Defect healing and charge transfer mediated valley polarization in MoS$_2$/MoSe$_2$/MoS$_2$ trilayer van der Waals heterostructures

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Abstract

Monolayer transition metal dichalcogenides (TMDC) grown by chemical vapor deposition (CVD) are plagued by a significantly lower optical quality compared to exfoliated TMDC. 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.\(^1\text{-}^{10}\) 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 of a given helicity.\(^11\text{-}^{13}\) 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.\(^2\text{-}^{14}\text{-}^{16}\) The interplay of spin-orbit coupling with broken inversion symmetry and time reversal symmetry locks the valley and spin degrees of freedom, making TMDC 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.\textsuperscript{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\textsuperscript{23–27} struggles to compete with exfoliated TMDC in terms of sample quality. Low temperature PL spectroscopy of CVD-grown MoS\textsubscript{2} and MoSe\textsubscript{2} reveals broad emission from defect bound excitons, which is significantly more intense than the free exciton peak\textsuperscript{28–30} and is related to chalcogen vacancies induced during the CVD growth.\textsuperscript{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.\textsuperscript{31–33} We investigate the optical properties of trilayer stacks composed of external CVD-grown MoS\textsubscript{2} flakes\textsuperscript{24} as capping layers and an internal CVD-grown MoSe\textsubscript{2} flake which has a smaller bandgap.\textsuperscript{34,35} Remarkably, this fabrication approach strongly suppresses the localized exciton emission in MoSe\textsubscript{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\textsubscript{2} donates chalcogen atoms to heal vacancy defects in MoSe\textsubscript{2}. Incorporating MoS\textsubscript{2} into the trilayer heterostructure furthermore allows us to demonstrate a new way to introduce valley polarization in MoSe\textsubscript{2}. Due to 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\textsubscript{2} to MoSe\textsubscript{2} after excitation in resonance with MoS\textsubscript{2} A exciton. This leads to non-zero steady state valley polarization in MoSe\textsubscript{2}, which has never been observed before under non-resonant 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 Fig. 1(a) and (b). Low temperature microPL (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 Fig. 1(c) and (d) were measured under nominally identical conditions with an excitation power of 100 µW (see Fig. 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 meV and 106 meV, respectively) related to emission from excitons bound to defect or charge impurity states. $^{28-30,41}$ A-exciton emission (labeled $X_A$ in Fig. 1(c)) 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 $\Delta R/R_s = (R - R_s)/R_s$, 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. $^{42}$ The reflectivity contrast spectrum of as-grown MoS$_2$ (see upper panel of Fig. 1(c)) 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 $^{43}$ and is very similar to the splitting determined with transmission measurements on similar samples. $^{34}$ The reflectivity contrast spectrum of as grown MoSe$_2$, shown in the central panel of Fig. 1(c) 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, $^{34}$ 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 (bottommost panel in Fig. 1(c)). 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 MoSe₂ PL (overall integrated intensity decrease by two and one orders of magnitude, respectively, see Fig. S2 in SI). The measured PL spectrum is dominated by narrow free neutral (X_A) and charged exciton (T) emission in MoSe₂ (low power FWHM of 11 meV and 10 meV, respectively, see Fig. S1 in SI), approaching the quality of exfoliated WSe₂ embedded in boron nitride (FWHM ~ 10 meV). 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 (see Fig. 1(c), bottom panel), blue shifted with respect to the A exciton peak of MoS₂ by 145 meV is attributed 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 eV 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 MoSe₂. 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 Fig. 1(d). 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 treatment²⁹ or the isoelectronic impurity substitution³⁰ 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.⁵¹ 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 functionalisation, 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 eV–1.5 eV range.⁵²,⁵³ 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 neighbouring layers.

We have also calculated the band structures of a perfect MoSe$_2$ monolayer, MoSe$_2$ monolayer with one Se vacancy, and MoSe$_2$ monolayer with one Se$\rightarrow$S substitution. We observe that Se vacancies introduce strongly localized states in the bandgap of MoSe$_2$, 0.92 eV above the top of the valence band (see Fig. 2). These are dispersionless and act as trap centers. Healing the Se vacancy with S substitution restores the band structure of a nearly perfect MoSe$_2$ monolayer. In the studied 5 $\times$ 5 supercell model (2% Se$\rightarrow$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 Fig. S2 of SI. Additional insights is provided by the spatial correlation of the PL intensity of the MoS$_2$ and MoSe$_2$. The integrated spatial map of the MoSe$_2$ A exciton is shown in Fig. 3(a). 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$_2$ incorporated in a heterostructure, by extract $\mu$PL spectra. We show in Fig. 3(b) 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 Fig. 3(c), we overlay the intensity map of MoS$_2$ with that of MoSe$_2$, forcing the areas having the lowest signal from the latter to be transparent. These areas correspond to zones where the signal from MoS$_2$ is highest. We quantify the observed intensity (anti)correlation by plotting in Fig. 3(d) the ratio between the intensity of A exciton in one material normalized by the total emission of both
materials \( I_{\text{MoX}_2}/(I_{\text{MoS}_2} + I_{\text{MoSe}_2}) \), where \( X = \text{S or Se} \). It can be noted that when the emission of \( \text{MoSe}_2 \) becomes more pronounced, the emission of \( \text{MoS}_2 \) decreases correspondingly. This is fully consistent with charge transfer. In positions where the three layers overlap efficiently, charge transfer induces a quenching of the \( \text{MoS}_2 \) PL. At the same time, the PL from \( \text{MoSe}_2 \) is particularly intense at these positions owing to efficient defect healing, but still weaker than in as grown \( \text{MoSe}_2 \) samples (see Fig. S2 in SI).

Photoluminescence excitation (PLE) spectroscopy is a useful tool to investigate more thoroughly the charge transfer processes. We focus our measurements on \( \text{MoSe}_2 \) incorporated in a trilayer stack. In Fig. 4(a), 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 \( \text{MoSe}_2 \).\textsuperscript{54} The integrated intensity is consistently lower than this maximum at other excitation energies, including those corresponding to resonances in \( \text{MoS}_2 \) (see for example the weak peak corresponding to \( \text{MoS}_2 X_A \), appearing as a shoulder of the main PLE peak in Fig. 4(a)). This is the exact opposite of what is observed in a heterostructure system where energy transfer has been 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.\textsuperscript{55} 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 \( \text{MoS}_2 \). For resonances with both A and B exciton of \( \text{MoS}_2 \), the emission intensity is enhanced more for \( \text{MoSe}_2 \) A exciton than for the trion. This is consistent with the presence of a large n-type background doping (free electrons) in CVD-grown \( \text{MoSe}_2 \), which gives rise to strong charged exciton emission even in the absence of gating (see Fig. 1(a)).
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 emission of the neutral exciton as compared to the trion.

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 Fig. 4(b), where a negligibly small DCP, defined as $\text{DCP} = [I_{\sigma_1} - I_{\sigma_2}]/[I_{\sigma_1} + I_{\sigma_2}]$, is observed across the entire energy range of interest. When the excitation energy of the laser was 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 Fig. 4(c). The valley polarization is quantified by a slightly positive DCP at energies around A exciton and trion of MoSe$_2$ (see Fig. 4(c)). In Fig. 4(d) 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 Fig. 4(d)), 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 polarized 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 Fig. 4(e). 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, similarly to non-resonant excitation (see Fig. 4(d)). Resonant excitation in MoS$_2$ creates valley polarization for a duration estimated in the hundreds of femtoseconds range.$^{58}$ Charge transfer in van der Waals heterostructures is an ultra fast 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, owing to 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 inter-valley scattering rate due to electron-hole exchange interaction.$^{59}$ 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.

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Supporting Information Available

The following files are available free of charge.

Supporting information: Low temperature µPL spectra, comparison of µPL spectra of as-grown versus trilayer samples, temperature dependent µPL spectra and time-resolved PL.

Methods

Sample preparation

The sample with MoS$_2$/MoSe$_2$/MoS$_2$ trilayer stacks, schematically shown in Fig. 1(a), was obtained by two separate transfer steps using a wet transfer KOH method.$^{32}$ First of all, the upper-MoS$_2$ was transferred onto the as-grown MoSe$_2$ monolayer on sapphire.$^{24,34}$ 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$_2$
stacks) were first spin coated with PMMA 950 at 1500 rpm for 60 s and baked at 180°C for 5 minutes. The films were detached in KOH (30%) at moderate temperatures (70°C), washed 3 times in deionized water, transferred onto sapphire with the stacking layer (MoSe$_2$ or bottom-MoS$_2$) and dried at 50°C for 30 minutes. The PMMA was removed by dipping the sample in acetone for 12 hours, 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 (MoSe$_2$/MoS$_2$, MoS$_2$/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 Fig. 1(b). 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 50× 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 5 K, 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 μm step). The integrated intensity of given features (e.g. A exciton...
emission) has been obtained by performing Gaussian fitting of the measured µPL 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 $5 \times 5$ supercells (see Fig. 2).

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

Table 1: Structural parameters of MoS$_2$/MoSe$_2$ defective heterostructures giving the lattice constant ($a$) and interlayer metal-to-metal distances ($d$).

| System            | $a$ (Å) | $d$ (Å) |
|-------------------|---------|---------|
| MoS$_2$ 1L        | 3.171   | -       |
| MoSe$_2$ 1L       | 3.251   | -       |
| MoS$_2$/MoSe$_2$  | 3.214   | 6.21    |
| Model 1           | 3.206   | 6.30    |
| Model 2           | 3.203   | 6.26    |

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 Å 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$_2$.

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Graphical TOC Entry
Figure 1: (a) Ball and stick model of MoSe$_2$ layer sandwiched between two MoS$_2$ flakes. (b) Optical micrograph of a representative transfer area. (c) Low temperature µPL spectra (colored curves) and reflectivity contrast (grey curves) of as-grown MoS$_2$, MoSe$_2$ monolayers and MoS$_2$/MoSe$_2$/MoS$_2$ trilayer stack. (d) PL spectra of trilayer stack measured using different spot sizes. The spectra are vertically offset for clarity. $X_A$ indicates A exciton and T denotes the trion (charged A exciton).
Figure 2: (a)–(c) Atomic representation of a perfect MoSe$_2$ monolayer, the MoSe$_2$ monolayer with 1 Se vacancy, and the MoSe$_2$ monolayer with 1 S substitution, respectively. (d)–(f) Calculated corresponding band structures. Fermi level (horizontal dashed lines) is shifted to the top of the valence band. Fundamental bandgaps are indicated.
Figure 3: (a) Spatial map of the integrated intensity of A exciton of encapsulated MoSe$_2$. 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) µPL 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$_2$ X$_A$ overlaid on the same spatial map of MoSe$_2$ X$_A$. (d) Integrated intensity of MoSe$_2$ X$_A$ and MoS$_2$ X$_A$ as a function of the intensity of MoSe$_2$ X$_A$. 
Figure 4: (a) Normalized integrated intensity of MoSe$_2$ X$_A$ as a function of the excitation energy. Polarization resolved µPL spectra and DCP of MoSe$_2$ excited (b) far off MoS$_2$ X$_A$ resonance and (c) on resonance with MoS$_2$ X$_A$. (d) Integrated DCP as a function of the excitation energy. (e) Schematic illustration of spin transfer under excitation resonant with MoS$_2$ X$_A$. 