Deciphering asymmetric charge transfer at transition metal dichalcogenide–graphene interface by helicity-resolved ultrafast spectroscopy

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Transition metal dichalcogenide (TMD)/graphene (Gr) heterostructures constitute a key component for two-dimensional devices. The operation of TMD/Gr devices relies on interfacial charge/energy transfer processes, which remains unclear and challenging to unravel. Fortunately, the coupled spin and valley index in TMDs adds a new degree of freedom to the charges and, thus, another dimension to spectroscopy. Here, by helicity-resolved ultrafast spectroscopy, we find that photoexcitation in TMDs transfers to graphene by asynchronous charge transfer, with one type of charge transferring in the order of femtoseconds and the other in picoseconds. The rate correlates well with energy offset between TMD and graphene, regardless of compositions and charge species. Spin-polarized hole injection or long-lived polarized hole can be achieved with deliberately designed heterostructures. This study shows helicity-resolved ultrafast spectroscopy as a powerful and facile approach to reveal the fundamental and complex charge/spin dynamics in TMD-based heterostructures, paving the way toward valleytronics and optoelectronic applications.

INTRODUCTION

Two-dimensional (2D) van der Waals heterostructures, deliberately designed and stacked by different materials [e.g., graphene (Gr), boron nitride, and transition metal dichalcogenides (TMDs)], could integrate the strength of constituent materials to achieve new functionalities. Among them, heterostructures consisting of semiconducting TMD with tunable electronic band structure and strong light-matter interaction (1, 2) and semimetal graphene with conical band structure and extremely high carrier mobility (3, 4) have been extensively used as a key component in optoelectronic, spintronic, and photonic devices. There, TMD acts as a light absorption or emission semiconductor layer and graphene acts as a conducting layer for charge transfer or injection (5–13).

The operation of TMD/Gr-based devices relies on the photoinduced charge (electron and hole) or energy transfer process at the interface. An in-depth understanding of the interfacial dynamics is essential for interpreting the operation principles, optimizing the performance, and boosting their practical applications. Considering their band alignment, in principle, both electron/hole and energy transfer from TMD to graphene can occur after photoexciting the TMD layer. Previous spectroscopy studies have suggested ultrafast charge/energy transfer at the TMD/Gr interface (8, 14–21). However, revealing the exact excited state relaxation pathways and dynamics has been challenging. Conventional transient absorption (TA) spectroscopy conveys carrier population information but can hardly discriminate different species and pathways, as electrons/holes/excitons in TMDs all contribute to TA signal similarly through band filling and renormalization effects (22–26). A very recent time- and angle-resolved photoemission study, averaging over hundreds of chemical vapor grown WS2/Gr epitaxial heterostructures, shows ultrafast (<200 fs, instrument response limited) hole transfer from photoexcited WS2 to graphene with a ~1 ps charge separation, exhibiting an asymmetric behavior (16). However, this technique imposes severe restrictions on sample preparations (size, orientation, and coverage) and measurement conditions (pump fluence and substrate) and cannot apply facilely to different heterostructures in a definitive way, which hinders the drawing of a general physical picture about excited state dynamics in TMD/Gr heterostructures.

Fortunately, monolayer TMDs exhibit two inequivalent valleys (K and K’) and coupled spin-valley index because of the broken inversion symmetry and strong spin-orbital coupling (27–29). This not only provides a unique platform for spin-valleytronics study (10–13, 30, 31) but also adds a new polarization degree of freedom to charges and, thus, a new dimension to optical spectroscopy. Helicity-resolved TA spectroscopy, combining population and polarization of photoexcited carriers, offers a new opportunity to probe carrier dynamics in real time and potentially can decipher complex excited dynamics in TMD-based heterostructures. In this study, we show helicity-resolved TA spectroscopy as a powerful and facile tool to reveal the complex photoinduced interfacial charge/energy transfer process in TMD/Gr heterostructures. We observed highly asynchronous electron and hole transfer from photoexcited TMD to graphene. For example, interfacial electron (hole) transfer is 1.43 ps (0.21 ps) for WS2/graphene and 0.15 ps (2.28 ps) for WSe2/graphene. The asymmetric charge transfer process can be attributed to different accepting density of states (DOS) in graphene, which is determined by energy offset between TMD and graphene. We observe a generally linear relationship between charge transfer rate and energy offset, regardless of TMD compositions and charge species.

RESULTS

Extracting polarization dynamics of excitons and electron/hole charges in TMDs as reference

In this part, we first performed helicity-resolved TA measurements on TMD monolayers and TMD/TMD type II heterostructures to obtain the spin polarization properties of excitons and electron/hole charges in TMDs as reference standard. The samples were prepared with mechanical exfoliation and stacking (see Materials and
Methods). The absorption spectra of all heterostructures are shown in fig. S1. In helicity-resolved TA measurements (see Materials and Methods for details), we excite samples using a circularly polarized pump pulse with energy slightly (~50 meV) above TMD A exciton resonance to create intralayer excitons in a specific valley (e.g., K) of TMD and probe transmitted light intensity change ΔT/T of a white light continuum with the same circular polarization (SCP) or opposite circular polarization (OCP) conditions (Fig. 1A). The imbalance of exciton population in K and K’ valleys of TMD monolayers leads to TA difference around A exciton resonance (25, 26). The 2D color plot of TA spectra of the WSe2 monolayer under SCP and OCP conditions is shown Fig. 1B (top and bottom panels, respectively). A few representative TA spectra at indicated delay times (0.2, 0.6, and 4 ps) are compared in Fig. 1C for a better view. Similar TA kinetics for the total population (ΔPop/ΔT) are shown in figs. S2 to S4.

The TA signal of TMDs stems from both exciton/charge band filling effect and Coulombic effect (e.g., bandgap renormalization) (22–26). While the former effect is sensitive to charge/exciton occupation in a specific valley, the latter would apply to both K and K’ valleys (23–26). At an early time (0.2 ps), the OCP spectra (∆T_{OCP}) have a dispersive line shape with absorption (bleach) in the lower (higher) energy side around WSe2 A exciton resonance, which can be mainly ascribed to band renormalization effect. Meanwhile, the SCP spectra (∆T_{SCP}) show a dominant bleach feature at exciton resonance due to the combined effect of band filling and renormalization (25, 26). While the sum of them yields the total population (ΔPop = ∆T_{SCP} + ∆T_{OCP}) of photoexcited excitons, this represents the imbalanced exciton densities in K and K’ valleys. This difference vanishes within 5 ps, indicating the equilibration between K and K’ valleys by intervalley scattering.

To extract the exciton polarization dynamics, we spectrally integrated SCP and OCP TA signal in the range of A exciton resonance and calculated the degree of valley polarization (Pol) by Pol = (∆T_{SCP} – ∆T_{OCP})/(∆T_{SCP} + ∆T_{OCP}). Both Pop and Pol kinetics for the WSe2 monolayer are plotted in Fig. 1D, and those for other TMD monolayers are plotted in figs. S2 to S4. While Pop shows a lifetime of tens of picoseconds, Pol decays mostly with a lifetime of ~180 fs for the WSe2 monolayer. We observe a similar behavior in other TMD monolayers with Pol showing a lifetime of ~570 and ~240 fs for WS2 and MoSe2, respectively. The subpicosecond depolarization process can be attributed to ultrafast intervalley scattering through electron-hole exchange interaction (δ in Fig. 1A) (32–38). We note that the valley polarization lifetime of MoSe2 monolayer is too short to be resolved at room temperature (fig. S4), which is consistent with previous observations (39) and can be ascribed to the lower depolarization energy threshold in MoSe2 (40). Therefore, MoSe2 is not included in this study.

We then performed the same helicity-resolved TA measurements on the WSe2/WS2 type II heterostructure (Fig. 2A) with ultrafast (<30 fs) interfacial charge transfer (Fig. 2B) (26, 41–46) to suppress electron-hole exchange interaction and extract polarization dynamics of individual electron and hole charges. We first focus on the hole depolarization process (β) after ultrafast electron transfer by exciting and probing WSe2 in heterostructure (Fig. 2C). After photoexciting WSe2 with a circular polarized light, electron transfers to WS2 with a lifetime of ~30 fs, leaving a valley-polarized hole in WSe2 (note S1 and fig. S5). The hole polarization (Polh) and population (Pop_h) kinetics are shown in Fig. 2D. Also shown in gray

Fig. 1. Helicity-resolved TA spectroscopy measurements on monolayer WSe2. (A) Scheme of helicity-resolved TA measurements and electron-hole exchange interaction (δ). Valley-polarized excitons are photoexcited by a circularly polarized pump pulse and probed by SCP/OCP conditions in monolayer TMD. (B) The 2D color plot of TA spectra of a representative WSe2 monolayer under SCP and OCP. (C) Comparison of representative TA spectra at indicated delay times of the WSe2 monolayer under SCP and OCP. (D) The spectrally integrated TA kinetics for the total population (Pop = ∆T_{SCP} + ∆T_{OCP}) and the degree of valley polarization (Pol) kinetics, calculated by Pol = (∆T_{SCP} – ∆T_{OCP})/(∆T_{SCP} + ∆T_{OCP}).
line is the exciton polarization kinetics (Pol_{ex}) of the WSe_{2} monolayer for comparison. Compared to excitons with a ~180 fs polarization lifetime, the hole in WSe_{2} has a much longer polarization lifetime (~18 ps) and can be attributed to suppressed electron-hole exchange interaction (26, 47, 48). We then focus on the electron depolarization process (α) after ultrafast hole transfer by exciting and probing WS_{2} in heterostructure (Fig. 2E). The hole transfers from photoexcited WS_{2} to WSe_{2} with a lifetime of ~40 fs (note S2 and fig. S6), leaving electrons in WS_{2} with a long population lifetime as shown by Pop_{e} kinetics in heterostructure (Fig 2F, red line). In contrast, the electron polarization kinetics (Pol_{e}; Fig. 2F, green circles) exhibits an ultrafast decay with a lifetime of ~80 fs, even faster than the exciton polarization decay in the WS_{2} monolayer (Fig. 2F, gray dashed line). A similar short electron depolarization lifetime in TMD has also been previously observed (33, 34).

We summarize our findings above: The electron, hole charges, and exciton in monolayer WS(Se)_{2} has a distinctly different polarization lifetime of <100 fs, >10 ps, and hundreds of femtoseconds, respectively. The orders of magnitude faster electron depolarization than hole depolarization can be ascribed to much smaller spin-orbit splitting in the conduction band than the valence band, facilitating the spin-conserved electron intervalley scattering process at room temperature (33, 34, 49). For excitons, despite large valence band splitting, the presence of electron markedly shortens hole polarization lifetime through electron-hole exchange interaction, leading to subpicosecond exciton depolarization (but still slower than electron polarization) (32–37). Since each excited state species (electron/hole/exciton) has its own characteristic polarization kinetics, the combination of population and polarization from helicity-resolved TA spectroscopy provides an exciting opportunity to

Fig. 2. Intervalley scattering of electrons (α) and holes (β) after charge transfer. (A) Schematic diagram of the WSe_{2}/WS_{2} heterostructure. (B) Type II band alignment and charge transfer process between WS_{2} and WSe_{2}. (C) Scheme of electron transfer and hole depolarization processes. After photoexcitation of WSe_{2}, photoinduced electron transfers from WSe_{2} to WS_{2} with a lifetime of ~30 fs, and valley-polarized hole in WSe_{2} decays with a lifetime of 18 ps. (D) Population (Pop_{h}) and polarization (Pol_{h}) kinetics of valley-polarized holes in WSe_{2}. The dashed gray line shows the exciton polarization (Pop_{ex}) kinetics in monolayer WSe_{2}. (E) Scheme of hole transfer and electron depolarization processes. After photoexcitation of WS_{2}, photoinduced hole transfers from WS_{2} to WSe_{2} with a lifetime of ~40 fs, and valley-polarized electron in WS_{2} decays with a lifetime of 80 fs. (F) The population (Pop_{e}) and the polarization (Pol_{e}) kinetics of valley-polarized electrons in WS_{2}. The dashed gray line shows the exciton polarization (Pol_{ex}) kinetics of monolayer WS_{2}.
potentially decipher the charge transfer mechanism in TMD-based heterostructures.

**Revealing charge transfer dynamics in TMD/Gr heterostructures**

Having established the methodology and obtained polarization kinetics of different species as reference, we moved to the WS₂/Gr heterostructure to reveal the interfacial charge/energy transfer dynamics after WS₂ light absorption (Fig. 3A). The optical image of a representative WS₂/Gr heterostructure sample is shown in Fig. 3B, where we can clearly identify the monolayer and heterostructure regions. The PL and absorption spectra of monolayer and heterostructure regions are shown in Fig. 3 (C and D, respectively). The ~2 eV peak on PL and absorption spectra corresponds to WS₂ A exciton transition, which is red-shifted slightly in heterostructure. The PL intensity of WS₂ in heterostructure is markedly (~10²) quenched compared to the monolayer, suggesting ultrafast charge or energy transfer from the photoexcited WS₂ to graphene. Unlike in TMD/TMD type II heterostructures, where charge transfer pathways can be inferred from band alignment, in TMD/Gr heterostructures, electrons, holes, and excitons photogenerated in TMDs can transfer across the interface to graphene (8, 14–20).

To decipher them, we performed helicity-resolved TA spectroscopy on WS₂/Gr heterostructures. The complete TA spectra under SCP and OCP conditions are shown in fig. S7. The population (Pop_{WS₂/Gr}) and polarization (Pol_{WS₂/Gr}) kinetics of WS₂ in heterostructure are shown in Fig. 3E. Also shown in Fig. 3E are polarization kinetics for electron (Pol_e) and exciton (Pol_ex) in WS₂ for reference. From TA results, Pop_{WS₂/Gr} shows a fast decay with a single exponential lifetime of 1.43 ps, which, by itself, is difficult to interpret. Meanwhile, Pol_{WS₂/Gr} exhibits a much faster decay with a lifetime of 210 fs, which is even faster than Pol_ex (570 fs) but slower than Pol_e (80 fs) of WS₂. This result precludes energy transfer process as a dominant process, which otherwise should show similar Pol_{WS₂/Gr} kinetics to Pol_ex. The ultrafast electron transfer process (before hole transfer) can also be excluded, which otherwise should lead to a longer Pol_{WS₂/Gr} than Pol_ex. Therefore, this ultrafast polarization decay process in WS₂/Gr can only be attributed to the hole transfer process, which effectively accelerates hole polarization decay and quenches the PL. The slower picosecond population decay thus can be ascribed to electrons remaining in WS₂. With this, the photoexcitation dynamics in the WS₂/Gr heterostructure can be drawn as in Fig. 3F, where the ultrafast hole transfer occurs first followed by slower electron transfer. The hole transfer kinetics is directly given by Pop_{WS₂/Gr} with a lifetime of 210 fs, and Pol_{WS₂/Gr} yields electron transfer kinetics with a lifetime of 1.43 ps. The electron and hole transfer in the WS₂/Gr heterostructure exhibits a highly asymmetric behavior. Previous temporally and spatially resolved optical measurement by Zhao’s group, despite no species discrimination and rate information, also suggests asynchronized interfacial electron and hole transfer in the WS₂/Gr heterostructure (18). A very recent angle- and time-resolved photoemission spectroscopy study with extreme ultraviolet pulse from Gierz’s group also shows rapid hole transfer from the photoexcited WS₂ to graphene with a ~1 ps charge separation lifetime (16). Compared to previous studies, the helicity-resolved TA spectroscopy that we show here is a direct and facile approach, without restrictions on sample or environment conditions, and thus is generally applicable to different heterostructures. In addition to carrier population as in conventional spectroscopy, it also provides rich valley polarization information of photoexcited carriers. A very recent study combining TA and ultrafast terahertz spectroscopy shows a fast (~1 ps) electron trapping to defects in WS₂, leading to

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**Fig. 3. Optical characterization and charge transfer mechanism in the WS₂/Gr heterostructure.** (A) Schematic diagram of the TMD/Gr heterostructure. (B) Optical image of a representative WS₂/Gr sample with monolayer and heterostructure regions. (C) PL spectra of WS₂ and the WS₂/Gr heterostructure by 532-nm excitation. (D) Absorption spectra of WS₂, graphene monolayers, and the WS₂/Gr heterostructure. (E) The population (red line) and polarization (green circles) kinetics of WS₂/Gr with 2.05-eV photoexcitation. The dashed gray line shows the exciton polarization dynamics in monolayer WS₂. (F) Scheme shows the charge transfer pathways and lifetimes in WS₂/Gr heterostructures.
fast decay on TA spectra and nanosecond long-lived holes in graphene (21). By carefully inspecting the TA results of WS$_2$ and WS$_2$/Gr heterostructure, we did not observe such a fast decay process in the WS$_2$ monolayer (fig. S8) or a long-lived differential-like feature from interfacial electric field (fig. S9) as in a previous study (21). Therefore, we believe that defect trapping plays a negligible role in this short time scale and that the 1.43 ps decay represents electron transfer to graphene instead of to defects. The sample from different preparation methods (direct chemical vapor growth versus mechanical exfoliation from a single crystal) could be the major reason for this difference.

By helicity-resolved TA spectroscopy, we also observed asynchronous charge transfer dynamics in the MoS$_2$/Gr heterostructure with an ultrafast polarization decay (faster than exciton polarization decay) and a slow population decay of MoS$_2$ (fig. S10), similar to that in the WS$_2$/Gr heterostructure. Single exponential fitting on population and polarization decay kinetics yields a ~130 fs ultrafast hole transfer followed by a ~7.91 ps electron transfer after photoexciting MoS$_2$ in the MoS$_2$/Gr heterostructure.

We now focus on the WSe$_2$/Gr heterostructure, which shows a very different behavior. The complete helicity-resolved TA spectra of WSe$_2$/Gr are shown in fig. S11. The population ($Pop_{\text{WSe}_2/\text{Gr}}$) and polarization ($Pol_{\text{WSe}_2/\text{Gr}}$) kinetics of WSe$_2$ in heterostructure are shown in Fig. 4A, together with the electron ($Pol_e$) and exciton ($Pol_{\text{ex}}$) polarization kinetics of the WSe$_2$ monolayer for reference. $Pop_{\text{WSe}_2/\text{Gr}}$ shows a typical fast decay in a few picoseconds, which is similar to the population decay in other TMD/Gr heterostructures but difficult to interpret on its own. Meanwhile, $Pol_{\text{WSe}_2/\text{Gr}}$ shows an interestingly biphasic decay behavior with an ultrafast decay component in ~0.5 ps and the long-lived component with negligible decay in a few picoseconds. The long-lived polarization component is substantially longer than the exciton polarization lifetime, which can only be ascribed to the valley-polarized hole remaining in WSe$_2$ with quenched electron-hole exchange interaction from prior electron transfer. The initial ultrafast polarization decay in ~0.5 ps, similar to exciton polarization decay, is due to the presence of electrons in WSe$_2$. Therefore, the initial ultrafast polarization decay component directly yields electron transfer kinetics with a single exponential lifetime of 150 fs. After the initial ultrafast electron transfer, the much slower population decay kinetics $Pop_{\text{WSe}_2/\text{Gr}}$ can be ascribed to the hole transfer process, showing a lifetime of 2.28 ps. The asymmetric charge transfer dynamics after WSe$_2$ light absorption in the WSe$_2$/Gr heterostructure are shown schematically in Fig. 4B.

**DISCUSSION**

We have shown above a convenient approach for deciphering photoinduced charge/exciton transfer pathways and rates in TMD/Gr heterostructures by helicity-resolved TA spectroscopy. Our results indicate that ultrafast charge transfer plays a dominant role at the TMD/Gr interface. In Table 1, we summarize the lifetimes of electron ($\tau_e$) and hole ($\tau_h$) transfer from the photoexcited TMD monolayer.
to graphene in different TMD/Gr heterostructures. Apparently, they all exhibit highly asymmetric charge transfer behaviors with one type of charge (electron or hole) transferring in the ultrafast femtosecond time scale and the other in picoseconds.

According to Fermi’s golden rule and neglecting electron/hole wave function distribution difference in TMDs, the electron/hole transfer rate from TMD to graphene can be approximated to be proportional to the available DOS in graphene accepting electrons/holes (16, 18, 19). The electron/hole accepting DOS in graphene depends on the energy offset (\( \Delta E \)) between the conduction band minimum (CBM)/valence band maximum (VBM) of TMDs and graphene Dirac point. The band offset for electron (\( \Delta E_e \)) and hole (\( \Delta E_h \)) transfer is also listed in Table 1 (3, 50). Because of linear band dispersion in graphene (4), a larger \( \Delta E \) corresponds to a larger accepting DOS in a linear manner. For WS\(_2\) and MoS\(_2\), where \( \Delta E_h \) for hole is significantly larger than that of electron, hole transfer is much faster than electron. The opposite behavior can be observed in WSe\(_2\). We further plotted all charge transfer rates (1/\( \tau \)) from three kinds of TMD/Gr heterostructures as a function of \( \Delta E \) in Fig. 5. A larger \( \Delta E \) generally shows a faster charge transfer in a monotonically way, regardless of TMD compositions and charge species. This is significant, as it shows that DOS acts as a universal valve for regulating charge transfer in TMD/Gr heterostructures. Therefore, energy offset provides an effective and general way to assess and tune the charge transfer dynamics, thanks to the linear band dispersion of graphene. This nice correlation between charge transfer rate and energy offset also suggests negligible contribution from defect trapping.

The helicity-resolved TA spectroscopy, by combining carrier population and polarization degrees of freedom, should be generally applicable to TMD heterostructures and adds a new dimension to ultrafast spectroscopy. Besides TMD/Gr heterostructures, in principle, it can also help decipher the complex excited state relaxation pathways in the TMD/metallic contact (e.g., Au, Ag, and 1T phase TMD) interface where electron, hole, and energy transfer can occur. Not only for TMD/(semi-)metal heterostructures but helicity-resolved TA spectroscopy can also unravel the interfacial charge transfer mechanisms in TMD/TMD type I or type II heterostructures where the charge transfer pathways were only inferred from calculated band alignment previously (26, 41–47, 51–53). As an important example, previous studies have shown ultrafast and efficient energy transfer in TMD/TMD type I heterostructures, but the underlying mechanism has been under intense debate, where both Förster and Dexter energy transfer mechanisms have been invoked (52, 54). We performed helicity-resolved TA spectroscopy on a prototypal WSe\(_2\)/MoTe\(_2\) type I heterostructure and found a polarization lifetime of 75 fs and a population lifetime of 480 fs in the photoexcited WSe\(_2\) (fig. S12). This indicates that the energy transfer process in the WSe\(_2\)/MoTe\(_2\) type I heterostructure occurs through an ultrafast (75 fs) hole transfer process and a relatively slower (480 fs) electron transfer from the photoexcited WSe\(_2\) to MoTe\(_2\). Such asymmetric electron/hole charge transfer rate also correlates very well with CBM/VBM offset in the WSe\(_2\)/MoTe\(_2\) heterostructure, confirming the universal role of DOS in dictating the interfacial charge transfer process.

Last, with the understanding of the charge transfer behavior in TMD/Gr heterostructures, the spin injection and valley/spin polarization can be manipulated with delicately designed TMD/Gr heterostructures. As shown above, spin-polarized hole injection from TMD to graphene at room temperature can be achieved in WS\(_2\)/Gr and MoS\(_2\)/Gr heterostructures where hole transfers before exciton depolarization via electron-hole exchange interaction. On the basis of the rates for hole transfer and the competing spin polarization in TMDs, excitingly, the hole polarization can maintain 73 and 65% of its initial value in WS\(_2\)/Gr and MoS\(_2\)/Gr, respectively, after injection. Even faster hole transfer and thus higher injected hole polarization could be achieved with TMDs with even lower VBM. As electrons in TMD lose spin polarization in less than 100 fs, spin-polarized electron injection from TMD to graphene with maintained and long-lived polarization in graphene, which is a critical aspect for the application of TMD/Gr systems for optospintronics, would remain a big challenge. On the other hand, as shown in Fig. 4A, ultrafast interfacial electron transfer in WSe\(_2\)/Gr can prolong hole polarization in WSe\(_2\) by reducing electron-hole exchange interaction. Unfortunately, the polarized hole decays quickly by a fast hole transfer process and such short hole lifetime potentially constrains the valleytronics applications. To simultaneously prolong the hole polarization and population lifetime, as a proof of concept, we manufactured WSe\(_2\)/WS\(_2\)/Gr heterostructures where electron transfers to graphene and hole remain in WSe\(_2\) with WS\(_2\) as an intermediate layer (Fig. 4D). The helicity-resolved TA spectra of the WSe\(_2\)/WS\(_2\)/Gr heterostructure are shown in fig. S13, and the hole polarization (Pop\(_{WSe_2/WS_2/Gr}\)) and population (Pop\(_{WSe_2/WS_2/Gr}\)) kinetics are shown in Fig. 4C. With the WS\(_2\) intermediate layer, which facilitates interfacial electron transfer but blocks hole transfer to graphene, the population and polarization lifetime of hole in WSe\(_2\) at room temperature can be markedly prolonged to be 165 and 113 ps, respectively. A similar intermediate layer approach has been used previously to achieve long charge separation lifetime in graphene/TMD heterostructures (55). Here, we extend this approach to markedly

| TMD/Gr | \( \tau_e \) (ps) | \( \Delta E_e \) (eV) | \( \tau_h \) (ps) | \( \Delta E_h \) (eV) |
|--------|-----------------|-----------------|-----------------|-----------------|
| WS\(_2\)/Gr | 1.43           | 0.79            | 0.21            | 1.50            |
| MoS\(_2\)/Gr | 7.91           | 0.54            | 0.13            | 1.70            |
| WSe\(_2\)/Gr | 0.15           | 1.24            | 2.28            | 0.86            |

**Table 1.** Electron and hole transfer lifetime (\( \tau \)) and energy offset (\( \Delta E \)) in TMD/Gr heterostructures.

**Fig. 5.** The plot of charge transfer rate (1/\( \tau \)) versus energy offset (\( \Delta E \)). Red circles and blue squares are the electron and hole transfer rate from three different TMD/Gr heterostructures, respectively. The error bar for rate is from multiple measures on multiple samples, and that for driving force is set to be 0.3, considering the uncertainty of theoretical calculation. The gray dashed line is drawn for eye guidance.
prolong the photoexcited carrier spin lifetime. With ~100 ps hole polarization lifetime at room temperature, extremely high-efficiency polarized hole extraction could be possible. This manipulation paves the way toward next-generation highly efficient valleytronic and optoelectronic applications.

In summary, we show that the helicity-resolved TA spectroscopy, by combining both carrier population and polarization information, provides a powerful and feasible approach to monitor the transient motion of electron/hole in TMDs and decipher the charge/energy transfer pathways and rates in TMD/Gr heterostructures. We found that photoexcited electrons and holes in TMDs transfer to graphene by an asynchronous process, with one type of charge transferring in ultrafast femtosecond timescale and the other in picoseconds. For example, interfacial electron (hole) transfer is 1.43 ps (210 fs) for WS₂/Gr and 150 fs (2.28 ps) for WSe₂/graphene. These highly asymmetric charge transfer rates correlate well with different accepting DOS in graphene, which is given by relative band alignment between TMD and graphene. By an asynchronous charge transfer mechanism, the spin-polarized hole injection to graphene or long-lived polarized hole can be achieved in the deliberately designed TMD/Gr heterostructure. This study provides important guidance for manipulating spin injection and polarization in TMD/Gr heterostructures and paves the way toward next-generation spintronic and optoelectronic applications.

MATERIALS AND METHODS

Sample fabrication

Monolayer TMDs were mechanically exfoliated onto gel films and fused silica substrates from bulk crystals (HQ Graphene). We fabricated TMD/Gr heterostructures by dry pickup and stacking method (56). The samples were annealed for 2 hours at 180°C in high vacuum before measurements.

Steady-state optical measurements

Absorption and photoluminescence (PL) measurements of samples were performed on a homebuilt microscope setup. The absorption spectra were measured with a supercontinuum laser (NKT Photonics, SuperK COMPACT) by normalizing the transmitted light from the sample on the substrate to that from the bare substrate. The transmitted light was collected and analyzed by liquid nitrogen-cooled detectors (PyLon 100B, Princeton Instruments). PL spectra were obtained with a 532 nm laser excitation.

Helicity-resolved TA measurements

The experiment setup for TA measurements has been described in our previous work (26). Basically, the fundamental beam from Ytterbium doped Potassium–Gadolinium Tungstate (Yb:KGW) laser (PHAROS, Light Conversion Ltd.) was divided into several light beams and sent to a microscopic ultrafast spectrometer (mFemto-TA100, Time-Tech Spectra LLC). There, one was focused onto an yttrium-aluminum-garnet crystal to generate a continuum white light as probe light. The other was introduced to a noncollinear optical parametric amplifier to generate a pump beam with pulse duration <35 fs. The delay time between pump and probe was controlled by a high-resolution motorized delay stage (Newport). Both beams were combined and focused by a microscope with a 70× reflective objective to a spot size <1 μm. The transmitted probe light was collected by liquid nitrogen-cooled detectors (PyLon 100B, Princeton Instruments) with the pump beam filtered by a polarizer, and the TA signal was calculated by normalizing the probe spectra from pumped ones to that from unpumped ones. The probe light is horizontally polarized, and the polarization of pump light can be tuned by a half-wave plate. Then, pump and probe light pass a quarter-wave plate (1/4λ) together and focused by a microscope. We set the fast axis direction of 1/4λ plate at a 45° angle to the polarization direction of the probe beam to get a circularly polarized light. When the pump light is the same polarization direction as the probe light, the helicity of the pump light after 1/4λ plate is the same as the probe light, which we denote as SCP. When the polarization direction of the pump light is perpendicular to the polarization direction of the probe light, the helicity of the pump light and probe light is opposite, which we denote as OCP. All measurements were performed at room temperature.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/34/eabg2999/DC1

REFERENCES AND NOTES

1. A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli, F. Wang, Emerging photoluminescence in monolayer MoS₂. Nano Lett. 10, 1271–1275 (2010).
2. K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, Atomically thin MoS₂: A new direct-gap semiconductor. Phys. Rev. Lett. 105, 136805 (2010).
3. Y. J. Yu, Y. Zhao, S. Ryu, L. E. Brus, K. S. Kim, P. Kim, Tuning the graphene work function by electric field effect. Nano Lett. 9, 3430–3434 (2009).
4. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, Two-dimensional gas of massless Dirac fermions in graphene. Nature 438, 197–200 (2005).
5. M. Massicotte, P. Schmidt, F. Vialla, K. G. Schädler, A. Reserbat-Plantey, K. Watanabe, T. Taniguchi, K. J. Tielrooij, F. H. Koppens, Picoscosecond photoresponse in van der Waals heterostructures. Nat. Nanotechnol. 11, 42–46 (2016).
6. L. Britnell, R. M. Ribeiro, A. Eckmann, R. Jalil, B. D. Belle, A. Mishchenko, Y. J. Kim, R. V. Gorbachev, T. Georgiou, S. V. Morozov, A. N. Grigorenko, A. K. Geim, C. Casiraghi, A. H. Castro Neto, K. S. Novoselov, Strong light-matter interactions in heterostructures of atomically thin films. Science 340, 1311–1314 (2013).
7. F. H. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, M. Polini, Photodetectors based on graphene, other two-dimensional materials and hybrid systems. Nat. Nanotechnol. 9, 780–793 (2014).
8. E. Lorchat, L. E. P. Lopez, C. Robert, D. Lagarde, F. Froehlich, T. Taniguchi, K. Watanabe, X. Marie, S. Bercaud, Filtering the photoluminescence spectra of atomically thin semiconductors with graphene. Nat. Nanotechnol. 15, 283–288 (2020).
9. T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y. J. Kim, A. Gholinia, S. J. Haigh, O. Makarovsky, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov, A. Mishchenko, Vertical field-effect transistor based on graphene-WSe₂ heterostructures for flexible and transparent electronics. Nat. Nanotechnol. 8, 100–103 (2013).
10. Y. K. Luo, J. Xu, T. Zhu, G. Wu, E. J. McCormick, W. Zhan, M. R. Neupane, R. K. Kawakami, Opto-valleytronic spin injection in monolayer MoS₂/Few-layer graphene hybrid spin valves. Nano Lett. 17, 3877–3883 (2017).
11. A. Avsar, D. Unuchek, J. Liu, O. L. Sanchez, K. Watanabe, T. Taniguchi, B. Ozyilmaz, A. Kis, Opto-spintronics in graphene via proximity coupling. ACS Nano 11, 11678–11686 (2017).
12. M. Grimura, J. Fabian, Graphene on transition-metal dichalcogenides: A platform for proximity spin-orbit physics and opto-spintronics. Phys. Rev. B 92, 155403 (2015).
13. E. Lorchat, S. Azzini, T. Cherry, T. Taniguchi, K. Watanabe, T. W. Ebbesen, C. Genet, S. Bercaud, Room-temperature valley polarization and coherence in transition metal dichalcogenide–Graphene van der Waals heterostructures. ACS Photonics 5, 5047–5054 (2018).
14. G. Froehlich, E. Lorchat, S. Bercaud, Charge versus energy transfer in atomically thin graphene-transition metal dichalcogenide van der Waals heterostructures. Phys. Rev. X 8, 011007 (2018).
15. J. He, N. Kumar, M. Z. Bellus, H. Y. Chiu, D. He, Y. Wang, H. Zhao, Electron transfer and coupling in graphene-tungsten disulfide van der Waals heterostructures. Nat. Commun. 5, 5622 (2014).
16. S. Aeschlimann, A. Rossi, M. Chávez-Cervantes, R. Krause, B. Arnoldi, B. Stadtmuller, M. Aeschlimann, S. Forti, F. Fabbri, C. Coletti, I. Gierz, Direct evidence for efficient ultrafast charge separation in epitaxial WS₂/graphene heterostructures. Sci. Adv. 6, eaay0761 (2020).
28. D. Xiao, G. B. Liu, W. Feng, X. Xu, Y. H. Zhang, W. Zheng, S. Krasel, Z. Chen, Z. M. Wang, K.-J. Tielrooij, M. Bonn, A. H. Joutenep, H. I. Wang, Long-lived carrier separation following pump-polarization-dependent ultrafast charge transfer in graphene/WSe$_2$ heterostructures. Opt. Express 15, 62–67 (2018).

29. F. Ceballos, M. G. Ju, S. D. Lane, X. C. Zeng, H. Zhao, Highly efficient and anomalous charge transfer in van der Waals trilayer semiconductors. Nano Lett. 17, 1623–1628 (2017).

30. L. Wu, Y. Chen, H. Zhou, H. Zhu, Ultrafast energy transfer of both bright and dark excitons in 2D van der Waals heterostructures beyond dipolar coupling. ACS Nano 13, 2341–2348 (2019).

31. Y. Li, H. Zhou, Y. Chen, Y. Zhao, H. Zhu, Efficient hot-electron extraction in two-dimensional semiconductor heterostructures by ultrafast resonant transfer. Nano Lett. 16, 4087–4093 (2016).

32. D. S. Koda, F. Bechtstedt, M. Marques, L. K. Teles, Trends on band alignments: Validity of Anderson's rule in SnS$_2$ and SnSe$_2$-based van der Waals heterostructures. Phys. Rev. B 97, 165402 (2018).

33. F. Ceballos, M. G. Ju, S. D. Lane, X. C. Zeng, H. Zhao, Highly efficient and anomalous charge transfer in van der Waals trilayer semiconductors. Nano Lett. 17, 1623–1628 (2017).

34. L. Wu, Y. Chen, H. Zhou, H. Zhu, Ultrafast energy transfer of both bright and dark excitons in 2D van der Waals heterostructures beyond dipolar coupling. ACS Nano 13, 2341–2348 (2019).

35. Y. Li, H. Zhou, Y. Chen, Y. Zhao, H. Zhu, Efficient hot-electron extraction in two-dimensional semiconductor heterostructures by ultrafast resonant transfer. Nano Lett. 16, 4087–4093 (2016).

36. D. S. Koda, F. Bechtstedt, M. Marques, L. K. Teles, Trends on band alignments: Validity of Anderson's rule in SnS$_2$ and SnSe$_2$-based van der Waals heterostructures. Phys. Rev. B 97, 165402 (2018).

37. F. Ceballos, M. G. Ju, S. D. Lane, X. C. Zeng, H. Zhao, Highly efficient and anomalous charge transfer in van der Waals trilayer semiconductors. Nano Lett. 17, 1623–1628 (2017).

38. L. Wu, Y. Chen, H. Zhou, H. Zhu, Ultrafast energy transfer of both bright and dark excitons in 2D van der Waals heterostructures beyond dipolar coupling. ACS Nano 13, 2341–2348 (2019).

39. Y. Li, H. Zhou, Y. Chen, Y. Zhao, H. Zhu, Efficient hot-electron extraction in two-dimensional semiconductor heterostructures by ultrafast resonant transfer. Nano Lett. 16, 4087–4093 (2016).

40. D. S. Koda, F. Bechtstedt, M. Marques, L. K. Teles, Trends on band alignments: Validity of Anderson's rule in SnS$_2$ and SnSe$_2$-based van der Waals heterostructures. Phys. Rev. B 97, 165402 (2018).

41. F. Ceballos, M. Z. Bellus, H. Y. Chiu, H. Zhao, Ultrafast charge separation and indirect exciton formation in a MoS$_2$/MoSe$_2$ van der Waals heterostructure. ACS Nano 8, 12771–12774 (2014).

42. X. Hong, J. Kim, S. F. Shi, Y. Zhang, C. Jin, Y. Sun, C. Tongay, J. Wu, Y. Zhang, F. Wang, Ultrafast charge transfer in atomically thin MoS$_2$/WS$_2$ heterostructures. Nat. Nanotechnol. 9, 682–686 (2014).

43. H. Chen, X. Wen, J. Zhang, T. Wu, Y. Gong, X. Zhang, J. Yuan, C. Y. J. Lou, P. M. Ajayan, W. Zhuang, G. Jiang, J. Zheng, Ultrafast formation of interlayer hot excitons in atomically thin MoS$_2$/WS$_2$ heterostructures. Nat. Commun. 7, 12512 (2016).

44. Z. Ji, H. Hong, J. Zhang, Q. Zhang, W. Huang, T. Cao, R. Qiao, C. Liu, J. Liang, C. Jin, L. Jiao, K. Shi, S. Meng, K. Liu, Robust stacking-independent ultrafast charge transfer in MoS$_2$/WS$_2$ bilayers. ACS Nano 11, 12020–12026 (2017).

45. H. Zhou, H. Zhu, Y. Chen, H. Zhu, Dielectric environment-robust ultrafast charge transfer between two atomic layers. J. Phys. Chem. Lett. 10, 155–159 (2019).

46. J. Kim, C. Jin, B. Chen, H. Cai, T. Zhao, P. Lee, S. Kahn, K. Watanabe, T. Taniguchi, S. Tongay, M. F. Crommie, F. Wang, Observation of ultralong valley lifetime in WSe$_2$/MoS$_2$ heterostructures. Sci. Adv. 3, e1705018 (2017).

47. P. Rivera, K. L. Seyler, H. Yu, J. R. Schlabey, J. Yan, D. G. Mandsur, W. Yao, X. Xu, Valley-polarized exciton dynamics in a 2D semiconductor heterostructure. Science 351, 688–691 (2016).

48. P. Dey, L. Yang, C. Robert, G. Wang, B. Urbaszek, X. Marie, S. A. Crooker, Gate-controlled spin-valley locking of resident carriers in WSe$_2$ monolayers. Phys. Rev. Lett. 119, 137401 (2017).

49. D. S. Koda, F. Bechtstedt, M. Marques, L. K. Teles, Trends on band alignments: Validity of Anderson's rule in SnS$_2$ and SnSe$_2$-based van der Waals heterostructures. Phys. Rev. B 97, 165402 (2018).

50. F. Ceballos, M. G. Ju, S. D. Lane, X. C. Zeng, H. Zhao, Highly efficient and anomalous charge transfer in van der Waals trilayer semiconductors. Nano Lett. 17, 1623–1628 (2017).

51. L. Wu, Y. Chen, H. Zhou, H. Zhu, Ultrafast energy transfer of both bright and dark excitons in 2D van der Waals heterostructures beyond dipolar coupling. ACS Nano 13, 2341–2348 (2019).

52. Y. Li, H. Zhou, Y. Chen, Y. Zhao, H. Zhu, Efficient hot-electron extraction in two-dimensional semiconductor heterostructures by ultrafast resonant transfer. J. Chem. Phys. 153, 044705 (2020).

53. D. Kozawa, A. Carvalho, I. Vierzhibitskiy, F. Giustiniano, Y. Miyachi, S. Mouri, A. H. Castro Neto, K. Matsuda, G. Eda, Evidence for fast interlayer energy transfer in MoS$_2$/WS$_2$ heterostructures. Nano Lett. 16, 4087–4093 (2016).

54. S. D. Lane, H. Zhou, Unipolar optical doping and extended photocarrier lifetime in graphene by band-alignment engineering. Nano Futures 2, 035003 (2018).

55. P. J. Zomer, M. H. D. Guimarães, J. C. Brant, N. Tombros, B. J. van Wees, Fast pick up technique for high quality heterostructures of bilayer graphene and hexagonal boron nitride. Appl. Phys. Lett. 105, 013101 (2014).

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