Dresden, Germany
June 05-09, 2-17

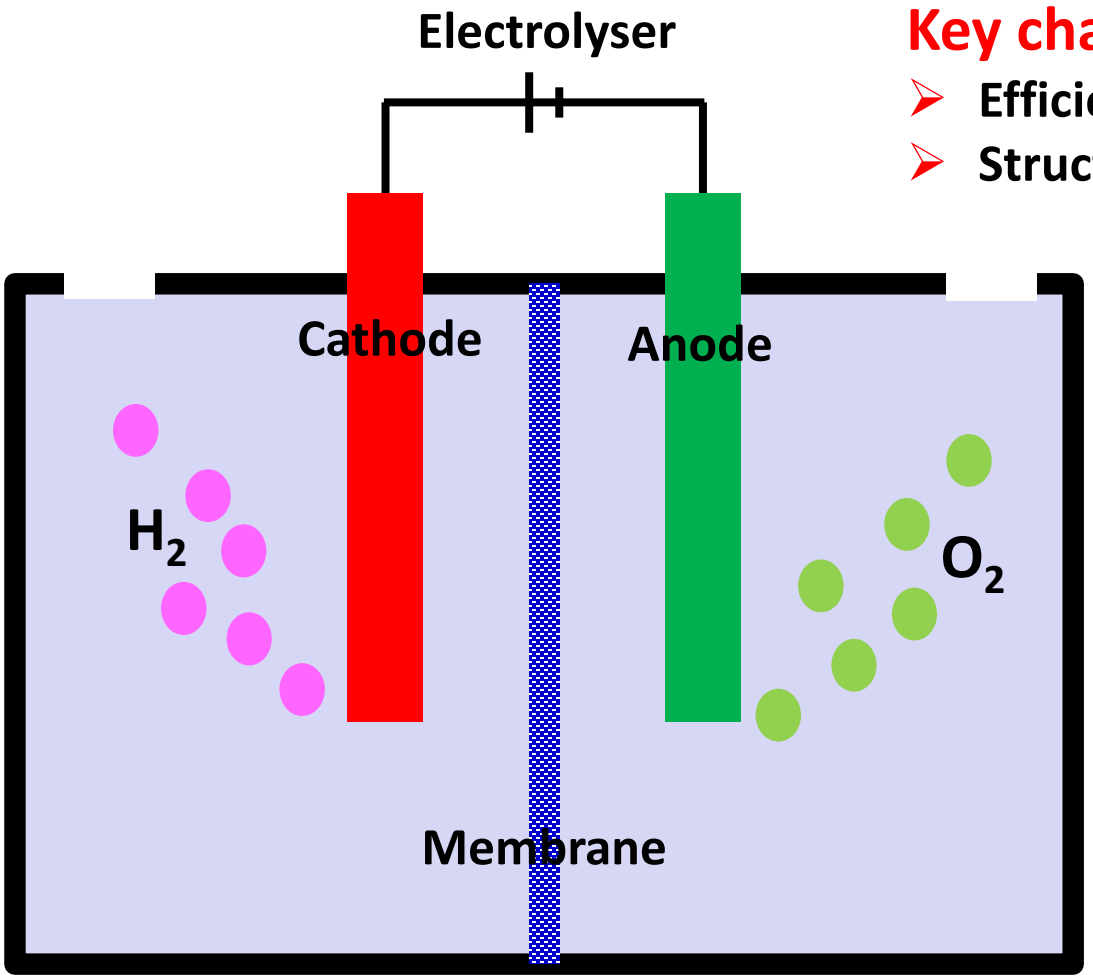
Efficient Hydrogen Production by Tailoring Electrocatalysts with Fast Water Dissociation Kinetics

Jian Zhang, Xinliang Feng

Chair for Molecular Functional Materials, cfaed, TU Dresden,
Dresden, Germany

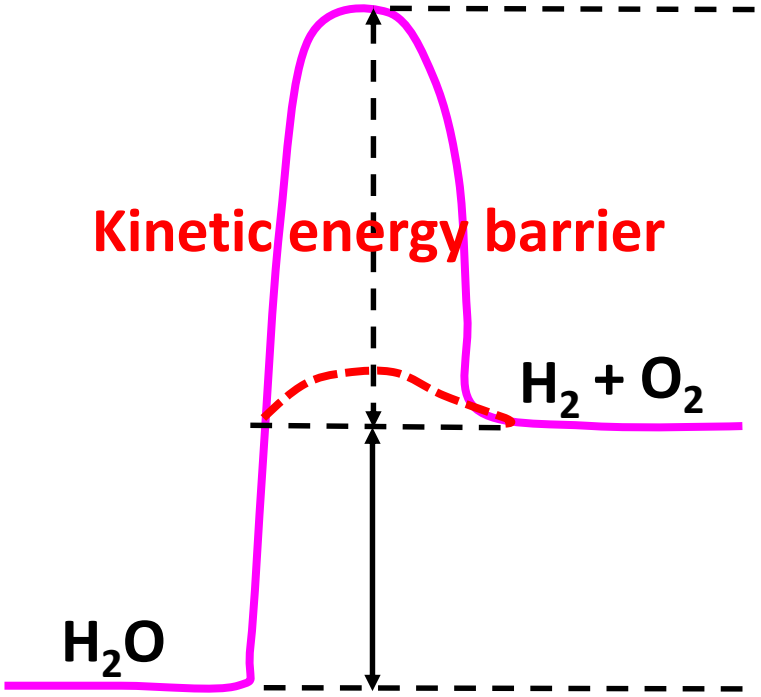
June 06, 2017

Introduction



Key challenges:

- Efficient, stable, low-cost HER catalysts;
- Structure of active sites.



Hydrogen evolution reaction (HER):

Acidic media: $2H^+ + 2e^- \longrightarrow H_2$

Alkaline media: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Noble metal Pt:

Overpotential: 30 mV at 10 mA/cm²;

Tafel slope = 30 mV/decade.

M. G. Walter, et al, *Chem. Rev.* 2010, 110, 6446-6473.

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.

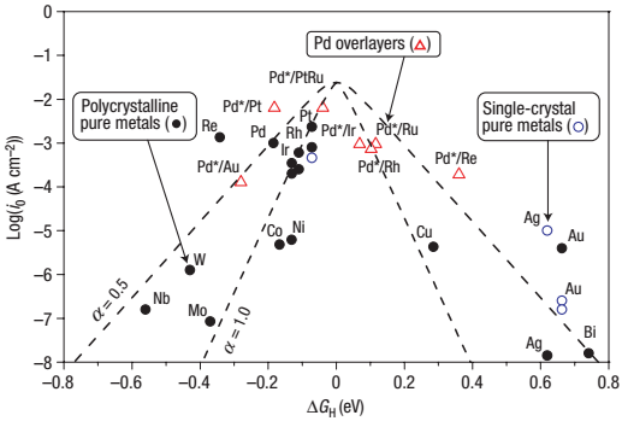
Motivation

HER mechanism in acidic solutions:

Volmer: $H^+ + e^- \longrightarrow H^*$

Tafel: $H^* + H^* \longrightarrow H_2$

Heyrovsky: $H^* + e^- + H^+ \longrightarrow H_2 + OH^-$

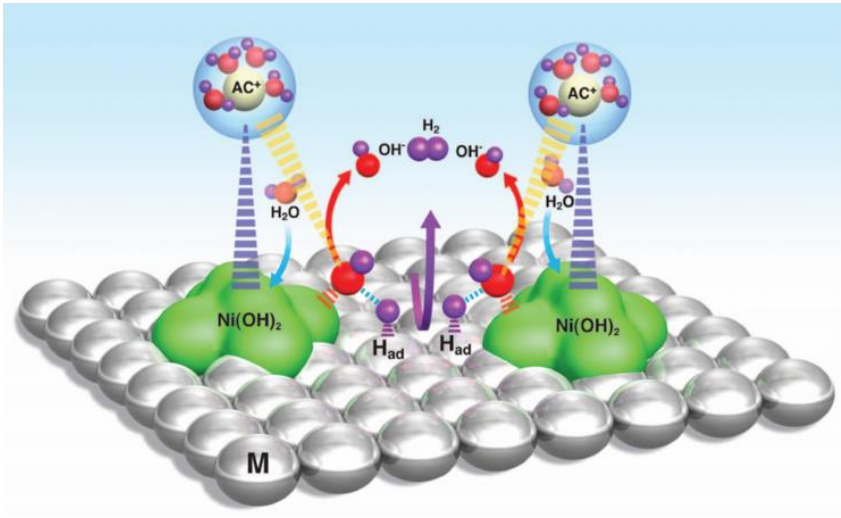


HER mechanism in basic solutions:

Volmer: $H_2O + e^- \longrightarrow OH^- + H^*$

Tafel: $H^* + H^* \longrightarrow H_2$

Heyrovsky: $H^* + e^- + H_2O \longrightarrow H_2 + OH^-$

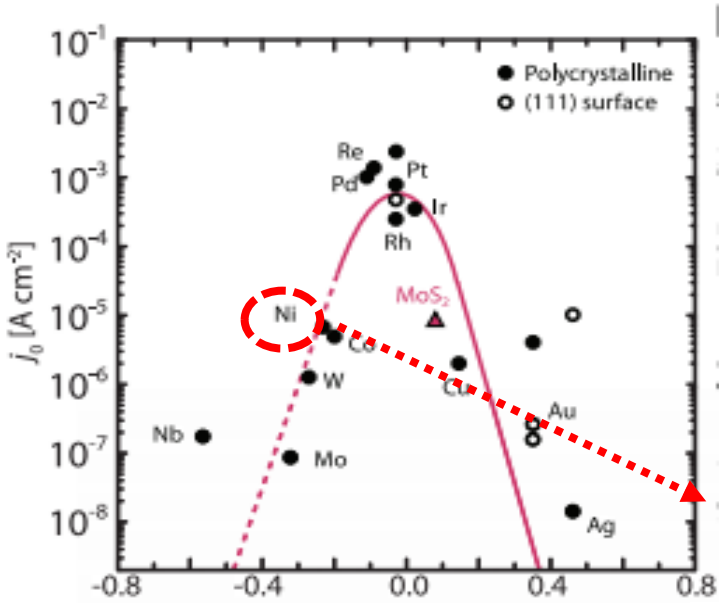


Key rate-limited step:

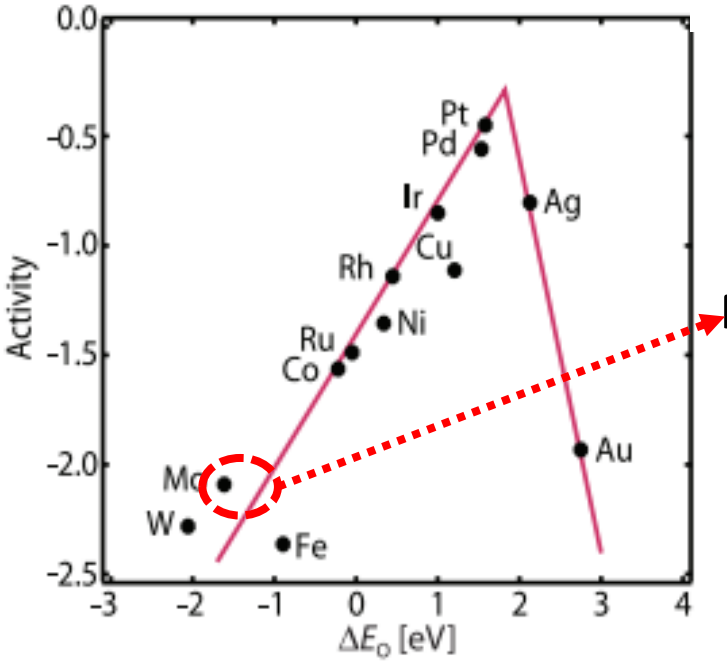
Dissociation of H_2O or Combination of H* into H_2

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

Motivation



Ni: strong H adsorption



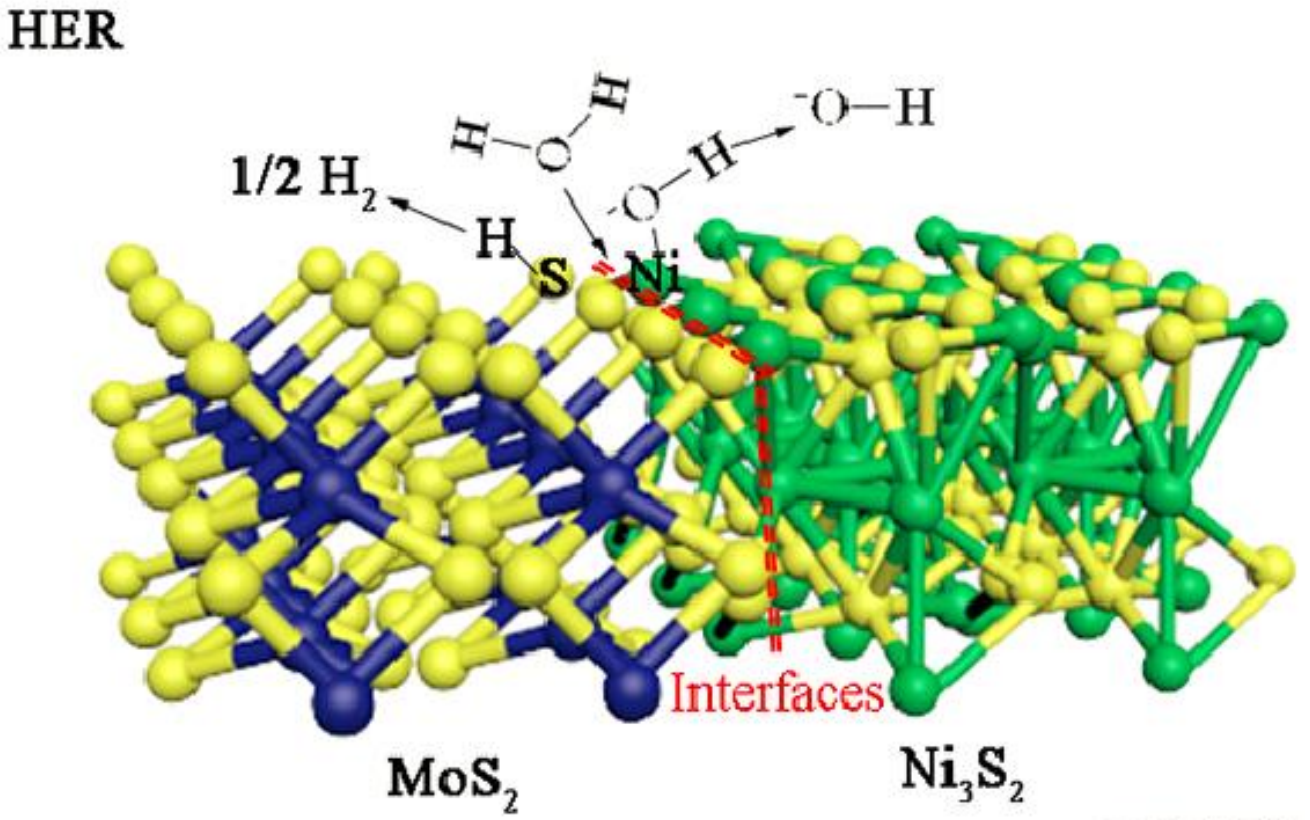
Mo: strong O adsorption

Accelerated Volmer step

MoNi-based catalysts: facilitate water dissociaton.

R. Subbaraman, et al, *Nat. Mater.*, 2012, *11*, 550–557.

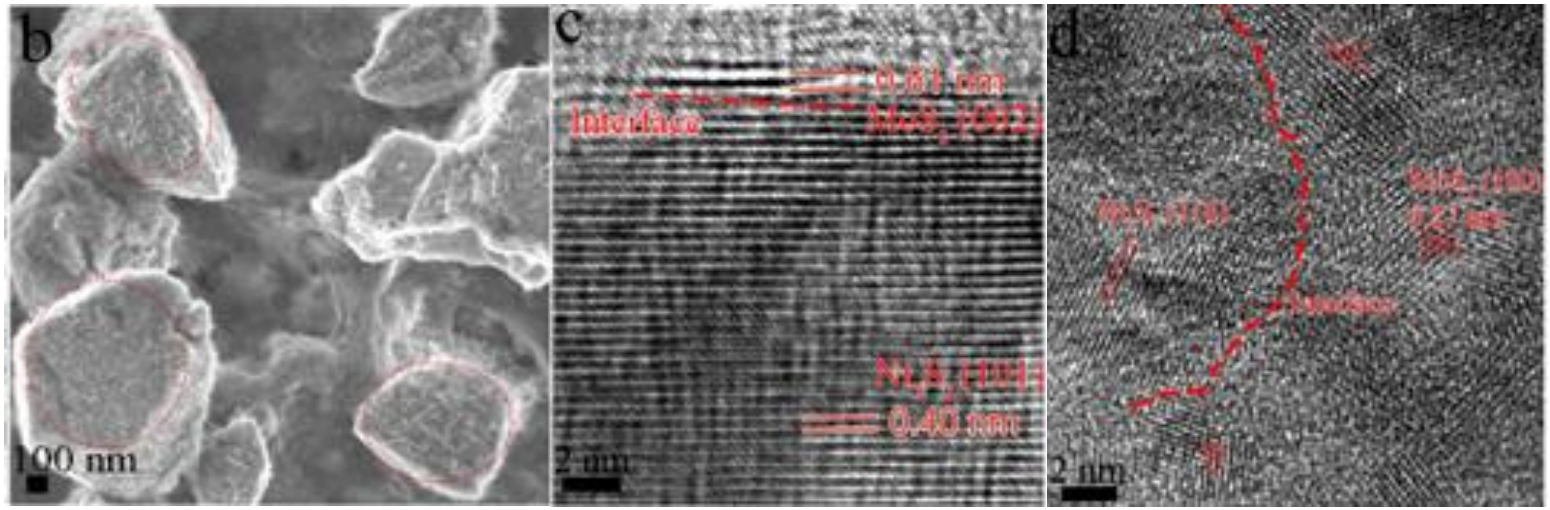
Interface Engineering



Interface engineering to improve the chemisorption interactions of hydrogen and oxygen-containing intermediates on the catalysts, facilitating the dissociation of water molecules into H_2 and O_2.

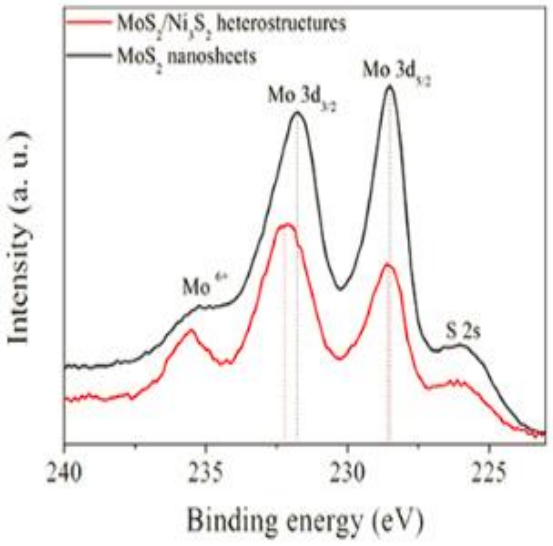
J. Zhang, et al, Angew. Chem. Int. Ed. 2016, 128,6814.

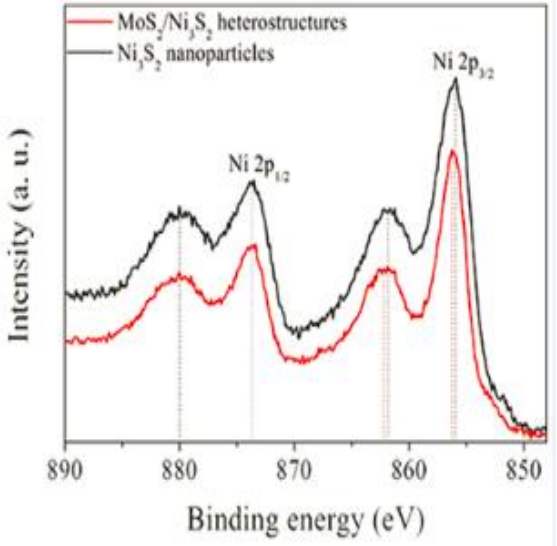
MoS_2/Ni_3S_2 heterostructures



MoS_2 nanosheets (~7.8%) on Ni_3S_2 nanoparticles

Interfaces between the (002) and (100) facets of MoS_2 and the (101) and (110) surfaces of Ni_3S_2

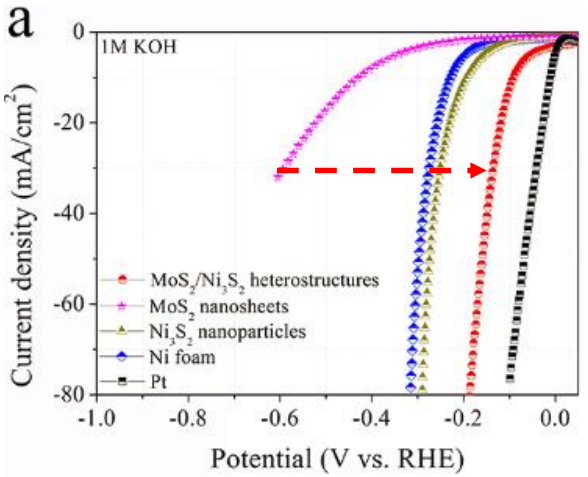


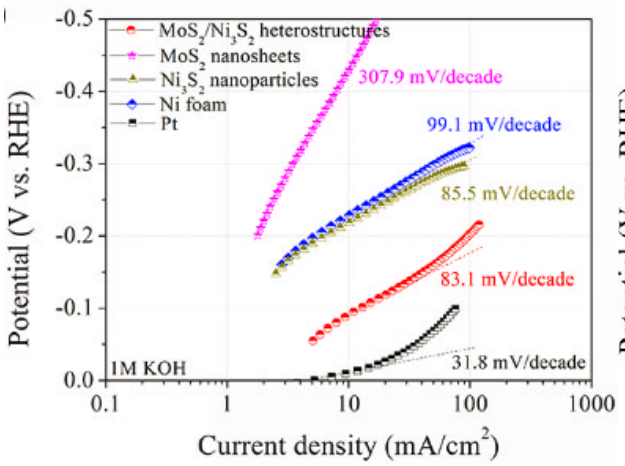


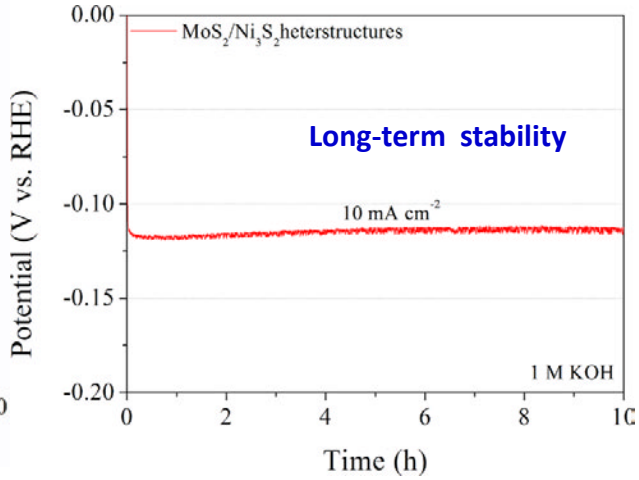
The XPS shifts strongly suggest the existence of strong electronic interactions between Ni_3S_2 and MoS_2, which implies the establishment of coupling interfaces.

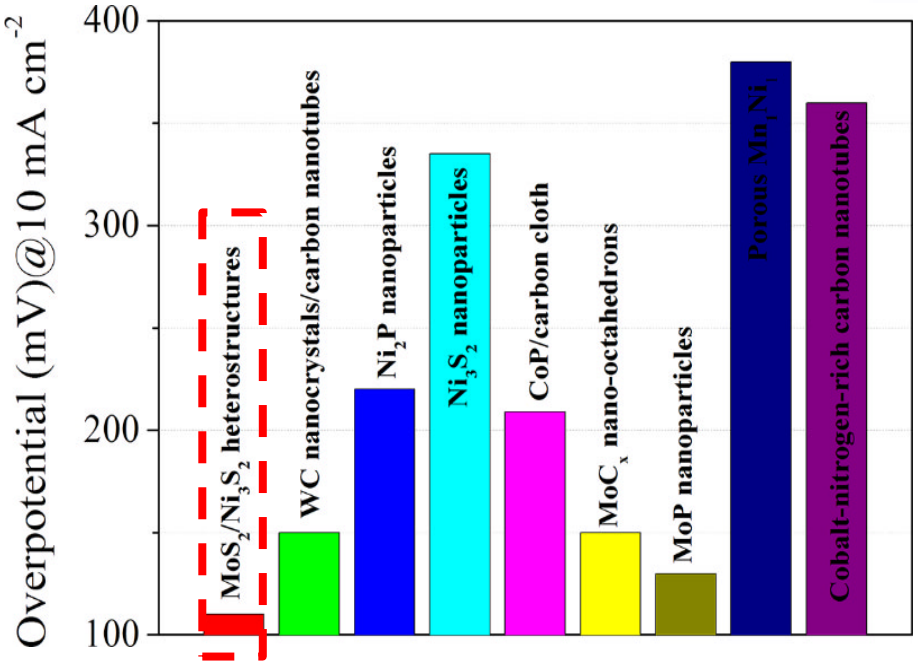
J. Zhang, et al, Angew. Chem. Int. Ed. 2016, 128,6814.

HER activity







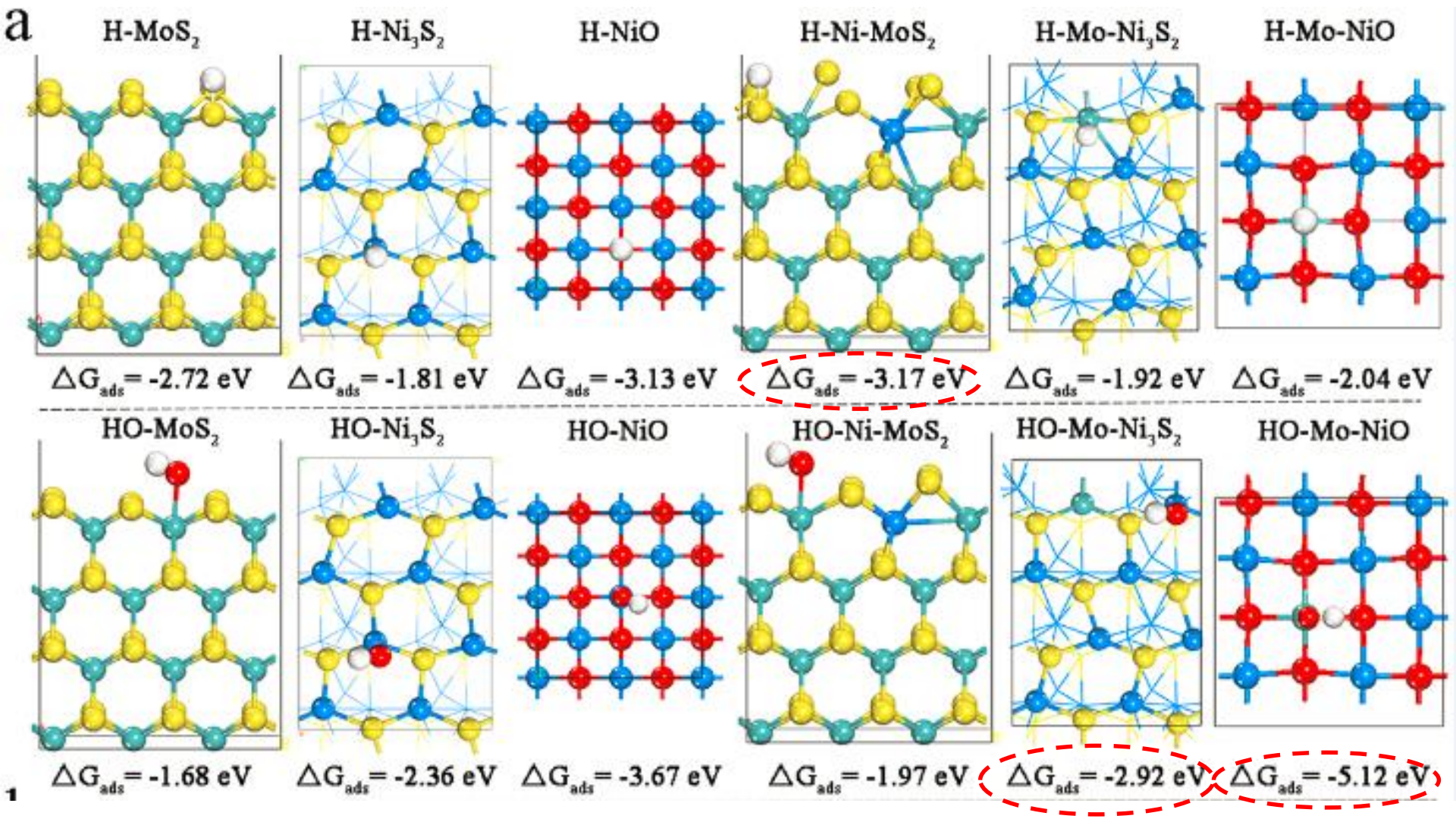


Onset overpotential: 50 mV

Overpotential at 10 mA/cm^2: 110 mV

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

DFT calculations

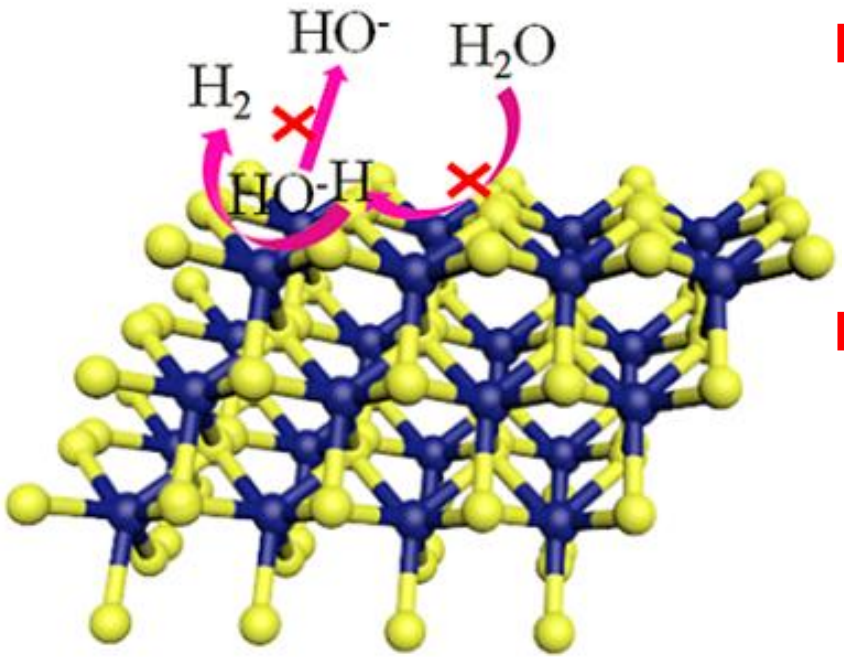


J. Zhang, et al, Angew. Chem. Int. Ed. 2016, 128,6814.

Engineering active sites

MoS_2 for HER in basic solutions:

MoS_2:

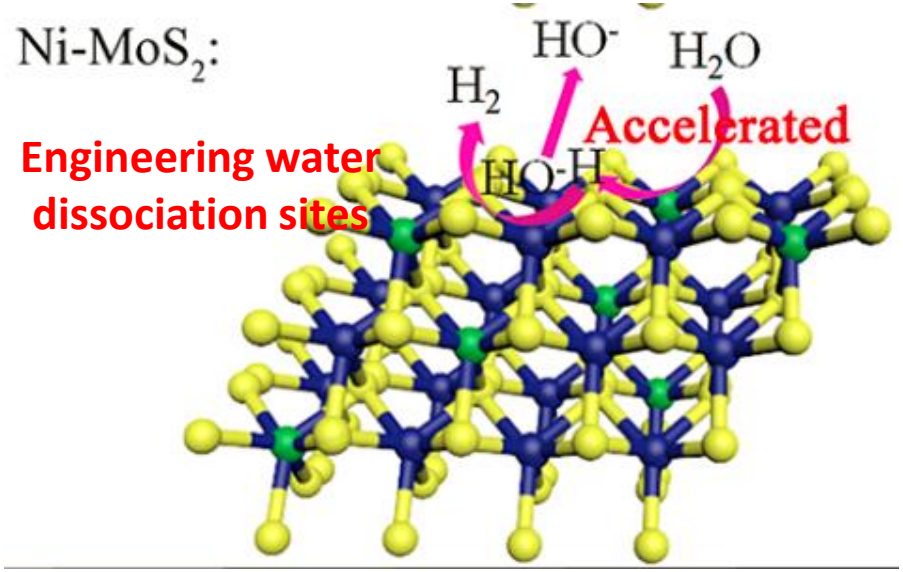


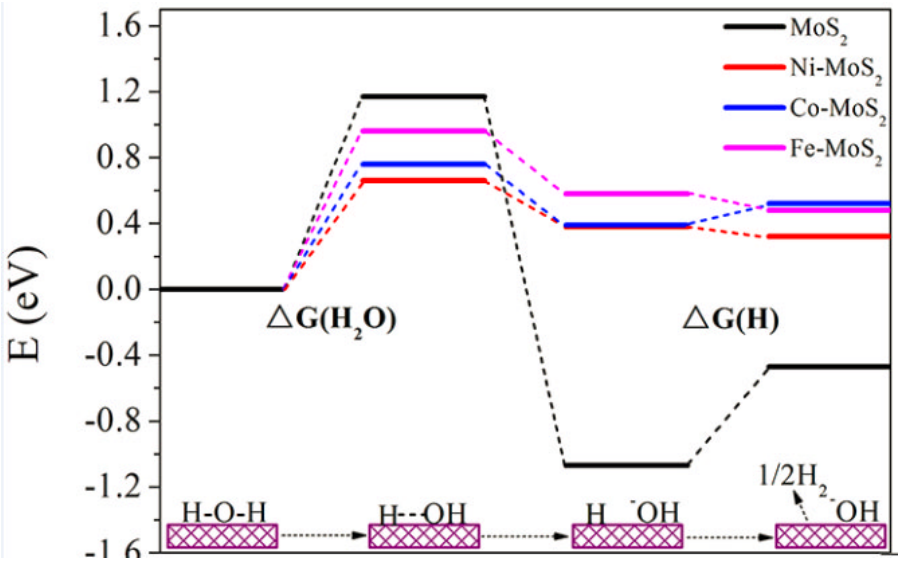
- Large kinetic energy barrier of water dissociation on MoS_2 catalysts;
- Strong adsorption interaction of the formed ^{-}OH on MoS_2 catalysts.

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.

DFT calculations





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

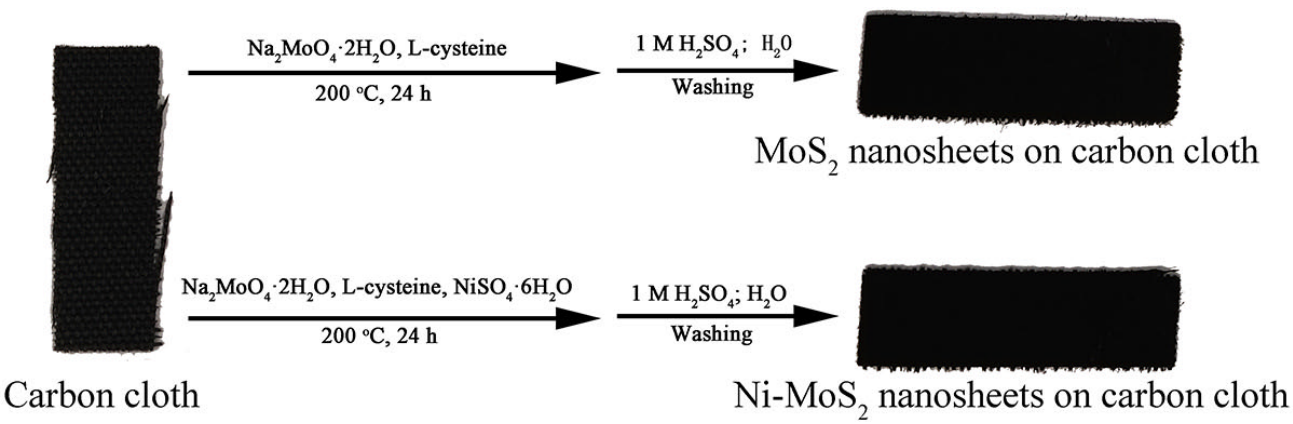
- **The kinetic energy barrier of water dissociation was decreased from 1.17 eV on MoS_2 to 0.66 eV on $Ni\text{-}MoS_2$;**
- **The desorption of ^-OH was facilitated on $Ni\text{-}MoS_2$;**

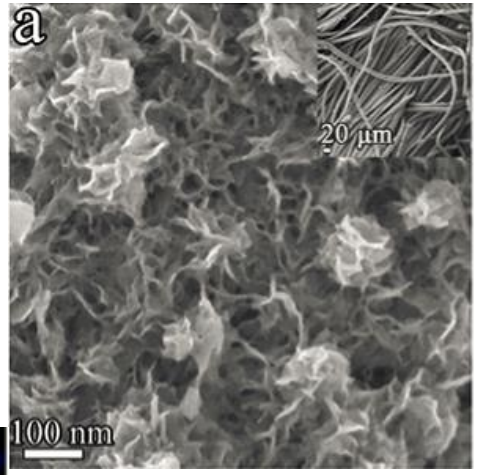
	△G(H_2O) (eV)	G(OH) (eV)	△G(H) (eV)
MoS_2	1.17	-5.24	0.60
$Ni\text{-}MoS_2$	0.66	-3.46	-0.10
$Co\text{-}MoS_2$	0.76	-3.46	-0.06
$Fe\text{-}MoS_2$	0.96	-3.36	0.13

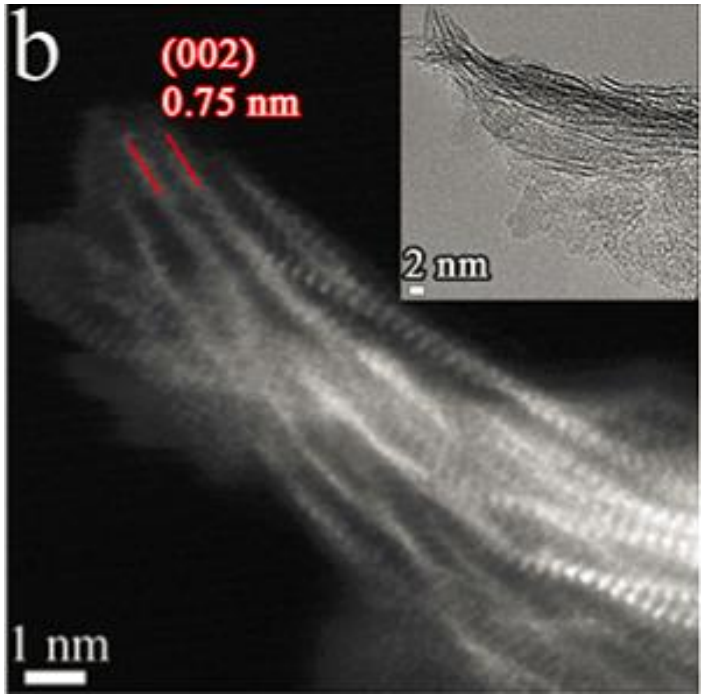
Dr. Tao Wang, Laboratoire de Chimie, CNRS, France

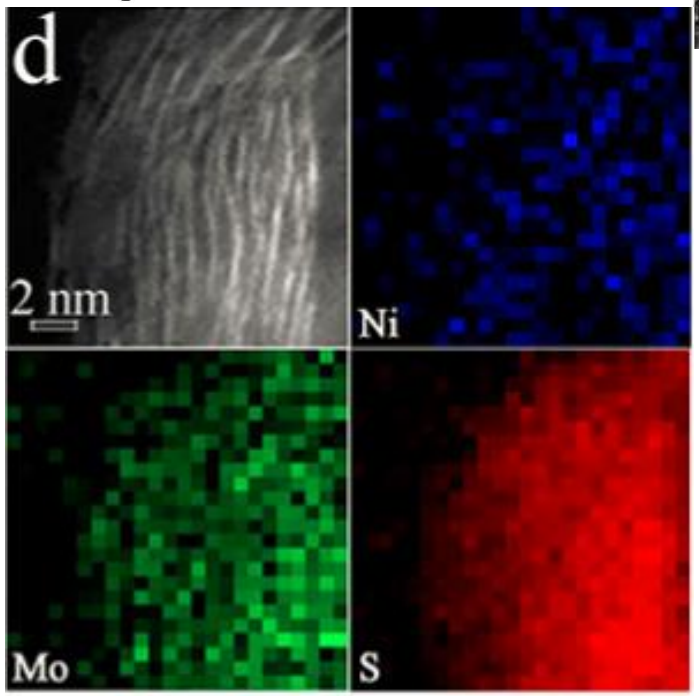
J. Zhang, *et.al*, *Energy Environ. Sci.*, 2016, 9, 2789.

Morphology







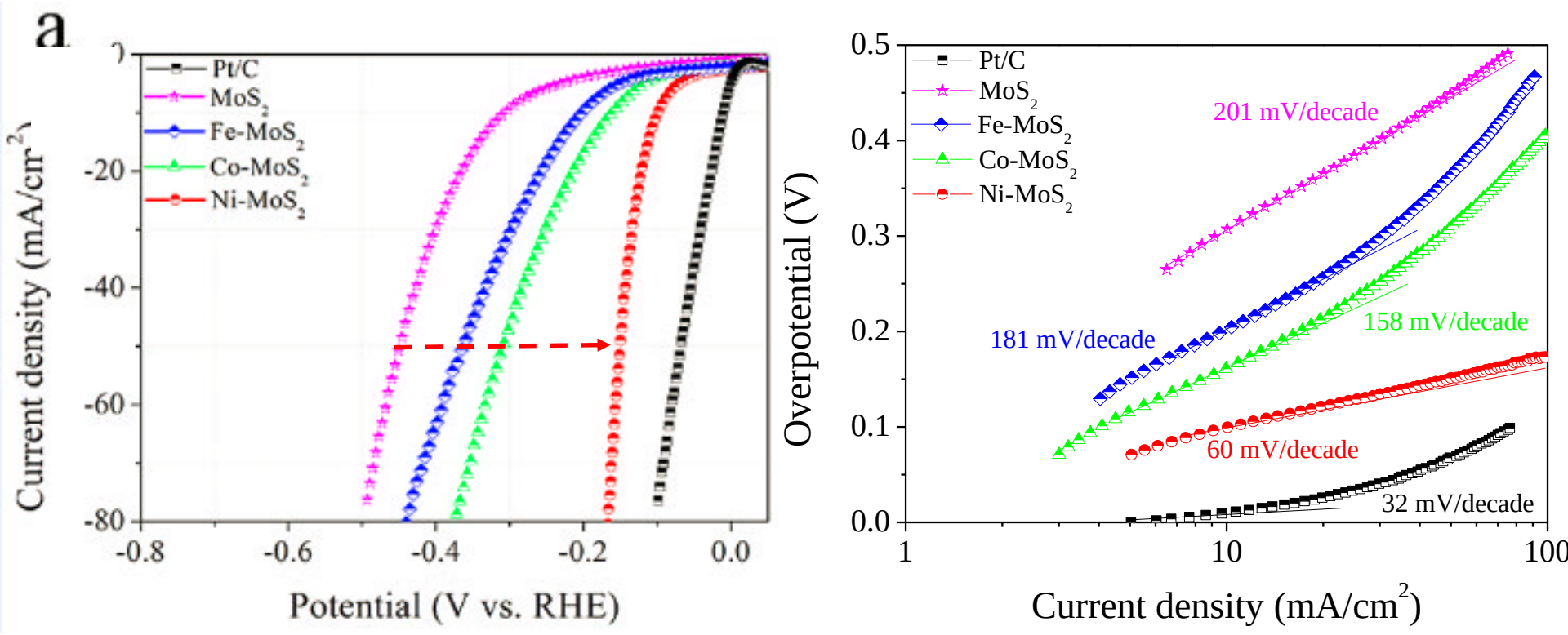


Ni atoms were homogeneously doped into crystalline MoS_2 nanosheets.

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

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

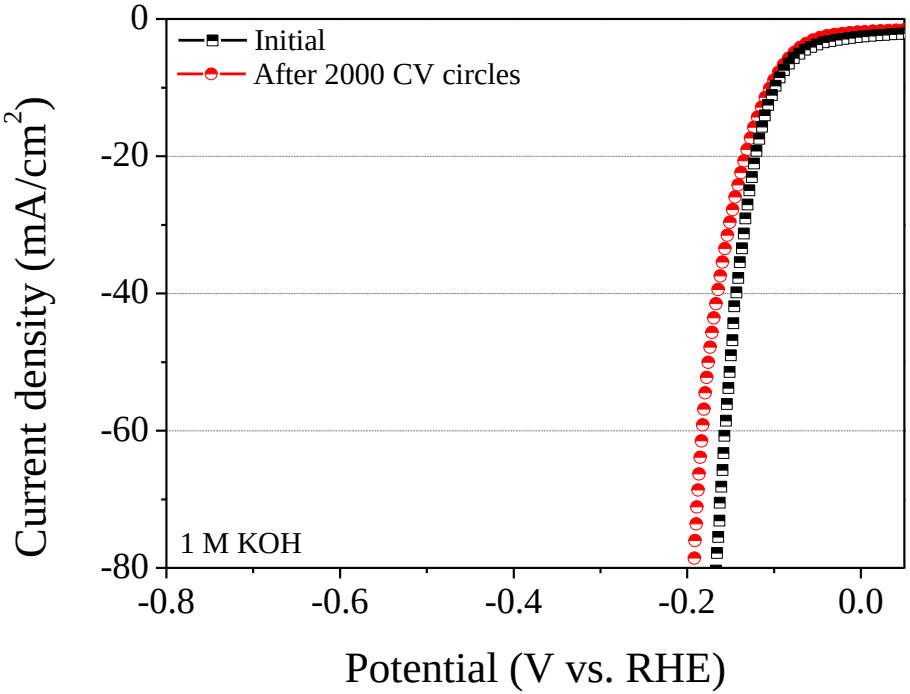
HER activity

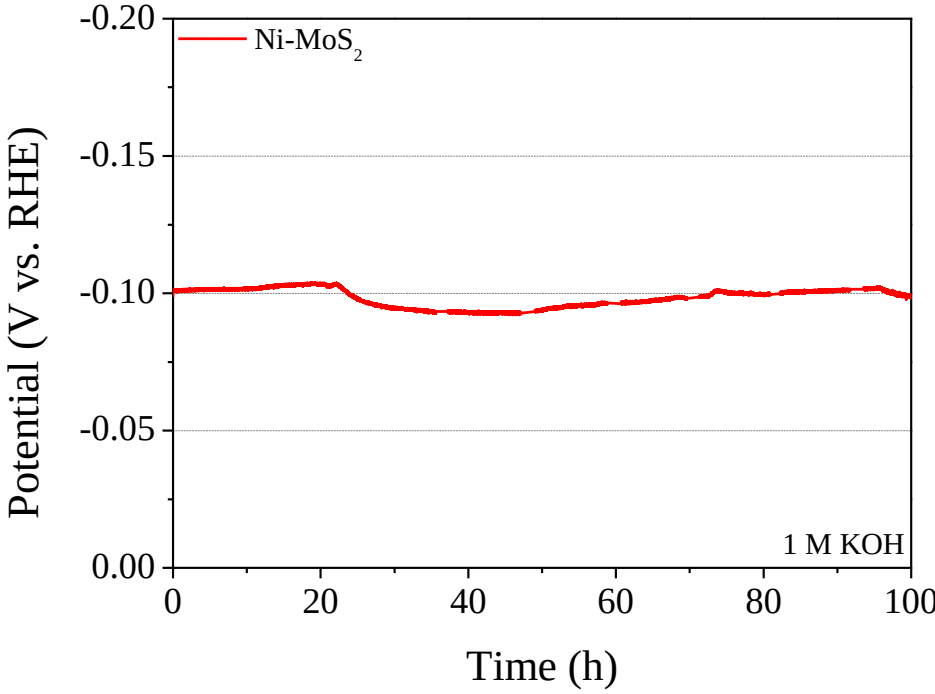


Overpotential at 10 mA/cm²: 98 mV. **Tafel slope: 60 mV per decade.**

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

Stability

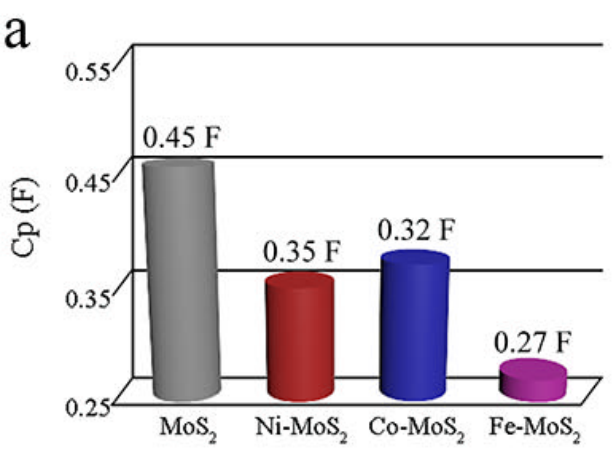


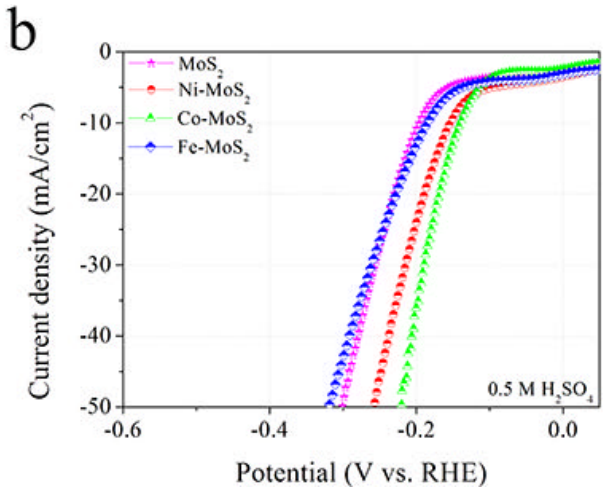


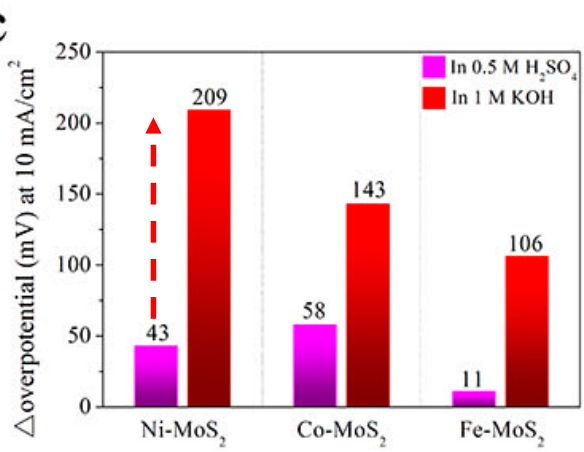
Increased overpotential: ~8 mV **Long-term stability**

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

Cp and HER







Electrochemical capacitances (Cp)

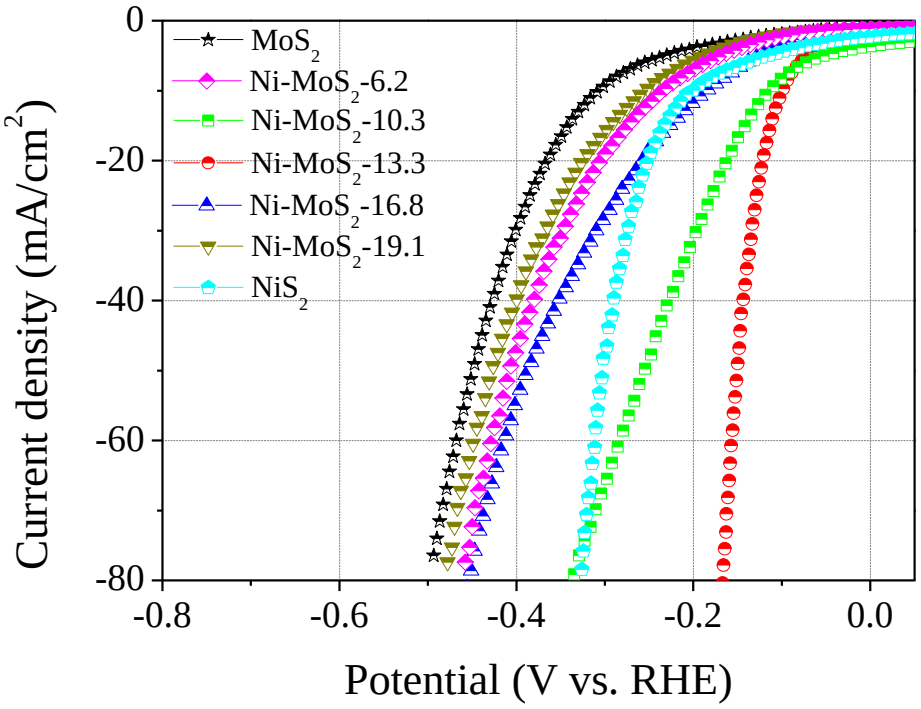
HER in 0.5 M H_2SO_4 solution

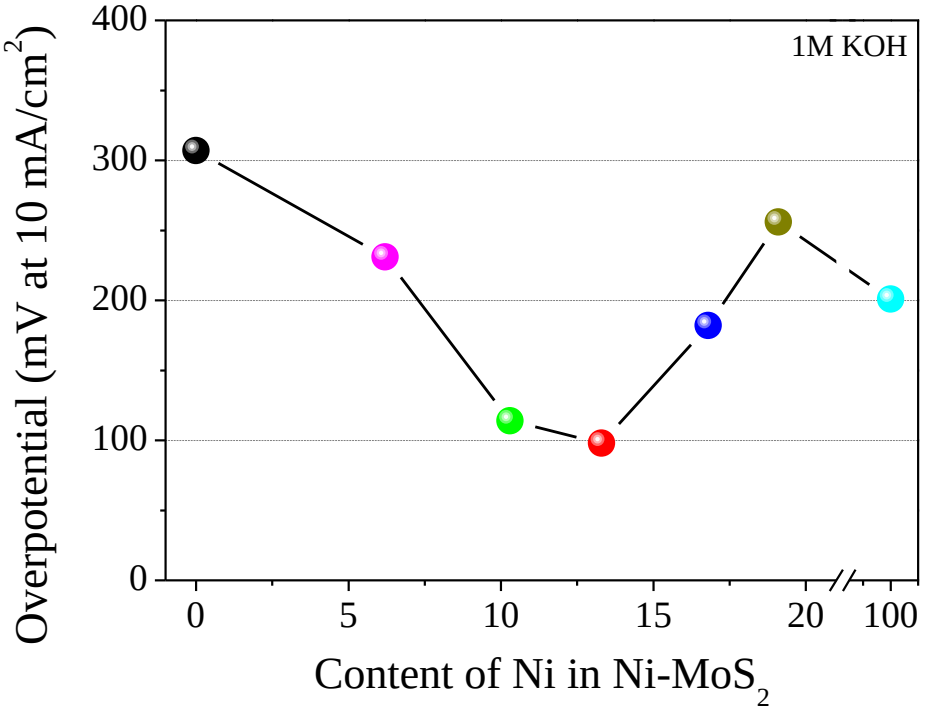
- Decreased Cp from **0.45 F** of MoS_2 to **0.35 F** of Ni-MoS_2;
- Overpotential$_{\text{at 10 mA/cm2}}$ after Ni doping: **43 mV** in 0.5 M H_2SO_4 and **209 mV** in 1 M KOH.

The excellent HER activity of the Ni-MoS_2 catalysts originates from **the improved HER kinetics and accelerated water dissociation**, rather than the active surface area and hydrogen adsorption property.

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

Doping content



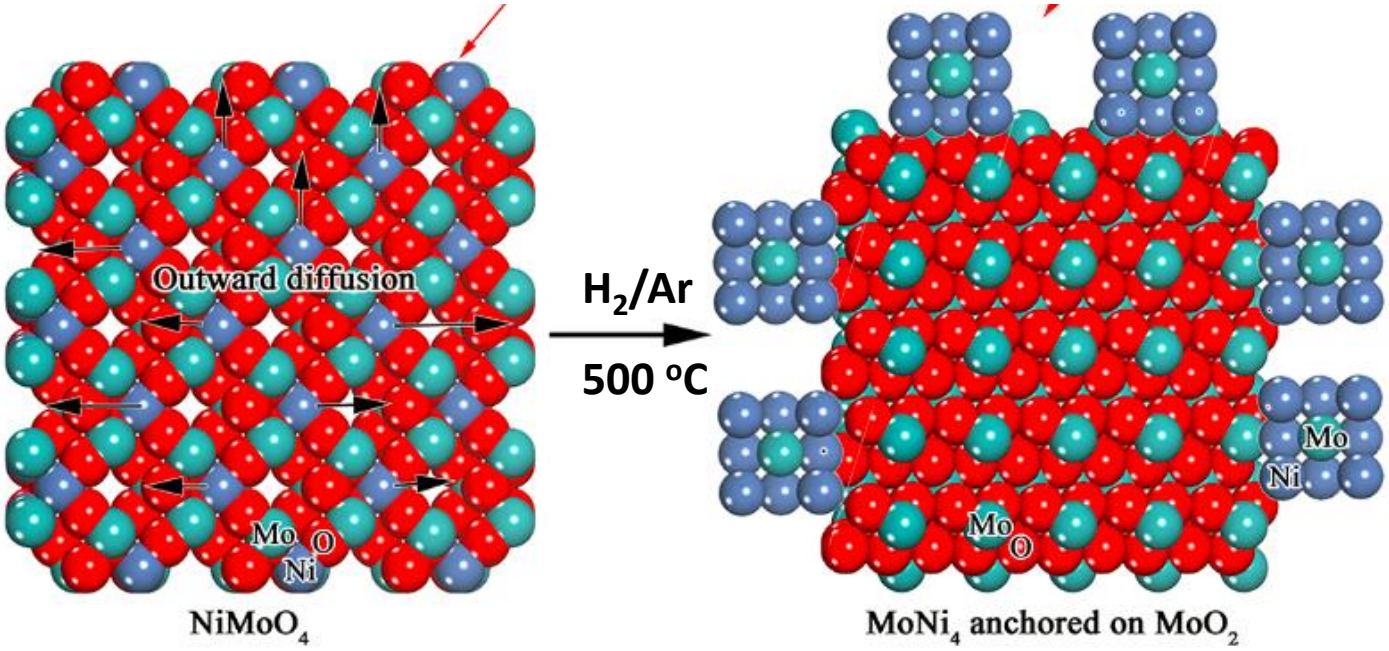


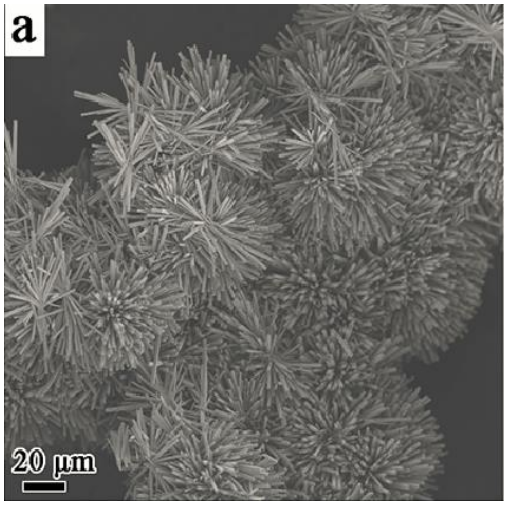
Ni content in Ni-MoS_2: 13.3 %

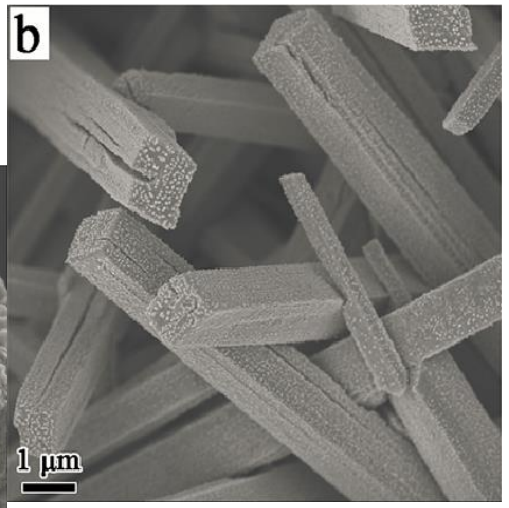
J. Zhang, *et.al*, *Energy Environ. Sci., 2016, 9, 2789.*

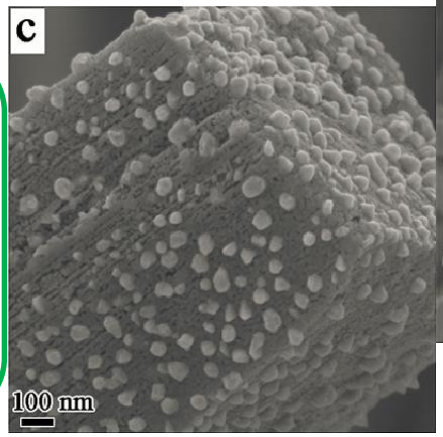
Engineering active sites

Out-diffusion of Ni





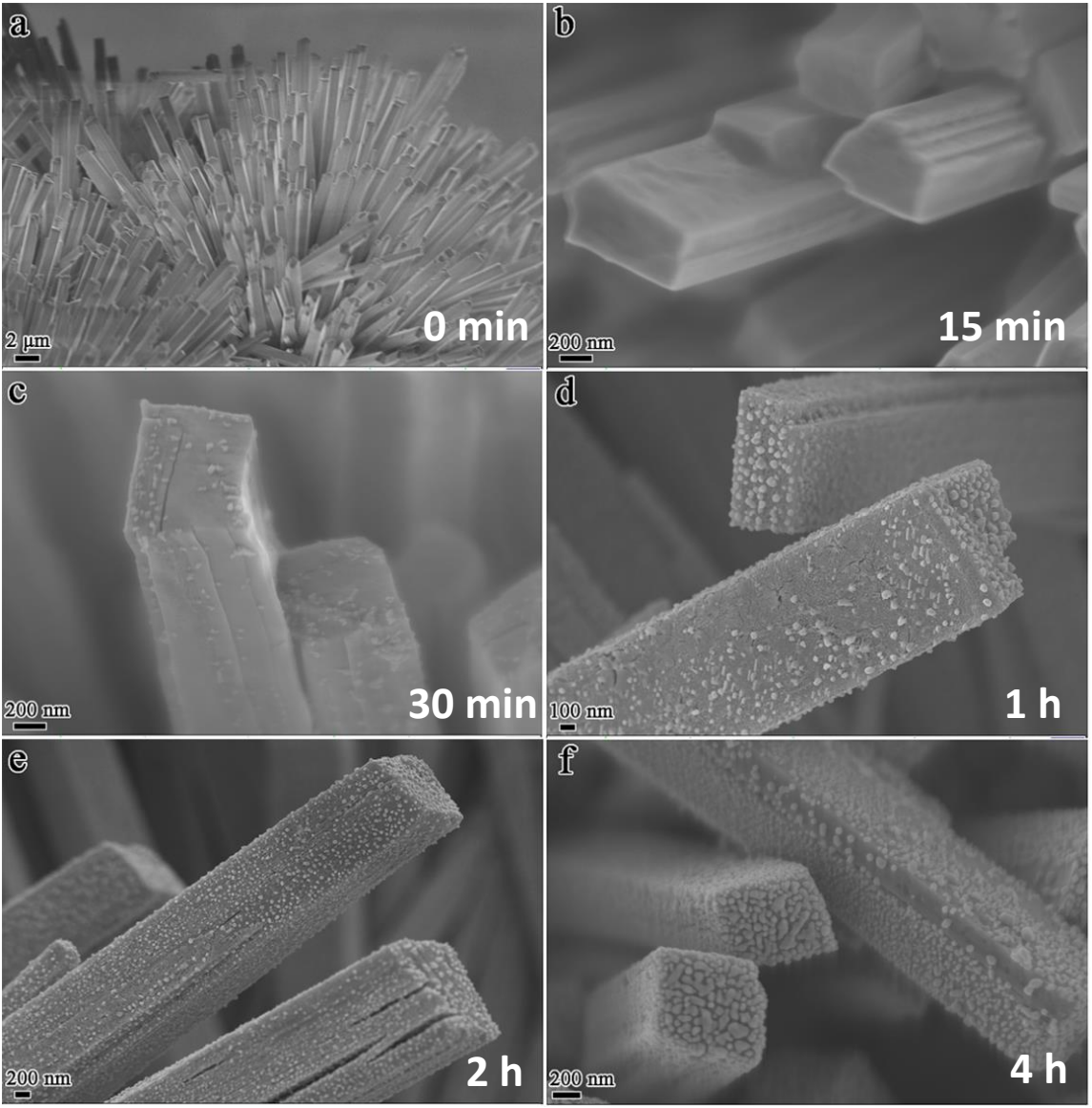


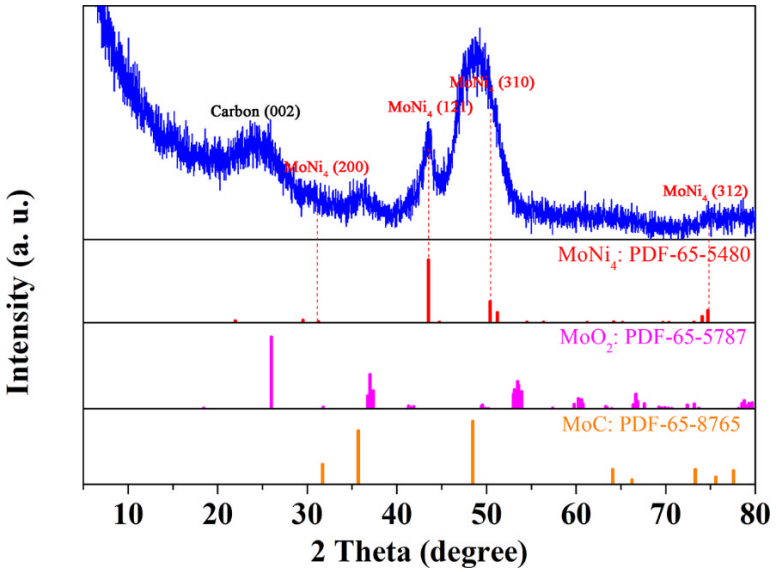


$MoNi_4$ nanoparticles are synthesized on the surfaces of MoO_2 cuboids supported by nickel foam.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

Growth of $MoNi_4$

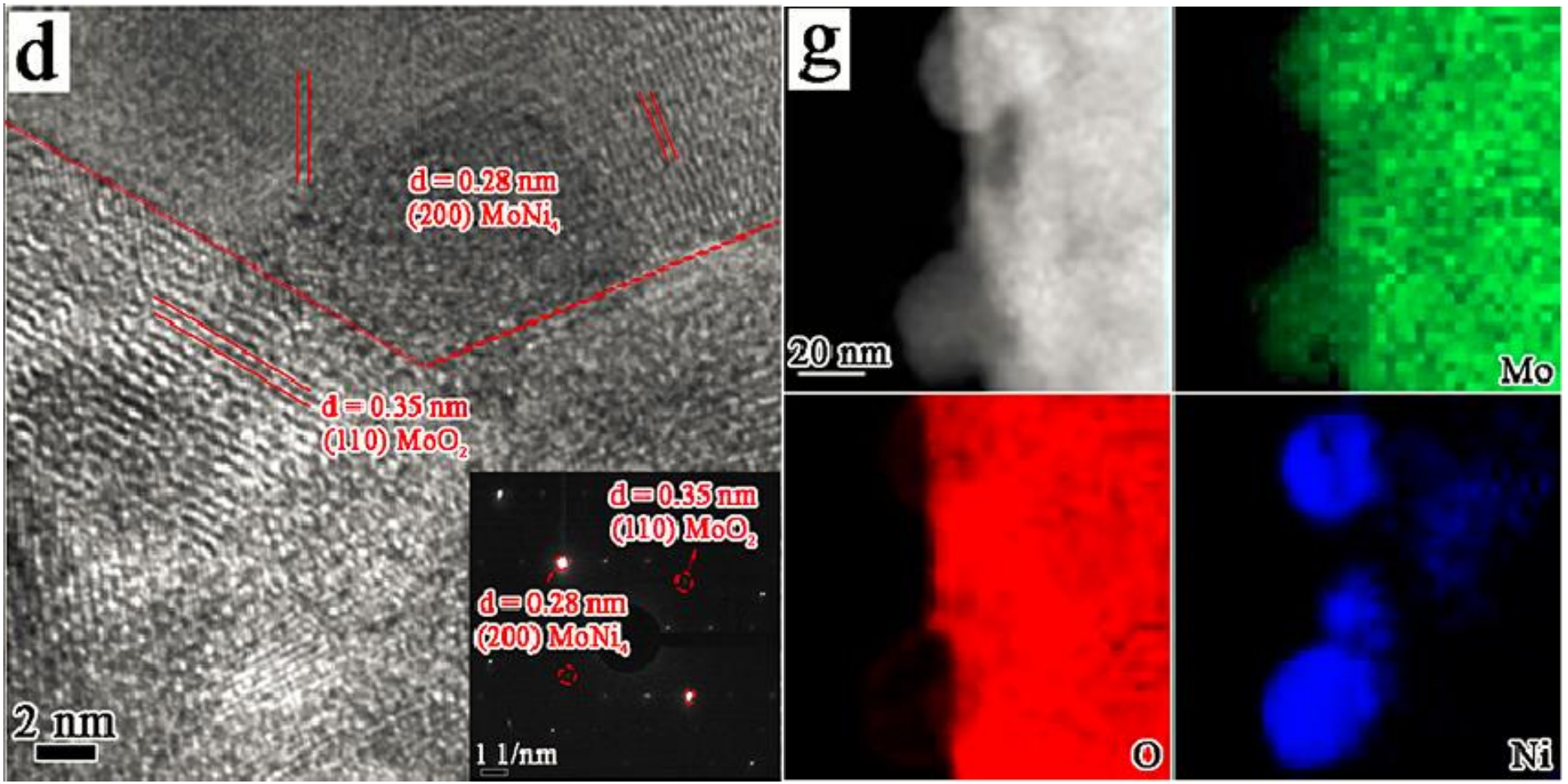




$MoNi_4$ nanoparticles (20-100 nm) gradually grow on the MoO_2 cuboids (0.5 - 1 μm).

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

$MoNi_4$ catalysts

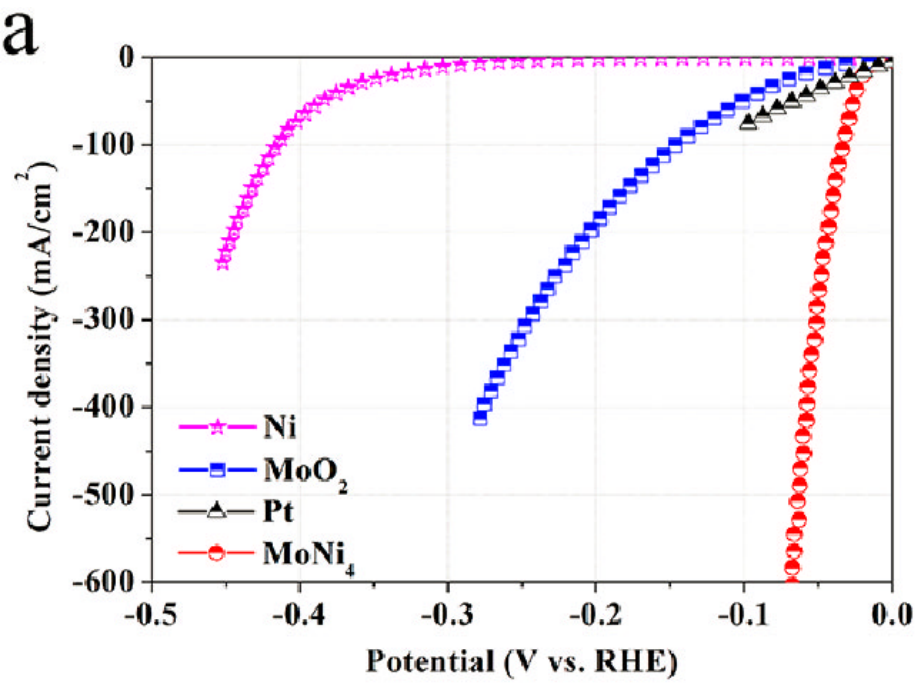


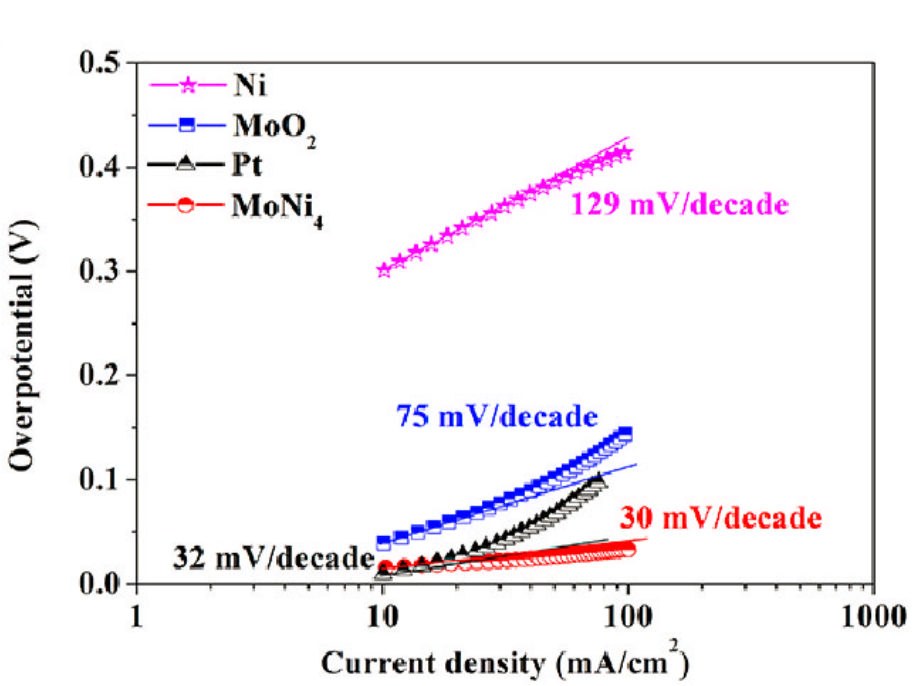
Exposed surfaces: $MoNi_4$ (200) and MoO_2 (110);
The molar ratio of Ni to Mo: 3.84:1.

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

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

HER activity

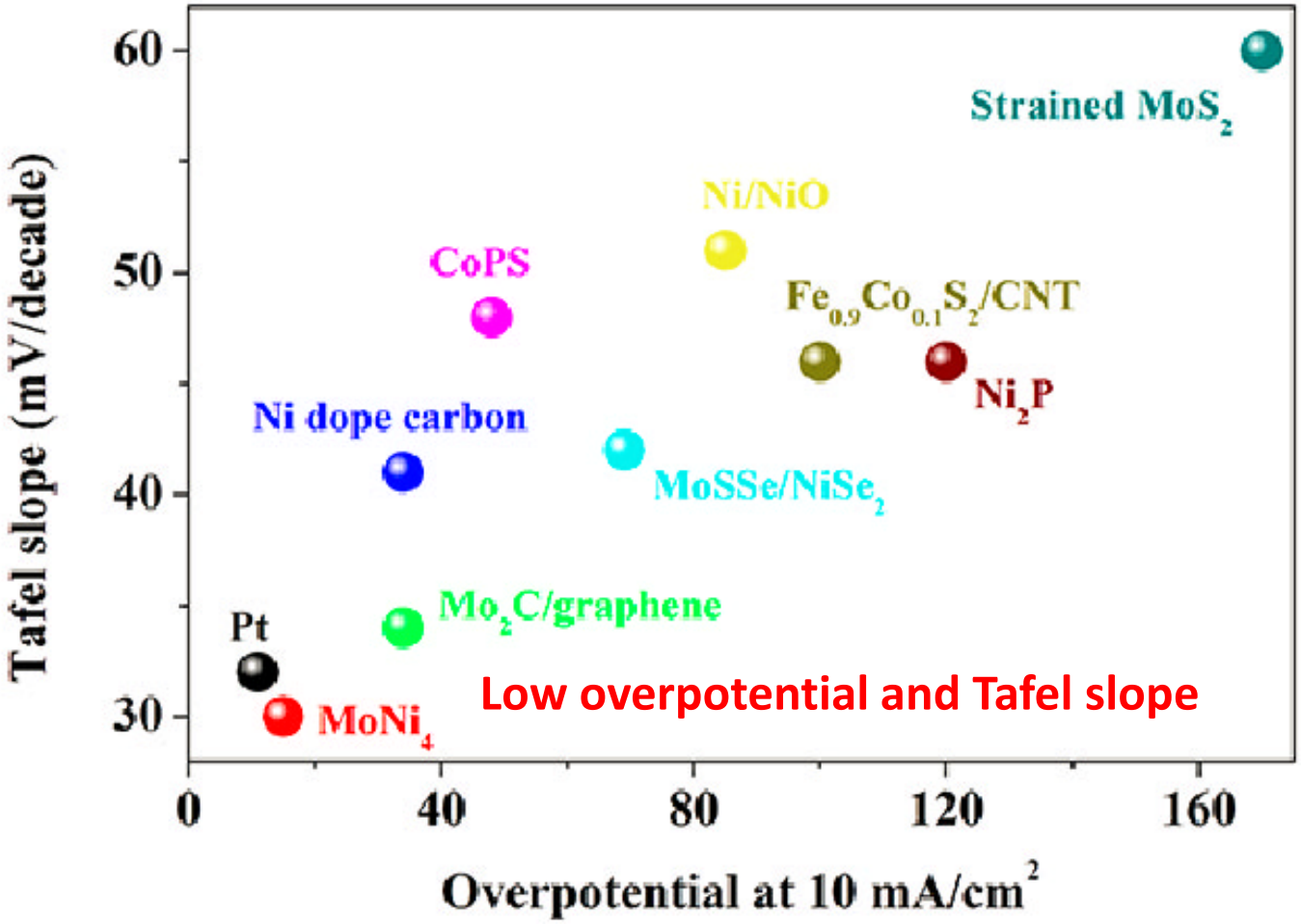




Overpotential at 10 mA/cm²: 15 mV, which is comparable to Pt/C.
Tafel slope: 30 mV/decade, suggesting
a fast water dissociation kinetics.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

HER activity

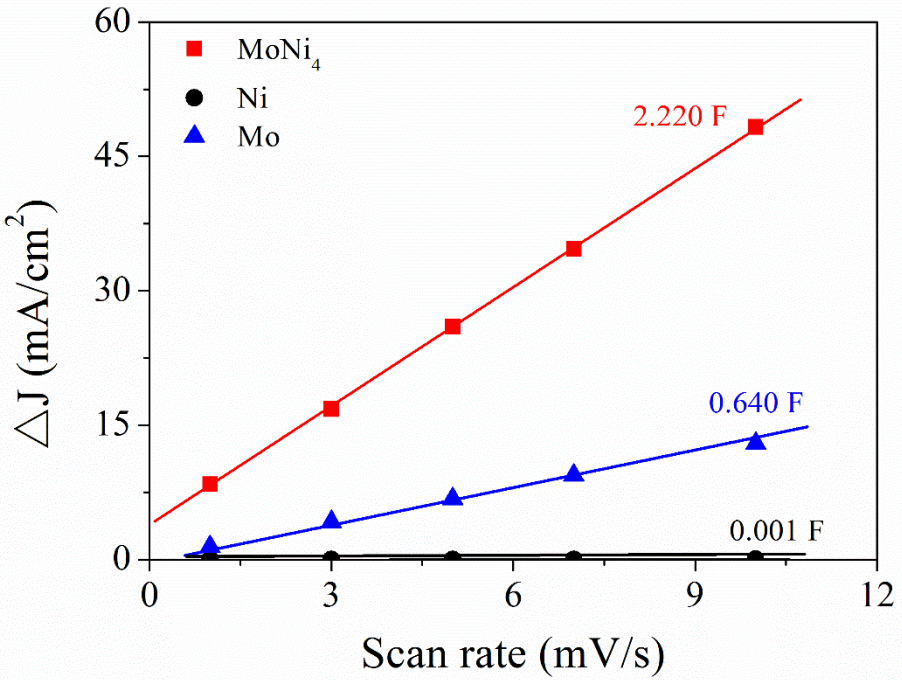


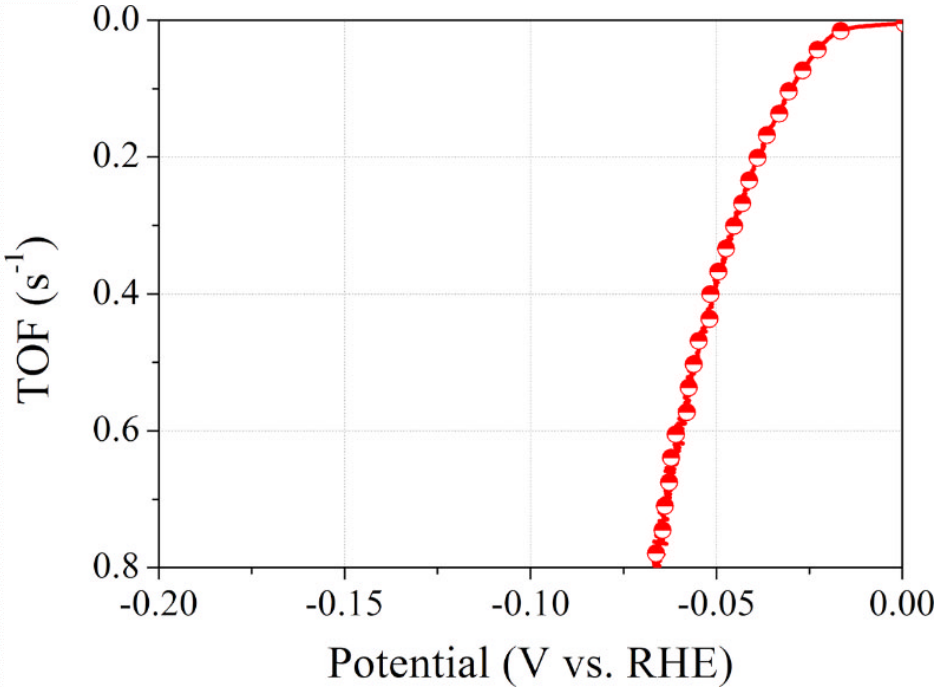
Strained MoS_2: Li H, et al. *Nat. Mater.* 2015, 15, 48;
Ni_2P: Popczun EJ, et al. *J. Am. Chem. Soc.* 2013, 135, 9267;
Ni/NiO: Gong M, et al. *Nat. Commun.* 2014, 5, 4695;
Mo_2C/graphene: Li J-S, et al. *Nat. Commun.* 2016, 7, 11204.

CoPS: Caban-Acevedo M, et al, *Nat. Mater.* 2015, 14, 1245;
$MoSSe/NiSe_2$: Zhou H, et al. *Nat. Commun.* 2016, 7, 12765;
Ni-doped carbon: Fan L, et al. *Nat. Commun.* 2016, 7, 10667.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

TOF



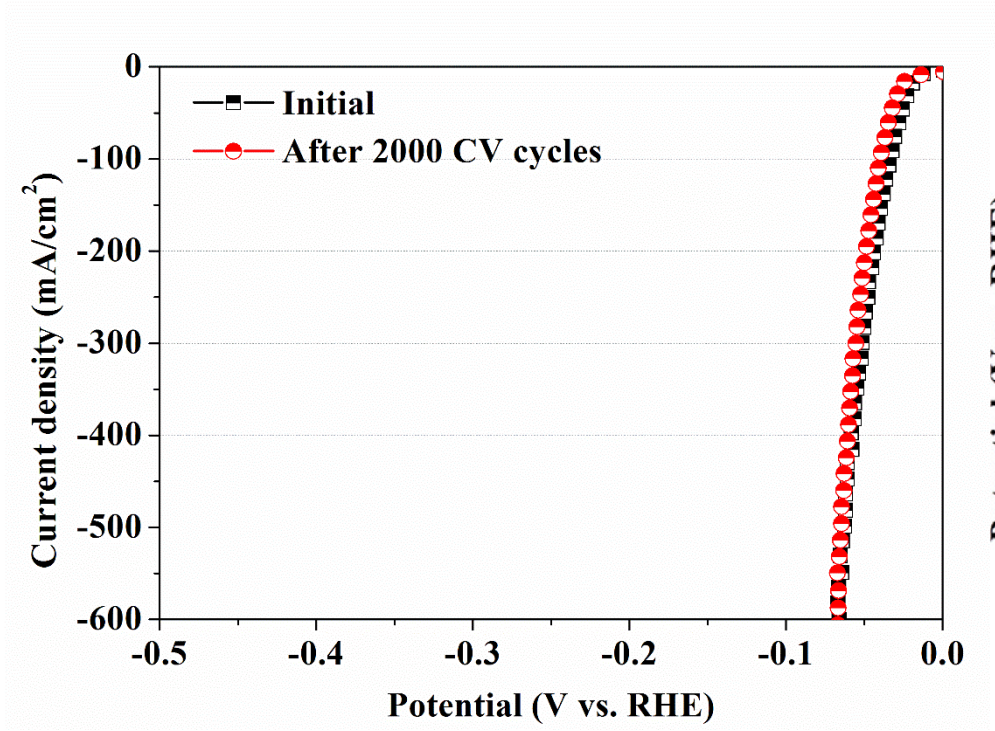


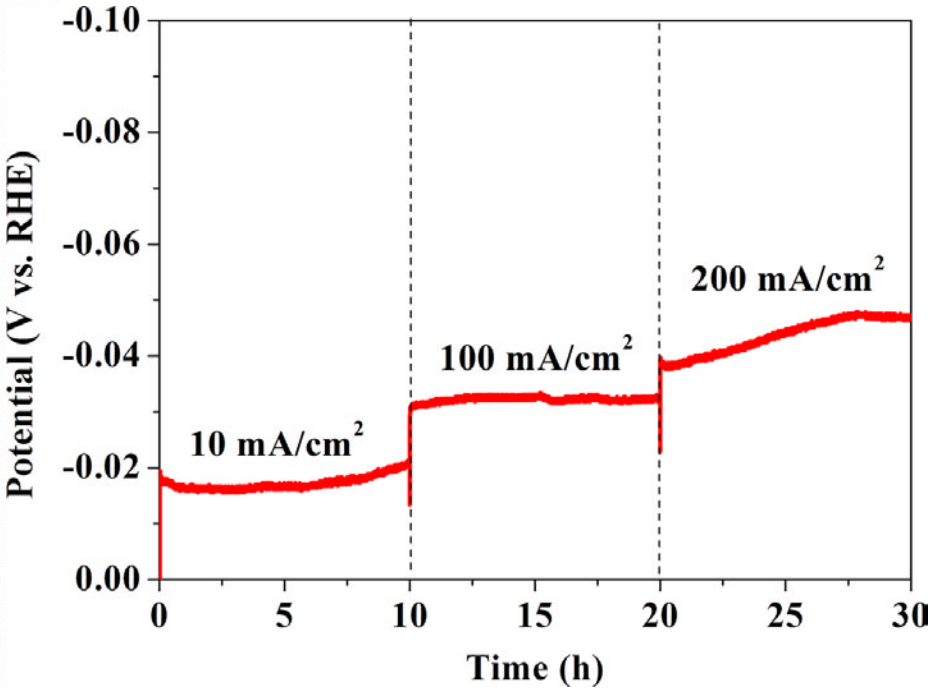
Electrochemcal double layer capacitance: 2.22 F.

TOF value: 0.4 s^{-1} at a low overpotential of 50 mV.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

HER Stability



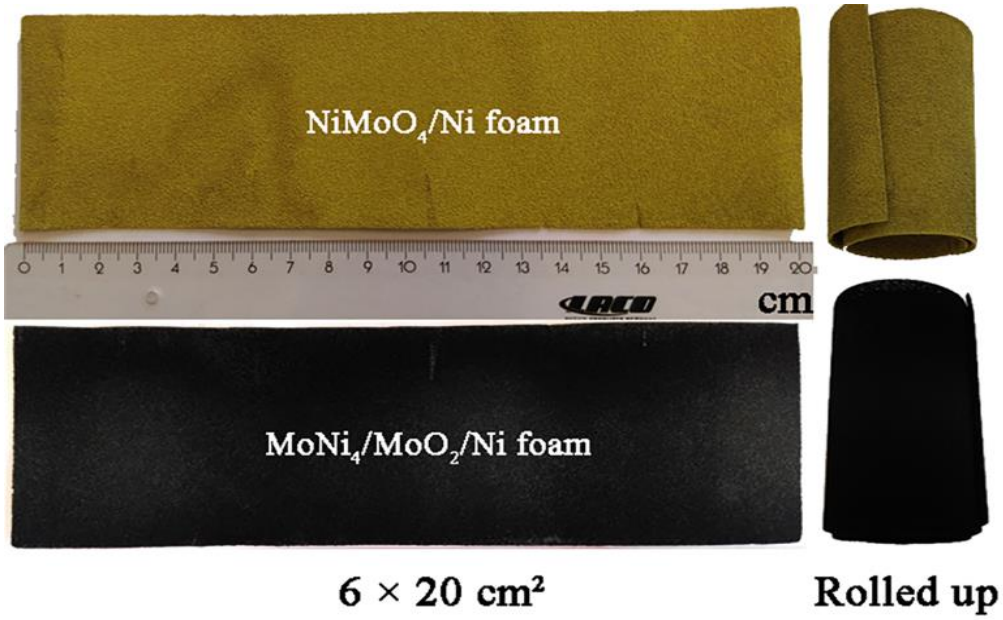


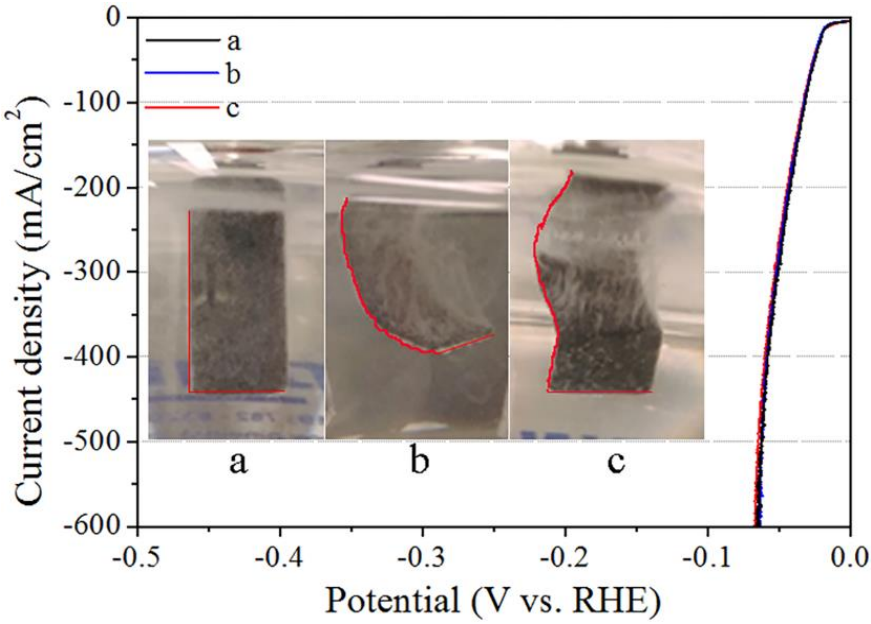
Overpotential at 10 mA/cm² increased by only 6 mV.

Excellent long-term stability.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

Flexibility



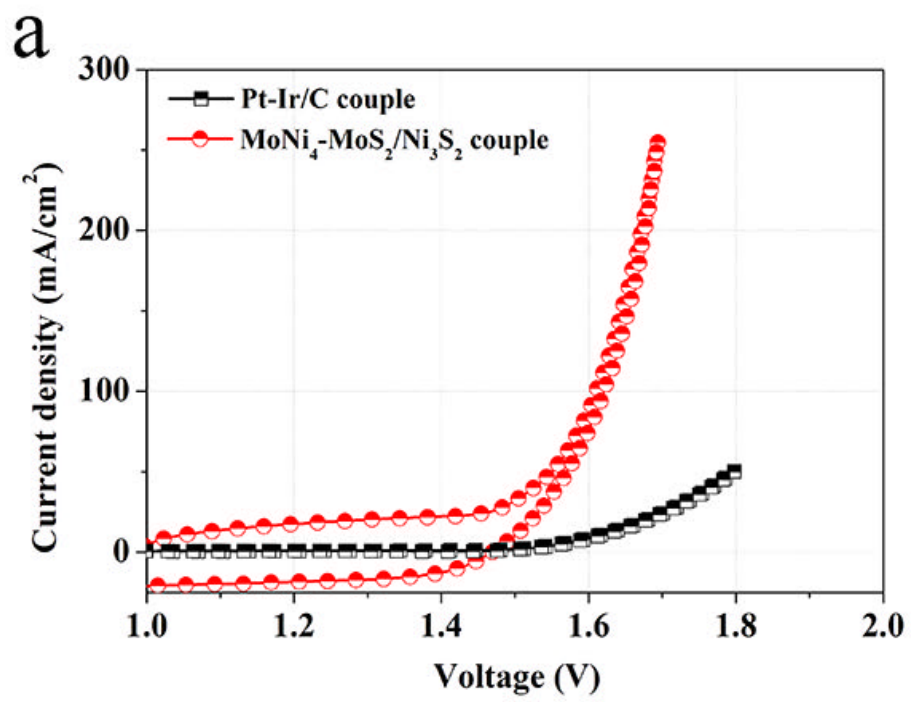


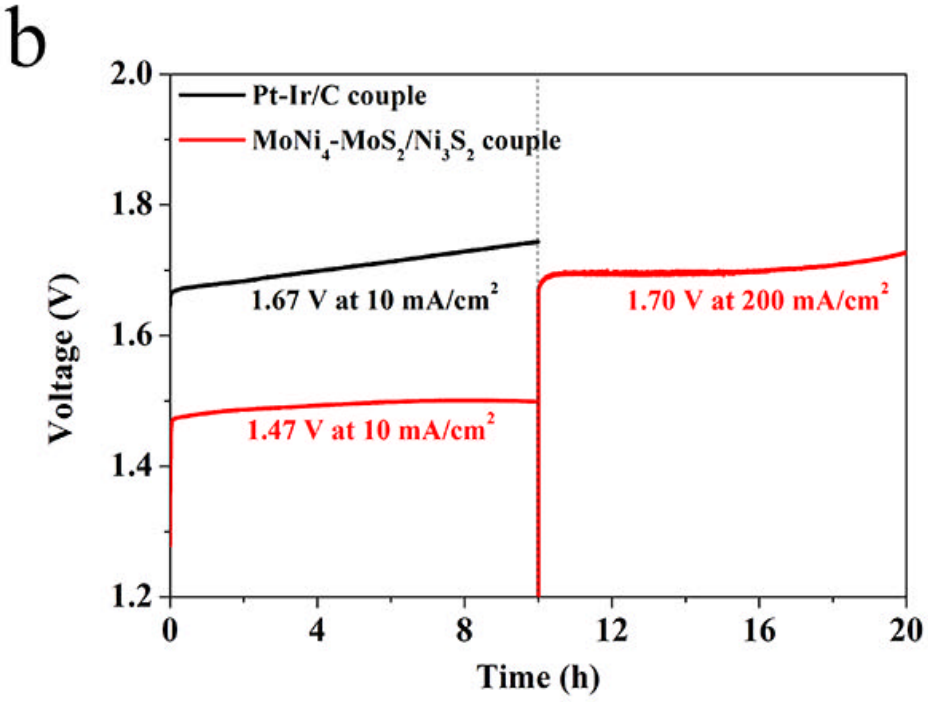
Large-scale synthesis of $MoNi_4$ electrocatalysts;

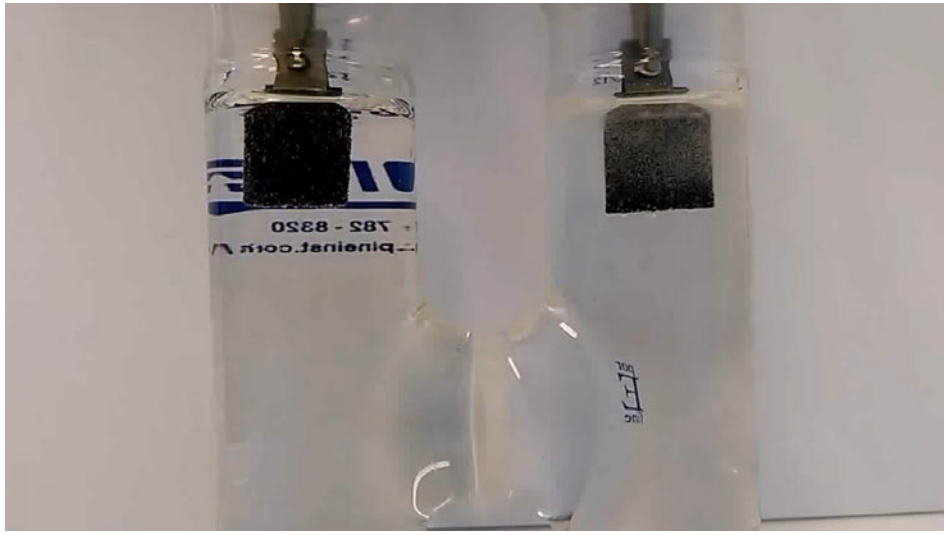
Outstanding stability.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

Electrolyzer





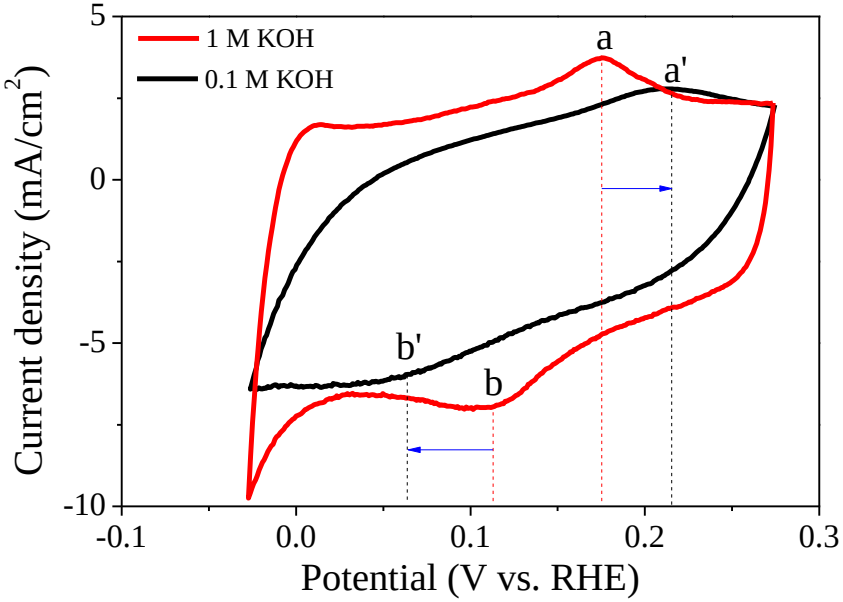


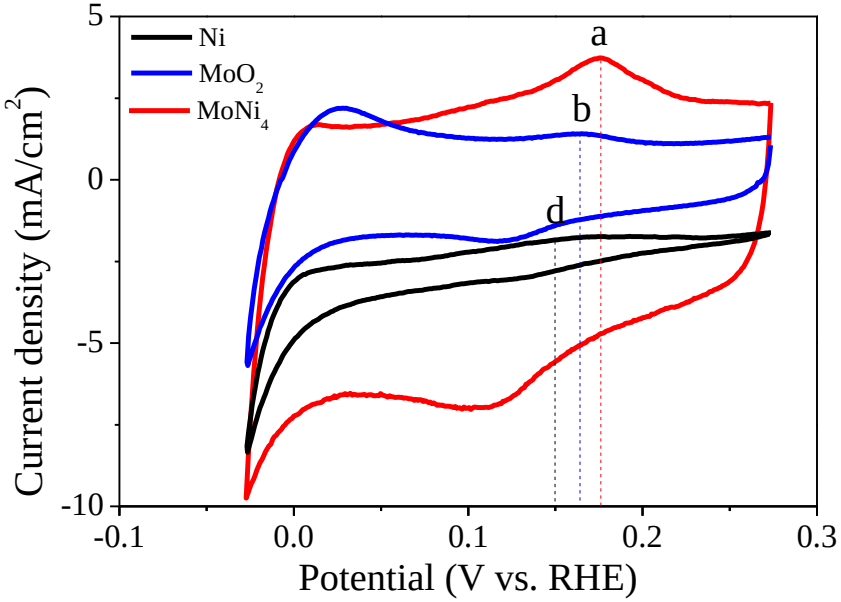
Combined overpotential:

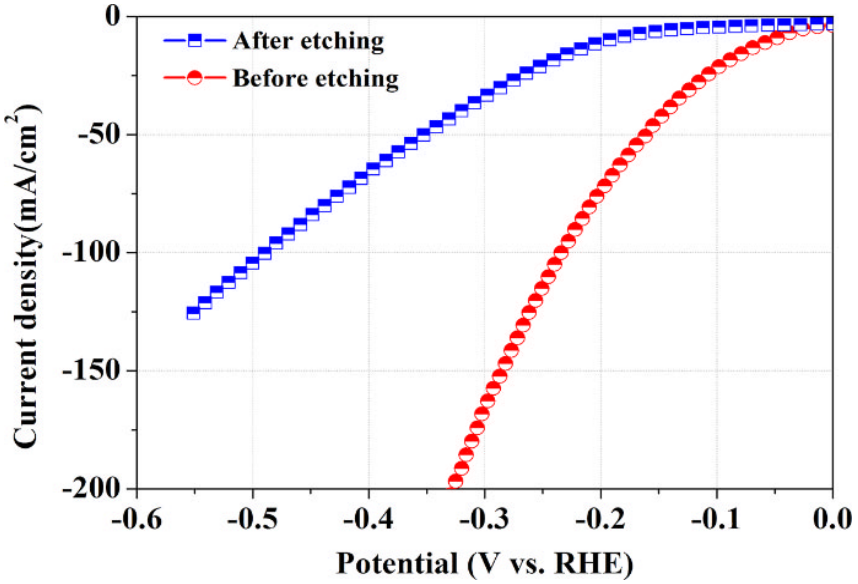
240 mV at 10 mA/cm².

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

Active centers



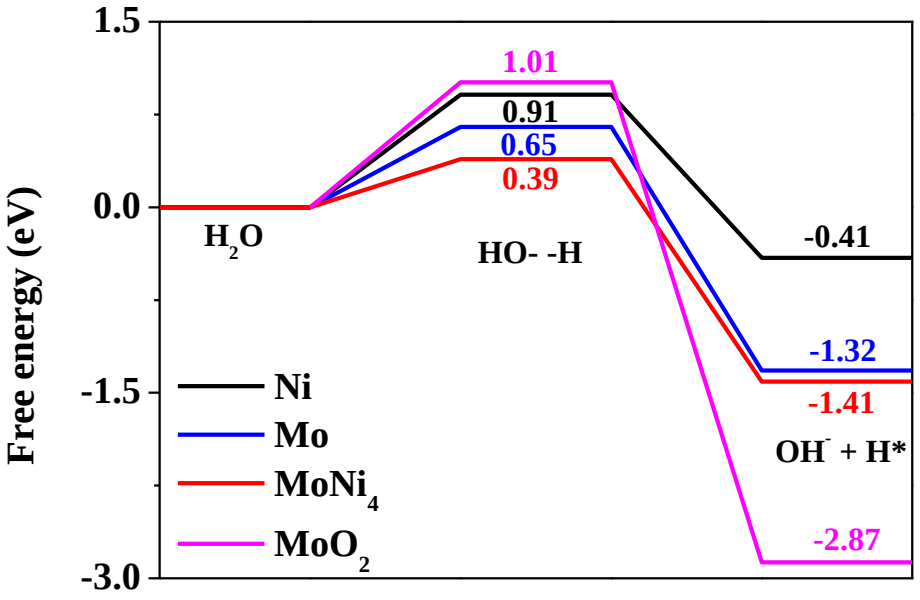


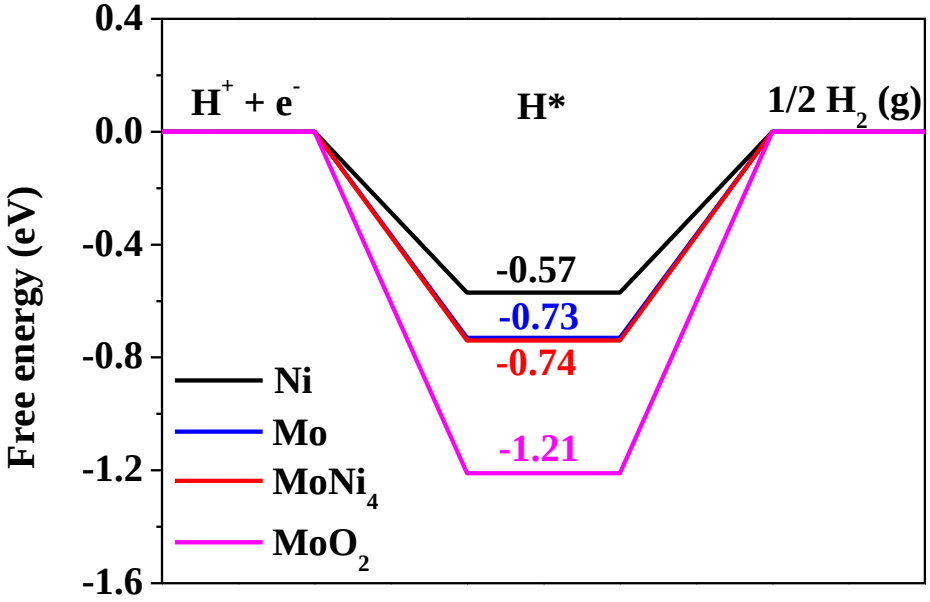


Adsorption: water molecule or OH;
Adsorption: anodic shift;
Onset overpotential: increased from 0 mV to 133 mV;
$MoNi_4$ are active centers

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

DFT calculations





The energy barrier of the Volmer step is largely decreased to 0.39 eV on $MoNi_4$, which is even lower than the 0.44 eV for the Pt.

Dr. Tao Wang, Univ Lyon, Ens de Lyon, CNRS, Université Lyon 1.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

Conclusions and outlook

- Water dissociation is more important than the H-adsorption in alkaline solution;
- MoNi-based active sites can largely lower the kinetic energy barrier of the Volmer;
- Developing new NiMo-based catalysts with excellent water dissociation kinetics;
- Understanding the alkaline HER mechanism and probe the adsorption states of H_2O, H and OH intermediates.

J. Zhang, *et.al*, *Nat. Commun.*, 2017, 8, 15437.

Acknowledgement

Ulrike Polnick
Guangbo Chen
Panpan Zhang
Gang Wang
Faxing Wang
Hanjun Sun
Tao Zhang
Yang Hou
Shaohua Liu

Prof. Xinliang Feng (TUD)
Dr. Tao Wang (CNRS)
Dr. Zhongquan Liao (IKTS)
Dr. Xiaodong Zhuang (TUD)
Prof. Pan Liu (SJTU)
Prof. Mingwei Chen (Tohoku University)
Prof. Ehrenfried Zschech (IKTS)
Dr. Bernd Rellinghaus (IFW)
Dr. Darius Pohl (IFW)

Funding Supports

DFG, BMBF, BASF, UPGRADE, Insolcell, ERC NANOGRAPH, ERC 2DMATER, Graphene Flagship, Cfaed Cluster, Talga, ESF

cfaed CENTER FOR ADVANCING ELECTRONICS DRESDEN

DRESDEN concept

TECHNISCHE UNIVERSITÄT DRESDEN

Thanks for your attention

Enjoy a nice journey in Dresden