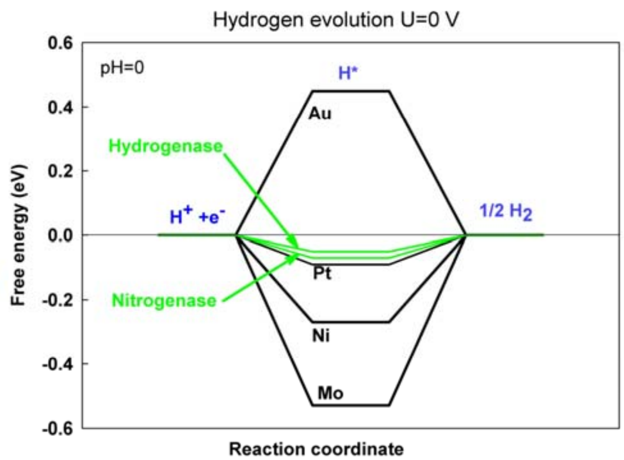


# How does nature make Hydrogen?

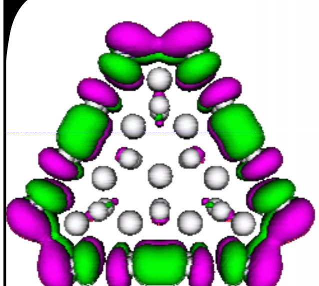
Nitrogenase:

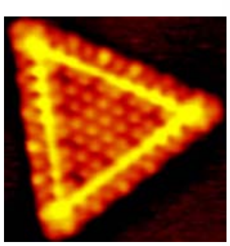


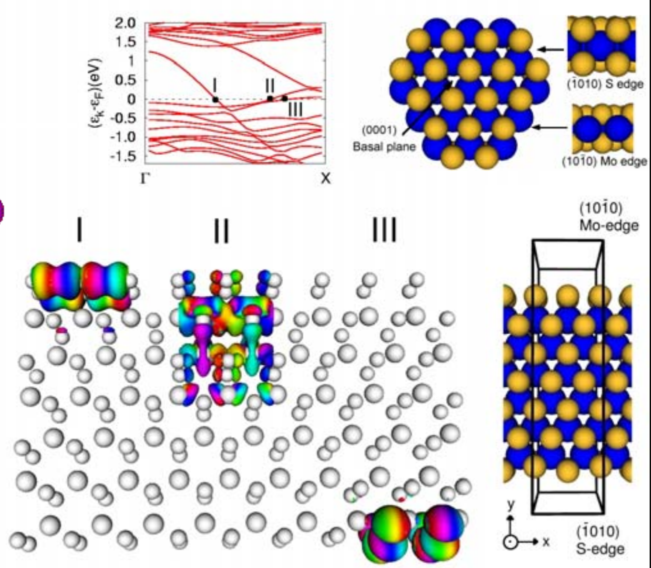



**B. Hinnemann and J.K Nørskov, *J. Am. Chem. Soc.* 126, 3920 (2004)**
**Hydrogenase: Per Siegbahn, Adv. Inorg. Chem. 56, 101 (2004).**

# The Nano effect: The edges of $MoS_2$ are metallic

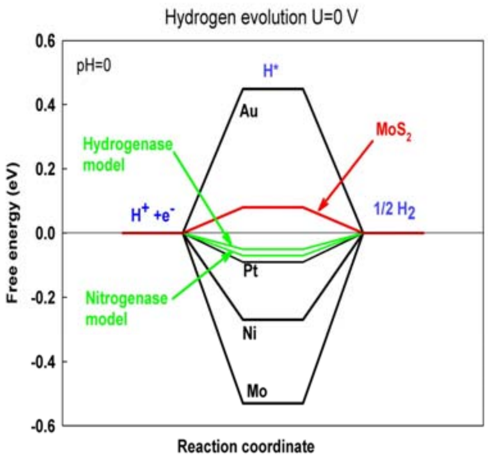


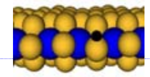
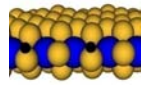
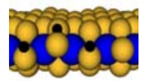
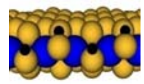





Bollinger, Jacobsen, Besenbacher, Nørskov *Phys. Rev. Lett.* 87, 196803 (2001).

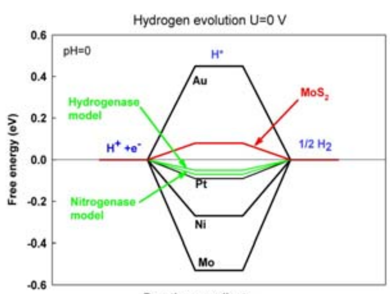
## $MoS_2$ as a catalyst for hydrogen evolution

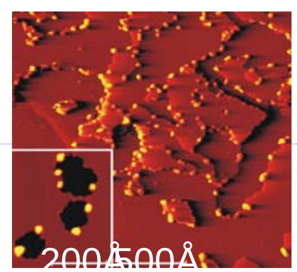



| | Model with four rows | Differential free energy (eV) |
|---|---|---|
| 25% |  | -0.33 |
| 50% |  | 0.08 |
| 75% |  | 0.76 |
| 100% |  | 0.79 |

- The coverage cannot be changed continuously.
- Probably only coverage changes between 25% and 50% contribute.

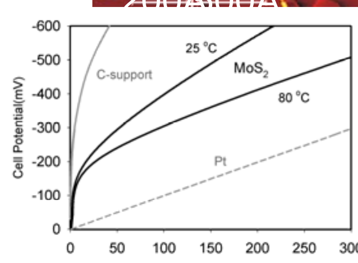
## Measurements on $MoS_2$ on Graphite




Are edge states really the active sites?

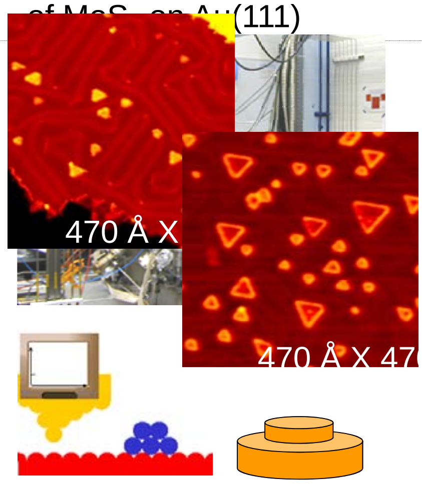
What is the activity per site ?



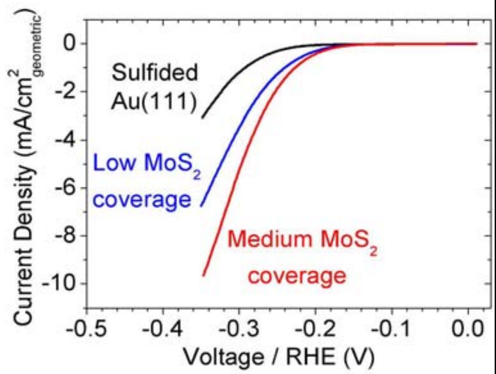

B. Hinnemann, P.G. Moses, J. Bonde, K. P. Jørgensen, J.H. Nielsen, S. Horch, I. Chorkendorff, and J.K. Nørskov, *J. Am. Chem. Soc.*, 127 (2005) 5308-5309.

## Combining surface science and electrochemistry

1) Synthesis and STM of $MoS_2$ on Au(111)



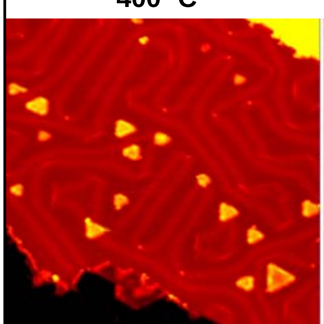
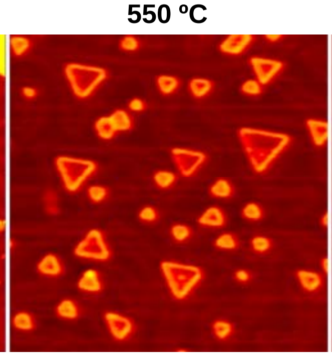
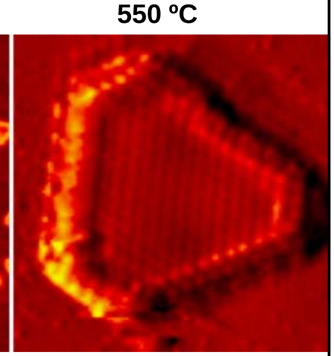

2) Measure electrochemical activity of the $MoS_2$ just



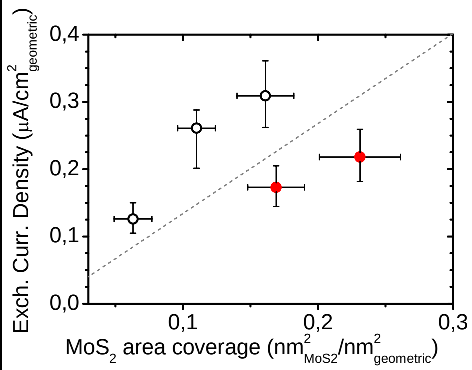

T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, Science 137 (2007) 100

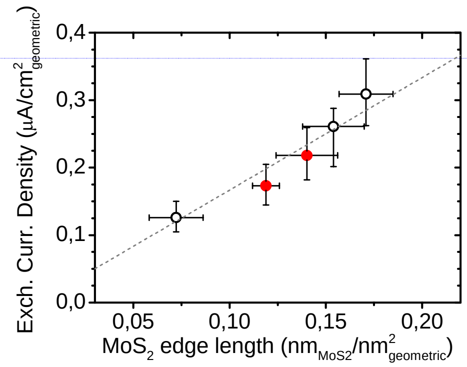
## Variation of the $MoS_2$ nano-particles

- Prepare a sample set of $MoS_2$ nanoparticles on Au(111) with variations:
  - **coverage:** controlled by Mo deposition rate / time.
  - **particle size:** controlled by sintering at elevated temperatures.

| 400 ºC | 550 ºC | 550 ºC |
|---|---|---|
|  |  |  |
| 470 Å x 470 Å | 470 Å x 470 Å | 60 Å x 60 Å |

# Exchange current density



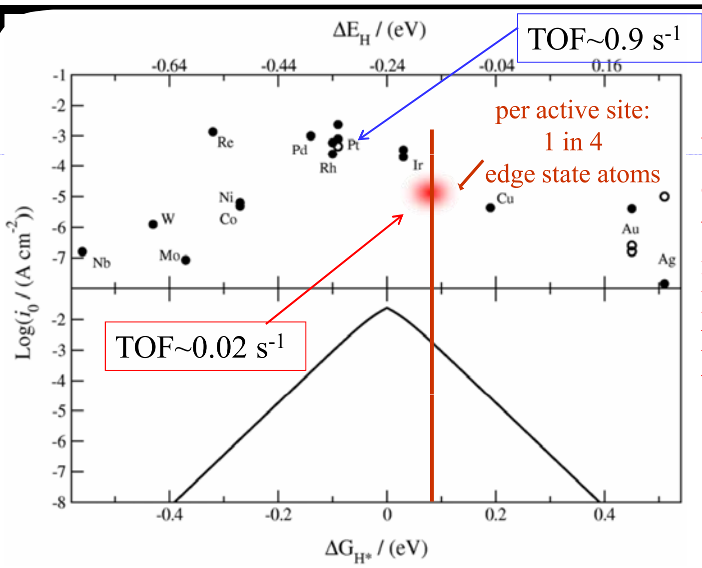




○ Annealed to 400 ºC

● Annealed to 550 ºC

T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, Science 137 (2007) 100

# $MoS_2$ on the volcano

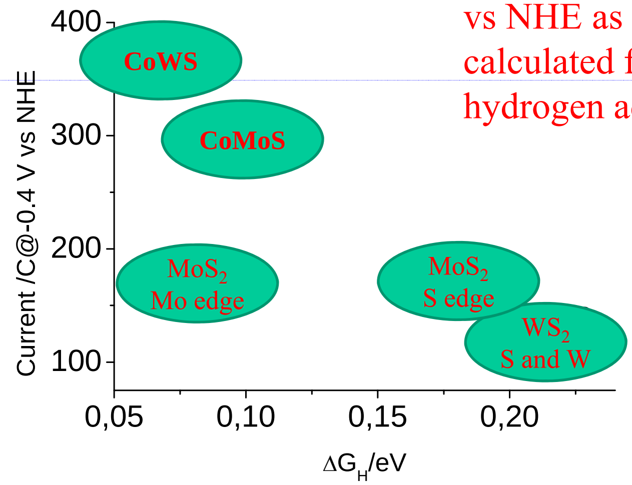



We now know exactly where to look for improvement: Increase the hydrogen bonding to the edge!

T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, Science 137 (2007) 100

# Overall trends

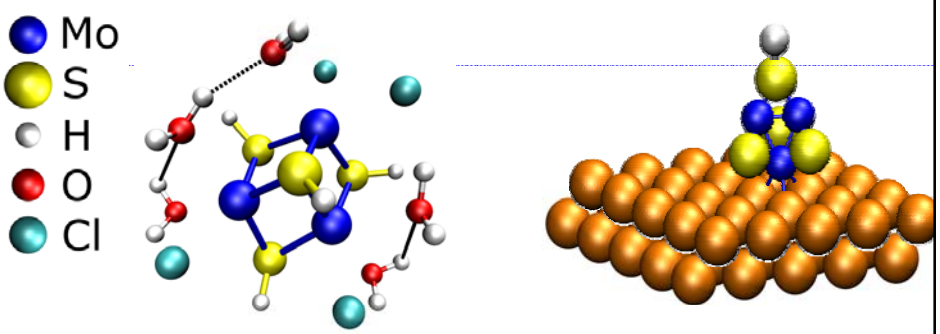
Normalized current at -0.4 V vs NHE as a function of the calculated free energies of hydrogen adsorption.




J. Bonde, P. G. Moses, T. F. Jaramillo, J. K. Nørskov, I. Chorkendorff Faraday Discussions. 140 (2008) 219-231.

# $Mo_3S_4$ going small

## Incomplete Cubanes $[Mo_3S_4]^{4+}$

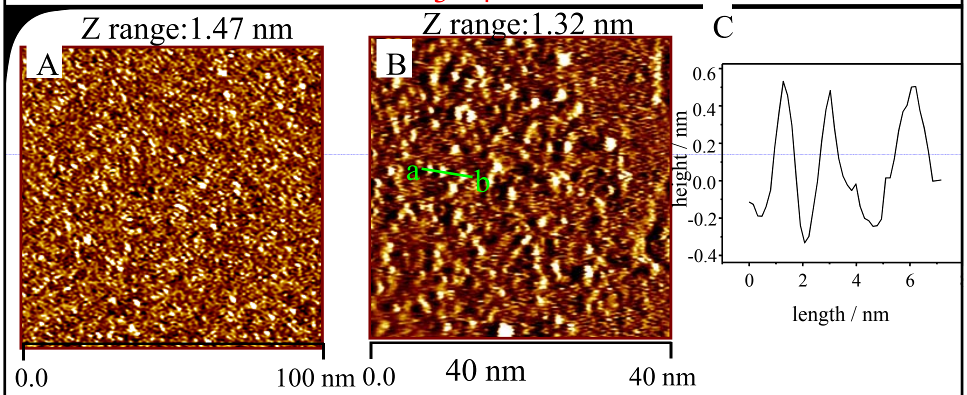



**4 $Cl^-$ to ensure charge neutrality**

The smallest entity of the active site of $MoS_2$ ?

**T. F. Jaramillo, J. Zhang, B. Lean Ooi, J. Bonde, K. Andersson, J. Ulstrup, I. Chorkendorff, J. Phys. Chem. 112 (2008) 17492.**

## STM of $Mo_3S_4$ on activated HOPG

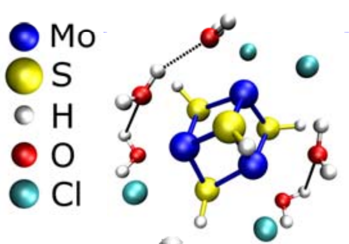


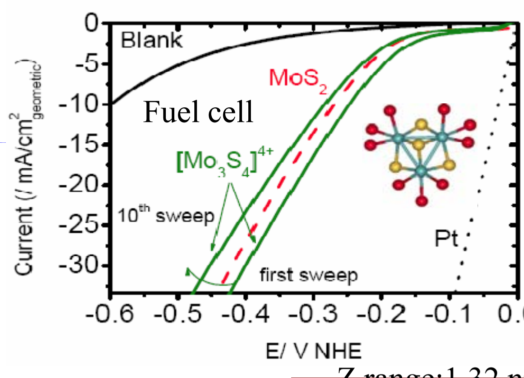

- Coverage of $Mo_3S_4$ molecule (most likely including ligands) on HOPG is approx. 1.0 (± 0.1) $x10^{13}$ molecules /$cm^2$
- Each molecule is ca. 2.0 (± 0.5) nm in diameter. Close-packed coverage is ~ 3.2 (± 0.8) x $10^{13}$ molecules /$cm^2$**.**

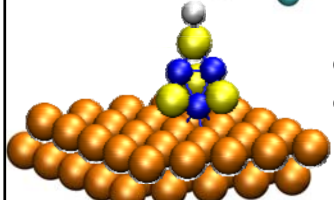
T. F. Jaramillo, J. Zhang, B. Lean Ooi, J. Bonde, K. Andersson, J. Ulstrup, I. Chorkendorff, J. Phys. Chem. 112 (2008) 17492.

## $Mo_3S_4$ going small

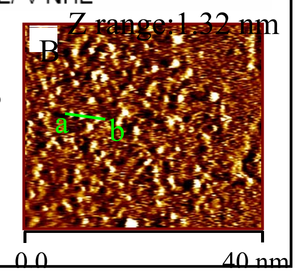
The smallest entity of the active site of $MoS_2$ ?



On graphite HOPG
Coverage $1*10^{13}$ $cm^{-2}$~1%

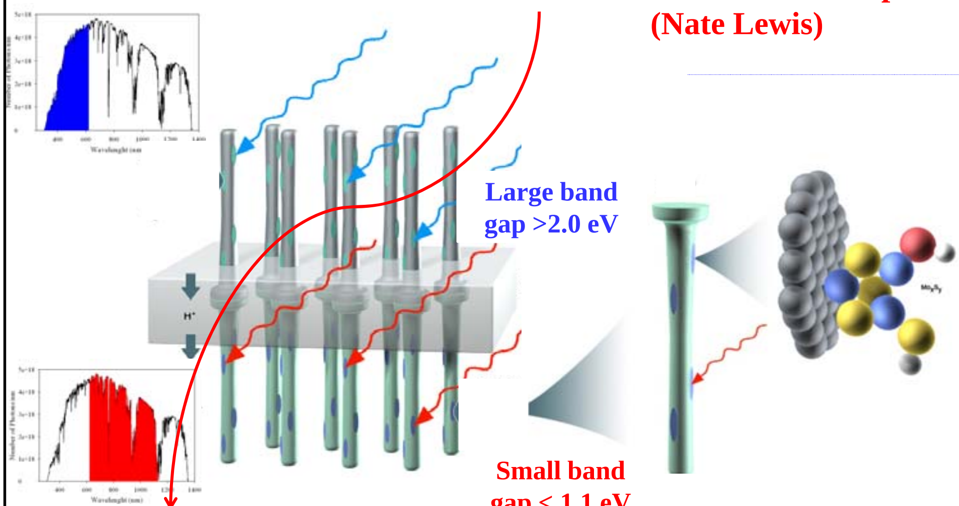



T. F. Jaramillo, J. Zhang, B. Lean Ooi, J. Bonde, K. Andersson, J. Ulstrup, I. Chorkendorff, J. Phys. Chem. 112 (2008) 17492.

# The dream device

$H_2O + 4h^+ \longrightarrow O_2 + 4H^+$

**The Helios concep (Nate Lewis)**

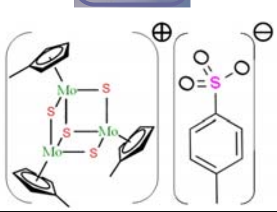



$4H^+ + 4e^- \longrightarrow 2H_2$

# Preparation

**Drop-casting**

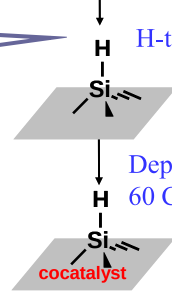
20 *u*L $Mo_3S_4$ dissolved in Dicloromethane and MeOH 1:1



**p-type (100) Si**

**HF etch**

H-terminated Si(100)

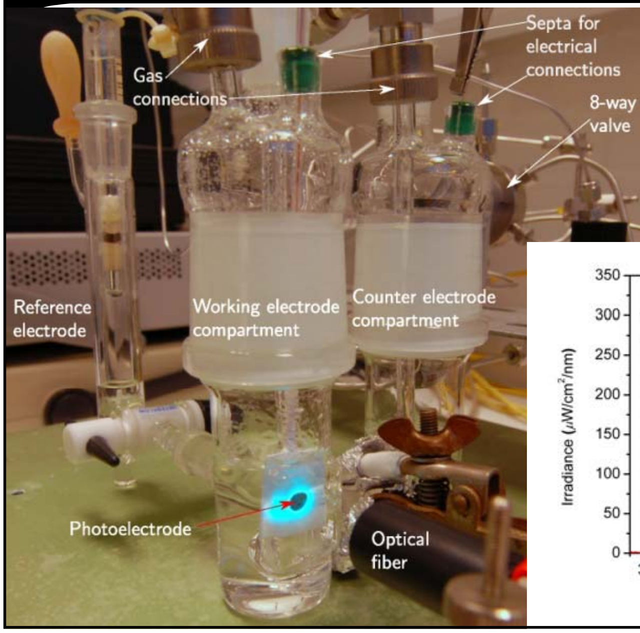



Deposit cubane and heat to 60 C to remove solvent

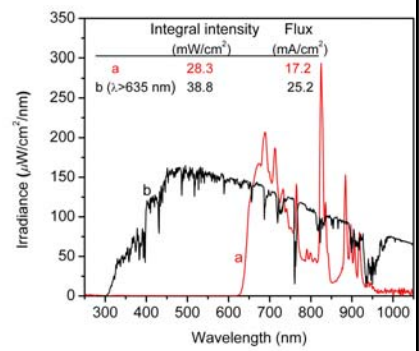
Transfer to cell

Xenon lamp with a combinatorial filters
1 M $HClO_4$ bubbling with hydrogen

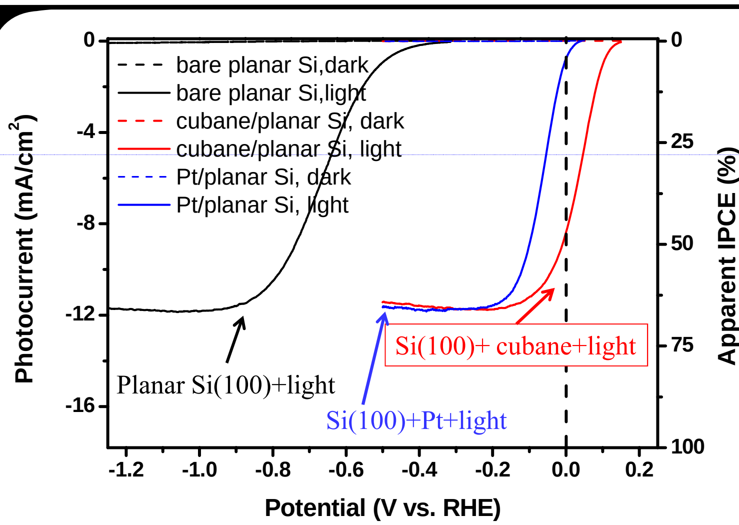
# Experimental




1000 W Xenon Lamp
"AM1.5G filter“ +
635 nm long-pass filter




# Effect of cubane on PEC activity



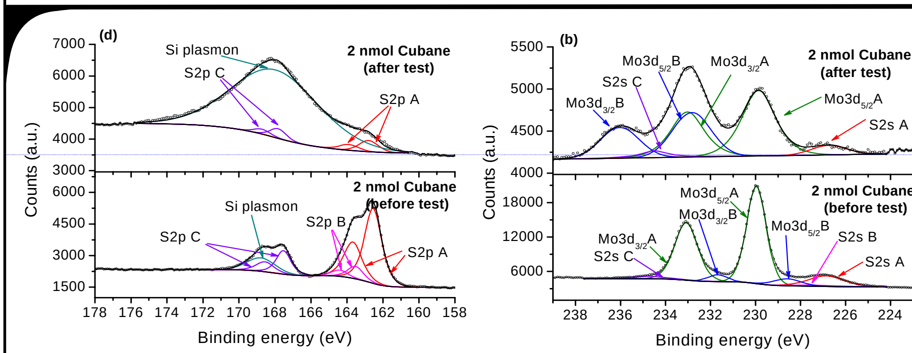

**Issues:**
Planar Si limited by low surface area

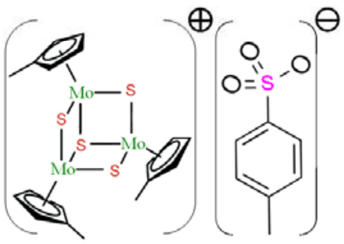
Minority carrier (e) has long diffusion length to reach the surface

The current reaches 8.4 mA/cm$^2$ over cubane/Si at 0 vs. RHE

The Pt/planar Si was prepared by photolelectrochemical reduction from 25 uM $H_2PtCl_6$ in 1M $HClO_4$

## XPS of 2nmol cubane before and after test




2 nmol-Mo: S: S(sulfonate) = **3**:**3.8**:**0.9**

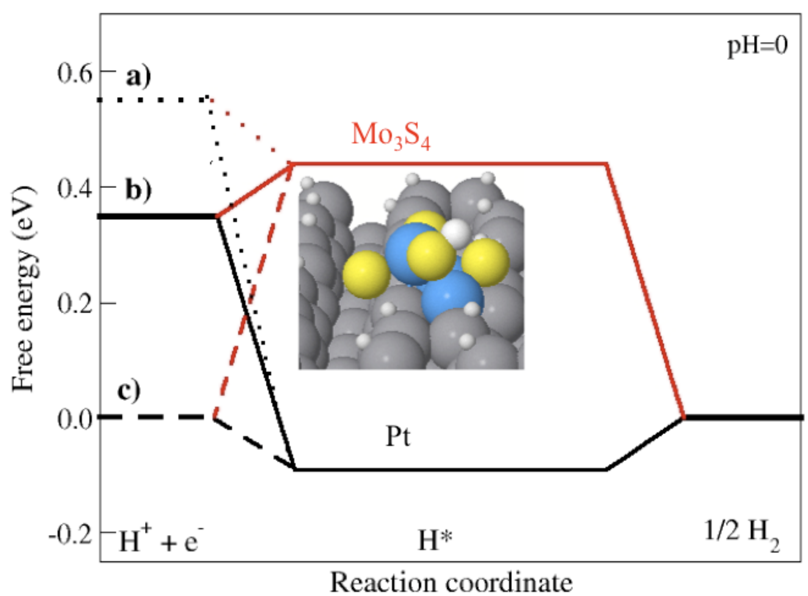
**After test**

2 nmol-Mo: S: S(sulfonate) = **3**:**2,7**:**2**

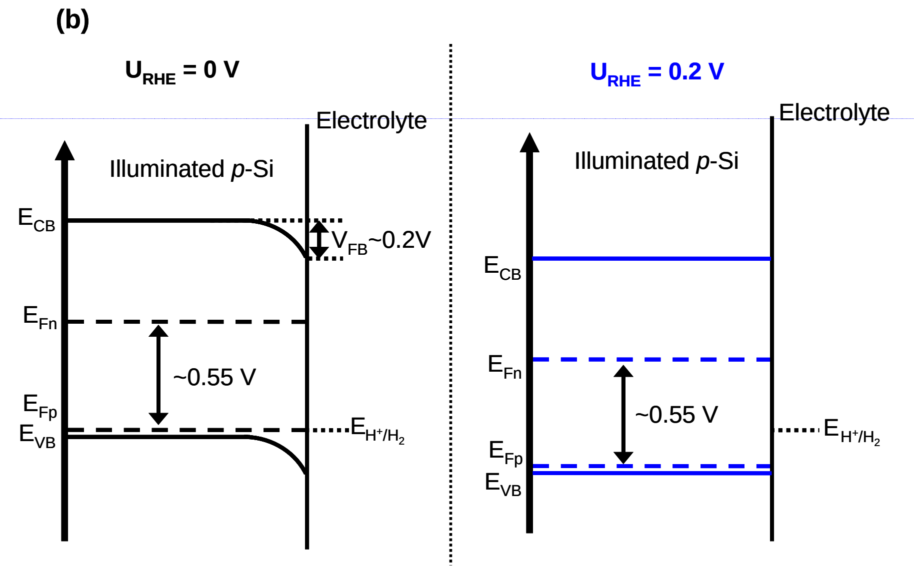
Obliviously deactivated by exposure to air by oxidation

Cubane coverage ~ 1% of a ML~$2*10^{17}m^{-2}$

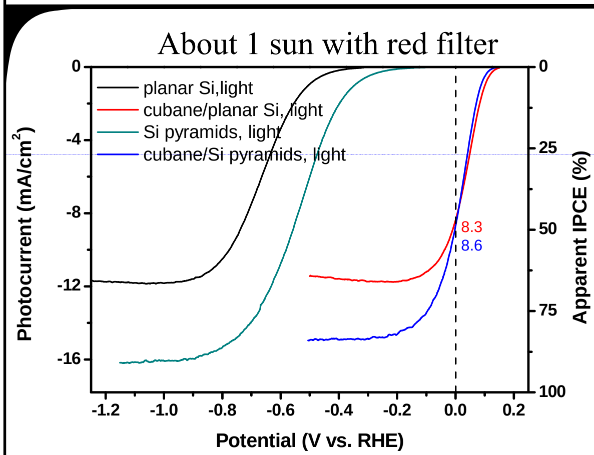
## Theoretical considerations

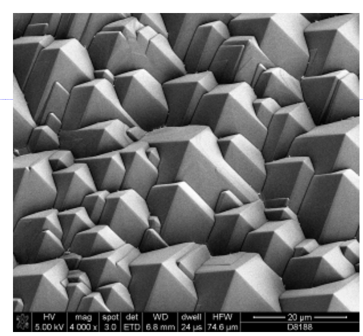


## The flat-band is shutting it of




## Si-pyramids: A Definite Enhancement

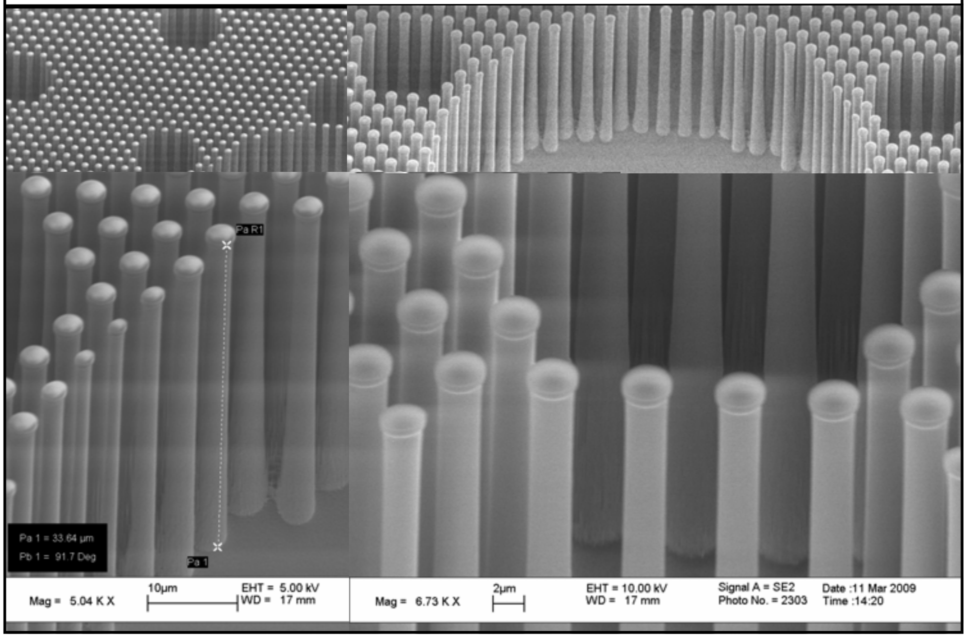


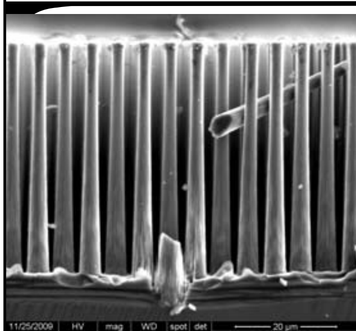
Microstructuring with 0.35 M KOH and IPA

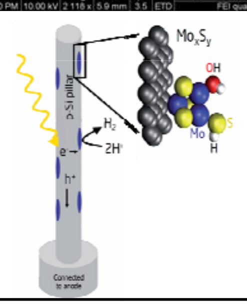
- The limiting current over Si pyramids was enhanced by 30% compared to planar Si
- Pyramid structure facilitates the release of hydrogen bubbles produced on the photoelectrode surface

## Surface Enhancement

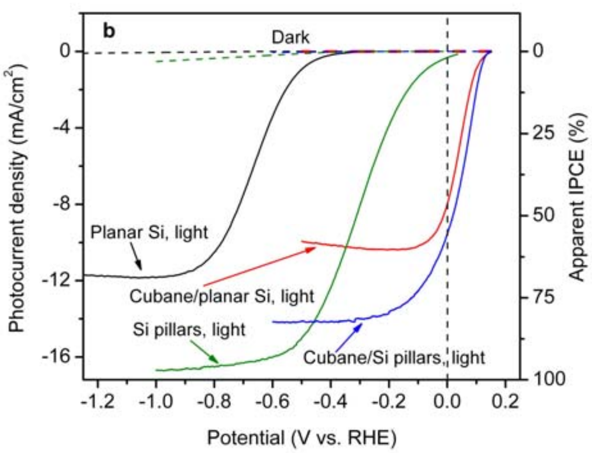



## Measurements on pillared structures



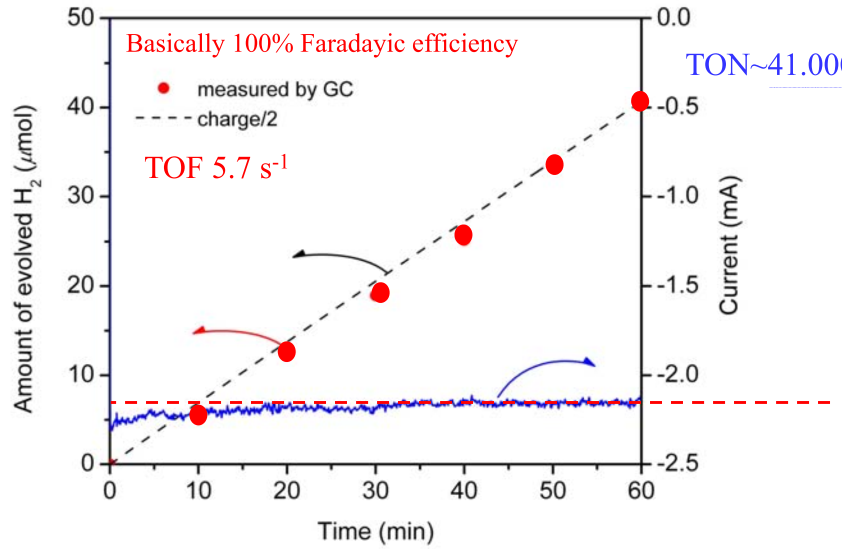



- UV-lithography and dry-etching of silicon
- 3 µm diameter circular w 6 µm spacing
- Hexagonal pattern and 60 µm long
- 32000 pillars/mm$^2$ increased area of ~15

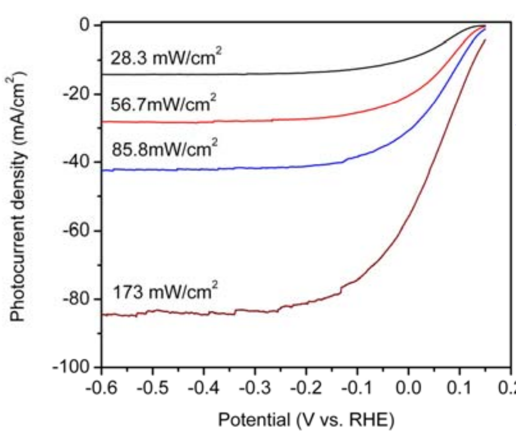


# Hydrogen evolution and stability

Pillars, (λ > 620nm, 28.3 mW/cm$^2$, Area ~0.25 cm$^2$, $V_{bias}$=0.0V




# The pillared structure scales linear with light intensity

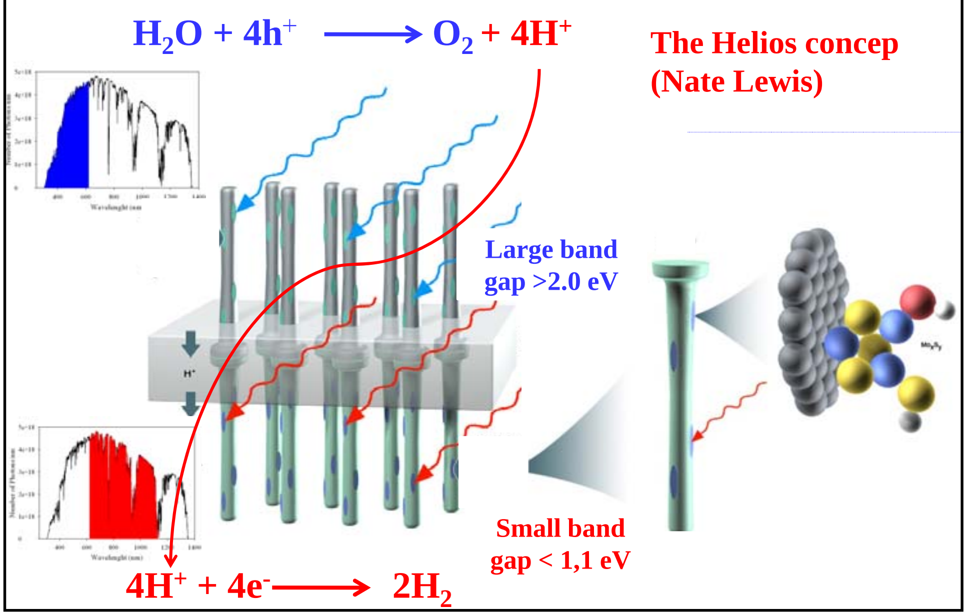


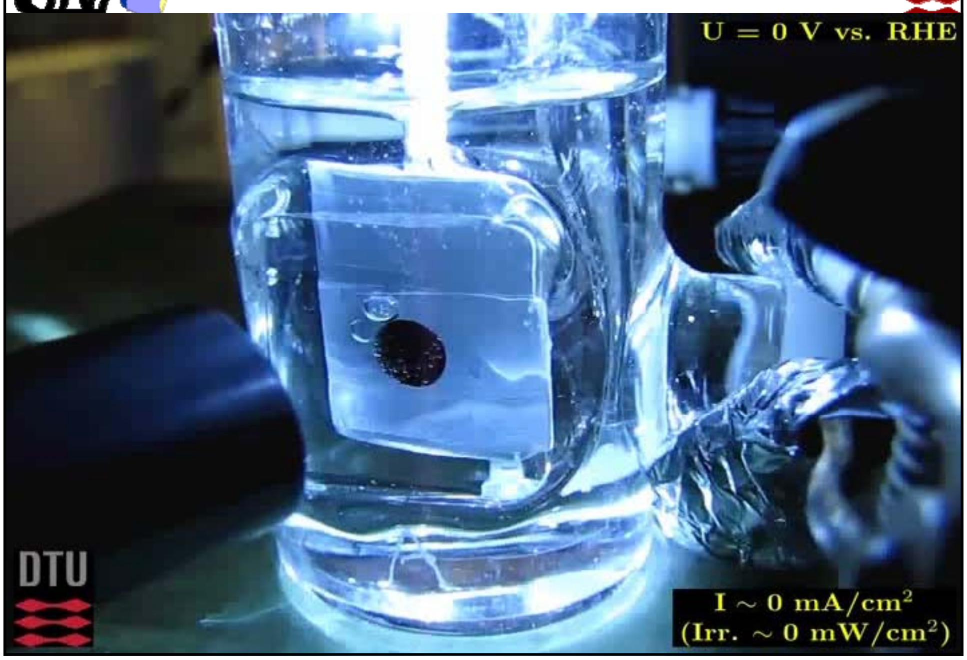

Could be important if focusing the light.

Naturally Si(100) is way too Expensive, but Nate Lewis have made extensive studies in optimizing growth of such pillared structure by much cheaper CVD processes.

Boettcher S. W. *et al.*: Energy-conversion properties of vapor-liquid-solid grown Silicon wire-array photocathodes. *Science* **327**, 185-187 (2010).

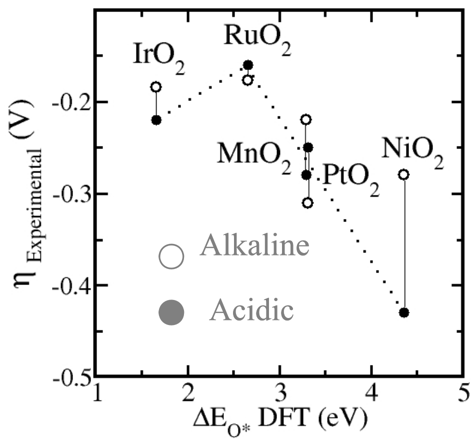
## The dream device: The real challenge



## The Oxygen evolution is the hard part

Experiments from: S. Trasatti. *Electrochimica Acta.* **29**, (1984), 1503.

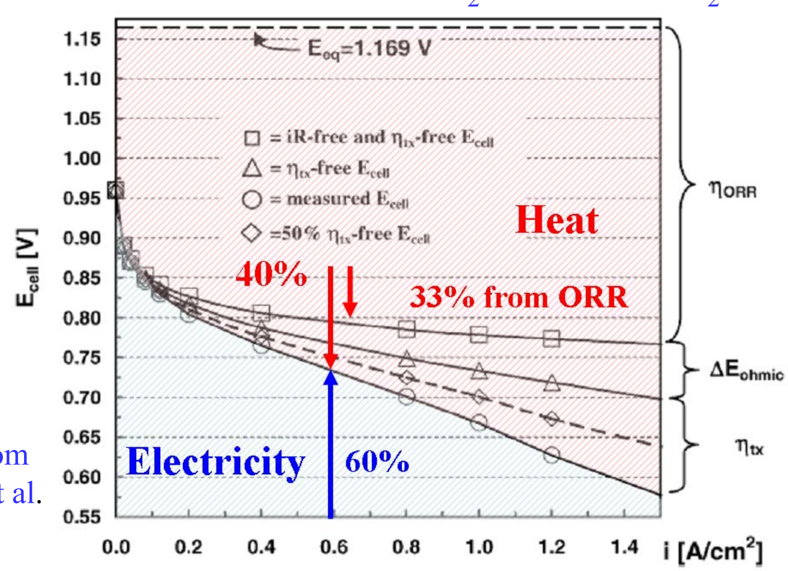



Must be combined with a 2.0 eV band gap material that is stable under extreme oxidizing conditions

H.A. Hansen, Rossmeisl, 2008

## The Major loss in ORR and OER

The anode reaction in a fuel cell: $O_2 + 4H^+ + 4e^- = 2H_2O$

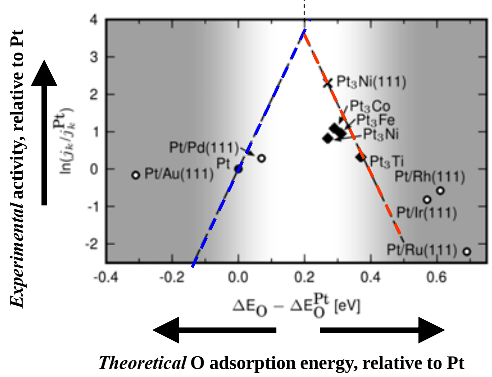



Adapted from Gasteiger et al.

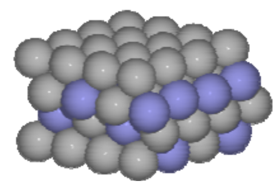
## Theoretical trends for oxygen reduction

**Using $\Delta E_O$ as a 'descriptor' for Pt alloys**

**O binds too strongly:** | **O binds too weakly:**




**All catalysts with 'Pt-skin' overlayers**

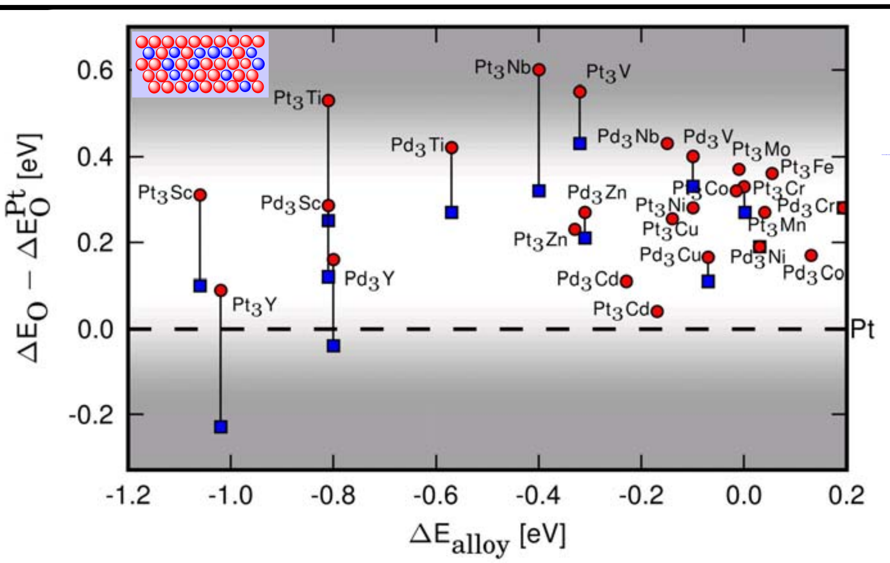


**Need to search for new Pt-alloy catalyst with**

$$\Delta E_O - \Delta E_O^{Pt} \sim 0.2 \text{ eV}$$

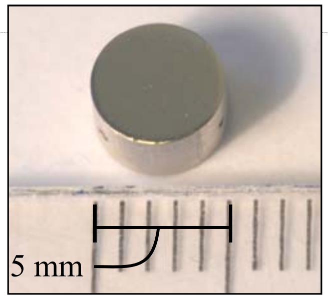
Experimental data from: Zhang et al Angew. Chem. Int. Ed., 2005; Stamenkovic et al, Angew. Chem, Int. Ed 2006; Stamenkovic et al, Science, 2007

## Screening of $Pt_3X$ and $Pd_3X$ alloys




Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

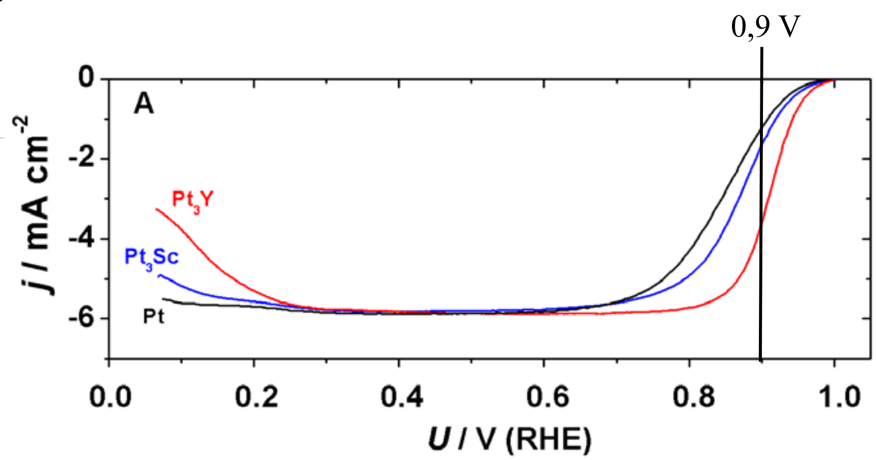
## Experimental verification of theory: Activity measurements of Pt, $Pt_3Y$ and $Pt_3Sc$




Polycrystalline Pt, $Pt_3Sc$ and $Pt_3Y$ disc electrodes cleaned and characterised under ultra high vacuum conditions.

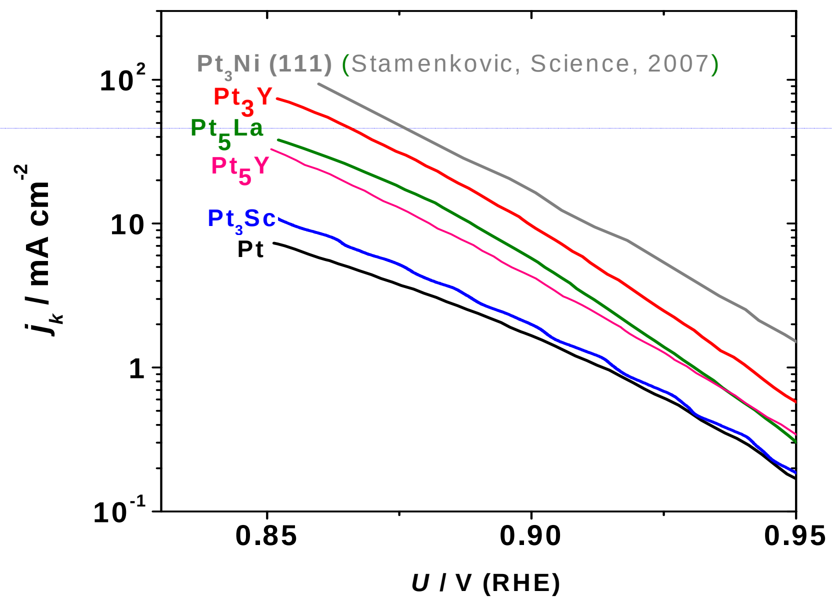
Rotating disc electrode (RDE) measurements in liquid cell with $O_2$-saturated 0.1 M $HClO_4$ solution, at room temperature.

## Measured polarization curves




Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

## Kinetic current at 60 ºC, (now including $Pt_3Sc$ and $Pt_5Y$ and $Pt_3La$)

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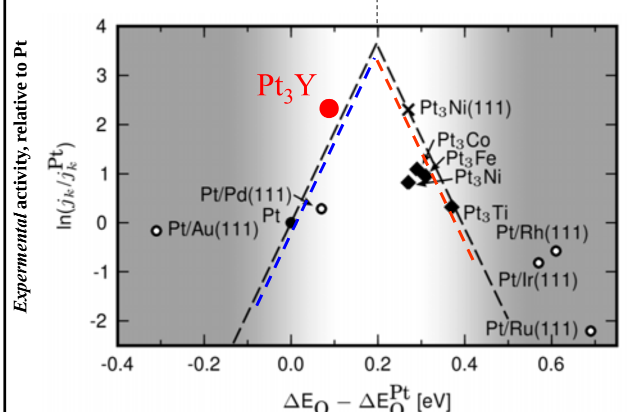


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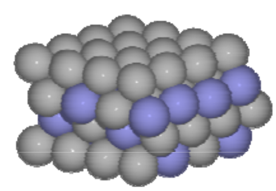

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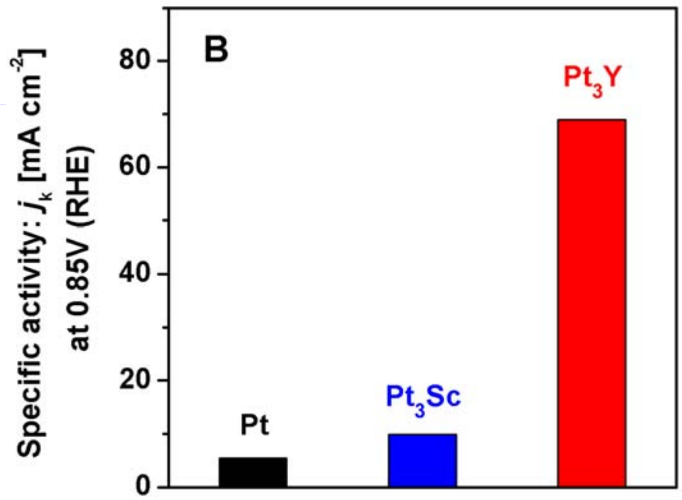
Experimental data from: Zhang et al Angew. Chem. Int. Ed., 2005; Stamenkovic et al, Angew. Chem, Int. Ed 2006; Stamenkovic et al, Science, 2007

# Kinetic rates




Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

# Summary of Approach

- Inspiration by the Nitrogenase enzyme leads us to $MoS_2$ or WS2 which in **nano-particulate** form are showing useful characteristic for HER and can be promoted by Co
- Even smaller entities like the incomplete cubanes display interesting effects and the overpotential may be reduced when considering the moderate current for photoelectrolysis
- The Cubanes can be coupled to p-Si nano-structures and the over potential can be negated by utilizing the otherwise useless part of the solar spectrum matching a say 10 % efficiency for water splitting.
- Ultimate goal is to produce and average energy by for example coupling the hydrogen production with storable fuels like $NH_3$ or $CH_3OH$ by direct hydrogenation of $N_2$ or $CO_2$

# New Nano-materials

It might be a good idea for mankind to be in some sort of balance with Nature

We need a Revolution on the Energy Production

We need super bright people You_!!!!