Research article

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Valley depolarization in downconversion and upconversion emission of monolayer WS₂ at room temperature

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Abstract: Benefiting from strong photon–exciton and phonon–exciton interactions in atomic thickness, transition metal dichalcogenides (TMDCs) are viewed as one promising platform for exploring elementary excitonic photoluminescence (PL) and intrinsic spin–valley properties at the monolayer limit. Despite well-studied Stokes downconversion (DC) PL, the anti-Stokes upconversion (UC) PL has been recently reported in TMDC monolayers, which mainly focus on UC mechanisms while detailed valley-related dynamical processes are unwittingly less concerned. Here, we carry out an in-depth investigation on both DC and UC emission features of monolayer WS₂ at room temperature, where UC PL persists with energy gain up to 190 meV. The PL excitation and power-dependent experiments clearly distinguish the origins of DC PL and UC PL, which refer to saturated absorption and phonon-assisted transition from charged trions to neutral A-excitons. And contrast valley properties are observed in DC and UC scenarios with polarization-resolved PL and pump–probe measurements. According to the experimental facts, phenomenological dynamical DC and UC scenarios are modeled with intervalley depolarization taken into consideration, in which intermediates from spontaneous intervalley depolarization account for the observed emission and valley properties. This work can help understand the light–matter interactions and valley properties in monolayer TMDCs.

1 Introduction

Photoluminescence (PL) is an elementary light–matter interaction process, in which downconversion (DC) PL is the general Stokes process in emission of semiconductors, resulting in the energy or frequency of an emitted photon smaller than that of the absorbed one. In contrast to the DC PL, the other one PL mode, namely upconversion (UC) PL, describes an anti-Stokes process, in which the material absorbs photons with lower energy and then reemits corresponding photons with some energy gain. As often referred to optical refrigeration and laser cooling, the UC PL phenomenon has been well explored and demonstrated in glass doping with rare-earth elements [1–3], quantum wells [4–7] and other semiconductors [8, 9] at cryogenic conditions. Recently, monolayer transition metal dichalcogenides (TMDCs) are found to be direct bandgap semiconductors with visible PL [10–16] and much higher quantum efficiency than traditional semiconductor materials [17, 18], where solid dipoles of excitons dominate the optical properties due to strong Coulomb binding effect [19–25]. Benefiting from enhanced photon–exciton [26–37] and phonon–exciton interaction strength [38–41] in a low dimensional scale, as observed in graphene and V–V binary materials [42, 43], TMDCs are viewed as one promising platform for exploring UC PL at the monolayer limit. And there are some research studies reporting the UC PL observed in monolayer TMDCs, for example, two-photon absorption–induced UC PL of B-exciton at 4 K [44] and phonon-mediated doubly resonant UC PL with an energy gain of 30 meV up to 250 K [45] in monolayer WSe₂, as well as multiphonon–induced UC PL with an energy gain of 150 meV in monolayer WS₂ at room temperature [46]. However, these research studies mainly focus on the excitonic conversion mechanism during the UC PL process, and the underlying dynamical transition process and intrinsic valley properties of monolayer TMDCs are

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unwittingly less concerned to some extent. Considering the strong excitonic and phonon–exciton interactions in monolayer TMDCs, the relationship between valley depolarization and UC PL process is still blurred. In this way, a deeper study of dynamical valley depolarization mechanism during the UC PL process may bring a new understanding of valleytronics based on TMDCs.

In this work, we investigate both DC PL and UC PL in monolayer WS₂. We not only explore the properties of DC PL and UC PL but also focus on the valley properties in these two opposite PL modes. We observe the UC PL, from charged trions to neutral excitons, with energy gain up to 190 meV at room temperature. Valley properties are measured, and different dynamical parameters related to valley depolarization, including initial polarization and exciton lifetime, are analyzed and discussed for both DC PL and UC PL scenarios. Finally, phenomenological valley

depolarization processes are modeled and discussed according to the experimental results, which well explain the observation of PL and valley properties in monolayer WS₂.

2 Results and discussion

Figure 1a presents the optical image of two WS₂ monolayers grown by the chemical vapor deposition method on the Si/SiO₂ substrate and marked as S1 and S2. All the results presented here are of S1 sample and those of S2 sample are presented in Supplementary material. The Raman spectrum of monolayer WS₂ is shown in Figure 1b, and the Raman interval between out-of-plane A_{1g} mode and in-plane E_{2g}¹ mode is around 61.7 cm⁻¹, which is in accordance with previous reports [47, 48]. The schematic of DC PL and

Figure 1: Downconversion (DC) and upconversion (UC) processes in monolayer WS₂.

(a) Optical image of monolayer WS₂ on Si/SiO₂ substrate. (b) Raman spectrum of monolayer WS₂. (c) The schematic of DC and UC processes. GS is the ground state. X_T, X_A and hot represent the trions, A-excitons and hot carriers, respectively. Red and blue lines represent the excitation process by off-resonance energy. Gray lines indicate the emission of A-excitons through DC and UC processes. (d) The PL spectrum of monolayer WS₂ excited by 512-nm continuous-wave laser at room temperature. The dash lines show the filter edges.

UC PL processes in monolayer WS_2 is illustrated in Figure 1c. Generally, the hot carriers are firstly generated by the photons with energy above the bandgap and then relax toward the band edge and are finally recombined with radiatively emitting photons, with energy centered at the resonance of A-exciton in DC PL. However, it is found that the A-exciton emission can also occur with excitation energy below the bandgap. In this case, trions, created by incident light with energy on the tail of resonance [45, 46], are somehow converted into A-excitons and then recombine radiatively, which is defined as UC PL. The prototypical PL spectrum excited by 512-nm continuous-wave laser at room temperature is presented in Figure 1d, with trion and exciton emission intensities and peaks fitted by the Lorentz model. During the following PL-related experiments, a short-pass filter and a long-pass filter are used, with the edge at 1.96 and 2.06 eV, respectively. And emission of A-excitons with excitation energy below 1.96 eV (above 2.06 eV) is described as UC PL (DC PL), with corresponding off-resonance energy (Δ) defined as the difference between the excitation energy (E_{ex}) and the peak

energy of A-exciton $E_A = 2.04$ eV in monolayer WS_2 , namely $\Delta = E_{\text{ex}} - E_A$.

2.1 Properties and origins of DC PL and UC PL

For detailed information about DC PL and UC PL, photoluminescence excitation (PLE) experiments are performed. As presented in Figure 2a and c, the intensity of both DC PL and UC PL depends on off-resonance energy, with the shape of the PL spectra and the peaks of the A-exciton nearly unchanged. Surprisingly, the A-exciton emission even remains detectable within 190 meV range of off-resonance energy, exceeding the reported 150 meV energy gain in previous research of monolayer WS_2 [46]. To quantitatively analyze the emission properties in DC PL and UC PL, the PL intensity of A-exciton resonance is integrated and normalized in log scale, shown in Figure 2b and d, which obey an evident linear relationship with the off-resonance energy. In this way, the integrated DC PL and

Figure 2: Photoluminescence excitation (PLE) spectra in downconversion (DC) and upconversion (UC) processes.

(a) DC PL and (c) UC PL spectra under variable excitation energy. Normalized intensity of (b) DC PL and (d) UC PL in log scale, linearly depending on the off-resonance energy.

UC PL intensity is described as $I = A \cdot e^{-k\Delta}$, where I and Δ are integrated PL intensity and the off-resonance energy, respectively. The fitted parameter k is defined as the fitting slope in Figure 2b and d, representing the decrement of integrated PL intensity with off-resonance excitation. Interestingly, the absolute value of k in UC PL (0.0252/meV) is one order larger than that in DC PL (0.0026/meV) when ignoring the sign. According to this contrast, we believe that the underlying origins of DC PL and UC PL should be different.

In addition to the PLE results, we then also carry out power-dependent PL experiments to explore the underlying origins of DC PL and UC PL. As shown with log–log plot in Figure 3a and b, the DC PL intensity reveals linear dependence on excitation power when the incident power is relatively low (0.1–0.5 μW). With the incident power increasing, the DC PL intensity finally shows obvious sublinear dependence (0.37 and 0.38), which indicates a saturated absorption trend. Similarly, the UC PL intensity

also shows linear dependence on low excitation power with log–log plot in Figure 3c and d. However, under high excitation power, the slopes still persist to be 0.81 and 0.9 in UC PL, which are much higher than that in DC PL.

Though the slopes of DC PL and UC PL intensity similarly change from linear dependence to sublinear dependence, the underlying origins are believed to be totally different according the PLE results in Figure 2 and power-dependent PL intensity behaviors. Apart from the saturated absorption in the DC PL process, the origin of UC PL may be much complex, such as nonlinear two-phonon absorption process and exciton Auger scattering. The linear slopes of UC PL intensity under small incident power exclude the possibility of two-phonon absorption and exciton Auger scattering progress; otherwise, a superlinear trend would be expected [44]. In previous UC PL study of monolayer TMDCs, optical phonons are proved to be necessary to maintain both the momentum and energy conservation in the UC process from trions to A-excitons. With

Figure 3: Power-dependent photoluminescence (PL) intensity in downconversion (DC) PL and upconversion (UC) PL. (a), (b) The DC PL intensity shows a saturated trend. (c), (d) The slope of UC PL intensity persists under high incident power.

participation of phonons, UC PL intensity starts with linear dependence at small density of trions when phonons are relatively abundant. With the consumption of phonons and the growing density of trions, it shows a slightly sub-linear trend, which is different from that in saturated DC PL process. The stable slopes in UC PL here, up to 0.81 and 0.9, represent an efficient excitonic many-body interaction effect even under high excitation power in our experiments.

2.2 Valley properties in DC and UC scenarios

After revealing the emission behaviors and origins in DC and UC scenarios, now we turn to their valley properties. As discussed above, excitonic and phonon–exciton interactions are strong in monolayer WS₂, which is proved in

our efficient UC PL results. In view of the absorption of phonons in the UC scenario, which cannot be regarded as a reverse process of hot carrier cooling in DC process, we assume that the depolarization mechanisms may be different in DC and UC. Moreover, unlike spontaneous DC process driven by carrier energy offset, UC is assisted by one or multiphonons when the off-resonance energy is tuned. In this way, the valley property would be influenced or even modulated by the off-resonance energy.

We perform polarization-resolved PL measurements in both DC and UC scenarios under right circularly polarized lasers with variable excitation energy and calculate the degree of polarization (DOP) as $DOP = \frac{I_{\sigma-} - I_{\sigma+}}{I_{\sigma-} + I_{\sigma+}}$, where $I_{\sigma-}$ and $I_{\sigma+}$ represent the intensity of right and left circularly polarized component signals, respectively. And as illustrated in Figure 4a and b, DOP decreases with the growing

Figure 4: Polarized photoluminescence (PL) spectra and average lifetime of A-excitons in downconversion (DC) and upconversion (UC) scenarios.

(a) Polarized PL spectra in DC process. (b) Polarized PL spectra in UC process. (c) Degree of polarization (DOP) value and lifetime of A-excitons, presented by circles and squares, respectively.

absolute value of off-resonance energy in both DC PL and UC PL, which clearly means the valley polarization preserves more efficiently under near-resonance excitation. In addition, the DOP in UC PL is much lower than that in DC PL, and the valley polarization quickly vanishes in UC PL with off-resonance energy from -70 to -130 meV. It is worth noticing that the DOP value can only reflect the resultant distribution of valley polarized excitons in steady states after the depolarization process. Deeper information about the depolarization dynamics cannot be obtained from polarization-resolved PL spectra alone. And as analyzed in previous reports, the resultant valley polarization of A-excitons can be related to dynamical parameters [28, 49–52], which is described by $\text{DOP} = \frac{P_0}{1 + \tau_x/\tau_v}$, where the P_0 , τ_x and τ_v denote the initial exciton polarization, exciton lifetime and valley lifetime, respectively. It is clearly seen that the valley properties of A-excitons can be influenced by these three independent parameters, which is complicated for clarification. For discussion, we firstly assume that the variation of τ_v in the same sample is neglectable at 295 K room temperature since it depends on the intrinsic spin-flip process of A-excitons according to previous report [43], and therefore variations of P_0 and τ_x dominate the DOP behavior in the DC PL and UC PL scenarios. Limited by the experimental instruments, it is difficult to precisely measure the value of initial exciton valley polarization P_0 . Instead, we lay P_0 aside and turn to the exciton lifetime τ_x by performing pump-probe (transient absorption spectrum) measurements with different off-resonance energies. After analyzing and fitting the dynamical exciton recombination signals (see more details in Supplementary material), we deduce the average exciton lifetime, which is presented with DOP values in Figure 4c. And there are two intriguing observations when taking both the measured DOP value and exciton lifetime into account. Firstly, the

average exciton lifetime slightly decreases when pumped with near-resonant excitation in the DC scenario, contributing to the rising DOP in DC PL. But contrastingly, the exciton lifetime in the UC scenario shows a totally opposite trend with excitation from off-resonance to near-resonance energy. Secondly, the DOP value is supposed to intuitively increase based on smaller lifetime in UC PL under the assumption of a constant P_0 . However, valley polarization gradually vanishes with decreasing exciton lifetime. Additionally, the experimental fact demonstrates that the DOP value of UC PL is obviously smaller than that of DC PL, though the measured lifetimes in both DC and UC scenarios are in the same order. And these changed exciton lifetimes would not result in such evident modulation of DOP alone, considering the small decrement in DC (from 30.7 to 26.9 ps) and anomalous increment in UC (from 15.2 to 28 ps) when pump energy is tuned from off resonance to near resonance. Therefore, we believe that the underlying P_0 is variable and can be effectively modulated in both DC and UC processes, which is not well studied but actually dominates and further complicates the unique valley property in monolayer WS_2 . In this way, variable P_0 and exciton lifetime imply different depolarization mechanisms between DC and UC scenarios.

2.3 Depolarization-assisted conversion model

According to our experimental results and analysis, we present a phenomenological roadmap to illustrate the observed valley properties during DC and UC scenarios, as shown in Figure 5. It is worth noticing that this roadmap is basically result oriented and only characteristic processes and results are shown, while detailed dynamical parameters

Figure 5: The depolarization model in downconversion (DC) and upconversion (UC) scenarios.

(a) Direct conversion channels from trions and hot carriers in $-K$ valley into the A-excitons in K valley are forbidden. (b) With intermediate depolarization of trions and hot carriers, possible conversion occurs from trions and hot carriers in $-K$ valley into the A-excitons in K valley.

of depolarization are not presented. And possible depolarization channels including D'yakonov–Perel mechanism [53, 54], Maialle–Silva–Sham mechanism [55–57] and Elliot–Yaffet mechanism [58, 59] are discussed in Supplementary material. We firstly consider a universal and basic depolarization model shown in Figure 5a. It starts from the photogenerated trions (hot carriers), created in the $-K$ valley, on set of right circularly polarized UC excitation (DC excitation). Considering the energy and momentum mismatches between the $-K$ and K valleys, we then assume that the trions and hot carriers in $-K$ valley, marked by X_T^{-K} and X_H^{-K} , would not directly transfer into the A-excitons in K valley. Under this assumption, only intrinsic and spontaneous depolarization process of A-exciton, from $-K$ (X_A^{-K}) to K (X_A^K) valleys, is involved. The whole depolarization in Figure 5a therefore consists of three independent dynamical processes with the following forms:

$$(1) X_H^{-K} \rightarrow X_A^{-K},$$

The photogenerated hot carriers are spontaneously downconverted into A-excitons during an ultrafast relaxation process in $-K$ valley.

$$(2) X_T^{-K} + \sum_{i=1}^N P_n^i \rightarrow X_A^{-K}, (N = 1, 2, 3 \dots),$$

The photogenerated trions are upconverted into A-excitons with the assistance of one phonon or multiphonons depending on the energy gain in $-K$ valley, where phonon is marked by P_n .

$$(3) X_A^{-K} \rightarrow X_A^K.$$

Finally, A-excitons converted from both DC and UC process in $-K$ valley partly transfer into A-excitons in K valley with degenerate resonant energy, inducing the valley depolarization.

This model shown in Figure 5a seems to be reliable until theoretical valley polarization behavior is concerned. Since intravalley DC and UC processes would not contribute to the intervalley depolarization of A-excitons, intervalley depolarization only takes effect when X_A^{-K} is formed and transferred into X_A^K ; the DOP values measured from polarization-resolved DC PL and UC PL should be identical in theory. This is totally different from the observed valley properties that are proved to be effectively modulated by the off-resonance excitation. Additionally, very finite (far below 100%) valley polarization can be observed with near-resonance excitation in DC PL and UC PL spectra out of A-exciton resonance, implying that the intervalley depolarization process is not limited to A-excitons. In this way, the depolarization model is corrected on the basis of Figure 5a, and two intermediates, X_H^{-K} for hot carriers and X_T^K for trions in K valley, are added in

Figure 5b. Similar to Figure 5a, trions and hot carriers in $-K$ valley are still supposed to obey the conservation of both energy and momentum, so they cannot directly turn into the A-excitons in K valley. However, an indirect transition with the help of intermediates is no longer inaccessible in this roadmap. According to the model in Figure 5b, the dynamical expressions are then corrected as follows which are separately discussed in DC and UC scenarios.

Depolarization of $X_H^{-K} \rightarrow X_A^K$ in the DC scenario,

$$(1) X_H^{-K} \rightarrow X_A^{-K} \text{ and } X_H^{-K} \rightarrow X_H^K,$$

The photogenerated hot carriers in $-K$ valley would experience two different physical processes. In addition to the same intravalley conversion into X_A^{-K} in Figure 5a, an additional intervalley conversion into hot carriers in K valley would also partly occur in an ultrafast timescale (via long-range exchange effect, carrier–carrier scattering or carrier–phonon scattering effect).

$$(2) X_A^{-K} \rightarrow X_A^K \text{ and } X_H^{-K} \rightarrow X_A^K.$$

Finally, X_A^K in the DC scenario is formed, which originates from two physical processes. One is the intervalley depolarization process of X_A^{-K} , while the other one is an intravalley DC process in K valley.

And similarly, depolarization of $X_T^{-K} \rightarrow X_A^K$ in the UC scenario,

$$(1) X_T^{-K} \rightarrow X_T^K,$$

The photogenerated hot carriers in $-K$ valley would experience two different physical processes. In addition to the same intravalley conversion into X_A^{-K} in Figure 5a, an additional intervalley conversion into hot carriers in K valley would also partly occurs in an ultrafast timescale (via long-range exchange effect, carrier–carrier scattering or carrier–phonon scattering effect).

$$(2) X_T^{-K} + \sum_{i=1}^N P_n^i \rightarrow X_A^{-K}, (N = 1, 2, 3 \dots) \text{ and}$$

$$X_T^{-K} + \sum_{i=1}^N P_n^i \rightarrow X_T^K, (N = 1, 2, 3 \dots),$$

Subsequent intravalley UC process occurs in both $-K$ and K valleys, with the assistance of optical phonons to compensate the energy mismatch. Since the energy gain is identical in $-K$ and K valleys, these two UC processes occur with the same conversion rate. One portion of X_A^K is generated.

$$(3) X_A^{-K} \rightarrow X_A^K.$$

Finally, A-excitons converted from UC process in $-K$ valley partly transfer into the other one portion of X_A^K with degenerate resonant energy. As can be seen above, the introduced intermediates X_H^{-K} and X_T^{-K} influence valley

property in DC and UC scenarios, respectively, which matches well with the experimental fact of contrasting DOP values in Figure 4c.

We then carry out some discussions about these conversion processes referred in Figure 5b to further estimate the depolarization model. Generally, the dynamical rate of each conversion process dominates this result-oriented depolarization model. As reported in previous research studies [49, 50, 57, 60, 61], the intervalley depolarization can quickly take effect (on the order of 1 ps) at room temperature, which means effective intervalley transition spontaneously happens from $X_H^K/X_A^K/X_T^K$ to $X_H^K/X_A^K/X_T^K$ with a very fast rate in Figure 5b. And in Stokes DC scenario, the hot carriers driven by energy offset spontaneously relax to the band edge within several hundred femtoseconds [15]. The dynamical rate of DC process exceeds intervalley transition, verified by the residual 13% DOP value of A-excitons under near-resonance excitation. And with larger off-resonance energy, the intervalley transition between hot carriers is enhanced to some extent, which is in accordance with the weaker valley property as shown in the DC PL scenario of Figure 4c. As for the UC scenario, one phonon or combination of multiphonons is needed, depending on the energy gain. Unlike spontaneous DC process driven by energy offset, the conversion rate (or possibility) from trion to A-excitons in anti-Stokes UC process obeys Fermi's golden rule, reported by Jones et al. [45]. We follow this calculation method and roughly obtain conversion rates of 0.07, 0.02 and 0.006 ps⁻¹ for off-resonance energy at -70, -100 and -130 meV, respectively. The conversion rate sharply decreases with off-resonance excitation, inducing a higher portion of X_T^K into X_T^K . And the valley property of generated A-exciton totally vanishes when off-resonance reaches -130 meV, as illustrated by polarization-resolved UC PL in Figure 4c. Moreover, the conversion rate is theoretically proportional to phonon population (related to energy gain) [45], which follows an averaged thermal distribution as $1/\exp\left(\frac{|\Delta|}{k_B T} - 1\right)$, where $|\Delta|$, k_B and T represent energy gain, Boltzmann constant and 295 K room temperature, respectively. We find that this relationship is not identical but pretty similar to the PLE intensity behavior of the UC scenario in Figure 2d. In this way, the depolarization model matches well with our observations in both DC and UC scenarios.

3 Conclusion

In summary, we have established an in-depth investigation on the emission features and valley properties of

monolayer TMDCs in both DC and UC scenarios at room temperature. The PLE measurements are conducted, and two variation slopes with difference of one magnitude in log-log scale are observed, which implies the different underlying emission mechanisms. UC PL is observed with energy gain up to 190 meV. Subsequent power-dependent experiments clarify the origins of DC PL and UC PL, which refer to saturated absorption and phonon-assisted conversion from trions to excitons. Valley properties are measured with polarization-resolved PL spectra, and two contrast valley polarization behaviors are found in DC PL and UC PL scenarios. We deduce different valley depolarization parameters for DC PL and UC PL scenarios. And finally, a phenomenological valley depolarization model is introduced and discussed according to our experimental results. This work can help understand the many-body interactions and valley properties of monolayer TMDCs.

4 Materials and methods

Raman, PL and pump-probe measurements are done by lab-built systems. A 532-nm continuous-wave laser is utilized as excitation during Raman measurement. The integration time is set as 1 (10) second in DC PL (UC PL) measurements. For polarization-resolved PL measurements, a quarter-wave plate and a polarizer with horizontal polarization are set in front of the spectrometer. And in this case, the detected polarization is controlled by rotating the quarter-wave plate. For pump-probe measurements, a Ti:sapphire femtosecond laser is used to provide ultrashort pulses with 800 nm center wavelength. The main portion of the femtosecond laser is sent to an optical parametric amplifier with tunable output energy as pump light. A small power portion is sent through a sapphire crystal to generate a white light continuum as the probe beam. Then, decay signals of A-exciton are analyzed and fitted to obtain dynamical lifetimes. All experiments are carried out at room temperature.

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References

- [1] D. V. Seletskiy, R. Epstein, and M. Sheik-Bahae, "Laser cooling in solids: advances and prospects," *Rep. Prog. Phys.*, vol. 79, p. 96401, 2016.
- [2] D. V. Seletskiy, S. D. Melgaard, S. Bigotta, A. Di Lieto, M. Tonelli, and M. Sheik-Bahae, "Laser cooling of solids to cryogenic temperatures," *Nat. Photonics*, vol. 4, pp. 161–164, 2010.
- [3] R. I. Epstein, M. I. Buchwald, B. C. Edwards, T. R. Gosnell, and C. E. Mungan, "Observation of laser-induced fluorescent cooling of a solid," *Nature*, vol. 377, pp. 500–503, 1995.
- [4] E. Finkels, M. Potemski, P. Wyder, L. Viña, and G. Weimann, "Cooling of a semiconductor by luminescence up-conversion," *Appl. Phys. Lett.*, vol. 75, pp. 1258–1260, 1999.
- [5] G. Rupper, N. H. Kwong, and R. Binder, "Large excitonic enhancement of optical refrigeration in semiconductors," *Phys. Rev. Lett.*, vol. 97, p. 117401, 2006.
- [6] S. Eshlaghi, W. Worthoff, A. D. Wieck, and D. Suter, "Luminescence upconversion in GaAs quantum wells," *Phys. Rev. B*, vol. 77, p. 245317, 2008.
- [7] J. B. Khurgin, "Role of bandtail states in laser cooling of semiconductors," *Phys. Rev. B*, vol. 77, p. 235206, 2008.
- [8] N. Akizuki, S. Aota, S. Mouri, K. Matsuda, and Y. Miyauchi, "Efficient near-infrared up-conversion photoluminescence in carbon nanotubes," *Nat. Commun.*, vol. 6, p. 8920, 2015.
- [9] J. Zhang, D. Li, R. Chen, and Q. Xiong, "Laser cooling of a semiconductor by 40 kelvin," *Nature*, vol. 493, pp. 504–508, 2013.
- [10] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nat. Nanotechnol.*, vol. 7, pp. 699–712, 2012.
- [11] S. W. Han, H. Kwon, S. K. Kim, et al., "Band-gap transition induced by interlayer van der Waals interaction in MoS₂," *Phys. Rev. B*, vol. 84, p. 45409, 2011.
- [12] K. F. Mak, "Atomically thin MoS₂: a new direct-gap semiconductor," *Phys. Rev. Lett.*, vol. 105, 2010, <https://doi.org/10.1103/physrevlett.105.136805>.
- [13] E. S. Kadantsev and P. Hawrylak, "Electronic structure of a single MoS₂ monolayer," *Solid State Commun.*, vol. 152, pp. 909–913, 2012.
- [14] L. Han, J. Wang, Y. Ma, et al., "Enhanced directional emission of monolayer tungsten disulfide (WS₂) with robust linear polarization via one-dimensional photonic crystal (PhC) slab," *Nanophotonics*, p. 20200294, 2020.
- [15] H. Li, X. Zheng, Y. Liu, Z. Zhang, and T. Jiang, "Ultrafast interfacial energy transfer and interlayer excitons in the monolayer WS₂/CsPbBr₃ quantum dot heterostructure," *Nanoscale*, vol. 10, pp. 1650–1659, 2018.
- [16] J. Wang, H. Li, Y. Ma, et al., "Routing valley exciton emission of a WS₂ monolayer via delocalized Bloch modes of in-plane inversion-symmetry-broken photonic crystal slabs," *Light Sci. Appl.*, vol. 9, p. 148, 2020.
- [17] D.-H. Kang, S. R. Pae, J. Shim, et al., "An ultrahigh-performance photodetector based on a perovskite-transition-metal-dichalcogenide hybrid structure," *Adv. Mater.*, vol. 28, pp. 7799–7806, 2016.
- [18] O. Salehzadeh, N. H. Tran, X. Liu, I. Shih, and Z. Mi, "Exciton kinetics, quantum efficiency, and efficiency droop of monolayer MoS₂ light-emitting devices," *Nano Lett.*, vol. 14, pp. 4125–4130, 2014.
- [19] C. Zhang, A. Johnson, C.-L. Hsu, L.-J. Li, and C.-K. Shih, "Direct imaging of band profile in single layer MoS₂ on graphite: quasiparticle energy gap, metallic edge states, and edge band bending," *Nano Lett.*, vol. 14, pp. 2443–2447, 2014.
- [20] A. Chernikov, T. C. Berkelbach, H. M. Hill, et al., "Exciton binding energy and nonhydrogenic rydberg series in monolayer WS₂," *Phys. Rev. Lett.*, vol. 113, p. 76802, 2014.
- [21] M. M. Ugeda, A. J. Bradley, S.-F. Shi, et al., "Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor," *Nat. Mater.*, vol. 13, pp. 1091–1095, 2014.
- [22] G. Wang, X. Marie, I. Gerber, et al., "Giant enhancement of the optical second-harmonic emission of WSe₂ monolayers by laser excitation at exciton resonances," *Phys. Rev. Lett.*, vol. 114, p. 97403, 2015.
- [23] D. Y. Qiu, F. H. da Jornada, and S. G. Louie, "Optical spectrum of MoS₂: many-body effects and diversity of exciton states," *Phys. Rev. Lett.*, vol. 111, p. 216805, 2013.
- [24] Z. Ye, T. Cao, K. O'Brien, et al., "Probing excitonic dark states in single-layer tungsten disulphide," *Nature*, vol. 513, pp. 214–218, 2014.
- [25] K. He, N. Kumar, L. Zhao, et al., "Tightly bound excitons in monolayer WSe₂," *Phys. Rev. Lett.*, vol. 113, p. 26803, 2014.
- [26] M. Bieniek, M. Korkusiński, L. Szulakowska, P. Potasz, I. Ozfidan, and P. Hawrylak, "Band nesting, massive Dirac fermions, and valley Landé and Zeeman effects in transition metal dichalcogenides: a tight-binding model," *Phys. Rev. B*, vol. 97, p. 85153, 2018.
- [27] S. Tongay, J. Zhou, C. Ataca, et al., "Broad-range modulation of light emission in two-dimensional semiconductors by molecular physisorption gating," *Nano Lett.*, vol. 13, pp. 2831–2836, 2013.
- [28] K. F. Mak, K. He, J. Shan, and T. F. Heinz, "Control of valley polarization in monolayer MoS₂ by optical helicity," *Nat. Nanotechnol.*, vol. 7, pp. 494–8, 2012.
- [29] J. S. Ross, S. Wu, H. Yu, et al., "Electrical control of neutral and charged excitons in a monolayer semiconductor," *Nat. Commun.*, vol. 4, p. 1474, 2013.
- [30] Z. Gong, G.-B. Liu, H. Yu, et al., "Magnetoelectric effects and valley-controlled spin quantum gates in transition metal dichalcogenide bilayers," *Nat. Commun.*, vol. 4, p. 2053, 2013.
- [31] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer MoS₂ transistors," *Nat. Nanotechnol.*, vol. 6, pp. 147–50, 2011.
- [32] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, "Spin and pseudospins in layered transition metal dichalcogenides," *Nat. Phys.*, vol. 10, pp. 343–50, 2014.
- [33] M. R. Molas, K. Nogajewski, A. O. Slobodeniuk, J. Binder, M. Bartos, and M. Potemski, "The optical response of monolayer, few-layer and bulk tungsten disulfide," *Nanoscale*, vol. 9, pp. 13128–13141, 2017.

- [34] G. Plechinger, P. Nagler, A. Arora, et al., “Trion fine structure and coupled spin–valley dynamics in monolayer tungsten disulfide,” *Nat. Commun.*, vol. 7, 2016, <https://doi.org/10.1038/ncomms12715>.
- [35] B. Wen, Y. Zhu, D. Yulistira, et al., “Ferroelectric-driven exciton and trion modulation in monolayer molybdenum and tungsten diselenides,” *ACS Nano*, vol. 13, pp. 5335–43, 2019.
- [36] J. Pei, J. Yang, T. Yildirim, H. Zhang, and Y. Lu, “Many-body complexes in 2D semiconductors,” *Adv. Mater.*, vol. 31, p. 1706945, 2019.
- [37] J. Shi, Y. Li, Z. Zhang, et al., “Twisted-angle-dependent optical behaviors of intralayer excitons and trions in WS_2/WSe_2 heterostructure,” *ACS Photonics*, vol. 6, pp. 3082–3091, 2019.
- [38] K. Wei, Y. Sui, Z. Xu, et al., “Acoustic phonon recycling for photocarrier generation in graphene- WS_2 heterostructures,” *Nat. Commun.*, vol. 11, p. 3876, 2020.
- [39] K. Kaasbjerg, K. S. Thygesen, and K. W. Jacobsen, “Phonon-limited mobility in *n*-type single-layer MoS_2 from first principles,” *Phys. Rev. B*, vol. 85, p. 115317, 2012.
- [40] B. R. Carvalho, L. M. Malard, J. M. Alves, C. Fantini, and M. A. Pimenta, “Symmetry-dependent exciton-phonon coupling in 2D and bulk MoS_2 observed by resonance Raman scattering,” *Phys. Rev. Lett.*, vol. 114, p. 136403, 2015.
- [41] J. Jadcak, A. Delgado, L. Bryja, Y. S. Huang, and P. Hawrylak, “Robust high-temperature trion emission in monolayers of $Mo(S_ySe_{1-y})_2$ alloys,” *Phys. Rev. B*, vol. 95, p. 195427, 2017.
- [42] J. He, L. Tao, H. Zhang, B. Zhou, and J. Li, “Emerging 2D materials beyond graphene for ultrashort pulse generation in fiber lasers,” *Nanoscale*, vol. 11, pp. 2577–2593, 2019.
- [43] S. Guo, Y. Zhang, Y. Ge, S. Zhang, H. Zeng, and H. Zhang, “2D V-V binary materials: status and challenges,” *Adv. Mater.*, vol. 31, p. 1902352, 2019.
- [44] M. Manca, M. M. Glazov, C. Robert, et al., “Enabling valley selective exciton scattering in monolayer WSe_2 through upconversion,” *Nat. Commun.*, vol. 8, p. 14927, 2017.
- [45] A. M. Jones, H. Yu, J. R. Schaibley, et al., “Excitonic luminescence upconversion in a two-dimensional semiconductor,” *Nat. Phys.*, vol. 12, pp. 323–327, 2016.
- [46] J. Jadcak, L. Bryja, J. Kutrowska-Girzycka, et al., “Room temperature multi-phonon upconversion photoluminescence in monolayer semiconductor WS_2 ,” *Nat. Commun.*, vol. 10, p. 107, 2019.
- [47] H. R. Gutiérrez, N. Perea-López, A. L. Elías, et al., “Extraordinary room-temperature photoluminescence in triangular WS_2 monolayers,” *Nano Lett.*, vol. 13, pp. 3447–3454, 2013.
- [48] S. Zheng, L. Sun, X. Zhou, et al., “Coupling and interlayer exciton in twist-stacked WS_2 bilayers,” *Adv. Opt. Mater.*, vol. 3, pp. 1600–1605, 2015.
- [49] Y. Miyauchi, S. Konabe, F. Wang, et al., “Evidence for line width and carrier screening effects on excitonic valley relaxation in 2D semiconductors,” *Nat. Commun.*, vol. 9, p. 2598, 2018.
- [50] D. Lagarde, L. Bouet, X. Marie, et al., “Carrier and polarization dynamics in monolayer MoS_2 ,” *Phys. Rev. Lett.*, vol. 112, p. 47401, 2014.
- [51] A. Neumann, J. Lindlau, L. Colombier, et al., “Opto-valleytronic imaging of atomically thin semiconductors,” *Nat. Nanotechnol.*, vol. 12, pp. 329–334, 2017.
- [52] T. Cao, G. Wang, W. Han, et al., “Valley-selective circular dichroism of monolayer molybdenum disulphide,” *Nat. Commun.*, vol. 3, p. 887, 2012.
- [53] I. Žutić, J. Fabian, and S. Das Sarma, “Spintronics: fundamentals and applications,” *Rev. Mod. Phys.*, vol. 76, pp. 323–410, 2004.
- [54] R. Hanson, L. P. Kouwenhoven, J. R. Petta, S. Tarucha, and L. M. K. Vandersypen, “Spins in few-electron quantum dots,” *Rev. Mod. Phys.*, vol. 79, pp. 1217–1265, 2007.
- [55] C. Jin, J. Kim, M. I. B. Utama, et al., “Imaging of pure spin-valley diffusion current in WS_2 - WSe_2 heterostructures,” *Science*, vol. 360, p. 893, 2018.
- [56] M. Z. Maialle, E. A. de Andrada e Silva, and L. J. Sham, “Exciton spin dynamics in quantum wells,” *Phys. Rev. B*, vol. 47, pp. 15776–15788, 1993.
- [57] T. Yu and M. W. Wu, “Valley depolarization due to intervalley and intravalley electron-hole exchange interactions in monolayer MoS_2 ,” *Phys. Rev. B*, vol. 89, p. 205303, 2014.
- [58] B. Zhu, H. Zeng, J. Dai, Z. Gong, and X. Cui, “Anomalously robust valley polarization and valley coherence in bilayer WS_2 ,” *Proc. Natl. Acad. Sci. U. S. A.*, vol. 111, p. 11606, 2014.
- [59] Y. Yafet, “Calculation of the *g* factor of metallic sodium,” *Phys. Rev.*, vol. 85, pp. 478–478, 1952.
- [60] T. Yan, J. Ye, X. Qiao, P. Tan, and X. Zhang, “Exciton valley dynamics in monolayer WSe_2 probed by the two-color ultrafast Kerr rotation,” *Phys. Chem. Chem. Phys.*, vol. 19, pp. 3176–81, 2017.
- [61] J. Huang, T. B. Hoang, T. Ming, J. Kong, and M. H. Mikkelsen, “Temporal and spatial valley dynamics in two-dimensional semiconductors probed via Kerr rotation,” *Phys. Rev. B*, vol. 95, p. 75428, 2017.

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