

pubs.acs.org/journal/apchd5

Article

# Light Absorption and Emission Dominated by Trions in the Type-I van der Waals Heterostructures

Hyemin Bae, ◆ Suk Hyun Kim, ◆ Seungmin Lee, Minji Noh, Ouri Karni, Aidan L. O'Beirne, Elyse Barré, Sangwan Sim, Soonyoung Cha, Moon-Ho Jo, Tony F. Heinz,\* and Hyunyong Choi\*



powerful method to control the alignment of energy bands of atomically thin 2D materials. Under light illumination, the optical responses are dominated by Coulomb-bound electron—hole quasiparticles, for example, excitons, trions, and biexcitons, whose contributions accordingly depend on the types of heterostructures. For type-II heterostructures, it has been well established that light excitation results in electrons and holes that are separated in different layers, and the radiative recombination is dominated by the interlayer excitons. On the contrary, little is known about the



corresponding optical responses of type-I cases. Understanding the optical characteristics of type-I heterostructures is important to the full exploration of the quasiparticle physics of the 2D heterostacks. In this study, we performed optical spectroscopy on type-I vdW heterostacks composed of monolayer MoTe<sub>2</sub> and WSe<sub>2</sub>. Photoluminescence and reflection contrast spectroscopy show that the light absorption and emission are dominated by the Coulomb-bound trions. Importantly, we observed that the MoTe<sub>2</sub> trion emission gets stronger compared with the exciton emission under resonant light excitation to the WSe<sub>2</sub> trion absorption state, especially in the WSe<sub>2</sub>/MoTe<sub>2</sub>/WSe<sub>2</sub> heterotrilayer. A detailed study of photoluminescence excitation further reveals that the chargetransfer mechanism is likely responsible for our observation, which differs from the exciton-dominated dipole–dipole energy transfer in type-II structures. Our demonstration implies that the type-I vdW heterostack provides new opportunities to engineer the light– matter interactions through many-body Coulomb-bound states.

**KEYWORDS:** transition-metal dichalcogenide, trion emission, type-I van der Waals heterostructure, two-dimensional material, van der Waals interface

he use of vdW heterostacking using transition-metal dichalcogenides (TMDs) opens up new avenues to study a variety of intriguing optoelectronic properties that are not easily accessible in conventional bulk solids.<sup>1-4</sup> Because the lattice mismatch does not impose limits on forming arbitrary heterointerfaces, dramatic changes in the magnetic, electronic, and optical properties have been introduced to both lateral<sup>5,6</sup> and vertical junctions $^{7-10}$  in addition to the recent discovery of the twist-angle-dependent Moiré superlattices.<sup>11-13</sup> An extensively investigated structure is the type-II heterostructure. In this case, when light illumination takes place in the heterostructures composed of semiconductors MX<sub>2</sub> and WX<sub>2</sub> (M = Mo or W and X = S or Se) with different work functions, electrons and holes are transferred into different layers of TMDs, and the light absorption and emission show new oscillators whose optical selection rules,<sup>16-20</sup> emitted photon helicities,<sup>21</sup> and charge-transfer characteristics<sup>22-24</sup> exhibit different optical responses compared with those of monolayer TMDs. Type-II heterostructures also result in new quasiparticles, such as long-lived interlayer excitons,<sup>14,25</sup> locally trapped

Moiré excitons,<sup>26,27</sup> Bose-like exciton condensation,<sup>28</sup> and tunable Mott insulators.<sup>29</sup>

The strong 2D Coulomb interaction can host stable charged excitons, called trions, whose effects on the optical responses are profound, sometimes dominant over the exciton effects.<sup>15,30,31</sup> Other than the type-II vdW heterostructures, different choices of TMDs can also offer opportunities to engineer the band alignment with a straddling energy gap. In this type-I heterostructure, because the electrons and holes reside in the same layer, the binding energy of exciton complexes is expected to be greatly enhanced. Therefore, it is highly crucial to investigate the roles of many-body Coulomb-bound states in the absorption and emission of light and the

Received: December 22, 2020 Published: June 11, 2021







**Figure 1.** (a) Optical microscope image of the heterostructure using the ML of WSe<sub>2</sub> and MoTe<sub>2</sub> on the Si/SiO<sub>2</sub> substrate. The scale bar is 10  $\mu$ m. Schematic of the heterobilayer and heterotrilayer device. (b) Heterobilayer and (c) heterotrilayer exhibit a type-I band alignment.

corresponding correlation between the photogenerated exciton complexes.

In this study, we investigate the optical responses of type-I vdW heterostructures, composed of monolayers (MLs) of WSe<sub>2</sub> and MoTe<sub>2</sub>. Photoluminescence (PL) and reflection contrast (RC) were performed to study the spectral features of the light emission as well as the photon-energy-dependent absorption characteristics. In addition, we performed photoluminescence excitation (PLE) spectroscopy to investigate the spectral correlation between the light absorption in high-energy-gap WSe<sub>2</sub> and the light emission in the low-band-gap MoTe<sub>2</sub>. The experiments were done on both the heterobilayer and the heterotrilayer, from which we conclude that the Coulomb-bound trions are the key contributors to the optical responses of the type-I heterostacks, and the charge-transfer process is likely dominant over the dipole-mediated energy transfer.

Figure 1a is the optical microscope image of the fabricated heterobilayer and heterotrilayer using MLs of WSe<sub>2</sub> and MoTe<sub>2</sub>. (See the Sample Preparation section for details.) Each ML of WSe<sub>2</sub> and MoTe<sub>2</sub> is mechanically exfoliated from the bulk crystals, and they are stacked using a dry-transfer method on a Si/SiO<sub>2</sub> (300 nm) substrate. Thin hexagonal boron nitride (hBN) was used to encapsulate the top and bottom of the heterostacks, which protects the samples from unwanted possible contamination during the experiments.<sup>32,33</sup> For the measurements, the sample was mounted on a liquid-helium-cooled cryostat at a coldfinger temperature of 70 K. (See the Optical Measurements for details.) Figure 1b,c shows the estimated energy band alignment of the WSe<sub>2</sub>/MoTe<sub>2</sub> heterobilayer and heterotrilayer using the work functions from ref 34. Indeed, the conduction band minimum and

valence band maximum are both located in the  $MoTe_2$  layer, reflecting the type-I band alignment.

We first performed PL spectroscopy to understand the light emission characteristics of the heterostructures. The excitation source is a standard He–Ne laser (photon energy 1.96 eV) that enables the previously described gap excitation of our samples. The on-resonant excitation was performed using PLE spectroscopy. Figure 2a shows the PL spectra of MoTe<sub>2</sub>ML (blue line) and the heterobilayer (red line) as well as the heterotrilayer (purple line). The heterotrilayer PL spectra were



**Figure 2.** (a) PL spectra of ML  $MoTe_2$  (blue line),  $WSe_2/MoTe_2$  heterobilayer (red line), and  $WSe_2/MoTe_2/WSe_2$  heterotrilayer (purple line) are shown. Inset: PL spectra of ML WSe<sub>2</sub> (green line) and heterobilayer (red line, ×100) are shown. (b) PL spectra of ML MoTe<sub>2</sub>, heterobilayer, and heterobilayer, with the peak heights normalized to the exciton peaks. The filled blue, red, and purple areas are the Lorentzian fits to the trion and exciton resonances.

normalized to compensate for the 10% of top - WSe<sub>2</sub> layer screening effect. Whereas an exciton peak was seen at 1.17 eV for ML MoTe<sub>2</sub>, additional luminescence was observed at 1.148 eV for both the heterobilayer and the heterotrilayer. For the heterobilayer and heterotrilayer, there are two strong luminescence peaks at 1.148 and 1.17 eV that we attribute to the trion and exciton resonance, respectively. The peak at the red side of the exciton peak is confirmed as a trion peak by its spectral position and the excitation power-dependent PL measurement.<sup>35–37</sup> We set the intensity of the ML MoTe<sub>2</sub> exciton to be 100% as our reference. In the heterobilayer, for the MoTe<sub>2</sub> exciton, the peak height does not change, that is, the intensity of 100%. The newly appeared trion peak is  $\sim$ 50% compared with the MoTe<sub>2</sub> exciton peak; this implies that the overall PL intensity is ~150% compared with the ML MoTe<sub>2</sub>. In the trilayer case, for the MoTe<sub>2</sub> exciton, the peak height is decreased by 40%, resulting in a spectrally integrated intensity of 60%. The trion peak of intensity is enhanced by 10%, resulting in a total PL intensity of 55%. The exciton and trion contribute  $\sim 115\%$  to the total PL intensity

The inset of Figure 2a shows the PL spectra of the WSe<sub>2</sub> ML and the heterobilayer in a higher photon energy range of 1.65 to -1.75 eV. For the ML WSe<sub>2</sub>, there are two strong luminescence peaks at 1.69 and 1.73 eV, which we attribute to the trion and exciton light emission that originated from  $WSe_{2}$ , respectively. Interestingly, the PL spectra of the heterobilayer show no optical responses in the WSe<sub>2</sub> spectral region, implying that the light emission from the heterobilayer is strongly quenched (~99.8%) compared with that of the isolated ML WSe<sub>2</sub>. This quenched response implies that the photogenerated carriers experience rapid interlayer charge transfer to an energetically favorable lower state. These observations, that is, the PL spectra in the MoTe<sub>2</sub> and WSe<sub>2</sub> spectral range, can be understood by the type-I band alignment of our heterostack. If our heterobilayer is type-II, then no exciton PL should be observed from the MoTe<sub>2</sub> spectral region because electrons and holes are separated into different layers so that the radiative recombination of the intralayer excitons should be suppressed.

In Figure 2b, the spectra are normalized by the MoTe<sub>2</sub> exciton peak emission intensity to clarify the relative MoTe<sub>2</sub> trion emission contribution. The filled area represents the contribution of the MoTe<sub>2</sub> exciton and trion, fitted using a Lorentzian.<sup>38</sup> A further examination of the relative ratio  $\eta$  of the PL intensity for the trion and exciton, that is,  $\eta = I_{\rm trion}/$  $I_{\text{exciton}}$  reveals that  $\eta$  seemingly increases from 0.49 for the heterobilayer to 0.92 for the heterotrilayer. The largely enhanced  $\eta$  can be explained by the two considerations. First, although the ML MoTe<sub>2</sub> is surrounded by a barrier-like ML WSe<sub>2</sub>, the intrinsic light emission properties, that is, the emission energy and the line width of ML MoTe2, are preserved because of the weak interlayer vdW interaction. Furthermore, because our heterobilayer and heterotrilayer are stacked randomly, we are less likely to observe additional luminescence from the Moiré excitons.<sup>11-13,26,27</sup> Second, our exfoliated WSe<sub>2</sub> flakes are slightly n-doped; the parent bulk crystal is n-doped. This induces an intrinsic electron doping to the MoTe<sub>2</sub> layer, resulting in the enhanced trion emission. Because the MoTe<sub>2</sub> trion states in the heterotrilayer can be more easily populated than the heterobilayer due to the extra electron injection from WSe<sub>2</sub>, the light emission from the MoTe<sub>2</sub> trions is more dominant than the heterobilayer case.

Because PL can probe only the lowest bright emission state, we employ RC spectroscopy to examine the absorptive Coulomb-bound states.<sup>27</sup> Figure 3a shows the RC spectra of



**Figure 3.** (a) RC spectra of each region are shown for ML WSe<sub>2</sub> (green line), MoTe<sub>2</sub> (blue line), heterobilayer (red line), and heterotrilayer (purple line). The vertical dashed lines indicate the WSe<sub>2</sub> trion and exciton absorption energies. (b) Real (blue line) and imaginary (red line) parts of the complex absorbance spectra  $A(\omega)$  of the WSe<sub>2</sub>/MoTe<sub>2</sub> heterobilayer calculated by Kramers–Kronig constrained analysis. We see that the real part of  $A(\omega)$  has two peaks that match well with the WSe<sub>2</sub> exciton peak and the WSe<sub>2</sub> trion peak position of WSe<sub>2</sub>PL spectra data.

each spatial region of our heterostructure: ML MoTe<sub>2</sub>(blue line), ML WSe<sub>2</sub>(green line), the heterobilayer (red line), and the heterotrilayer (purple line). The ML  $MoTe_2$  layer is essentially featureless; the broadly varying absorption may originate from the scattered light of SiO<sub>2</sub> and hBN layers. In ML WSe<sub>2</sub>, we observe a strong absorption from the A exciton, whereas the trion absorption is almost negligible. On the contrary, the heterobilayer and the heterotrilayer exhibit absorption features near the WSe<sub>2</sub> trion resonance. From the RC measurements, we can infer that the WSe<sub>2</sub> trion states in the heterobilayer and the heterotrilayer contribute more to the optical absorption than the WSe<sub>2</sub> exciton states. In Figure 3b, the Kramers-Kronig constrained analysis<sup>31</sup> was applied to calculate the complex valued absorbance spectra  $A(\omega)$  for the  $WSe_2/MoTe_2$  heterobilayer, confirming that the WSe\_2 exciton peak and the WSe<sub>2</sub> trion peak coincide with the WSe<sub>2</sub> PL spectra data. The sample absorbance was calculated from the RC data with Kramers-Kronig constrained analysis.<sup>31</sup> The dielectric function was modeled by a sum of 200 equally spaced Lorentzian functions over the spectral range of interest, 1.6 to 1.8 eV, as follows

$$\varepsilon(\omega) = \sum_{j} \frac{\omega_{p,j}^{2}}{\omega_{j}^{2} - \omega^{2} + i\Gamma\omega}$$

Here  $\omega_{p,j}$  is the *j*th oscillator strength fitting parameter, and  $\omega_j = 1.6 + j \times 0.001$  (in eV) is the *j*th resonance energy (broadening parameter  $\Gamma = 10$  meV). The absorbance curve in Figure 3b is calculated by  $A(\omega) = \frac{-i\omega d}{c} \varepsilon(\omega)$ . We see that the real part of the  $A(\omega)$  has two peaks, which match well with the WSe<sub>2</sub> exciton peak and the WSe<sub>2</sub> trion peak positions of the WSe<sub>2</sub>PL spectrum.

To investigate the spectral correlation of the trion absorption and emission in  $WSe_2$  and  $MoTe_2$ , we performed PLE on the ML MoTe<sub>2</sub>, heterobilayer, and heterotrilayer. Figure 4a-c shows the 2D plots of the corresponding PLE data



**Figure 4.** (a) 2D plot of PLE data for MoTe<sub>2</sub>, (b) the heterobilayer, and (c) the heterotrilayer at 70 K. The vertical black dashed lines represent the MoTe<sub>2</sub> trion and exciton luminescence states, and the horizontal white dashed lines are the WSe<sub>2</sub> trion and exciton absorption states. (d) The trion–exciton intensity ratio  $\eta$  is shown as a function of the excitation energy, displaying the dominance of the trion in the heterotrilayer compared with the heterobilayer.

for each region. In the Figure, the vertical black dashed lines represent the MoTe<sub>2</sub> trion (1.148 eV) and MoTe<sub>2</sub> exciton (1.17 eV) luminescence energies determined from Figure 2, and the horizontal white dashed lines are the WSe<sub>2</sub> trion (1.690 eV) and the WSe<sub>2</sub> exciton (1.725 eV) absorption energies obtained from Figure 3. For the region of the ML MoTe<sub>2</sub> alone, a single luminescence peak at 1.17 eV was observed regardless of the excitation photon energy. This reflects that the above-gap absorption of free carriers and the subsequent radiative recombination of the band-edge excitons are dominant in the ML MoTe<sub>2</sub> optical response. When probing the heterostructures, however, we see that the PLE contains very different luminescence spectral structures that strongly depend on the excited photon energy. In particular, we observed an additional luminescence peak at 1.148 eV, which is 22 meV lower than the  $MoTe_2$  exciton PL of the heterobilayer. Interestingly, the PL intensity is strongly enhanced when the excited photon energy is at 1.69 eV for the heterobilayer. Inferring from the RC measurement of Figure 3, this excited photon energy matches the WSe<sub>2</sub> trion absorption resonance. When the excited photon energy is away from the WSe<sub>2</sub> trion, the MoTe<sub>2</sub> trion luminescence is weaker. This supports the notion that the MoTe<sub>2</sub> trion emission is enhanced by the WSe<sub>2</sub> trion absorption.

The heterotrilayer PLE (Figure 4c) is qualitatively different from the heterobilayer PLE (Figure 4b). The PL emission is largely dominated by the MoTe<sub>2</sub> trion emission at 1.69 eV (black vertical line). The enhanced  $MoTe_2$  trion emission by the WSe<sub>2</sub> trion absorption, a feature similarly observed in heterobilayer, is more pronounced in the heterotrilayer. A distinct feature compared with the heterobilayer is that the MoTe<sub>2</sub> exciton emission, which presumably occurs at 1.17 eV, is marginally small regardless of the excitation photon energy, exhibiting the dominant role of the trion absorption over the exciton absorption in the light emission. The ratio of PL intensity for the trion and exciton  $\eta$  is plotted as a function of the excitation energy in Figure 4d, which indicates that the correlation between the light absorption ( $WSe_2$  trion absorption) and emission (MoTe<sub>2</sub> trion emission) reaches the spectral maximum in both of the heterostacks and is much stronger in the heterotrilayer (max: $\eta = 2.5$ ) than in the heterobilayer (max: $\eta$  = 1.3). This feature can be understood by the presence of n-doped WSe<sub>2</sub> in both sides of  $MoTe_2$ , which further helps the trion formation. Such on-resonance  $\eta$  values are far stronger than the above-gap excitation case in Figure 2 of  $\eta = 0.92$  in the heterotrilayer and  $\eta = 0.49$  in the heterobilayer. This significant enhancement under the onresonance excitation implies that the  $MoTe_2$  trion formation is

different from the ground-state or the background electron transfer.

A prior study on the WSe<sub>2</sub>/MoTe<sub>2</sub> type-I heterostructure<sup>39-44</sup> suggests that the dipole-dipole energy transfer induces the neutral exciton "transfer": The WSe2 exciton recombination releases energy to excite the MoTe<sub>2</sub> carrier over the quasiparticle gap and creates excitons in the MoTe<sub>2</sub> layer. Adopting the same mechanism to explain our trion feature, however, raises some issues. A common feature observed both in the heterobilayer and heterotrilayer is that no spectral correlation was seen between the WSe<sub>2</sub> exciton absorption and the MoTe<sub>2</sub> trion emission; the only relevant exciton complexes are the WSe<sub>2</sub> trion for the light absorption and the MoTe<sub>2</sub> trion for the light emission. If the MoTe<sub>2</sub> trion is created by the released energy from the WSe<sub>2</sub> trion recombination, then the WSe<sub>2</sub> exciton should be able to create the MoTe<sub>2</sub> trion as well. This contradicts our observation of the PLE spectral correlations.

A close examination of the energy spectrum of light excitation and the MoTe<sub>2</sub> luminescence provides another clue to the origin of the MoTe<sub>2</sub> trion emission. In the heterobilayer, we see that the MoTe<sub>2</sub> exciton emission is activated by a wide spectral range (~200 meV) of light excitation around the WSe<sub>2</sub> exciton energy (Figure 4b). In contrast, the MoTe<sub>2</sub> trion emission occurs within a narrow energy window ( $\sim 20 \text{ meV}$ ) around the WSe<sub>2</sub> trion absorption state in both the heterobilayer and the heterotrilayer. This implies that the creation mechanism is different between the MoTe<sub>2</sub> exciton and trion. For the MoTe<sub>2</sub> exciton, it can be created by the dipole-dipole energy transfer via the energy released from WSe<sub>2</sub> exciton recombination. One can attribute the wide acceptance range of MoTe<sub>2</sub> exciton emission to the energy-mediated transfer process, where the required energy criteria for the stable exciton creation are not very important. On the contrary, the MoTe<sub>2</sub> trion is likely directly transferred from the WSe<sub>2</sub> trion. This is because the narrow spectral window of the MoTe<sub>2</sub> trion emission requires an exact amount of energy for the stable trion creation in WSe<sub>2</sub> and the subsequent charge transfer.

Because we assumed that the trion can transfer from WSe<sub>2</sub> to MoTe<sub>2</sub>, we can develop a rate-equation model for the creation, transfer, and decay of the neutral exciton and trion in the WSe<sub>2</sub>/MoTe<sub>2</sub> heterobilayer stack. We define four variables,  $N_{\rm WE}$ ,  $N_{\rm WT}$ ,  $N_{\rm ME}$  and  $N_{\rm MT}$ , as the excitons in WSe<sub>2</sub>, trions in WSe<sub>2</sub>, excitons in MoTe<sub>2</sub>, and trions in MoTe<sub>2</sub>, respectively. The dynamic rate equations for these populations are as follows.<sup>45</sup>

$$\begin{aligned} \frac{\mathrm{d}N_{\mathrm{WE}}}{\mathrm{d}t} &= P_{\mathrm{W}} - (k_{\mathrm{E}\rightarrow\mathrm{T}}^{\mathrm{W}} + k_{\mathrm{WE}} + k_{\mathrm{inter}} + k_{\mathrm{E}}^{\mathrm{W}\rightarrow\mathrm{M}})N_{\mathrm{WE}} \\ \frac{\mathrm{d}N_{\mathrm{WT}}}{\mathrm{d}t} &= k_{\mathrm{E}\rightarrow\mathrm{T}}^{\mathrm{W}}N_{\mathrm{WE}} - (k_{\mathrm{WT}} + k_{\mathrm{inter}} + k_{\mathrm{T}}^{\mathrm{W}\rightarrow\mathrm{M}})N_{\mathrm{WT}} \\ \frac{\mathrm{d}N_{\mathrm{ME}}}{\mathrm{d}t} &= P_{\mathrm{M}} + k_{\mathrm{E}}^{\mathrm{W}\rightarrow\mathrm{M}}N_{\mathrm{WE}} - (k_{\mathrm{ME}} + k_{\mathrm{inter}} + k_{\mathrm{E}\rightarrow\mathrm{T}}^{\mathrm{M}})N_{\mathrm{ME}} \\ \frac{\mathrm{d}N_{\mathrm{MT}}}{\mathrm{d}t} &= k_{\mathrm{E}\rightarrow\mathrm{T}}^{\mathrm{M}}N_{\mathrm{ME}} + k_{\mathrm{T}}^{\mathrm{W}\rightarrow\mathrm{M}}N_{\mathrm{WT}} - (k_{\mathrm{MT}} + k_{\mathrm{inter}})N_{\mathrm{MT}} \end{aligned}$$

Here we defined a number of variables to describe the rate of creation, transfer, and decay of excitons and trions.  $P_W(P_M)$  is the exciton creation rate by optical excitation in WSe<sub>2</sub> (MoTe<sub>2</sub>).  $k_{WE}$ ,  $k_{WT}$ ,  $k_{ME}$ , and  $k_{MT}$  are the relaxation rates of excitons in WSe<sub>2</sub>, trions in WSe<sub>2</sub>, excitons in MoTe<sub>2</sub>, and trions in MoTe<sub>2</sub>, respectively.  $k_{E\rightarrow T}^W$  ( $k_{E\rightarrow T}^M$ ) is the transformation rate from excitons to trions in WSe<sub>2</sub> (MoTe<sub>2</sub>).  $k_E^{E\rightarrow T}$  and  $k_T^{W\rightarrow M}$  are the WSe<sub>2</sub>-to-MoTe<sub>2</sub> transfer rates of excitons and trions, respectively. Finally, we defined  $k_{inter}$  to describe the interface-defect-induced decay rates. In addition to the PL peak height analysis, we analyzed the temperature dependence of the PL line width from the MoTe<sub>2</sub> ML and the heterobilayer and obtained the rates assuming the steady state.

$$k_{\text{inter}} = 8.221 \times 10^{12} \text{ s}^{-1}$$
$$k_{\text{ME}} = 3.361 \times 10^{11} \text{ s}^{-1}$$
$$k_{\text{MT}} = 2.223 \times 10^{12} \text{ s}^{-1}$$
$$k_{\text{WE}} = 7.03 \times 10^{11} \text{ s}^{-1}$$
$$k_{\text{E} \rightarrow \text{T}}^{\text{W}} = 3.72 \times 10^{11} \text{ s}^{-1}$$

By this simple model, we obtained the creation, transfer, and decay rates of excitons and trions in the heterobilayer. We see the four different k values,  $k_{E\to T}^W$ ,  $k_{WE}$ ,  $k_{inter}$ , and  $k_E^{W\to M}$ , are the flow weights of the four pathways that the WSe<sub>2</sub> excitons take, such as transforming into the trion, relaxing within WSe<sub>2</sub>, relaxing in the interface defect, and transferring into MoTe<sub>2</sub>, respectively. Now we focus on the WSe<sub>2</sub>-to-MoTe<sub>2</sub> trion transfer. From the ML MoTe<sub>2</sub> PL data with no significant trion peak, we assume that the trion generation rate from the MoTe<sub>2</sub> exciton  $k_{E\to T}^M$  is negligible. This leads to the following equation.

$$k_{\rm T}^{\rm W \to M} = \frac{(k_{\rm MT} + k_{\rm inter})N_{\rm MT}}{N_{\rm ME}}$$

We see that the WSe<sub>2</sub>-to-MoTe<sub>2</sub> transfer rate of trions,  $k_{\rm T}^{{\rm W}\rightarrow{\rm M}}$ , is directly proportional to the population ratio  $N_{\rm MT}/N_{\rm ME}$  the trion/exciton PL peak height ratio of the heterostack,  $\eta$ . In the case of the above-gap excitation ( $\eta = 0.49$ ), the calculated value of  $k_{\rm T}^{{\rm W}\rightarrow{\rm M}}$  is 5.12 × 10<sup>12</sup> s<sup>-1</sup>. As we vary the excitation wavelength, we can compare the trion transfer rate for onresonance and above-gap excitation. For resonant PL excitation ( $\eta = N_{\rm MT}/N_{\rm ME} = 1.3$ ), the trion transfer rate  $k_{\rm T}^{{\rm W}\rightarrow{\rm M}}$  is 1.36 × 10<sup>13</sup> s<sup>-1</sup>, which is 260% larger compared with the above-gap excitation case. Under this model, we find that resonant excitation supports the creation of trions in the heterobilayer system.

In summary, we have investigated the light absorption and emission in the type-I vdW heterostructures. In contrast with the type-II heterostructure, where the light emission is strongly quenched, we observed the enhanced light emission of excitons and trions in the type-I heterostacks. The light emission intensity was larger at the  $MoTe_2$  trion than at the exciton emission. RC measurements confirm that there indeed exists a trion absorption state in our type-I structure, which is absent in the isolated MLs of WSe<sub>2</sub> and MoTe<sub>2</sub>. Interestingly, the enhanced MoTe<sub>2</sub> trion emission is pronounced when the light excitation is at the WSe<sub>2</sub> trion absorption energy. On the contrary, no such resonant feature was observed for the MoTe<sub>2</sub> exciton luminescence. Thus we conclude that the chargetransfer process, rather than the dipole—dipole energy transfer, is likely responsible for the trion-dominated light absorption and emission in the type-I vdW stacks.

## SAMPLE PREPARATION

The samples used in this experiment were prepared by mechanical exfoliation.<sup>1–5</sup> The WSe<sub>2</sub> and MoTe<sub>2</sub> crystals were purchased from 2D Semiconductors. Small pieces of WSe<sub>2</sub> and MoTe<sub>2</sub> bulk crystals were exfoliated onto the polydimethylsiloxane (PDMS). We then found ML WSe<sub>2</sub> and MoTe<sub>2</sub> flakes whose thicknesses were confirmed by the image analysis based on the computational algorithm.<sup>6</sup> The bottom hBN, ML WSe<sub>2</sub>, ML MoTe<sub>2</sub> and top hBN flake were subsequently transferred to a Si/SiO<sub>2</sub> (300 nm) substrate by the dry-transfer method<sup>7</sup> using a piezo stage. Thin hBN was used to encapsulate the top and bottom of the heterostacks, which protected the samples from possible air contamination during the experiments.<sup>8–10</sup> During the procedure, the layers were stacked with extreme care, which helped to prevent any unwanted formation of microbubbles between the layers. Finally, the stacked sample was annealed at 150 °C for 2 h in a vacuum environment.

#### OPTICAL MEASUREMENTS

The constructed optical setups were used to perform various optical measurements simultaneously: PL, RC, and PLE spectroscopy. For the PL spectroscopy, the samples were excited by the He-Ne laser with a photon energy of 1.96 eV. For the RC measurement, a tungsten halogen lamp was used for the broadband white-light source. For the PLE spectroscopy, the broadband excitation beam was first generated by a supercontinuum pulsed laser source (NKT Photonics, with a repetition rate 20 MHz and a pulse width of 400 fs), and the excitation color was selected by a diffraction grating monochromator (Princeton Instrument) in the wavelength range of 600-850 nm with a spectral resolution of 1 nm. All of the beams were focused on the sample with a microscope objective lens (spot size of 2 to 3  $\mu$ m). To cover the spectral ranges of the WSe<sub>2</sub> A exciton and the MoTe<sub>2</sub> A exciton, we measured the signals using a spectrometer equipped with a Peltier-cooled Si charge-coupled device (CCD) (for the visible to near-IR range, 300–1000 nm) and a liquid-nitrogen-cooled InGaAs CCD array detector (for the IR range, 800–1700 nm), respectively. The laser excitation power was controlled by a set of ND filters with various optical densities.

### AUTHOR INFORMATION

#### **Corresponding Authors**

- Hyunyong Choi Institute of Applied Physics and Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea; orcid.org/0000-0003-3295-1049; Email: hy.choi@snu.ac.kr
- Tony F. Heinz Department of Applied Physics and Photon Science, Stanford University, Stanford, California 94305,

United States; SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States; • orcid.org/ 0000-0003-1365-9464; Email: tony.heinz@stanford.edu

### Authors

- **Hyemin Bae** Institute of Applied Physics, Seoul National University, Seoul 08826, Korea
- Suk Hyun Kim Institute of Applied Physics and Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea
- Seungmin Lee School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea
- Minji Noh Institute of Applied Physics and Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea
- **Ouri Karni** Department of Applied Physics and Photon Science, Stanford University, Stanford, California 94305, United States
- Aidan L. O'Beirne Department of Applied Physics and Photon Science, Stanford University, Stanford, California 94305, United States
- Elyse Barré Department of Applied Physics and Photon Science, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0003-2119-0707
- Sangwan Sim Division of Electrical Engineering, Hanyang University, Ansan 15588, Korea; in orcid.org/0000-0001-9877-8272
- Soonyoung Cha Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), Pohang 37673, Republic of Korea; Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea
- Moon-Ho Jo Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), Pohang 37673, Republic of Korea; Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea; orcid.org/0000-0002-3160-358X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsphotonics.0c01942

## **Author Contributions**

◆H.B. and S.H.K. contributed equally to this work. H.C. conceived the main idea. H.B., S.L., and M.N. carried out the device fabrication. H.B., S.H.K., and S.L. performed the PL, PLE, and RC measurements. S.S., O.K., A.L.O., E.B., S.C., M.-H.J., and T.F.H. discussed the main results and data modeling. T.F.H. and H.C. supervised the work. H.B., S.H.K., and S.L. wrote the manuscript with input from all authors. All authors contributed to the analysis and interpretation of the results and the preparation of the manuscript.

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the New Faculty Startup Fund from Seoul National University. H.B., S.L., M.N., and H.C. were supported by the NRF through the government of Korea (MSIP) (grants NRF-2018R1A2A1A05079060, NRF-2021R1A2C3005905), the Creative Materials Discovery Program (grant 2017M3D1A1040828), the Scalable Quantum Computer Technology Platform Center (grant 2019R1A5A1027055), and the Institute for Basic Science (IBS), Korea under project code IBS-R014-G1-2018-A1. H.C. was supported by LG Yonam Foundation of Korea. O.K. acknowledges the support of the Viterbi Fellowship of the Erna and Andrew Viterbi Department of Electrical Engineering, Technion, Israel, and of the Koret Foundation, CA, USA. E.B. is supported by the National Sciences and Engineering Research Council (NSERC) of Canada PostGraduate Scholarship for Doctoral program (PGS-D), PGSD3-502559-2017, and the National Science Foundation (NSF) newLAW program, award 1741691.

## REFERENCES

(1) Geim, A. K.; Grigorieva, I. V. Van der Waals heterostructures. *Nature* **2013**, 499 (7459), 419–25.

(2) Jin, C.; Ma, E. Y.; Karni, O.; Regan, E. C.; Wang, F.; Heinz, T. F. Ultrafast dynamics in van der Waals heterostructures. *Nat. Nanotechnol.* **2018**, *13* (11), 994–1003.

(3) Rivera, P.; Yu, H.; Seyler, K. L.; Wilson, N. P.; Yao, W.; Xu, X. Interlayer valley excitons in heterobilayers of transition metal dichalcogenides. *Nat. Nanotechnol.* **2018**, *13* (11), 1004.

(4) Özçelik, V. O.; Azadani, J. G.; Yang, C.; Koester, S. J.; Low, T. Band alignment of two-dimensional semiconductors for designing heterostructures with momentum space matching. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *94* (3), 035125.

(5) Yu, H.; Wu, Y.; Liu, G. B.; Xu, X.; Yao, W. Nonlinear valley and spin currents from Fermi pocket anisotropy in 2D crystals. *Phys. Rev. Lett.* **2014**, *113* (15), 156603.

(6) Zhang, Y. J.; Oka, T.; Suzuki, R.; Ye, J. T.; Iwasa, Y. Electrically Switchable Chiral Light-Emitting Transistor. *Science* **2014**, 344 (6185), 725–728.

(7) Lee, C. H.; Lee, G. H.; van der Zande, A. M.; Chen, W.; Li, Y.; Han, M.; Cui, X.; Arefe, G.; Nuckolls, C.; Heinz, T. F.; Guo, J.; Hone, J.; Kim, P. Atomically thin p-n junctions with van der Waals heterointerfaces. *Nat. Nanotechnol.* **2014**, *9* (9), 676–81.

(8) Gong, Y.; Lin, J.; Wang, X.; Shi, G.; Lei, S.; Lin, Z.; Zou, X.; Ye, G.; Vajtai, R.; Yakobson, B. I.; Terrones, H.; Terrones, M.; Tay, B. K.; Lou, J.; Pantelides, S. T.; Liu, Z.; Zhou, W.; Ajayan, P. M. Vertical and in-plane heterostructures from  $WS_2/MoS_2$  monolayers. *Nat. Mater.* **2014**, *13* (12), 1135–42.

(9) Zhang, K.; Zhang, T.; Cheng, G.; Li, T.; Wang, S.; Wei, W.; Zhou, X.; Yu, W.; Sun, Y.; Wang, P.; Zhang, D.; Zeng, C.; Wang, X.; Hu, W.; Fan, H. J.; Shen, G.; Chen, X.; Duan, X.; Chang, K.; Dai, N. Interlayer Transition and Infrared Photodetection in Atomically Thin Type-II MoTe<sub>2</sub>/MoS<sub>2</sub> van der Waals Heterostructures. *ACS Nano* **2016**, *10* (3), 3852–8.

(10) Furchi, M. M.; Pospischil, A.; Libisch, F.; Burgdorfer, J.; Mueller, T. Photovoltaic effect in an electrically tunable van der Waals heterojunction. *Nano Lett.* **2014**, *14* (8), 4785–91.

(11) Zhang, C.; Chuu, C.-P.; Ren, X.; Li, M.-Y.; Li, L.-J.; Jin, C.; Chou, M.-Y.; Shih, C.-K. Interlayer couplings, Moire patterns, and 2D electronic superlattices in MoS<sub>2</sub>/WSe<sub>2</sub> hetero-bilayers. *Sci. Adv.* **2017**, 3 (1), e1601459.

(12) Zhang, N.; Surrente, A.; Baranowski, M.; Maude, D. K.; Gant, P.; Castellanos-Gomez, A.; Plochocka, P. Moiré Intralayer Excitons in a MoSe<sub>2</sub>/MoS<sub>2</sub> Heterostructure. *Nano Lett.* **2018**, *18* (12), 7651–7657.

(13) Liu, K.; Zhang, L.; Cao, T.; Jin, C.; Qiu, D.; Zhou, Q.; Zettl, A.; Yang, P.; Louie, S. G.; Wang, F. Evolution of interlayer coupling in twisted molybdenum disulfide bilayers. *Nat. Commun.* **2014**, *5*, 4966. (14) Kim, J.; Jin, C.; Chen, B.; Cai, H.; Zhao, T.; Lee, P.; Kahn, S.; Watanabe, K.; Taniguchi, T.; Tongay, S.; Crommie, M. F.; Wang, F. Observation of ultralong valley lifetime in WSe<sub>2</sub>/MoS<sub>2</sub> heterostructure. *Sci. Adv.* **2017**, *3*, No. e1700518.

(15) Choi, C.; Huang, J.; Cheng, H.-C.; Kim, H.; Vinod, A. K.; Bae, S.-H.; Özçelik, V. O.; Grassi, R.; Chae, J.; Huang, S.-W.; Duan, X.; Kaasbjerg, K.; Low, T.; Wong, C. W. Enhanced interlayer neutral

excitons and trions in trilayer van der Waals heterostructures. *npj* 2D Mater. Appl. 2018, 2 (1), 30.

(16) Li, Y.; Cui, Q.; Ceballos, F.; Lane, S. D.; Qi, Z.; Zhao, H. Ultrafast Interlayer Electron Transfer in Incommensurate Transition Metal Dichalcogenide Homobilayers. *Nano Lett.* **2017**, *17* (11), 6661–6666.

(17) Jones, A. M.; Yu, H.; Ghimire, N. J.; Wu, S.; Aivazian, G.; Ross, J. S.; Zhao, B.; Yan, J.; Mandrus, D. G.; Xiao, D.; Yao, W.; Xu, X. Optical generation of excitonic valley coherence in monolayer WSe<sub>2</sub>. *Nat. Nanotechnol.* **2013**, *8* (9), 634–8.

(18) Jones, A. M.; Yu, H.; Ross, J. S.; Klement, P.; Ghimire, N. J.; Yan, J.; Mandrus, D. G.; Yao, W.; Xu, X. Spin-layer locking effects in optical orientation of exciton spin in bilayer WSe<sub>2</sub>. *Nat. Phys.* **2014**, *10* (2), 130–134.

(19) Krasnok, A.; Alù, A. Valley-Selective Response of Nanostructures Coupled to 2D Transition-Metal Dichalcogenides. *Appl. Sci.* **2018**, 8 (7), 1157.

(20) Yu, H.; Liu, G.-B.; Yao, W. Brightened spin-triplet interlayer excitons and optical selection rules in van der Waals heterobilayers. 2D Mater. 2018, 5 (3), 035021.

(21) Mak, K. F.; He, K.; Shan, J.; Heinz, T. F. Control of valley polarization in monolayer  $MoS_2$  by optical helicity. *Nat. Nanotechnol.* **2012**, 7 (8), 494–8.

(22) Rigosi, A. F.; Hill, H. M.; Li, Y.; Chernikov, A.; Heinz, T. F. Probing Interlayer Interactions in Transition Metal Dichalcogenide Heterostructures by Optical Spectroscopy: MoS<sub>2</sub>/WS<sub>2</sub> and MoSe<sub>2</sub>/WSe<sub>2</sub>. *Nano Lett.* **2015**, *15* (8), 5033–8.

(23) Velusamy, D. B.; Kim, R. H.; Cha, S.; Huh, J.; Khazaeinezhad, R.; Kassani, S. H.; Song, G.; Cho, S. M.; Cho, S. H.; Hwang, I.; Lee, J.; Oh, K.; Choi, H.; Park, C. Flexible transition metal dichalcogenide nanosheets for band-selective photodetection. *Nat. Commun.* **2015**, *6*, 8063.

(24) Yu, Y.; Hu, S.; Su, L.; Huang, L.; Liu, Y.; Jin, Z.; Purezky, A. A.; Geohegan, D. B.; Kim, K. W.; Zhang, Y.; Cao, L. Equally efficient interlayer exciton relaxation and improved absorption in epitaxial and nonepitaxial  $MoS_2/WS_2$  heterostructures. *Nano Lett.* **2015**, *15* (1), 486–91.

(25) Latini, S.; Winther, K. T.; Olsen, T.; Thygesen, K. S. Interlayer Excitons and Band Alignment in MoS<sub>2</sub>/hBN/WSe<sub>2</sub> van der Waals Heterostructures. *Nano Lett.* **2017**, *17* (2), 938–945.

(26) Seyler, K. L.; Rivera, P.; Yu, H.; Wilson, N. P.; Ray, E. L.; Mandrus, D. G.; Yan, J.; Yao, W.; Xu, X. Signatures of moiré-trapped valley excitons in  $MoSe_2/WSe_2$  heterobilayers. *Nature* **2019**, 567 (7746), 66–70.

(27) Jin, C.; Regan, E. C.; Wang, D.; Iqbal Bakti Utama, M.; Yang, C.-S.; Cain, J.; Qin, Y.; Shen, Y.; Zheng, Z.; Watanabe, K.; Taniguchi, T.; Tongay, S.; Zettl, A.; Wang, F. Identification of spin, valley and moiré quasi-angular momentum of interlayer excitons. *Nat. Phys.* **2019**, *15* (11), 1140–1144.

(28) Fogler, M. M.; Butov, L. V.; Novoselov, K. S. High-temperature superfluidity with indirect excitons in van der Waals heterostructures. *Nat. Commun.* **2014**, *5*, 4555.

(29) Binder, J.; Howarth, J.; Withers, F.; Molas, M. R.; Taniguchi, T.; Watanabe, K.; Faugeras, C.; Wysmolek, A.; Danovich, M.; Fal'ko, V. I.; Geim, A. K.; Novoselov, K. S.; Potemski, M.; Kozikov, A. Upconverted electroluminescence via Auger scattering of interlayer excitons in van der Waals heterostructures. *Nat. Commun.* **2019**, *10* (1), 2335.

(30) Lui, C. H.; Frenzel, A. J.; Pilon, D. V.; Lee, Y. H.; Ling, X.; Akselrod, G. M.; Kong, J.; Gedik, N. Trion-induced negative photoconductivity in monolayer MoS<sub>2</sub>. *Phys. Rev. Lett.* **2014**, *113* (16), 166801.

(31) Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly bound trions in monolayer  $MoS_2$ . *Nat. Mater.* **2013**, 12 (3), 207–11.

(32) Cadiz, F.; Courtade, E.; Robert, C.; Wang, G.; Shen, Y.; Cai, H.; Taniguchi, T.; Watanabe, K.; Carrere, H.; Lagarde, D.; Manca, M.; Amand, T.; Renucci, P.; Tongay, S.; Marie, X.; Urbaszek, B. Excitonic Linewidth Approaching the Homogeneous Limit in MoS<sub>2</sub>- Based van der Waals Heterostructures. Phys. Rev. X 2017, 7 (2), 021026.

(33) Man, M. K.; Deckoff-Jones, S.; Winchester, A.; Shi, G.; Gupta, G.; Mohite, A. D.; Kar, S.; Kioupakis, E.; Talapatra, S.; Dani, K. M. Protecting the properties of monolayer  $MoS_2$  on silicon based substrates with an atomically thin buffer. *Sci. Rep.* **2016**, *6*, 20890.

(34) Gong, C.; Zhang, H.; Wang, W.; Colombo, L.; Wallace, R. M.; Cho, K. Band alignment of two-dimensional transition metal dichalcogenides: Application in tunnel field effect transistors. *Appl. Phys. Lett.* **2013**, *103* (5), 053513.

(35) You, Y.; Zhang, X.; Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R.; Heinz, T. F. Observation of biexcitons in monolayer WSe<sub>2</sub>. *Nat. Phys.* **2015**, *11* (11), 477–481.

(36) Marceddu, M.; Saba, M.; Quochi, F.; Lai, A.; Huang, J.; Talapin, D. V.; Mura, A.; Bongiovanni, G. Charged excitons, Auger recombination and optical gain in CdSe/CdS nanocrystals. *Nanotechnology* **2012**, 23, 015201.

(37) Hou, X.; Kang, J.; Qin, H.; Chen, X.; Ma, J.; Zhou, J.; Chen, L.; Wang, L.; Wang, L.; Peng, X. Engineering Auger recombination in colloidal quantum dots via dielectric screening. *Nat. Commun.* **2019**, *10*, 1750.

(38) Koirala, S.; Mouri, S.; Miyauchi, Y.; Matsuda, K. Homogeneous linewidth broadening and exciton dephasing mechanism in MoTe<sub>2</sub>. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, 93 (7), 075411.

(39) Li, M.; Bellus, M. Z.; Dai, J.; Ma, L.; Li, X.; Zhao, H.; Zeng, X. Ch A type-I van der Waals heterobilayer of WSe<sub>2</sub>/MoTe<sub>2</sub>. *Nanotechnology* **2018**, *29*, 335203.

(40) Wu, L.; Chen, Y.; Zhou, H.; Zhu, H. Ultrafast Energy Transfer of Both Bright and Dark Excitons in 2D van der Waals Heterostructures Beyond Dipolar Coupling. ACS Nano 2019, 13 (2), 2341–2348.

(41) Yamaoka, T.; Lim, H. E.; Koirala, S.; Wang, X.; Shinokita, K.; Maruyama, M.; Okada, S.; Miyauchi, Y.; Matsuda, K. Efficient Photocarrier Transfer and Effective Photoluminescence Enhancement in Type I Monolayer  $MoTe_2/WSe_2$  Heterostructure. *Adv. Funct. Mater.* **2018**, *28* (35), 1801021.

(42) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric field effect in atomically thin carbon films. *Science* **2004**, *306*, 666–669.

(43) Ross, J. S.; Wu, S.; Yu, H.; Ghimire, N. J.; Jones, A. M.; Aivazian, G.; Yan, J.; Mandrus, D. G.; Xiao, D.; Yao, W.; Xu, X. Electrical control of neutral and charged excitons in a monolayer semiconductor. *Nat. Commun.* **2013**, *4*, 1474.

(44) Castellanos-Gomez, A.; Buscema, M.; Molenaar, R.; Singh, V.; Janssen, L.; van der Zant, H. S. J.; Steele, G. A. Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping. 2D *Mater.* **2014**, *1* (1), 011002.

(45) Kozawa, D.; Carvalho, A.; Verzhbitskiy, I.; Giustiniano, F.; Miyauchi, Y.; Mouri, S.; Castro Neto, A. H.; Matsuda, K.; Eda, G. Evidence for Fast Interlayer Energy Transfer in MoSe<sub>2</sub>/WS<sub>2</sub> Heterostructures. *Nano Lett.* **2016**, *16* (7), 4087–4093.