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Atomic-scale Chemical Manipulation of Materials in the Scanning Transmission Electron Microscope under Controlled Atmospheres

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Transmission electron microscopy (TEM) is typically used as an observational tool, often in a remote location far away from the rest of the experimental setup. This limits the capabilities of the method in terms of suitable samples and direct integration into experimentation. Since TEM is based on passing energetic electrons through a specimen and allowing them to interact with its nuclear and electronic structure, it is inevitable that prolonged exposure leads to structural changes ("beam damage") especially in nonmetallic and light materials. This damage arises through three different main mechanisms: (1) knock-on damage caused by elastic scattering of electrons from the nuclei in the specimen, (2) electronic excitations and ionization of the sample due to inelastic scattering from the electronic structure of the specimen, and (3) chemical reactions that occur between the specimen and molecules of the residual gases in the microscope column that have been cracked by the electron beam. Despite being harmful in the context of imaging, these processes can also be used intentionally to alter the specimen under investigation. In this presentation, we will introduce the use of the Nion UltraSTEM 100 dedicated scanning TEM (STEM) device in Vienna [1] as an integral part of an ultrahigh vacuum setup for materials growth and manipulation with the additional capability to carry out atomic-resolution microscopy under controlled gaseous environments [2].

In our device, we can vary the pressure during observation between 10^{-10}–10^{-6} mbar for a number of different gases. In the initial experiments presented here, we exposed single-layer graphene and its ubiquitous carbon-based contamination to the electron beam in atmospheres of air, H_2, N_2, O_2 and H_2O vapor. Due to the high electron mobility in graphene, the only damage mechanism under ideal vacuum conditions in this material is knock-on damage, which is practically nonexistent at the 60 kV acceleration voltage used here [3]. We show that air leaked into the microscope column during the experiment is efficient in cleaning graphene samples from contamination, but ineffective in damaging the pristine lattice. Our experiments also show that exposure to O_2 and H_2O lead to a similar result, oxygen providing an etching effect nearly twice as efficient as water, presumably due to the two O atoms per molecule. H_2 and N_2 environments have no influence on etching.

Although pristine graphene remains unchanged even in O_2 environment under the electron beam, the stability of graphene edges show a drastically different behavior. As predicted through atomistic simulations already years ago [4], the armchair edge is stable against electron irradiation at 60 kV at a pressure of 10^{-10} mbar (Figure 1). However, in oxygen atmosphere this structure is very rarely observed, whereas the zigzag edge can be imaged, occasionally even with attached oxygen atoms. We attribute the instability of the armchair edge under oxygen to its ability to absorb a large number of oxygen atoms between the carbon-carbon bonds, which destabilizes the edge against irradiation. At the zigzag edge, the most likely absorption position for the oxygen atoms is at the edge, where they do not alter the graphene structure.

Similar processes and the extended experimental setup can also be used for chemical manipulation within the bulk of 2D materials. For example, a graphene sample can be first cleaned in the microscope column with a laser (445 nm tunable 6 W diode laser) [5] aimed through a view port, transferred to a manipulation chamber with evaporators and a plasma ion source [6] for the introduction of defects that act as chemically reactive sites [7] and can be used as nucleation points for later chemical manipulation in the microscope column.

Overall, our results show that the residual gas environment in typical TEM instruments (with pressures exceeding 10^{-7} mbar) can have a large influence on the observations, and show that chemical etching of carbon-based structures can be effectively carried out with oxygen. Further, the 1-Å-sized electron probe in a STEM device combined with controlled atmosphere around the sample provide the possibility for chemical manipulation of materials at the sub-nanometer resolution opening the way towards nanostructures that can not be created via any other means.

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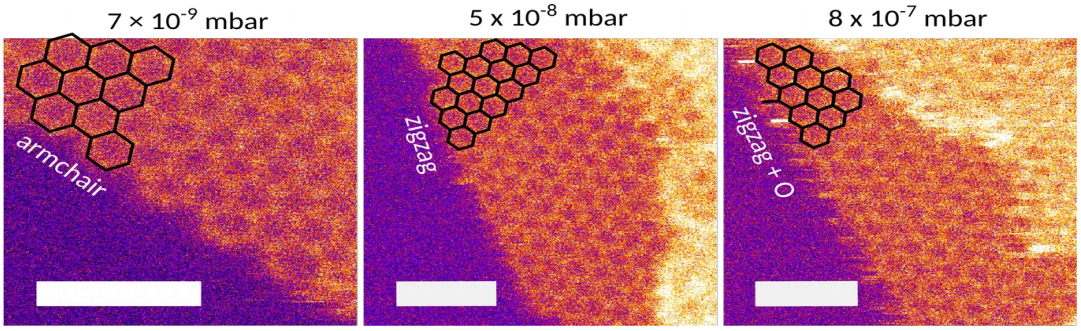

Figure 1. STEM medium angle annular dark field (MAADF) images of graphene edges at different oxygen pressures (marked over each frame), as imaged with the Nion UltraSTEM 100 in Vienna at 60 kV (beam convergence semi-angle 30 mrad, detector semi-angular range 60–200 mrad). Scale bars are 1 nm.