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Electron Microscopic Studies with Grapheme

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Graphene is a crystalline single layer of carbon atoms that can be viewed as an individual atomic plane extracted from graphite [1]. It has attracted a tremendous interest due to its outstanding electronic properties [2-5]. With a thickness of only one carbon atom, freely suspended mono-layer graphene is the thinnest possible membrane that is conceivable with currently known materials. Yet, it is remarkably stable under high-energy electron irradiation and thus opens unprecedented opportunities for electron microscopic studies [6-15]. On the one hand, the graphene membrane structure and its defects are of outstanding interest for the science and applications of this promising new material. Static deformations, topological defects, various vacancy configurations or dislocations have been detected by transmission electron microscopy (TEM) [6-8]. On the other hand, graphene membranes can serve as a perfect sample support for transmission electron microscopy. Its contribution to the TEM image signal can be filtered out completely, and adsorbed atoms and molecules on the graphene sheet can be imaged as if they were suspended in free space [8-10, 16]. Two examples, showing images of defects in graphene and of a low contrast molecular-scale adsorbate, are given below. The preparation of graphene membranes for TEM has been described elsewhere [7,12]. We use an imaging-side aberration corrected FEI Titan 80-300, operated at 80kV. The spherical aberration is set to ca. 10µm and imaging is done at Scherzer defocus. Atoms appear black under these conditions. The extraction voltage of the gun is set to 2kV in order to minimize the energy spread of the source [17]. Image sequences are recorded on the CCD camera and a drift-compensated averaging (5 to 10 frames) is used to improve the signal to noise ratio. The first image (Fig. 1a) shows a large defect-free single layer graphene sample. At 80kV, graphene is stable up to high doses of electron irradiation: In this case no defect was observed up to the end of a long image sequence with a total dose of 4·109 e-/nm2. Indeed, holes are rarely observed to form within a clean area, they mostly appear within or at the rim of a contamination region. This indicates that at 80kV, beam-induced chemical processes are the primary source of radiation damage for graphene. The situation is very different for higher acceleration voltages. The same sample was now touched briefly at an acceleration voltage of 300kV (dose ca. 107 e-/nm2), and then imaged again at 80kV. Unfortunately, a ~2hr wait was required to obtain stable conditions after switching the high tension, giving defects plenty of time to relax. Nevertheless, significant changes are found after this small dose. Most remarkably, the defective areas do not exhibit any “simple” vacancy configurations. We observe single-layer carbon patches incorporated into the membrane (Fig. 1b), where the atoms are still in a sp^2-bonded configuration with three neighbors but the hexagonal structure is perturbed. By comparison with the ideal lattice, we find that there are a few atoms missing from these areas, giving the membrane locally a lower density than the ideal lattice. This indicates that, after only a few atoms have been knocked out by the 300kV electron beam, about ~1nm-sized areas reconstruct around these defects as a consequence in order to satisfy the dangling bonds. As a second example, we show imaging of an amorphous, molecular-size adsorbate on the graphene sheet. Fig. 2 shows a single-layer graphene sheet with an adsorbate that itself is also mostly a single-layer carbon structure. The lattice of the graphene sheet has been removed by Fourier filtering. Although single exposures (Fig. 2a,b) can yield useful information, an average of several exposures is desirable in order to improve the signal to noise ratio. By following the image sequence,

we find that the adsorbate moves and also rotates on top of the graphene sheet, while the structure appears to remain mostly intact across several exposures. Therefore, we use an alignment algorithm that compensates for both translation and rotation. Such an algorithm is found in the StackReg plugin for the ImageJ software [18] (using the "rigid body" alignment). By applying it *after* the graphene lattice was removed by a Fourier filter, this now compensates for the drift and rotation of the adsorbate only. Figs. 2c,d now shows an 8-frame average of the adsorbate structure, clearly revealing the atomic structure in this amorphous piece of contamination (a structural model is overlaid in Fig. 2d). The appearance and contrast of the adsorbate resembles the defective regions in the graphene sheet, which strongly indicates that this adsorbate also predominantly consists of carbon. Again, nearly all of the atoms are bonded to three neighbors, i.e. we are looking at a sp^2-bonded planar but amorphous network of carbon atoms. Thus, by using the graphene membrane as a support and an acceleration voltage that does not damage the graphene membrane itself, the atomic configuration of a thin, non-periodic (amorphous) adsorbate can be resolved.

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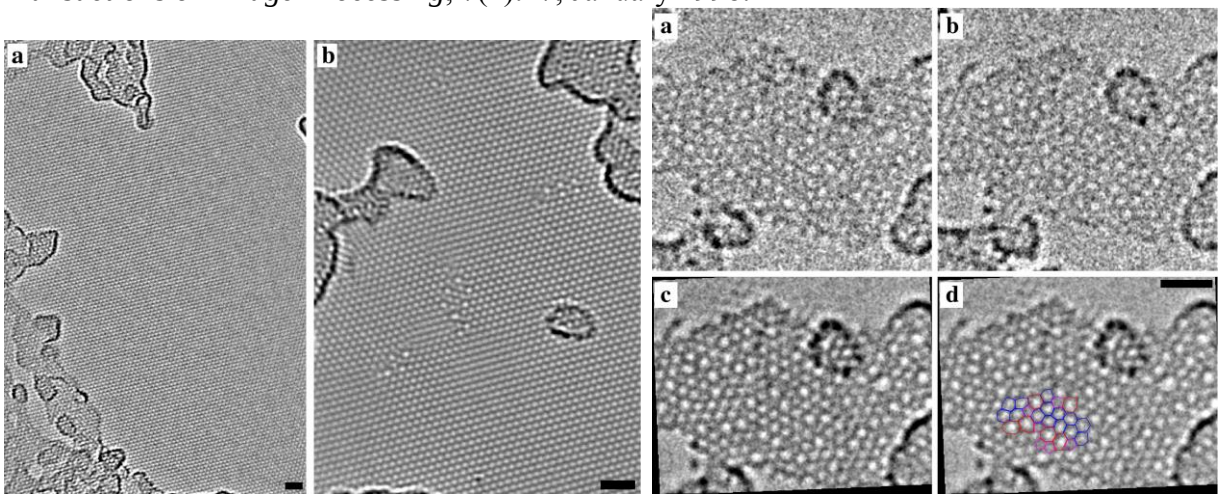

Figure 1: Defect-free graphene membrane, stable up to high doses at 80kV. (b) Graphene membrane briefly touched at 300kV; then imaged at 80kV. Scale bars are 1nm.

Figure 2: Adsorbate on a grapheme membrane. The lattice of the graphene sheet was removed by Fourier filtering. (a,b) Two exposures from an image sequence, where the adsorbate has slightly moved and rotated. (c,d) Drift- and rotation-compensated average of 8 exposures, clearly revealing the twodimensional amorphous structure. (d) Atomic model superimposed on part of the structure (atoms at the vertices, blue: carbon hexagons, red: heptagons, pink: pentagons). Scale bar 1nm.

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