From functionalizing inorganic two-dimensional materials on the level of single atoms towards molecular imaging of organic two-dimensional materials

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Prerequisite for functionalizing two-dimensional inorganic materials using the electron beam in a transmission electron microscope is the detailed understanding of the beam electron - sample interactions. We derive this basic knowledge from atomically-resolved, time-dependent in-situ TEM imaging of inorganic two-dimensional (2D) transition metal dichalcogenides (TMDs) using the chromatic- and spherical-aberration-corrected low-voltage SALVE instrument operating in the voltage range between 80kV and 20kV.

We show for different single-layer TMDs that in dependence of the electron accelerating voltage and applied electron dose the defect formation can be initiated. Applying this knowledge, in-situ and ex-situ structural and chemical transformations of different freestanding TMDs and of more rarely reported TMPTs (TM phosphorus tri-chalcogenides) are performed and verified by complementary ab-initio calculations.

For lateral heterostructures we show near-atomically sharp junctions with a typical extent of 3 nm for the covalently bonded MoSe2-WSe2 interface and use this knowledge to explain the considerably narrowed optical transition linewidth in the PL and Raman spectroscopy. Further we show proof-of-principle experiments in which we transfer electron-exposed TMD flakes from a TEM grid to arbitrary substrates to directly relate the results of the photoluminescence and transport measurements to their structural origin.

For vertical few-layer heterostructures we study the effect of interlayer excitons in WSe2 located in the low-loss range of the EELS spectrum. In few-layer graphene heterostructure we discuss the Li crystal nucleation mechanism from in-situ studies of a miniaturized electrochemical cell, where reversibly single-crystalline bilayer graphene is lithiated and delithiated in controlled manner using an electrochemical gate confined to a device protrusion.

The knowledge gained for the study of 2D inorganic materials we apply to the study of 2D polymers and 2D metal-organic frameworks (MOFs), however, not surprisingly, functionalization and even atomically-resolved imaging is hindered due to much lower resilience of the organic material during electron irradiation. We present key strategies to achieve nevertheless higher resolution in high-resolution TEM images of imine-based 2D polymer films, which include the selection of a surprisingly low electron accelerating voltage of 120kV for achieving a resolution of 1.9A, enabling imaging the linker molecules. Further, we study experimentally and computationally the role of different organometallic bonds and hydrogen content on electron radiation stability, using a group of four structurally similar Cu-based 2D MOFs.

We summarize our results in one sentence that 2D materials and lower-voltage atomic (molecular) resolution TEM/STEM are just made for each other