LVEM for 2D Materials

Background

This report will present how LVEM benefits research and scientific advancements supporting the field of two dimensional (2D) materials research, which have shown steadily increasing interest in research and commercialization in the past decade.

2D Materials

Materials thinned to their physical limits as planar layers are commonly referred to as "2D Materials." The most notable example is graphene, a single atomic layer of carbon atoms in two dimensional honeycomb lattice. Additional examples include hexagonal boron nitride (h-BN), transition-metal dichalcogenides (TMDC), and MXenes. (Castellanos-Gomez, 2016). 2D materials have a range of diversity of properties, from metallic conductors to semiconductors to dielectric materials, and their applications range from electronics to sensors to energy storage to biomedical treatments and devices. (Bhimanapati, 2015)

Electron Microscopy in 2D Materials

Transmission Electron Microscopy (TEM) is an excellent characterization tool for obtaining visual images and micrographs of nanosized structures. Electron diffraction is also possible with TEM instruments, allowing investigation of the hexagonal lattice structures commonly found in 2D materials. Additionally, the lower accelerating voltages of LVEM offer enhanced contrast of carbon-based materials and low atomic weight materials compared to the higher accelerating voltages used in other TEM instruments.

LVEM Enhanced Contrast

The LVEM offers enhanced contrast of organic and low atomic weight samples compared to traditional TEM, directly on the as-prepared samples. The enhanced contrast of low atomic weight atoms including carbon, nitrogen, oxygen commonly comprising the composition of 2D materials enables clear visualization of structures.

Low accelerating voltages in TEM are especially useful in imaging 2D materials such as graphene. For example, reports have demonstrated how the lower accelerating voltages are particularly useful at preventing sample damage induced by the electron beam, and is helpful at preserving the matrix surrounding the materials. (Bell, 2014). Accelerating voltages as low as 5 kV are reported to provide enhanced contrast benefits that drive preferential selection of lower voltages when available for organic materials. (Drummy, 2014)

Sample preparation for LVEM can improve the final image quality. For example, when using carbon support films, selection of films that are 10 nm thick instead of 30 nm thick will significantly increase electron transmittance. The benefits of this include improved image quality, reduce risk for sample dehydration effects, more reproducibility in sample preps, and reduced chromatic aberration from non-elastic scattering of the incident beam in the sample. (Sintorn, 2013)

LVEM

Both the LVEM 5 and the LVEM 25 provide a versatile tool for studying 2D materials. For either a researcher or a laboratory manager, there are several well-established operational and business advantages to LVEM compared to traditional TEM instruments to help meet the demands for high quality facilities competing for limited resources, and meet the goals of providing cost-effective approaches.

LVEM Financial & Operational Advantages vs HVTEM:

- Lower initial cost
- Lower operating cost
- Easier operation
- Easier maintenance
- Smaller laboratory footprint
- No specialized site prep required

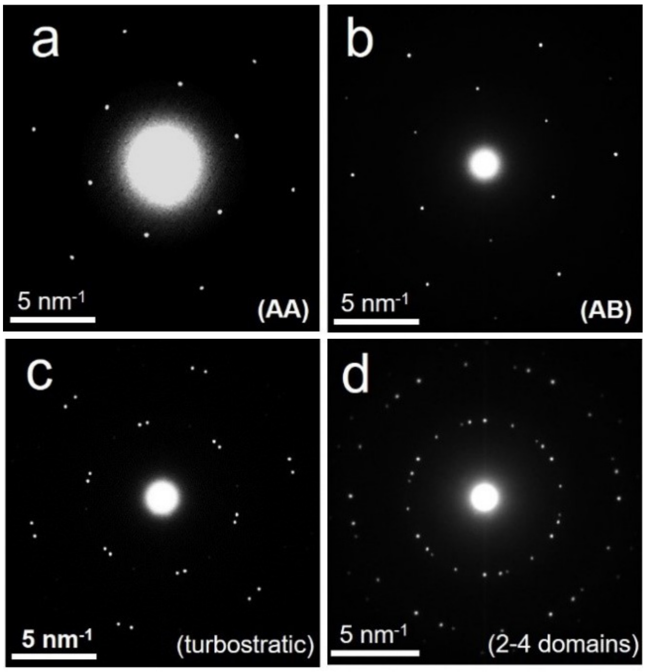
The significantly lower initial cost of a new LVEM instrument compared to even a used TEM is a tremendous advantage, allowing routine access to electron microscopy images when otherwise unobtainable and freeing up larger budgets for other critical tasks.

Additionally, placement of an LVEM is possible in many laboratories, making for much more efficient collection of routine characterization data. Much as low-cost instruments are ubiquitous in synthesis labs for initial screening characterization, LVEM enables electron microscopy to now become a rapid, affordable and easy microscopy tool, eliminating the need for costly core user facilities often found only at major research universities.

LVEM for the study of diamane

Genuine diamane is a new member of the nanocarbon 2D material family. It consists of two crystalline sp^3-bonded carbon layers for which half of the carbon atoms are hydrogenated while the other half bond the two layers to each other. This wide band-gap semiconducting material has potential applications in nanoelectronics, nanooptics, quantum information processing, ultrathin protective coatings, composite materials, resonators and miniaturized electronics and biomedical devices. The material stability was computationally predicted in 2009, and recently the LVEM was among the tools used to provide evidence of the successful synthesis of stable genuine diamane. (Piazza, 2021) The group used a hot-filament-promoted hydrogenation process, at low pressure and at low temperature to efficiently hydrogenate bilayer graphene and to subsequently convert them into stable diamane. Genuine diamane can be produced by the chemisorption of hydrogen atoms on the “top” and “bottom” surfaces of bilayer graphene (2LG) and the subsequent interlayer bonding between sp^3-bonded carbon atoms, if the stacking sequence of the pristine 2LG is AA or AB. The number of layers can be increased, thereby generating what the group calls “diamanoids” with different properties (e.g., different gap values) possible depending upon whether the stacking sequence is based on an ABC or AAA sequence. The use of graphene with the right number of layers and the right stacking sequence is therefore of the utmost importance when investigating genuine diamane and diamanoids.

The LVEM in its electron diffraction mode is used to determine both the number of layers and the stacking sequence of pristine 2LG films. Thanks to the use of an electron energy as low as 5 keV, it was possible to obtain evidence, for the first time, of single 2LG domains made from either AA stacking, AB stacking, or from two randomly stacked single-layer graphene (1LG), otherwise designated as twisted 2LG. The 2LG-AB discriminates from 2LG-AA by the three-fold symmetry of the spot intensity distribution on the inner diffraction ring. The 2LG-AA discriminates from 1LG by the significant lower intensity of the spot intensity on the outer ring. These differences are observable at 5 keV but not at 60–100 keV, as confirmed by calculations. The reason is the following: when dealing with ultrathin crystallized materials (graphene, diamane, diamanoids), their images in the reciprocal space are made of reciprocal nodes which are elongated into rods in the z direction. For an electron energy of 100 keV, the Ewald sphere is large enough for its surface to be approximated as a plane. However, the lower the electron energy, the shorter the Ewald sphere radius, inducing the Ewald sphere surface to intersect the various reciprocal rods at different heights, thereby generating diffraction patterns exhibiting the same spots but with variable intensities, or even with some spots missing. Studies by Piazza have revealed that the spot intensities may vary dramatically with the electron energy, which has never been previously considered in the literature. (Piazza, 2021)



Discriminating bilayer graphene with different stacking sequence is possible at very low accelerating voltages, a unique feature enabled by the LVEM5. (Piazza, 2021)

As a first, diffraction patterns of single bilayer graphene domain with AB stacking were found. The single bilayer graphene domain with AB stacking discriminates from AA counterpart by the three-fold symmetry of the spot intensity distribution on the inner ring of the diffraction patterns. This cannot be observed at 60–100 keV. This result will motivate the use of multi-wavelength electron diffraction (definitely including energy as low as 5–10 keV) as a new tool for identifying stacking sequences in 2D materials.

Conclusion

LVEM is an enabling technology for the characterization of 2D materials. The lower voltage of the beam enhances contrast of these materials while reducing the risks of beam-induced damage to samples. Using electron diffraction with LVEM allows for confirmation of the hexagonal lattice structure of planar one layer materials, and the identification of the stacking patterns of bilayer and multilayer assemblies of 2D materials.

As the world's best low voltage electron microscopes, the Delong LVEM 5 and LVEM 25 continue to contribute to many scientific disciplines beyond 2D materials, including nanotechnology, cell biology, materials science, higher education, environmental toxicology, and energy research.

References:

Bell DC, Mankin M, Day RW, Erdman N. Successful application of Low Voltage Electron Microscopy to practical materials problems. Ultramicroscopy. 2014 Oct 1;145:56–65.

Bhimanapati GR, Lin Z, Meunier V, Jung Y, Cha J, Das S, Xiao D, Son Y, Strano MS, Cooper VR, Liang L. Recent advances in two-dimensional materials beyond graphene. ACS nano. 2015 Dec 22;9(12):11509–39.

Castellanos-Gomez A. Why all the fuss about 2D semiconductors?. Nature Photonics. 2016 Apr;10(4):202–4.

Drummy LF. Electron microscopy of organic–inorganic interfaces: Advantages of low voltage. Ultramicroscopy. 2014 Oct 1;145:74–9.

Piazza F, Monthioux M, Puech P, Gerber IC, Gough K. Progress on Diamane and Diamanoid Thin Film Pressureless Synthesis. C. 2021 Mar;7(1):9.

Sintorn IM, Nordström R, Haag L, Coufalova E, Drsticka M. Factors influencing high quality low voltage TEM imaging of biological routinely stained specimen. InMicroscopy Conference (MC) 2013 (pp. 321–322).

About the author:

Robert I. MacCuspie, Ph.D., has over twenty years of experience in nanotechnology and materials characterization. Career highlights include leading the team that developed the silver nanoparticle reference materials at the National Institute of Standards and Technology, the first faculty and Director of Nanotechnology and Multifunctional Materials Program at Florida Polytechnic University, and over five years of consulting at the business-science interface from MacCuspie Innovations, helping companies commercialize and educate on technologies to improve human health.