Revealing Surface Species on Electrochemical Cell Electrodes in Operando

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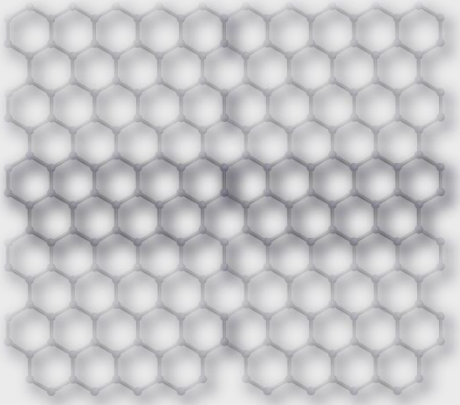
Research activities

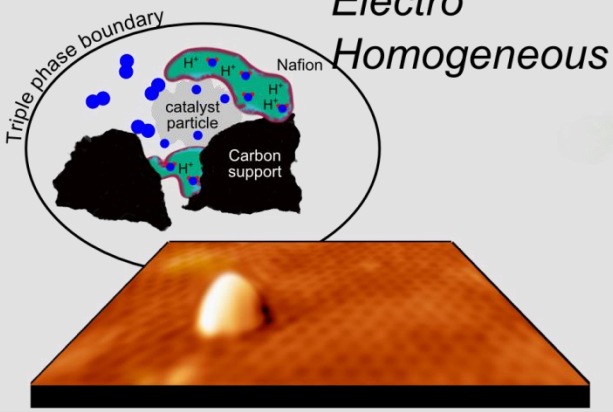
Graphene functionalization

Hydrogenation of SLG/FLG



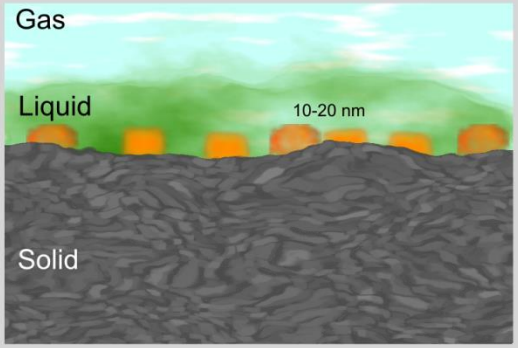
Catalysis

Heterogeneous
Electro
Homogeneous



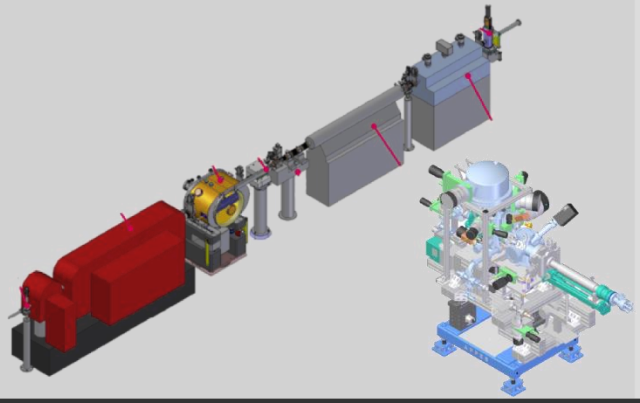
Water

Interfacial water



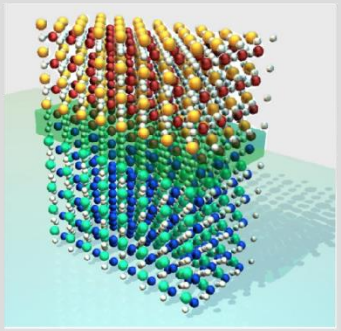
Instrumentation

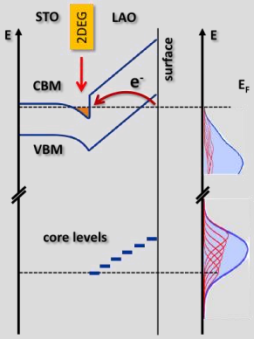
AP HAXPES / Beamline



Hetero-junctions

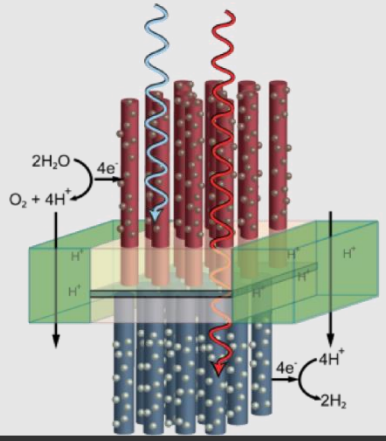
$LaAlO_3/SrTiO_3$





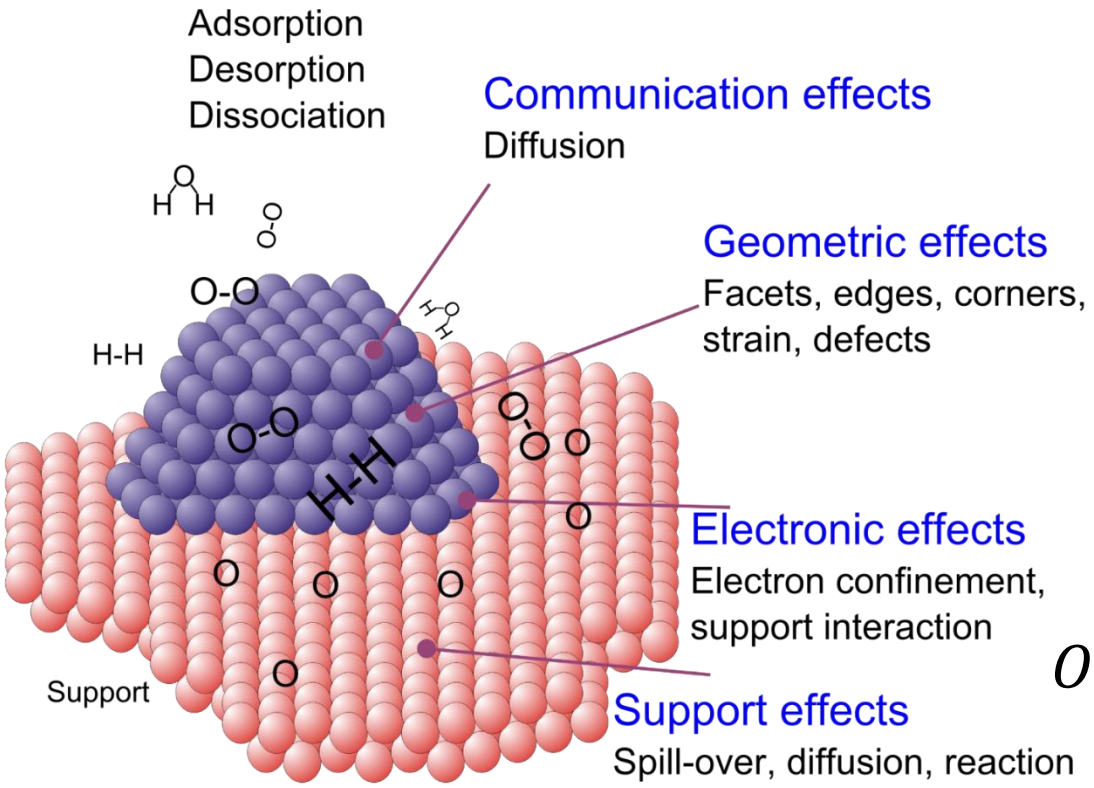
Artificial photosynthesis

Water splitting



Surface chemistry

What determines catalytic activity?



Water formation-fuel cell
Water splitting-Electrochemical
Water splitting-photoelectrochemical

$$H_2O \leftrightarrow OH* + H^+ + e^-$$
$$OH* \leftrightarrow O* + H^+ + e^-$$
$$O* + H_2O \leftrightarrow OOH* + H^+ + e^-$$
$$OOH* \leftrightarrow O_2 + H^+ + e^-$$

Understanding the fundamental principles of electrocatalysis

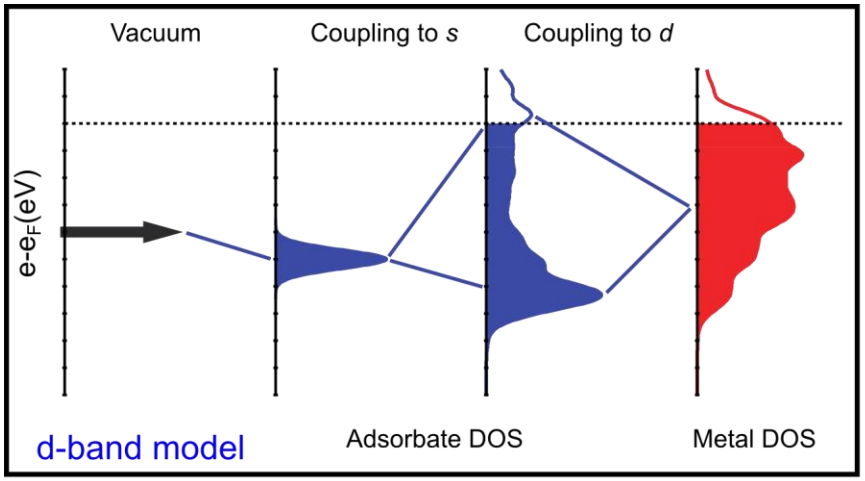
<u>Goal</u>: Understanding the fundamental principles of electrocatalysts under realistic operating conditions

Water splitting
Water formation

1.23 V (Thermodynamically)

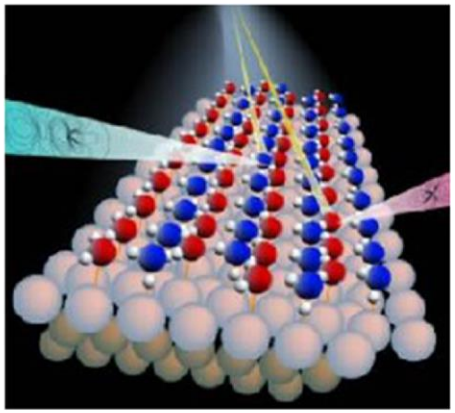
Local electronic structure

Change in local electronic structure at an atom upon adsorption on a simple metal



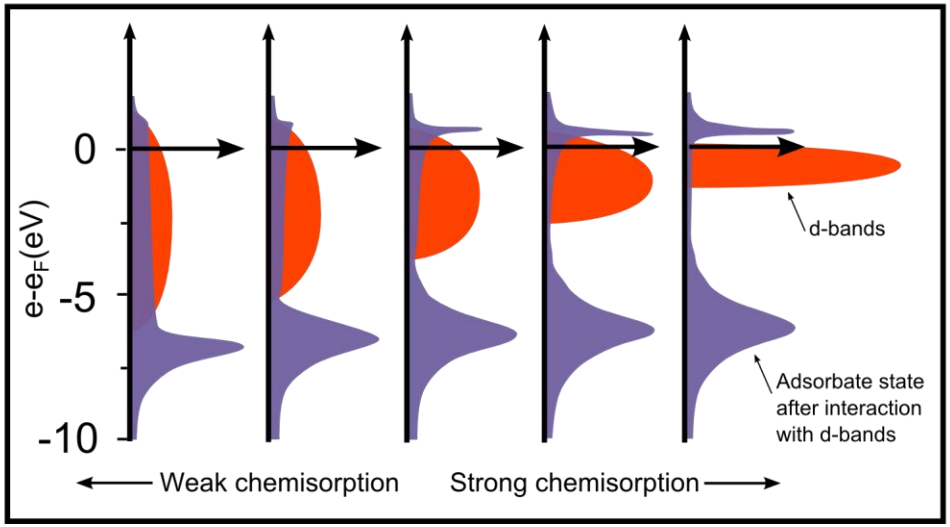
What determines the strength of the adsorbate-metal interaction?

-Physisorption
-Chemisorption
(molecular and dissociative)



Local DOS projected onto an adsorbate state interacting with the d-bands

Position of the d-band center determines the strength of the adsorbate-metal bonding



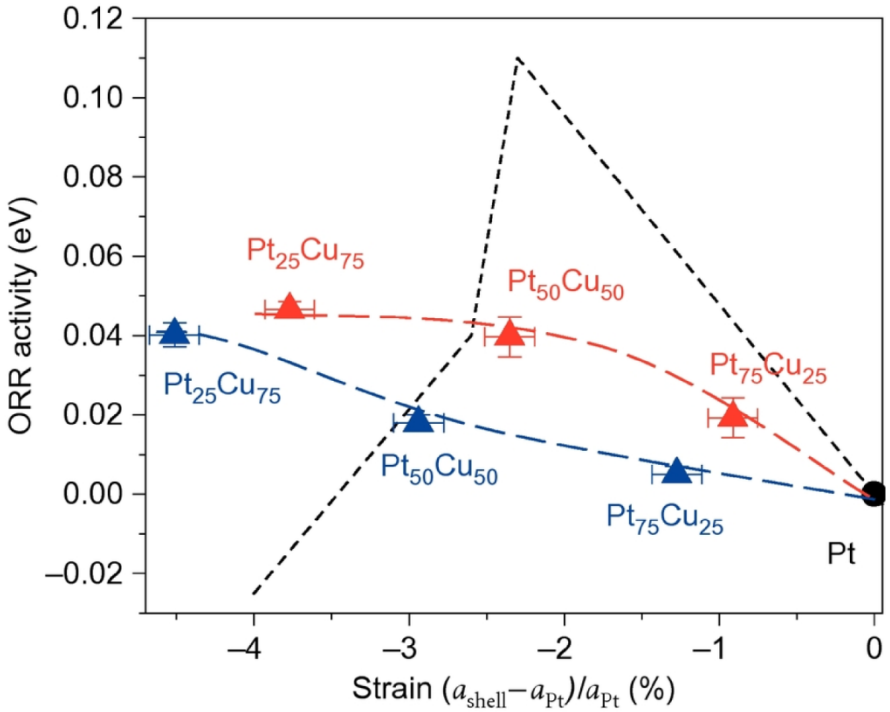
Compressive strain

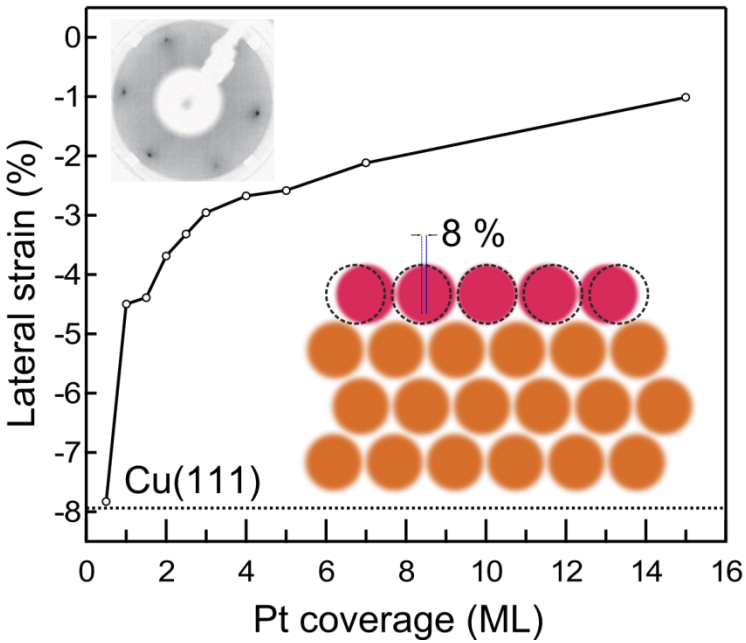
Coverage dependent compressive strain on Pt films

Experimental finding: Increase in ORR activity with strain

DFT prediction: Moderate compressive lattice strain is predicted to enhance the rate of ORR

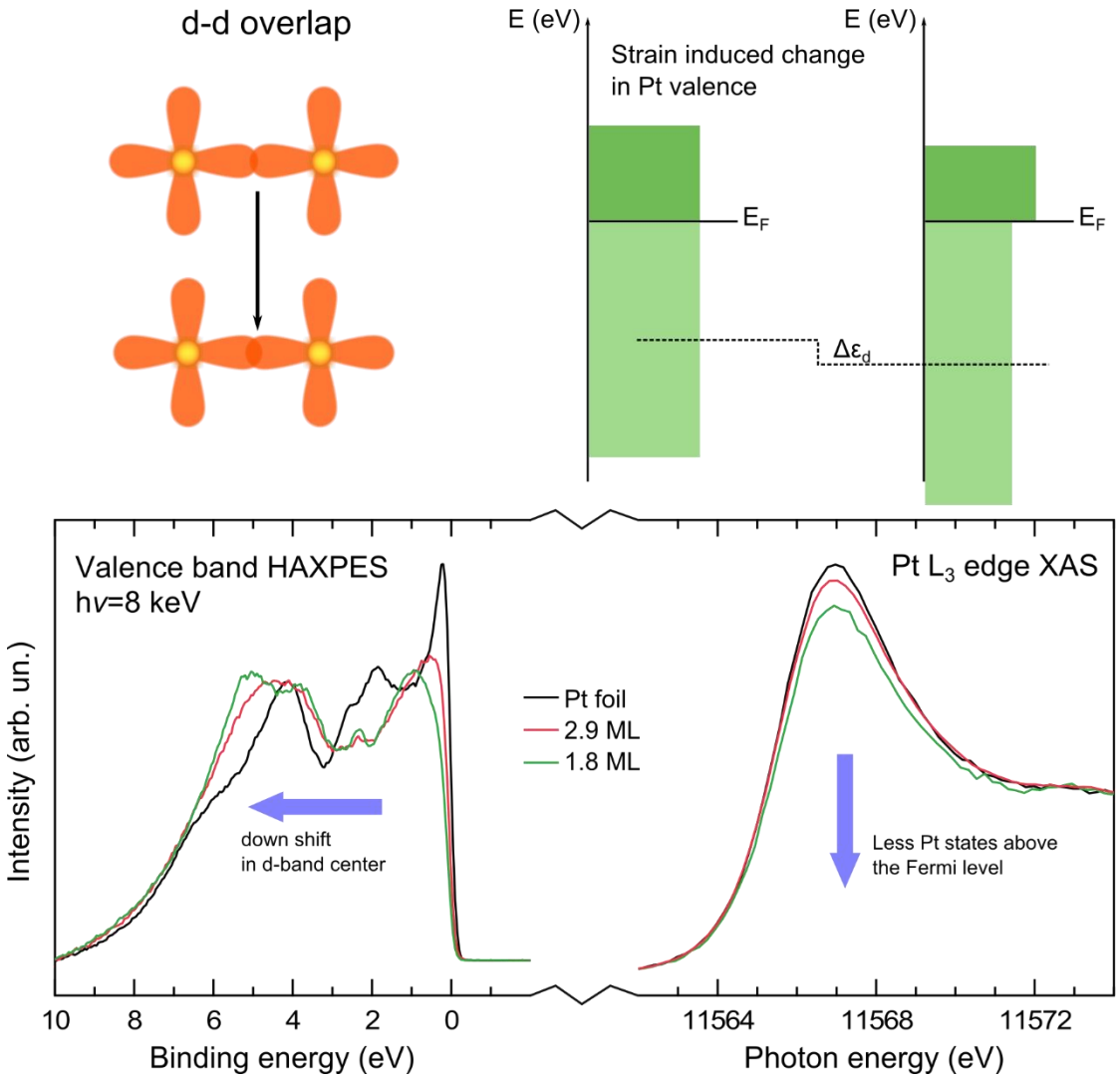
On Cu(111) surface, platinum overlayer is compressed but it relaxes with increasing thickness





d-band center

Pt 5d valence band XPS and Pt L_3 edge XAS

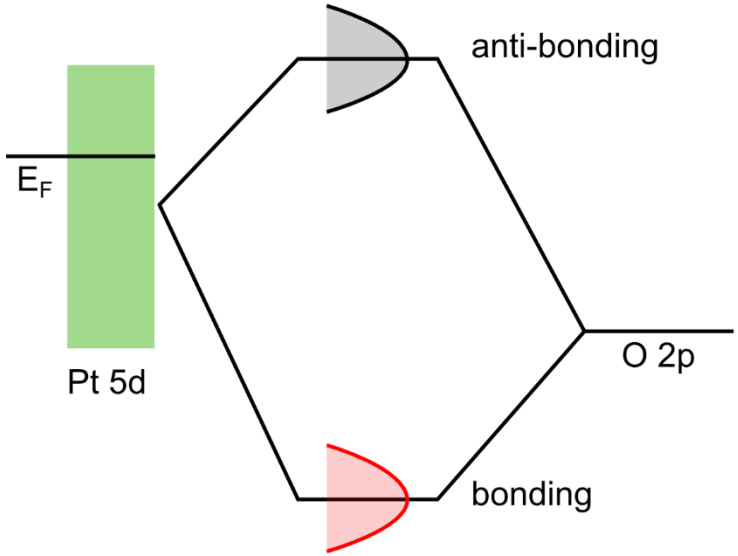


Strain induced change in the overlap between d-states leading to a change in the d-band width.

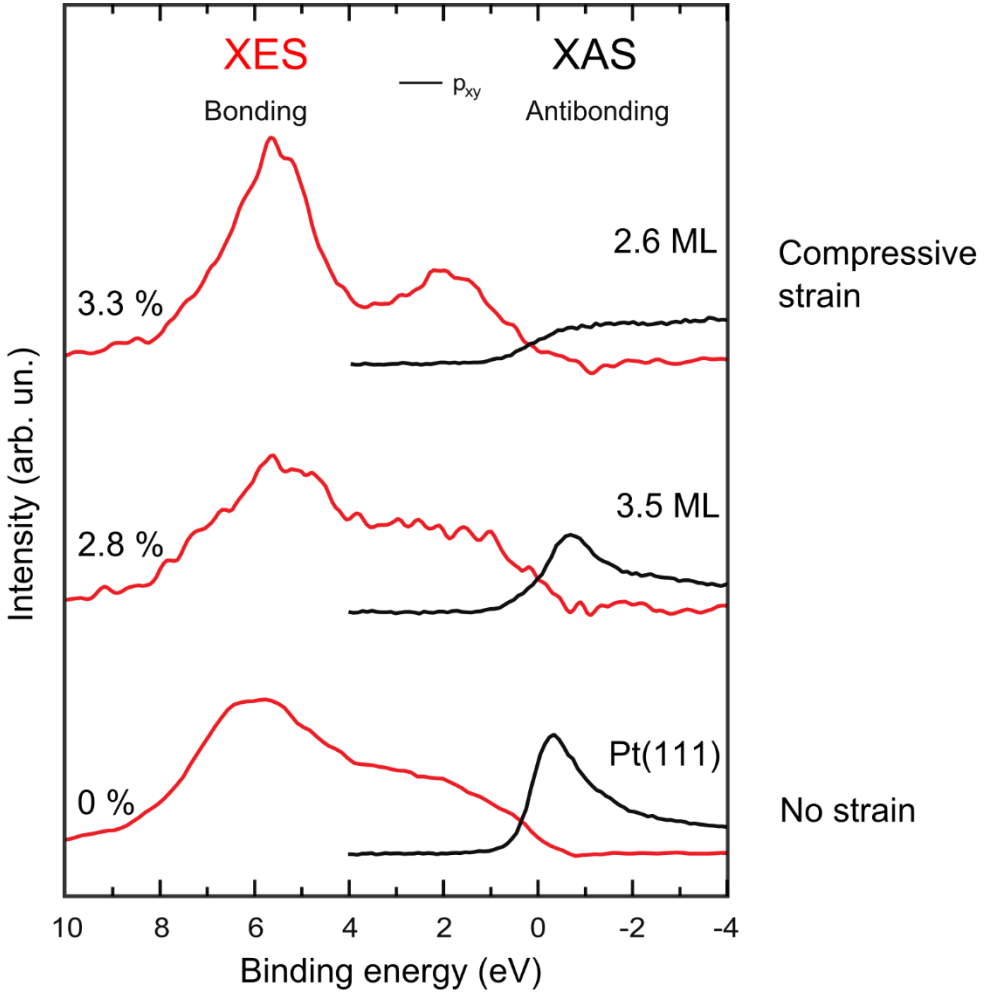
Change in the d-DOS, shift of the d-band center can be probed by spectroscopy.

Electronic structure of adsorbate

O K-edge XAS and XES



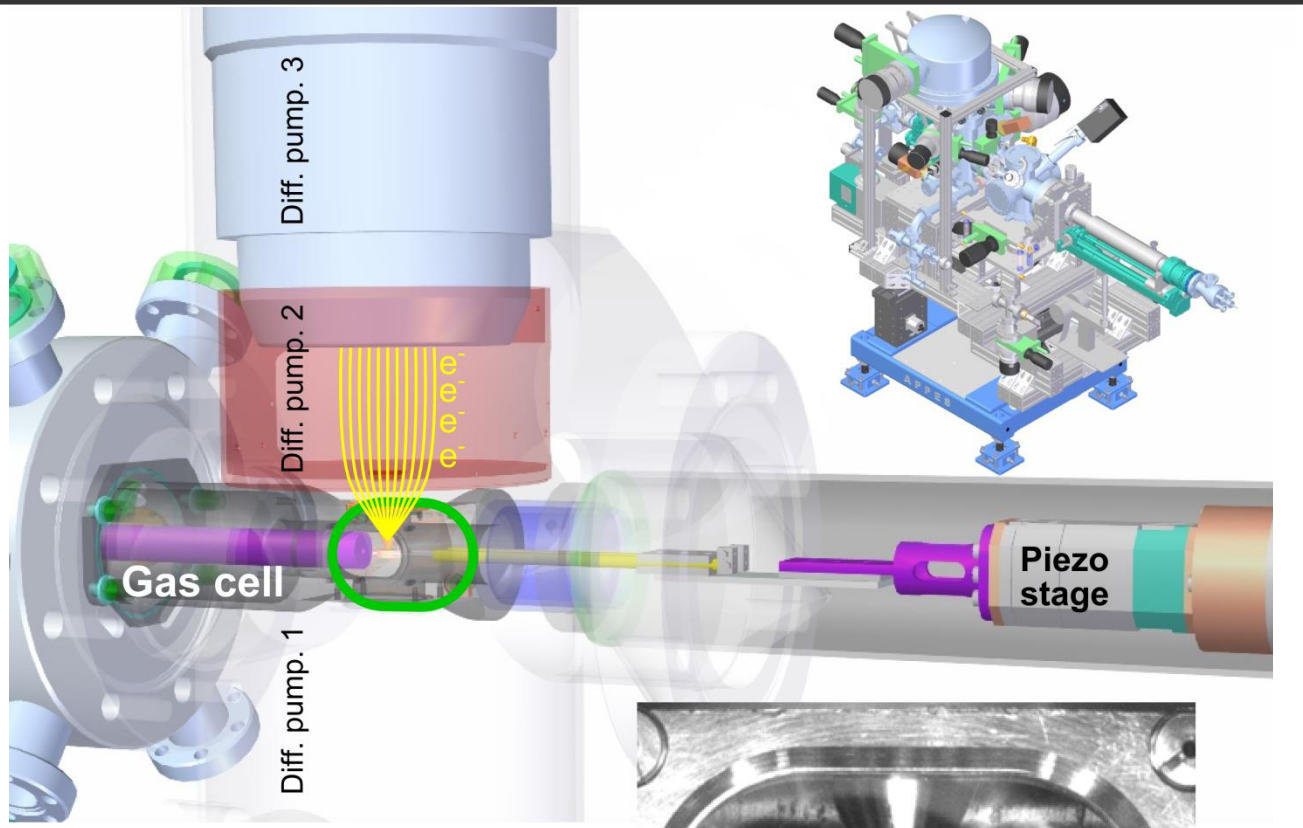
Populated antibonding states:
Weak Pt-O chemical bond

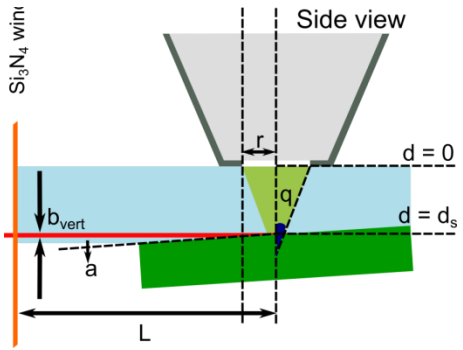


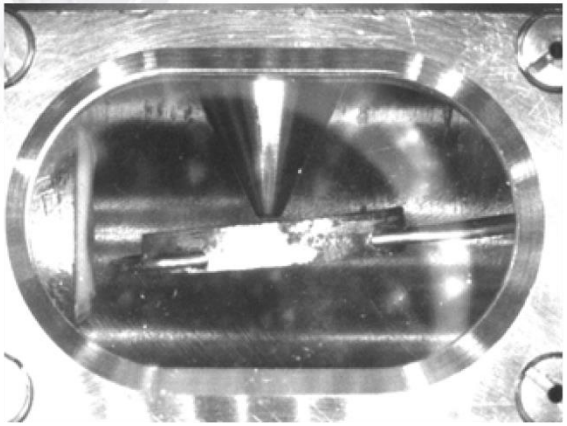
Nat. Chem. 2, 454–460 (2010)

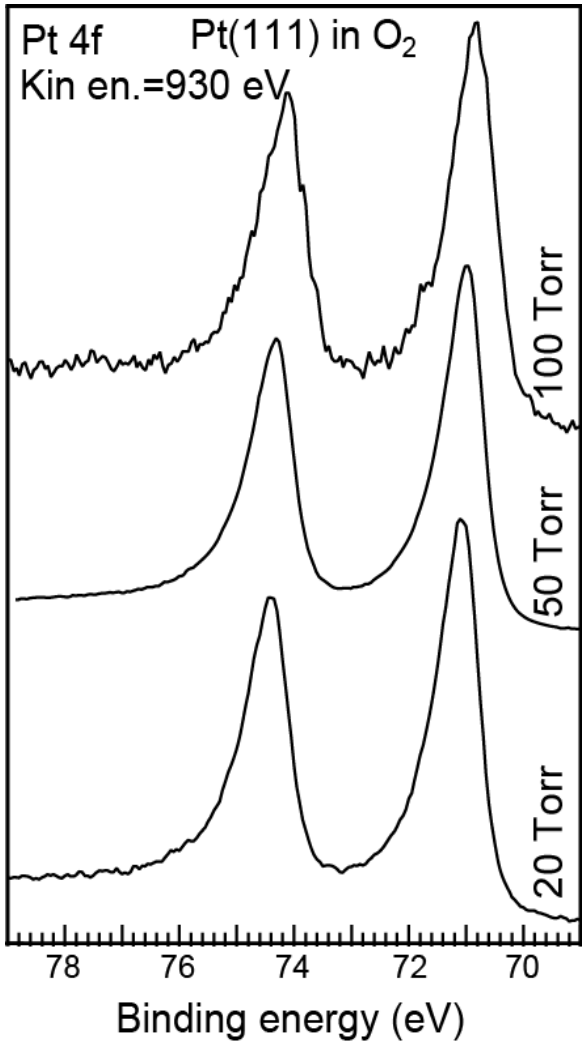
Ambient Pressure X-Ray Photoelectron Spectroscopy

Gas cell concept



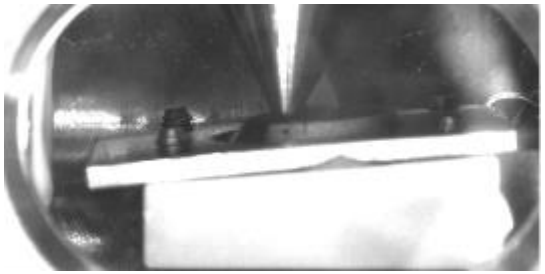






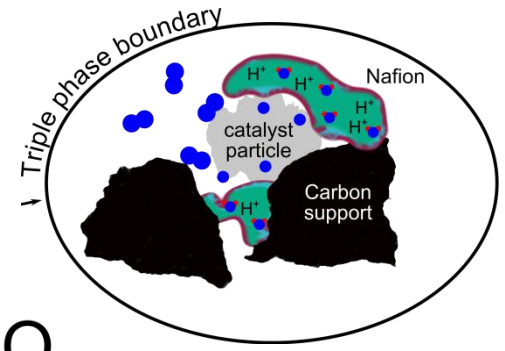
In operando XPS concept

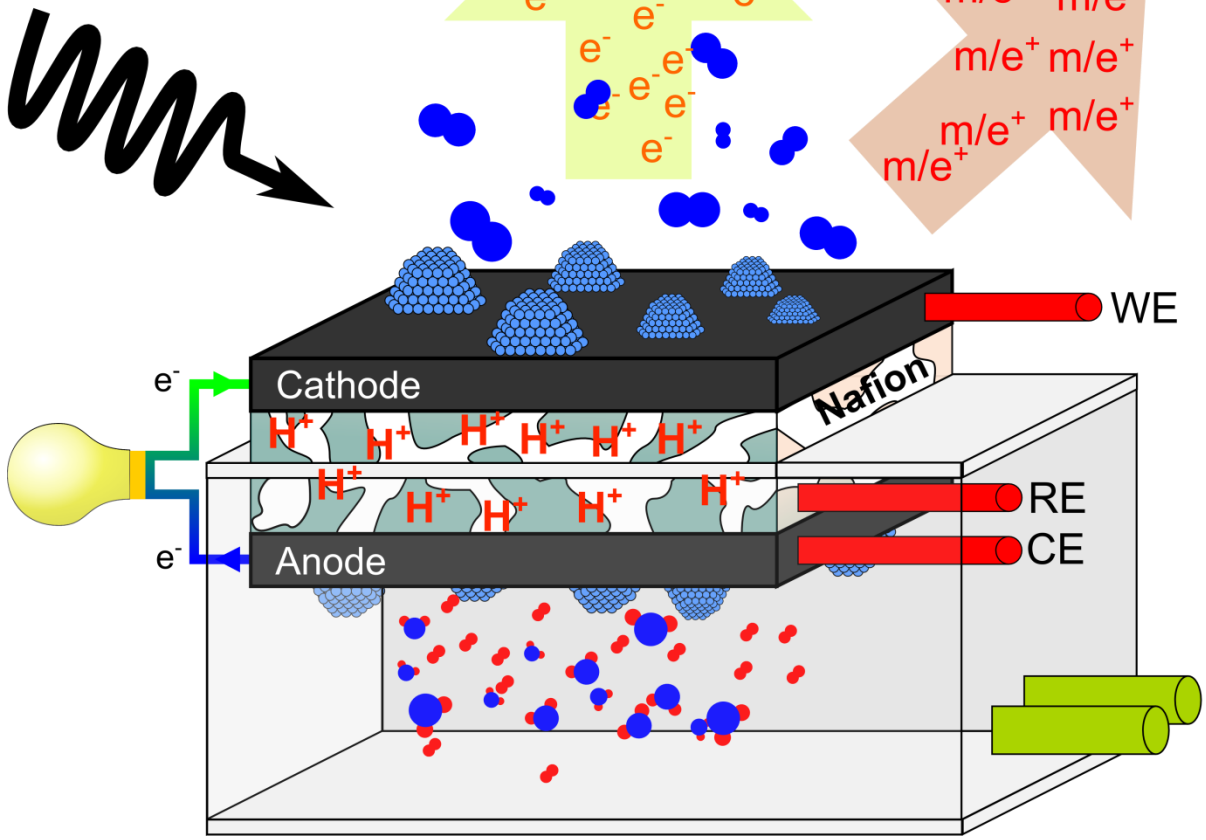
A cell design for battery and electrochemistry reactions



To a electron spectrometer

To a mass spectrometer





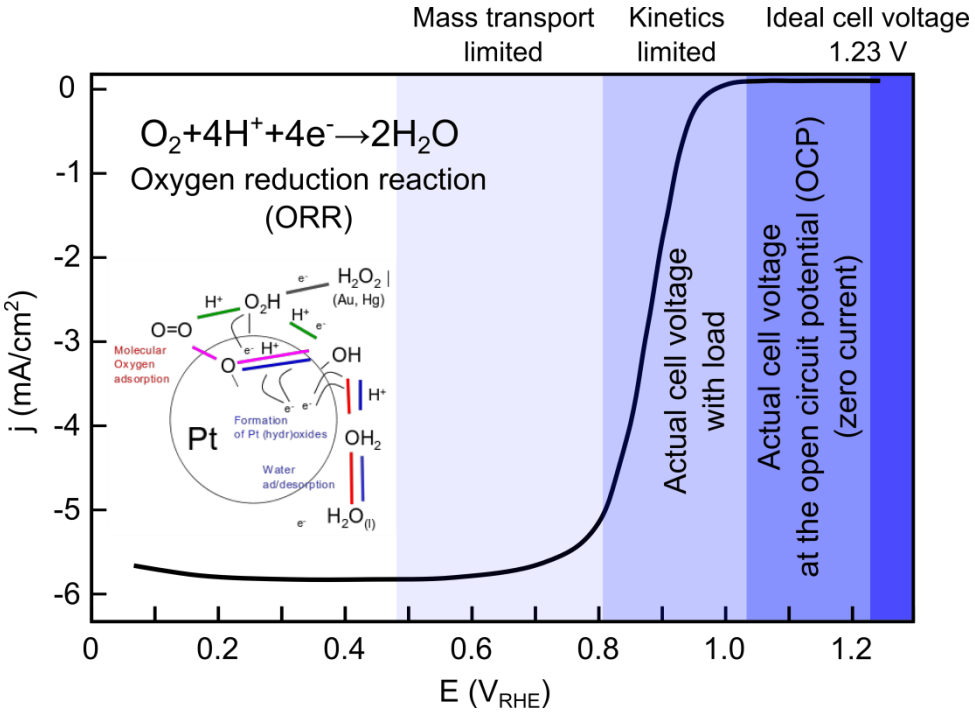
O_2

ORR on Pt
OER on IrO_2
OER on IrO_2/RuO_2
OER on Mn doped TiO_2
HER on MoS_3/MoS_2

H_2, H_2O

ORR on Pt nano-particles

O 1s XPS: As P(O_2) increased

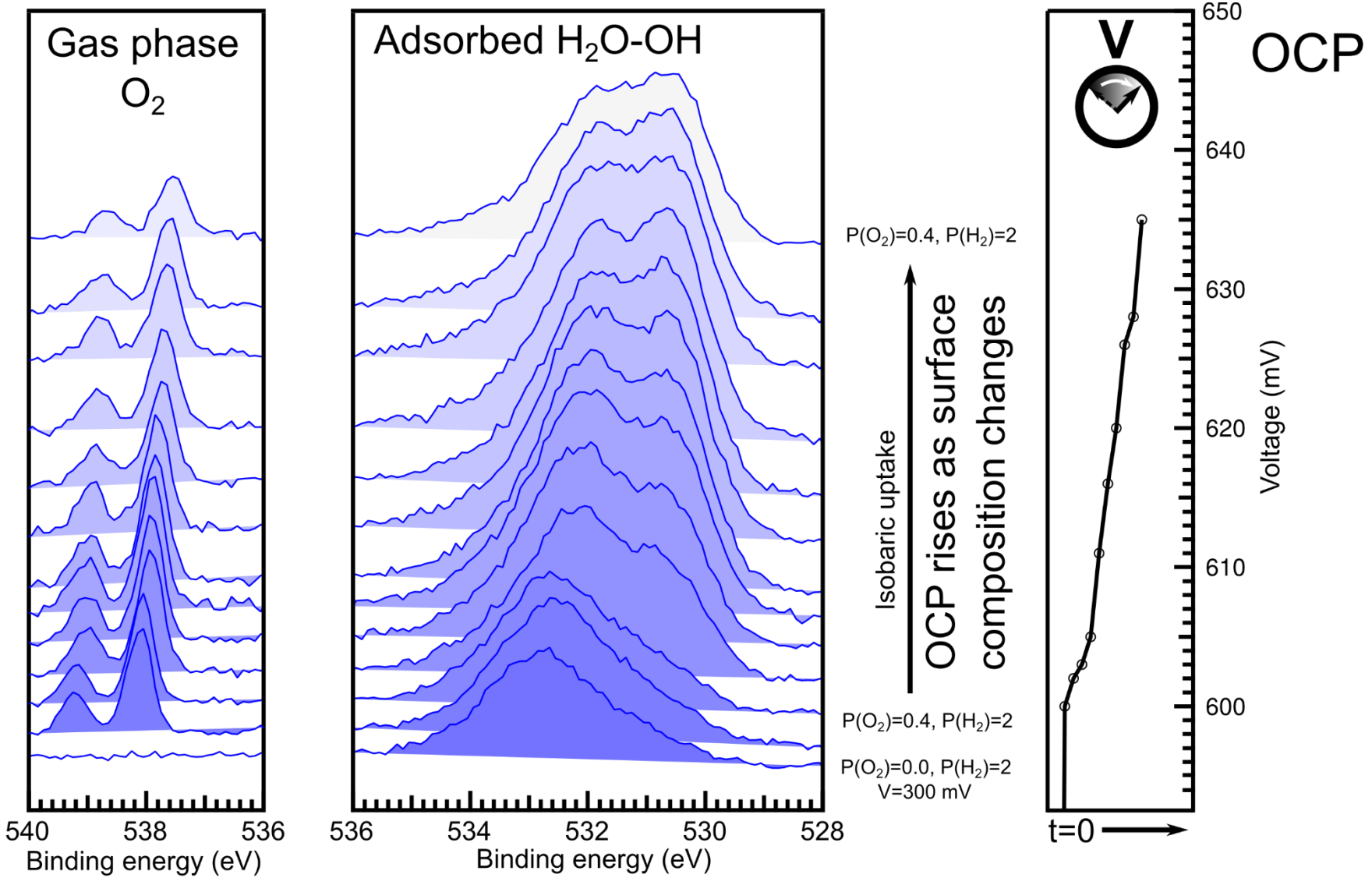


Overall $2H_2+O_2\leftrightarrow 2H_2O$

Oxidation	Reduction
$2H_2\leftrightarrow 4H^++4e^-$	$O_2+4H^++4e^-\leftrightarrow 2H_2O$
$\leftarrow$HER	$\leftarrow$OER

Pt PEM fuel cell

O 1s XPS: Operando fuel cell OCP

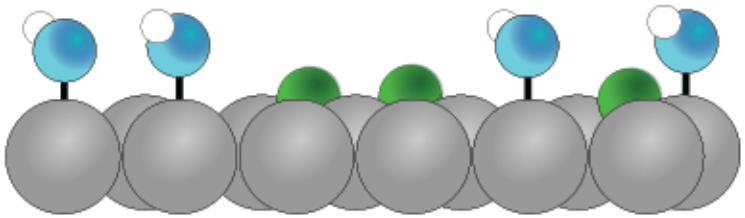


Open Circuit Results

O1s 670 eV
P_{back}= Fixed
P_{Front}= Fixed

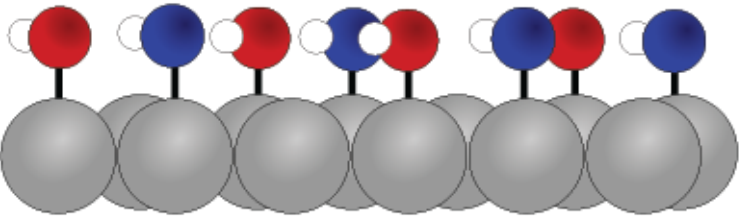
529.9 eV
OH-O

531eV
OH-O

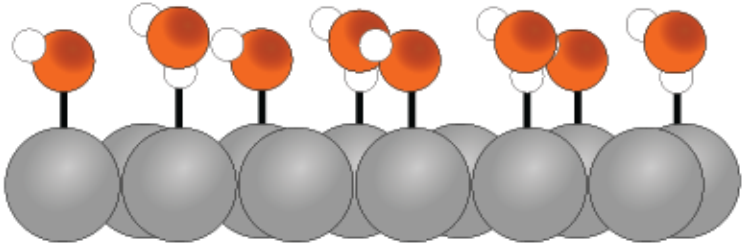


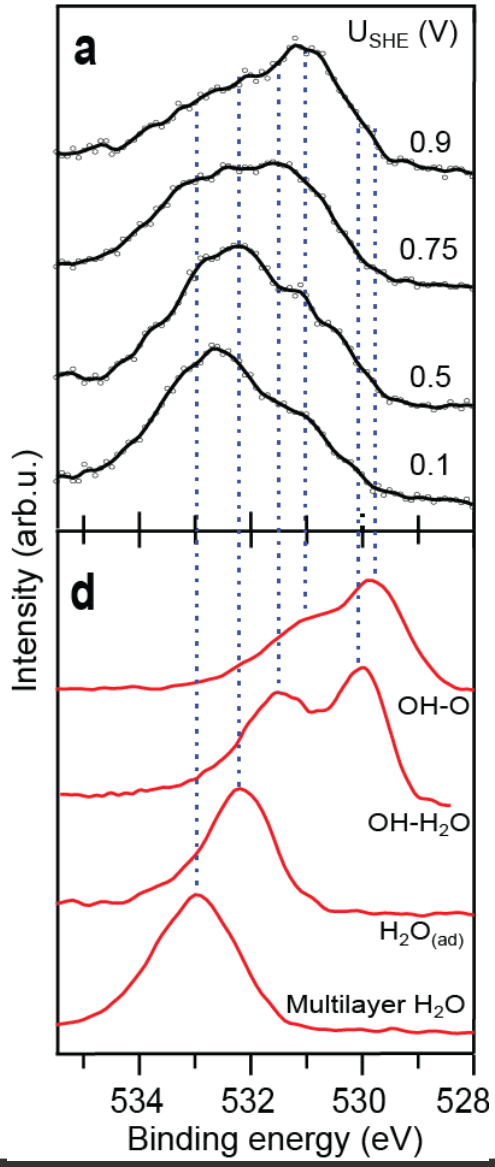
531.6 eV
OH-H_2O

530.1 eV
H_2O-OH



532.2 eV
$H_2O_{(ad)}$

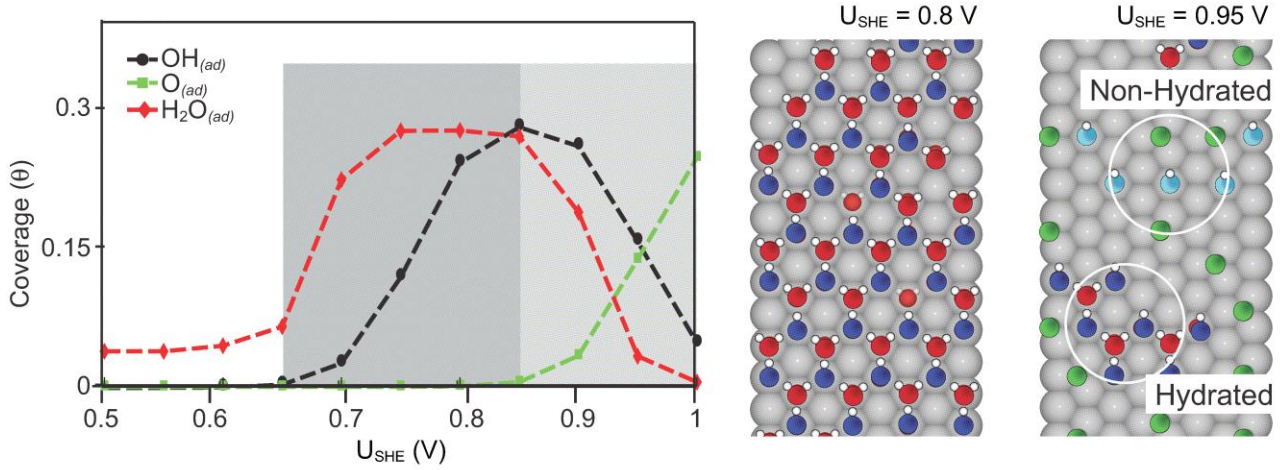


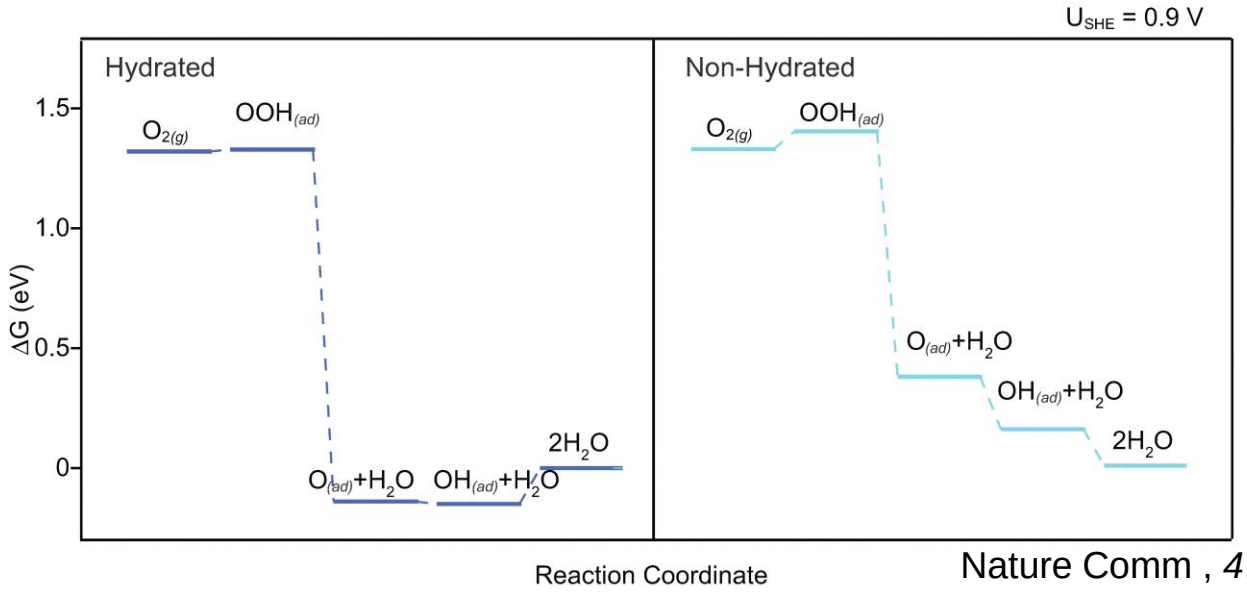


Nature Comm. , *4*, 2817 (2013)

Oxygenated species on running FC

Calculated coverages of oxygen, OH and water as a function of potential



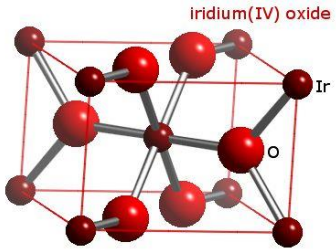


Nature Comm , *4*, 2817 (2013)

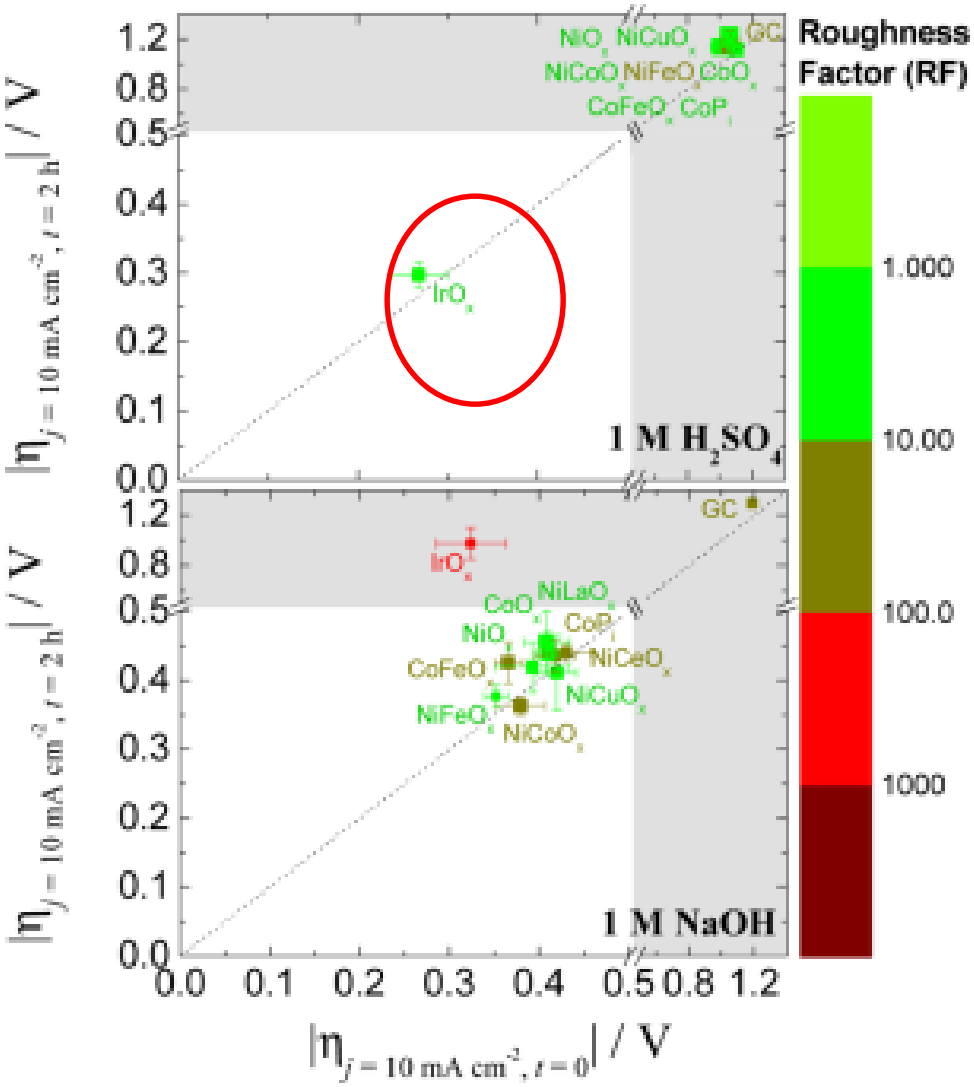
Why Iridium Oxide (IrO_2)?

All intermediates can be observed in either the O1s or Ir4f signals

Ideal system for first APXPS look into OER
Low overpotential
Stable in acid



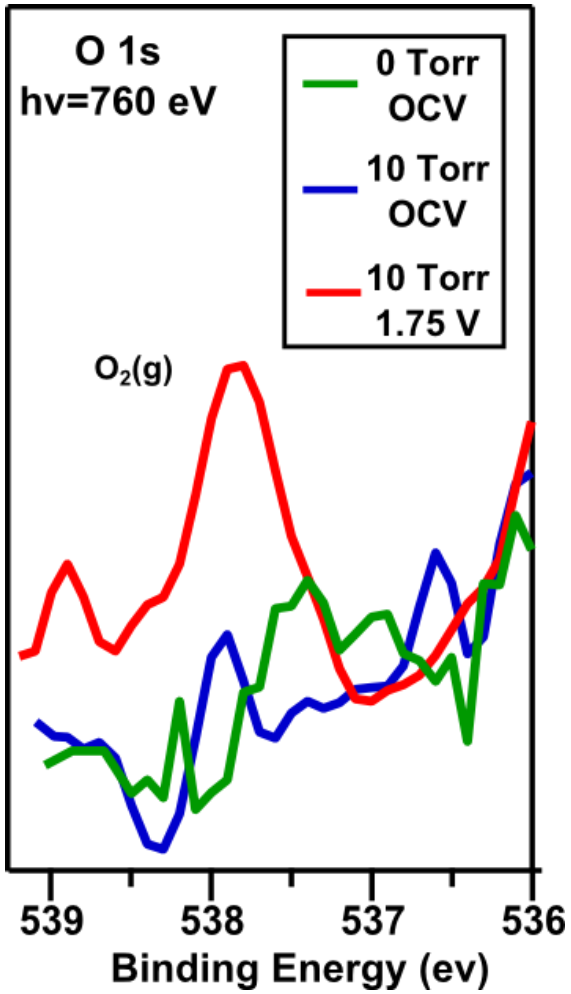
$$H_2O \leftrightarrow OH* + H^+ + e^-$$
$$OH* \leftrightarrow O* + H^+ + e^-$$
$$O* + H_2O \leftrightarrow OOH* + H^+ + e^-$$
$$OOH* \leftrightarrow O_2 + H^+ + e^-$$

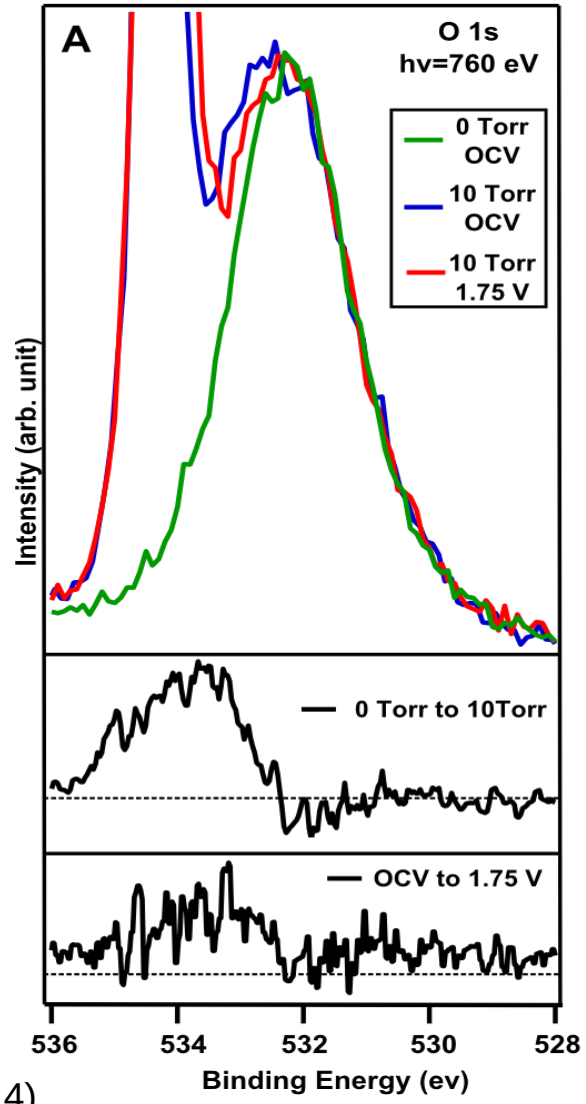


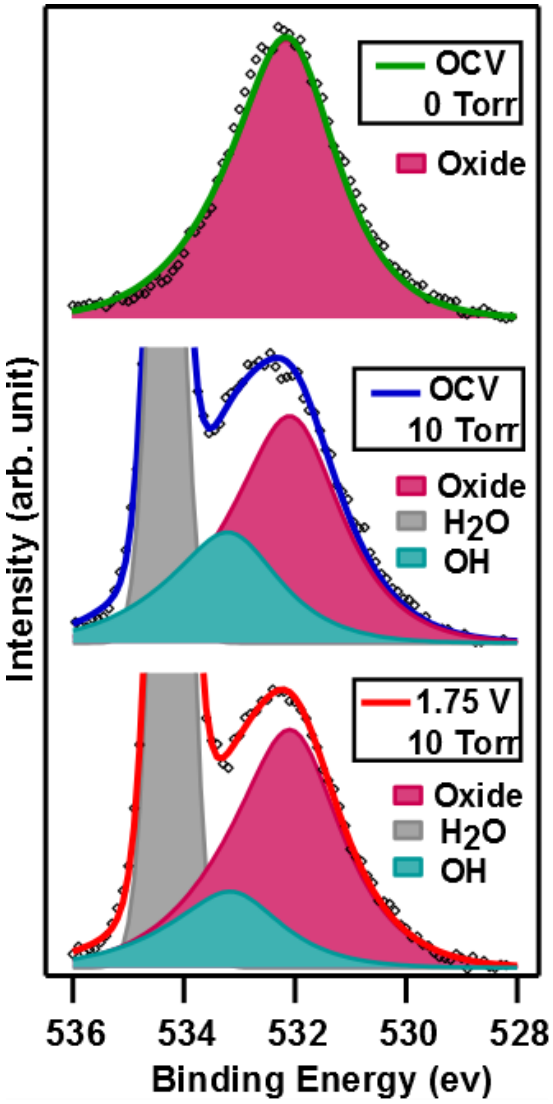
C. McCrory, et al. *J. Am. Chem. Soc.*, **2013**, 135, 16977–16987

Operando changes

O 1s XPS



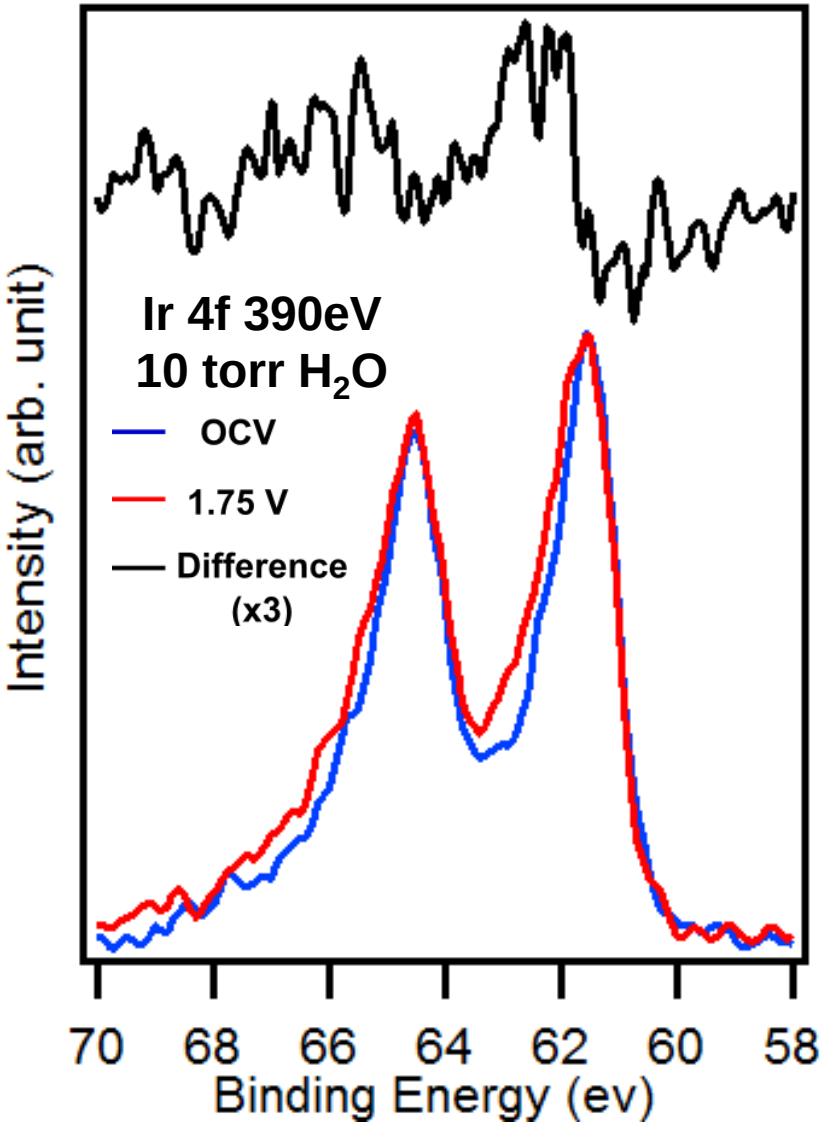


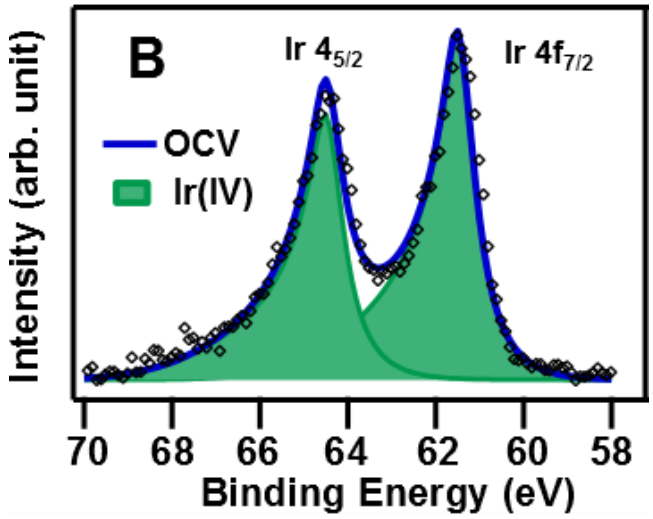


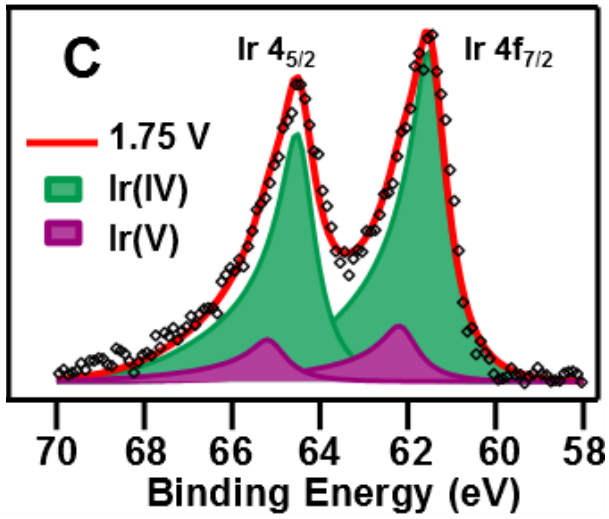
Angew. Chem. Int. Ed., 53, 7169 (2014)

In operando electrochemically induced changes

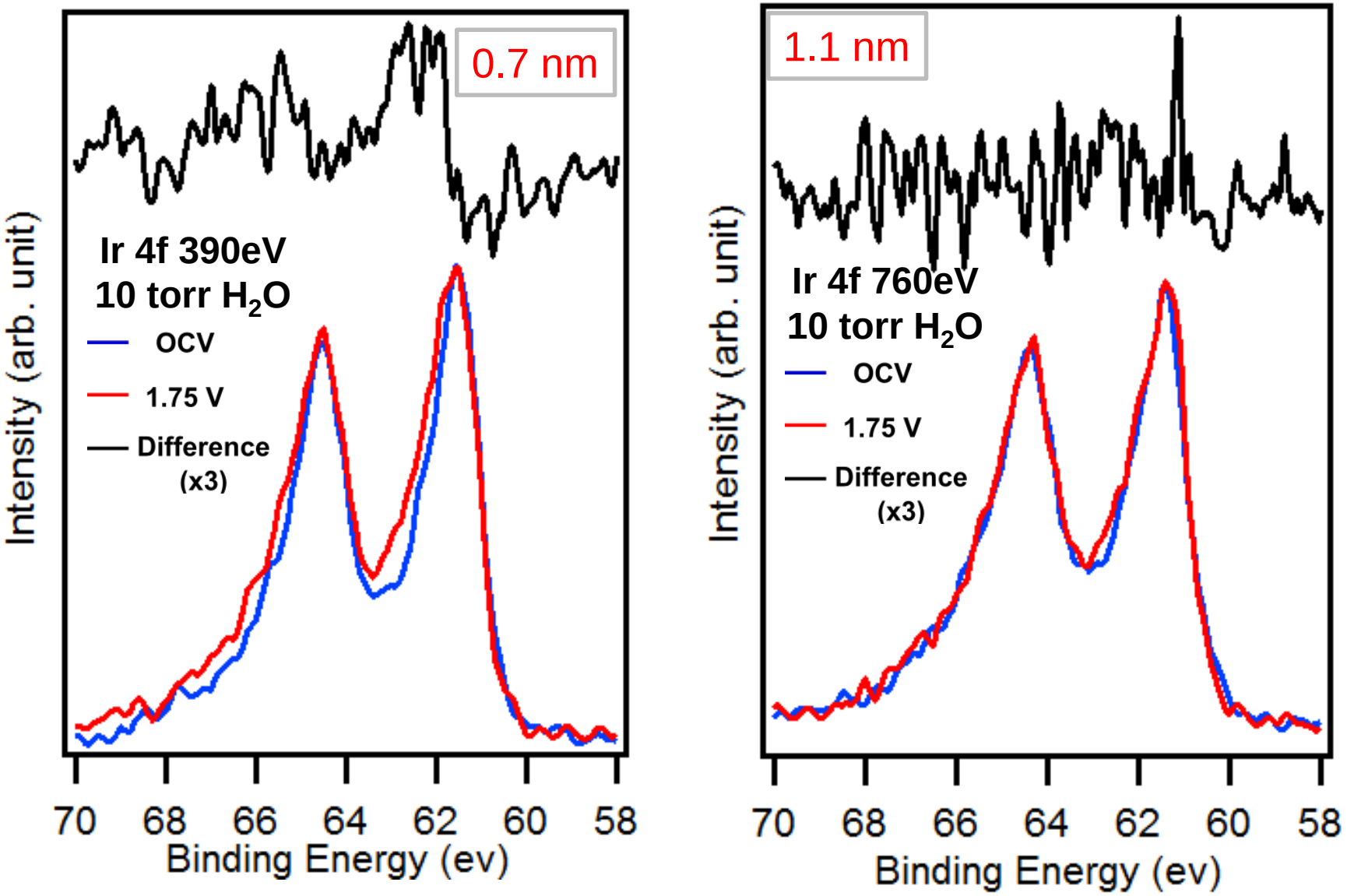
Ir 4f XPS







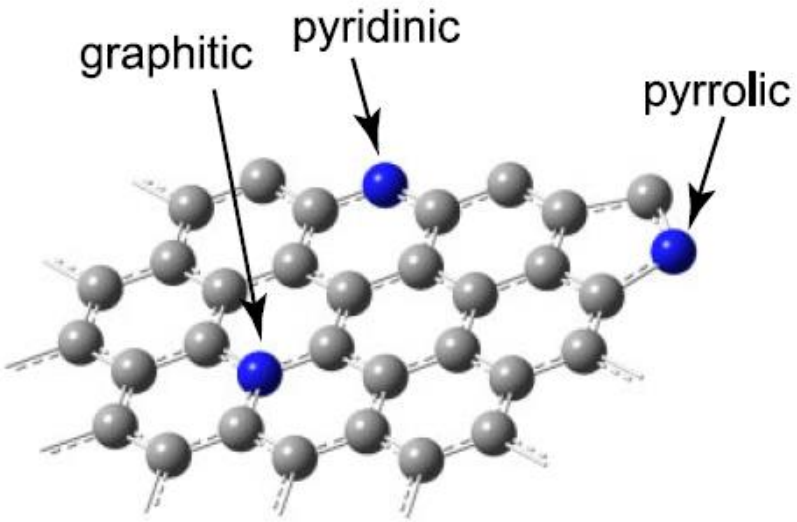
Reaction takes place on the surface



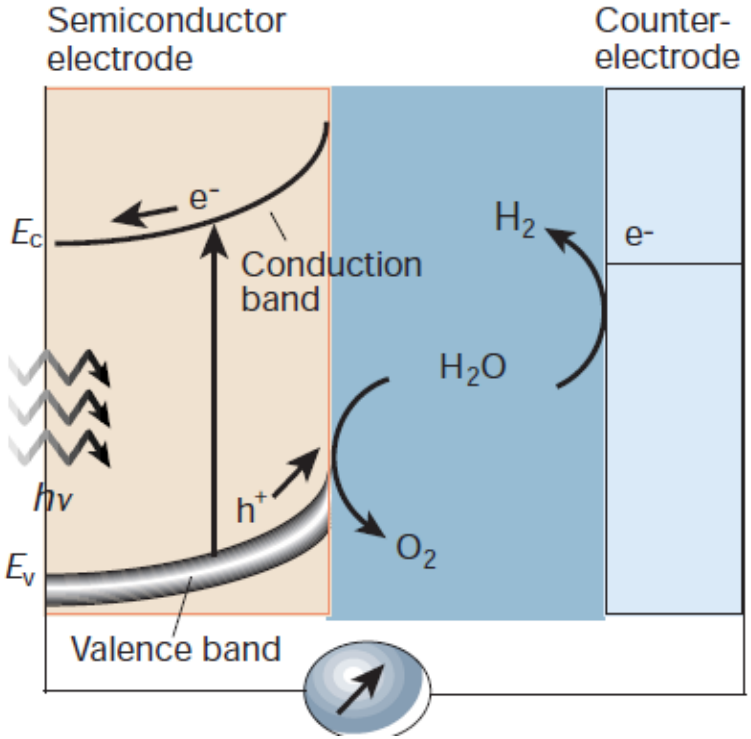
Current research

ORR and OER (photoelectrochemical)

N-doped graphene as a ORR catalyst



$BiVO_4$/CoOx for OER
TaON/CoOx for OER



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