Elettra
Sincrotrone
Trieste

Unveiling the local properties of nanomaterials using x-ray photoelectron spectromicroscopy

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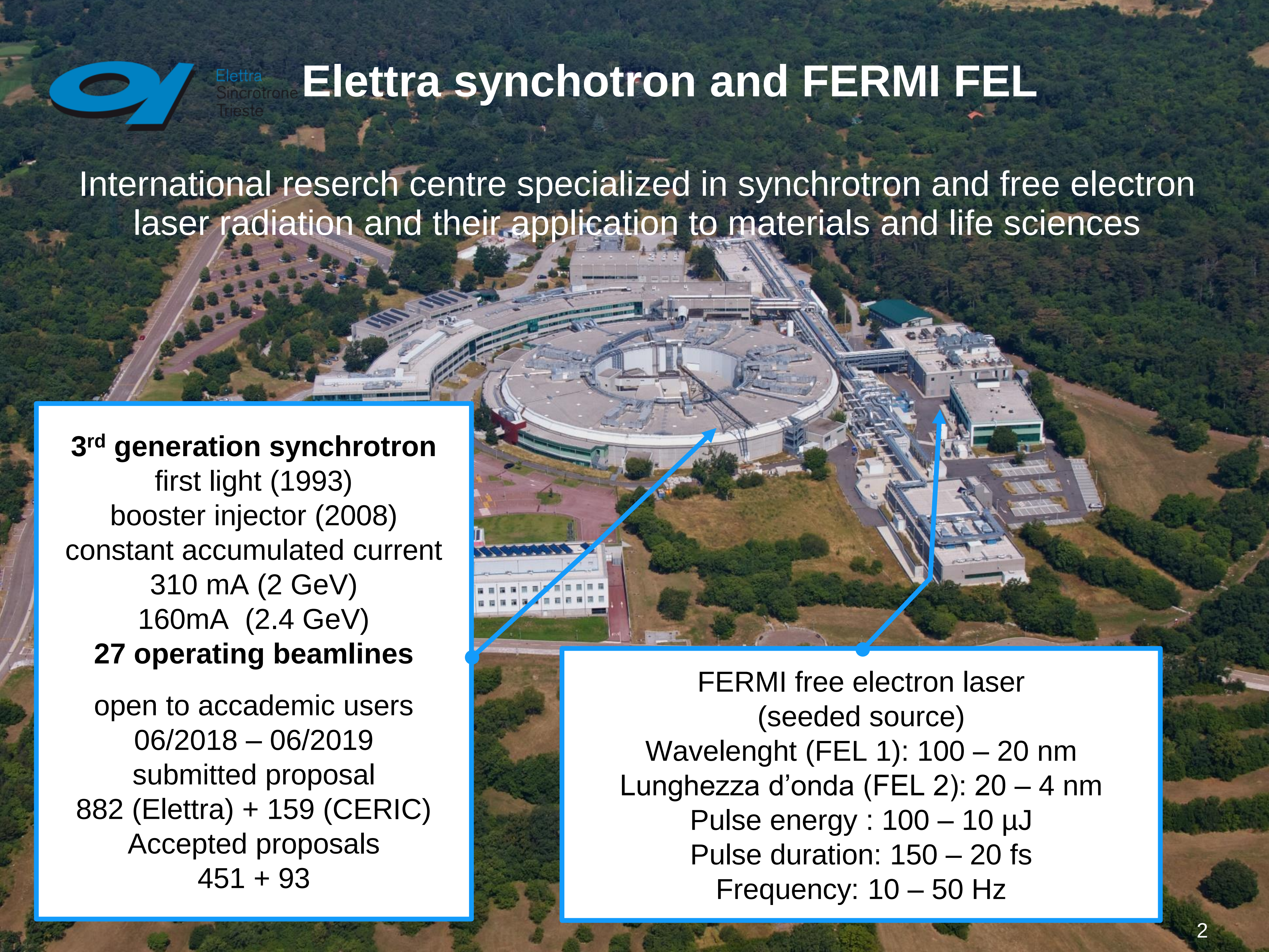


Elettra Sincrotrone Trieste

Elettra synchrotron and FERMI FEL

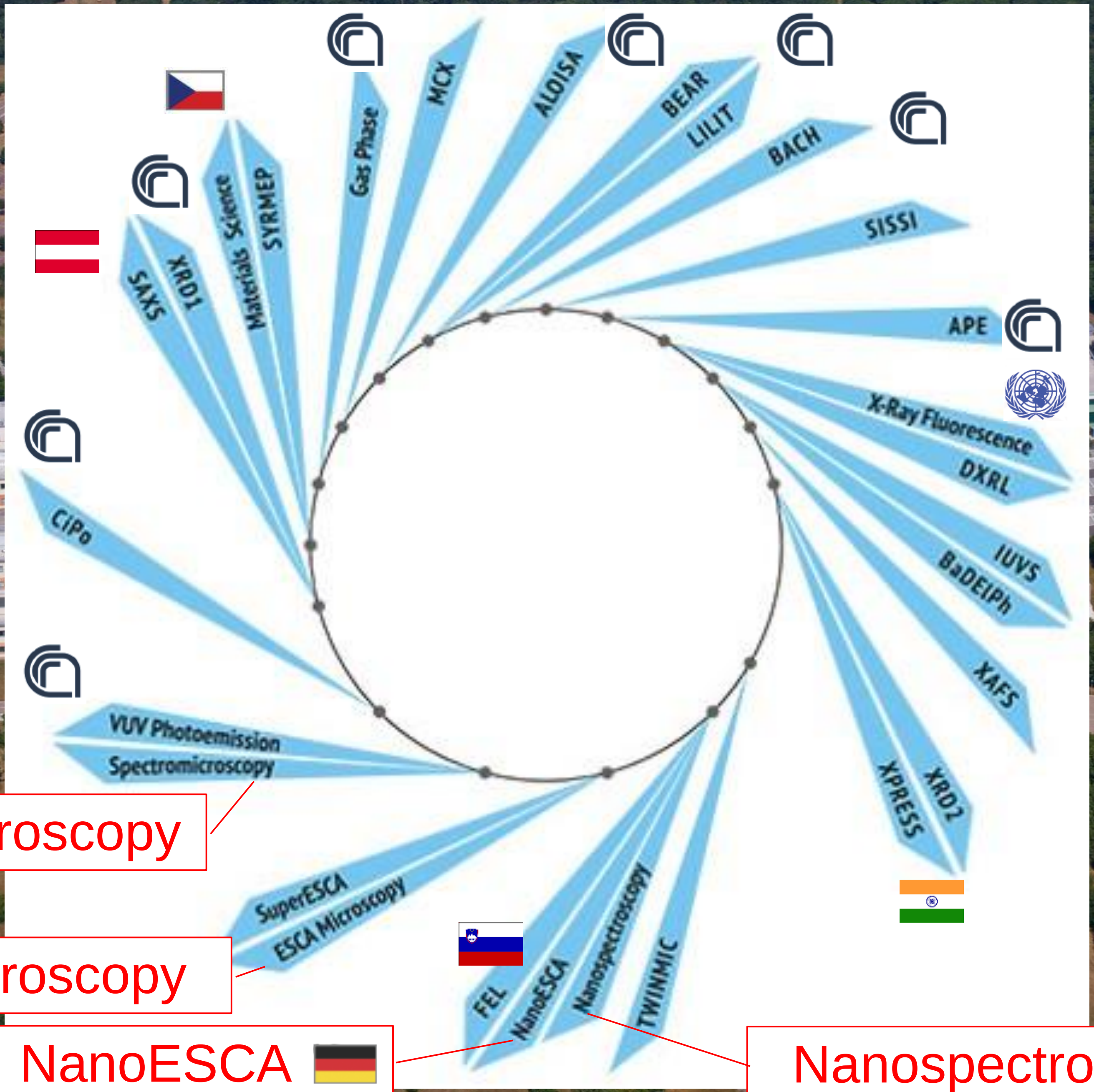
International reserch centre specialized in synchrotron and free electron laser radiation and their application to materials and life sciences

3rd generation synchrotron
first light (1993)
booster injector (2008)
constant accumulated current
310 mA (2 GeV)
160mA (2.4 GeV)
27 operating beamlines

open to accademic users
06/2018 – 06/2019
submitted proposal
882 (Elettra) + 159 (CERIC)
Accepted proposals
451 + 93

FERMI free electron laser
(seeded source)
Wavelenght (FEL 1): 100 – 20 nm
Lunghezza d'onda (FEL 2): 20 – 4 nm
Pulse energy : 100 – 10 µJ
Pulse duration: 150 – 20 fs
Frequency: 10 – 50 Hz

Elettra photoemission spectromicroscopes



Spectromicroscopy

ESCAmicroscopy

NanoESCA

Nanospectroscopy

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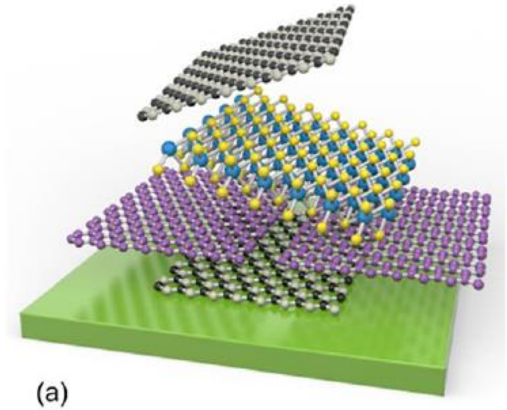
Outlook – materials & applications


(a)

<u>Nanomaterials</u>

Electronic and optical devices
Magnetic devices
Corrosion protection...
Catalysis and electro-chemistry

Goal
understand/control their properties at the microscopic scale!

- ❑ Crystal Structure / Morphology
- ❑ Chemical / Electronic Structure
- ❑ Magnetic Structure
- ❑ Interfacial interactions

} **Synchrotron-based Spectromicroscopes**

ESCA Microscopy Beamline

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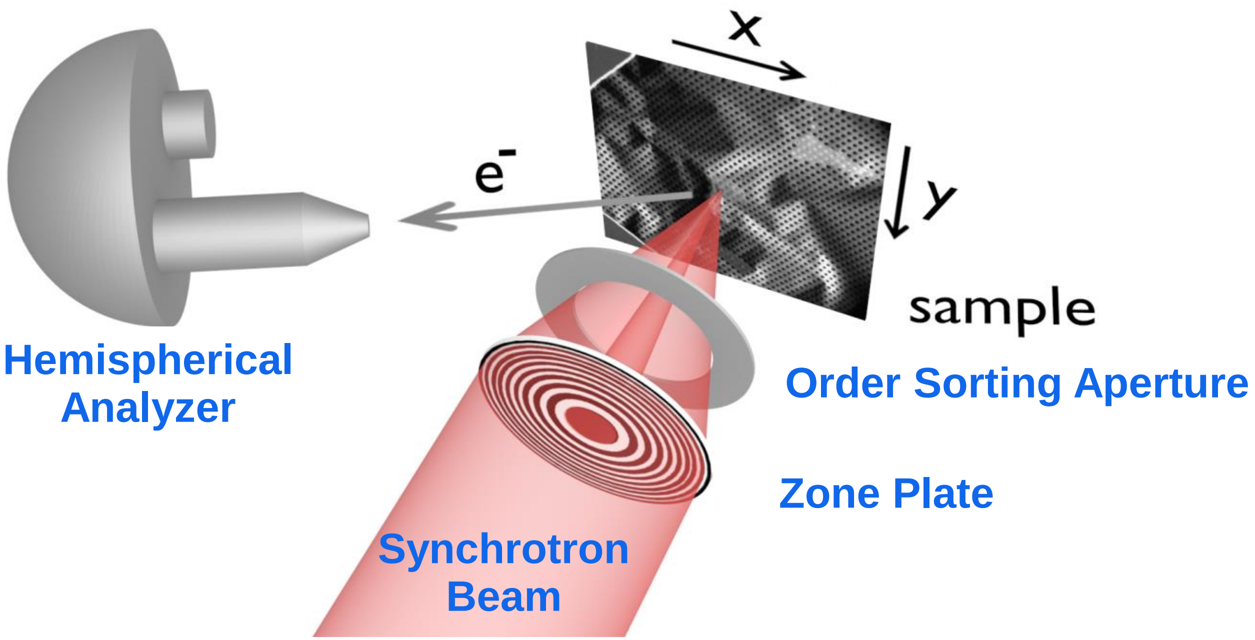
Scanning Photoelectron Microscope (SPEM)

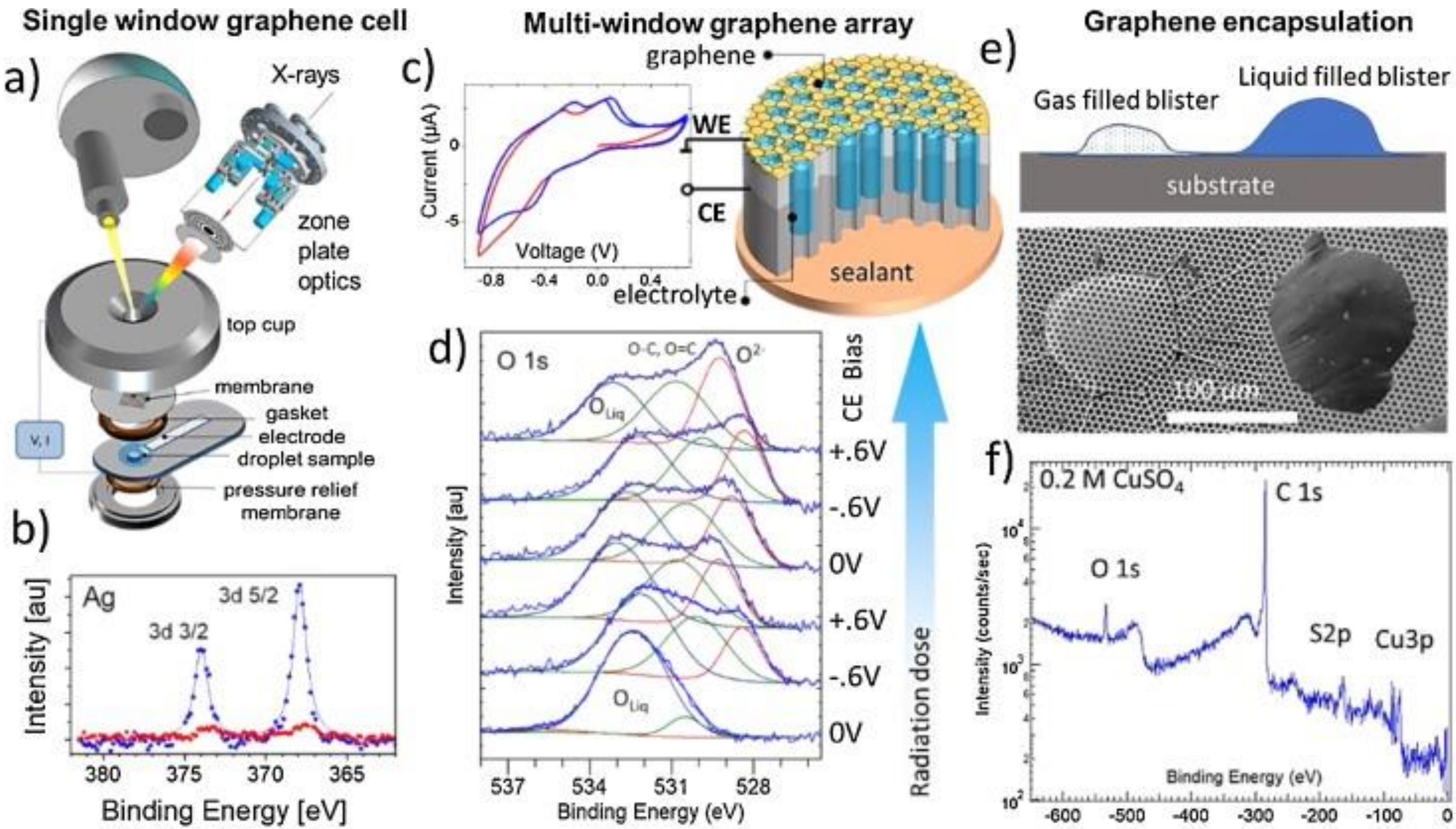


- Linearly Polarised Undulator
- Photon energy range: 400 – 1200 eV
- Overall Energy resolution: ~180meV @ 500 eV
- Beam Spot size at the sample: > 130 nm @ 500 eV

Contact: luca.gregoratti@elettra.eu

https://www.elettra.eu/elettra-beamlines/escamicroscopy.html

Graphene environmental cells: probing liquids

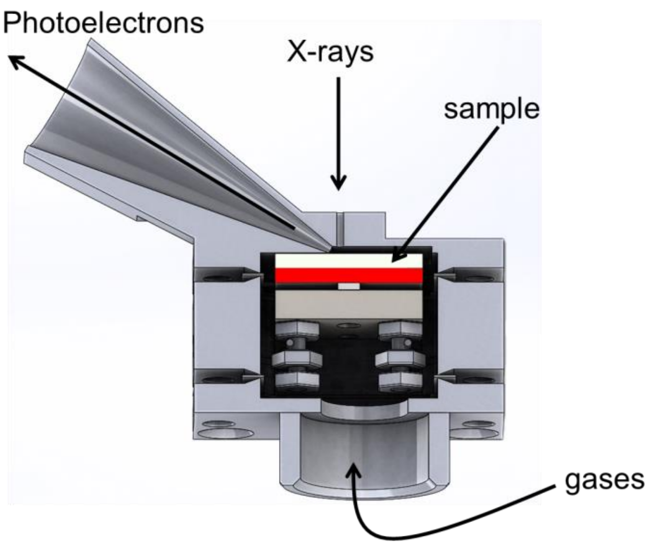


$AgNO_3$ solution — Radiolysis — $CuSO_4$ solution

M. Amati et al., J. Electron Spec. Rel. Phenomena, in press (2020)

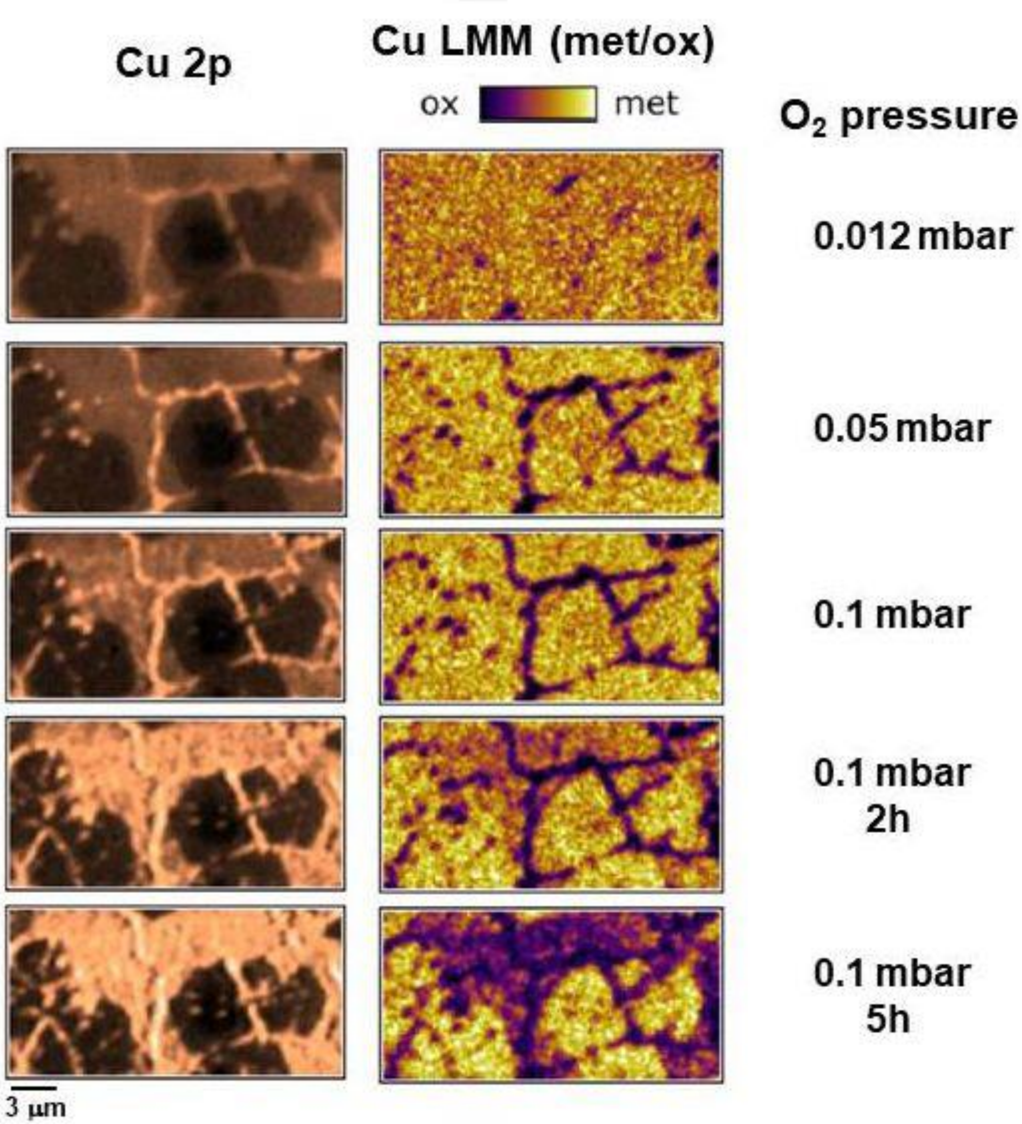
Operando photoemission microscopy

Highlighting the Dynamics of Graphene Protection toward the Oxidation of Copper Under Operando Conditions



Near Ambient Pressure Cell for NAP-XPS spectromicroscopy

(custom set up for pressure up to 1 mbar)



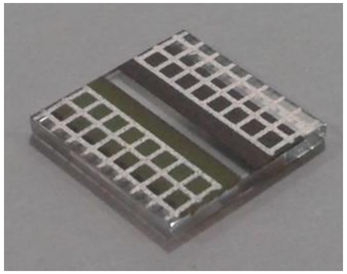
M. Scardamaglia et al., ACS Appl. Mater. Interfaces 11, 29448 (2019)

Characterization of a single-chamber solid oxide fuel cell

(in collaboration with B. Bozzini, Università del Salento, Italy)

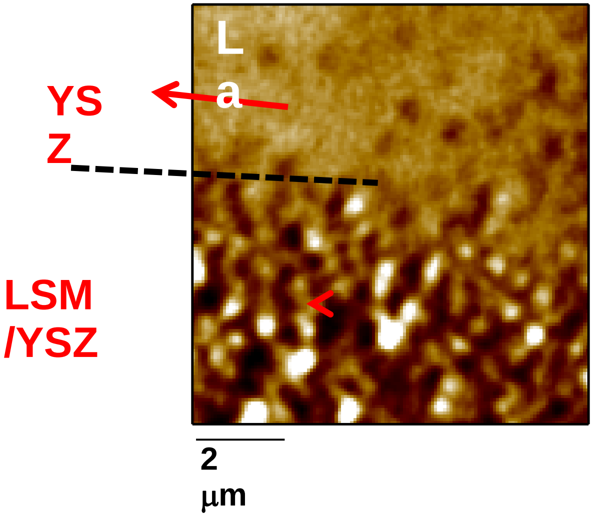
- *In operando* near-ambient pressure characterization of an operating single chamber solid oxide fuel cell (SC-SOFC)

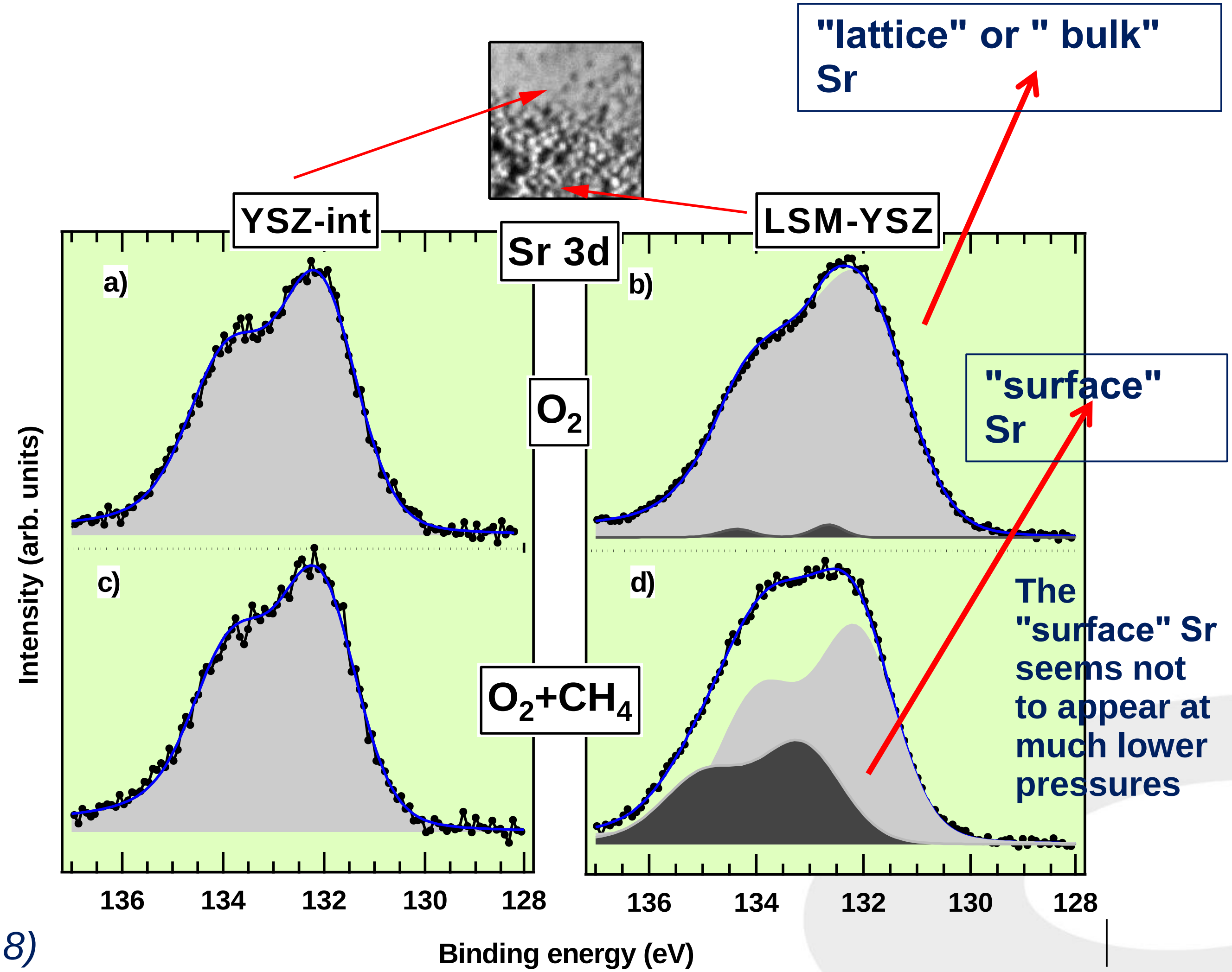
T= 923 K with a CH_4/O_2 gas mixture; P_{max}=0.1 mbar



NiO – anode
LSM – cathode
YSZ – electrolyte

SPEM map of the interface





B. Bozzini et al. Topics in Catalysis (2018)

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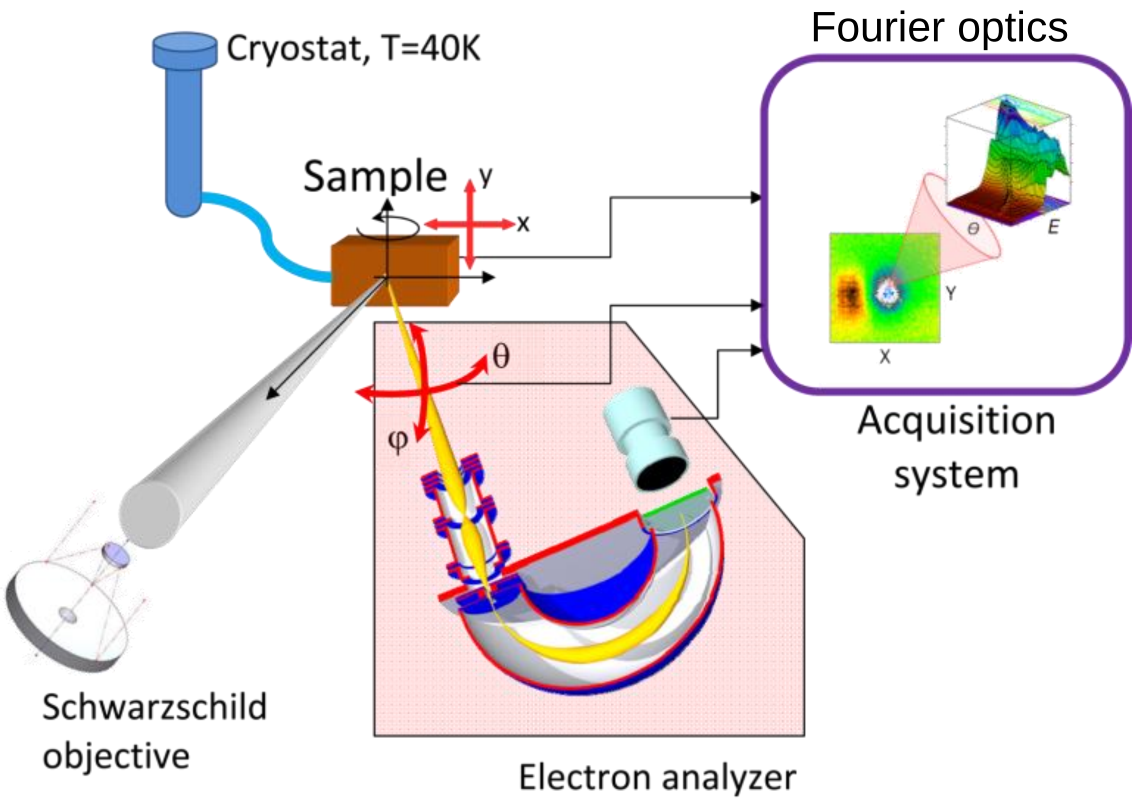
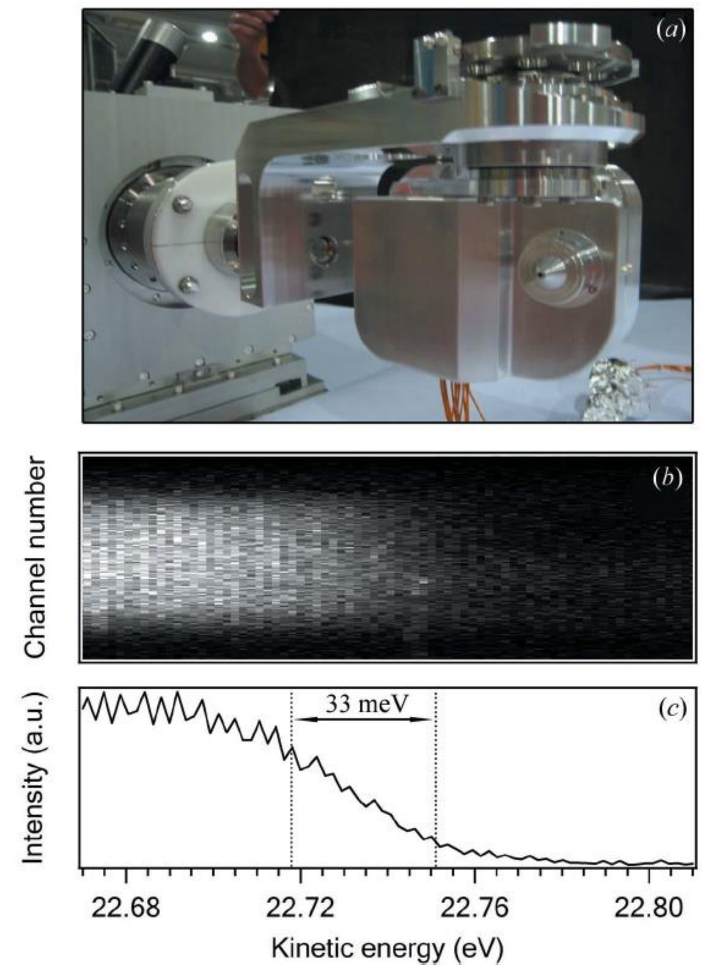
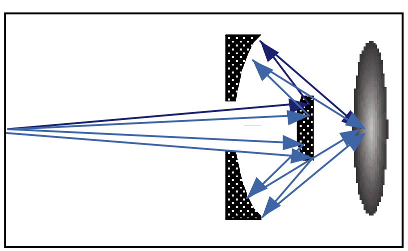
Spectromicroscopy beamline

microspot angle resolved x-ray photoemission spectroscopy





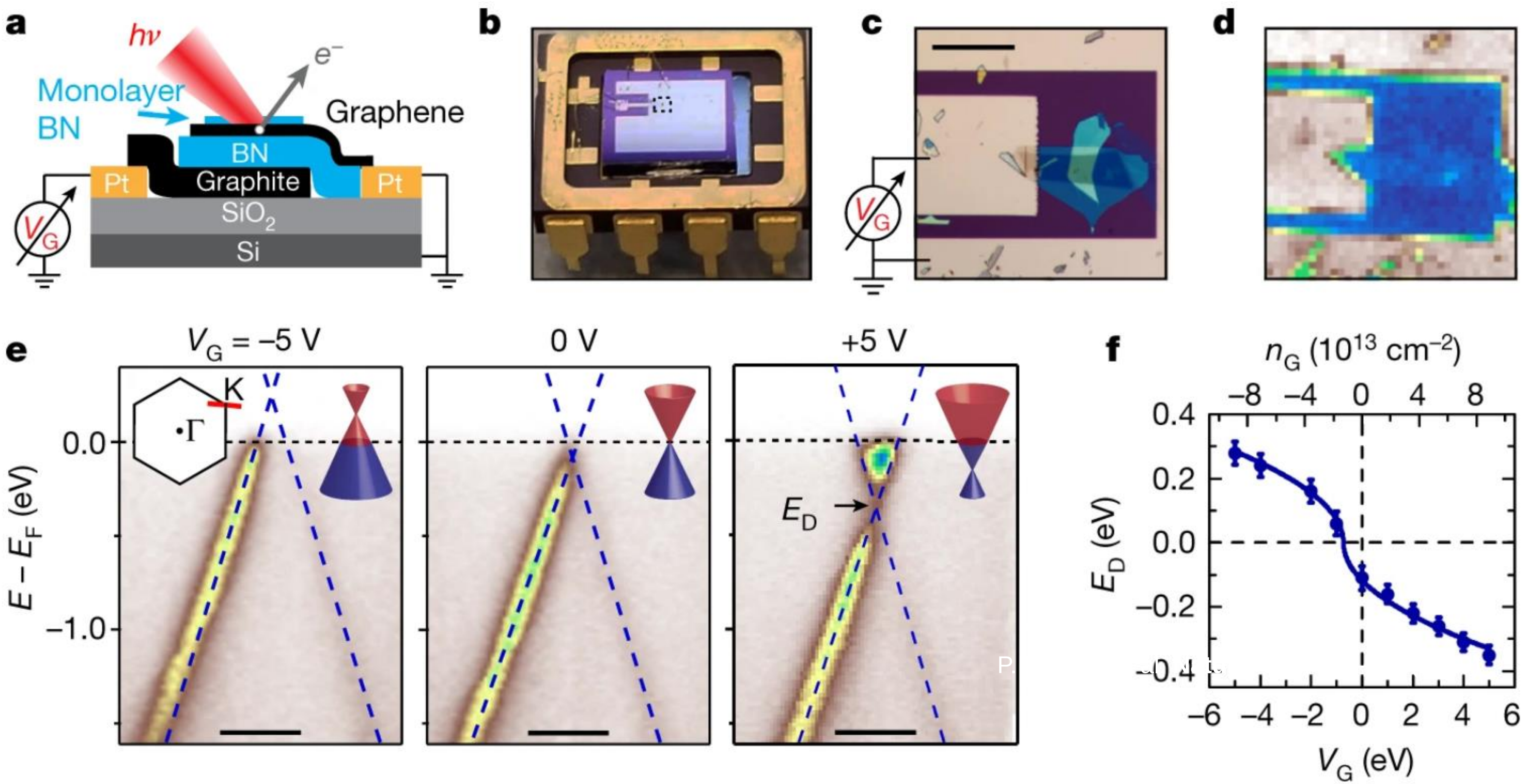


Resolution, 0.6 µm
25-50 meV, ±0.3° .
High photon flux>10^{10-11} ph sec^{-1}
Two possible energies: 27 eV with <1% scattered background and 74 eV with <20% scattered background.
Vacuum <$1.5x10^{-10}$ mbar.

Contact:
alexei.barinov@elettra.eu

Dudin *et al.*, *Journal of Synchrotron Radiation, Vol. 17 - 4 (2010)*

Visualizing electrostatic gating of monolayer graphene

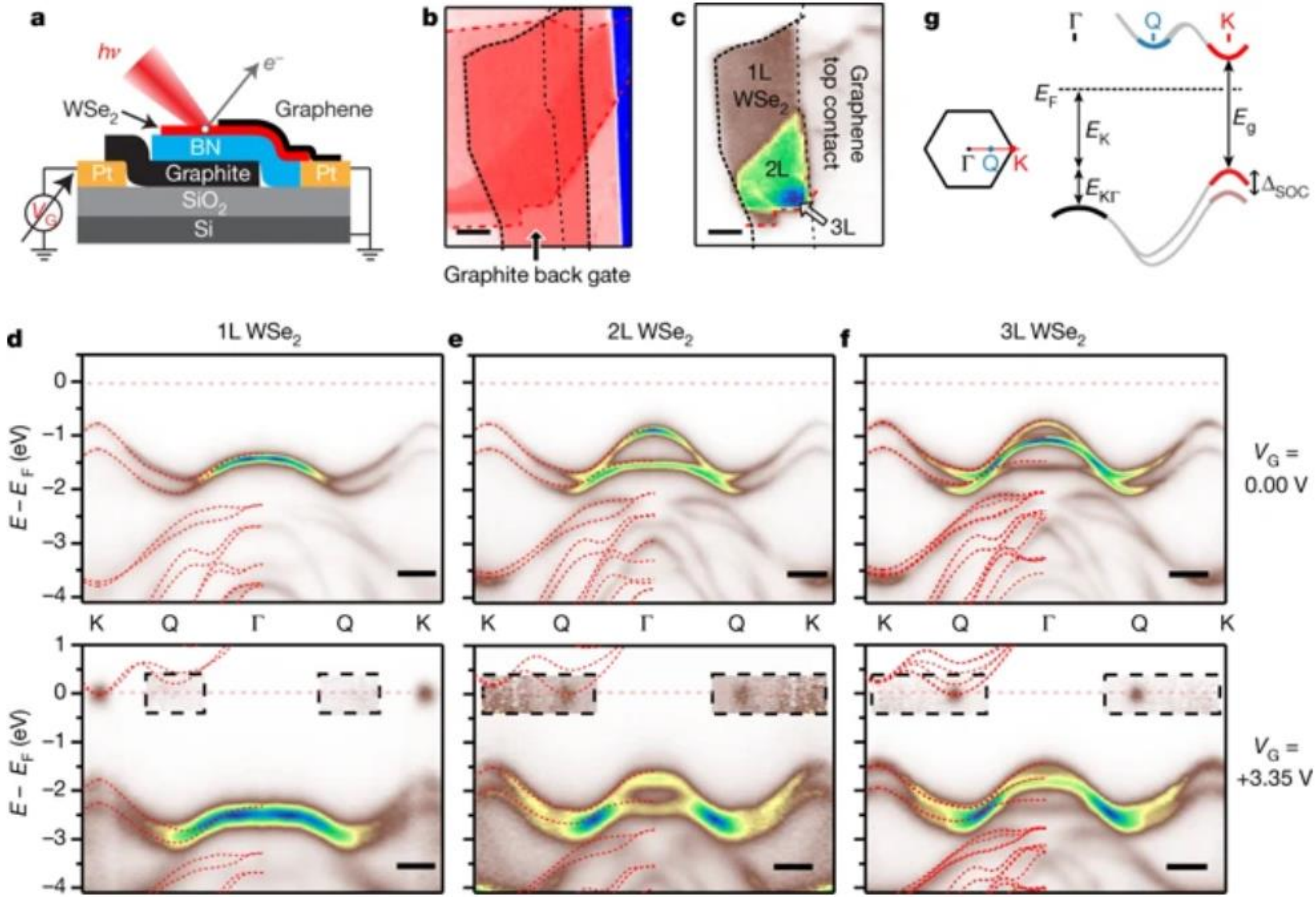


LETTER

https://doi.org/10.1038/s41586-019-1402-1

P. Nguyen *et al.*, **Nature 572**, 220–223 (2019)

Visualizing electrostatic Layer-number-dependent CBE in WSe_2

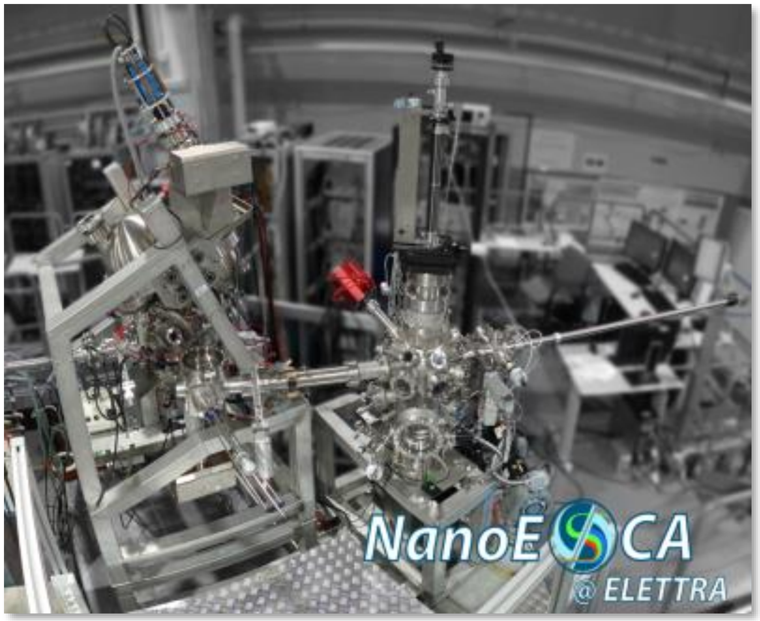


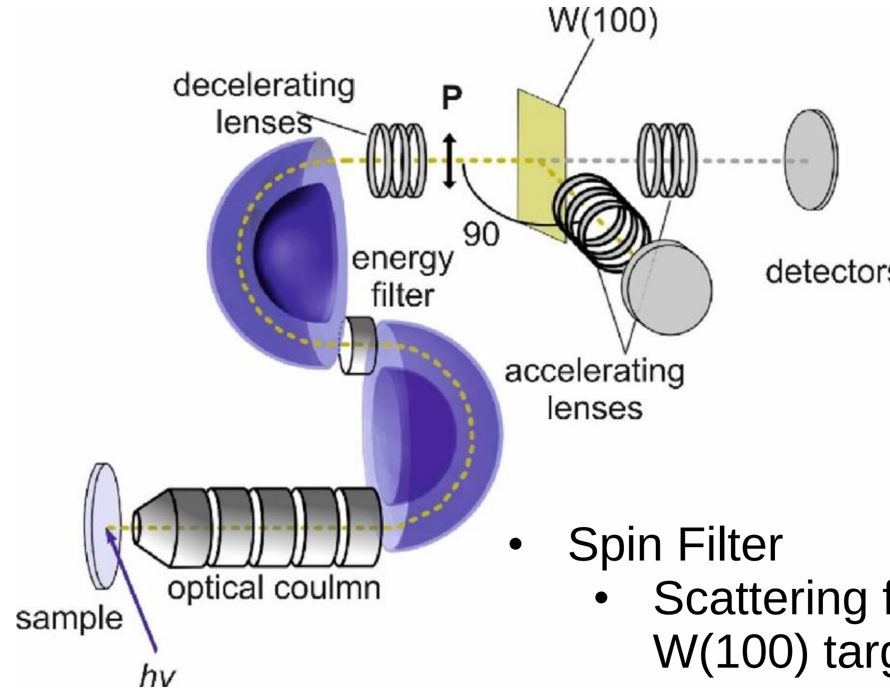
P. Nguyen *et al.*, **Nature 572**, 220–223 (2019)

JÜLICH
FORSCHUNGSZENTRUM

NanoESCA beamline

microspot angle resolved x-ray photoemission spectroscopy

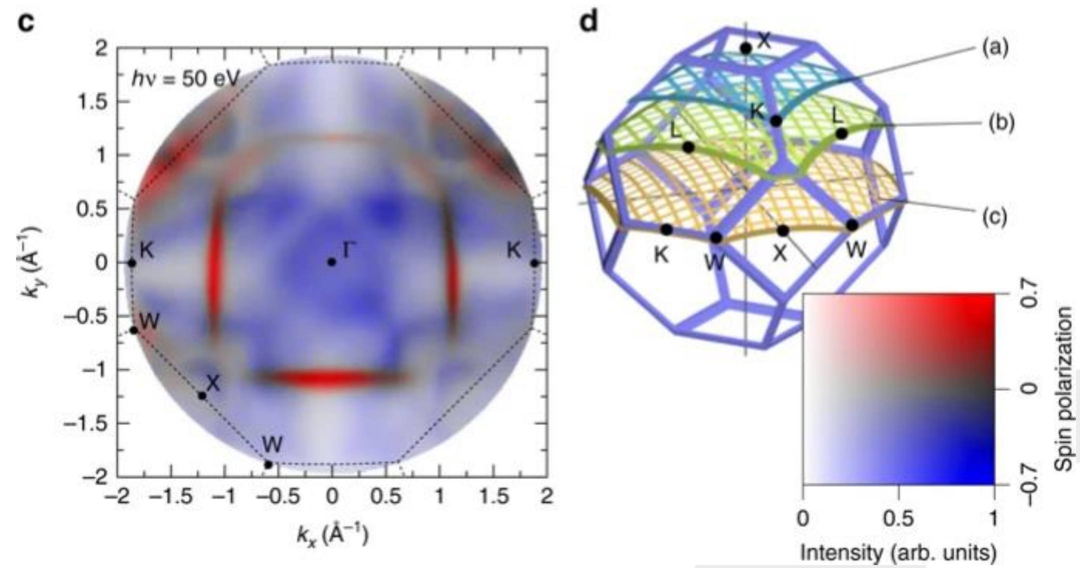




- Spin Filter
  - Scattering from W(100) target

- hv: 20 – 1000 eV, ***s p*** and **c+/c-** pol.
- Energy Filter: ΔE ~ 70 meV
  - ➢ **Real Space** (100 nm)
  - ➢ **Reciprocal Space**
  - ➢ µ-ARPES: spot size ~ 12-4 µm

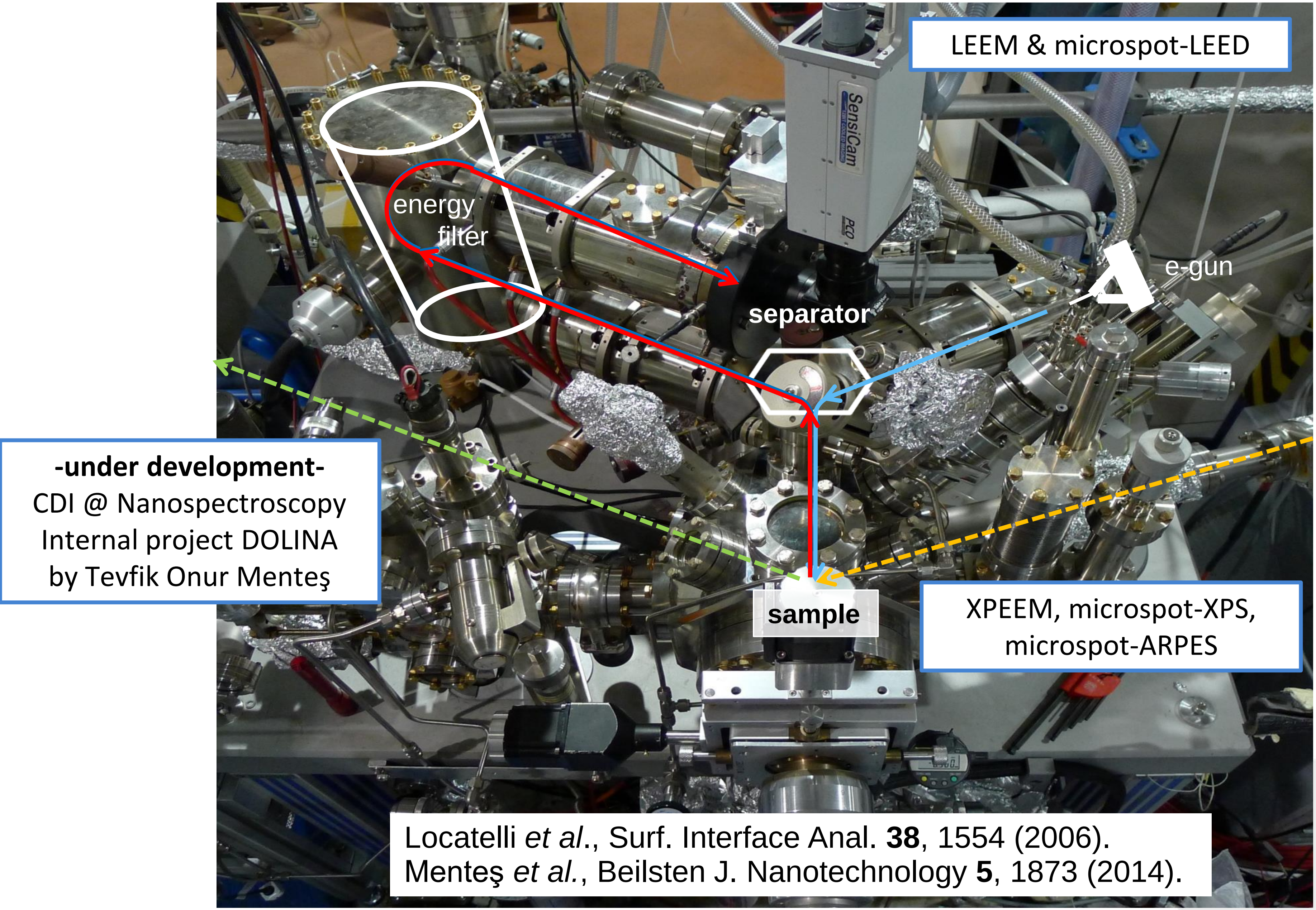
Contact: vitaliy.feyer@elettra.eu



C. Tusche *et al*., *Nature Communications, Vol. 9 - 1, pp. 3727 (2018)*

The SPELEEM @ Nanospectroscopy

Full-field, soft x-rays (25-1000eV) or low energy electrons as probe



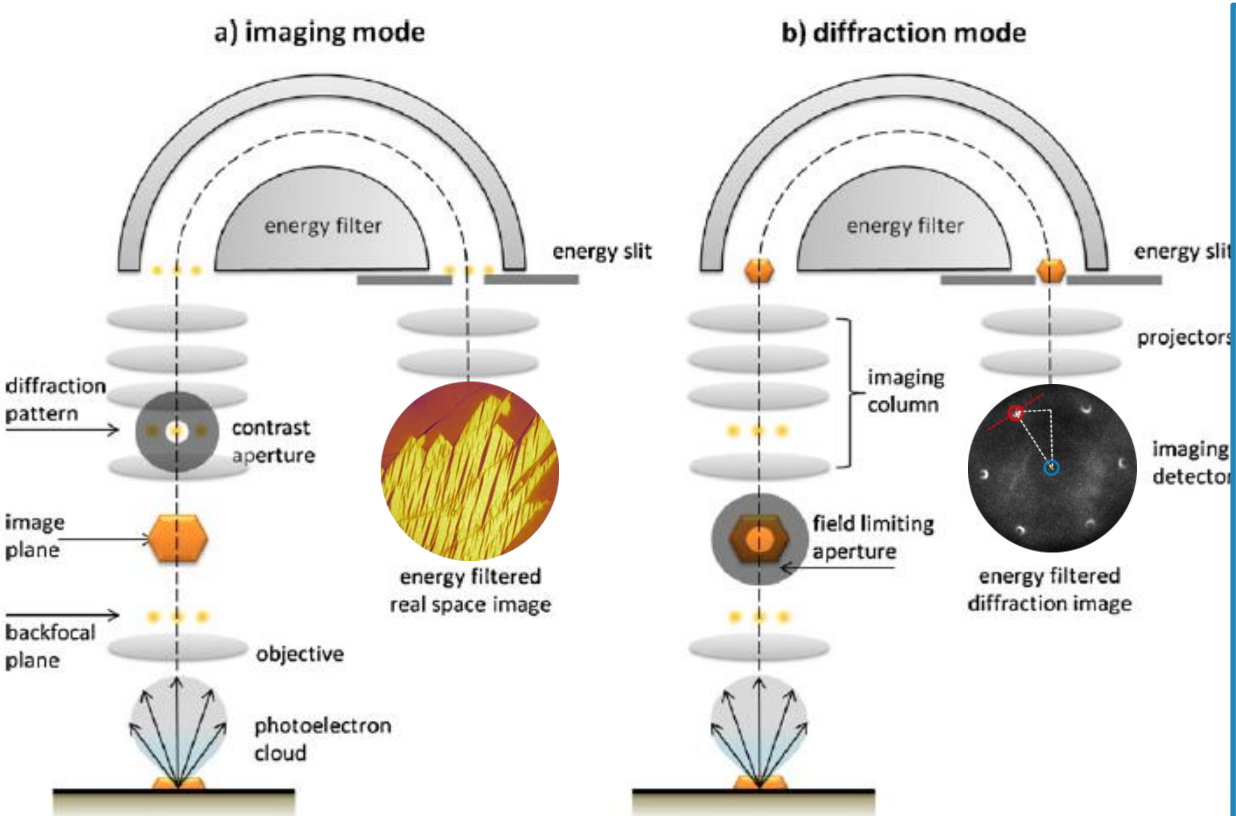
Locatelli *et al*., Surf. Interface Anal. **38**, 1554 (2006).
Menteş *et al*., Beilsten J. Nanotechnology **5**, 1873 (2014).

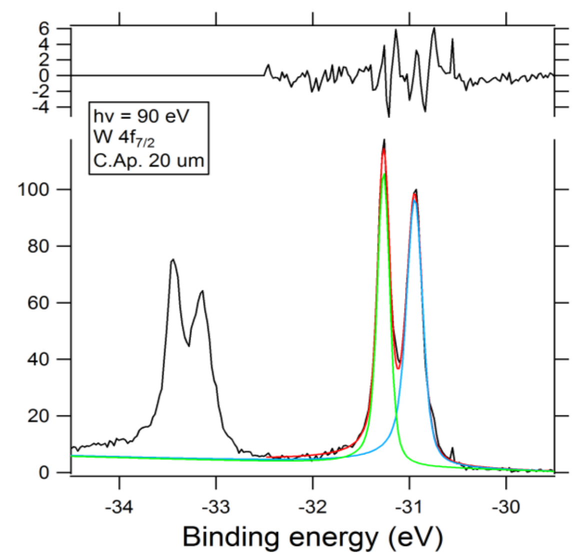
SPELEEM multi-method analysis

Spectroscopic imaging
XAS-PEEM / XPEEM / LEEM

microprobe-diffraction
ARPES / LEED

microprobe-spectroscopy
Fast-XPS





T. O. Menteş et al.
Beilstein J. Nanotechnol. 5, 1873–1886 (2014).

energy resolution
µXPS : 0.11 eV

spatial resolution
LEEM : 10 nm
XPEEM : 25 nm

energy resolution
XPEEM : 0.3 eV

Detector blanking available for time-resolved XMCD-PEEM: see Ultramicroscopy 202, 10-17 (2019)

Limited: to 2 microns in dia.
Energy resolution:
ARPES: 0.3 eV
angular resolution
ARPES: 0.01 Å^{-1}

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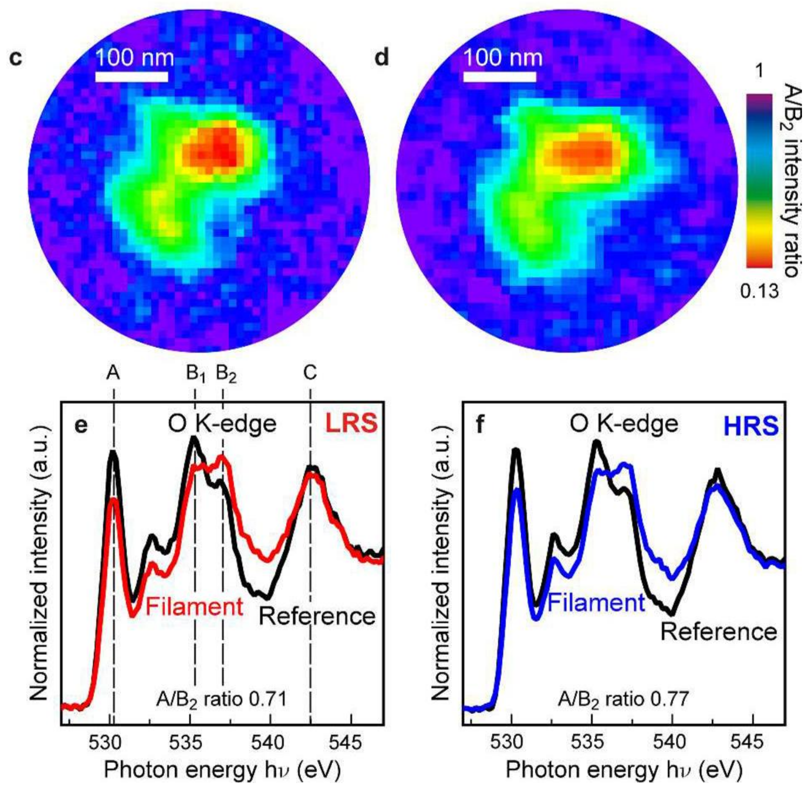
XAS-PEEM and mu-ARPES

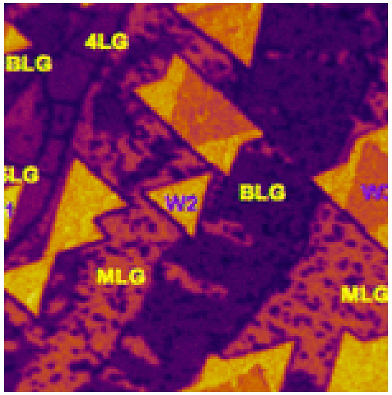
- ✓ microscopic origin of resistance variability in memristor devices

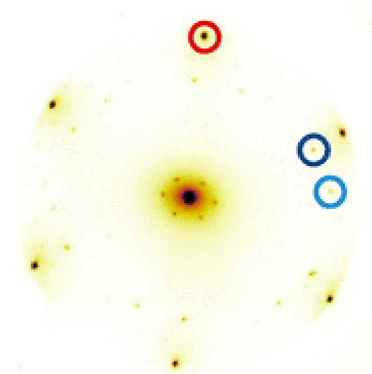


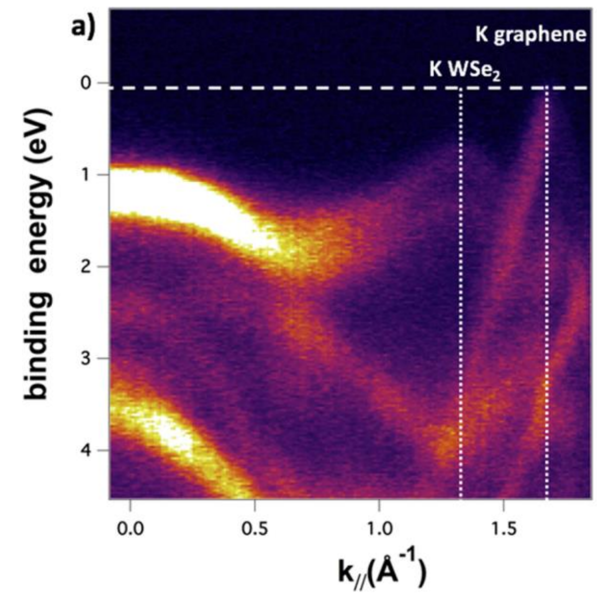
XAS at high lateral resolution reveals oxidaition state at filaments

C. Baeumer *et al*., ACS Nano 11, 6921 (2017).
See also: C. Baeumer *et al*., Nano Lett. 19, 54–60 (2019).

- ✓ Electronic Properties at the WSe_2–Graphene Interface





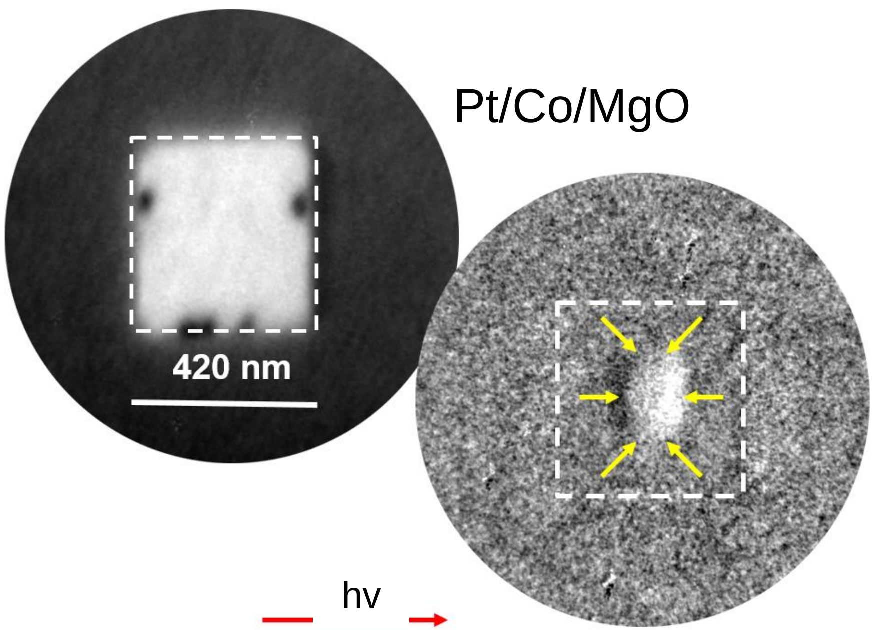


Unique combination of crystal and electronic structure information

S. Agnoli *et al*.,
ACS Appl. Nano Mater. 1 (3), 1131–114 (2018)

SPELEEM examples: magnetic imaging at high lateral resolution

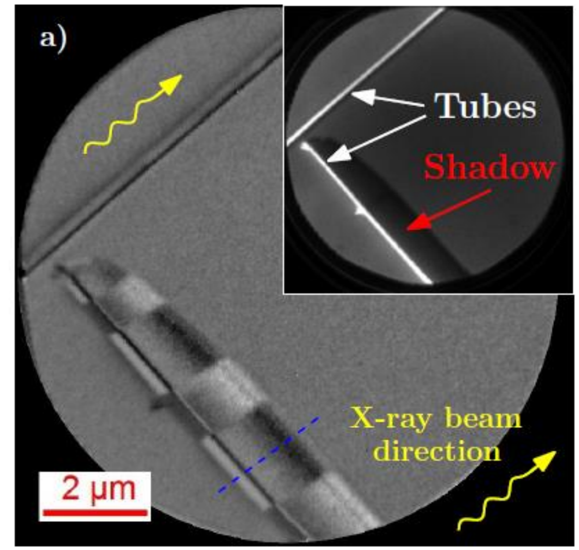
- ✓ First observation of chiral skyrmions at room temperature



O. Boulle *et al*., Nat. Nanotech. **11**, 449–454 (2016)
doi: 10.1038/nnano.2015.315

More recently, «Current-Driven Skyrmion Motion and SHE»
R. Juge *et al*., Phys Rev. Appl. 12. 044007 (2019)

- ✓ Magnetism in Nanowires



Fast Domain Wall Motion in cylindrical magnetic NW
M. Schöbitz *et al*., Phys Rev. Lett., accepted (2019)

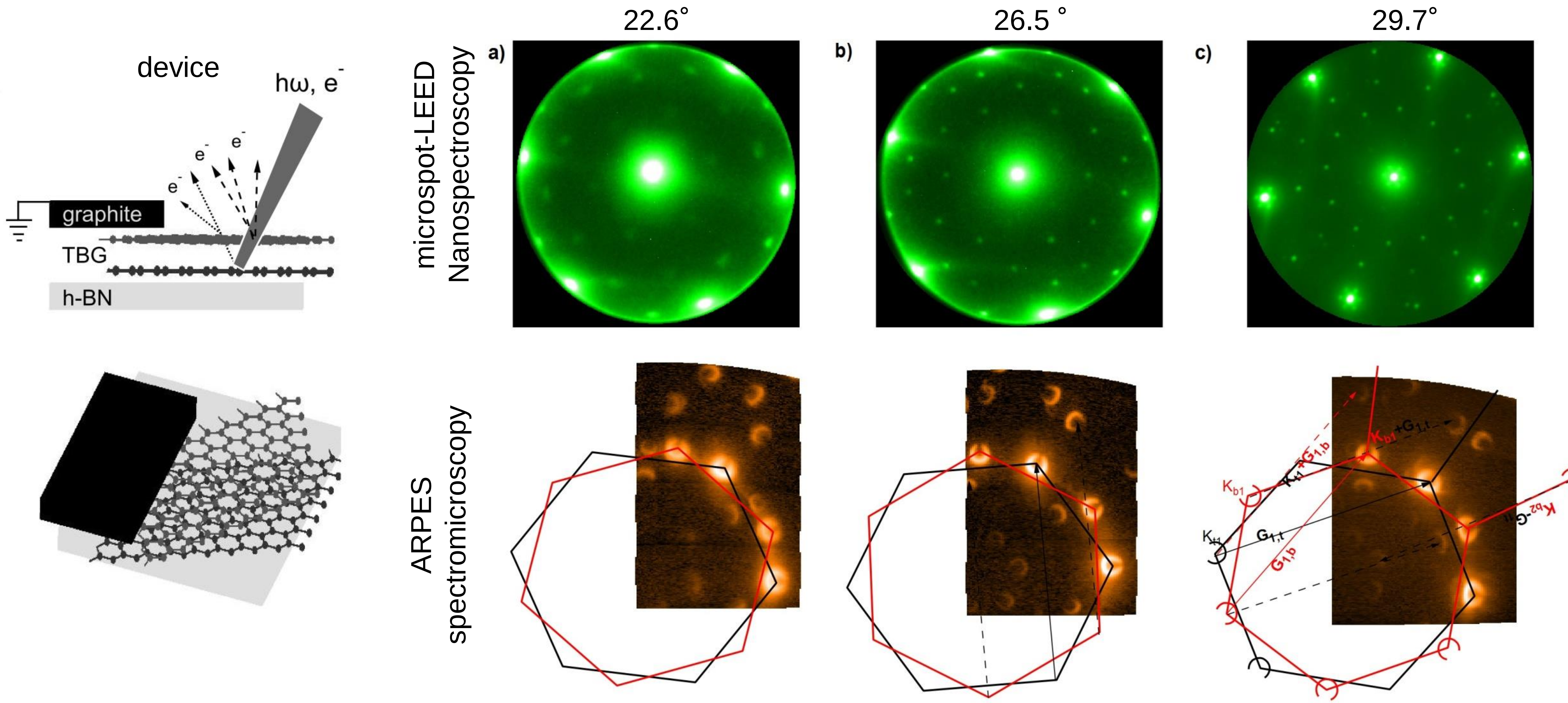
Flux-closure domains in high aspect ratio electroless-deposited CoNiB nanotubes
M. Staňo *et al*., SciPost Phys. 5, 038 (2018)

Quantitative analysis of shadow XMCD-PEEM
S. Jamet *et al*., Phys. Rev. B 92, 144428 (2015)

Bloch-point DW in cylindrical magnetic NW
S. Da Col *et al*., Phys. Rev. B 89, 180405(R) (2014).

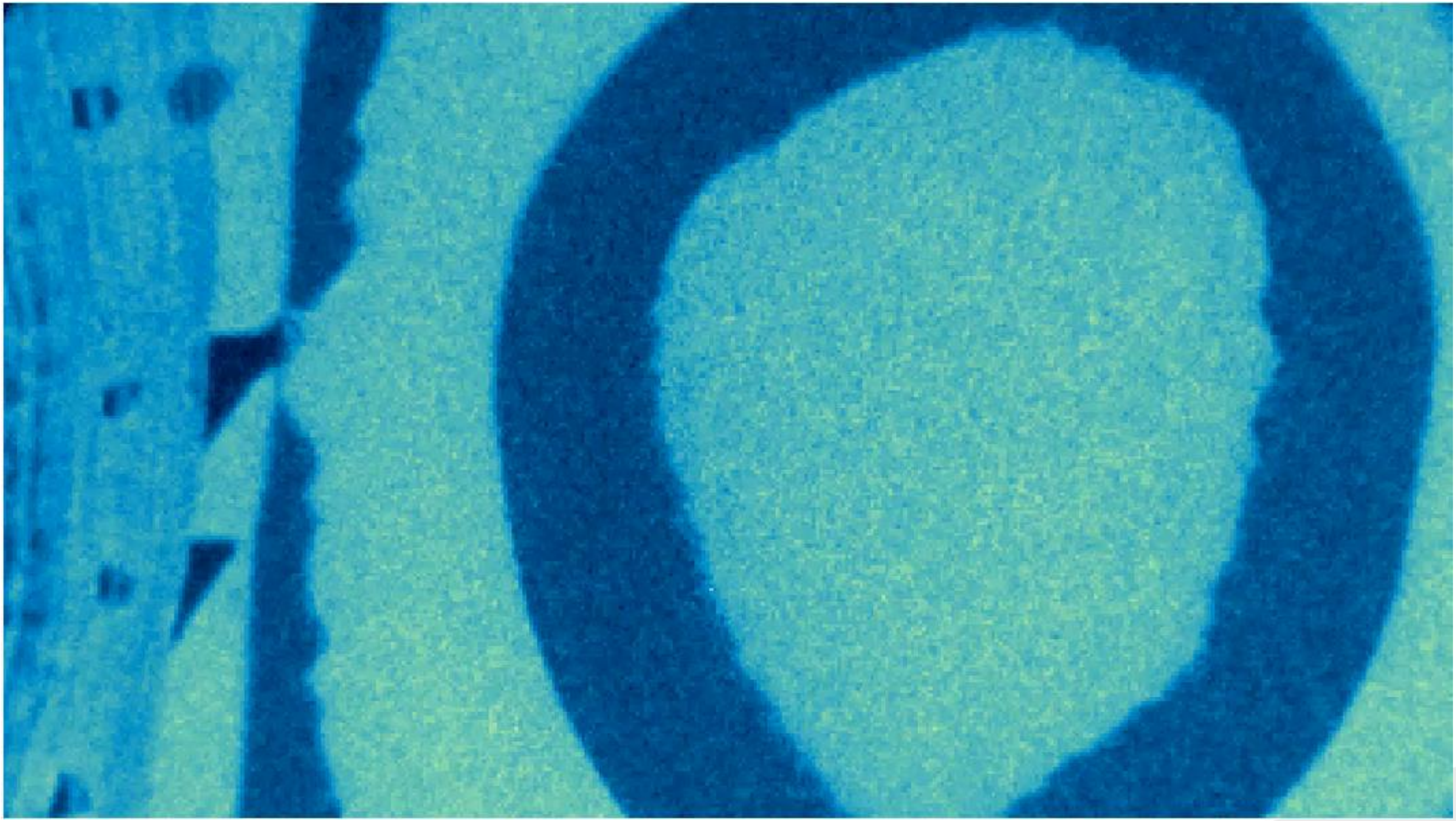
Artificially fabricated 2D heterostacks

- ✓ Combining LEEM & microspot LEED with ARPES capabilities (energy resolution in particular) is highly desirable!
- ✓ Example: twisted graphene/h-BN (Graphene institute, Manchester, UK)



M. Hamer, A. Barinov, R. Gorbachev *et al.*, in preparation

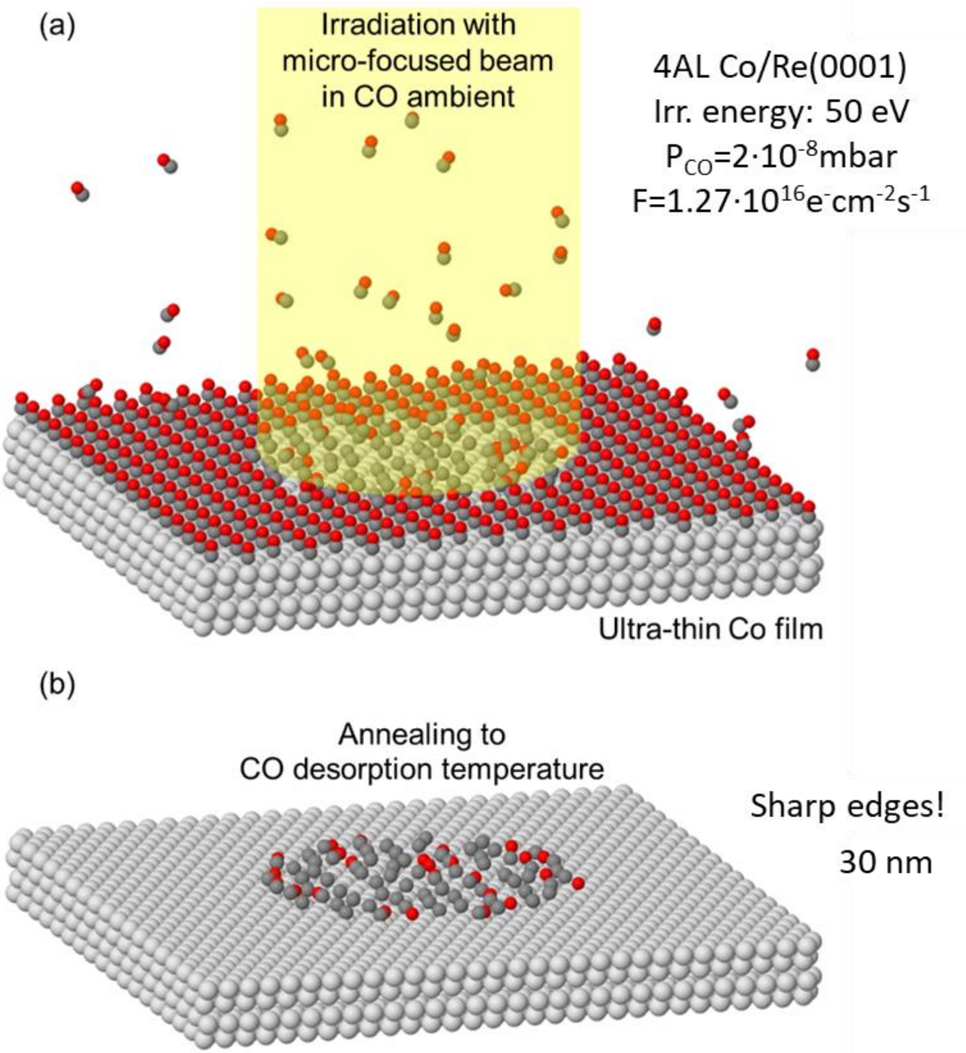
LEEM Imaging: thin film growth

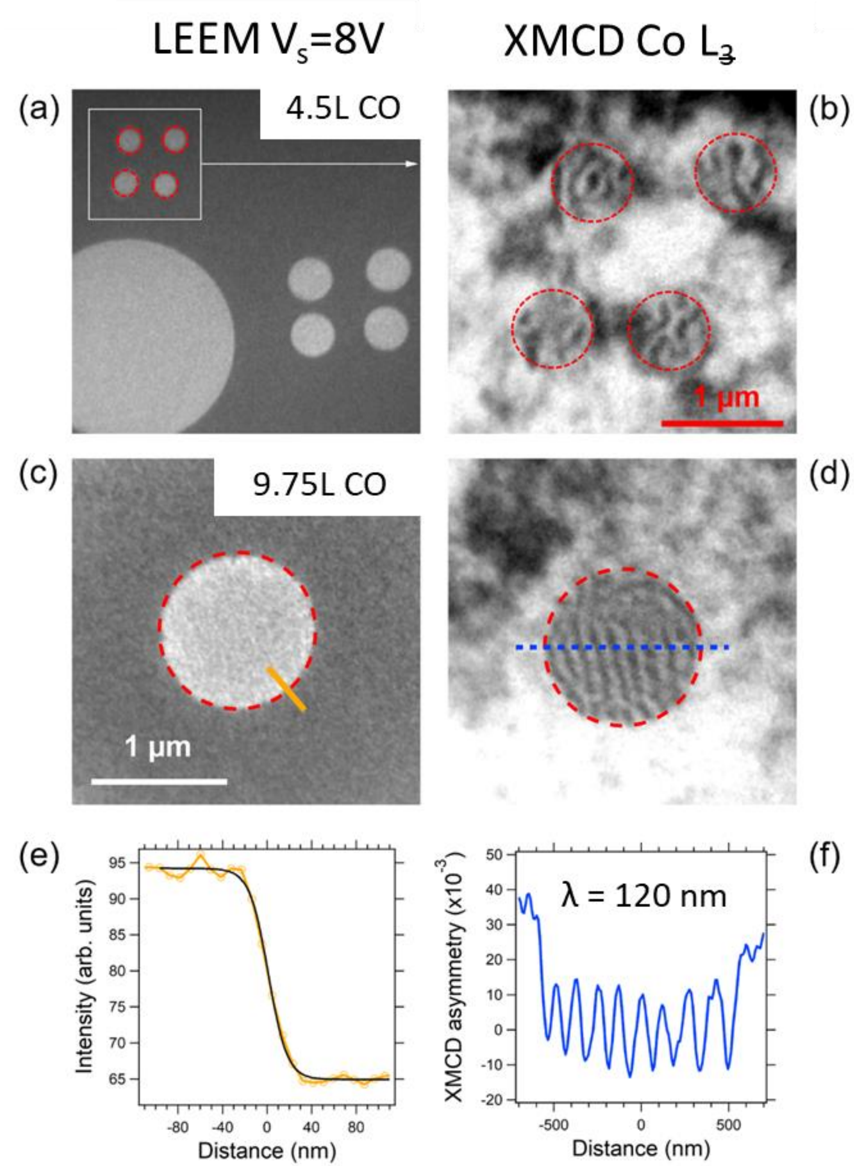


Thickness dependent intensity modulations
Co/Re(0001) at T= 460K

electron-beam assisted carbon lithography

Similar to FXBIP and FEBIP

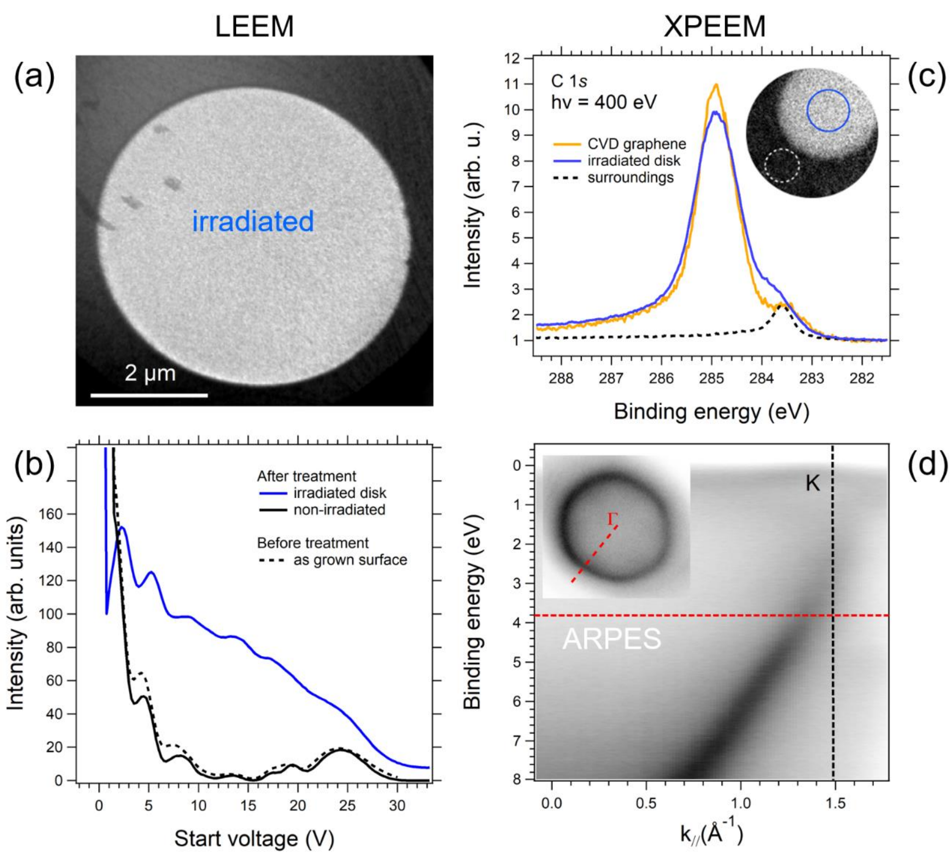




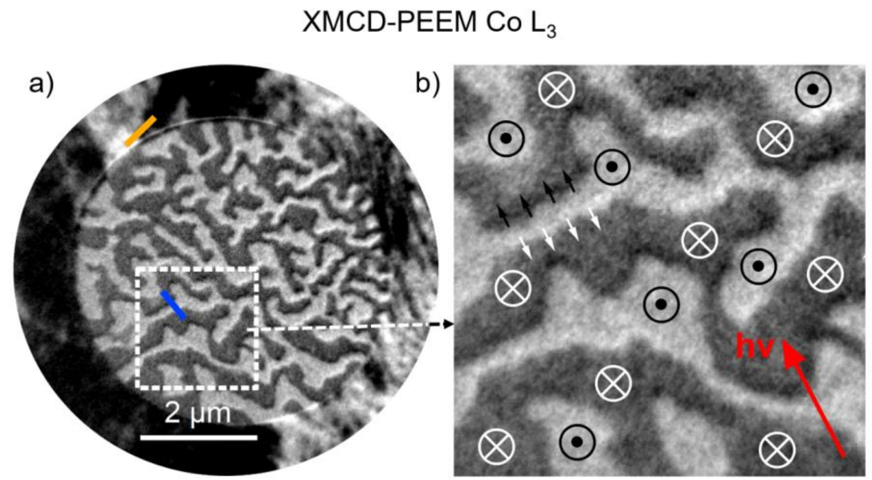
P. Genoni et *al.*, ACS Applied Materials & Interfaces **10**(32), 27178–27187 (2018)

Chemistry and magnetism of gr/Co/Re(001)

CO exposures of the order or in excess of 1000 L → ML amount of carbon on the surface, which transforms to graphene upon annealing at 380° C.



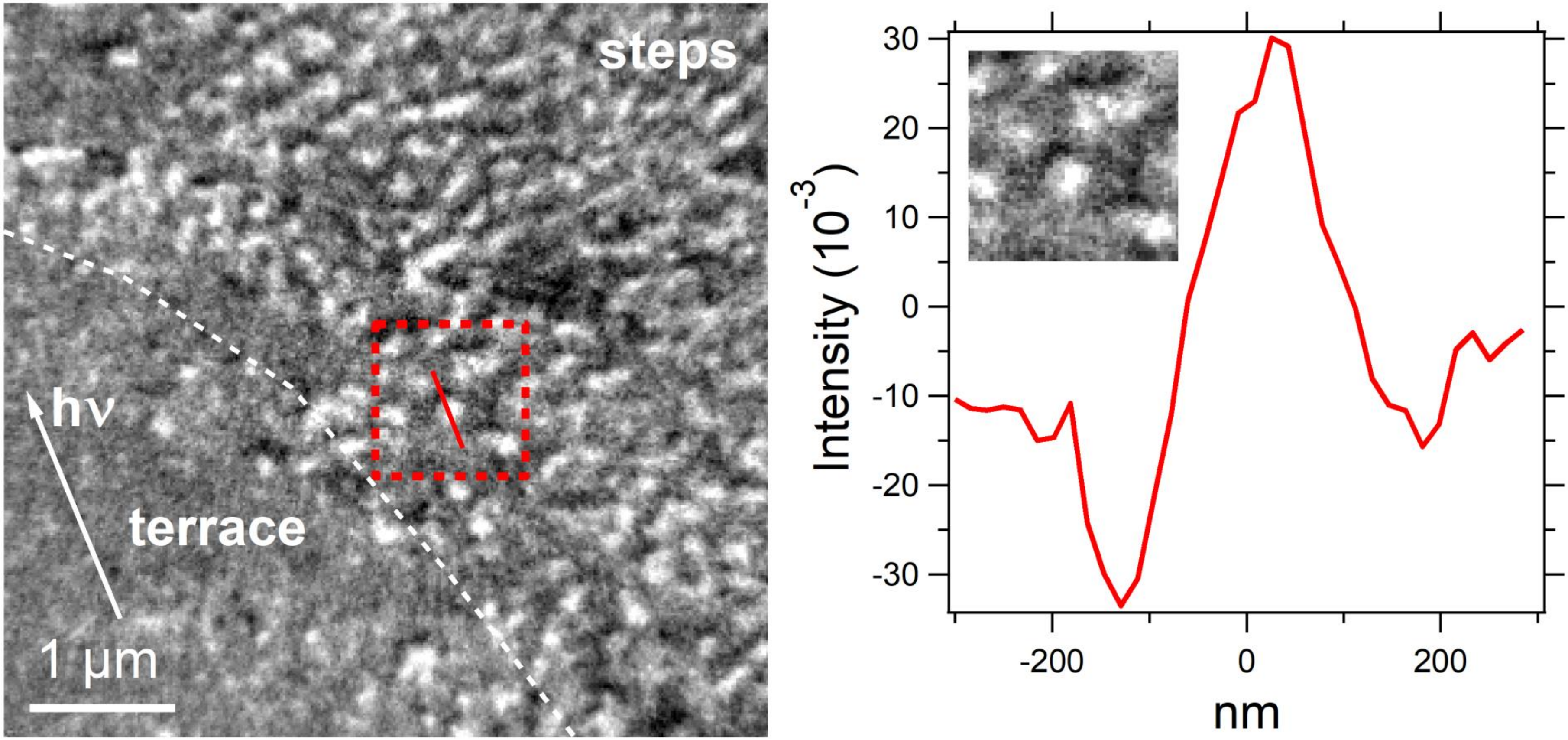
✓ enhanced perpendicular magnetic anisotropy



- Neél magnetic domains with right handed chirality
- Dzyaloshinskii-Moriya interaction →
- Skyrmion bubbles observed upon magnetization reversal

P. Genoni *et al*., ACS Applied Materials & Interfaces 10(32), 27178–27187 (2018)
F. Genuzio *et al*.,
J. Phys. Chem. C 123(13), 8360-8369 (2019);
IEEE Transactions on Magnetics 55(2), 1-4 (2019);

XMCD-PEEM imaging of a hysteresis cycle



F. Genuzio *et al*., IEE Transactions on Magnetics - Conferences (2018).
doi: 10.1109/TMAG.2018.2868423;

Elettra Sincrotrone Trieste

Summary

photoemission microscopes available at Elettra: SPEM, XPEEM

- ❑ Nanometer-range lateral resolution
- ❑ LEEM in-situ preparation with surface science methodology
- ❑ time-resolved studies using stroboscopic approach
- ❑ Magnetic imaging
- ❑ Capabilities in operando experiments
- ❑ SPEM @ near ambient pressure

microprobe ARPES

- ❑ Spectromicroscopy beamline
- ❑ NanoESCA (also spin-resolved)