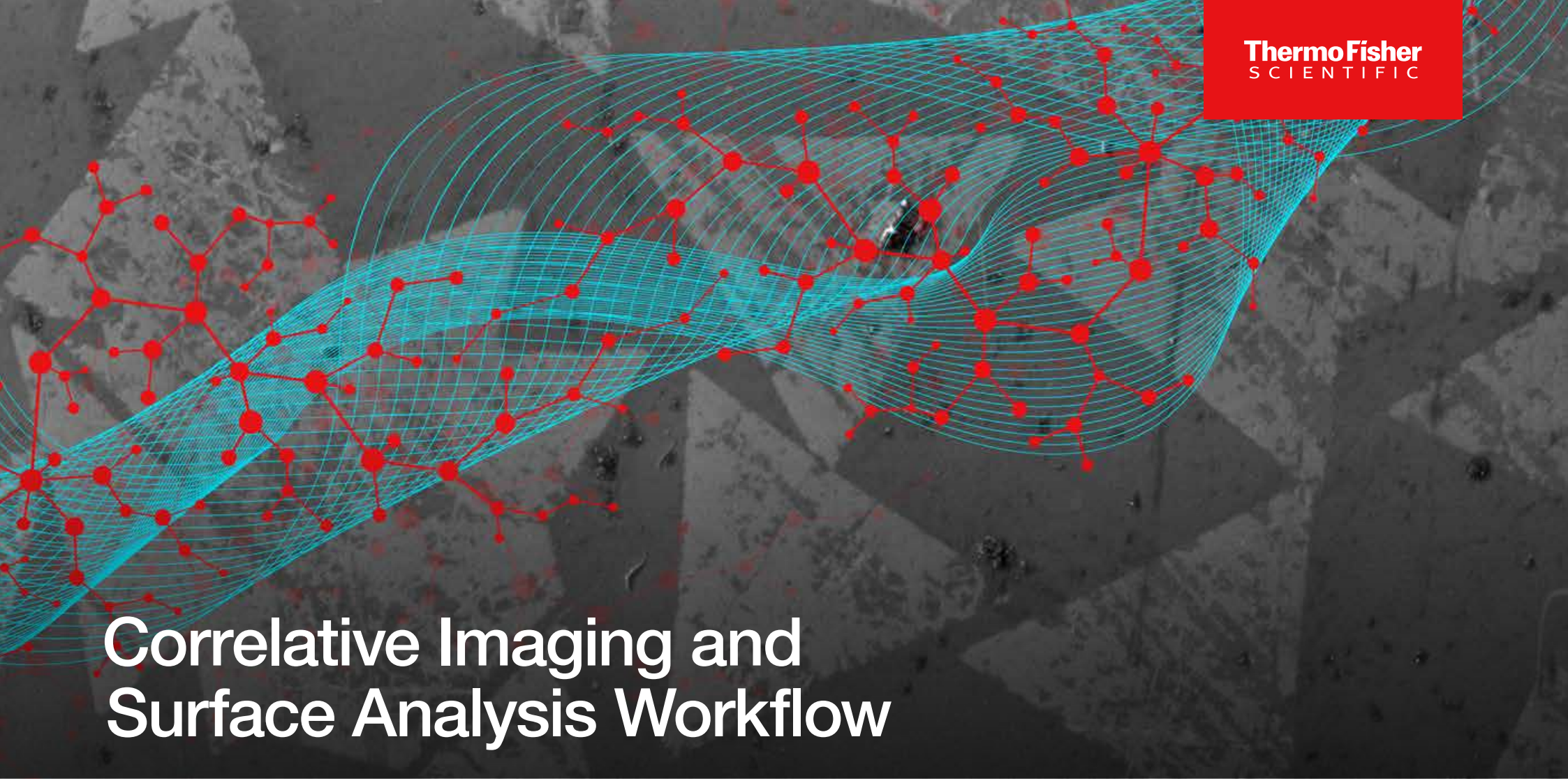

ThermoFisher SCIENTIFIC

Correlative Imaging and Surface Analysis Workflow

Harness the combined powers of SEM and XPS

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A full understanding of your sample often requires analysis on different instruments. Imaging a sample in a scanning electron microscope (SEM) and acquiring the composition with energy dispersive X-ray spectroscopy (EDS) might not reveal the surface chemistry that is crucial to understanding a material's performance. Conversely, knowledge of the surface chemistry of a sample may need more high-resolution imagery to fully capture how the interplay between chemistry and structure is affecting the behavior of a material. By using the Thermo Scientific™ Correlative Imaging and Surface Analysis (CISA) Workflow, you can combine datasets from our X-ray photoelectron spectroscopy (XPS) and SEM instruments to more fully understand your samples.

In this eBook, we will describe the information obtained from each instrument and share example case studies to demonstrate how the CISA Workflow is used.

Introduction

Understanding the surface of a material is important for a wide variety of applications such as Li-ion battery electrodes, metal components, and advanced nanomaterials.

Knowing both the chemical composition and the structure is crucial to gaining this understanding. However, several different experimental methods might need to be used. To that end, ensuring that data is obtained from the same regions of interest is vital to allow correlation of the results.

The CISA Workflow is designed to make this understanding simple to achieve by bringing together data from SEMs and surface analysis systems.

Samples are mounted onto a special sample holder, maintaining their position in each system. Typically, XPS is done first, followed by SEM, but the order can be reversed if SEM is required to find regions of interest first. Thermo Scientific Maps™ Software is then employed to correlate images and spectroscopy, using automated tools to match the output from the instruments.

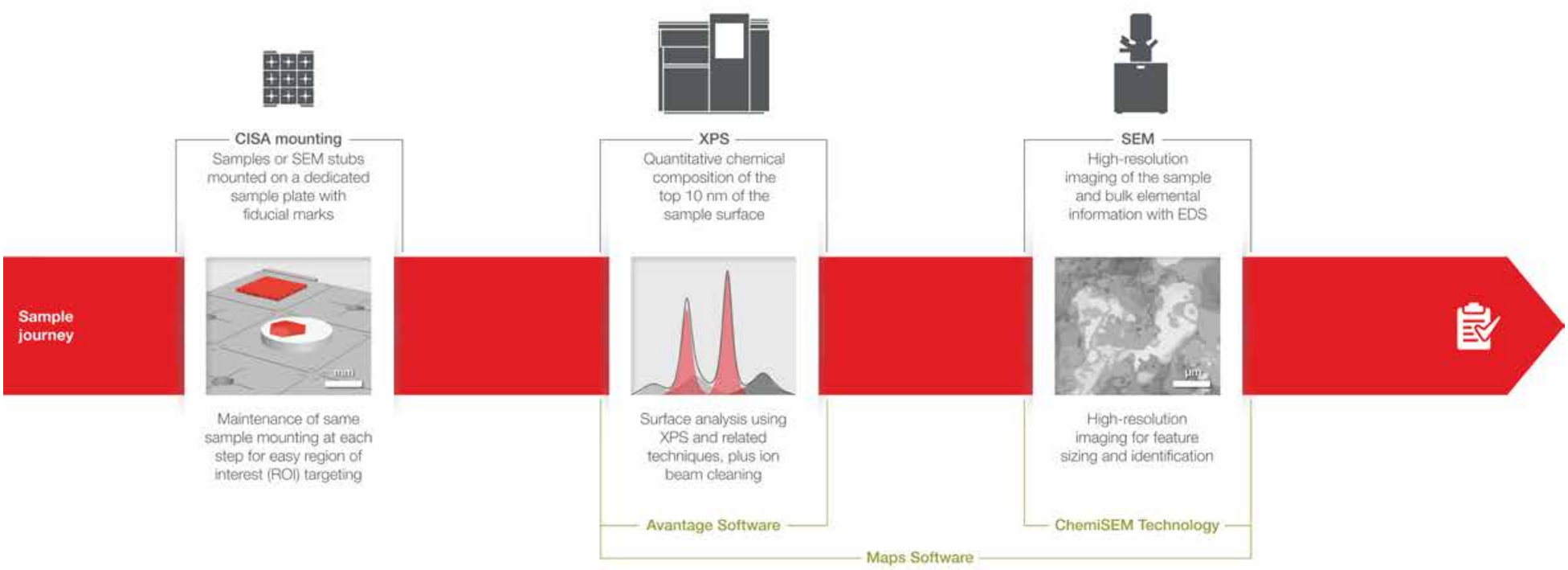


Figure 1. CISA Workflow using Thermo Scientific XPS and SEM instruments with Thermo Scientific software.

Get to know XPS

A surface layer (see Figure 2) is defined as being up to three atomic layers thick (~1 nm), depending upon the material.

Layers up to approximately 10 nm are considered ultra-thin films, and layers up to approximately 1 µm are thin films. The remainder of the solid is referred to as bulk material. This terminology is not definitive, however, and the distinction between the layer types can vary depending upon the material and its application. The surface represents a discontinuity between one phase and another; therefore, the physical and chemical properties of the surface are different from those of the bulk material. These differences affect the topmost atomic layer of the material to a large extent. In the bulk of the material, an atom is surrounded on all sides in a regular manner by atoms composing that material. Because a surface atom is not surrounded by atoms on all sides, it has bonding potential, which makes the surface atom potentially more reactive than atoms in the bulk.

XPS can measure the elemental composition, empirical formula, chemical state, and electronic state of the elements within a material. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays and measuring the kinetic energy of the electrons that are emitted from the top 0–10 nm of the material being analyzed.

A photoelectron spectrum (see Figure 3 for an example) is recorded by counting ejected electrons over a range of electron kinetic energies. Peaks appear in the spectrum due to atoms emitting electrons of a characteristic energy. The energies and intensities of the photoelectron peaks enable identification and quantification of all surface elements except hydrogen and helium.

Because photoelectrons can travel only a short distance in matter (0–10 nm) before losing energy, XPS is very surface-sensitive. The real strength of XPS, however, is its ability to investigate the chemical bonding states of surface elements. If you measure the kinetic energy of the photoelectron peaks in finer detail, you see that, even for the same element, the peak energy may shift depending on the surface chemistry. This is known as the chemical shift. The ability to detect and quantify this shift is what makes XPS such a powerful analytical technique.

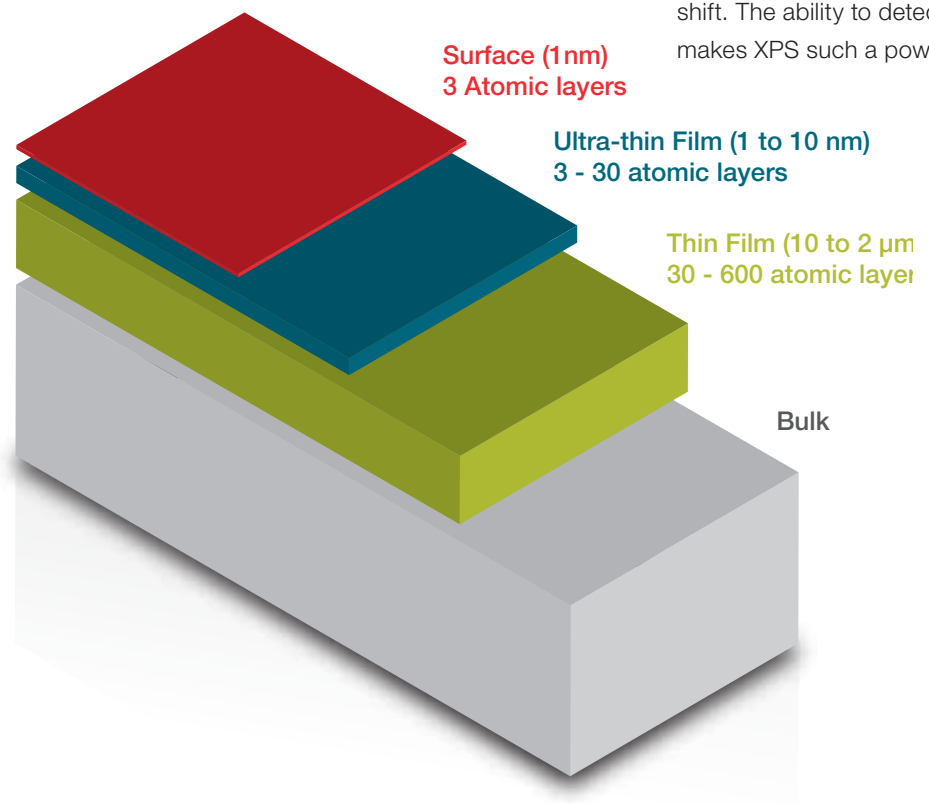


Figure 2. The modified layer is often far too thin to be characterized with most techniques. The extreme surface sensitivity of XPS ensures that only the top few nanometers of the sample are analyzed.

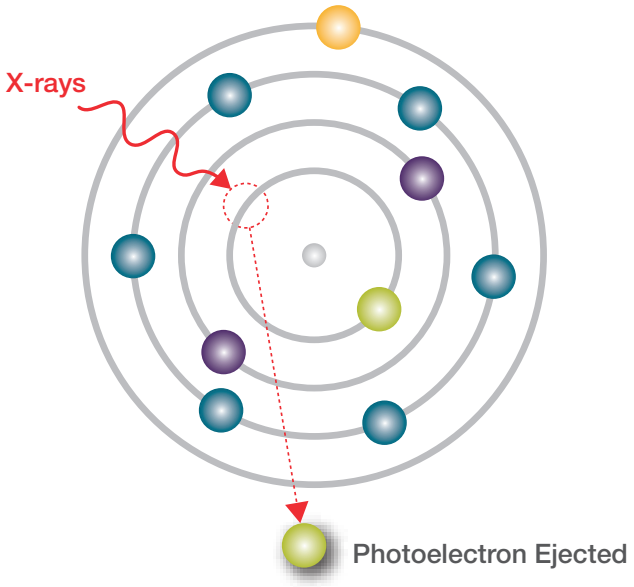
Basic XPS theory

The surface is comprised of atoms of the various elements present. As shown in the simple diagram here, the nucleus is surrounded by electrons at different orbitals. The energy each electron has within the orbital is referred to as the binding energy, which varies depending on the orbital's proximity to the nucleus. When the surface is irradiated with X-rays, energy is supplied, and, if the energy supplied is greater than the electron binding energy, the electron can leave the atom—an ionization event. These electrons are referred to as photoelectrons, as they are the result of an interaction involving X-ray photons.

The analyzer of the spectrometer counts the number of photoelectrons with a particular kinetic energy as it scans the energy range. The binding energy can then be calculated. A peak therefore corresponds to electrons from a specific orbital in an element's atom, providing three important bits of information:

1. Peak—provides information as to which element the photoelectron came from.
2. Orbital—in conjunction with the element, mostly defines the binding energy.
3. Shifts—small changes in binding energy are also caused by the chemical environment; these can also be seen as small shifts in the peak position. The act of forming a chemical bond changes the outer, or valence, electrons, adding or losing an electron in the case of an ionic compound, for example. This will change the amount of attractive force the core electrons experience, and so causes a change in the binding energy.

Learn more about XPS and surface analysis



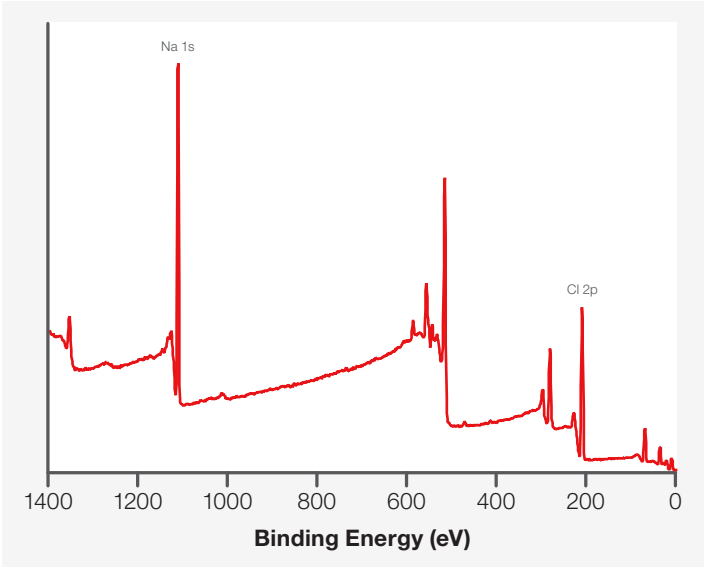


Figure 3. Schematic of the XPS process and a representative survey spectrum. The major XPS peaks used for quantification of sodium and chlorine from a sample of sodium chloride are indicated.

Get to know SEM and EDS

Scanning electron microscopy (SEM) has developed into a critical tool within numerous research fields, spanning everything from materials science to forensics and industrial manufacturing, and even to life sciences.

As soon as microscopic information about the surface or near-surface region of a specimen is needed, SEM becomes a necessary tool. For that reason, the method finds applications in nearly every branch of science, technology, and industry. Floor-model and desktop SEMs offer the flexibility and versatility to meet a wide range of academic and industrial needs:

- Support for large and heavy samples
- Excellent imaging quality for the most challenging materials or the smallest details
- Dynamic experimentation

Energy dispersive X-ray spectroscopy (EDS) is the analysis of X-rays that are emitted by the atoms of the sample under excitement of the incoming electron beam. EDS is a commonly used technique in electron microscopy because it is a fast, accurate, and non-destructive technique that provides local information of a microvolume. This makes EDS highly attractive for many research fields such as metallurgy, surface analysis, and mineralogy.

Learn more about how SEM and EDS work

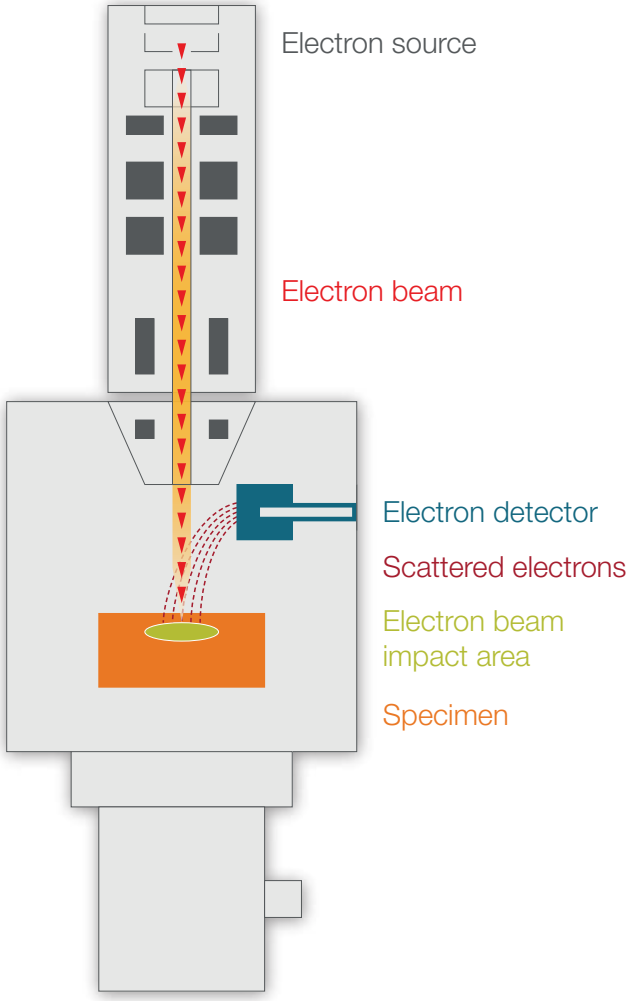


Figure 4. Schematic of a scanning electron microscope. The sample is raster scanned beneath the electron beam, generating an image of the sample's topography.

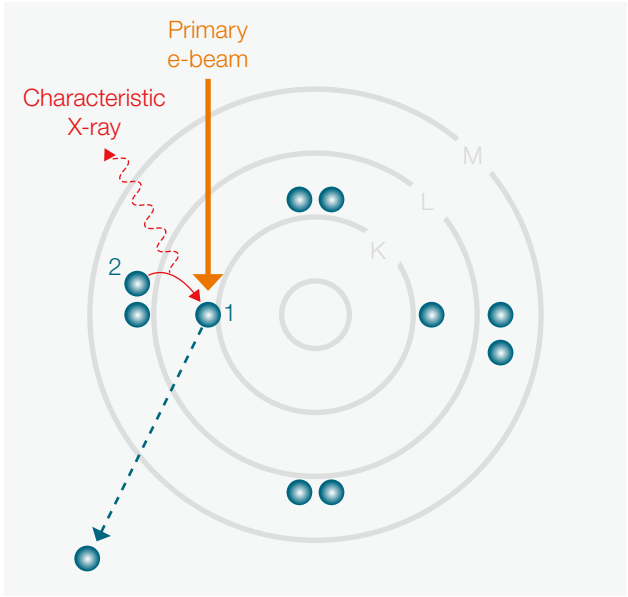


Figure 5. Schematic of the X-ray emission process that makes EDS analysis possible. The emitted X-ray carries crucial information about the identity of the atom.

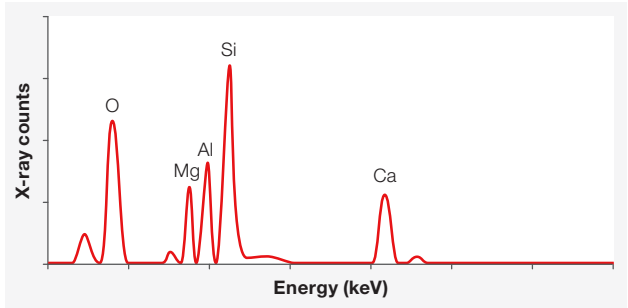


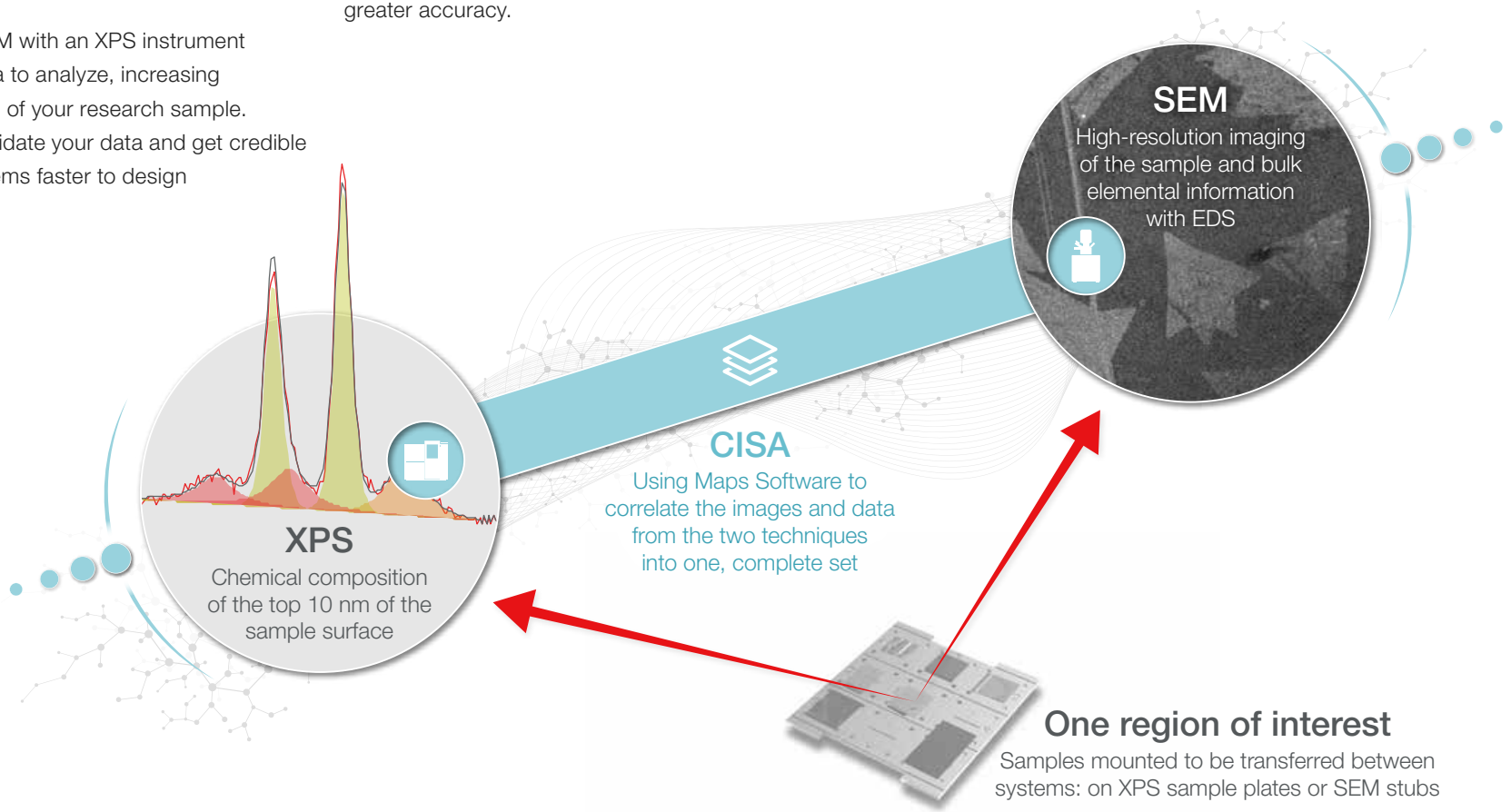
Figure 6. As the name implies, EDS is a spectral technique. The SEM generates X-rays across an energy spectrum up to the beam energy used (e.g., 15 kV). An EDS detector collects these X-rays all at once. The shape and height of the peaks in the spectrum are indicative, in part, of the relative concentration of the elements.

Combining XPS with SEM

By combining XPS with SEM analysis, you can now accurately add chemical information with high resolution to the structural information from the microscope.

The combination of an SEM with an XPS instrument results in more robust data to analyze, increasing your overall understanding of your research sample. Consequently, you can validate your data and get credible information to solve problems faster to design better materials.

Using the CISA Workflow, you can an export images with stage coordinates from XPS to SEM and SEM to XPS to easily target exact point-of-interest sample transferal between systems. Another benefit of this combination is that you can also easily confirm alignment of datasets, ensuring that the data from each system was collected at the same position for greater accuracy.



Maps Software

Scientists and researchers rely increasingly on nanoscale observations to inform the latest advances in research and analysis.

It has, however, become apparent that high-resolution observations lose much of their utility in the absence of the larger macroscopic context. Observations from multiple sources must be linked, providing the necessary multi-scale and multi-modal insight for truly valuable data.

Thermo Scientific Maps™ Software provides a powerful imaging workflow automation package within an easy-to-use and robust platform. With just a few clicks, you can collect impactful data while preserving the context of your observations.

The CISA Workflow utilizes Maps Software to enable you to easily target the exact point-of-interest when transferring the sample, guaranteeing better data correlation between XPS and SEM tools for more comprehensive surface analysis.

Use cases

The CISA Workflow offers reliable "best-in-field" performance and accuracy between two surface analysis techniques across several applications, such as batteries, polymers, catalysts, and metals.

Use case 1: Batteries

The electrodes of a Li-ion cell are typically comprised of compressed powder, held together by a binder material. Using both SEM and XPS to see how the material changes with cycling is common; however, ensuring that similar areas are being analyzed can be challenging. In this example, the electrode had been exposed to air and was transferred on the same sample mount between the Thermo Scientific Nexsa™ G2 XPS System and the SEM.

The sample was analyzed first with XPS to determine fluorine chemical states. Both inorganic fluoride and organic fluorine chemistries were detected. The exact locations of the compounds could not been seen by XPS mapping. Once transferred into the SEM, the grain structure of the powder could be seen, and regions where accumulations of the binder were present could be identified.

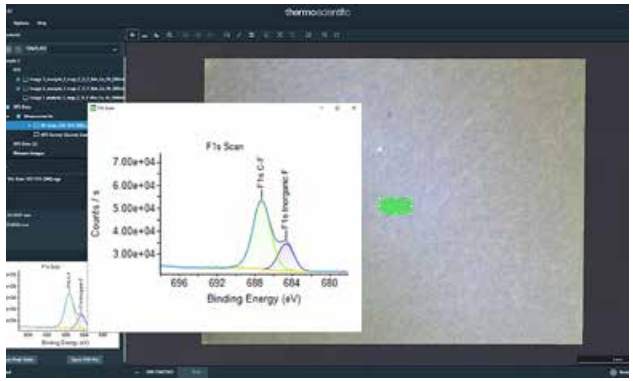


Figure 4. XPS analysis points with associated data.

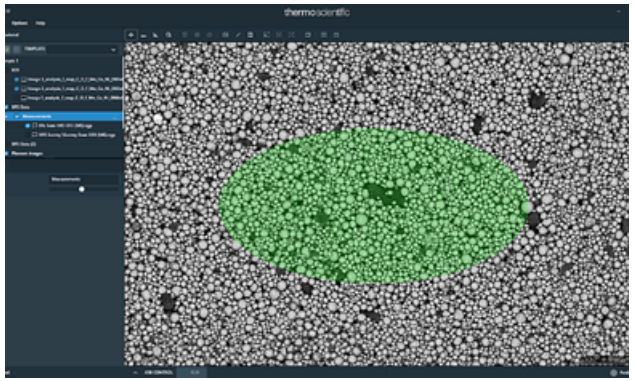


Figure 5. SEM image added as layer.

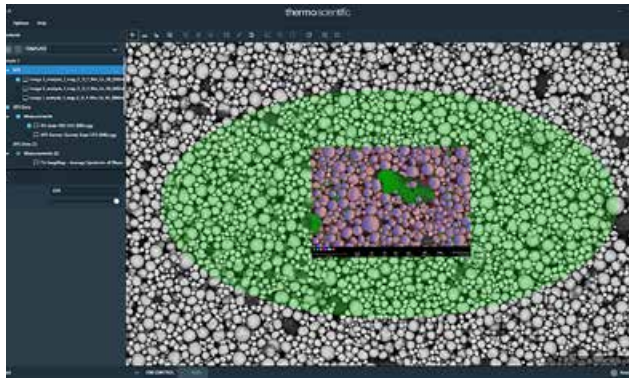


Figure 6. EDS analysis in the SEM.

Use case 2: 2D materials

Materials like single-layer MoS_2 or graphene are being investigated for their potential uses in a wide variety of applications in electronics, medicine, and composite materials. In this example, a sample of single-layer MoS_2 deposited on a silicon oxide surface was analyzed. The special properties exhibited compared to the bulk material equivalents can be tailored to a specific application by careful modification of chemistry or structure.

Understanding these properties can be done using the CISA Workflow. The surface can be visualized using SEM, but the layers are too thin to be seen easily with EDS analysis. XPS cannot resolve the structures of the layer, but can easily detect that the material is present and quantify any chemical changes that have occurred. On the Nexsa G2 XPS System, it is also possible to have a Raman spectrometer that is co-incident with the XPS analysis position. Raman spectroscopy is a powerful tool for the analysis of 2D materials and can be used to great effect to understand the presence of defects and the number of layers present, in addition to obtaining molecular information.

View application note

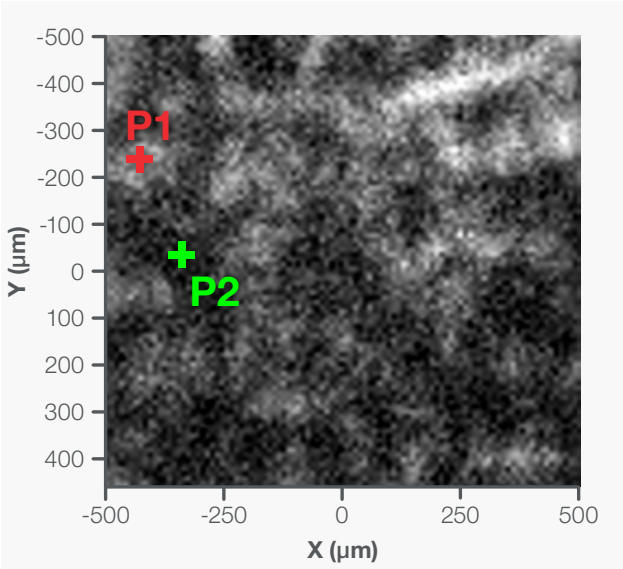


Figure 7. Elemental quantification with small spot XPS.

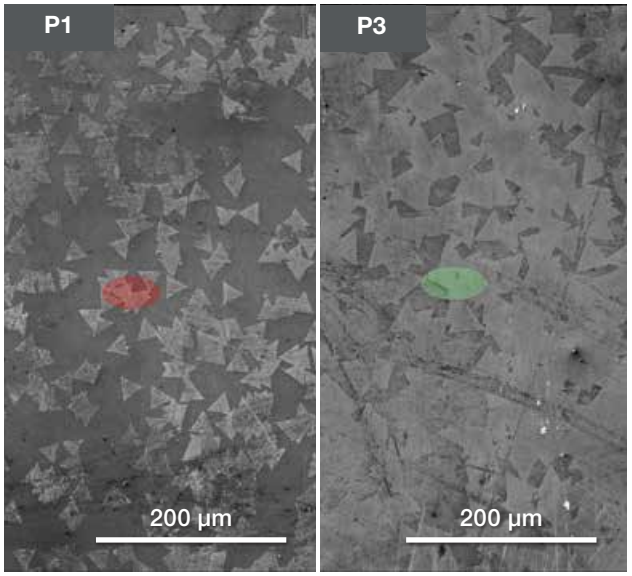
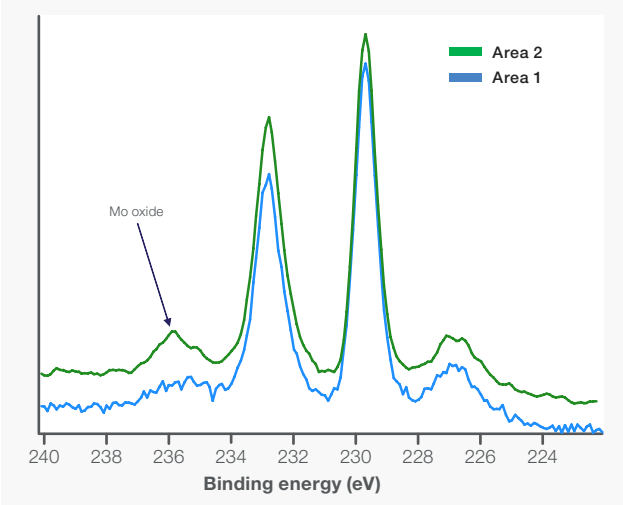


Figure 9. SEM shows lower density of triangular structures in area with single-layer MoS_2.



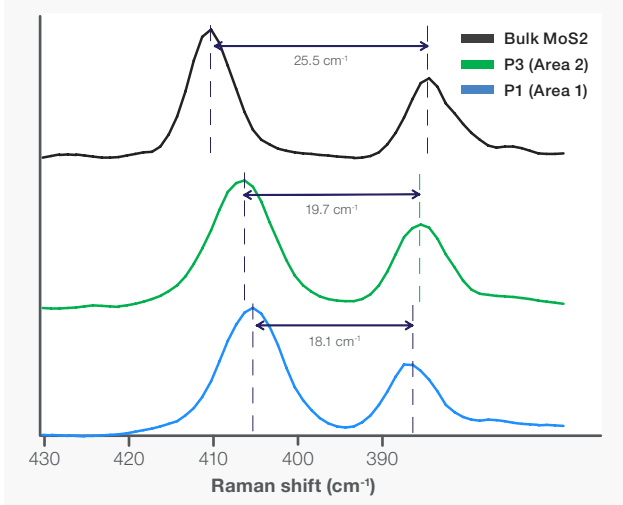


Figure 8. XPS-Raman analysis of MoS_2 (left: Mo3d XPS; right: Raman spectroscopy).

Use case 3: Antimicrobial fabrics

Textiles' ubiquity has led to ongoing interest in the improvement of their properties, such as decreased flammability, water repellency, stain resistance, strengthening, and antimicrobial protection. Textiles are particularly important for medical applications, being used in a wide variety of products ranging from bandages to personal protective equipment (PPE) such as masks. Increased antimicrobial properties are achieved through a variety of means, including the application of coatings as well as treatment with various additives such as nanoparticles.

This case study, which was a collaboration with the University of Belgrade, the CISA Workflow was used to analyze polypropylene fabrics modified with copper nanoparticles. Researchers determined that a novel "green" approach to antimicrobial nanoparticle treatment was efficient and effective at eliminating bacteria from the material, clearly showing how the addition of holistic XPS-SEM characterization can accelerate novel materials research.

View application note

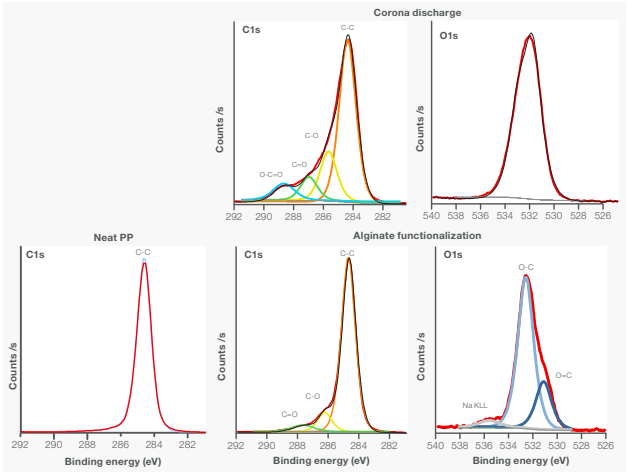
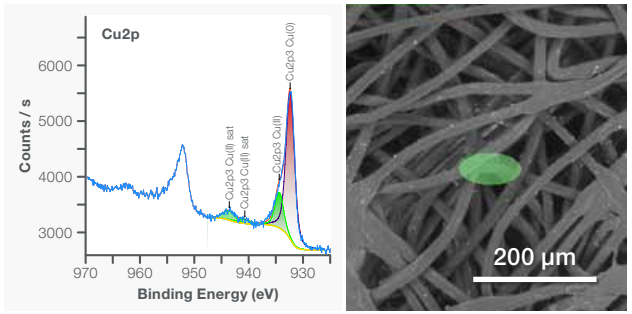


Figure 11. High-resolution XPS spectra of carbon and oxygen signal in Samples A-C (untreated PP, corona-treated PP, and alginate-functionalized PP).



Name	Peak BE	Atomic %
C 1s	285.38	87.9
O 1s	532.74	9.7
Cu 2p	933.26	2.4

Figure 13. Top) SEM image showing the distribution of copper nanoparticles across the PP fabric following reduction with $NaBH_4$. Bottom) XPS atomic distribution data for the highlighted region.

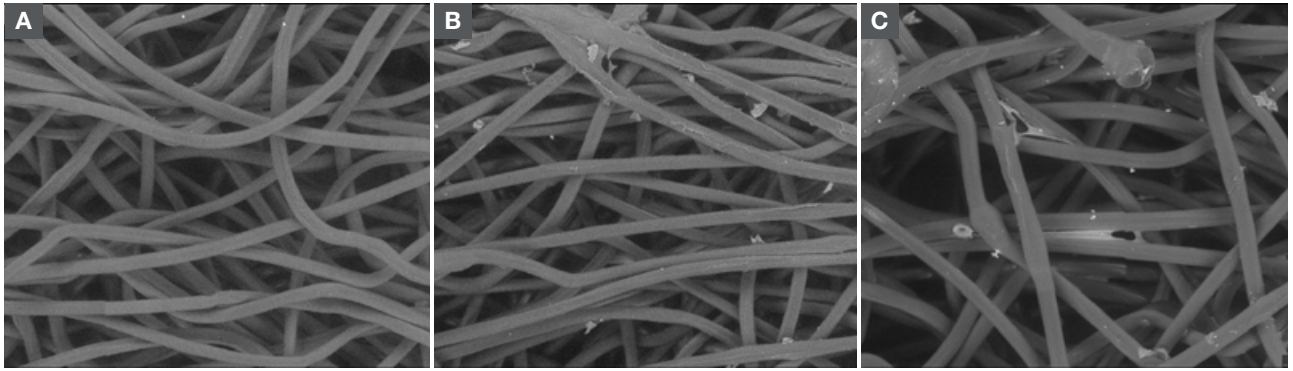


Figure 12. Polypropylene Samples A–C imaged with scanning electron microscopy.

Microorganism	Inoculum	Control PP	CPP + ALG + Cu ($NaBH_4$)	CPP + ALG + Cu (Ascorbic acid)
E. coli (ATCC 25922)	4.1 × 106	1.1 × 106	<10	<10
S. aureus (ATCC 25923)	8.0 × 105	5.0 × 105	<10	<10
C. albicans (ATCC 24433)	6.0 × 105	1.0 × 105	<10	<10

Table 1. Number of microbial colonies (CFU/mL).

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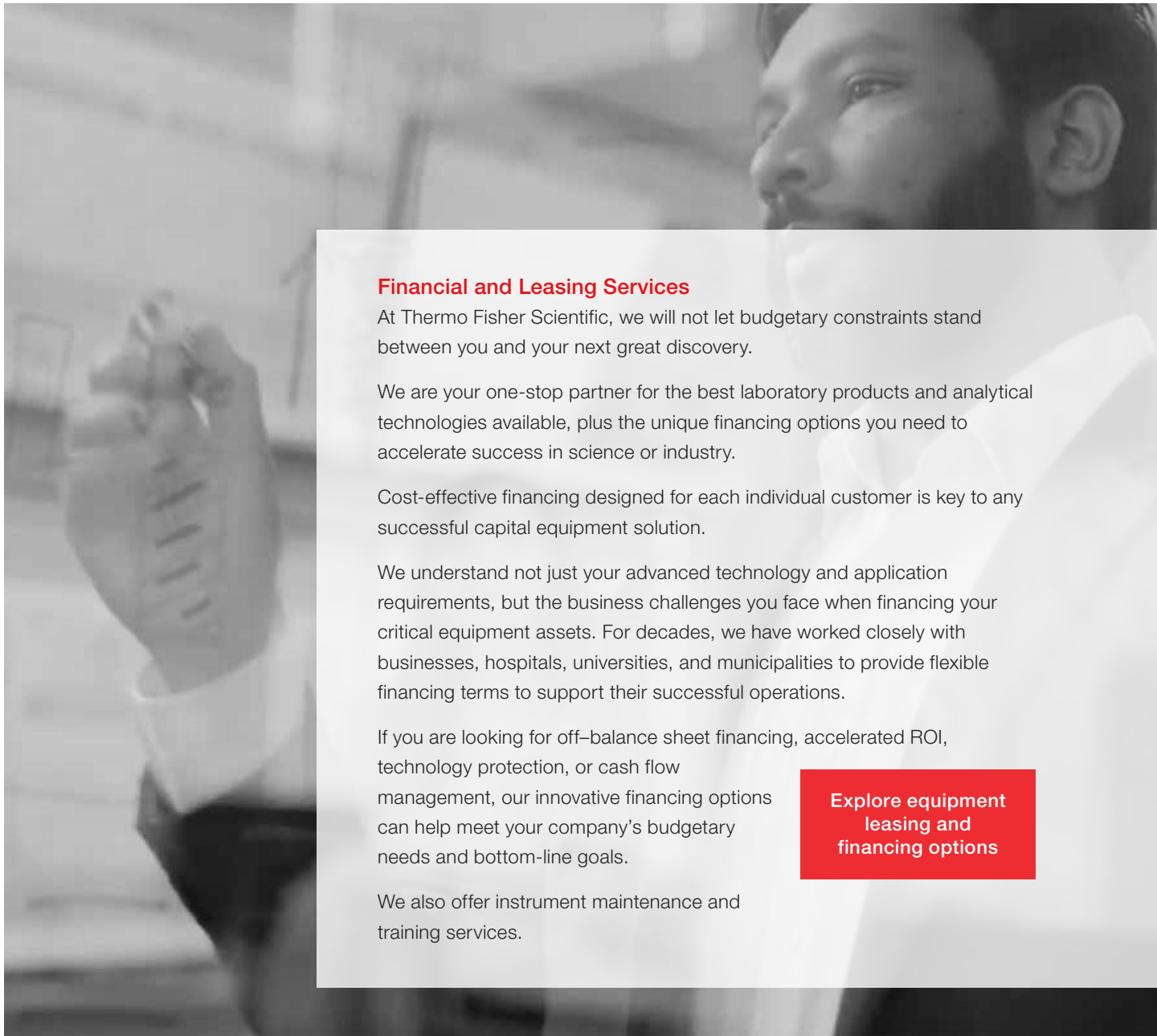

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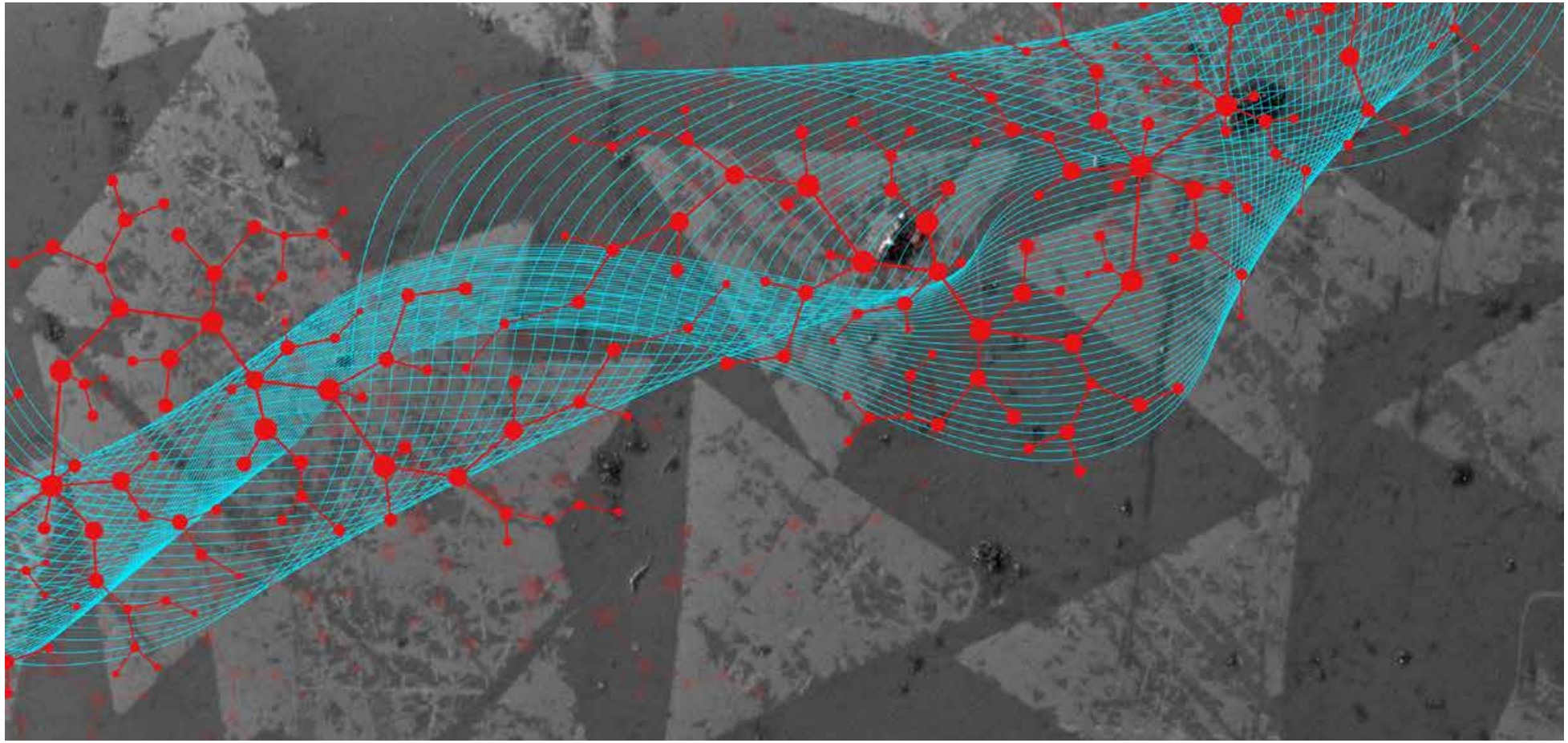

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