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Trion-Mediated Förster Resonance Energy Transfer and Optical Gating Effect in WS_2/hBN/$MoSe_2$ Heterojunction

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Abstract

Van der Waals two-dimensional layered heterostructures have recently emerged as a platform, where the interlayer couplings give rise to interesting physics and multifunctionalities in optoelectronics. Such couplings can be rationally controlled by dielectric, separation, and stacking angles, which affect the overall charge or energy transfer processes, and emergent potential landscape for twistronics. Herein, we report the efficient Förster resonance energy transfer (FRET) in WS_2/hBN/$MoSe_2$ heterostructure, probed by both steady-state and time-resolved optical spectroscopy. We clarified the evolution behavior of the electron-hole pairs and free electrons from the trions, *i.e.*, ~59.9% of the electron-hole pairs could transfer into $MoSe_2$ by FRET channels (~38 ps) while the free electrons accumulate at the WS_2/hBN interface to photogate $MoSe_2$. This study presents a clear picture of the FRET process in two-dimensional transition metal dichalcogenides heterojunctions, which establishes the scientific foundation for developing the related heterojunction optoelectronic devices.

Keywords: 2D materials, transition metal dichalcogenides, trion, van der Waals heterostructure, Förster resonance energy transfer, photogating, optical spectroscopy,

Energy transfer refers to the nonradiative transfer of an electronic excitation from a donor to an acceptor. This process avoids the emission and reabsorption events, thus possessing a high energy conversion efficiency.[1] Energy transfer can be divided into Dexter and Förster type, whereas the former is based on electron exchange thus only works in the close proximity (<1 nm); while the latter depends on dipole-dipole coupling and works in a relatively long distance (r) with a $1/r^6$ dependence in the molecular dye system.[2, 3] During the past three decades, Förster resonance energy transfer (FRET) has been intensively studied for various important optoelectronic applications including solar cell,[4] light-emitting diode,[5] and laser.[6] Such applications in optoelectronics are highly compatible with recently emerged two-dimensional (2D) van der Waals materials. Due to the reduced dimension and strong confinement in the 2D limit, the dipole-dipole coupling strength is proportional to $1/r^4$, rather than $1/r^6$ in 3D confinement, enabling a stronger interaction strength and more pronounced long-range characteristics.[7, 8]

2D materials such as graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDs) offer a platform to study fundamental physics in a single atomic layer limit.[9, 10] Monolayer TMDs hold high stability and sizeable direct bandgap covering from visible to near-infrared spectrum. Due to the reduced dielectric screening effect, monolayer TMDs feature strong excitonic emission even at room temperature with a binding energy of several hundred meV.[11] Many-body effect of the excitonic species is strong and highly sensitive to the doping level, allowing the characterization and manipulation of trions or even biexctions.[12, 13] Inversion symmetry breaking and strong spin-orbit coupling enable more exciting physics, including valleytronics and spin-forbidden dark states.[14, 15] Since monolayer TMD heterojunctions usually form type II band alignment, optically excited electrons and holes are readily separated and then accumulate in the opposite monolayers. Pump-probe method has proven such charge transfer process in the heterostructure to be ultrafast (~100 fs).[16-21] The appropriate material combination and careful stacking, *e.g.*, $MoSe_2$ and WSe_2, can form strong interlayer exciton with long lifetime and novel valleytronic properties.[22, 23] Besides charge transfer, energy transfer is another important interaction between semiconducting emitters, which are widely studied in quantum dots and organic molecules but much less in 2D material heterojunctions.[24-30] Recently, by performing photoluminescence excitation (PLE) spectroscopy, FRET has been demonstrated in type II $MoSe_2/WS_2$ heterojunction.[31] On the contrary, energy transfer at $MoTe_2/WSe_2$ interface is demonstrated to be Dexter type by pump-probe method, thus both direct and indirect exciton from the donor could transfer and contribute to the acceptor emission.[32] Although FRET has been achieved in 2D material heterojunctions, it is simply attributed to a dipole-dipole coupling between excitons.[31, 33] However, due to the reduced Coulomb screening effect and high intrinsic doping, 2D TMDs feature diverse emission species, including exciton, trion and even biexciton emission. The population and lifetime of different excitonic species are quite different, thus, one needs to be extremely careful when dealing with the dynamics in 2D TMD heterojunctions.[12, 34, 35]

Here, we experimentally investigate the energy transfer process in WS_2/hBN/$MoSe_2$ heterojunction. By 532 nm (above WS_2 bandgap) excited photoluminescence (PL) mapping, we observe an enhancement of $MoSe_2$ exciton (X^0) emission, accompanied by the quenching of WS_2 trion (X^-)

emission. Such energy transfer occurs *via* a 3 nm hBN spacer, implying a clear signature of FRET. In combination with the shortening of WS_2 X^- PL lifetime, our study unambiguously reveals that FRET happens between X^- of WS_2 and X^0 of $MoSe_2$, *i.e.*, trion-exciton coupling owing to the strong coupling strength and a long intrinsic lifetime of X^-, rather than the direct exciton-exciton coupling proposed in literature.[31, 33]

RESULTS AND DISCUSSION

All the heterojunctions are fabricated with standard stamp-assisted dry transfer method in the nitrogen-filled glovebox to minimize the influence from trapped moisture. After transfer, 5/60 nm chromium/gold electrodes are patterned by standard electron beam lithography process, followed by a high vacuum (10^{-6} mbar) annealing at 200 °C for 2 hours to enhance the interlayer coupling. All the optical spectroscopies presented in this paper are taken at 80 K in a liquid nitrogen-cooled cryostat unless otherwise stated.

Figure 1a shows the schematic structure and the optical image of the typical device. Here, monolayer WS_2, ~3 nm thick hBN, and monolayer $MoSe_2$ are stacked layer by layer to form a heterojunction with distinct regions composing of: (I) WS_2/hBN/$MoSe_2$ (orange square in the sample image); (II) hBN/$MoSe_2$ (green circle) and (III) WS_2/hBN. Therefore, the influence of WS_2 on the optical properties of $MoSe_2$ (or *vice versa*) can be qualitatively and quantitatively compared. Figure 1b-d illustrates the PL mapping data for $MoSe_2$ X^0, X^- and X^0/X^- ratio excited by a 532 nm continuous-wave (CW) laser from the white dashed square in the bottom of Figure 1a. Compared to the case of $MoSe_2$ in region II, the $MoSe_2$ X^0 emission in the region I is enhanced by a factor of ~2.1 while the X^- emission is decreased by a factor of ~2/3 (Figure 1b, c), leading to a much higher $MoSe_2$ X^0/X^- ratio (Figure 1d), as reflected in the extracted PL spectra (Figure 1e). The changes of peak position and full width at half maximum (1.64 eV and 7 meV for X^0; 1.61 eV and 11 meV for X^-) are negligible due to nearly identical dielectric environment ($MoSe_2$ is sandwiched between SiO_2 and hBN). The enhancement of X^0 emission is attributed to the FRET from WS_2 as detailed later, while the X^- emission quenching results from the optical gating effect (p-doping) induced by the electron accumulation at the WS_2/hBN interface.

The optical gating scenario was confirmed by the Raman spectroscopy at the same position, which shows a small redshift of $MoSe_2$ A_{1g} mode by ~0.12 cm^{-1} in the region I (Figure 1f, full-scale spectra is shown in Supplementary Figure 3a). As previously shown in literature, the A_{1g} mode of TMDs is sensitive to the doping level due to the strong electron-phonon coupling.[36] Hence, the small redshift here is the direct evidence of weak p-doping.[36] For WS_2, the PL is dominated by X^- emission. The stacking of hBN/$MoSe_2$ quenched the WS_2 X^- emission intensity by almost half, suggesting the exciton energy transfer from WS_2 X^- to $MoSe_2$ X^0 (Figure 1e).

Then, the excitation wavelength was tuned to 671 nm, *i.e.*, below WS_2 bandgap excitation (Supplementary Figures 1, 4). All the $MoSe_2$ X^0, X^- and X^0/X^- ratio are quite homogeneous among the whole sample, indicating the absence of optical gating, charge, or energy transfer (Supplementary Figure 4 b-e). The absent interlayer interaction leads to the negligible peak shift of $MoSe_2$ A_{1g} mode as expected (Supplementary Figure 4f). This result confirms the FRET and optical gating scenery with 532 nm excitation from another perspective. Meantime, the interference effect from the SiO_2 substrate is ruled out by repeating the result on a transparent sapphire substrate, as detailed in Supplementary Figure 5.

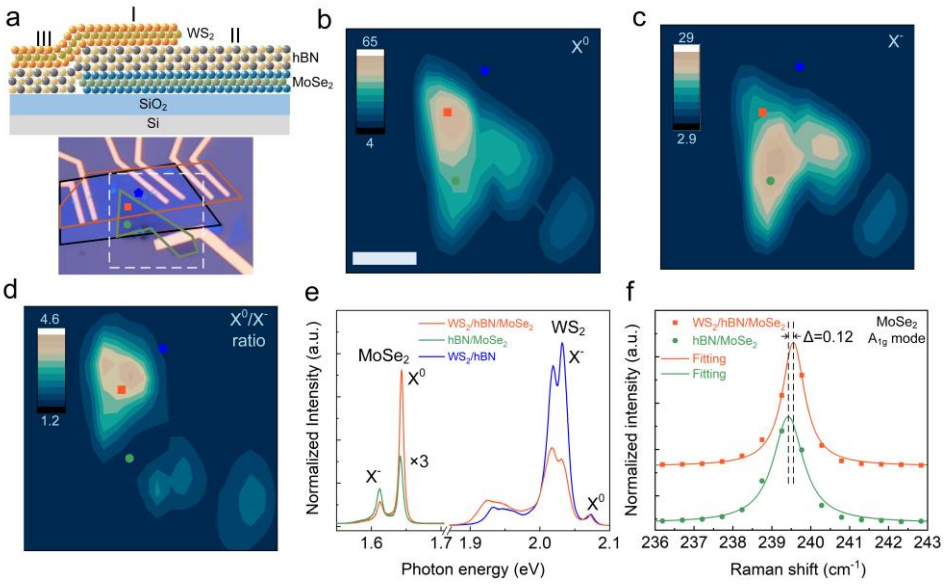

Figure 1. Sample image and optical spectroscopy of the monolayer WS_2/few-layer hBN/monolayer $MoSe_2$ heterojunction excited by 532 nm laser. Orange, black and green sketch denote WS_2, hBN and $MoSe_2$, respectively. White dashed square indicates the mapping area. Same color indication holds along this paper. a Device structure and optical image. b-d PL mapping of $MoSe_2$ X^0 (b), X^- (c) and X^0/X^- ratio (d) over the white dash square indicated in (a). e, f PL (e) and Raman (f) spectra in the corresponding sample position. The scale bar in (b) is 5 μm.

For comparison, we fabricated another typical heterostructure device consisting of a multilayer WS_2 (~10 nm), hBN dielectric layer, and monolayer $MoSe_2$, as presented in Figure 2a. As seen from the spectroscopy mapping excited by 532 nm laser, the $MoSe_2$ X^0 is quite uniform in the whole sample area, indicating no energy transfer (Figure 2b). The absence of FRET results from the negligible interaction between the indirect exciton in multilayer WS_2 and the direct exciton in monolayer $MoSe_2$.[32, 37] The significant difference from the FRET scenery in Figure 1 confirms the origin of the FRET process, *i.e.*, from the direct dipole-dipole coupling. Meanwhile, the $MoSe_2$ X^- emission is quenched by a factor of ~3/5 at the region I, in agreement with the photogating scenery, *i.e.*, photo-generated electrons accumulate at the WS_2/hBN interface (Figure 2c, e). The redshift of $MoSe_2$ A_{1g} mode is 0.2 cm^{-1} in the region I, slightly larger than 0.12 cm^{-1} in the monolayer case in Figure 1, indicating the slightly stronger p-doping effect, which results from the higher optical absorption and larger density of states in multilayer than monolayer WS_2 (Figure 2f). Similarly, the excitation wavelength was then tuned to 671 nm, which shows a negligible change of $MoSe_2$ X^0 emission due to the absence of FRET, as expected (Supplementary Figure 6).

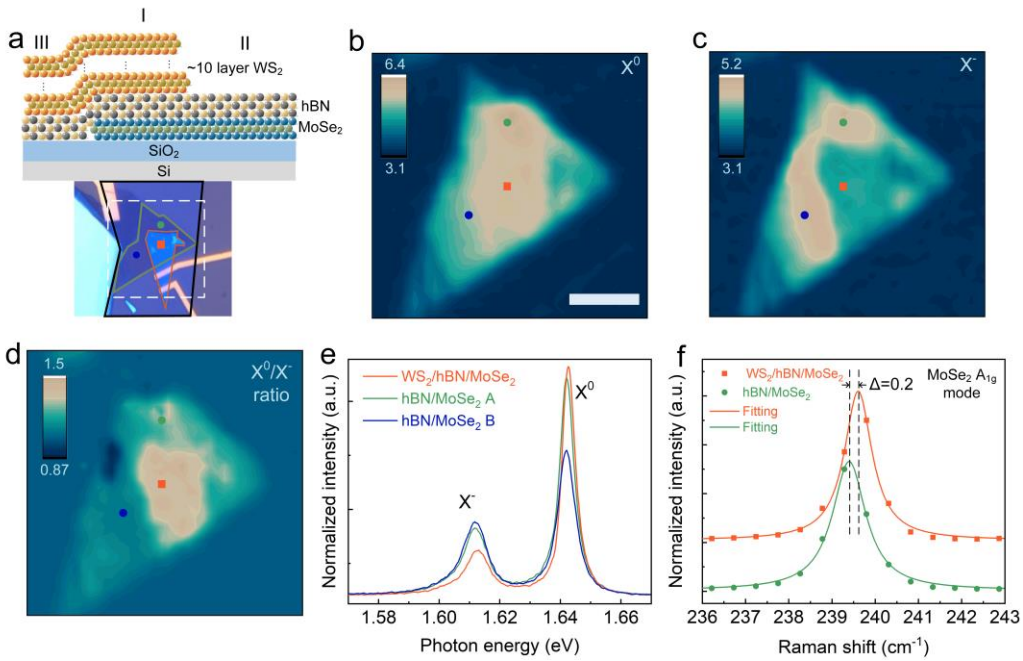

Figure 2. The sample image and optical spectroscopy of the multilayer WS_2/few-layer hBN/monolayer $MoSe_2$ heterojunction excited by 532 nm laser. a Device structure and optical image. b-d PL mapping of $MoSe_2$ X^0 (b), X^- (c) and X^0/X^- ratio (d) over the white dash square indicated in (a). e, f PL (e) and Raman (f) spectra in the corresponding sample position. The scale bar in (b) is 5 μm.

To understand the band alignment, which dominates the interlayer interactions in the heterojunction, we performed the electrical *I-V* measurement, as shown in Figure 3. The tunneling heterojunctions in the region I of Figures 1 and 2 cannot operate due to the poor conductance of TMD monolayers and the insulating hBN layer. Hence, we use the heterojunctions of monolayer WS_2/monolayer $MoSe_2$ and multilayer WS_2/few-layer hBN/multilayer $MoSe_2$ instead (Figure 3, Supplementary Figure 8). In Figure 3a, the WS_2 and $MoSe_2$ layers are biased and grounded, respectively. The linear scale *I-V* curve at different temperatures shows the typical diode characteristics, with a negative turn-on voltage and rectification ratio of ~10^5 at room temperature (Figure 3b). Since the majority carrier in both WS_2 and $MoSe_2$ are electrons, the negative turn-on voltage is an indicator that the conduction band (CB) of WS_2 lies above $MoSe_2$, in agreement with the band alignment calculated by Heyd-Scuseria-Ernzerhof (HSE06) method.[38] This result is also supported by the negative turn-on voltage in the *I-V* curve of the multilayer WS_2/few-layer hBN/multilayer $MoSe_2$ heterojunction (Supplementary Figure 8b). With increasing temperature, the current increases while the turn-on voltage decreases monotonously, implying the thermionic-emission-dominated transport mechanism (Supplementary Figure 9).

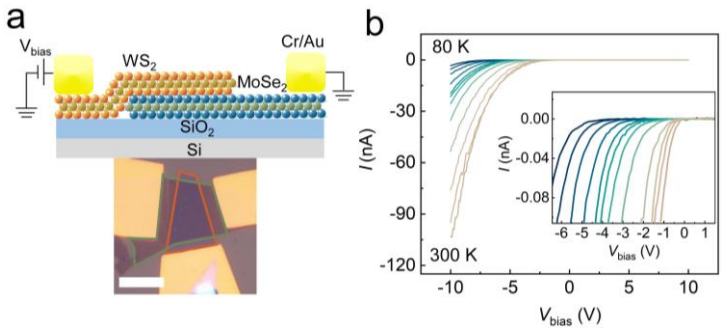

Figure 3. Electrical performance of the monolayer WS_2/monolayer $MoSe_2$ device. a The heterojunction device image and structure. The scale bar is 5 μm. b Linear scale *I-V* performance from 80 K to 300 K with an increment of 20 K. Inset: the zoom-in image of the low bias part.

The dynamic processes in the heterojunction were evaluated by the time-resolved PL (spectral resolution ~2 nm), as plotted in Figure 4. The lifetime of WS_2 X^0 (2.07 eV) on hBN, X^- (2.03 eV) on hBN and hBN/$MoSe_2$ are measured to be 13.8±0.3, 57.4±0.4, and 23.3±0.5 ps, respectively, after deconvolution and fitting with a single exponential decay function $I = I_0 e^{-\frac{t}{\tau}}$ (Figure 4 a-c). It should be emphasized that the radiative recombination of exciton in the 2D system is very fast due to the small exciton Bohr radius and the large exciton optical oscillator strength, *i.e.,* in sub-

picosecond to picosecond timescale, as demonstrated in numerous theoretical and pump-probe investigations.[34, 35, 39-41] The WS_2 X^0 lifetime approaches the temporal resolution of our testing system, as learnt from the comparison between the experimental data and the instrument response function (IRF) curve (Figure 4a). Such a short lifetime indicates that WS_2 X^0 tends to recombine radiatively rather than transfer to the acceptor. However, it should be noted that the WS_2 PL is dominated by X^- emission, which forms within ~2 picoseconds after exciton formation (Figure 1e)[42]. The radiative lifetime of WS_2 X^- (57.4±0.4 ps) is much longer than that of the X^0 due to the difficulty for the electron dissociated from the X^- to find an unoccupied state in the band.[34, 39] As a result, in the heterojunction, the electron-hole pair from X^- in WS_2 tends to transfer into $MoSe_2$ and recombine by emitting a X^0 photon. We can calculate the FRET rate ($1/\tau_{FRET}$) and efficiency (η_{FRET}) according to the formula, $1/\tau_{FRET}=1/\tau_{het}-1/\tau_{donor}$ and $\eta_{FRET}=1-\tau_{het}/\tau_{donor}$, in which τ_{donor} and τ_{het} denote the 1/e lifetime of the WS_2 X^- on hBN and hBN/$MoSe_2$, respectively.[26, 43] The corresponding value τ_{FRET} is ~38.4 ps and η_{FRET} is 59.9%, matching well with the ~50% attenuation of the WS_2 X^- intensity as indicated by the steady-state PL spectra (Figure 1e). During the FRET process, the electrons dissociated from the X^- accumulate at the WS_2/hBN interface, leading to the optical gating effect as aforementioned.

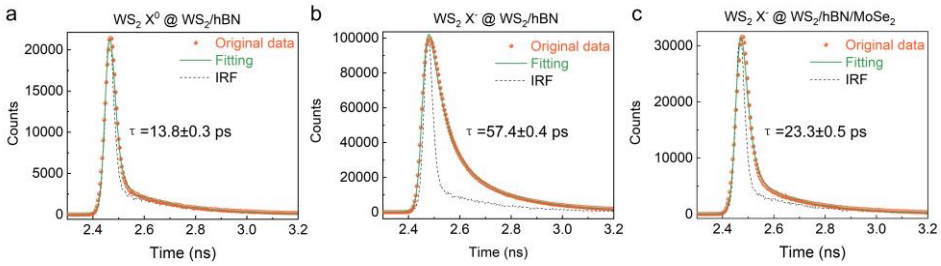

Figure 4. The time-resolved PL of WS_2 measured at 80 K. a X^0 at WS_2/hBN, b X^- at WS_2/hBN, and c X^- at WS_2/hBN/$MoSe_2$. The IRF is provided as a reference.

Besides, we used COMSOL to numerically simulate the FRET rate in monolayer WS_2/few-layer hBN/monolayer $MoSe_2$ heterojunction. We first check the exciton FRET dynamics by placing a dipole inside the WS_2 monolayer with the $MoSe_2$ monolayer as the absorber medium. The model and the distribution of the electric field are shown in Supplementary Figure 11. The exciton FRET

rate, Γ_{X^0FRET}, is calculated by [44-46]

$$\Gamma_{X^0FRET} = \frac{2}{\hbar}\frac{\mathrm{Im}(\varepsilon_{MoSe2}(\omega_{exc}))}{4\pi}\int_{MoSe2}\mathbf{E}\bullet\mathbf{E}^{*}dV \quad (1)$$

where $\varepsilon_{MoSe2}(\omega_{exc})$ is the $MoSe_2$ dielectric function at the exciton frequency of the WS_2, **E** is the electric field induced by an oscillating exciton dipole $\mu e^{-i\omega_{exc}t}$ (μ is dipole moment) and the integral is taken over the $MoSe_2$ layer. The in-plane dipole in WS_2 has a $\mu = 13$ Debye, with other parameters shown in Supplementary Table 2.[11, 47] Accordingly, the computed Γ_{X^0FRET} is: $\Gamma_{X^0FRET} = 2.1\times10^{10}\ s^{-1}$, corresponding to the FRET transfer time τ_{X^0FRET}=47.6 ps. This value is significantly longer than WS_2 exciton lifetime (<13.8 ps) and trion formation lifetime (both lie in the range from sub-picosecond to several picoseconds)[34, 35, 39-42], excluding the exciton as the donor of FRET. Similarly, we check the trion ET dynamics, as detailed in Supplementary Figure 12. The estimated trion energy transfer rate Γ_{X^-ET} is $\Gamma_{X^-ET} = 1.85\times10^{13}\ s^{-1}$, corresponding to a transfer time of 0.054 ps, which is faster than the exciton FRET rate $\left(\Gamma_{X^0FRET} = 2.10\times10^{10}\ s^{-1}\right)$ and meantime shorter than the trion lifetime in WS_2 (57.4 ps). The Γ_{X^-ET} is faster than the value obtained experimentally (38.4 ps) due to the following reasons: 1) the trion lifetime in the heterojunction is close to the IRF, which may cause some overestimation of the lifetime, so as the underestimation of FRET rate; 2) the formula (1) was developed to estimate the exciton FRET rate, which may need a coefficient of correction in the trion ET rate calculation. Further theoretical work is required to get a deeper understanding of the underlying physics.

Based on the preceding optical spectroscopy and transport measurements, we can conclude the realistic band alignment models for three different scenarios as shown in Figure 5. The dynamics in the monolayer WS_2/hBN/monolayer $MoSe_2$ heterojunction include three steps, *i.e.*, (I) the formation of trions in WS_2 within ~2 ps on optical pumping; (II) ~40.1% trions recombine *via* the

recombination of electron-hole pair in the time scale of ~57 ps; (III) the tunneling of the dominant electron-hole pairs (~59.9%) into $MoSe_2$ *via* FRET in the time scale of ~38 ps (Figure 5a). The electrons generated in step (II) accumulate at the WS_2/hBN interface and serve as the photogate. In contrast, the laser excitation only induces excitons and trions in hBN/monolayer $MoSe_2$ (Figure 5b). In multilayer WS_2/hBN/monolayer $MoSe_2$, the optically generated electrons accumulate at the WS_2/hBN interface and gate the $MoSe_2$, leading to the exciton-dominated emission in the PL spectrum (Figure 5c).

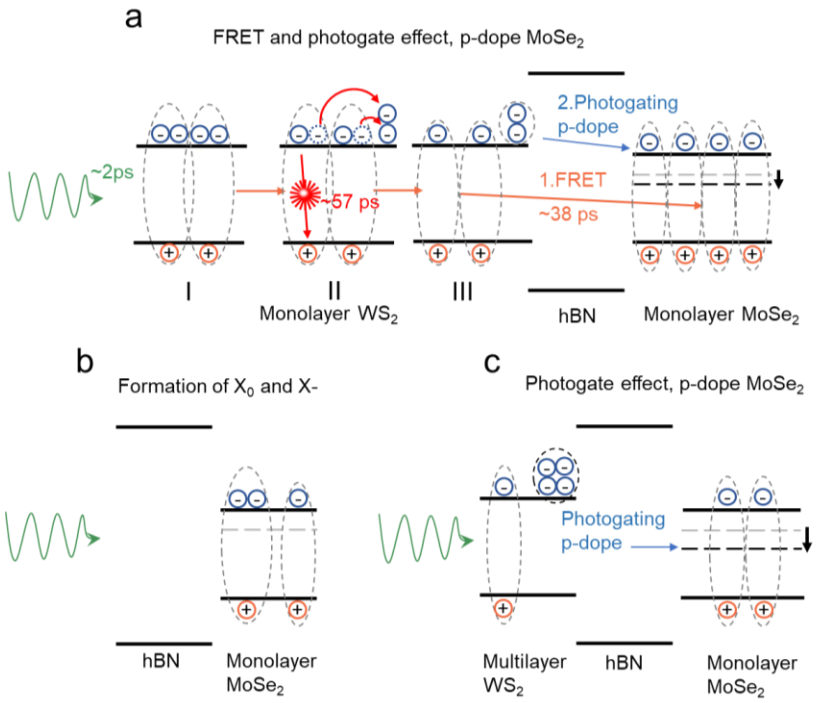

Figure 5. Schematic band diagrams and dynamic processes in different heterojunctions with above WS_2 bandgap excitation. a Monolayer WS_2/hBN/monolayer $MoSe_2$, b hBN/monolayer $MoSe_2$, c multilayer WS_2/hBN/monolayer $MoSe_2$. The dashed line in $MoSe_2$ indicates the Fermi level.

CONCLUSIONS

In conclusion, we have demonstrated a clear picture of the energy transfer dynamics in 2D WS_2/hBN/$MoSe_2$ heterojunction. Specifically, the dynamics are mediated by the trions, in which ~59.9% electron-hole pairs from the trions transfer into $MoSe_2$ *via* FRET channels (τ_{FRET} ~38.4 ps) and the rest ~40.1% recombine by emitting photons in WS_2 (τ_{donor} ~57.4 ps), while the extra electrons accumulate at the WS_2/hBN interface to photogate $MoSe_2$. These results are experimentally revealed by both the steady-state and the time-resolved optical spectroscopy and further supported by the numerical simulations. This mechanism is different from the dipole-dipole

interaction in the molecular system, and also different from the direct exciton-exciton interaction in 2D TMD heterojunctions reported to date. The understanding of the underlying physics lays the foundation for engineering the interlayer energy transfer in the 2D limit and realizing FRET-based high-performance optoelectronic devices.[48]

METHODS

Sample Preparation. TMD samples are first exfoliated from bulk crystals (hq Graphene) to polydimethylsiloxane stamps and then transferred layer by layer on SiO_2 (300 nm)/Si substrate in a nitrogen-filled glovebox. A poly(methyl methacrylate) A4 (Microchem, USA) resist was spin-coated on the sample and then baked at 150 °C for 10 min. We then used a scanning electron microscope (JEOL 7001F) equipped with the nanometer pattern generation system to pattern electrodes. The exposed chip was immersed in methyl isobutyl ketone: isopropanol (3:1) mixed solution for 90 s to finalize developing. After developing, the sample was loaded into a thermal evaporator (Elite Engineering, Singapore) to deposit a Cr/Au film with a thickness of 5/50 nm. Subsequently, the chip was immersed in acetone for lift-off procedure, followed by rinsing with isopropanol and then drying with nitrogen gas. The sample was ready after a high vacuum (10^{-6} mbar) annealing at 200 °C for 2 hours.

Optical Spectroscopy Measurement. (1) For the absorption measurement, we used a microspectrophotometer (Craic 20) to measure the small size sample, and it is capable of measuring the sample size down to 10 μm. The spectral range can be covered from 400 to 2100 nm. (2) PL and Raman spectroscopy mapping were conducted on a spectrometer with a 800 mm focal length (Horiba-JY Evolution) equipped with a liquid nitrogen-cooled CCD detector. Samples were put in a continuous flow cryostat fixed on an xyz translation stage. The optical signals are collected by a 50× long work distance objective. All the measurements were carried out at a low temperature of 80 K with an excitation power ~10 μW. (3) The time-resolved photoluminescence spectroscopy measurement was performed with a home-built confocal micro-PL setup. Samples were also put in the cryostat operated at 80 K. A Ti: sapphire femtosecond laser with ~100 fs pulses at 80 MHz is used as the excitation source. The emission of the laser is frequency-doubled to output 400 nm

pulses and is focused (50× objective lens, NA = 0.65) onto the sample. The time-resolved photoluminescence emission is first spectrally resolved with a spectrometer with a focal length of 320 mm (Horiba-JY iHR320), and photons after the exit slit of the spectrometer are detected with an avalanche detector connected to a time-correlated single-photon counting module (PicoHarp 300). The excitation power is ~ 5 μW.

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ASSOCIATED CONTENT

Supporting Information Available: Absorption, Raman and PL spectra from different samples; *I-V* performance and fitting; PL lifetime fitting; details of numerical simulations. This material is available free of charge *via* the Internet at http://pubs.acs.org.

Competing interests:

The authors declare no competing interests.

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