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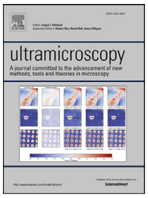

A short story of imaging and spectroscopy of two-dimensional materials by scanning transmission electron microscopy☆

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ABSTRACT

Here we present a short historical account of when single adatom impurities where first identified in two-dimensional materials by scanning transmission electron microscopy (STEM). We also present a study of the graphene low-loss (below 50 eV) response as a function of number of layers using electron energy-loss spectroscopy (EELS). The study shows that as few as three layers of graphene behave as bulk graphite for losses above 10 eV We also show examples of how point and extended defects can easily be resolved and structural dynamics can be readily capture by using aberration-corrected STEM imaging. Finally, we show that the new generation of monochromators has opened up possibilities to explore new physics with an electron microscope. All these capabilities were enabled by the development of spherical aberration correctors and monochromators, where Ondrej Krivanek has played a key role.

1. Introduction

It has been just over ten years since the first two-dimensional (2D) material (i.e. graphene) was first isolated [1], and the scientific excitement about its remarkable physical properties has not decreased. Now there are many more known 2D materials [2,3], with equivalent or complementary properties to graphene, that are being exploited for a broad range of technological applications. However, despite the wide spread efforts in creating proof-of-concept devices, today (late 2016), still not much is known about the atomic structure-property relationships of point and extended defects of 2D materials.

As pointed out in 2009 by one of the recipients of the 2010 Nobel Prize for "groundbreaking experiments in graphene" Prof. Andrew Geim [1], the main challenge in researching the influence of defects in the 2D materials physical properties is that "there has been an absence of experimental tools that could define structures with atomic precision" [4]. It is precisely here that aberration corrected scanning transmission electron microscopy (STEM) has really become a game changer in the field of 2D materials. STEM, thanks to aberration correction, is probably the only analytical technique where the structure [5], chemistry [6], bonding [7–9], spin [10], optical and plasmonic properties [5,11,12] of 2D materials can be studied with atomic precision and single atom sensitivity.

All the exciting materials physics that is now available to pursue with the STEM would not be possible without the tremendous achievements and contributions of Ondrej Krivanek. In this Special Issue, we would like to tell a short anecdote of how we met Ondrej, witnessed his first involvement in imaging 2D materials, and how that lead us to study 2D materials with the STEM. Finally, we, will present some of our results in 2D materials.

I [JCI] met Ondrej Krivanek in the summer of 2002 during the Microscopy and Microanalysis meeting. I clearly remember the circumstances because it was my first international microscopy conference. The meeting was held in the beautiful city of Quebec, Canada. On the first day of the conference, my PhD advisor (Nigel Browning) told me and the other members of the group that we should attend a talk given by "Ondrej Krivanek" about "Albert Crewe". Originally, Prof. Crewe was scheduled to give a talk that

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had the title “Some Chicago Aberrations” [13]. However, due to health reasons, Prof. Crewe requested Ondrej to give the talk on his behalf. Despite having read papers by Ondrej [14,15], and frequently used the EELS Atlas that he helped to create [16], the pronunciation of his name did not ring a bell on my memory bank. I had the misfortune to ask my advisor who was “that Ondrej?” Needless to say I was non-sympathetically told to simply attend the talk.

The talk was captivating because Ondrej gave it as if it were a play. In the play he was interviewing Prof. Crewe and when he played the role of Crewe he would wear a jacket and change his accent a bit. When Ondrej was playing himself, he would take the jacket off and go back to be himself. I have to say that I did not forget his name after listening to his talk! During that meeting, and the many that followed, I had the opportunity to informally interact with Ondrej. I have been awed by the sharpness of his mind, the strength of his character, and his relentless inquisitive curiosity — with right-to-the-point questions, I might add — to find out as many details as he could on whatever topic we would be discussing at the time. Before moving to the scientific part of this manuscript, I would like to mention another story about Ondrej and how the event influenced us to get involved in studying 2D materials with the electron microscope.

The story took place in the Spring of 2009 at Oak Ridge National Laboratory (ORNL). The STEM Group was getting its first Nion UltraSTEM column. The microscope installation began in March 23rd 2009 [17]. During that spring and subsequently months we often saw Ondrej and Niklas Dellby at the Lab. The two are co-founders of Nion. One weekend, specifically in the afternoon of Saturday June 13th 2009 [17], I happened to be at the Lab to do some experiments. I went into the UltraSTEM room to get a sample from a desiccator without knowing that people were there. I saw Ondrej, Niklas and Matt Chisholm (from The STEM group) working with the instrument.

Ondrej was driving the microscope. Two things caught my attention. The first obvious thing was that Ondrej was on the operator position. I remember that my thoughts were on the lines of: “Here is ‘this guy’, who not only has helped inventing electron spectrometers [18], pioneered the field of electron energy-loss spectroscopy [19], developed the first working aberration corrector for STEM [20], built a new microscope column from the ground up [21] (more recently also including a sub 10 meV monochromator [22]), founded and has been managing a company that produces among the best electron microscopes in the world, but also still knows how to operate a state-of-the-art electron microscope!” I think I could say with great certainty that there are not many senior scientists out there, that have continuously contributed in so many areas of electron microscopy, and yet still go to an electron microscope room to dexterously operate a STEM as well as any of the best graduate students or postdocs would.

The second thing catching my attention was the material that Ondrej was studying with the electron microscope. That afternoon I witnessed among the first STEM experiments that imaged individual impurities of oxygen and nitrogen in monolayer graphene [23]. I was simply struck by the quality of the images. We could basically differentiate the chemical identity of individual atoms by simply comparing their relative contrast in the image. The research I had prepared for that afternoon was not important any more. I gladly stayed at the back of the room for a very long time admiring the stunning experiments without saying a word [24]. The experiments of that afternoon led to a *Nature* article [6] (that even got the cover of the journal), and helped propelling STEM as one of the main techniques to study the properties of two-dimensional materials with atomic resolution.

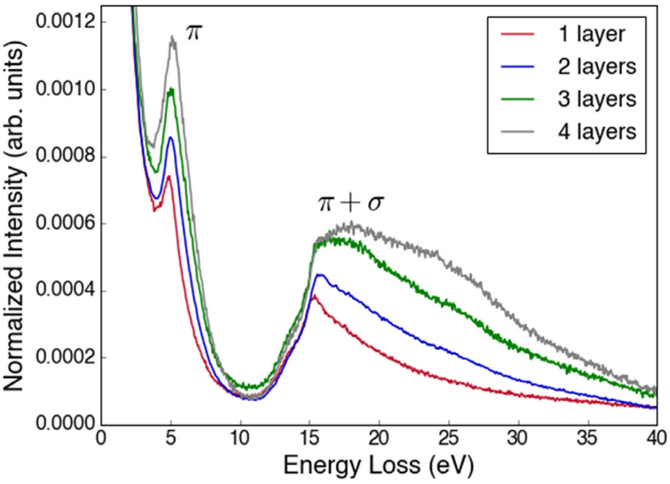

Fig. 1. Electron energy-loss spectra of one, two, three and four graphene layers. All the spectra contain two main features, known as the π and $\pi+\sigma$ peaks. The π and $\pi+\sigma$ peaks change with the number of layers by shifting their position to higher energies and augmenting their peak intensity. However, the $\pi+\sigma$ peak also changes its shape when graphene transitions from two to three layers. The shape of the EEL spectra for the 3 layers of graphene resembles that of graphite [25], indicating that for energy losses above 10 eV, as few as three graphene layers already present inelastic scattering features of bulk graphite.

2. Electron energy-loss spectra of single layer and multi layers graphene

Our first attempt to study graphene with the electron microscope began in mid 2010 by trying to image lithium intercalation in graphene. Graphene samples were prepared by a standard CVD method and transferred to a TEM Cu-grid as previously described in detail in Ref. [11]. However, despite our best attempts, the lithium intercalation in the graphene samples consistently failed. So instead, we decided to shift our efforts, and focus on understanding features that were consistently observed in the low-loss region of the electron energy-loss (EEL) spectra of samples of monolayer graphene without lithium. Another reason was that one of the authors of this manuscript (WZ) was desperately hoping to get some data for the upcoming M&M abstract submission deadline, and the lithium project was simply not taking off. The efforts were part of what later became the discovery that individual impurities in monolayer graphene could present sub nanometer localized EEL signals below 20 eV [11].

The first experimental EELS study of suspended monolayer graphene was performed in 2008 by Gass et al. [5] in the SuperSTEM facilities at the Daresbury Laboratory in the UK. Gass et al. observed that the low-loss region (below 50 eV) EEL spectra of graphene changed drastically going from one to five layers. However, in their original study, Gass et al. only showed data from one, two and five layers. EEL spectra from three and four layers were missing. Moreover, the spectra were rather noisy and accurately quantifying the exact position and relative intensity of the two main peaks in the spectra, labeled by the authors as the π and $\pi+\sigma$, was not possible.

Fig. 1 shows the EEL spectra of one to four layers of graphene acquired in ORNL’s Nion UltraSTEM 100 [21]. The microscope was operated at 60 kV acceleration voltage in order to avoid knock-on damage of the graphene lattice. A 30 mrad convergence angle, a 48 mrad collection aperture, an energy dispersion of 50 meV/pixel, and an electron beam with an energy resolution of 350 meV were used in the experiments. The spectra were obtained from regions free of defects and they were normalized to the maximum intensity of the zero loss-peak (ZLP) of each spectrum.

Three main characteristics can be directly observed from the EEL spectra shown in Fig. 1. There are two main peaks present in all the spectra: the first peak (π) located at $\sim$ 5 eV and the second peak ($\pi + \sigma$) located at ~15 eV The last characteristic is the extremely weak intensity of all the inelastically scattered peaks as compared to the ZLP intensity.

For the case of monolayer graphene, the π peak (including the ZLP tail) has an intensity of only 0.075% with respect to the maximum ZLP intensity. The intensity of the π peak (again including the ZLP tail) increases almost linearly with the number of layers, going from 0.075% for one layer to 0.087%, 0.104% and 0.117% for two, three and four layers, respectively.

We also can observe that the π peak position shifts from 4.90 eV to 5.05 eV, 5.07 eV and 5.19 eV for one to four layers, respectively. The π peak does not change in shape, in contrast to what occurs for the $\pi + \sigma$ peak.

The maximum intensity of the $\pi + \sigma$ peak increases from 0.038% to 0.045%, 0.055% and 0.059%, for one to four layers, respectively. While the peak positions shift from 15.4 eV to 15.6 eV, 16.5 eV and 18.1 eV, for one to four layers, respectively. However, as it can be observed in Fig. 1, the shape of the $\pi + \sigma$ peak is drastically altered going from two to three layers of graphene. A third broad peak becomes apparent at $\sim$ 25 eV for three and four layers of graphene. The third broad peak at $\sim$ 25 eV has been previously observed in graphite samples [25]. The result indicates that as few as three graphene layers already presents inelastic scattering features of bulk graphite for energy losses above 10 eV While for the π peak, its intensity increases linearly up to four layers.

Finally, it is important to point out the following when trying to study graphene with the STEM for energies below 4 eV, in particular by using new available monochromated instruments with energy resolutions of 30 meV or better. As it can be seen in Fig. 1, the ZLP tails for a non monochromated EEL spectra have intensities that are above 1 in 10,000 of the maximum ZLP intensity for excitations below 4 eV This means from a pure experimental measurement that phonons or optical excitations in graphene have intensities that are a 10,000th of the ZLP tail intensity — similar to those of inner shell cross sections. The same conclusion has been obtained theoretically by Rez [26]. Thus, minimizing the tail of the ZLP in monochromated spectra is just as important as achieving a small-width at half-maximum [26]. As of today (late 2016), we are not aware of any report resolving the phonon modes in graphene using monochromated aberration-corrected STEM.

3. Imaging of point and extended defects of 2D materials

As mentioned in the introduction, one of the main advantages of aberration correction is that it allows to study defects of 2D materials with unprecedented high spatial resolution. At an acceleration voltage of 60 kV, it is possible in STEM to image single layers of graphene, boron nitride and transition metal dichalcogenides (such as MoS_2) without or with minimal electron beam damage.

For the particular case of extended defects, such as grain boundaries, it is of particular interest to obtain not only structural information (how the atoms are arranged) but also how the electronic configuration of the atoms is affected by different bond lengths and angles. For instance, it has been shown that the C K-edge fine structure drastically changes at the edges of monolayer graphene, where C atoms have dangling bonds [7].

Similarly, it has been shown that the electronic structure of a single Si atom present as an impurity in monolayer graphene can change depending on how it is bonded [8,9]. Two different groups, at ORNL and SuperSTEM, have independently reported that a Si impurity can be bonded either with a sp^3 or a sp^2d configuration depending on whether the Si atom is three-fold or four-fold coordinate with the graphene lattice, respectively.

However, despite the relative early success in imaging the atomic structure of graphene grain boundaries with aberration corrected STEM [27], the bonding configuration of C atoms in the grain boundaries is still basically unknown. The culprit for the lack of EEL data in the grain boundaries is due to carbon contamination present on the graphene surfaces. Our experience is that the grain boundaries are consistently covered by carbon contamination. Consequently, the intrinsic carbon contamination tends to systematically migrate to the grain boundaries. We have had many collaborators during the last few years visiting ORNL asking us to look at their graphene samples to obtain images and spectra of the grain boundaries. Unfortunately, our efforts during several years of looking at graphene grain boundaries have not been very successful. Only in few occasions we have been able to image relative large pristine graphene grain boundaries. Fig. 2 (left panel) shows one of those successful attempts. The image shows a 28.5° graphene grain boundary composed of carbon rings containing five and seven C atoms. Although we have been able to acquire EEL spectra of such grain boundary in the low energy range (below 50 eV), it has not yet been possible to get EEL spectra containing the C K-edge due to contamination.

It is possible that in-situ heating, and a better treatment of the graphene surface when transferring the graphene layers to a TEM grid, will allow in the near future to obtain EEL spectra with fine structure information of the C K-edge. Such spectra should be able to reveal how the electrons behave in grain boundaries for carbon bonds beyond a standard sp^2 configuration. We are aware that many STEM groups (including the authors of this manuscript) are pursuing that goal and we look forward to see a successful experiment in the near future.

The right panel in Fig. 2 shows a single Mo vacancy in monolayer MoS_2. Mo vacancies are important in MoS_2 for the following reason. It has been theoretically predicted that the substitution of only few percent of Mo atoms by Mn [29] could produce a long-range ferromagnetic ordering in the material. This should make Mn-doped MoS_2 behave as a dilute magnetic semiconductor, which could then be used for spintronic applications. Although Mo vacancies can be generated during the CVD growth process, or by a posteriori ion and electron irradiation, no Mn substitution has been reported in the literature so far. We have been pursuing the substitution of Mo atoms by Mn atoms with our collaborators, such that we can then perform single atoms EELS experiments of the Mn impurities as done by Lin et al. in Japan [10]. Again, we look forward for STEM groups around the world reporting successful imaging and spectroscopy experiments of 3*d* transition metal impurities in MoS_2, or other transition metal dichalcogenide material for that matter.

4. Imaging of dynamics of defects in 2D materials

The successful application of low-voltage (in particular 60 kV) aberration corrected STEM ADF imaging to the study of 2D materials has made the term "gentle STEM", coined by Ondrej [30], popular in the microscopy community. This is mainly because the energy of the electron beam at such low accelerating voltage is below the knock-on damage threshold of the carbon atoms in perfect monolayer graphene; thus, prolonged illumination does not alter the graphene structure. However, such low-voltage "gentle STEM" conditions are not always damage-free: for semiconducting or insulating materials, such as MoS_2 and h-BN, ionization damage becomes more severe at lower voltages. In addition, the electron beam always transfer energy to the samples via direct momentum transfer. At 60 kV, a maximum energy of 10.8 eV can be transferred from the electron beam to carbon atoms. Thus, for carbon atoms with weaker bonding than that in perfect graphene lattice, e.g. those on graphene edges or defect sites or in fullerenes,

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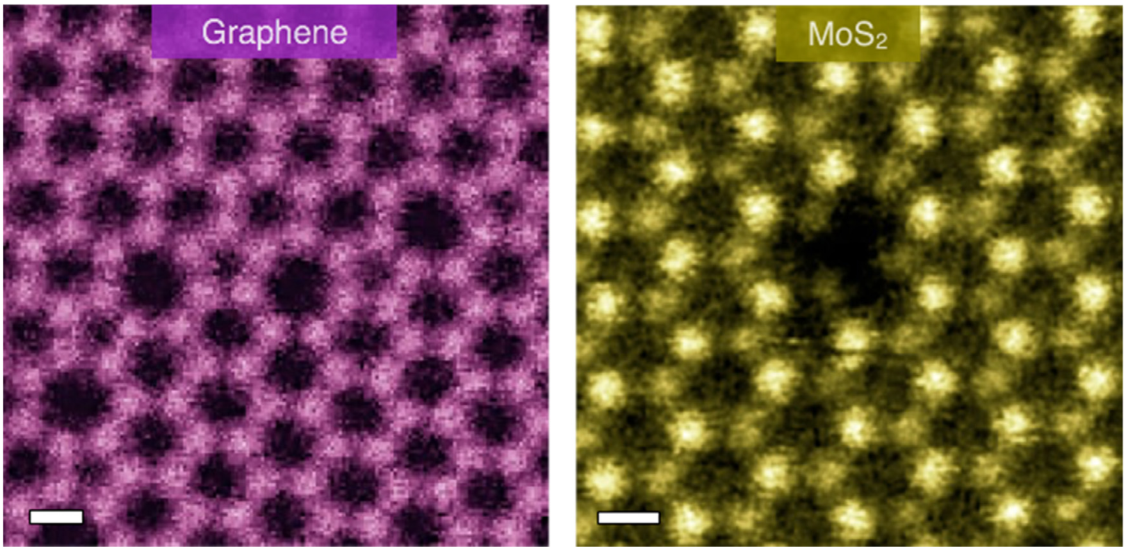

Fig. 2. Z-contrast images (as acquired) of monolayer graphene, and MoS_2 obtained in the Nion UltraSTEM 100, operating at 60 kV. The electron microscope at 60 kV has an information transfer of 0.106 nm, which is sufficient to resolve individual C, Mo, S atoms, point defects (such as a Mo vacancy in the MoS_2 lattice), and extended defects like the 28.5° graphene grain boundary shown in the figure. Scale bars are 0.2 nm. The MoS_2 right panel figure is adapted from Ref. 28.

energy transferred from 60 kV electron beam can still be sufficient to cause atomic motion. This could be viewed as structural damage, but in an optimistic way, it actually provides a very convenient and sometimes controllable way to explore the dynamics of defect structures.

Fig. 3 provides a time sequence of STEM-ADF images collected at 60 kV from a graphene edge. While the structure within the graphene lattice remained intact, the atomic arrangement of the carbon atoms along the edge (mostly zig-zag edge as shown in the first frame) continuously evolved under the illumination of the 60 kV electron beam. In addition, a Si atom attached to the graphene edge was seen to shuffle back and forth during the sequential imaging. In this case, the momentum transferred from the electron beam provides sufficient energy for the Si atom to overcome its diffusion barrier, so that this diffusion event can be excited and recorded simultaneously.

For the study of dynamical events, it is important to capture structural evolution with both atomic resolution and chemical information so that any compositional variation associated with the structural changes can be quantitatively analyzed. This is one of the main advantages of using sequential STEM-ADF imaging over phase contrast high resolution-TEM imaging for structural dynamics study, as the chemical information can be extracted from the image contrast. Thanks to the continuous development of aberration correction technique and the overall microscope platforms, low-voltage STEM-ADF images can now provide atomic resolution and good signal-to-noise (SNR) ratio for atom-by-atom chemical analysis even at fast acquisition. This has made possible many defect dynamics studies reported by our group and others. For example, the ADF images in Fig. 3 has sufficient SNR to identify the Si atoms based on image intensity quantification alone. Differentiation of a nitrogen atom from carbon in graphene lattice during a dynamical event has also been reported [31]. Further improvement on detector efficiency and combing with quantitative imaging method via electron counting technique [32] should allow for the study of more complex structural evolutions in 2D materials and beyond using sequential STEM-ADF techniques with improved temporal resolution.

5. New capabilities from ultra-high energy resolution EELS enabled by the new monochromators

The most exciting new development in electron microscopy in the past decade is probably monochromators with sub-20 meV (or even sub-10 meV) energy resolution [22]. Such unprecedented energy resolution has made it possible to detect vibrational spectrum inside an electron microscope [33,34] with nanometer resolution.

Fig. 4A compares the zero-loss peak profiles from a typical cold field-emission gun (CFEG) and from a monochromated Nion UltraSTEM-100 (also known as the Nion HERMES) with different energy selection slit widths. As can be seen, the energy resolution, measured by the full-width-at-half-maxima (FWHM) of the ZLP, can be improved by 5–20 times with the help of the monochromator. Importantly, the ZLP from CFEG has a rather asymmetric intensity distribution, with an extended ZLP tail. This can be largely corrected by the monochromator, leading to a more symmetric ZLP profile after monochromation. Even though the improvement of energy resolution itself is already quite impressive, a better way to highlight the benefit of a monochromator is to look at the ZLP plotted in log scale as shown in Fig. 4B. By increasing the energy resolution from 300 meV out of the CFEG to 60 meV out of the monochromator, the intensity at the ZLP tail in the low energy-loss regime, especially below 1 eV, drops by two orders of magnitude, as also listed in Table 1. In low-loss EELS, detection of many signals, such as phonon, optical absorption and exciton peaks in the infrared regime, has long been hindered by the poor energy resolution of (S)TEM, as these weak features can be easily overshadowed by the relatively high intensity of the ZLP tail. Decreasing the intensity of the ZLP tail in the low energy-loss regime by two orders of magnitude would, thus, be equivalent to an improvement of the "resolving power" in low-loss EELS by the same orders of magnitude, making detection of optical features in the infrared regime feasible [35].

Further increasing the energy resolution can bring the intensity of the ZLP tail even lower. For example, at 14 meV energy resolution, the ZLP intensity at $\sim$ 200 meV energy-loss is of the order of 10^{-4} with respect to the ZLP maximum. Since the intensity of vibrational peaks in the low-loss spectra is typically of similar order of magnitude ($10^{-5}\sim10^{-4}$) relative to the ZLP maximum [34], increasing the energy resolution to the sub-20 meV regime is critical

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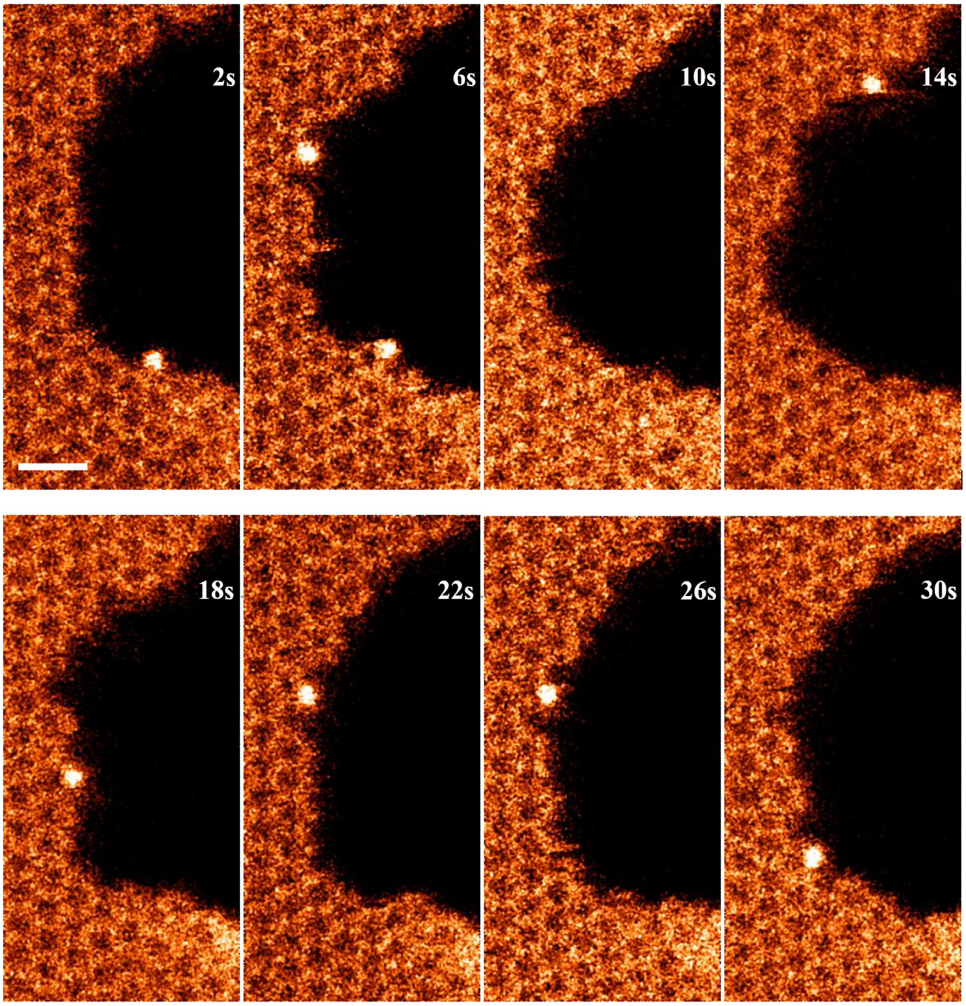

Fig. 3. Time sequence of ADF images showing the modification of a graphene edge and the diffusion of Si adatoms under 60 kV electron beam illumination. In the second frame, the Si atom was captured twice during the acquisition of the STEM-ADF image as it migrated from the top to the bottom along the graphene edge. Scale bar: 0.5 nm. Frame time: 2 s.

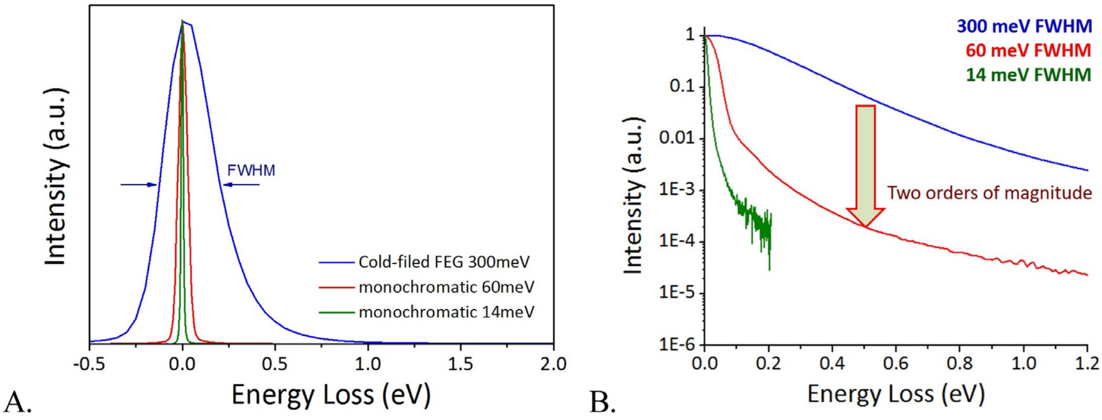

Fig. 4. Comparison of the ZLP from a CFEG with and without a monochromator. The resolving power at the low energy loss regime, especially below 1 eV, has been drastically improved by the monochromator. (A) ZLP plotted in linear scale showing the changes in FWHM. (B) ZLP plotted in log scale to highlight the suppression of the intensity at the ZLP tail.

for clear identification of vibrational modes using EELS. Meanwhile, as can also be seen from Fig. 4B, at very high energy resolution, when the full ZLP is recorded the exposure time of the spectrum has to be kept relatively short in order not to burn the spectrometer camera. This in turn leads to very poor SNR in the spectrum apart from the ZLP. For example, at ~ 200 meV, the noise level in the 14 meV FWHM spectrum is about the same as the signal, a new obstacle for detecting weak signals at very low energy-loss regime using monochromated EELS. Further development of low noise spectrometer detector and new data acquisition/processing schemes to reduce noise would help to realize the full potential of ultra-high energy resolution EELS.

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Table 1
Comparison of the intensity of the ZLP tail at different energy losses.

	CFEG	Monochromated	Improvement
Energy resolution (FWHM)	300 meV	60 meV	5 X
Intensity at 100 meV energy loss*	77%	1.2%	65 X
Intensity at 200 meV energy loss	44%	0.25%	176 X
Intensity at 300 meV energy loss	23%	0.1%	230 X
Intensity at 500 meV energy loss	5.6%	2×10^{-4}	280 X
Intensity at 1 eV energy loss	0.4%	4×10^{-5}	100 X

* Intensity of the ZLP tail at specific energy loss with respect to the ZLP maximum

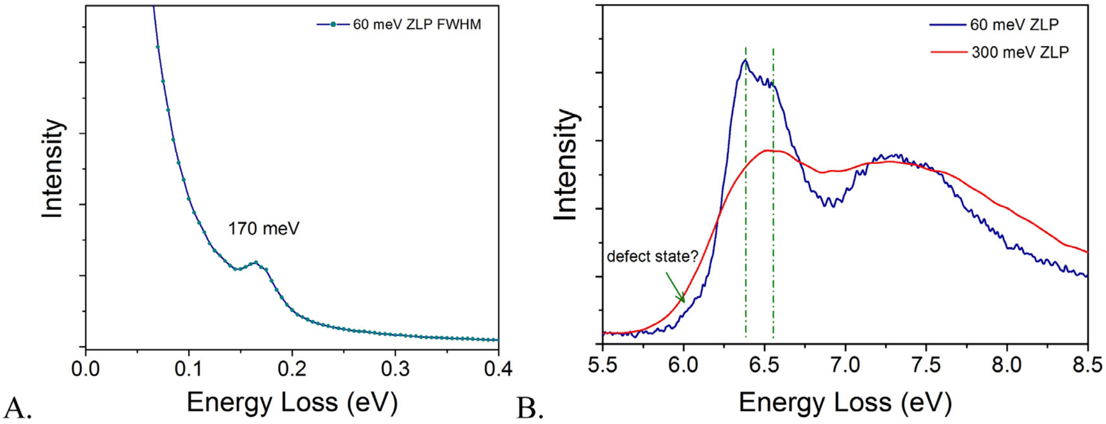

Fig. 5. Monochromated low-loss EELS from thin h-BN flakes (1–2 layers) showing the longitudinal optical (LO) phonon peak (A) and the plasmon peaks (B). The plasmon spectrum is also compared with a spectrum acquired without a monochromator (red curve).

Fig. 5 shows the low-loss EELS from thin h-BN flakes, collected with energy resolution of 60 meV. The weak peak at ~ 170 meV corresponds to the longtitudinal optical (LO) phonon in h-BN, as previously reported by Krivanek et al. [34], although with a lower energy resolution this phonon peak is not as prominent above the background as in the previous report. The improved energy resolution in monochromated EELS also brings new view to spectroscopy features well beyond the ZLP tail. As shown in Fig. 5B, the so-called "π plasmon" peak of h-BN consists of a sharp peak at ~ 6.5 eV and a shoulder at ~ 7.3 eV The monochromated EELS spectrum further reveals that the first sharp peak is indeed composed of two peaks, separated by ~ 170 meV, which is beyond the energy resolution of typical EELS spectra without a monochromator. Revealing the origins of these peaks requests for theoretical input, but monochromated EELS certainly provides the capability to explore these new spectroscopy features.

6. Summary

Here we present a short and first-hand story of how individual impurities of 2D materials were first quantitatively investigated using STEM Z-contrast imaging at the atomic scale. That research was originally carried out by Ondrej Krivanek when installing the first Nion aberration corrected column at ORNL. What is rather astonishing is that Ondrej also participated in the design of the corrector, the whole column system (stage, vacuum system, condenser and projector lenses, detectors, *etc.*), the spectrometer and even in the software used to acquire and analyze the images and spectra.

We also presented EEL spectra data of single and multilayer graphene. We show that with three layers, the graphene low-loss spectrum behaves as bulk graphite above 10 eV We discussed how future experiments in graphene and MoS_2 could reveal new information regarding the electronic behavior of C atoms beyond sp^2 bonding, and the long-range magnetic ordering of MoS_2. Moreover, we show that the new generation of monochromators has opened up possibilities to explore physics with an electron microscope that was only at the reach of synchrotron facilities.

We now look forward to the new discoveries in material physics that the recently developed monochromators in STEM will bring. Again, Ondrej has been essential in this area by designing and delivering the new monochromators. One thing for sure, Ondrej's contributions to electron microscopy are going to be present for many future generations of scientists.

We also really look forward to see what Ondrej and his team have for us around the corner. Perhaps a truly atomically-stable cryo-stage will join the monochromated aberration-corrected STEM in the near future?

Competing financial interest

The authors declare no competing financial interest.

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