PIER Graduate Week 2017

Interdisciplinary lecture and workshop week for PhD students

9 – 12 OCT 2017

CFEL / Bahrenfeld Campus / Hamburg

Ambient Pressure X- Ray Photoelectron Spectroscopy of catalytically active interphases (Part II)

Axel Knop (knop@fhi-berlin.mpg.de)

Fritz-Haber-Institut der MPG

Department of Inorganic Chemistry

Faradayweg 4-6

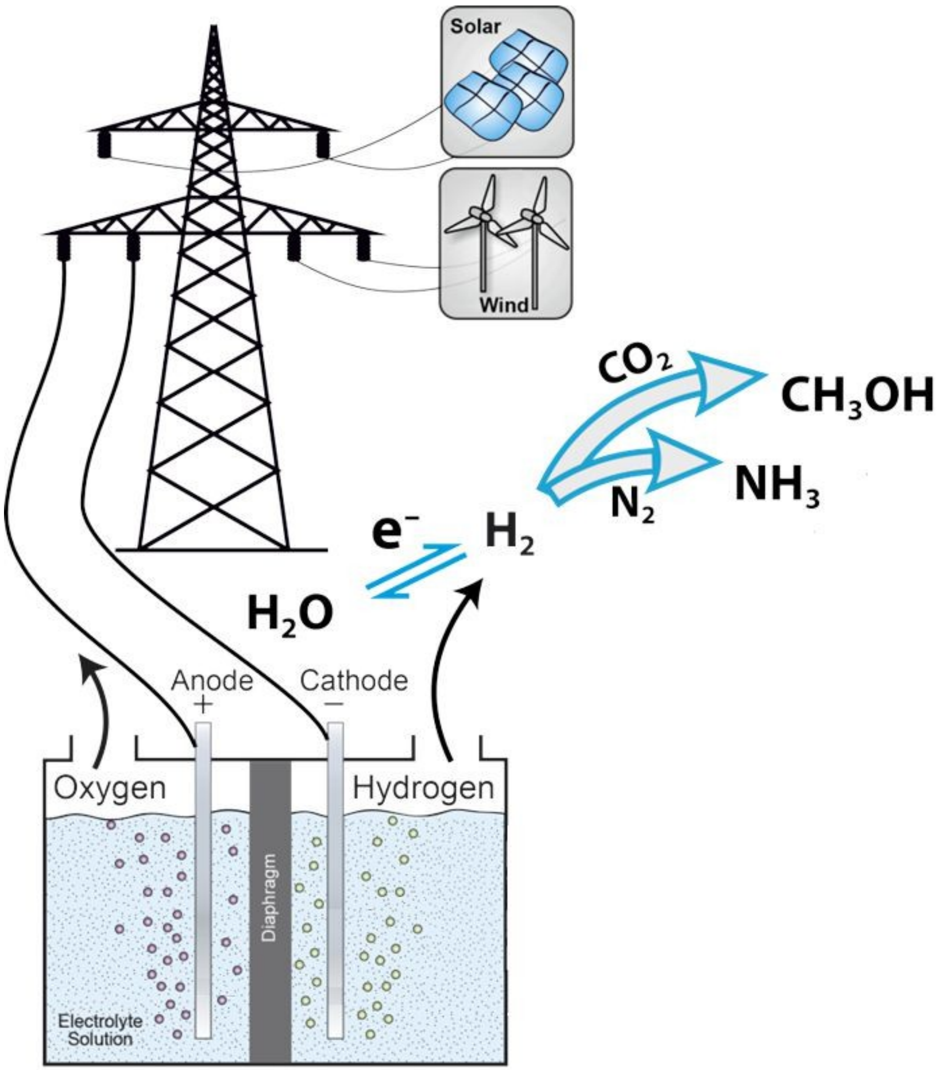
14195 Berlin

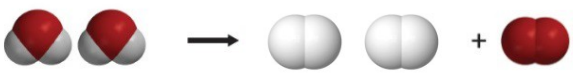
MAX-PLANCK-GESELLSCHAFT

AC FHI

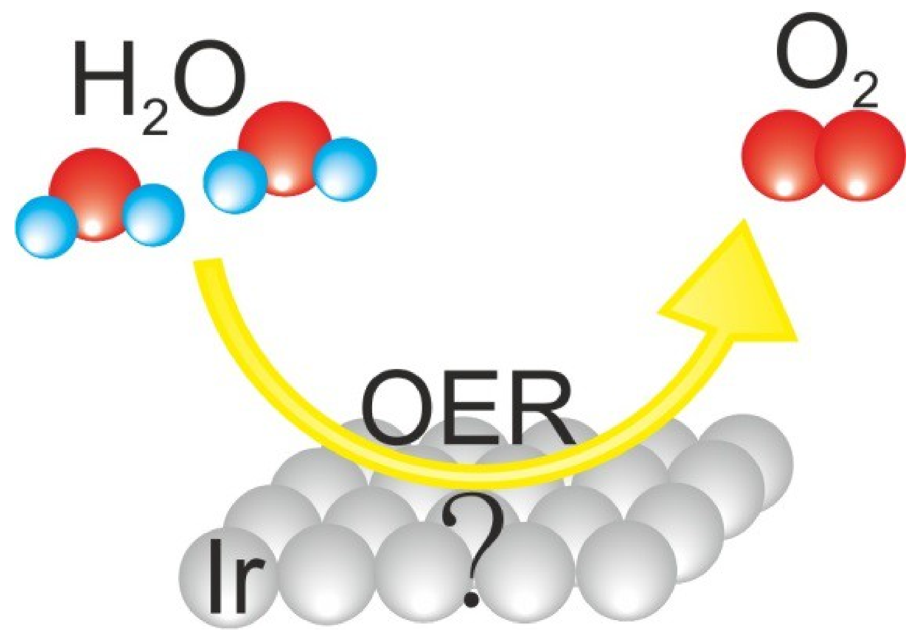
Motivation

Chemical energy storage and conversion



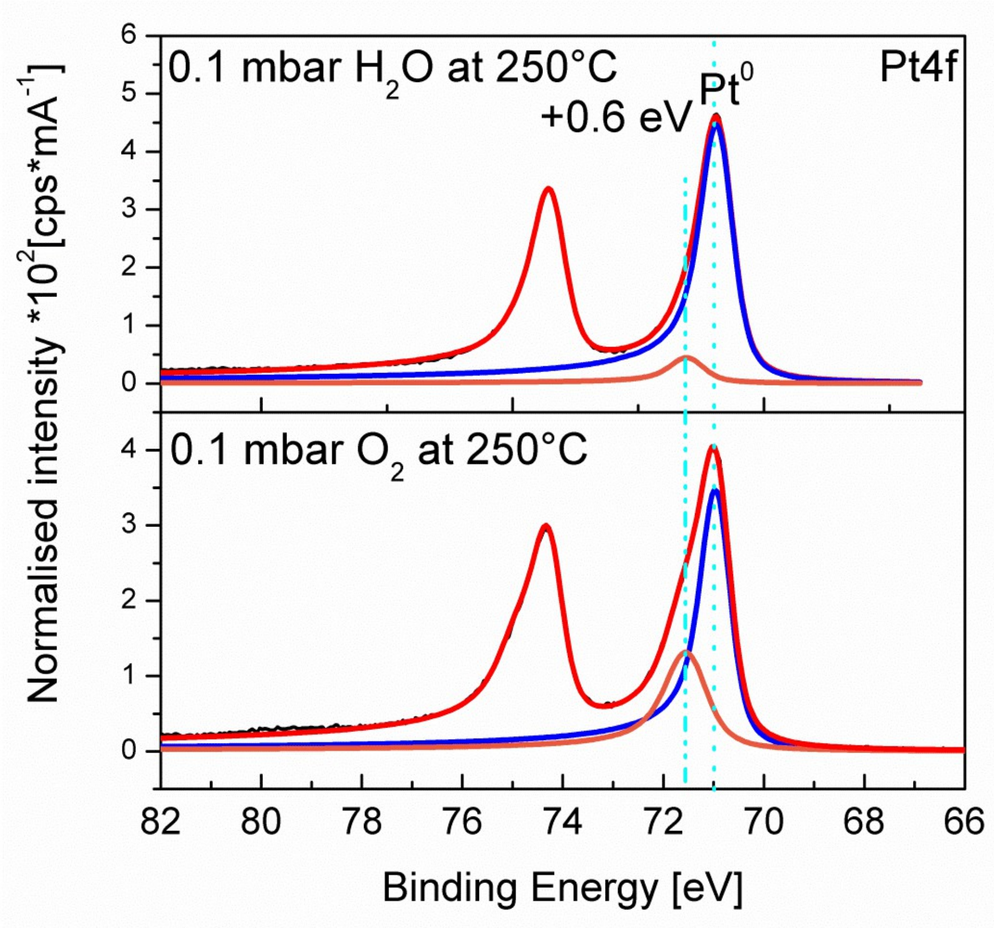


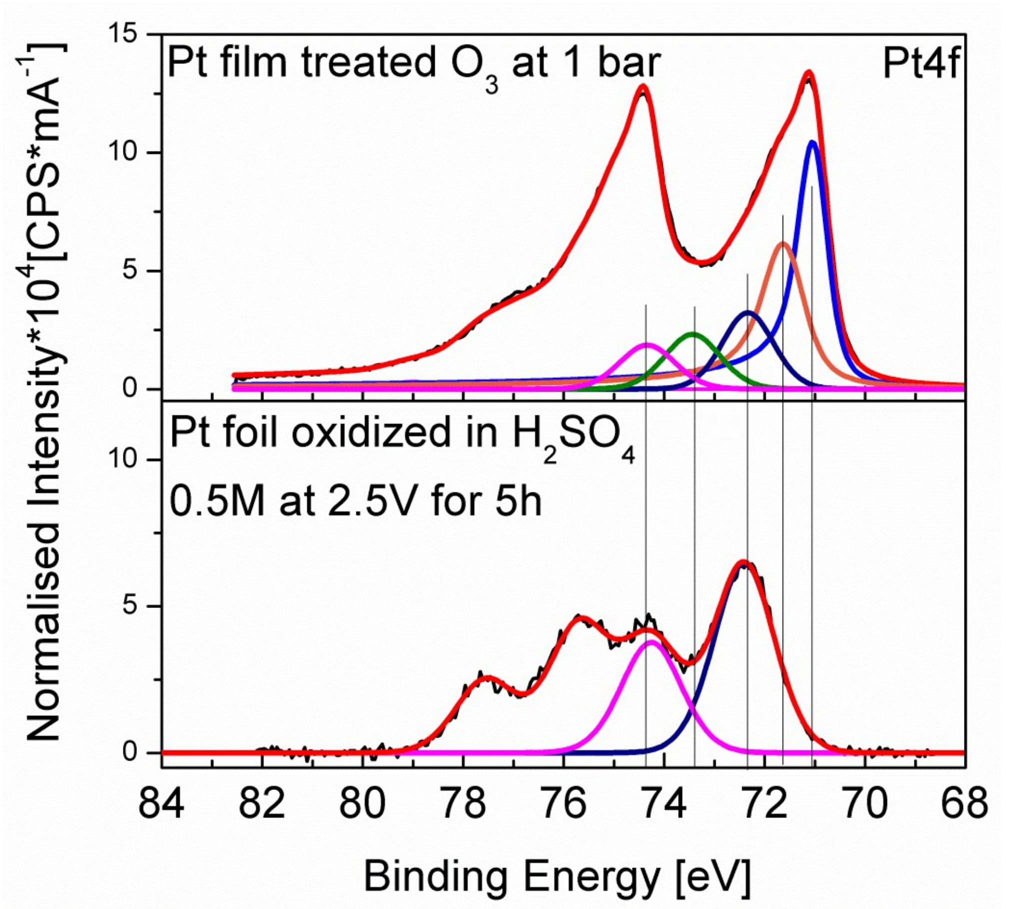
- Water splitting



Background

- Pt as a model system to study the nature of the surface species upon OER (oxygen evolution reaction)

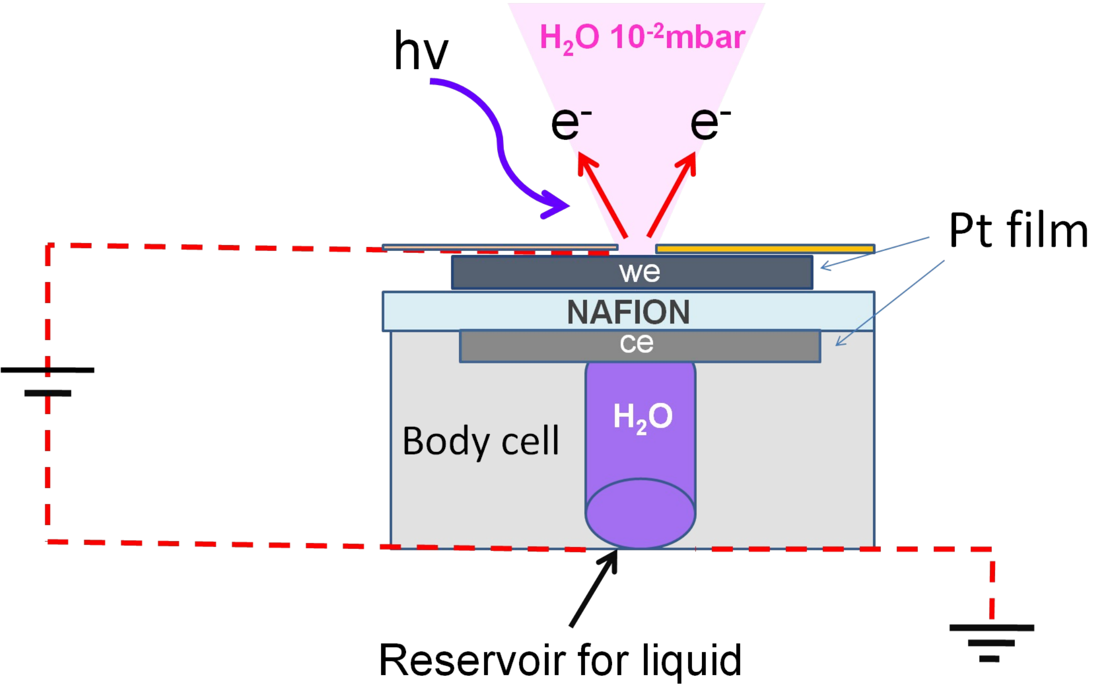


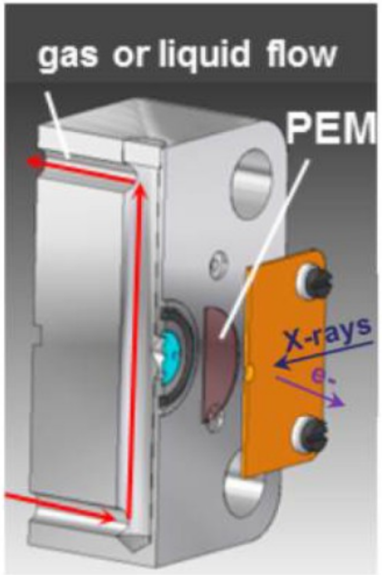


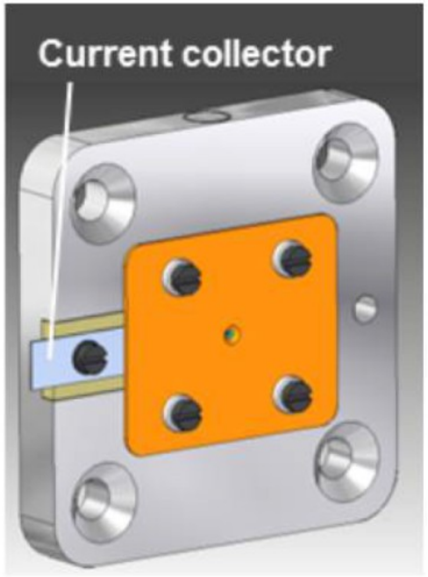
In-situ electrochemical cell

Limitation of the state of the art NAP-XPS end-station at the soft X-ray ISISS beam line (HZB)

- No liquid electrolyte
- Low pressure (not possible to investigate liquid/solid interface)
- Restriction to conductive material (charging issue in XPS)



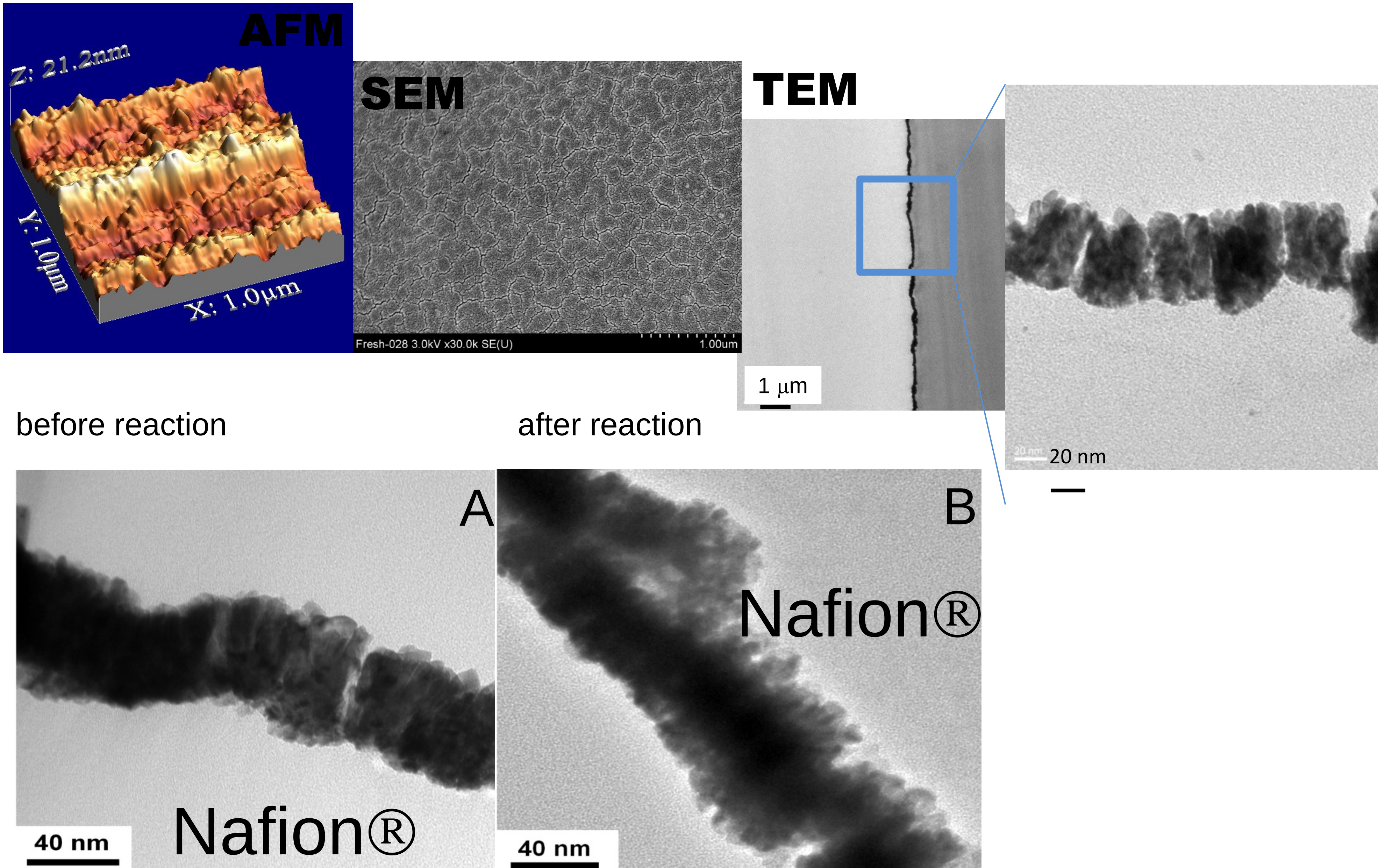




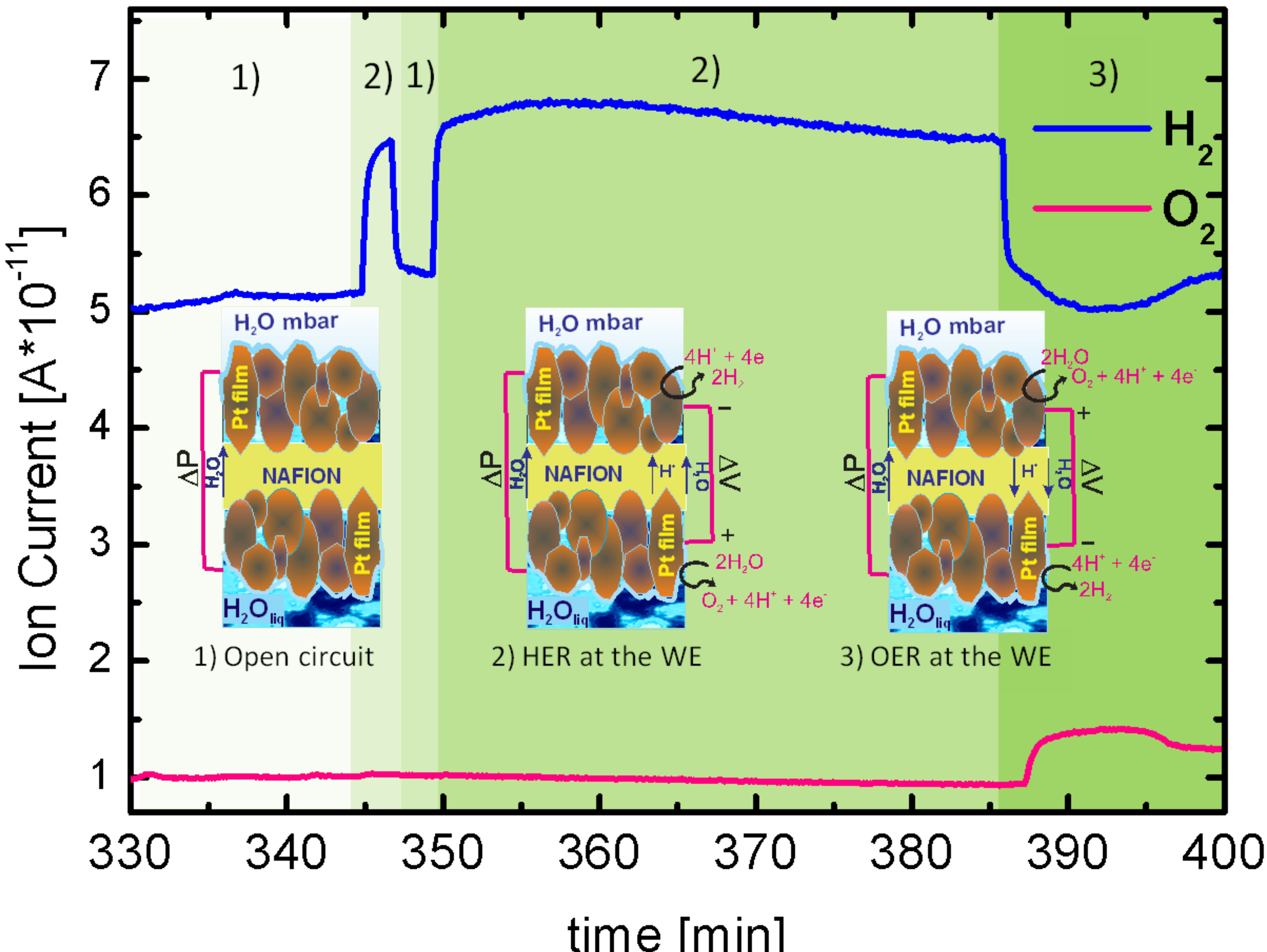
Fermi level of the CE is aligned with the Fermi level spectrometer

R. Arrigo

Pt Electrode Structure

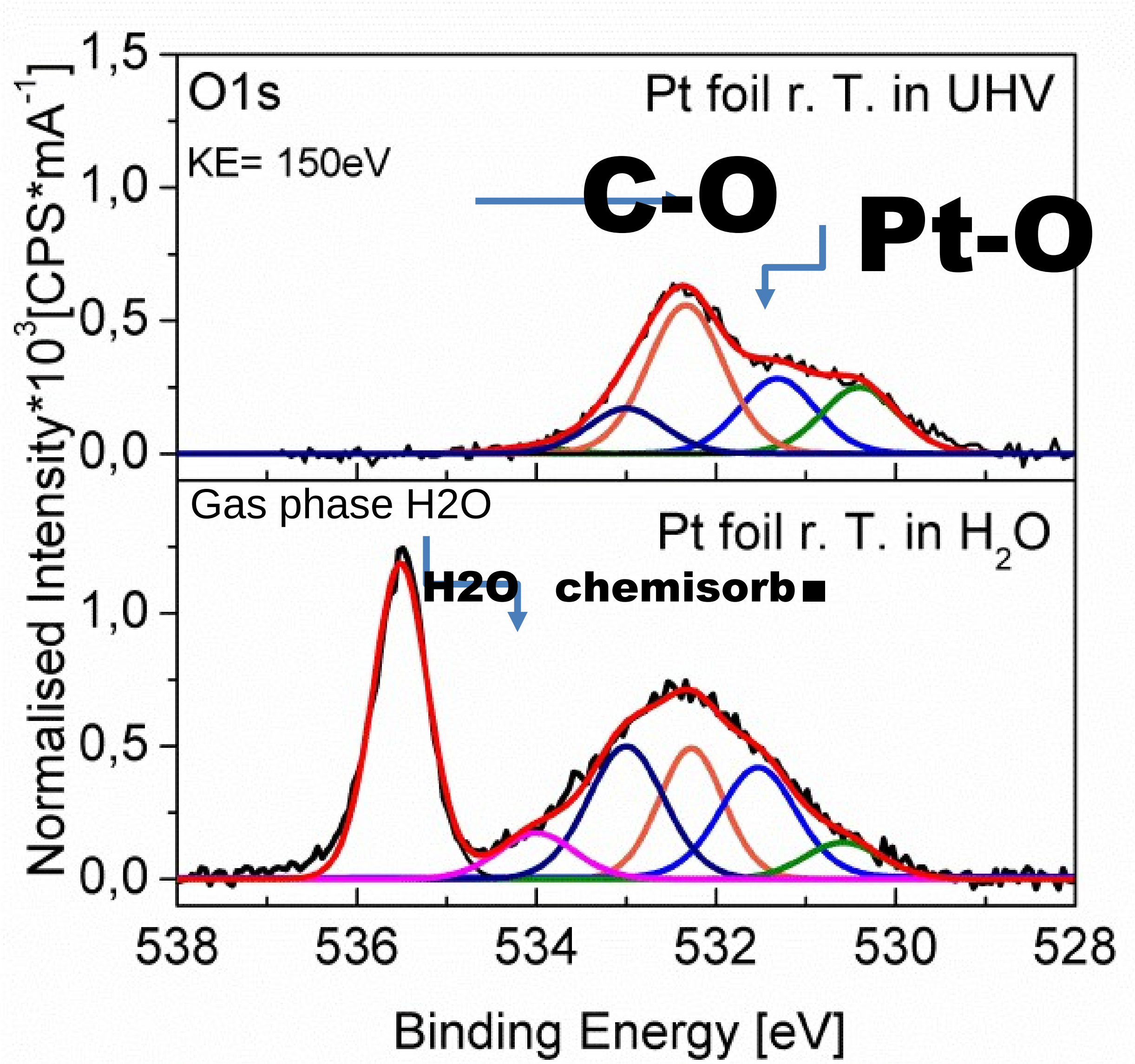


Electrochemical cell:MS



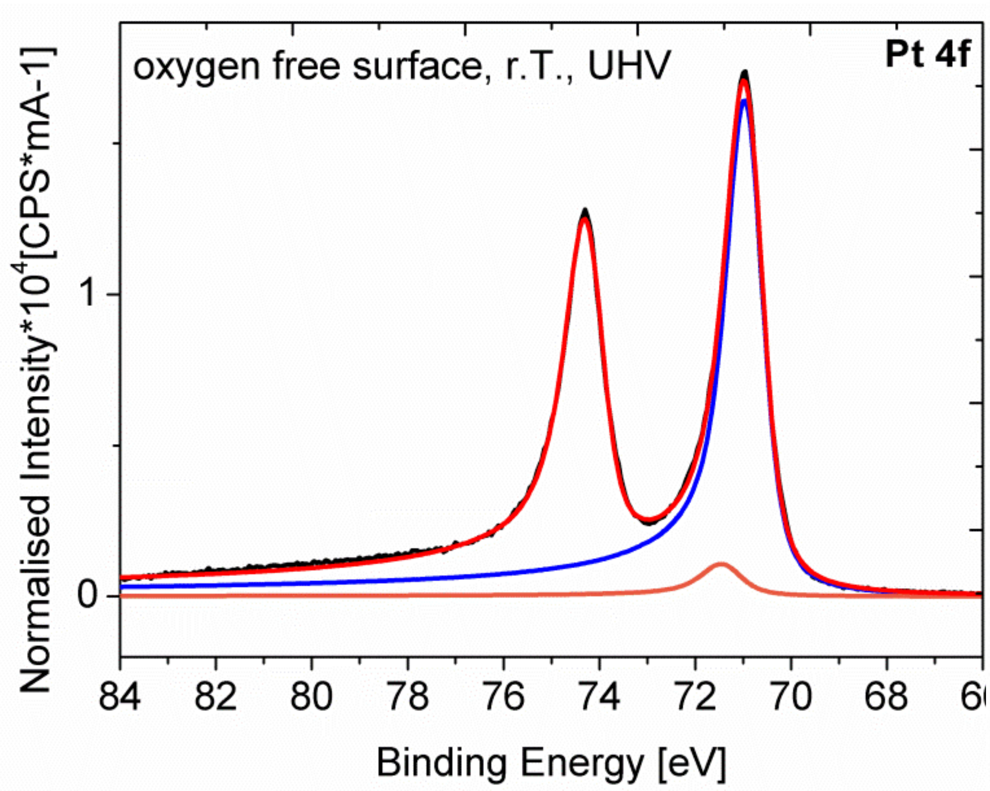
O species on Pt

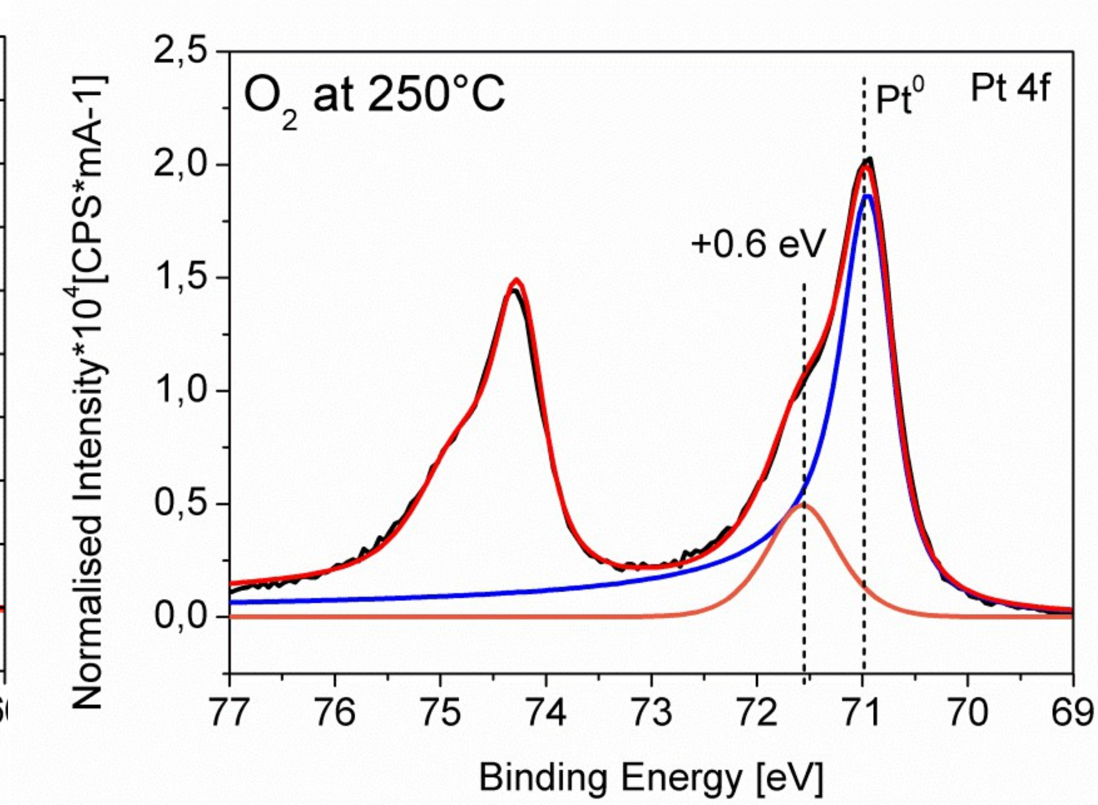
Polycrystalline Pt foil at 25°C



Pt species

Polycrystalline Pt foil previously treated in O2 at 250°C to remove the C

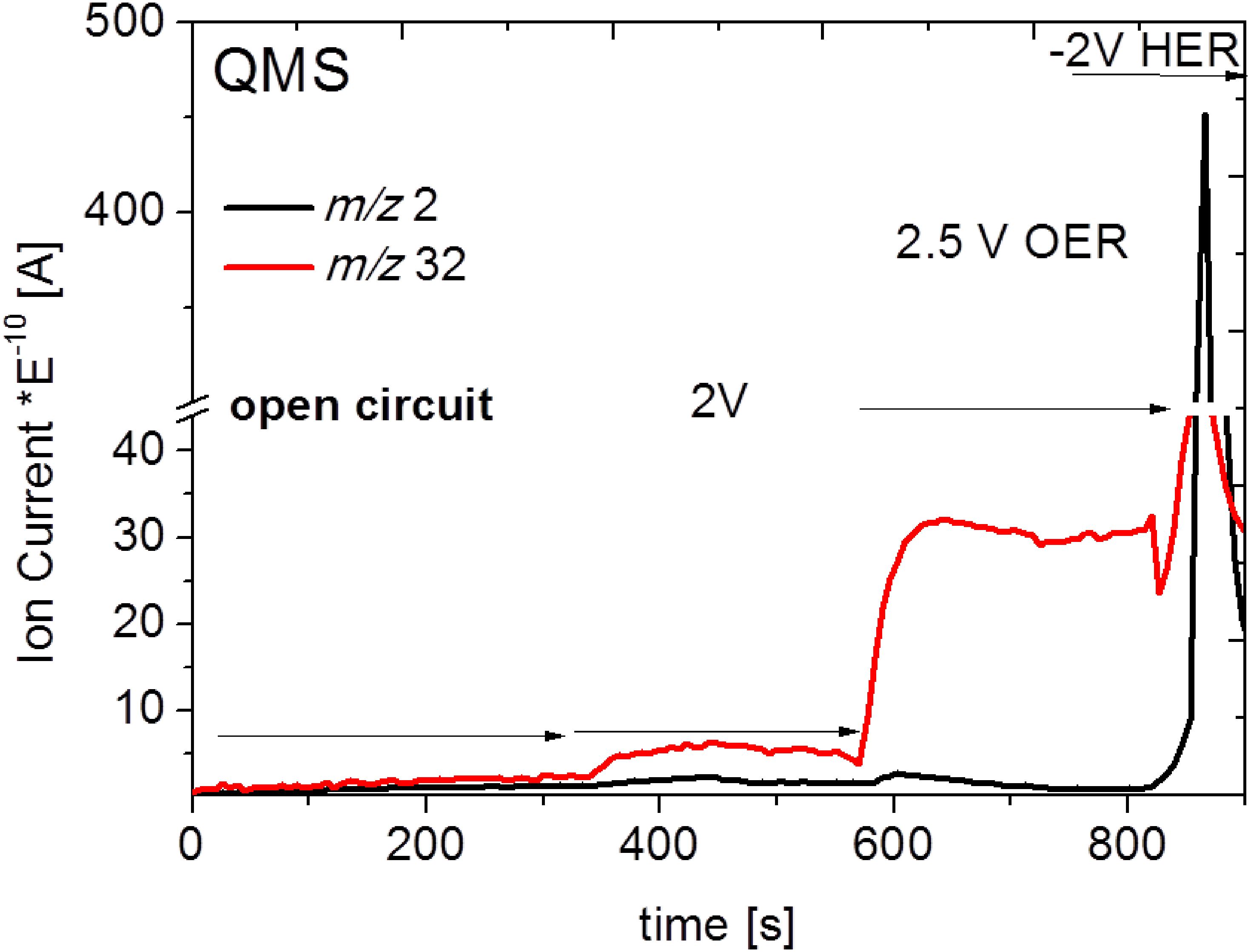




Specie	Pt0	Pt 1	Pt 2
BE [eV] +/-0.05	70.95	+ 0.6	+1.3

In-situ study during OER: QMS

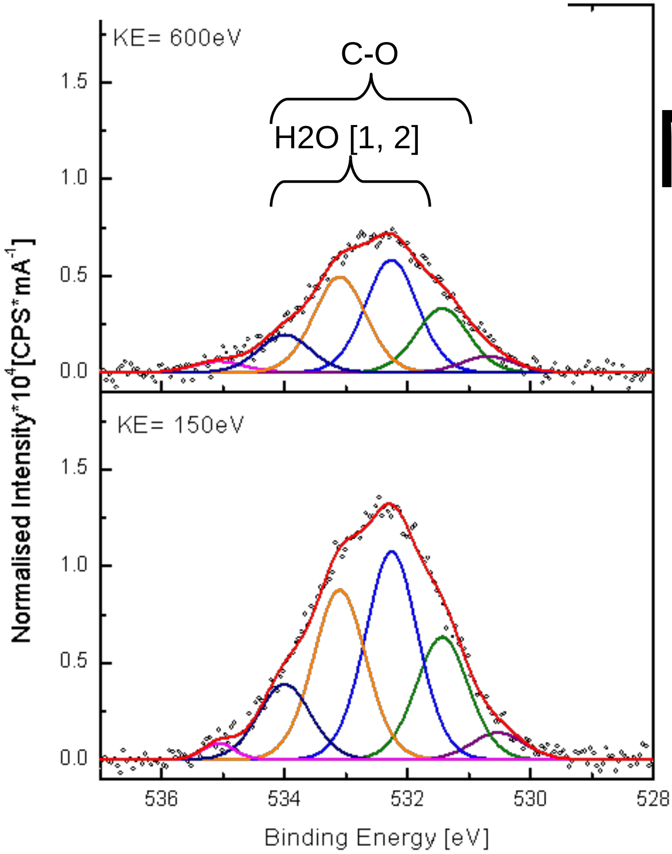
Two electrode-system



In-situ XPS during OER: O1s

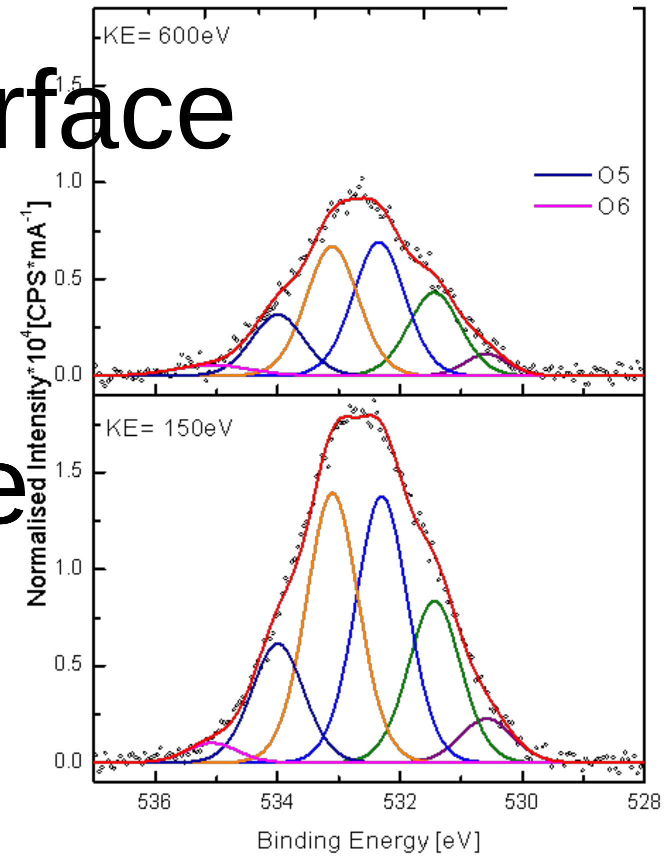
VWE= 2V

VWE= 2.5V



Near surface

surface

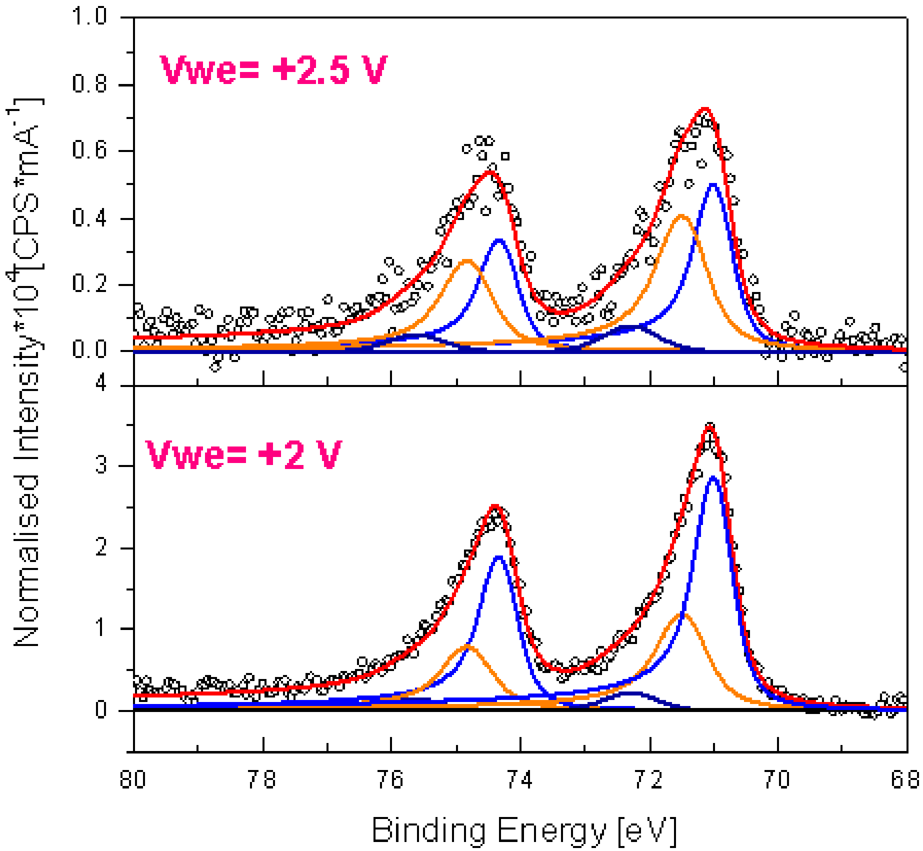


Specie	O2	O3	O4	O5	O6
BE [eV] +/-0.05	530.6	531.5	532.2	533	534

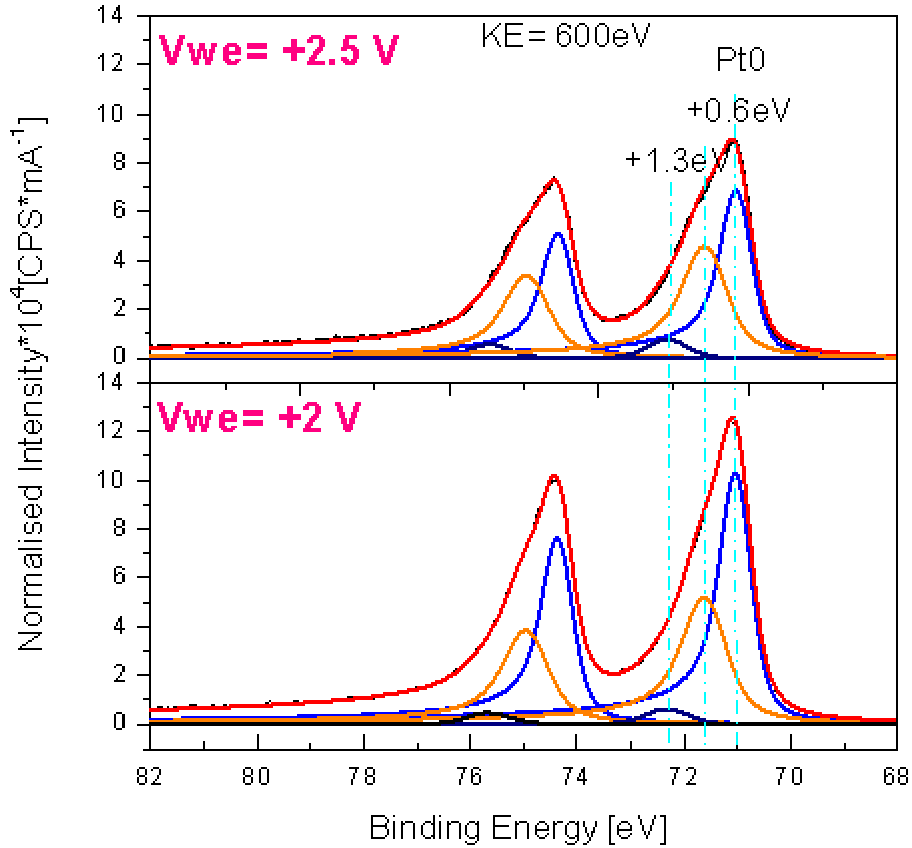
[1]S. Yamamoto, Journal of physics: condensed matter **2008,** 20, 184025
[2]M. Salmeron, Faraday discussion, **2009**, 141, 221-229

In-situ XPS during OER: Pt4f

KE= 150 eV



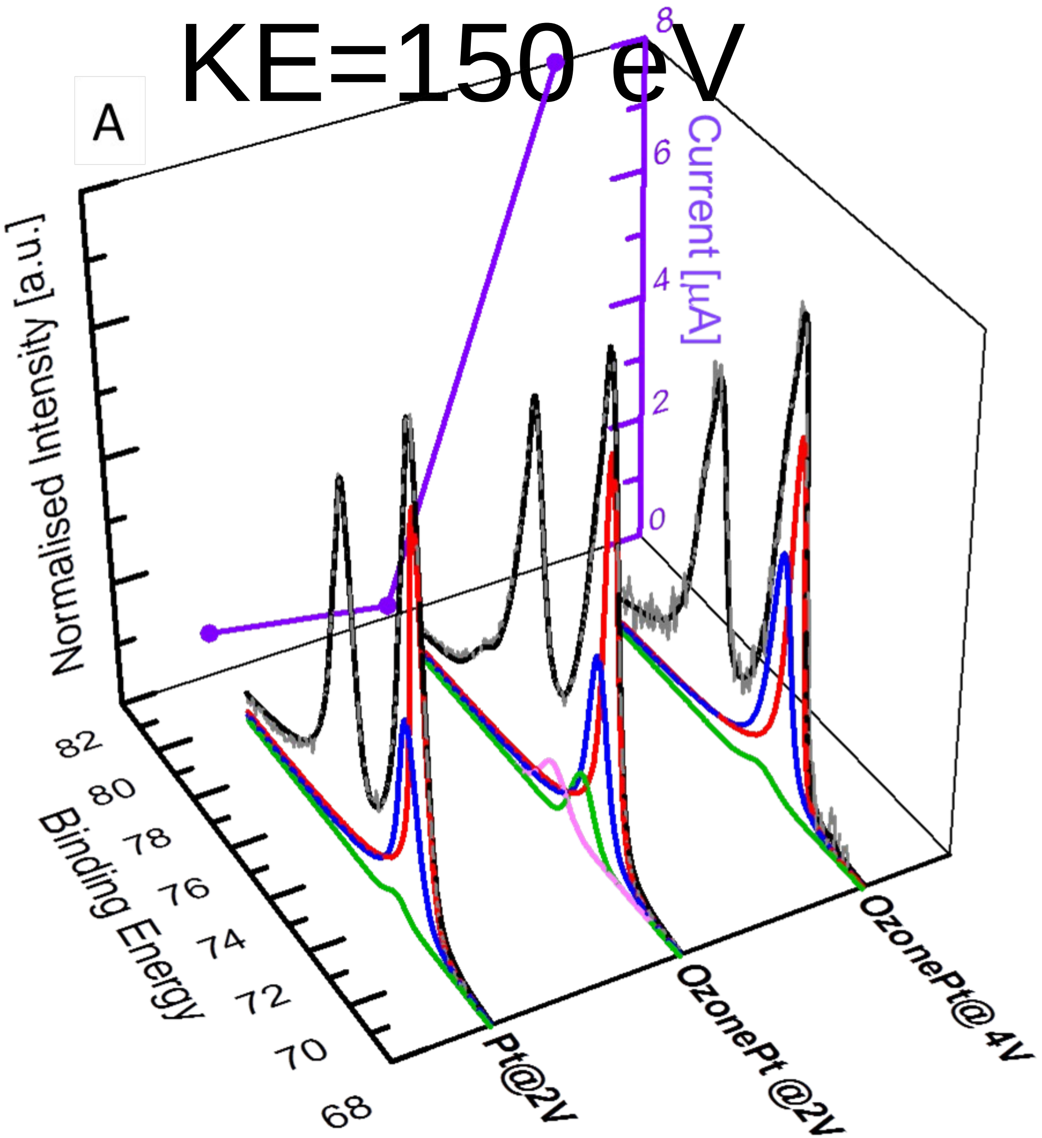
KE= 600 eV



Pt0= 71 eV
Pt(1)=71.6eV electronically modified Pt species due to O
Pt(2)= 72.3 eV (Pt2+)

Specie	Pt0	Pt 1	Pt 2
BE [eV] +/-0.05	70.95	+ 0.6	+1.3

In-situ XPS: three electrodes

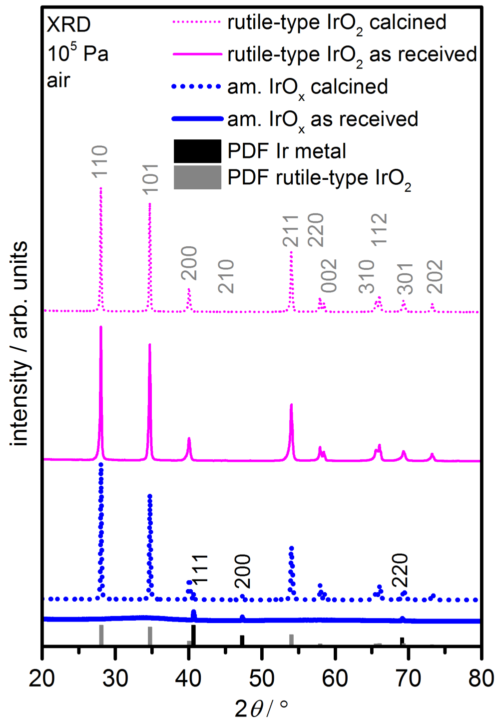


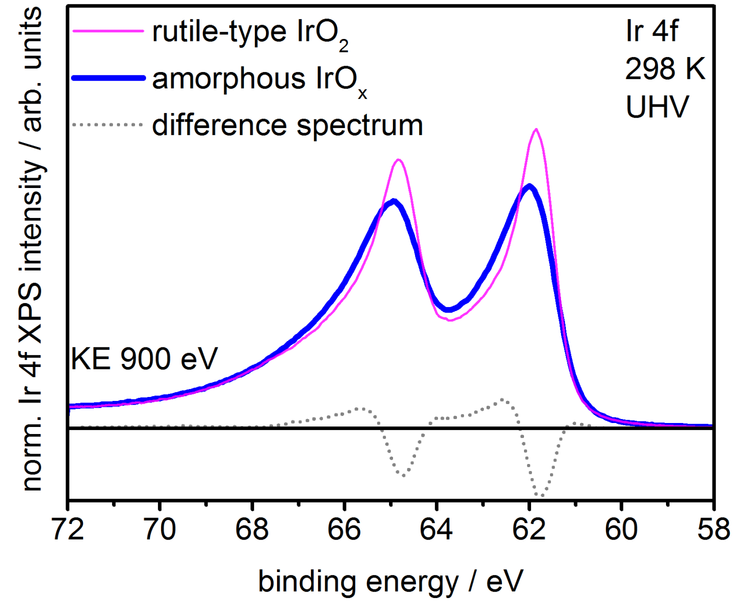
R. Arrigo et al., Angew. Chemie 2013

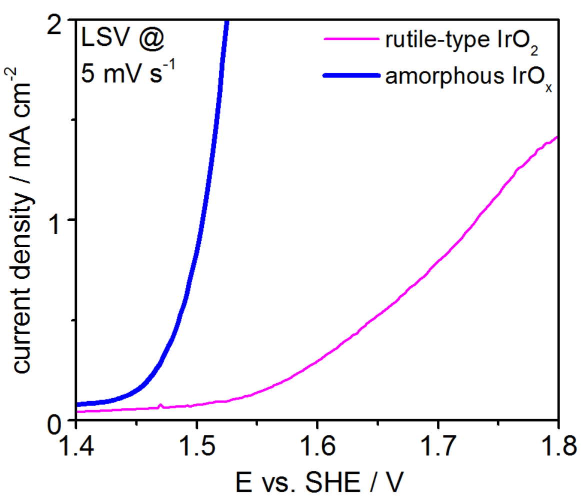
Summary

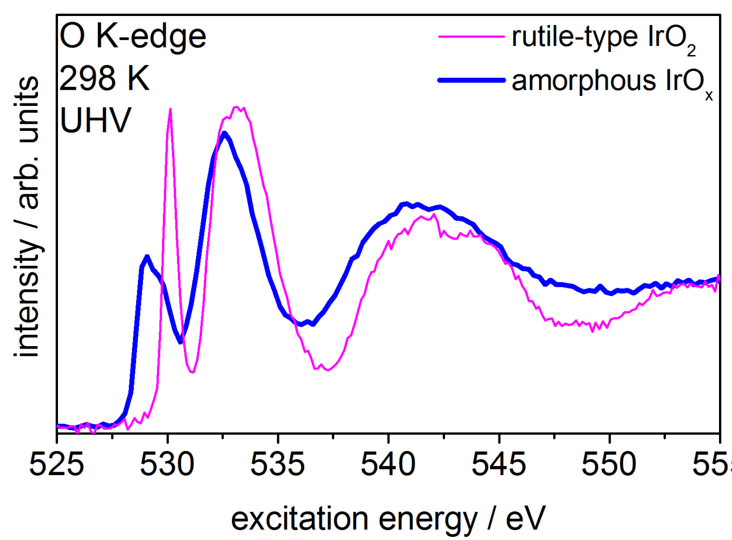
- The designed cell is suitable for investigating electrochemical processes
- The QMS and XPS shows the response of the system when switching from open circuit potential to OER or HER
- The initial state of Pt film contains beside Pt0 a Pt$\delta+$ component ΔBE +0.6 eV attributed to electronically modified Pt by O species.
- Increasing the potential from 2 to 2.5 V increase the Pt$\delta+$ as well as the Pt2+ component (ΔBE +1.3 eV) as consequence of the enhancement of the oxygen population.
- The presence of Pt2+ species is not beneficial for OER. OER rate is related to the Pt$\delta+$

OER-active and -inactive iridium oxides



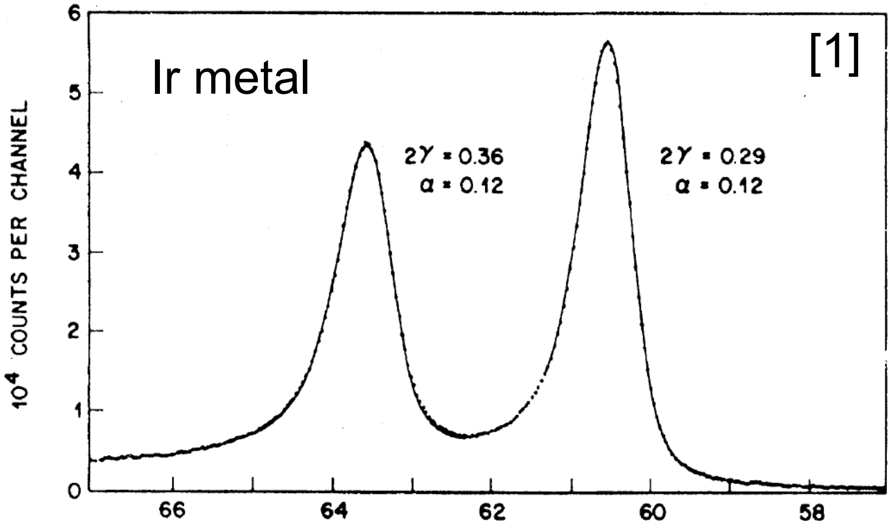


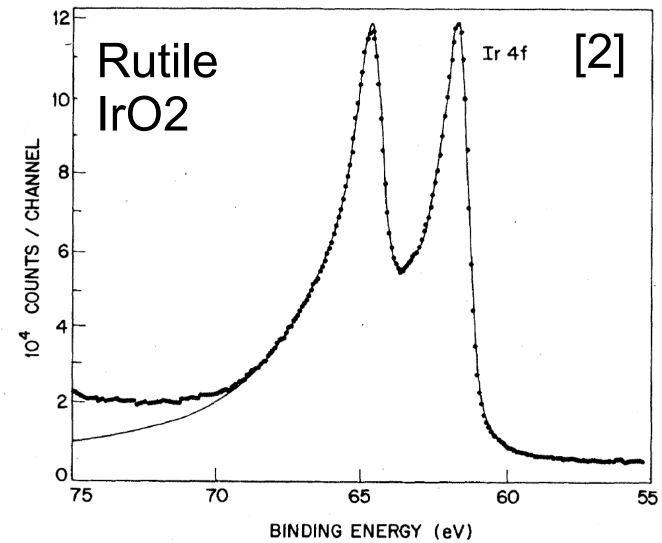




Surf. Interface Anal. 2016

How to describe the electronic structure of iridium and its oxides? Literature overview

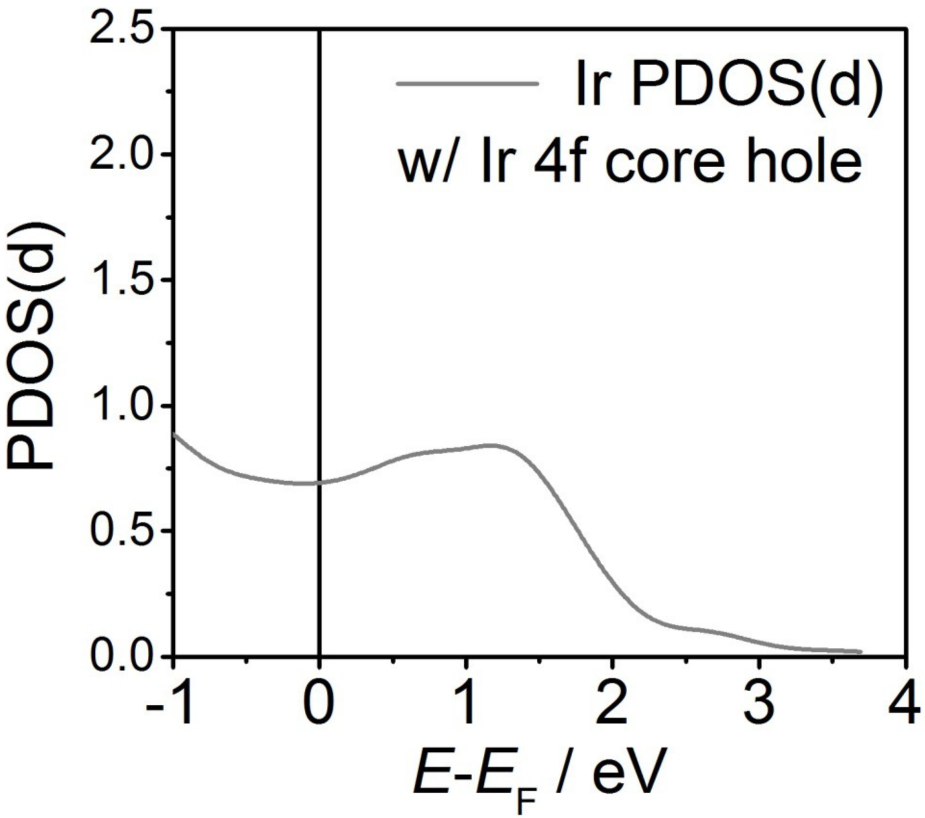




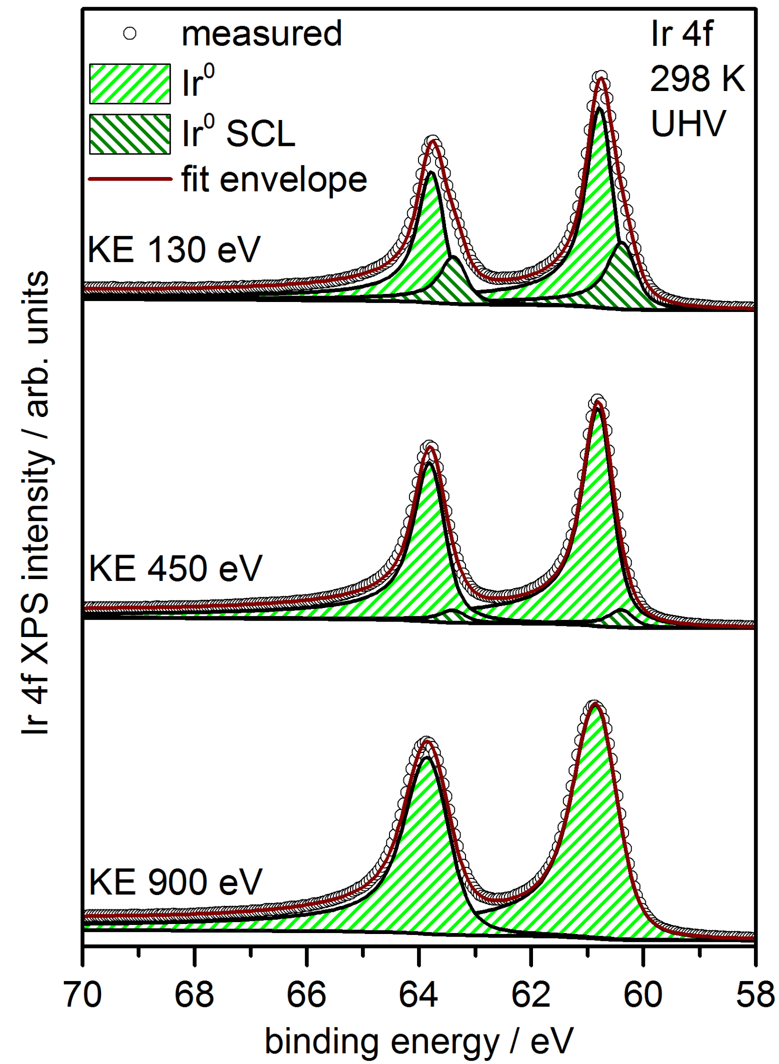
[1]G. K. Wertheim, S. Hüfner, *Phys. Rev. Lett.* **1975**; *35*, 53. [2]G. K. Wertheim, H. J. Guggenheim, *Phys. Rev. B* **1980**; *22*, 4680.

How to describe the electronic structure of iridium and its oxides?
Ir metal: DS line shape holds

Calculation



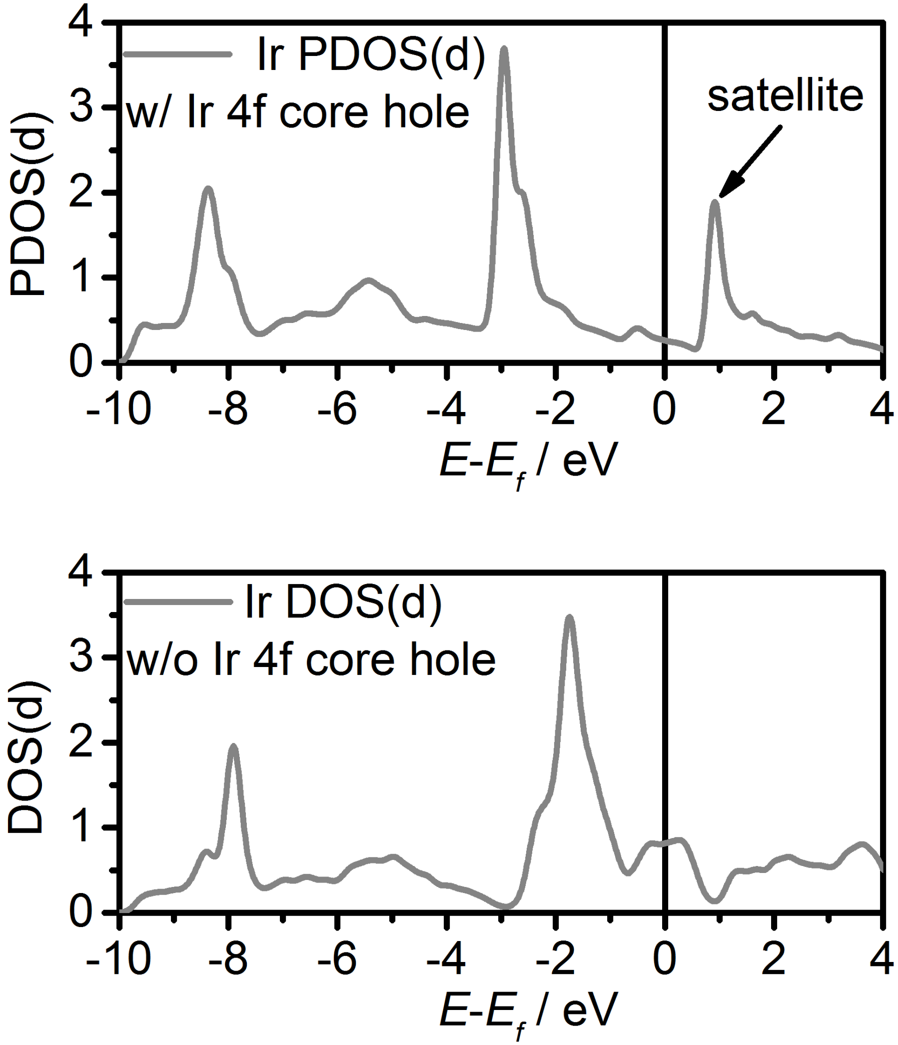
Experiment



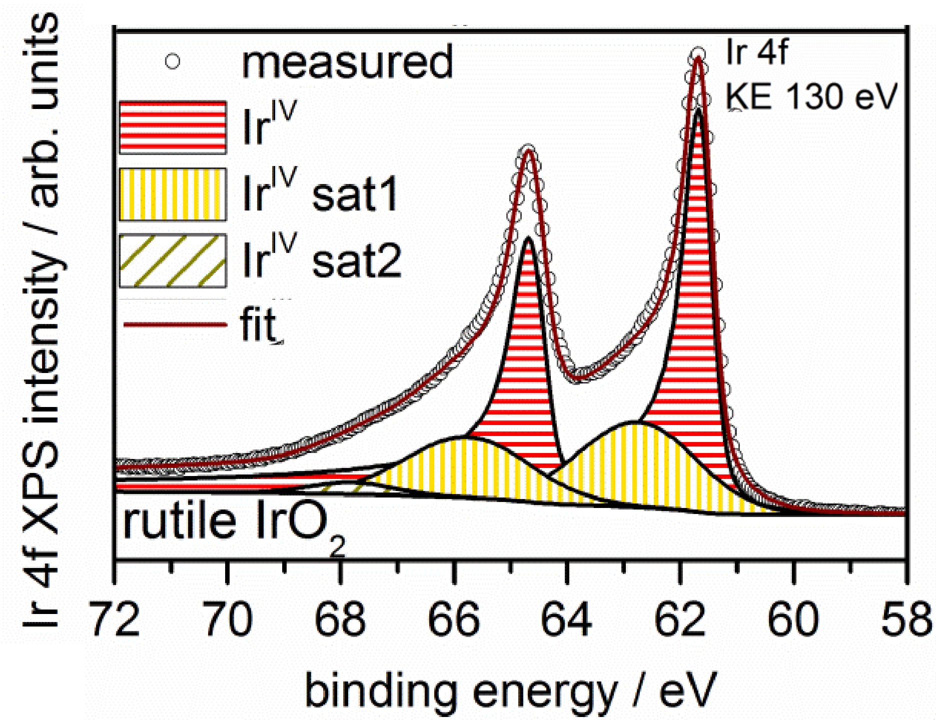
Surf. Interface Anal. 2016

How to describe the electronic structure of iridium and its oxides?
Rutile-type IrO2: DS line shape complemented with satellites

Calculation



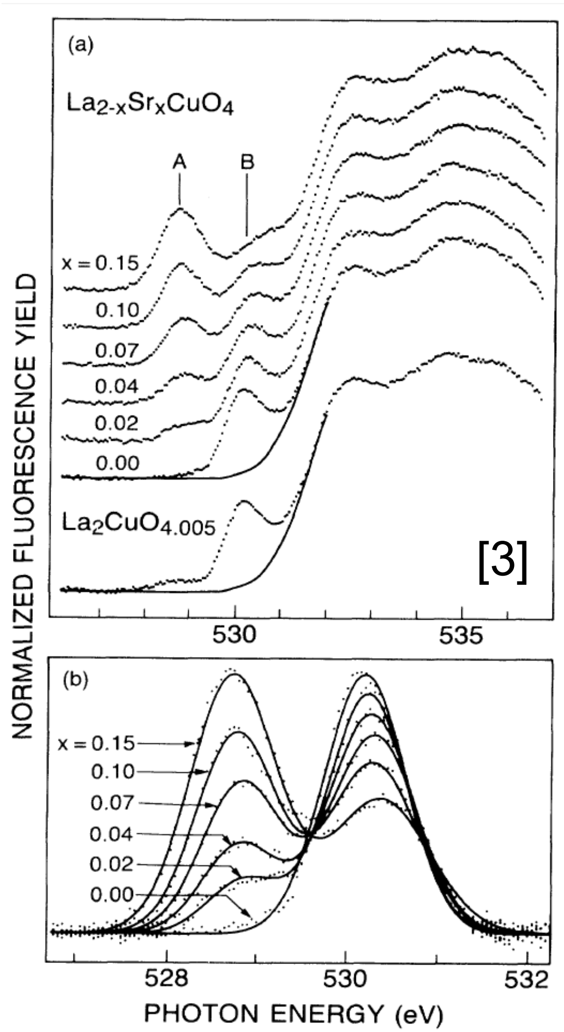
Experiment



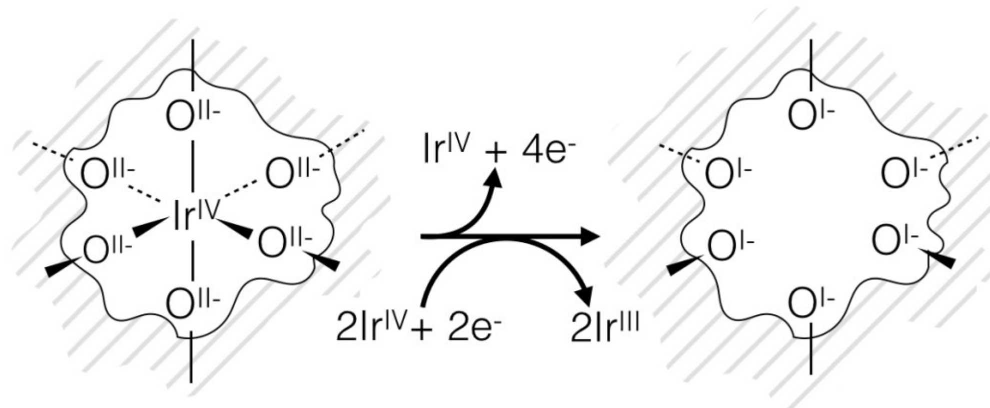
Surf. Interface Anal. 2016

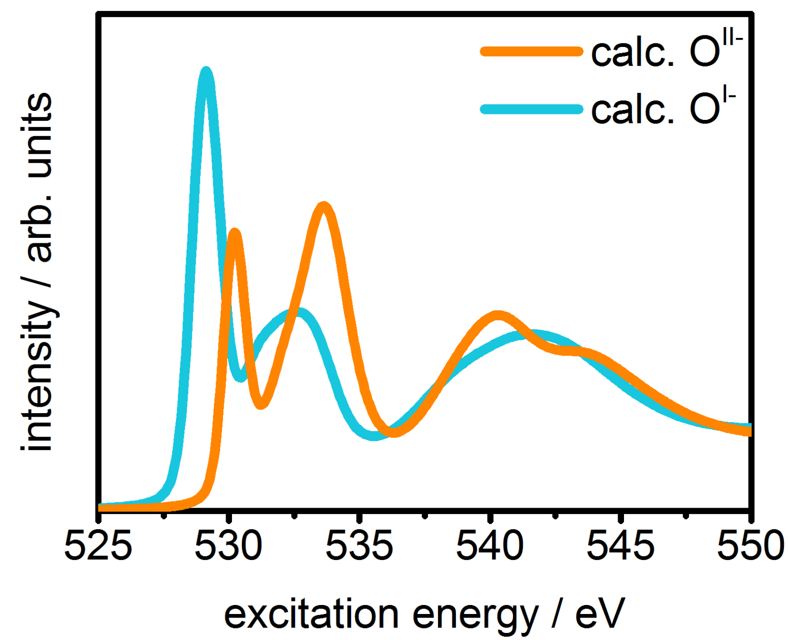
Hole doping: origin of absorption pre-edge feature

Hole doping in superconductors



Defect model for iridium oxide

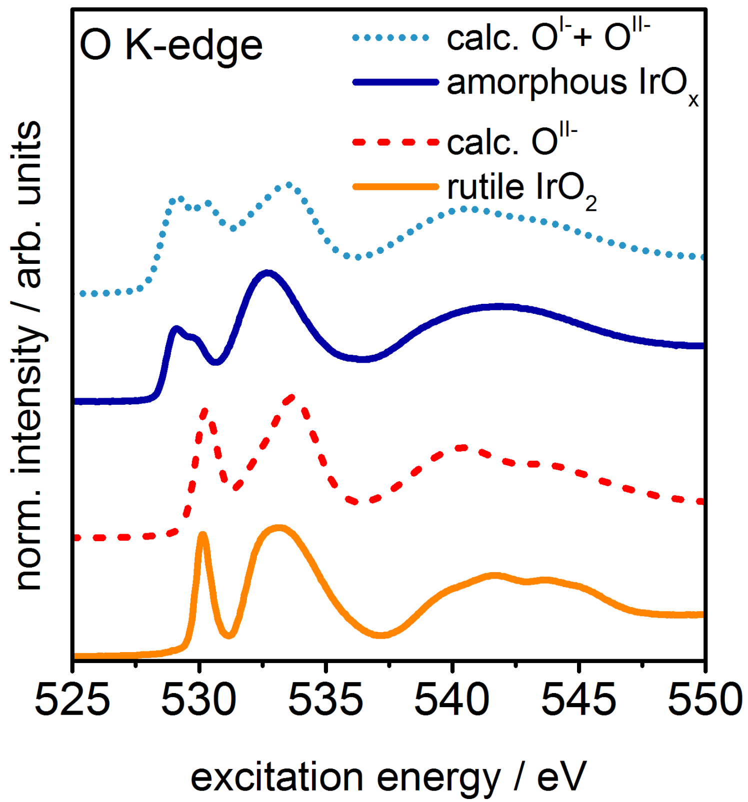


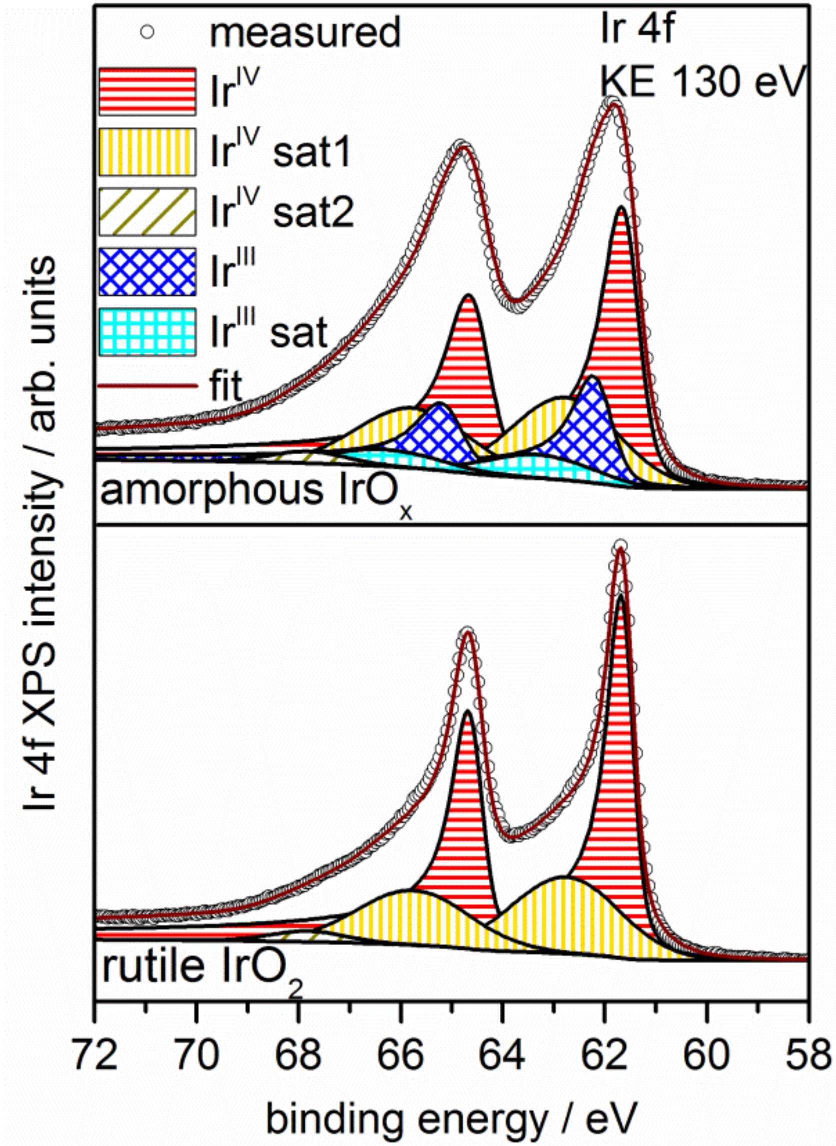


[3]C. T. Chen *et al.*, *Phys. Rev. Lett.* **1991**; *66*, 104.

Surf. Interface Anal. 2016

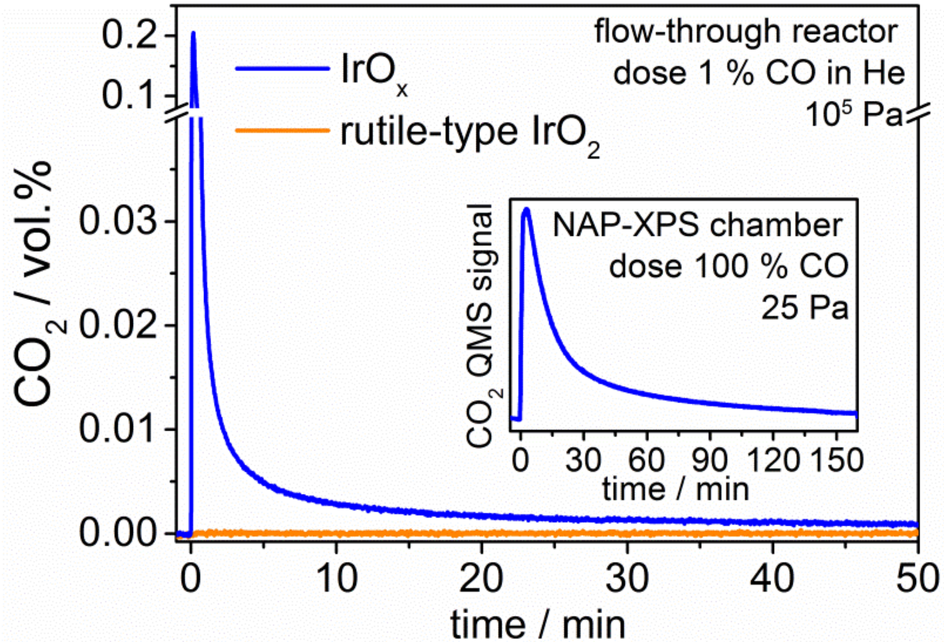
How to describe the electronic structure of iridium and its oxides?
Amorphous IrOx: Electronic defects in anionic and cationic framework

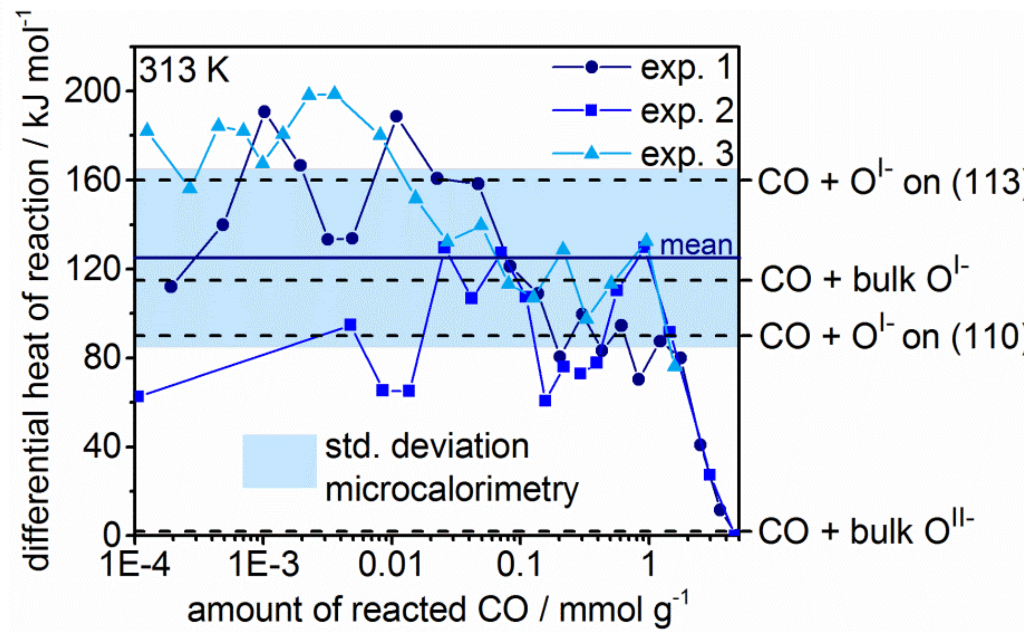




Surf. Interface Anal. 2016

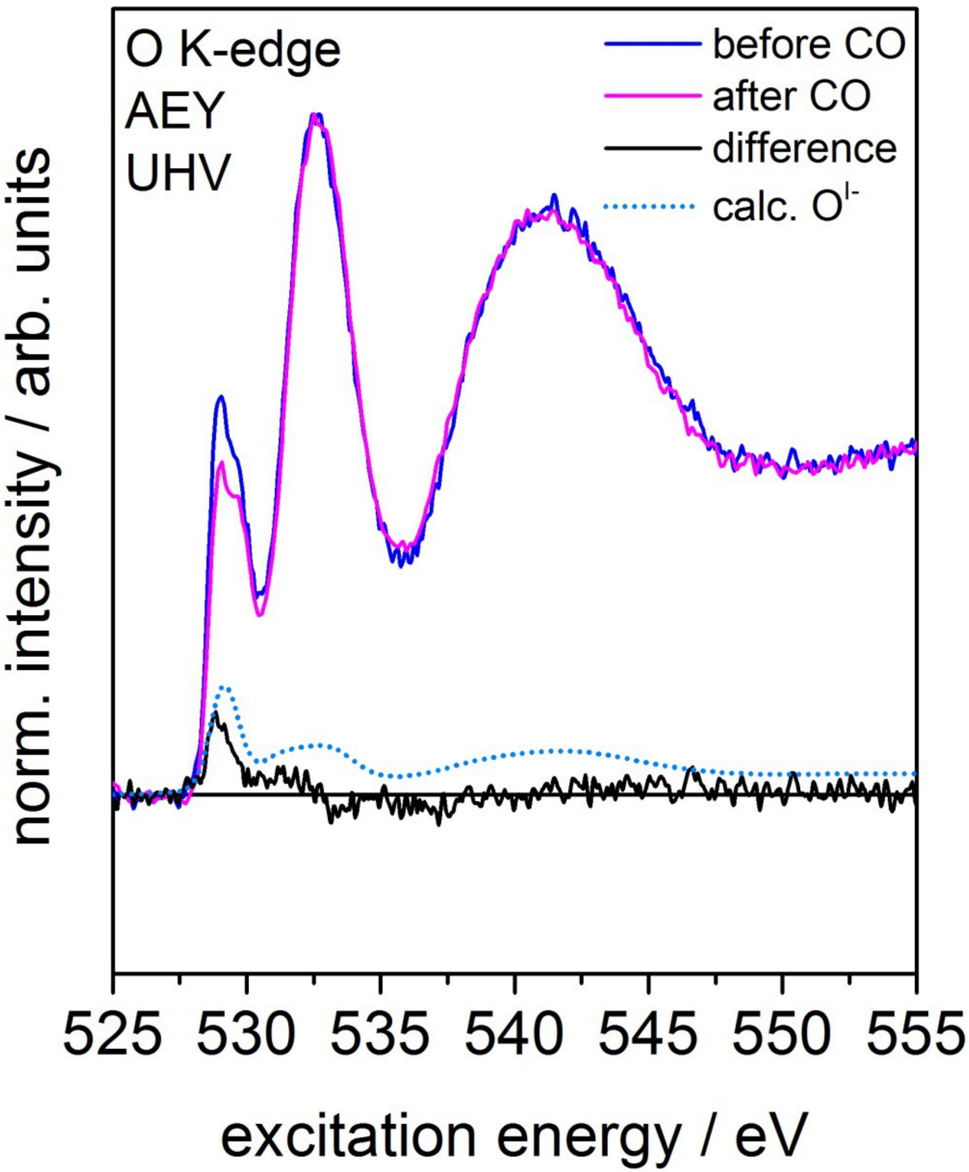
OER-active IrOx oxidizes CO at room temperature without externally dosed O2

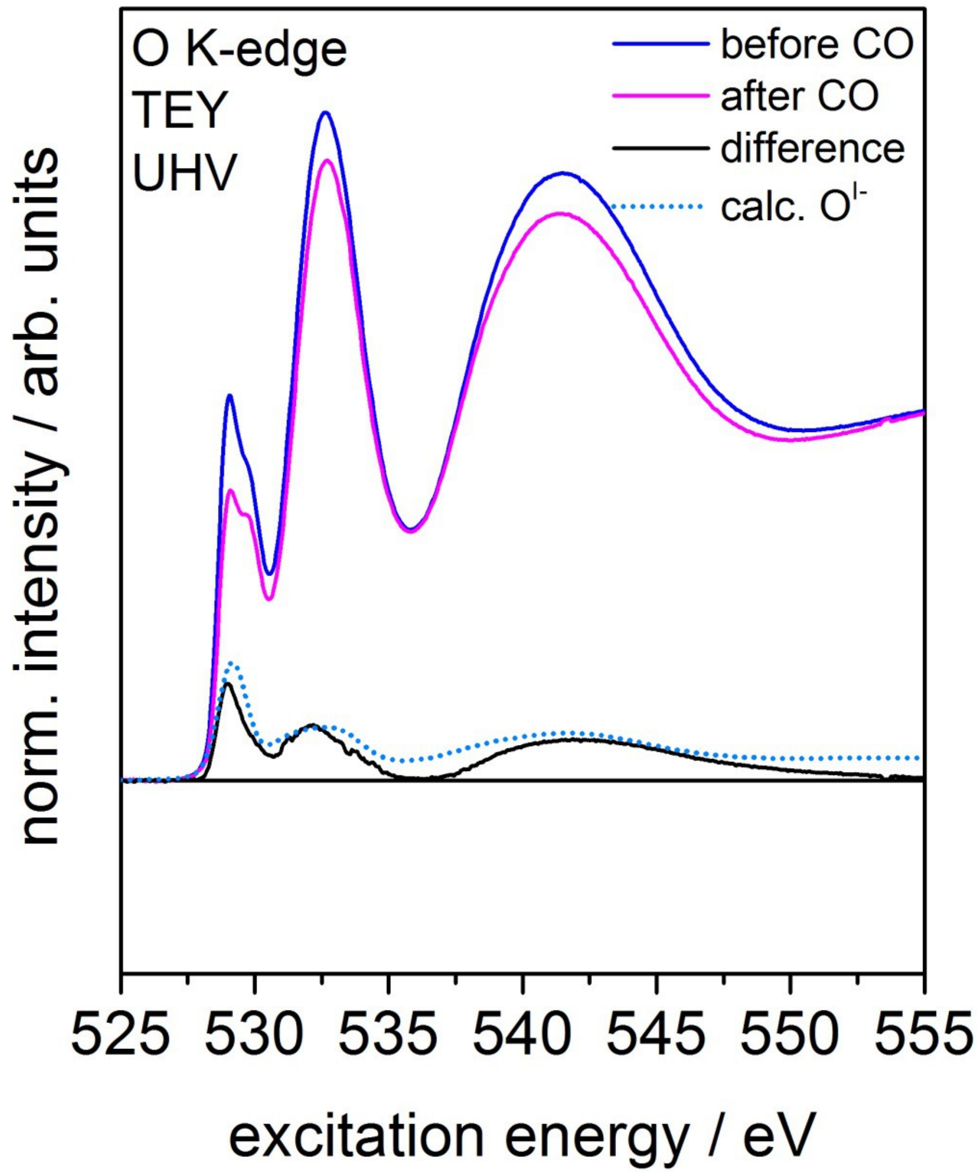




Chem. Sci. 2016

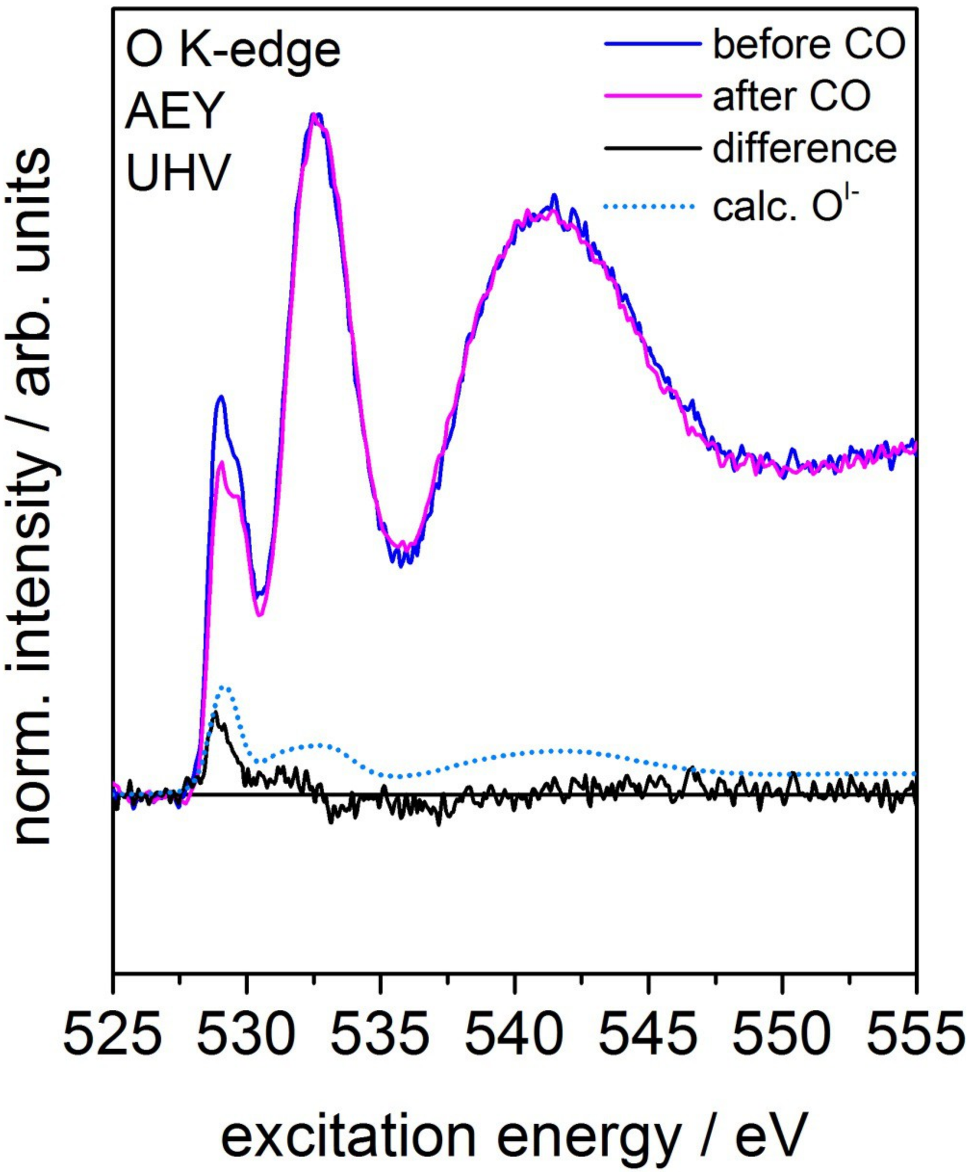
CO experiments on amorphous IrOx
NEXAFS

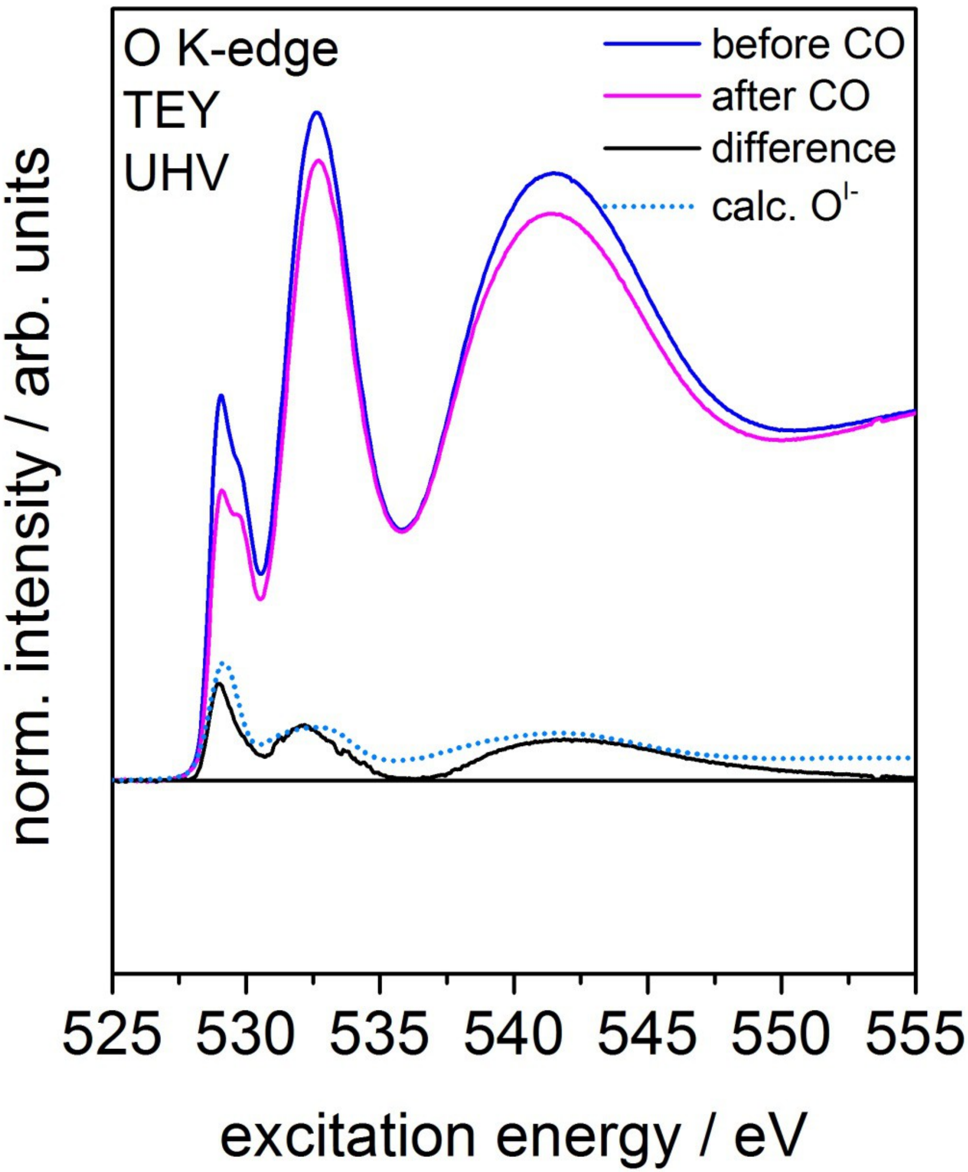




Chem. Sci. 2016

CO experiments on amorphous IrOx
NEXAFS

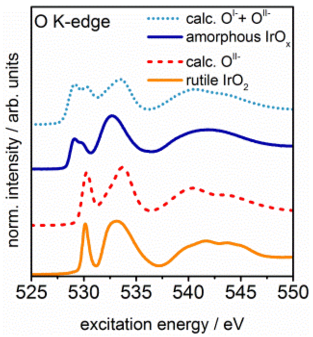


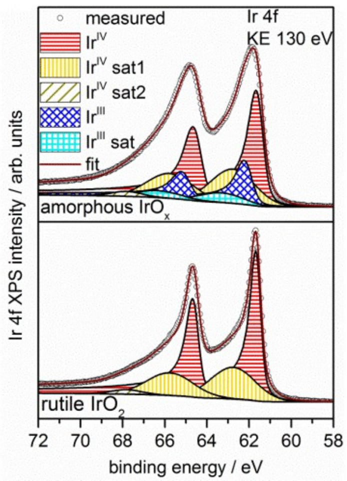


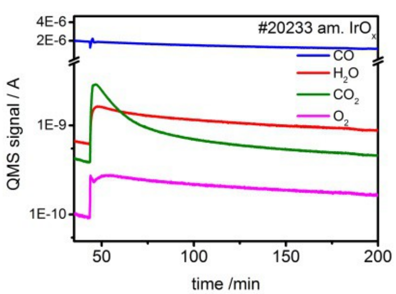
Chem. Sci. 2016

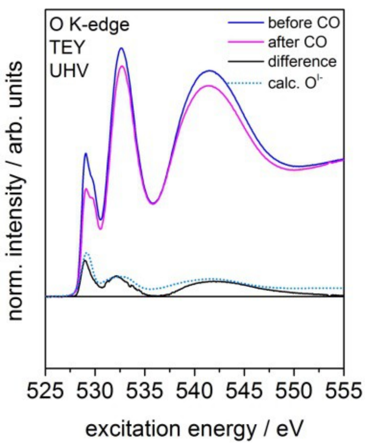
Summary

- Electronic structure of iridium metal, rutile-type IrO2, and of an amorphous IrOx has been described
- Electronic defects in the anionic and cationic framework seem to favor OER activity
- MS and microcalorimetry have shown that amorphous IrOx oxidizes CO at low temperatures (starting at ~230 K)
- NEXAFS reveals concomitant decrease of pre-edge feature at ~529 eV



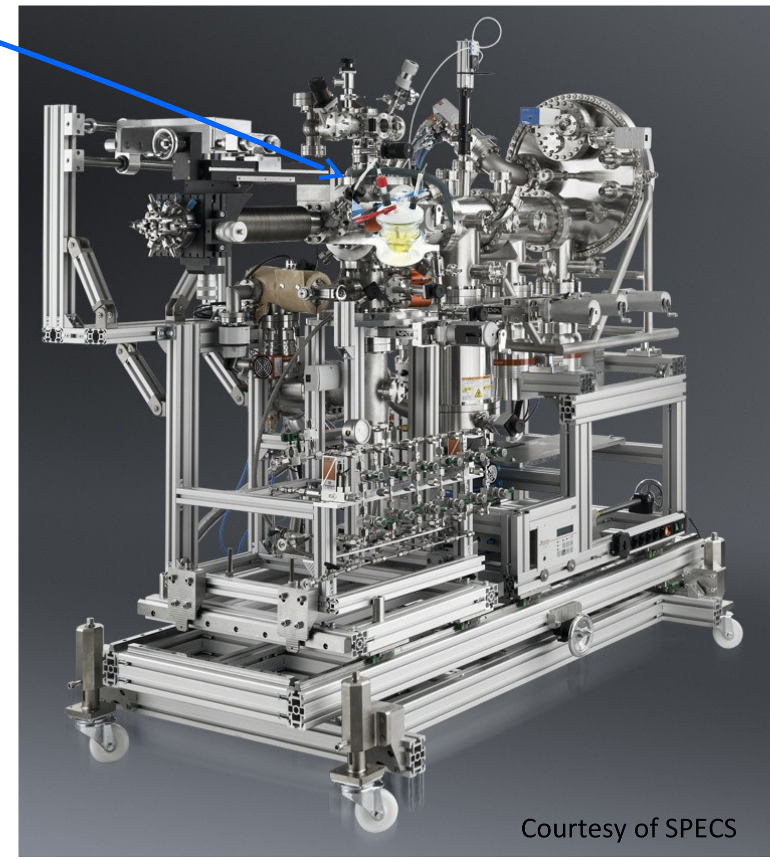






Identifying OER-active iridium oxide surface species

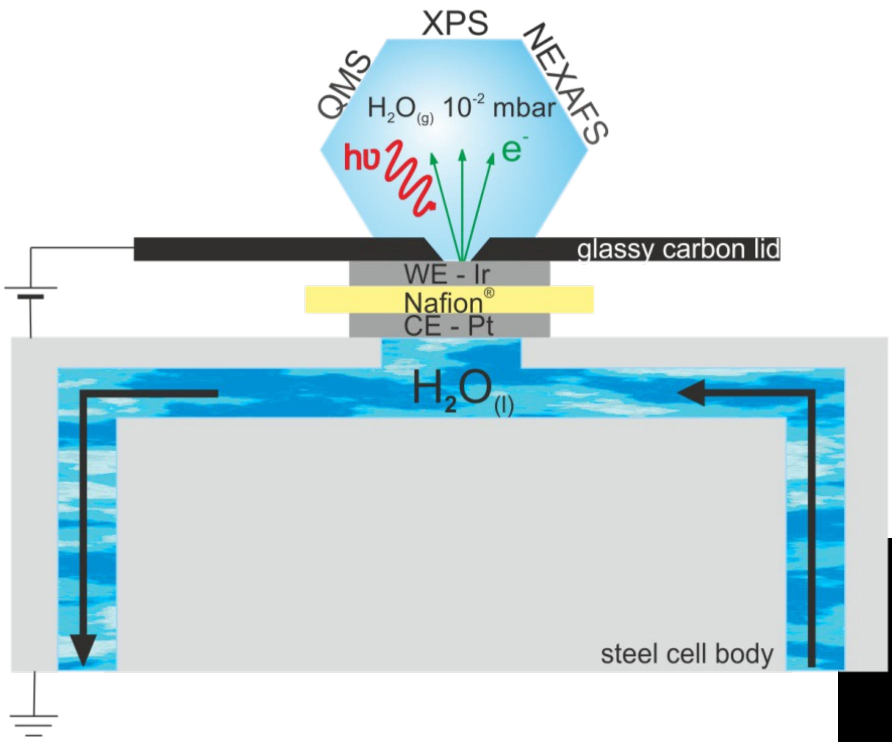
http://www.bio-logic.info/instruments/potentiostat-sp-200/



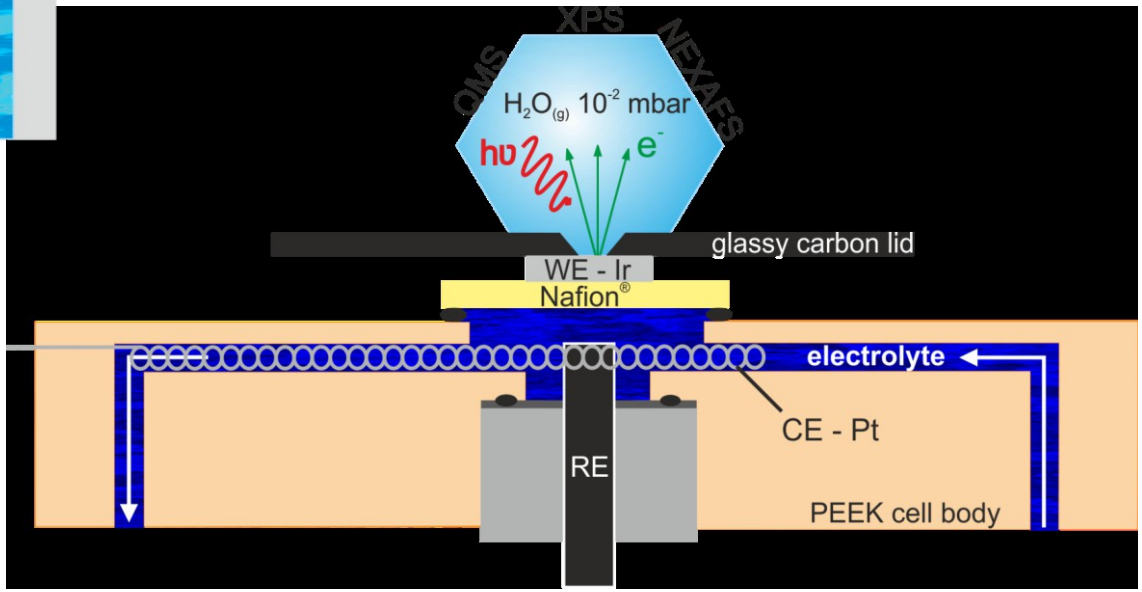
Courtesy of SPECS

Nafion®-based cell concepts for *in-situ* XPS and NEXAFS

2-electrode cell

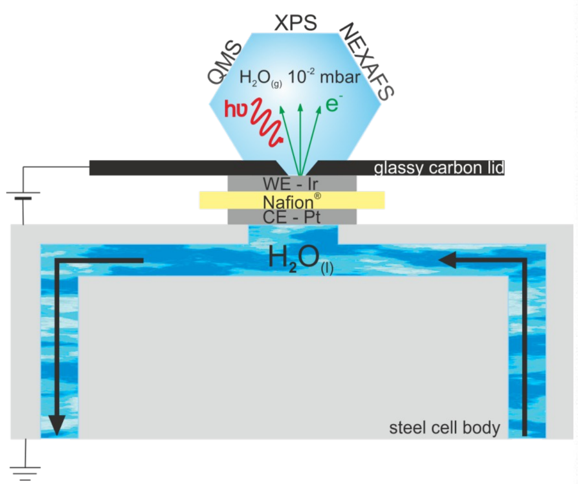


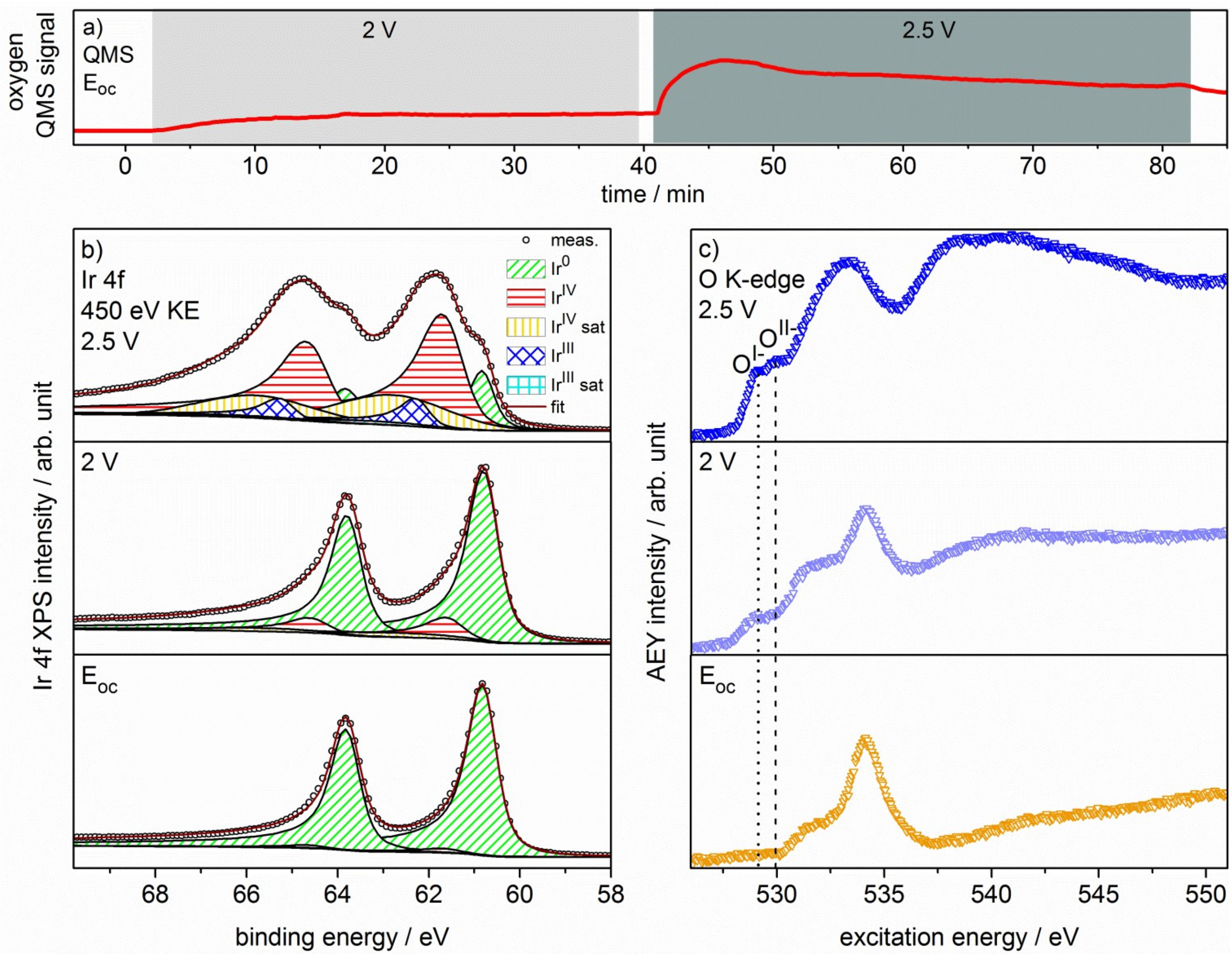
3-electrode cell



Ir/Pt-coated Nafion® in 2-electrode setup during OER

#18111:
Ir-coated Nafion® 117
sputter time: 120 s
electrolyte: H2O/Nafion
p:5*10-2 mbar
ring currentNEXAFS: 300 mA

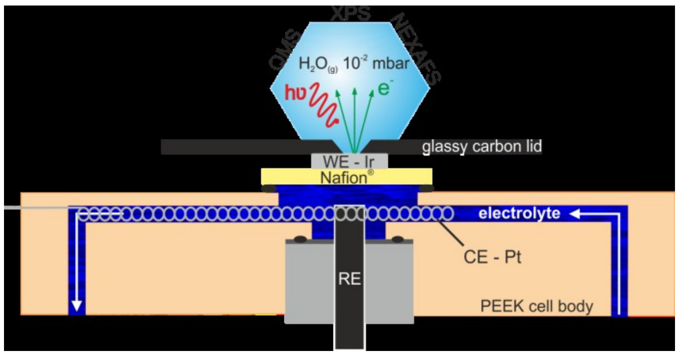


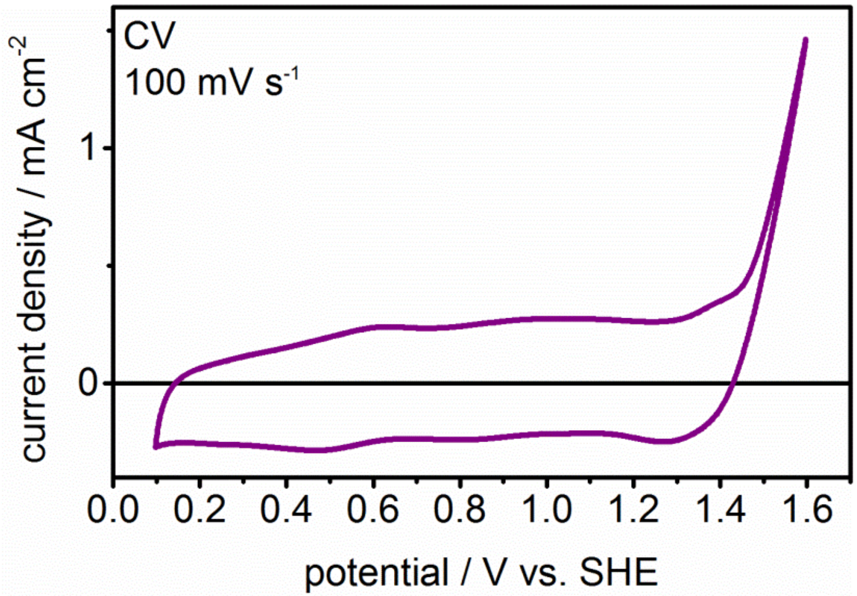


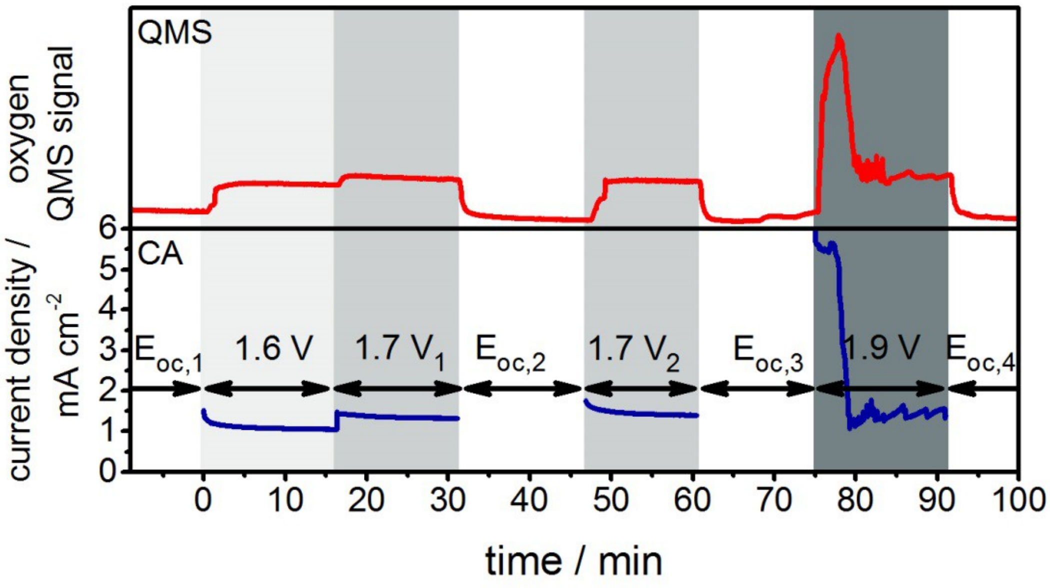
Submitted to Chem. Science

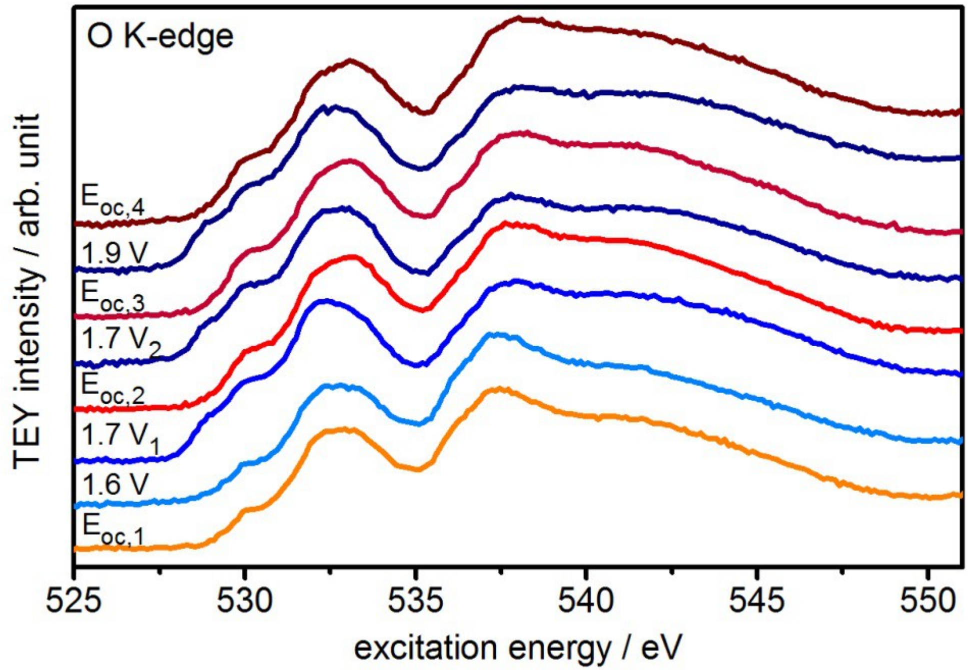
Ir-coated Nafion® in 3-electrode setup during OER

#23898:
Ir-coated Nafion® 117
sputter time: 60 s
electrolyte: 0.1 M H2SO4
pNEXAFS:4.5*10-3 mbar
ring currentNEXAFS: ~13 mA









Ir-coated Nafion® in 3-electrode setup during OER

#23894:

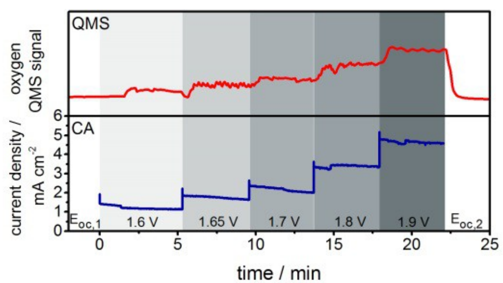
Ir-coated Nafion® 117

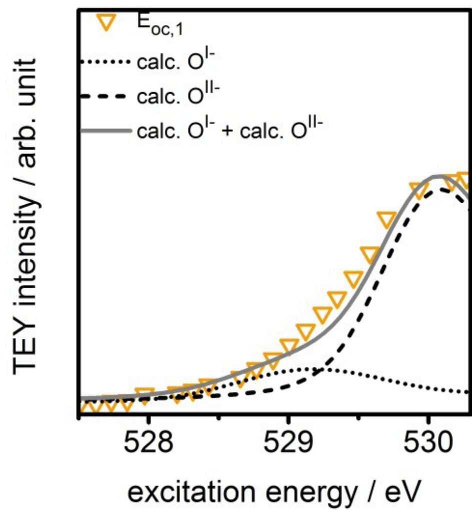
sputter time: 180 s

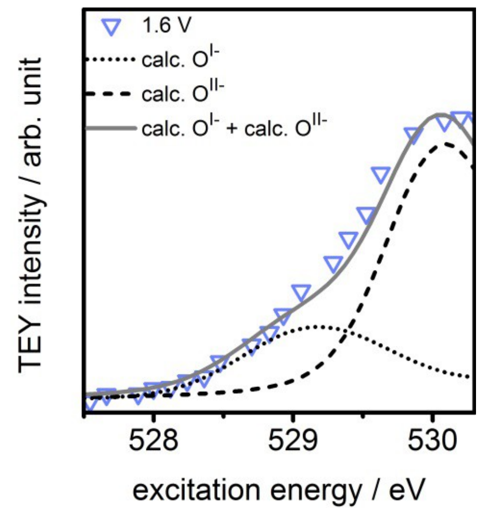
electrolyte: 0.1 M H2SO4

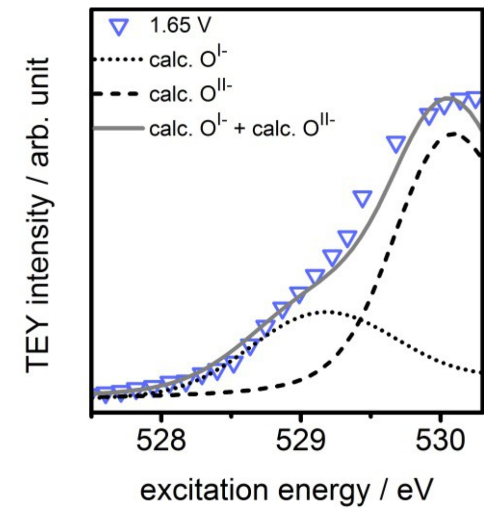
pNEXAFS:5*10-3 mbar

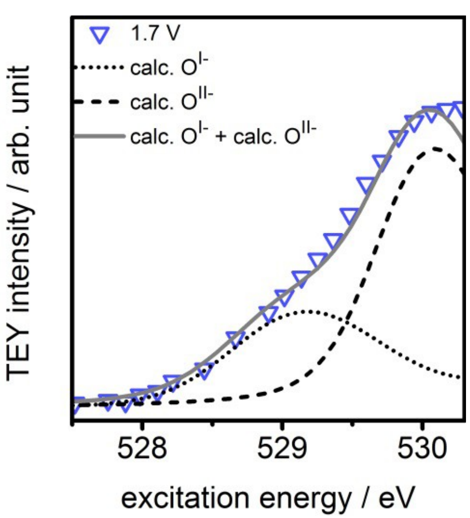
ring currentNEXAFS: ~70 mA

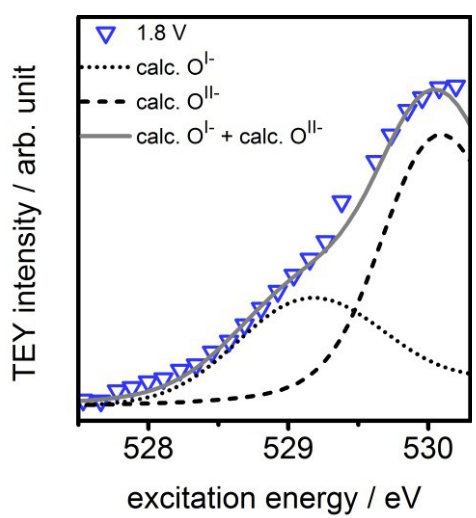


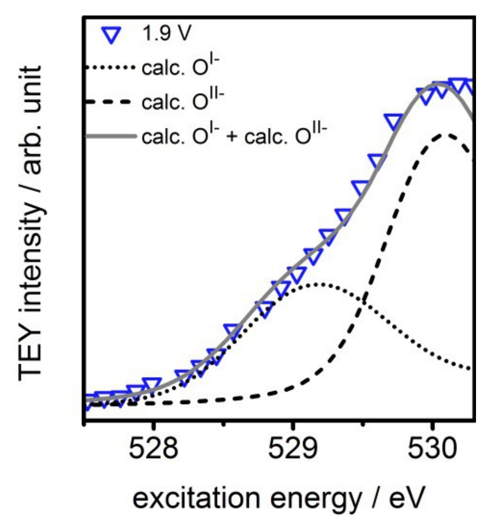


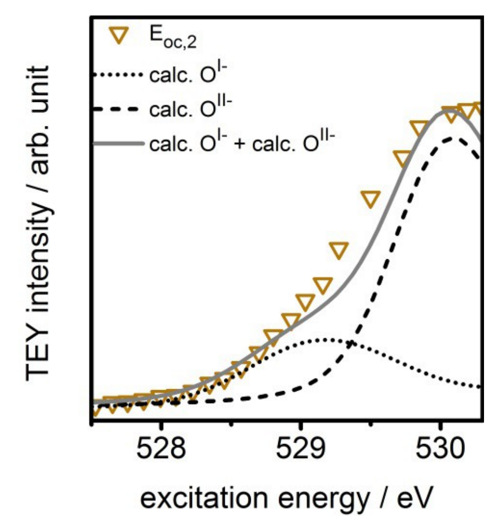








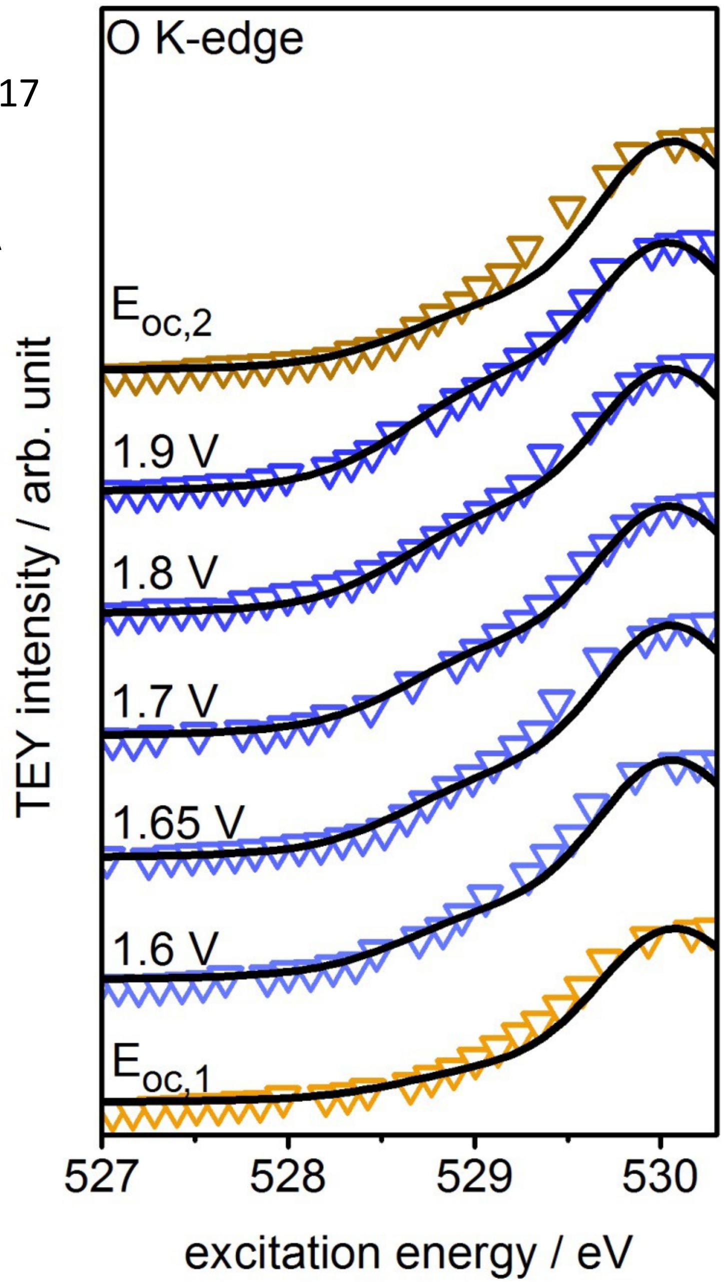


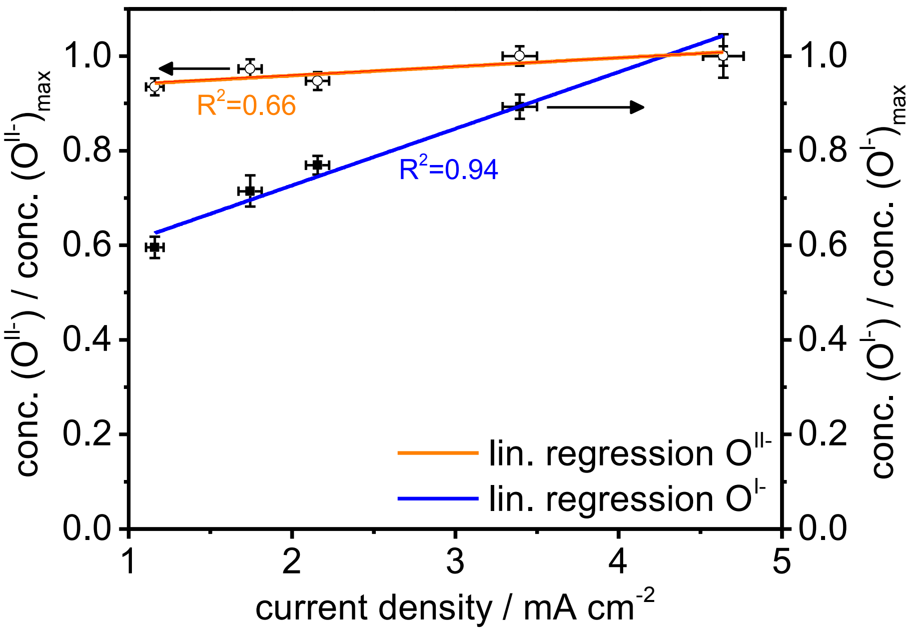


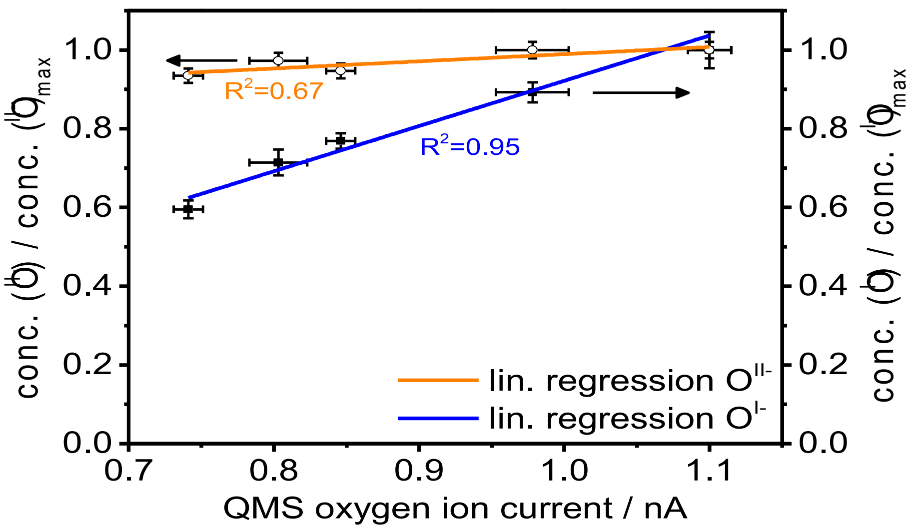
Chem. Science 2017

Ir-coated Nafion® in 3-electrode setup during OER

#23894:
Ir-coated Nafion® 117
sputter time: 180 s
electrolyte: 0.1 M H2SO4
pNEXAFS:5*10-3 mbar
ring currentNEXAFS: ~70 mA

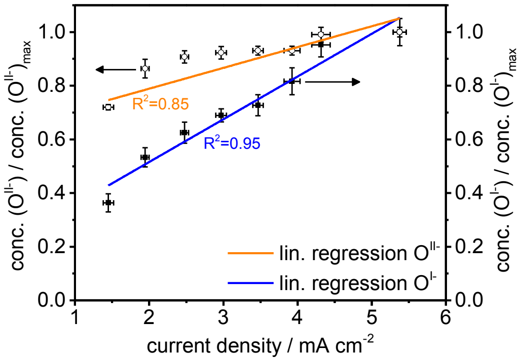






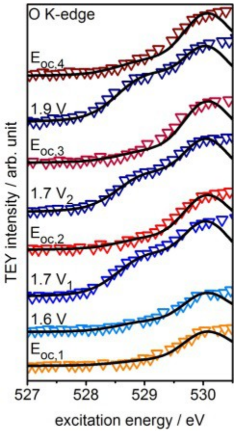
Chem. Science 2017

What we have learnt from in situ measurements



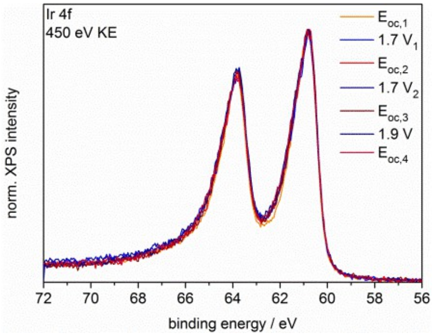
... rough linear relationship between OI- concentration and current density is observed

... part of OI- and also OII- are switched on and off with potential

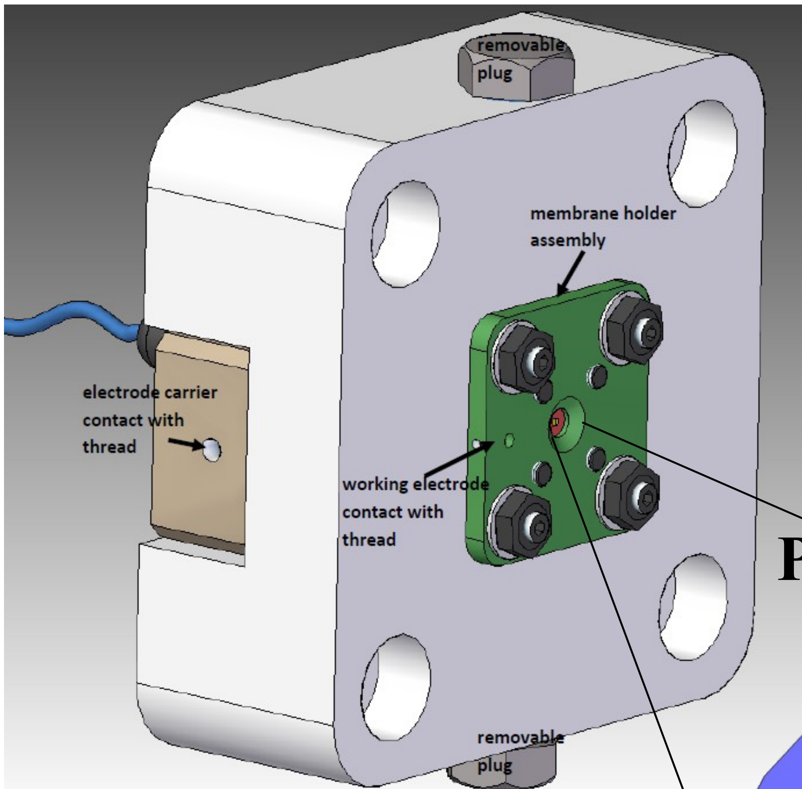


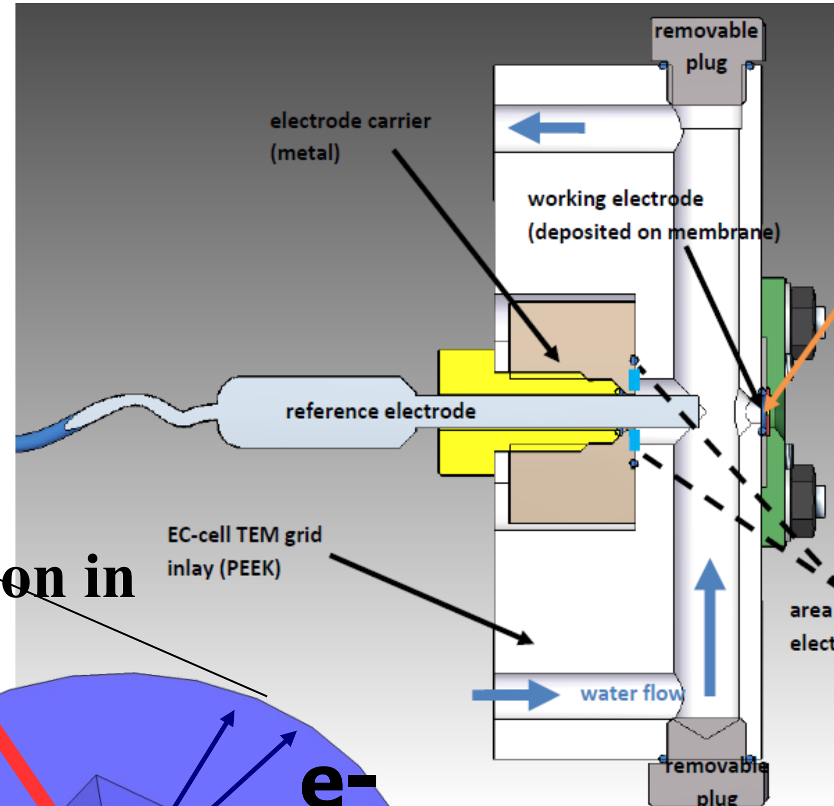
... O K-edge is sensitive probe to monitor OI- species

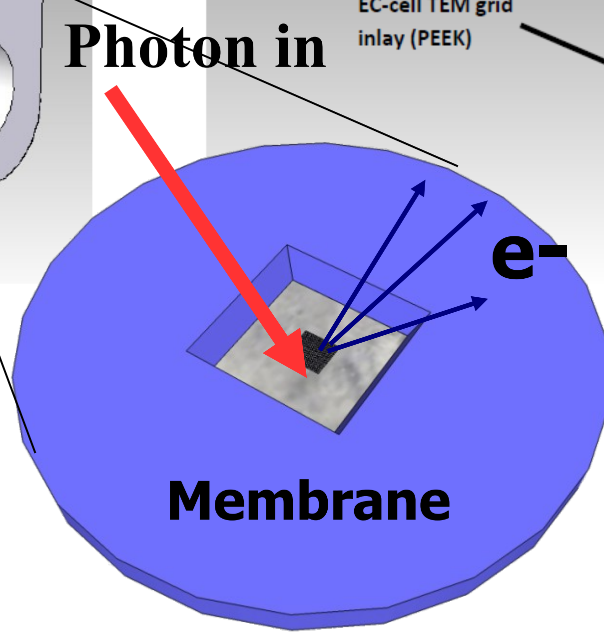
... only very subtle changes are observed in Ir 4f and O 1s XPS



New design: HPXPS cell

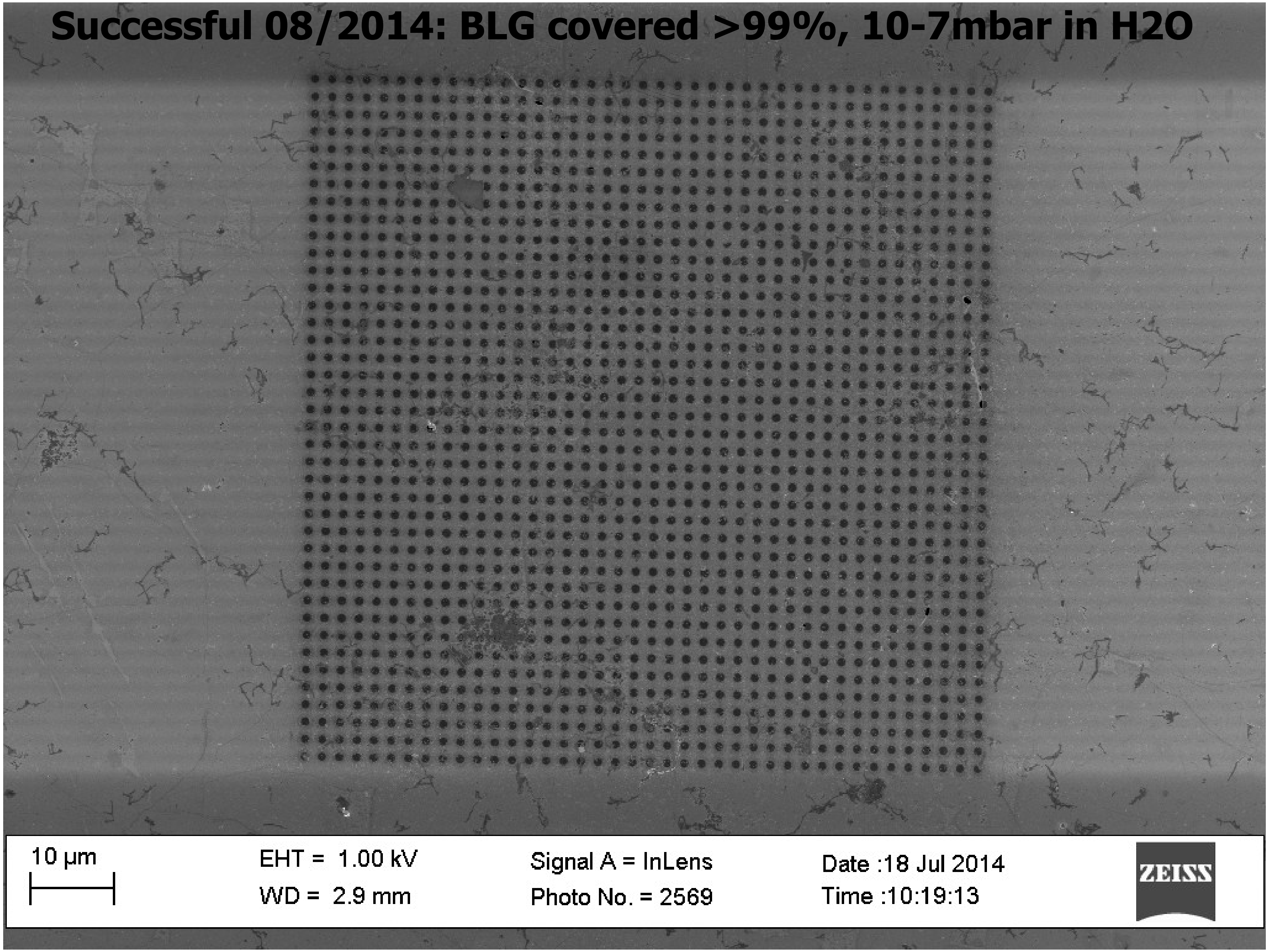




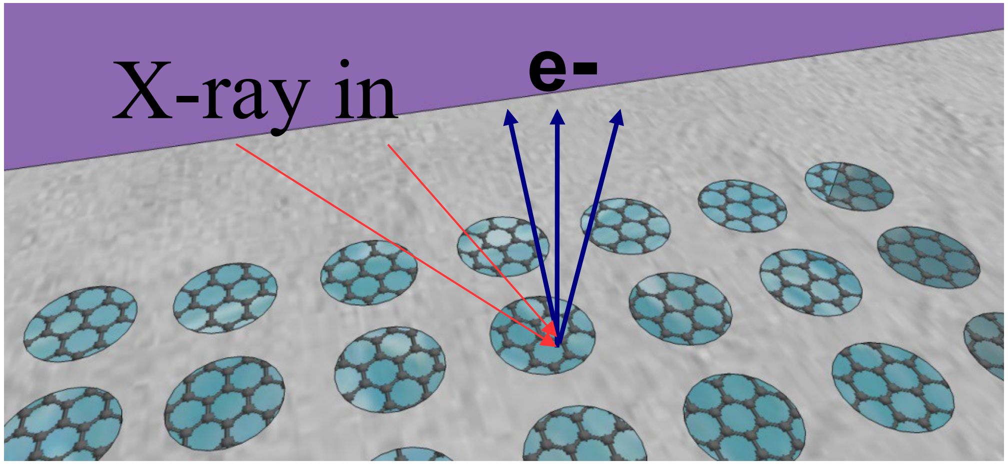


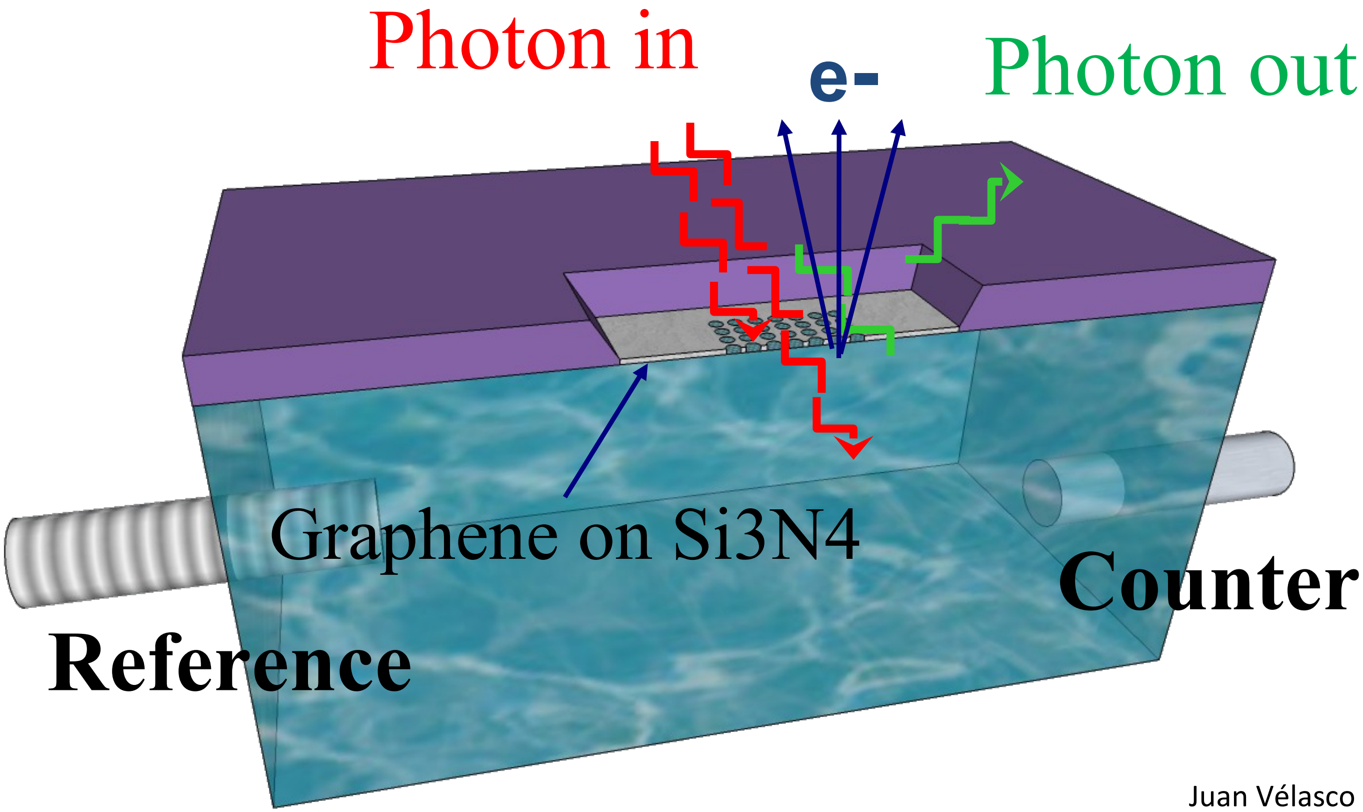
Juan Vélasco et al., Angew Chem. 2015

BLG coverage rate > 99%



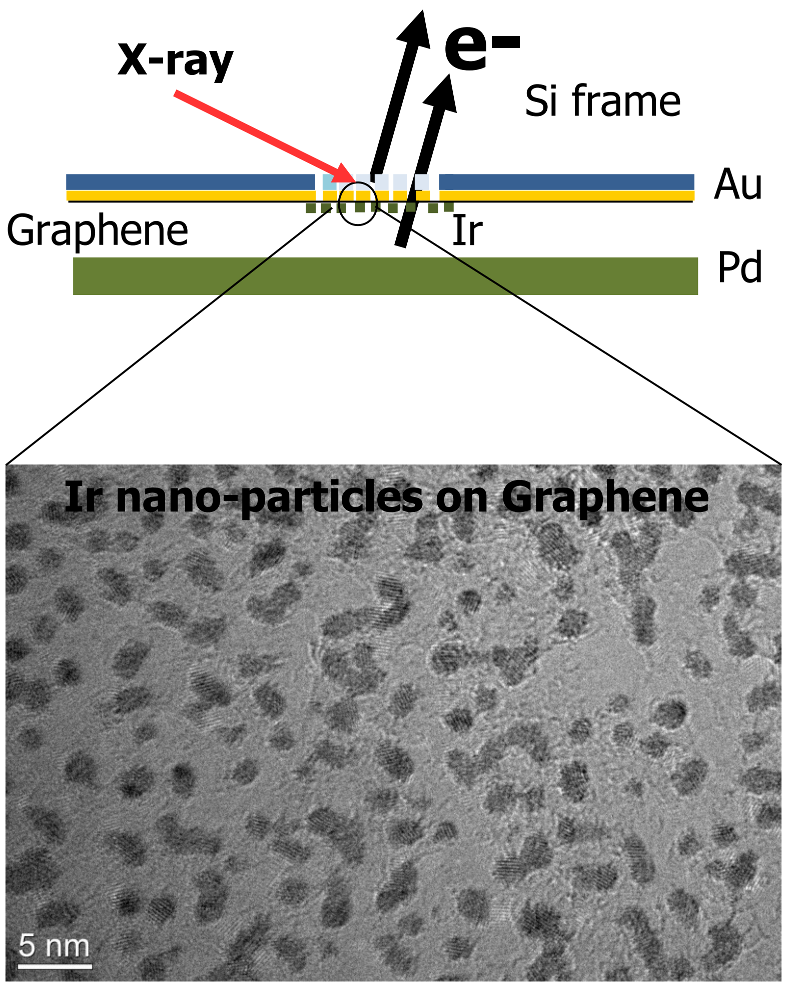
Graphene membrane

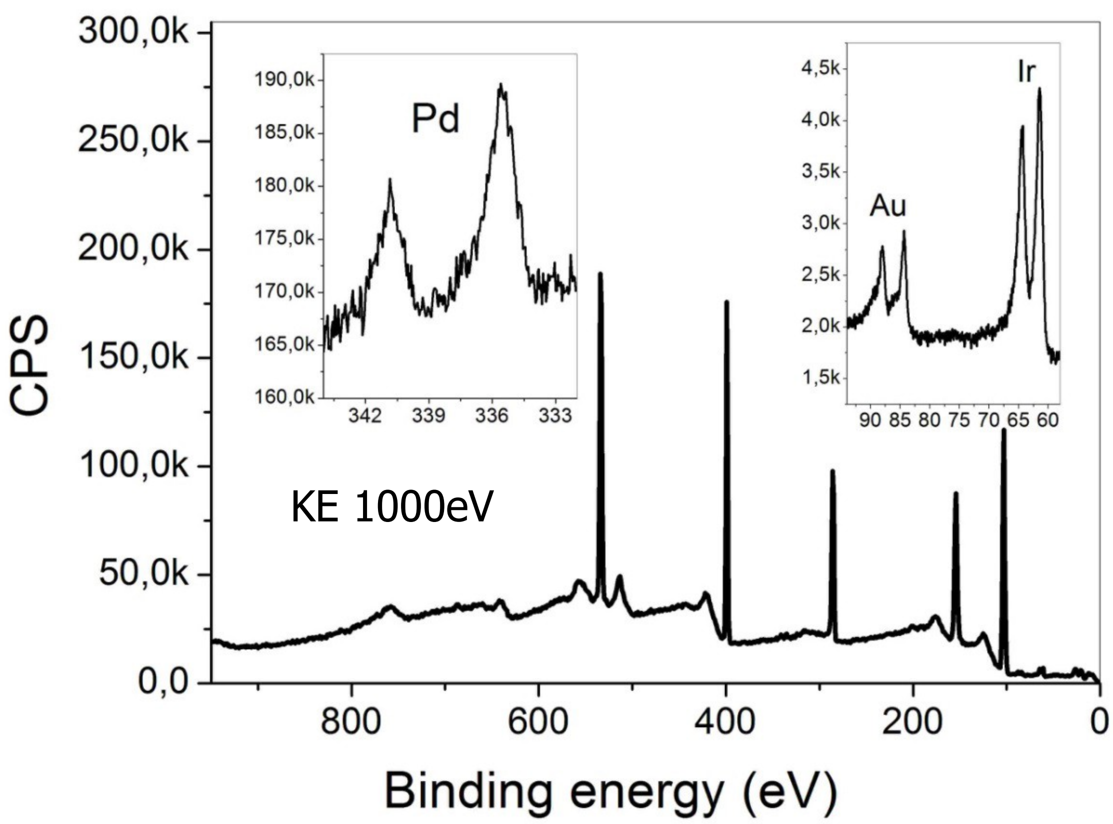




Juan Vélasco et al., Angew Chem. 2015

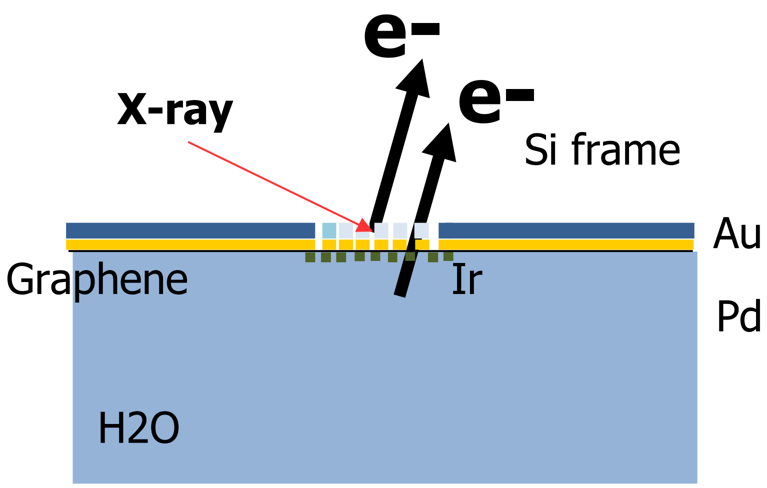
Pd UHV: Transmission test

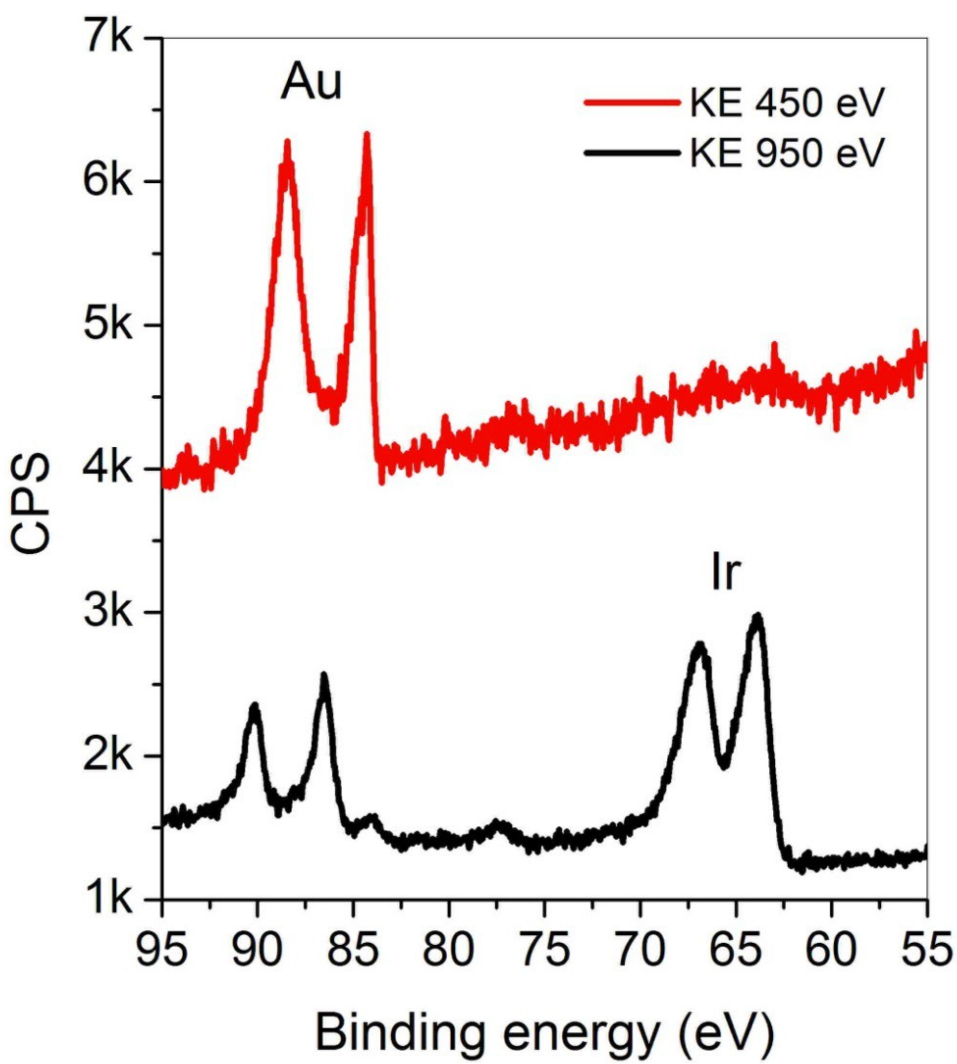




Juan Vélasco et al., Angew Chem. 2015

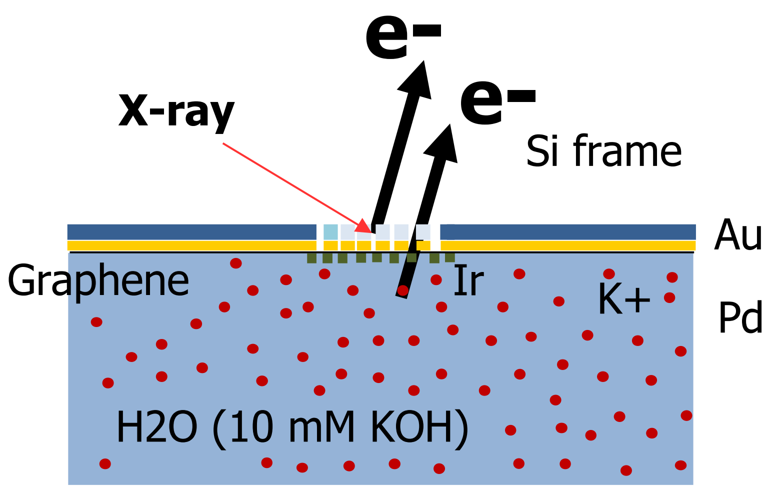
Cell filled with DI-water

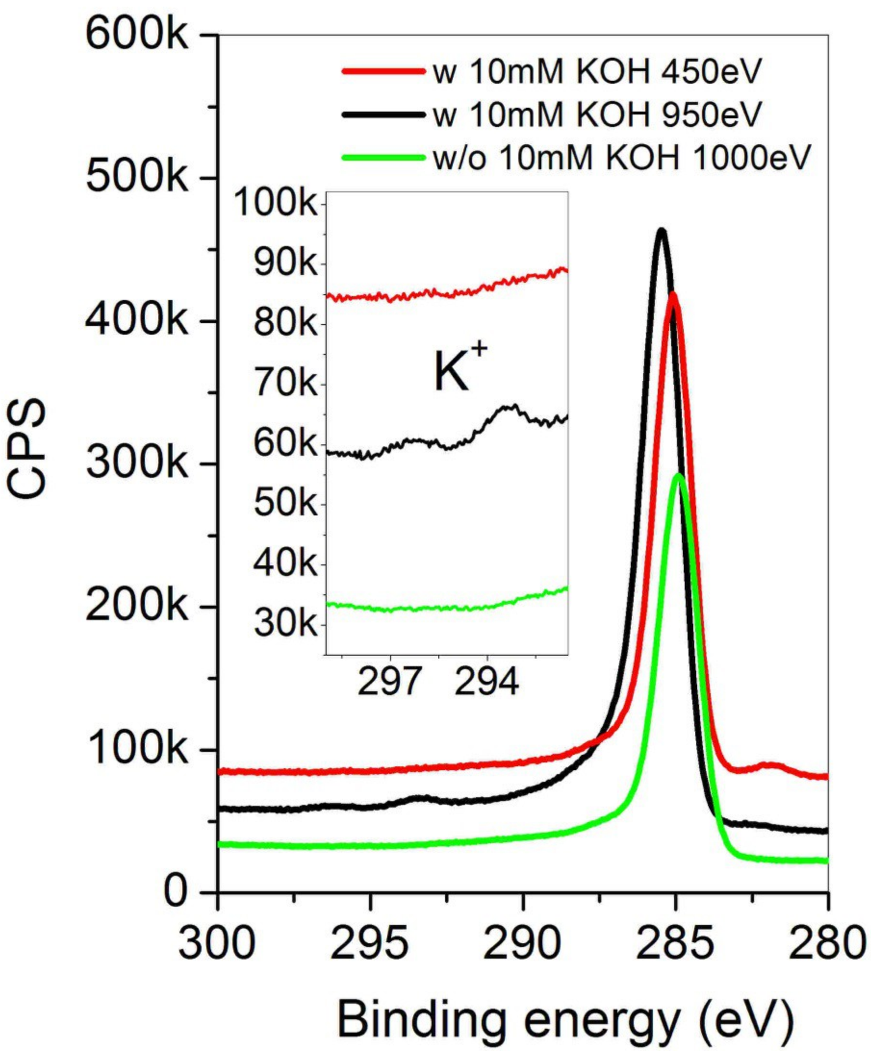




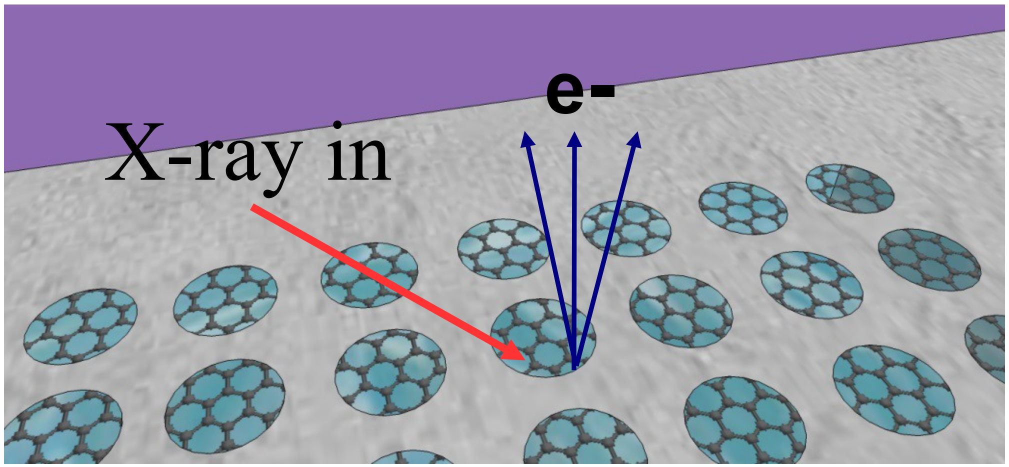
Juan Vélasco et al., Angew Chem. 2015

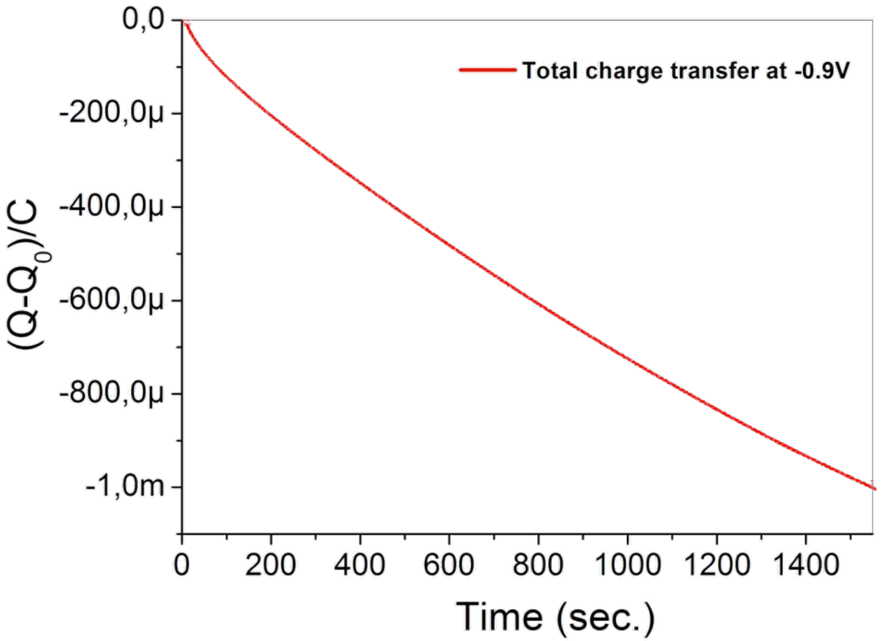
Cell filled with 10mM KOH



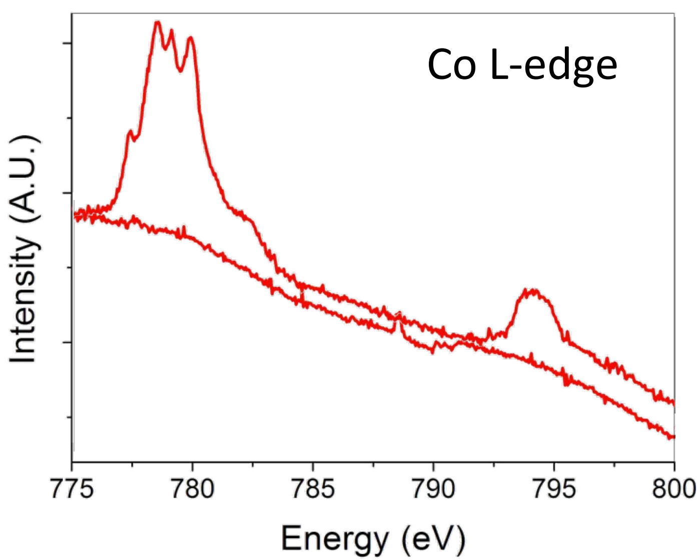


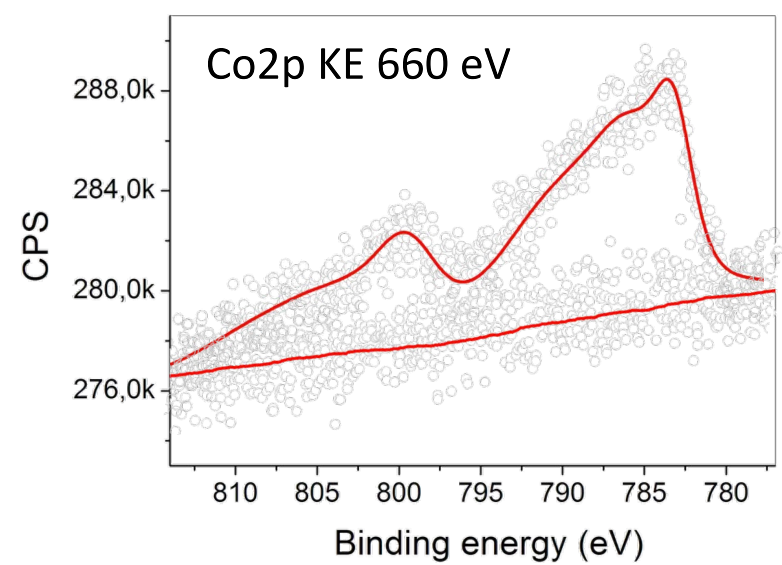
Electroplating (4 mM CoSO4)





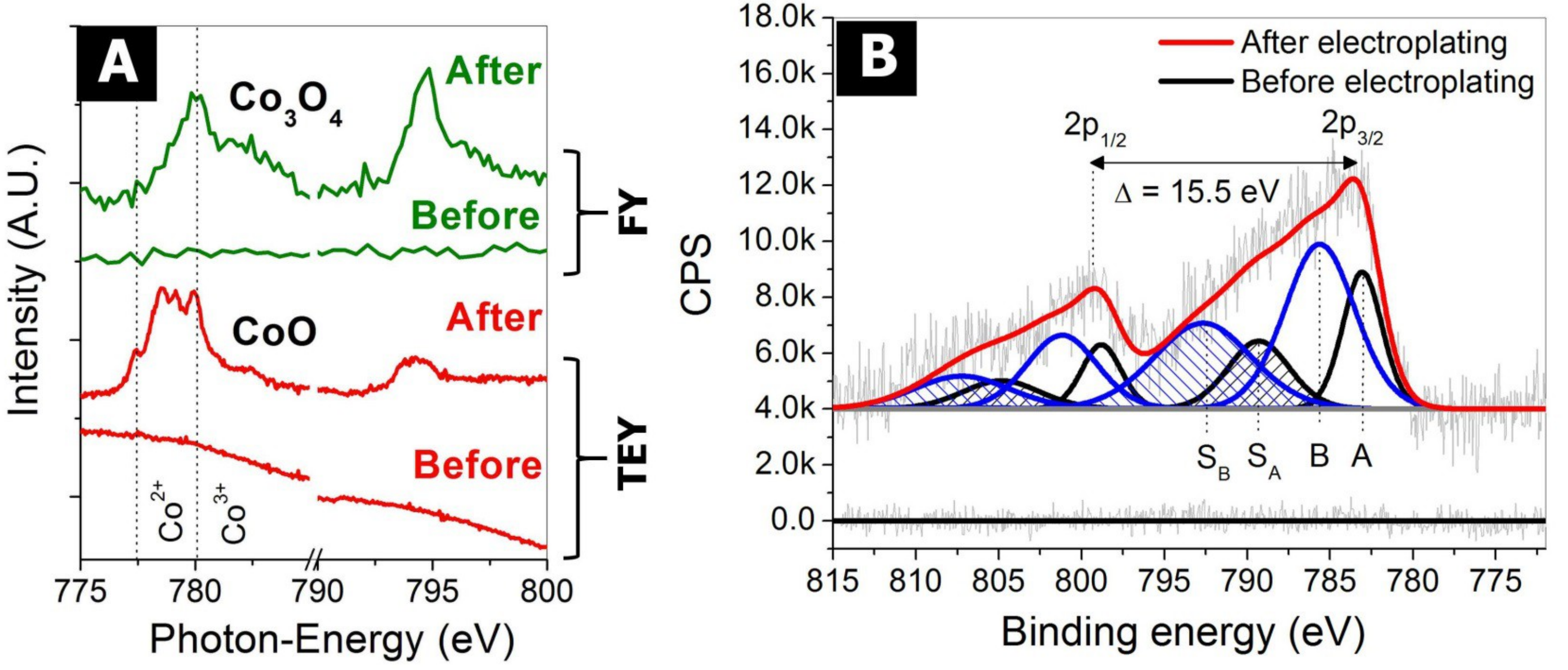
- Metall electroplated (Co)





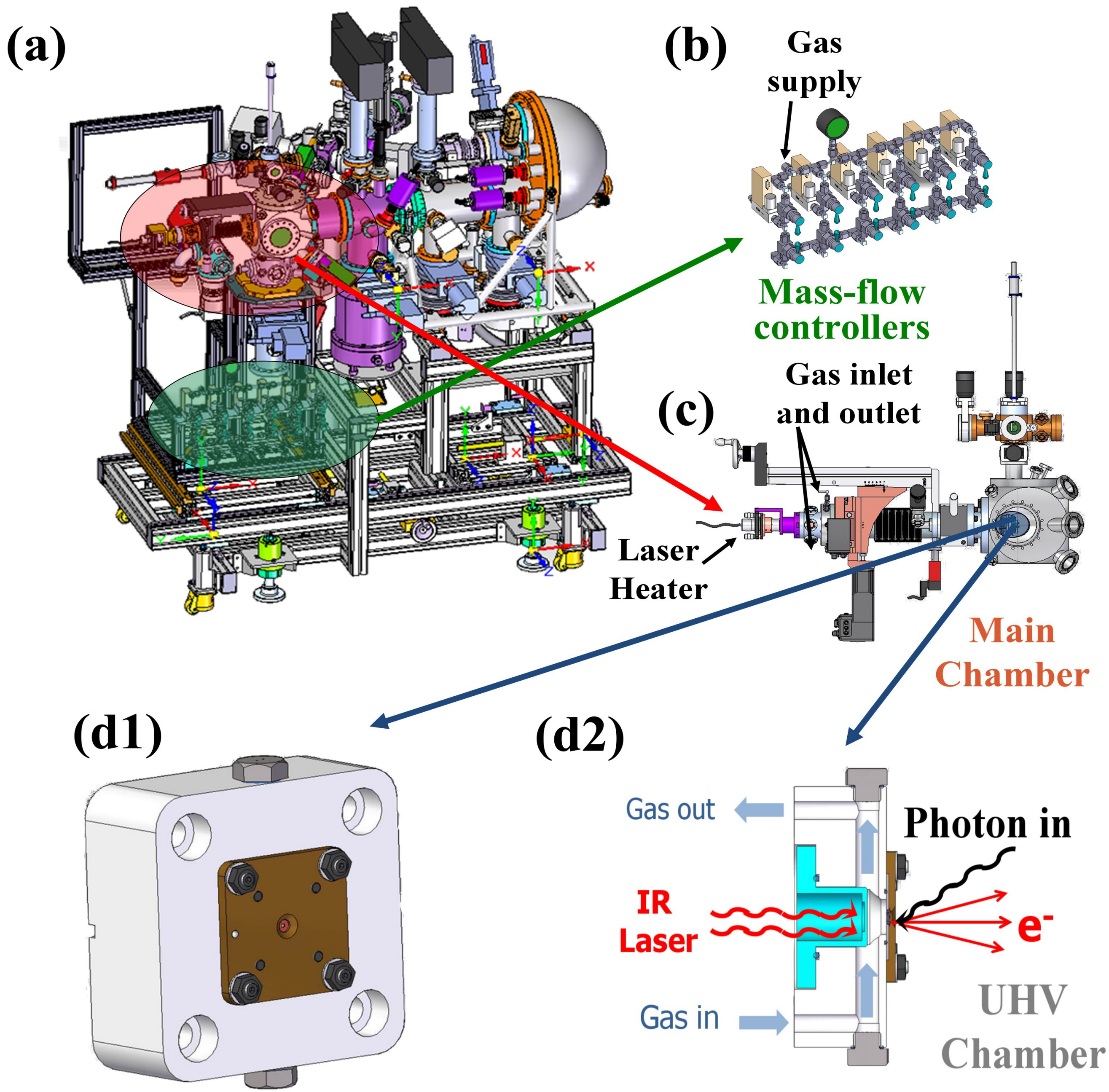
Juan Vélasco et al. Angew. Chemie 2015

Anchorage of Co on Graphene



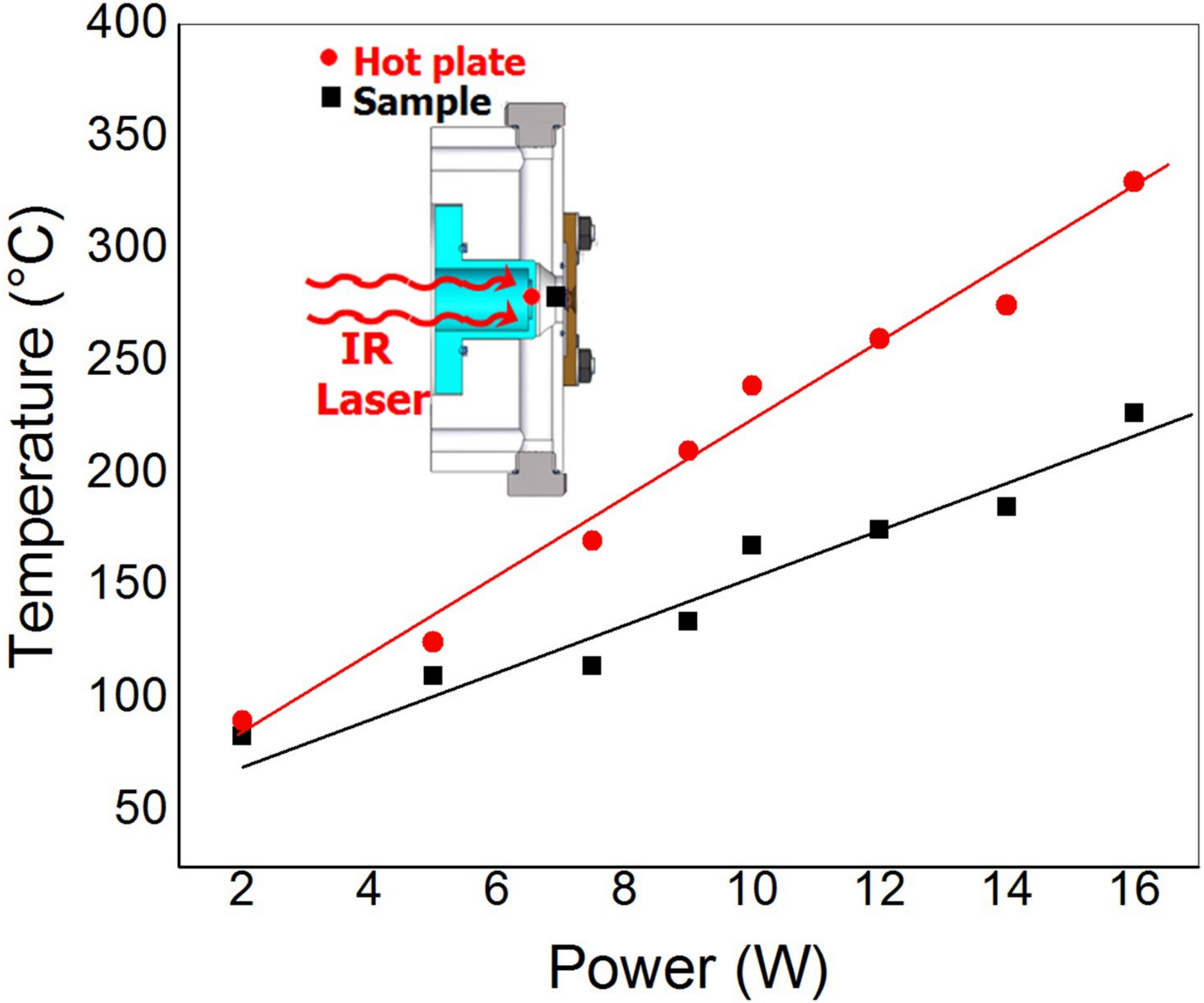
Juan Vélasco et al., Angew Chem. 2015

Solid gas phase reactions at 1 bar



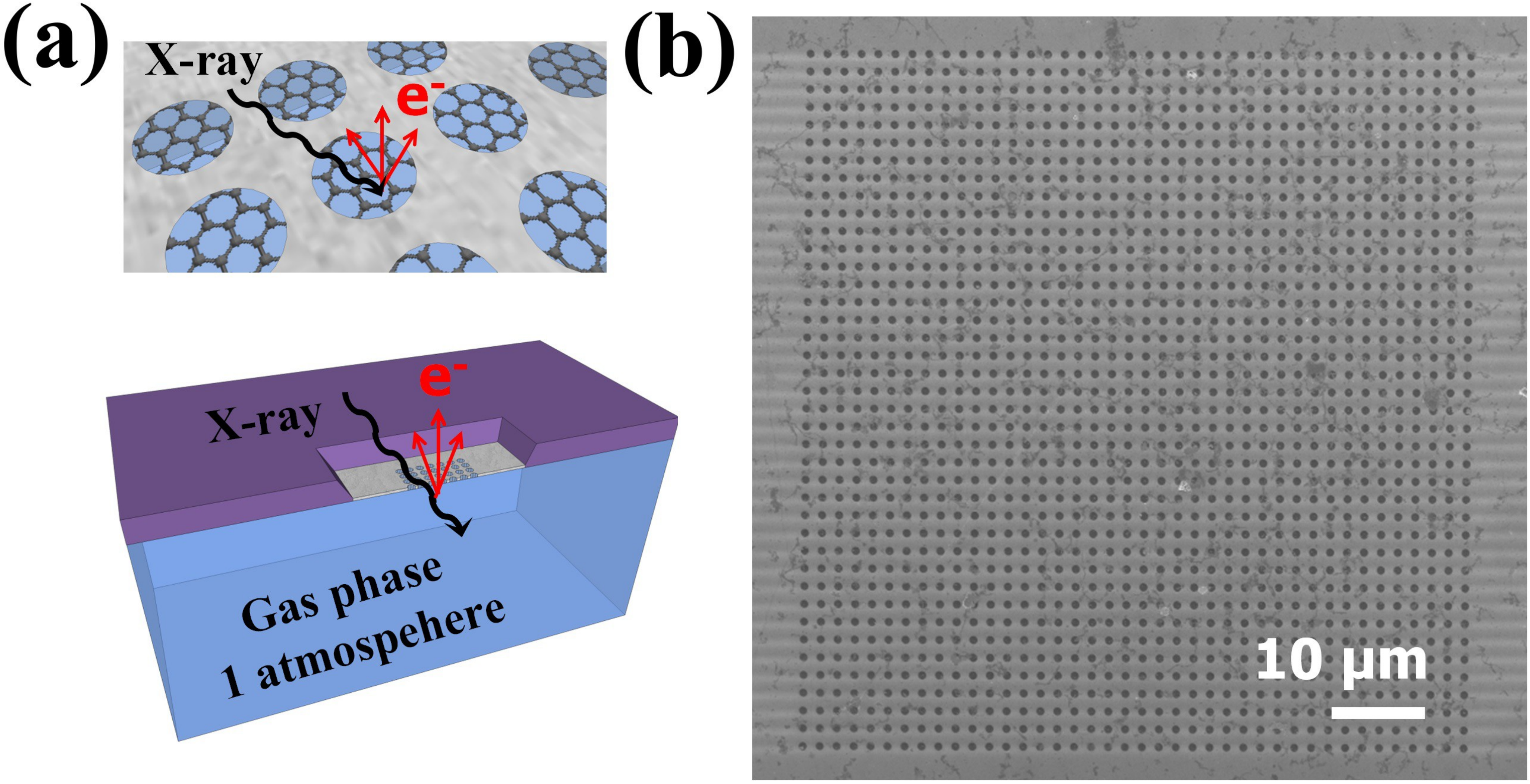
Velasco et al. Rev. Sci. Instr. 2016

Sample heating using an IR Laser



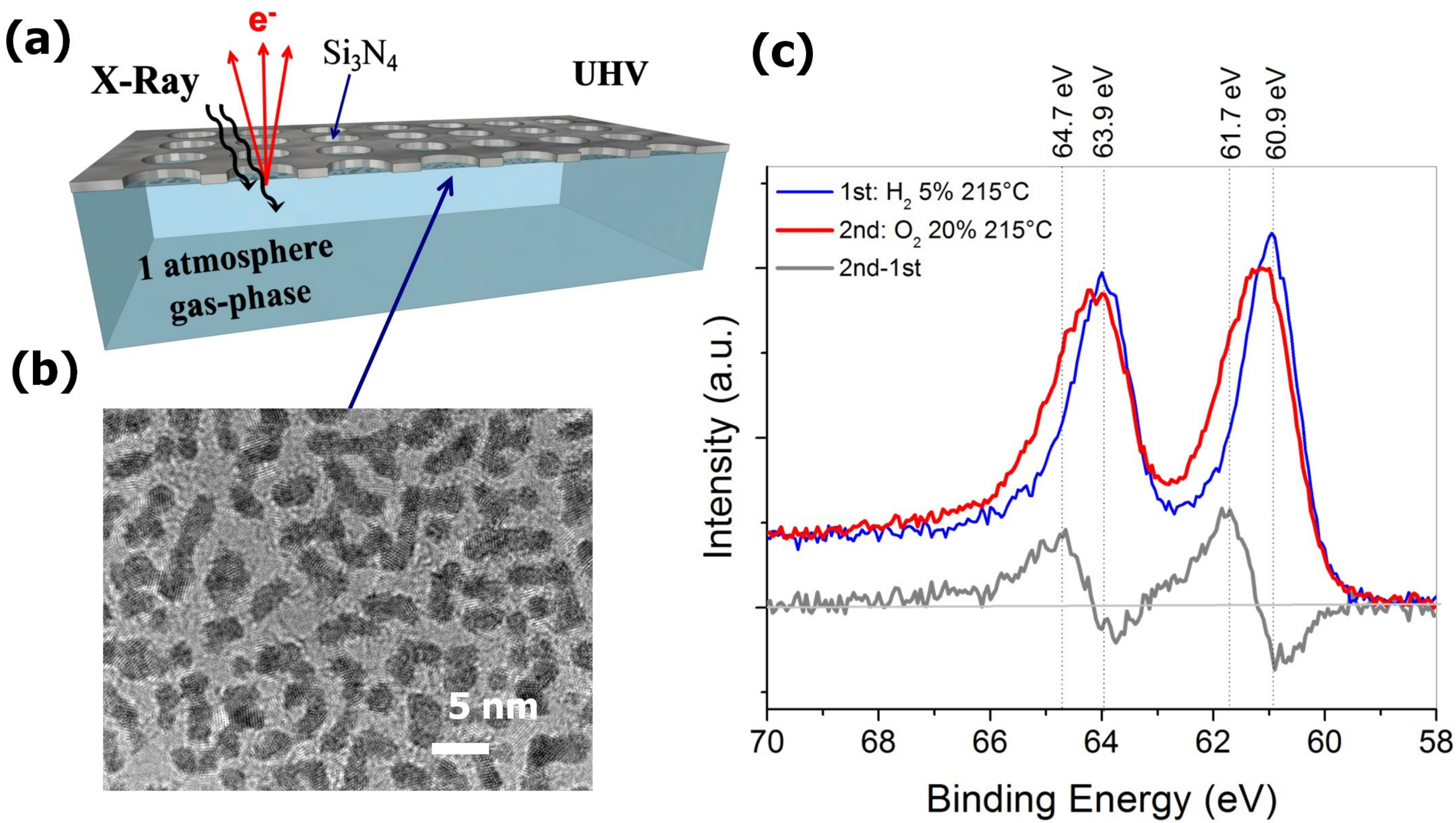
Velasco et al. Rev. Sci. Instr. 2016

The reaction cell



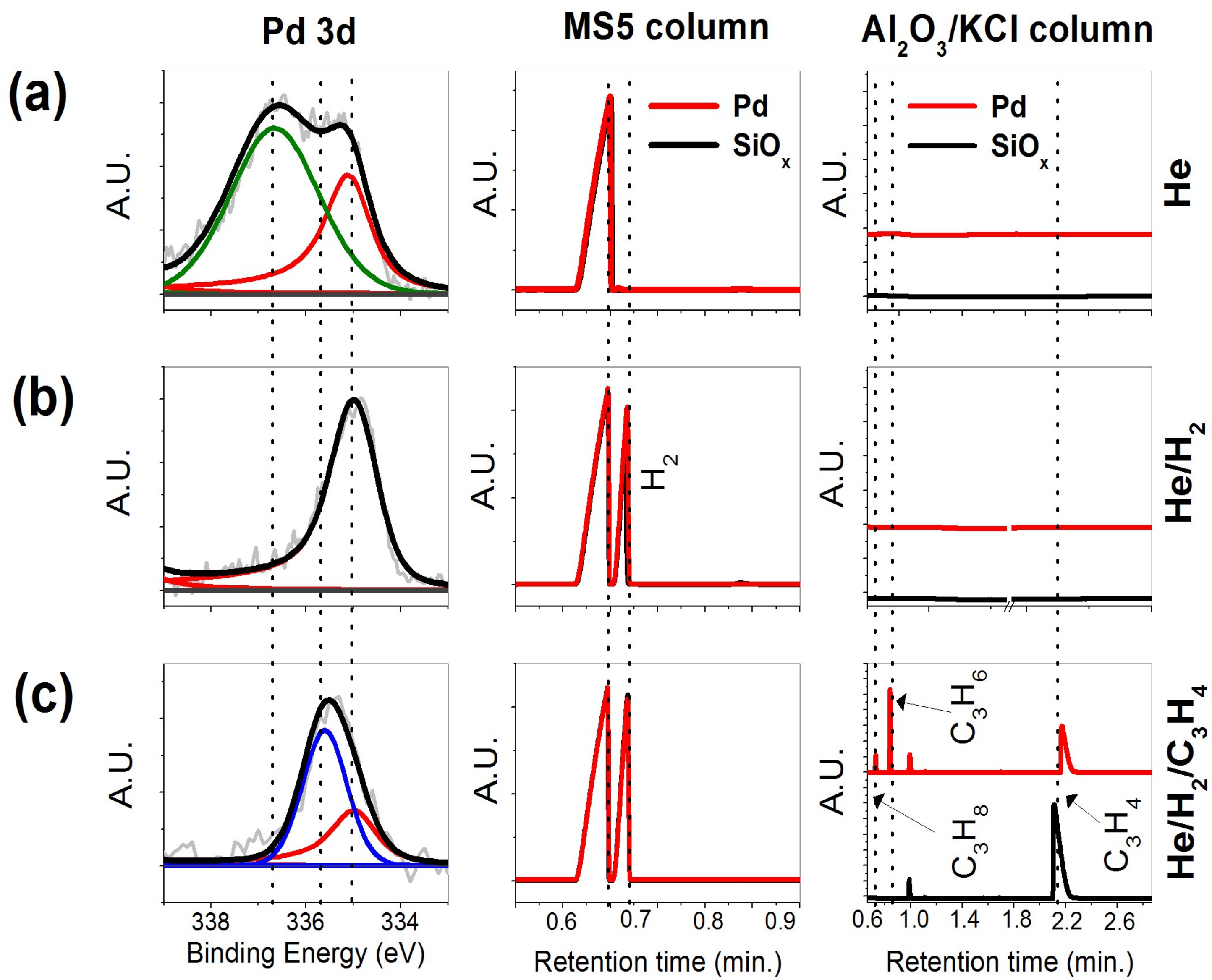
Velasco et al. Rev. Sci. Instr. 2016

The oxidation and reduction of Ir



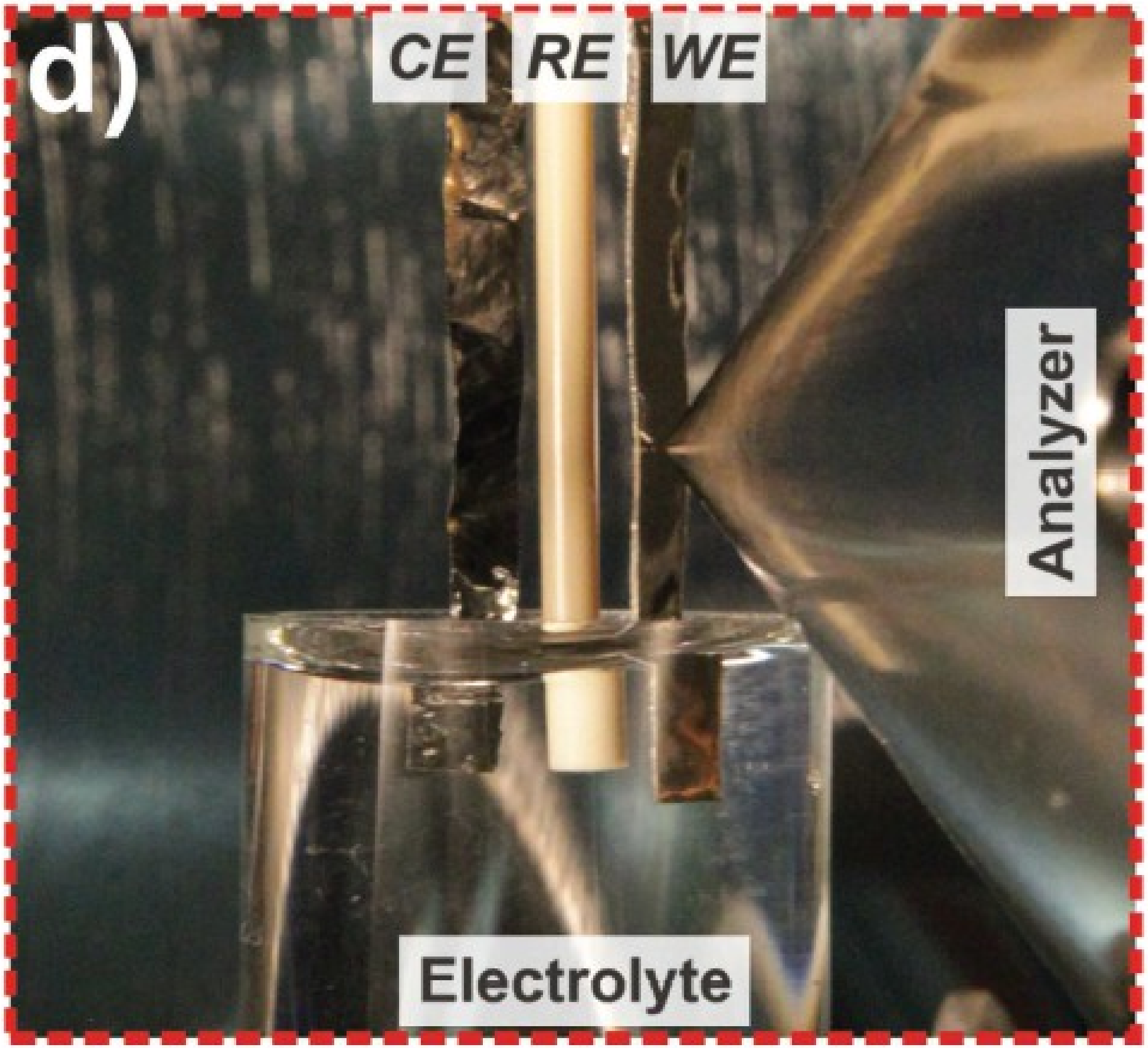
Velasco et al. Rev. Sci. Instr. 2016

The selective hydrogenation of alkynes to alkenes



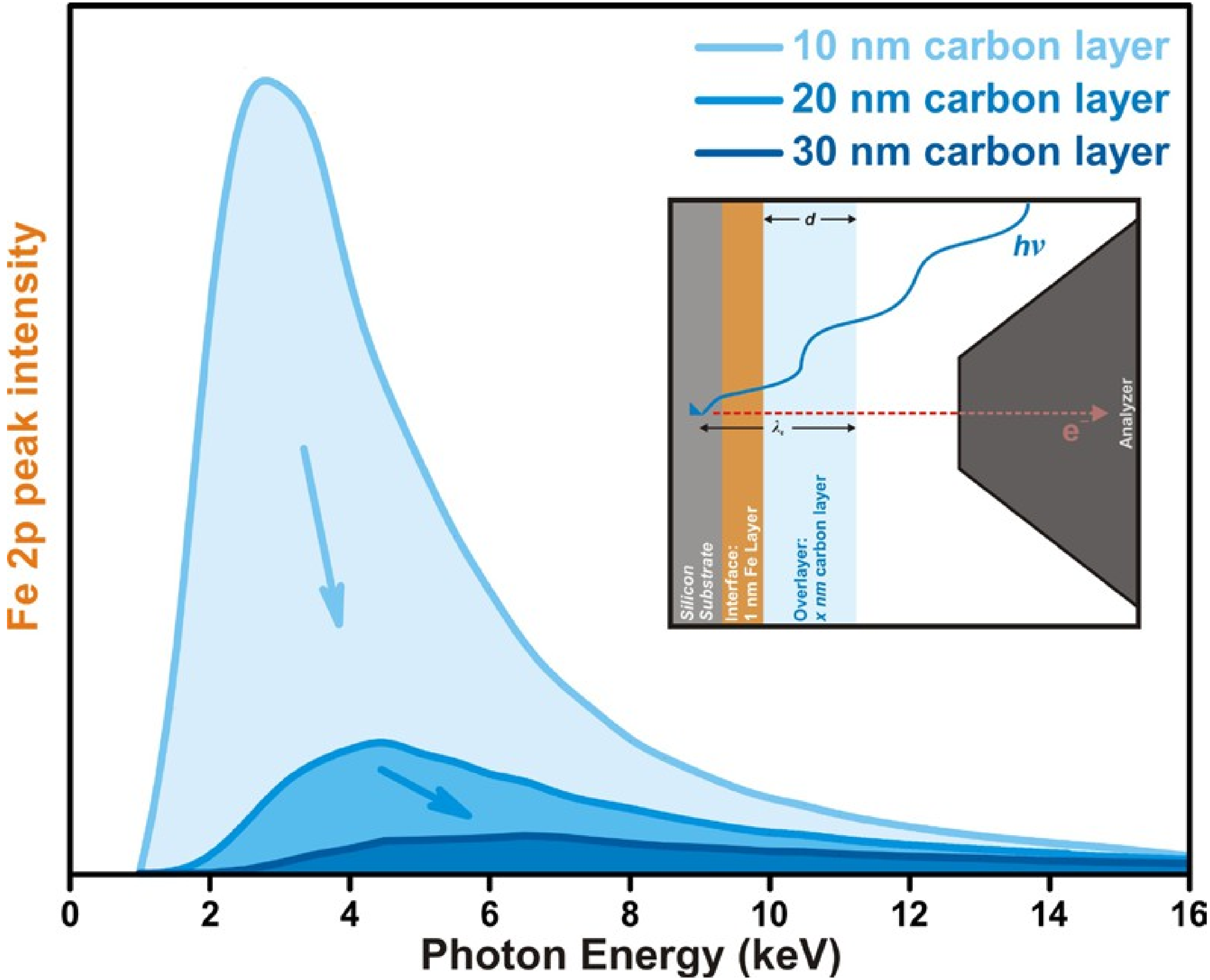
Velasco et al. Rev. Sci. Instr. 2016

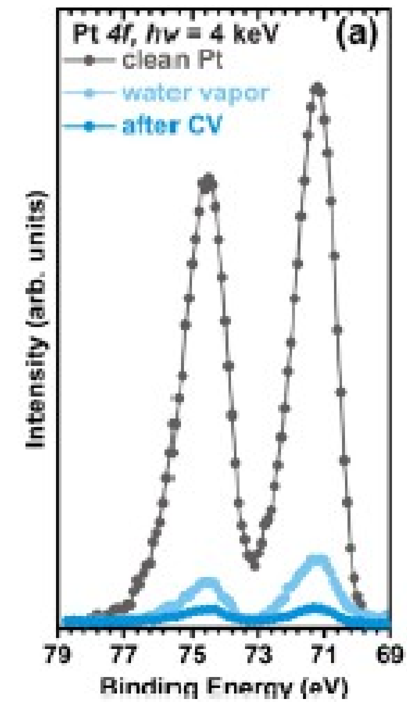
Dip &Pull



S. Axnanda et al. Scientific Reports 2015

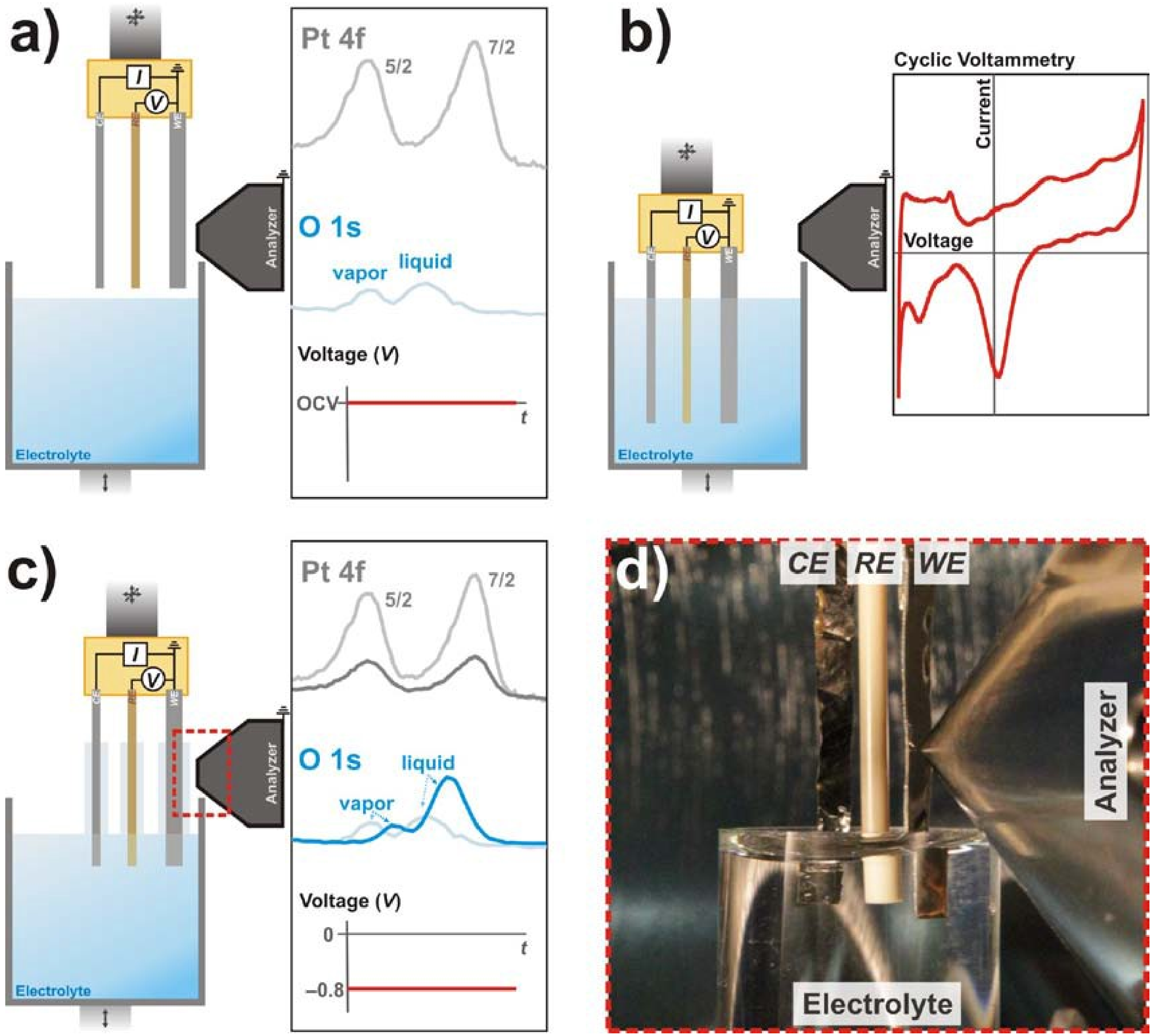
Dip &Pull





S. Axnanda et al. Scientific Reports 2015

Dip &Pull



S. Axnanda et al. Scientific Reports 2015

EMIL

* with permission from
Verlagsgruppe Öttinger

EMIL *

HZB SISSY

CAT

Solar Energy Materials In-Situ
Spectroscopy at the Synchrotron:
Photovoltaic related material and
solar cell development

CATalysis research for
sustainable energy supply
(MPG/FHI)

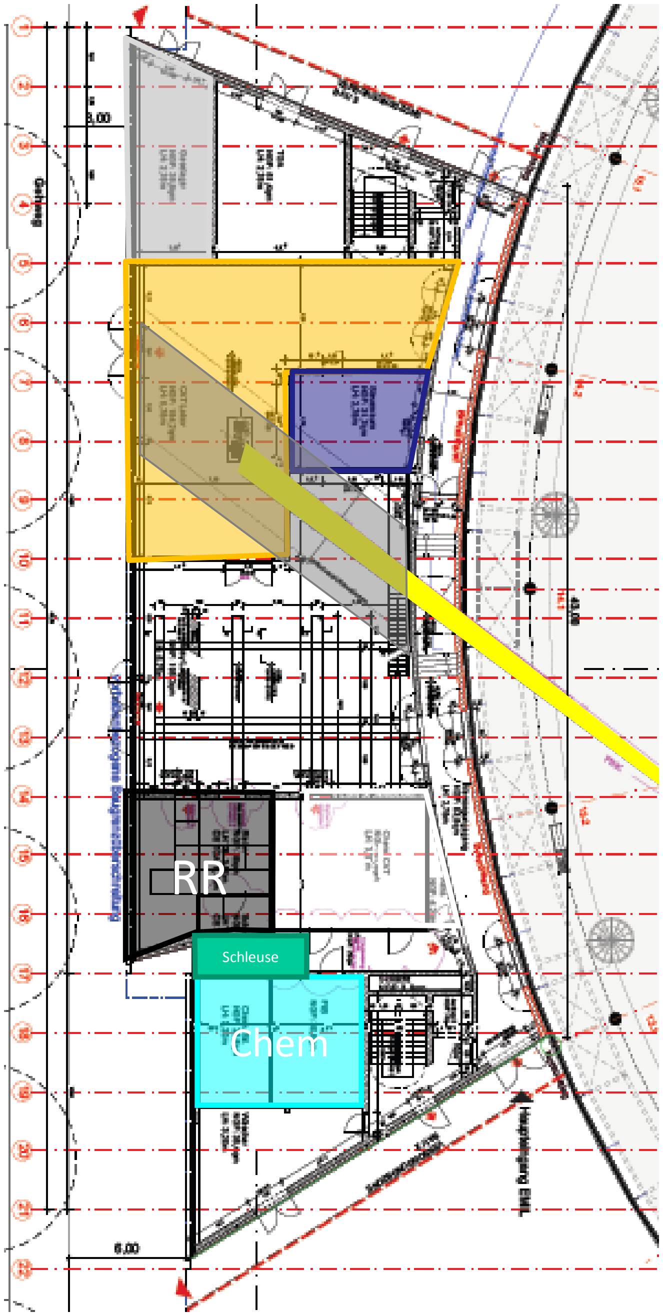
research alliance between HZB and MPG

State of the art deposition tools

Ambient pressure XPS

Synchrotron based analytics in a wide energy range (80 eV – 8000 eV)

EMIL Lab: An extension to BESSY II



Gas Storage

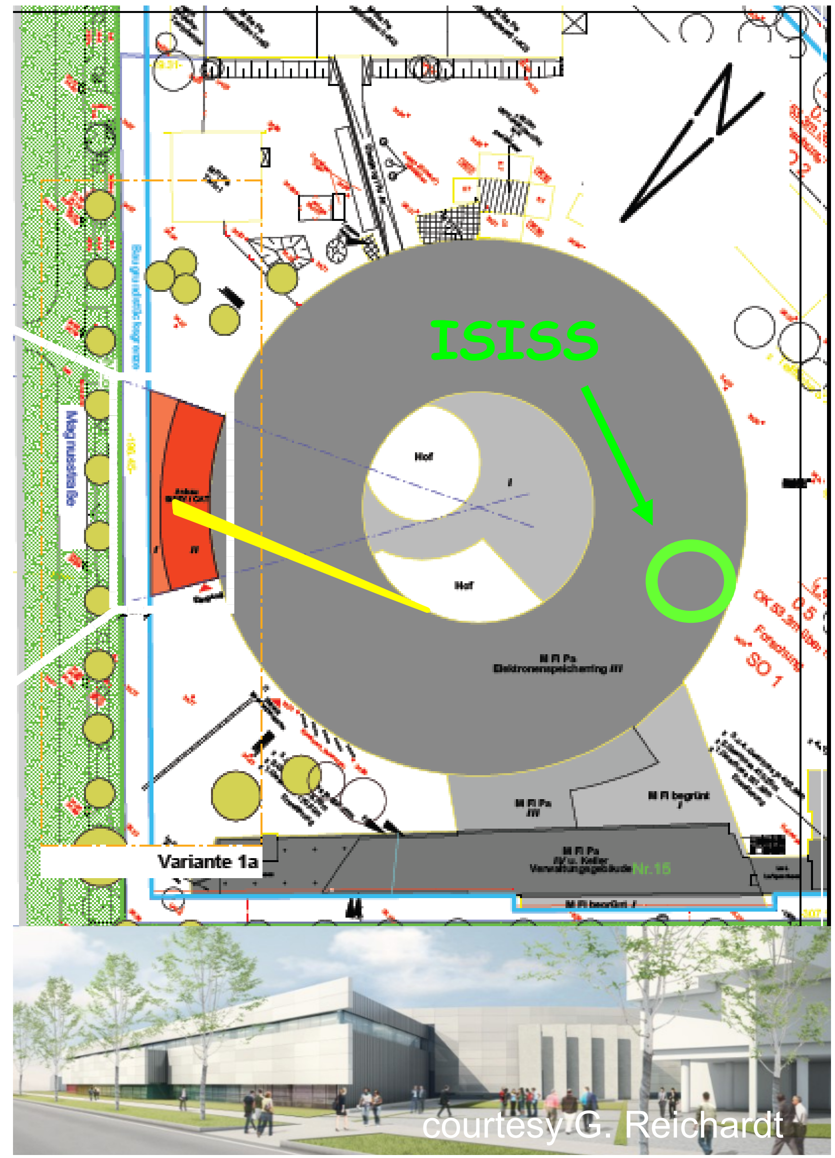
CAT-Lab

Control Room

Clean Room

FIB-Lab

Chem-Lab



EMIL project at BESSY II (HZB + MPG)

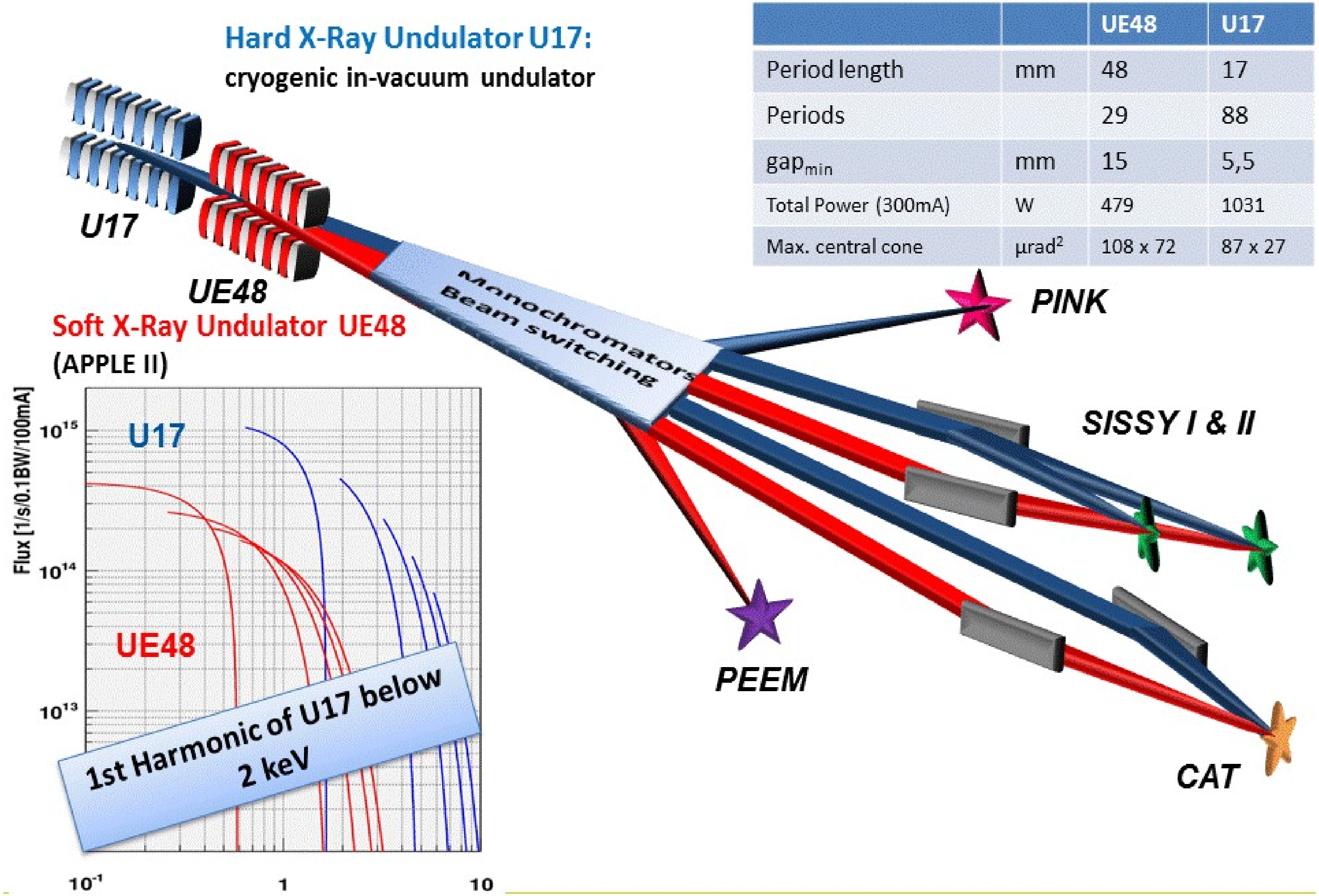
EMIL lab

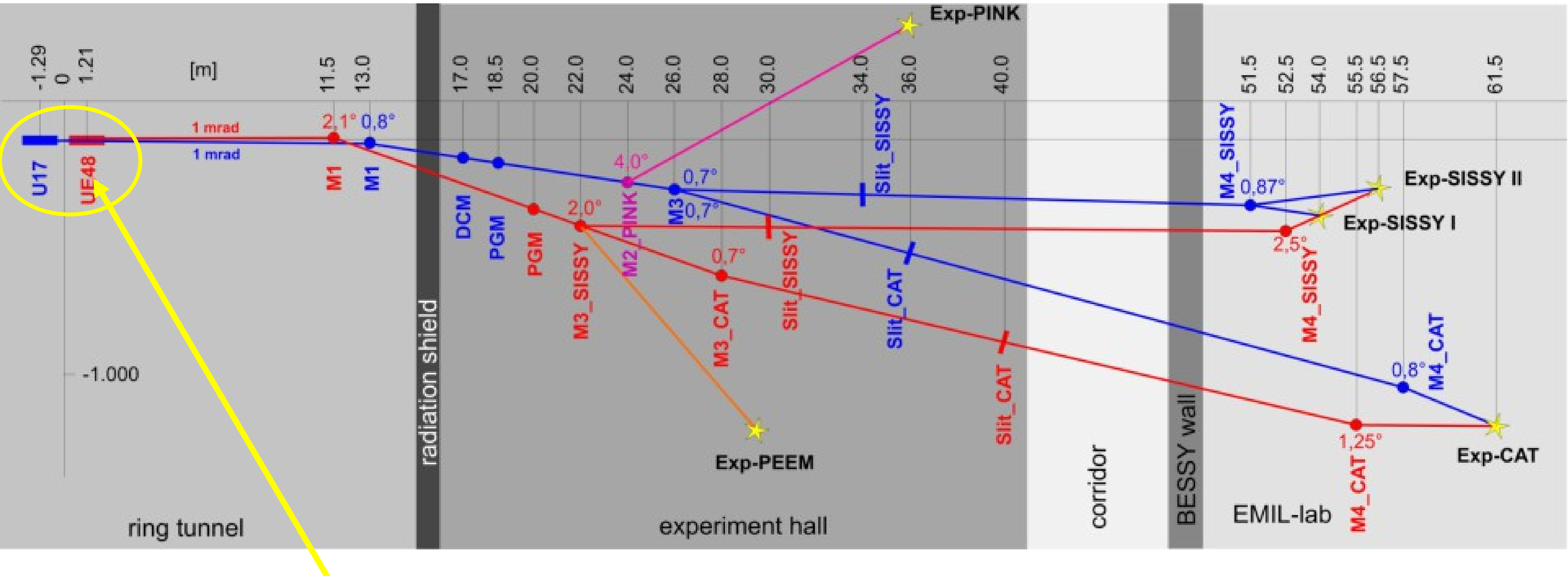
2 undulators covering the energy range 80 to 10000 eV

Energy Materials In-Situ Laboratory

EMIL

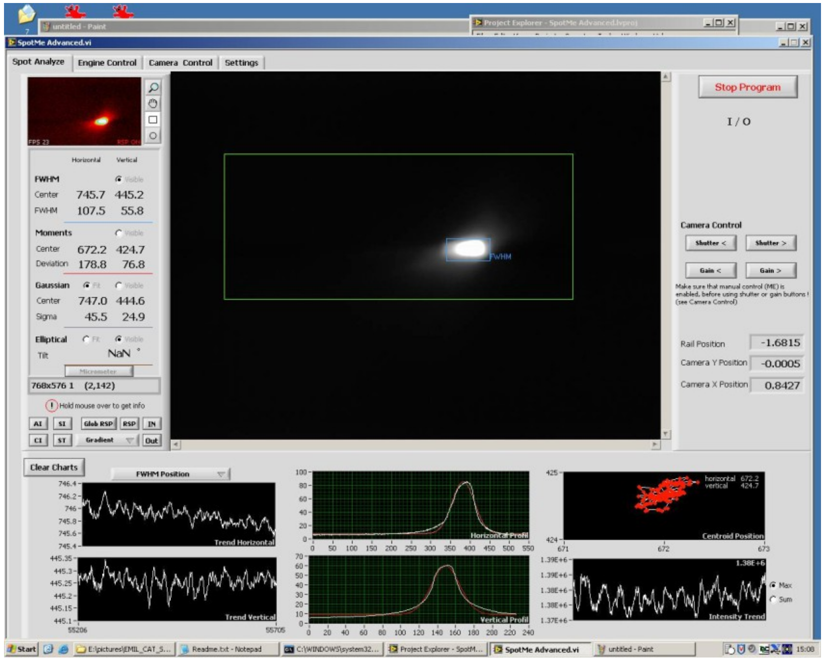
		UE48	U17
Period length	mm	48	17
Periods		29	88
gap_{min}	mm	15	5,5
Total Power (300mA)	W	479	1031
Max. central cone	μrad^2	108 x 72	87 x 27

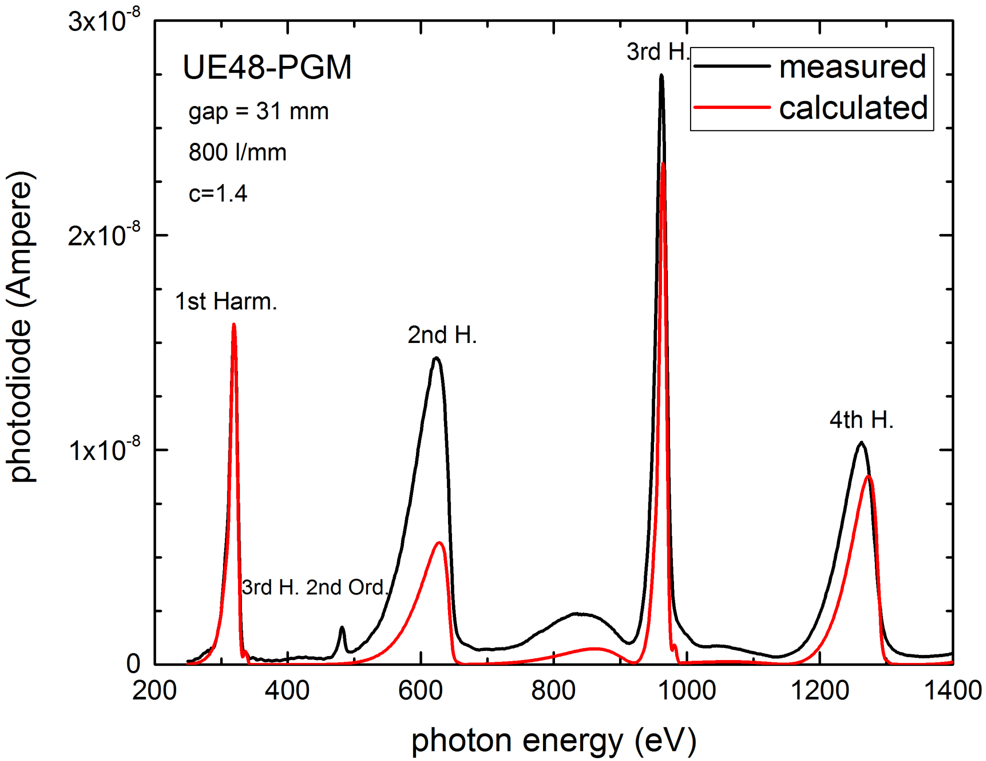




2 undulators

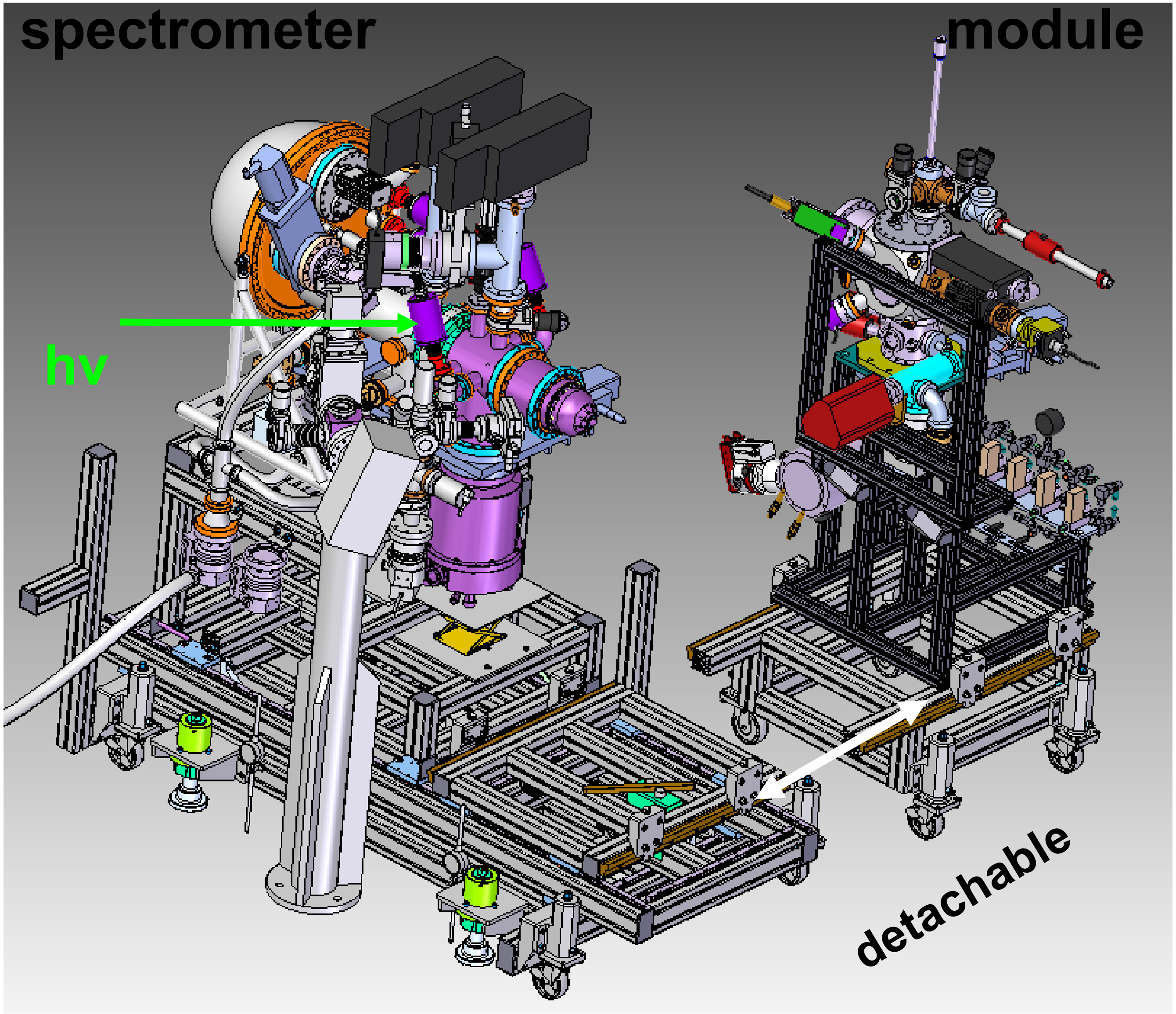
First X-Rays in CAT (23.08.17)





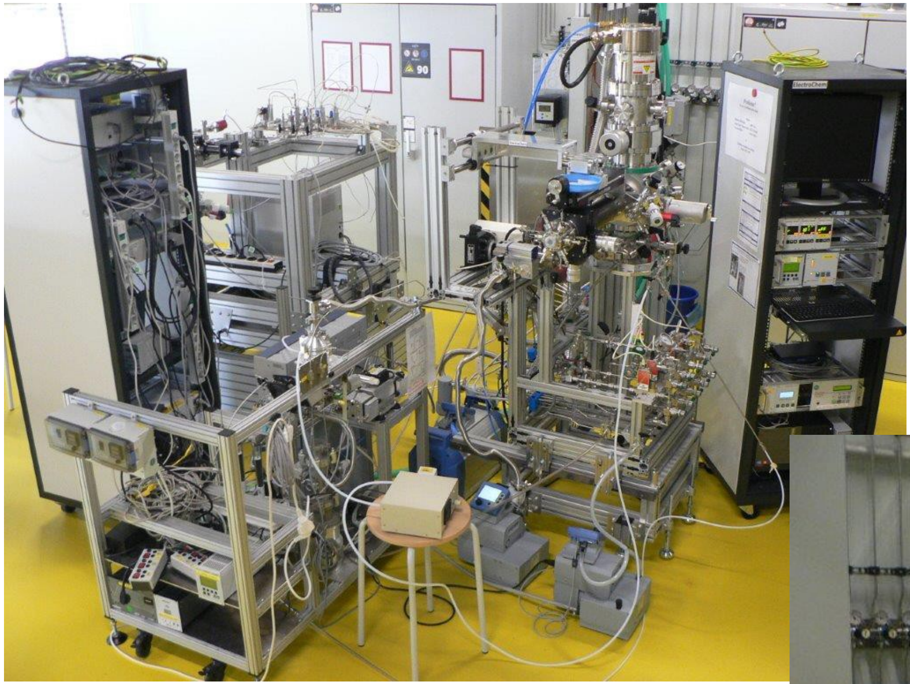
Infrastructure

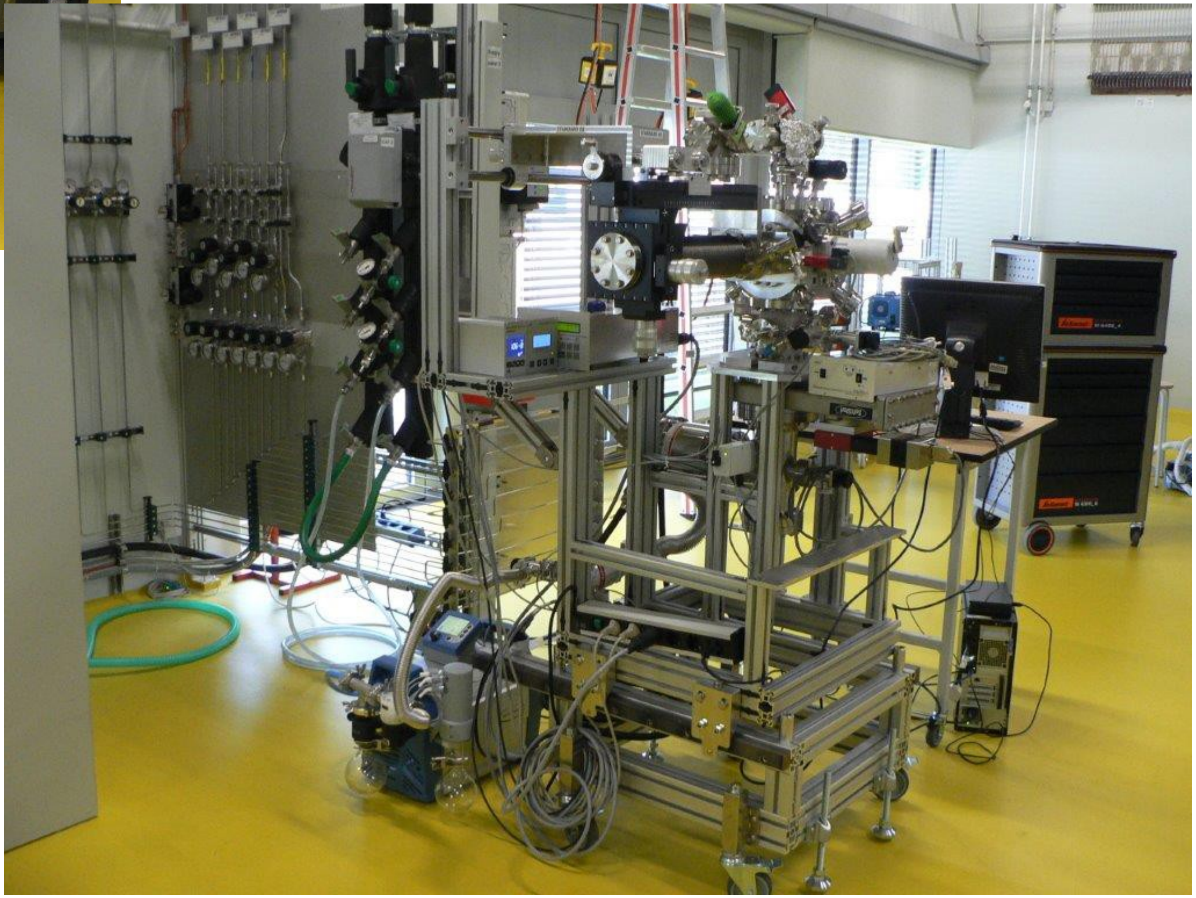
Modular design in AP-XPS



- XPS cell module can easily be exchanged and thus adapted to needs of users
- detached XPS cell module is a **fully operable stand-alone unit**

Operation site for stand-alone modules





Infrastructure