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Understanding Imaging Contrast at Low Acceleration Voltages Exemplified on Two-dimensional Materials and Properties of Advanced Two-dimensional Materials by Low-voltage TEM

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A new type of transmission electron microscopes operating at electron energies between 80keV and 20keV is developed to obtain structural and electronic properties of advanced low-dimensional material at the atomic scale. It allows to undercut most of the pristine material's knock-on damage thresholds and enables sub-Angstroem resolution in a single-exposure image down to 40keV by correcting not only the geometrical aberrations of the objective lens but also its chromatic aberration [1,2,3,4]. The increased HRTEM image contrast with decreasing voltage is demonstrated in a systematic voltage-dependent HRTEM study of graphene and $MoTe_2$. Comparison between simulated and experimental images show quantitative fit.

Cc/Cs-corrected imaging allows the use of most elastically and inelastic scattered electrons for image formation, without the loss of beam intensity resulting from monochromation. In combination with an imaging energy filter, it is possible to form atomic-resolution EFTEM images using plasmon-loss or core-energy-loss electrons. For atomic-resolution energy-filtered TEM not only correction of the chromatic aberration of the objective lens is required but also the performance of the imaging energy filter must satisfy the conditions that primarily chromatic distortions and non-isochromaticity are kept very small. We show energy-filtered transmission electron microscopy (EFTEM) imaging of graphene at atomic resolution for large energy windows. Previous works demonstrated lattice contrast from ionization-edge signals such as the $L_{2,3}$ edges of silicon or titanium [5,6]. However, the direct interpretation as chemical information was found to be hampered by contributions from elastic contrast from dynamic scattering due to thick samples. We demonstrate that the elastic contrast is preserved even in the ionization-edge signal of a one light-atom thin sample – graphene - and conclude that any atomic-resolution EFTEM image cannot be interpreted in terms of pure chemical contrast [7].

During the HRTEM imaging process, however, the interaction between beam electrons and the material can result in changes of the 2D material's atomic structure due to inelastic channels [8] but so far there is no quantitative microscopic theory describing the relation between electronic excitations and damage creation. Here we show that non-adiabatic Ehrenfest dynamics combined with time-dependent density-functional theory (TD-DFT), along with constrained DFT molecular dynamics, allow to understand the experimentally observed defect production in 2D MoS_2 under electron beam energies in the range of 20-80 keV [9]. To image the pristine structure of a 2D material, sophisticated sample preparation methods must be employed to reduce these effects [10]. We find that from the evolution of defect under defined electron exposure, the number of intrinsic defect can be determined.

However, not only the structure of the pristine material is of interest. With the defined and shaped electron beam also defined properties can be engineer. Thus, we show the dynamics of single point defects and of extended defect formation in $MoTe_2$, WSe_2 and/or WS_2 and understand their formation characteristics and their properties from related first principle calculations [11]. In the case of $TaSe_2$ we demonstrate the

creation of commensurate charge density wave (CDW) in a monolayer 1T-$TaSe_2$ [12], and show that the CDW's order varies due to an increase in the S/Se vacancies [13].

To determine the electronic structure of 2D materials, low-loss spectra of MoS_2 and WS_2 are studied by momentum-resolved (MR)-EELS. Firstly, the A and B exciton peaks are observed in the spectrum of pristine WS_2, and the change of the peaks due to electron-beam-induced interactions is investigated over time. HRTEM images of the illuminated WS_2 area show the destruction of the sample region over time and allow linking the variation of the electronic properties to the observed structural changes. Secondly, for monolayer MoS_2, few-layer $MnPS_3$ [14], as well as few-layer freestanding $FePS_3$ [15], MR-EELS spectra for the ΓK and ΓM directions are shown. Our calculations support the experimental results providing insight into layer-number-dependent changes in the electronic properties of $FePS_3$ as result of lowering the dimensionality.

Finally, we intercalate bilayer graphene by lithium and study the in-situ lithiation and delithiation between bilayer graphene, with emphasis on understanding the nucleation process of the new high density crystalline Li- phase [16].

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