

Supplementary information:

Post-Synthesis Modifications of Two-Dimensional MoSe₂ or MoTe₂ by Incorporation of Excess Metal Atoms into the Crystal Structure

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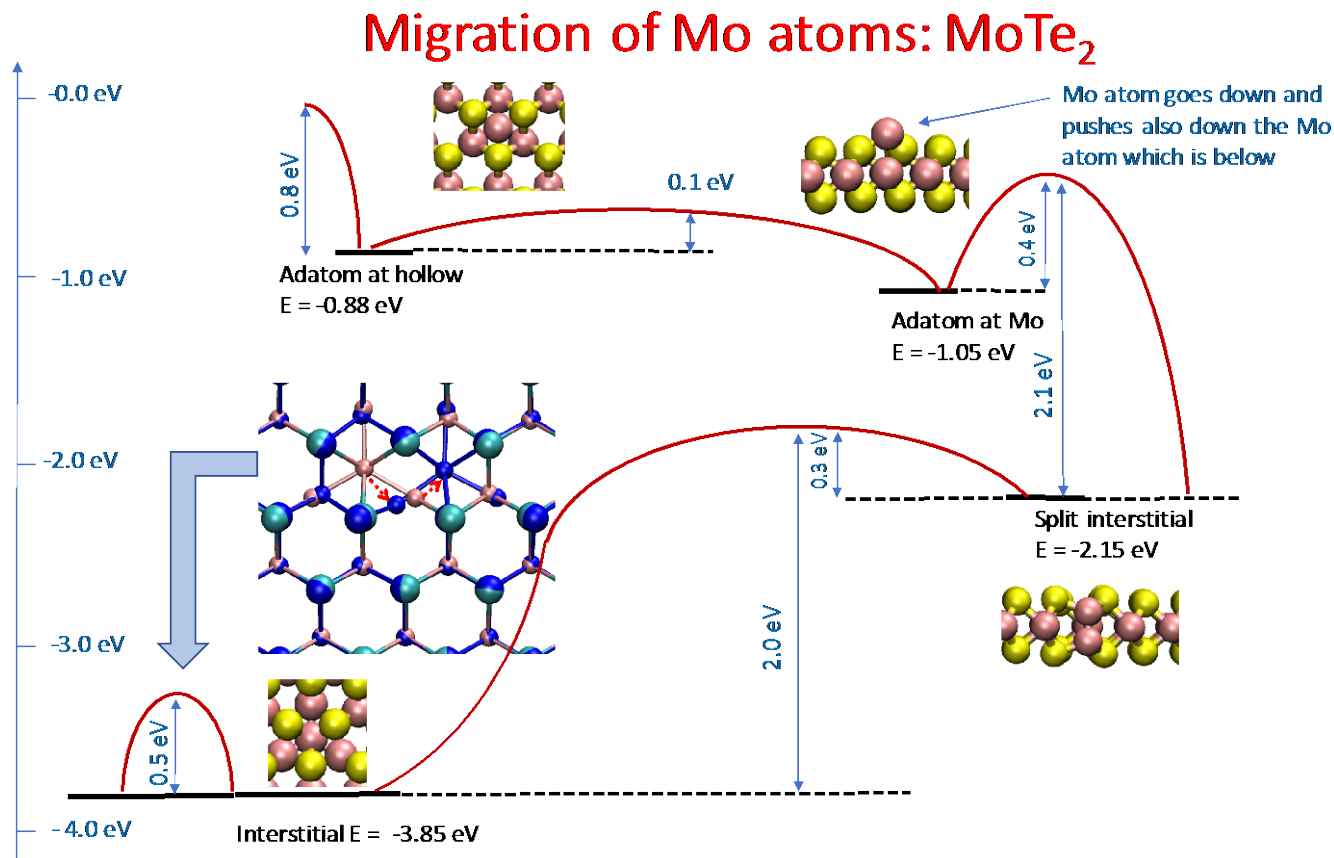


Figure S1. Energetics and migration barriers of Mo atoms adsorbed on MoTe₂ sheet, as revealed by NEB DFT calculations. Yellow balls represent Te atoms, pink ones stand for Mo. Zero energy corresponds to isolated Mo atom and MoTe₂ sheet. Mo atom adsorbed on the MoTe₂ surface will take a position on top of a Mo atom, then both will form a split interstitial, followed by a transformation to the interstitial (middle of hexagon) configuration. The interstitial can migrate within the plane by exchange mechanism with a migration barrier of 0.5 eV. The migration path shown in the middle of the figure. Note that the atoms are colored differently for the initial and final configurations. Mo interstitials should be mobile at $T > 200$ K and do not reappear on the surface.

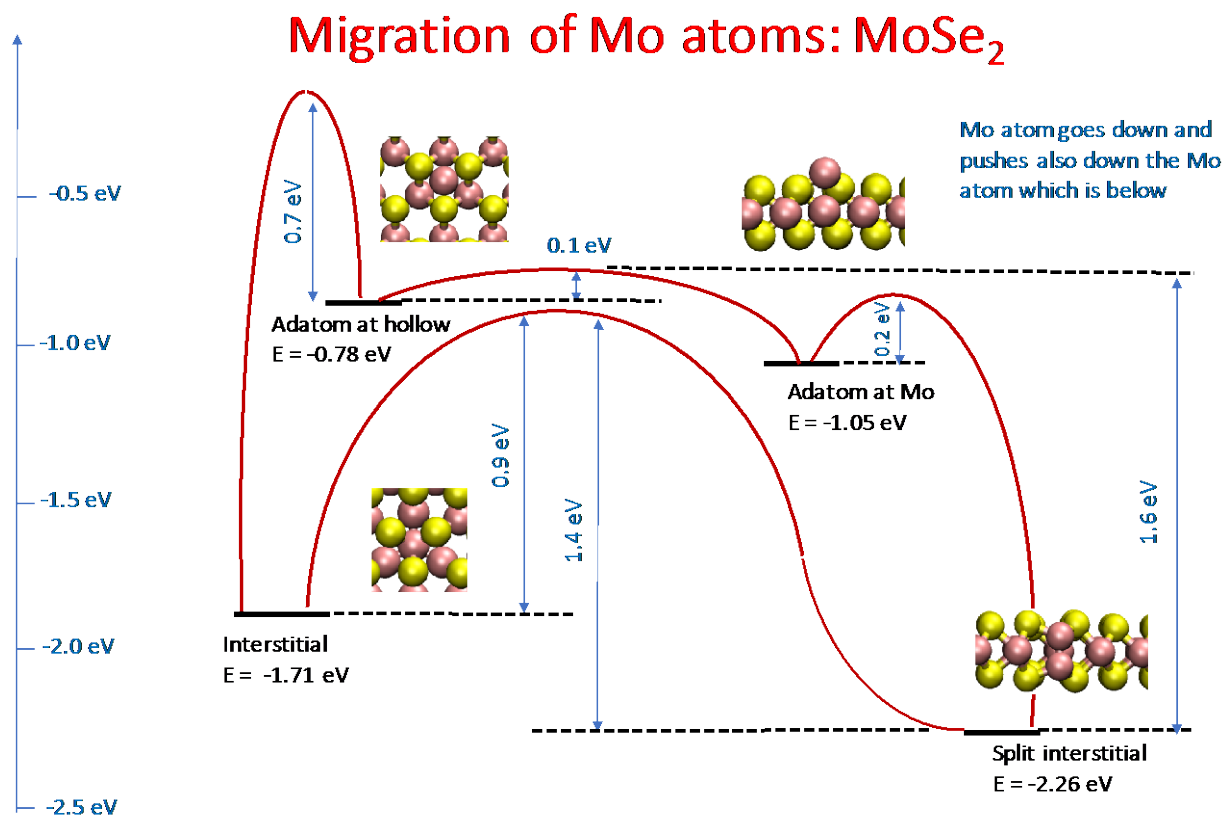


Figure S2. Energetics and migration barriers of Mo atoms adsorbed on MoSe₂ sheet, as revealed by NEB DFT calculations. Yellow balls represent Se atoms, pink ones stand for Mo. Zero energy corresponds to isolated Mo atom and MoTe₂ sheet. Mo atom adsorbed on the MoSe₂ surface will take a position on top of a Mo atom, then both will form a split interstitial, which is the lowest energy configuration. The interstitial can migrate with a barrier of ~ 1.5 eV either within the plane through the interstitial position or by resurfacing.

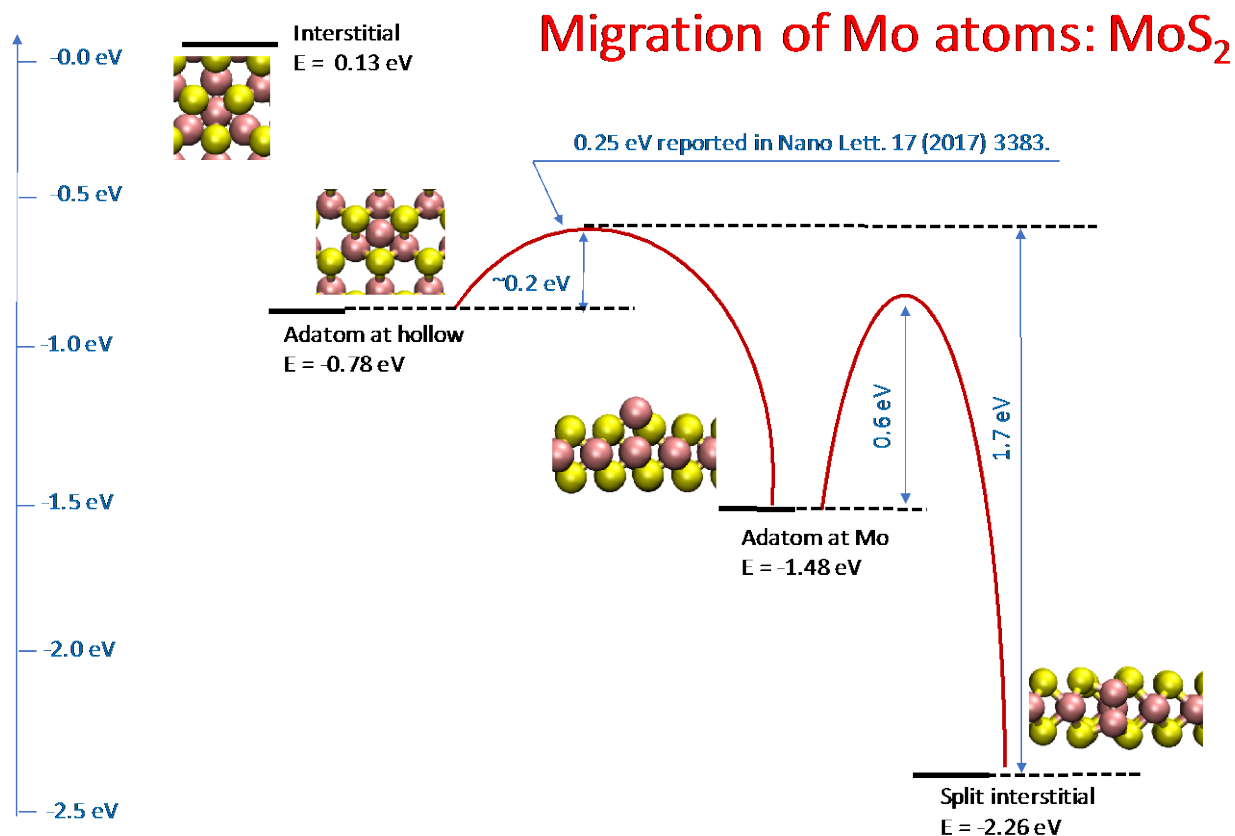


Figure S3. Energetics and migration barriers of Mo atoms adsorbed on MoS₂ sheet, as revealed by NEB DFT calculations. Yellow balls represent S atoms, pink ones stand for Mo. Zero energy corresponds to isolated Mo atom and MoTe₂ sheet. Mo atom absorbed on the MoS₂ surface will take a position on top of a Mo atom, then both will form a split interstitial, which is the lowest energy configuration. The interstitial can migrate with a barrier of $\sim 1.7 \text{ eV}$ by resurfacing.

It is worthwhile pointing out that surface modifications with MTBs naturally induces IDs. Such IDs will have different stacking relative to the second layer than the natural 2H-stacking of Mo-dichalcogenides. It is known that the stacking and interlayer interactions does influence the band maximum at the Γ -point. Consequently, there may be a small error in the above measurements at the Γ -point due to broadening of the VBM by the formation of IDs. Thus we performed also measurements for the shift of the VBM at the K-point. The results of these measurements are shown in Fig. S4. The same trend for the shift of the VBM is observed at the K-point as for the Γ -point. However, a slightly larger upward shift of the VBM at the K-point are measured of 160 meV and 50 meV for MoTe₂ and MoSe₂, respectively. This slight variation is consistent with a small relative shift of the VBM at the Γ - and K- points due to modifications of interlayer interactions as the consequence of the formation of IDs.

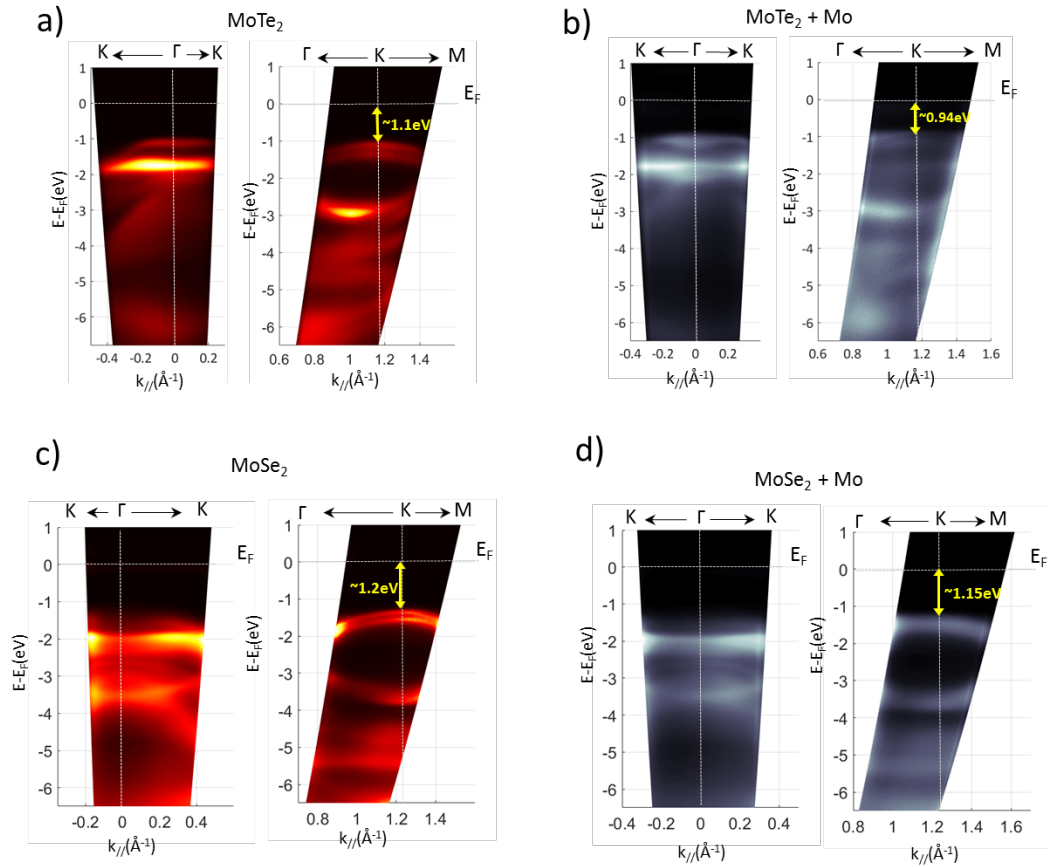


Figure S4. ARPES studies of MoTe₂ and MoSe₂ single crystal surface before and after MTB formation. He-I ARPES spectra of the MoTe₂ single crystal before and after Mo deposition at 350°C are shown in (a) and (b) respectively. He-I ARPES spectra of the MoSe₂ single crystal before and after Mo deposition at 350°C are shown in (c) and (d) respectively. The change in the valence band maximum at the K-point before and after formation of MTBs is indicated for both samples.