



華中師範大學

明德、厚學、求實、篤行  
The Xiao Group

# Organic Electrosynthesis Using Heterogeneous Catalysts Modified Electrodes

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Supervisor: Prof. Liang-Qiu Lu  
Prof. Wen-Jing Xiao

Sep. 10, 2023

The Xiao Group

# Outline

## ✓ **Background**

- Introduction of electrolytic cell
- Two types of electrolysis
- The representation of heterogeneous catalysts modified electrodes

## ✓ **Anodic oxidation reaction**

## ✓ **Cathodic reduction reaction**

## ✓ **Summary**

# Outline

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- Introduction of electrolytic cell
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- The representation of heterogeneous catalysts modified electrodes

## ✓ Anodic oxidation reaction

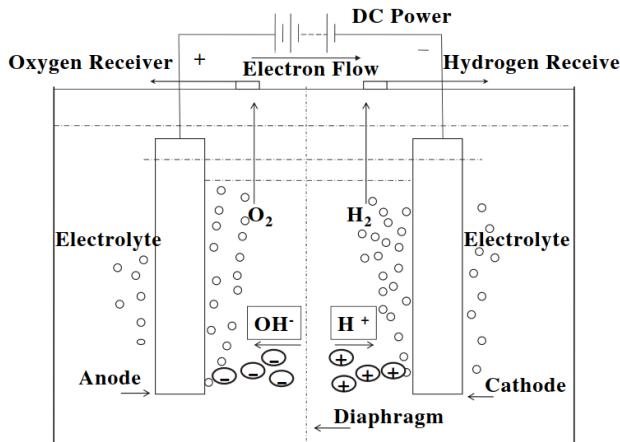
## ✓ Cathodic reduction reaction

## ✓ Summary

# Background

## ■ Introduction of electrolytic cell

- ✓ Electrolytic cell : a **non-spontaneous** reaction is driven by an external source of **current**.
- ✓ The electrode at which **oxidation** occurs is called the **anode**; the electrode at which **reduction** occurs is called the **cathode**



$$\text{Anode: } \varphi_a = \varphi_{a,e} + \eta_a = \varphi^\theta - \frac{RT}{ZF} \ln \frac{1}{a} + \eta_a$$

$$\text{Cathode: } \varphi_c = \varphi_{c,e} - \eta_c = \varphi^\theta - \frac{RT}{ZF} \ln \frac{1}{a} - \eta_c$$

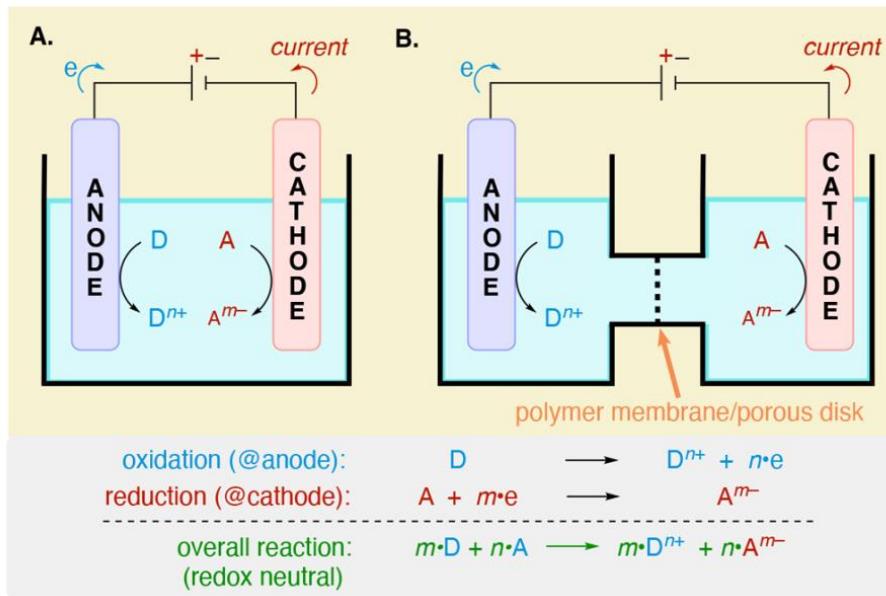
$$\text{Decomposition potential: } E_d = \varphi_a - \varphi_c = E_r + \eta_a + \eta_c$$

$\varphi^a \downarrow$  : Being oxidized first;

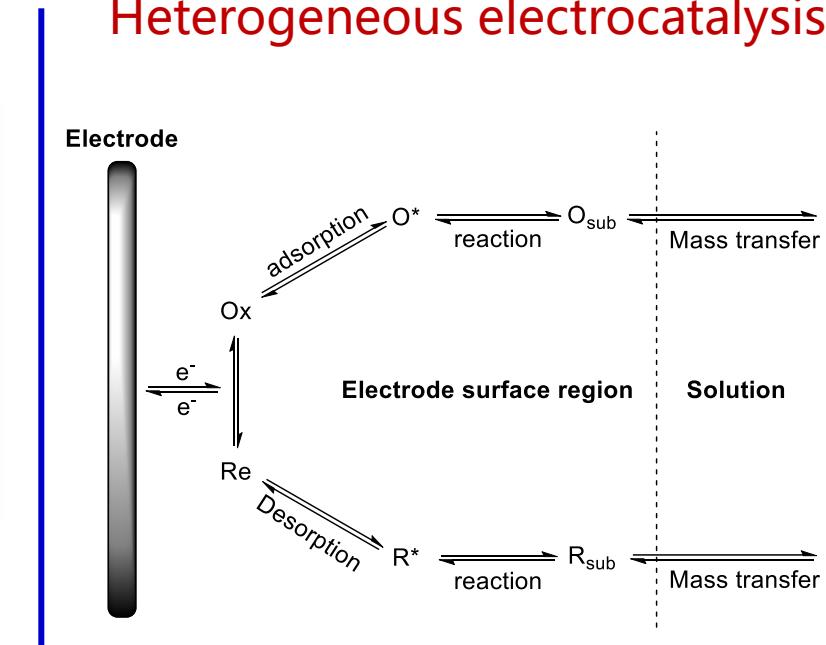
# Background

## ■ Introduction of electrolytic cell

### The type of Electrolytic cell



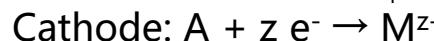
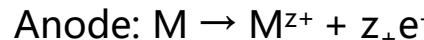
### Heterogeneous electrocatalysis



- ◆ **Undivided cell: a starting material, intermediate, or product is unable to undergo reaction at the opposite electrode**
- ◆ **Adsorption and desorption are essential for selectivity**

# Background

## ■ Introduction of electrolytic cell- the current density



取得失电子数为 $z$ , 通入的电量为 $Q$ , 发生反应的物质的量为 $n$ , 电流为  $i$

$$Q = nzF, \text{ or } n = \frac{Q}{zF}, i = \frac{dQ}{dt}$$

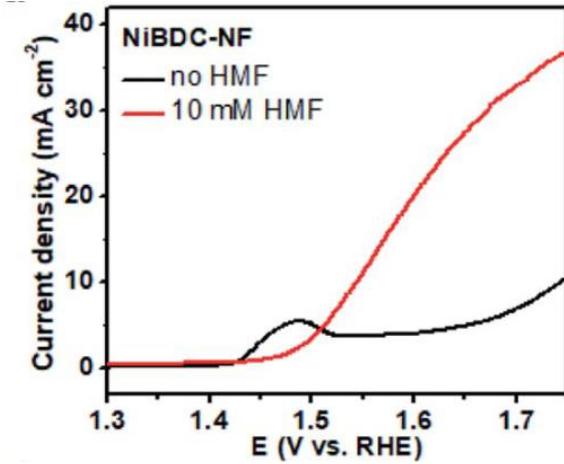
$$V = \frac{dn}{dt} = \frac{d(\frac{Q}{zF})}{dt} = \frac{1}{zF} * \frac{dQ}{dt} = \frac{i}{zF}$$

Surface area ( $A$ ) needs to be taken into account

$$V = \frac{i}{zFA} = \frac{j}{zF}, j \text{ is the current density}$$

- ◆ The current density represents the rate of reaction
- ◆ The potential indicates the difficulty of reaction

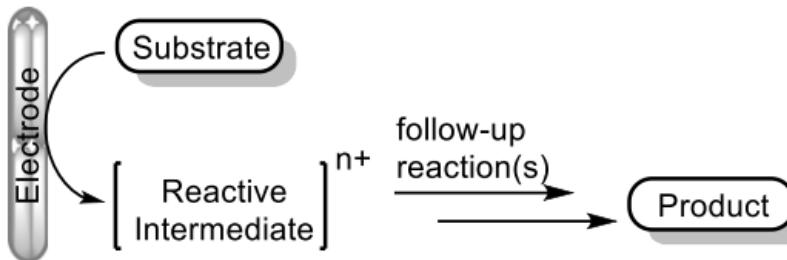
For example:



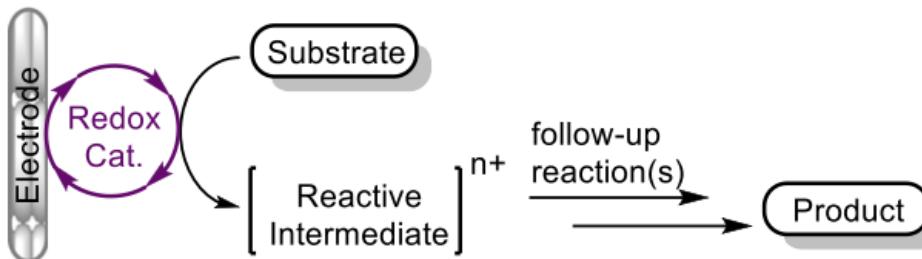
# Background

## ■ Two types of electrolysis

(A) Direct electrolysis



(B) Indirect electrolysis



- Redox potential of the substrate
- Limited substrate range
- Difficult compatibility of sensitive groups

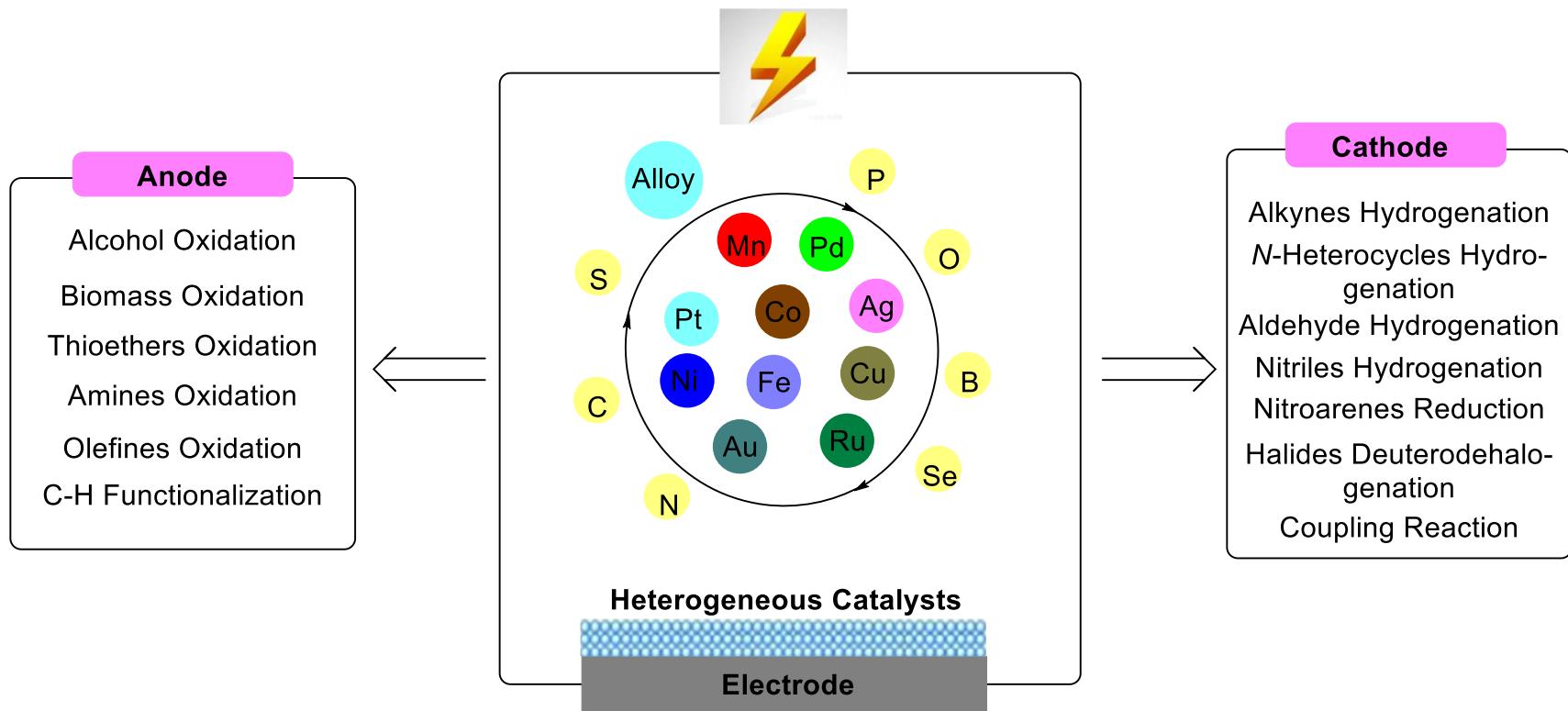
- Avoid excessive oxidation/reduction
- The selectivity of the product is controllable
- Easy recyclability

**Homogeneous electrolysis: diffusion of the electrocatalyst, unrecyclable**

**Heterogeneous electrolysis: increased active surface area and electron transfer, recyclability.**

# Background

## ■ The representation of heterogeneous catalysts modified electrodes



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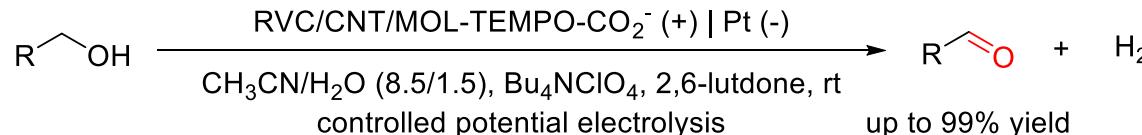
## ✓ Anodic oxidation reaction

## ✓ Cathodic reduction reaction

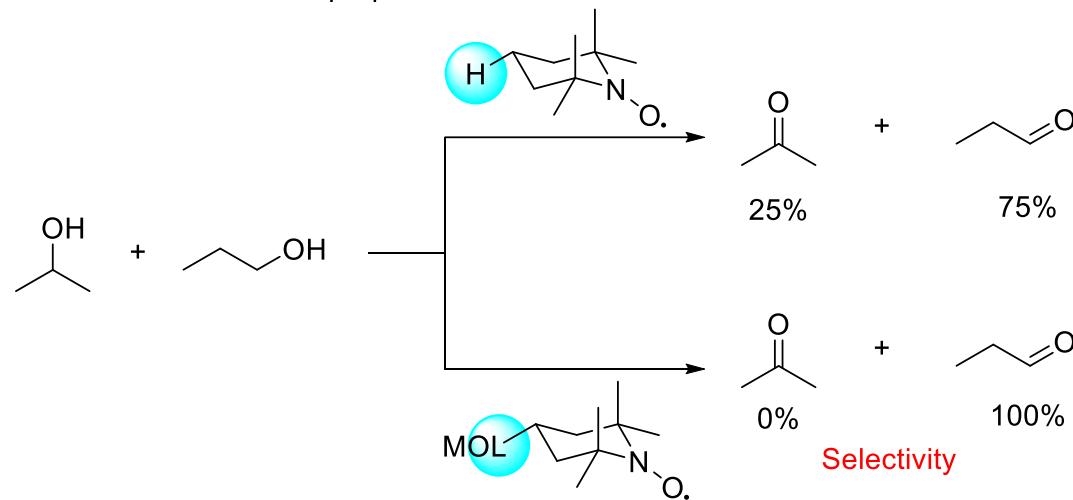
## ✓ Summary

# Anodic oxidation reaction

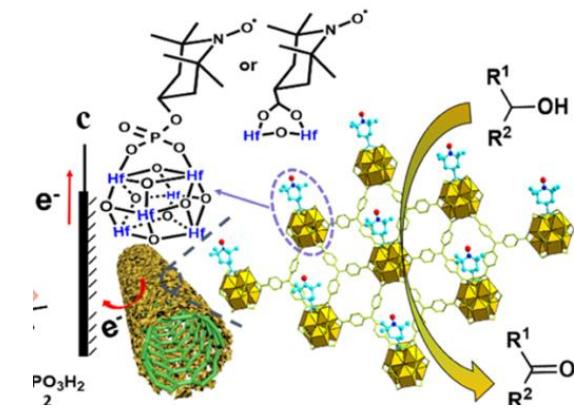
## ■ Two-Dimensional Metal–Organic Layers to Conductivity Constraint



Selective oxidation of *n*-propanol:



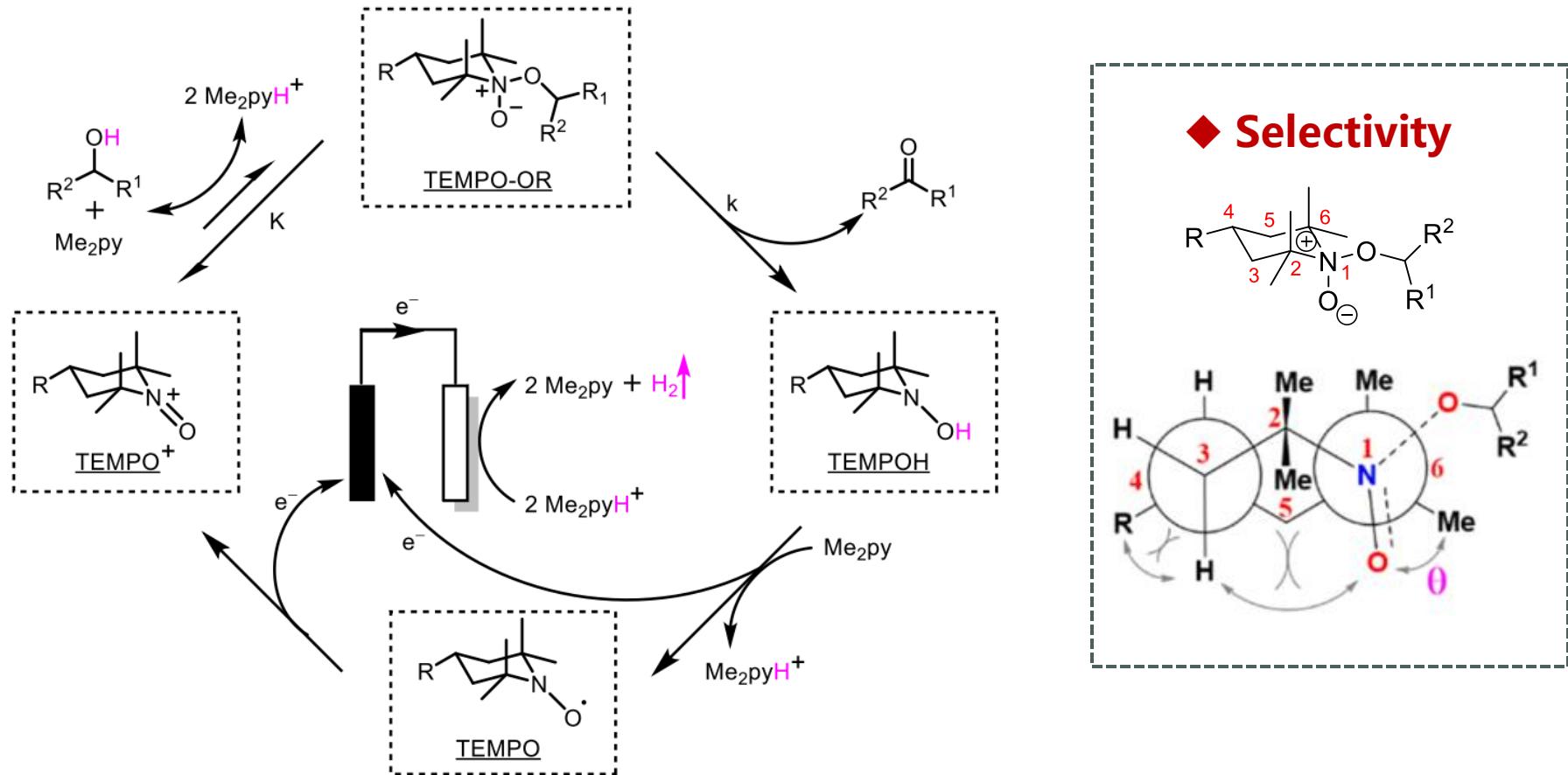
◆ CNT/MOL Assembly endowed the selectivity for primary versus secondary alcohols



◆ Enhancing conductivity by decreasing the transport distance of the electron and the hole

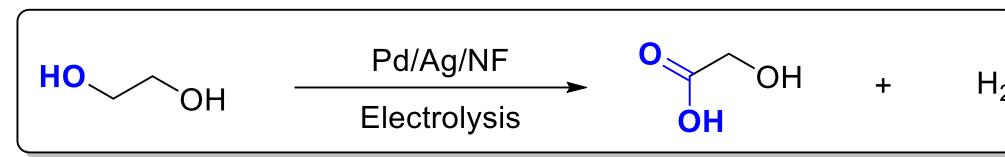
# Anodic oxidation reaction

## ■ Two-Dimensional Metal–Organic Layers to Conductivity Constraint



# Anodic oxidation reaction

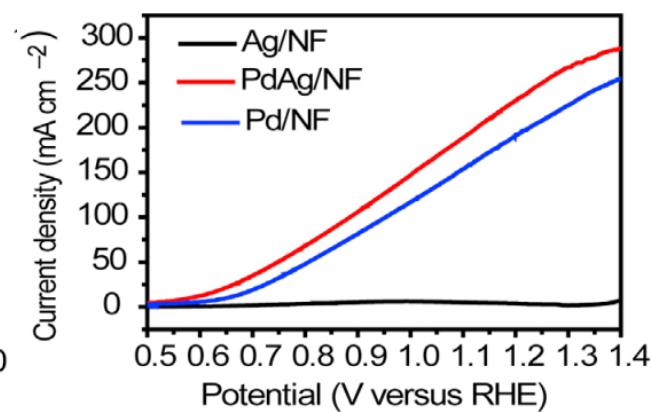
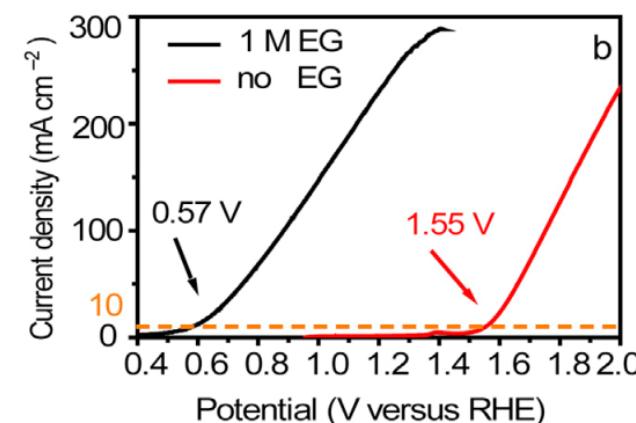
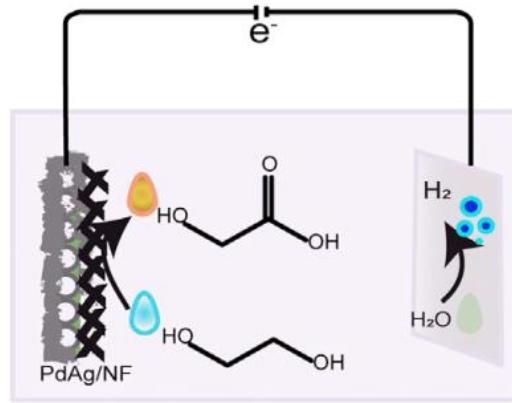
## ■ Architecture–Performance Relationship in Bifunctional Multilayer Electrodes



□ High selectivity

□ high-purity hydrogen

□ high-value-added product



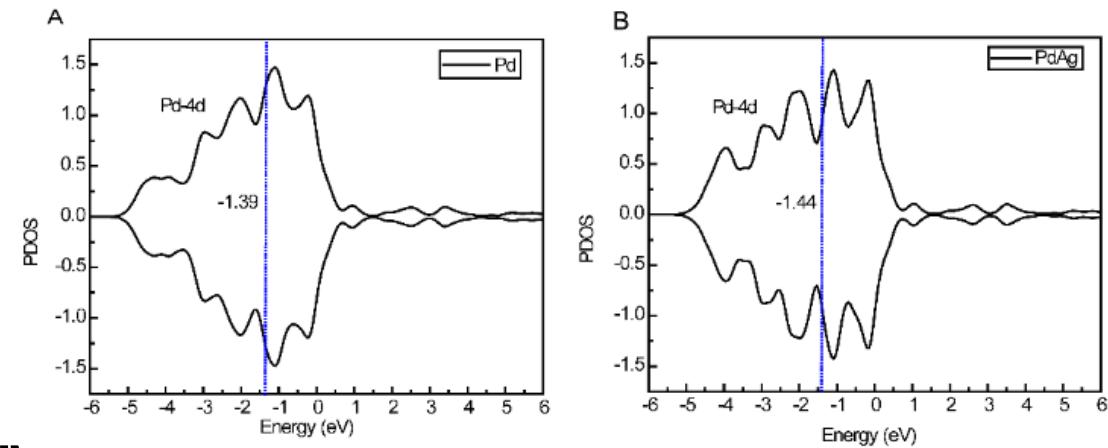
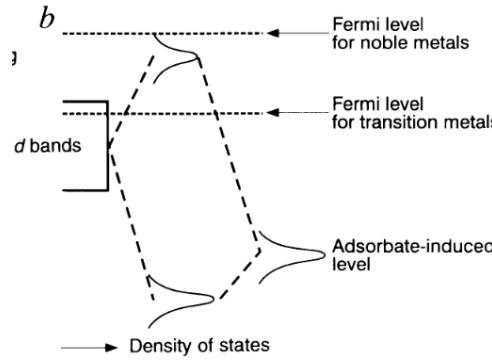
◆ Lower than that of the oxygen evolution reaction

J.-L. Shi et al. *Chem Catalysis*. 2021, 1, 941–955

# Anodic oxidation reaction

## ■ Architecture–Performance Relationship in Bifunctional Multilayer Electrodes

### ◆ How to prevent further oxidation?

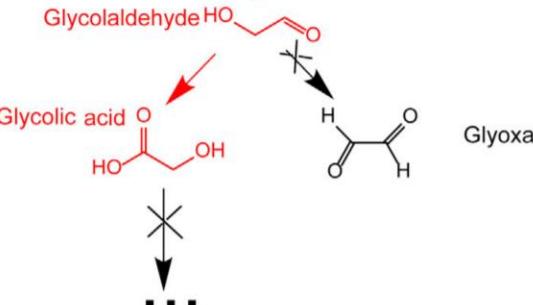
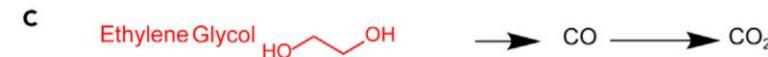
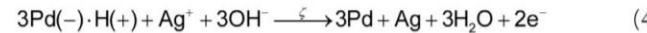
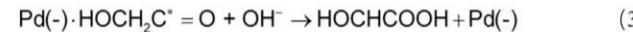
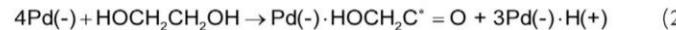
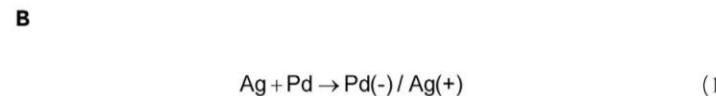
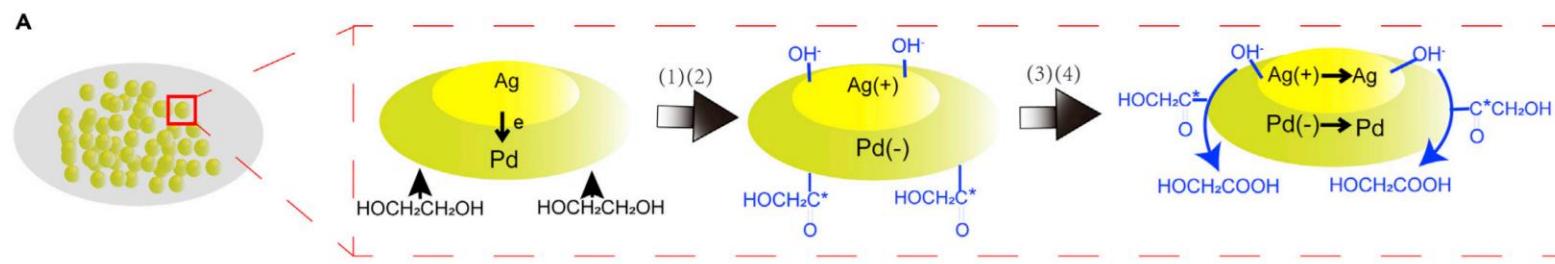


- ◆ 费米能级以下填充电子,以上不填充。
- ◆ 反键态填充电子,则不利于吸附
- ◆ 反键态高于费米能级不填充电子
- ◆ d能带中心靠近费米能级,利于吸附

- ◆ Ag的加入(PdAg/NF)导致表Pd的d能带中心偏离费米能级,从1.39 eV到1.44 eV
- ◆ 导致表面钯对产物的吸附能降低,易于解离
- ◆ 避免产物被进一步氧化为乙二酸

# Anodic oxidation reaction

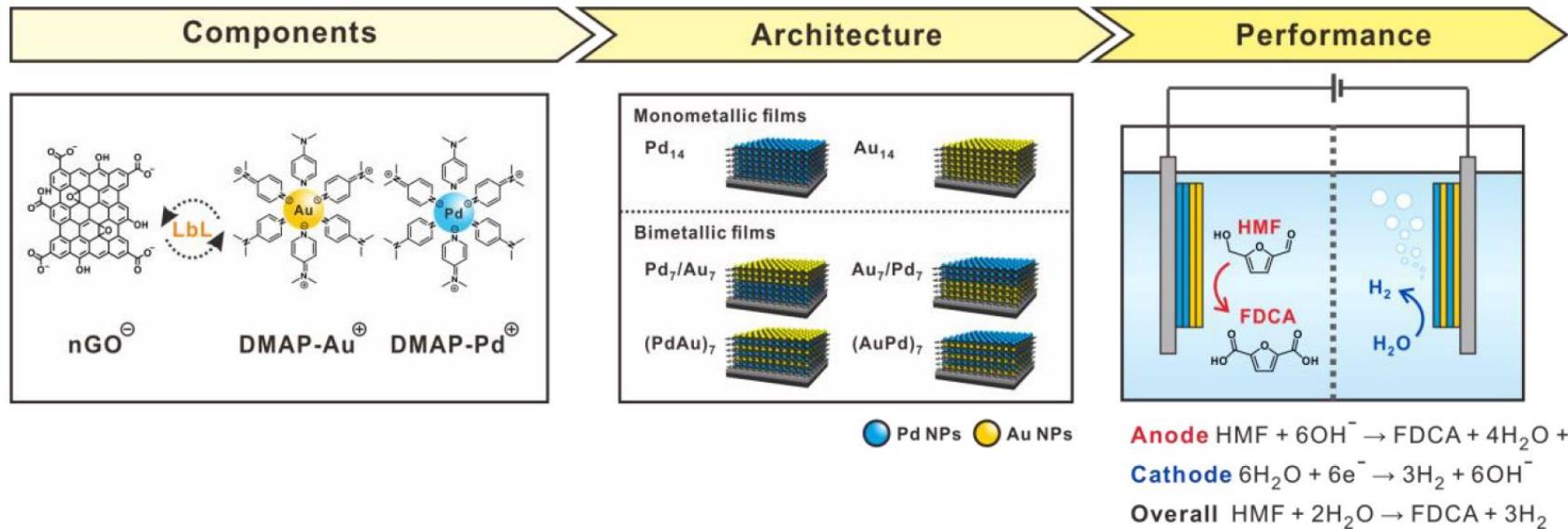
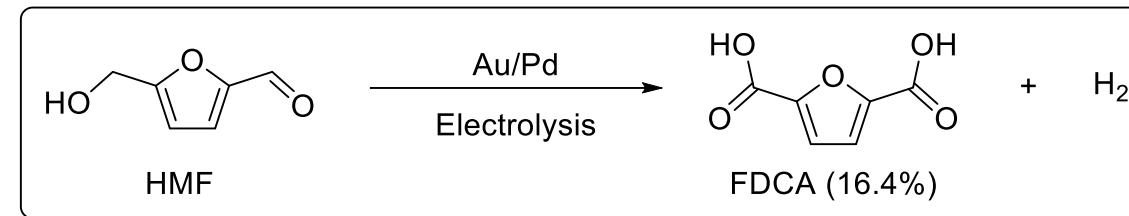
## ■ Synergetic catalytic effect between Pd and Ag



J.-L. Shi et al. *Chem Catalysis*. 2021, 1, 941–955

# Anodic oxidation reaction

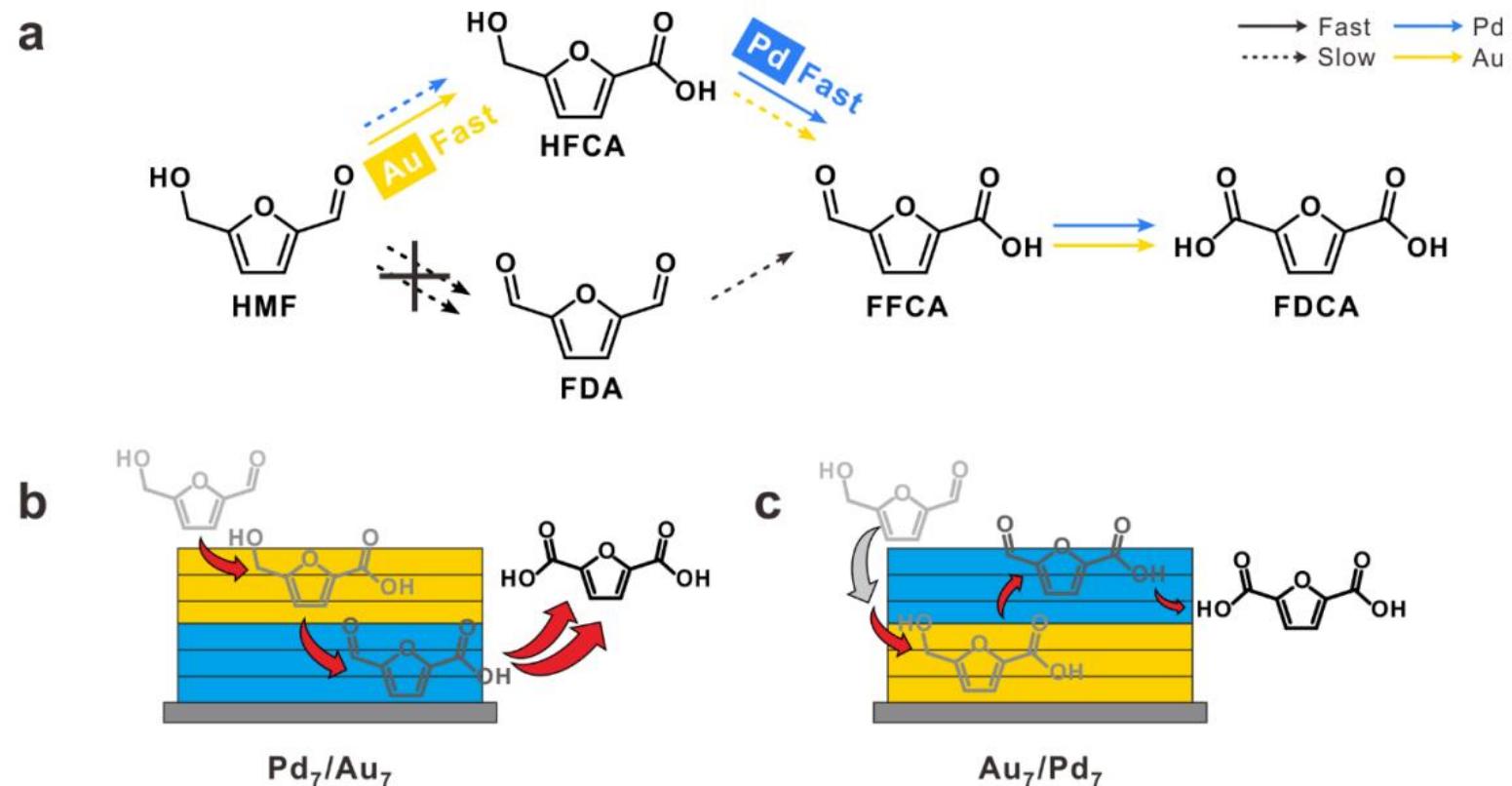
## ■ Architecture–Performance Relationship in Bifunctional Multilayer Electrodes



B. U. Kim et al. ACS Nano. 2020, 14, 6812–6822

# Anodic oxidation reaction

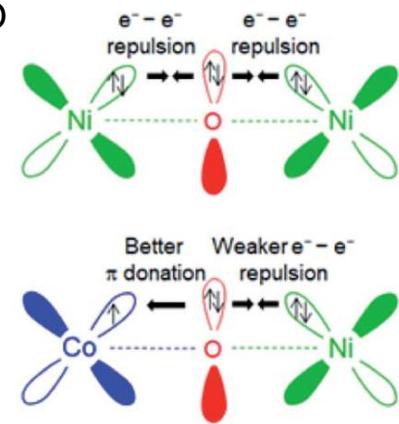
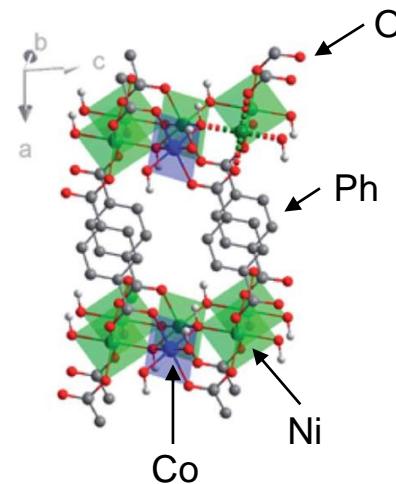
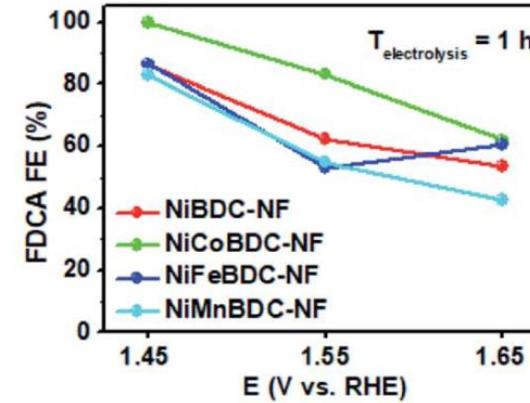
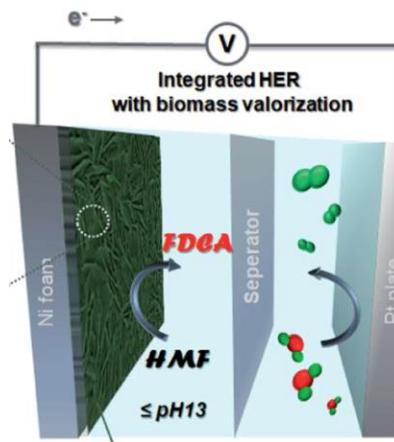
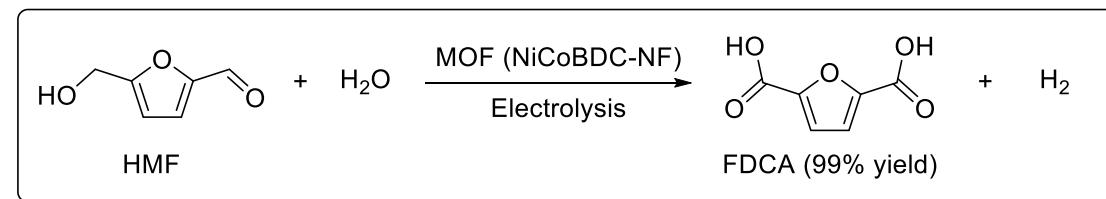
## ■ Architecture–Performance Relationship in Bifunctional Multilayer Electrodes



B. U. Kim et al. *ACS Nano*. 2020, 14, 6812–6822

# Anodic oxidation reaction

## ■ 2D MOFs catalyst for electrocatalytic HMF oxidation



NiCoBDC-NF

$\downarrow$

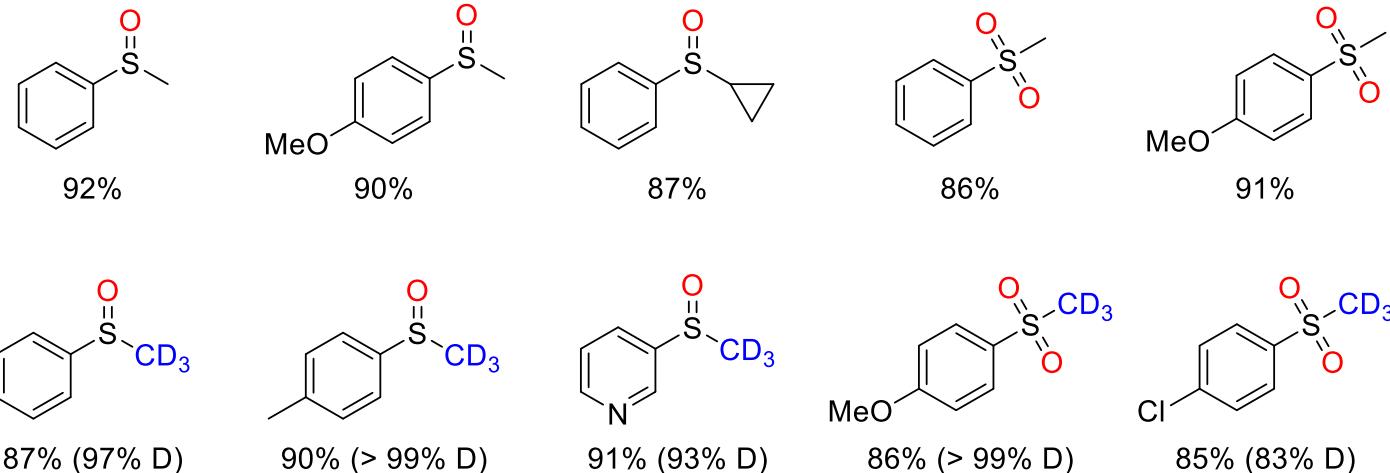
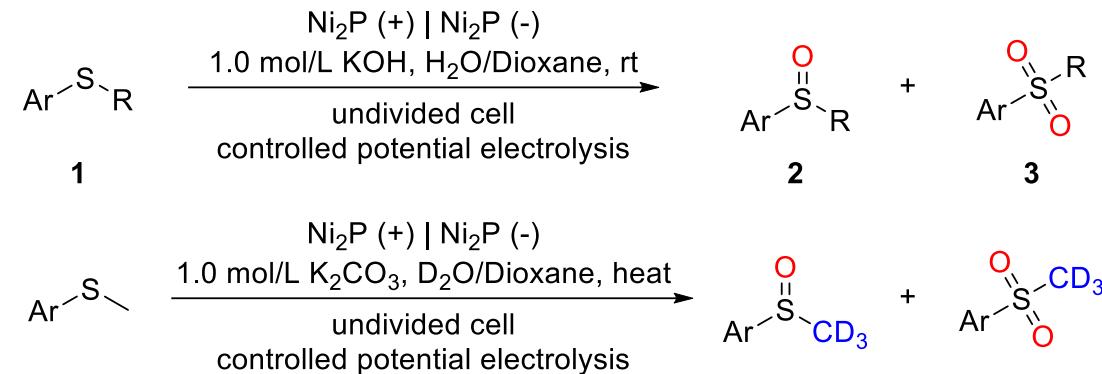
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  +  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  + Terephthalic acid + Nickel foam (NF)

◆ Best catalyst:  
NiCoBDC-NF

◆ The formation of high valence nickel species

# Anodic oxidation reaction

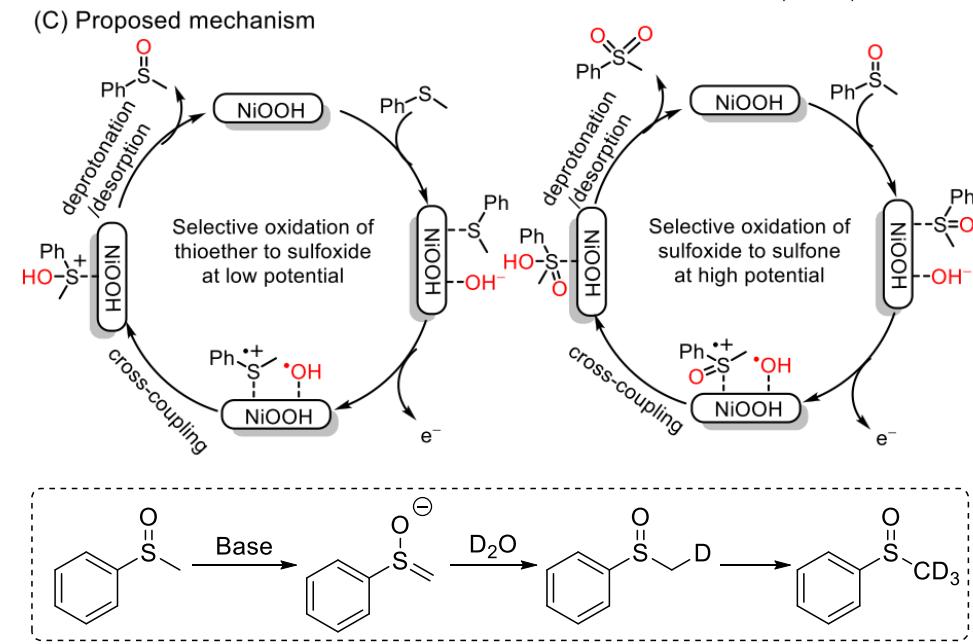
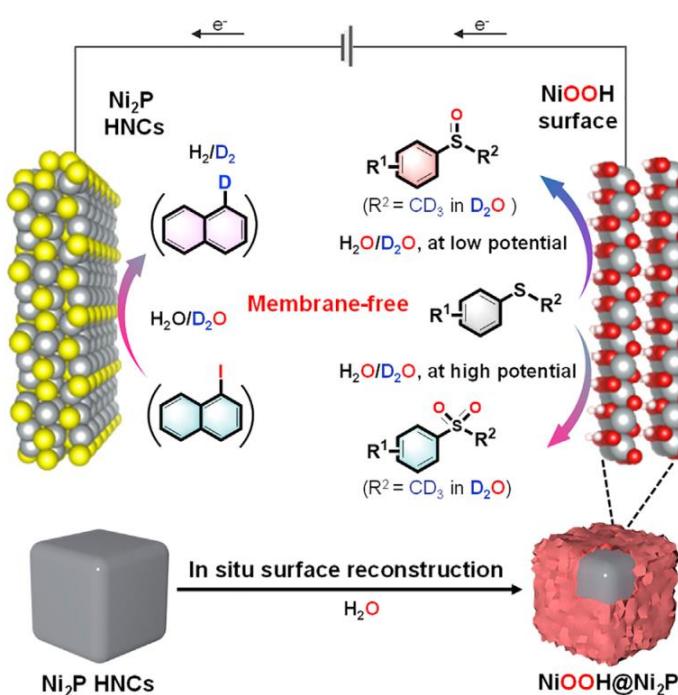
## ■ Ni<sub>2</sub>P Hollow nanocubes modified electrode for selective thioether electrooxidation



B. Zhang et al. *Cell Reports Physical Science*. 2021, 2, 100462-100479

# Anodic oxidation reaction

## ■ Ni<sub>2</sub>P Hollow nanocubes modified electrode for selective thioether electrooxidation

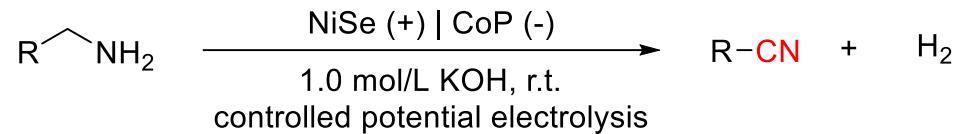


◆ Ni<sub>2</sub>P is used as both cathode and anode material

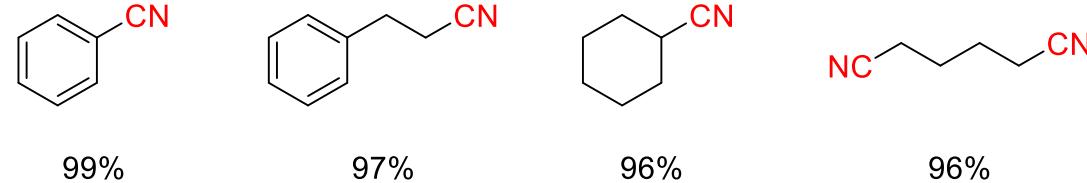
◆ The selective oxidation is realized by adjusting the working voltage

# Anodic oxidation reaction

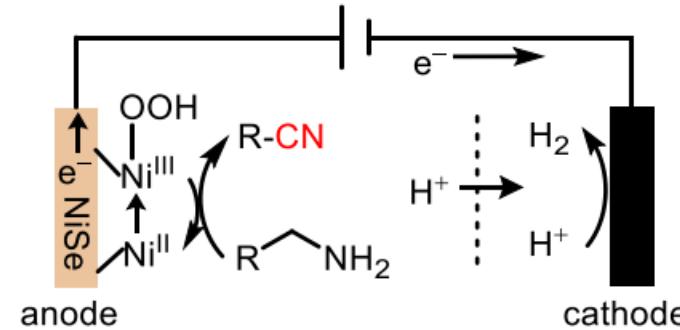
## ■ NiSe nanorod modified electrode for primary amines electrooxidation.



Representative substrate scope:



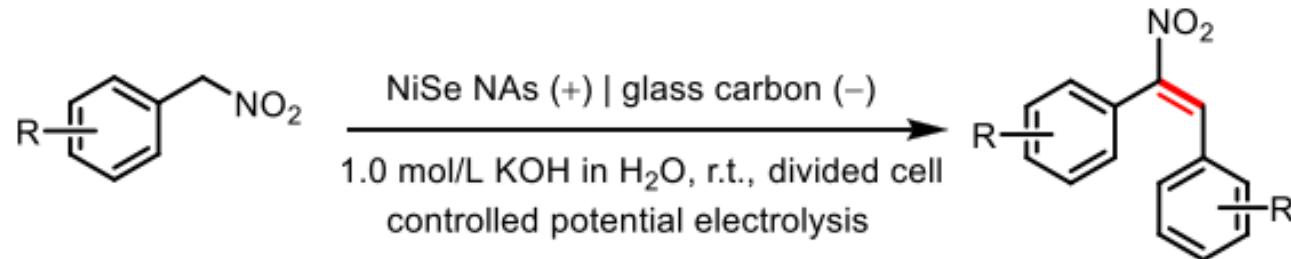
Proposed mechanism:



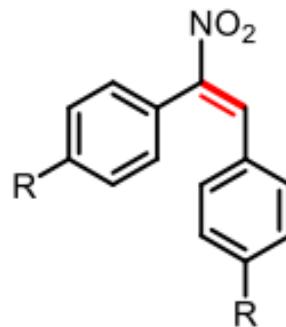
B. Zhang et al. *Angew.Chem.Int.Ed.* **2018**, 57, 13163-13166

# Anodic oxidation reaction

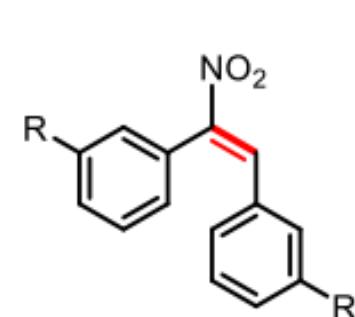
## ■ NiSe NAs modified electrode for electrochemical self-coupling reaction



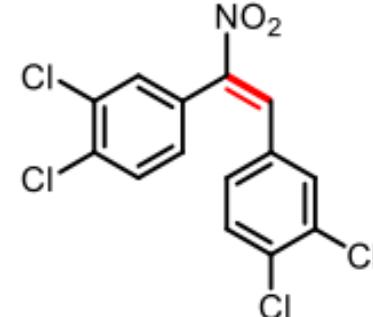
(B) Representative substrate scope



$\text{R} = \text{H}$ , con. 96%, sel. 91%  
 $\text{R} = \text{CH}_3$ , con. 90%, sel. 87%  
 $\text{R} = \text{F}$ , con. 93%, sel. 91%  
 $\text{R} = \text{Cl}$ , con. 94%, sel. 88%



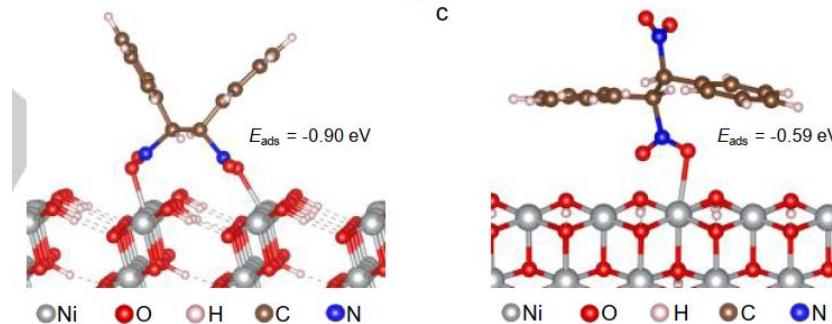
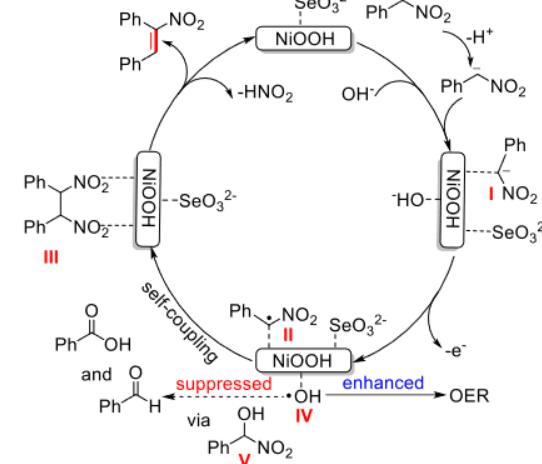
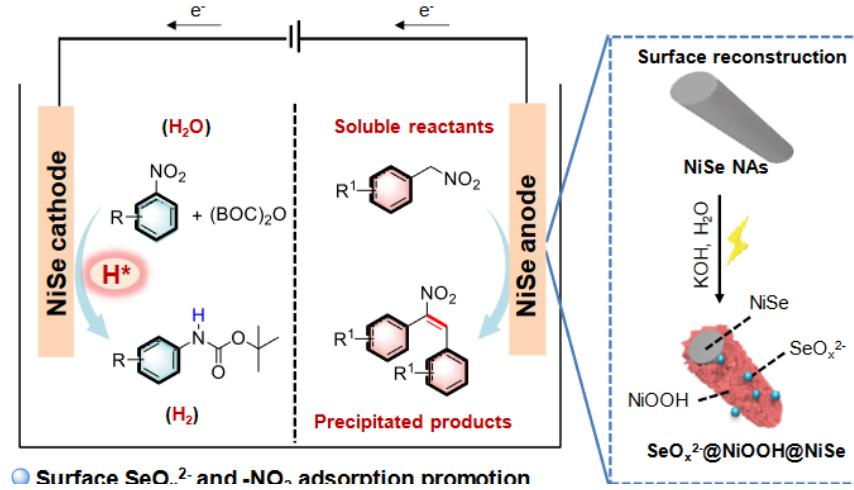
$\text{R} = \text{CH}_3$ , con. 89%, sel. 87%  
 $\text{R} = \text{F}$ , con. 85%, sel. 89%  
 $\text{R} = \text{Cl}$ , con. 89%, sel. 87%



con. 94%, sel. 84%

# Anodic oxidation reaction

## ■ NiSe NAs modified electrode for electrochemical self-coupling reaction

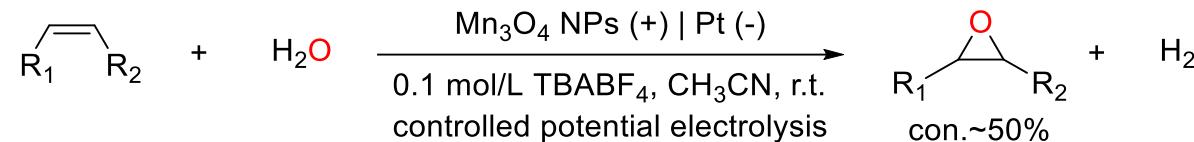


- ◆ *Z*- 和 *E*-nitroethene are similar Gibbs free energies
- ◆ The preferential adsorption of two -NO<sub>2</sub> groups on electrode surface can dominate the *E*-isomer product

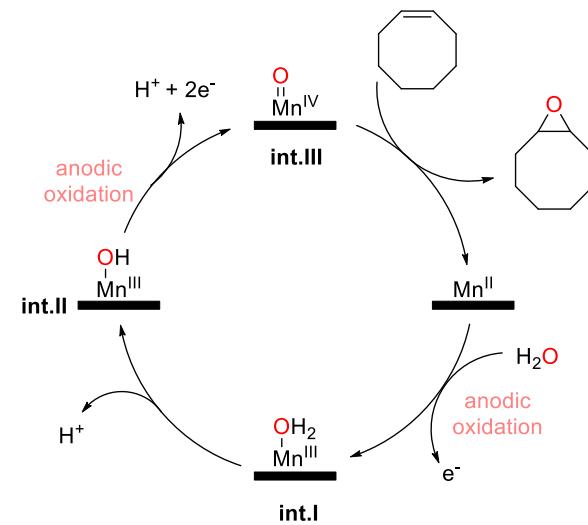
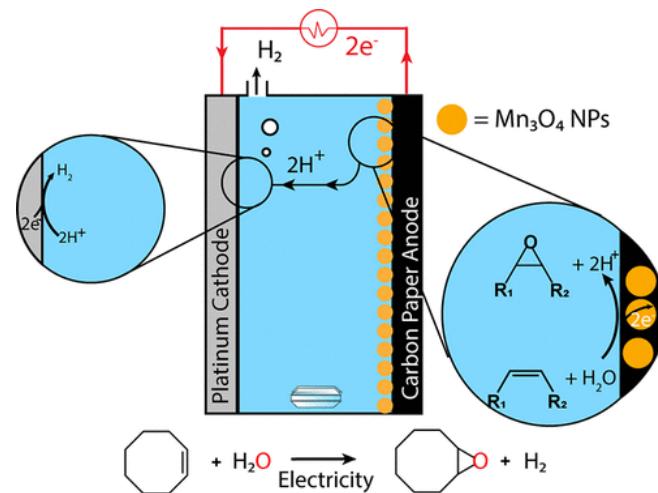
B. Zhang et al. *Angew.Chem.Int.Ed.* **2021**, *60*, 22010–22016

# Anodic oxidation reaction

## ■ Mn<sub>3</sub>O<sub>4</sub> NPs modified electrode for epoxidation of olefins



Proposed mechanism:



D.-T. Yang et al. *J.Am.Chem.Soc.* 2019, 141, 6413–6418

# Outline

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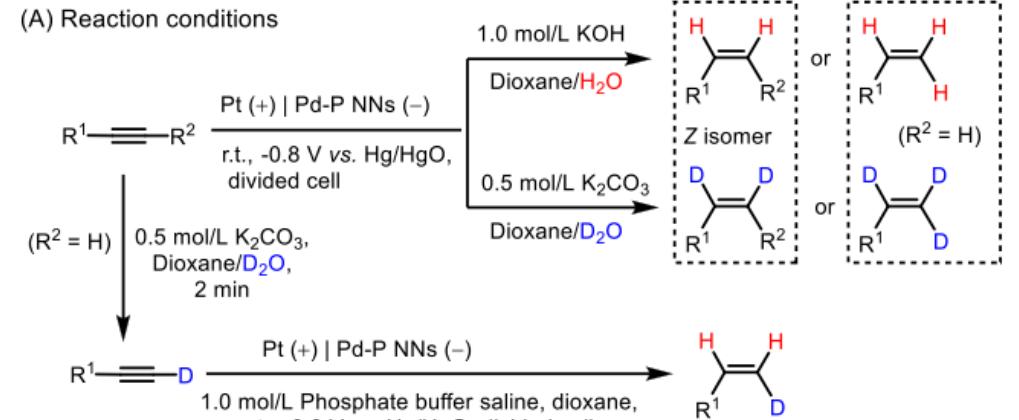
## ✓ Anodic oxidation reaction

## ✓ Cathodic reduction reaction

## ✓ Summary

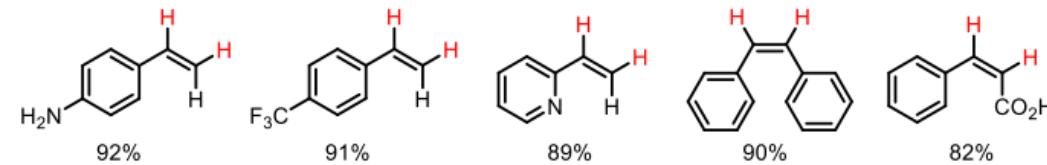
# Cathodic reduction reaction

## ■ Pd-P NNs modified electrode for electrocatalytic semihydrogenation of alkynes.

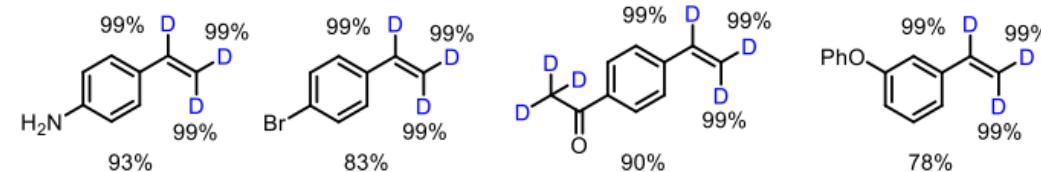


(B) Representative substrate scope

Semihydrogenation



Trideuterated alkenes

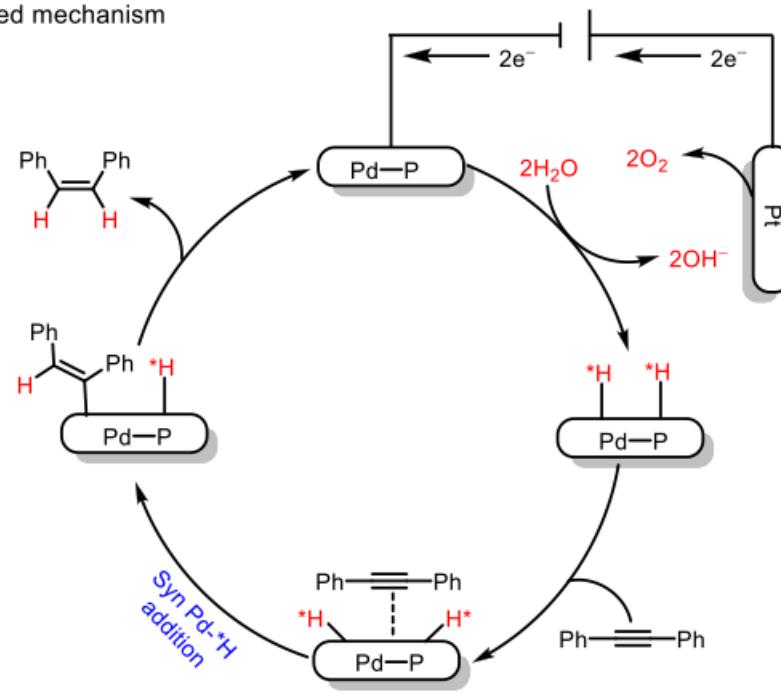


B. Zhang et al. *Angew.Chem.Int.Ed.* **2020**, 59, 21170–21175

# Cathodic reduction reaction

## ■ Asymmetric Cyclopropanation and Cyclopropenation

(C) Proposed mechanism



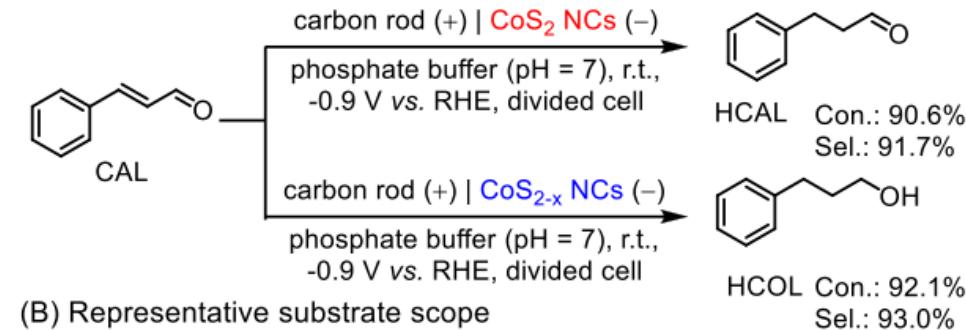
**The incorporation of P into Pd**

- ◆ **Over hydrogenation**: decrease the number of H atoms
- ◆ **Adsorption of alkyne**: more preferential adsorption of the Pd-P to  $\text{C}\equiv\text{C}$   $\pi$  bond than  $\text{C}=\text{C}$
- ◆ **Hydrogenation of alkynes**: the stronger bonding of  $\text{H}^*$

B. Zhang et al. *Angew.Chem.Int.Ed.* **2020**, 59, 21170–21175

# Cathodic reduction reaction

■ **CoS<sub>2</sub> and CoS<sub>2-x</sub> NCs modified electrodes for selective electrocatalytic hydrogenation of  $\alpha, \beta$ -unsaturated aldehydes.**

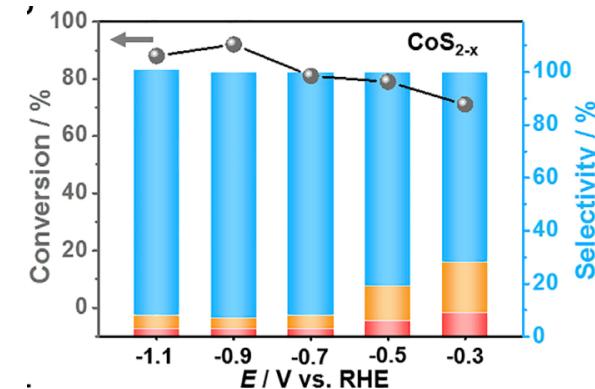
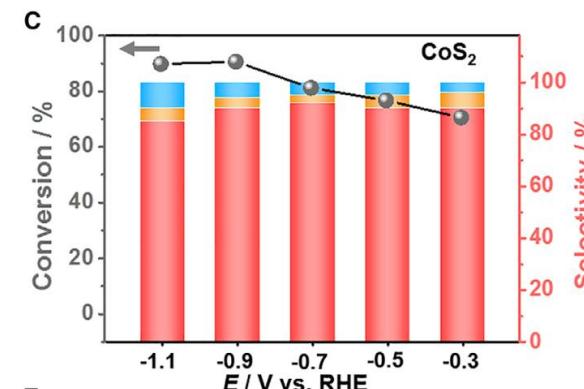
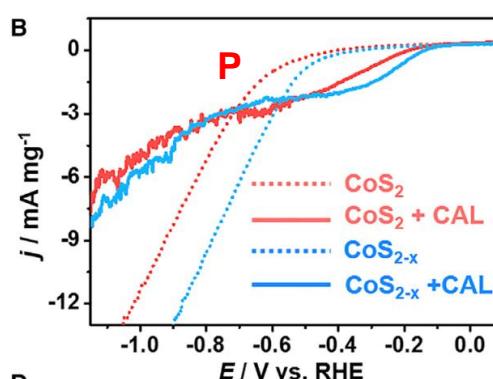
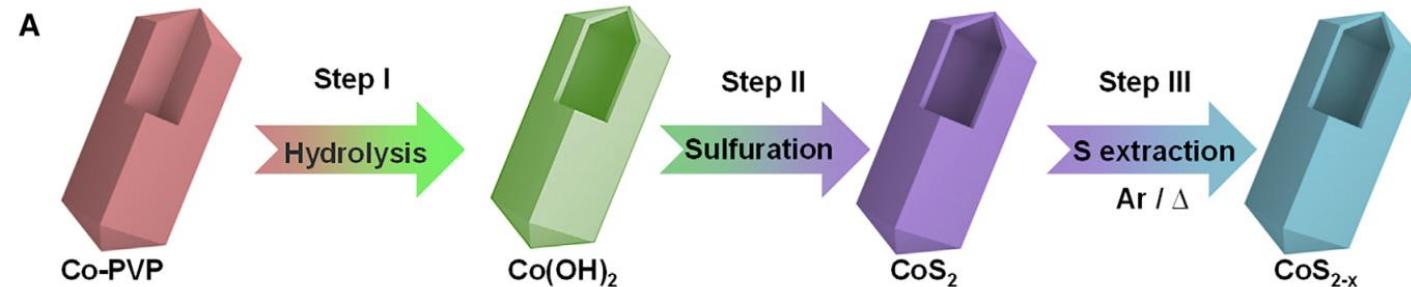


Substrate	CoS <sub>2</sub> NCs	CoS <sub>2-x</sub> NCs
	 Con.: 86.3% Sel.: 88.7%	 Con.: 88.1% Sel.: 92.6%
	 Con.: 72.0% Sel.: 84.3%	 Con.: 76.5% Sel.: 84.6%
	 Con.: 87.2% Sel.: 76.8%	 Con.: 90.2% Sel.: 89.3%

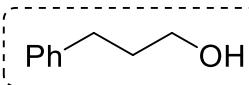
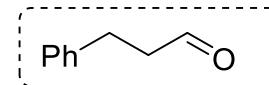
B. Zhang et al. *Cell Reports Physical Science*. **2021**, 2, 100337-100353.

# Cathodic reduction reaction

■ CoS<sub>2</sub> and CoS<sub>2-x</sub> NCs modified electrodes for selective electrocatalytic hydrogenation of  $\alpha, \beta$ -unsaturated aldehydes.

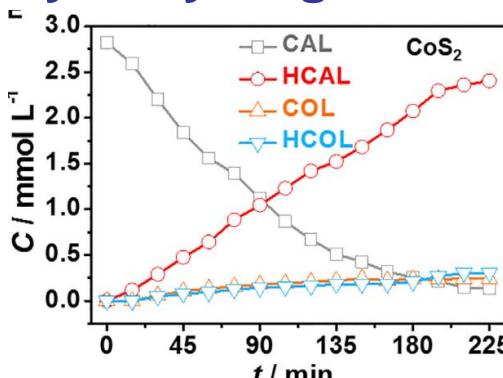


**P:** Due to the dominant HER

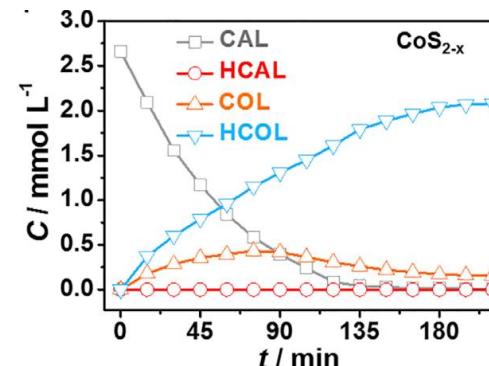


# Cathodic reduction reaction

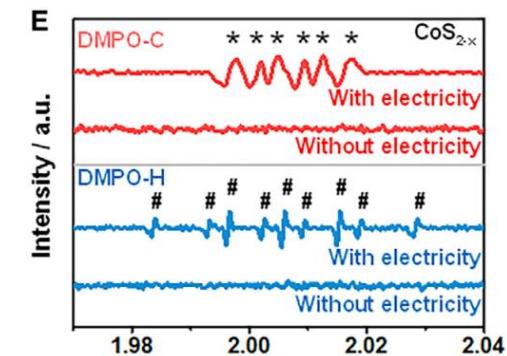
■ CoS<sub>2</sub> and CoS<sub>2-x</sub> NCs modified electrodes for selective electrocatalytic hydrogenation of  $\alpha, \beta$ -unsaturated aldehydes.



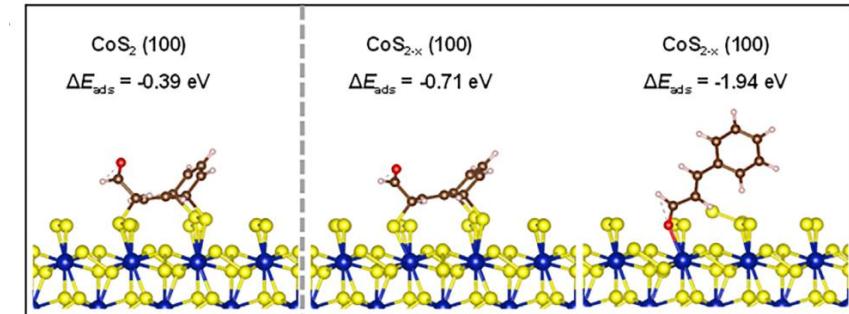
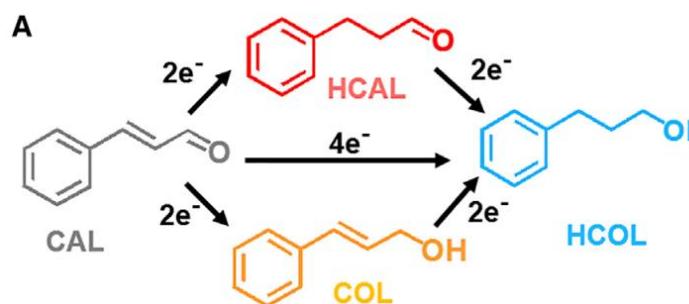
**CAL → HCAL**



**CAL → COL → HCOL**



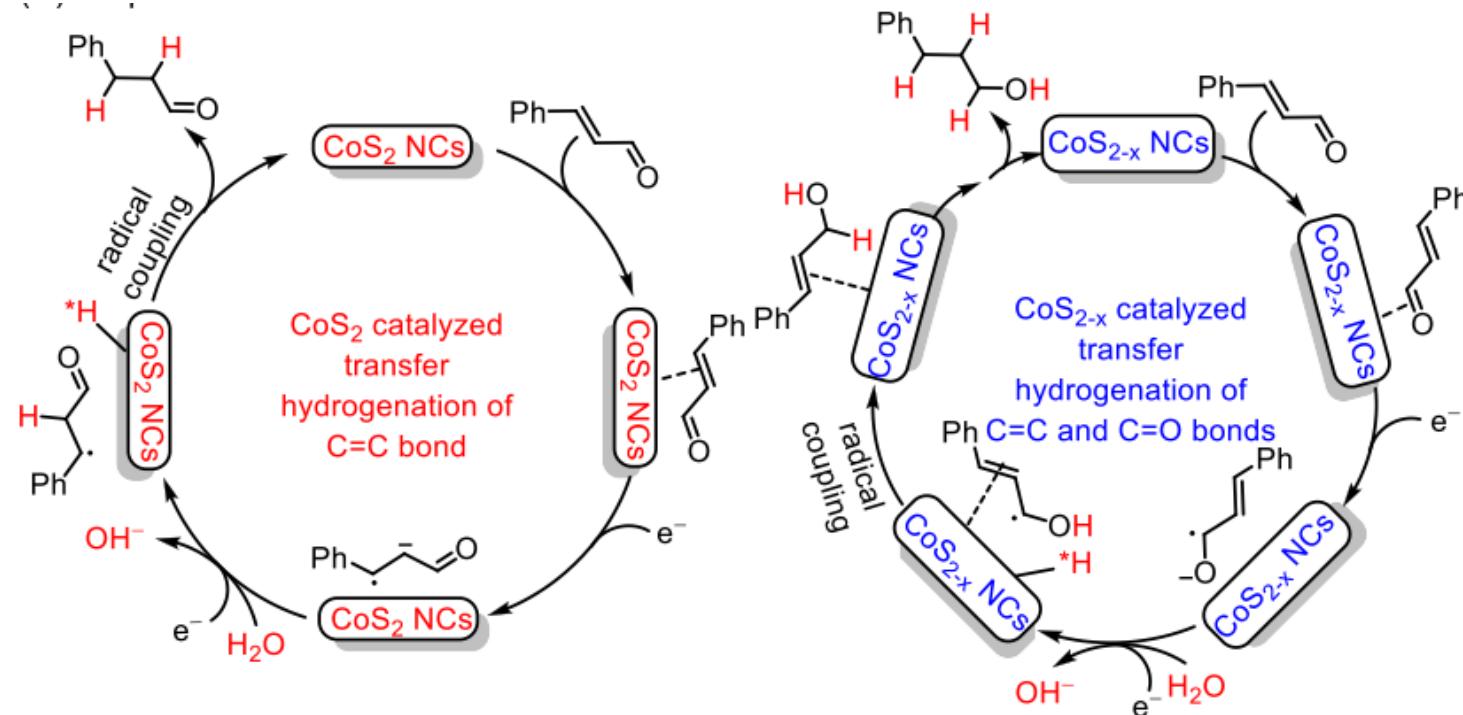
**H and C radical**



◆ Sulfur vacancies: Different groups have different adsorption energy

# Cathodic reduction reaction

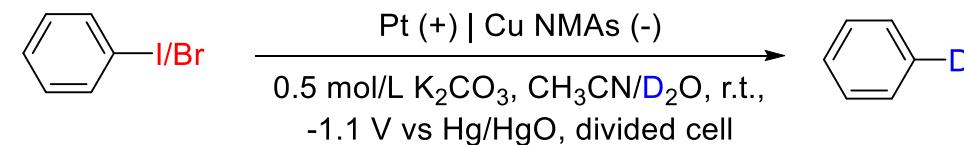
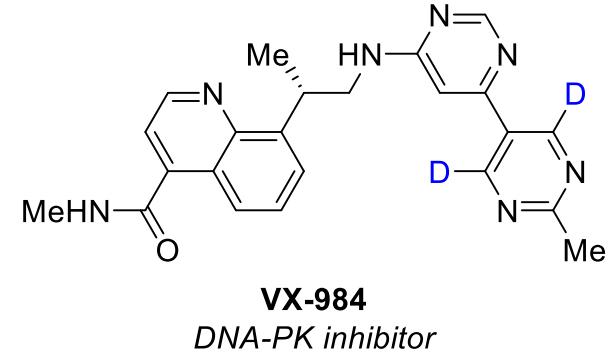
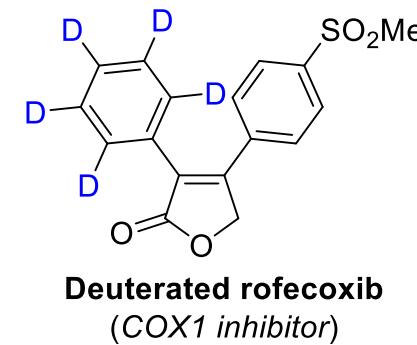
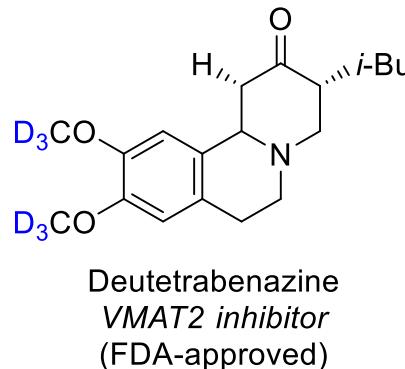
■ CoS<sub>2</sub> and CoS<sub>2-x</sub> NCs modified electrodes for selective electrocatalytic hydrogenation of  $\alpha, \beta$ -unsaturated aldehydes.



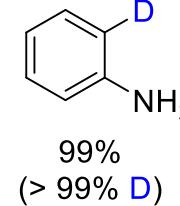
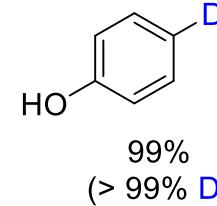
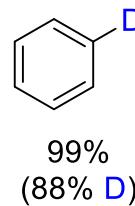
B. Zhang et al. *Cell Reports Physical Science*. 2021, 2, 100337-100353.

# Cathodic reduction reaction

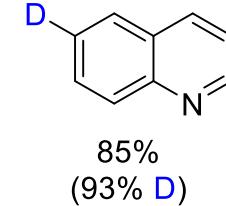
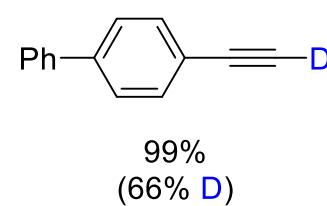
## ■ Cu NWAs modified electrode for radicals coupled reaction



C-I to C-D:



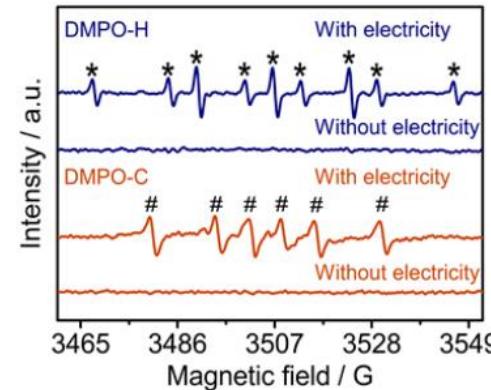
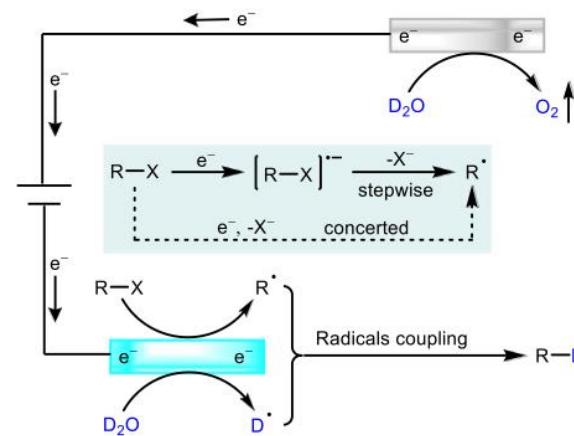
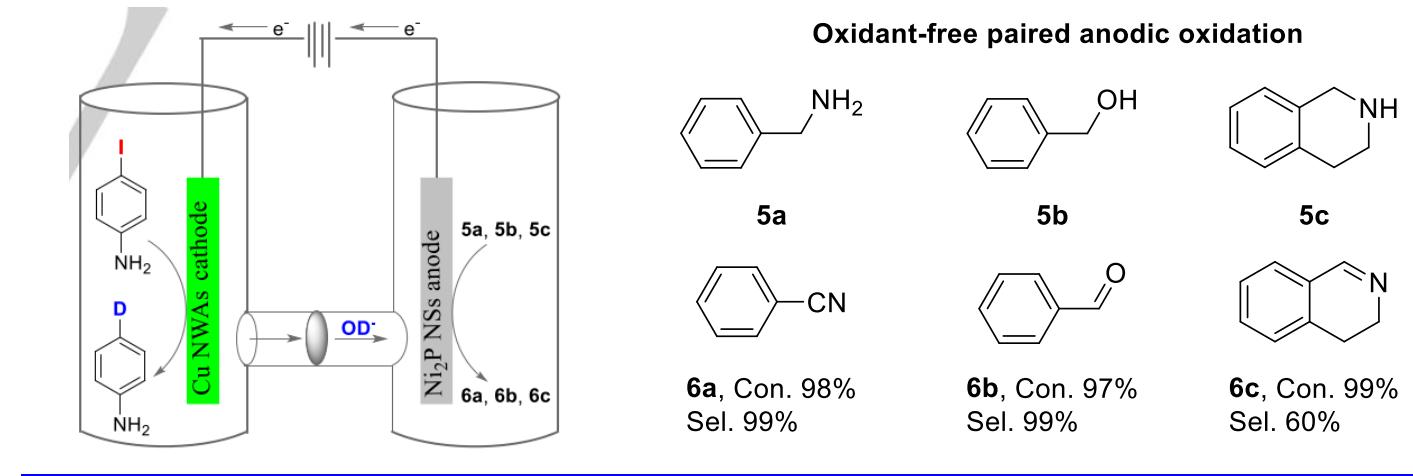
C-Br to C-D:



B. Zhang et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 18527 – 18531.

# Cathodic reduction reaction

## ■ Cu NWAs modified electrode for radicals coupled reaction



B. Zhang et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 18527 – 18531.

# Outline

## ✓ Background

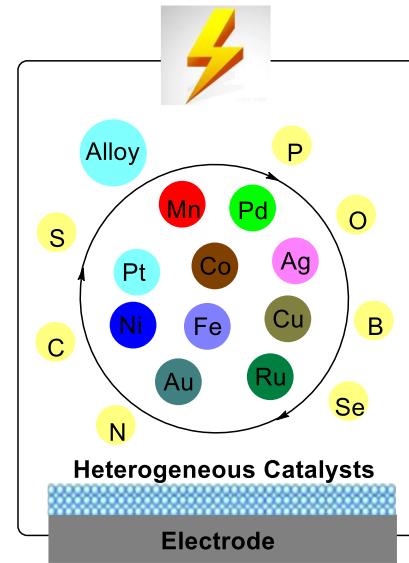
- Introduction of electrolytic cell
- Two types of electrolysis
- The representation of heterogeneous catalysts modified electrodes

## ✓ Anodic oxidation reaction

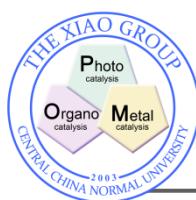
## ✓ Cathodic reduction reaction

## ✓ Summary

# Summary



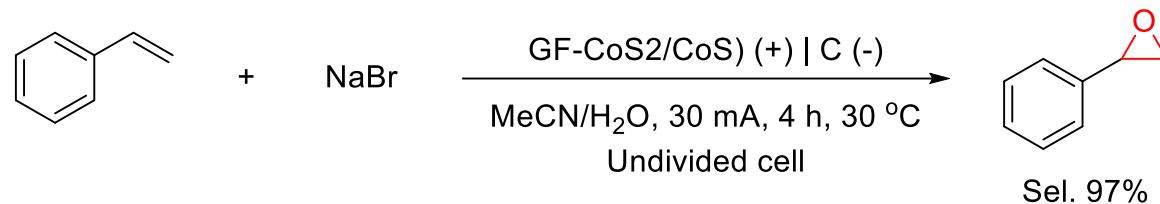
- ◆ Integrating heterogeneous electrocatalysts into electrode surfaces expands the range of traditional organic electrosynthesis
- ◆ Heterogeneous electrocatalysts can be specifically and rationally designed to incorporate catalytic sites and have broad application prospects
- ◆ Despite there are some difficulties to overcome, heterogeneous electrocatalysts provide a promising platform for advancing electrocatalytic conversions of organic molecules to value-added products



*Thanks for your kind attention !*

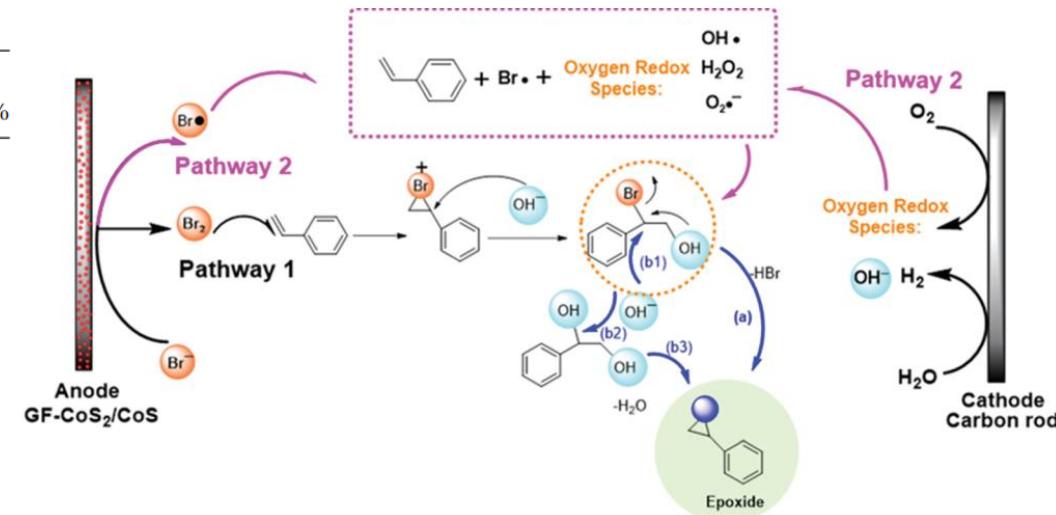
# Anodic oxidation reaction

## ■ GF-CoS<sub>2</sub>/CoS anode for electrocatalytic epoxidation



Proposed mechanism:

Sr. no.	Scavenger	Mediator	Conditions	Epoxide %
1	Divided cell	NaBr	Air	0%
2	—	NaBr	Argon	51%
3	—	Na <sub>2</sub> SO <sub>4</sub>	Air	0%
4	—	Na <sub>2</sub> SO <sub>4</sub>	Argon	0%
5	—	Na <sub>2</sub> SO <sub>4</sub>	O <sub>2</sub>	4%
6	D-Mannitol (OH <sup>•</sup> radical)	NaBr	Air	42%
7	BHT (common radical)	NaBr	Air	0%
8	Peroxidase (H <sub>2</sub> O <sub>2</sub> degradation)	NaBr	Air	72%
9	TEMPO (common radical)	NaBr	Air	5%

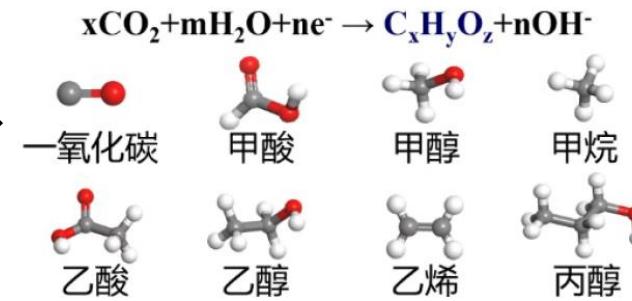


Xuefeng Qian et al. *Org. Chem. Front.* **2022**, 9, 436-444

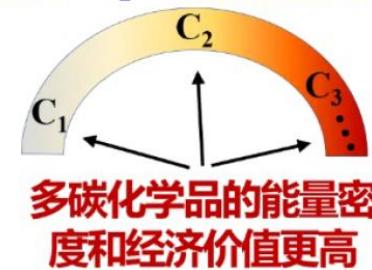
# Background

## ■ Application of electrochemical technology

**电催化反应特点：简单、清洁、无需添加额外的氧化还原试剂**



**电还原CO<sub>2</sub>→有价值化学品**



依据动力学，单位时间生产或消耗的物质的量，即  
**反应速度**可表示为

$$v = -(\frac{dn_{ox}}{dt}) = -(\frac{dn_e}{dt}) = \frac{dn_{Red}}{dt} = i/zF$$

i表示电化学反应的电流；Q表示电化学反应通过的电量；t表示电流通过的时间；z表示电极反应电子的计量数， $dn_{ox}$ 等分别表示电解产生或消耗的各对应物种的量和电子的物质的量，v为电极反应进行的速度

此式表示在不同情况下电化学反应速度的大小可以通过流过的电流大小表示

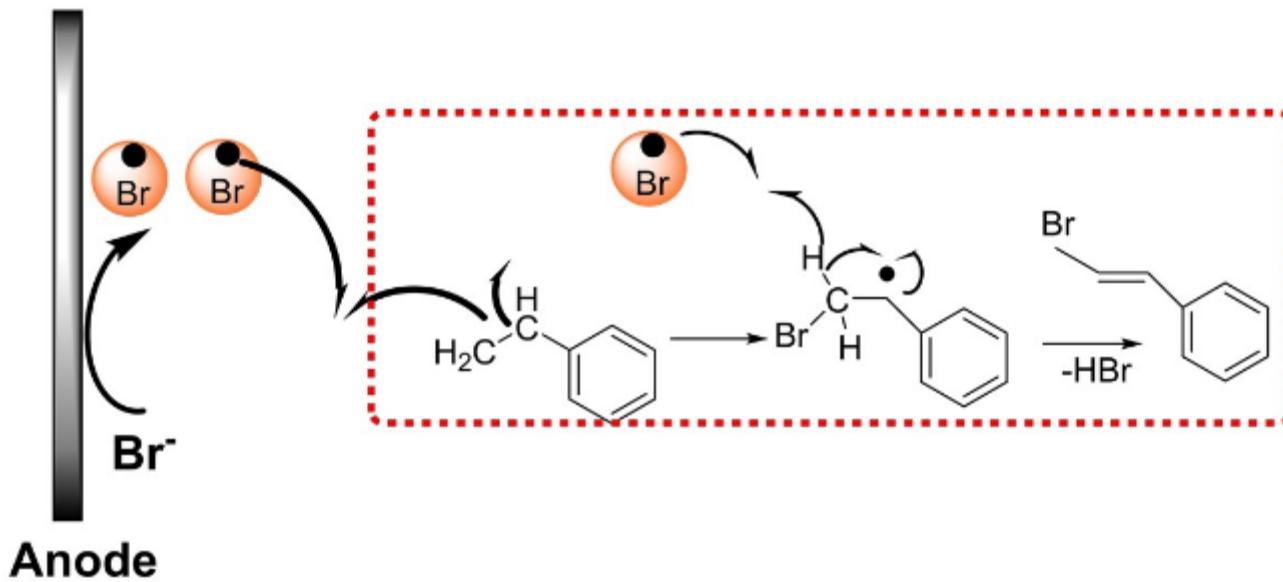
由于电极反应是界面上发生的异相过程，其反应速度常用单位面积的电流密度来表示：

$$v = i/zFA = j/zF$$

A为电极表面积，j是电流密度 ( $\text{A/cm}^{-2}$ )

由于 $nF$ 是一常数，所以 $j$ 完全取决于 $v$ ，即 $j$ 可以表示电极反应的速度。在电化学中电流密度就是电化学反应速度的同义语。

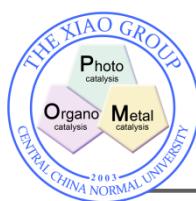
对于发生在异相界面的电极反应，施加在工作电极上的电势大小表示了电极反应的难易程度，而流过的电流则表示了电极表面上发生反应的速度。



**Fig S8** The mechanism of the  $\beta$ -bromostyrene formation.

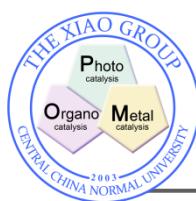
在一定的电流密度下，电极电位与平衡电位的差值称为该电流密度下的过电位或超电势，用符号 $\eta$ 表示。即  $\eta = E - E_{\text{平}}$ ，过电位 $\eta$ 是表征电极极化程度的参数，在电极过程动力学中有重要的意义。习惯上取过电位为正值。因此规定阴极极化 $\eta_c = E_{\text{平}} - E_c$ ；阳极极化时， $\eta_a = E_a - E_{\text{平}}$ 。

对于同一电化学体系，通过的电流越大，电极电势偏离平衡值越大



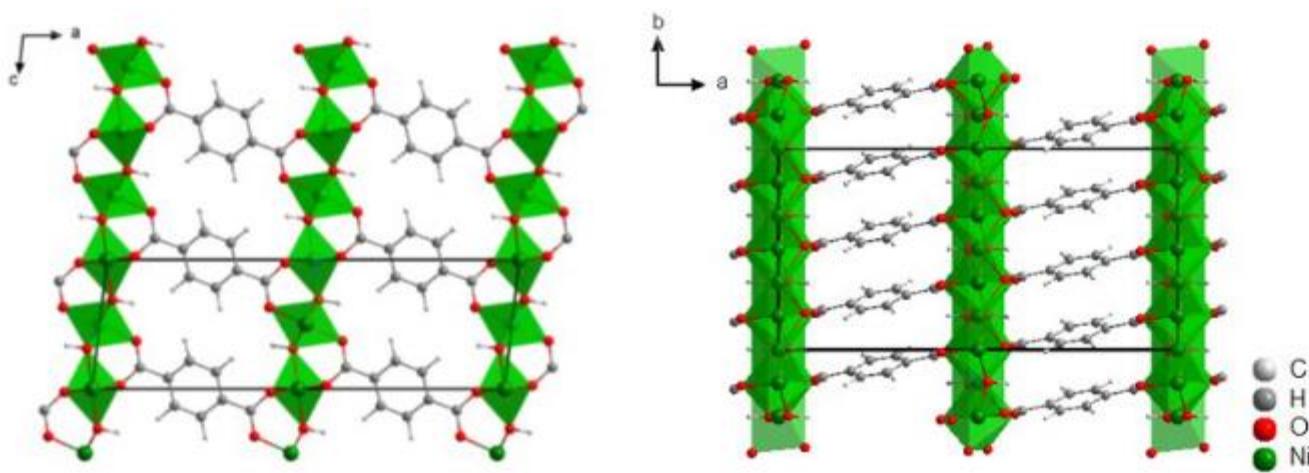
## 电极产生极化的原因：

电极极化现象是极化与去极化两种矛盾作用的综合结果，其实质是电极反应速度跟不上电子运动速度而造成的电荷在界面的积累，即产生电极极化现象的内在原因正是电子运动速度与电极反应速度之间的矛盾。



## 电极反应特点

1. 电极反应的速度不仅与温度、压力、溶液介质、固体表面形态，传质条件等有关，而且受施加于电极/溶液界面电位的强烈影响。如：电极电势每改变1V可是电极反应速度改变 $10^{10}$ 倍。所以，电极反应的速度可以通过改变电极电势加以控制，因为通过外部施加到电极上的电位，可以自由地改变反应的活化能，电极反应的特点



**Figure S5.** Crystal structure diagram of the 2D MOFs NiBDC with the molecular formula of  $[\text{Ni}_3(\text{OH})_2(1,4\text{-BDC})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ .

There are two other efficiencies calculated based on the energy changes of the water electrolysis reaction, known as the *Faradic efficiency* and the *thermal efficiency*. They use the Gibbs free energy change and enthalpy change of water decomposition reaction as the energy input, respectively. Both  $\eta_{\text{Faradic}}$  and  $\eta_{\text{Thermal}}$  adopt the theoretical energy requirement plus energy losses as the energy input. As shown in Equations (7) and (8).

$$\eta_{\text{Faradic}} = \frac{\Delta G}{\Delta G + \text{Losses}} = \frac{E_{\Delta G}}{E_{\text{cell}}} \quad (7)$$

$$\eta_{\text{Thermal}} = \frac{\Delta H}{\Delta G + \text{Losses}} = \frac{E_{\Delta H}}{E_{\text{cell}}} \quad (8)$$

a Hypothesized Mechanism for  $\alpha$ -Nitrotoluene Electrooxidation to *E*-Nitroethene

