Recent XAFS development and its application in Shanghai Synchrotron Radiation Facility

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上海同步辐射光源 Shanghai Synchrotron Radiation Facility

中国科学院上海高等研究院 Shanghai Advanced Research Institute, Chinese Academy of Sciences

SINAP 中国科学院上海应用物理研究所 Shanghai Institute of Applied Physics, Chinese Academy of Sciences

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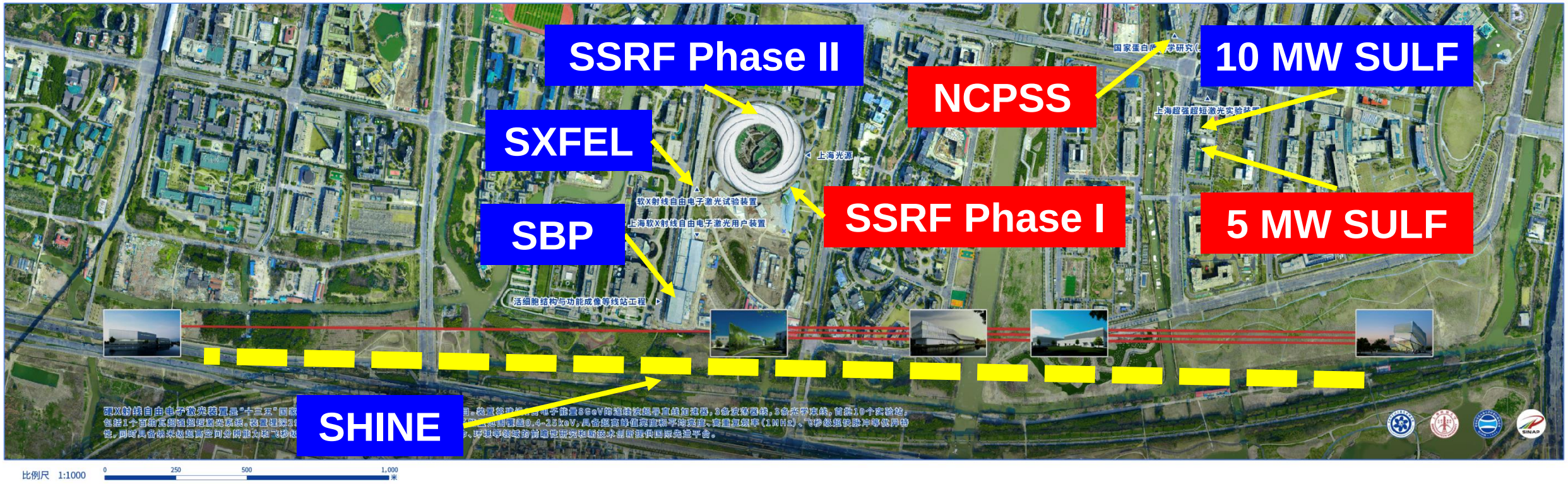
Zhangjiang Comprehensive National Science Center



We will actively participate in the construction of Zhangjiang comprehensive National Science Center, join the international club.

Outline

- **X-ray Spectroscopy Platforms in SSRF**
  - BL14W1-XAFS beamline
  - D-line/E-line/RMB/Hard X-ray Spectroscopy beamline
- **X-ray Spectroscopy Platforms in SHINE**
- **Application of X-ray Spectroscopy in Catalysis**

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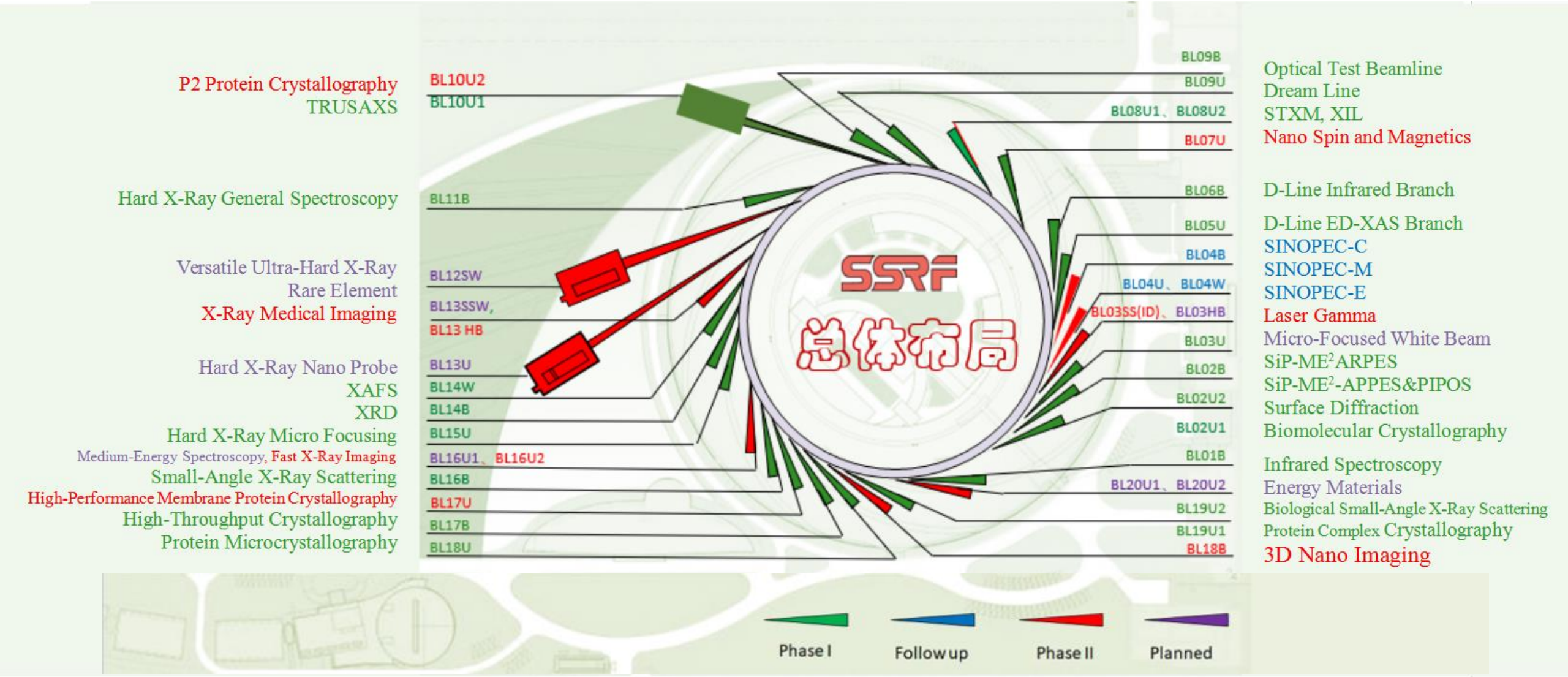
SSRF Beamlines layout



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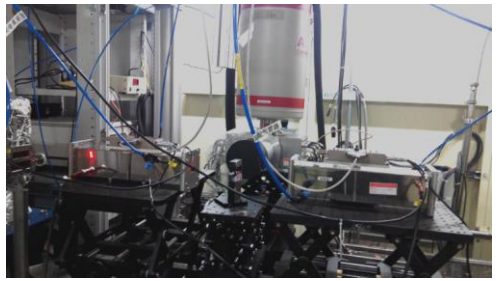
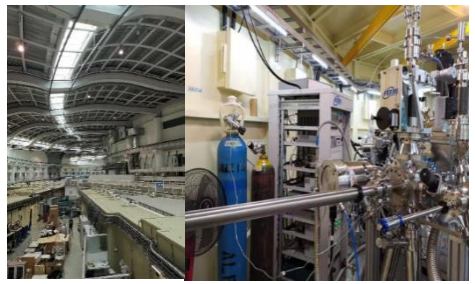
X-ray Spectroscopy Platforms at SSRF



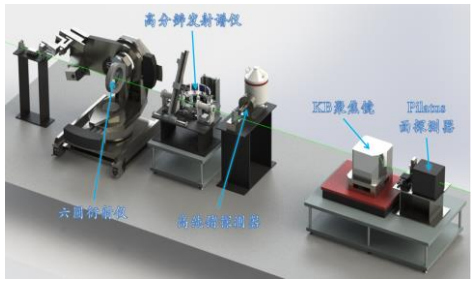
BL14W1-XAFS

Hard X-ray Spectroscopy

Dynamic D-line



Energy Material E-line



Radioactive Materials Beamline

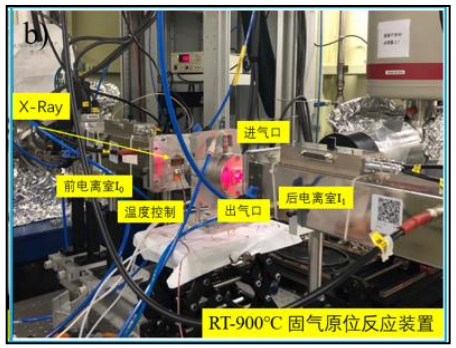
原位XAFS

QXAFS

DXAFS+IR

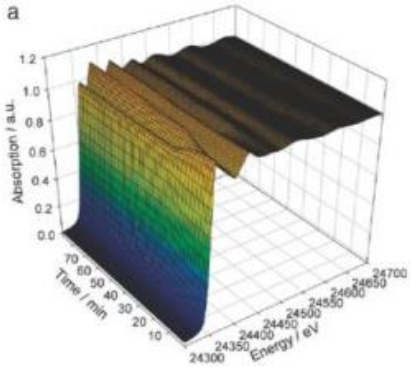
APPES/STM/XES/XRS....

XES/micro-spectroscopy



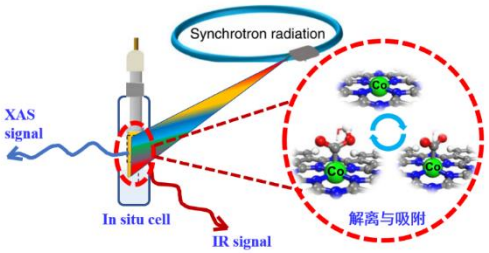
2005

2009

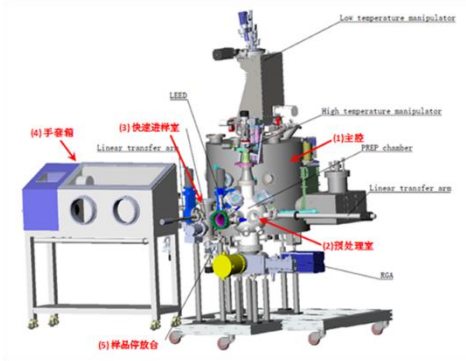


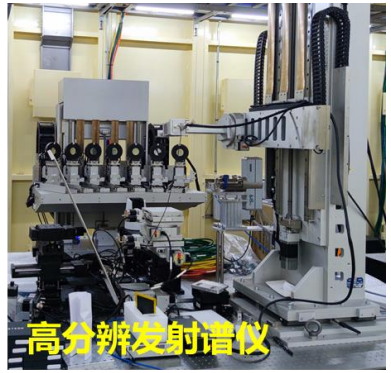
2016

2018



2020





2022

Timeline of construction

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Spectroscopy Methods in BL14W1

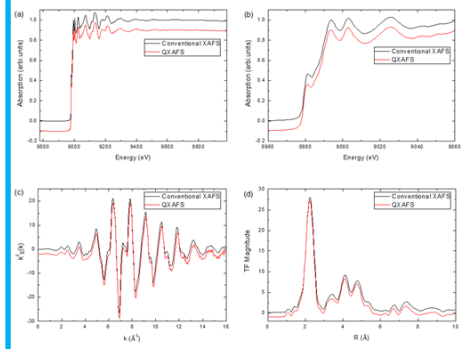
High energy resolution spectroscopy


Single/multiple-crystal Johann spectrometer

TRXEOL

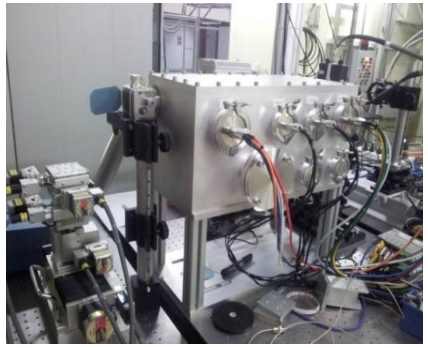
TRXEOL system

QXAFS



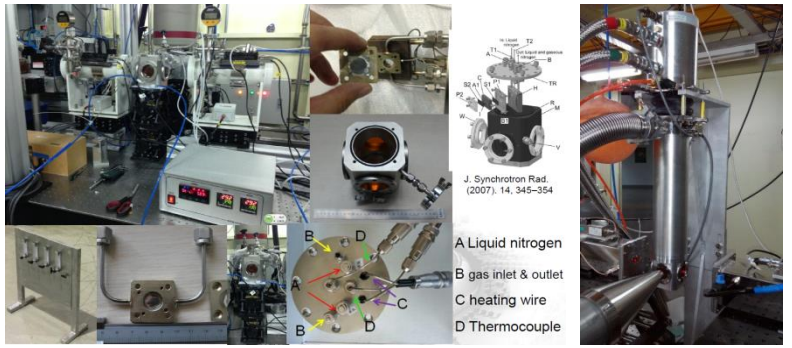
QXAFS result

High pressure XAFS




K-B/capillary isoelectric focusing

In situ/operando XAFS



High-temperature/low-temperature cells

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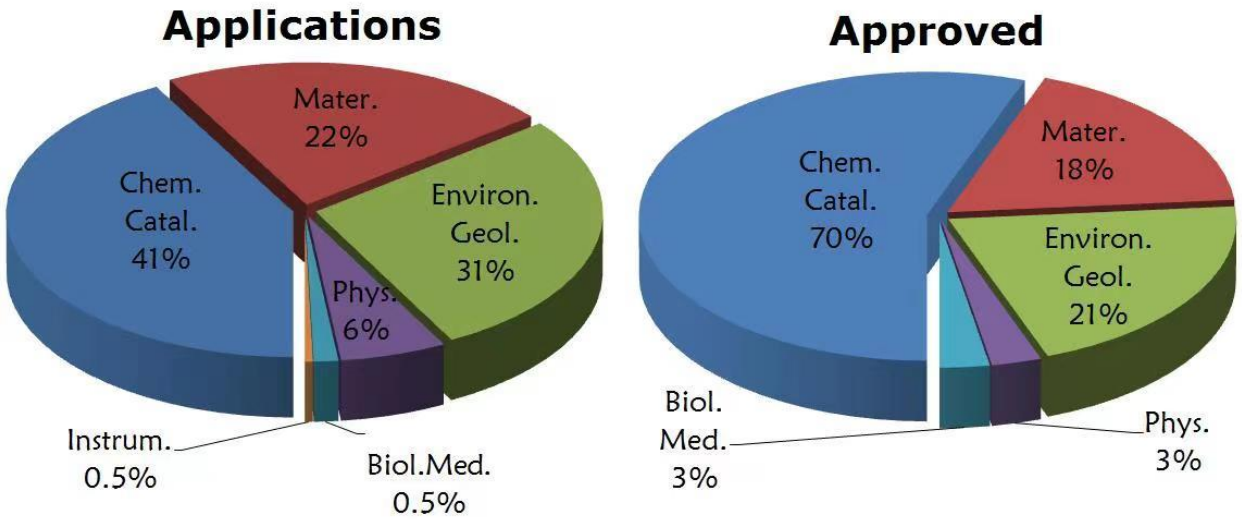
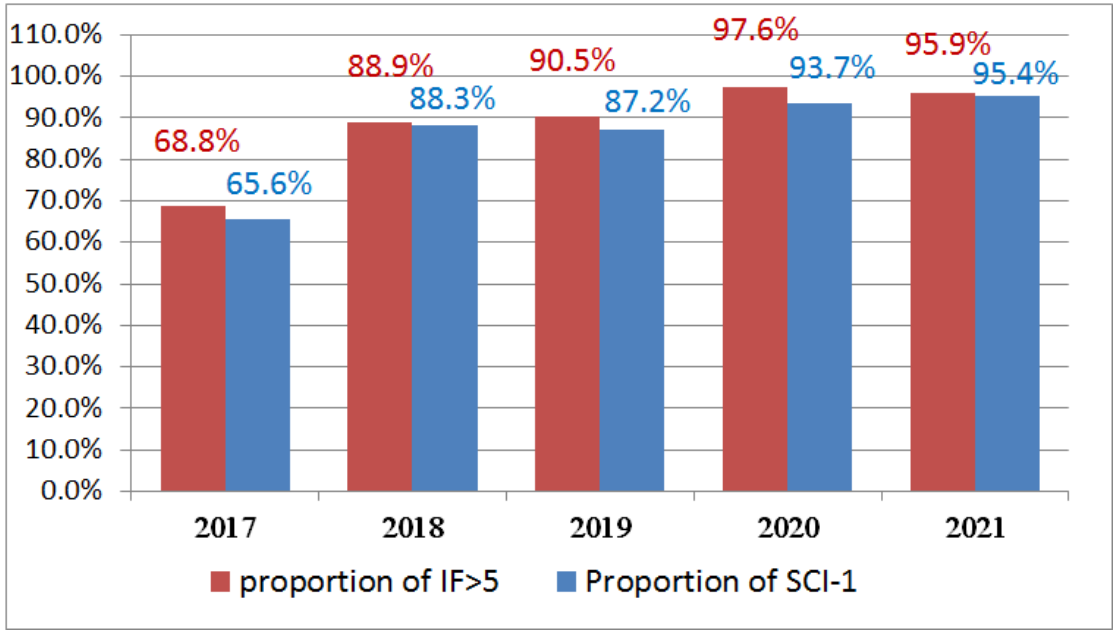
Users' Research Achievement of BL14W1





Chemistry (catalysis) has always been the field with the largest demand and highest quality output.

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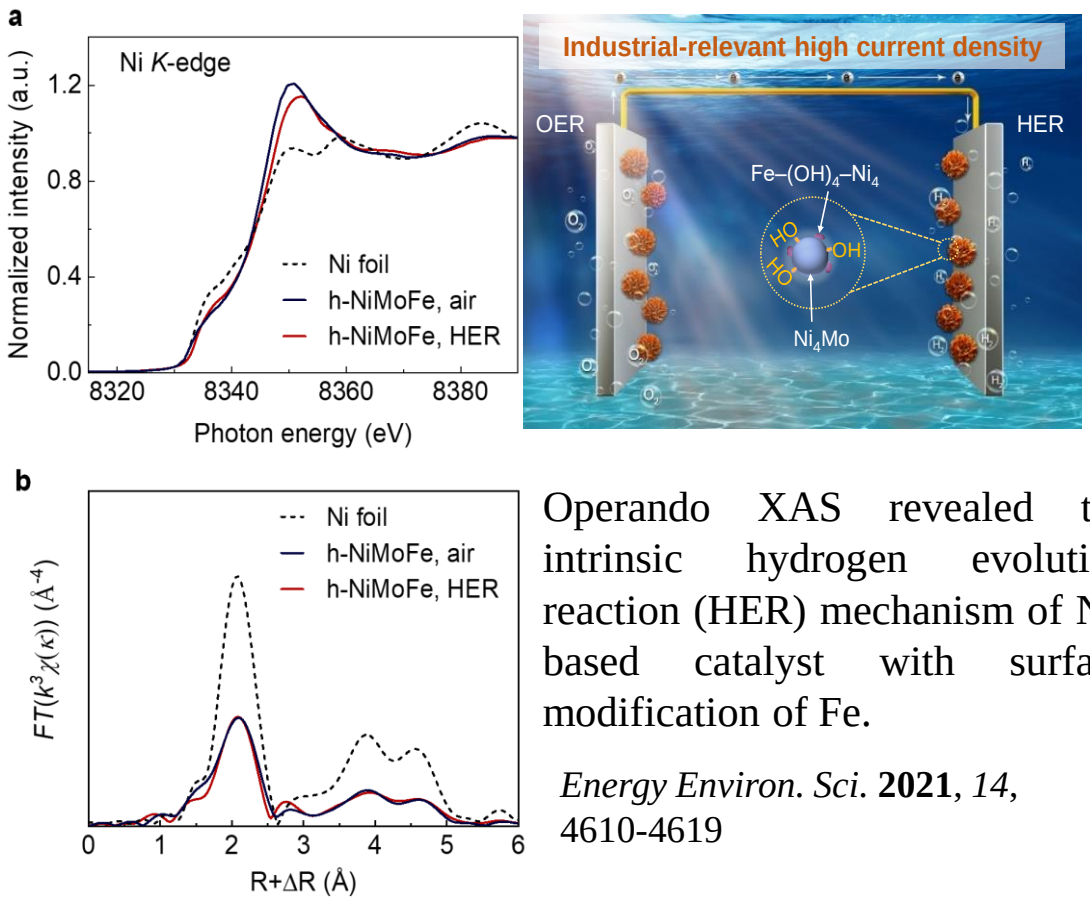
Hard X-ray Spectroscopy Beamline

Main Techniques:

- Transmission XAFS
- Fluorescence XAFS
- Quick Scanning XAFS
- Combined XAFS and XRD
- Operando XAFS

Hard X-ray Spectroscopy Beamline

Energy range	5~30 keV
Spot size	$500 \times 500\ \mu m^2$
Photon flux	4×10^{11}phs/s@10 keV, Si(111)
Energy resolution	2×10^{-4}@10keV, Si(111) 5×10^{-5}@10keV, Si(311)
Time resolution	~100 ms



Operando XAS revealed the intrinsic hydrogen evolution reaction (HER) mechanism of Ni-based catalyst with surface modification of Fe.

Energy Environ. Sci. **2021**, *14*, 4610-4619

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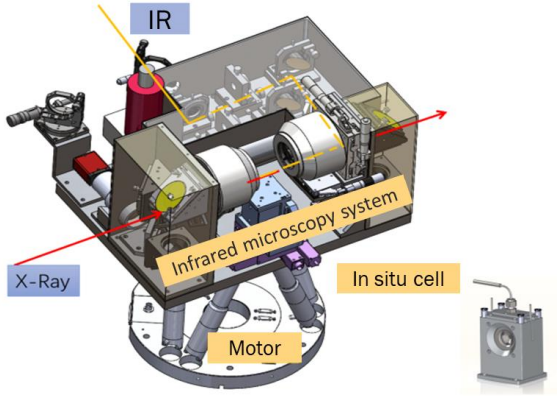
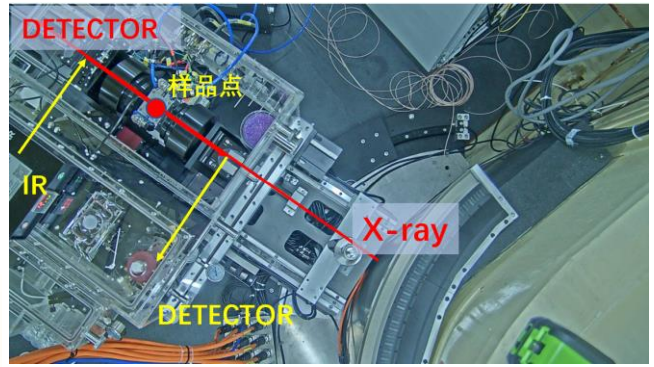
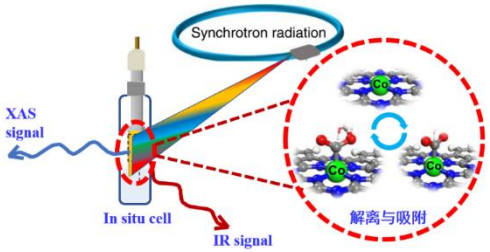
Design and Layout of D-line

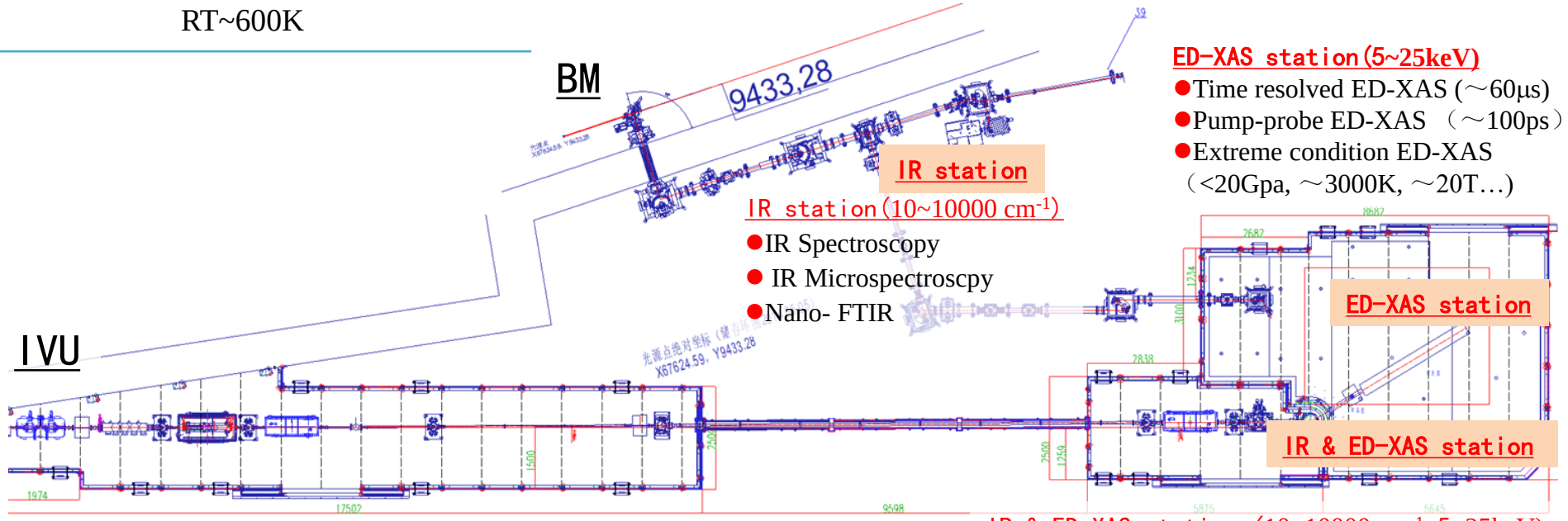
ED-XAS & IR

Energy range	5~25 keV; 100~1000 cm^{-1}
Spot size	20×20 μm^2; 100×100 μm^2@1000 cm^{-1}
Photon flux	3.8×10^{12}phs/s·300eV BW@7keV; 10^{13}phs/s·0.1%BW@4200 cm
Energy resolution	2×10^{-4}@Cu K-edge; 16cm^{-1}
Time resolution	~10 ms(FTIR), ~60 μs(ED-XAS)
In situ cell temperature	RT~600K









IR station (10~10000 cm^{-1})
- IR Spectroscopy
- IR Microspectroscpy
- Nano- FTIR

ED-XAS station (5~25keV)
- Time resolved ED-XAS (～60μs)
- Pump-probe ED-XAS （～100ps）
- Extreme condition ED-XAS （<20Gpa, ～3000K, ～20T…）

IR & ED-XAS station (10~10000 cm^{-1}, 5~25keV)
- Time-resolved IR+ ED-XAS（~ms）

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Science Object of E-line

Focusing on surface interface chemistry, electrochemistry, self-assembly, and photoelectric conversion, etc.

Electronic structure

- Occupied state
- Unoccupied state

Spatial dimention

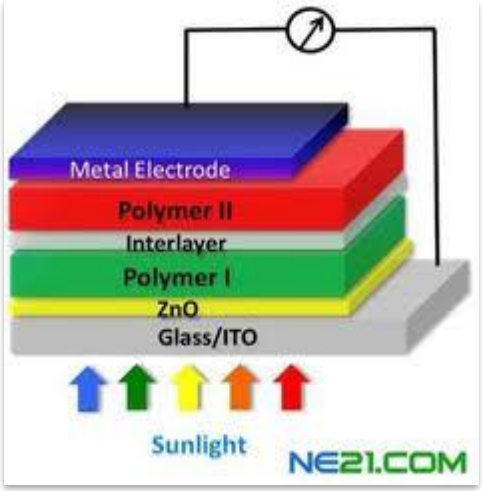
- Surface and interface
- Bulk

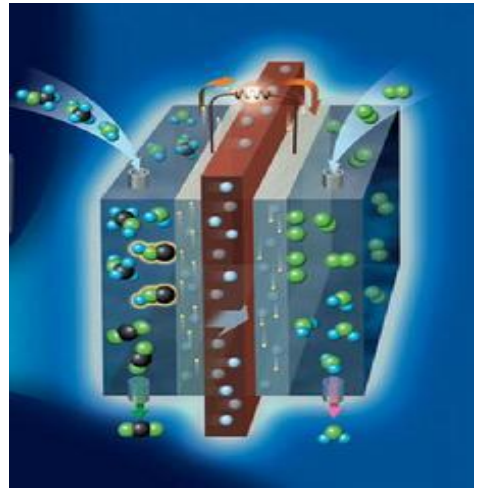
Operando measurement

- Temperature and pressure
- Electronic/magnetic field

- Measurement methods:
  XAS, XES, XRS, APPES, RXES, REXS

- **Understanding the reaction mehanism**
- **Regulating the reaction performance**





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Design and Layout of E-line

IVU23

Hard Branch

XES/XRS

hv: 2.3 keV-18 keV

Energy resolution: 4eV@ 6keV
HERFD-XAFS

Merging branch with hard and soft X-ray

XANES/AP-XPS

hv: 130eV -10 keV

EPU56

Soft branch

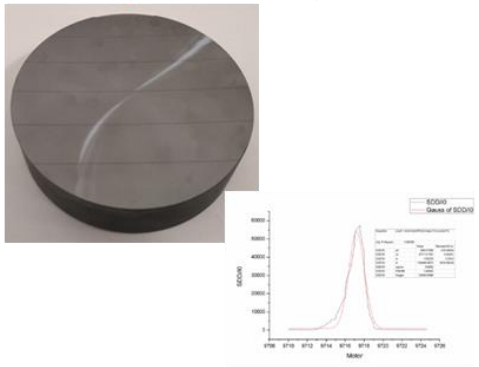
REXS+RIXS

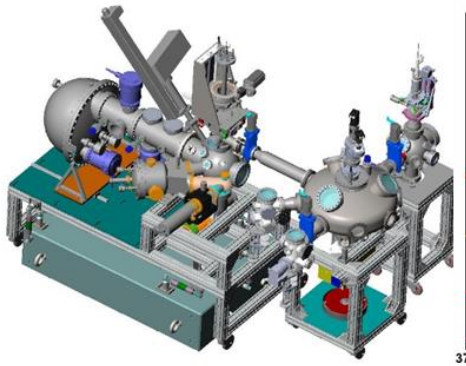
hv: 130eV -2 keV

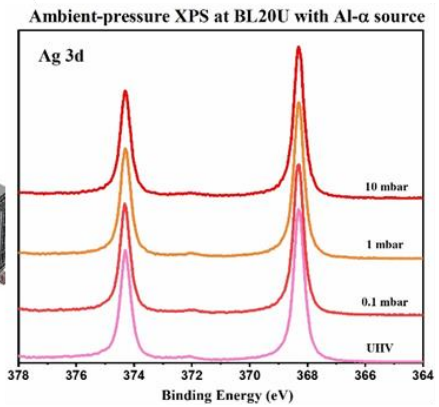
Energy resolution: 4000@ 445eV RIXS

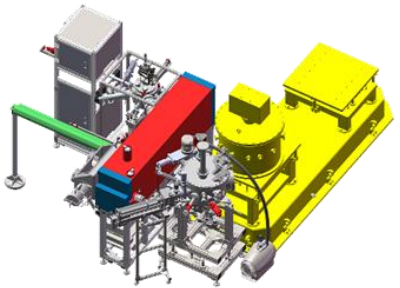
7-crystal XES

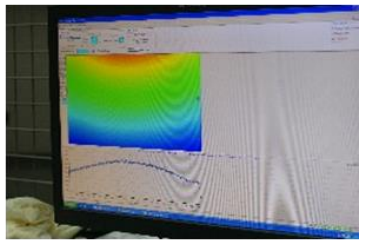
Crystal analyzer











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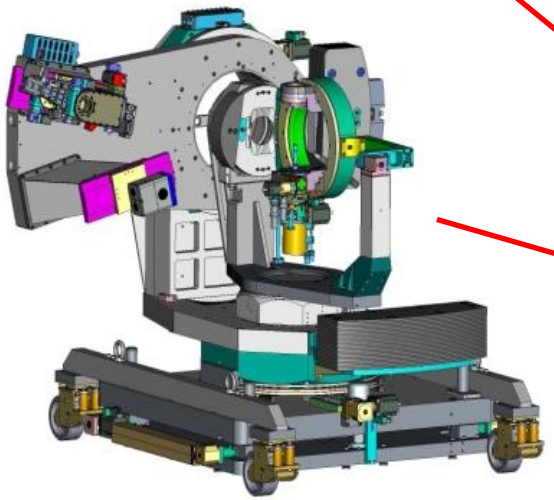
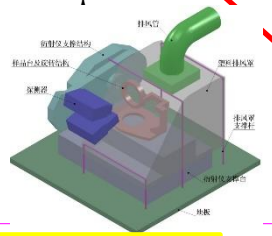
Radioactive Materials Beamline (RMB)

HRXPD station(5~50 keV)

- XRD, GIXRD
- High Resolution X-ray Powder Diffraction（HRXPD）



Ventilation system



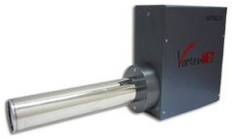
Cabinet for interim sample storage

Micro-beam station(5~35keV)

- μ-XAFS,
- μ-XRD

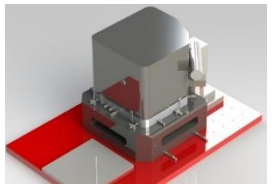
RMB Beamline

HRXPD station



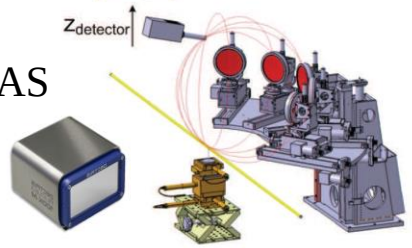
Micro-beam station

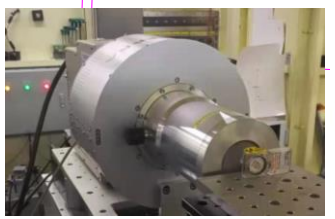
XAS & HR-XAS/XES station

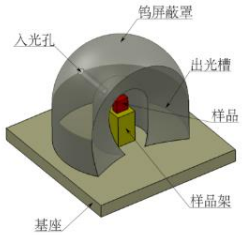


XAS & HR-XAS/XES station (3~50 keV)

- XAS
- HR-XAS
- XES







Tungsten shielding of sample

Outline

- **X-ray Spectroscopy Platforms in SSRF**
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10 End-Stations @ SHINE Facility

FEL-I Hard X-ray End-stations

- HSS: Hard X-ray Scattering and Spectroscopy
- **CDS:** Coherent Diffraction Endstation for Single Molecules and Particles
- **SEL:** Station of Extreme Light

➢ **XFEL + 100 PW Laser System**

FEL-II Soft X-ray End-stations

- **AMO:** Atomic, Molecular, and Optical Science
- **SES:** Spectrometer for Electronic Structure
- **SSS:** Soft X-ray Scattering and Spectroscopy

Tsu-Chien Weng

FEL-III Hard X-ray End-stations

- HXS: Hard X-ray Spectroscopy
- **SFX:** Serial Femtosecond Crystallography
- **CDE:** Coherent Diffraction Imaging
- **HED:** High Energy Density Science

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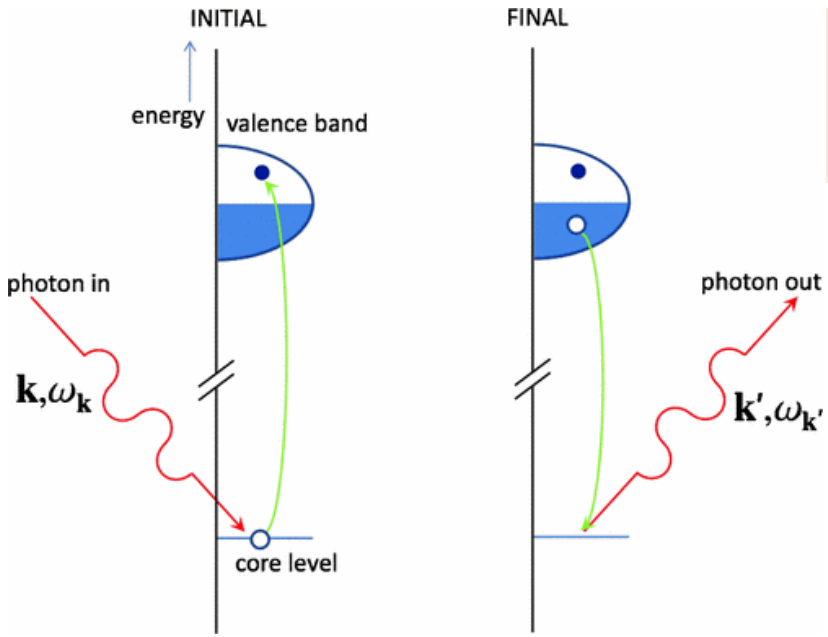
Hard X-ray Scattering & Spectroscopy Endstation

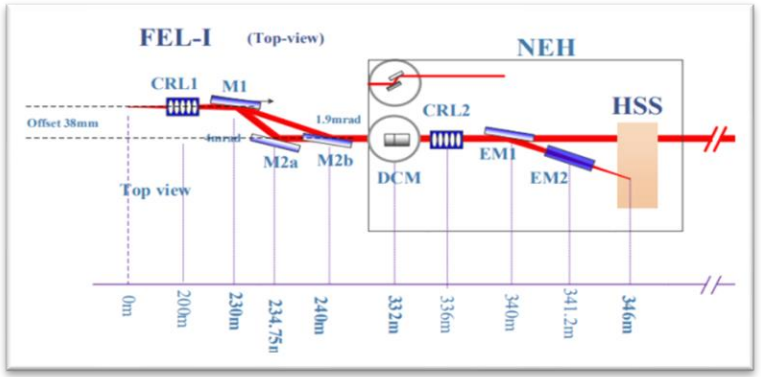
Measuring the element excitation in quantum associated materials in the case of energy, momentum and time.

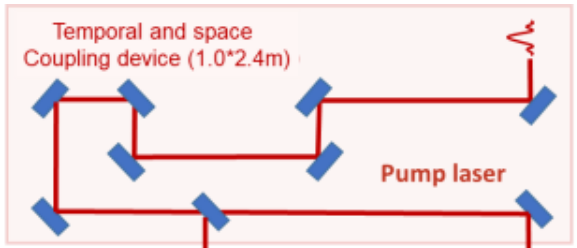


Rev. Mod. Phys. 83, 705 (2011)

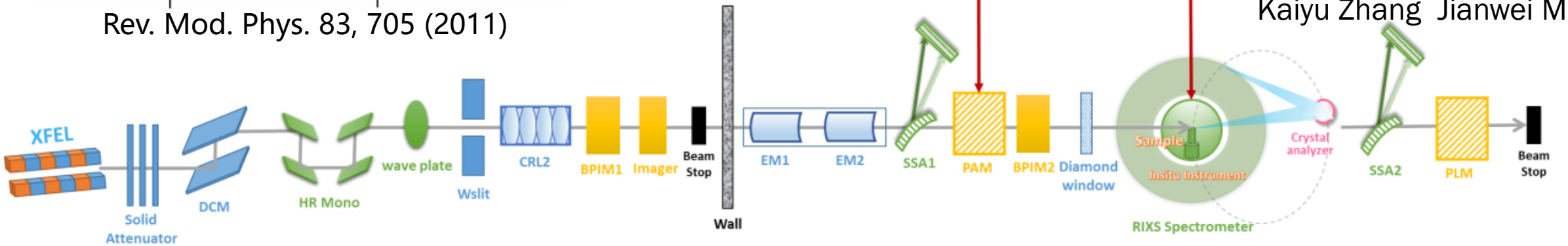
- **RIXS**
- **HERFD-XAS**

Energy range: 3-15 keV





Kaiyu Zhang Jianwei Meng



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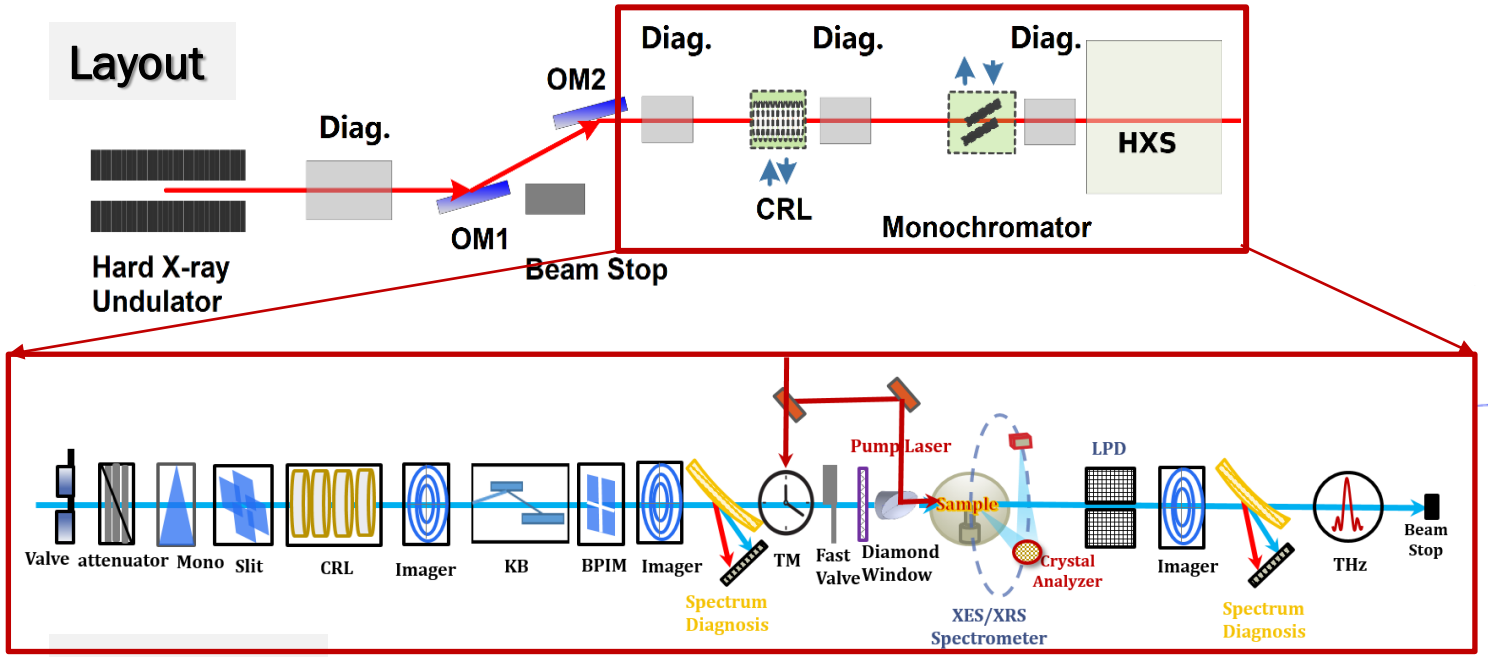
Hard X-ray Spectroscopy Endstation

FEL-III

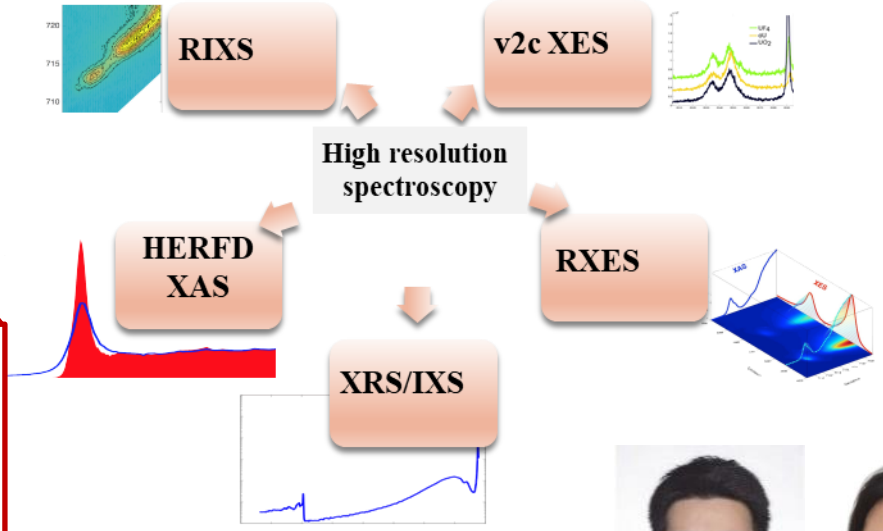
Layout



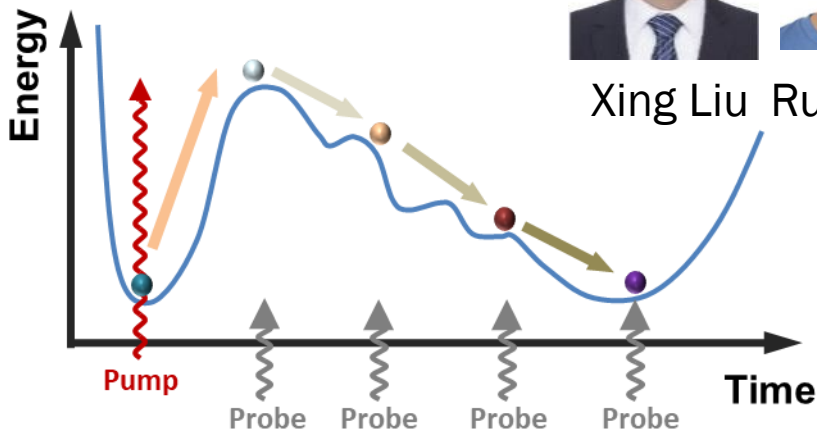
Parameters

Parameters	Unit	Values
Distance from source point	m	350
Photon energy range	keV	10–25
X-ray energy resolution	(ΔE/E)	Si(111):2.0×10^{-4} @ 10 keV Si(311):5×10-^{5}@10keV
Spot size	μm × μm	5~100μm
Experimental techniques	Non-resonant XES, RXES, XAS (XANES, EXAFS), XRS, XDS and IXS	

High Energy Resolution



High Time Resolution



Xing Liu Ruixue Zhu

Peng Liu

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- **Application of X-ray Spectroscopy in Catalysis**

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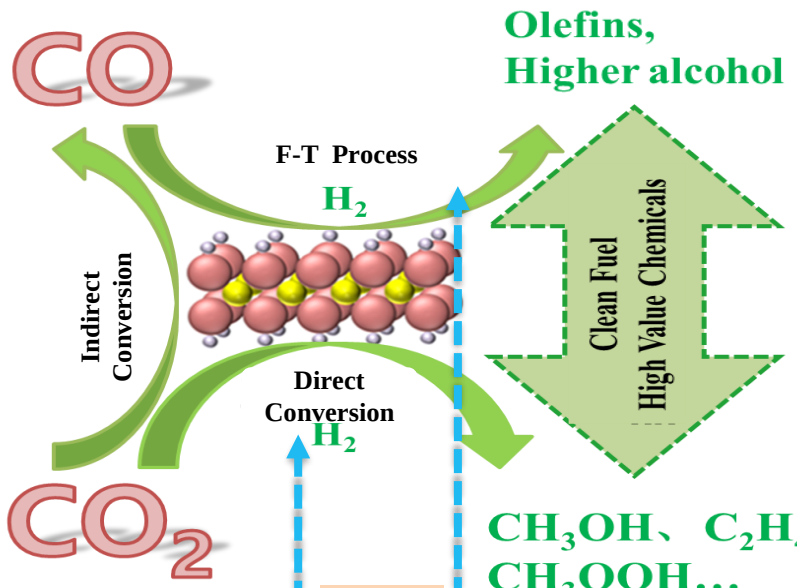
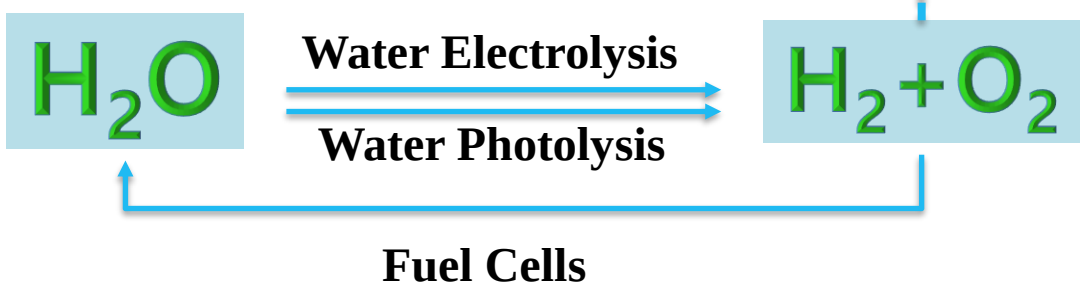
Toward Great Strategy Demand

Carbon Conversion



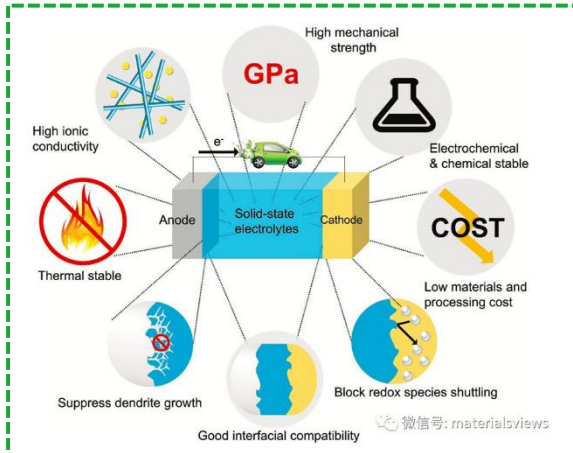
Hydrogen Energy Development



Ultimate goal

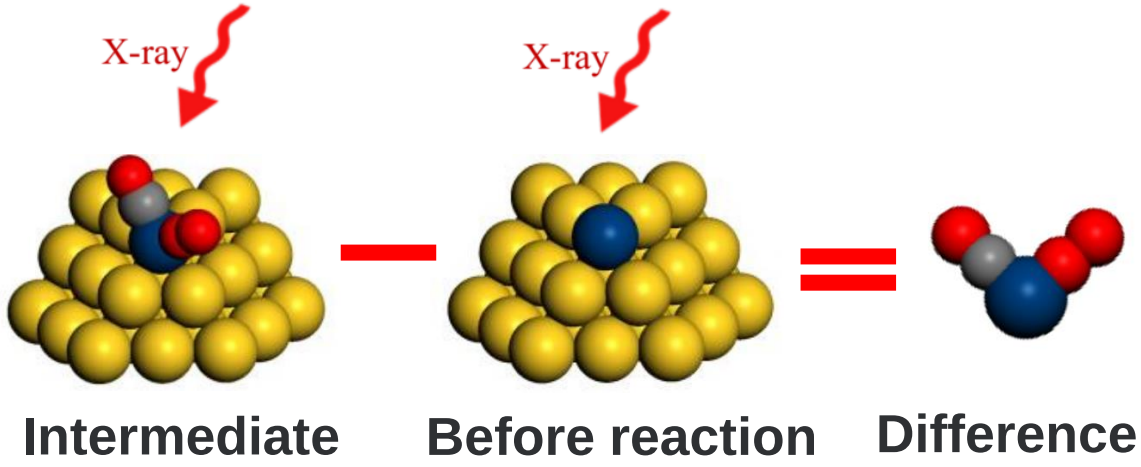
Emission = Eliminate

Li-ion Battery



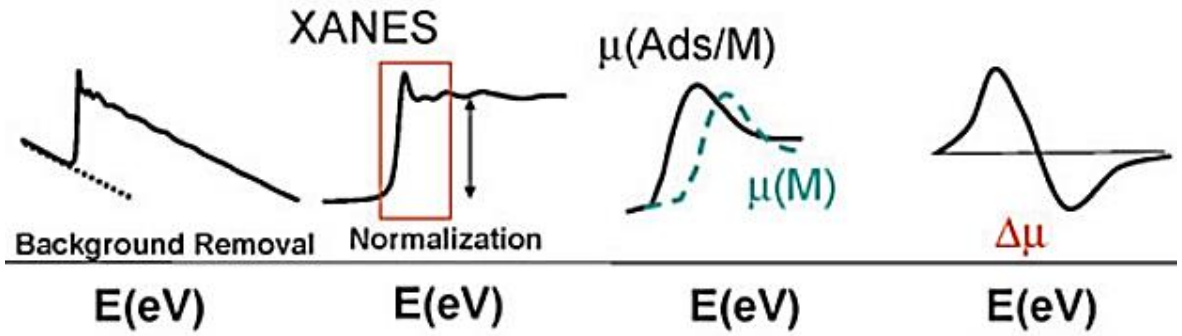
Difference spectra —— surface information

Difference technique ($\Delta\mu$)



$$\Delta\mu = \mu(\mathrm{Ad/M}) - \mu(\mathrm{M})$$

Surface sensitive



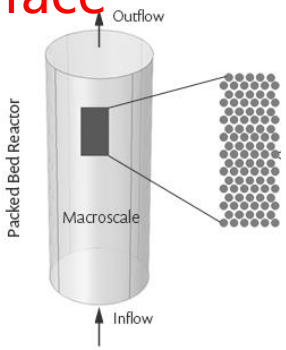
Shortage：weak intensity

Phys. Chem. Chem. Phys., **2010**, *12*, 5514–5534

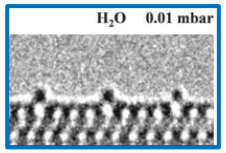
In Situ Spectroscopy Reveals Proton Transfer in EDL

Thermocatalysis:

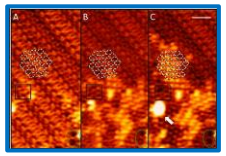
- Solid-Gas interface



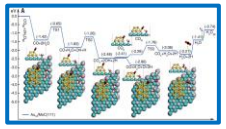
ETEM

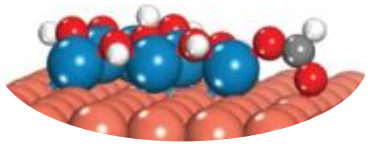


STM



DFT

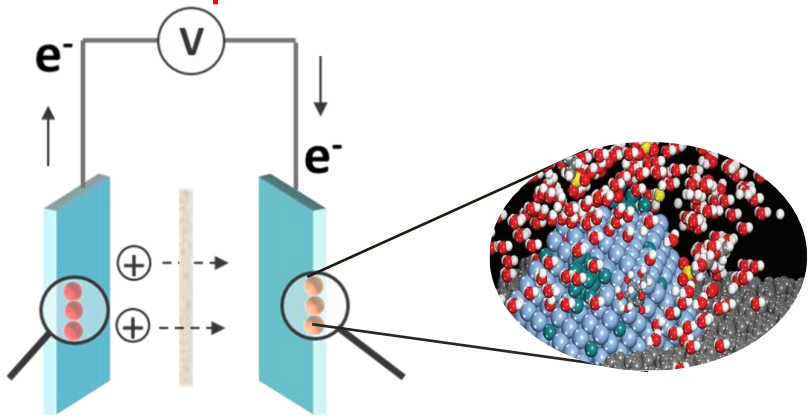




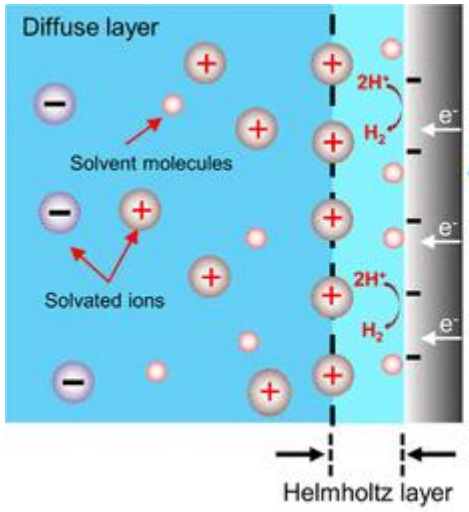
Building a catalytic reaction model

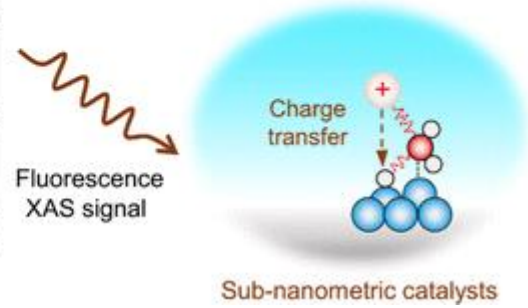
Electrocatalysis:

- Solid-Liquid interface



EDL

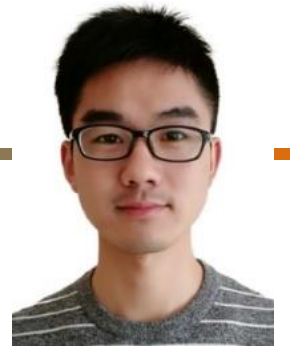




Solvent effect at the solid-liquid interface

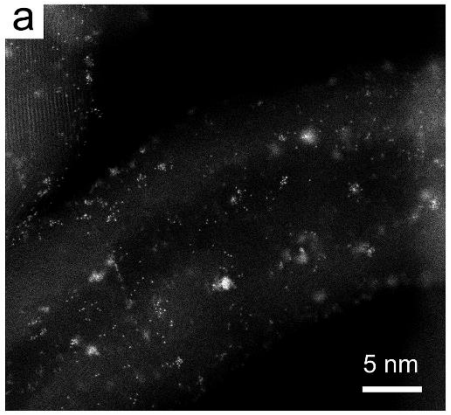
上海同步辐射光源
Shanghai Synchrotron Radiation Facility

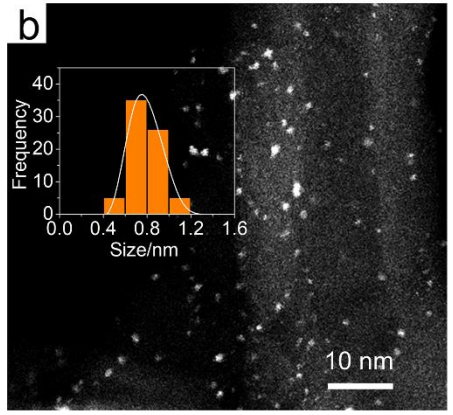
HER @ Sub-Nanometric Platinum

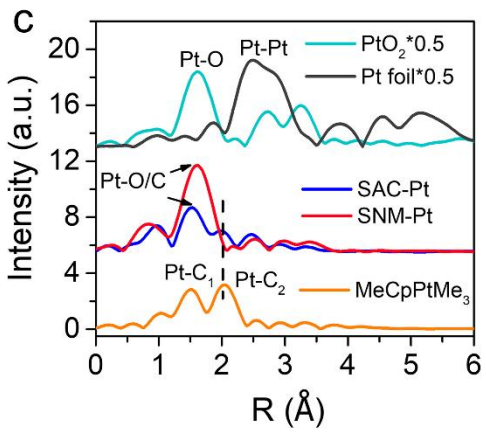


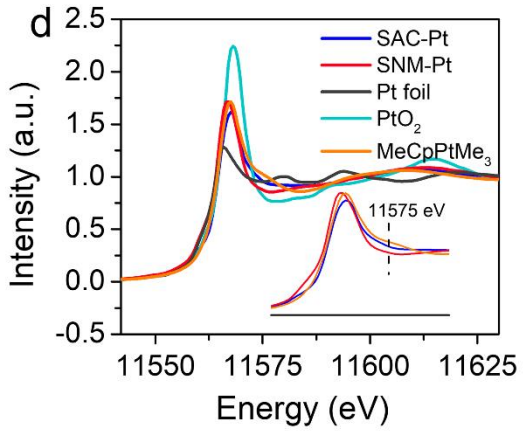
Hao Zhang

Characterization PtO_x

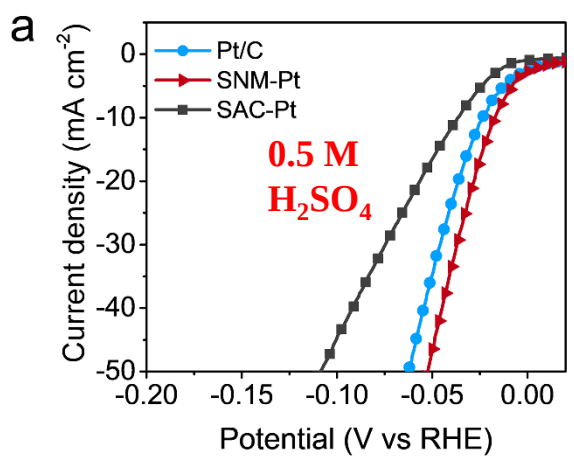


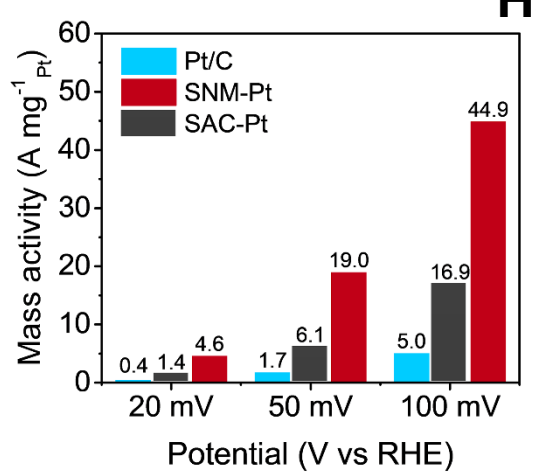






Performance >commercial Pt/C

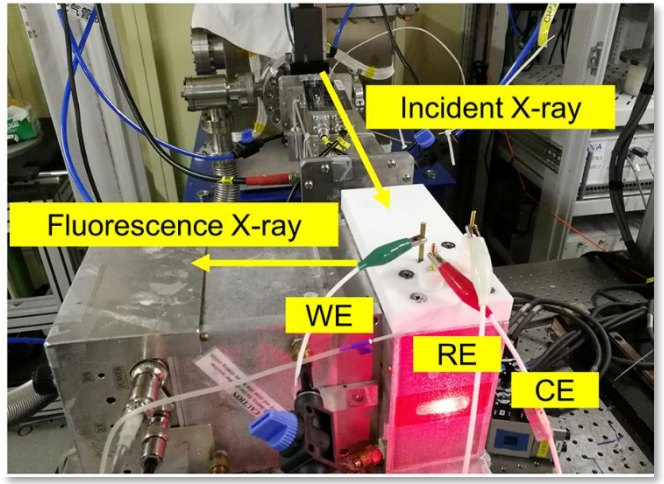


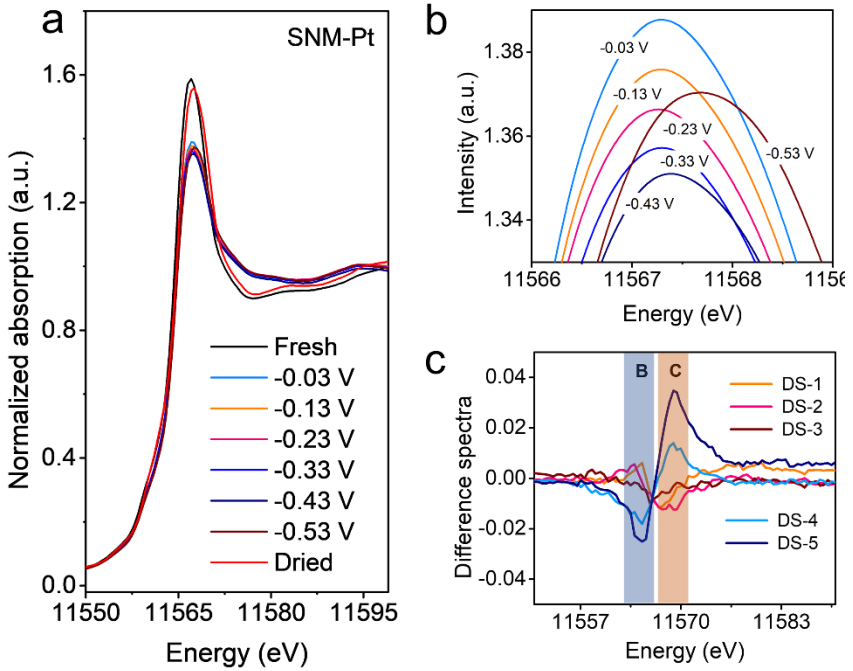


- Only 18 mV overpotential at 10 mA/cm^2 (23mV for commercial Pt/C)
- high mass activity (19 A/mg Pt *vs* 1.7 A/mg Pt of Pt/C at an overpotential of 50 mV)

ACS Appl. Mater. Interfaces **2021**, *13*, 47252−47261

Operando XAFS Reveals Structural Evolution

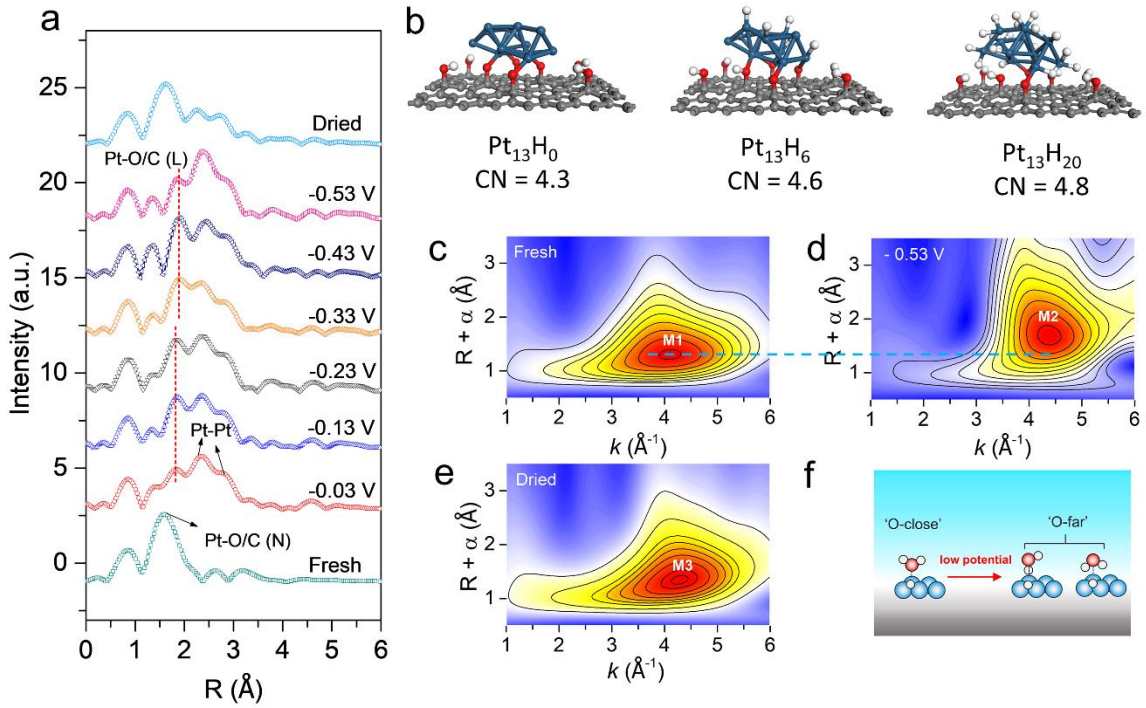


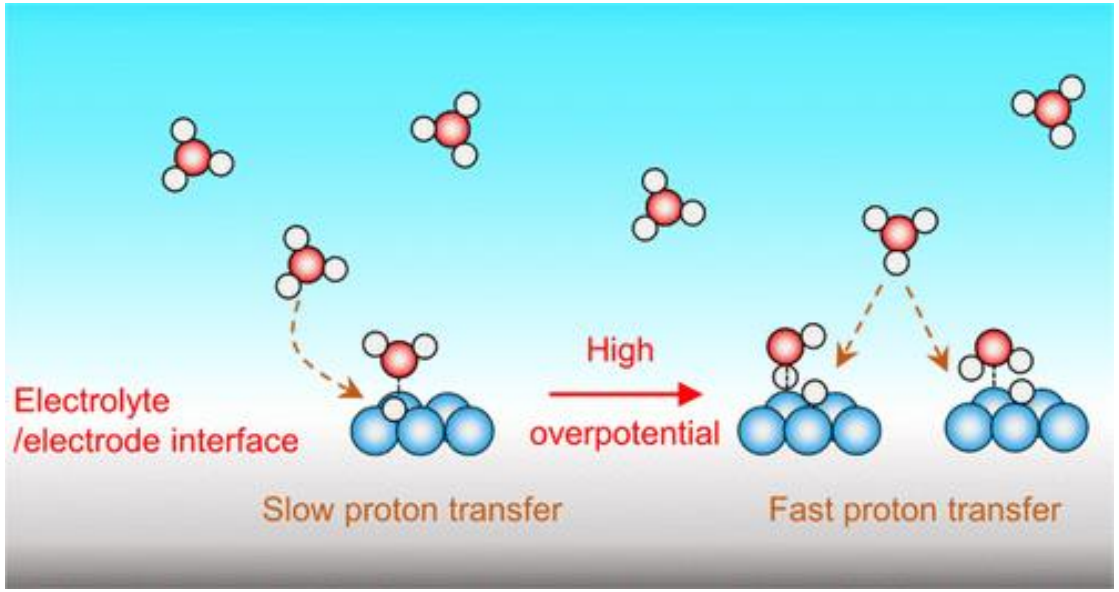


PtO_x —HER→ Pt clusters —Re-oxidation→ PtO_x

- In high potential region, the white-line intensity decreasing→**Pt-C/O bond breaking**
- In low potential region, the white-line intensity increasing→**increase in hydrogen coverage on the Pt surface**

Structure-performance Relationship





The simultaneous increases in Pt−O (L) radial distance and hydrogen coverage at the SNM-Pt/electrolyte interface are closely correlated, which implies that more flexible interfacial water more efficiently transfers the proton through the EDL interface and leads to a faster reaction rate for HER.

XANES —— spatial configuration

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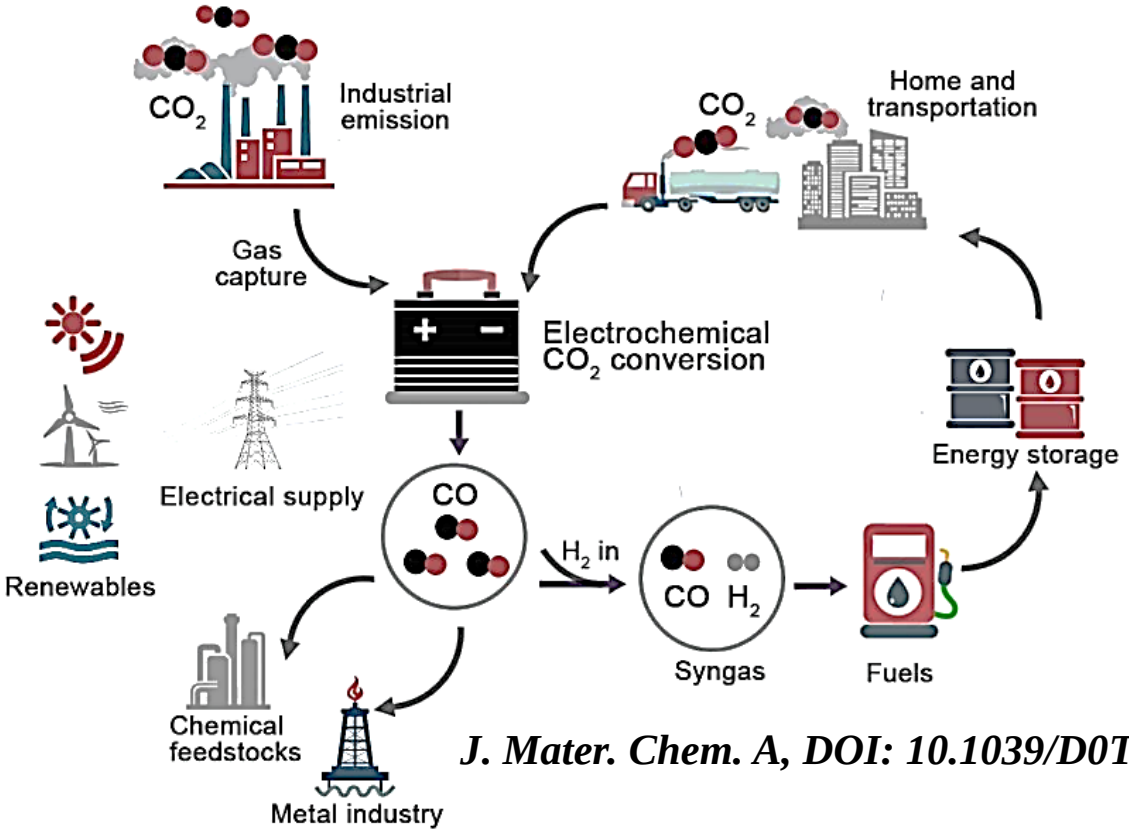
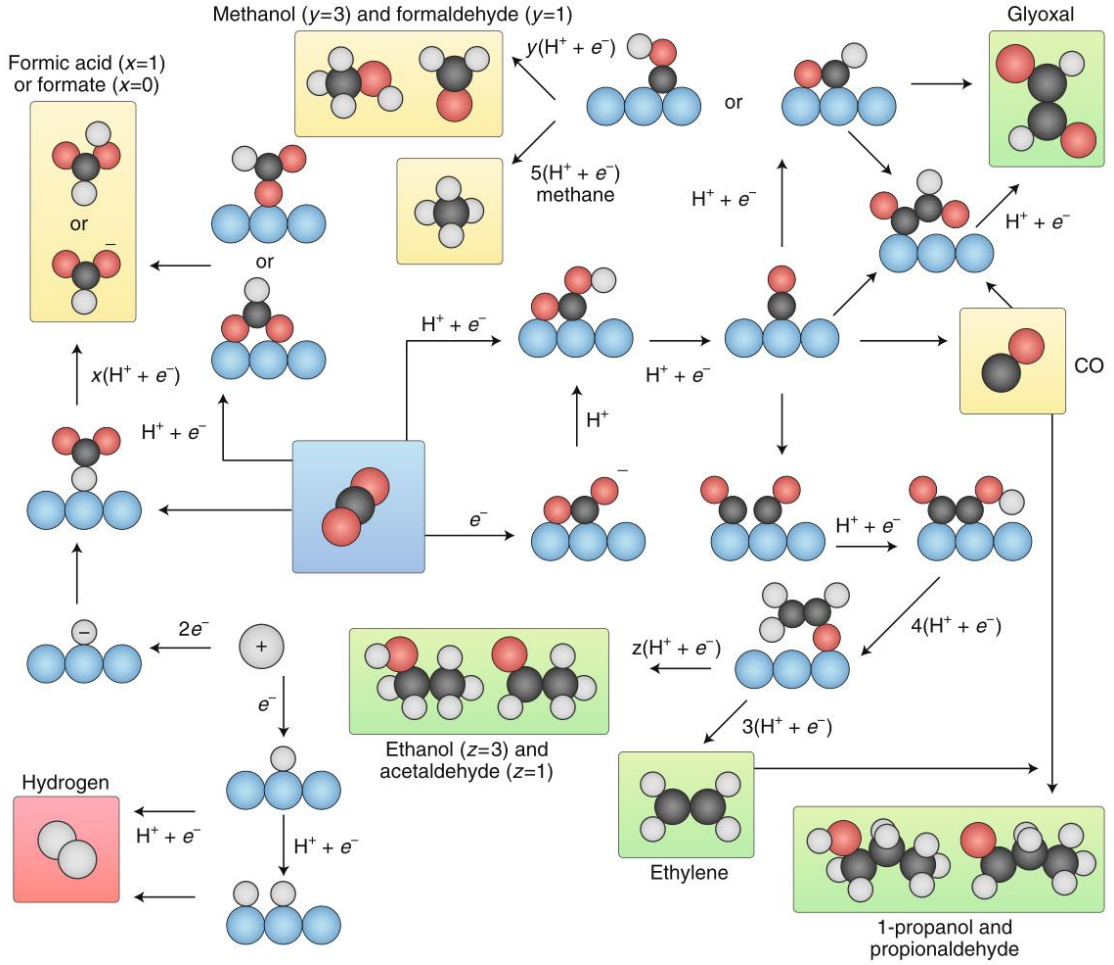
CO_2 Reduction Reaction (CO_2RR)

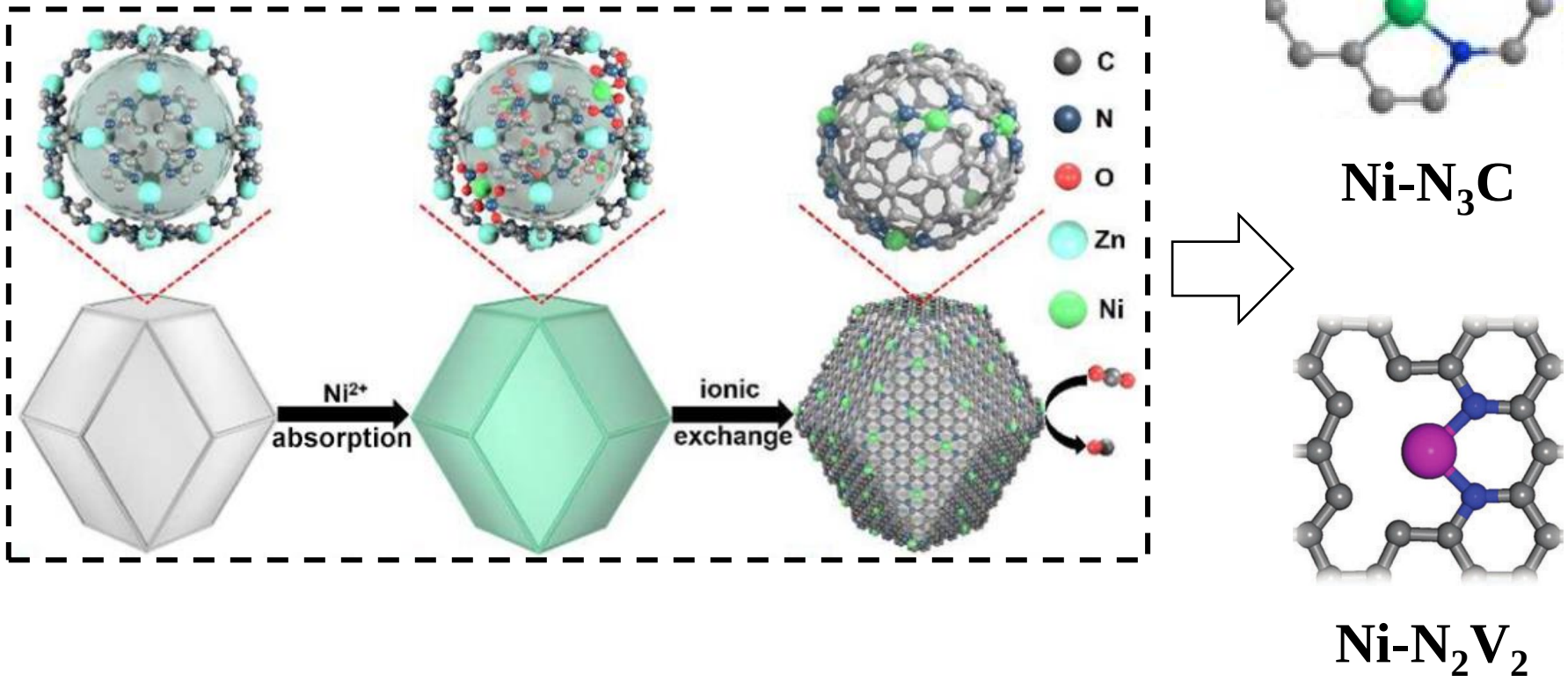
- Peaking carbon dioxide emissions before 2030
- Achieving carbon neutrality before 2060



J. Mater. Chem. A, DOI: 10.1039/D0TA03525D



Synthesis of Ni SAC based on ZIF-8



Although the same synthesis method was performed, different atomic structures was obtained. The coordination environment of ZIF-8 Ni SACs has not been determined.

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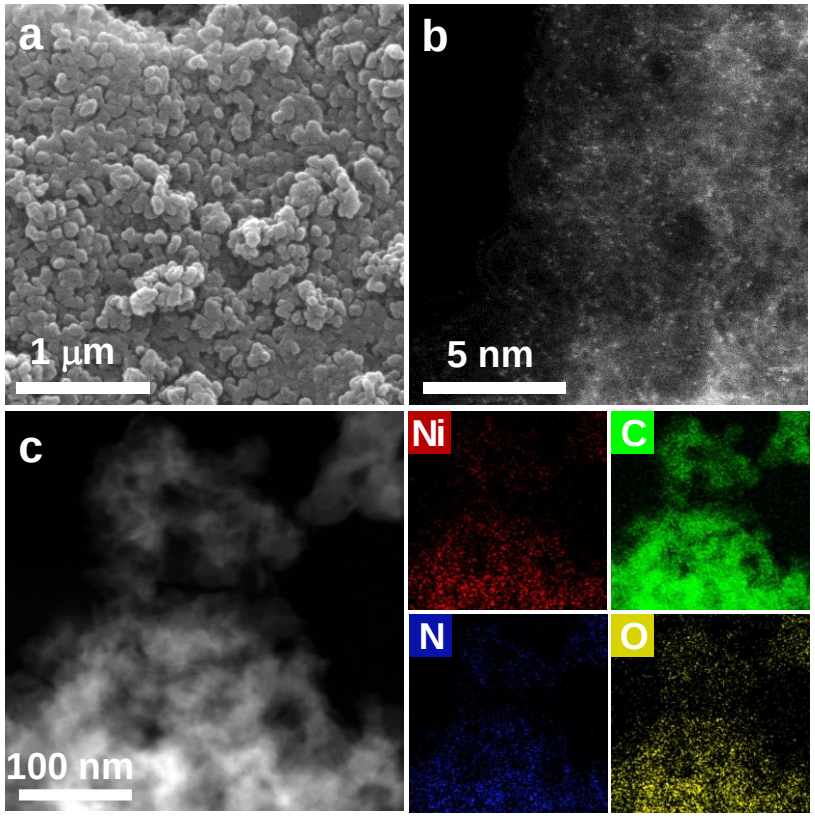
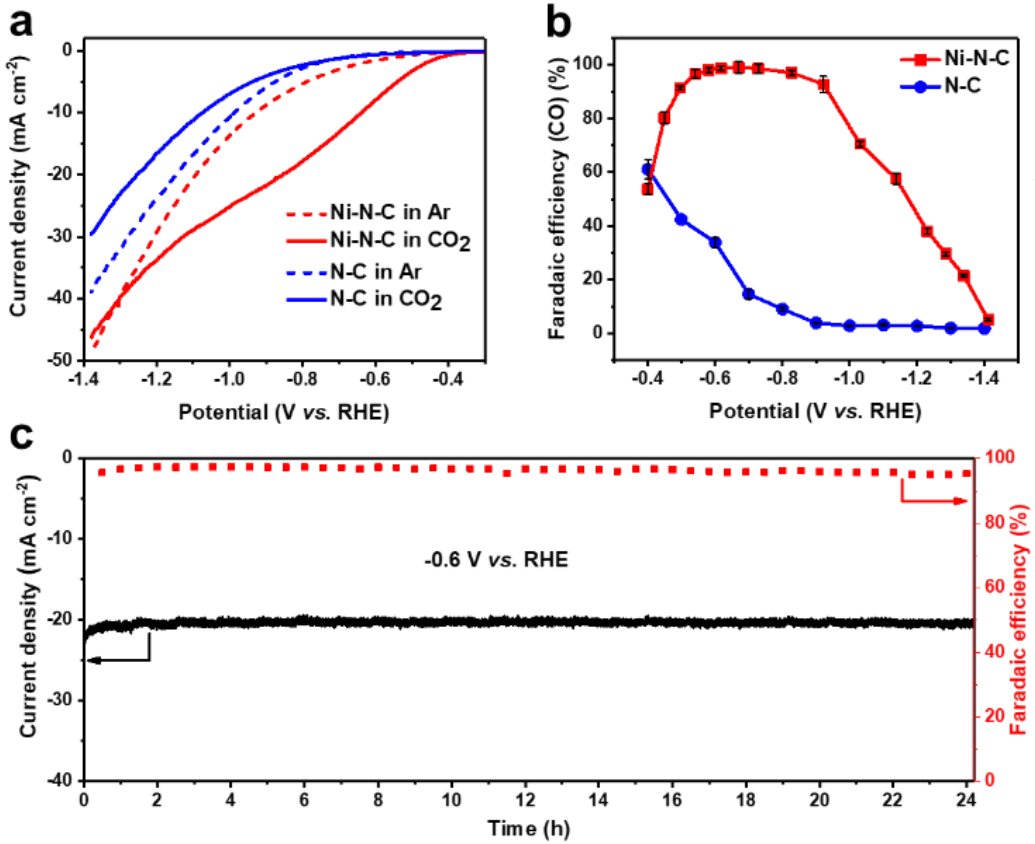
CO_2RR based on Ni SAC





Potential-dependent Volcanic Selectivity

The production of CO became predominant in the range of **−0.5 to −0.9 V**. The highest CO Faradaic efficiency of **99%** was achieved at a potential of −0.67 V.

ACS Catal. 2022, **12**, 14, 8676–8686

上海同步辐射光源
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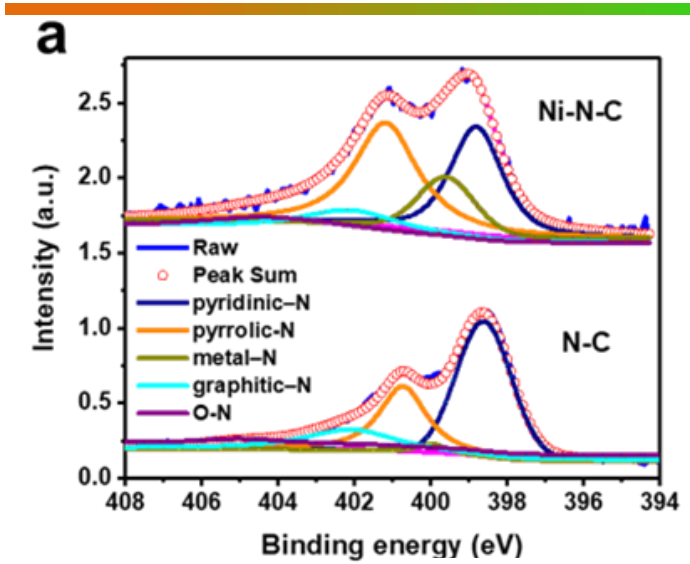
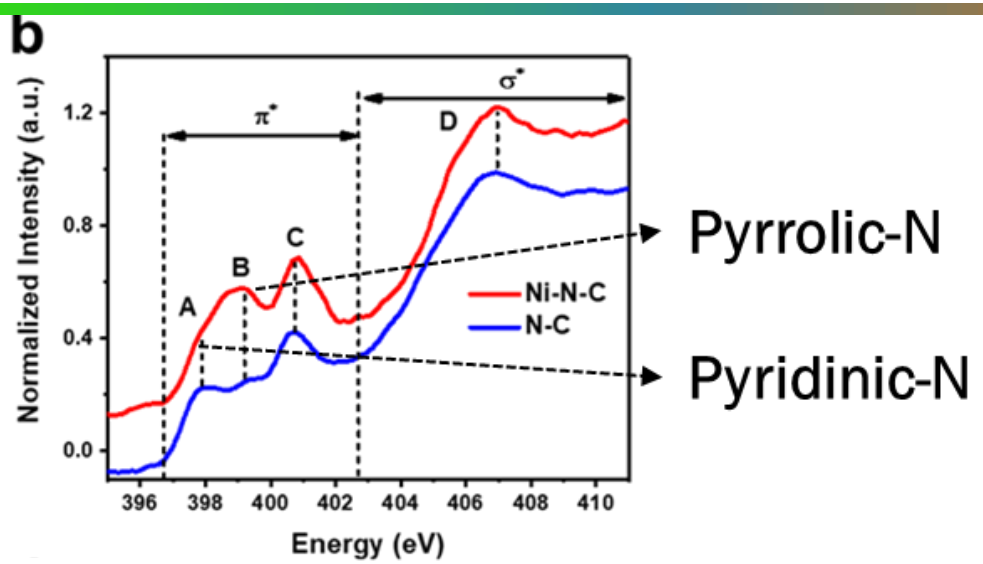
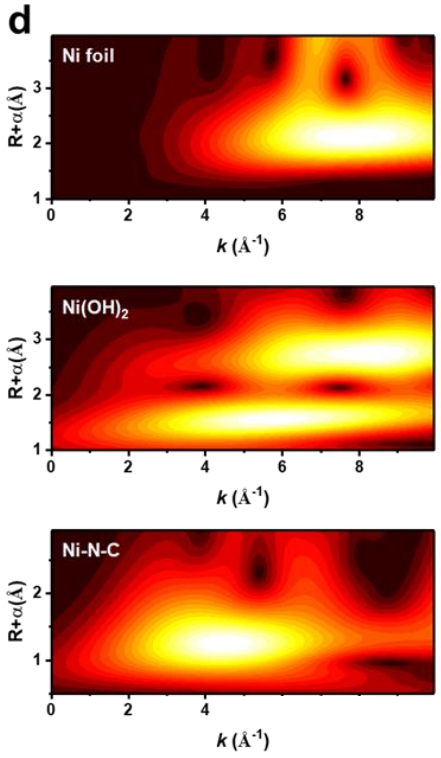
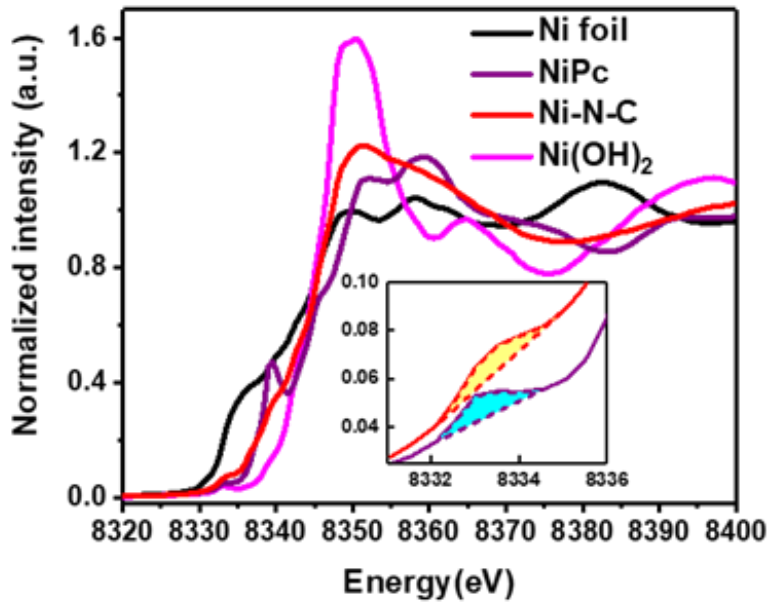
Spectroscopy methods uncover the atomic structure









The Ni species are **atomically dispersed** and mainly bonds with **pyrrole-type N species**.

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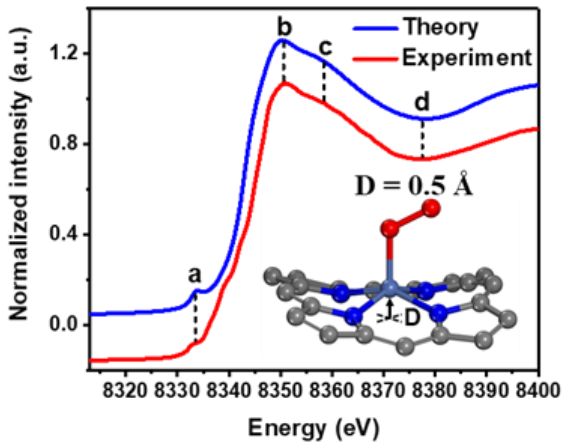
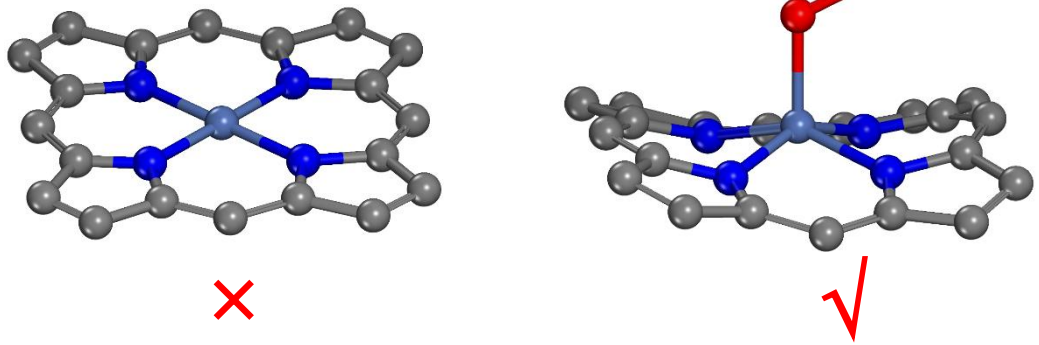
XANES simulation determines fine configuration





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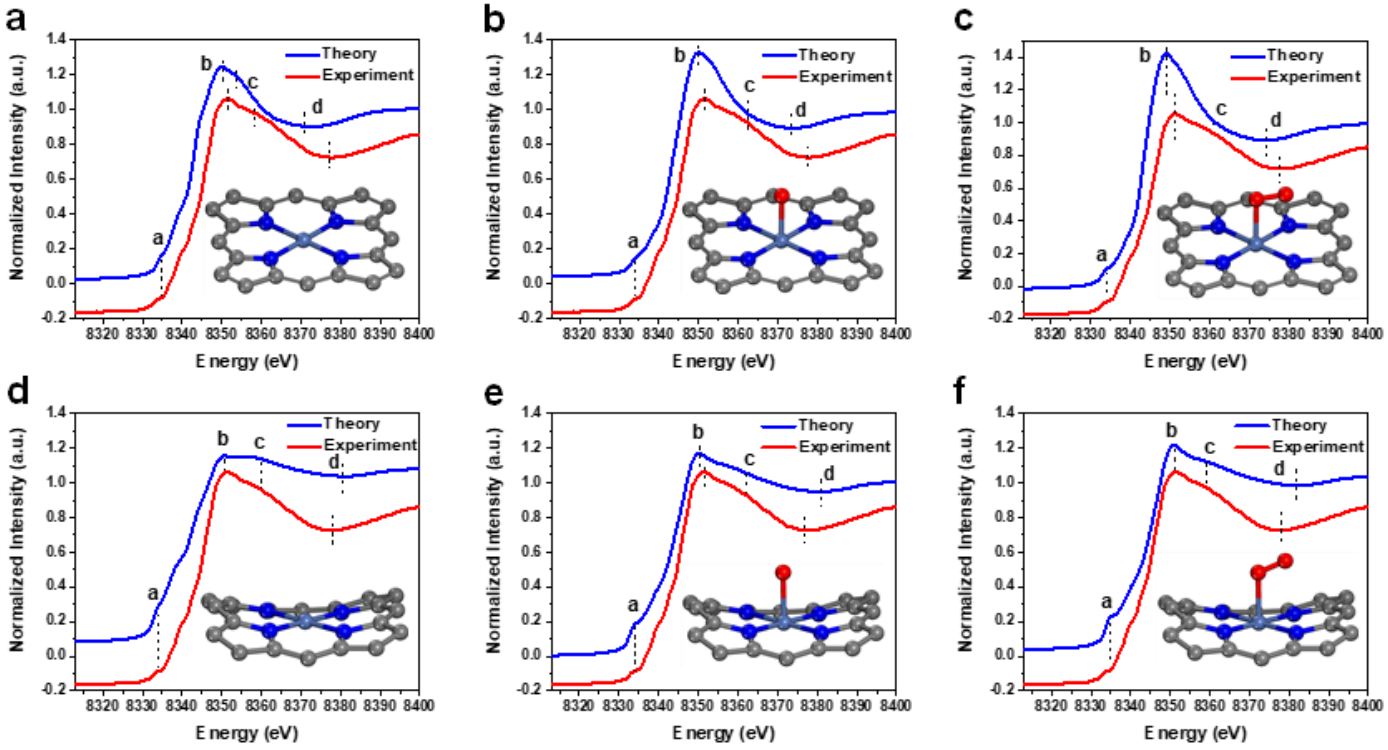

Disordered pyrrole-type Ni-N_4O_2 with the Ni center out of the N_4 plane

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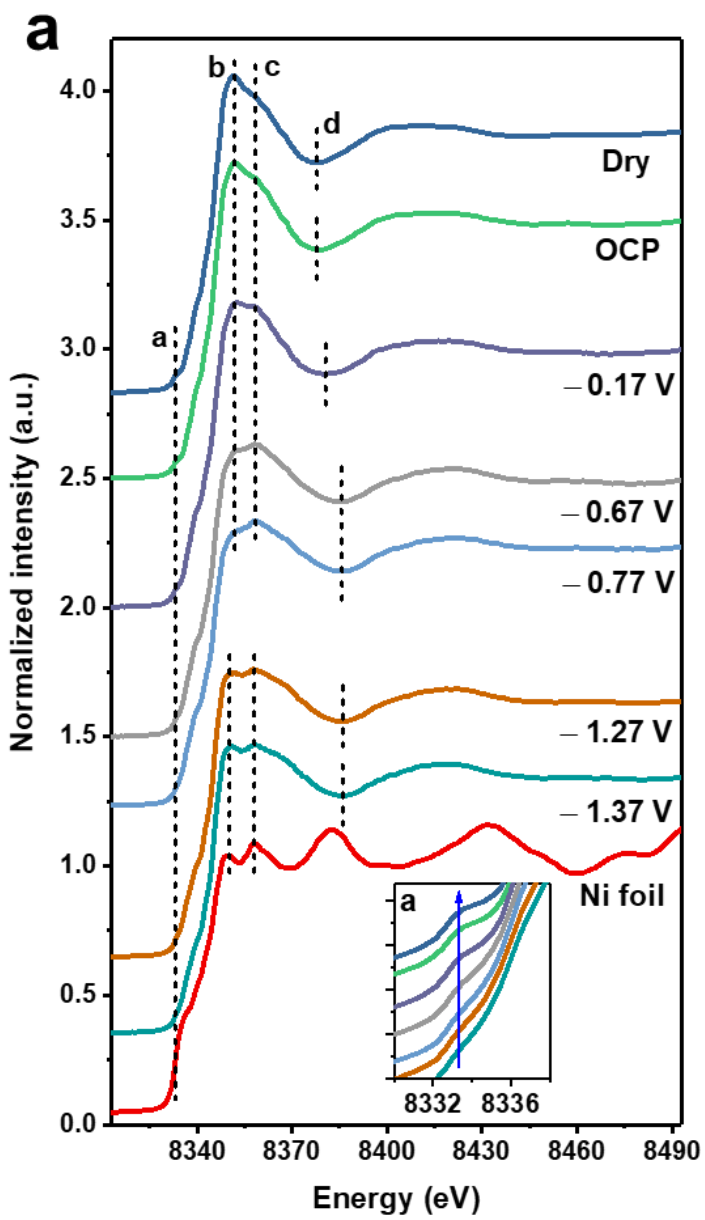
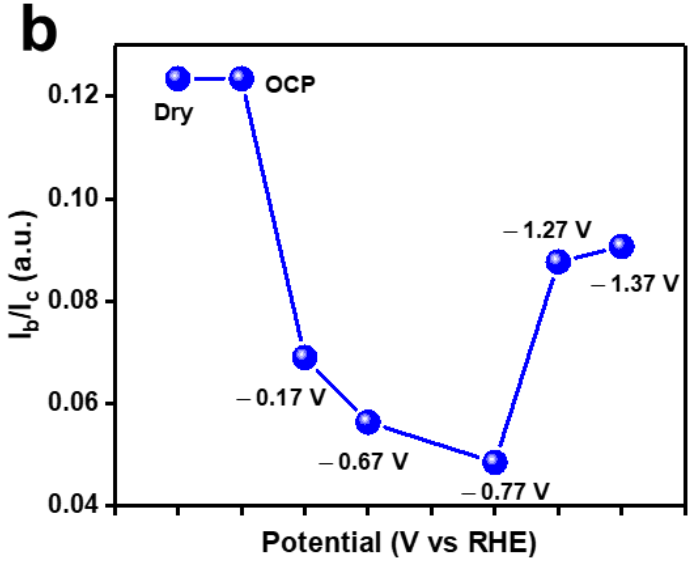
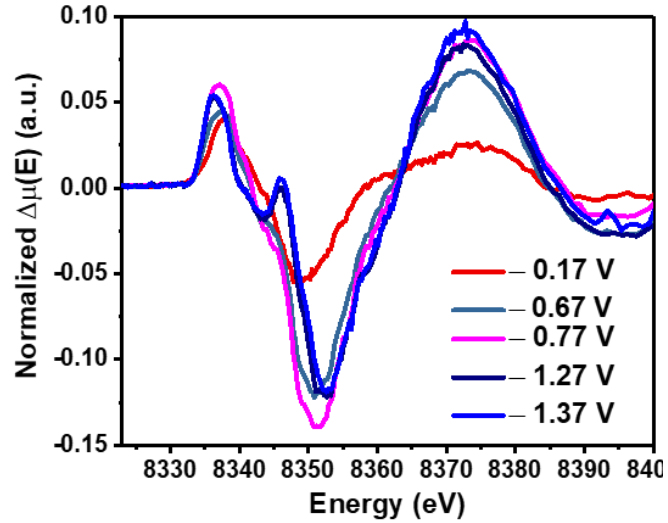
Operando XAFS analysis







The applied potential induced local structure changes.

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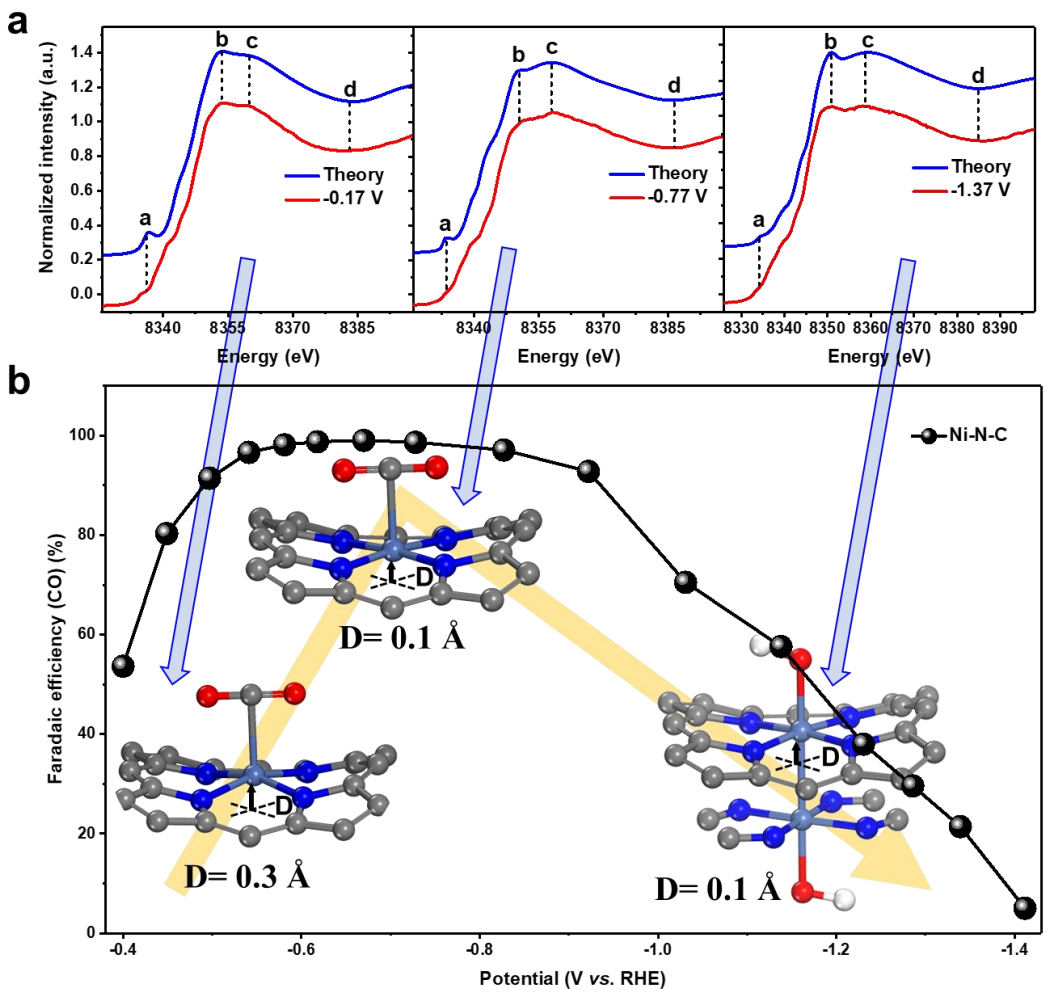
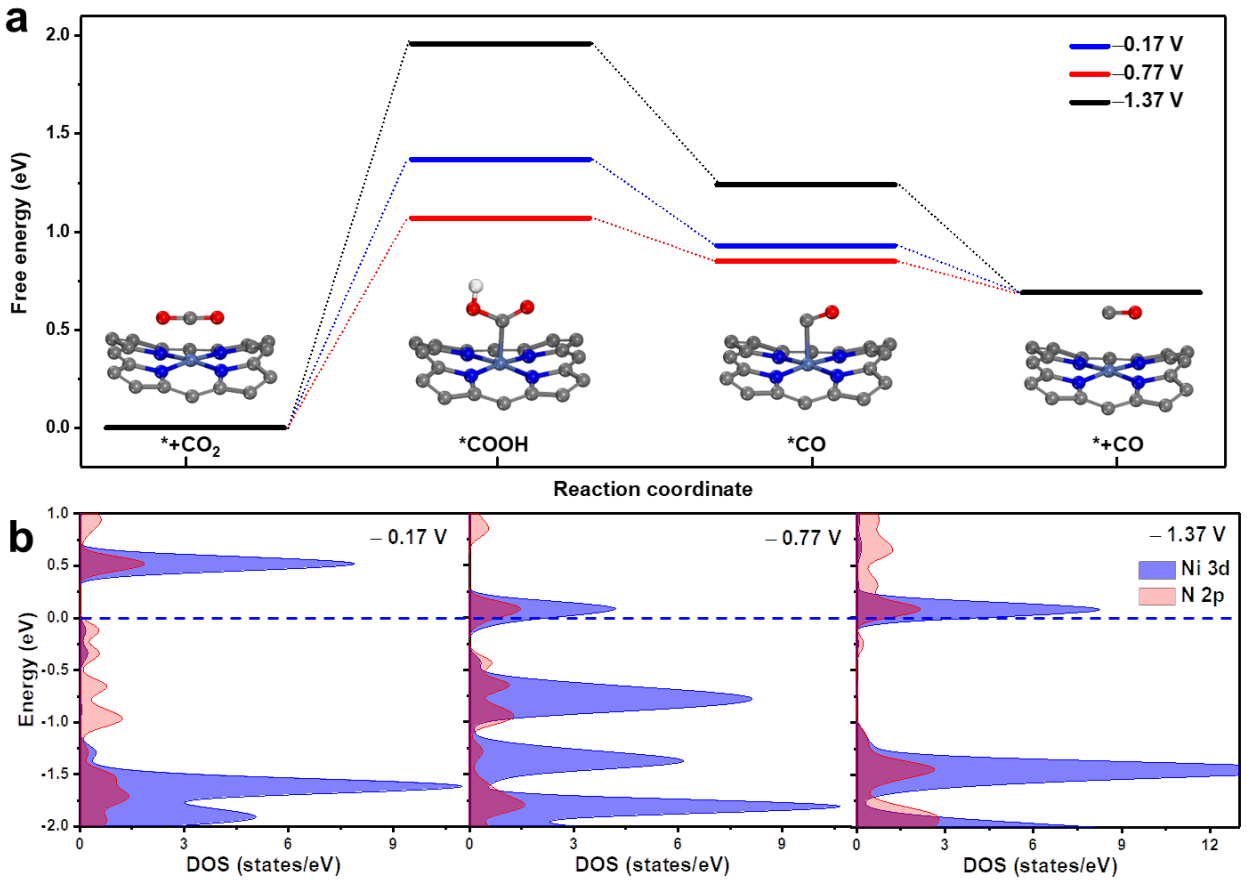
Shanghai Synchrotron Radiation Facility

XANES simulation

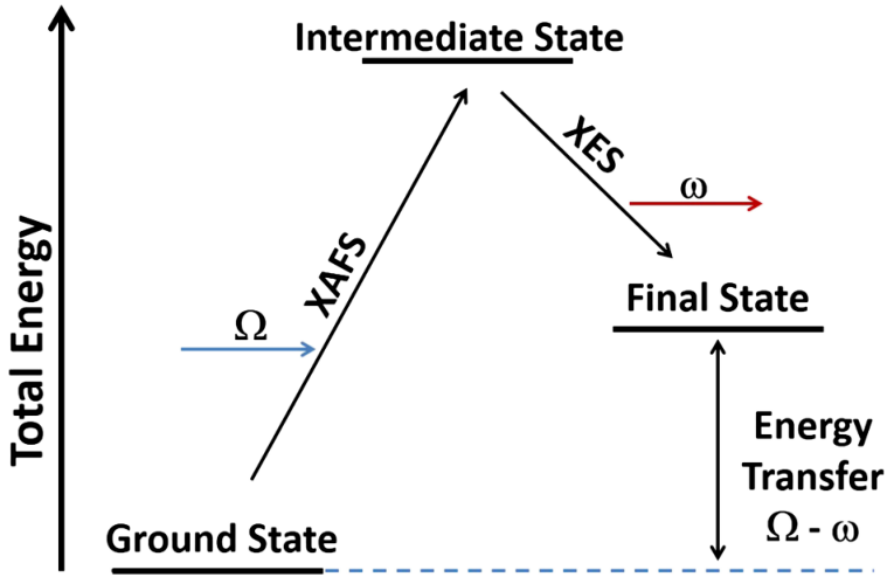


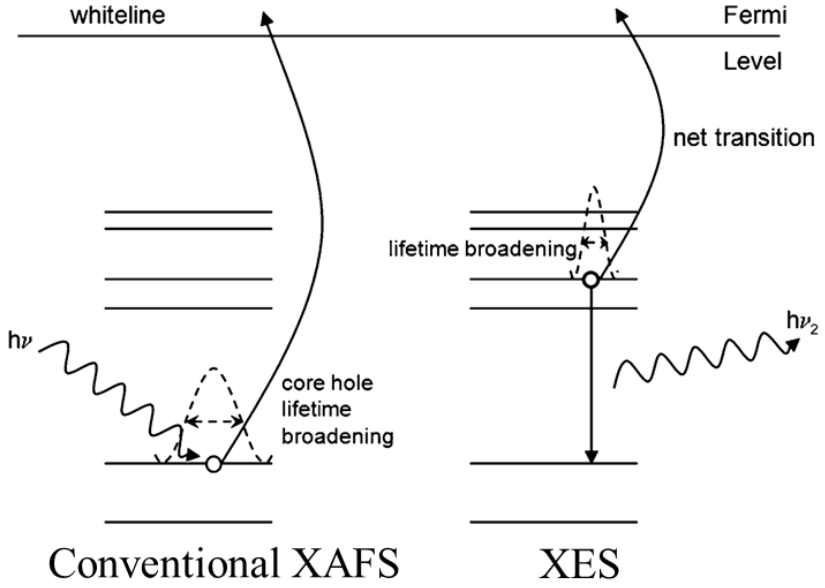


The change of the structure of the active site regulates the electronic state and thus affects **potential-dependent volcanic selectivity changes.**

High energy resolution of XES

High energy-resolution XES





The resolution of X-ray spectroscopy is related to the life broaden of the final state.

Heisenberg uncertainty

$$\Delta E = \hbar / t$$

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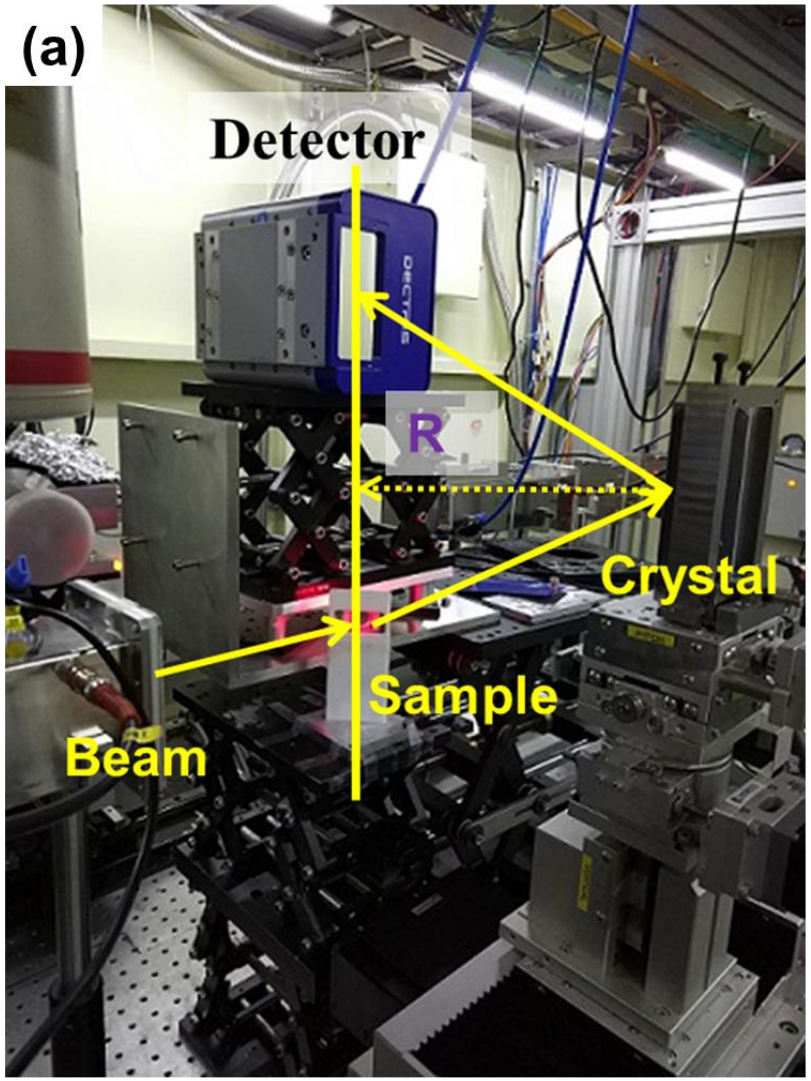
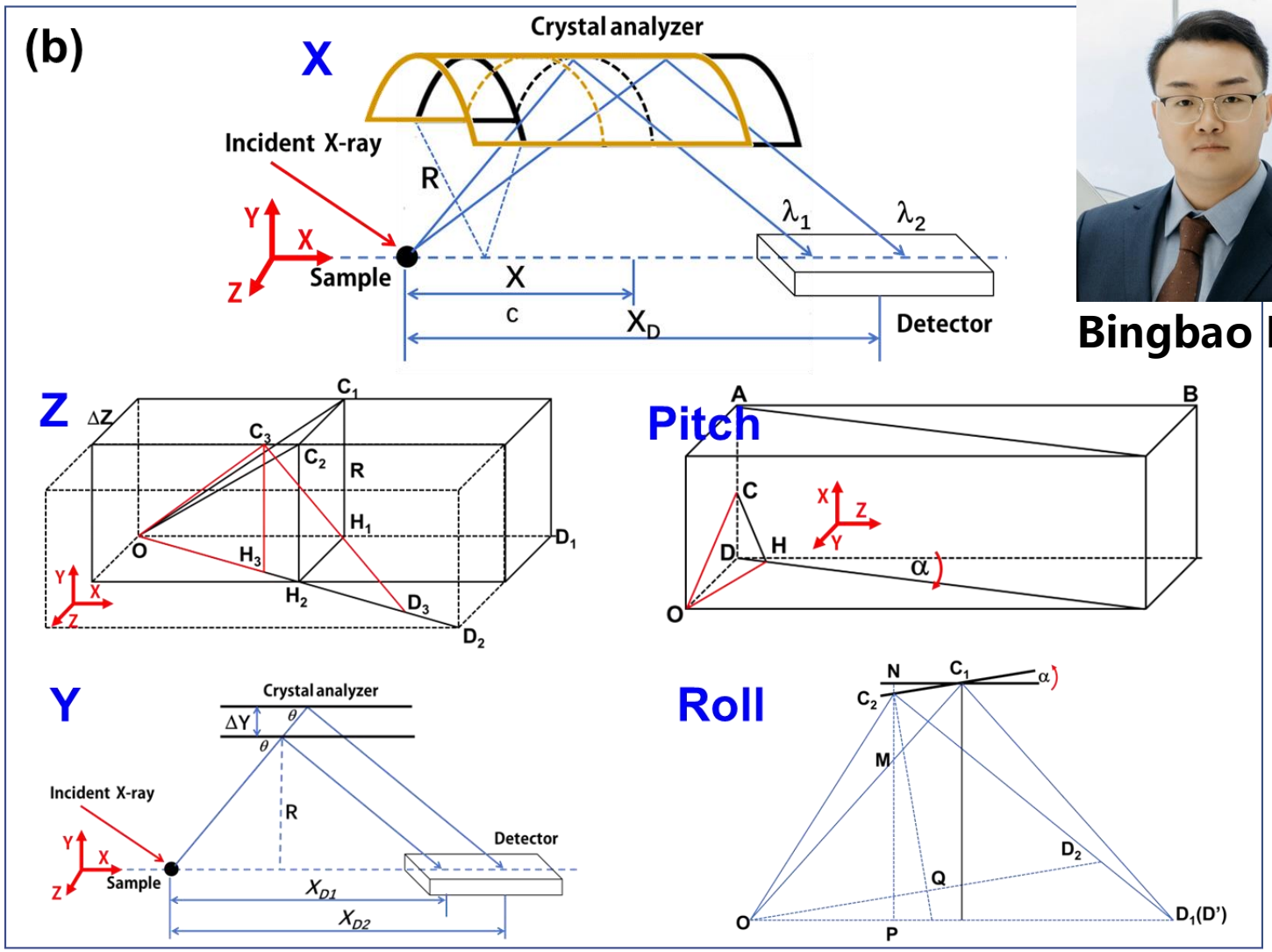
High Energy Resolution X-ray Spectroscopy





Bingbao Mei

Von Hamos spectrometer

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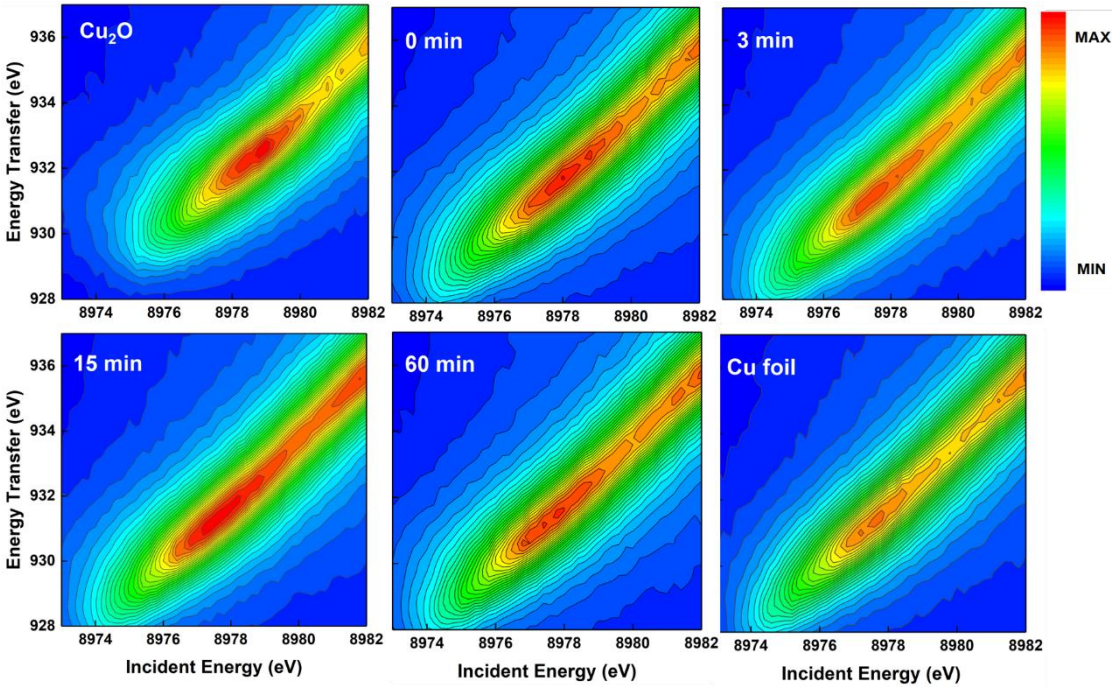
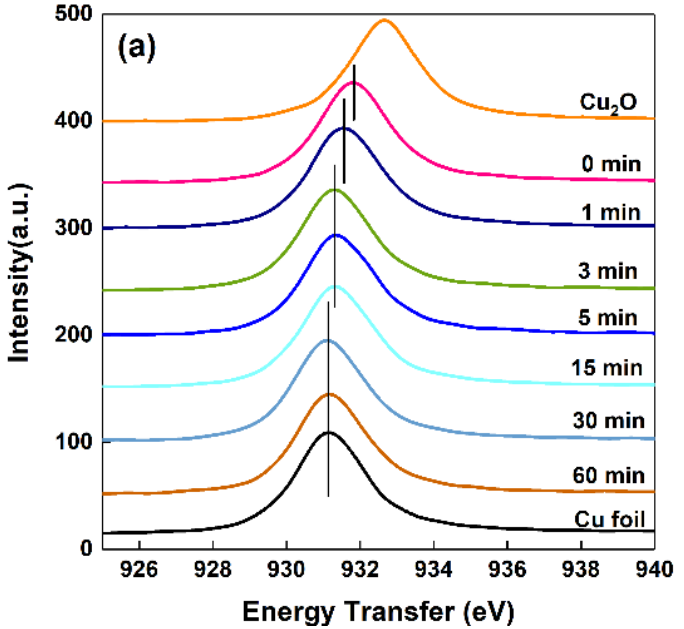
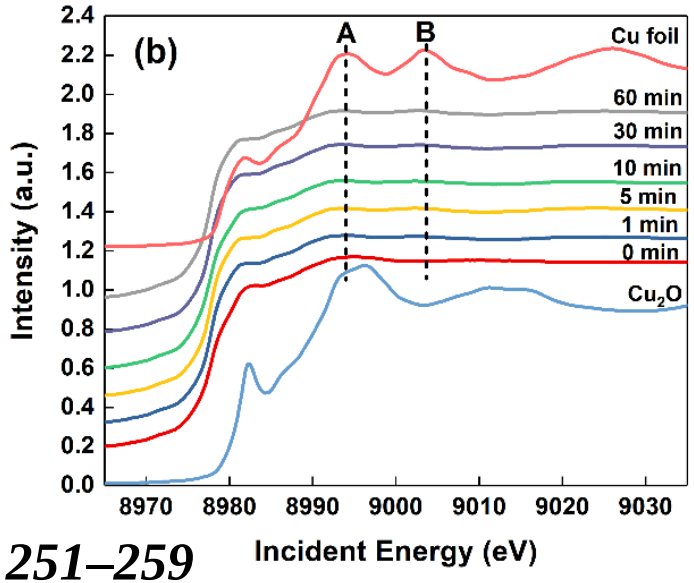
Operando XES analysis of Cu_2O/Cu film



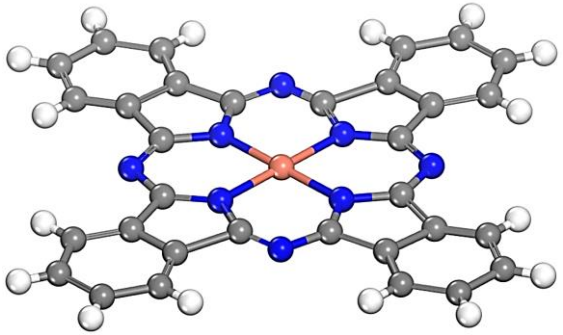




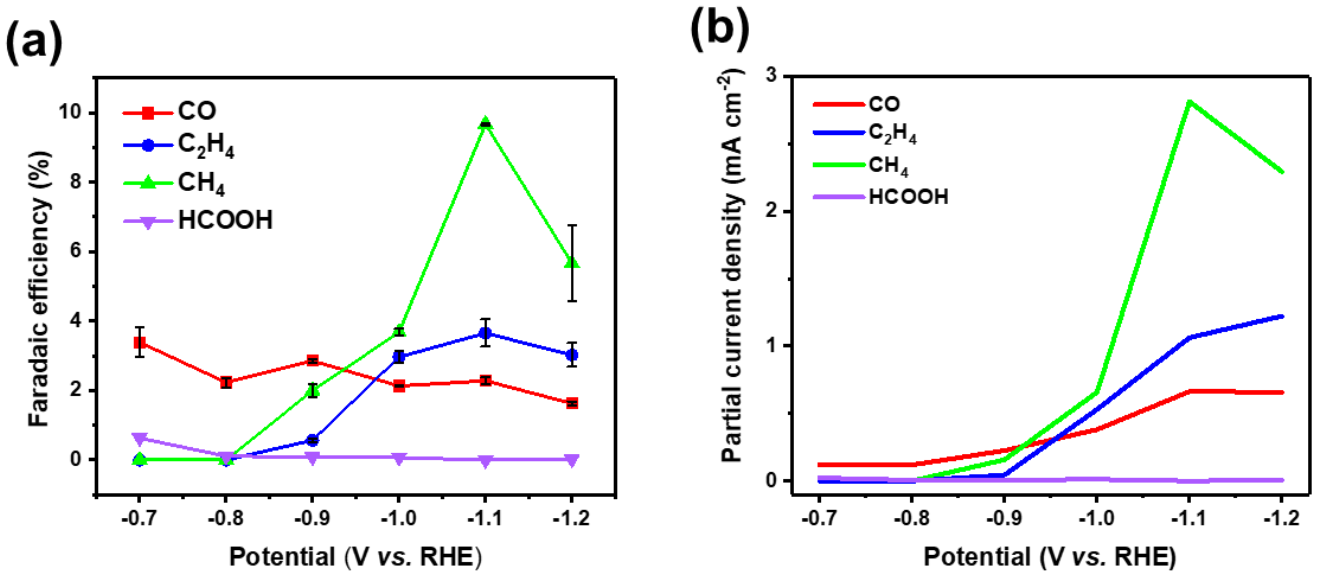
It is challenging to gain further information about the structure and chemical state of these thick samples based only on XAFS due to the strong **self-absorption affect**.

Bingbao Mei, Zheng Jiang, et al. X-Ray Spectrometry. 2019, 49, 251–259*

CuPc model catalyst for CO_2RR

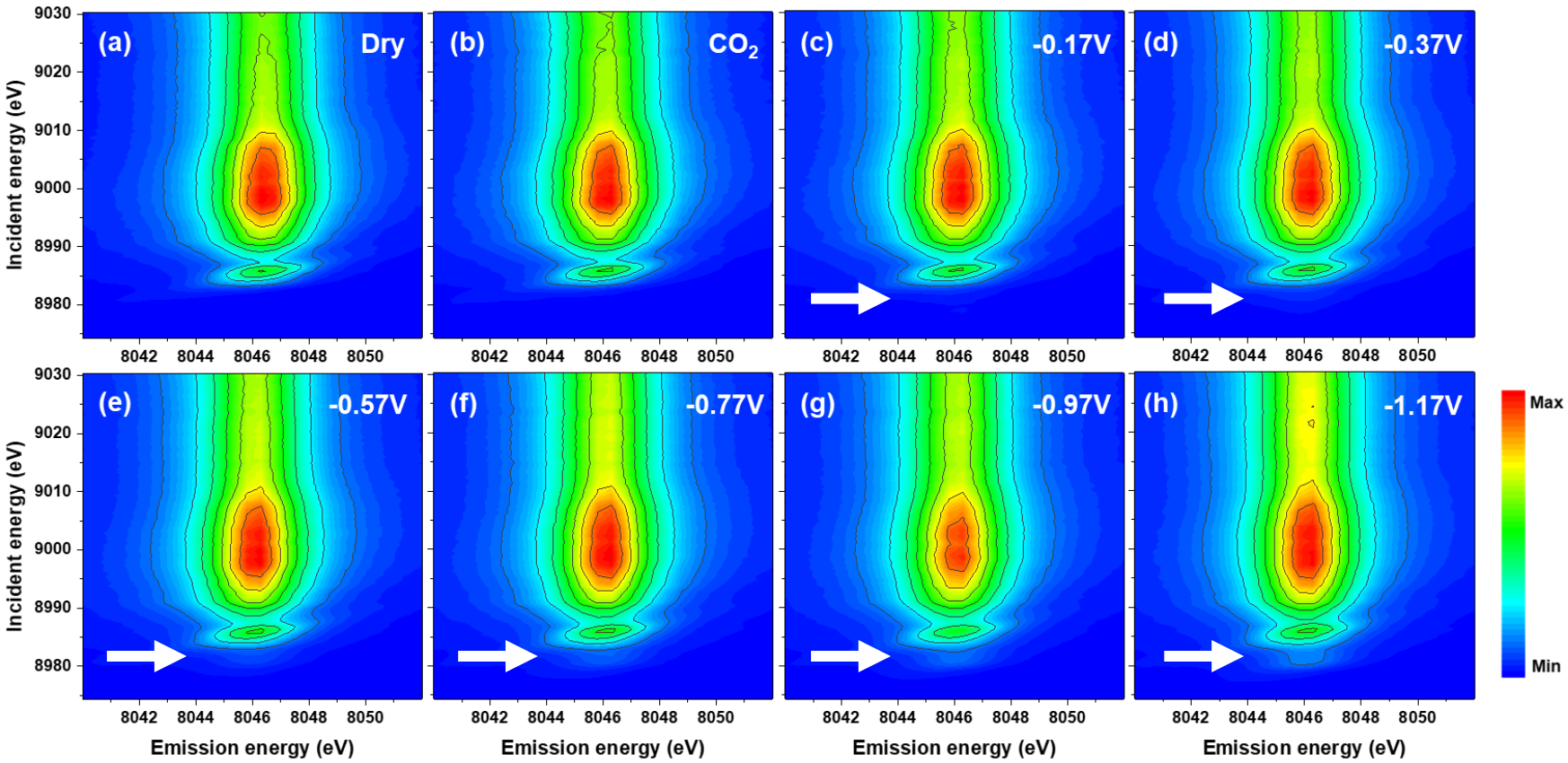


- Defined atomic configuration of CuN_4C_8
- Guiding the study of SACs



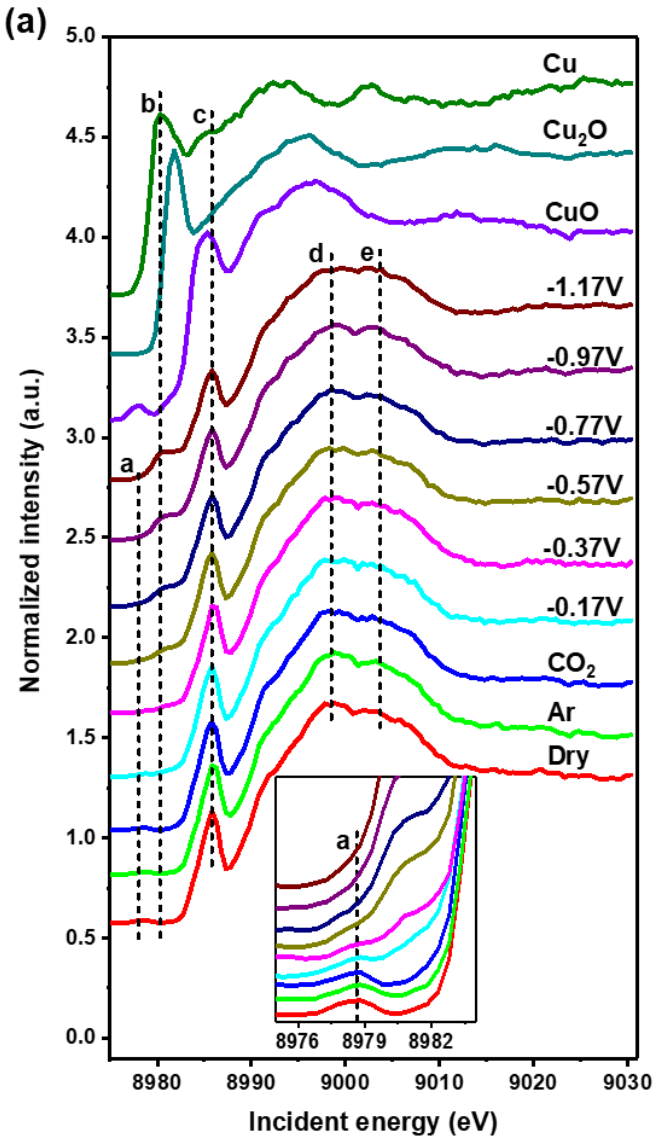
Journal of Energy Chemistry, 64 (2022) 1–7

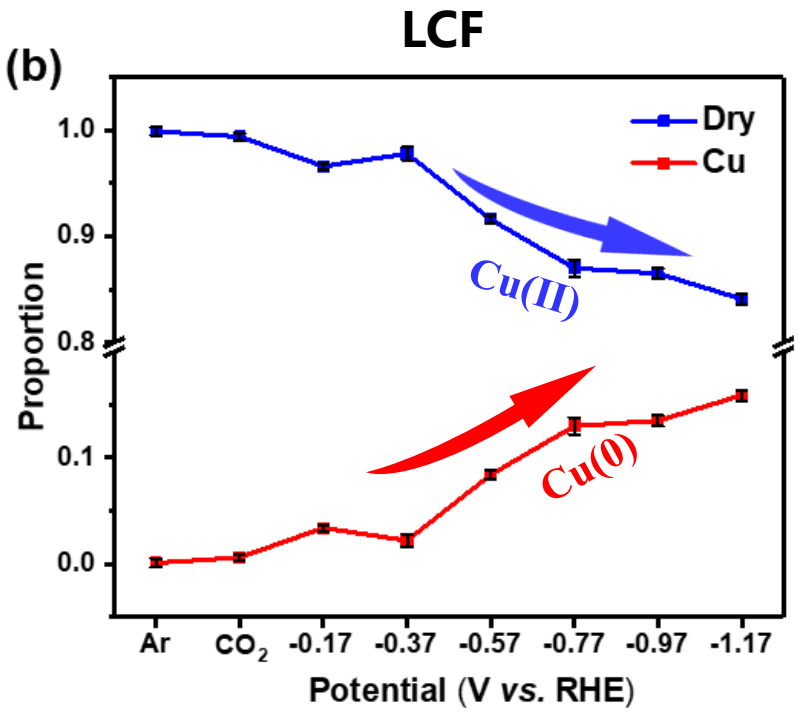
Operando XES identified the structural evolution



Gradual strengthen of contour center at 8980 eV as the potential increases indicates the formation of a novel structure.

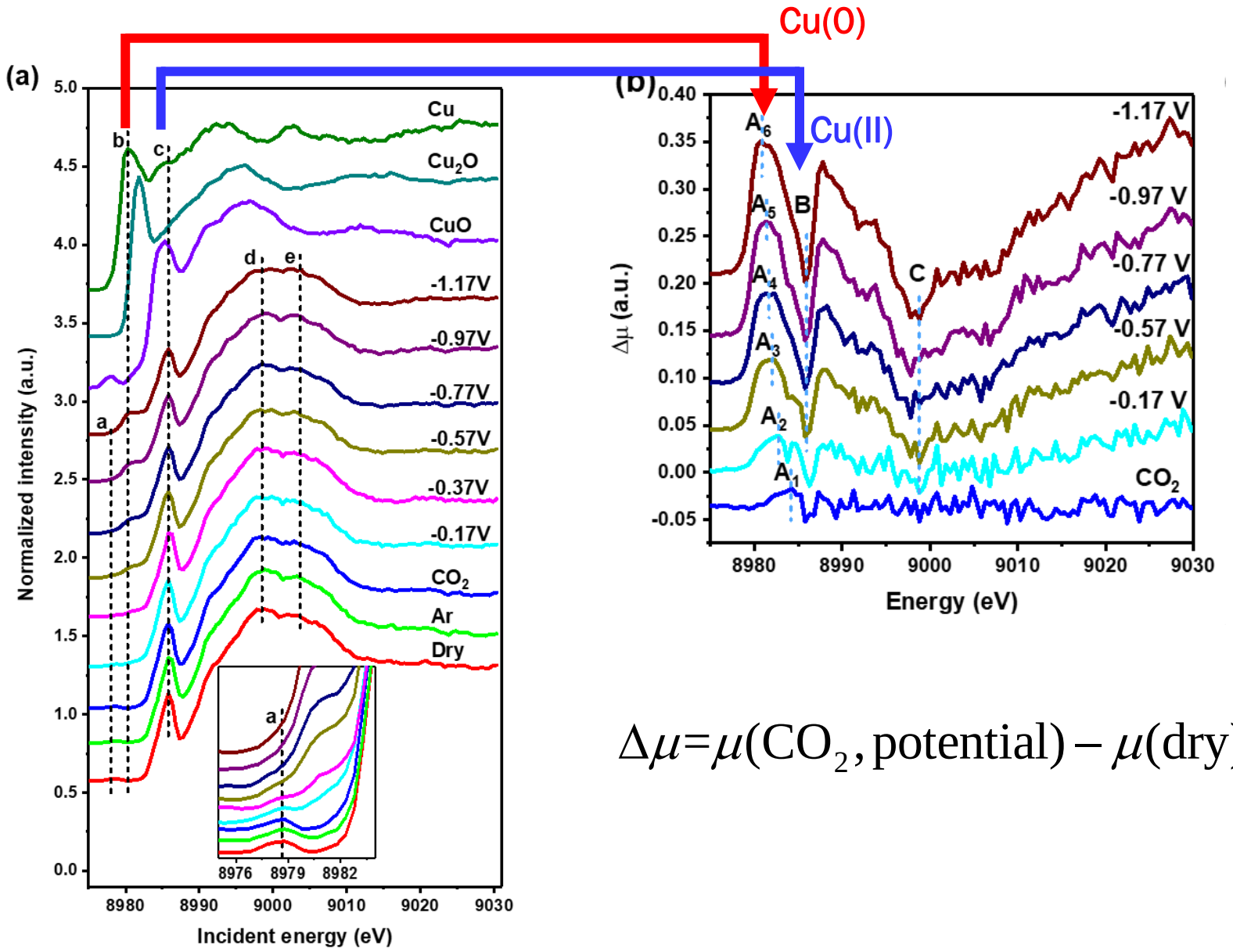
■ Peak fitting and LCF determined the component changes





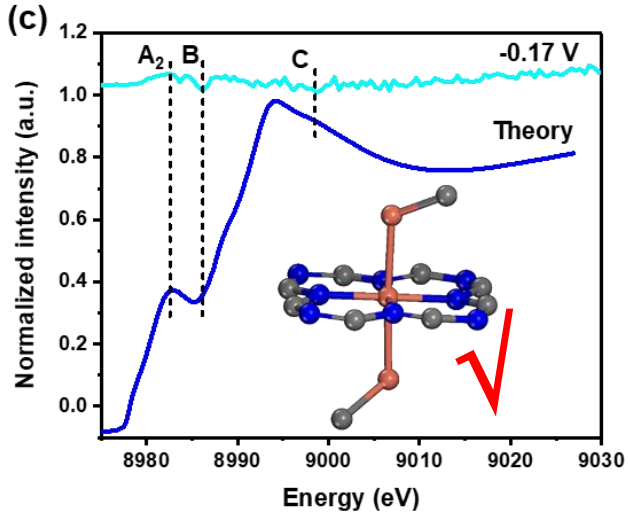
The applied potential directly induced the structural transformation of Cu(II) to Cu(0)

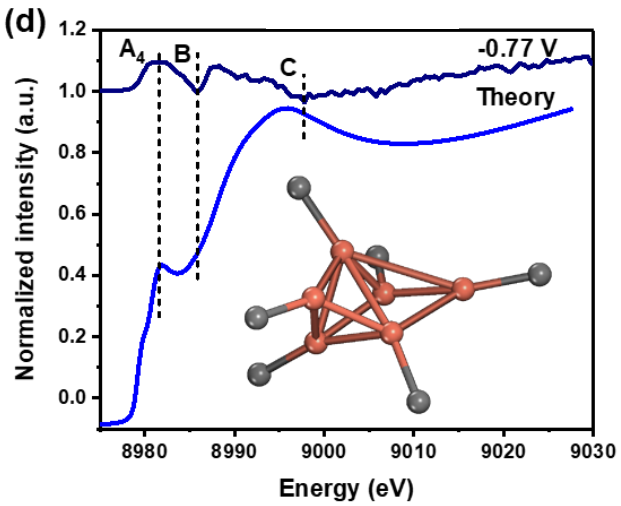
HERFD-XANES Δμ analysis

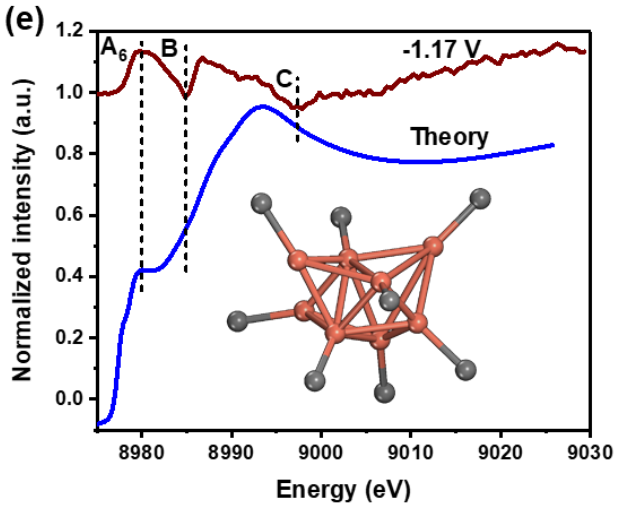


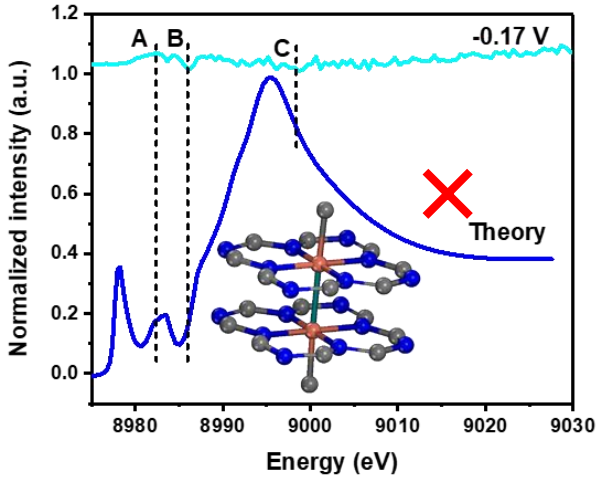
$$\Delta\mu = \mu(\mathrm{CO_2}, \mathrm{potential}) - \mu(\mathrm{dry})$$

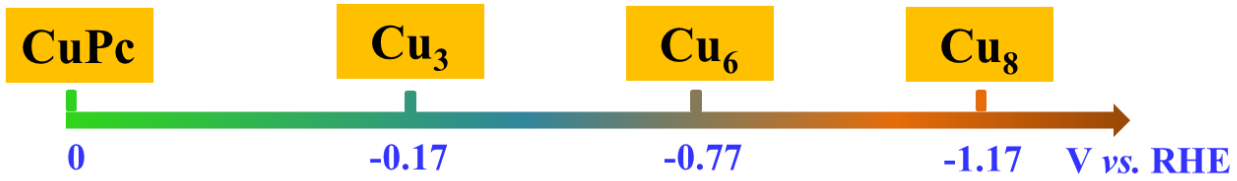
■ HERFD-XANES simulation based on Δμ











Cu clusters offer active sites for C-C coupling

上海同步辐射光源
Shanghai Synchrotron Radiation Facility

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