ETH zürich

Advanced Electron Microscopy CCMX November 2022

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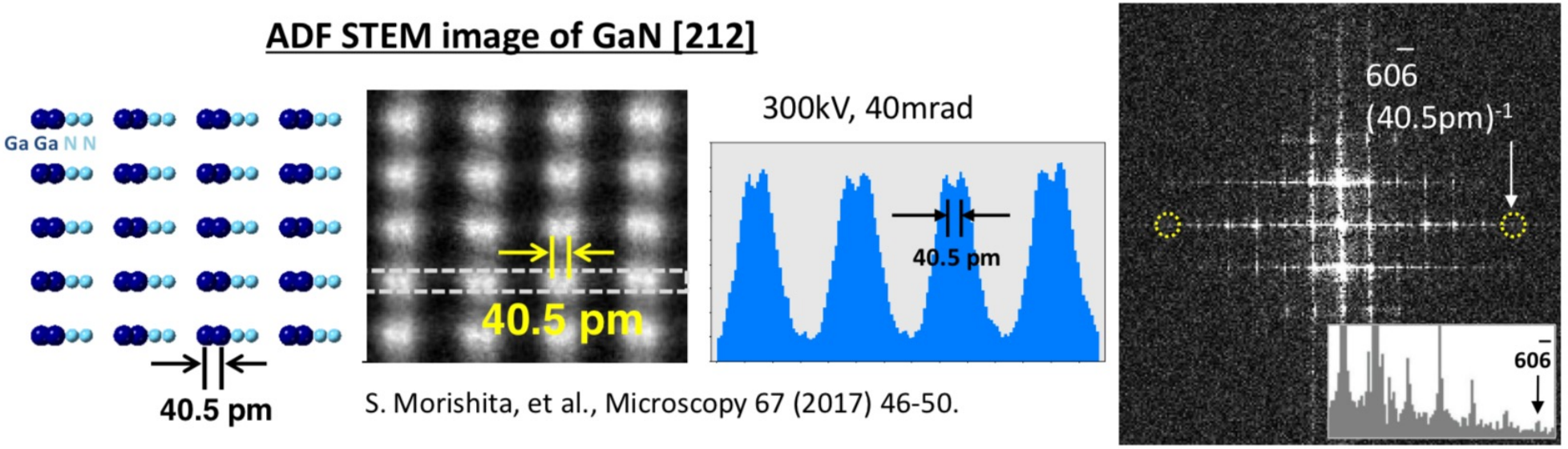
Technical Director TEM ScopeM / ETH Zürich

ScopeM

SPATIAL RESOLUTION: DO WE NEED MORE?

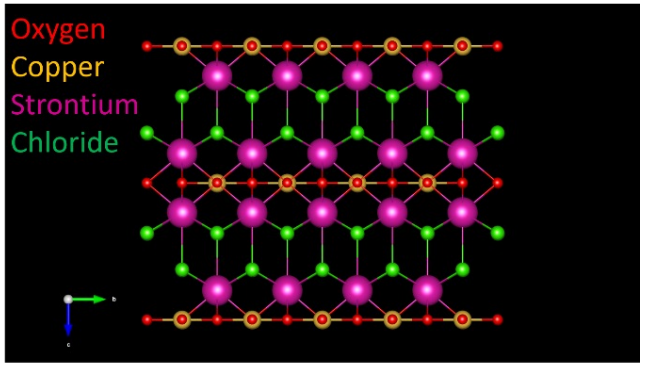


EELS:

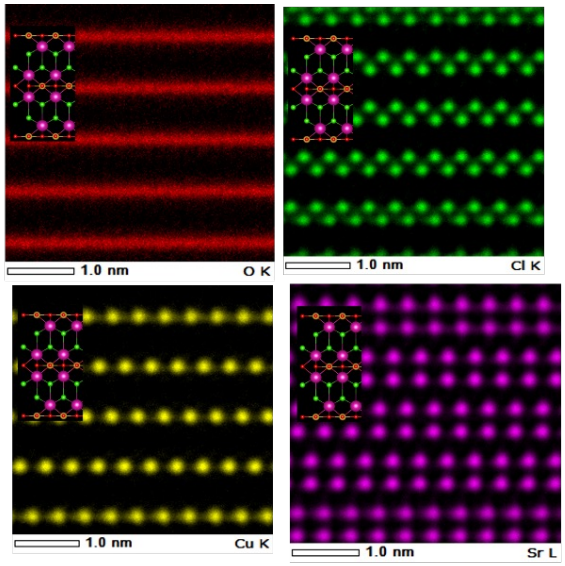
- 4meV
- Electron counting system

What do we actually need?

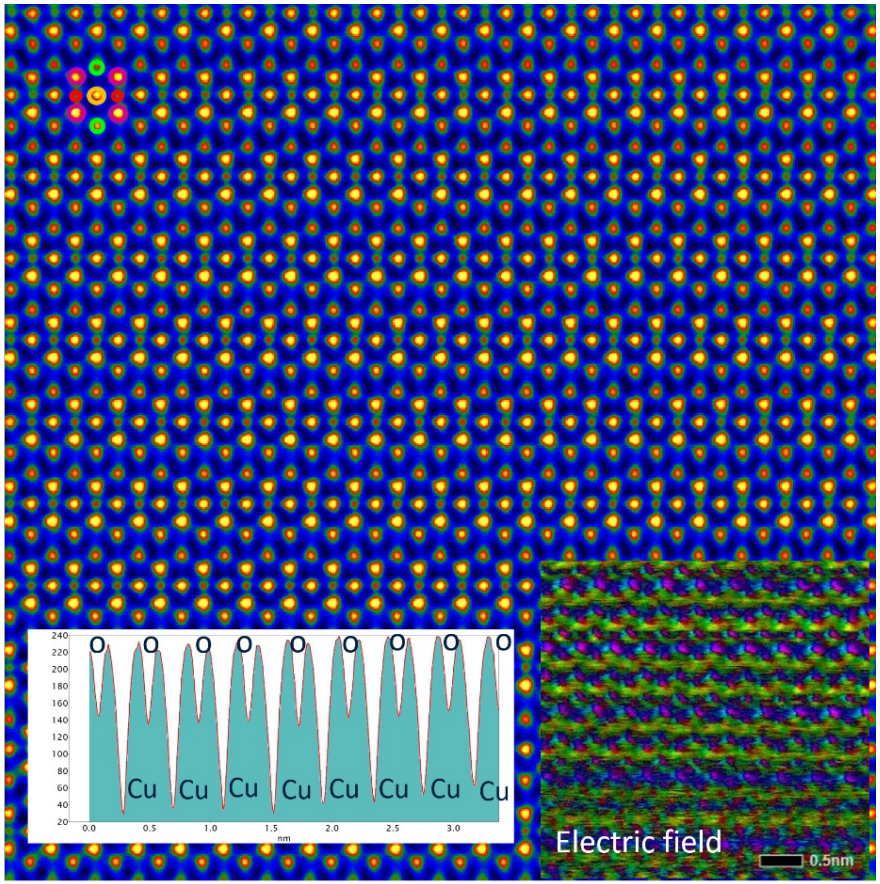
Typical characterization (Cuprate):



Vizualisation of the crystal structure $Sr_2CuO_2Cl_2$ along the [100] axis.



EDS map with the corresponding crystal structure

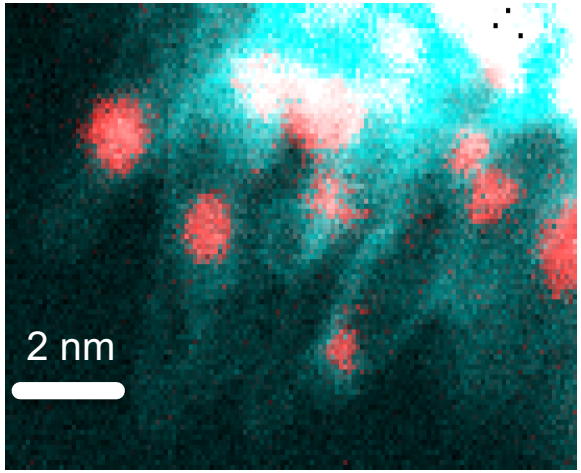


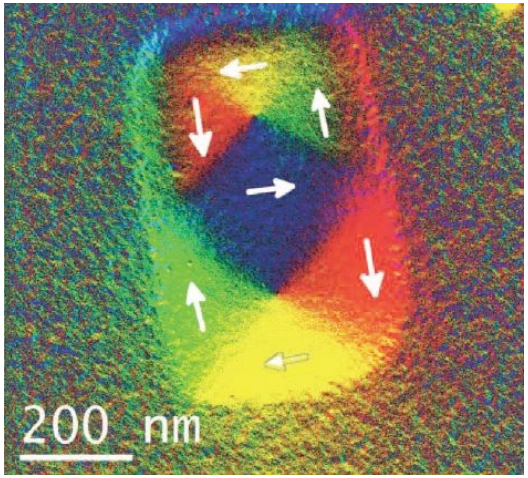
Annular Bright Field Image of $Sr_2CuO_2Cl_2$ *along the 001 axis. Insights shows a intensity profile along the* CuO_2 *stack, intensity dip corresponds to atoms. The electric field map's color corresponds to the field orientation*

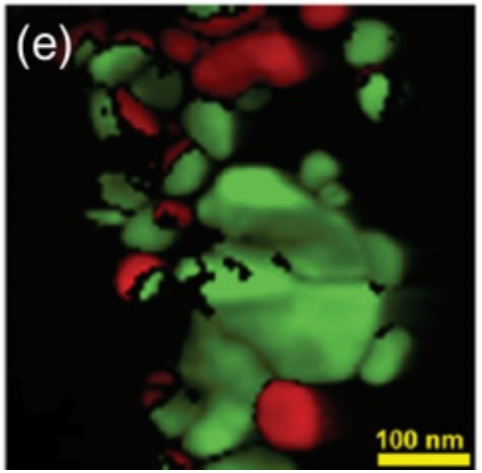
- Nano-characterisation.
- Environmental control – in-situ TEM.
- Example of Advanced Electron Microscopy.
- Summary and Outlook.

OUTLINE

Toward state of the art nano-characterisation







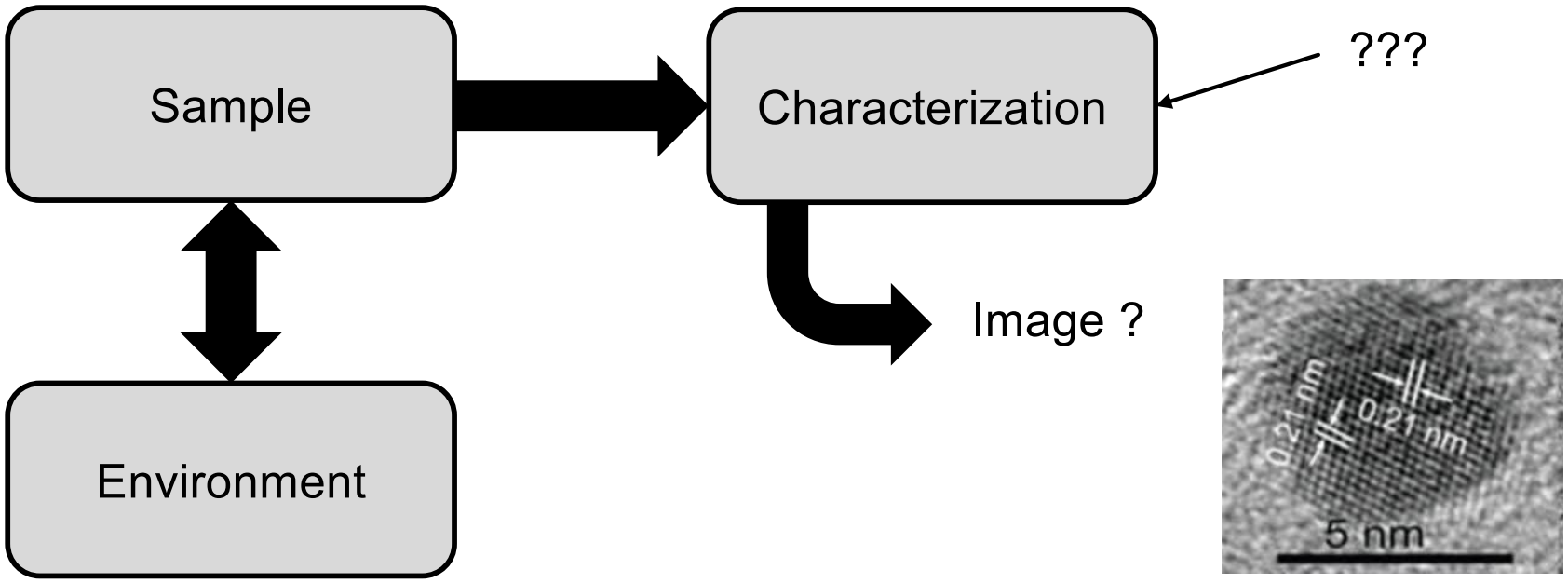
Left: Ga nanoparticle @ carbon nanotube
Middle: Field map in Iron Oxide
Right: Lithium cell sample. R: $LiFePO_4$, G: $FePO_4$

Nano-characterisation

Toward material property understanding

What is nano-characterization

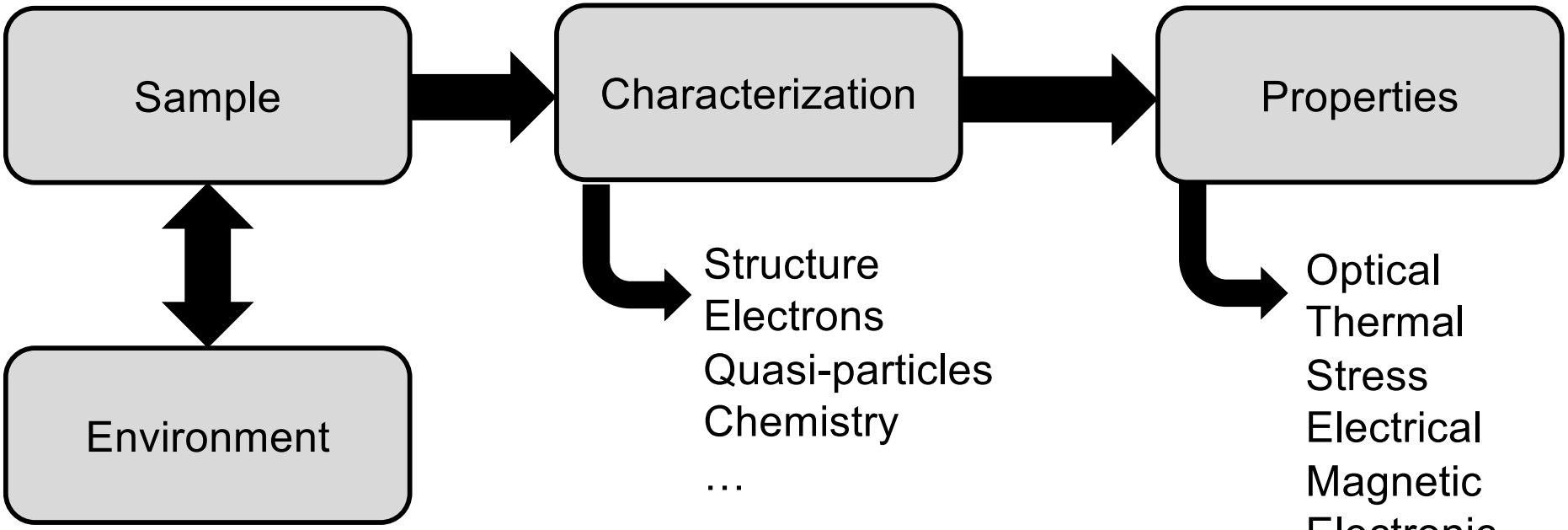
Instrumental technique to obtain local information at the nano-scale on a given sample to understand how the local structure affects the material properties



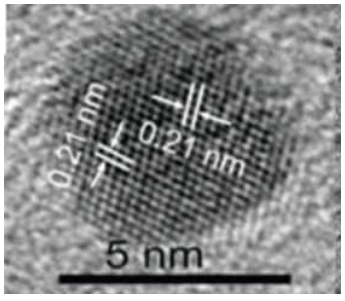
Example: Graphene Quantum dots – Which colors do they emit?

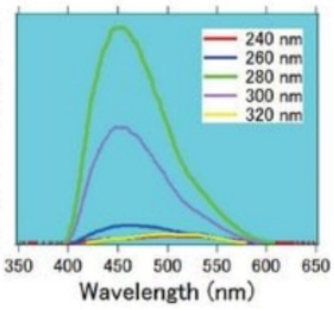
What is nano-characterization

Atomic position ≠ Local properties

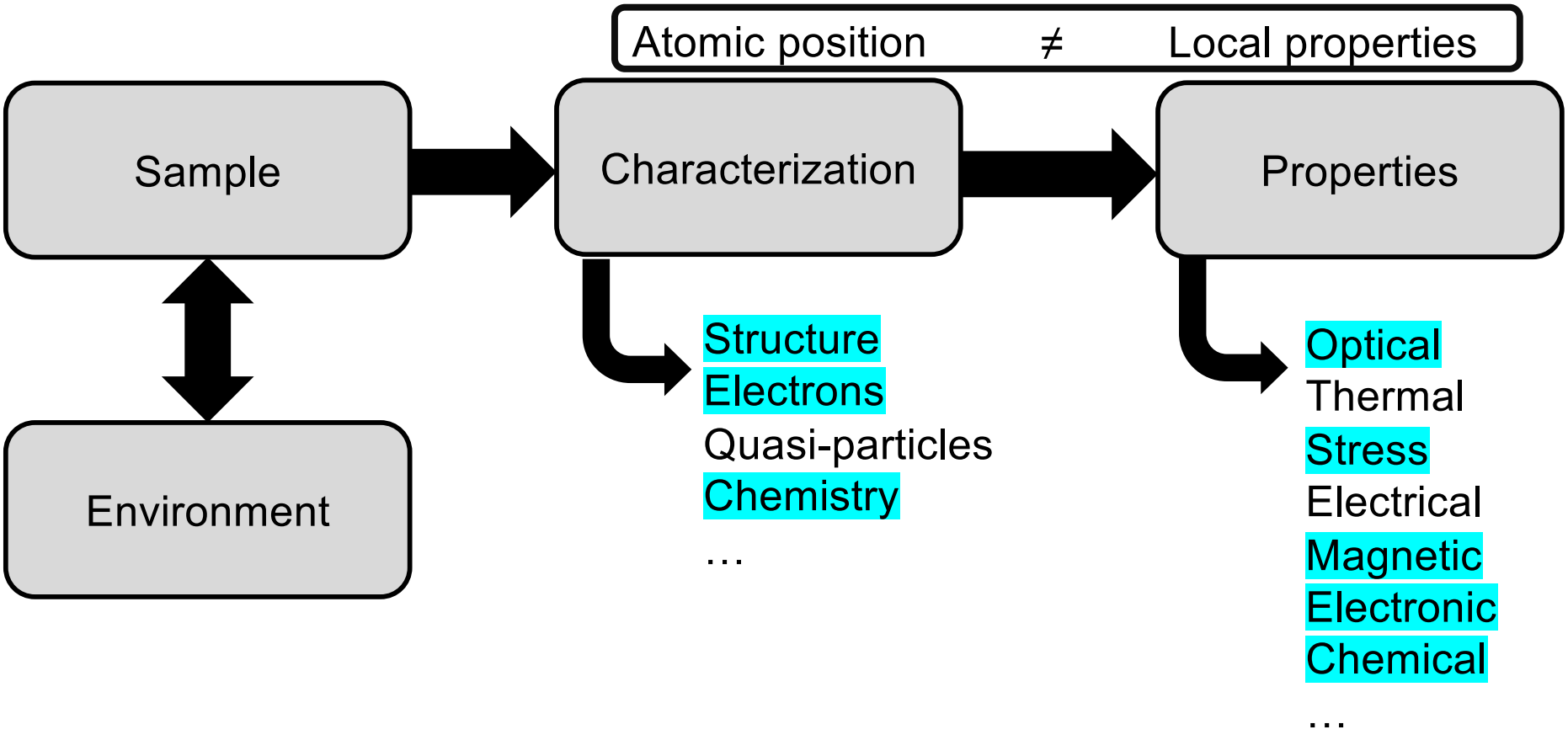


Example: Quantum dots – Which colors do they emit?
electronic structure -> optical properties



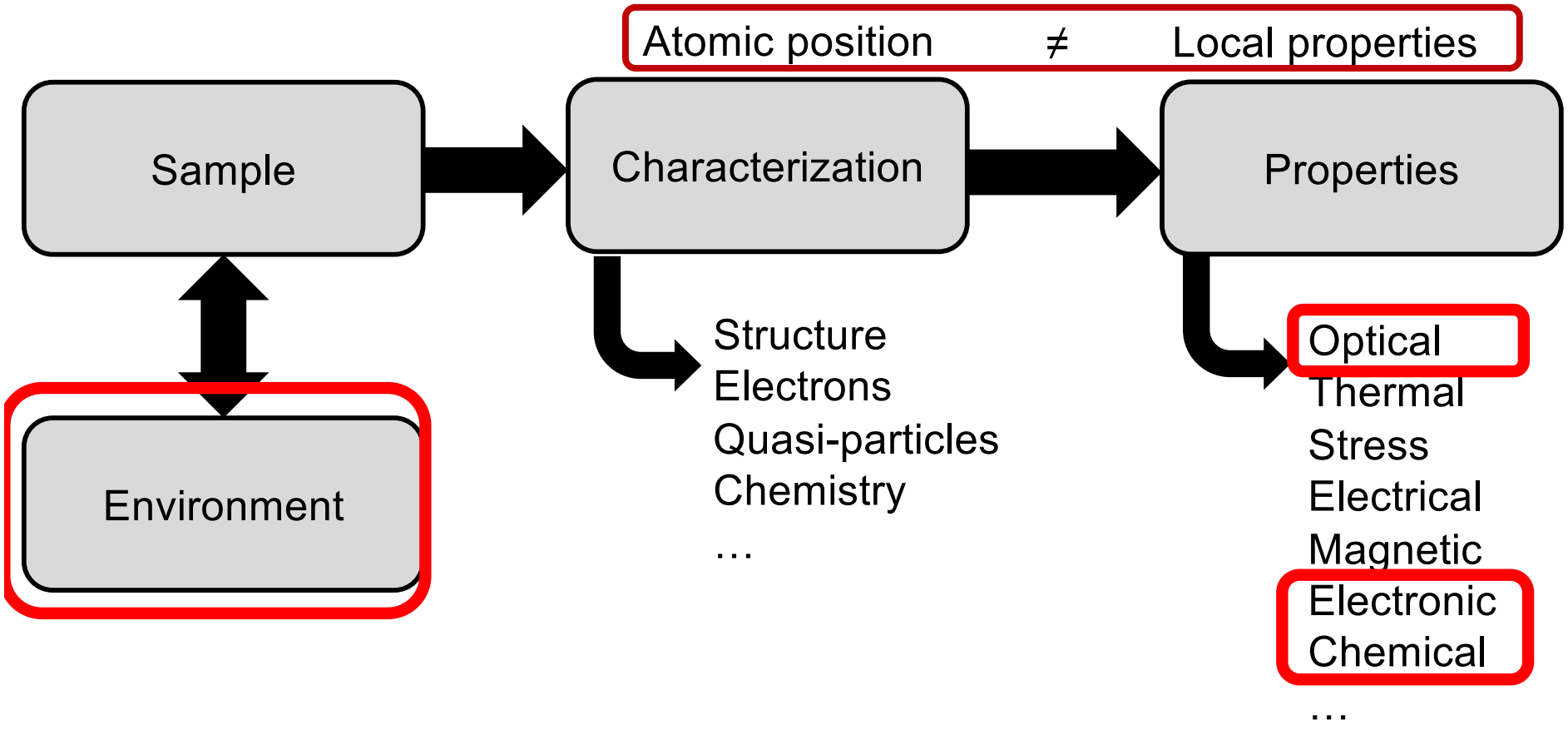


What is nano-characterization



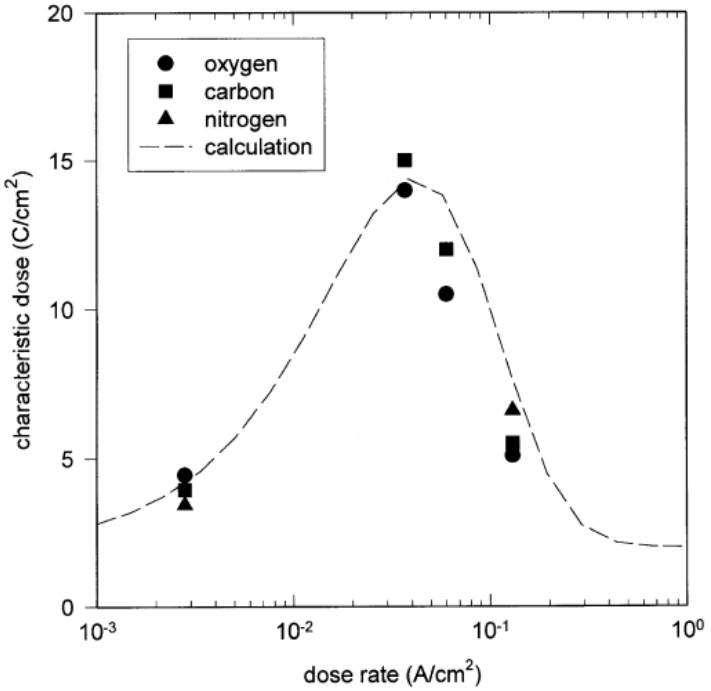
ScopeM capability

What is nano-characterization



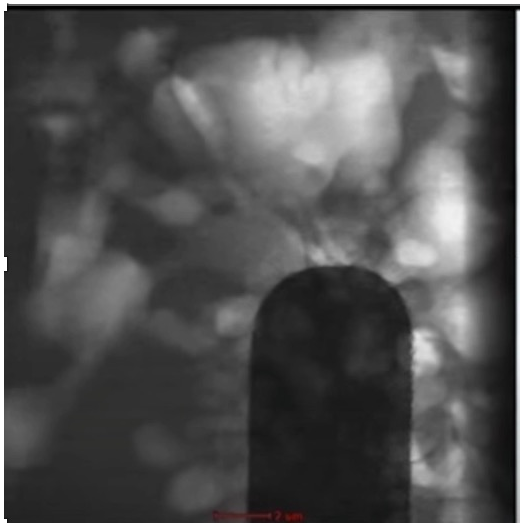
Beam-Sample interaction

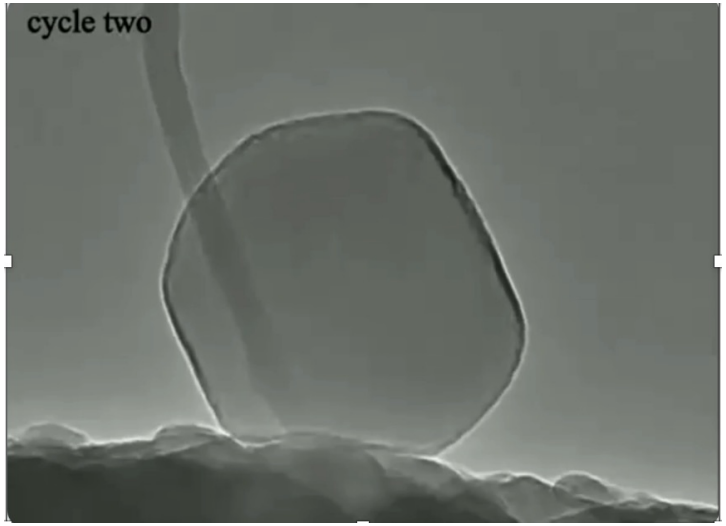
- Damages:
  - **Knock-on damage (elastic scattering)**
    Important in conducting specimens
    Often reduced by lowering microscope kV
  - **Radiolysis (inelastic scattering)**
    Reduced by cooling, encapsulating specimen
  - **Electrostatic charging (inelastic scattering)**
    Reduced by lowering beam current
    Conductive coating
  - **Contamination**
  - **Heating**
    Secondary event

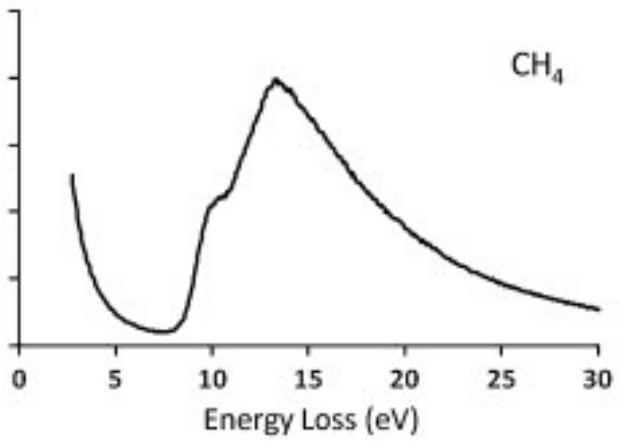


current density

Very complicated
Still not well understood







Left: Lithium Dendrite growth
Middle: NaO_2/CO_2 battery[2]
Right: EELS of CH_4[3]

Environmental control

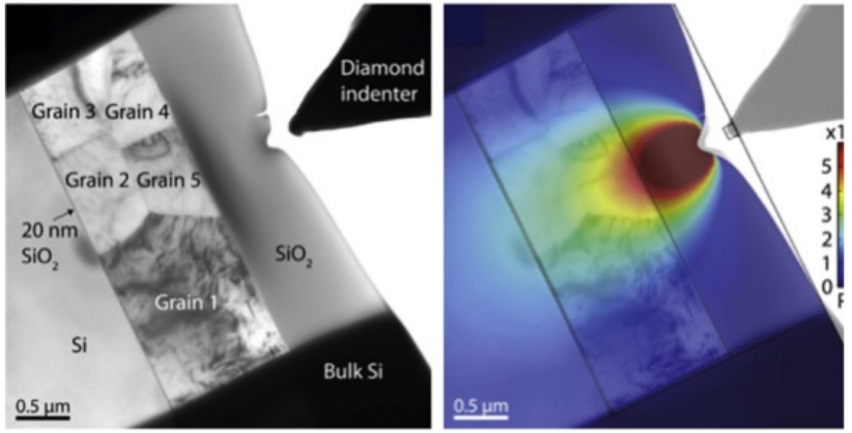
In-situ TEM

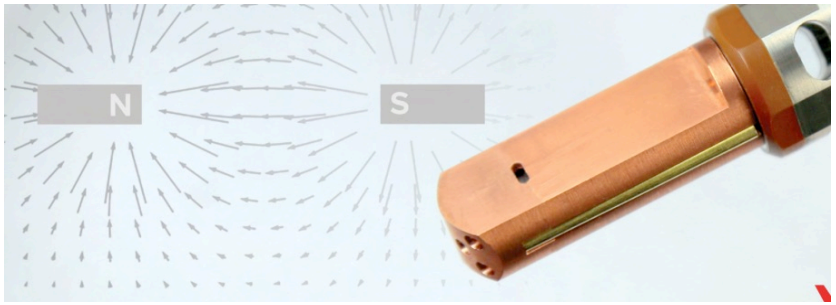
ScopeM

1: *R.L. Mehdi et al. Nano Lett. 2015, 15, 2168−2173*
2: Liu et al. ACS Nano 2010, 14, 13232-13245
3: Crozier et al. Ultramicroscopy 111-3, 2011

What type of control do we have on the environment

- Gas
- Liquid
- Biasing (contact or bias)
- Heating (resistor or MEMS)
- Cooling (LN_2 or LHe)
- Mechanical (Tensile strain, nano-indention, MEMS)
- Magnetic Field



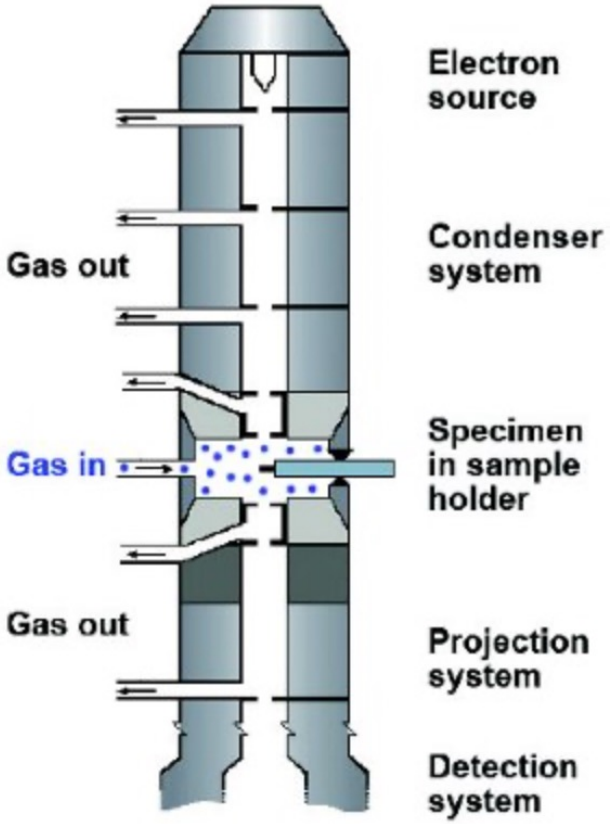


De Knoop Scr. Mater., 74 (2014), pp. 44-47

Gas in-situ 1: E-TEM

Advantages:
- Any sample holder
- Robust gas mixing system
- No need for windows
- Direct observation of the experiment
- EELS possible

Disadvantage:
- Dedicated TEM
- Pressure low (max:20mbar)
- STEM performance limited by diaphragm

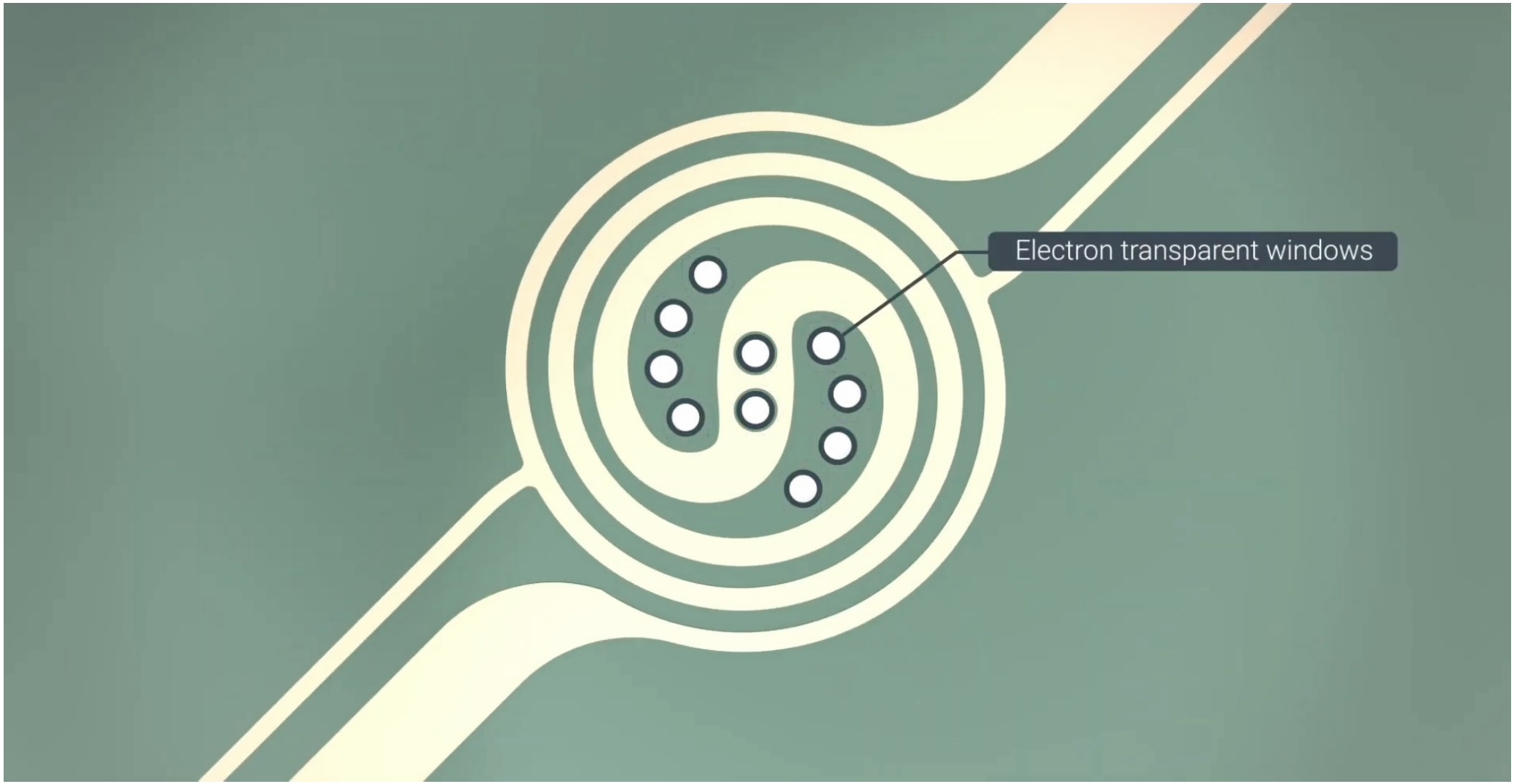


Gas in-situ 2: MEMS cell

Advantages:
- Higher pressure (up to 1bar)
- Any microscope
- Highly customizable

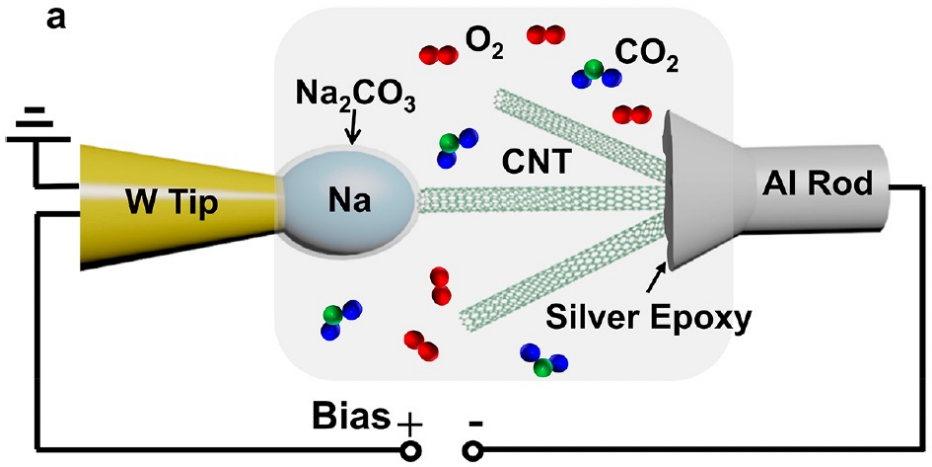
Disadvantage:
- SiN window
- EELS very difficult
- Image deteriorated by windows

Gas in-situ 2: MEMS based Gas cell holder



Dens climate holder, available at ScopeM

Gas example: Charge Discharge NaO_2/CO_2 battery



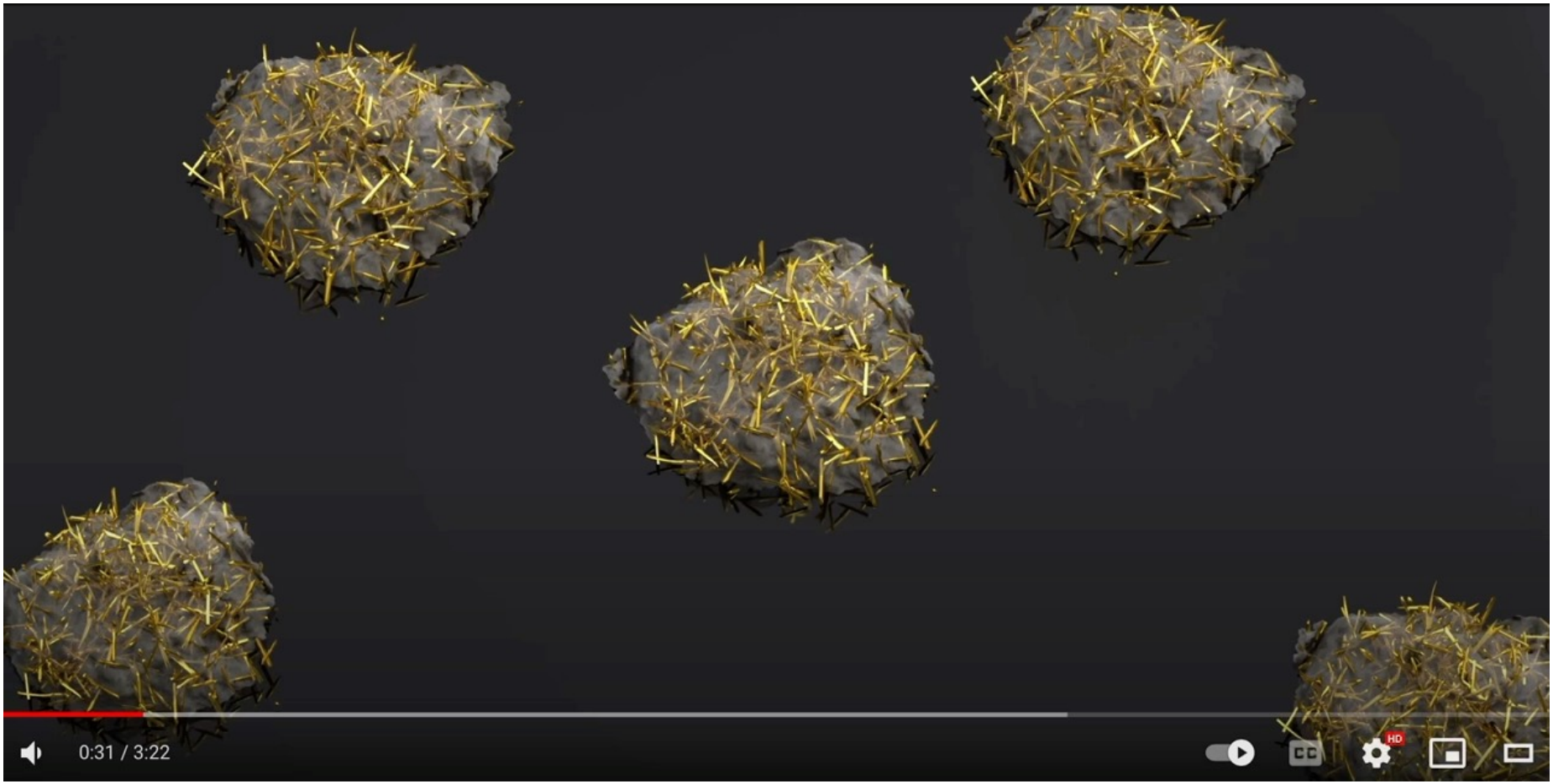
In Situ Electrochemical Study of $Na-O_2/CO_2$ Batteries in an Environmental Transmission Electron Microscope

Qiunan Liu, Yongfu Tang,* Haiming Sun, Tingting Yang, Yong Sun, Congcong Du, Peng Jia, Hongjun Ye, Jingzhao Chen, Qiuming Peng, Tongde Shen, Liqiang Zhang,* and Jianyu Huang*

Cite This: *ACS Nano* 2020, 14, 13232–13245 Read Online

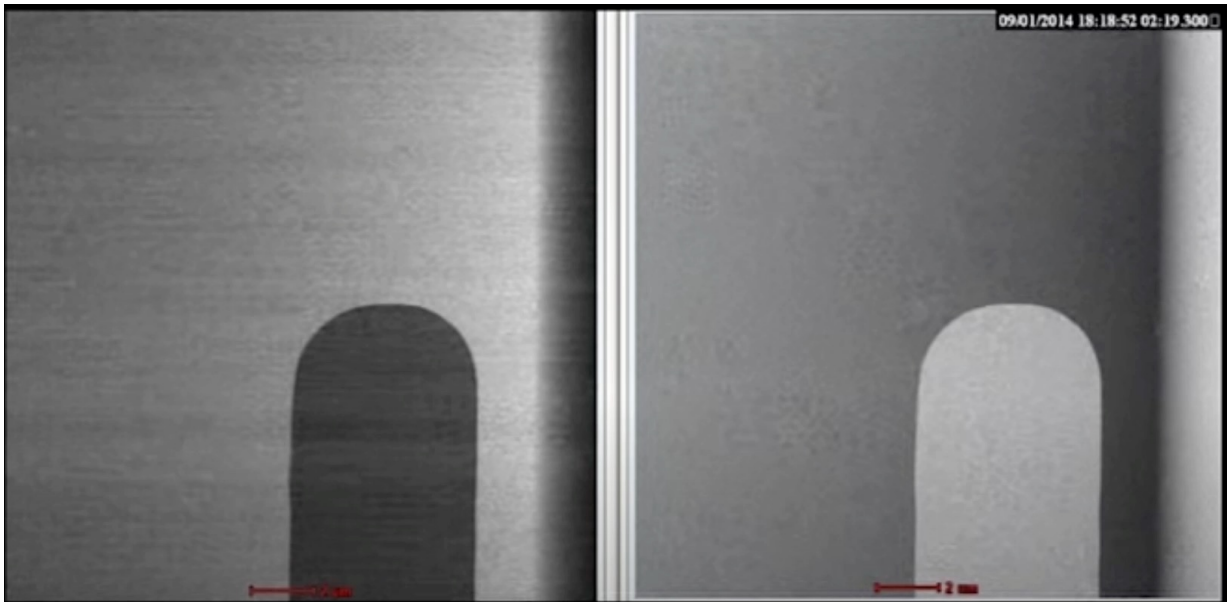
ScopeM

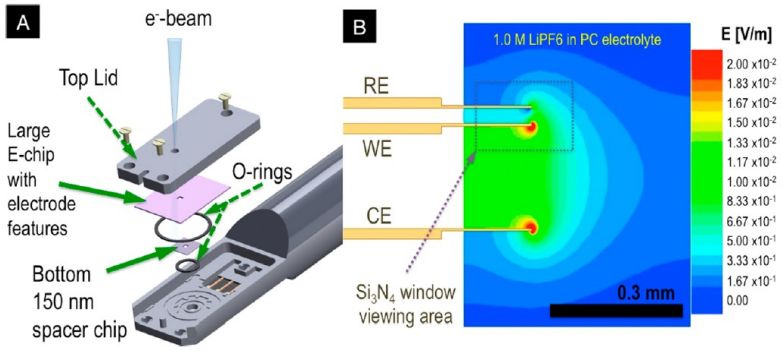
MEMS based liquid cell holder



Protochips Poseidon holder, available at ScopeM

Liquid Cell example: Lithium Dendrite growth

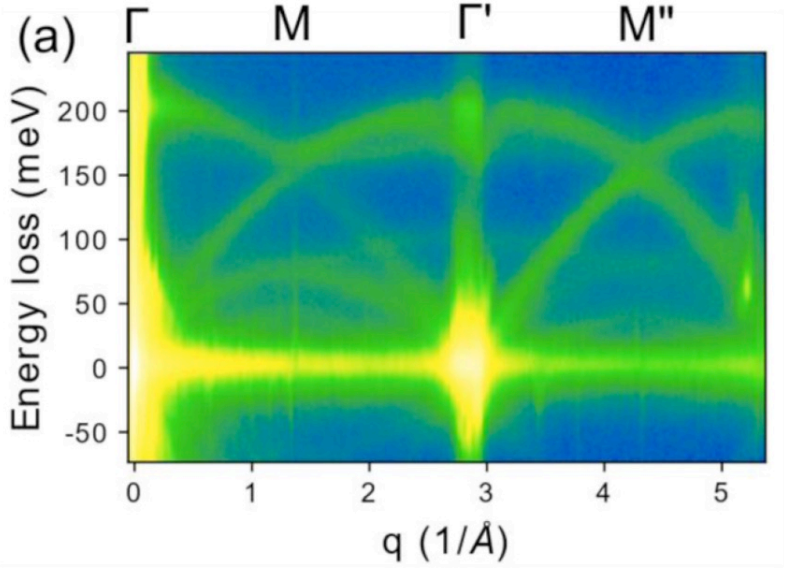


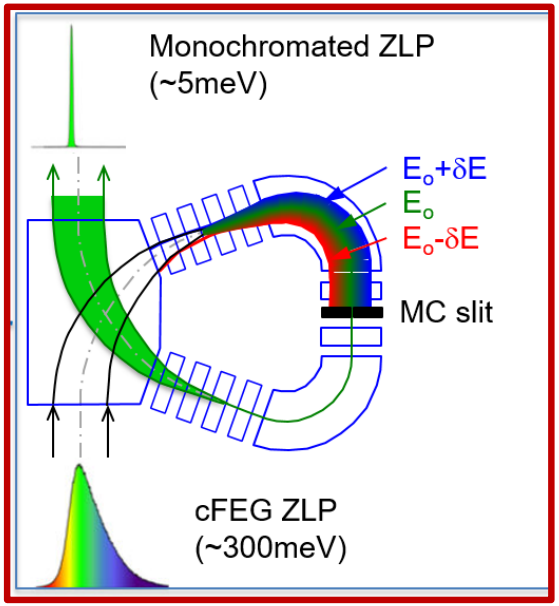


NANO LETTERS
Letter
pubs.acs.org/NanoLett

Observation and Quantification of Nanoscale Processes in Lithium Batteries by Operando Electrochemical (S)TEM

B. L. Mehdi,*,† J. Qian,‡ E. Nasybulin,‡ C. Park,§ D. A. Welch,∥ R. Faller,∥ H. Mehta,⊥ W. A. Henderson,‡ W. Xu,‡ C. M. Wang,⊥ J. E. Evans,⊥ J. Liu,‡ J. -G. Zhang,‡ K. T. Mueller,⊥,# and N. D. Browning†



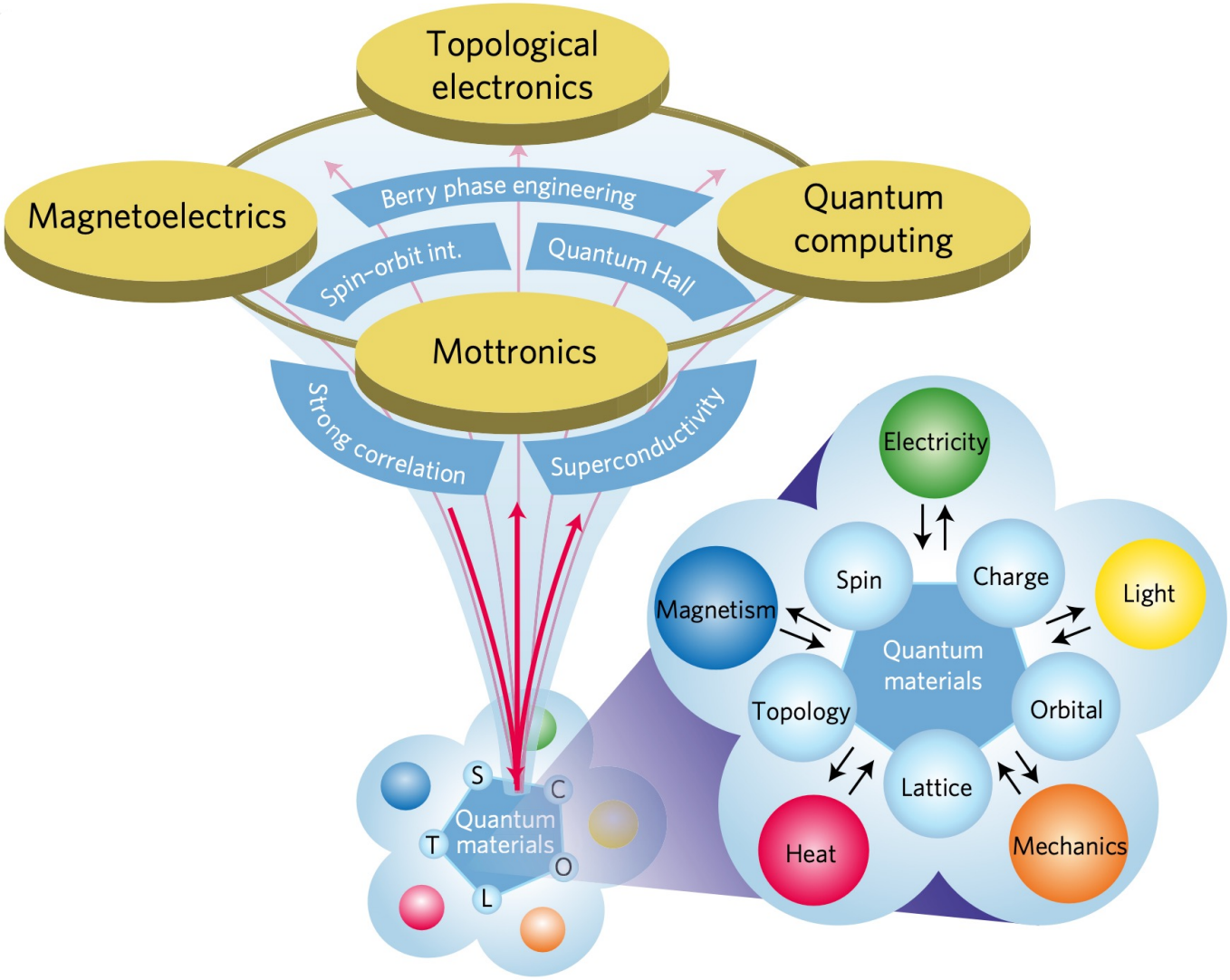


Left: phonon map hBN
Right: monochromator schema

Electronic properties

Application for quantum material

Quantum Materials = Condensed Matter

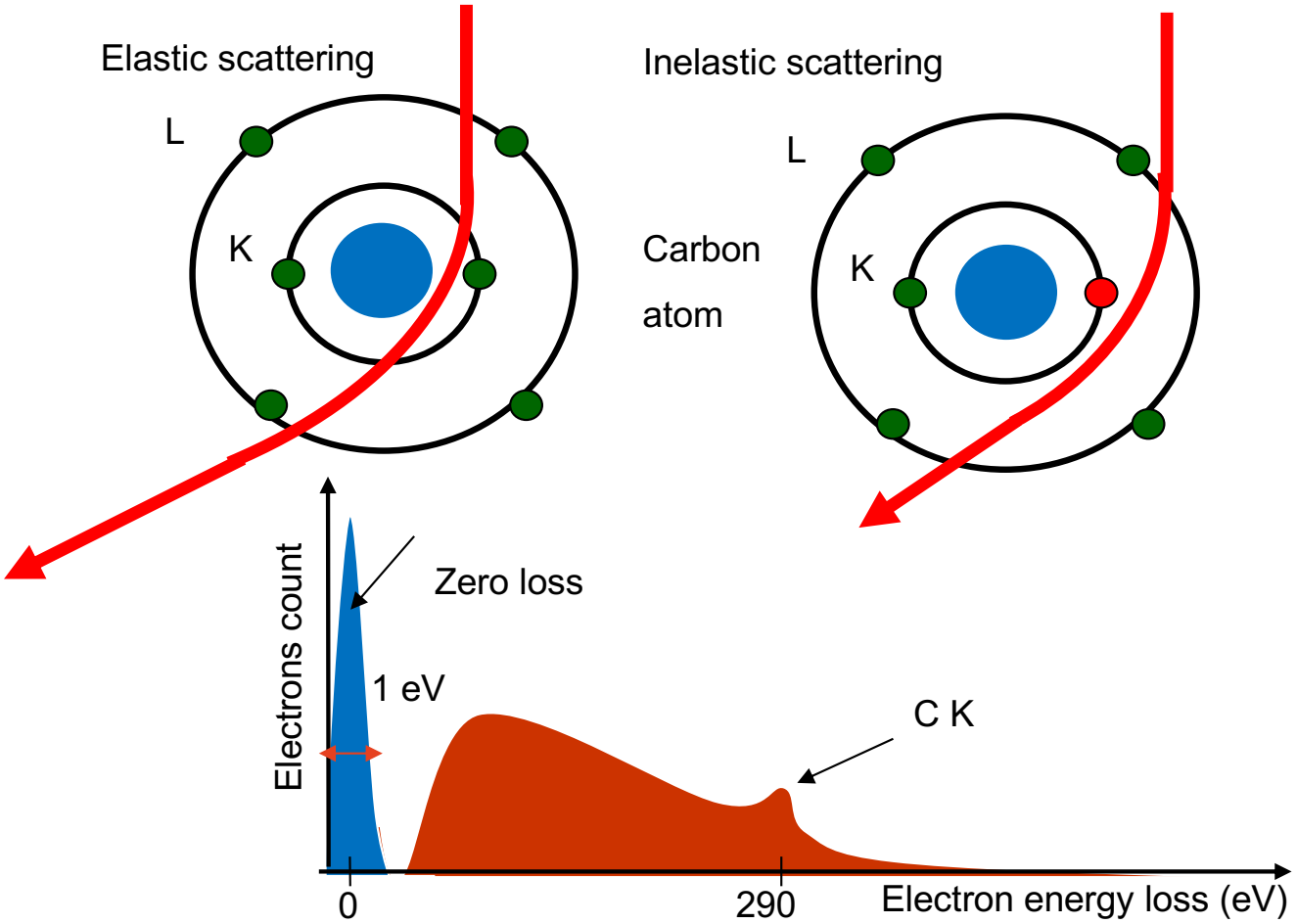


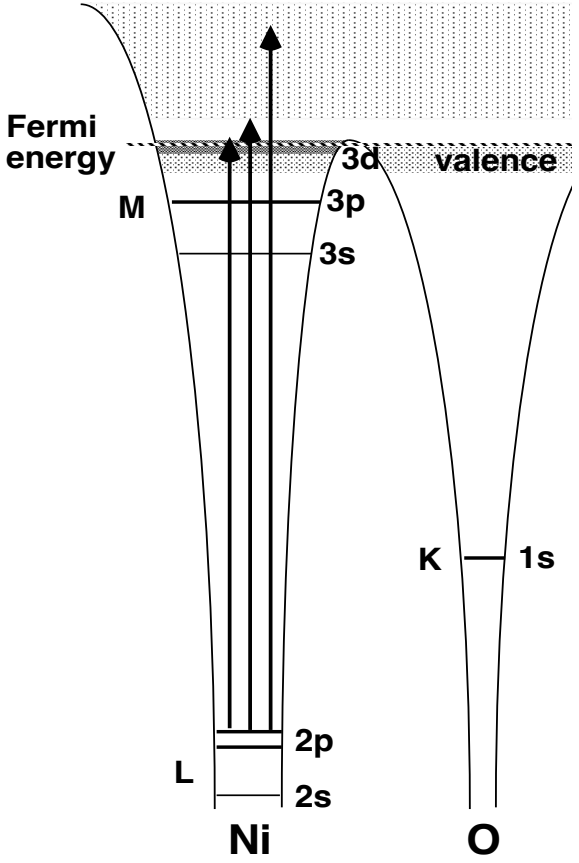
Example:
- Quantum dots
- 2D Films and interface
- Superconductors
- Nanotubes.

Applications:
- Batteries
- Super capacitors
- Quantum Computing
- Bio-sensing

Tokura et al. Nature Physics 13, 2017

Introduction to EELS





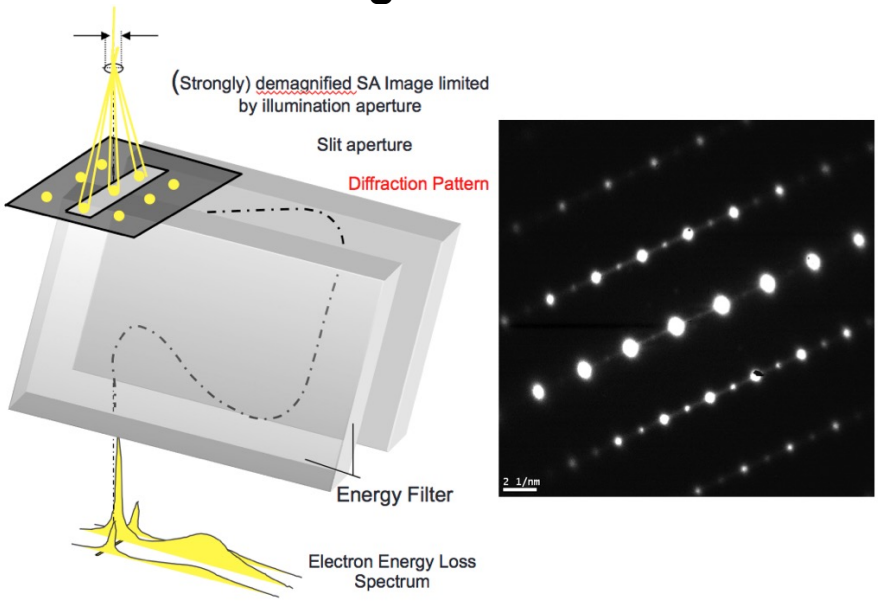
Core-Loss:
- Bonding
- Valence State
- **Spin***
- **Charge**
- **Orbital**

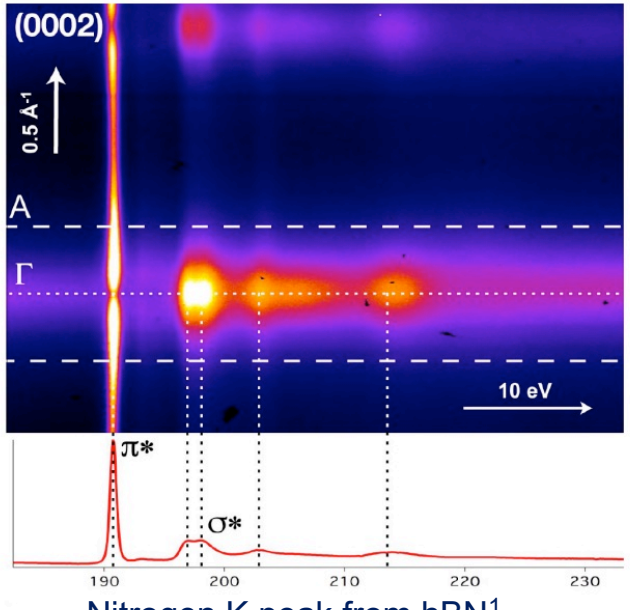
Topology?

Valence EELS:
- Band structure
- Optical properties
- Dielectric properties
- **Lattice**
- Temperature

How to access topological properties

- **Schematic of Angular Resolved EELS:**





Nitrogen K peak from hBN[1]

- **Limitation Angular Resolved EELS:**
  - Inelastic σ decreased with $1/q^2$. -> High q but very weak signal
    - ➢ **Sensitive detector**
  - q resolution proportional to beam parallelism
    - ➢ **Nanobeam parallel setup**
  - Multiple scattering involving low q, tails
    - ➢ **Monochromator**

ScopeM

1:Loiseau et al. PRB 96 (2017)

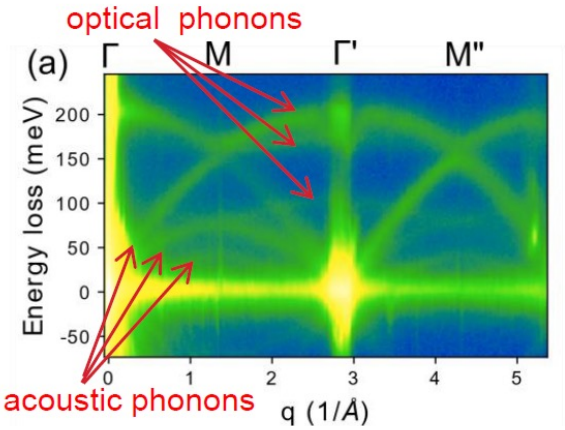
QSTEM: NION STEM for energy Momentum EELS

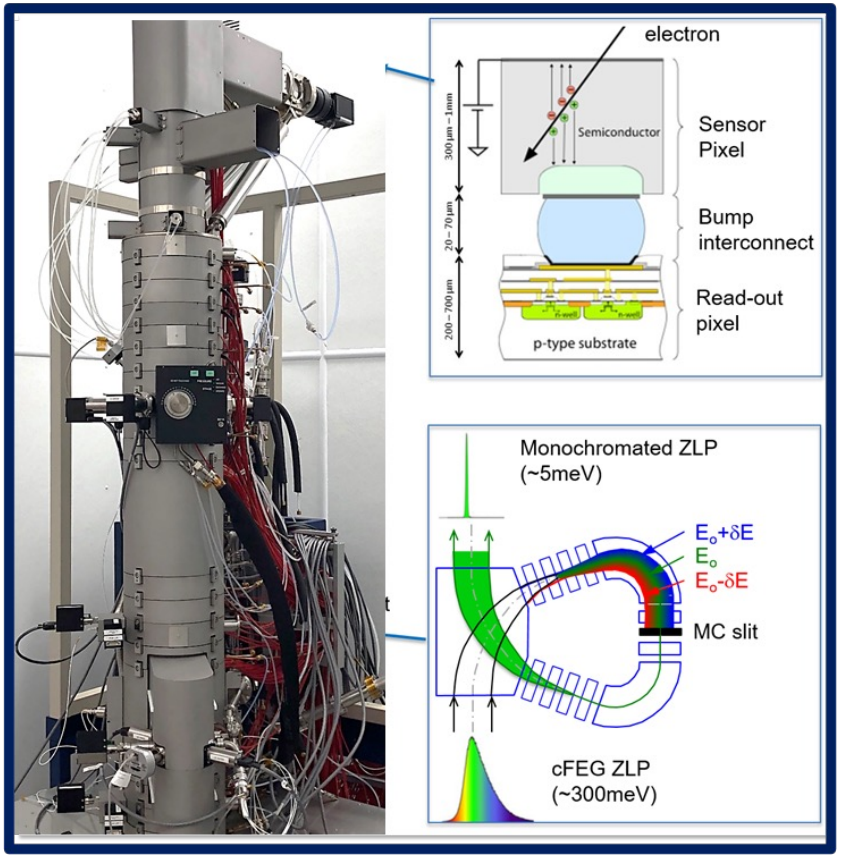
2017

- 4meV at 60kV
- 130pm at 60kV
- High Momentum up to 6Å^{-1}

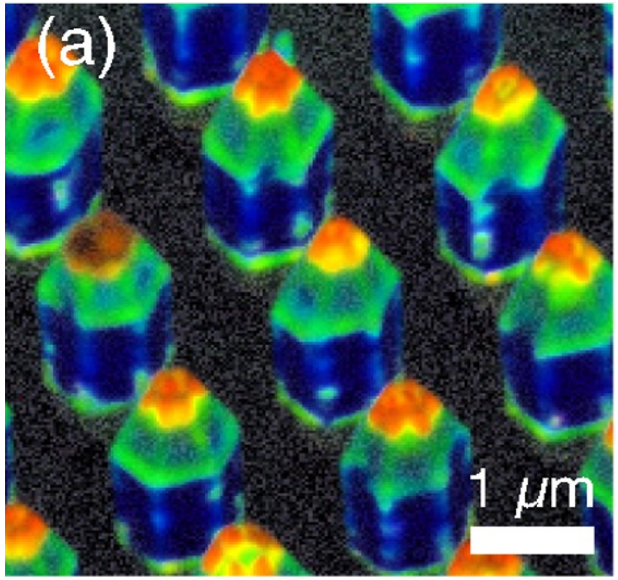
2024

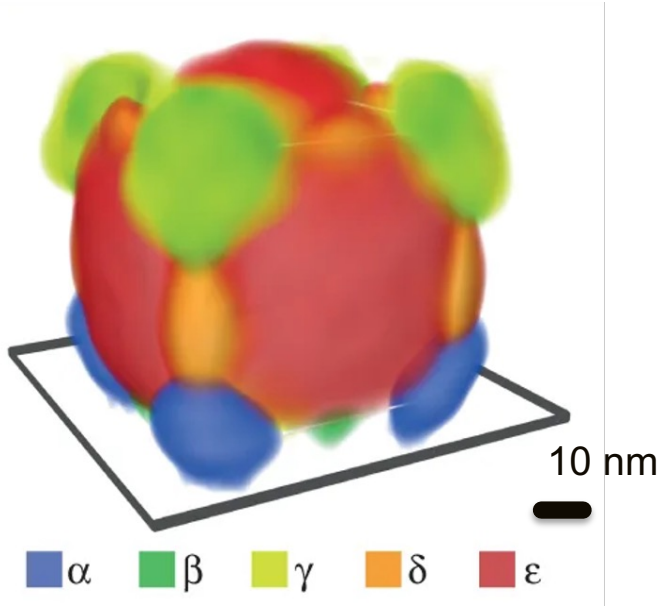
- Helium temperature
- Magnetic control





Applications: Batteries, Super capacitor, Quantum Computing, Quantum-sensing, nanomaterials





Left: CL GaN nanorods
Right: CL tomography

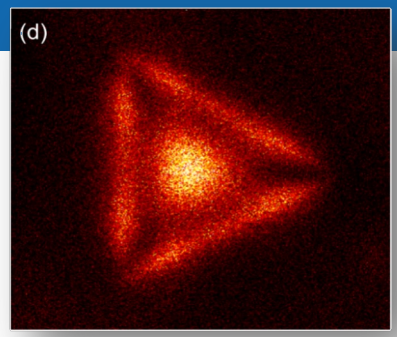
Optical properties

Exploring Nano-optics

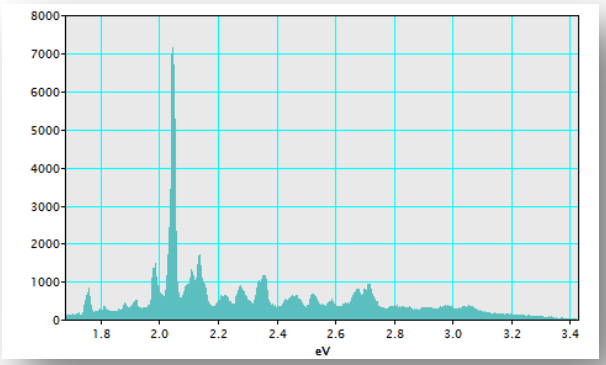
Tu et al. Nanotechnology 27-2 (2016)
Nicoletti, de la Pena et al. Nature 502, 2013.

LIGHT EMISSION

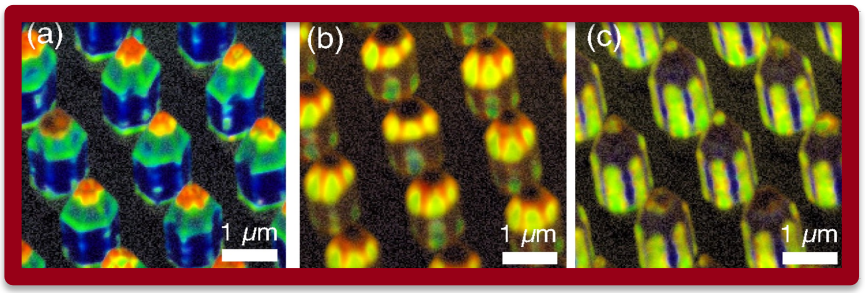
- Light emission phenomena:
  - Electronic Physics:
    - Free Electrons -> Plasmon
    - Quantum confinement
    - Interband emission
    - Excitons (e-h pairs bound by coulomb attraction)
  - Vibronic Systems
    - Molecular materials
    - Luminescent defects and impurities (phosphors, diamonds...)
  - Vibrational Physics
    - Phonons (IR)
  - Nonlinear Optics



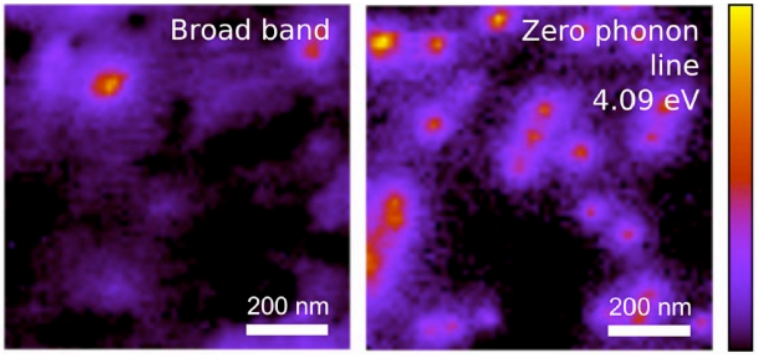
Surface plasmon resonance mode in 800nm gold prism



Phosphor nanoparticles – Y_2O_3:Eu (red)



Real-color images from CL spectrum for GaN nanorods with different growth conditions.



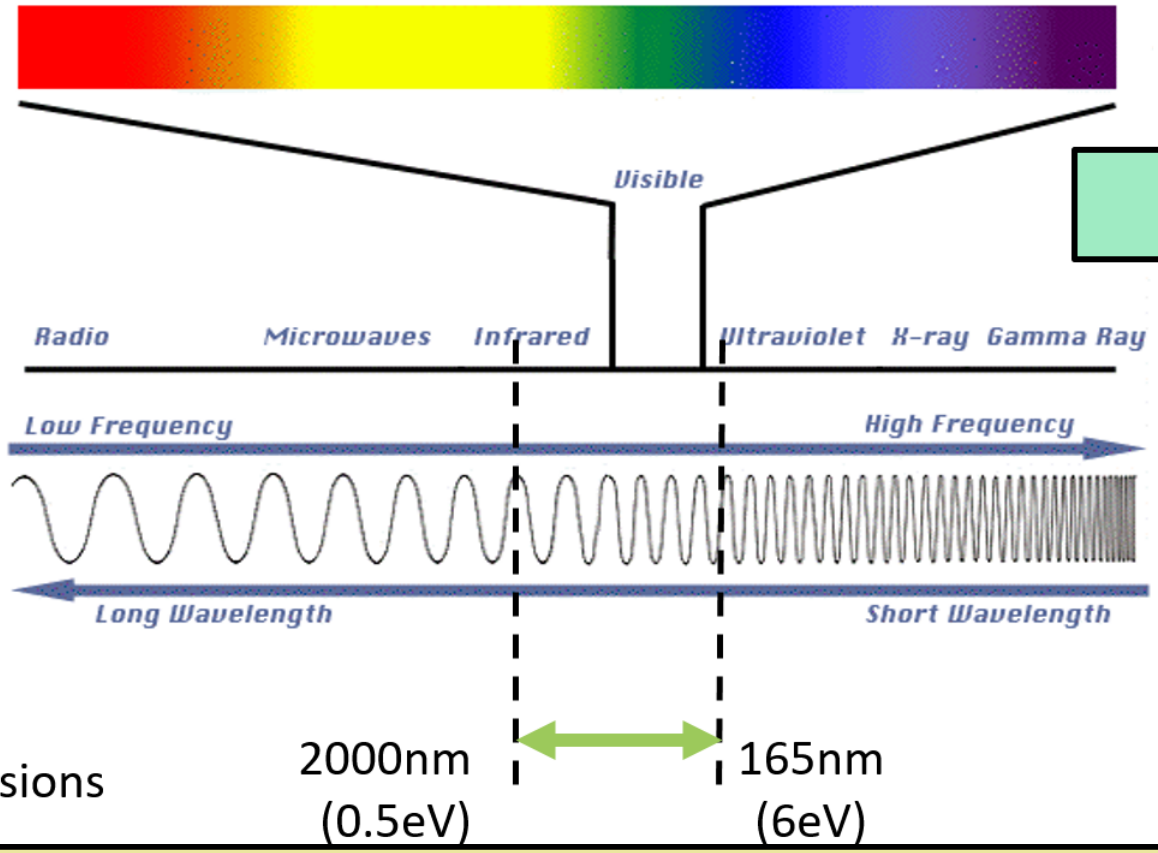
NV center in nanodiamonds[1]

ScopeM

1: L.Tizei et al. Nanotechnology 2012, 23, 175702

Electromagnetic spectrum

Exact wavelength (energy) is characteristic of a particular electronic transition



EDS (keV)

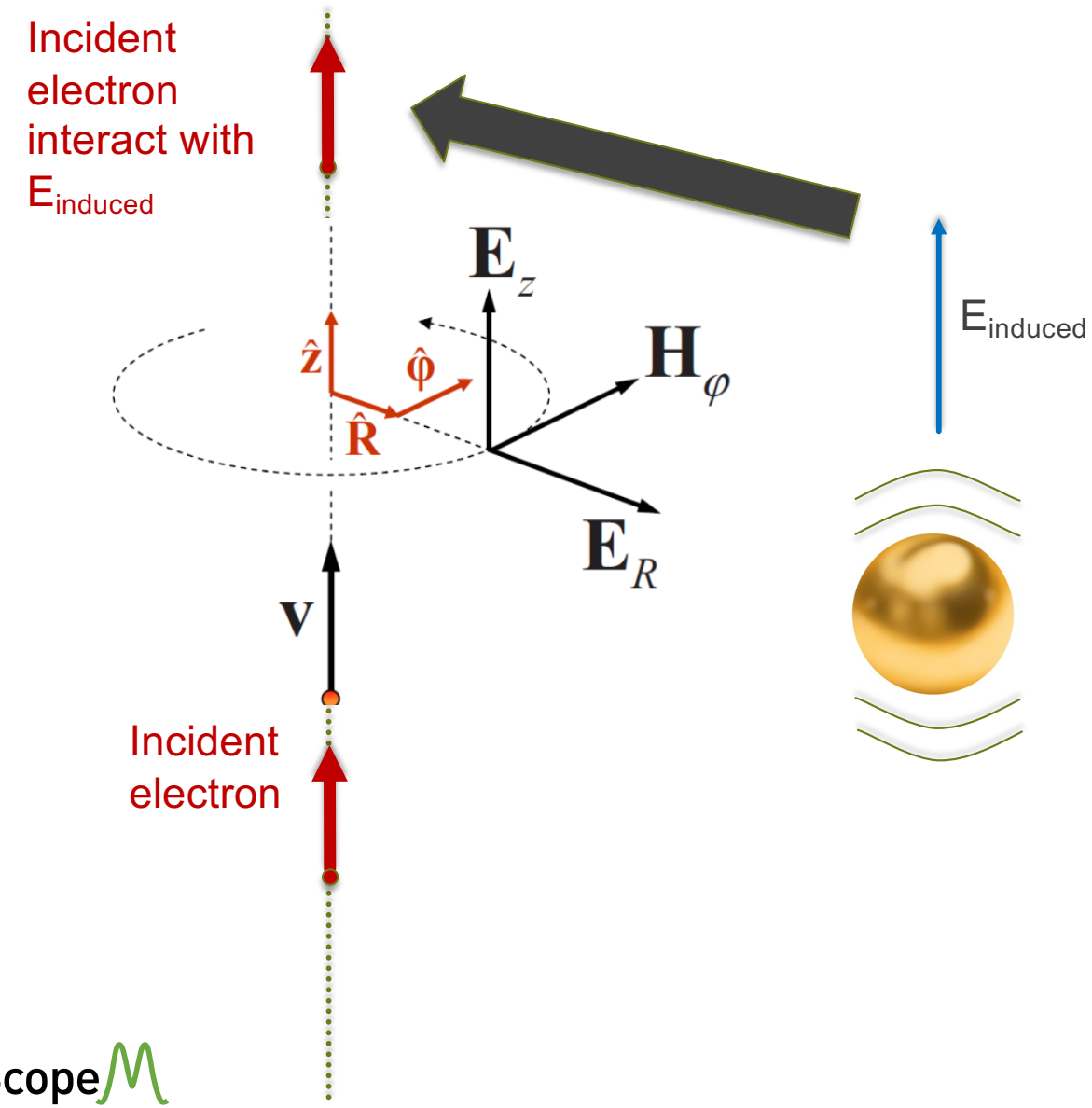
Typical CL emissions

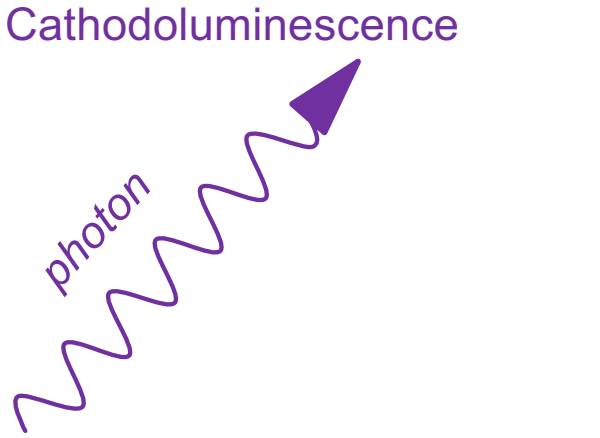
2000nm (0.5eV)

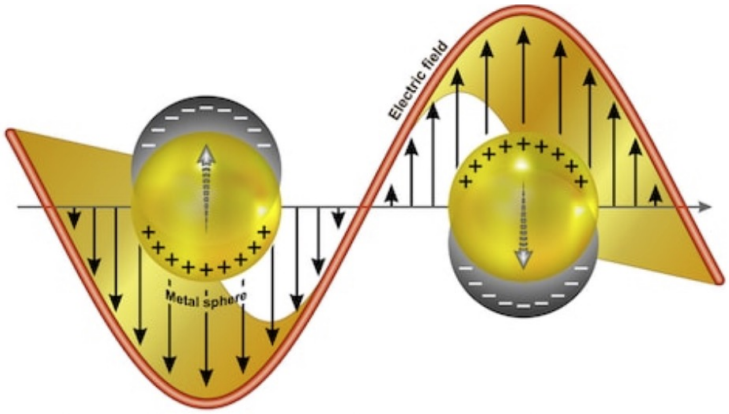
165nm (6eV)

EELS (0 – 3000eV)

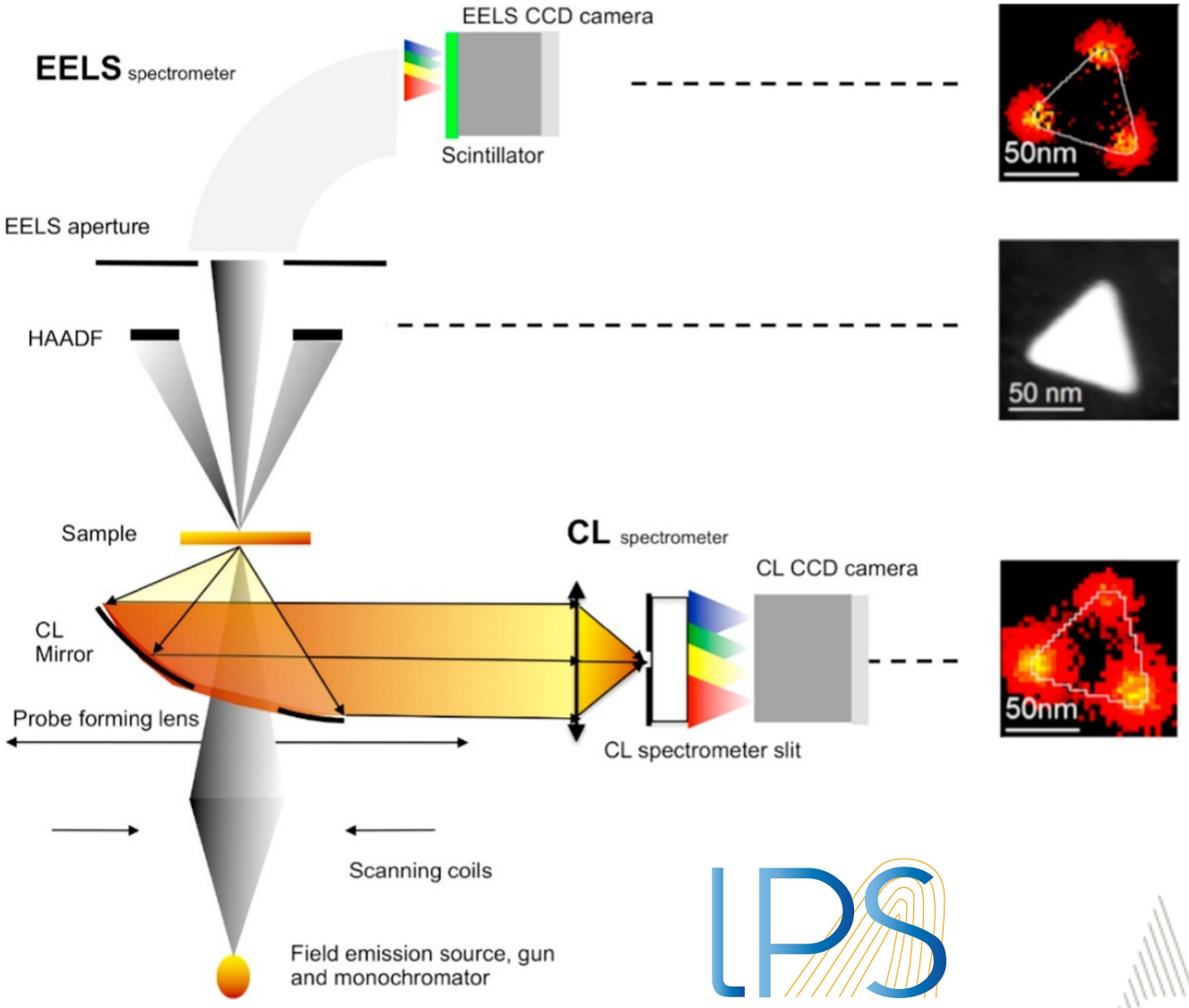
How to probe optical properties at the nanoscale

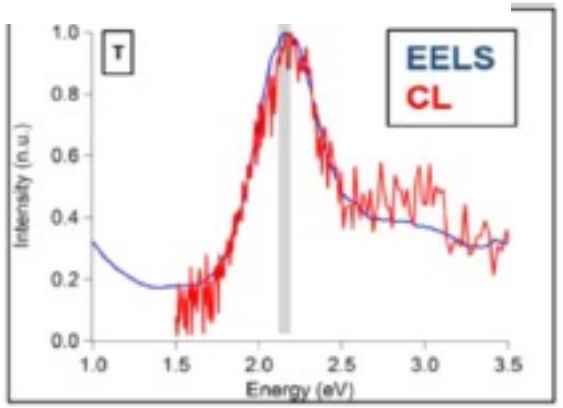






Cathodoluminescence and EELS





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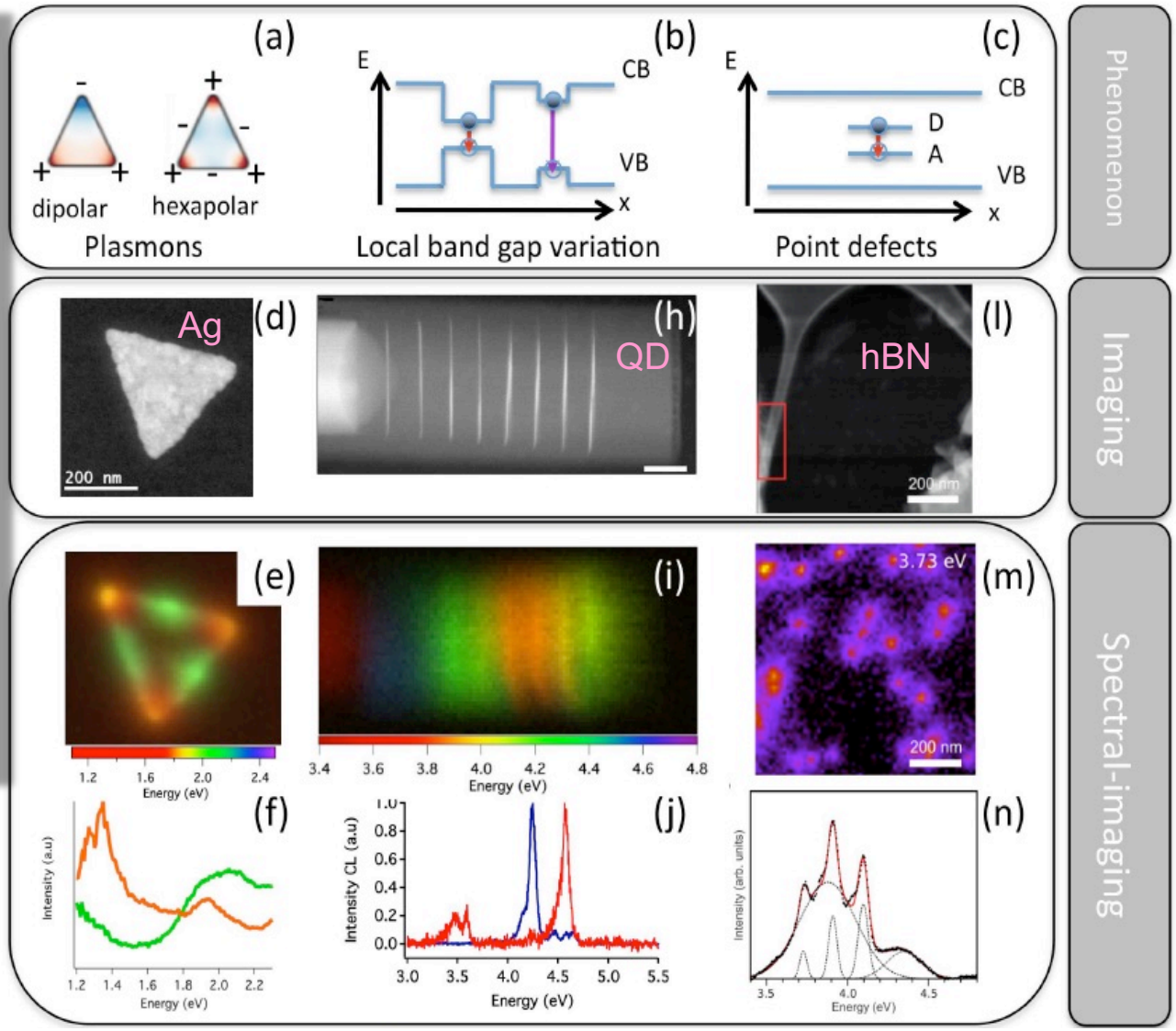
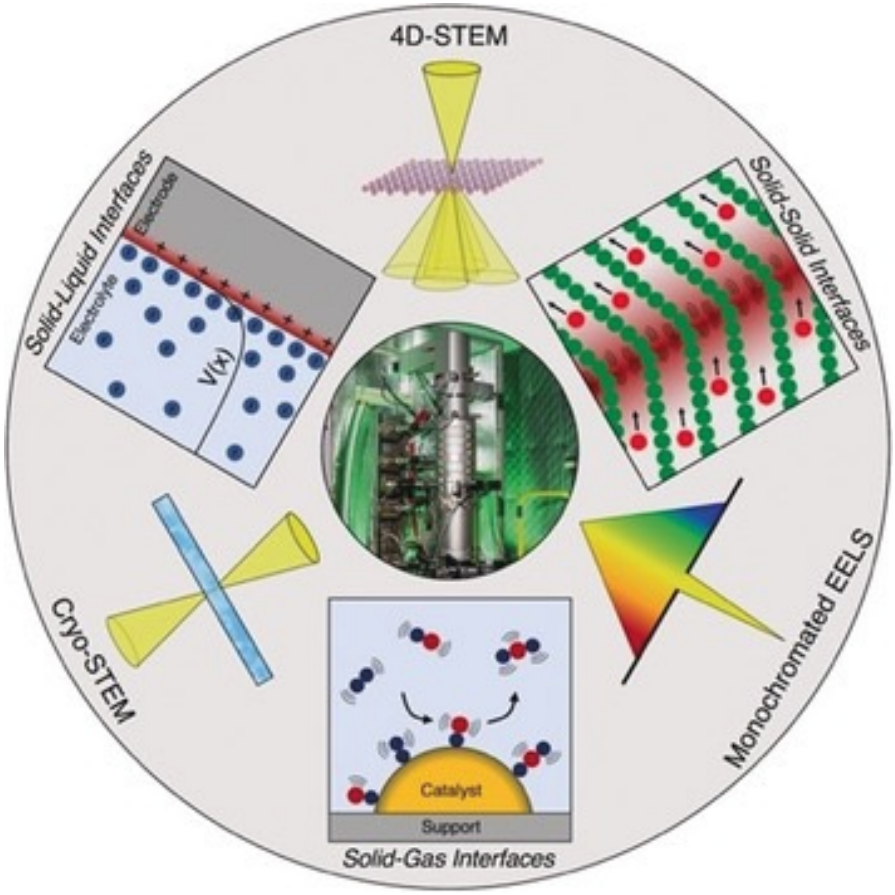
LPS ORSAY

attolight™

Current State of the art in nano-optics

- Cathodoluminescence (TEM/SEM)
- EELS (Visible to Microwave)
- Resolution down to single atomic defects
- Angular distribution
- Pico-second speed





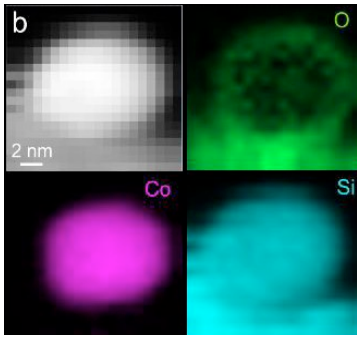
Chemical properties

From solid to gas

Chemical properties

Basic Chemistry:

- - Element Identification (EELS/EDS)
- - Mainly Bulk
- - Resolution VS speed



Co/SiO2 system by EELS

F.Yang Chem. Sci., 2021,

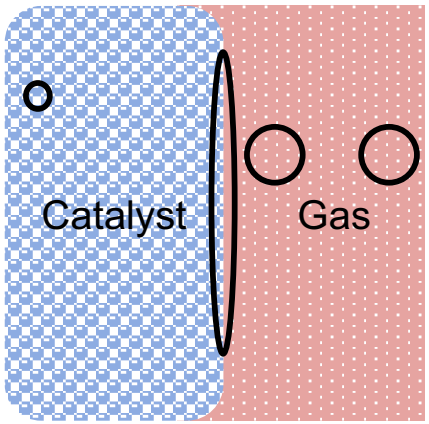
Interface Chemistry:

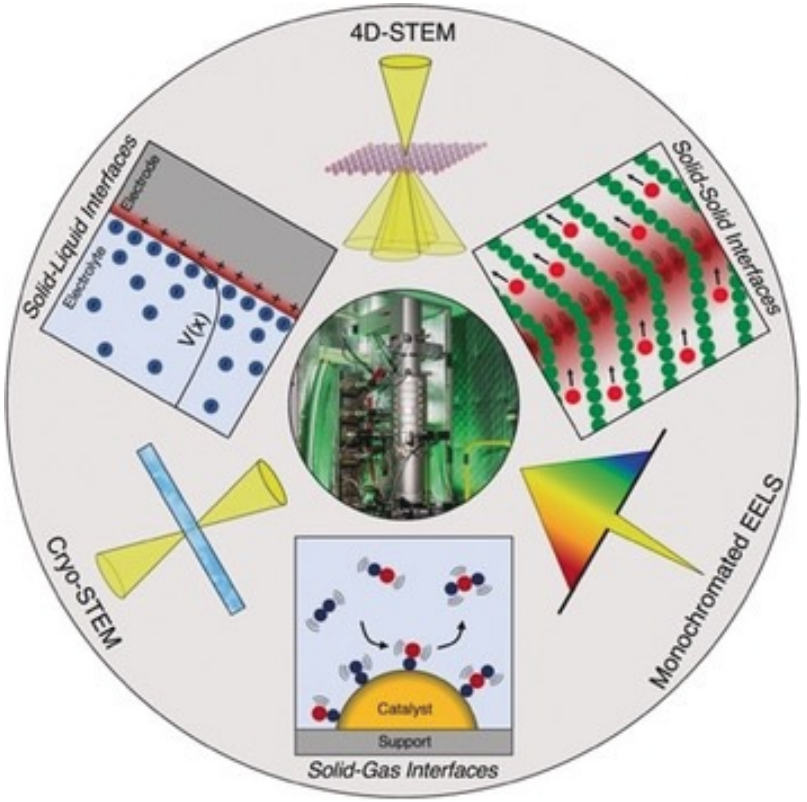
- "Useful Chemistry"
- Much more challenging
- Often Invisible (ions, electrons, gas,…)

➢ Surface Chemistry

➢ Gas Chemistry

➢ Liquid Chemistry

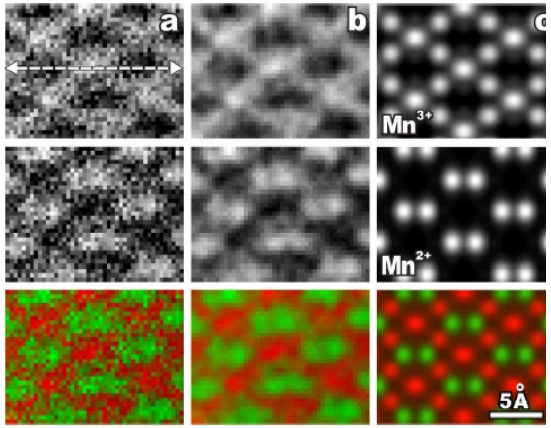


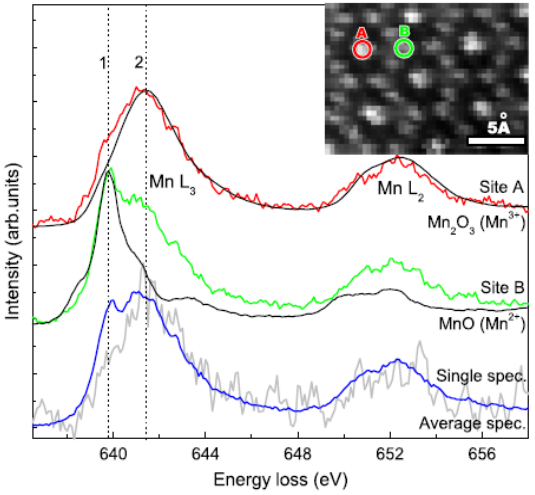


ScopeM

Chemical Bonds

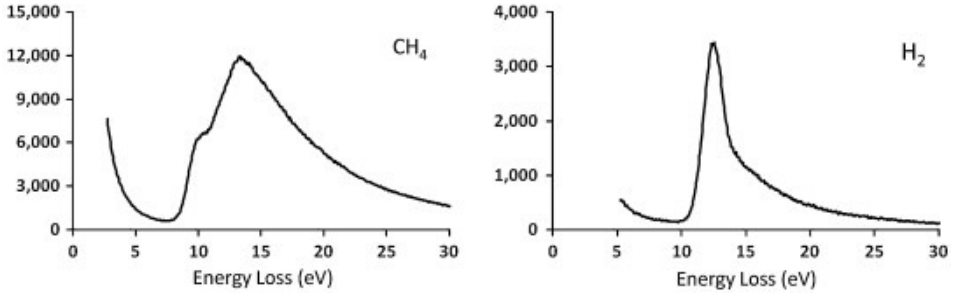
- Inorganic solid : Density of States. Normal EELS

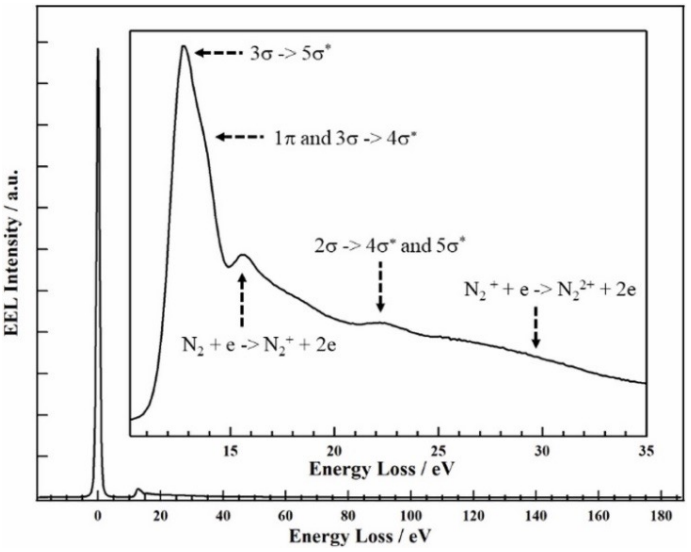




H. Tan et al., *Phys Rev Lett.*, **107** (2011) 107602

- Gas : Similar but technically challenging

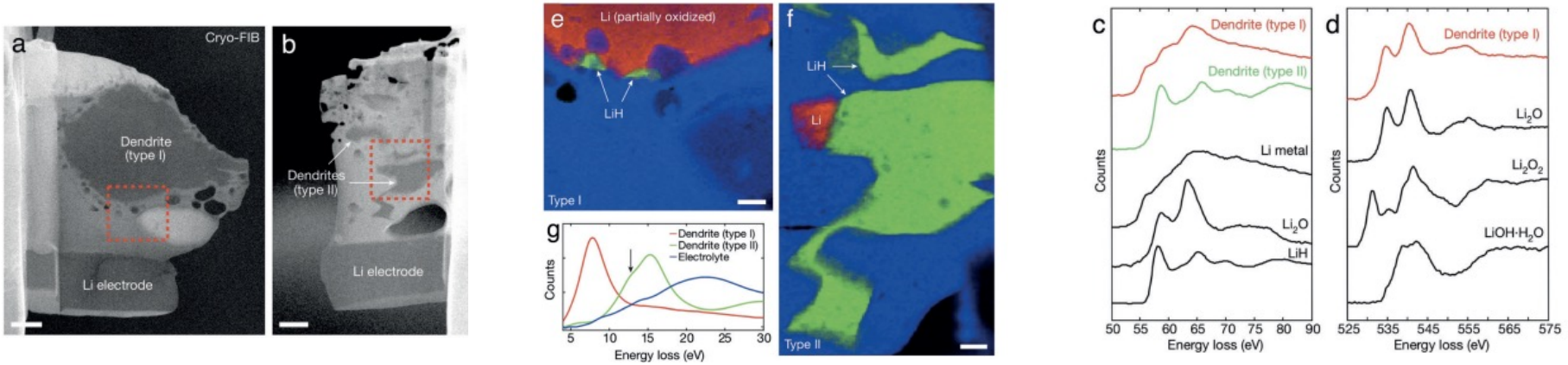




Crozier et al. Ultramicroscopy 111-3, 2011

Chemical Bonds

- Solid-liquid interface: frozen



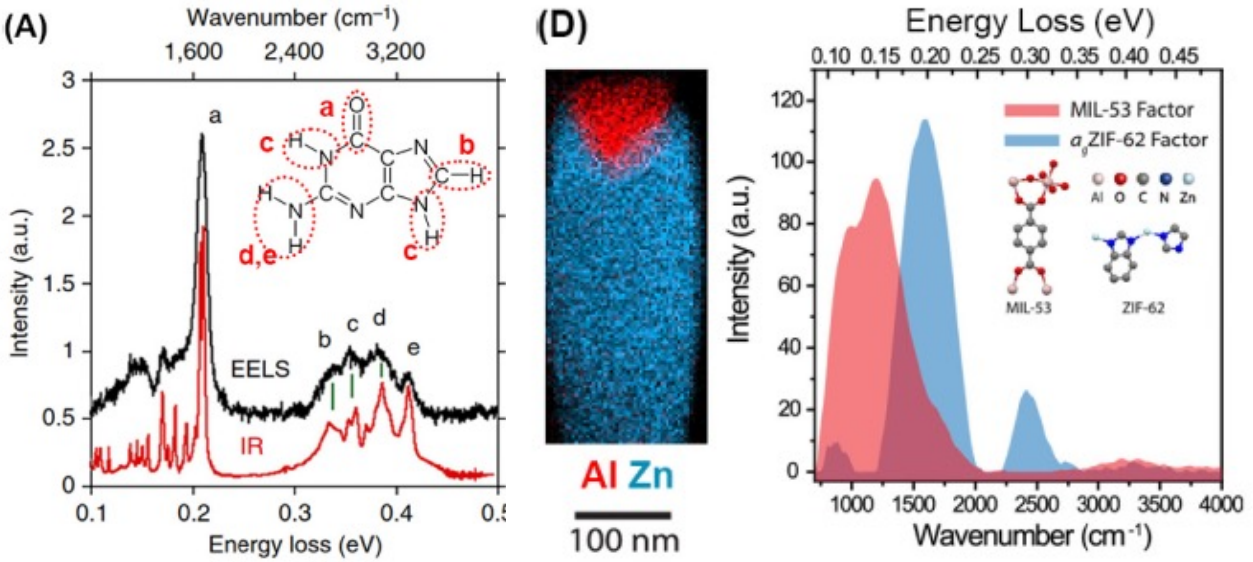
STEM-EELS of dendrite – electrolyte interface

El Baggari et al. PNAS 2018-115

- Organic or hybrid molecules:

➢ Vibrational Spectroscopy

- In-situ Vibrational EELS ~ 2025



Rez et al. Nat Com. 7, 10945

Collins et al. Nano Lett. 20 - 2020

- Experiments in Electron Microscopy should be designed with a clear plan in mind: Sample – Environment – Properties
- Characterization should be a mean for properties analysis.
- Various stimuli can be applied to samples (gas, bias, magnetic field…)
- Advanced techniques can give us direct insight on many properties such as the chemistry, the electronic structure or the optical properties.

Summary and Outlook