Atomic-resolution studies of materials by monochromated, aberration-corrected STEM

Ondrej L. Krivanek

Nion Co., 11511 NE 118th St, Kirkland, WA 98034, USA, and
Dept of Physics, Arizona State University, Tempe, AZ 85287, USA
Email: krivanek@nion.com

Aberration-corrected scanning transmission electron microscopes (ACSTEMs) are able to form intense electron probes as small as 0.5 Å in diameter, and to image and spectroscopically analyze single atoms in-situ. When equipped with a high-performance monochromator and electron energy loss spectrometer (EELS), ACSTEM is also able to analyze the vibrational properties of materials at an energy resolution of about 10 meV. This allows different types of chemical bonds present in organic materials to be detected spectroscopically, the hydrogen content of solids to be analyzed, and radiation damage to be avoided by performing aloof beam spectroscopy. This short paper briefly reviews the history of aberration-corrected STEM, summarizes several of the more recent developments, and charts the most promising future directions.

The first successful aberration corrector for a STEM was built in Cambridge UK by Krivanek and Dellby, in 1997 [1]. Aberration-corrected STEM then progressed to the first sub-Å resolution electron microscope images ever obtained directly (i.e., without image reconstruction) [2], and it has since been universally adopted as a powerful method for imaging and analyzing materials at atomic resolution. Fig. 1 illustrates the kind of analysis that is now readily possible: acquiring an EEL spectrum from a single atom, and using the spectrum's fine structure to determine the atomic environment of the atom [3]. Analyzing atomic columns is easier experimentally than probing single atoms, and atomic-resolution maps of crystalline specimen can now be readily obtained both by EELS and energy-dispersive X-ray spectroscopy (e.g. [4]).

More recently, Nion has introduced an ACSTEM equipped with a monochromator, called "High Energy Resolution Monochromated EELS STEM" (HERMES™). The monochromator is placed at ground potential, and it employs two new stabilization schemes that have enabled it to reach better than 10 meV energy resolution (Fig. 2). It has opened up a new field of electron microscopy: ultra-high energy resolution electron spectroscopy (UHERES), which is now allowing vibrational spectra to be acquired in the electron microscope [5]. The new technique analyzes the vibrations of the atomic nuclei in the sample, not the excitations of the sample's electrons that are probed by "regular" EELS. UHERES spectra are similar to those obtained by infrared (IR) and Fourier Transform IR (FTIR) spectroscopies, but at much better spatial resolution.

UHERES is able to detect hydrogen and analyze its bonding, even though hydrogen used to be a very difficult element to detect by electron microscopy. Being very light, hydrogen's elastic scattering cross-section is much smaller than the cross-sections of other elements, and it does not give rise to core loss edges that could be used for detecting it by EELS, nor to characteristic X-rays. Fig. 3 shows the detection of hydrogen and of other bonds involving light atoms in guanine [6]. The EEL spectrum does not match the energy resolution of the IR one, but it is able to resolve the peaks due to different types of bonds present in guanine, as shown schematically in the figure. The spatial resolution is about 50 nm, i.e. about 100x better than for standard IR.

The principal (dipole) component of the vibrational signal is highly delocalized: it comes from a sample region typically about 50 nm in diameter. Vibrational spectra of radiation-sensitive samples can therefore be acquired with the electron beam stationed 10-50 nm outside the area being probed, in a so-called "aloof beam" geometry. This has been used when collecting the data of Fig. 3 [6]. Not exposing the sample directly to the electron beam protects it from being damaged by high-energy (interband, plasmon and inner shell loss) excitations, and allows vibrational spectra to be collected from "fragile" organic samples such as those containing hydrogen.

Very recently, it has been shown that atomic vibrations may be mapped in a substantially damage-free way by moving the electron probe in discrete steps of 10 nm or more, and thereby collecting useful spectra from undamaged regions located a few nm from the electron beam [7]. If this turns out to be generally applicable to the majority of biological samples, it is likely to become a very powerful method of biological nanoanalysis. At the same time, there is a non-dipole component of the vibrational spectra that is localized on the atomic scale, and ways are being explored to enhance this signal in radiation-resistant materials so that vibrational spectra are acquired at nm-level or better spatial resolution [8].

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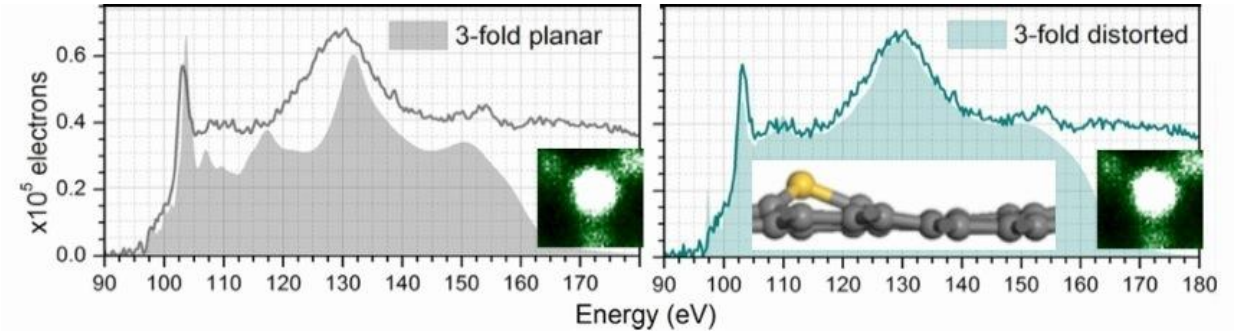

Fig. 1. EEL $L_{2,3}$ spectrum from a Si atom replacing a single C atom in graphene (line) and theoretical fits (solid spectra). Inserts show "tracking images" acquired during the signal acquistion. The right fit allowed the Si atom to "pop out" 0.95 Å from the graphene plane (inset) and gave a much better agreement. (Ref. [2]).

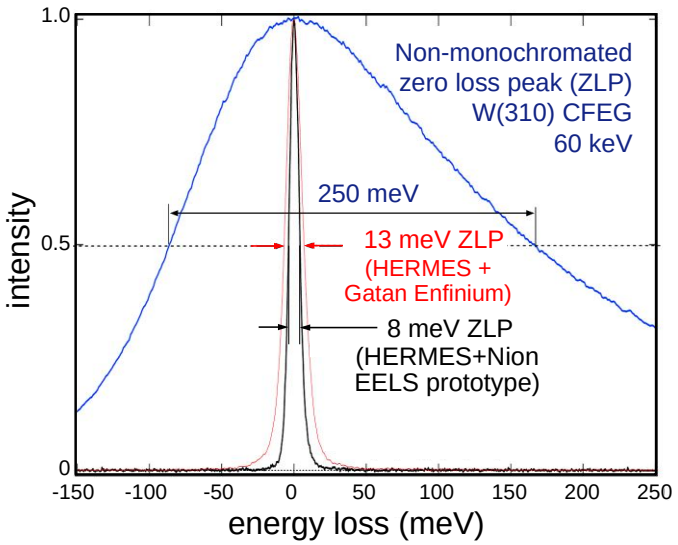

Fig. 2. Full-widths at half-maximum (FWHMs) of zero loss peaks (ZLPs) recorded with an unmochromated cold field emission gun (CFEG, blue curve), and with the monochromated Nion HERMES™ system (red and black curves).

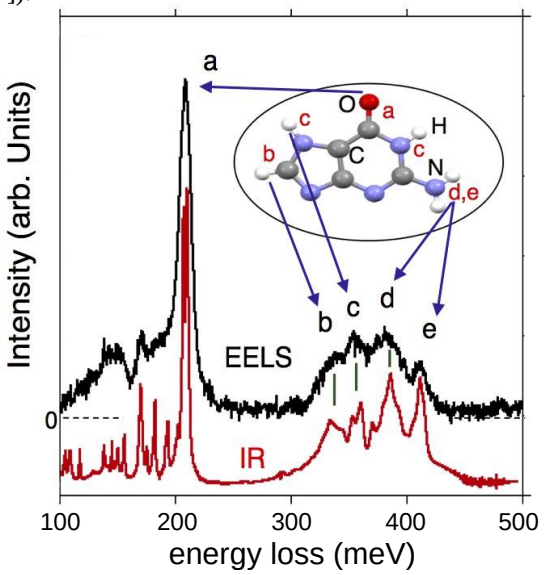

Fig. 3. Black: electron energy loss spectrum (EELS) of guanine recorded with the electron beam positioned 30 nm outside a guanine crystal. Red: IR spectrum of guanine. The inset shows the guanine molecule and which bonds give rise to which spectral features.