2D Materials Nanosculpting in the Transmission Electron Microscope and Bioelectronics Applications

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Understanding, shaping and manipulating matter at atomic scale remains one of the major contemporary challenges in science and technology. Electron beams constitute powerful tools to shape and modify materials with atomic resolution inside a transmission electron microscope (TEM). I will describe experiments where we push the limits of device size to atomic scale in 2D materials from graphene to metaldichalcogenides (MoS_2, WS_2, $MoTe_2$ and alloys) and phosphorene, and expand their function and precision, while addressing fundamental questions about structure and properties at nanometer and atomic scales. To realize TEM compatible devices, we transfer as-grown 2D materials onto suitable holes, or the 2D materials can be grown directly across apertures, and we develop custom chips and holders designed for specific device applications in mind.

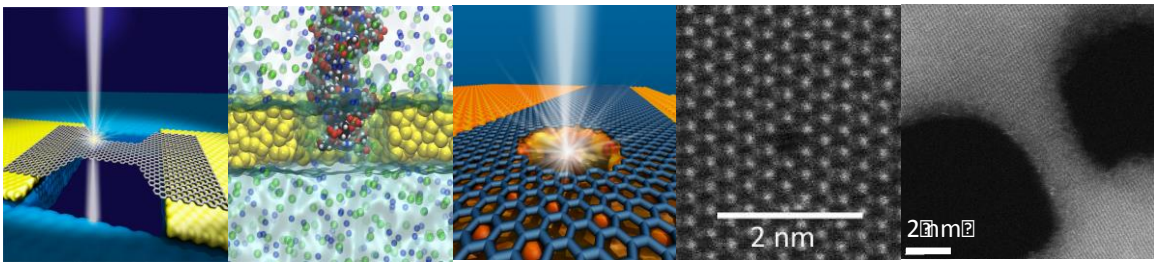
Experiments are performed *in situ* and *ex situ TEM*. *In situ TEM* experiments include fabrication of nanoribbons and field-effect-transistors from novel two-dimensional materials down to sub-nm widths, and *in situ* electrical measurements including measurements of resistance vs. width for nanoribbons with different atomic structure, determining the effects of electron irradiation dose and current annealing on defect creation and healing and the change in electrical resistance. When these experiments are combined with Raman spectroscopy, the Raman peak shifts can then be used as a quantitative diagnostic tool to characterize defect density.

Ex situ TEM experiments include the ultrafast, all-electronic detection and analysis of biomolecules by driving them through tiny holes – or nanopores – in thin membranes, including the efforts towards mapping a human genome under 10 min. As molecules are driven through nanopores in solution, they block the ion current flow, typically resulting in current reductions from which molecule's physical and chemical properties are inferred. DNA, proteins, microRNA and other biomolecules can be analyzed. Many of these molecules are important biomarkers for a broad range of illnesses and it is therefore beneficial to develop platforms that have the necessary resolution to detect and count a small number of biomarkers quickly. More broadly, nanopores whose diameters, compositions and functions we are trying to control, could detect, count, filter and analyze different kinds of particles. For example, nanopores could quickly quantify the charge and shape of nanoparticles, or they could be used as subzeptoliter mixing volumes for the electrically-controlled synthesis of nanoparticles.

The temporal, spatial resolution and sensitivity in nanopore experiments have been improved over the last few years thanks to advanced materials, improved measurement protocols, device designs and new electronics. The improvements of resolution are due to improved precision in nanopore fabrication using electron beam drilling in the TEM (the ability to make smaller and thinner nanopores), the development of nanopore-supporting

chips with low capacitance (< 1pF) to lower the high frequency noise, and of custom amplifier designs with low input capacitance. Specifically, I will describe the design and fabrication of low-capacitance glass chips to support 2D membranes, and describe DNA translocation measurements that represent the fastest ion current recordings through nanopores reported to date (up to 10 MHz).

Finally, I will also describe alternative uses of nanopores created in or near two-dimensional nanowires to highly localize molecules in the nanowire's proximity and then use the nanowire's electrical response to probe the molecule's presence and properties. Specifically, I will describe the nanofabrication of graphene nanoribbons with nanopores and measurements of ionic current through the nanopore during the passage of double-stranded DNA molecules near the ribbon, along with the simultaneous response of the neighboring graphene nanoribbon due to changes in the surrounding electric potential.



From left to right: Illustrations of nanoribbon sculpting with the electron beam; passage of a DNA molecule through a nanopore; illustration of nanopore drilling with an electron beam inside of the TEM; one-atom-large nanopore in a MoS_2 sheet; armchair phosphorene nanoribbon sculpted in the AC-TEM.

Selected references: Danda *et al*., ACS Nano 11 (2), 1937, 2017; Shekar *et al*., Nano Letters 16 (7), 4483, 2016, Masih Das *et al*., ACS Nano 10 (6), 5687, 2016; Rodriguez-Manzo *et al*., ACS Nano 10 (4), 4004, 2016 & ACS Nano 9 (6), 6555, 2015; Parkin *et al*., ACS Nano 10 (4), 4134, 2016; Qi *et al.*, ACS Nano 9(4), 3510, 2015; Balan *et al.*, Nano Letters 14 (12), 7215, 2015; Balan *et al*., Scientific Reports 5, 17775, 2015; Puster *et al*., Small, 22 (47), 6309, 2015; Drndic, Nature Nanotechnology 9, 743, 2014; Qi *et al.*, Nano Letters 14 (8), 4238, 2014; Rosenstein *et al*., Nature Methods, 9 (5), 487, 2012.