Recent advances in spatially-resolved spectroscopy combining photon and monochromated electron beams in a STEM

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In scanning transmission electron microscopy (STEM), following the advent of aberration correctors, a more recent breakthrough has been the development of new-generation monochromators, preserving the brightness of electron sources, and thus opening the way to new applications in Electron Energy-Loss Spectroscopy (EELS). More than just improving spectral resolution (now available in combination with atomic resolution), monochromation in EELS has given access to a whole new range of low-energy elementary excitations (down to the infrared range) with nanoscale resolution. The field of nano-optics using fast electron beams has been booming in recent years, boosted by recent developments in experiments combining photons and electrons in the microscope: cathodoluminescence (EELS), electron energy-gain spectroscopy (EEGS), photon-induced near-field electron microscopy, etc. Further advances are still to be expected by pushing the limits of time resolution, both as instrumentation advances and for accessing new physical information.

I will review some of our latest results obtained in the field. This will encompass the observation by monochromated EELS/CL combined measurements of the nanoscale modification of WS$_2$ monolayers trion emission by local electromagnetic environment [1] the mapping of high-quality plasmons in copper nanostructures [2] or the three-dimensional vectorial imaging of surface phonon polaritons in MgO nanocubes [3].

Very recently, we have developed new acquisition schemes making use of a Timepix3 direct electron detector providing sub 10 ns time resolution over arbitrary EELS energy ranges [4]. In parallel, we are developing new schemes aiming at synchronizing a continuous electron beam with (in some cases pulsed) photon beams, as a complement to approaches using a pulsed electron gun. I will put the emphasis on two recently developed spectroscopies:

- Electron Energy-Gain Spectroscopy [5] and ultra-high EEGS with sub meV (100 µeV) energy resolution
- a new type of time-correlated experiments based on coincidence (time-correlated) measurements between inelastic electron scattering (EELS) and photon emission (CL) events. I will show how this newly developed spectroscopy (so called Cathodoluminescence Emission spectroscopy) can image energy transfer pathways at the nanometer scale [6].

References
Engineering polar states in multiferroic Sr$_{1-x}$Ba$_x$MnO$_3$ thin films

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Fundamental physics of perovskite oxides is governed by subtle changes in stoichiometry and crystal symmetry. Particularly in thin films, the interplay between chemistry and structure can be altered by fine-tuning the conditions for epitaxial growth. A good example is the family of multiferroics AMnO$_3$ (A= Ca, Sr, Ba) perovskite, antiferromagnets in which ferroelectricity driven by the off-centering of the magnetic cation Mn$^{4+}$ can emerge through selective crystal distortions [1].

In this talk we review our research on the family of Sr$_{1-x}$Ba$_x$MnO$_3$ (SBMO, $0 \leq x \leq 0.5$) thin films. We demonstrate that in epitaxial thin films it is possible to tailor the polar atomic displacements as a function of the composition, by tuning key growth conditions. Cs-corrected scanning transmission electron microscopy (STEM) [2] combined with X-ray diffraction (XRD) has allowed us to determine the local polarization at the nanoscale as a function of the induced crystalline structure and composition. Polarization is intimately linked to the sign and magnitude of epitaxial strain and can be tuned either in-plane or out-of-plane with respect to the substrate plane (see Figure 1), by the appropriate choice of the substrate-induced strain, Ba doping and the O content —induced by controlled annealing [3].

![Figure 1](image)

**Figure 1.** (a) XRD of selected SBMO thin films. (b) ABF-STEM image of an Sr$_{0.6}$Ba$_{0.4}$MnO$_3$ epitaxial film, observed along the $\langle110\rangle$ direction. (c) Average atomic displacements of O and Mn, and deduced polarization components ($x$: in-plane direction, $z$: out-of-plane direction).

**References**


MEMS-based in-situ TEM: Exploring Untapped Opportunities in Battery Research, Catalysis and Electrochemistry

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We introduce our technology for in situ studies inside transmission electron microscope (TEM), where next to heating and biasing studies, also environmental studies (i.e. in gaseous or liquid environments) are made possible. The systems rely on a Micro Electro-Mechanical System (MEMS)-based device as a smart sample carrier, which contains an integrated set of biasing electrodes or an integrated microheater, to enable in situ electrochemistry, battery research, catalytic studies and failure analysis, among others. As a result, the system provides users with the capability to visualize exciting dynamics in vacuum or liquid/gas environments as a function of different stimuli. In order to provide meaningful results and address historical challenges, our MEMS device controls the flow direction and ensures the gas/liquid will always pass through the region of interest. Thereby, the developed systems offer the opportunity to define the mass transport and control the kinetics of the reaction. Furthermore, the system’s modularity enables the user to remove the tip, referred to as a “lab-on-a-cartridge”, which can be inserted in the Synchrotron, in order to enable powerful correlative studies while keeping the environmental conditions constant. We believe that our developments will play a fundamental role in addressing many of the research questions within battery optimization, fuel cells, (electro)catalysis, as well as for advanced materials.

FIGURE 1. Different systems have been developed, all MEMS-based, to enable in-situ studies as a function of multiple stimuli.

References
High Angle Liquid Cell TEM Tomography and 3D Reconstruction in Liquid

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Liquid-Cell (LC) electron microscopy (EM) is a rapidly emerging field in TEM [1]. While 2-D LC observations are very common for inorganic materials and biological systems, studies of objects in 3-D in liquid are scarce mainly due to very limited available tilt range of the current LC holders (e.g. usually ±35°). To perform electron tomography, LCs need to reach high angular ranges, preferably more than 140° (±70°) to obtain a reliable 3D model. Since such LC do not exist currently, we have developed a prototype “tomographic” LC (labelled as Tomochip) by modifying a commercial LC (K-Kit from Bio MA-TEK), whose original total inclination angular range is about 60° (±30°) [2]. The central part of such LC viewing window can be tilted ±70° with an effective observation area of about 100µm x 25µm. We found that when LC spacer is between 100-200 nm, it is very probable that samples (e.g. crystals) may stay still inside the liquid for long periods of times (e.g. several minutes), which is adequate in order to perform 3D tomography experiments within the liquid.

We have studied (beam-induced) 3D crystals of Flufenamic acid (FFA) grown in our Tomochip at 120 kV. We minimized total tomography acquisition time by performing 10° tilt steps from -50° to 50° , while crystals were maintained still inside the liquid during tilt. We have also studied 3D Carbon particles within water in a Tomochip where images were collected from 70° to 70°, every 5°. In both cases TomoJ (v2.6) plugin for tomographic reconstruction of the ImageJ (v1.53e) image processing program has been used. 3D image tomography was reconstructed using Total Variation Minimization reconstruction algorithm (Figure 1).

![Figure 1. 3D view of FFA crystals within liquid cell](image)

References
Combining High-Speed and High-Sensitivity: The application of Counting Detectors for EELS, EFTEM and 4D-STEM

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The number of electrons in a beam can be parsed in many ways, but the total number is fixed. The faster you go, the fewer electron you have at each data point leaving you starved for counts. The same can be said for other data acquisition modes that parses the electrons into finer bins, such as increasing the energy dispersion to achieve better EELS resolution or reducing the energy selecting slit size to get sharper energy filtered images. The final limit of your experiment may not be the resolution of the hardware, but the Poisson or “shot” noise associated with counting discrete events. For a signal with N electrons, you can never have better noise than SQRT(N).

The advent of counting detectors for electrons have revolutionized electron microscopy in many ways, but they too cannot get around the SQRT(N) limit. However, due to the fast readout rate and sharp point spread function of these cameras, the traditional methods of acquiring electron microscopy data have been turned on their heads. In this presentation, we will discuss and illustrate the strategies for acquiring EELS, EFTEM and 4D STEM data using electron counting detector to optimally use the fixed number of electron available in the system. We will draw on examples from high-speed multimodal data acquisition and extreme low dose EELS fine structure analysis to demonstrate these strategies.
Cryoelectron microscopy: a revolution in structural biology

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Electron microscopy is an old technique -it has been in use for more than 90 years-, and whereas in Material Science it soon showed its great potential in structure determination, this has not been the case with biological molecules. The two main problems for this practical limitation are: a) the inability to find ways of preserving the three-dimensional structure of the molecules, which is maintained by weak bonds that are easily destroyed by electron radiation; b) the inability of properly determining the angular position of the particles during the tomographic, three-dimensional reconstruction procedure. Part of the first problem can be overcome with the use of very low temperatures, and thus the name of cryoelectron microscopy. The rest of the limitation were successfully solved around 10 years ago, resulting in a revolution that is dominating structural biology and soon cell biology. The talk will deal with a description of the problems, show how they have been solved and what are the avenues that cryoelectron microscopy offers to biology.

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Structural Biology in the Liquid State: Amyloid-β40 aggregation visualized by Liquid-Phase TEM

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Liquid phase transmission electron microscopy LP EM offers remarkable capabilities with regard to imaging label-free, time-resolved structures in their native liquid media by removing the artefacts caused by traditional drying or cryogenic treatments. One of the most exciting applications of LP EM is the investigation of cell molecular machinery structures such as proteins. The liquid nature of the sample offers novel opportunities such as accessing previously inaccessible protein states or the possibility of 3D structure reconstruction by applying tomographic methods. The free movement of soft objects in LP EM allows for screening proteins’ structural landscape during the imaging process. Such a feature provides a unique selling point for the technique for structural biology investigations.

We propose the combination of all-atom simulations with imaging via LP EM to complement protein structural studies with dynamic investigations. We have employed LP EM to investigate Amyloid-β (Aβ) aggregation. Aβ is a short 39–42 amino acid peptide that aggregates into larger assemblies, including neurotoxic oligomers, fibrils, and plaques. This process is highly associated with Alzheimer’s disease and has been of great interest to drug development research. The details of the aggregation pathway remain elusive, with much of the current knowledge arising from computational simulations and chemical kinetics investigations. We have been able to visualise processes including oligomers attaching to the surface of fibres, an essential step in secondary nucleation of Aβ and one of the most critical aggregation steps to consider for developing oligomer-targeting drugs. We have also been able to visualise the growth of a short fibril over a 10s video. This investigation demonstrates the capabilities of LP EM for imaging molecular aggregating systems over time in solution and in-situ. Although still in the early stages, the presented findings promise to provide relevant and novel biological information on Aβ aggregation pathways.
Cryo-CLEM with FIB-SEM for life science

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In the latest few years, correlative microscopy has been the state of art, growing up very fast and making it a very broad technique. The most important thing is the relation between light and electron microscopy, inside the same region of interest, in different temperature conditions (room or cryogenic), in order to preserve the original states of biological samples. Sometimes, sample preparation causes changes or artifacts in the sample, so this is the mean reason to consider working in cryogenic conditions as a good choice.

FIB-SEM instruments are very important because they allow a great number of applications, above all, in life science. In this work, we will focus on the Cryo-FIB-SEM workflow, from cryo-light microscopy to cryo-TEM observation, through different sample preparation, performed inside the FIB-SEM. [1] [2]

This work aims to be a compilation of different applications that can be carried out with Focused Ion Beams systems.

References


Correlative super resolution and electron microscopy methods for nanomedicine

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Correlative light and electron microscopy (CLEM) entails a group of multimodal imaging techniques that are combined to pinpoint to the location of fluorescently labelled molecules in their ultrastructural context. Correlative super resolution and electron microscopy is one CLEM modality in which super resolution microscopy is used instead of conventional fluorescence microscopy techniques. Single-molecule localization microscopy (SMLM) is one of the super resolution microscopy families, offering excellent resolution (5–25 nm), multi-colour imaging and quantification capability with single-particle precision. Thus, the improved resolution of SMLM leads to a nanoscale localization precision of the specific fluorescent labels in the ultrastructural reference space provided by EM.

Super-resCLEM methods have been mainly applied to biological samples; here we introduce it for synthetic materials. The decoration of nanoparticles with functional moieties is a key strategy to achieve cell targeting in nanomedicine. The interplay between size and ligand number is crucial for the formulation performance and needs to be properly characterized to understand nanoparticle structure–activity relations. However, there is a lack of methods able to measure both size and ligand number at the same time and at the single particle level. We address this issue by introducing a super-resCLEM method, specifically by combining one type of SMLM (DNA-PAINT) with TEM.

Moreover, we are now applying super-resCLEM methods to learn about the trafficking of different nanomaterials inside cancer cells.

\textbf{FIGURE 1.} Super-resCLEM of a PLGA-PEG nanoparticle: functional ligands are counted by DNA-PAINT, while TEM provides the morphology and size.

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\textbf{References}

Advanced computational methods for EELS spectroscopy data

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Electron Energy Loss Spectroscopy (EELS) in the Transmission Electron Microscope (TEM) is a powerful tool to access materials atomic composition, oxidation state and optoelectronic properties at the nanoscale, and even with atomic resolution. With recent improvements in TEM instrumentation and EELS spectrometers, it is now possible and even frequent that in EELs experiments large Spectrum Images are obtained, containing a huge amount of data. So the problem arises of how to analyze this data in a fast and reliable way, independently of user biases, and allowing to access all the information contained therein.

In this work, we will address different approaches to EELS data analysis. First of all, the software that has been developed to perform oxidation state calculations. Then, strategies involving multivariate statistical analysis (MSA) for dimensionality reduction of the problem at hand. These strategies are composed by a family of multivariate statistics tools used to analyze large datasets involving many variables, such as Principal Component Analysis (PCA) and Independent Component Analysis (ICA). Finally, recent Big Data approaches based upon Clustering, Neural Networks and Support Vector Machines strategies will be presented.

**FIGURE 1.** Robustness of Support Vector Machines against noise, depending on the kernel used, for Fe oxidation state classification.

References

What do historical bricks from Auschwitz, clothes with caffeine encapsulated and surgical masks against COVID-19 have in common?

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They have in common that they can all be rapidly (and easily) characterized by Scanning Electron Microscopy (SEM). SEM is a user-friendly complete technique to characterize a wide variety of samples for different applications, from cultural heritage objects and textiles, to cosmetics and innovative nanomedicines.

As a first example we will show how SEM was used to characterize the moulds colonizing historical brick from barracks at the Auschwitz II-Birkenau State Museum in Oświęcim. In addition, this biodeterioration could be eradicated by the antifungal activity of Polyoxometalate-Ionic Liquids \cite{1}, which appeared to exert toxic effects on fungal conidia, as evidenced by enviromental SEM imaging. These results are promising for a future use on historical objects and in other mineral-based materials.

Another example is the development caffeine-encapsulated textile fibers, in order to reduce body fat while using these functional clothing. We will show that the metal-organic framework MIL-53(Al) \cite{2} can encapsulate caffeine due to its lightness, flexibility, porosity, chemical affinity and adsorption capacity. Energy-Dispersive X-ray Analisys (EDX) was used to quantify the amount of capsules incorporated into the textile fibers and SEM imaging was used to investigate the presence of caffeine capsules after scouring, and washing processes.

In the last example we will focus on the fight against COVID-19 by studying surgical masks. A new low-cost method to generate antiviral coatings on filter materials using silver nanoparticles and polyethyleneimine relied heavily on the use of SEM micrographs to verify the homogeneity of the silver distribution on the polymer fibers. The antiviral coatings were tested against COVID-19, obtaining inactivation yields greater than 99.9\% \cite{3}.

References

Applications of Dual Beam in cryogenics conditions

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The Dual Beam technique (FIB-SEM) is a smart solution to characterize a wide range of materials and to obtain nanoscale information about their structure and properties. It also allows the design and patterning of nanostructures opening new research lines in fields like nanoelectronics, sensors and quantum technologies.

In this work, we focus on three applications of cryogenic Dual Beam, performed in the Thermo Fisher Nova Nanolab 200 installed at the LMA, upgraded with a cryo-station (by Quorum Technologies) to operate in a wide range of temperatures, from 100 K up to 320 K.

1) We have used a cryo fracture to analyze the structure inside soft and electron sensitive alginate with cells in their natural state. Cryo fracture images allow to analyze the natural state of the cells inside a hidrogel [1]

2) Several materials can change their microstructure during Transmission Electron Microscopy (TEM) sample preparation, so it is necessary the cryo-preparation of electron-transparent lamellas for TEM to minimize damage by ion irradiation. The example of SrFeO$_{3-\delta}$ thin films will be shown [2].

3) Focused electron or ion beam induced deposition (FEBID/FIBID) techniques enable the patterning of metallic nanostructures thanks to the electron/ion beam decomposition of precursor molecules supplied by a gas injection system (GIS) and adsorbed on the substrate surface. The use of cryogenic conditions permits to create a condensate of precursor molecules on the surface, so that the growth rate of the deposits is several orders of magnitude faster than at room temperature. We will show the example of Co nanostructures grown by Cryo-FIBID [3]

Electron microscopy of ferroelectric incommensurate spin crystals

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The rapid improvement in materials growth and processing techniques has produced novel structures with unique functionalities. Electron microscopy plays a key role in understanding the structure of these novel materials and controlling them at an atomic level. Ferroics can form vortices and skyrmions under particular boundary conditions. Here, we focus on the formation of modulated ferroelectric vortices in PbTiO$_3$ sandwiched between two SrRuO$_3$ electrodes on SrTiO$_3$ buffered DyScO$_3$ (110) substrate. The local structure is resolved using a combination of STEM and conventional TEM. Two orthogonal modulations were revealed, in agreement with the model. This incommensurate polar crystal[1] may be an equivalent to the incommensurate spin crystals in ferromagnetic materials.

FIGURE 1. Vortex arrays with a second cycloidal modulation along the vortex core.

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References
Structural and Electronic Couplings in Rare-earth Nickelate Superlattices

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Rare-earth nickelate oxides display an abrupt metal-insulator transition that is strongly influenced by their characteristic Ni-O-Ni bond angle, which regulates the degree of overlapping between the O 2p and Ni 3d electronic orbitals.\cite{1} Although the physical mechanisms ruling this transition are well understood, little is known about the characteristic length-scales over which their distinct electronic phases can be established.

In this work, we directly address this aspect by using aberration-corrected scanning transmission electron microscopy in combination with electron energy-loss spectroscopy (STEM-EELS) to thoroughly characterize the structural, electronic and chemical properties of a series of \([\text{NdNiO}_3]_m/\text{[SmNiO}_3]_n\) superlattices (SLs), being \textit{m} the number of pseudocubic (PC) unit cells in each nickelate layer and \textit{n} the total amount of repetitions of the periodic unit. These SLs are found to display a novel type of electronic coupling that is attributed to the interfacial energetics of the system.\cite{2}

First, we acquire atomically-resolved EELS compositional maps to demonstrate that the nickelate interfaces are atomically sharp, with a minimal degree of cationic intermixing. Second, we determine the length-scale associated to the structural couplings established at the nickelate interfaces by measuring the evolution of the Ni-O-Ni bond angle across them from high-quality annular bright field (ABF) images. A remarkably short coupling length is observed of just 1 PC unit cell, which is much shorter than that associated to their displayed electronic coupling (around 8 PC unit cells).

Finally, we use monochromated EELS to locally determine the electronic state of each individual nickelate layer. The acquired EELS spectrum images not only enable us to determine the electronic state of each individual nickelate layer but also to generate electronic phase maps with ~single unit cell resolution (pixel size around 4Å). The width of the metallic-insulating phase boundaries can be also estimated from these maps, which is observed to be remarkably short (around 2–4 PC unit cells).\cite{3}

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References
A new giants step in Crystallography: Structure Determination based on Electron Diffraction

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Structure determination of nano-crystals using 3D Electron Diffraction (3D ED) has lived in the last decade a revolution based on the introduction of protocols for 3D acquisition and analysis of electron diffraction data [1]. Experiments were performed in adapted transmission electron microscopes using different data collection protocols being the most recent approach to the continuous data collection with a high-sensitive shutterless detector while the goniometer is rotating [2]. In 2021 two new commercial devices appeared in the market. Dedicated Electron Diffractometers from the companies Eldico Scientific (Switzerland) and Rigaku Corporation/JEOL Ltd. (Japan) were made available. Focused on these new dedicated devices, we launched the project proposal “Electron Diffractometer for the Structural Determination of Nano-crystalline Material” (EQC2021-006956-P) which was granted with 1.495.000 € for the acquisition of an Electron Diffractometer. Objective of the project was to create a national service available for the scientific community in Spain. The type of samples expected should include drugs, natural products, pigments, zeolites, minerals, semi-conductors, metal-organic framework (MOF), covalent organic framework (COF), proteins and any nano-crystalline material.

During 2022 the available equipment was tested with selected samples which included a pharmaceutical co-crystal sensitive to radiation, chiral molecules with the aim to determine the absolute configuration, a vacuum sensitive pharmaceutical hydrate, an organometallic gold compound, a MOF and Cystine, the crystalline cell of which stands out for having a long axis (60 Å). With the tests, the following questions should be cleared:

• Is vacuum hindering the measurement of a part of the samples?
• How can radiation damage be avoided?
• Is cooling of samples really necessary?
• Are dynamical diffraction effects a problem or an advantage?
• Is it necessary to have available different detector lengths?

Finally the public tender realized in summer 2022 was awarded to Rigaku Corporation/JEOL Ltd. which will deliver in spring 2023 an Electron Diffraction Integrated Platform XtaLAB Synergy-ED with temperature and cryo-preparation attachments.

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Electron Crystallography: The TEM as an Electron Diffractometer for the Structural Analysis of Sub-Microcrystals

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Electron crystallography has gained a lot of attention during the last years due to the introduction of different technological advances that make the acquisition and processing of three-dimensional electron diffraction (3D ED) in a transmission electron microscope (TEM) much feasible [1]. This includes hybrid pixel detectors of high dynamic range and negligible read-out times, goniometric stages with improved stability and, recently, the commercial availability of dedicated electron diffractometers. Nevertheless, the initial ideas of 3D ED are already 25 years old and TEMs that are not specifically designed for ED applications can be perfectly used as electron nano-diffractometers [2-3].

In this context, this work shows how an acquisition routine can be set in any TEM for the automated collection of 3D ED data in a systematic and reliable way for crystal structure analysis, so-called Fast-ADT [4]. The methodology is used to demonstrate how a new incommensurate modulated structure of Ca\textsubscript{2}SiO\textsubscript{4} and a novel polymorph of a red organic dye (Disperse Red 1) can be fully determined and refined from ED datasets obtained from the routine use of such setup. On another fashion, the TEM is also portrayed here as a x-ray free electron laser for serial protein crystallography. TEM grids can be scanned for suitable protein crystals in a low-dose automated setting, and single-oriented ED patterns can be collected by exposing them to the electron beam until their crystallinity is lost, resulting in good signal-to-noise individual patterns. The acquisition and indexing of diffraction data from lysozyme crystals sealed by graphene layers in their mother liquor is given as an example on the use of a TEM for serial ED experiments [5].

**FIGURE 1.** Representative electron diffraction patterns from A) an incommensurate modulated structure of Ca\textsubscript{2}SiO\textsubscript{4} and B) a lysozyme crystal in its mother liquor.

**References**

AXON: An In-situ TEM Software Platform Streamlines Image Acquisition, Metadata Synchronization and Data Analysis, Enabling Deeper Understanding, and Improved Reproducibility of In-situ Experimental Results

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A recurring refrain within the in-situ community is the need to develop minimum requirements for reporting experiment conditions and parameters to improve analysis and enable the reproducibility of results by other researchers [1]. The need to standardize reporting and enable other researchers to access metadata created during microscopy experiments was recently highlighted by Sarkans et al. as a general area for improvement within the wider biological imaging community [2,3].

Protochips recently introduced AXON, a software solution designed to address needs in image stabilization and metadata consolidation. In this talk, scientific examples of in situ applications will be presented and the role metadata analysis had on deriving scientific conclusions (Figure 1). In addition, specific applications will be presented on a new tool which utilizes machine vision technology to calibrate beam current, record dose rates and total accumulated dose within the sample area, and include this information directly into the image metadata for subsequent analysis (Figure 2.) With these advances, utilization of the AXON platform for in-situ experiments easily enables the application of FAIR principles to in-situ data management, and facilitates more robust analysis, data mining and review of in-situ experiments by outside researchers, increasing productivity and ultimately elevating the field of in-situ TEM.

Fig. 1 Alignment and analysis of metadata

Fig. 2 Visualization of dose metadata

References
New TEM instrumentation and upgrades: present and future prospects at the Barcelona ELECMI node

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In this talk we will summarize the ongoing upgrades and future prospects in terms of instrumentation at the Barcelona node of the ICTS ELECMI. Starting with a brief historical overview up to the present state of the instrumentation in the node, we will cover the background of expertise and know-how accumulated by both the technical staff and the community of users along the years, and what can be expected in the near future with the arrival of new instrumentation.

Regarding the aforementioned new instrumentation, the main focus of this talk will be on the specifications and applications of the new probe-corrected (S)TEM JEOL NeoARM 200cF. The acquisition of this microscope by the University of Barcelona was possible through the cooperation with different partners (IBEC, IDIBELL, IDIBAPS, FHSJD) in a coordinated FEDER project (MERIT). Its extremely flexible configuration, dose control capabilities and sensitive cameras allow for state of the art applications in a wide range of systems from Materials Science to Life Sciences. We will highlight the very strong capabilities for in situ experimentation of the instrument, including liquid cell holders, heating and biasing holders and cryogenic holders, as well as the possibilities offered by the installation of a direct detection Gatan K3 camera after the EELS energy filter both for imaging and spectroscopy applications, among other many features.

Equipped in the new TEM, but also in the existing conventional JEOL J2100 and JEOL J2010F microscopes in the node, we will cover the recent upgrade of the electron beam precession systems by Nanomegas that was prioritized in the ICTS technological plan. Applications of precession-assisted 4D STEM and reciprocal space tomography techniques already present at the node will see its possibilities and performance improved.

Finally, we will briefly cover the future applications of the dual beam FIB/SEM instrument that will also arrive at the node, with applications in Life Sciences and Materials Science. In this talk, we will focus mainly in its application to sample preparation both conventional and for MEMS chips, given the strong in situ focus of the new JEOL NeoARM.

Acknowledgements

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Atomic-level handedness determination of chiral crystals using aberration-corrected scanning transmission electron microscopy

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The local determination of the handedness of a nanocrystal at the atomic-level in real-space imaging has been very challenging, due to the well-known fact that chiral information is lost in a two-dimensional projection. Herein, we present a method for handedness determination by atomic-resolution imaging using aberration-corrected STEM. Enantiomorphic structures can be distinguished through chiral dependent features in two-dimensional projections by comparing a tilt-series of high-resolution images along different zone axes. The method has been successfully applied to verify the specific enantiomorphic forms of tellurium and tantalum silicide crystals, and it has the potential to open up new possibilities for rational synthesis and characterization of chiral crystals.

![Figure 1](image)

**FIGURE 1.** Handedness determination of a Te crystal. (a) Tilt-series of Te structural models with $P\bar{3}21$ and $P3\bar{2}21$ space groups. (b) STEM-ADF images along $[010]$ and $[120]$ zone axes, indicating a left-handedness.

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**References**

New JEOL developments on cutting edge time resolved microscopy field.

Guillaume Brunetti

JEOL (Europe) SAS

“Since 1949, JEOL’s legacy has been one of the most remarkable innovations in the development of instruments used to advance scientific research and technology. JEOL has 60 years of expertise in the field of electron microscopy, more than 50 years in mass spectrometry and NMR spectrometry, and more than 40 years of e-beam lithography leadership.

Recently JEOL has acquired the American company IDES. IDES's unique technology will upgrade the JEOL TEM systems to "ultrafast time resolved TEMs" capable of capturing still and dynamic images in nano seconds to femtoseconds and recording them with nanometer-scale spatial resolution. These innovative systems can be used to explore dynamic and quantum phenomena beyond the reach of conventional TEM. In the future, the system can also be upgraded to support applications in life sciences such as studies of protein movement.

These new integrations will also offer unique technologies related to high speed electrostatic deflection and compressive sensing. These technologies can be integrated into TEM as accessories to provide minimum damage, high throughput TEM image acquisition in an order of micro second time resolution.
Advanced Electron microscopy; a perfect tool to elucidate the key role of atomically thin CeO₂ surface layers on nanoparticles with applications in Energy and the encapsulation of bioactive natural products used as Green Agrochemicals

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Advanced electron microscopy provides a battery of techniques that can be applied to understand the properties of various nanomaterials. In this context, imaging (HAADF, iDPC) and spectroscopy techniques (EELS and ESD) have been combined to elucidate the key role of atomically thin CeO₂ surface layers on catalytic nanoparticles and to optimise the encapsulation process of bioactive natural products.

High-temperature redox cycles are shown to induce reversible reducibility modifications in CeO₂/TiO₂ catalysts [1]. Advanced electron microscopy has evidenced that the response to high temperature redox aging treatments of the catalyst supported on titania is highly complex. Not only different Ce-Ti phases with an ordered structure of Ce³⁺ and Ti⁴⁺ are presented (Ce₅TiO₉ and Ce₂Ti₂O₇), also atomically thin layers, which are distributed both over the surface and at the grain boundaries between rutile TiO₂ crystallites are observed. In the case of Ce-containing monolayers; two different structures are found; coherent growth onto the surface of rutile crystallites and atomically thick Ce-containing patches depicting a compressed fluorite type structure. The whole set of structural data and the comparison with previous studies [2], clearly point out that the improvement in reducibility observed is linked to the formation of highly dispersed ceria nanostructures, particularly in the form of extended monolayers.

The encapsulation of bioactive natural products has emerged as a relevant tool for modifying the poor physicochemical properties often exhibited by agrochemicals. The characterization of this new structures is particularly challenging, since damage effects of the extremely beam sensitive systems adds up to the requirement of discriminating the two (host-guest) organic components. In this context, we present the characterization of two different natural products morphologies; lactones encapsulated in organic nanotubes[3] and ortho-disulfides encapsulated in functionalized Zinc-MOFs [4]. Both systems have demonstrated to have a better performance than the nonencapsulated compounds, reinforcing their use as natural-product-based herbicides with direct applications in agriculture.

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References
Electron Beam Damage Mitigation Strategies

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Since the invention of the electron microscope scientists have been arguing about how the electrons affect or even damage the sample. Life scientists have always looked at ways to increase contrast, and reduce beam damage, for improving productivity (throughput) and performance (resolution) when studying biological structures. Now materials science is commanding similar tactics, especially for beam-sensitive specimens. Many material classes such as polymers, 2D materials, zeolites, MOFs (metal organic frameworks) require a frugal use of the electrons that have transited through the sample in order to minimize the damage they can cause. Here we will discuss recent developments as well as ongoing research and development projects at Thermo Fisher Scientific in the field of low-dose imaging and analysis.

Electron beam damage mitigation strategies consist of both hardware and software solutions requiring fewer primary electrons without sacrificing the signal-to-noise of generated data. In general, detectors must be made more sensitive and software-based imaging and analysis techniques must yield a higher contrast for a given dose.

On the hardware side, we discuss Panther STEM, our newly developed segmented detector with single electron sensitivity, Ultra-X the new super-sized EDX detector enabling EDX analysis of materials otherwise too beam sensitive and the Falcon 4i, the new direct electron detector with unprecedented DQE. On the software front, we focus on EDC (Electron Dose Control) package, as well as iDPC (integrated Differential Phase Contrast) for extreme low-dose STEM imaging.

In the last decade, bright-field (BF) STEM imaging techniques (ABF, e-ABF and OBF) have enjoyed a renaissance, because contrary to dark-field (DF) techniques, they allow for many more transmitted electrons to participate in the imaging process. Unfortunately, none of the BF techniques are linear and retrieving the object from the image is all but trivial. iDPC-STEM, on the other hand, is another imaging technique which uses close to all the transmitted electrons, but without the inconveniences of non-linear BF imaging. iDPC-STEM was first utilized as the actual integration of the DPC vector field to resolve the iDPC scalar field by Ivan Lazić, et al. [1, 2]. For a thin sample, the DPC vector field represents the projected electric field, which when integrated yields the projected electrostatic potential field (φ) of the sample [1, 2]. iDPC-STEM is a one-to-one representation of the atomic model one is trying to resolve. (HA)ADF-STEM (φ²) also offers a direct representation of the atomic model, albeit for heavy elements only, whereas iDPC visualizes the entire periodic table, down to hydrogen [3]. In short, iDPC yields a HAADF-like contrast, but with the added benefit that light elements are also imaged. iDPC-STEM has successfully been utilized to image MOFs [4] and zeolites [5,6] with unprecedented resolution under very low-dose conditions. Figure 1 is an example of a MOF (UiO-66) imaged with a total dose of 22 e⁻/Å².
Finally, we discuss our soon-to-be-launch Electron Dose Control (EDC) package, which not only controls and manages the dose automatically, but also documents it and provides the user with accurate count of electron dose. Moreover, by taking advantage of single electron sensitivity and linearity of Panther STEM system, it is able to measure the exact number of electrons per pixel in each STEM image, and hence open up possibilities toward accurate quantitative analysis.

References

Figure 1. A 200kV iDPC-STEM example of a MOF (UiO-66) imaged with 22 e/Å². The probe current was 0.5pA, the frame time 10s and the convergence angle 10mrad.
Magnetic deposits by FEBID

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Focused Electron Beam Induced Deposition (FEBID) is a powerful technique for growing functional nanostructures with high resolution. Specifically, 3D ferromagnetic nanowires can be grown on virtually any surface, including cantilevers [1]. In order to obtain the desired ferromagnetic properties, the nanofabrication parameters such as e-beam voltage, e-beam current, precursor gas type and precursor gas flux have to be very well controlled [2]. In the case of growing cobalt deposits, there is high influence of the beam current and the gas pressure in the metal purity. However, iron growth is not highly dependent on flux and current to achieve high purity.

The chemical characterization of cobalt and iron nanowires by transmission electron microscopy has revealed that the internal composition of the nanowire is mainly cobalt or iron. Nevertheless, an external surface oxidation layer of 3-5 nm appears after the exposition to ambient atmosphere [3], as show in Figures 1a and 1b.

Ferromagnetic nanostructures such as 3D nanowires have potential applications in magnetic sensing, e.g. in Magnetic Force Microscopy (MFM) [4,5]. In particular, nanowires with sharp tips (Figure 1c) are required for MFM because they get rid of non-magnetic interactions and have high lateral resolution (15-20 nm). Moreover they provide low invasiveness (sample-tip magnetic interaction). This is the reason why they are suitable for measurements of soft magnetic materials such as skyrmions. The FEBID tips are also better than conventional tips for measurements of magnetic materials in liquid environment, such as measurements of magnetic biomaterials.

![Chemical characterization by transmission electron microscopy of Co (a) and Fe (b) nanowires grown by FEBID. (c) 3D Fe nanowire with sharp tip.](image)

**FIGURE 1.** Chemical characterization by transmission electron microscopy of Co (a) and Fe (b) nanowires grown by FEBID. (c) 3D Fe nanowire with sharp tip.

**References**

Four-dimensional scanning transmission electron microscopy techniques for materials characterization

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Recent advances in ultra-fast segmented and pixelated detectors for the scanning transmission electron microscope (STEM) allow us now to acquire of a full image of the transmitted electron probe as it is scanned over the sample, producing a four-dimensional (4D) STEM dataset. The term 4D-STEM in fact refers to recording 2D images of a converged electron probe, or convergent beam electron diffraction pattern (CBED), while the electron beam is raster scanned over a 2D grid of probe positions in real space, as schematized in Fig. 1. This new dimension in electron microscopy offers a plethora of information on the materials structure, composition or electrostatic potential and brings the possibility to develop new computational imaging methods\cite{1}. Furthermore, 4D-STEM data is also sensitive to the spatial distribution of transmitted electrons on the detector plane and hence, to electric and magnetic fields in materials\cite{2}.

This talk will introduce the 4D-STEM technique and discuss how it enables new insights into the physical properties of materials.

\textbf{FIGURE 1.} Schematic of a 4D STEM experiment showing an incident electron beam (yellow) scanned over a SrTiO\textsubscript{3} sample with the corresponding CBED patterns at each probe position.

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TEM insight into defects in ionic conductor thin layers and their effect in fast transport.

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Tuning oxygen mass transport properties at the nanoscale offers a promising approach for developing high performing energy materials. Several strategies for engineering interfaces with enhanced oxygen diffusivity and surface exchange have been proposed. However, the origin and the magnitude of such local effects remain largely undisclosed to date due to the lack of direct measurement tools with sufficient resolution. One potential candidate to retrieve the hidden information is the Transmission Electron Microscope (TEM), a powerful instrument that allows the local observation of structures with sub Å resolution. Atomic resolution in both structural and analytical images is commonplace, and the ever-increasing size of the latter has been the driving force behind the application of big data algorithms to segment and extract the relevant information from spectra [1,2].

Here we focus on a series of materials with mixed electronic and ionic conduction properties (La_xSr_{1-x}MO_3 with X = Mn, Cr and (Co,Fe)) where crystalline defects have been determined as the most efficient conduction pathways. Here we show that the adequate characterization of these defects in terms of local order, strain and stoichiometry is an unavoidable step in the understanding of their functional properties. Supported by Atom Probe Tomography results [3], in this work we present the capabilities of several TEM related techniques to unveil the local phenomena at the atomic scale that ultimately govern the macroscopic properties of electrochemical devices, thus illuminating the path for charge transport engineering in epitaxially grown thin layers.

References