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Interface Engineering Modulated Valley Polarization in MoS₂/hBN Heterostructure

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Abstract: Layered transition metal dichalcogenides (TMDs) provide a favorable research platform for the advancement of spintronics and valleytronics because of their unique spin-valley coupling effect, which is attributed to the absence of inversion symmetry coupled with the presence of time-reversal symmetry. To maneuver the valley pseudospin efficiently is of great importance for the fabrication of conceptual devices in microelectronics. Here, we propose a straightforward way to modulate valley pseudospin with interface engineering. An underlying negative correlation between the quantum yield of photoluminescence and the degree of valley polarization was discovered. Enhanced luminous intensities were observed in the MoS₂/hBN heterostructure but with a low value of valley polarization, which was in stark contrast to those observed in the MoS₂/SiO₂ heterostructure. Based on the steady-state and time-resolved optical measurements, we reveal the correlation between exciton lifetime, luminous efficiency, and valley polarization. Our results emphasize the significance of interface engineering for tailoring valley pseudospin in two-dimensional systems and probably advance the progression of the conceptual devices based on TMDs in spintronics and valleytronics.

Keywords: molybdenum disulfide; hexagonal boron nitride; valley polarization; photoluminescence quantum yield; relaxation time



Citation: Li, F.; Zhang, H.; Li, Y.; Zhao, Y.; Liu, M.; Yang, Y.; Yao, J.; Min, S.; Kan, E.; Wan, Y. Interface Engineering Modulated Valley Polarization in MoS₂/hBN Heterostructure. *Nanomaterials* **2023**, *13*, 861. <https://doi.org/10.3390/nano13050861>

Academic Editor: Stefano Agnoli

Received: 26 January 2023

Revised: 15 February 2023

Accepted: 24 February 2023

Published: 25 February 2023



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1. Introduction

Two-dimensional (2D) polarized materials, including ferromagnets [1], ferroelectrics [2], and ferrovalley materials [3,4], demonstrate peculiar behaviors at the quantum realm. Valley pseudospin, which represents the energy band extremes in momentum space, normally exists in periodic solid materials [5,6]. The addressability of valley pseudospin enables the utilization of the momentum states of carriers as a brand-new paradigm in data coding and information handling. Using the research strategies of spintronics [7,8] for reference, a similar concept, valleytronics, arose naturally and vigorously [9]. The novel scientific connotation associated with the manipulation of the valley degree of freedom may result in a transformative impact. Referring to theoretical predictions about the intrinsic properties closely related to the valley pseudospin, rapid experimental advances [10–14] have been performed to observe and manipulate the valley polarization in a way similar to real spin.

Recently, the successful isolation and further experimental characterizations of 2D materials, including but not limited to graphene, hexagonal boron nitride (hBN), and TMDs, enriched our cognition of valley physics [15]. The spatial symmetry breaking along with the time-reversal symmetry enable two sets of the individually addressable valleys, K and K' points in the first Brillouin zone, for TMDs [16]. Especially when the layered TMDs, such as MoS₂, WS₂, and MoSe₂, are mechanically exfoliated from bulk-phase crystals and thinned down to monolayers, a marvelous transition in their electronic structure occurs, viz the evolution from an indirect bandgap to a direct one. The direct bandgaps of monolayer TMDs normally lie in the near-infrared and visible spectral ranges of approximately

1~2 eV, suitable for the investigation of valley pseudospin-related optoelectronic applications. Van der Waals (vdW) heterostructures composed of 2D materials offer a fascinating research platform for tailoring artificial composite constructions with unique properties, novel phenomena [17,18], and widespread potential applications [19–21]. The concept of engineering material properties via fabricating mixed-dimensional vdW heterostructures can also be employed to manipulate valley polarization with great convenience and low cost for spintronics and valleytronics [22,23].

Here, we performed circularly polarization-dependent photoluminescence (PL) measurements upon MoS₂ monolayers transferred atop *h*BN nanoflakes and SiO₂/Si wafers at room temperature, prepared with the chemical vapor deposition (CVD) method. Substantial variations were observed in these two vertically stacked systems, MoS₂/*h*BN and MoS₂/SiO₂, especially in their luminous performance. An underlying opposite relationship between the intensity of luminescence and the degree of valley polarization was observed. Specifically, a stronger exciton luminescence was observed in the MoS₂/*h*BN heterostructure but with a lower degree of valley-polarized emission, while a weaker luminous performance and a higher degree of valley polarization were obtained in the MoS₂/SiO₂ heterostructure. We infer that there exists a connection to be examined between the luminous efficiency and the valley polarization. According to the time-resolved circularly polarization-dependent PL measurements, a lower degree of valley polarization is observed in samples that exhibit longer exciton lifetimes. Our work reveals an inverse relationship between luminescence efficiency and the valley polarization value, and emphasizes the significance of interface engineering for modulating the intrinsic new degrees of freedom in ultrathin 2D polarized materials. It may potentially deepen our understanding of 2D quantum systems and advance the realization of the emerging practical applications for next-generation information storage and processing.

2. Materials and Methods

Large-area, continuous MoS₂ monolayers with a lateral size of several millimeters were routinely prepared with a standardized CVD process in a commercial dual-temperature-zone furnace [24,25] using high-purity S and MoO₃ powders as the solid-state powder sources. Mechanically exfoliated *h*BN flakes were transferred atop SiO₂/Si wafers with a 285 nm oxidation layer before CVD growth. Highly purified argon was employed as the transport gas. The growth temperature and the required time parameters we used for the CVD process are shown in the inset of Figure 1a. The programming temperatures for the two respective zones, in which the S and MoO₃ powders were placed, were elevated from room temperature to 160 and 650 °C in 40 min and remained unchanged for 5 min. Once the reaction and deposition processes finished, it was cooled naturally. Generally speaking, the typical growth of MoS₂ crystals atop SiO₂/Si normally results in equilateral triangle shapes under thermodynamically stable conditions. As shown in the optical microscopy image, the MoS₂ samples were successfully deposited onto the 285 nm SiO₂/Si wafer with some mechanically exfoliated *h*BN flakes randomly distributed atop its surface (Figure 1a). It can be observed that numerous discrete MoS₂ monolayers connected to each other and merged into a continuous single-layer film. The continuous single-layer film typically exhibits a lateral dimension up to several hundreds of micrometers, beneficial for probing many discrete locations within a sample via an optical means. Yu et al. previously reported that, unlike the growth of MoS₂ on SiO₂ substrates, the growth of MoS₂ on *h*BN normally follows a lattice alignment epitaxial growth mode [26], where two structurally equivalent 0° and 60° stacked MoS₂/*h*BN are presented.

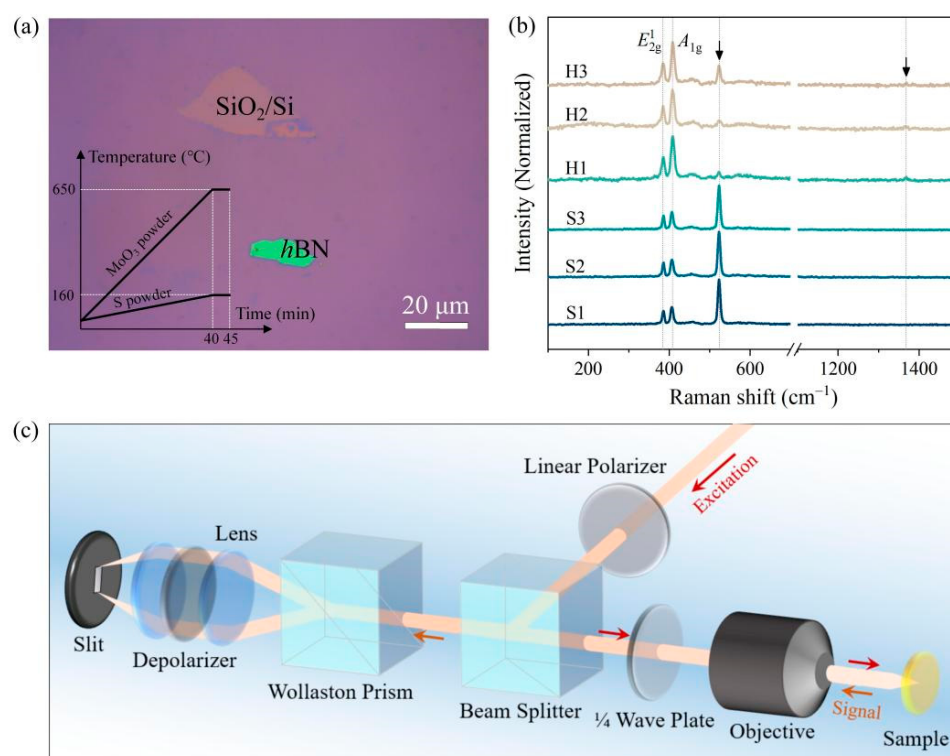


Figure 1. (a) Optical image of continuous MoS_2 monolayer films prepared with the CVD method. There is a typical $h\text{BN}$ flake obtained with mechanical exfoliation on the commonly used SiO_2 (285 nm)/ Si wafer before CVD growth. Inset: Temperature and time parameters for the CVD growth of the MoS_2 monolayers. (b) Typical Raman spectra obtained from the MoS_2 monolayer prepared atop $h\text{BN}$ (H1, H2, and H3) and SiO_2 (S1, S2, and S3). (c) The schematic diagram of the experimental setup for collecting the circularly polarized photoluminescence signals from the MoS_2 sample.

Figure 1b presents the Raman scattering spectra acquired from six distinct locations, corresponding to the MoS_2 samples prepared atop the $h\text{BN}$ and SiO_2 substrates, respectively. The characteristic feature located at approximately 520.7 cm^{-1} is attributed to the underneath Si substrate used for wavenumber calibration. Due to the reliability and repeatability of our synthetic strategy, we can observe two characteristic peaks of MoS_2 , E_{2g}^1 and A_{1g} , as well as the signal from $h\text{BN}$ ($\approx 1366.4 \text{ cm}^{-1}$), as shown in the Raman spectra labeled as H1–H3, confirming that MoS_2 is successfully grown on the $h\text{BN}$ flake. The peak interval between the two characteristic features of MoS_2 , E_{2g}^1 and A_{1g} , can help us determine the number of layers of the MoS_2 samples quantitatively and rapidly (Appendix A). One accessible mode for $h\text{BN}$ is the in-plane E_{2g} mode located at approximately 1366.4 cm^{-1} (Appendix B).

The vdW heterostructures comprised of 2D materials serve as an inspiring platform for tailoring physicochemical properties, exploring novel quantum effects, and ultimately fabricating conceptually new devices [17,18]. A classical paradigm is the demonstration of the fascinating Hofstadter butterfly observed in artificial vertically stacked moiré superlattices comprised of graphene and $h\text{BN}$ [27,28]. The strategy to tailor material properties with interface engineering is also available for the vertically stacked structure comprised of TMDs and $h\text{BN}$, which enables the exploration of valley polarization. The circular polarization-sensitive PL measurement was performed in a home-made micro-zone setup as displayed in Figure 1c. The linearly polarized excitation light is converted to the circularly polarized one by a broadband quarter-wave plate. A $50\times$ objective (N.A. 0.55) is used to collect the emission signals from the MoS_2 monolayers. The left-handed and right-handed circularly polarized light signals (σ^+ and σ^-) are converted to horizontal and vertical linearly polarized light signals ($I_{\sigma^+ \rightarrow \sigma^+}$ and $I_{\sigma^+ \rightarrow \sigma^-}$), respectively, via a broadband

quarter-wave ($1/4\lambda$) plate. The two linearly polarized light beams can be separated in real space with a Wollaston prism and then focused to two spots positioned at the entrance slit of the spectrometer equipped with the charged coupled device (CCD) cooled at -75°C . The intensities of these two orthogonally linearly polarized beams, corresponding to the $\sigma+$ and $\sigma-$ components of the PL signal, are recorded simultaneously with the CCD. By doing so, we greatly reduce the error caused by laser power fluctuation. The steady-state circularly polarized PL spectra were captured under resonant excitation with a continuous-wave 633 nm laser. For the time-resolved PL measurements, a pulsed linearly polarized Ti:sapphire laser with the wavelength of 405 nm was employed.

3. Results and Discussion

3.1. Crystal Structure of MoS_2 and the Coupled Valley-Spin Excitonic Transition Rules

Transmission electron microscopy (TEM) provides a powerful tool for examining the morphology and lattice structure of low-dimensional materials. As shown in Figure 2a, a MoS_2 monolayer triangle was transferred atop a carbon-film-coated TEM copper microgrid in the presence of a relatively complete geometric morphology. The recorded selected area electron diffraction (SAED) spots (inset, Figure 2a) exhibit a typical hexagonal pattern, consistent with that of MoS_2 . The lattice spacings of approximately 0.27 nm and 0.16 nm are clearly visible along the $\{100\}$ and $\{110\}$ planes of MoS_2 , respectively (Figure 2b). The atomic-level resolution TEM image along with the corresponding SAED patterns demonstrate that the CVD-synthesized MoS_2 monolayer possesses excellent crystal quality with a hexagonal lattice structure.

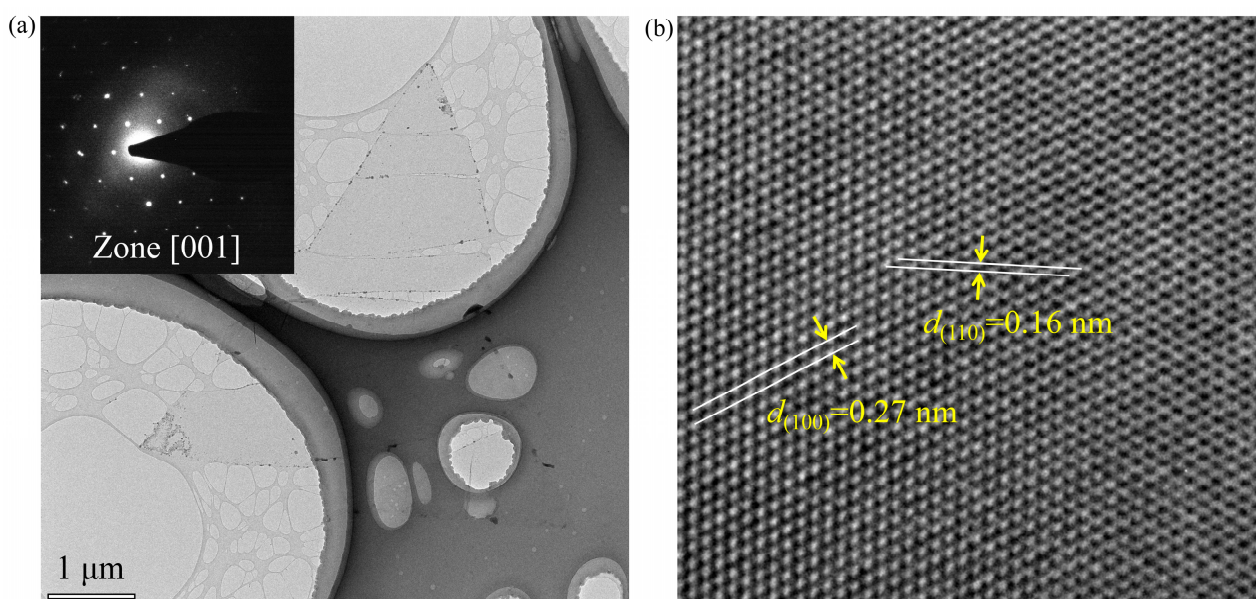


Figure 2. (a) TEM image of a MoS_2 monolayer triangle transferred atop a carbon-film-coated copper microgrid. Inset: SAED patterns recorded along the zone [001] axis of MoS_2 . (b) Atomic-level resolution TEM image of MoS_2 . A periodic triangular packing arrangement of transition metal molybdenum atoms is clearly observed.

From the top view of the crystal structure in MoS_2 , a hexagonal honeycomb lattice structure can be observed that generates two sets of degenerate-but-not-equivalent valleys, K and K', at the edges of the first Brillouin zone (left panel, Figure 3a). These valleys that are degenerate in energy exhibit a huge splitting in the valence band ($\Delta_v = \sim 148 \text{ meV}$) induced by spin-orbit coupling and a much smaller one in the conduction band ($\Delta_c = \sim 3 \text{ meV}$), which is also depicted for completeness (right panel, Figure 3a), for the MoS_2 monolayer [29–32]. The K and K' valleys are differentiated by the opposite spin orientations corresponding to the valence band maximum (VBM) and conduction band minimum

(CBM). As schematically displayed in the right panel of Figure 3a, combined with the time reversal symmetry, the spin orientations of the K and K' valleys are anti-symmetric, enabling a locking of the spin and the valley degree of freedom. The remarkable difference guarantees the valley-dependent optical selection rules that the direct excitonic transitions should obey, including A and B, in the MoS₂ monolayer. To be specific, the circularly polarized lights with left-handed helicity ($\sigma+$) excite the excitonic transitions in the K valleys exclusively, whereas those lights with right-handed helicity ($\sigma-$) only couple to the K' valleys. In our previous report [24], we reported that the A excitonic emission from the MoS₂ monolayer on the *h*BN flake exhibited a ubiquitous enhancement compared with that on SiO₂/Si. As plotted in Figure 3b,c, the intensities of the PL signals from MoS₂ on *h*BN are much stronger than those obtained from MoS₂ on SiO₂, both under 633 nm and 488 nm excitation.

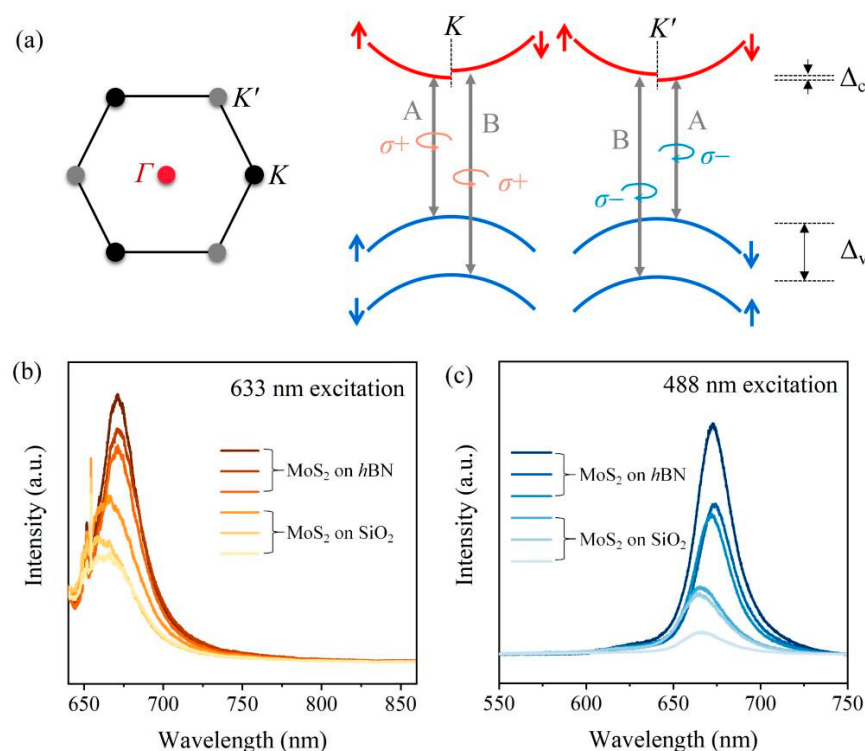


Figure 3. (a) Schematic illustration of the coupled valley-spin excitonic transition rules at the K and K' valleys in momentum space, where $\Delta_c(\Delta_v)$ denotes the amplitude of the energy splitting induced by spin-orbit coupling in the CBM and VBM in the MoS₂ monolayer. (b,c) PL spectra obtained from the representative MoS₂ samples on *h*BN and on SiO₂. The excitation wavelengths are 633 nm (b) and 488 nm (c).

3.2. Steady-State Circularly Polarized PL Spectra

The valley polarization-resolved luminous property appears a typical representative among the abundant unique physical properties for the MoS₂ monolayer. The vertical stacking of MoS₂ and *h*BN enables us to explore the valley polarization utilizing our home-made circular polarization PL measurement system. We further performed the PL measurements upon the MoS₂ monolayer on *h*BN and SiO₂ under resonant excitation with a 633 nm laser, widely employed in valley pseudospin-related luminous property investigation. The value for the degree of valley polarization obtained from the MoS₂ monolayers with different substrates underneath was calculated based on the measured polarization-resolved PL spectra involving $\sigma-$ and $\sigma+$ components. As shown in Figure 4a and b, we obtained the PL spectra by using the 1.96 eV (633 nm) laser radiation as excitation,

that is with the left-handed helicity ($\sigma+$) on resonance with the A excitonic transition. We determined the degree of valley polarization quantitatively [10,11] as

$$P = \frac{I_{\sigma+ \rightarrow \sigma+} - I_{\sigma+ \rightarrow \sigma-}}{I_{\sigma+ \rightarrow \sigma+} + I_{\sigma+ \rightarrow \sigma-}} \quad (1)$$

where $I_{\sigma+ \rightarrow \sigma+}$ and $I_{\sigma+ \rightarrow \sigma-}$ denote the intensities of the left-handed and right-handed circularly polarized PL signals, respectively, which are excited with a left-handed circular excitation laser. As plotted in Figure 4c, the average valley polarization values, ranging from 656 nm to 676 nm, were calculated to be 0.207 for MoS₂ on SiO₂ and 0.080 for MoS₂ on *h*BN. It can be observed, among the wavelength range of the direct A excitonic emission for the MoS₂ monolayer, the valley polarization for MoS₂ on *h*BN is always lower than that observed from the MoS₂ monolayers on SiO₂.

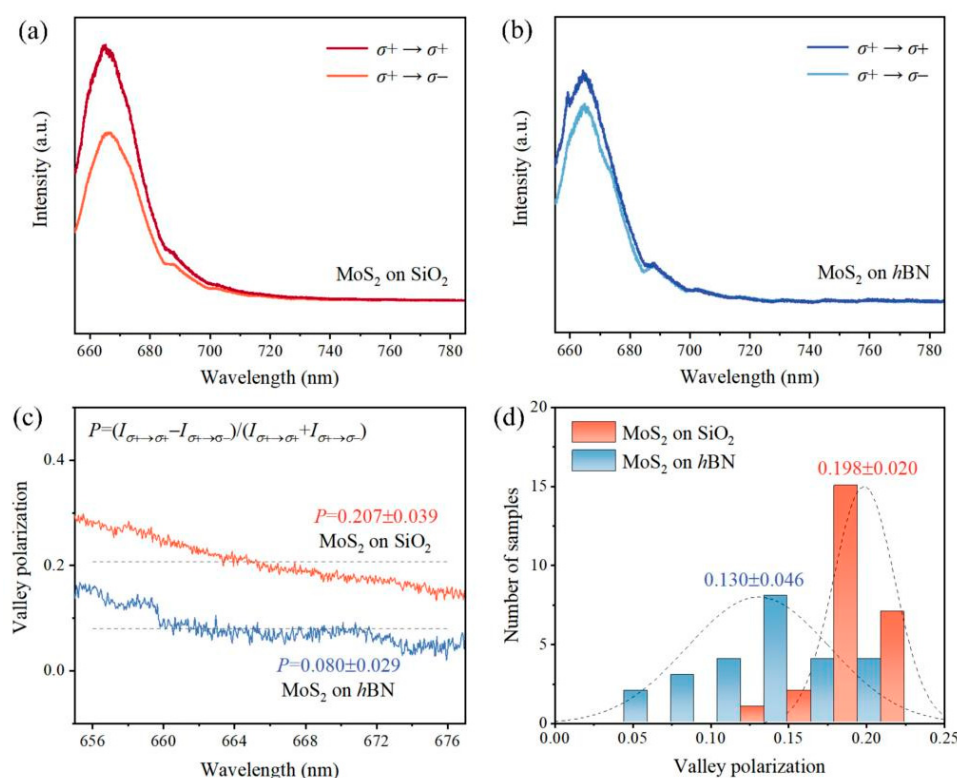


Figure 4. (a,b) Room-temperature circularly polarized PL spectra obtained from the MoS₂ monolayers on SiO₂ and *h*BN under a resonant continuous-wave excitation. (c) Degree of valley polarization determined with $P = (I_{\sigma+ \rightarrow \sigma+} - I_{\sigma+ \rightarrow \sigma-}) / (I_{\sigma+ \rightarrow \sigma+} + I_{\sigma+ \rightarrow \sigma-})$, where $I_{\sigma+ \rightarrow \sigma+}$ and $I_{\sigma+ \rightarrow \sigma-}$ represent the intensities of the left-handed and right-handed circularly polarized PL components, respectively. (d) Statistical histogram of the calculated valley polarization value for the MoS₂ monolayers on SiO₂ (orange) and on *h*BN (blue) summarized from 50 samples. The summarized valley polarization values are 0.198 for MoS₂ on SiO₂ and 0.130 for MoS₂ on *h*BN.

Based on the numerical analyses of 25 MoS₂ monolayer samples on *h*BN, the statistical average for the degree of valley polarization is $P = 0.130 \pm 0.046$ (Figure 4d), which demonstrates a relatively low degree of valley polarization in the MoS₂/*h*BN heterostructure at room temperature (300 K). In stark contrast to that, the degree of valley polarization for the MoS₂ monolayer deposited atop the SiO₂ wafer under the identical measurement conditions is relatively high. The statistical average value equals approximately 0.198 ± 0.020 from which an important message can be delivered that the interaction widely existent in 2D materials/supporting substrates may play a critical role in the modulation of valley pseudospin in 2D polarized materials. Combined with the measurement results men-

tioned above, an enhanced PL intensity and a reduced valley polarization are observed in the MoS₂/hBN heterostructure. Why does there exist a noticeably opposite relationship between luminous intensity and valley polarization? To answer this question and further clarify the underlying mechanism, we further performed the time-resolved circularly polarization-dependent PL measurements at room temperature.

For the steady-state conditions excited with a continuous wave (CW) laser, the degree of valley polarization, P , can be determined with

$$P = \frac{P_0}{1 + \frac{2\tau_e}{\tau_v}} \quad (2)$$

under a rate model, where P_0 denotes the initial polarization, and τ_e and τ_v represent the exciton and valley relaxation times, respectively. The derivative process is provided in Appendix C. The value of P increases with either an increase in valley lifetime τ_v or a decrease in exciton lifetime τ_e , as clearly observed from Equation (2). Previous reports did not identify the influence of substrates on the valley relaxation time τ_v for MoS₂, among which the measured values are close numerically and even the supporting substrates are different. All the as-synthesized MoS₂ monolayers shown in Figure 4 were excited with exactly the same excitation wavelength, pumping power, and exposure time, and exposed to nearly the identical environment. Thus, it is assumed that the valley relaxation time τ_v and the initial polarization P_0 are the same. It can be inferred that the degree of valley polarization P will decrease if the exciton relaxation time increases.

3.3. Time-Resolved Circularly Polarized PL Spectra

According to the theory in semiconductor physics, the exciton relaxation time τ_e is closely related to both radiative and non-radiative recombination times through the following relational expression:

$$\frac{1}{\tau_e} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \quad (3)$$

The time parameters, τ_r and τ_{nr} , represent the radiative and non-radiative lifetimes, respectively. For transition metal dichalcogenides, the non-radiative lifetimes can be orders of magnitude shorter than the radiative recombination times. In other words, the magnitude relationship $\tau_{nr} \ll \tau_r$ exists in MoS₂ monolayers. Hence, there exists an approximation relation $\tau_e \approx \tau_{nr}$. For a certain material, the radiative recombination time τ_r can be regarded as a constant. Since the luminous intensity is in direct proportion to quantum yield (QY),

$$QY = \frac{1}{1 + \frac{\tau_r}{\tau_{nr}}} \approx \frac{1}{1 + \frac{\tau_r}{\tau_e}} \quad (4)$$

If the radiative recombination time remains unchanged, a longer exciton relaxation time will lead to a higher QY and, thus, an enhanced PL intensity.

We further performed time-resolved photoluminescence (TRPL) measurements to examine the exciton dynamics and capture the corresponding fluorescence lifetime with which our hypothesis mentioned above may be verified. The measured TRPL spectra are plotted in Figure 5. Two systems, including the MoS₂ monolayers deposited atop hBN and SiO₂, were measured, which behave remarkably different from each other in the intensity of luminescence and the degree of valley polarization. A pulsed, linearly polarized Ti:sapphire laser with the wavelength of 405 nm was employed to pump the direct excitons into the two degenerate-but-not-equivalent valleys, K and K', in the MoS₂ monolayer simultaneously via an optical means. The pulsed optical pumps were realized with an optical parametric amplification. The subsequent luminescent signals created from the K and K' valleys could then be collected and directed to a time-resolved CCD detector. The dynamic experimental results were quite similar to those observed in the steady-state PL measurement results.

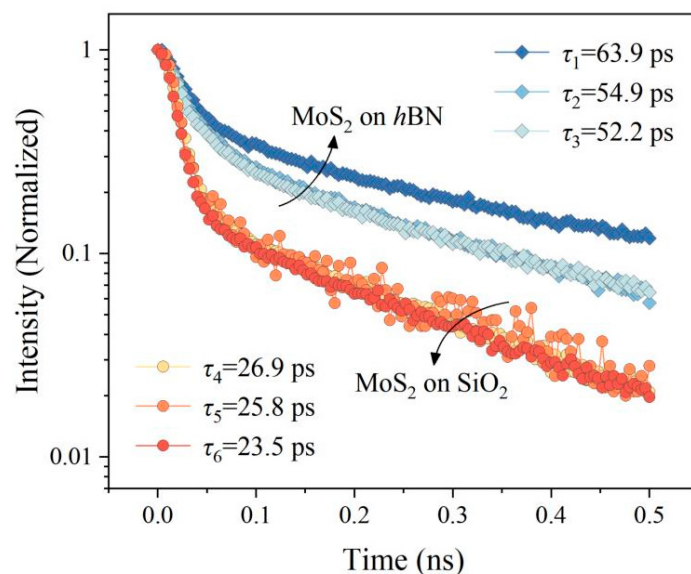


Figure 5. The circularly polarized time-resolved PL spectra obtained from the MoS₂ monolayers on hBN and SiO₂, all of which were measured at room temperature. By the deconvolution fitting, the exciton lifetimes could be obtained.

As mentioned above, the MoS₂ monolayers on hBN and SiO₂ display noticeably different PL intensity as well as distinguishing valley polarization behaviors. The time-resolved emission spectra measured from these samples, as presented here, also exhibit significantly different exciton attenuation kinetics. MoS₂ on hBN possesses a longer exciton lifetime than MoS₂ on SiO₂. Compared with SiO₂, hBN is chemically inert and has no defect states or hanging bonds on its surface. This may result in less disorder to the MoS₂ monolayer [33], which is mainly stemmed from extrinsic effects, for example, defects and trap states. The difference in the exciton relaxation time explains the enhanced PL intensity and lower valley polarization of MoS₂ on hBN.

4. Conclusions

In conclusion, we successfully synthesized a MoS₂ monolayer on hBN nanoflakes via the CVD method and performed room-temperature circularly polarized PL measurements upon the MoS₂ samples with different substrates underneath. We observed that there exists an apparent inverse correlation between the intensity of PL signals and the value of valley polarization, which originates from the variations in exciton relaxation time. Compared to MoS₂ monolayers atop SiO₂, the MoS₂ monolayers atop hBN exhibit a relatively low degree of valley polarization. An enhanced PL intensity and a longer exciton lifetime were also experimentally consolidated in the MoS₂/hBN system. Our discovery suggests a pathway to tailor carrier dynamics via crystal modification, which can be realized by introducing an appropriate amount of defects or non-radiative recombination sites. By doing so, the room-temperature valley polarization can be effectively modulated, and the coupling between degenerate valleys can be attenuated, which provides new strategies for the realization of state-of-the-art devices in spintronics and valleytronics.

Author Contributions: F.L., H.Z., Y.Z. and M.L. performed the CVD synthesis and sample characterization measurements (Micro-Raman and PL); analyzed and interpreted the corresponding data; and drafted the article. Y.L., Y.Y., J.Y. and S.M. performed the TEM characterizations. E.K. and Y.W. conceived the project and revised the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China (Nos. 12004182, T2125004, and 11774173), Jiangsu Province Science Foundation (No. BK20200481), the China

Postdoctoral Science Foundation (No. 2021M691587), the Fundamental Research Funds for the Central Universities (Nos. 30920021152, and 30920041115), and Funding of NJUST (No. TSXK2022D002).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data concerning this study are contained in the present manuscript and in previous articles, whose references have been provided.

Acknowledgments: The authors are grateful to Yu Ye and Lun Dai from Peking University for helpful discussion.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Li et al. proposed a general thickness identification technique for atomic-scale, few-layer MoS₂ on dielectric substrates [34], such as SiO₂. The peak interval between the two characteristic features of MoS₂, E_{2g}^1 and A_{1g} , can determine the number of layers of the MoS₂ samples quantitatively and rapidly.

The zoom-in Raman spectrum of the MoS₂ monolayer on SiO₂ is provided in Figure A1a. We can clearly observe the characteristic modes E_{2g}^1 and A_{1g} of MoS₂, the peak interval ($\sim 19.8 \text{ cm}^{-1}$) between which is consistent with the criterion for CVD-synthesized MoS₂ monolayers on SiO₂. Figure A1b plots the Raman spectra obtained from 1L, 2L, and 3L MoS₂ on SiO₂, the thickness of which was determined with the atomic force microscope technique. The three characteristic peaks located among $360\sim 540 \text{ cm}^{-1}$ correspond to two characteristic peaks of MoS₂, E_{2g}^1 and A_{1g} , as well as the signal from the underneath Si substrate (520.7 cm^{-1}). In the series of Raman spectra, corresponding to 1L, 2L, and 3L MoS₂, there exists a monotonous variation trend in the peak interval between E_{2g}^1 and A_{1g} .

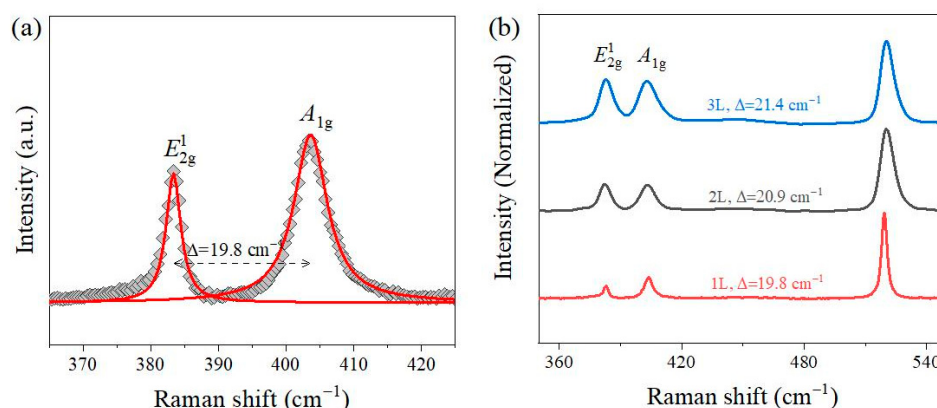


Figure A1. (a) Zoom-in Raman spectrum of 1L MoS₂. (b) Typical Raman spectra obtained from 1L, 2L, and 3L MoS₂ prepared atop SiO₂. The Raman peak located at approximately 520.7 cm^{-1} corresponding to Si is used for wavenumber calibration and intensity normalization.

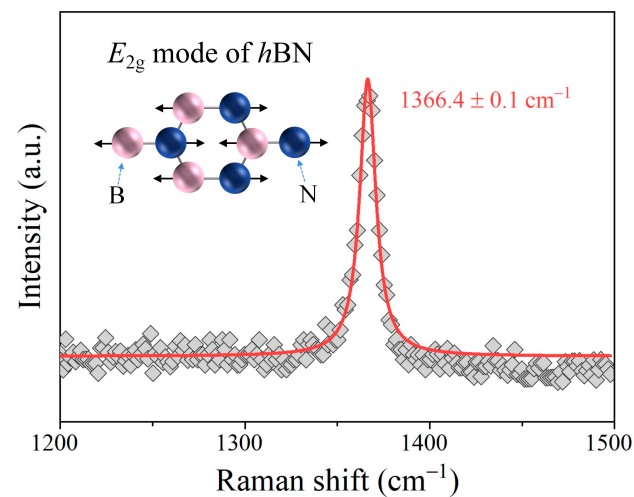
The detailed values of peak positions, as shown in Figure A1b, are summarized in Table A1. With the increasing number of layers, there exists a decrease in the peak position of E_{2g}^1 mode, an increase in the peak position of A_{1g} mode, and an increase in the peak interval Δ , consistent with the experimental results previously reported by Li et al. [34]. As mentioned above, it is a feasible calibration method to determine the number of layers of the few-layer MoS₂ samples based on the amplitude of the peak interval Δ .

Table A1. The Raman spectral peak positions of few-layer MoS₂.

Number of Layer	E_{2g}^1 (cm ⁻¹)	A_{1g} (cm ⁻¹)	Δ (cm ⁻¹)
1	383.4	403.2	19.8
2	382.3	403.2	20.9
3	382.1	403.5	21.4

Appendix B

Raman scattering spectroscopy provides a non-destructive technique for studying *h*BN. One accessible mode is the in-plane E_{2g} mode at approximately 1366.4 cm⁻¹ [35]. As displayed in Figure A2, a narrow feature is a representative of highly ordered, defect-free *h*BN. As we can observe from Figure 1b, the two characteristic peaks of MoS₂, E_{2g}^1 and A_{1g} , as well as the signal from *h*BN (≈ 1366.4 cm⁻¹) obtained from the samples labeled as H1 to H3 in the main text, indicate that MoS₂ is successfully synthesized atop the mechanically exfoliated *h*BN flakes.

**Figure A2.** Raman peak located at approximately 1366.4 cm⁻¹ corresponding to *h*BN. The left top schematic image indicates the Raman-active mode E_{2g} of *h*BN.

Appendix C

Under a rate model [10], the rate equation for the neutral exciton populations at the two degenerate-but-not-equivalent K and K' valleys can be mathematically described as follows:

$$\frac{dn_K}{dt} = g_K - \frac{n_K}{\tau_{nr}} - \frac{n_K}{\tau_{exciton \rightarrow trion}} - \frac{n_K - n_{K'}}{\tau_v} \quad (A1)$$

$$\frac{dn_{K'}}{dt} = g_{K'} - \frac{n_{K'}}{\tau_{nr}} - \frac{n_{K'}}{\tau_{exciton \rightarrow trion}} + \frac{n_K - n_{K'}}{\tau_v} \quad (A2)$$

where g_K and $g_{K'}$ represent the excitation rate optically pumped by left-handed helicity ($\sigma+$) coupled to the excitonic transitions in the K valleys and right-handed helicity ($\sigma-$) coupled to the K' valleys, respectively. Besides, τ_{nr} , $\tau_{exciton \rightarrow trion}$, and τ_v denote the non-radiative relaxation time, the scattering relaxation time from neutral exciton to charged tightly bound trion [36,37], and the intervalley relaxation time between K and K' valleys, respectively. In fact, under a relatively high measuring temperature [36] or a relatively low carrier injection concentration [37], as in our experiments, the scattering process from exciton to trion can be ignored, which means $\tau_{exciton \rightarrow trion}$ can be viewed as an infinite.

Under the steady-state excitation for the neutral exciton (A) generated in the K valley, as employed in our experiment, the right-handed helicity excitation is zero, viz $g_{K'} = 0$, and the material system is in a state of dynamic equilibrium, which indicates that

$$\frac{dn_K}{dt} = \frac{dn_{K'}}{dt} = 0 \quad (\text{A3})$$

We determine the degree of valley polarization quantitatively as

$$P = \frac{I_{\sigma+\rightarrow\sigma+} - I_{\sigma+\rightarrow\sigma-}}{I_{\sigma+\rightarrow\sigma+} + I_{\sigma+\rightarrow\sigma-}} \quad (\text{A4})$$

based on the polarization-dependent PL intensities. The valley polarization can also be written as

$$P = \frac{n_K - n_{K'}}{n_K + n_{K'}} \quad (\text{A5})$$

based on the polarization-dependent PL intensities. Thus, for the steady-state conditions excited with a CW laser, the degree of valley polarization, P , can be determined with

$$P = \frac{1}{1 + \frac{2\tau_{nr}}{\tau_v}} \quad (\text{A6})$$

According to the theory in semiconductor physics, the exciton relaxation time τ_e is closely related to both radiative and non-radiative recombination times through the following relational expression, $\tau_e^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$, in which the time parameters, τ_r and τ_{nr} , represent the radiative and non-radiative lifetimes, respectively. For transition metal dichalcogenides, the non-radiative lifetimes can be orders of magnitude shorter than radiative recombination times, viz $\tau_{nr} \ll \tau_r$. Hence, there exists an approximation relation $\tau_e \approx \tau_{nr}$. Considering the derivation in initial polarization that is closely related to some parameters, including but not limited to excitation laser wavelength, exposure time, and possible intervalley generation, we multiply the numerator with a coefficient P_0 additively:

$$P = \frac{P_0}{1 + \frac{2\tau_e}{\tau_v}} \quad (\text{A7})$$

Consequently, the less-than-perfect (much lower than the ideal 100%) degree of valley polarization observed in the circularly optical measurement results is attributed to inevitable intervalley processes and the competition between the valley lifetime τ_v and the recombination relaxation time τ_e .

References

1. Wang, Q.H.; Bedoya-Pinto, A.; Blei, M.; Dismukes, A.H.; Hamo, A.; Jenkins, S.; Koperski, M.; Liu, Y.; Sun, Q.-C.; Telford, E.J.; et al. The magnetic genome of two-dimensional van der Waals materials. *ACS Nano* **2022**, *16*, 6960–7079. [CrossRef]
2. Zhang, D.; Schoenherr, P.; Sharma, P.; Seidel, J. Ferroelectric order in van der Waals layered materials. *Nat. Rev. Mater.* **2022**, *8*, 25–40. Available online: <https://www.nature.com/articles/s41578-022-00484-3> (accessed on 17 October 2022). [CrossRef]
3. Chu, J.; Wang, Y.; Wang, X.; Hu, K.; Rao, G.; Gong, C.; Wu, C.; Hong, H.; Wang, X.; Liu, K.; et al. 2D polarized materials: Ferromagnetic, ferrovalley, ferroelectric materials, and related heterostructures. *Adv. Mater.* **2021**, *33*, 2004469. [CrossRef]
4. Sheng, K.; Chen, Q.; Yuan, H.K.; Wang, Z.Y. Monolayer CeI_2 : An intrinsic room-temperature ferrovalley semiconductor. *Phys. Rev. B* **2022**, *105*, 075304. Available online: <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.105.075304> (accessed on 14 February 2022). [CrossRef]
5. Xiao, D.; Yao, W.; Niu, Q. Valley-contrasting physics in graphene: Magnetic moment and topological transport. *Phys. Rev. Lett.* **2007**, *99*, 236809. Available online: <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.99.236809> (accessed on 7 December 2007). [CrossRef]
6. Xiao, D.; Chang, M.-C.; Niu, Q. Berry phase effects on electronic properties. *Rev. Mod. Phys.* **2010**, *82*, 1959. Available online: <https://journals.aps.org/rmp/abstract/10.1103/RevModPhys.82.1959> (accessed on 6 July 2010). [CrossRef]
7. Han, W. Perspectives for spintronics in 2D materials. *APL Mater.* **2016**, *4*, 032401. [CrossRef]

8. Ahn, E.C. 2D materials for spintronic devices. *npj 2d Mater. Appl.* **2020**, *4*, 17. Available online: <https://www.nature.com/articles/s41699-020-0152-0> (accessed on 18 June 2020). [CrossRef]
9. Schaibley, J.R.; Yu, H.; Clark, G.; Rivera, P.; Ross, J.S.; Seyler, K.L.; Yao, W.; Xu, X. Valleytronics in 2D materials. *Nat. Rev. Mater.* **2016**, *1*, 16055. Available online: <https://www.nature.com/articles/natrevmats201655> (accessed on 23 August 2016). [CrossRef]
10. Mak, K.F.; He, K.; Shan, J.; Heinz, T.F. Control of valley polarization in monolayer MoS₂ by optical helicity. *Nat. Nanotechnol.* **2012**, *7*, 494–498. Available online: <https://www.nature.com/articles/nnano.2012.96> (accessed on 17 June 2012). [CrossRef]
11. Cao, T.; Wang, G.; Han, W.; Ye, H.; Zhu, C.; Shi, J.; Niu, Q.; Tan, P.; Wang, E.; Liu, B. Valley-selective circular dichroism of monolayer molybdenum disulphide. *Nat. Commun.* **2012**, *3*, 887. Available online: <https://www.nature.com/articles/ncomms1882> (accessed on 6 June 2012). [CrossRef]
12. Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X. Valley polarization in MoS₂ monolayers by optical pumping. *Nat. Nanotechnol.* **2012**, *7*, 490–493. Available online: <https://www.nature.com/articles/nnano.2012.95> (accessed on 17 June 2012). [CrossRef]
13. Mak, K.F.; McGill, K.L.; Park, J.; McEuen, P.L. The valley Hall effect in MoS₂ transistors. *Science* **2014**, *344*, 1489–1492. [CrossRef]
14. Ye, Y.; Xiao, J.; Wang, H.; Ye, Z.; Zhu, H.; Zhao, M.; Wang, Y.; Zhao, J.; Yin, X.; Zhang, X. Electrical generation and control of the valley carriers in a monolayer transition metal dichalcogenide. *Nat. Nanotechnol.* **2016**, *11*, 598–602. Available online: <https://www.nature.com/articles/nnano.2016.49> (accessed on 4 April 2016). [CrossRef]
15. Liu, X.; Hersam, M.C. 2D materials for quantum information science. *Nat. Rev. Mater.* **2019**, *4*, 669–684. Available online: <https://www.nature.com/articles/s41578-019-0136-x> (accessed on 19 August 2019). [CrossRef]
16. Xu, X.; Yao, W.; Xiao, D.; Heinz, T.F. Spin and pseudospins in layered transition metal dichalcogenides. *Nat. Phys.* **2014**, *10*, 343–350. Available online: <https://www.nature.com/articles/nphys2942> (accessed on 30 April 2014). [CrossRef]
17. Ciarrocchi, A.; Tagarelli, F.; Avsar, A.; Kis, A. Excitonic devices with van der Waals heterostructures: Valleytronics meets twistrionics. *Nat. Rev. Mater.* **2022**, *7*, 449–464. Available online: <https://www.nature.com/articles/s41578-021-00408-7> (accessed on 31 January 2022). [CrossRef]
18. Wu, X.; Chen, X.; Yang, R.; Zhan, J.; Ren, Y.; Li, K. Recent Advances on tuning the interlayer coupling and properties in van Der Waals heterostructures. *Small* **2022**, *18*, 2105877. [CrossRef]
19. Lee, D.; Lee, J.J.; Kim, Y.S.; Kim, Y.H.; Kim, J.C.; Huh, W.; Lee, J.; Park, S.; Jeong, H.Y.; Kim, Y.D.; et al. Remote modulation doping in van der Waals heterostructure transistors. *Nat. Electron.* **2021**, *4*, 664–670. Available online: <https://www.nature.com/articles/s41928-021-00641-6> (accessed on 13 September 2021). [CrossRef]
20. Liu, L.; Kong, L.; Li, Q.; He, C.; Ren, L.; Tao, Q.; Yang, X.; Lin, J.; Zhao, B.; Li, Z.; et al. Transferred van der Waals metal electrodes for sub-1-nm MoS₂ vertical transistors. *Nat. Electron.* **2021**, *4*, 342–347. Available online: <https://www.nature.com/articles/s41928-021-00566-0> (accessed on 26 April 2021). [CrossRef]
21. Tao, Q.; Wu, R.; Li, Q.; Kong, L.; Chen, Y.; Jiang, J.; Lu, Z.; Li, B.; Li, W.; Li, Z.; et al. Reconfigurable electronics by disassembling and reassembling van der Waals heterostructures. *Nat. Commun.* **2021**, *12*, 1825. Available online: <https://www.nature.com/articles/s41467-021-22118-y> (accessed on 23 March 2021). [CrossRef]
22. Chen, Y.; Ma, J.; Liu, Z.; Li, J.; Duan, X.; Li, D. Manipulation of valley pseudospin by selective spin injection in chiral two-dimensional perovskite/monolayer transition metal dichalcogenide heterostructures. *ACS Nano* **2020**, *14*, 15154–15160. [CrossRef]
23. Kumar, A.; Yagodkin, D.; Stetzuhn, N.; Kovalchuk, S.; Melnikov, A.; Elliott, P.; Sharma, S.; Gahl, C.; Bolotin, K.I. Spin/valley coupled dynamics of electrons and holes at the MoS₂-MoSe₂ interface. *Nano Lett.* **2021**, *21*, 7123–7130. [CrossRef]
24. Wan, Y.; Zhang, H.; Wang, W.; Sheng, B.; Zhang, K.; Wang, Y.; Song, Q.; Mao, N.; Li, Y.; Wang, X. Origin of improved optical quality of monolayer molybdenum disulfide grown on hexagonal boron nitride substrate. *Small* **2016**, *12*, 198–203. [CrossRef]
25. Wan, Y.; Zhang, H.; Zhang, K.; Wang, Y.; Sheng, B.; Wang, X.; Dai, L. Large-scale synthesis and systematic photoluminescence properties of monolayer MoS₂ on fused silica. *ACS Appl. Mater. Interfaces* **2016**, *8*, 18570–18576. [CrossRef]
26. Yu, H.; Yang, Z.; Du, L.; Zhang, J.; Shi, J.; Chen, W.; Chen, P.; Liao, M.; Zhao, J.; Meng, J.; et al. Precisely aligned monolayer MoS₂ epitaxially grown on h-BN basal plane. *Small* **2017**, *13*, 1603005. [CrossRef]
27. Dean, C.R.; Wang, L.; Maher, P.; Forsythe, C.; Ghahari, F.; Gao, Y.; Katoch, J.; Ishigami, M.; Moon, P.; Koshino, M. Hofstadter’s butterfly and the fractal quantum Hall effect in moiré superlattices. *Nature* **2013**, *497*, 598–602. Available online: <https://www.nature.com/articles/nature12186> (accessed on 15 May 2013). [CrossRef]
28. Hunt, B.; Sanchez-Yamagishi, J.D.; Young, A.F.; Yankowitz, M.; LeRoy, B.J.; Watanabe, K.; Taniguchi, T.; Moon, P.; Koshino, M.; Jarillo-Herrero, P. Massive Dirac fermions and Hofstadter butterfly in a van der Waals heterostructure. *Science* **2013**, *340*, 1427–1430. [CrossRef]
29. Kośmider, K.; González, J.W.; Fernández-Rossier, J. Large spin splitting in the conduction band of transition metal dichalcogenide monolayers. *Phys. Rev. B* **2013**, *88*, 245436. Available online: <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.88.245436> (accessed on 23 December 2013). [CrossRef]
30. Ochoa, H.; Roldán, R. Spin-orbit-mediated spin relaxation in monolayer MoS₂. *Phys. Rev. B* **2013**, *87*, 245421. Available online: <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.87.245421> (accessed on 17 June 2013). [CrossRef]
31. Liu, G.-B.; Shan, W.-Y.; Yao, Y.; Yao, W.; Xiao, D. Three-band tight-binding model for monolayers of group-VIB transition metal dichalcogenides. *Phys. Rev. B* **2013**, *88*, 085433. Available online: <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.88.085433> (accessed on 26 August 2013). [CrossRef]

32. Stier, A.V.; McCreary, K.M.; Jonker, B.T.; Kono, J.; Crooker, S.A. Exciton diamagnetic shifts and valley Zeeman effects in monolayer WS₂ and MoS₂ to 65 Tesla. *Nat. Commun.* **2016**, *7*, 10643. Available online: <https://www.nature.com/articles/ncomms10643> (accessed on 9 February 2016). [[CrossRef](#)] [[PubMed](#)]
33. McCreary, K.M.; Currie, M.; Hanbicki, A.T.; Chuang, H.-J.; Jonker, B.T. Understanding variations in circularly polarized photoluminescence in monolayer transition metal dichalcogenides. *ACS Nano* **2017**, *11*, 7988–7994. [[CrossRef](#)] [[PubMed](#)]
34. Li, S.-L.; Miyazaki, H.; Song, H.; Kuramochi, H.; Nakaharai, S.; Tsukagoshi, K. Quantitative Raman spectrum and reliable thickness identification for atomic layers on insulating substrates. *ACS Nano* **2012**, *6*, 7381–7388. [[CrossRef](#)]
35. Maestre, C.; Toury, B.; Steyer, P.; Garnier, V.; Journet, C. Hexagonal boron nitride: A review on selfstanding crystals synthesis towards 2D nanosheets. *J. Phys. Mater.* **2021**, *4*, 044018. Available online: <https://iopscience.iop.org/article/10.1088/2515-7639/ac2b87/meta> (accessed on 18 October 2021). [[CrossRef](#)]
36. Ross, J.S.; Wu, S.; Yu, H.; Ghimire, N.J.; Jones, A.M.; Aivazian, G.; Yan, J.; Mandrus, D.G.; Xiao, D.; Yao, W.; et al. Electrical control of neutral and charged excitons in a monolayer semiconductor. *Nat. Commun.* **2013**, *4*, 1474. Available online: <https://www.nature.com/articles/ncomms2498> (accessed on 12 February 2013). [[CrossRef](#)]
37. Mak, K.F.; He, K.; Lee, C.; Lee, G.H.; Hone, J.; Heinz, T.; Shan, J. Tightly bound trions in monolayer MoS₂. *Nat. Mater.* **2013**, *12*, 207–211. Available online: <https://www.nature.com/articles/nmat3505> (accessed on 2 December 2012). [[CrossRef](#)] [[PubMed](#)]

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