

Graphene Electrodes for In-Situ Transmission Electron Microscopy of Electrochemical Processes

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Recent advances in the construction of environmental cells for in situ transmission electron microscopy (TEM) are allowing the direct imaging of wet, electrochemical processes with near atomic resolution. For many experiments a smooth, chemically stable, and highly conductive electrode is desirable. However, of the standard electrode materials, those that are most conveniently microfabricated into a fluid cell are generally metals with large atomic numbers – gold and platinum, for instance [13]. These materials interact strongly with the electron beam, interfering with sensitive detection of dynamical processes occurring at the electrode surface.

Graphene is derived from a standard electrochemical electrode material, graphite. While it is currently not available in many microfabrication facilities, it is otherwise ideal for the in situ TEM of electrochemical processes. Like the metals discussed above, it is highly conductive, chemically inert, and mechanically robust. However, it also has the great advantage of being electron transparent. Because of its low atomic number Z , a single layer of graphene scatters less than 0.5% of the incident electrons [4]. Using inexpensive laboratory tools, we construct single crystal graphene electrodes that have defined lateral geometries, thicknesses selected at the atomic level, and are located with micrometer precision. Here we describe how to fabricate fluid cell graphene electrodes for the purpose of in situ liquid TEM, and give preliminary results demonstrating reversible ion motion over these single crystal, electron transparent electrodes.

Graphene is deposited onto Si/SiO₂ (90nm oxide) chips via micromechanical exfoliation of natural graphite flakes. When desired we modify the lateral geometries of found graphene sheets using tungsten probe tips electrochemically sharpened with an alternating voltage in 1 M KOH. After taking optical images for reference, PMMA (450K, 2% in anisole) is spun onto the chip for 1 minute, slowly accelerating to 3000 rpm. The chip is baked on a hot plate at 100° C for 1 minute and carbon-tipped tweezers are used to remove PMMA from the perimeter of the chip. This step prevents the PMMA/graphene sheet from sticking to the chip's bare Si edges during transfer. The chip is then submerged in a 1 M solution of NaOH for ~1 hour. The oxide is etched away and the PMMA/graphene sheet floats to the surface [5]. The sheet is scooped out of solution using the (now bare Si) source chip and transferred to clean, deionized water. Repeating the previous step further removes residual NaOH.

The PMMA/graphene sheet is then moved onto a fluid cell window chip with prepatterned Cr/Au electrodes, which in turn is placed on a clean microscope slide. The PMMA/graphene sheet floats on the thin layer of water between it and the window chip. Using nearby thicker sheets of graphene as location references, the incipient graphene electrode is repositioned using micromanipulators over the target location (generally spanning the electron transparent window and the Cr/Au electrodes). The sheet is then left in air to dry until the PMMA/graphene sheet is firmly adhered to the window chip. Occasional nudges with the micromanipulators correct drifts that occur during the drying.

After the bulk of the water has evaporated the chip is placed on a hot plate at 100°C for 20 minutes to remove excess water. The PMMA is then gently removed by first reapplying a few drops of the PMMA solution, then applying drops of acetone and isopropanol, and finally drying with nitrogen. After inspecting the chip to verify the success of the transfer, the chip is soaked in acetone for several hours, dipped in isopropanol, and dried with nitrogen. At this point the membrane window is further thinned with a vapor HF etch if necessary, and the chip is annealed on a hot plate at 300° C. Finally, the fluid cell is assembled as previously reported [2].

Figure 1 shows STEM images of a completed cell with graphene electrodes under bias. In this instance the cell solution consists of water and uranyl nitrate salt. The uranium ($Z = 92$) in the uranyl ion generates excellent contrast, and can be seen to decorate the graphene electrodes (primarily on along the edges). Reversing the applied bias causes the ions to shift to the other electrode, as illustrated by the difference image on the right in Figure 1. *In situ* electron diffraction (Fig. 1 inset) reveals that both graphene electrodes are derived from the same single crystal, and that their relative orientation has been preserved in the transfer process.

References:

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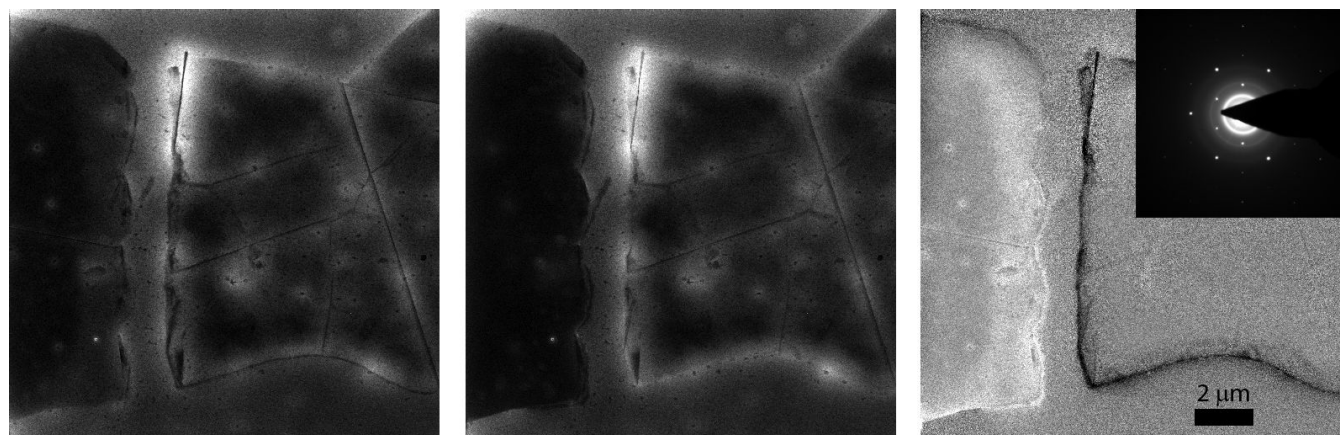


Figure 1. (left and center) Dark-field STEM images of two multi-layer graphene electrodes separated by $\sim 1\mu\text{m}$ via micromechanical sculpting. The graphene is enclosed in a fluid cell containing a saturated solution ($\sim 3\text{ M}$) of uranyl nitrate. The graphene electrodes are held at a potential difference of 1V, which causes the UO_2^{2+} ions to crowd the negatively charged electrode. The concentration of UO_2^{2+} ions at the electrode edges changes dramatically when the polarity of the potential difference is switched, which occurs between the left and center images. The rightmost image, the difference of the two STEM images to the left, highlights the ion shift. The electron diffraction pattern (inset) acquired from the electrode on the right shows a strong signal from the immersed crystalline carbon.