Chapter V: Heterogeneous catalysts for HER

Table of contents

I. Mechanistic aspects and benchmark

Mechanism of hydrogen evolution on a heterogeneous surface

In acidic conditions:

Discharge reaction (Volmer step) $H_3O^+ + e + cat \rightleftharpoons cat—H + H_2O$

Ion + atom reaction (Heyrovsky step) $cat—H + H_3O^+ + e \rightleftharpoons cat + H_2 + H_2O$

Combination reaction (Tafel step) $cat—H + cat—H \rightleftharpoons 2\,cat + H_2$

In neutral to basic conditions:

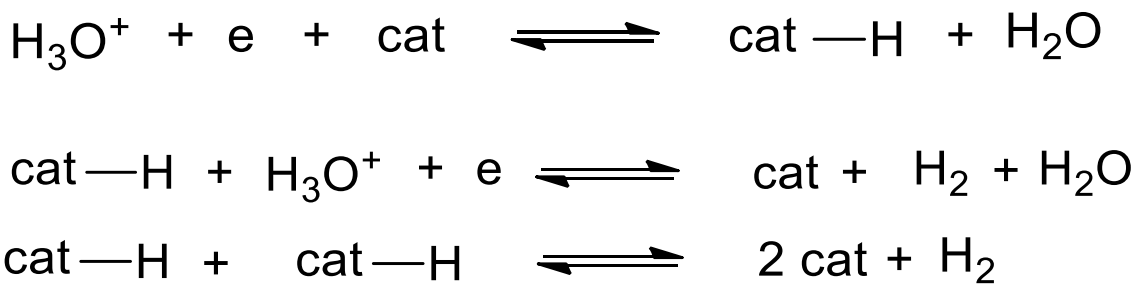
Discharge reaction (Volmer step) $H_2O + e + cat \rightleftharpoons cat—H + HO^-$

Ion + atom reaction (Heyrovsky step) $cat—H + H_2O + e \rightleftharpoons cat + H_2 + HO^-$

Combination reaction (Tafel step) $cat—H + cat—H \rightleftharpoons 2\,cat + H_2$

The catalyst serves to lower the energy of intermediates.

Catalytic performance correlates with M-H

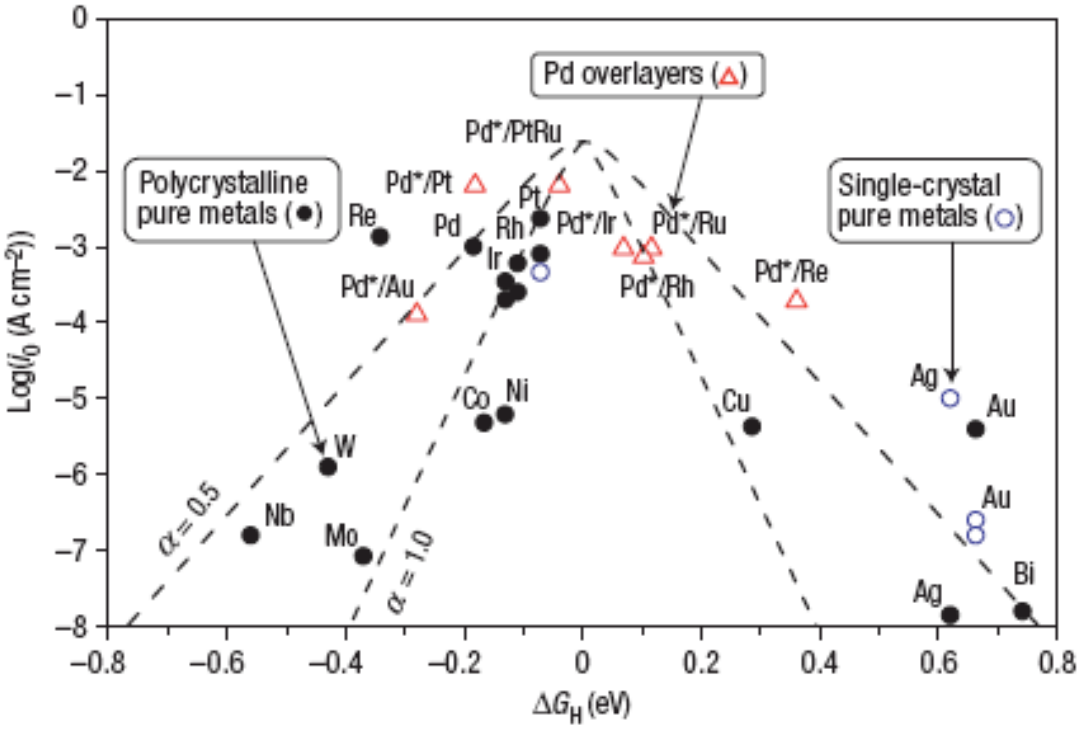


If M-H is too strong, then it is hard to get H out of M,
so the hydrogen formation step is not efficient.

If M-H is too weak, there is not enough stablization of M-H,
so the first step is not efficient.

A good comprise is to have a optimal value for M-H. Pt and other precious metals happen to have the more optimal M-H values. That is why they are good HER catalysts.

Hydrogen adsorption energy is related to catalyst performance



Free energy of absorption of H atom

Figure 1 **Volcano plot for the HER for various pure metals and metal overlayers.**

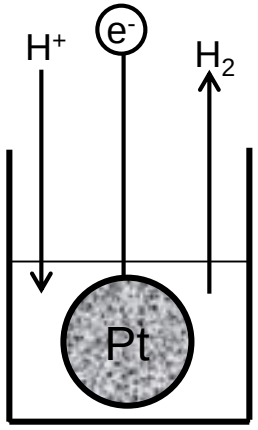
$$H^+ + e + cat \rightleftharpoons cat—H$$

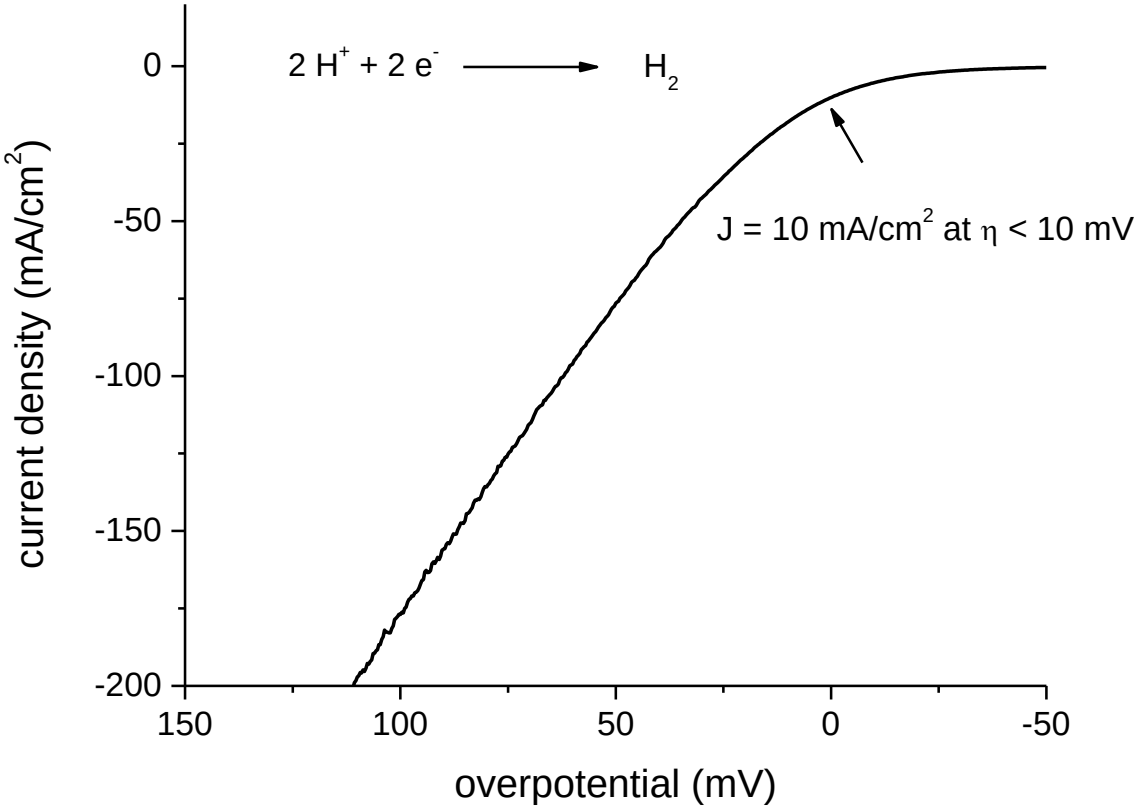
The M-H energy is a “descriptor” for catalysts

Greeley et. al., Nature Materials, 5 (2006) 909

Pt as a catalyst for hydrogen evolution

Pt is the best catalyst for HER.





Overpotential and energy efficiency

In electrochemistry, the potential is always measured against a reference electrode. We have already said that potential is a measure of energy input. To compare energy efficiency, the potential can be converted to **overpotential**.

Overpotential is the potential difference between a given potential under discussion and the thermodynamic potential for a reversible reaction.

η = E(working) – E(reversible)

The thermodynamic potential need to be measured or calculated separately.

In some literature, η is taken as an absolute value.

Overpotential and energy efficiency

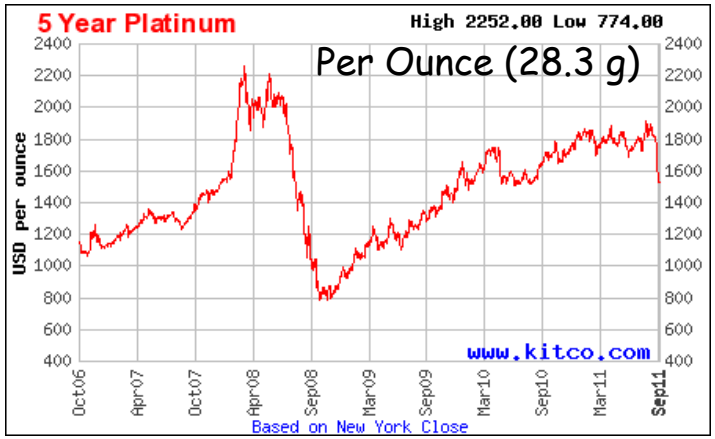
Overpotential is related to the energy efficiency of an electrochemical system.

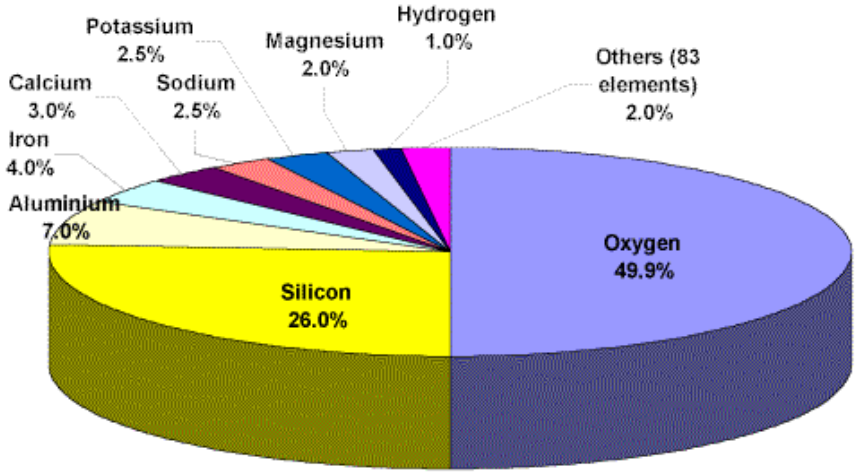
Considering for example water splitting.

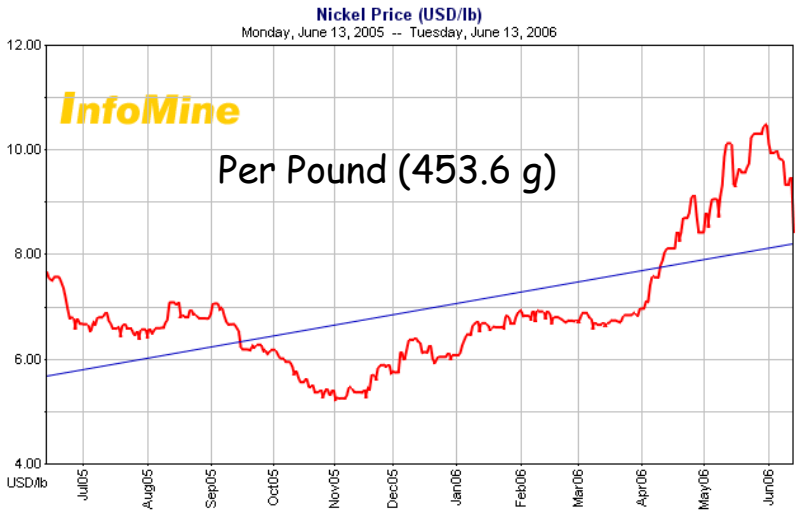
The overall thermodynamic voltage for the reaction is 1.23 V at room temp.
For a practical device, the total voltage is
$V = \eta(HER) + \eta(OER) + iR(electrolyte) + 1.23$
HER and OER are the hydrogen and oxygen evolution reactions. iR is the voltage loss from the resistance of electrolyte solution. Neglecting iR for the moment, if $\eta(HER) + \eta(OER) = 0.3$, then the efficiency is 1.23/1.53 = 80%. if $\eta(HER) + \eta(OER) = 0.6$, then the efficiency is lower than 1.23/1.83 = 67%.

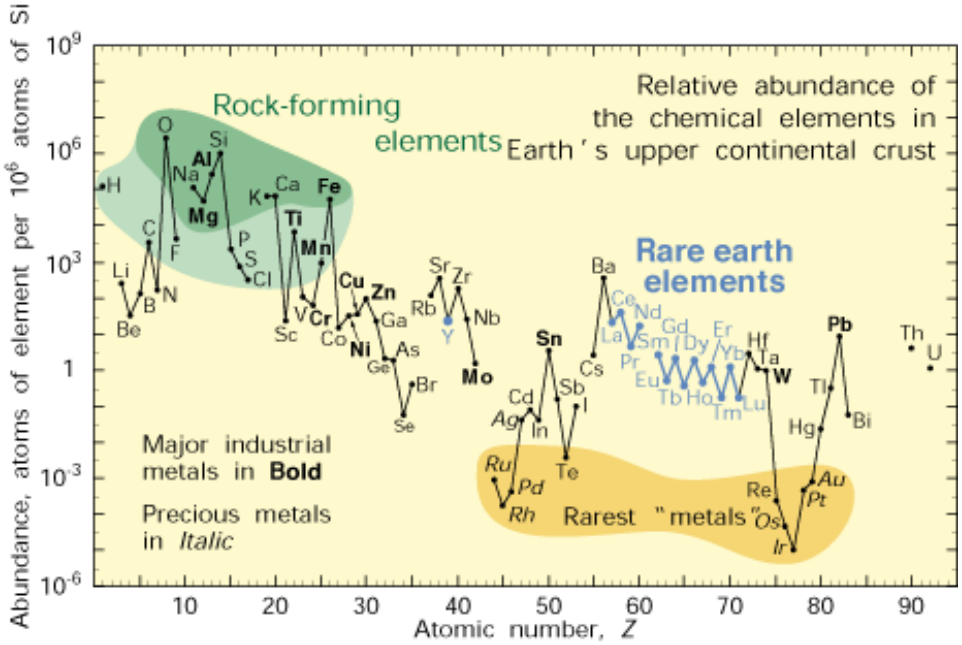
It is now clear that overpotential need to minimized while maintaining a rapid reaction rate for water splitting (high TOF). This is where catalysis comes in play. Without catalyst, both HER and OER are very slow even at a high overpotential (> 500 mV each).

Pt: Cost & Abundance?









Problem of Pt as HER catalyst

Rare:
Require 500 tons of Pt for HER for 1 TW of energy.
But < 200 tons of Pt produced a year;
Pt is used for many other processes such as fuel cells and car exhaust catalysts.
Faire to say – not enough Pt.

Expensive:
60 CHF per gram. Price will go up if Pt is used in a large industrial application.

Therefore, we need to develop HER catalysts that are:
(1)based on earth-abundant elements.
(2)Inexpensive.

Challenge: all good catalysts in the «Volcano plot» in page 5 are precious metals.

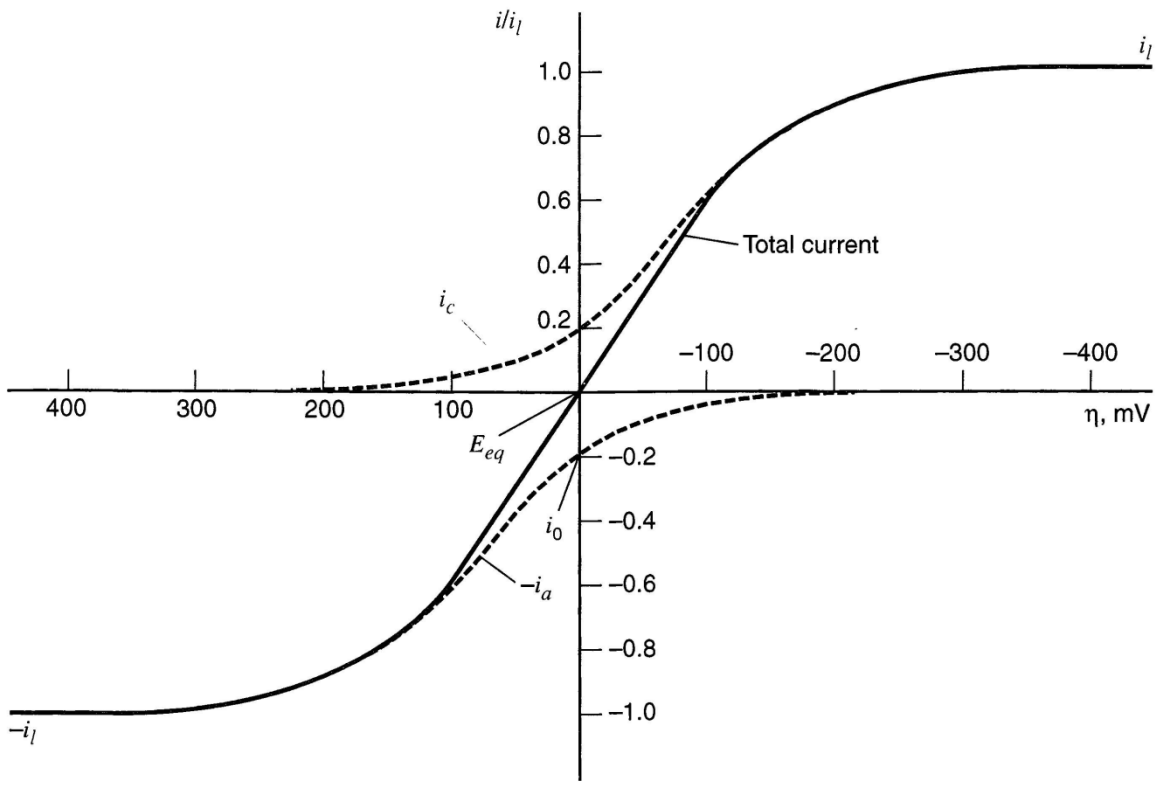
II. Tafel analysis

Now, we seek a quantitative description of the current-potential relation. We use a reversible reaction as the example. Here, we learn the concepts of exchange current density and Tafel slops. Importantly, the Tafel equation is introduced.

The exchange current density and Tafel slops are two common parameters that describe the kinetics of an electrochemical reaction.

This approach is not only used in reversible reactions, but also irreversible reactions. Even with a catalyst, HER and OER are often irreversible.

For a reversible reaction on surface: $Ox + e \leftrightarrow Red \quad E^o$



$$i = FAk^0 \left[C_{\mathrm{O}}(0,t) e^{-\alpha f (E - E^{0'})} - C_{\mathrm{R}}(0,t) e^{(1-\alpha) f (E - E^{0'})} \right]$$

f = F/RT, C_o, C_R = concentration
α = transfer coefficient

When $|\eta| >= 100$ mV, the back-reaction is insignificant and can be neglected

In electrochemistry, the Tafel equation is widely used:

$$\eta = a + b \log j$$

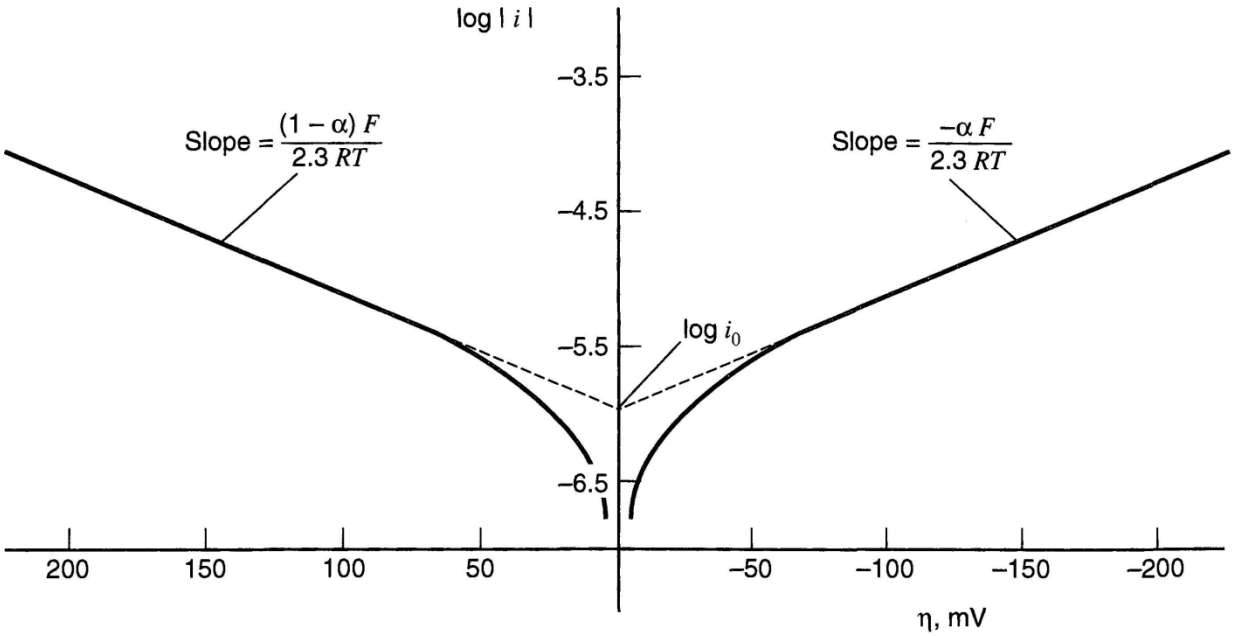
This equation correlates the thermodynamic energy input (η) with the rate of the reaction (j)

It has been deduced that $a = (2.3RT/\alpha F)\log j^o$, $b = -(2.3RT/\alpha F)$

j^o is called exchange current density
b is called Tafel slope
α Is called asymmetric factor, $0 < \alpha < 1$; often taken as 0.5

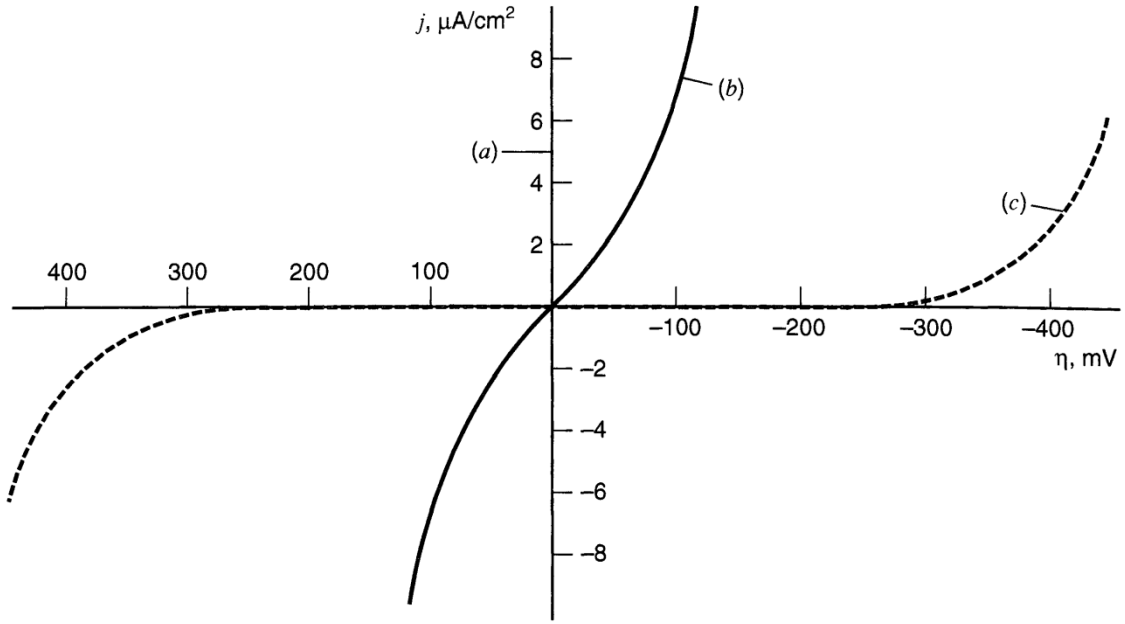
when $\alpha = 0.5$, b = 118 at r.t

Plot of log i and overpotential can give i_o and Tafel slope



In electrochemistry, we use current density to describe the reaction rate J = i/A, i is the current, and A is the surface area.

Effect of j_o on the current-potential plot

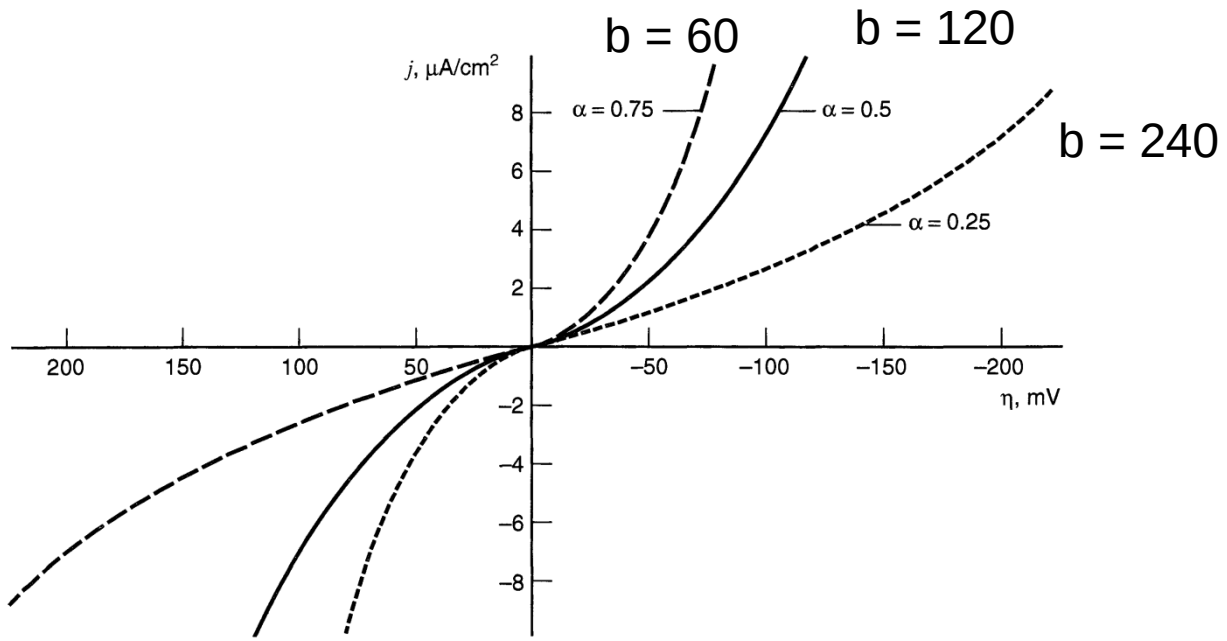


(a)j_o = 10^{-3} A/cm^2 (curve is indistinguishable from the current axis),
(b)j_0 = 10^{-6} A/cm^2, *(c)*j_0 = 10^{-9} A/cm^2. The Tafel slope is 120 for all curves.

A small exchange current density leads to a deteable current only at a high overpotential. In this case, the reaction appears irreversible (curve C).
Most catalytic HER, OER, and CO_2 reduction reactions have curves similar to C, that is, they appear irreversible.

Effect of Tafel slope on the current-potential plot

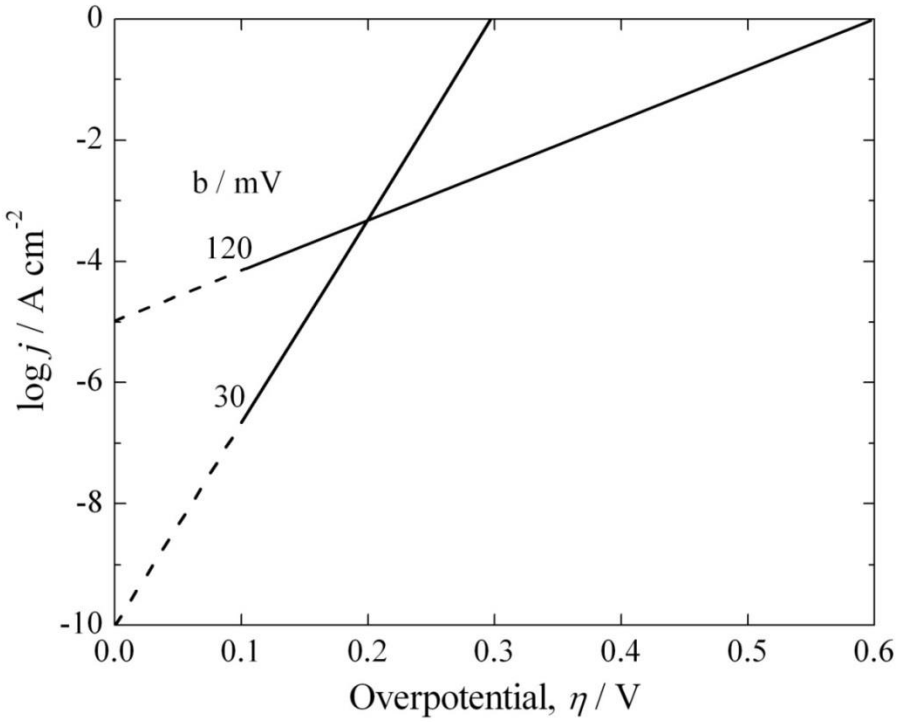
Tafel slope b = -(2.3RT/αF),



j_0 = 10^{-6} A/cm^2 for all curves with different Tafel slops.

A small Tafel slope is desriable as the current increases more rapidly with the increase of overpotential.

Exchange current density and Tafel slope can be used to judge the practicality of a catalyst for an electrochemical reaction.
A catalyst with a high exchange density and low Tafel slope is desirable.
If a catalyst cannot have both, then the situation is more complicated. The performance of catalyst depends on conditions.



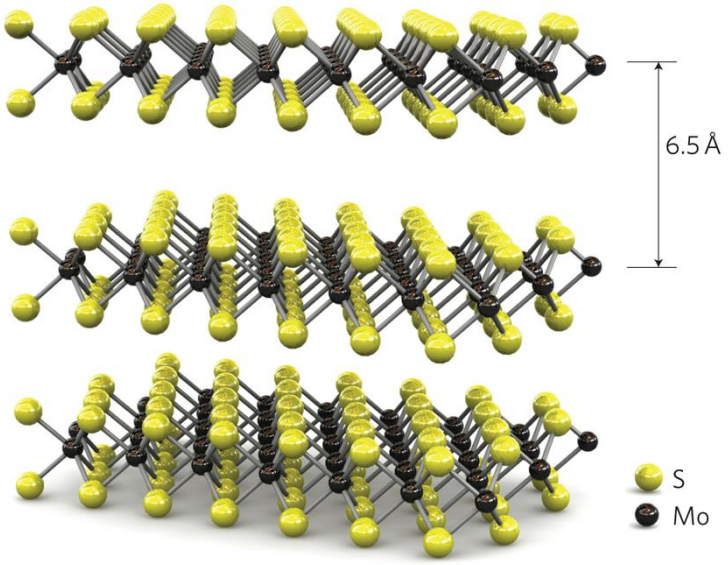
Comparison of two catalysts: one has a higher exchange current density but higher Tafel slope; the other has a lower exchange current density but lower Tafel slope.

What is a better catalyst ??? Depending on the conditions.
At a low overpotential, the catalyst gives a Tafel slope of 120 is preferred; at a high overpotential, the catalyst that gives a Tafel slope of 30 is preferred.

We will now present several case studies of non-precious HER catalysts (heterogeneous). We do not intend to know all existing catalysts in this course. Rather, we study representative and state-of-the-art catalysts. These examples expose us to an active area of research and its basic methodologies.

III. HER catalyzed by MoS_2

Background about MoS_2



MoS_2 is the main component of molybdenite, a mineral.

MoS_2 can also be synthesized by reacting MoO_3 with H_2S, or Mo with H_2S.

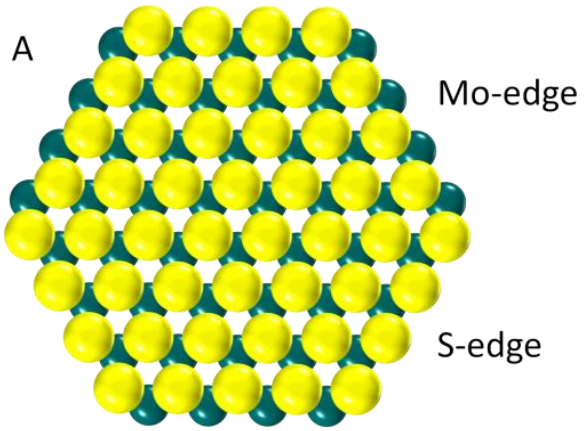
Both Mo and S are earth-abundant. Concentration in earth-crust: Mo: 1ppm; S: 400 ppm. Pt: 0.003 ppm.

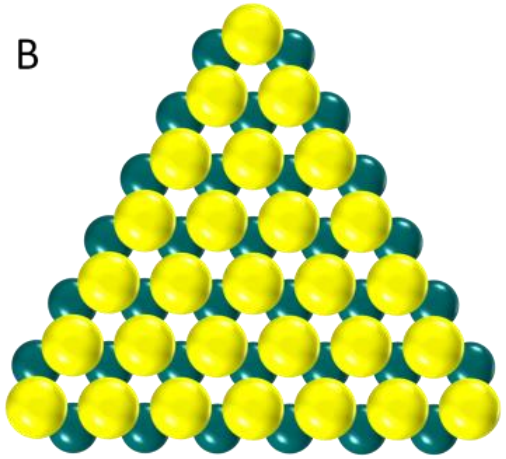
MoS_2 has a layer structure. Each layer of MoS_2 is held together by Van der Waals interaction. The distance between two layers is 6.5 Å.

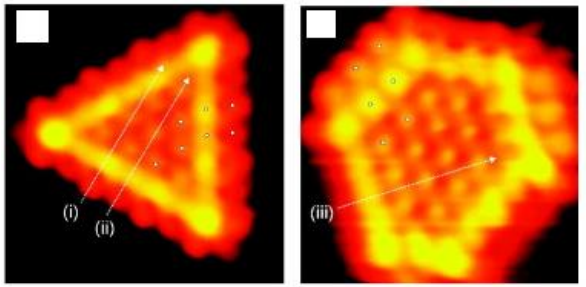
It is used as lubricant and as catalyst for hydrotreating of crude petro products, to remove sulfur impurities.

Layer structure of MoS_2

In each layer of MoS_2, the Mo and S atoms are packed in a hexagonal manner. The first layer is S, then Mo, and then S. For a hexagonal slab of MoS_2, there are two type of edges (Figure A). The Mo edge exposes Mo atoms; the S edge exposes S atoms.
It is possible to control the morphology of the MoS2 crystal, so a trigonal slab is formed (Figure B). Here, most of the edges are the Mo edges.
The shape of the crystal can be obseved by Sanning Tunnel Microscopy (STM). The bright spots in STM are metallic spots. In the case of MoS_2, they represent Mo atoms.

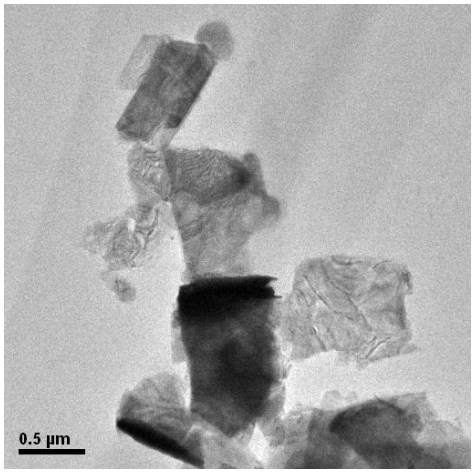




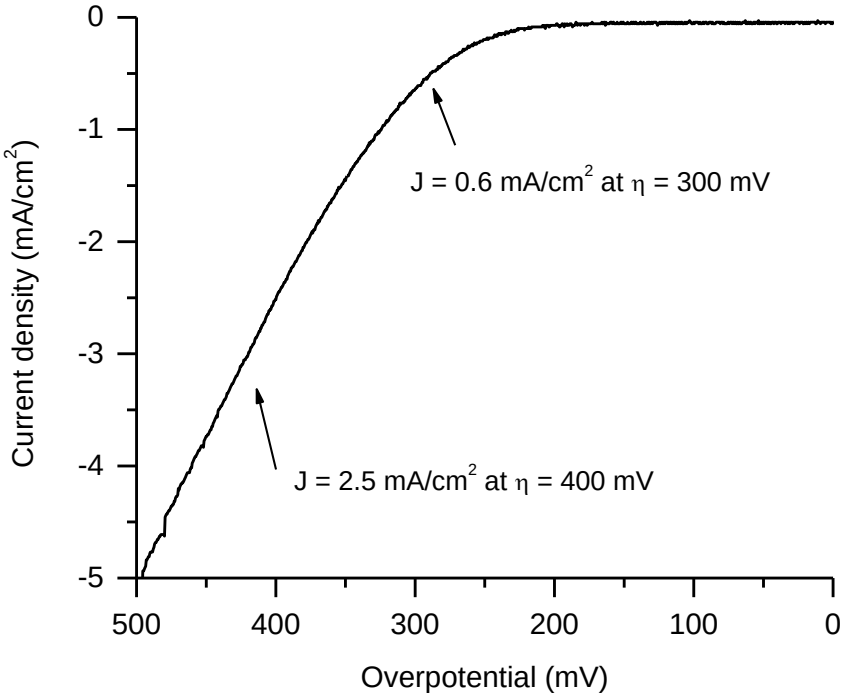


MoS_2 as HER catalyst

MoS_2 was studied in the 1970s as catalyst for hydrogen evolution. The activity is modest. Here I show you a current-potential curve (often called polarization curve in the literature) of MoS_2 microcrystals.



commercial MoS_2 particles
Particle size about 1 µm



We can see from the figure in the right that the current density is small at a high overpotential. So it looks like that MoS_2 is not a good HER catalyst. But the story does not stop here.

Catalyst Design for H_2 Evolution

- The next stage of the story took place in 2005. MoS_2 again drew attention thanks to a computationl study.

Research in heterogeneous catalysis is often empirical; but people are trying to add some rational design in the research. One way is to use computational chemistry. This is not easy, because catalysis is related to activation energy, and DFT still cannot get the activation energy to a good accuracy. On the other hand, the thermal energy of a reaction can be calculated at a reasonable accuray.

One can use this thermal energy to screen for a potential good catalyst. Because for a good catalyst for a multiple-step reactions, each step cannot be too exothermic or endothermic (regardless the reaction mechanism).

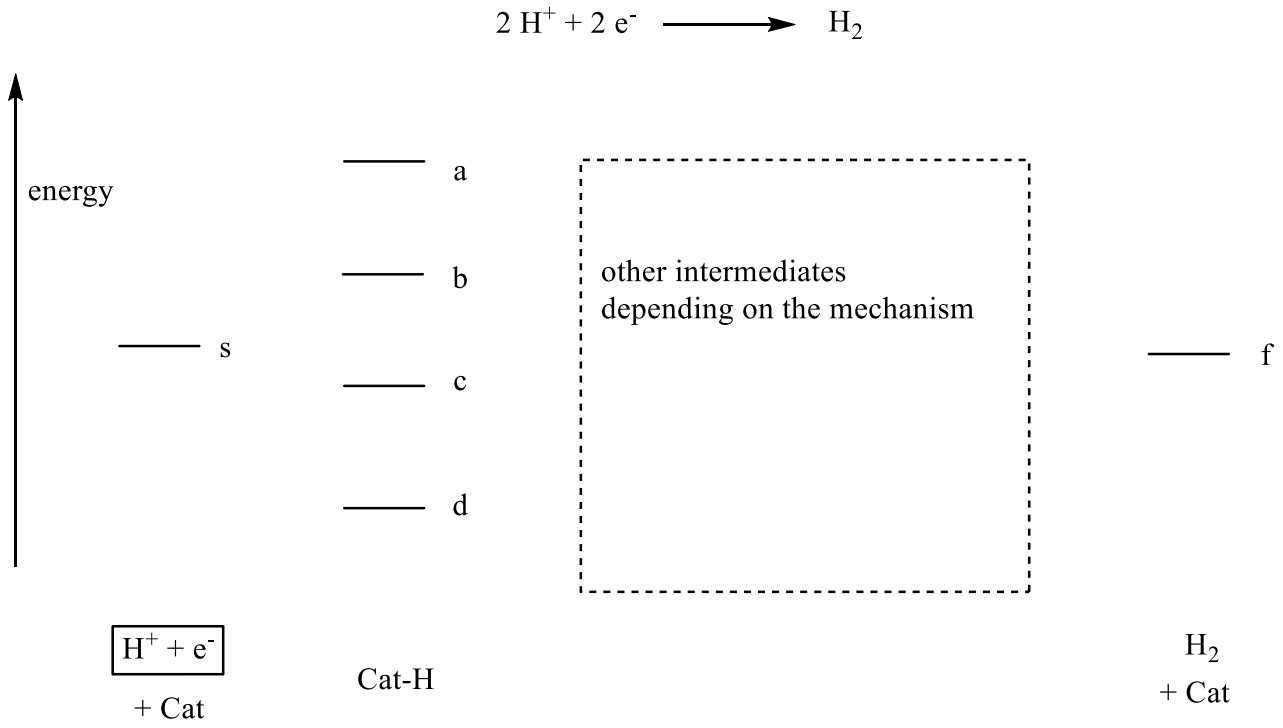
Catalyst Design for H_2 Evolution

$$2H^+ + 2e^- \rightleftharpoons H_2$$

discharge reaction	$H_3O^+ + e + cat \rightleftharpoons cat—H + H_2O$	(1)
ion + atom reaction	$H_3O^+ + e + cat—H \rightleftharpoons cat + H_2 + H_2O$	(2)
combination reaction	$cat—H + cat—H \rightleftharpoons 2\ cat + H_2$	(3)

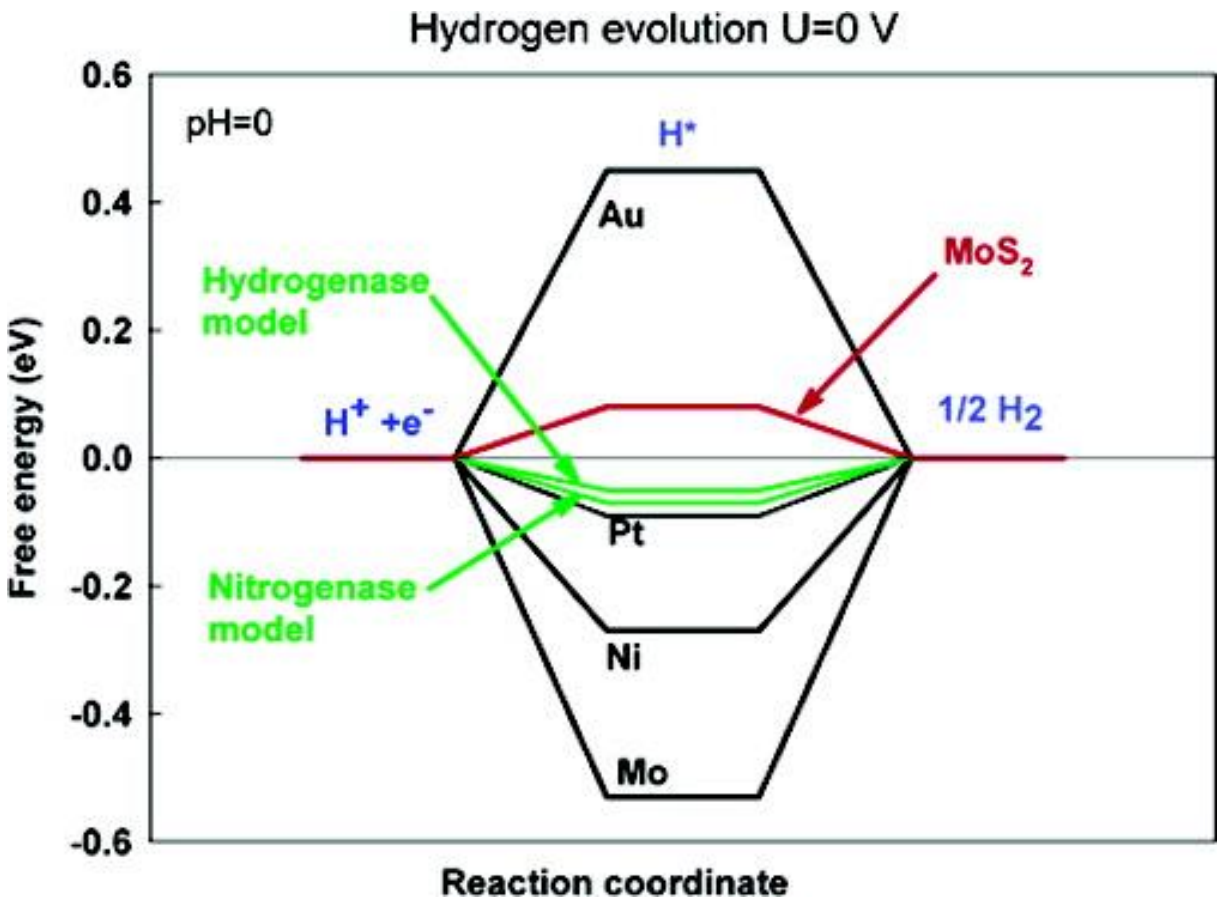
For HER, H_2 can be produced either by reaction (2) or by reaction (3). It depends on the catalyst.
As said, the calculation of activation barrier for each step is difficult.
However, the calculation of thermal energy for each step is possible.
For HER, one can even just compare the themal energy for reaction (1).

Catalyst Design for H_2 Evolution



A different catalyst would give a different intermediate Cat-H. The energies of these Cat-H are different. It could be a, b, c, or d. These energies can be calculated.
If this energy is too positive, e.g., is at a, then a large activation energy is required to reach a. The catalyst is not good.
If this energy is too negative, e.g., is at d, then to go out from d to reach the final state f, a large activation energy is again required. The catalyst is not good.
If the energy of Cat-H is at b or c, then the catalyst is «potentially» good.

DFT-Based Catalyst Design for H_2 Evolution



Ib Chorkendorff; Jens K. Nørskov; et al. *J. Am. Chem. Soc.* **2005,** 127, 5308-5309.

Explanation for the previous slide

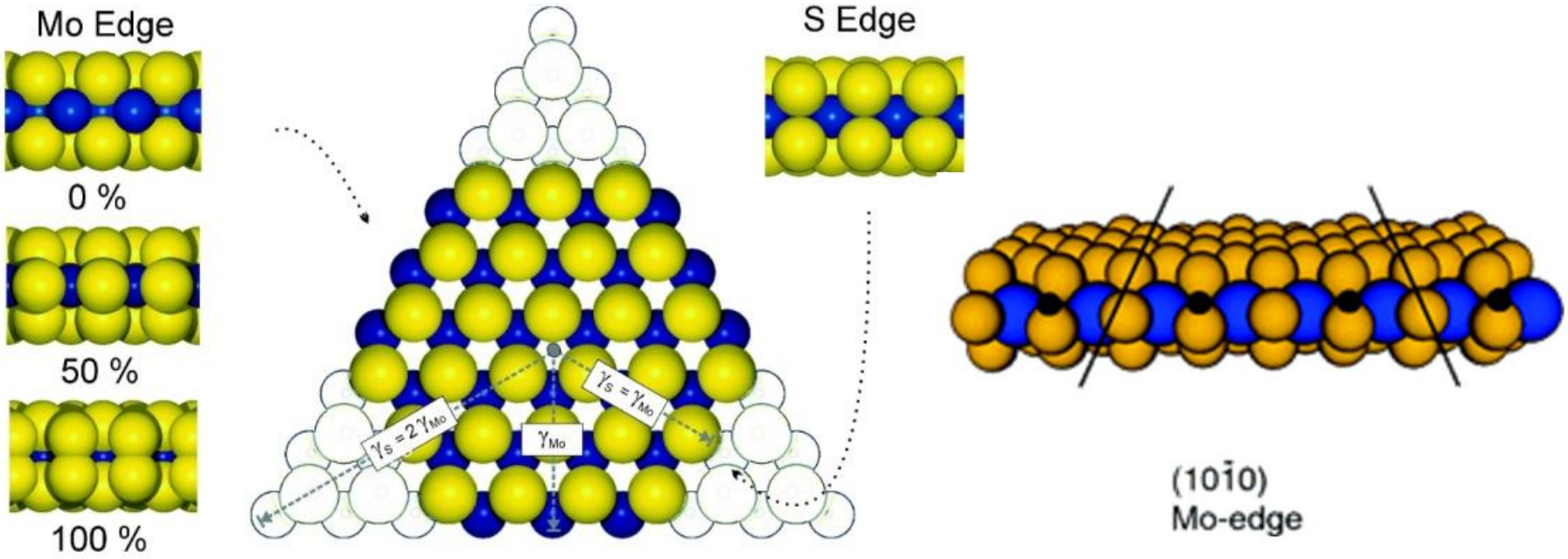
The energy of a hydrogen atom adsorbed on the surface of various catalysts have been calculated. This energy is equivalent to the thermal energy of the first step of hydrogen evolution, the discharge reaction.

Known good catalysts, such as Pt, hydrogenase, nitrogenase, are shown to have a small energy for hydrogen adsorption. In the case of Pt, the adsorption is shown to be energetically favored; this is confirmed by experiment.
Known bad catalysts, such as Au, Ni, and Mo, are shown to have a big energy for hydrogen adsorption.
So the DFT method seems to produce results that are consistent with experiments.

The authors screened some other potential catalysts. They found that a certain phase of MoS_2 might be a good catalyst, because the energy for hydrogen adsorption is not too big.
This is not just any MoS_2, but a special edge of MoS_2, that is used in the calculation.

We shall go back to the structure of MoS_2 slab again.

DFT-Based Catalyst Design for H_2 Evolution



A naked Mo edge is not stable; it is normally covered with some residual S. **The Mo edge, covered with 50% S, is shown by calculation to have a small energy for hydrogen adsorption.**

This is a nice prediction; but is it useful?

J. Am. Chem. Soc. **2005,** 127, 5308-5309.

In class literature reading and analysis:
Chorkendorff et al. *Science, 2007, 317, 100-102.*

Encounter state-of-the-art research;
Understand the scientific background (echo the course material);
Acquaint typical scientific methods;
Analyze how data are processed and how hypotheses are tested;
Learn how conclusions are formulated;
Critical reading and thinking.

After the reading, we have a question-answer period.
First, I ask you questions about the paper;
Second, you ask me questions about the paper.

Guideline for reading.

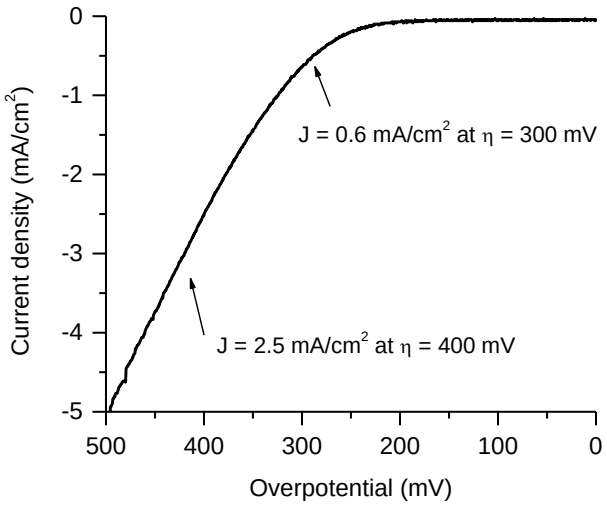
(1)Read at a normal speed; acquire an overview; formulate a few questions and options.
(2)Read again the part you have doubts. Write down the doubts if they persist.
(3)Formulate the answers to my questions; read more if necessary.

My questions:
(1)What is the general scientific question that motivates the study?
(2)What is the specific scientific question the study wants to address?
(3)Which experiments did the authors carry out to answer the questions?
Hint: (a) Sample preparation; (b) sample characterization; (c) electrochemial measurement.
(4) What are the key data obtained? What conclusion do they lead to?
(5) Do you think the experiments are valid? The interpretation of data was correct? The hypothesis was proven?
(6) What is the significance of this study?
(7) What is the weakness of the work?

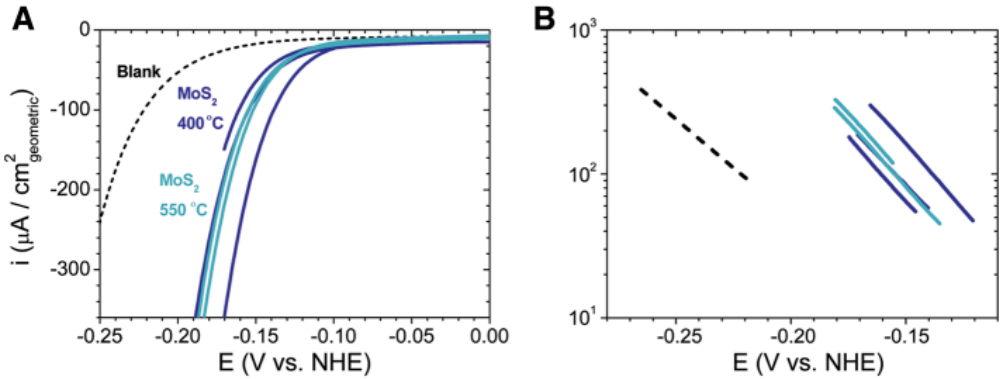
When the teacher asks a question and you're trying to avoid eye contact

HER by MoS_2

Recall, MoS_2 crystal is not a good HER catalyst



MoS_2 nanocrystal is much better HER catalyst than MoS_2 bulk crystal



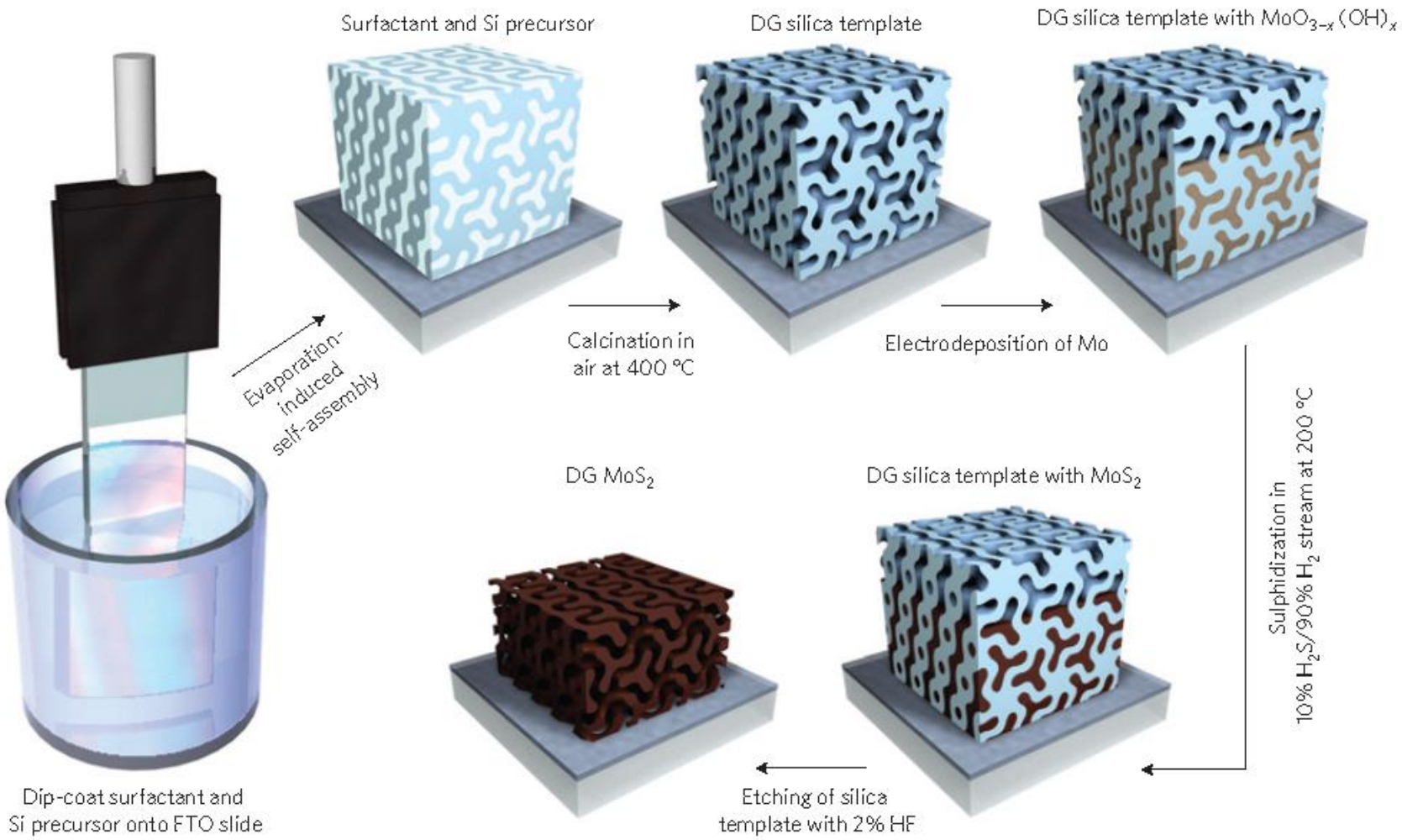
NHE is normal hydrogen electrode; at pH = 0, potential vs. NHE is negative of the overpotential for HER.

The Mo edge is responsible for HER. In MoS_2 nanocrystals, there are more edges than in MoS_2 bulk crystals. This is why the former is more active.

This study suggests that MoS_2 can be a good HER catalyst if the edge sites can be enriched in a MoS_2 sample. The work inspires a large body of work to develop MoS_2 materials as HER catalysts. We will see some examples.

IV. Development of MoS_2-based HER catalysts

First example: MoS_2 gyroid to expose more edge sites

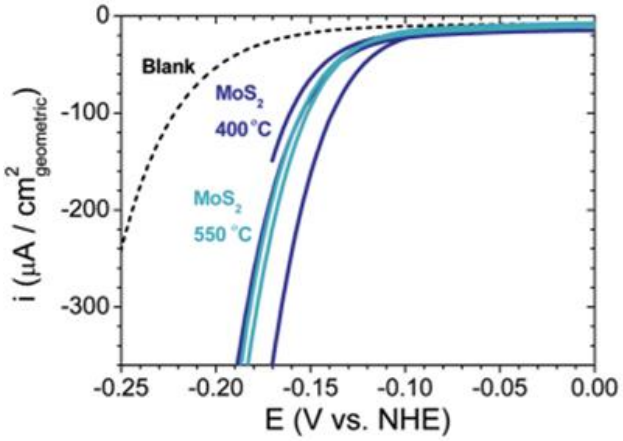


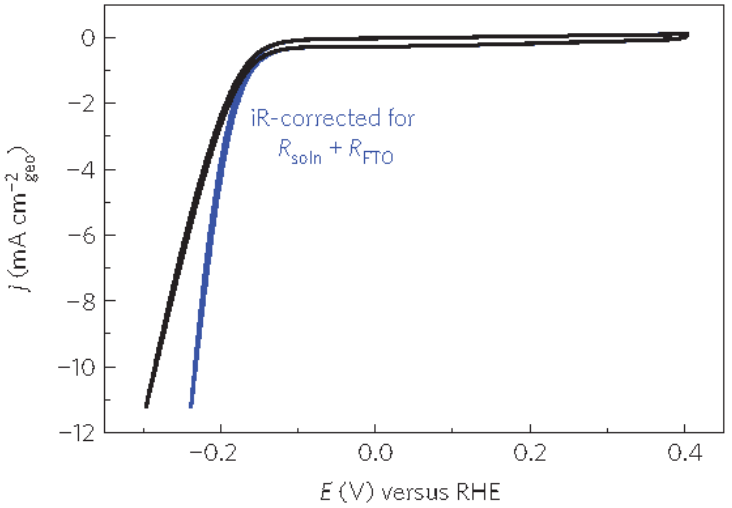
Synthesis procedure and structural model for mesoporous MoS_2 with a double-gyroid (DG) morphology.

Jaramillo et al. Nature Materials, 2012, DOI: 10.1038/NMAT3439

The previous image shows an approach to produce nanoporous thin films of MoS_2. First, a nanoporous silica (SiO_2) template is prepared. Mo oxide films were then deposited by electrochemistry to this template. The Mo oxide was converted to MoS_2 by reacting to a mixture of H_2S and H_2 at 200°C. The silica template was then removed to leave the gyroid MoS_2 film.

RHE is reversible hydrogen electrode; at any pH, potential vs. RHE is negative of the overpotential for HER.



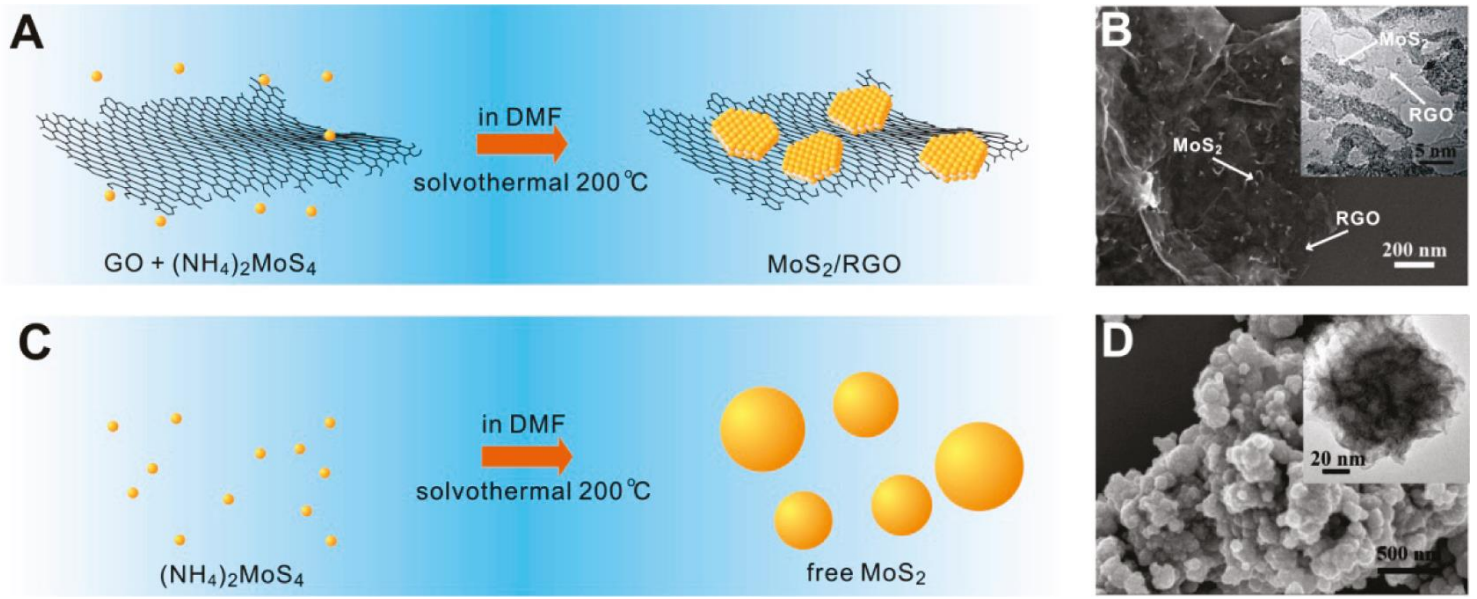


MoS_2 nanocrystal
Tafel slope: 60 mV/decade

MoS_2 gyroid film
Tafel slope: 50 mV/decade

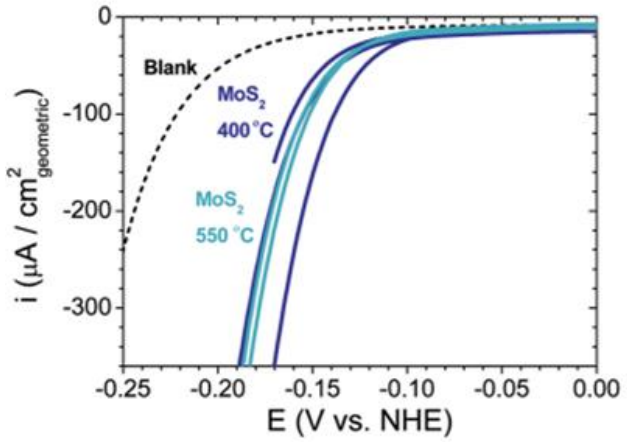
The gyroid film indeed shows a much higher activity than nanocrystals of MoS_2 in HER. J = 10 mA/cm^2 at η = 230 mV.

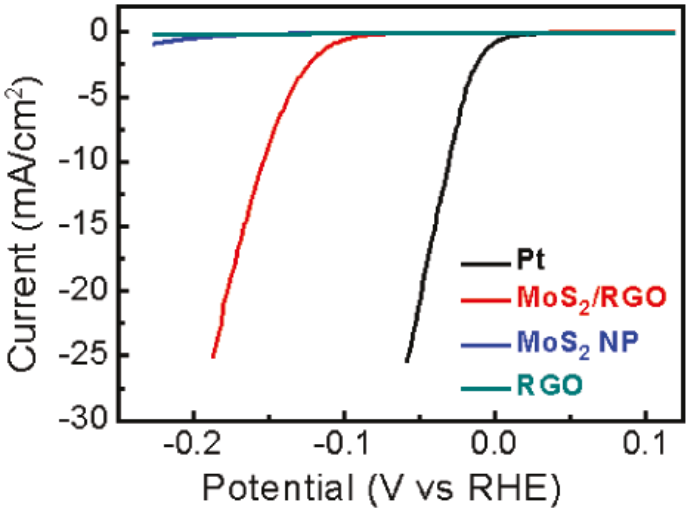
Example II: Disperse MoS_2 on conducting substrate to enhance surface area and electron transport



Reduced graphene oxide (RGO) is a very conductive substrate.
Deposition of MoS_2 on graphite makes small and well dispersed MoS_2 nanoparticles.
The synthesis is by solvothermal reaction in a closed vessel.
Electron microscopy is used to show the morphology.

Dai et al. J. Am. Chem. Sco. 2011, 133, 7296.





MoS_2 nanocrystal;
Tafel slope: 60 mV/decade

MoS_2 nanoparticle on RGO
Tafel slope: 40 mV/decade

The MoS_2/GRO shows a much higher activity than nanocrystals of MoS_2 in HER. J = 10 mA/cm^2 at η = 150 mV.

The enhancement is due to (1) high loading of well-dispersed catalyst; one can laod much more catalysts on a porous substrate like RGO than on planar Au. (2) higher real surface area; the RGO substrate has a high surface area. (3) Good electronic communication between MoS_2 and RGO.

Nanostructuring of MoS_2 to increase the surface area, to expose more edge sites, and to couple with porous and conductive substrates such as carbon nanotube, graphene, mesoporous carbon is an active area of research.

These studies were also inspired by the seminal work in 2005 and 2007 (DFT calculation and study of active site) we discussed earlier. So we can see that a good understanding of the origin of catalytic activity has a big impact in the development of catalyst.

However, there is one common pitfall of these type of studies: the catalyst is prepared in a sophisticated, energy intensive, costly, and non-scalable manner.

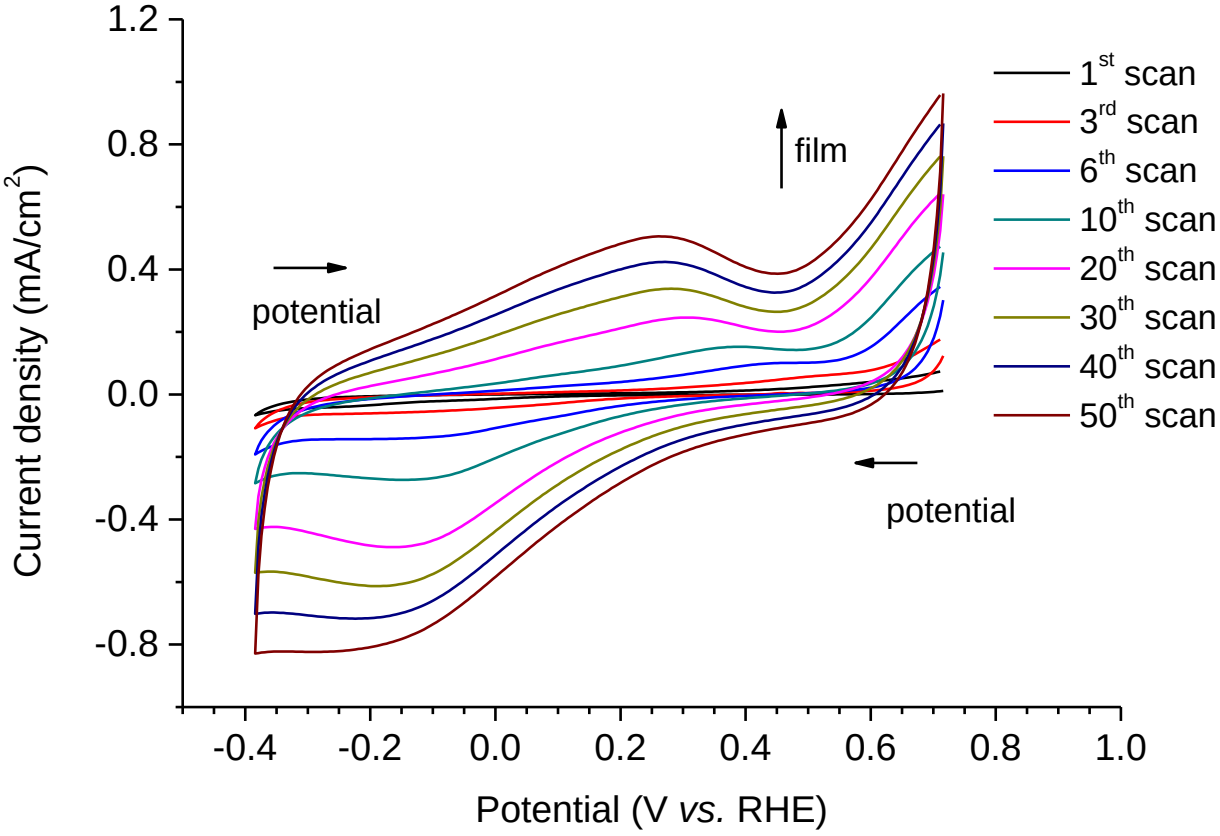
For real-world application, one needs to make catalyst accessible and scalable. After all, this is the only problem of Pt.

I will show you now an example of our own contribution to address this challenge.

The deposition of MoS catalyst

"MoS" film is produced when an electrode is subjected to potential cycling (0.7 to -0.4 V vs. RHE) in an aqueous solution containing $(NH_4)_2[MoS_4]$ at room temperature.

No expensive materials, no sophisticated instrument, no pressure, no heating …



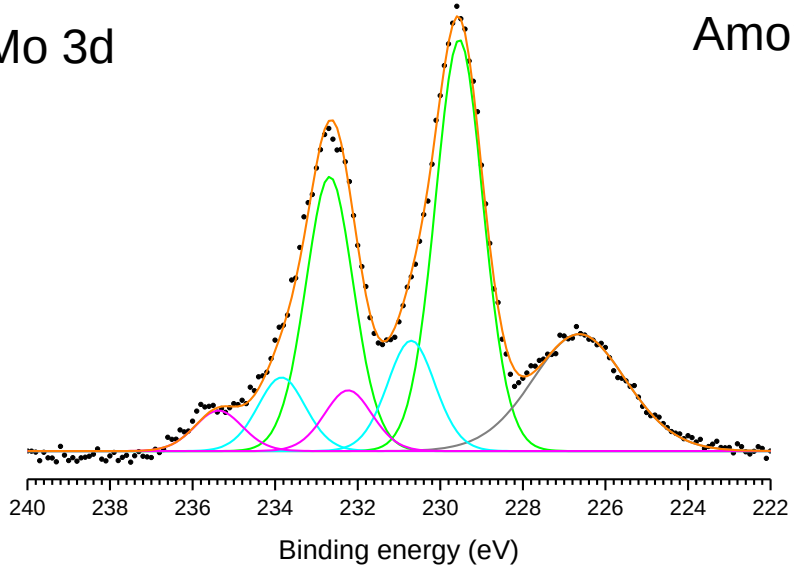
Characterization of Catalyst

Active species: amorphous MoS_{2+x}; $x < 1$. Characterization by X-ray photoelectrospectroscopy.
This species is chemically different from MoS_2; it is also structureally different, as it is amorphous, while MoS_2 is crystalline.

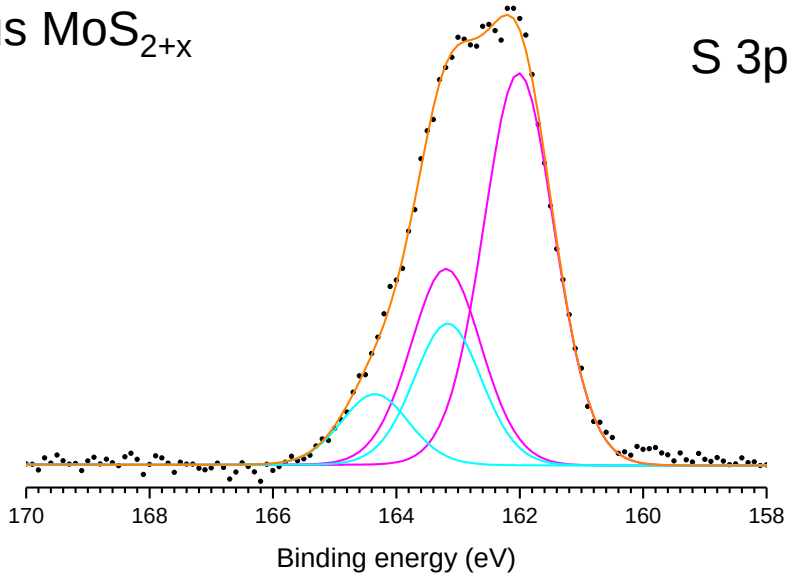
X-ray photoelectron spectroscopy (XPS)

Mo 3d

Amorphous MoS_{2+x}

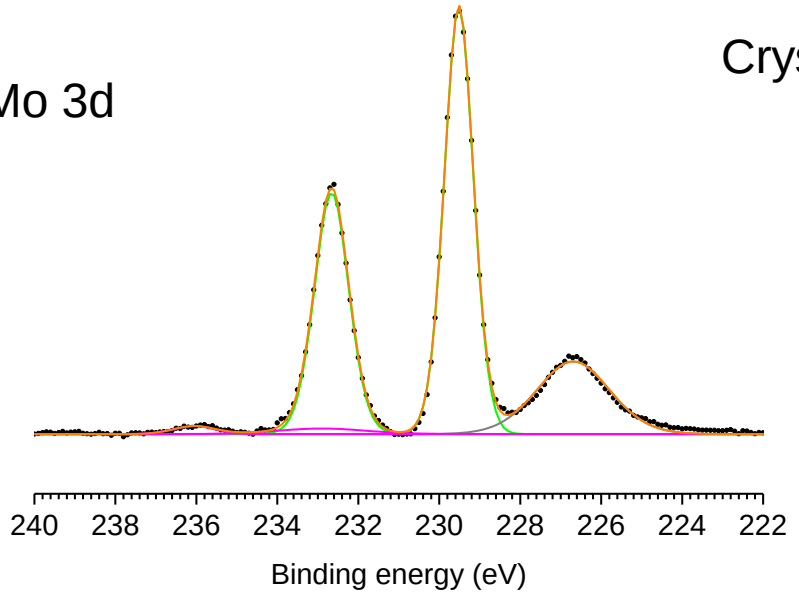


S 3p

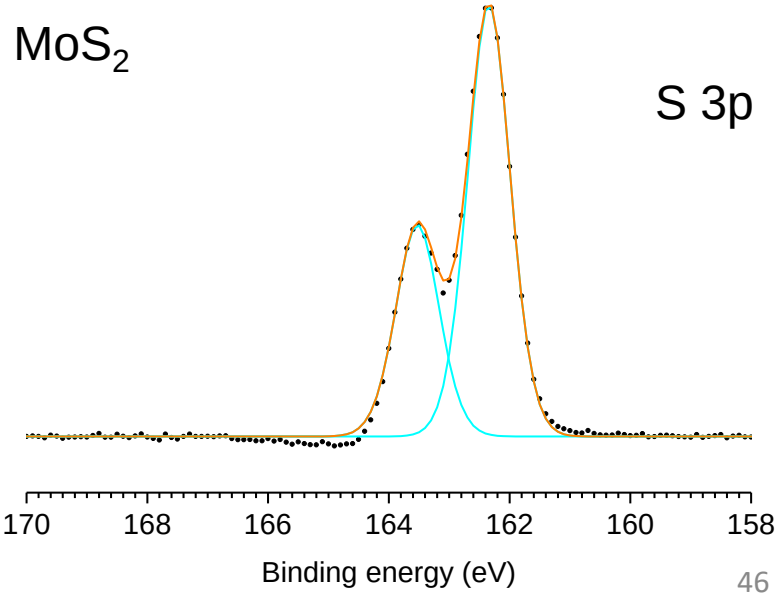


Mo 3d

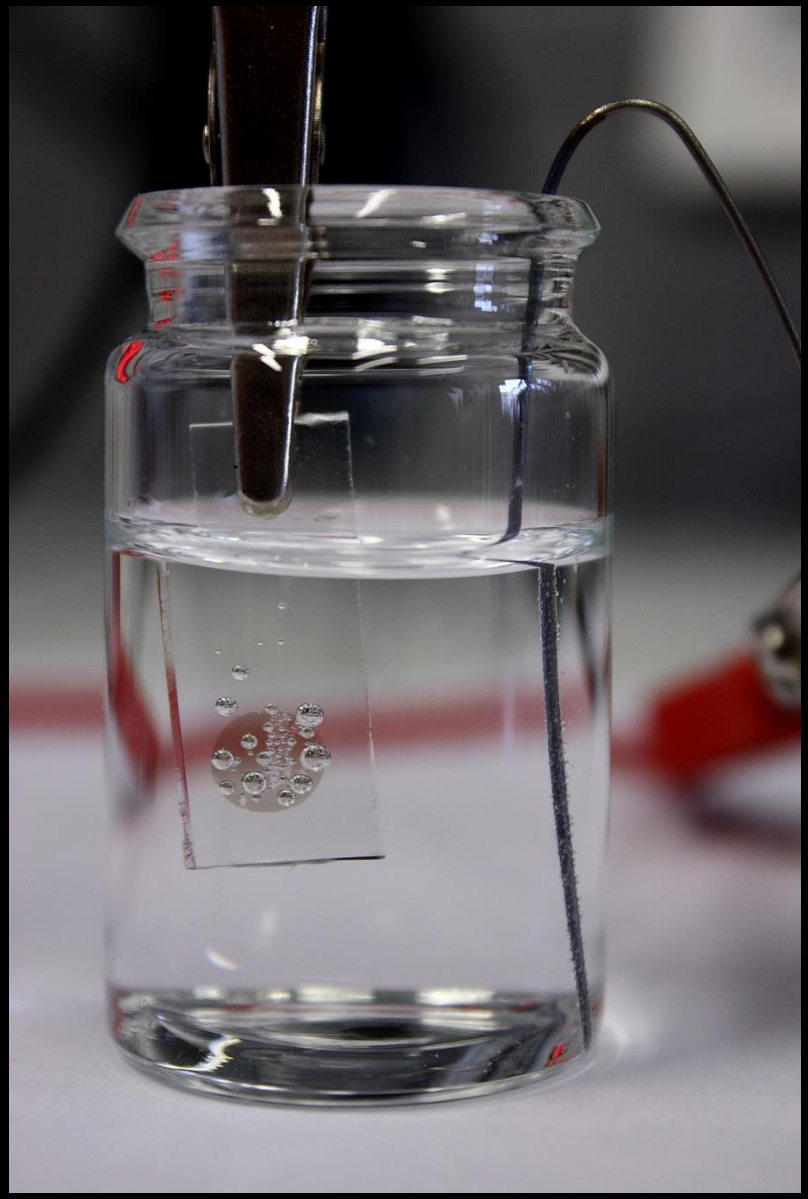
Crystalline MoS_2

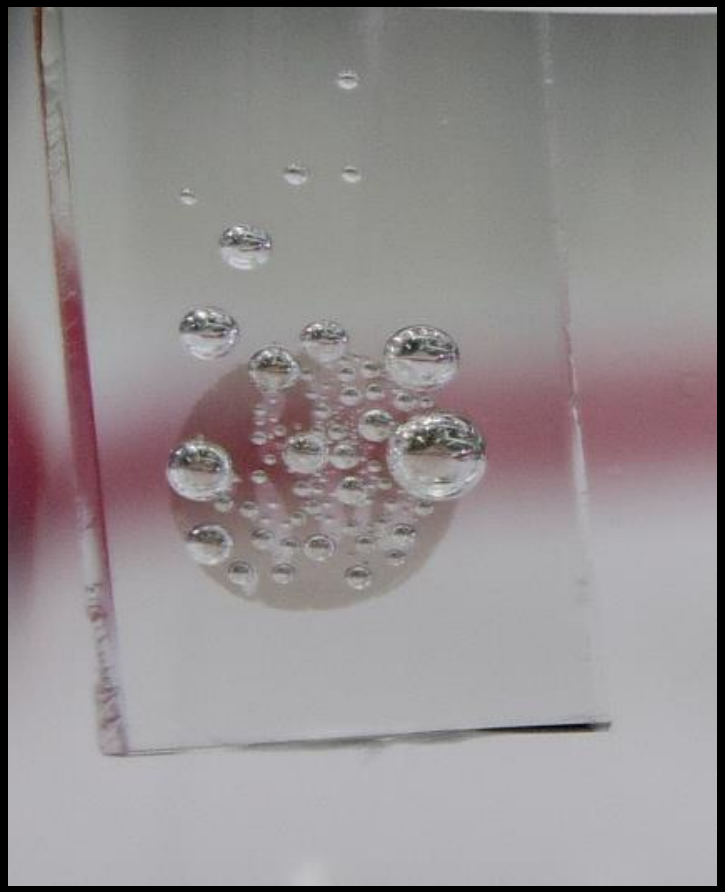


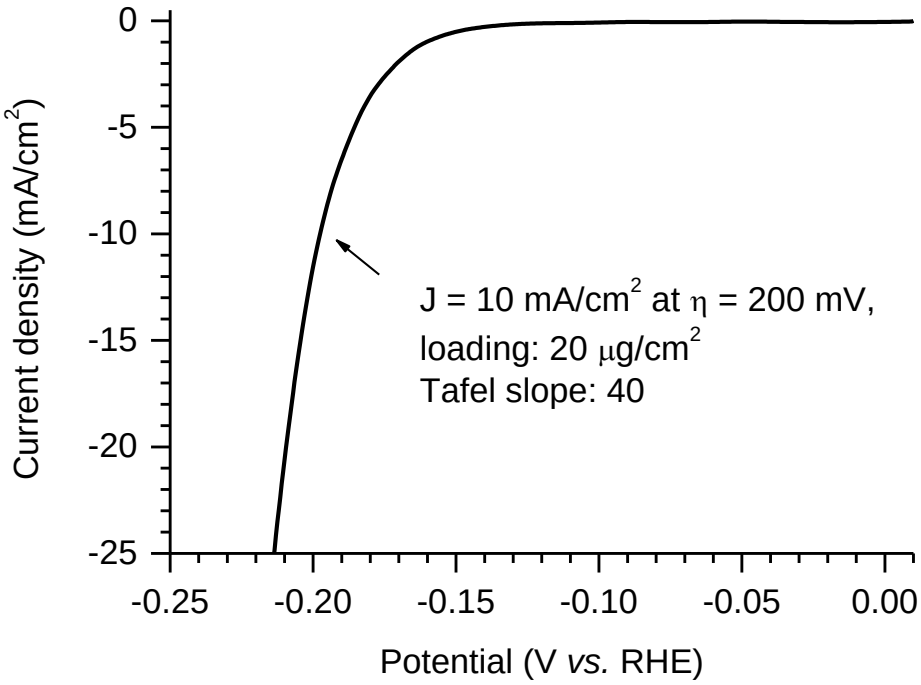
S 3p



Catalytic Property

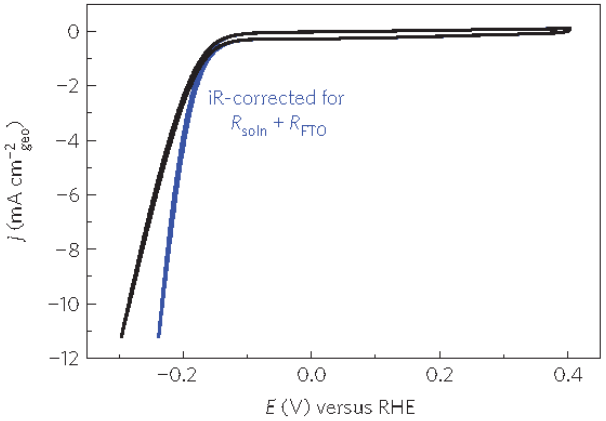




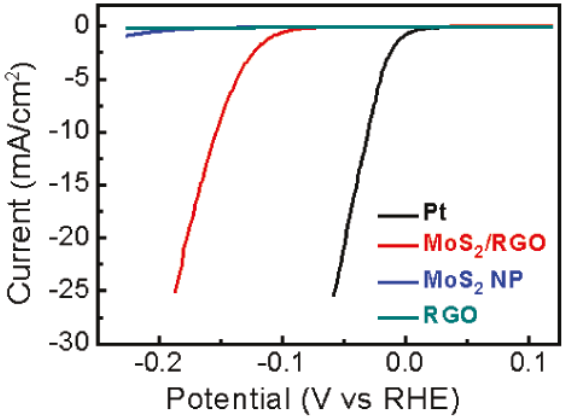


Catalytic performance of MoS_{2+x} film for HER:
Comparable to the best MoS_2 nanoparticles

Strength of MoS_x film:
Easy synthesis; scalable; inexpensive.



MoS_2 gyroid film
Tafel slope: 50 mV/decade
J = 10 mA/cm^2 at η = 230 mV



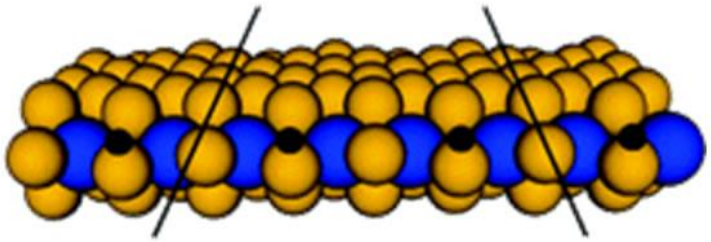
MoS_2 nanoparticle on GRO
Tafel slope: 40 mV/decade
J = 10 mA/cm^2 at η = 150 mV
Loading: 200 μg/cm^2

Hu et al. Chem. Sci. 2011, 2, 1262.

Why does amorphous MoS_{2+x} work

For MoS_2 bulk crystals, all sulfur ligands are saturated, therefore HER activity is poor

For MoS_2 nanocrystals, the sulfur ligands attached to the Mo edge adsorbs H atom



$(10\bar{1}0)$
Mo-edge

discharge reaction

$$H_3O^+ + e + cat \rightleftharpoons cat—H + H_2O$$

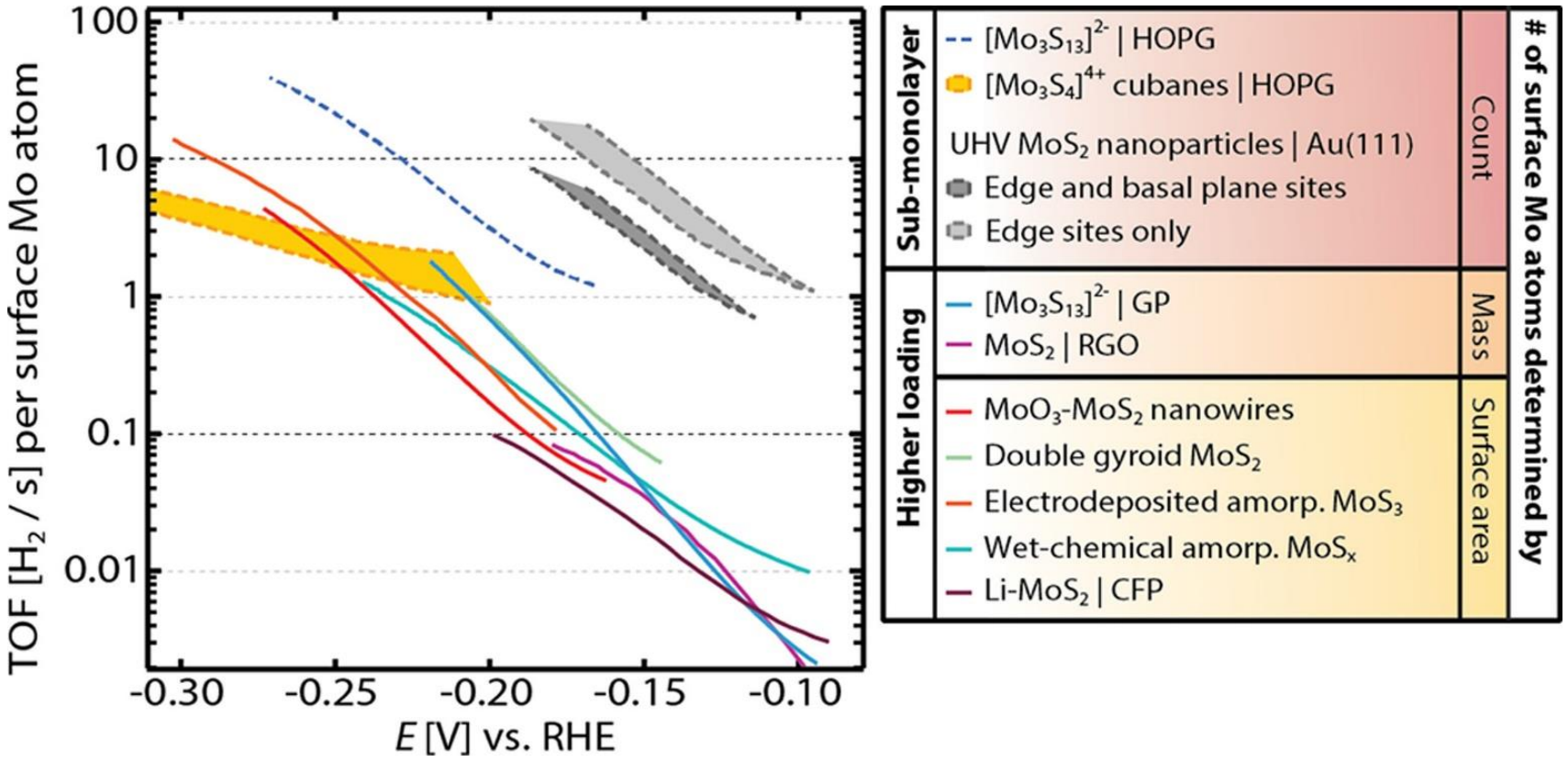
$$cat—H + H_3O^+ + e \rightleftharpoons cat + H_2 + H_2O$$

$$cat—H + cat—H \rightleftharpoons 2\,cat + H_2$$

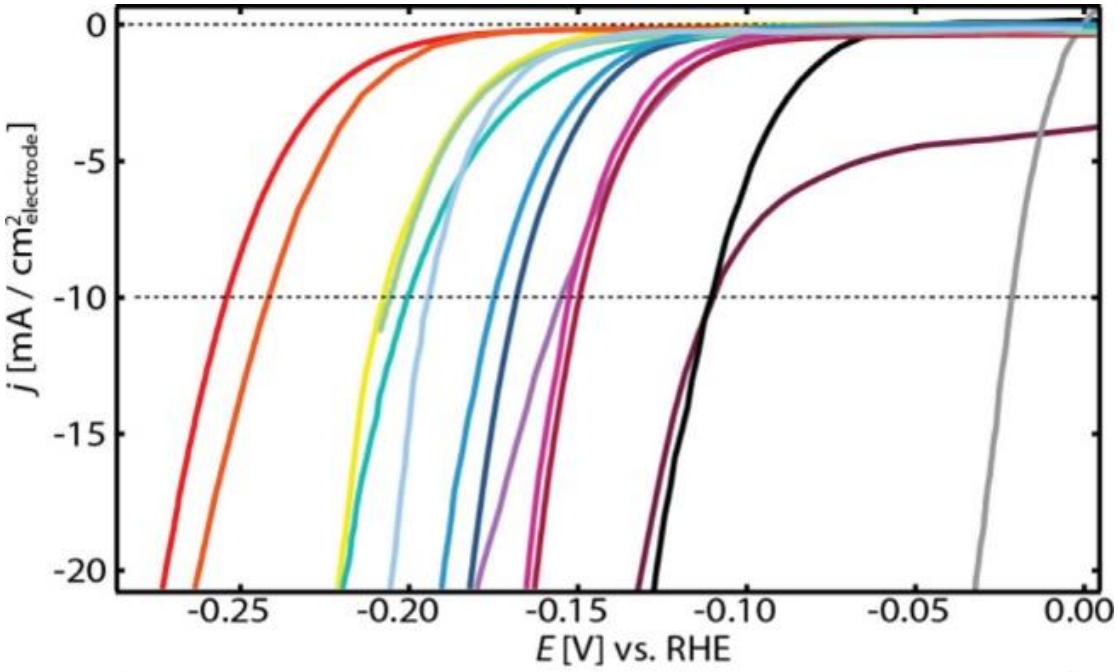
For amorphous MoS_{2+x}, there are plenty of defect sides, so there are plenty of unsaturated sulfur ligands. These sulfur ligands can engage in HER catalysis. Therefore, MoS_{2+x} can be more active than MoS_2 nanocrystals!

How do we compare activity?

Turnover frequencies of different molybdenum sulfide catalysts normalized to the number of surface Mo atoms



Linear sweep voltammograms demonstrating the total electrode activity different molybdenum sulfide catalysts.



	Reference	Potential for 10 mA/cm²geo [V] vs. RHE
MoO_3-MoS_2 nanowires	[54]	-0.254
Electrodeposited amorp. MoS_3	[69]	-0.242
1T - MoS_2	[71]	-0.207
Double gyroid MoS_2	[58]	-0.206
Wet-chemical amorp. MoS_x	[50]	-0.200
MoS_x | GP	[62]	-0.194
100 µg/cm² $[Mo_3S_{13}]^{2-}$ | GP	[96]	-0.174
Li_xMoS_2 | GP	[75]	-0.168
MoS_2 | RGO	[63]	-0.154
MoS_x | Piranha GP	[62]	-0.152
$[Mo_3S_{13}]^{2-}$ | anodized GP	This work	-0.149
Li-MoS_2 | CFP	[81]	-0.110
MoS_x | N-CNT	[126]	-0.110
Polycrystalline Pt	This work	-0.021

Summary of Case study of HER catalyzed by MoS_2

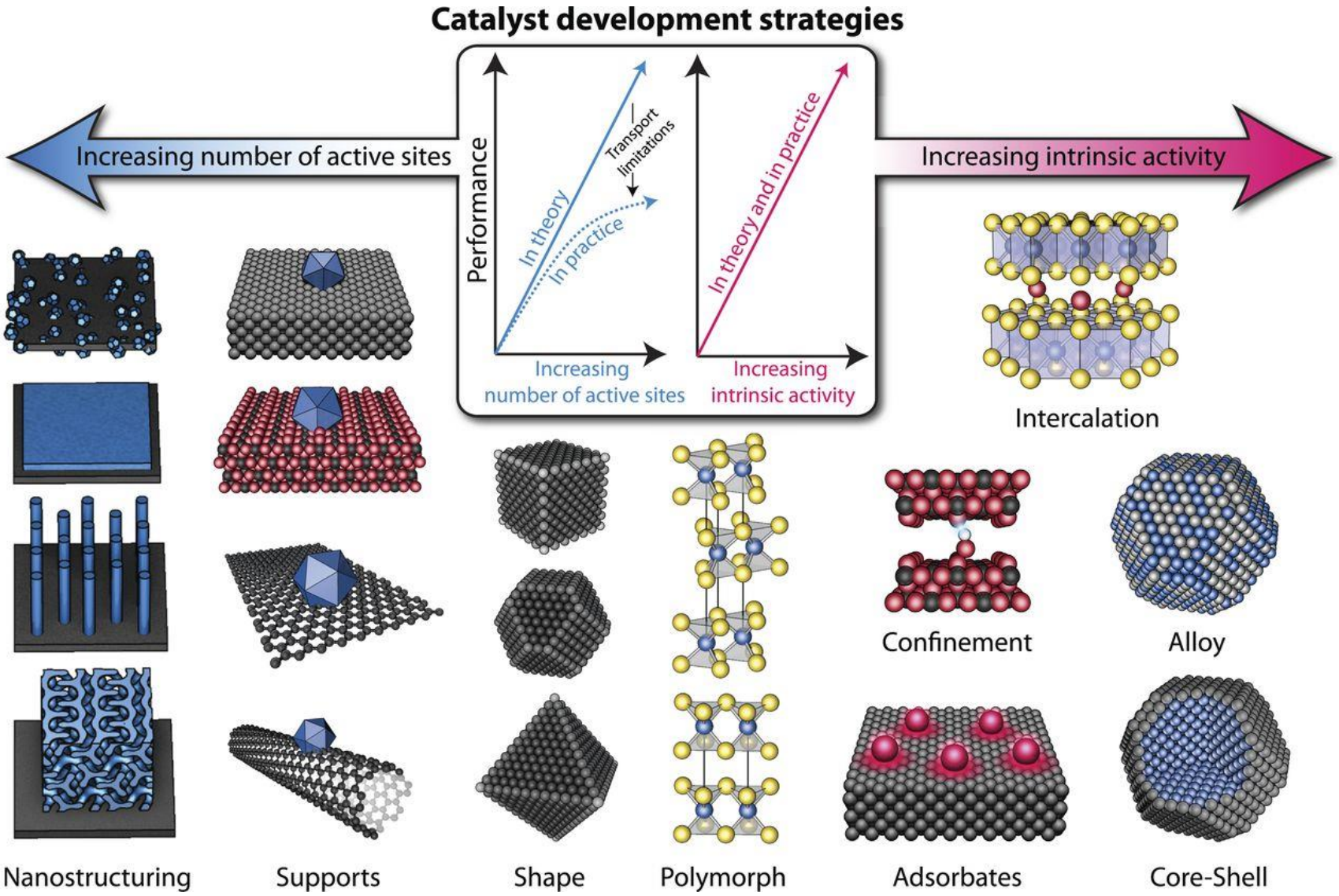
MoS_2 was deemed as an uninteresting catalyst for HER because the activity of bulk material was modest.

In an attempt for rational design of HER catalyst, DFT calculations were conducted on typical catalysts. The same calculations identified the edge site of MoS_2 as a potentially good catalyst for HER.

MoS_2 nanoparticles were prepared where the edge lengths were controlled. Experiments showed that the HER activity correlates with edge length. Nanoparticles rich in edge sites show enhanced HER activity compared with MoS_2 bulk material. This study points to a new direction in catalyst design.

Two examples of current research in MoS_2 catalysts are shown. Nanostructuring leads to much more active MoS_2 catalysts than simple nanoparticles.

A different approach in catalyst development is introduced – the viability and scalability of catalyst is addressed in the development of amorphous MoS_{2+x} catalysts.


Catalyst development strategies
Increasing number of active sites
Increasing intrinsic activity
Performance
In theory
Transport limitations
In practice
In theory and in practice
Increasing number of active sites
Increasing intrinsic activity
Intercalation
Confinement
Alloy
Nanostructuring
Supports
Shape
Polymorph
Adsorbates
Core-Shell

Conclusion

(1) Mechanism of HER on an electrode.
(2) Precious metals such as Pt are good catalysts. This is due to an optimal M-H energy.

(3) Non-precious catalysts are not as active and new materials need to be developed. While catalysis is often approached in an empirical manner, the development of MoS_2 and MoS_{2+x} materials shows that rational design of catalyst can be more efficient. This necessitate fundamental studies in both theory and experiments.

(4)Some common methods and tools in electrocatalysis are shown:
(i)Synthesis: solution chemistry; gas phase deposition; template synthesis;
(ii)Characterization: STM; Electron Microscopy; XPS
(iii)Electrochemistry: current-potential curve; Tafel slope
(iv)Theory: DFT