Ultrafast charge transfer in atomically thin MoS$_2$/WS$_2$ heterostructures

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1. Determination of band alignment in MoS\textsubscript{2}/WS\textsubscript{2} heterostructure

In general, electronic band alignment in heterostructure is determined by relative energy levels with respect to vacuum level and initial doping concentration. In this study, the MoS\textsubscript{2}/WS\textsubscript{2} layers is predicted to form a type-II heterostructure where conduction band minimum (CBM) is at MoS\textsubscript{2} and valence band maximum (VBM) is at WS\textsubscript{2} as described in Figure 1a. Such band alignment have been shown to be valid in several theoretical investigations, and is consistent with the physical consideration of ionization potential of Mo and W atoms. It is also consistent with our data on photoconductivity from the MoS\textsubscript{2}/WS\textsubscript{2} heterostructures.

1. Relative energy level calculation in literature

To date, there have been 5 theoretical investigations on MoS\textsubscript{2}/WS\textsubscript{2} heterostructures using different parameters by different groups (See Ref. 1-5). Although the quantitative energy levels differ in different studies, they all predict the same type-II band alignment. The DFT calculations also agree well with the experimentally determined valence band energies in MoS\textsubscript{2} and WSe\textsubscript{2} bulk crystals (See for example Ref 6).

MoS\textsubscript{2} and WS\textsubscript{2} have almost exactly the same atomic arrangement and bond length. The only difference in MoS\textsubscript{2} and WS\textsubscript{2} is the transition metal. The valance band maximum and conduction band minimum are composed of d-orbitals of transition metal and p-orbitals of sulfur. The 4d electrons in Mo have appreciably larger ionization energy than the 5d electrons in W. As a result, the valance band of MoS\textsubscript{2} has a larger ionization energy than that of WS\textsubscript{2}, and leads to the formation of a type-II band alignment in MoS\textsubscript{2}/WS\textsubscript{2} heterostructures.

2. Photocurrent measurements

We have performed photocurrent measurements on MoS\textsubscript{2}/WS\textsubscript{2} heterostructures at zero bias. We observed positive current flows from MoS\textsubscript{2} to WS\textsubscript{2} upon optical excitation of the MoS\textsubscript{2} layer as shown in Figure S1. This is consistent with efficient hole transfer from the MoS\textsubscript{2} layer to the WS\textsubscript{2} layer.

![Figure S1. Photocurrent measurement of MoS\textsubscript{2}/WS\textsubscript{2} heterostructure at zero bias. a. Schematic illustration of the photocurrent measurement. No bias was applied.](image)
applied between the electrodes. Optical radiation with photon energy below 1.907 eV was used to excite MoS\textsubscript{2} only. \textbf{b.} Measured photocurrent. The positive sign means the current is flowing from MoS\textsubscript{2} to WS\textsubscript{2}, a direct verification of the type-II band alignment.

2. Initial doping levels and built-in field in MoS\textsubscript{2}/WS\textsubscript{2} heterostructure

Reference 7 demonstrates that the exciton absorption peak of MoS\textsubscript{2} monolayers broadens upon both n- and p-doping due to the effect of trion states. Therefore gate-dependent optical absorption spectra of MoS\textsubscript{2} and WS\textsubscript{2} layers provide a convenient way to estimate the initial charge doping. Figure S2 shows our data on gate-dependent reflection spectra of MoS\textsubscript{2} and WS\textsubscript{2} layers using an ionic liquid gating. It shows that the MoS\textsubscript{2} is initially weakly n-doped and the as prepared WS\textsubscript{2} layer is largely intrinsic.

![Figure S2. Gate-dependent absorption spectra of pristine (a) MoS\textsubscript{2} and (b) WS\textsubscript{2}. Absorption peak starts broadening at -0.5 V (MoS\textsubscript{2}) and 1.6 V (WS\textsubscript{2}) due to optical transition from trions. At 0 V, MoS\textsubscript{2} is n-doped and WS\textsubscript{2} is largely intrinsic. This measurement is done in room temperature.](image)

The relative band alignment between isolated MoS\textsubscript{2} and WS\textsubscript{2} monolayers is illustrated in Figure. S3a. Upon the formation of the MoS\textsubscript{2}/WS\textsubscript{2} heterostructure, the Fermi level has to align in both materials. This can be achieved by a shift of the WS\textsubscript{2} Fermi energy without introducing a significant built in electrical field because the Fermi level in WS\textsubscript{2} is within the bandgap. Therefore we expect the band alignment in the MoS\textsubscript{2} and WS\textsubscript{2} heterostructures to form a type-II structure with a relatively weak built in electrical field, as illustrated in Figure S3b.
Figure S3. Illustration of Fermi level shift upon contact. a. Before contact, both materials have the same vacuum level and there is no electric field between them. MoS$_2$ is n-doped and WS$_2$ is more intrinsic, as determined in Figure S2. b. After contact, the Fermi level in the two materials will become the same. This can be achieved by a shift of the WS$_2$ Fermi energy without introducing a significant built in electrical field because the Fermi level in WS$_2$ will remain within the bandgap.

3. Effect of annealing on PL quenching and Raman

We annealed our samples in order to improve the contact between the MoS$_2$ and WS$_2$ layers. Based on the previous studies on 2D heterostructures,$^{8,9}$ we tried two different annealing conditions, and studied corresponding results in terms of PL quenching and lattice vibration: 120 °C for 6 hours and 300 °C for 3 hours, both at $10^{-5}$ mbar vacuum pressure. We found these two annealing conditions gave similar results.

Figure S4a demonstrates typical atomic force microscope image across the boundary of heterostructure and pristine WS$_2$ before and after annealing. Before annealing, there is significant PMMA polymer residue on top of the heterostructure (upper panel in Figure S4a). We observed a step increase at the boundary of the WS$_2$ layer and the MoS$_2$/WS$_2$ heterostructure, however the step height is affected by the polymer residue. After annealing, the polymer residues are significantly reduced (lower panel in Figure S4a), and height profile reveals a step height of 0.8 nm, which is comparable to the MoS$_2$ thickness (Figure S4b). We also measured photoluminescence spectra at 77 K and Raman spectra at room temperature before and after annealing. For the majority of the sample areas, we
did not observe significant change in PL quenching ratio after annealing (Figure S4c). However, the thermal annealing does help to improve the homogeneity of the heterostructure contact. In as prepared heterostructures, fluorescence quenching is very weak in some areas. The quenching ratio in these areas is significantly improved after thermal annealing. From these measurements we believe that the MoS$_2$ and WS$_2$ layers are largely in good contact, and thermal annealing can help improve the heterostructure homogeneity.

The effect of thermal annealing on the Raman spectra is also relatively weak, as shown in Figure S4d.

Figure S4. The effect of annealing on morphology, photoluminescence and Raman spectrum. a. AFM measurements before (upper panel) and after 300 ºC annealing (lower panel). Polymer residues on top of the surfaces are reduced after the thermal annealing. b. Height profiling from the annealed sample in the lower panel of a. A step height of ~0.8 nm is measured, in good agreement with the thickness of a monolayer MoS$_2$. c. Photoluminescence spectra of the heterostructure before and after annealing. d. Raman spectra of heterostructure before and after annealing.

4. Room temperature photoluminescence data

At room temperature, we observed strong PL quenching in the MoS$_2$/WS$_2$ heterostructure compared to isolated MoS$_2$ and WS$_2$ monolayers, as shown in
Figure S5. The behaviour is similar to that observed at 77 K as described in the main text and in Figure 2.

Figure S5. Photoluminescence (PL) spectra and mapping of MoS2/WS2 heterostructures at Room Temperature. a. Typical PL spectra of an isolated monolayer MoS2, an isolated monolayer WS2, and a MoS2/WS2 heterostructure. The bright exciton PL in isolated monolayer WS2 and MoS2 layers are strongly quenched in the heterostructure. b. Optical microscope image of a typical MoS2/WS2 heterostructure sample. The MoS2 layer covers everywhere in the image, and bright areas correspond to MoS2/WS2 heterostructures. c. PL mapping data taken from the dashed rectangle area in a. The color scale represents PL intensity at the MoS2 A-exciton resonance (1.87 eV). It clearly shows that MoS2 PL is strongly quenched in the heterostructure. Scale bar is 5 µm.

5. Pump-probe measurements on WS2 monolayers

Figure S6 shows transient absorption spectra of isolated WS2 monolayers when excited by 1.86 eV photons, which is significantly below the WS2 exciton resonance. No photo-induced signal above the noise can be observed, in striking contrast to that observed in MoS2 monolayers and MoS2/WS2 heterostructures (Figure 3a and 3b in the main text). This is consistent with the fact that no optical active transitions are available at pump wavelength in isolated WS2.

Figure S6. Transient absorption spectra on isolated WS2. Two dimensional plots of transient absorption spectra at 77 K from an isolated WS2 monolayer. The horizontal axis, vertical axis, and colour scale represent the probe photon energy,
pump-probe time delay, and the transient absorption signal, respectively. No pump-induced signal is observed from an isolated WS\textsubscript{2} monolayer above the noise level.

6. **Room temperature pump probe data**

Room temperature pump-probe data (Figure S7) exhibit similar behaviour to that at 77 K (Figure 3 in the main text) after excitation of the MoS\textsubscript{2} exciton transition. With 1.86 eV pump at a fluence of \( \sim 20 \mu J/cm^2 \), we obtained an initial density of electron hole pairs in MoS\textsubscript{2} layer similar to that in 77 K measurements described in the main text. From the position and width of resonances, we can assign the resonance features in the transient absorption spectrum of the heterostructure to the A-exciton and B-exciton in the WS\textsubscript{2} layer, and the feature in the isolated MoS\textsubscript{2} monolayer to its B-exciton. It demonstrates that hole transfer processes in MoS\textsubscript{2}/WS\textsubscript{2} heterostructures are efficient at room temperature as well.

![Figure S7. Transient absorption spectra of MoS\textsubscript{2}/WS\textsubscript{2} heterostructures. a. b. and c. Two-dimensional plots of transient absorption spectra at room temperature from a MoS\textsubscript{2}/WS\textsubscript{2} heterostructure (a) an isolated MoS\textsubscript{2} monolayer (b) and an isolated WS\textsubscript{2} monolayer (c) upon excitation energy corresponding to the MoS\textsubscript{2} A-exciton transitions (1.86 eV). The horizontal axis, vertical axis, and colour scale represent the probe photon energy, pump-probe time delay, and the transient absorption signal, respectively. Positive signals indicate a pump-induced decrease in absorption. d. and e. Transient absorption spectra for MoS\textsubscript{2}/WS\textsubscript{2} (magenta circle) and MoS\textsubscript{2} (green square) at 1 ps and 20 ps pump-probe delay, respectively. No pump-induced transient absorption is observed for WS\textsubscript{2} f. Linear absorption spectra of monolayers of MoS\textsubscript{2} (green line) and WS\textsubscript{2} (purple line). Although only MoS\textsubscript{2} A-exciton transitions are optically excited, transient absorption spectra in](image-url)
the MoS$_2$/WS$_2$ heterostructure are dominated by a resonance feature (magenta circles in d and e) corresponding to the WS$_2$ A-exciton transition (purple line in f), which is clearly distinguishable from the resonance feature corresponding to the MoS$_2$ B-exciton transition in an isolated MoS$_2$ monolayer (green squares in d and e and green line in f). It demonstrates unambiguously an efficient hole transfer from the photoexcited MoS$_2$ layer to the WS$_2$ layer in MoS$_2$/WS$_2$ heterostructures.

7. Room temperature ultrafast hole transfer

Figure S8 displays the ultrafast hole transfer in MoS$_2$/WS$_2$ heterostructure at room temperature. It shows the dynamic evolution of the WS$_2$ A-exciton resonance in the MoS$_2$/WS$_2$ heterostructure (Figure S8a), which can be compared to the transient absorption signal for the B-exciton resonance in an isolated MoS$_2$ monolayer (Figure S8b). We found that the rise time in both signals are almost identical, and it is limited by the laser pulse duration ~ 250 fs. In Figure S8b the MoS$_2$ monolayer is directly pumped, and the photo-induced signal should appear instantaneously. We could reproduce the ultrafast dynamics in the MoS$_2$ monolayer in Figure S8b by convoluting the instrument response function (the blue dashed curve in Figure S8b) with an instantaneous response in MoS$_2$. Using the same instrument response function for time convolution, we can then reproduce the experimentally observed signal in the heterostructure with a hole transfer time constant shorter than 50 fs (red line in Figure S8a). Therefore our results show that holes are transferred from the MoS$_2$ layer to the WS$_2$ layer within 50 fs after optical excitation of the MoS$_2$/WS$_2$ heterostructure in room temperature, similar to the 77 K measurements described in the text.

Figure S8. Ultrafast hole transfer dynamics from vertical cuts in Figure S7. a and b. a. The evolution of transient absorption signals at the WS$_2$ A-exciton resonance in the MoS$_2$/WS$_2$ heterostructure. b. The dynamic evolution of transient absorption signals at the MoS$_2$ B-exciton resonance in the isolated MoS$_2$ monolayer. Both signals show almost identical ultrafast rise time, which is limited by the laser pulse duration ~ 250 fs. By convoluting the instrument response function (blue dashed line in b) and an instantaneous response in MoS$_2$, we can reproduce the ultrafast dynamics in the MoS$_2$ monolayer (red trace in b). Similar
convolution shows that the rise time in MoS$_2$/WS$_2$ monolayer is around 25 fs (red trace in a), and has an upper limit of 50 fs. It demonstrates that holes can transfer from the photoexcited MoS$_2$ layer to the WS$_2$ layer within 50 fs in the MoS$_2$/WS$_2$ heterostructure at room temperature.

8. Comparison of A exciton dynamics with B exciton dynamics in MoS$_2$

Figure S9 shows the comparison between the pump-probe signals from MoS$_2$ A and B-exciton when the A-exciton transition is excited. The rising time of the pump-induced signal for A exciton and B exciton are almost indistinguishable at 77 K. This confirms that the ultrafast responses of both A- and B-excitons are instrument-limited. They provide an intrinsic calibration that allows us to determine accurately time zero in pump-probe studies.

Figure S9. Instrument-limited rising dynamics of (black) A and (red) B exciton resonances in MoS$_2$ at 77K. MoS$_2$ is excited with optical pump resonant to A-exciton. The rise times for A- and B-exciton signals are almost indistinguishable and limited by the instrument response.

References


