SUPPORTING INFORMATION

The Role of Excitons and Free Charges in the Excited-State Dynamics of Solution-Processed Few-Layer MoS_2 Nanoflakes

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1. Estimation of the nanoflake thickness

To obtain an estimate of the average number of layers in the solution-processed few-layer MoS_2 nanoflake thin films, the absorbance spectrum shown in Figure S1 was used.

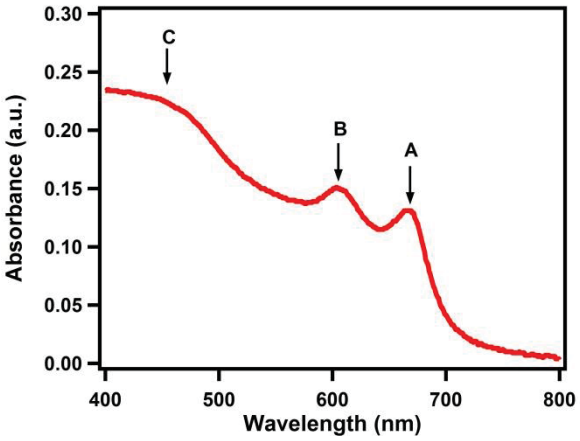

FIGURE S1. Absorption spectrum of the few-layer MoS_2 nanoflake thin film prepared by the self-assembly method. The arrows indicate the A, B and C excitonic transition peaks measured at 673, 611 and 453 nm, respectively.

The absorbance peaks at 611 nm (= 2.03 eV) and 673 nm (= 1.84 eV) are associated with the A and B excitonic transitions. These transitions take place at the K point of the Brillouin zone between a local conduction band minimum and two maxima of the valence bands that are largely energetically separated due to spin-orbit coupling.[1-2] An additional absorbance peak at higher energies, named excitons C (= 453 nm), is attributed to transitions from the valence band to the nested region of the conduction band or a transition from a deep valence band to the conduction band.[3-4] To estimate the average thickness of the MoS_2 nanoflakes the absorption coefficient[5] of bulk MoS_2 at the excitonic absorption peaks was

used and the thickness was found to be ~ 10 nm (representing an average thickness). The deposition method used to prepare the thin film of MoS_2 ensures that only one layer of nanoflakes is deposited on the substrate.[6-7] Thus, the average film thickness is used to estimate the average number of atomic layers in these nanoflakes, using the interlayer stacking distance of the bulk material (~ 0.62 nm) and found to be ~ 16. Taking into account the distribution of different flake thicknesses we estimate that the nanoflakes range from 10-20 atomic layers.

2. Additional TA data

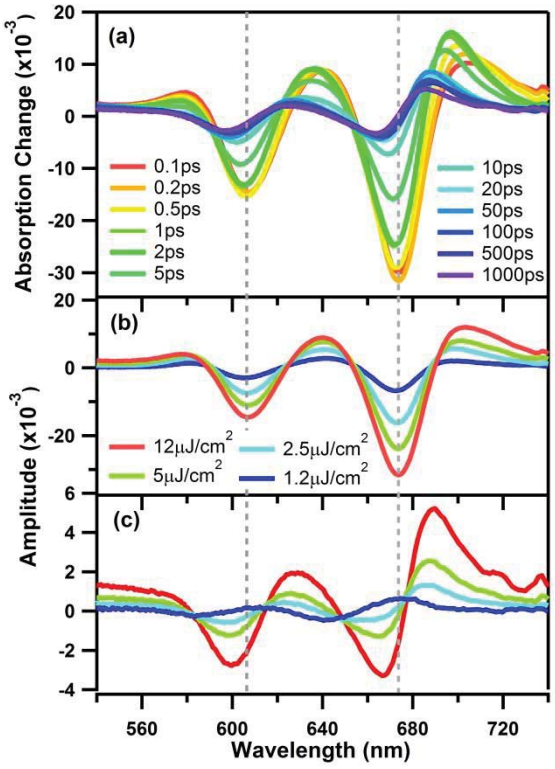

FIGURE S2**.** (a-c) TA spectra following excitation with a higher photon energy of ~3 eV (410 nm) at a) various time delays and a pump fluence of ~12 μJ/cm^2, and at pump fluences between 1.2-12 μJ/cm^2 at (b) early (t = 0.2 ps) and (c) long (t = 1 ns) times.

TA measurements were also performed using excitation at 400 nm; thus the photoexcited carriers possess more initial excess kinetic energy. The TA spectra at different time delays for an absorbed pump fluence of ~12 μJ/cm^2 are shown in figure S2a. Additionally, the TA spectra at early (t = 0.2 ps) and long (t = 1 ns) times at pump fluences between 1.2-12 μJ/cm^2 are included in Figures S2b and S2c, respectively.

For better visualization of the initial blue-shift observed at short time delays (see discussion in the main text), the TA spectra at fast time delays between 0.1-3 ps for a pump fluence of ~1.1 μJ/cm^2 (600 nm excitation) are shown in Figure S3.

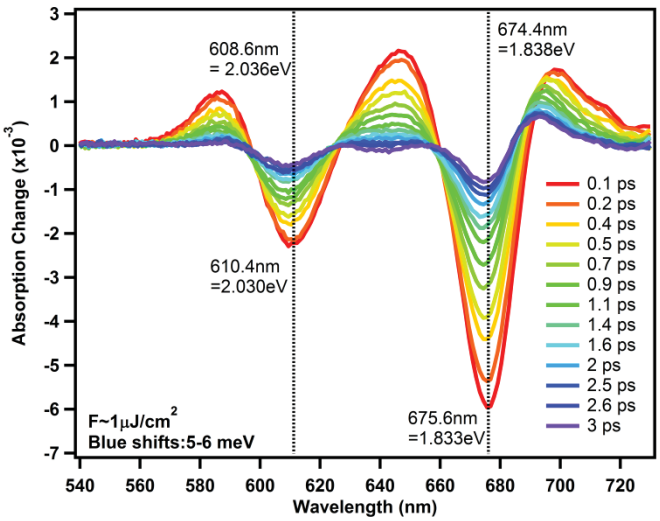

FIGURE S3. TA spectra in few-layer MoS_2 nanoflakes recorded following photoexcitation at 600 nm at an absorbed pump fluence of ~1.1 μJ/cm^2.

Figure S4 shows the results from the global analysis for the TA spectra recorded using excitation at 410 nm at various pump fluences. Similar observations to the ones made for excitation at 600 nm can be extracted. While the fast and show components show a gradual red shift with pump fluence and sub-linear dependence, the intermediate component does not

exhibit any shift even for the highest pump fluence used. Excitation at 410 nm results in the photogeneration of a higher density of charges, thus the shifts observed are larger and the contribution of the charges to the fast relaxation component is more important.

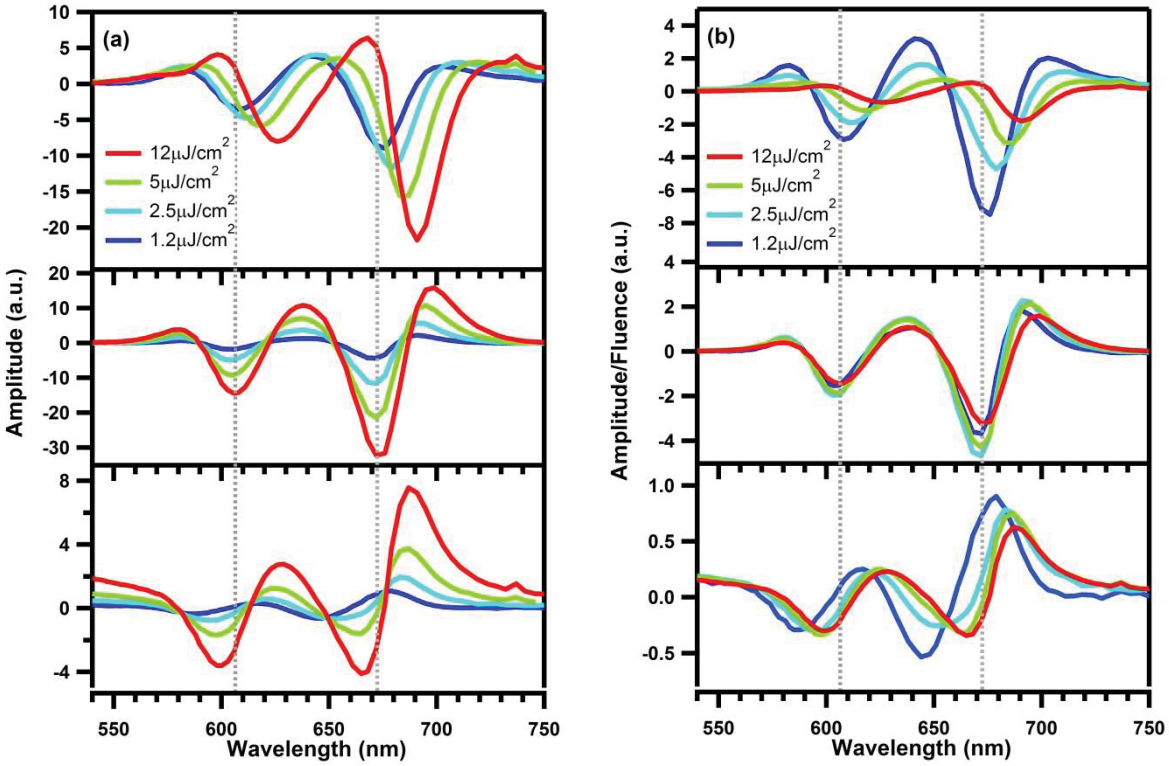

FIGURE S4. a) Amplitude spectra for excitation at 410 nm and different pump fluences between 1.2-12 μJ/cm^2 for the fast time constant of 0.5 ps (top), an intermediate one of 5.5 ps (middle) and the long (bottom) component. b) The respective amplitude spectra scaled with the pump fluence are shown.

References

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