Defect Healing and Charge Transfer-Mediated Valley Polarization in MoS$_2$/MoSe$_2$/MoS$_2$ Trilayer van der Waals Heterostructures

Alessandro Surrente,$^†$ Dumitru Dumcenco,$^‡$ Zhuo Yang,$^†$ Agnieszka Kuc$^§$:,$^∥$ Yu Jing,$^∥$ Thomas Heine,$^§$:,$^∥$ Yen-Cheng Kung,$^‡$ Duncan K. Maude,$^†$ Andras Kis,$^†$ and Paulina Plochocka$^∗$

†Laboratoire National des Champs Magnétiques Intenses, UPR 3228, CNRS-UGA-UPS-INSA, Grenoble and Toulouse, France
‡Electrical Engineering Institute and Institute of Materials Science and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
§Wilhelm Ostwald Institute of Physical and Theoretical Chemistry Leipzig, University of Leipzig, 04109 Saxony Germany
∥School of Engineering and Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

ABSTRACT: Monolayer transition metal dichalcogenides (TMDCs) grown by chemical vapor deposition (CVD) are plagued by a significantly lower optical quality compared to exfoliated TMDCs. In this work, we show that the optical quality of CVD-grown MoSe$_2$ is completely recovered if the material is sandwiched in MoS$_2$/MoSe$_2$/MoS$_2$ trilayer van der Waals heterostructures. We show by means of density functional theory that this remarkable and unexpected result is due to defect healing: S atoms of the more reactive MoS$_2$ layers are donated to heal Se vacancy defects in the middle MoSe$_2$ layer. In addition, the trilayer structure exhibits a considerable charge-transfer mediated valley polarization of MoSe$_2$ without the need for resonant excitation. Our fabrication approach, relying solely on simple flake transfer technique, paves the way for the scalable production of large-area TMDC materials with excellent optical quality.

KEYWORDS: Chemical vapor deposition, transition metal dichalcogenides, van der Waals heterostructures, defect healing, charge transfer mediated valley polarization

Monolayer transition metal dichalcogenides (TMDC) have a direct bandgap situated in the visible range, which makes them ideal building blocks for novel electronic and optoelectronic devices.$^1$–$^10$ The bandgap of monolayer TMDCs occurs at the inequivalent (but degenerate) K and K' points of the hexagonal Brillouin zone. The broken inversion symmetry of a TMDC monolayer combined with the time reversal symmetry imposes opposite magnetic moments at the K and K' valleys. This in turn determines the characteristic circular dichroism exhibited by these materials, wherein each valley can be addressed separately with circularly polarized light.$^{11}$–$^{15}$ Additionally, optical spectra are influenced by the strong spin–orbit coupling, which lifts the degeneracy of band states at the valence band edges, resulting in well-resolved A and B resonances, as observed in reflectivity or absorption spectra.$^2$,$^{14}$–$^{16}$ The interplay of spin–orbit coupling with broken inversion symmetry and time reversal symmetry locks the valley and spin degrees of freedom, making TMDCs attractive candidates for valleytronics.$^{17}$ The spin-valley index locking along with the large distance in the momentum space between K and K' valleys preserves the valley polarization observed in the degree of circular polarization (DCP) in helicity resolved photoluminescence emission.$^{18}$–$^{22}$

Applications require a scalable fabrication platform providing high-quality large-area monolayer TMDC. Unfortunately, the most promising approach today, namely chemical vapor deposition (CVD) growth$^{23}$–$^{27}$ struggles to compete with exfoliated TMDCs in terms of sample quality. Low-temperature photoluminescence (PL) spectroscopy of CVD-grown MoS$_2$ and MoSe$_2$ reveals broad emission from defect bound excitons, which is significantly more intense than the free exciton peak$^{28}$–$^{30}$ and is related to chalcogen vacancies induced during the CVD growth.$^{29}$,$^{30}$

Here, we demonstrate a novel approach to neutralize the intrinsic defects of CVD-grown TMDCs using flake transfer tools routinely employed in the fabrication of van der Waals heterostructures.$^{31}$–$^{33}$ We investigate the optical properties of trilayer stacks composed of external CVD-grown MoS$_2$ flakes$^{23}$ as capping layers and an internal CVD-grown MoSe$_2$ flake that has a smaller bandgap.$^{34}$,$^{35}$ Remarkably, this fabrication approach strongly suppresses the localized exciton emission in MoSe$_2$, yielding a low-temperature PL comparable to that observed in mechanically exfoliated samples. This striking result can be understood from density functional theory (DFT), which suggests that the more reactive MoS$_2$ donates chalcogen atoms to heal vacancy defects in MoSe$_2$. Incorporating MoS$_2$...
into the trilayer heterostructure furthermore allows us to demonstrate a new way to introduce valley polarization in MoSe$_2$. Because of the type II band alignment in TMDC heterojunctions,\textsuperscript{35} a significant charge transfer is observed in these systems.\textsuperscript{32,36,37} Our results show that spin of the hole is conserved upon charge transfer from MoS$_2$ to MoSe$_2$ after excitation in resonance with MoS$_2$ A exciton. This leads to nonzero steady-state valley polarization in MoSe$_2$, which has never been observed before under nonresonant excitation.\textsuperscript{38−40}

**Defect Healing.** The sample with MoS$_2$/MoSe$_2$/MoS$_2$ trilayer stacks and micrograph of a representative transfer area are schematically shown in Figure 1a,b. Low-temperature $\mu$PL (μPL) spectroscopy has been used to characterize as-grown CVD samples on the sapphire substrate (prior to any transfer process) and the trilayer MoS$_2$/MoSe$_2$/MoS$_2$ stack. All spectra shown in Figure 1c,d were measured under nominally identical conditions with an excitation power of 100 μW (see Figure S1 in Supporting Information (SI) for power dependent μPL spectra). The as-grown MoS$_2$ and MoSe$_2$ monolayers both show a broad PL feature (full width at half-maximum, fwhm, of 258 and 106 meV, respectively) related to emission from excitons bound to defect or charge impurity states.\textsuperscript{28−30,41} A-exciton emission (labeled $X_A$ in Figure 1c) is seen only as a weak peak or shoulder at higher energies. These assignments are confirmed by reflectivity contrast measured on the same spot. Reflectivity contrast is defined as $AR/R_0 = (R - R_s)/R_0$ where $R$ is the reflectivity spectrum measured on the sample and $R_s$ denotes the reflectivity spectrum measured on the substrate. In the case of transparent substrates such as sapphire, reflectivity contrast is proportional to the absorption of the sample.\textsuperscript{42} The reflectivity contrast spectrum of as-grown MoS$_2$ (see upper panel of Figure 1c) consists of a main peak at 1.937 eV and a higher energy, weaker feature at 2.085 eV, related to the spin−orbit split B exciton. The energy difference of 148 meV corresponds very well to theoretically predicted spin−orbit splitting of the valence band\textsuperscript{43} and is very similar to the splitting determined with transmission measurements on similar samples.\textsuperscript{34} The reflectivity contrast spectrum of as-grown MoSe$_2$, shown in the central panel of Figure 1c has a peak at 1.637 eV, which corresponds well to the high energy shoulder of the μPL spectrum and hence is assigned to A exciton. As in our previous study,\textsuperscript{34} we are unable to resolve the B exciton in reflectivity contrast measurements on as grown MoSe$_2$.

The optical properties of the trilayer stack are dramatically improved (bottom panel in Figure 1c). The most striking difference is the nearly total suppression of (i) emission from defect bound excitons, and (ii) significant quenching of both MoS$_2$ PL, barely seen as a weak peak at 1.929 eV, and of MoSe$_2$ PL (overall integrated intensity decreases by two and one orders of magnitude, respectively, see Figure S2 in SI). The measured PL spectrum is dominated by narrow free neutral ($X_A$) and charged exciton (T) emission in MoSe$_2$ (low power fwhm of 11 and 10 meV, respectively, see Figure S1 in SI), approaching the quality of exfoliated WSe$_2$ embedded in boron nitride (fwhm $\sim$10 meV).\textsuperscript{44} The free exciton emission overlaps with a weak broad background emission from the sapphire substrate (the narrow peak just below 1.8 eV corresponds to the emission from a color center in sapphire). The highest energy peak in the reflectivity contrast spectrum of the trilayer
impurity substitution have met with only partial success; related emission in MoSe2 in areas which are not fully capped. A broad low-energy peak starts to emerge, probably due to defect emission remains strongly suppressed. For larger spot sizes, a Figure 1d. For an excitation spot size of 10 μm, the peak related to MoS2 A exciton in the reheterostructure enabled us to resolve an additional peak at 1.87 eV in the reflectivity contrast spectrum, assigned to the B exciton of MoS2. The peak related to MoS2 A exciton in the reflectivity contrast spectrum is blue-shifted by 27 meV with respect to the corresponding PL peak. This Stokes shift has been attributed to the presence of a high doping level in MoS2, also present in our layers. On the low energy side of the μPL spectrum, the two distinct peaks at 1.674 and 1.645 eV are assigned to the A exciton and to the trion of MoSe2, respectively. The trion binding energy of 29 meV is very similar to that reported in other studies on MoSe2.

We assign the brighter emission from MoSe2 to intimate physical contact with MoS2, a procedure that can be material and to the defect healing effeminacy contrast spectrum, assigned to the B exciton of MoS2. The peak related to MoS2 A exciton in the reflectivity contrast spectrum is blue-shifted by 27 meV with respect to the corresponding PL peak. This Stokes shift has been attributed to the presence of a high doping level in MoS2, also present in our layers. On the low energy side of the μPL spectrum, the two distinct peaks at 1.674 and 1.645 eV are assigned to the A exciton and to the trion of MoSe2, respectively. The trion binding energy of 29 meV is very similar to that reported in other studies on MoSe2.

The high optical quality of the MoSe2 embedded in the heterostructure enabled us to resolve an additional peak at 1.87 eV in the reflectivity contrast spectrum, assigned to the B exciton of MoS2. The vastly improved optical properties suggest a defect healing process in which the contact with MoS2 is enough to drastically reduce the number of defects in MoSe2. The quenching of the intralayer emission in the trilayer is manifestation of a fast charge transfer mechanism related to the type II band alignment in MoS2/MoSe2 heterostructures. The weak luminescence of MoS2 is consistent with a background n-doping of the as grown layers and with an additional charge transfer after the formation of the heterostructure. We assign the brighter emission from MoSe2 (in the trilayer) to the hole transfer to an intrinsically n-doped material and to the defect healing effect, combined with luminescence resulting from higher energy states, similar to hot luminescence of direct exciton in multilayer MoSe2. The long-range optical uniformity of the trilayer stacks has been monitored by acquiring PL with a gradually defocused excitation beam. The acquired PL spectra are displayed in Figure 1d. For an excitation spot size of 10 μm, the defect emission remains strongly suppressed. For larger spot sizes, a broad low-energy peak starts to emerge, probably due to defect related emission in MoSe2 in areas which are not fully capped. These measurements are a proof of concept, demonstrating that this approach, when optimized, should enable the fabrication of large area CVD-grown heterostructures with excellent optical quality.

Previous attempts at improving the optical properties of CVD-grown MoSe2 using HBr treatment or the isoelectronic impurity substitution have met with only partial success; impurity-bound excitons still remained the most prominent component of the emission spectrum. Low-temperature PL spectra consisted in broad features, wherein free exciton emission could be identified only after fitting. The optical properties of exfoliated MoS2 have been improved by superacid treatment. In our case, the simple act of bringing MoSe2 in intimate physical contact with MoS2, a procedure that can be performed after growth and does not require any chemical functionalization, results in a virtually complete suppression of emission from the impurity-bound states and a spectrum in which the trion and exciton resonances can be clearly resolved. Our defect healing hypothesis is further supported by the results obtained from DFT simulations. We have calculated the gain of energy in a heterobilayer MoSe2/MoS2 using two models: A single Se vacancy in the MoSe2 layer (Model 1) and a single S vacancy in the MoS2 layer together with a single S substitution in the MoSe2 layer (Model 2). This corresponds to the transfer energy of a S atom from pristine MoS2 to heal a defect in MoSe2. We observe a significant energy gain of 18 kJ mol−1 (180 meV) per S transfer from MoS2 to the MoSe2 defect, which shows that defect healing in MoSe2 by MoS2 is thermodynamically favored. The formation energy of a S vacancy in a MoS2 monolayer has been theoretically estimated in the 1.3–1.5 eV range. We consider these as upper bounds for the energy barrier of the transfer of a S atom to fill a Se vacancy in MoSe2, because this is not a static process but a transfer between two neighboring layers.

We have also calculated the band structures of a perfect MoSe2 monolayer, MoSe2 monolayer with one Se vacancy, and MoSe2 monolayer with one Se—S substitution. We observe that Se vacancies introduce strongly localized states in the bandgap of MoSe2, 0.92 eV above the top of the valence band (see Figure 2). These are dispersionless and act as trap centers. Healing the Se vacancy with S substitution restores the band structure of a nearly perfect MoSe2 monolayer. In the studied S × S supercell model (2% Se—S substitutions), the bandgap increases by only 1 meV.

**Charge Transfer-Mediated Valley Polarization.** First signatures of charge transfer between the layers are seen in the comparison between PL intensities of as grown layers and trilayers, shown in Figure S2 of SI. Additional insights is provided by the spatial correlation of the PL intensity of the
MoS\textsubscript{2} and MoSe\textsubscript{2}. The integrated spatial map of the MoSe\textsubscript{2} A exciton is shown in Figure 3a. The signal is particularly intense at positions where the overlap between the three layers is good and the material does not have a large number of defects. This implies that the bright spots do not necessarily have a triangular shape. This map provides an additional opportunity to demonstrate the high degree of uniformity of the emission of MoSe\textsubscript{2} incorporated in a heterostructure, by extracting \(\mu\)PL spectra. We show in Figure 3b five \(\mu\)PL spectra measured at 10 \(\mu\)m distance from one another. The spectra have been normalized by the integration time. We note that emission from defect states is consistently absent in the five spectra and the similar line shape points to a good uniformity of the emission over the full mapped area. In Figure 3c, we overlay the intensity map of MoS\textsubscript{2} with that of MoSe\textsubscript{2}, forcing the areas having the lowest signal from the latter to be transparent. These areas correspond to zones where the signal from MoS\textsubscript{2} is highest. We quantify the observed intensity (anti)correlation by plotting in Figure 3d the ratio between the intensity of A exciton in one material normalized by the total emission of both materials \([I_{\text{MoX}}]/(I_{\text{MoS}} + I_{\text{MoSe}})\), where \(X = S\) or \(Se\). It can be noted that when the emission of MoSe\textsubscript{2} becomes more pronounced, the emission of MoS\textsubscript{2} decreases correspondingly. This is fully consistent with charge transfer. In positions where the three layers overlap efficiently, charge transfer induces a quenching of the MoS\textsubscript{2} PL. At the same time, the PL from MoSe\textsubscript{2} is particularly intense at these positions owing to efficient defect healing, but still weaker than in as-grown MoSe\textsubscript{2} samples (see Figure S2 in SI).

Photoluminescence excitation (PLE) spectroscopy is a useful tool to investigate more thoroughly the charge transfer processes. We focus our measurements on MoSe\textsubscript{2} incorporated in a trilayer stack. In Figure 4a, we show the PLE measured without making use of polarization optics. Both PLEs of the A exciton and trion have been normalized by the weakest intensity measured at an excitation energy of 1.999 eV in order to be able to compare the enhancement effects for the exciton and trion. The integrated intensities of both peaks show a pronounced maximum when the excitation energy is close to the resonance with the B exciton of MoSe\textsubscript{2}.\textsuperscript{54} The integrated intensity is consistently lower than this maximum at other excitation energies, including those corresponding to resonances in MoS\textsubscript{2} (see, for example, the weak peak corresponding to MoS\textsubscript{2} X\textsubscript{A}, appearing as a shoulder of the main PLE peak in Figure 4a). This is the exact opposite of what is observed in a heterostructure system where energy transfer has been demonstrated.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Figure 3. (a) Spatial map of the integrated intensity of A exciton of encapsulated MoSe\textsubscript{2}. The dashed line schematically illustrates the direction along which the spectra of panel b have been extracted. The colored circles mark the position within the map of the spectra having the corresponding color in panel b. (b) \(\mu\)PL spectra extracted at positions marked by circles of the corresponding color in panel a. The spectra are vertically offset for clarity. (c) Mapping of the integrated intensity of MoS\textsubscript{2} X\textsubscript{A} overlaid on the same spatial map of MoSe\textsubscript{2} X\textsubscript{A}. (d) Integrated intensity of MoSe\textsubscript{2} X\textsubscript{A} and MoS\textsubscript{2} X\textsubscript{A} as a function of the intensity of MoSe\textsubscript{2} X\textsubscript{A}.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Figure 4. (a) Normalized integrated intensity of MoSe\textsubscript{2} X\textsubscript{A} and T as a function of the excitation energy. Polarization-resolved \(\mu\)PL spectra and DCP of MoSe\textsubscript{2} excited (b) far off MoS\textsubscript{2} X\textsubscript{A} resonance and (c) on resonance with MoS\textsubscript{2} X\textsubscript{A}. (d) Integrated DCP as a function of the excitation energy. (e) Schematic illustration of spin transfer under excitation resonant with MoS\textsubscript{2} X\textsubscript{A}.}
\end{figure}
demonstrated. In such system, the emission intensity of one material is significantly enhanced when the excitation energy is resonant with excitonic transitions of the other material. This consideration allows us to safely rule out energy transfer between the different layers.

To investigate whether the trilayer stack shows charge transfer, we initially consider the normalized intensity of exciton and trion when the excitation energy is resonant with excitonic transitions of MoS$_2$. For resonances with both A and B exciton of MoS$_2$, the emission intensity is enhanced more for MoSe$_2$ A exciton than for the trion. This is consistent with the presence of a large n-type background doping (free electrons) in CVD-grown MoSe$_2$, which gives rise to strong charged exciton emission even in the absence of gating (see Figure 4a). For a MoS$_2$/MoSe$_2$ heterojunction, the band alignment promotes the transfer of holes from MoS$_2$ to MoSe$_2$. When we optically excite the trilayer stack, we induce a net transfer of holes from MoS$_2$ to MoSe$_2$, resulting in a relatively stronger exciton emission even in the absence of gating (see Figure 1a).

We also performed circular polarization resolved PLE focusing on MoSe$_2$ incorporated in a trilayer stack. When the excitation energy is far from resonance (A or B excitons of both materials), MoSe$_2$ shows an extremely small valley polarization. This is illustrated by the polarization-resolved μPL spectra of Figure 4b, where a negligibly small DCP, defined as DCP = \( [I_{\pm} - I_{\mp}] / [I_{\pm} + I_{\mp}] \), is observed across the entire energy range of interest. When the excitation energy of the laser is tuned to the proximity of the resonance with the A exciton of MoS$_2$, a significant valley polarization accumulates. An example of polarization-resolved spectra at an excitation energy resonant with A exciton of MoS$_2$ is shown in Figure 4c. The valley polarization is quantified by a slightly positive DCP at energies around A exciton and trion of MoSe$_2$ (see Figure 4c). In Figure 4d, we illustrate the excitation energy dependence of the integrated DCP (estimated by extracting the relevant integrated intensity of exciton and trion with Gaussian fits). We notice a significant increase of the integrated DCP at energies corresponding to the A exciton resonance of MoS$_2$ (see dashed line in Figure 4d) with a low energy shoulder possibly related to an enhanced DCP at excitation energies corresponding to MoSe$_2$ B exciton. Polarization-resolved electroluminescence of single and multilayer MoSe$_2$ as well as polarization-resolved PL of indirect excitons emitted by a WSe$_2$/MoSe$_2$ heterostructure have demonstrated higher degree of circular polarization. However, the mechanisms leading to polarization emission in these systems are fundamentally different from those yielding polarized PL of MoSe$_2$, which is virtually impossible to achieve unless the PL is excited using quasi-resonant excitation in X$_A$ of MoSe$_2$.

We ascribe the observed MoSe$_2$ valley polarization to the hole transfer from MoS$_2$ with a mechanism schematically illustrated in Figure 4e. We excite the trilayer stack with circularly polarized light with a given helicity and in resonance with the A exciton of MoS$_2$. The valley polarization directly created in MoSe$_2$ is quickly lost, which results in a negligible DCP, similar to nonresonant excitation (see Figure 4d). Resonant excitation in MoS$_2$ creates valley polarization for a duration estimated in the hundreds of femtoseconds range. Charge transfer in van der Waals heterostructures is an ultrafast process with upper bounds in the tens of femtoseconds range (hole transfer from MoS$_2$ has been reported to be faster than 50 fs$^{36}$). During this very rapid transfer, we assume that the hole spin (and thus valley due to the large spin orbit splitting in the valence band) is conserved, and because of the excess electron population in the MoSe$_2$ layer, the injected hole forms an exciton populating the valley corresponding to the helicity of the incoming light. These excitons have presumably a low kinetic energy (no excess energy of the photocreated hole), which slows down significantly the intervalley scattering rate due to electron–hole exchange interaction. As a result, this hole transfer is responsible for the observed valley polarization.

**Conclusions.** A detailed investigation of the optical properties of MoS$_2$/MoSe$_2$/MoS$_2$ trilayers reveals that stacking dramatically improves the optical quality of CVD-grown MoSe$_2$, essentially eliminating all defect bound exciton and MoS$_2$-related emission. These results open the way to using CVD-grown TMDCs for applications and studies that require materials with excellent optical quality. Photoluminescence spectra from MoSe$_2$ in a trilayer stack are dominated by narrow neutral and charged A exciton emission, resembling the spectrum of a high quality mechanically exfoliated flake. Density functional calculations confirm a defect healing scenario in which S atoms replace Se vacancies. Circular polarization resolved PL measurements demonstrate that MoSe$_2$ exhibits a significant valley polarization even when the excitation energy is far from the A exciton resonance. This behavior is the signature of an efficient spin-conserving hole transfer from MoS$_2$ to MoSe$_2$. Our approach provides a robust and straightforward method of healing defects in CVD-grown samples, which might also be beneficial for the transport properties of these materials.

**Methods. Sample Preparation.** The sample with MoS$_2$/MoSe$_2$/MoS$_2$ trilayer stacks, schematically shown in Figure 1a, was obtained by two separate transfer steps using a wet transfer KOH method. First of all, the upper-MoS$_2$ was transferred onto the as-grown MoSe$_2$ monolayer on sapphire. Subsequently, the MoS$_2$/MoSe$_2$ stack was transferred onto an as-grown bottom MoS$_2$ monolayer on sapphire. For both transfers, sapphire chips with material (upper-MoS$_2$ or MoS$_2$/MoSe$_2$ stack) were first spin coated with PMMA 950 at 1500 rpm for 60 s and baked at 180 °C for 5 min. The films were detached in KOH (30%) at moderate temperatures (70 °C), washed three times in deionized water, transferred onto sapphire with the stacking layer (MoSe$_2$ or bottom-MoS$_2$), and dried at 50 °C for 30 min. The PMMA was removed by dipping the sample in acetone for 12 h, followed by rinsing with isopropanol and drying in a N$_2$ flow. Such method provides a polymer clean interface of stacks and minimal damage of material caused by the transfer process. Using this method, a large area film with monolayer (MoS$_2$), bilayer (MoS$_2$/MoS$_2$, MoSe$_2$/MoS$_2$ and MoS$_2$/MoSe$_2$ stacks) and trilayer (MoS$_2$/MoSe$_2$/MoS$_2$ stack) was obtained. A micrograph of a representative transfer area is shown in Figure 1b. To determine the position of areas with different number of stacked layers, Ni markers were deposited.

**Optical Measurements.** For the optical characterization, the sapphire substrate was mounted on the cold finger of a He-flow cryostat. The excitation was provided either by a CW frequency-doubled solid-state laser emitting at 532 nm or by the frequency-doubled output of an optical parametric oscillator (OPO), synchronously pumped by a mode-locked Ti:sapphire laser. The typical temporal pulse width was 300 fs, with a repetition rate of 80 MHz. The excitation beam was focused on the sample by a 50X microscope objective, giving a spot size of approximately 1 μm and having a numerical aperture of 0.55. The emitted PL was collected through the
same objective and redirected to a spectrometer equipped with a liquid nitrogen cooled CCD camera or (for time-resolved measurements) to an imagining spectrometer and detected using a synchroscan streak camera with the temporal resolution set to 5 ps. All the spectra have been measured at 5K, unless otherwise specified.

For spatial mapping the emission has been monitored while the optical cryostat was displaced with respect to the microscope objective using high precision motorized $x$–$y$ translation stages ($1 \mu m$ step). The integrated intensity of given features (e.g., A exciton emission) has been obtained by Gaussian fitting of the measured $\mu$PL spectra.

**Density Functional Theory of Band Structure in MoSe$_2$/MoS$_2$ Heterobilayers.** We have calculated heterobilayers made of MoSe$_2$ and MoS$_2$ monolayers, using DFT as implemented in the Crystal09 software. We employed all-electron Gaussian-type bases of triple-quality, while Mo atoms were treated with the HAYWSC-311(d31)G basis with effective core potential set, together with the PBE gradient corrected density functional. London-dispersion interactions were accounted for using the approach proposed by Grimme (DFT-D3). Full optimization of atomic positions and lattice vectors was performed on both models: Model 1 with perfect MoS$_2$ monolayer and one Se vacancy in the MoSe$_2$ monolayer, and Model 2 with one S vacancy in the MoS$_2$ monolayer and one S substitution in the MoSe$_2$ monolayer. The models are built of 5 × 5 supercells (see Figure 2).

Geometry optimization only slightly alters the lattice geometry (see Table 1).

<table>
<thead>
<tr>
<th>System</th>
<th>$a$ (Å)</th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$ 1L</td>
<td>3.171</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$ 1L</td>
<td>3.251</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$/MoSe$_2$</td>
<td>3.214</td>
<td>6.21</td>
</tr>
<tr>
<td>Model 1</td>
<td>3.206</td>
<td>6.30</td>
</tr>
<tr>
<td>Model 2</td>
<td>3.203</td>
<td>6.26</td>
</tr>
</tbody>
</table>

For the large supercells, which still overestimate the defect density in experiment, the defects studied here do not introduce any drastic changes into the structural properties of the systems. However, we note that we are constrained with the commensurate models of a heterobilayer, in which the corresponding monolayers are slightly distorted compared with the relaxed monolayers 3.251 and 3.171 Å for MoSe$_2$ and MoS$_2$, respectively. For a perfect heterobilayer (3.214 Å), this gives 1.15% compression of MoSe$_2$ and 1.4% elongation of MoS$_2$.

### Associated Content

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b00904.

Low-temperature $\mu$PL spectra, comparison of $\mu$PL spectra of as-grown versus trilayer samples, temperature-dependent $\mu$PL spectra, and time-resolved PL (PDF)

### References
