Graphene 2018
June 26 - 29
Dresden (Germany)

DRESDEN concept

TECHNISCHE UNIVERSITÄT DRESDEN

Designing nanostructures and active sites of 2D materials for electrochemical water splitting

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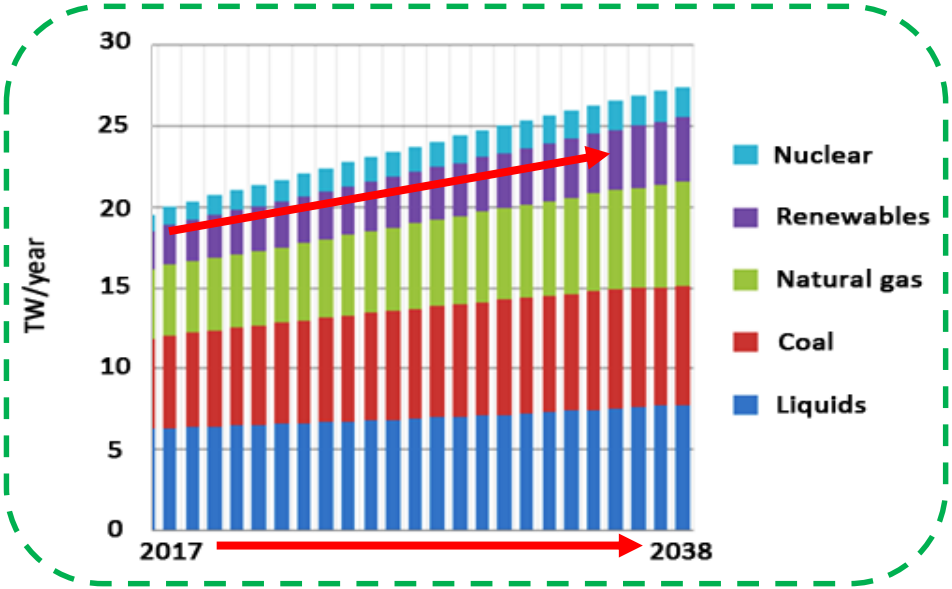
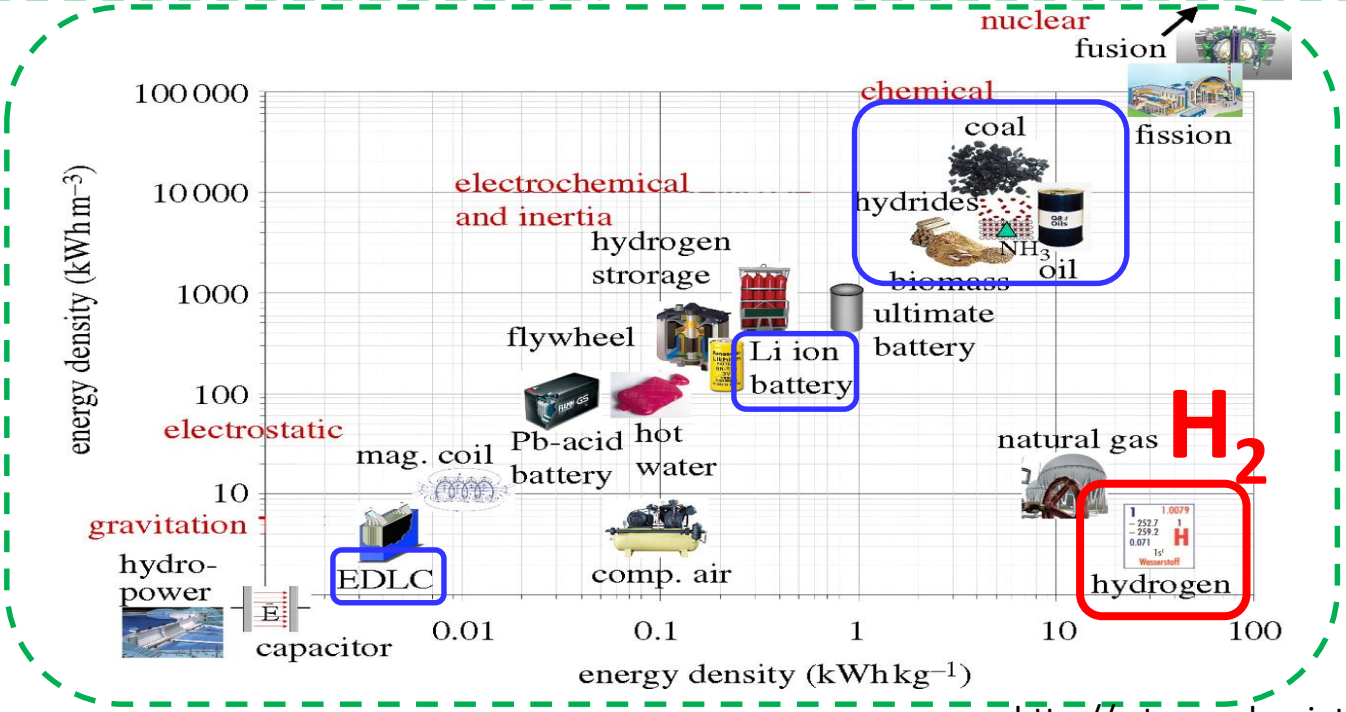
cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

June 27, 2018

Background





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Energy systems for hydrogen utilization

DRESDEN concept

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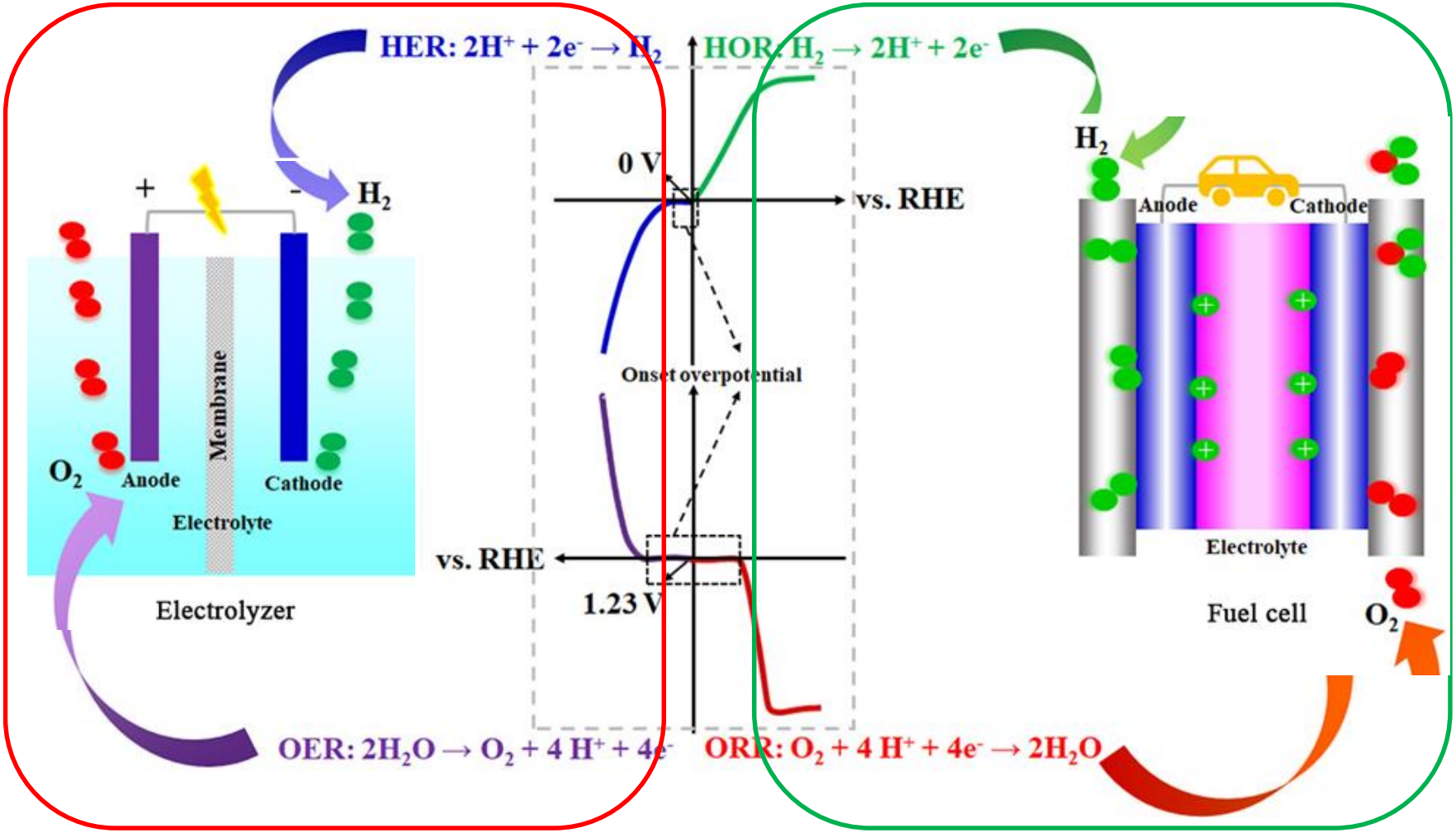
H_2 generation

H_2 combustion



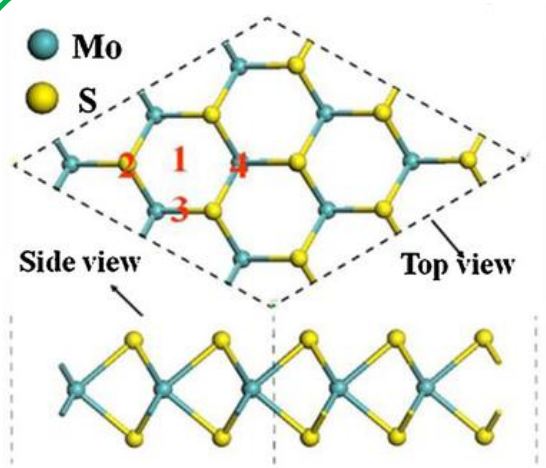
Pt and Pt alloy: the best HER electrocatalysts

Onset overpotential: ~0 mV;

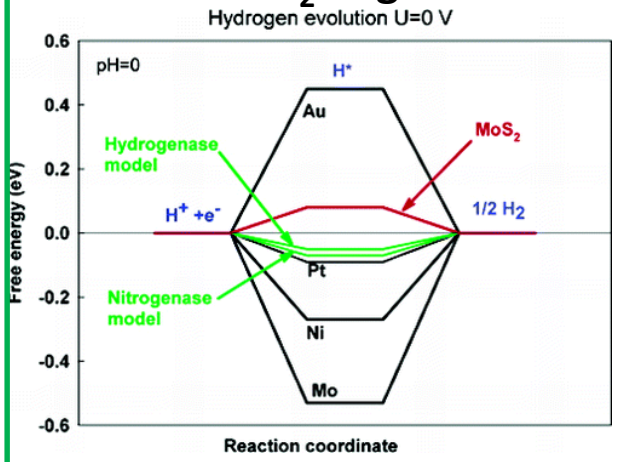
Overpotential at 10 mA/cm^2: ~30 mV;

J. Zhang, et.al, *Adv. Mater.* **2018**, accepted.

2D materials for hydrogen evolution

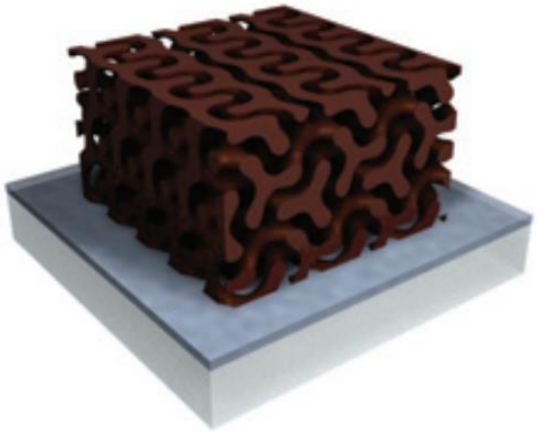


MoS_2 edges

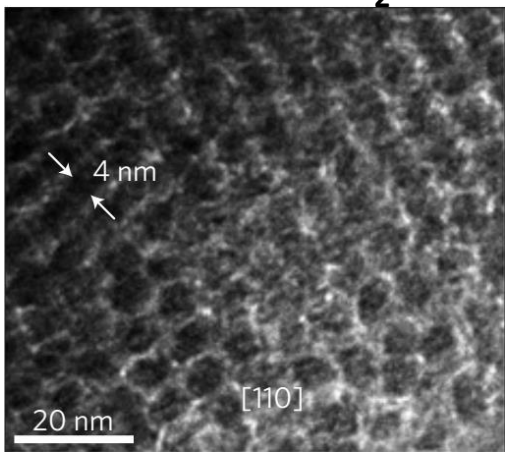


J. Am. Chem. Soc., **2005**, *127* (15), 5308.

Intrinsic activity

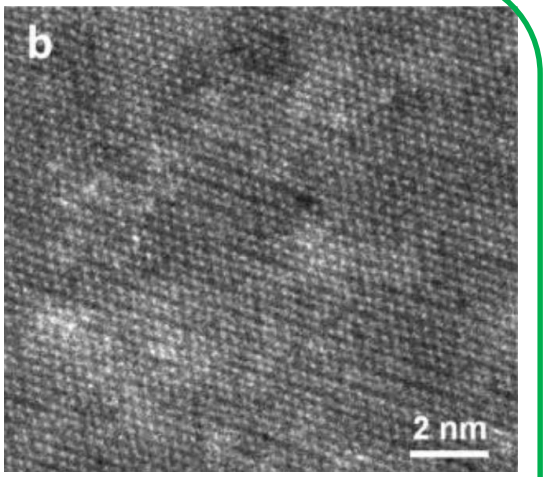


Porous MoS_2

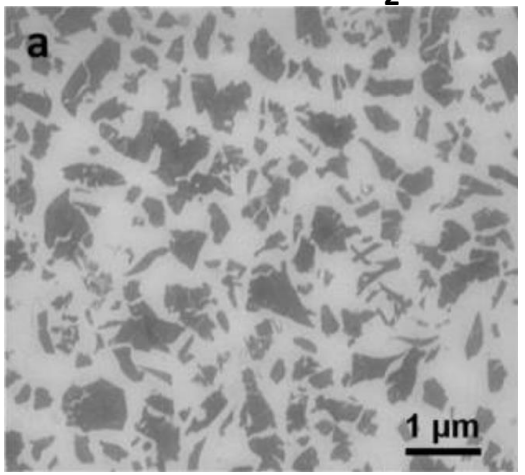


Nat. Mater. **2012**, 11, 963.

Abundant active sites



Metallic MoS_2



Nano Lett., **2013**, *13*, 6222.

Rapid charge transfer

TMD: transition-metal dichalcogenides

State-of-the-art

I. Advanced Pt-based HER catalysts

(i) Pt-based hybrid catalysts.

Science, **2011**, *334*, 1256.

Acidic solution

Alkaline solution ?

II. Pt-free catalysts

(i) Metal alloys-based HER catalysts

Electrochimica Acta, **2000**, *45*, 4151; *Energy Environ. Sci.*, **2011**, *4*, 3573; *ACS Catal.*, **2013**, *3*, 166.

(ii) Metal oxides, chalcogenides, carbides, phosphides, nitrides-based catalysts

Nat. Commun., **2014**, *5*, 4695; *Science*, **2007**, *317*, 100; *Nat. Commun.* **2016**, *7*, 11204; *Angew. Chem. Int. Ed.*, **2012**, *51*, 6131; *J. Am. Chem. Soc.*, **2013**, 135, 9267.

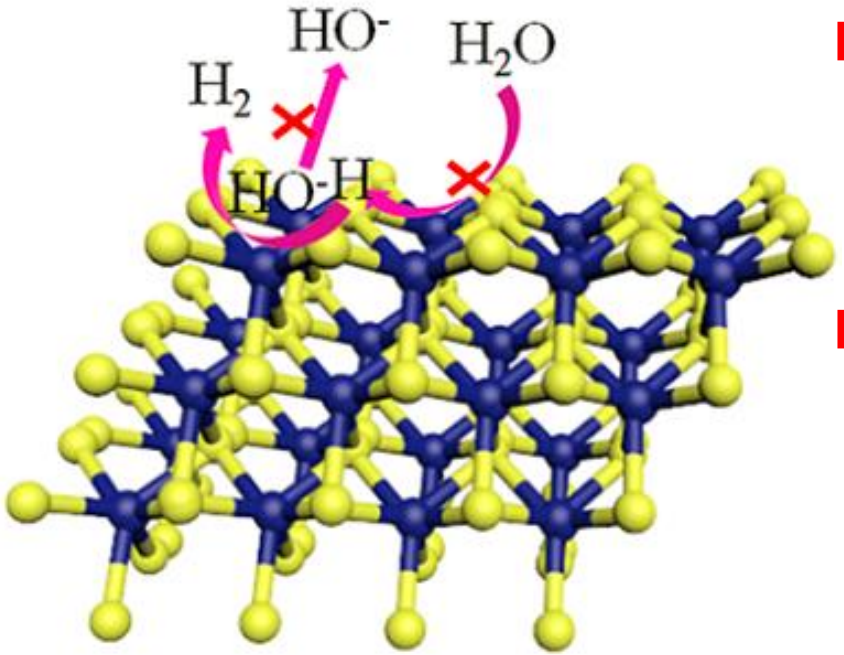
(iii) Carbon-based catalysts

Nat. Commun., **2016**, *7*, 10667; *Nat. Commun.*, **2015**, *6*, 7992; *Nat. Commun.*, **2015**, *6*, 8668; *Angew. Chem. Int. Ed.*, **2014**, *126*, 4461.

MoS_2 electrocatalysts

MoS_2 for HER in basic solutions:

MoS_2:

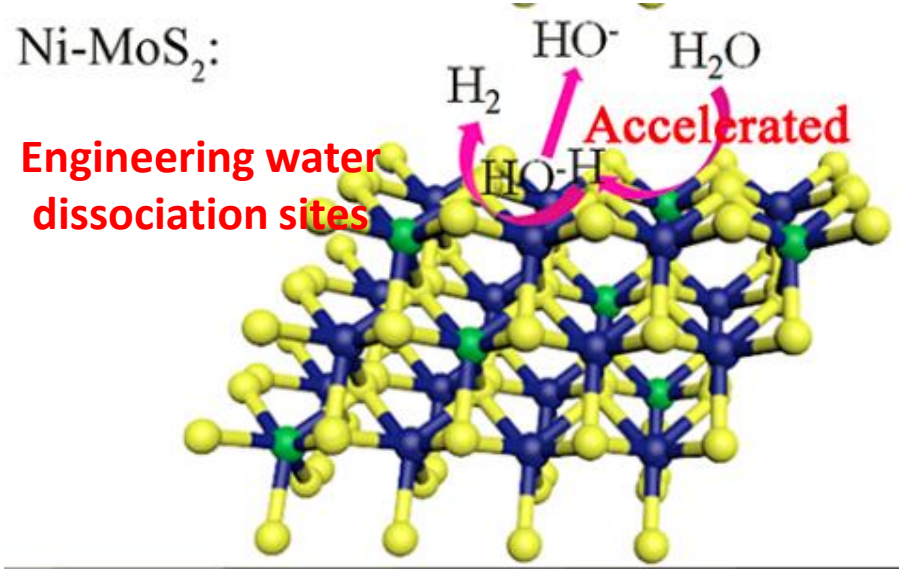


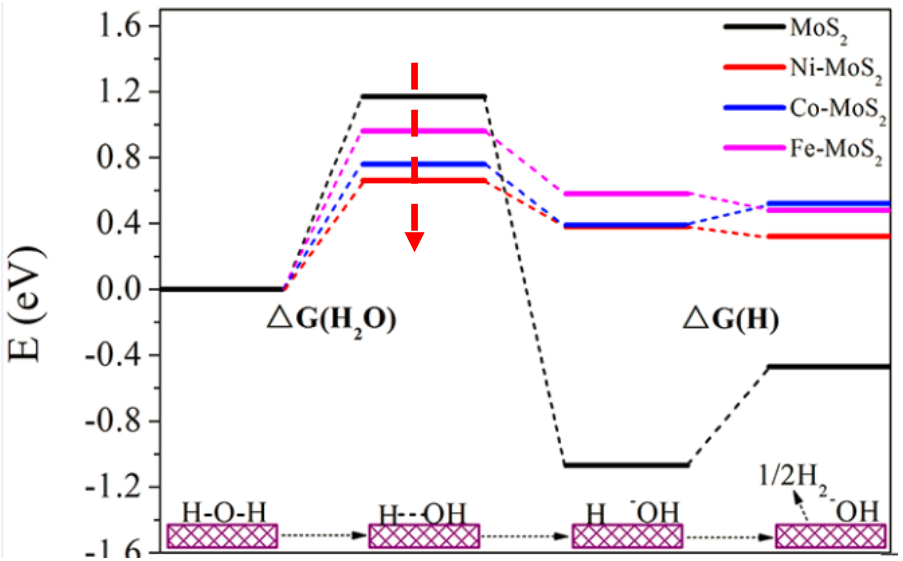
- Large kinetic energy barrier of water dissociation on MoS_2 catalysts;
- Strong adsorption interaction of the formed ^{-}OH on MoS_2 catalysts.

MoS_2 catalysts exhibit poor HER activity in basic solution.

R. Subbaraman, et al, *Science* **2011**, *334*, 1256-1260;
R. Subbaraman, et al, *Nat. Mater.* **2012**, *11*, 550-557.

Theoretical calculations





Ni doped MoS_2 ($Ni\text{-}MoS_2$):

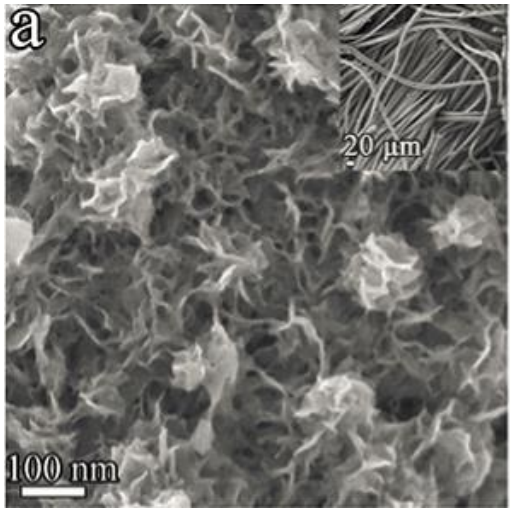
- The kinetic energy barrier of water dissociation was decreased from 1.17 eV on MoS_2 to **0.66 eV** on $Ni\text{-}MoS_2$;
- The **desorption** of ^{-}OH was facilitated on $Ni\text{-}MoS_2$;

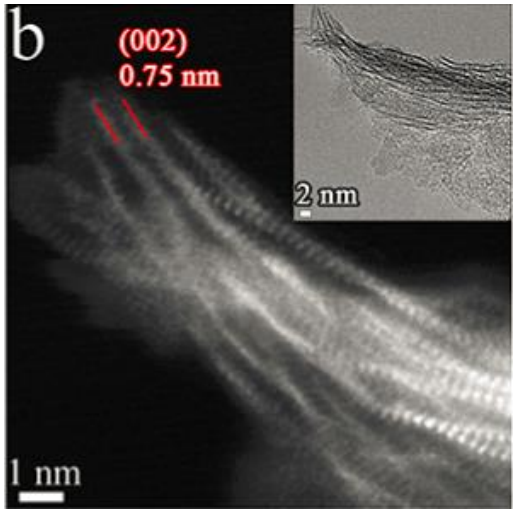
	△G(H_2O) (eV)	G(OH) (eV)	△G(H) (eV)
MoS_2	1.17	-5.24	0.60
$Ni\text{-}MoS_2$	0.66	-3.46	-0.10
$Co\text{-}MoS_2$	0.76	-3.46	-0.06
$Fe\text{-}MoS_2$	0.96	-3.36	0.13

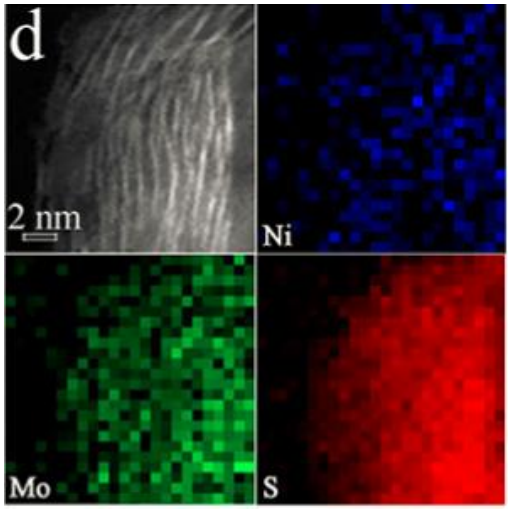
Dr. Tao Wang, SunCat center, Stanford University, USA

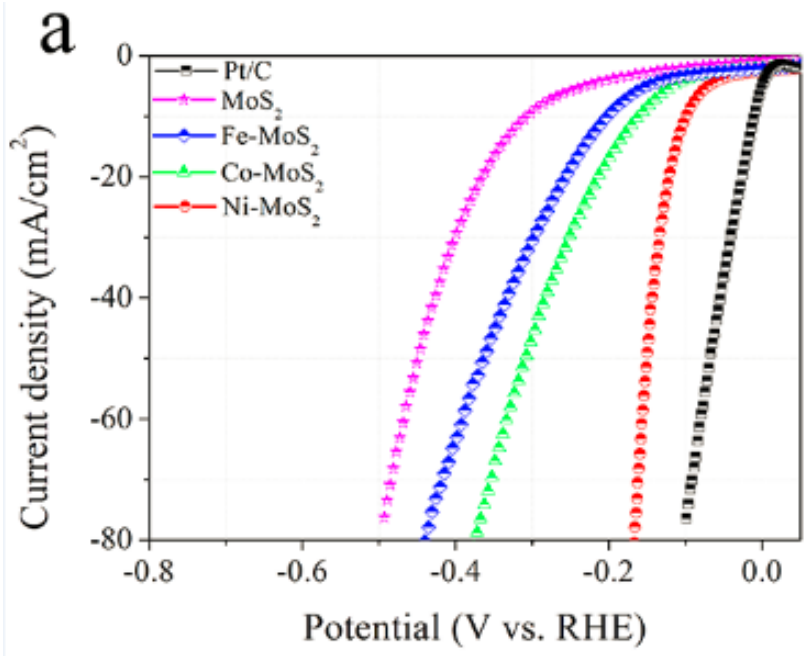
J. Zhang, *et.al*, *Energy Environ. Sci.*, **2016**, *9*, 2789.

Morphology







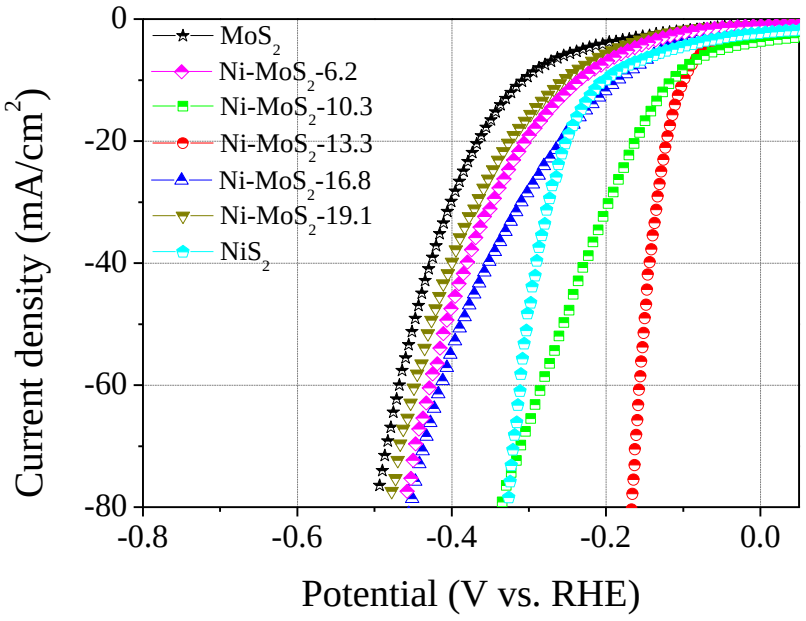


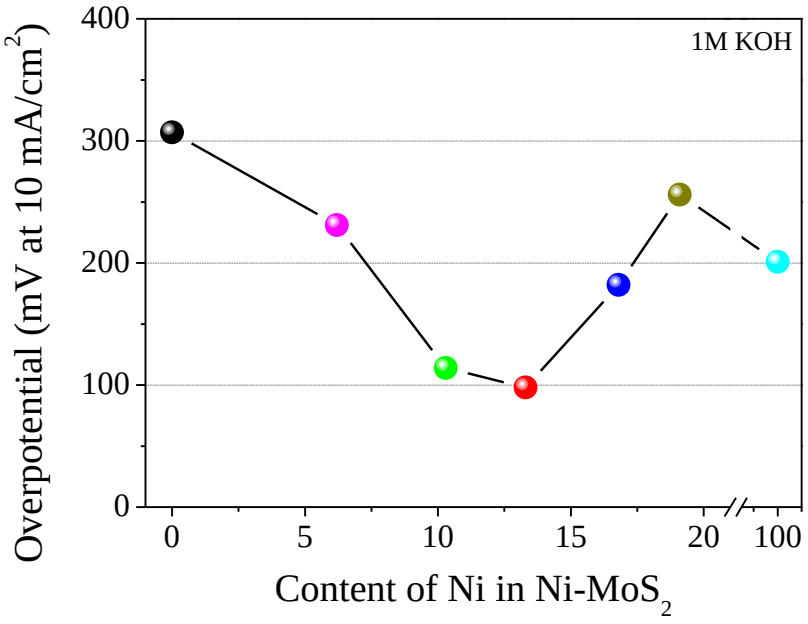
- Thichness: **< 10 nm**
- **Ni atoms** were doped into crystalline MoS_2 nanosheets.
- Overpotential at 10 mA/cm^2: **98 mV.**

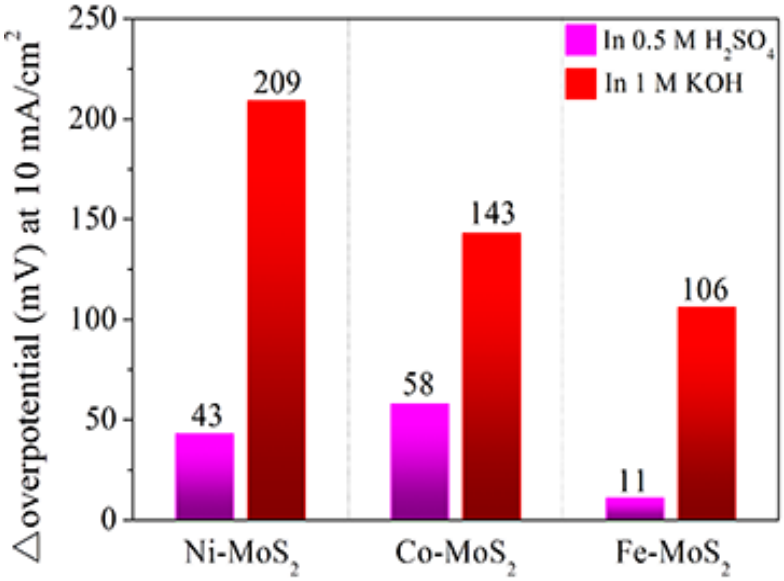
Dr. Pan Liu and Prof. Mingwei Chen, Tohoku University, Japan.

J. Zhang, *et.al*, *Energy Environ. Sci.*, **2016**, *9*, 2789.

Ni content



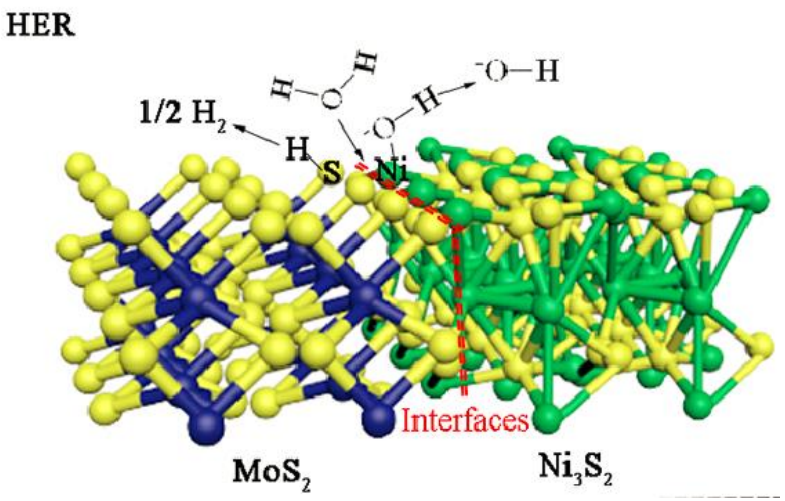


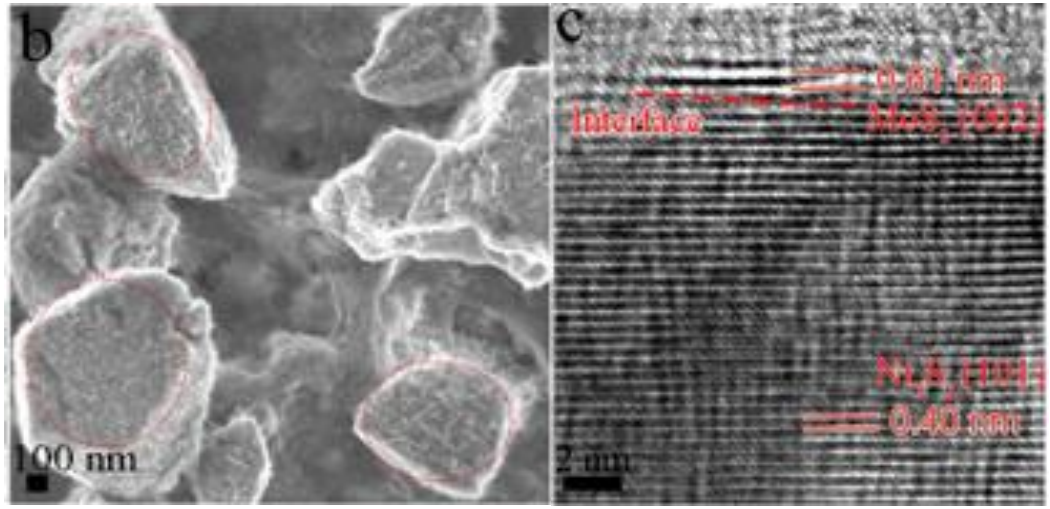


- Ni content in Ni-MoS_2: **13.3 %**
- The excellent HER activity of the Ni-MoS_2 catalysts originates from **accelerated water dissociation**, rather than the hydrogen adsorption property.

J. Zhang, *et.al*, *Energy Environ. Sci.*, **2016**, *9*, 2789.

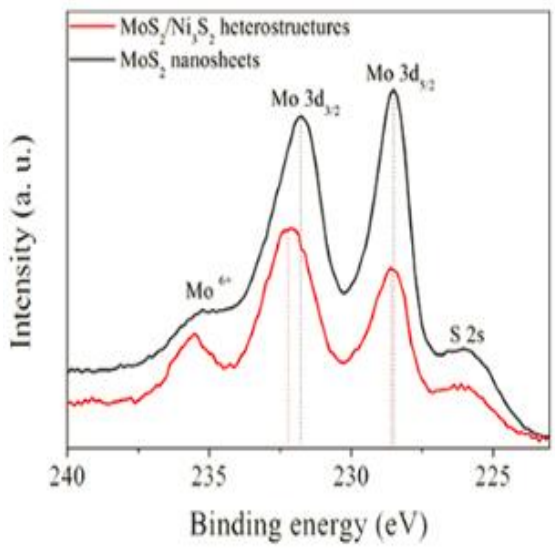
Interface Engineering: MoS_2/Ni_3S_2

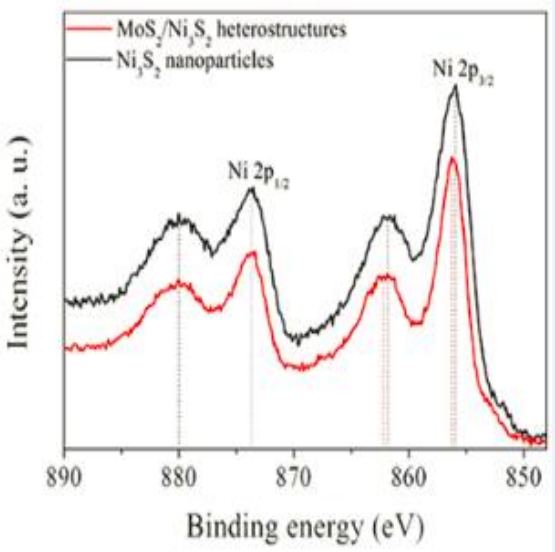




MoS_2 **nanosheets: ~7.8%**

Interfaces between MoS_2 and Ni_3S_2

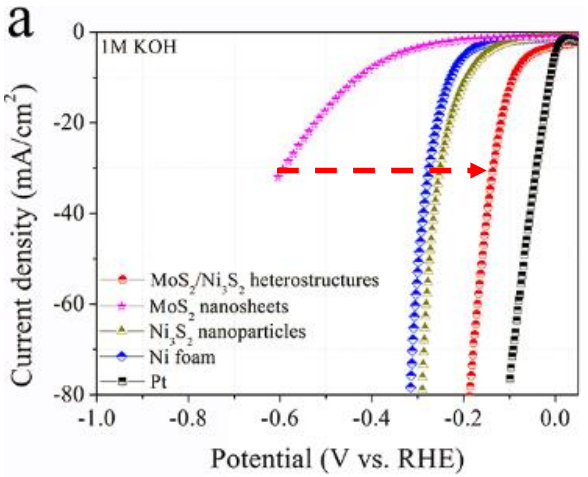


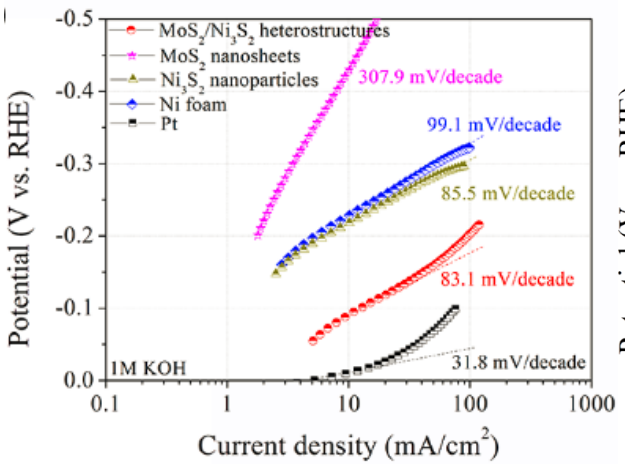


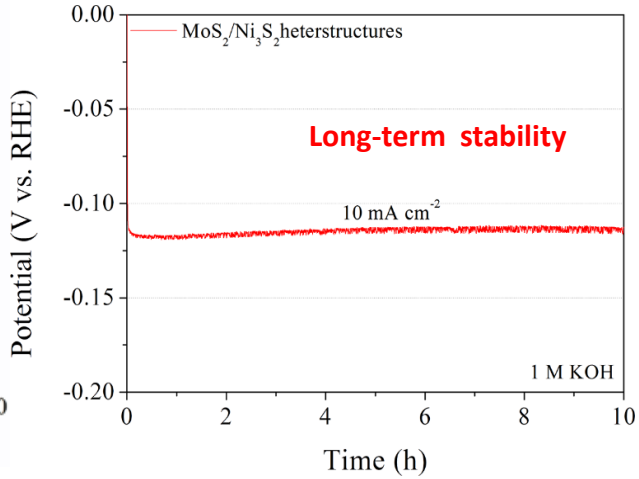
The XPS shifts strongly suggest the existence of **strong electronic interactions** between Ni_3S_2 and MoS_2, which implies the **establishment of coupling interfaces.**

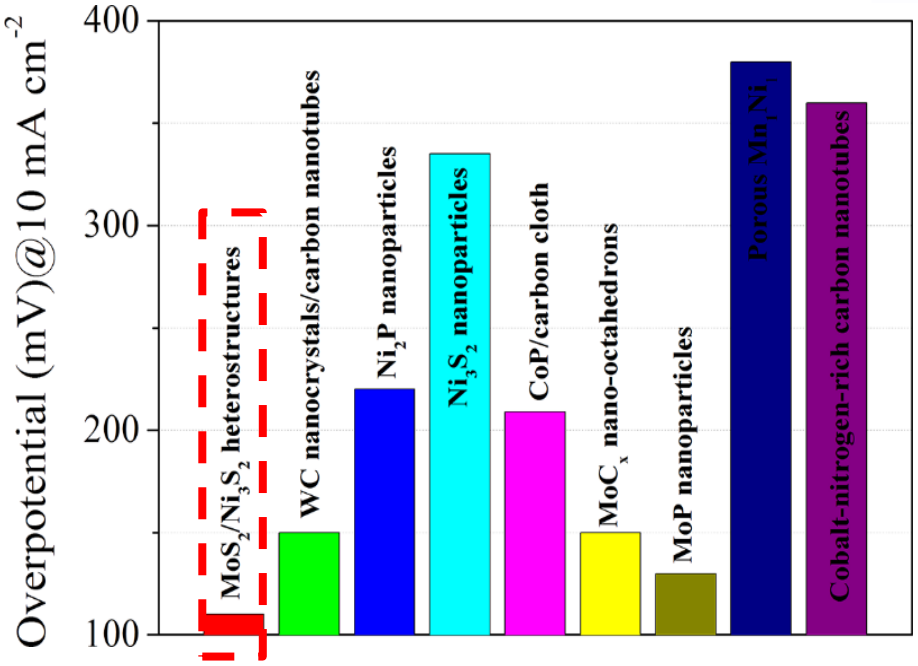
J. Zhang, *et al, Angew. Chem. Int. Ed.* **2016**, *128*, 6814.

HER activity







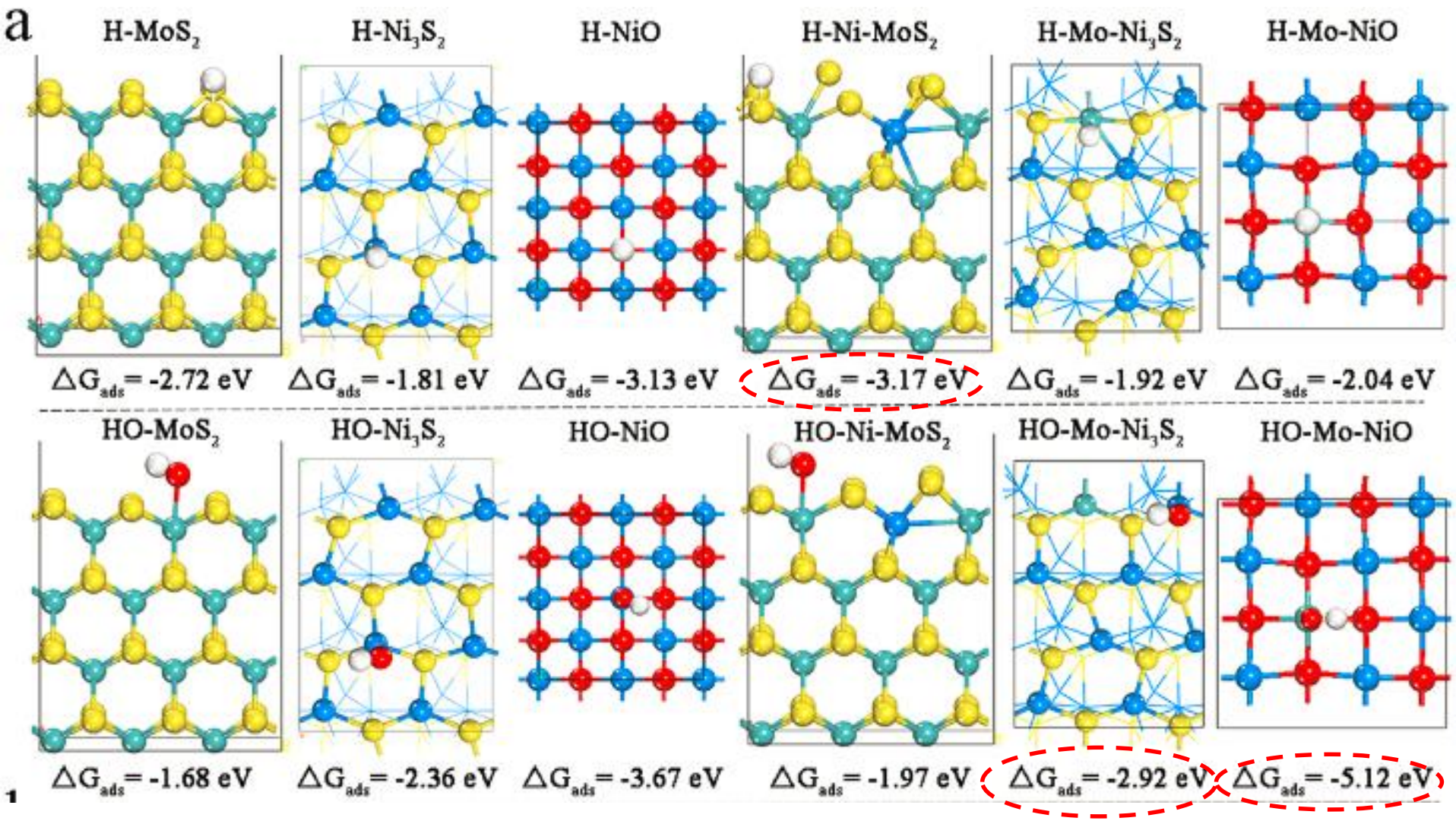


Onset overpotential: **50 mV**

Overpotential at 10 mA/cm^2: **110 mV**

J. Zhang, *et al, Angew. Chem. Int. Ed.* **2016**, *128*, 6814.

Theoretical calculations



J. Zhang, et al, Angew. Chem. Int. Ed. 2016, 128,6814.

NiFe-LDH

HER in alkaline solution:

$H_2O \rightarrow OH^- + 1/2\ H_2$

$H_2O + e^- + cat. \rightarrow H^*\text{-}cat + OH^-$, (Volmer step)

$2H^*\text{-}cat \rightarrow H_2\uparrow$ (Tafel step)

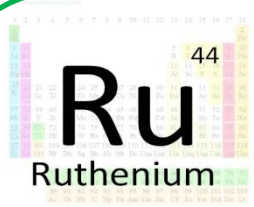
$H^*\text{-}cat + H_2O + e^- \rightarrow cat + OH^- + H_2\uparrow$

NiFe-LDH

- **Ni^{2+} centers: superior adsorption ability toward water molecules and OH intermediates**
- **Fe^{3+} centers: rather weak binding ability for hydrogen**

Poor water dissociation

→ Poor HER activity



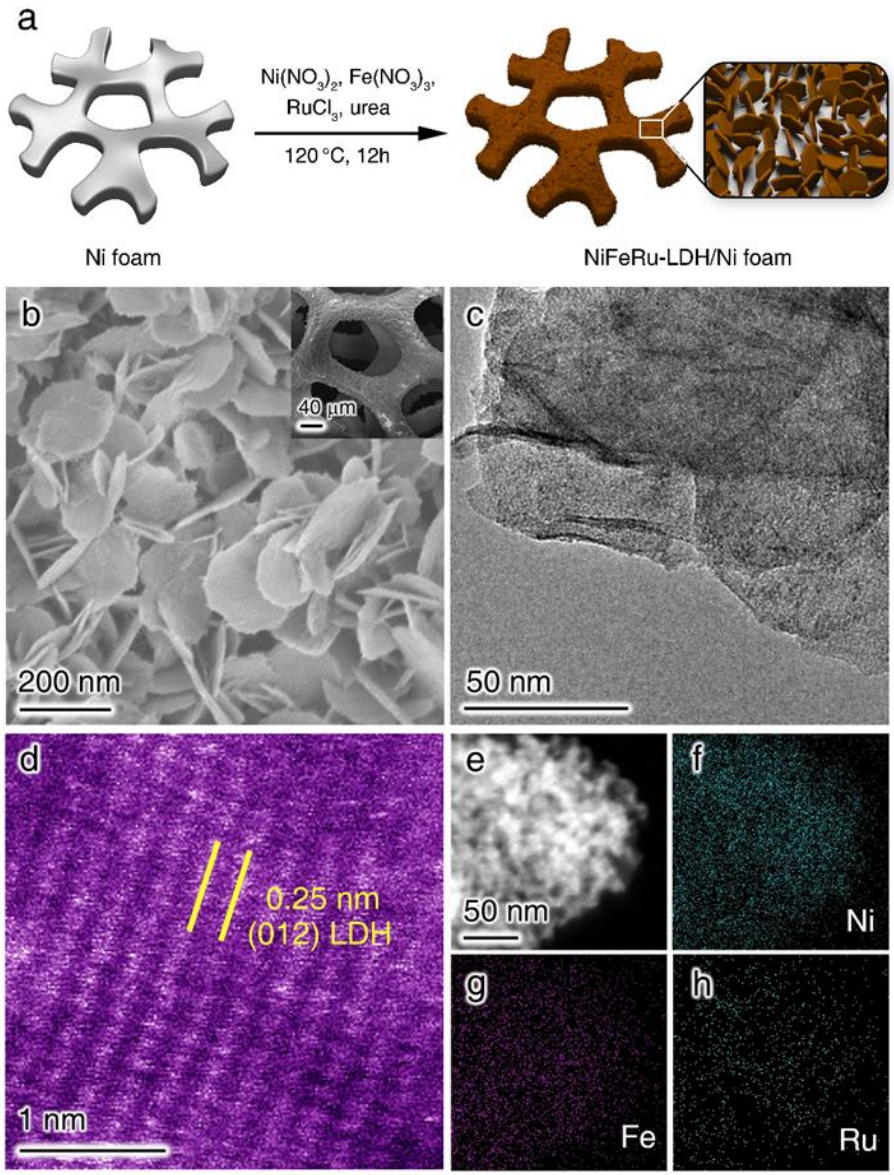
Excellent adsorption capabilities for both H- and O- containing intermediates

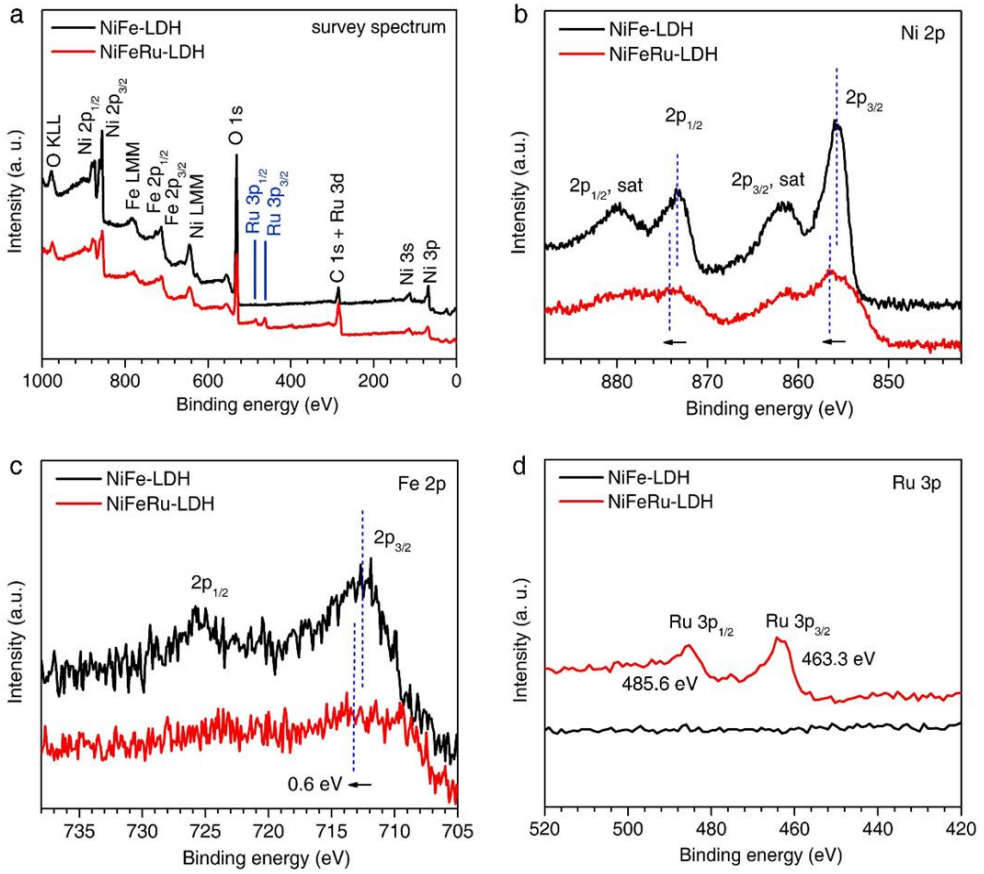
NiFeRu-LDH

- **Accelerate water dissociation kinetics;**
- **Enhance HER activity;**

Science, **2011**, *334*, 1256;
Science, **2017**, *355*, 146.

NiFeRu-LDH



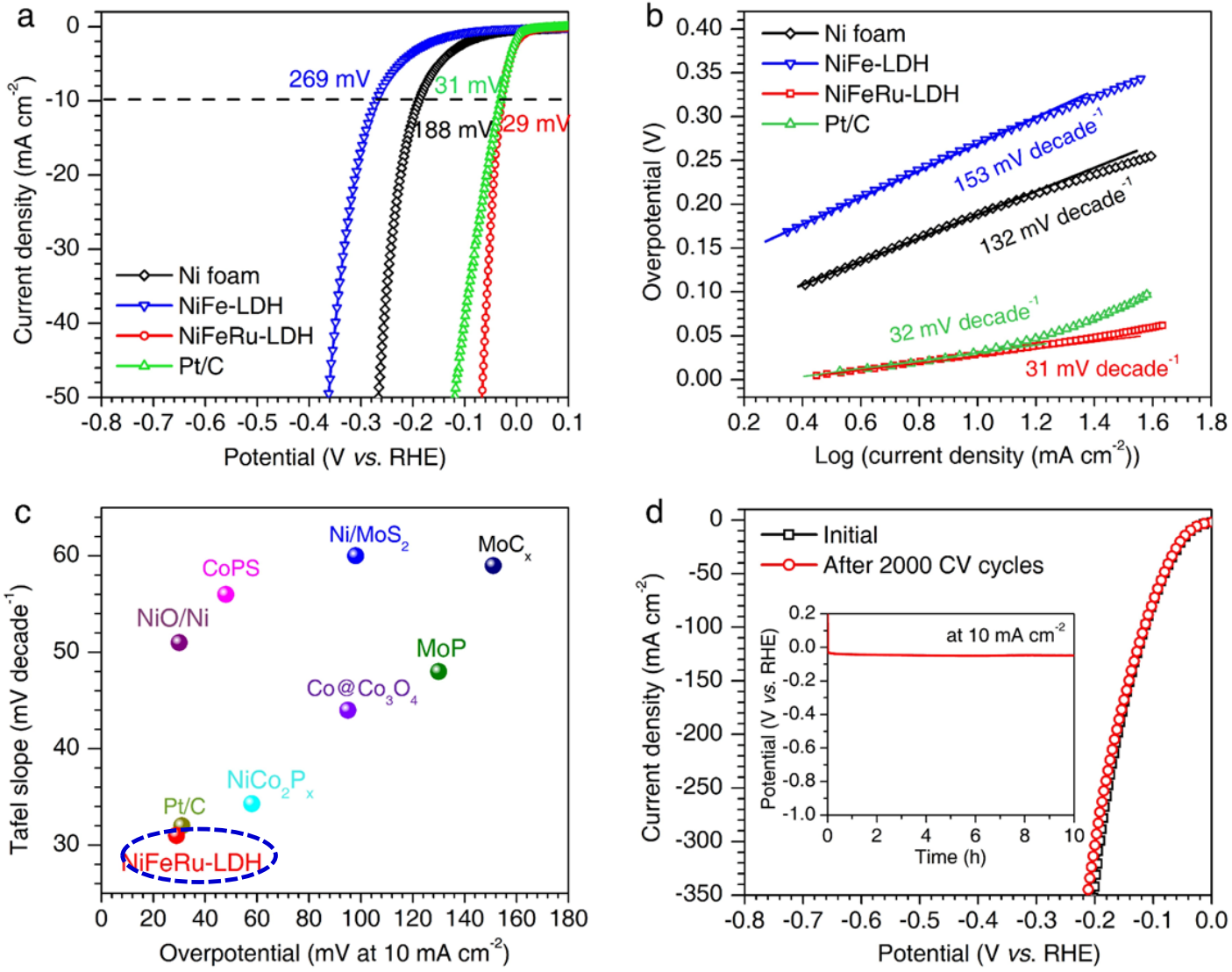


- Thickness: ~23 nm
- Doping of Ru: 16 at%.
- Electronic interaction.

Dr. Pan Liu and Prof. Mingwei Chen, Tohoku University, Japan.

G. Chen, et.al, Adv. Mater. **2018**, *30*, 1706279.

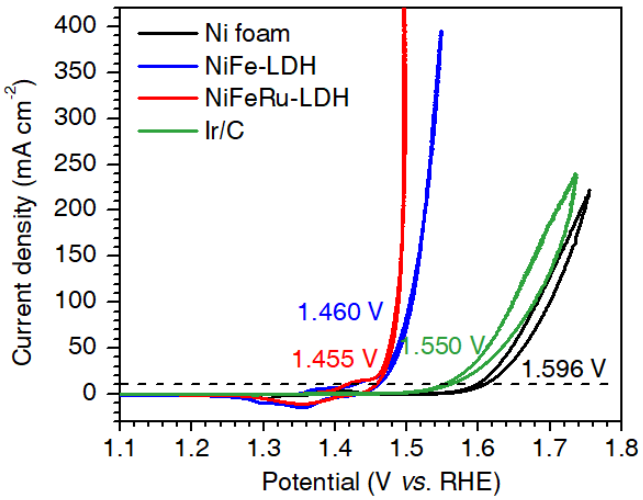
HER activity

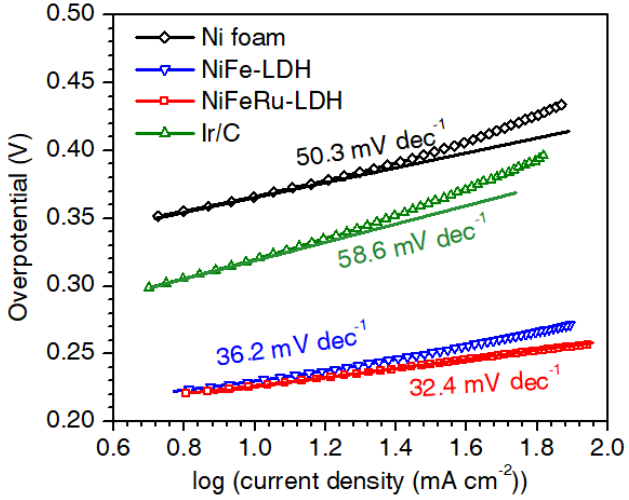


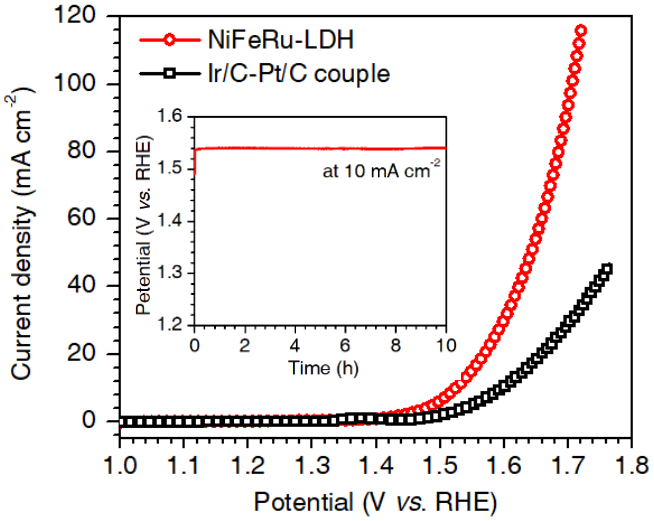
- Overpotential: 29 mV @ 10 mA cm^{-2}
- Tafel slope: 31 mV decade^{-1}. → accelerated Volmer step

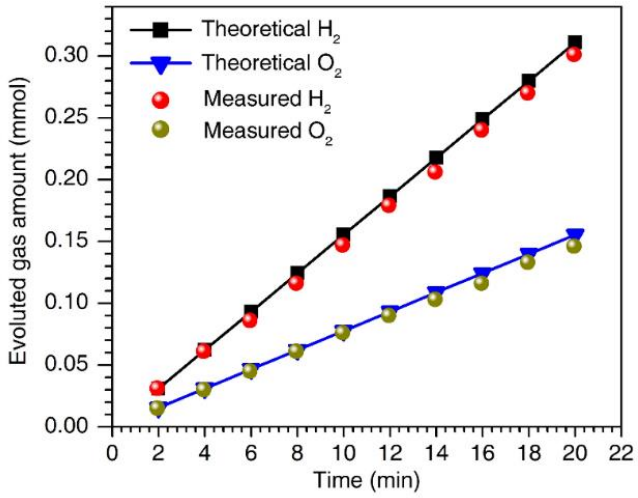
G. Chen, et.al, Adv. Mater. **2018**, *30*, 1706279.

OER and Overall water splitting





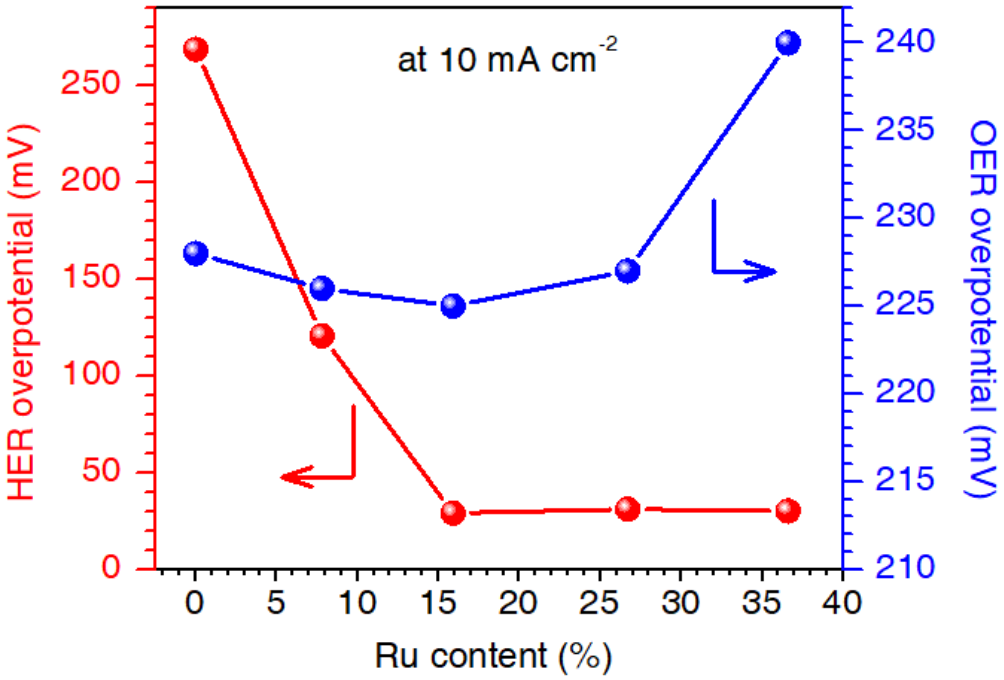


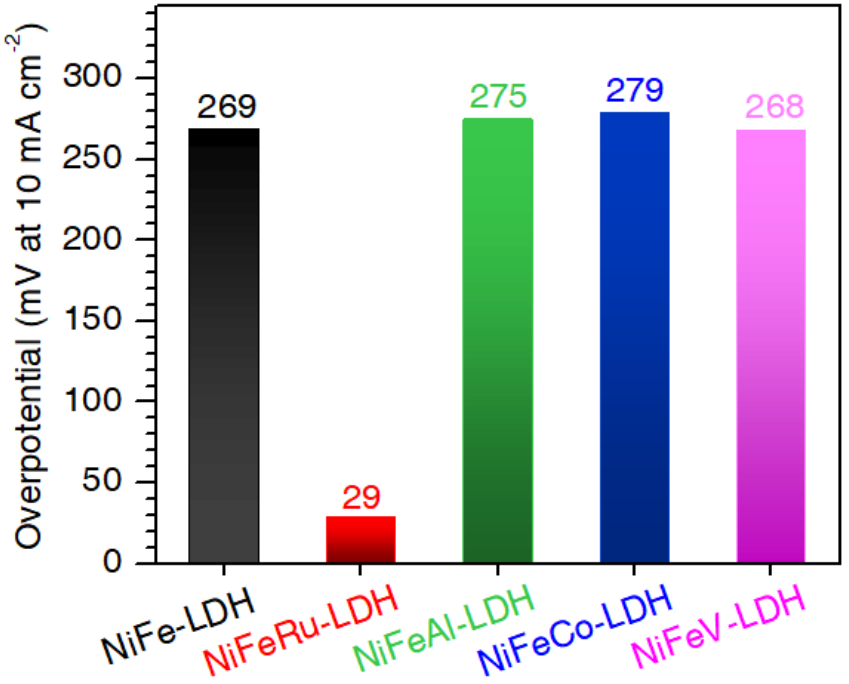


- OER overpotential: 225 mV @ 10 mA cm^{-2}
- Overall water splitting overpotential: 290 mV at 10 mA cm^{-2}

G. Chen, et.al, Adv. Mater. **2018**, *30*, 1706279.

Active sites

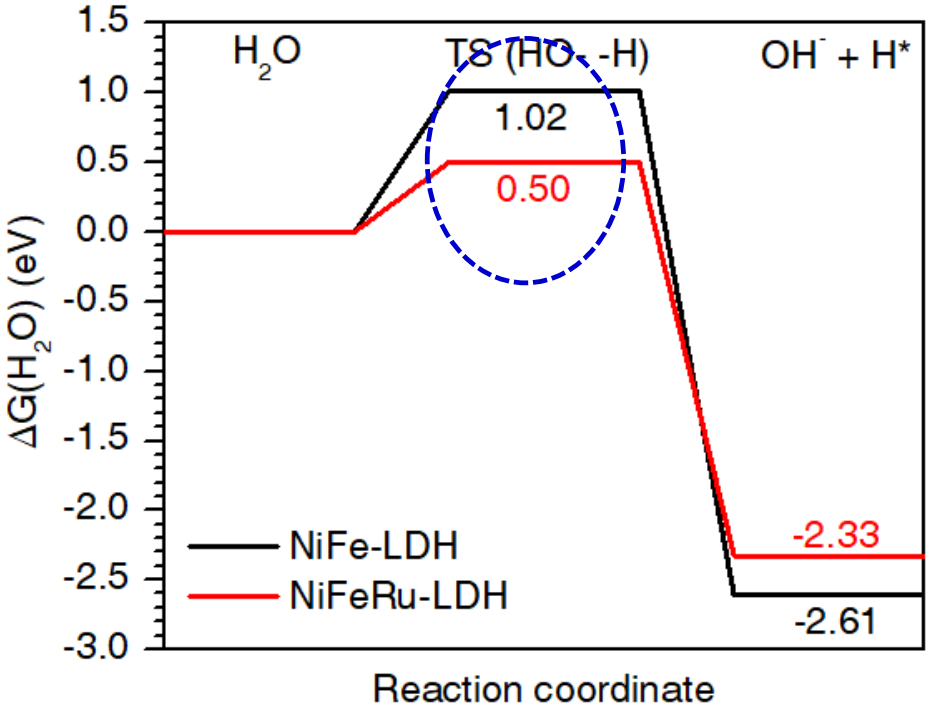


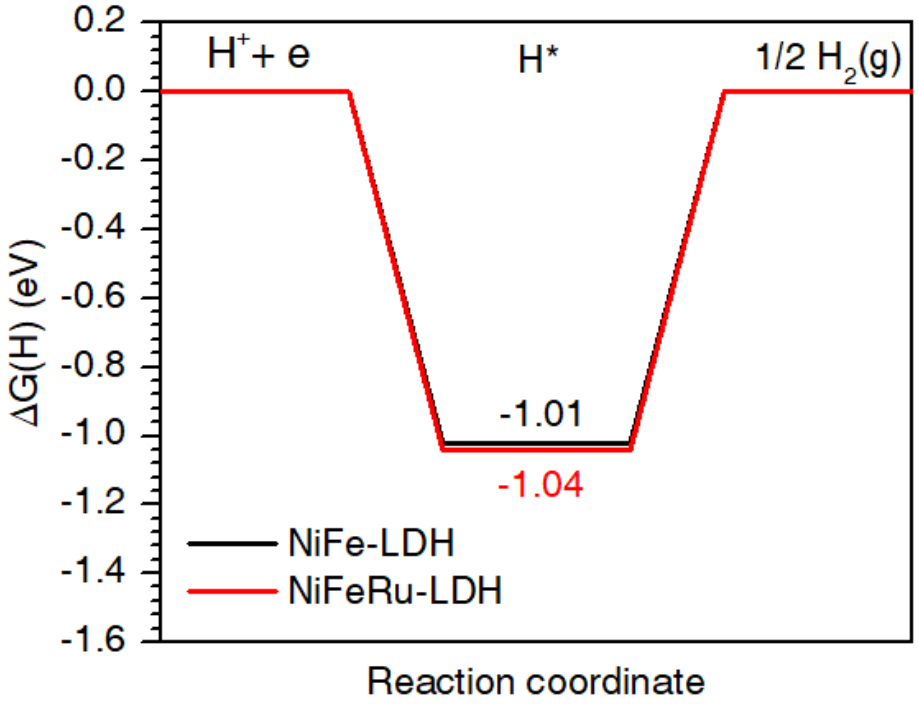


- **16%** Ru in NiFeRu-LDH;
- NiFe-LDH, **NiFeRu-LDH**, NiFeAl-LDH, NiFeCo-LDH, NiFeV-LDH.

G. Chen, et.al, Adv. Mater. **2018**, *30*, 1706279.

Theoretical calculations





Accelerated Water dissociation kinetics.

Dr. Tao Wang, SunCat center, Stanford University, USA

G. Chen, et.al, Adv. Mater. **2018**, *30*, 1706279.

Conclusions and outlook

- Water dissociation is the rate-limited step in alkaline solution;
- MoNi-based active sites can largely lower the kinetic energy barrier of the Volmer;
- Understanding the alkaline HER mechanism and probe the adsorption states of H_2O, H and OH intermediates;
- Engineering the water dissociation active sites for other 2D materials systems towards outstanding HER performance.

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