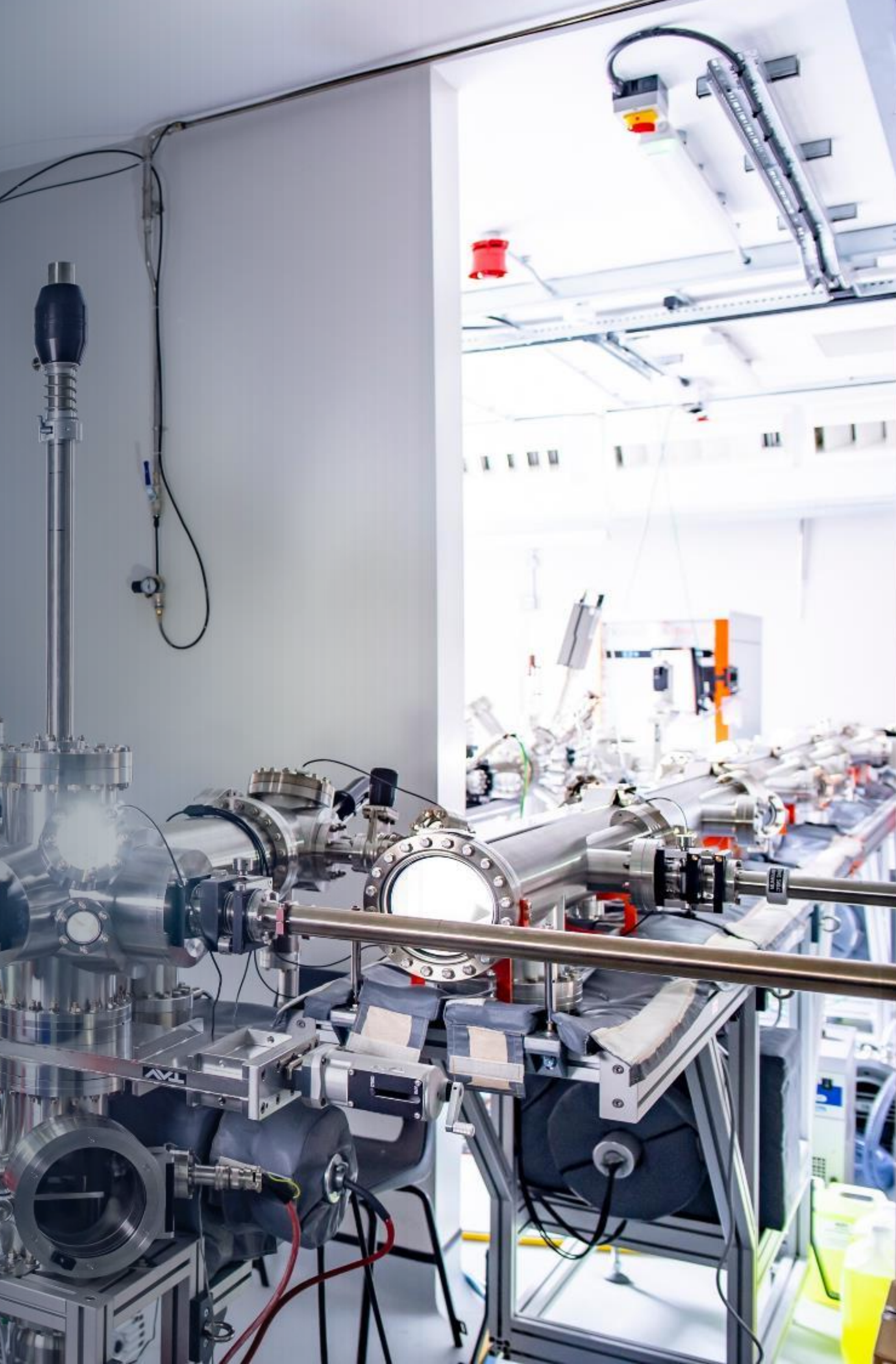
University of Nottingham
UK | CHINA | MALAYSIA

Near-ambient pressure XPS for in-situ studies of catalytic surfaces

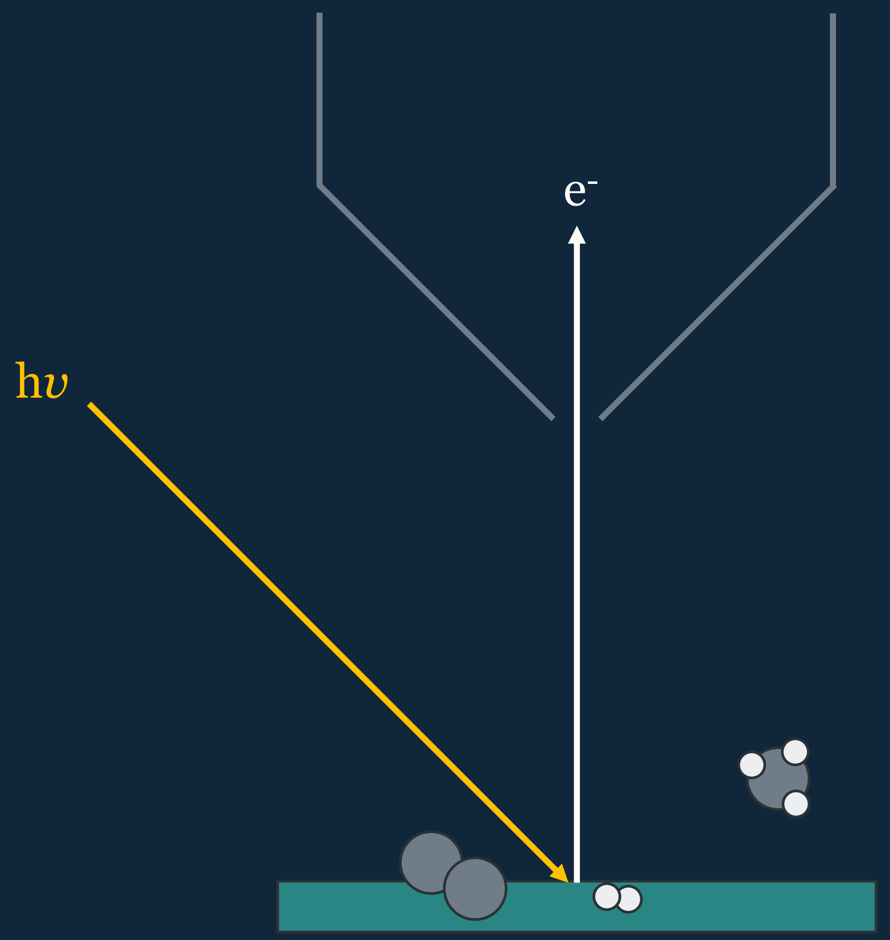
Dr. James N. O’Shea

School of Physics & Astronomy, University of Nottingham, UK



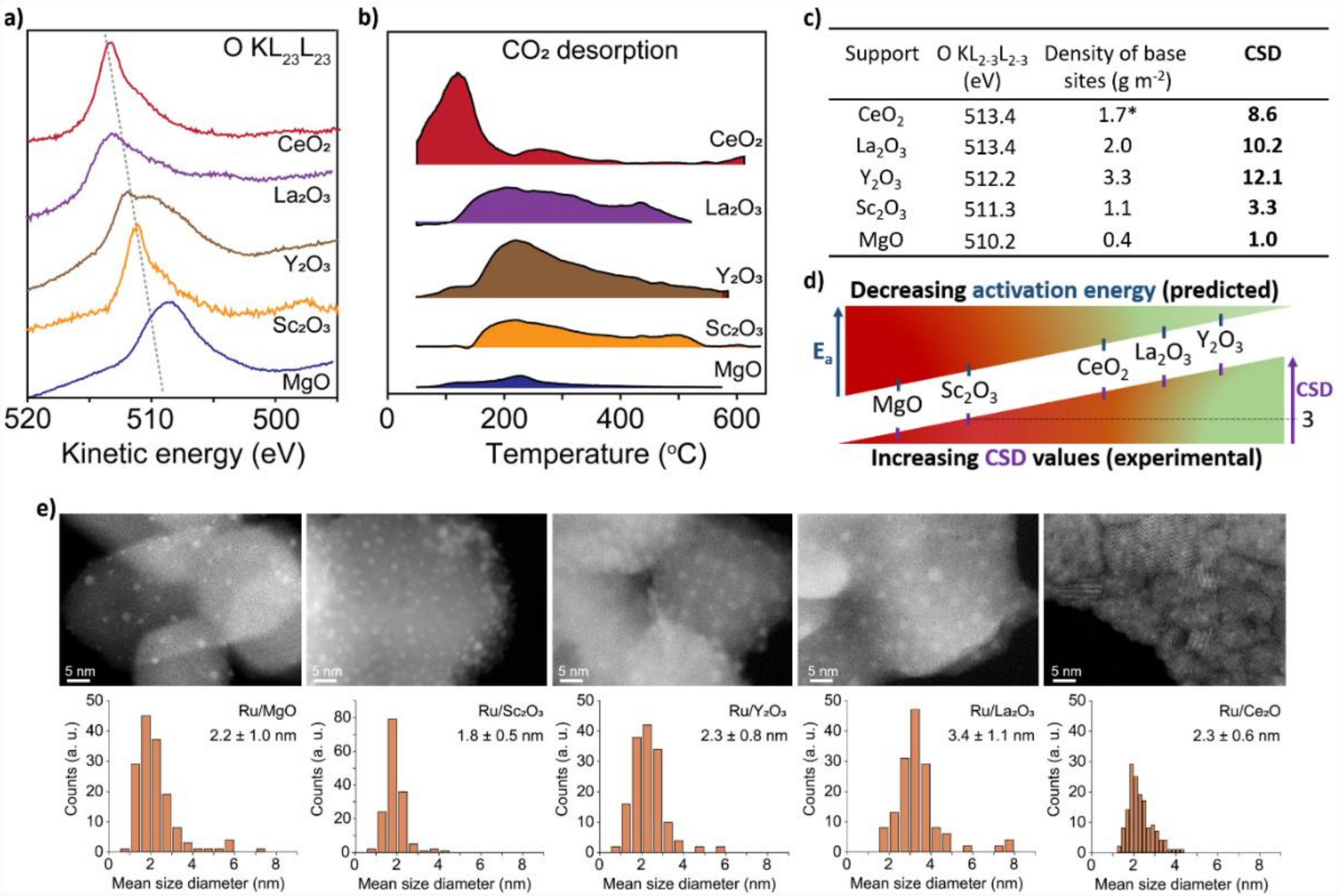
2nd LATAM MEETING ON GREEN AMMONIA AND POWER-to-X

XPS & it’s applications to catalytic surfaces



A Sole Descriptor Guiding the Selection of Catalyst Supports for Ammonia Synthesis

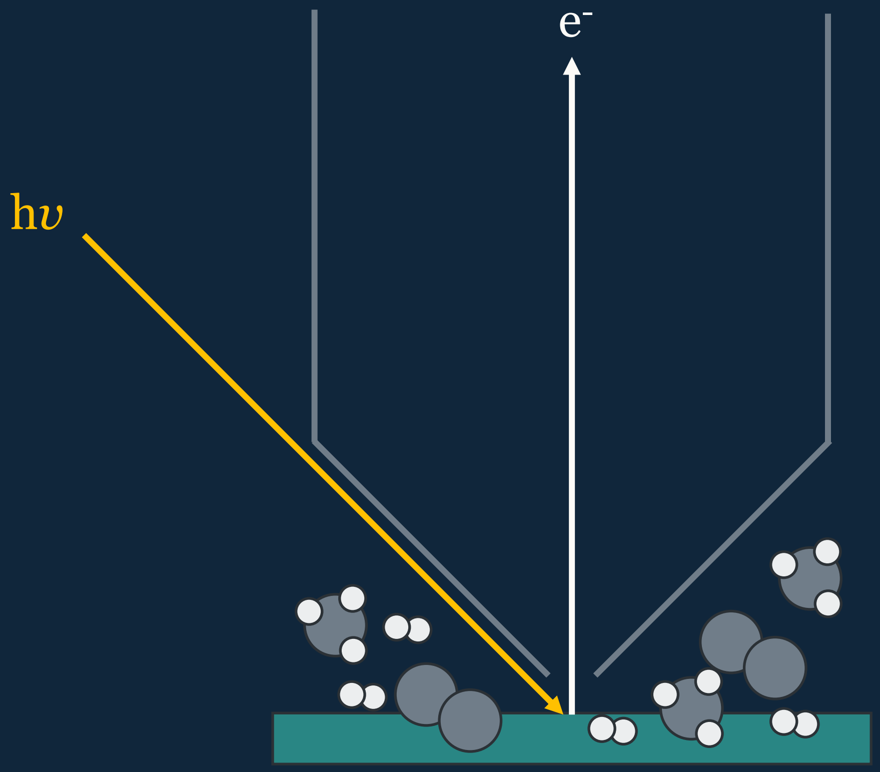
A. Weilhard, I. Popov, E. Kohlrausch, G. Aliev, L. S. Blankenship, L. T. Norman, S. Ghaderzadeh, L. Smith, M. Isaacs, J. N. O'Shea, A. Lanterna, W. Theis, D. Morgan, G. Hutchings, E. Besley, A. N. Khlobystov and J. Alves Fernandes



Support	O $KL_{2\text{-}3}L_{2\text{-}3}$ (eV)	Density of base sites (g m^{-2})	CSD
CeO_2	513.4	1.7*	**8.6**
La_2O_3	513.4	2.0	**10.2**
Y_2O_3	512.2	3.3	**12.1**
Sc_2O_3	511.3	1.1	**3.3**
MgO	510.2	0.4	**1.0**

A. Weilhard *et al*, In review (2025)

XPS & reaching for more realistic pressures



What does near-ambient pressure mean in the context of XPS?

10^{-10} mbar ---------- 10^{-6} mbar ---------- 10 mbar ---------- 200 bar

UHV

XPS

NAP-XPS

Industrial processes (ammonia synthesis)

Article

Operando probing of the surface chemistry during the Haber–Bosch process

https://doi.org/10.1038/s41586-023-06844-5

Received: 7 December 2022

Accepted: 7 November 2023

Published online: 10 January 2024

Christopher M. Goodwin[1,5]✉, Patrick Lömker[1], David Degerman[1], Bernadette Davies[2], Mikhail Shipilin[1], Fernando Garcia-Martinez[3], Sergey Koroidov[1], Jette Katja Mathiesen[1], Raffael Rameshan[4], Gabriel L. S. Rodrigues[1], Christoph Schlueter[3], Peter Amann[1,6] & Anders Nilsson[1]✉

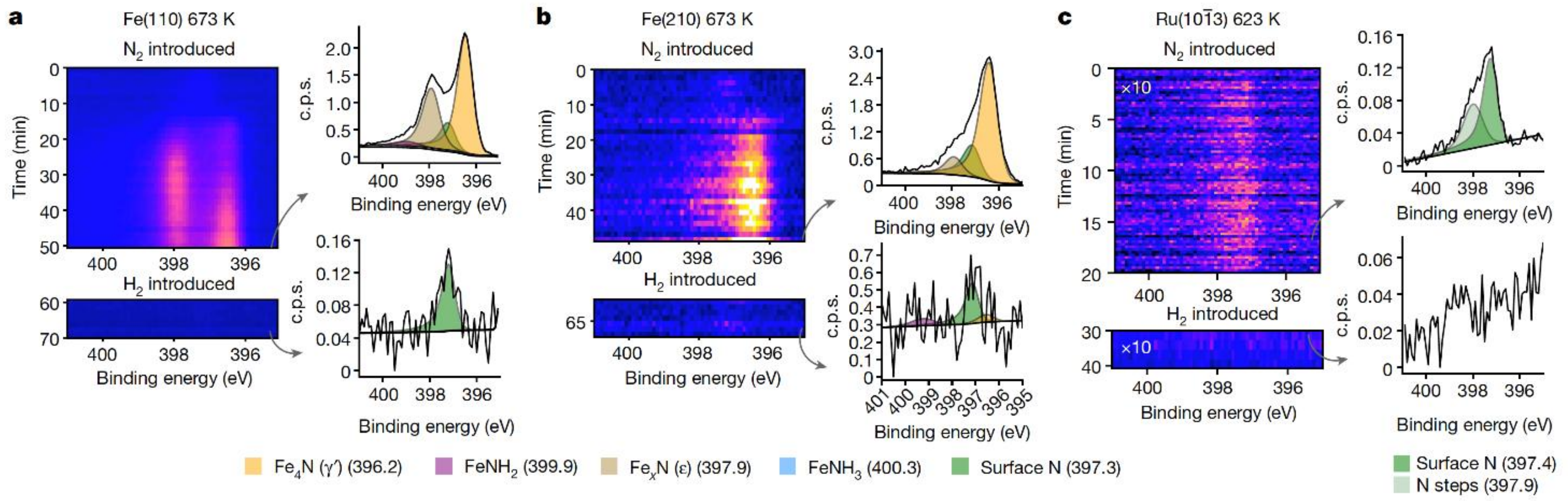
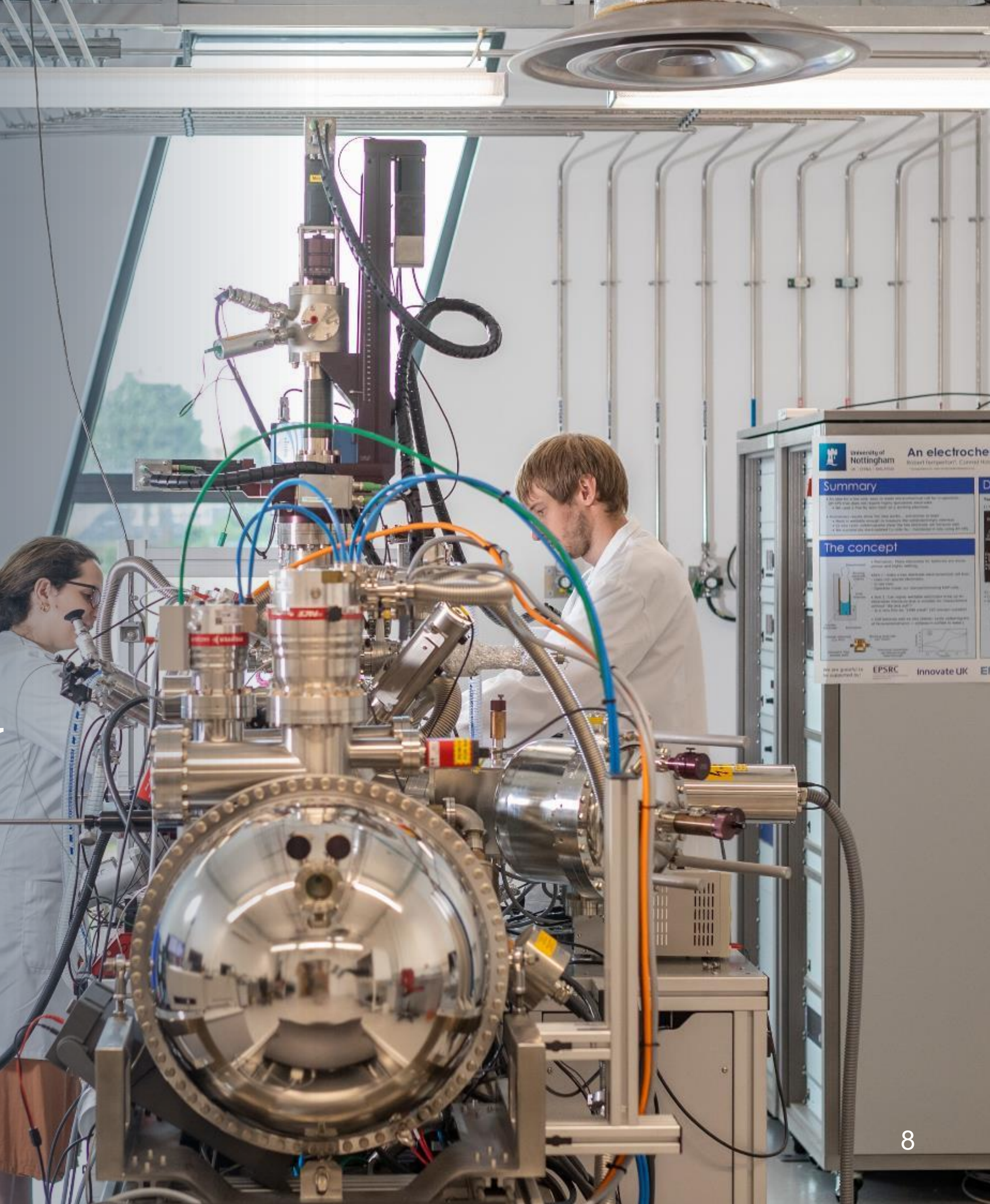


Fig. 2 | Nitride formation and depletion. The formation and depletion of nitride on the surface of each catalyst are shown as a function of time. At the top, the N_2 gas is introduced with a total pressure of 150 mbar and spectral collection begins. Then, after the nitride begins to stabilize, H_2 gas is introduced immediately in a 1:1 ratio with N_2 with a total pressure of 300 mbar, reducing the surface within the frame of the detector. Next to each time series are example spectra normalized to the background, with a grey arrow showing the frame it represents. **a**, The data for 673 K over Fe(110). **b**, The data for 673 K over Fe(210). **c**, The data for 623 K over Ru(10$\bar{1}$3). For Ru, the spectra shown are the summation of the entire time series. Note the difference in *y*-axis scale in the spectral figures.

The instrument

NAP-XPS

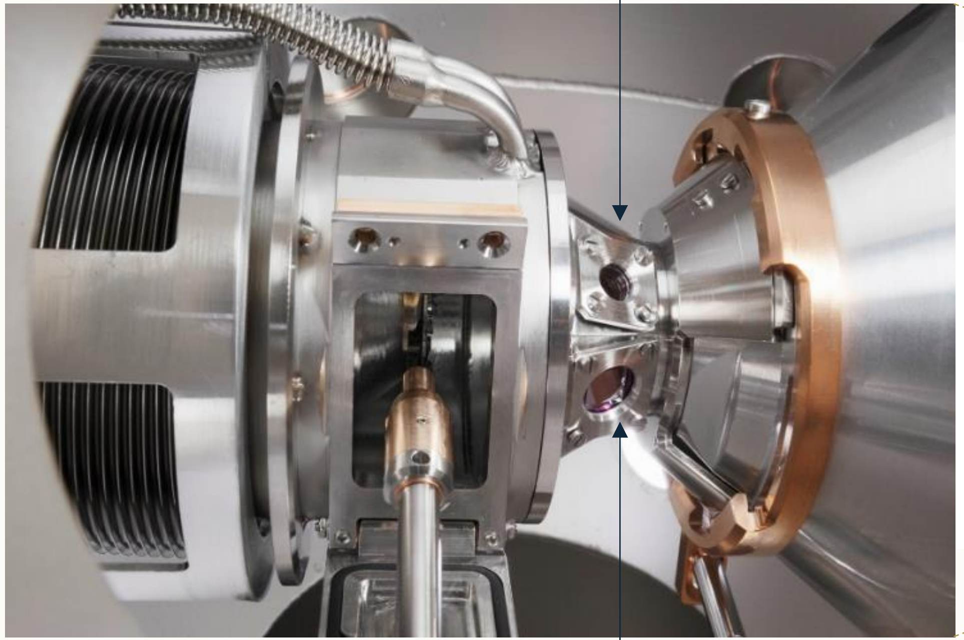
XPS
Gas-dosing
Mass-spectrometry
Excitation sources

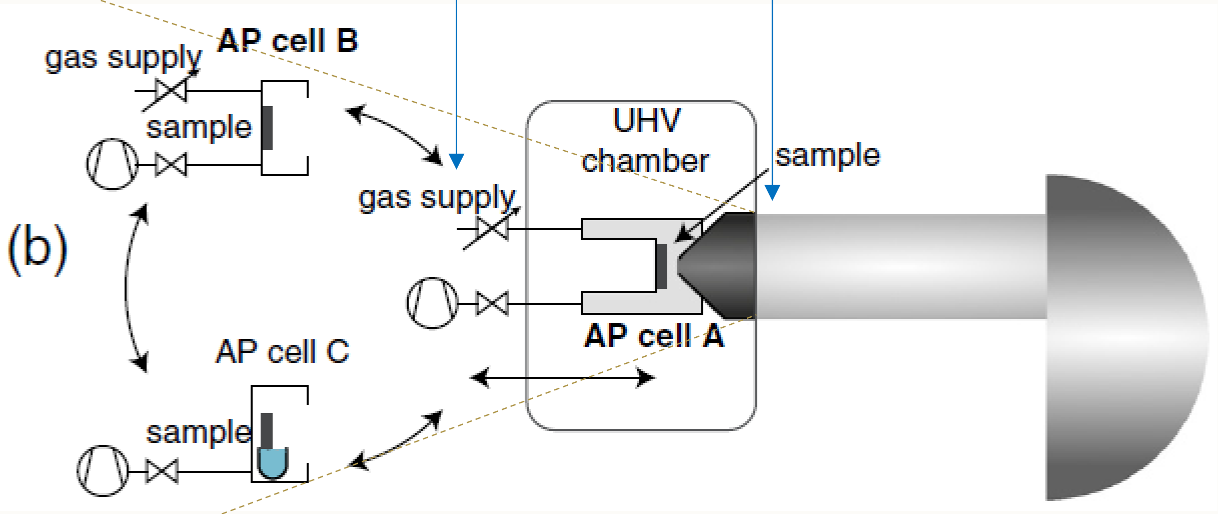


Bridging the pressure gap

X-rays

Mass-spectrometers





Visible & UV

UHV suitcase for sample transfer to other instruments

“Knowing the before-reaction part or after-reaction part is like studying a life with access only to the prenatal and postmortem states.”

- Gabor A. Somorjai, 1998

PCCP

PAPER

View Article Online
View Journal

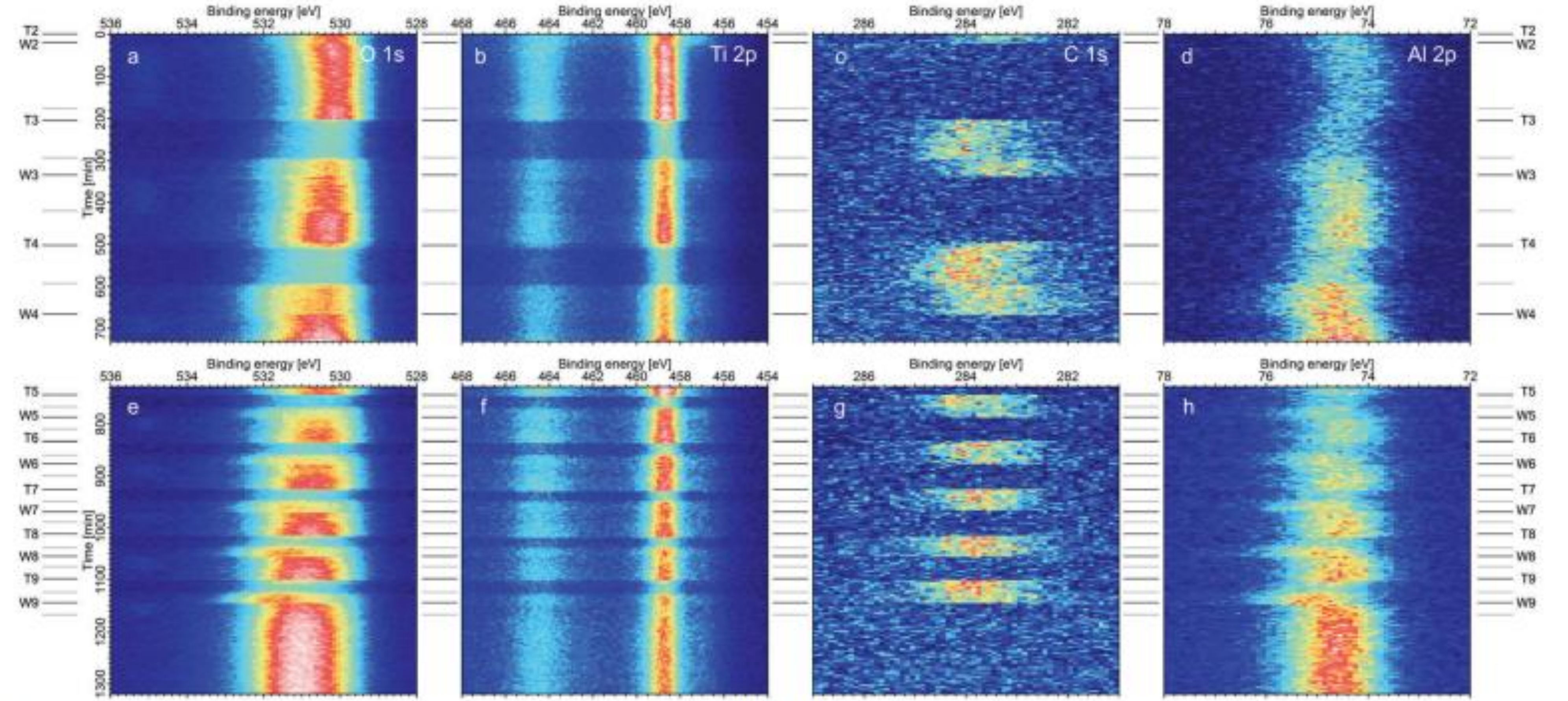


Fig. 2 *In situ* XPS measurements during cycles 2–9, labeled T2–T9 and W2–W9 for TMA and water half-cycles respectivly. Grey lines indicate purges of the cell to 1×10^{-2} mbar. From left to right, O 1s, Ti 2p, C 1s and Al 2p regions are shown. The break in the data (between plots a–d and e–h) represents a break in the experiment, apart from which the measurements were continuous. Each cycle of the four regions took approximately 3 minutes 45 seconds to measure.

Realtime ALD of Al_2O_3 growth on TiO_2

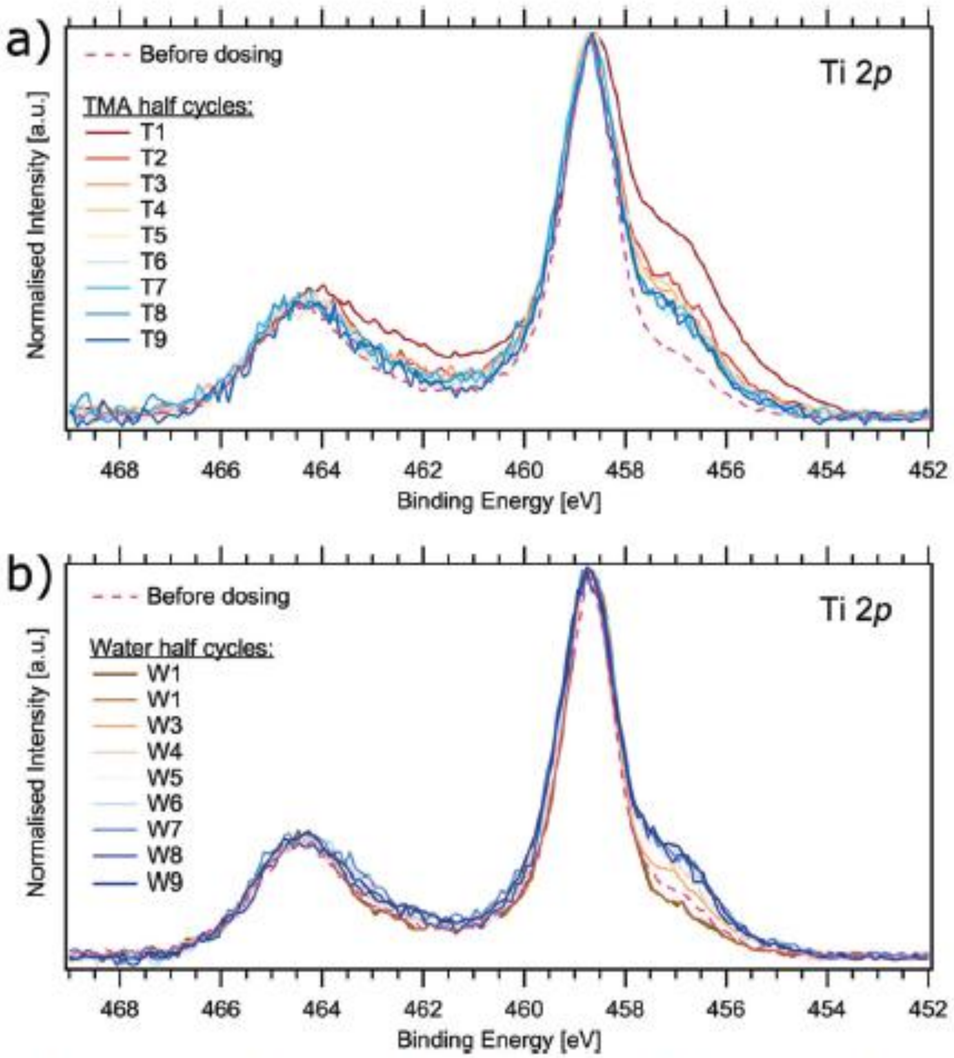


Fig. 3 Ti 2p spectra after each TMA (a) and water (b) half cycles that have been normalised to the height of the $Ti_{3/2}^{4+}$ peak. A spectrum prior to dosing is included for reference.

Ti^{3+} defects are created at the interface due to the reaction of the surface with tri-methyl aluminium

Ti^{3+} defects are healed by water exposure, but get locked-in at the interface after a full monolayer is formed.

An in situ exploration of subsurface defect migration to a liquid water-exposed rutile TiO_2(110) surface by XPS

SURFACE and INTERFACE ANALYSIS
WILEY

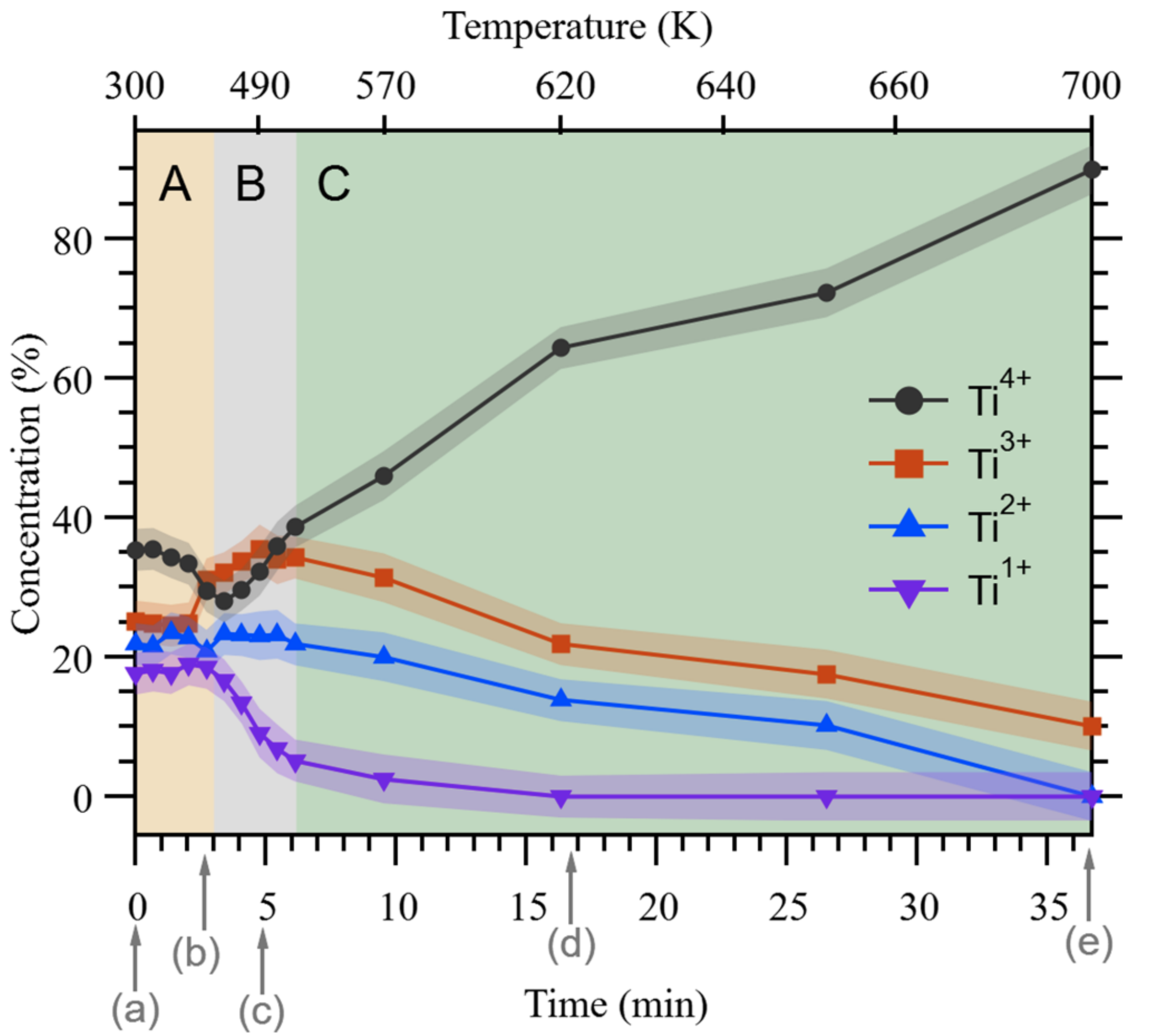
M. H. Mesbah Ahmed |

School of Physics & Astronomy, University of Nottingham, Nottingham, UK

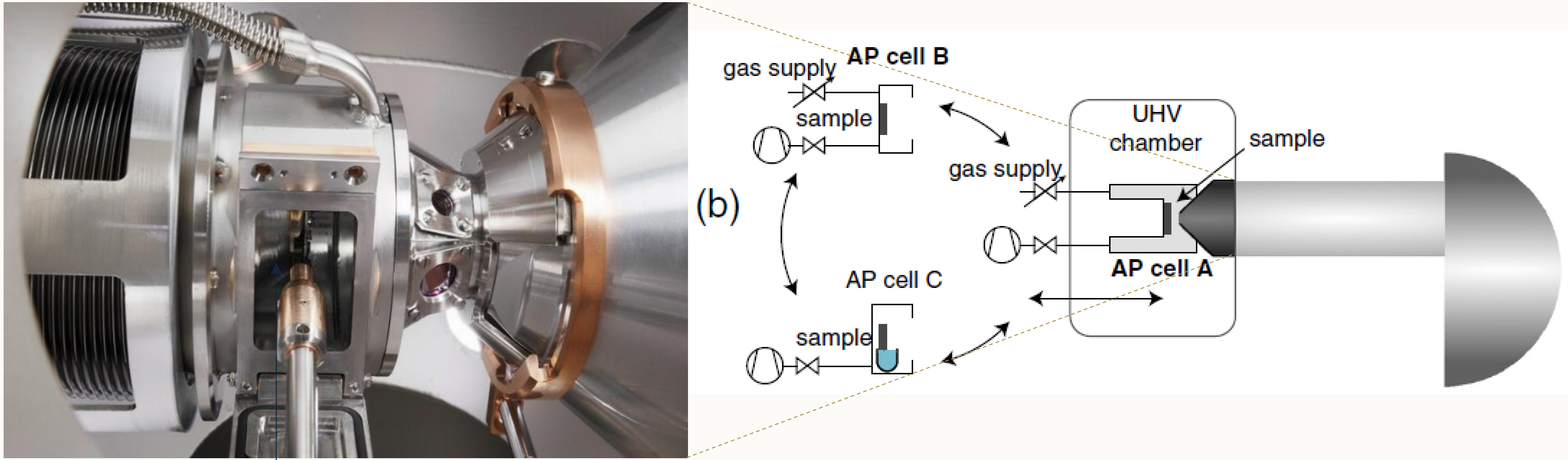
Correspondence
James N. O'Shea, School of Physics & Astronomy, University of Nottingham, Nottingham NG7 2RD, UK.
Email: J.Oshea@nottingham.ac.uk

Funding information
Engineering and Physical Sciences Research Council, Grant/Award Number: Doctoral Prize; Innovate UK, Grant/Award Number: ERA; University of Nottingham, Grant/Award Number: Propulsion Futures Beacon

Paper presented at the UK Surface Analysis Forum 40th Anniversary Meeting, University of Nottingham UK, 10-11 July 2019.

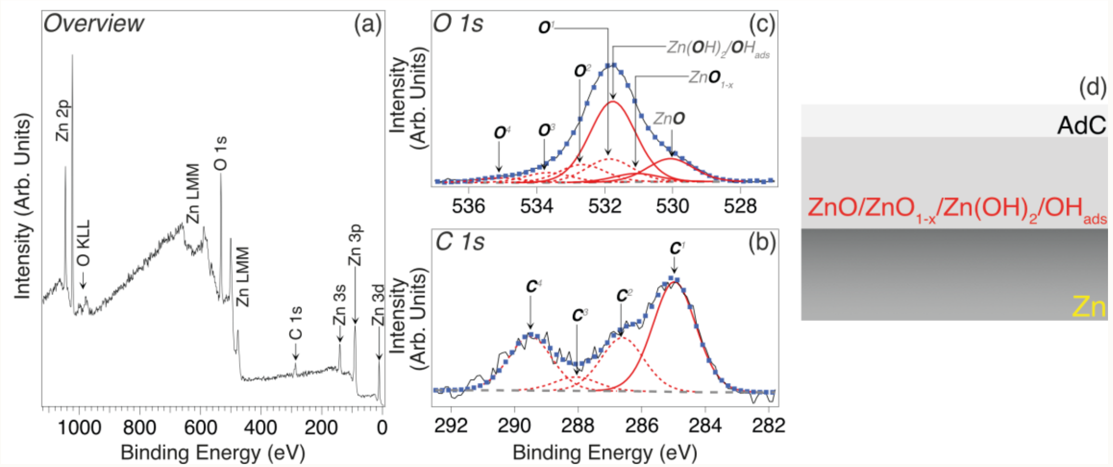


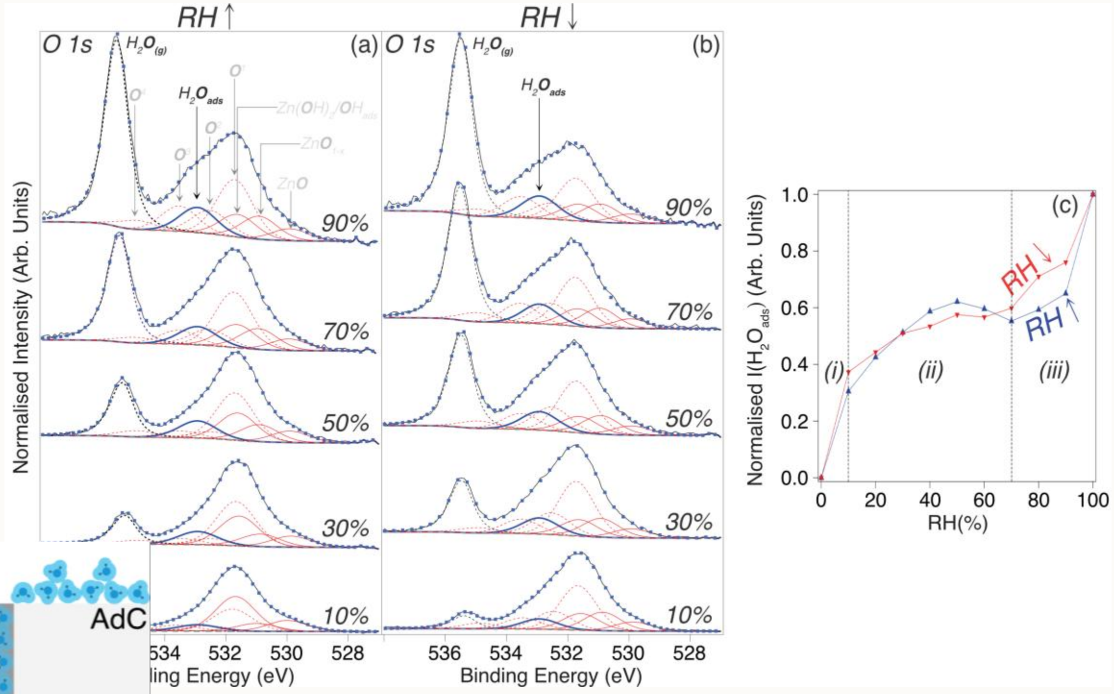
How do we get liquid water on the surface?

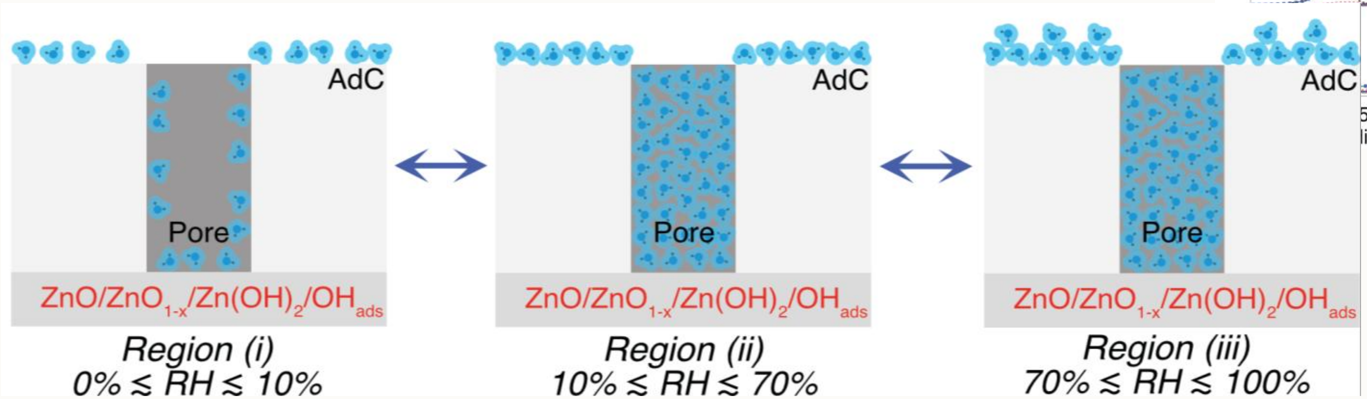


Peltier thermoelectric cooled sample

Complexity at a Humid Surface: Throwing Light on Atmospheric Corrosion







M. Dowhyj *et al*, Submitted to ACS Applied Materials & Interfaces (2024)

University of Nottingham
UK | CHINA | MALAYSIA

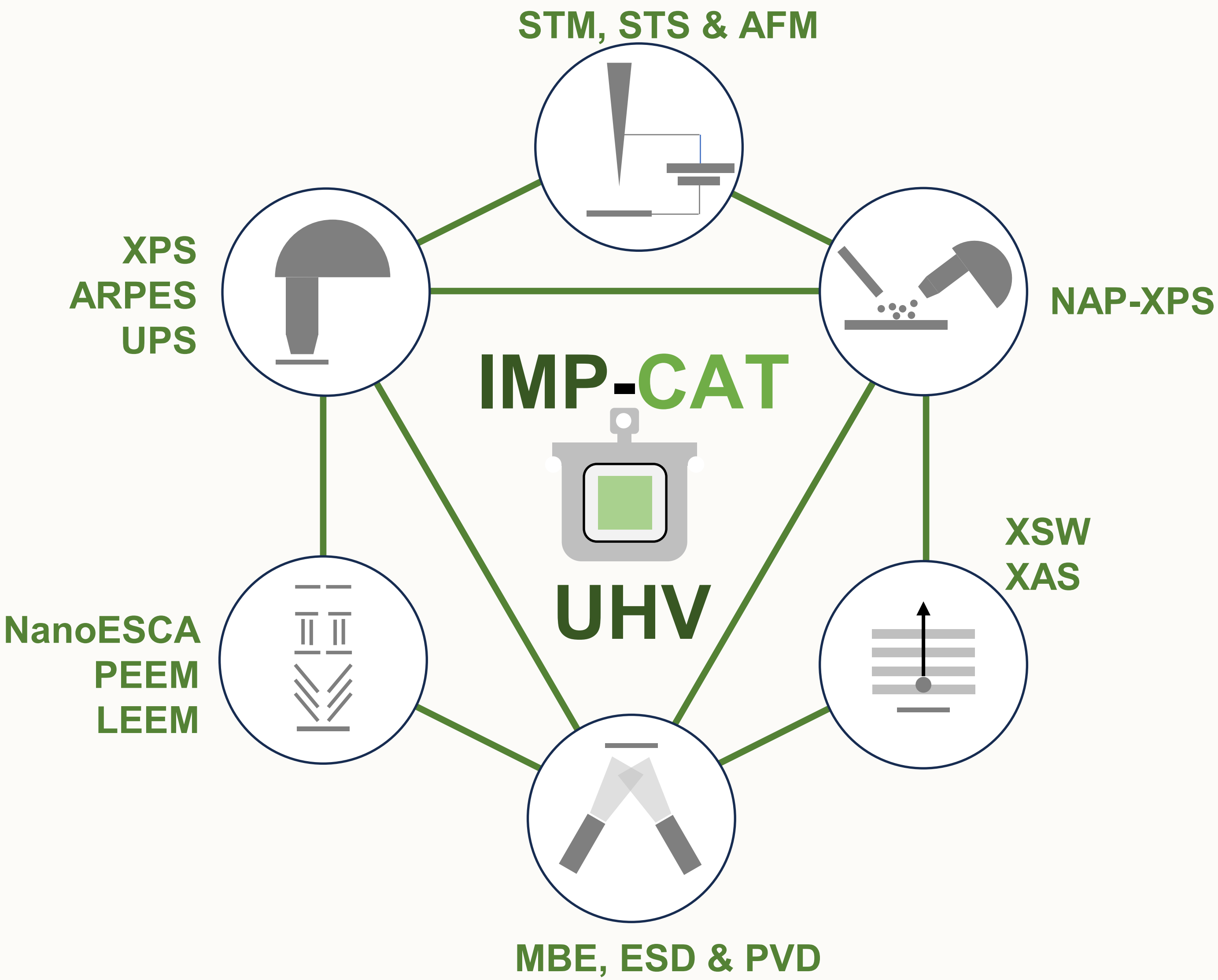
The growth of GaSe & oxidation to Ga_2O_3

EPI2SEM & NAP-XPS

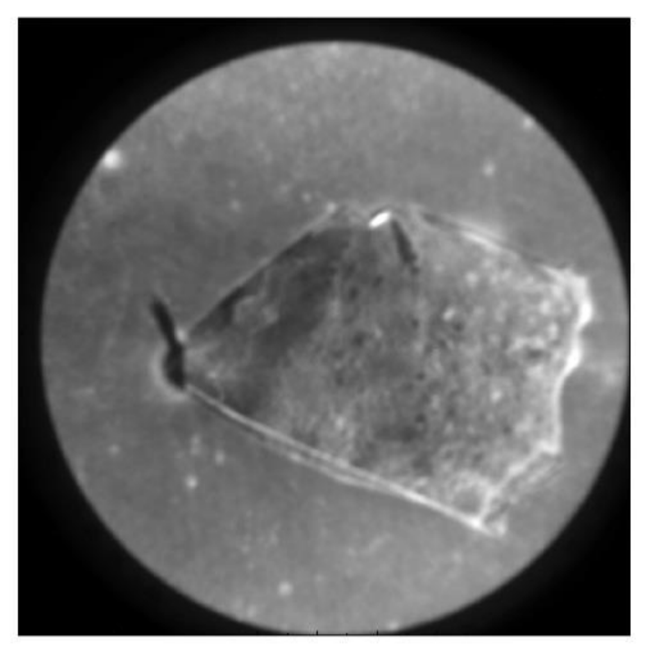
IMP-CAT

IMP-CAT

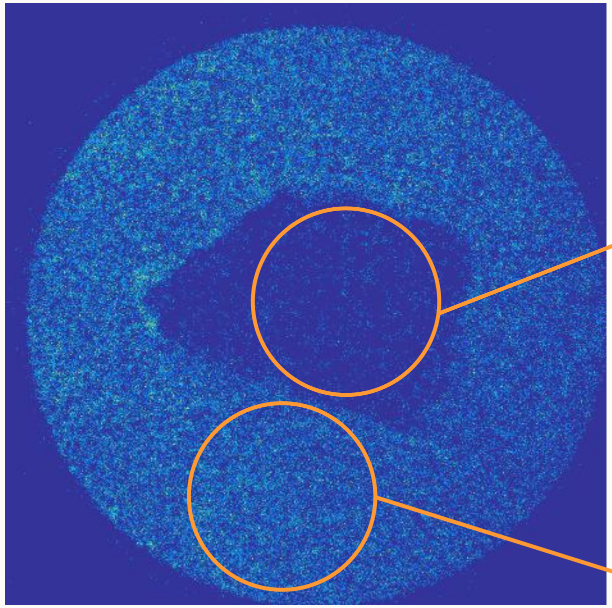
Interconnected Materals Preparation & Characterisation for Advanced Technologies



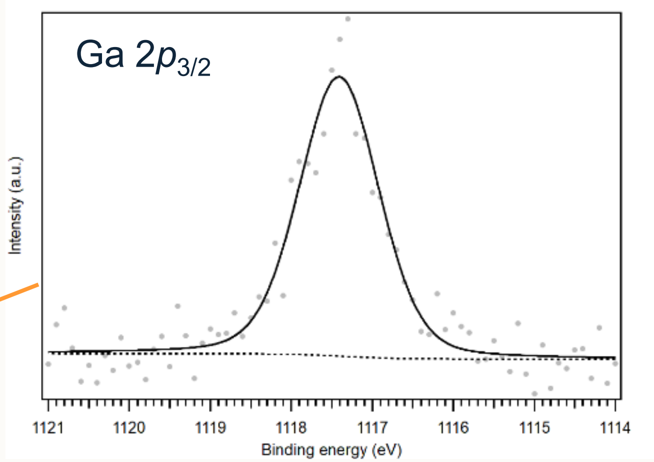
XPEEM of a 20 µm GaSe flake on Gold

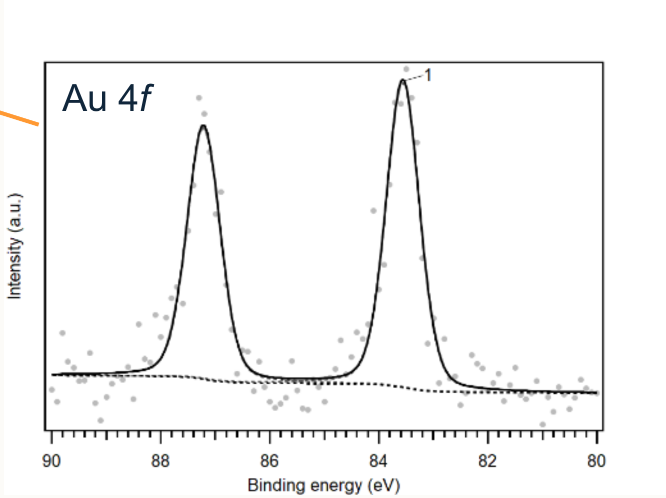


Hg-lamp image

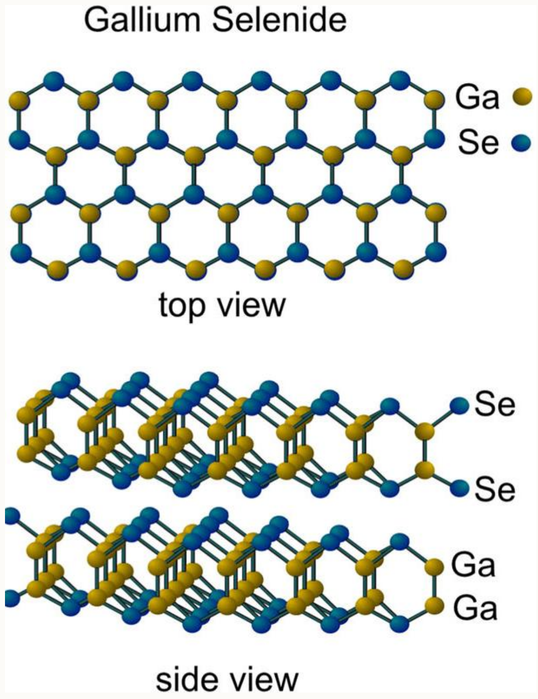


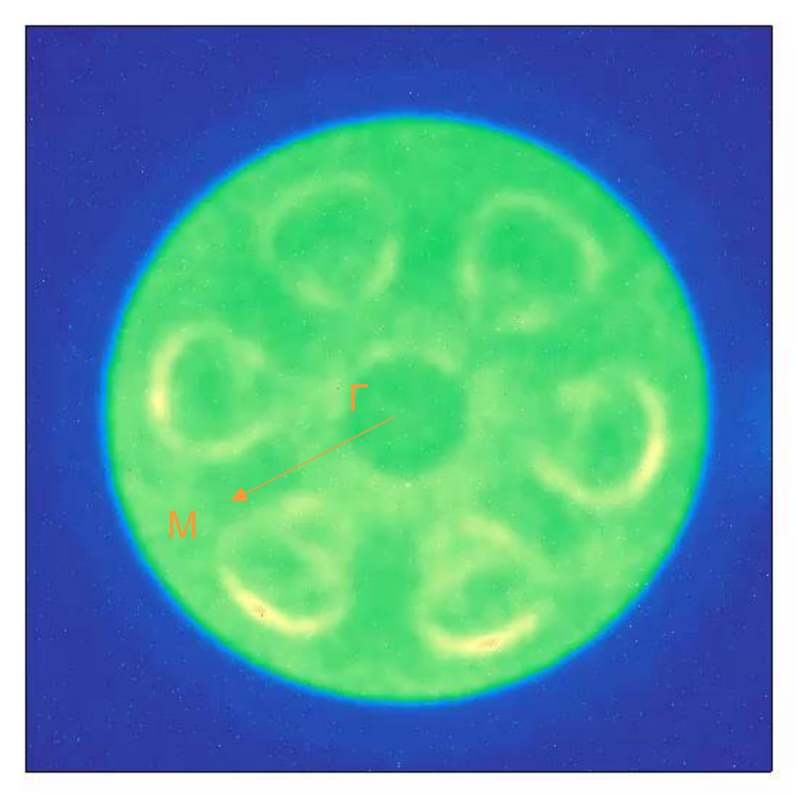
X-ray excited secondary electron image

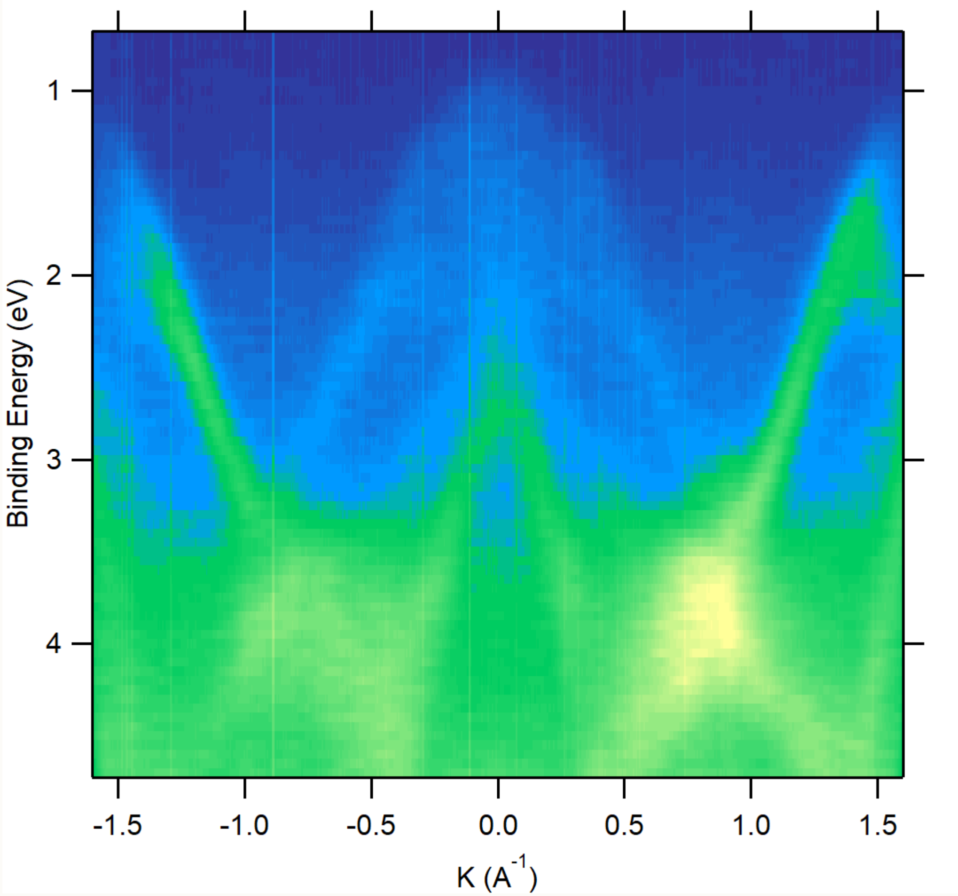




GaSe Flake (NanoESCA/ARPES)







NANO · MICRO small
www.small-journal.com

Epitaxy of GaSe Coupled to Graphene: From In Situ Band Engineering to Photon Sensing

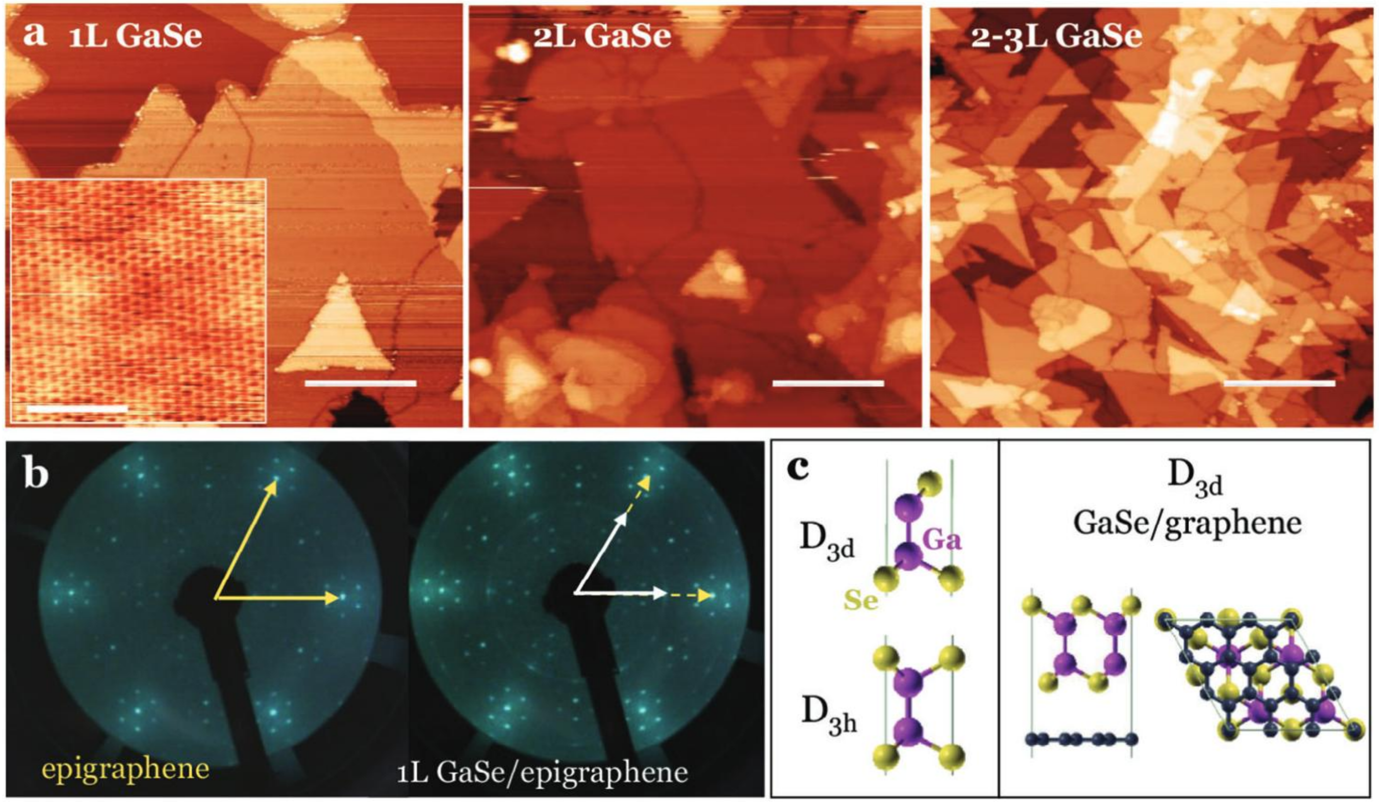
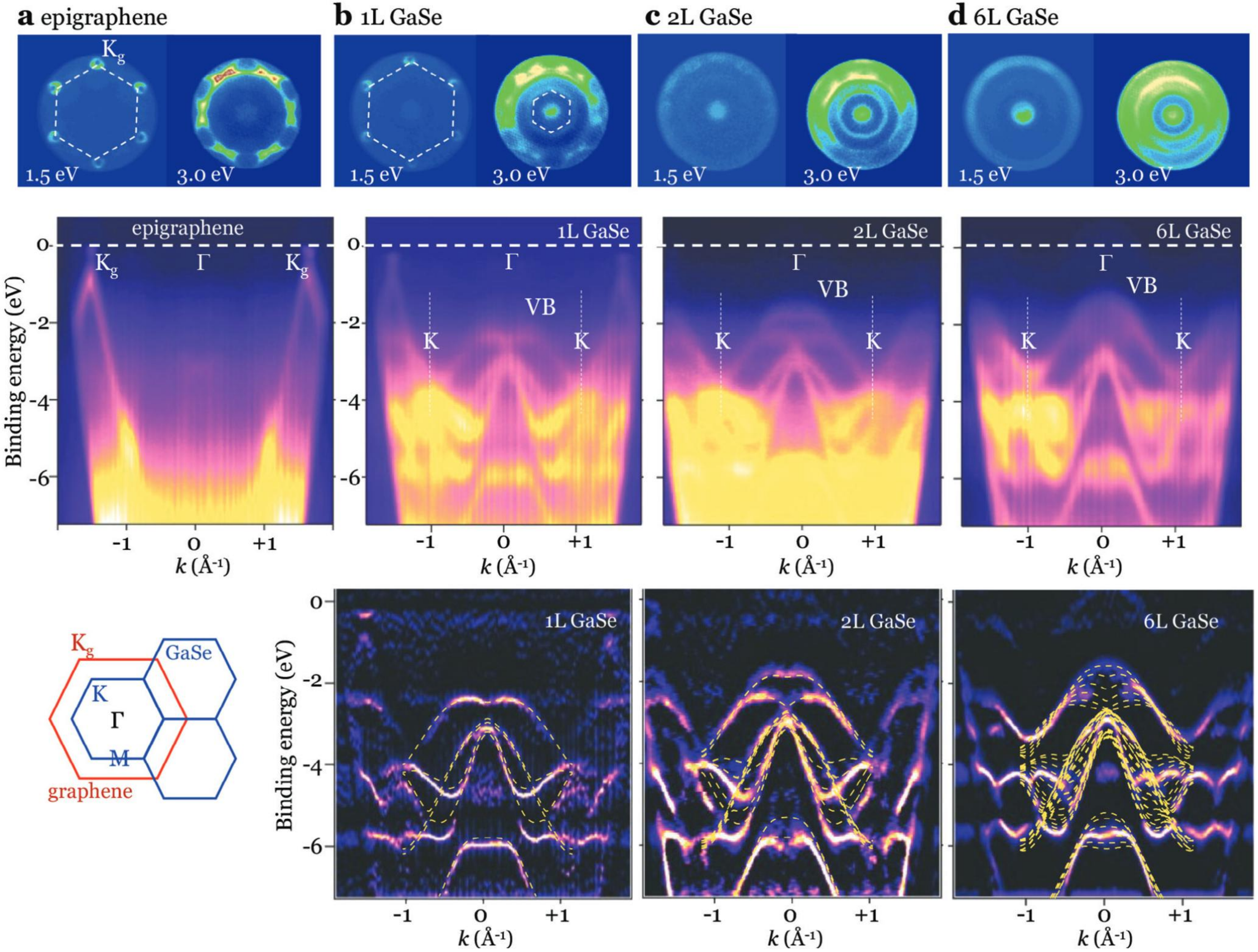
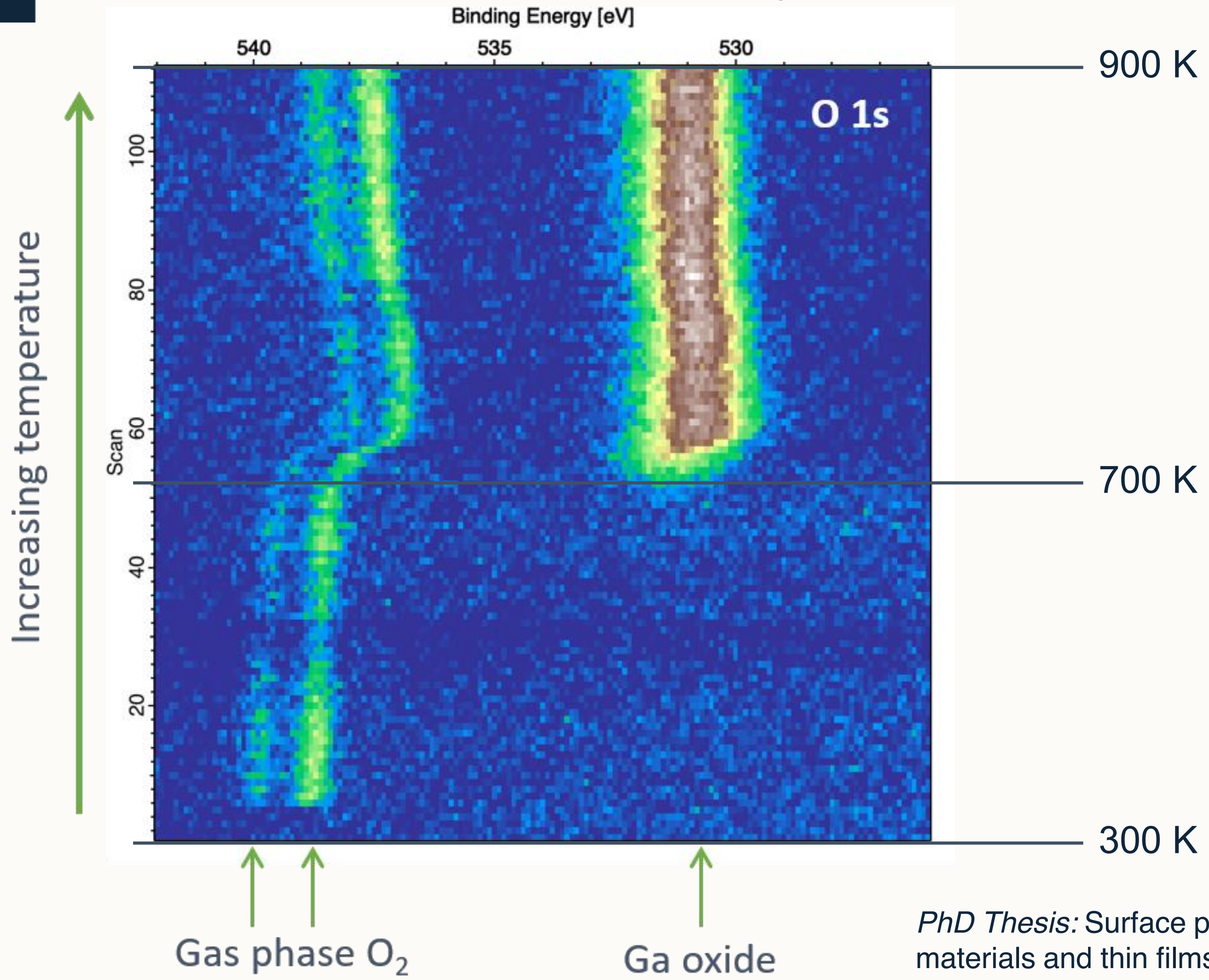


Figure 2. a) Scanning tunneling microscopy (STM) images for 1 layer (L), 2L, and 2–3L GaSe on epigraphene (scale bar = 200 nm). The inset (left) shows a high-resolution STM image for 1L GaSe (scale bar = 4 nm). b) Low energy electron diffraction (LEED) image for epigraphene (left) and for 1L GaSe on epigraphene (right). Arrows mark the diffraction spots for graphene (yellow, left and right) and 1L GaSe (white, right). Each of the spots for graphene is surrounded by six satellite spots associated with the $(6\sqrt{3} \times 6\sqrt{3})R30°$ buffer layer of SiC. c) Left: polymorphs of GaSe with axial-symmetry (D_{3h}) and centro-symmetry (D_{3d}). Right: In-plane and side views of D_{3d} GaSe on graphene, as modeled by density functional theory.

NANO · MICRO small
www.small-journal.com

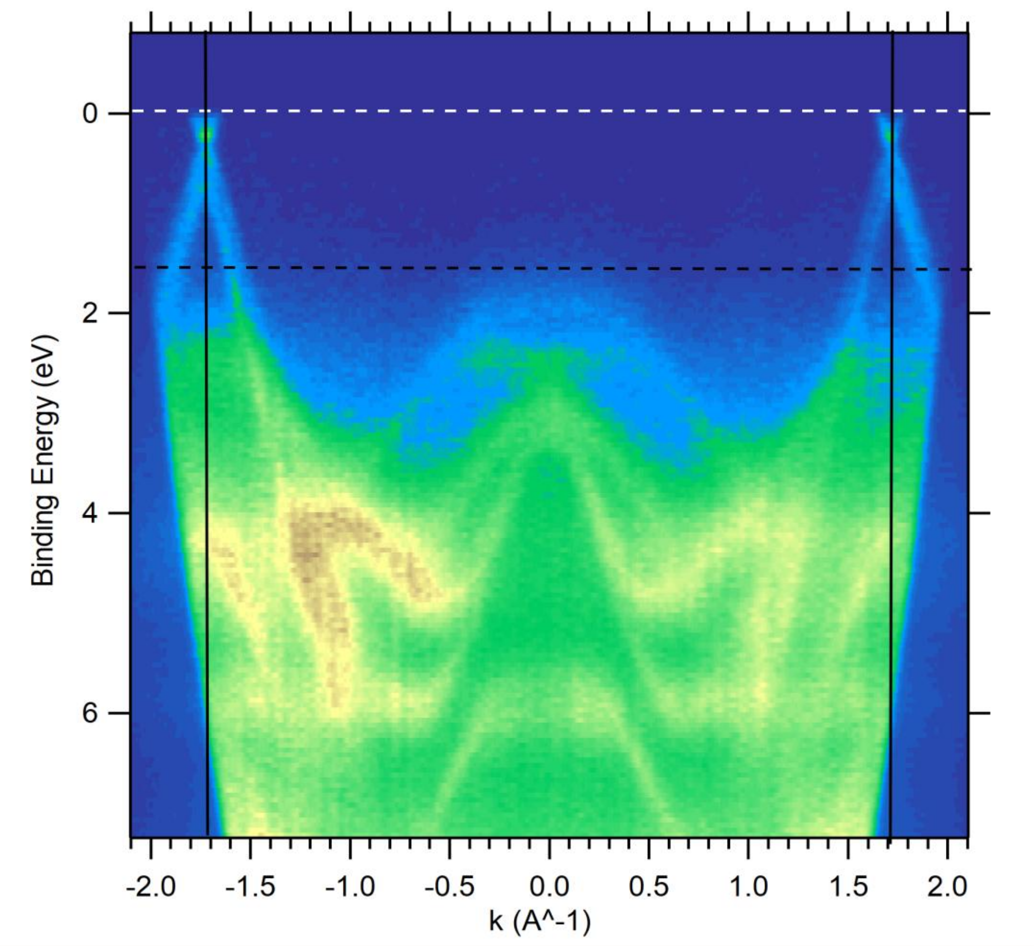


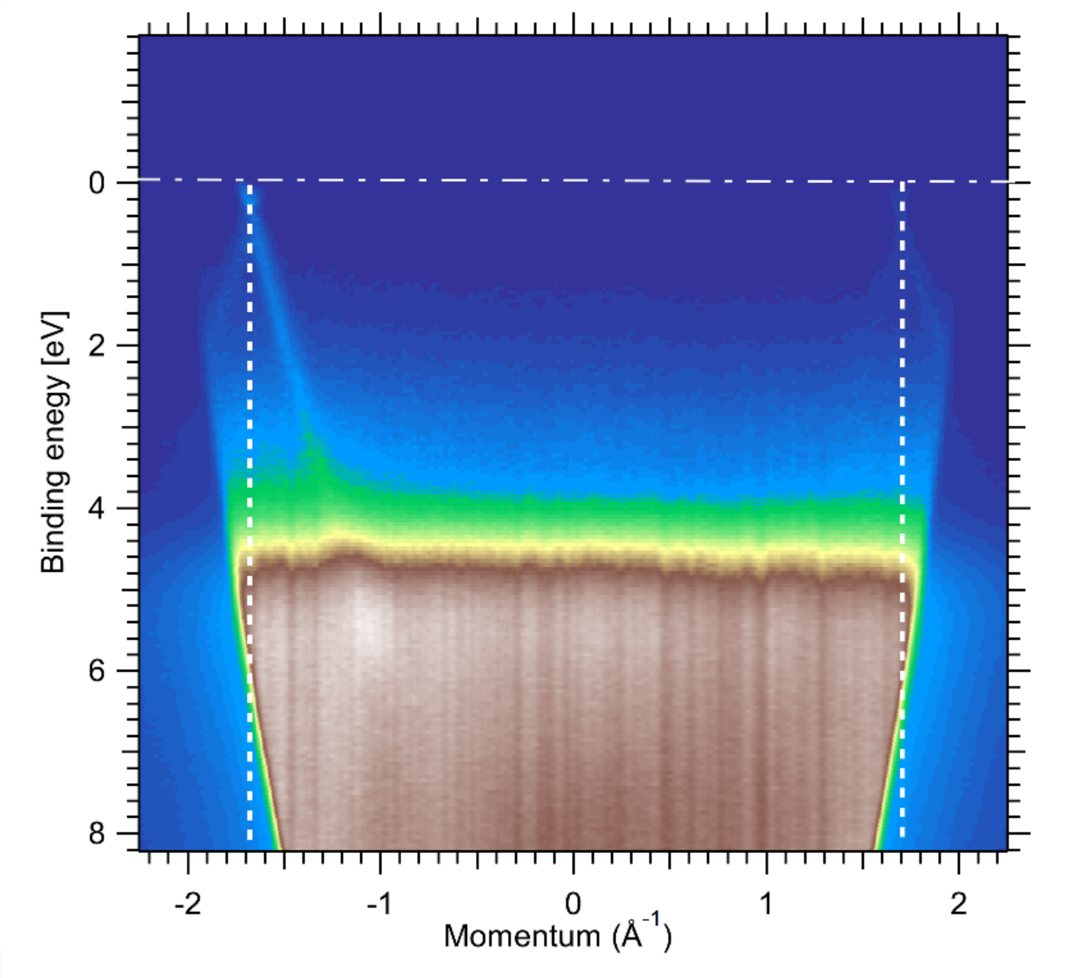
Oxidation of 3-layer GaSe to Ga_2O_3



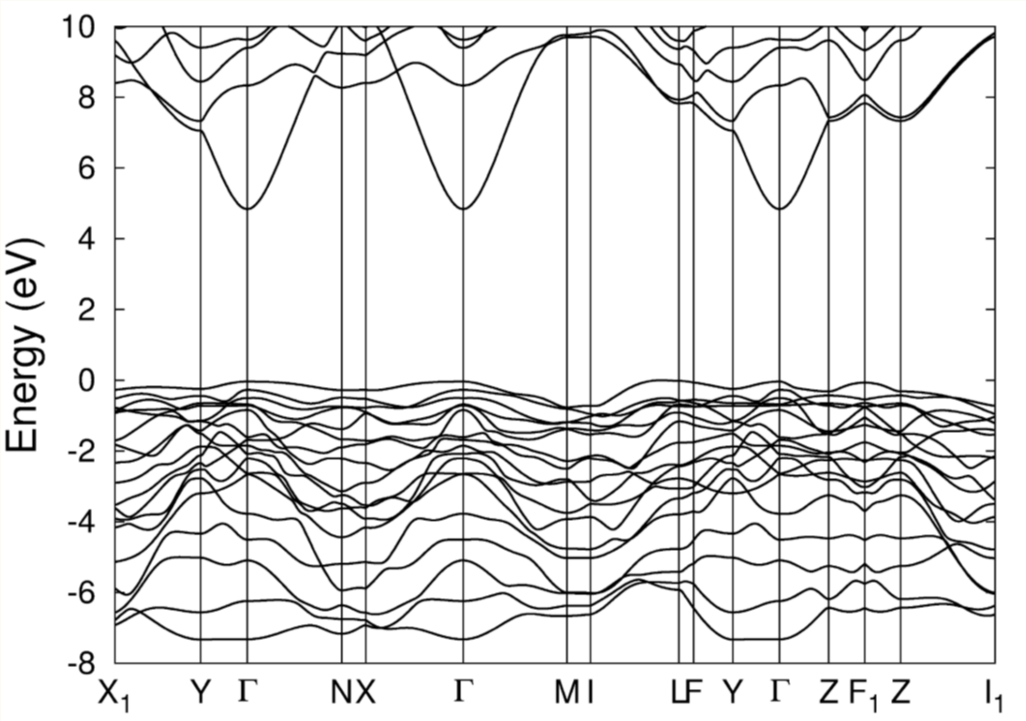
PhD Thesis: Surface properties & electronic band structure of 2D materials and thin films, K. Rahman (2024) – University of Nottingham

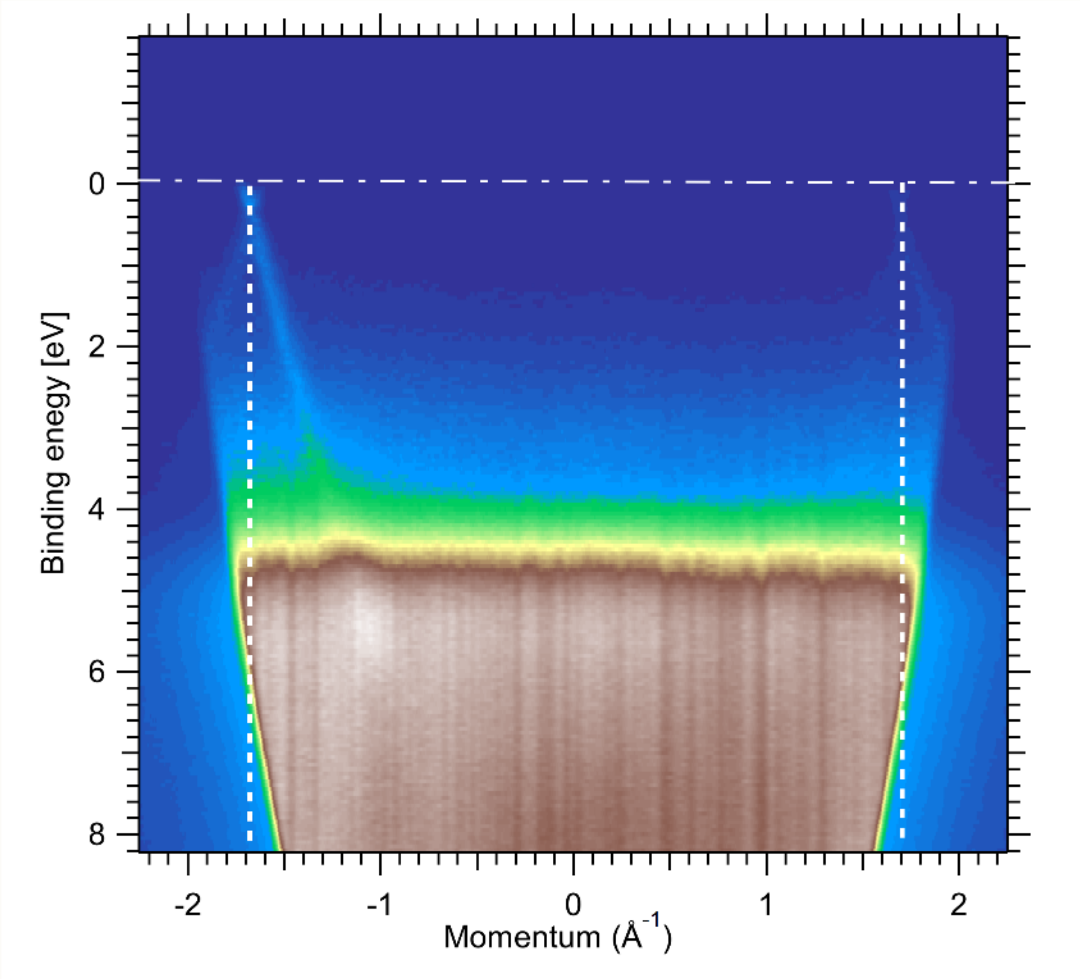
Oxidation of 3-layer GaSe to Ga_2O_3



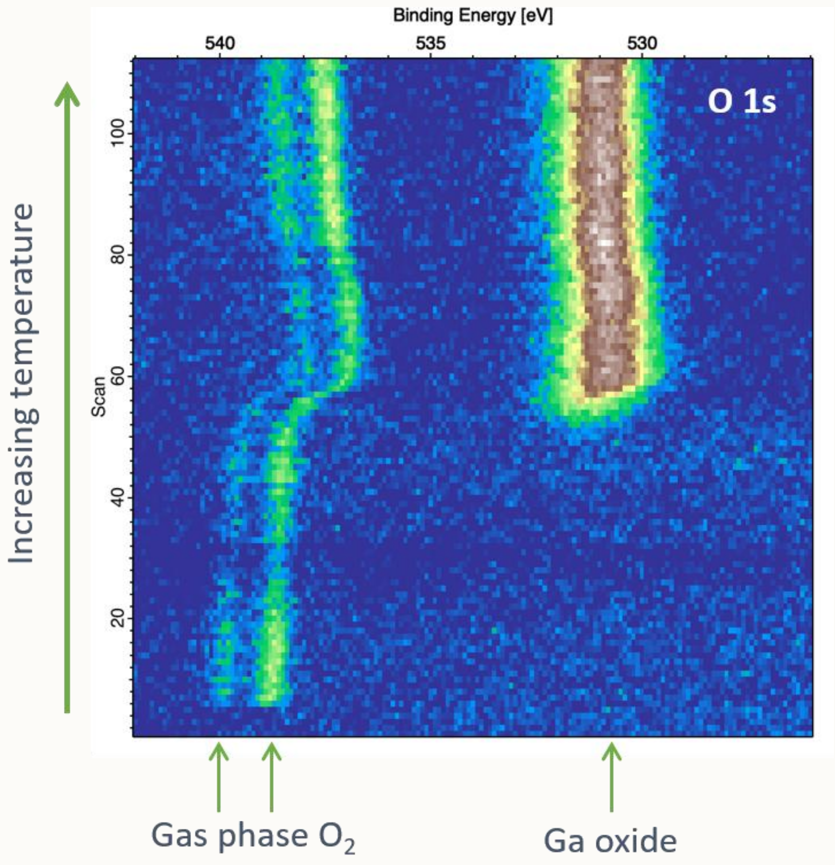


Oxidation of 3-layer GaSe to Ga_2O_3

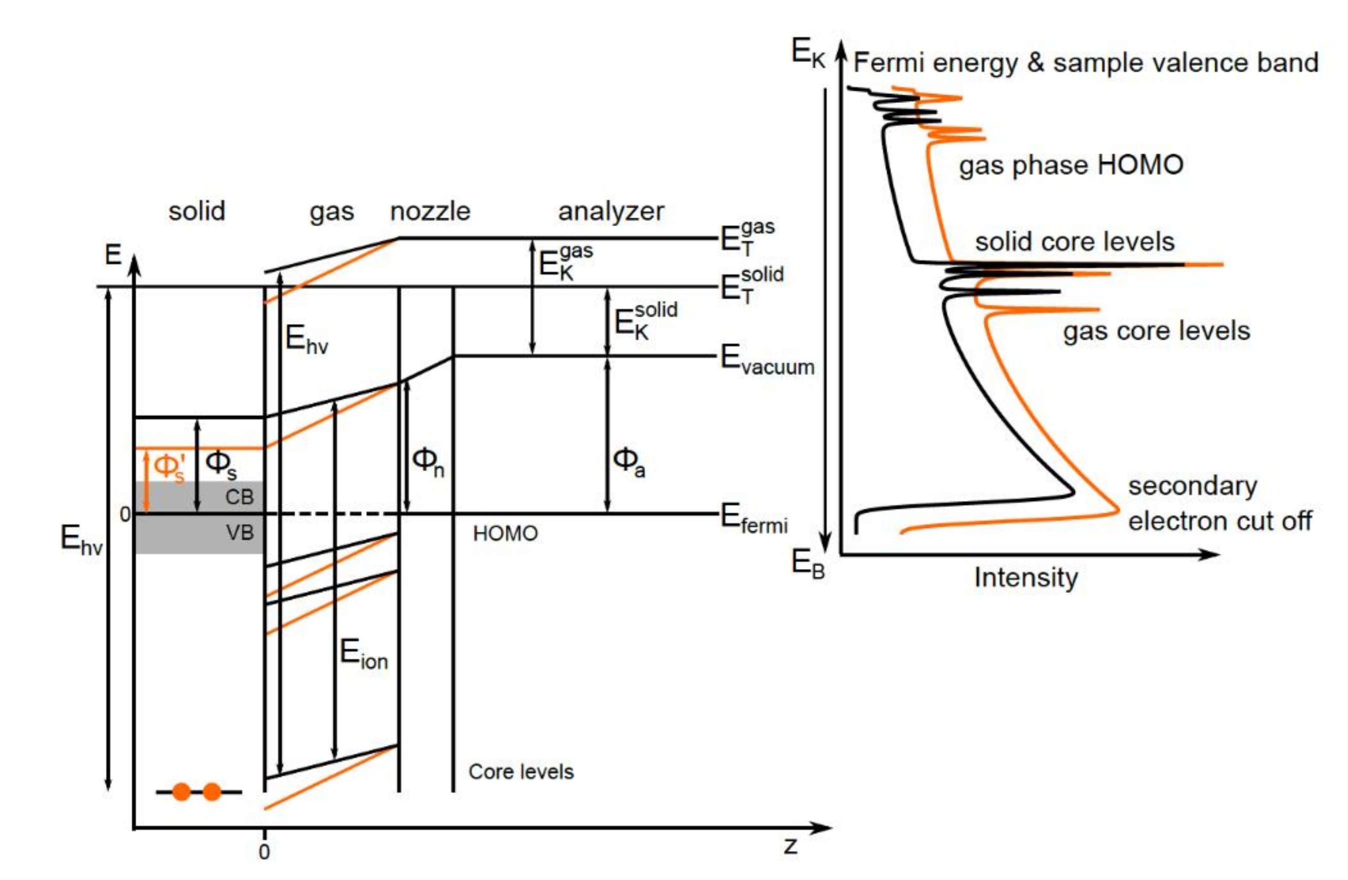




In-situ NAP-XPS probe of the work function

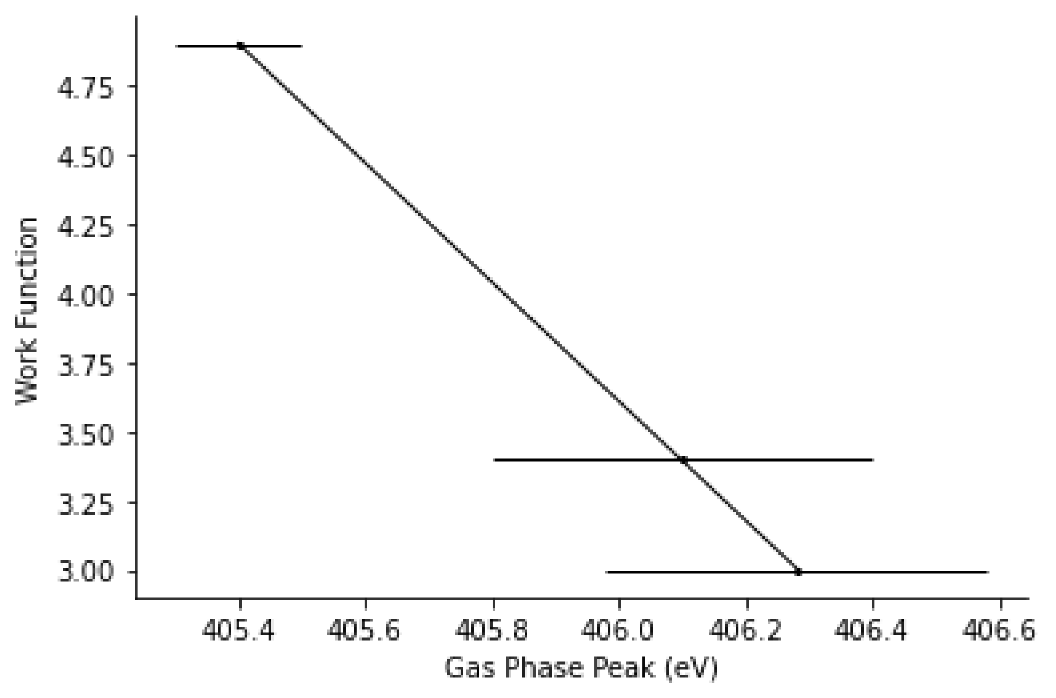


K. Rahman (2024) PhD Thesis



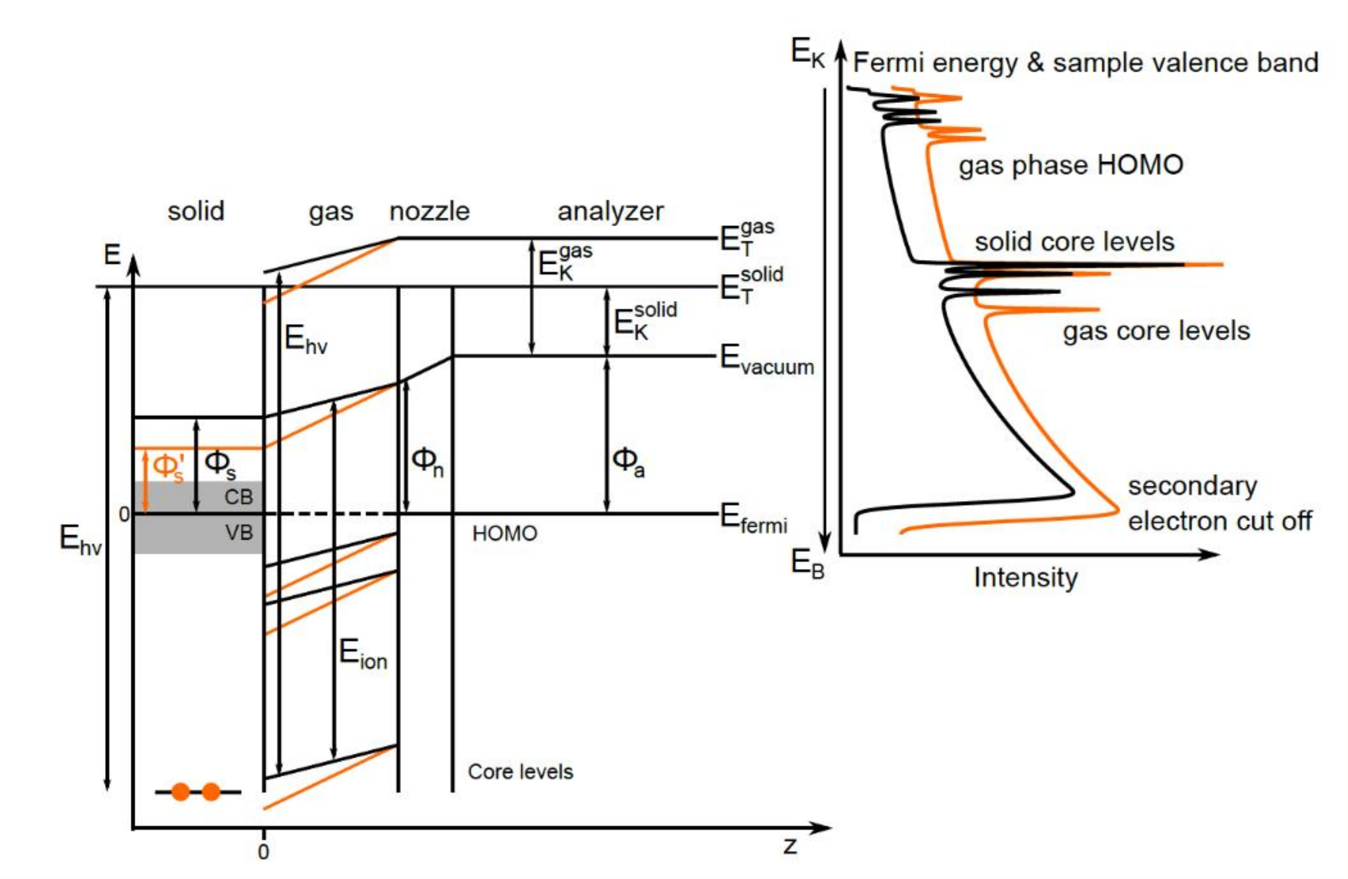
PhD Thesis: Synchrotron-based In Situ Electron Spectroscopy Applied to Oxide Formation and Catalysis J. Niclas (2017) – Lund University

Gas-phase XPS probe of the work function



4 mbar N_2 over Au, O/Al, and Al

M. Parker, B. Linton, J. N. O'Shea (Unpublished)



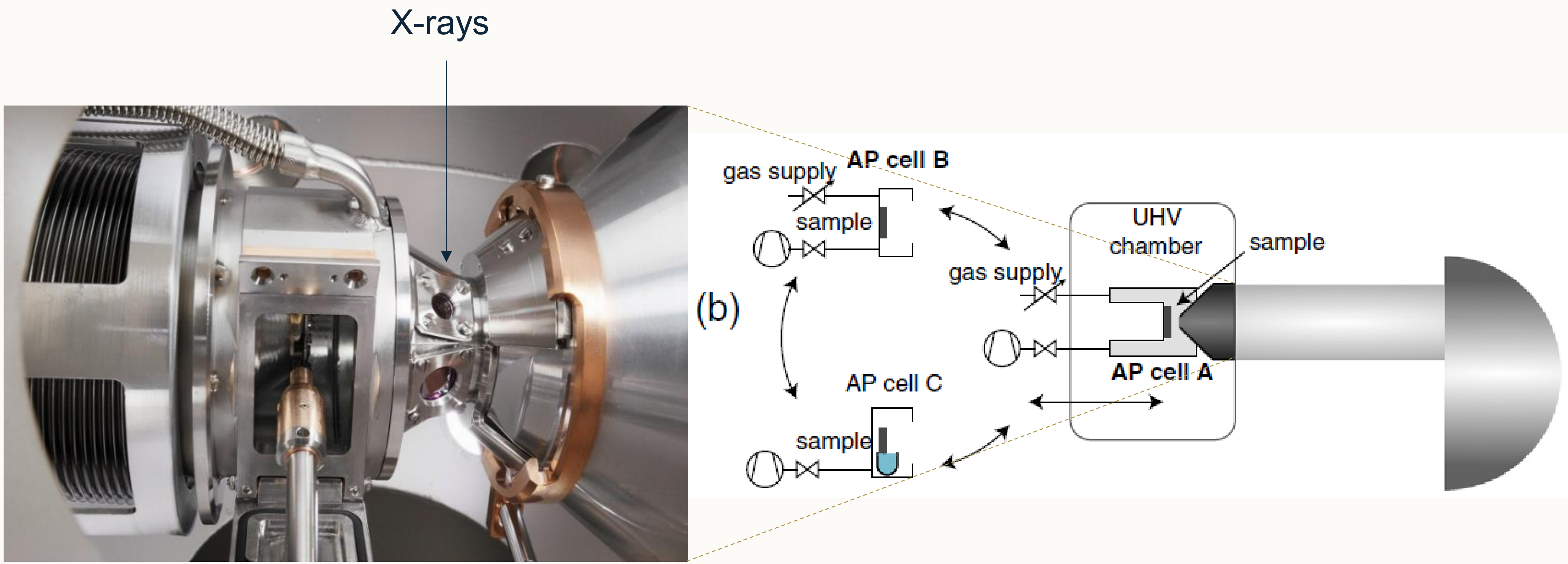
Synchrotron-based In Situ Electron Spectroscopy Applied to Oxide Formation and Catalysis J. Niclas (2017) PhD Thesis

What does near-ambient pressure mean in the context of electrochemical XPS?

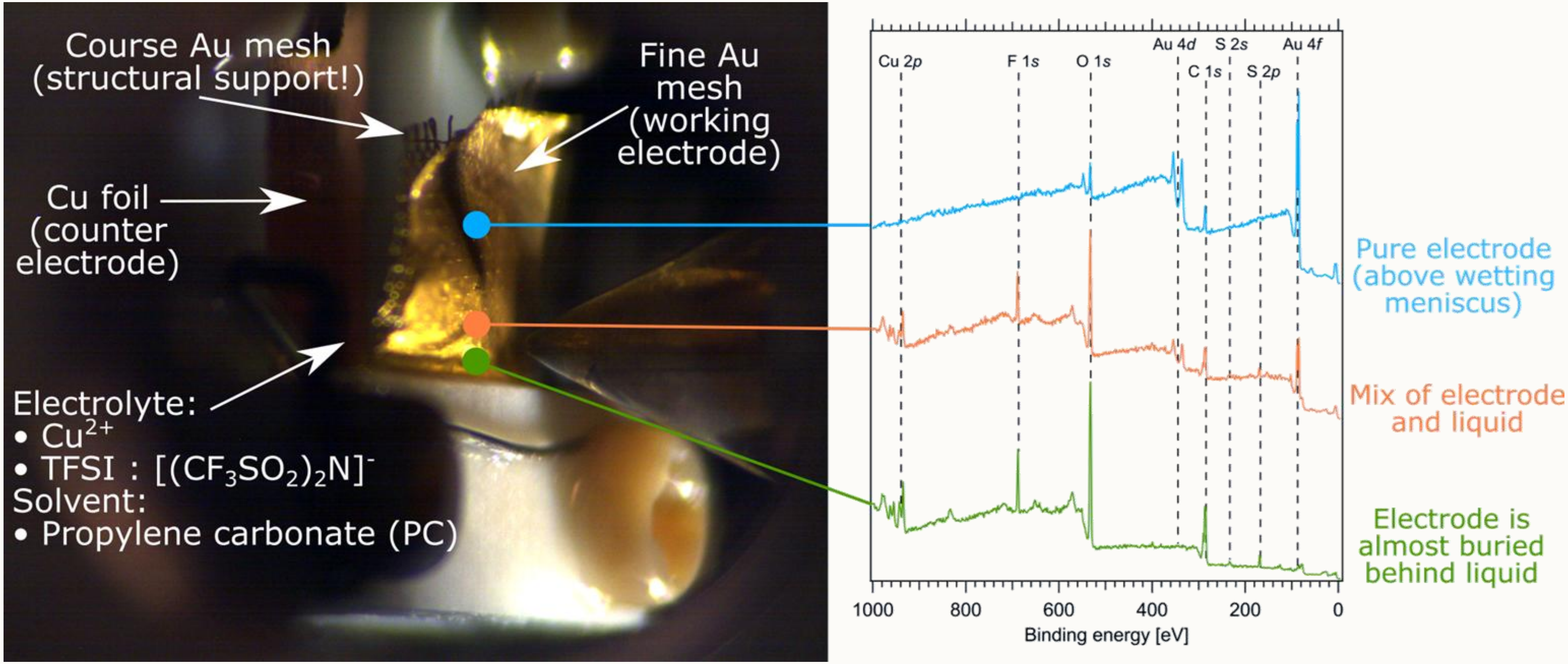
10^{-10} mbar ---------- 10^{-6} mbar ---------- 10 mbar ---------- 200bar

UHV — XPS — NAP-XPS — Industry

In-situ operando electrochemistry

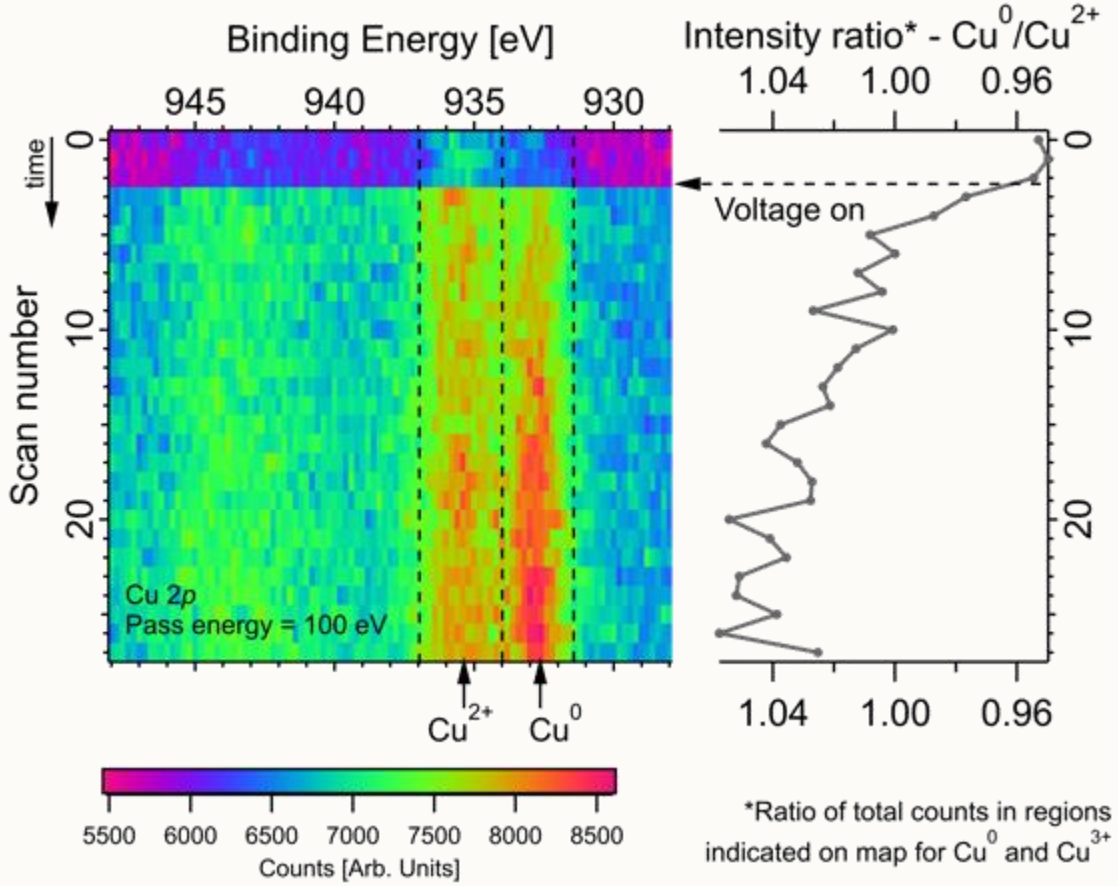


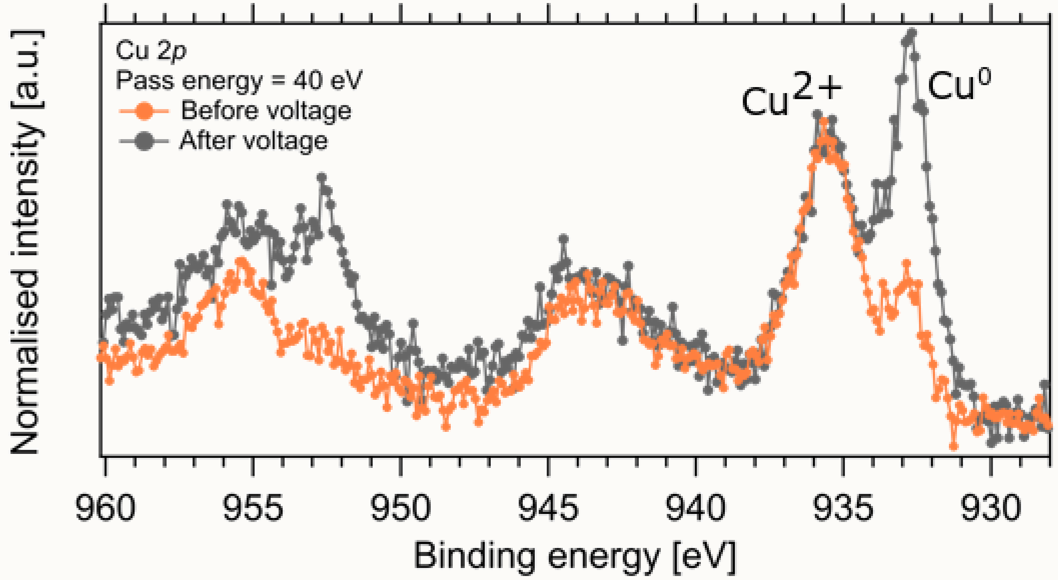
In-situ operando electrochemistry



R. H. Temperton, Unpublsihed

In-situ operando electrochemistry



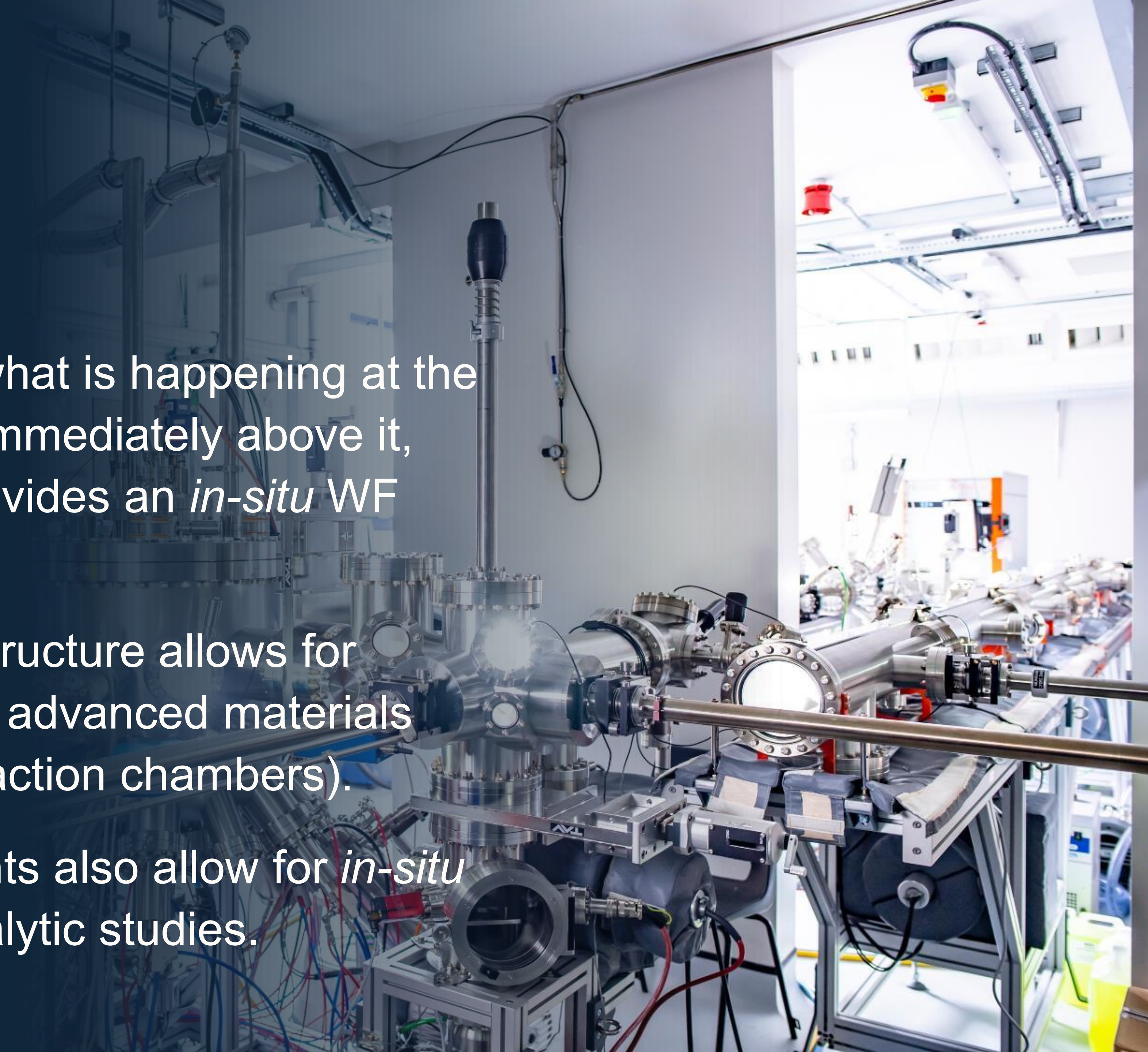


R. H. Temperton, Unpublsihed

University of Nottingham
UK | CHINA | MALAYSIA

Summary

- NAP-XPS allows us to see what is happening at the surface and the gas-phase immediately above it, **during the reaction** and provides an *in-situ* WF probe.
- The surrounding UHV infrastructure allows for transfer from instruments for advanced materials preparation (and coupled reaction chambers).
- Different sample environments also allow for *in-situ* electrochemical or photocatalytic studies.



Acknowledgements

Rob Temperton
Jack Hart
Mesbah Ahmed
Judy Castillo Rodriguez
Macarena Kroff Cortez
Molly Parker
Ben Linton
Jesum Alvez Fernandes
Andreas Weilhard
Anabel Lanterna

NAP-XPS funded by
Innovate UK
EPSRC

Amalia Patane
Peter Beton
Sergei Novikov
Tin Chen
Jonathan Bradford
Sabrina Rahman
James Felton
Mustaqeem Shifa
Adeem Ali M Azeer

EPI2SEM funded by
EPSRC

Thank you