Supplementary Information for

Reversed charge transfer in type Ⅰ $MoS_2/PtSe_2$ heterostructure probed by ultrafast two-dimensional electronic spectroscopy

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Section 1. Full range absorption spectra of the samples

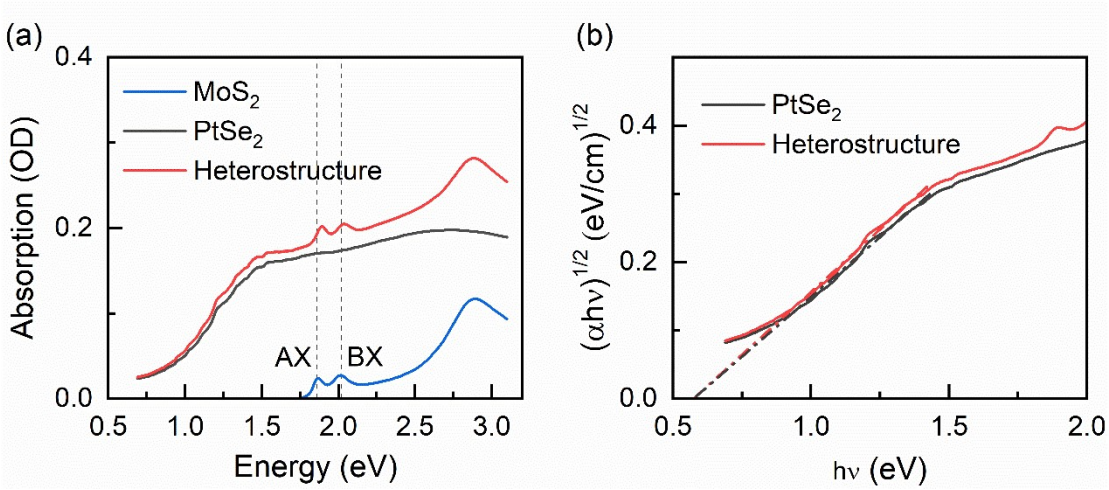

Fig. S1 (a) Full range absorption spectra of MoS_2, $PtSe_2$, and the heterostructure. (b) The Tauc plots of bare $PtSe_2$ and heterostructure which are obtained by: $(\alpha h\nu)^{1/2} = B(h\nu - E_g)$. Here, E_g represents for indirect bandgap, hν is photon energy (h = 4.13 × 10^{-15} eV · s is Planck's constant, ν is the frequency of the light), α is absorption coefficient and B is a constant. Thus, by extracting the intercept with the x-axis, the bandgap E_g can be determined by fitting the linear relationship between $(\alpha h\nu)^{1/2}$ and $h\nu$. The result shows that bare $PtSe_2$ and the $PtSe_2$ in the heterostructure have similar optical bandgap of 0.57 eV.

Section 2. Fitting procedure and time constants of the dynamics in transient transmission spectra

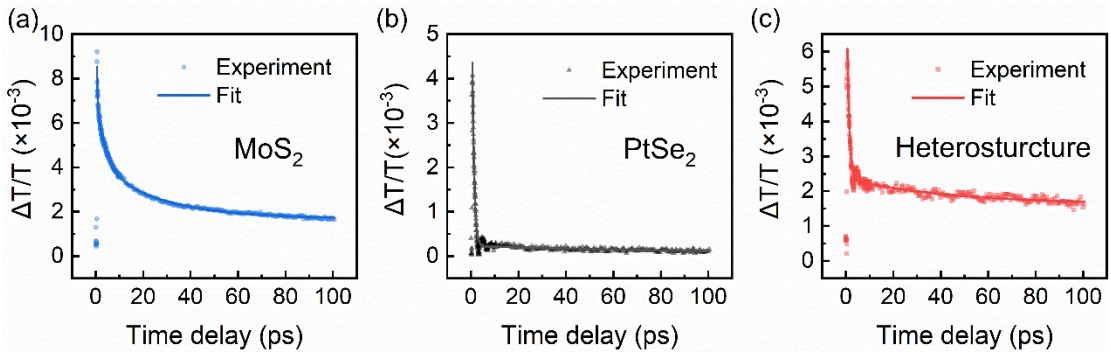

Fig. S2 Experimental peak dynamics (symbols) and multi-exponential fitting results (lines). (a) A exciton bleaching signal at 1.86 eV probe energy from the bare MoS_2 sample. (b) Bleaching signal at 1.87 eV probe energy from the bare $PtSe_2$ sample. (c) A exciton bleaching signal at 1.87 eV probe energy from the heterostructure sample.

Multi-exponential fitting is applied to extract the kinetic behavior in transient transmission data. The interested probe energy is selected to be the MoS_2 A exciton bleaching peak for bare MoS_2 (1.86 eV) and the heterostructure (1.87 eV). For bare $PtSe_2$, since its response is broadband, we also chose the signal at 1.87 eV to examine the relaxation dynamics. Note that the dynamics in bare $PtSe_2$ does not vary for different probe energy. The fitted results are reported in Figure S2 as solid lines, which well reproduce the experimental data (symbols), and the fitted time parameters are listed in Table S1.

We found that the dynamics of bare $PtSe_2$ (Fig. S2b) can be well fitted with a bi-exponential function $F_1(t)$,

$$F_1(t) = A_1\exp\left(-\frac{t}{\tau_1}\right) + A_2\exp\left(-\frac{t}{\tau_2}\right) + y_0. \quad (1)$$

in which the two time constants τ_1 and τ_2 represents defect trapping and Auger recombination, respectively.[1]

The dynamics of bare MoS_2 can be fitted with a three-exponential decay function $F_2(t)$,

$$F_2(t) = A_1\exp\left(-\frac{t}{\tau_1}\right) + A_2\exp\left(-\frac{t}{\tau_2}\right) + A_3\exp\left(-\frac{t}{\tau_3}\right) + y_0. \quad (2)$$

in which τ_1, τ_2, τ_3 represents for defects-assisted intraband scattering, fast trapping of excitons by surfaces defects and carrier–phonon scattering, respectively.[2] In equations (1-2), τ_i are decay times, A_i are the weights of the respective exponential

functions, and y_0 is the base line value.

The dynamics at the A exciton bleaching peak of the heterostructure can also be fitted with a bi-exponential function (Fig. S2a). Since the signal of the heterostructure at this probe energy contains both the $PtSe_2$ response and the A exciton dynamics of MoS_2, we assign the early time dynamics to be dominant by the $PtSe_2$. The latter decay constant is mainly contributed by A exciton relaxation dynamics because the signal of $PtSe_2$ is much weaker than that of MoS_2 in this probe energy (see Fig. 2g in the main text). Table S1. Fitted time constants from the multi-exponential decay model.

Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
MoS_2	0.26 ± 0.02	3.93 ± 0.21	26.37 ± 1.45
$PtSe_2$	0.78 ± 0.01	136.74 ± 22.65	—
Heterostructure	0.86 ± 0.03	44.89 ± 9.05	—

Section 3. Peak dynamics in 2DES maps

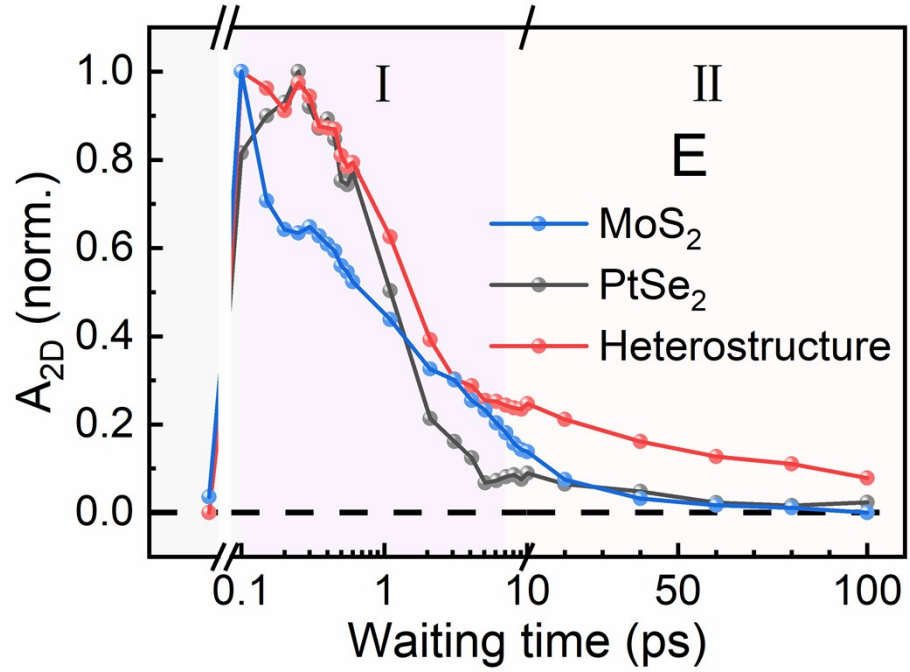

Fig. S3 Normalized peak dynamics of the region marked as E in the 2DES maps in Figure 3c. Region E corresponds for the A exciton bleaching response in MoS_2 and the heterostructure.

Before 2 ps, the signal in the heterostructure decays slower compared to that of bare $PtSe_2$, suggesting the existence of charge transfer, which prolongs the relaxation as the charges are separated in different materials. Further, there is an additional slow decay after a few picoseconds in the heterostructure, much slower than that of bare MoS_2. This feature is consistent with the results in region C (fig .4c), corresponding to Auger-assisted secondary charge transfer.

Reference

1. H. J. Shin, S. Bae and S. Sim, *Nanoscale*, 2020, **12**, 22185.
2. H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing and L. Huang, *ACS Nano*, 2013, **7**, 1072.