

Supplementary material

Exciton-Driven Two-Step Charge Transfer in MoS₂- WSe₂ Heterostructures Revealed by Valley-Resolved Broadband Pump–Probe Spectroscopy

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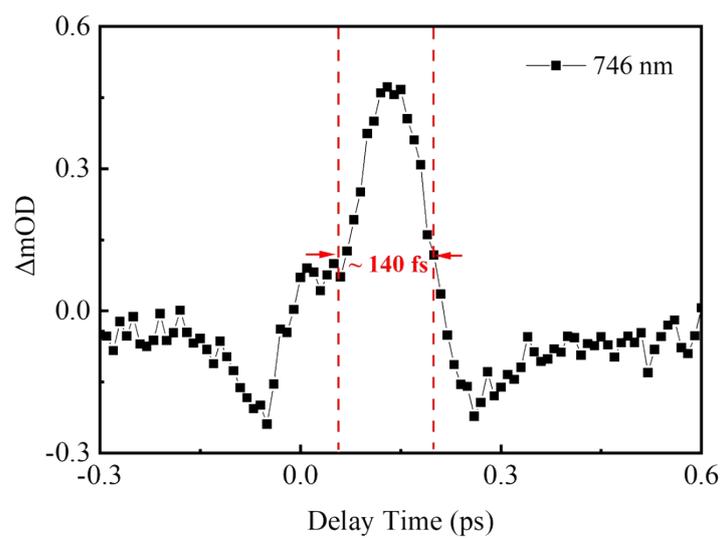


Figure S1 Instrument response function (IRF) with a ~ 140 fs FWHM. The IRF was measured via cross-correlation between the 750 nm pump and the white-light probe at 746 nm on sapphire.

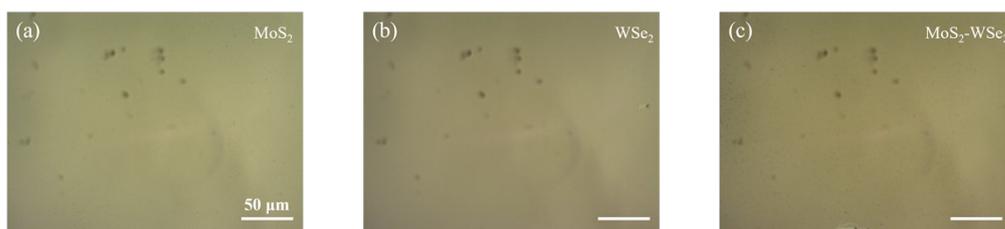


Figure S2 The optical images of MoS₂, WSe₂, MoS₂-WSe₂ heterostructure (HS).

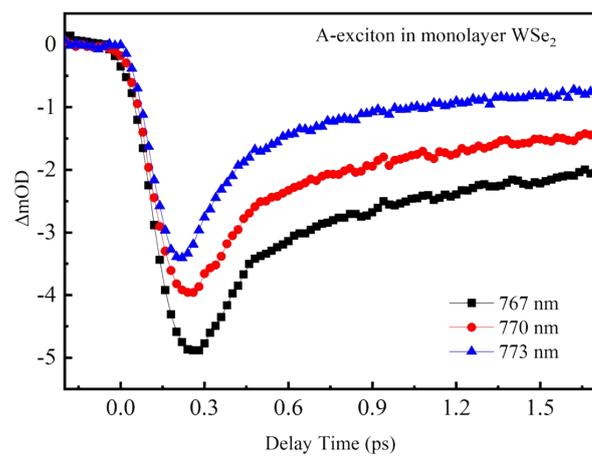


Figure S3 Dynamics of the A-exciton in monolayer WSe₂.

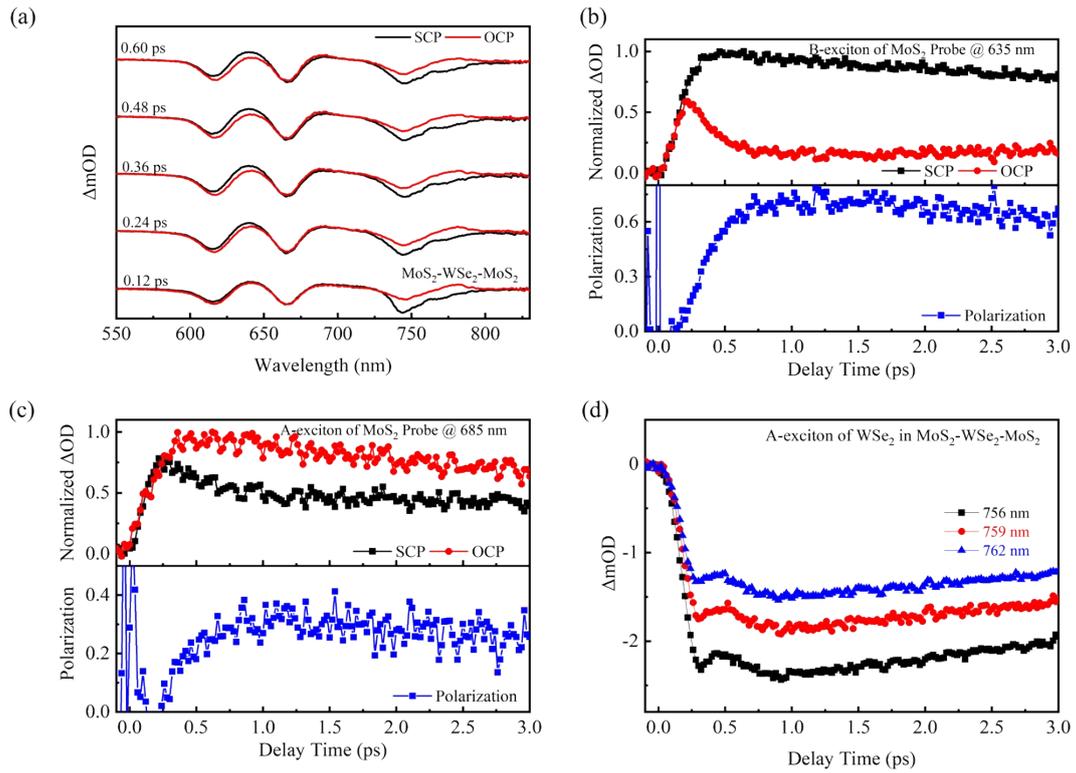


Figure S4 a) TA spectra of MoS₂-WSe₂-MoS₂ trilayer HS. SCP and OCP dynamics (top panel) and spin-valley polarization dynamics (bottom panel) of b) B-exciton and c) A-exciton in MoS₂ within the MoS₂-WSe₂-MoS₂ HS. (c) Dynamics of the A-exciton in WSe₂ within the MoS₂-WSe₂-MoS₂ HS.

Supplementary Note 1: Discussion of alternative interpretations for the rising component in the WSe₂ ground-state bleaching signal

The ~1 ps rising component observed in the WSe₂ A-exciton ground-state bleaching (GSB) dynamics (Fig. 3c) is a key signature of the charge transfer process. We have considered three alternative interpretations suggested during review:

- i. **Relaxation of residual electrons in WSe₂.** This process describes intralayer cooling of electrons that remain in the WSe₂ conduction band. However, such electron relaxation does not increase the hole population at the valence band maximum and therefore cannot produce a rise in the GSB signal. We thus rule out this mechanism.
- ii. **Back-transfer of electrons from MoS₂ to WSe₂.** This process would reduce hole occupancy at the valence band maximum via recombination and should manifest as a decay component in the GSB signal. The observed feature is a rise, and no corresponding decay is seen in the MoS₂ GSB kinetics (Fig. 3a-b). Back-transfer is therefore not a meaningful contributor.
- iii. **Valence-band hole filling by higher-energy electrons.** We interpret this possibility as the relaxation of hot holes from higher-lying valence band states to the valence band maximum. This process increases the band-edge hole population and produces a rise in the GSB signal, consistent with our observation. The absence of this feature in monolayer WSe₂ (Fig. S3) confirms that it is not intrinsic hole cooling but is specifically enabled by the ultrafast electron extraction, which leaves behind a distribution of hot holes. This assignment provides a symmetric picture with the electron relaxation dynamics inferred from the delayed valley polarization build-up in MoS₂.