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

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To functionalize and image two-dimensional inorganic materials using the electron beam in a transmission electron microscope, a prerequisite is the detailed understanding of the beam electron - sample interaction is required. 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 rarely reported TMPTs (TM phosphorus tri-chalcogenides) are performed and varified 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 $MoSe_2$-WSe_2 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 as function of the twist-angle and material. 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. Moreover this resolution allowed even imaging the molecular nature of interstitial defects, which was interpreted by means of quantum mechanical calculations. 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.