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Engineering Valley Polarization of Monolayer WS₂: A Physical Doping Approach

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Abstract

The emerging field of valleytronics has boosted intensive interests in investigating and controlling valley polarized light emission of monolayer transition metal dichalcogenides (1L TMDs). However, so far, the effective control of valley polarization degree in monolayer TMDs semiconductors are mostly achieved at liquid helium cryogenic temperature (4.2 K), with the requirements of high magnetic field and on-resonance laser, which are of high cost and unwelcome for applications. To overcome this obstacle, it is depicted that by electrostatic and optical doping, even at temperature far above liquid helium cryogenic temperature and under off-resonance laser excitation, a competitive valley polarization degree can be achieved. The circular polarized photoluminescence (PL) measurement on monolayer WS₂ with various carrier concentrations at 80 K reveals that the electrostatic doping is able to induce continuous, more than 3-fold increase of polarization degree of charged exciton (trion) emission. Moreover, a sizable enhancement of trion polarization degree is depicted by increasing excitation laser power through photo-induced electron doping effect. Within low excitation range, such power dependence is in line with electrostatic doping results, indicating a general doping dependent valley relaxation mechanism, which agrees well with the theory of carrier screening effects on intervalley scattering process. These results demonstrate the tunability corresponds to an effective magnet field of ~ 10 T at 4.2 K. The findings reported here not only serve as a strategical reference to future experiments based on valley polarization of monolayer TMDs with various external or native carrier densities, but also provide an alternative approach towards enhanced polarization degree, which denotes an essential step towards practical valleytronic applications.

Introduction

Layered transition-metal dichalcogenides (TMDs) semiconductors have been demonstrated to carry the spin-like degree of freedom known as valley pseudospin, which can be optically generated and detected via circularly polarized photoluminescence (PL) spectra.^[1-4] In specific, this two-fold valley degree of freedom (DOF) directly corresponds to the optical bandgap of +K and -K valley in the Brillouin zone.^[5] Due to strong spin-orbit coupling and broken inversion symmetry, together with time-reversal symmetry, spin and valley DOFs are coupled in monolayer TMDs.^[6] This property enables selectively pumping +K (-K) valley with left (right) hand circular light excitations to create an imbalanced carrier population between two valleys. Realizing such net valley polarization is an essential step for developing valleytronic devices.^[7-11] Resulted from the opposite selection rules of two valleys, controlling valley polarization in monolayer TMDs by optical helicity is achievable. As experimentally measured, the circular polarization degree (P_c) reflects the population ratio between two valleys which generate light emissions with opposite helicity. Ideally, if photo-excited carriers are fully polarized within single valley, this value should be approaching 100%. However, the reported values of P_c in monolayer TMDs vary from 2% to nearly 100% among different TMD semiconductors,^[12-16] which are mainly attributed to intervalley scattering process from the selectively pumped valley to the opposite one.^[16-18] As for the PL measurements, various approaches have been adopted to obtain a sizable P_c , like applying magnetic field, cooling down to liquid helium cryogenic temperature, using near resonant light excitation or building van der Waals heterostructure.^[1,3,12,19-24] More practical and desirable methods could be electrical and optical control of valley polarization in TMDs at non-cryogenic temperature and off-resonance conditions. Towards this goal, one of the most effective means is in-situ carrier doping by physical or chemical approaches.^[25-27] The introduced resident carriers in TMDs not only tailor the exciton species, but are expected to considerably tune the valley

polarization dynamics which dominates P_c values as well.^[28,29] In previous reports, the changes of valley polarization/relaxation dynamics due to carrier doping have been noticed but haven't been investigated systematically and the mechanism remains elusive.^[13, 21, 30, 31] In addition, the unintentional doping and localized states in TMD samples play important roles to influence their optical properties, which may lead to discrepancies in experiments using layered TMD samples with different initial electronic states.^[32,33] Therefore, probing correlations between valley polarization and carrier concentration is crucial for future manipulations and potential applications based on valleytronic properties in TMD samples prepared by mechanical exfoliation or chemical vapor deposition (CVD) with various native and/or external carrier doping from environment and laser excitation.

Inspired by a recent theoretical study together with an experimentally proved framework based on carrier screening effects on excitonic valley relaxation in 2D semiconductors,^[34,35] here we designed a strategy to greatly enhance P_c at liquid nitrogen temperature. Doping dependent circularly polarized PL spectra of monolayer WS₂ at temperature of 80 K under off-resonance excitation (2.33 eV) are studied. The carrier density of the sample is controlled by electrostatic and optical doping. The evolution of neutral and charged exciton emission states have been extracted. Surprisingly the electrostatic doping drives continuous increase of P_c for charged exciton emission. Besides, by controlling photoexcitation strength, a considerable modulation of polarization degree is also depicted, parallel with the electrical doping effects. By comparing these findings with a general doping dependent valley relaxation mechanism and previous reports on exciton dynamics, we reveal the correlation between P_c and physical doping. Our results demonstrate the tunable valley polarization degree under low cost and Helium-free condition, equally effective as conducted under 10 T magnetic field.^[36] We successfully enriched the understanding of valley relaxation process by

electrostatic and optical doping means, which denotes an essential step towards practical valleytronic applications.

Results and discussion

Polarization-resolved PL measurements of the mechanically exfoliated monolayer WS₂ were conducted under excitation from a σ^+ circular polarized 532 nm (2.33 eV) laser and filtered with σ^+/σ^- helicity to measure the emission from +K/-K valley (**Figure 1a**). The polarization degree P_c is calculated by the equation:

$$P_c = \frac{I(\sigma^+) - I(\sigma^-)}{I(\sigma^+) + I(\sigma^-)} \quad (1)$$

where $I(\sigma^+) / I(\sigma^-)$ denotes the left/right hand circular polarization resolved PL intensity. Based on optical selection rule, σ^+ (σ^-) excitation solely couples to excitonic transitions in the +K (-K) valley and the corresponding light emission should carry single handedness. However, as schematically shown in **Figure 1b**, when the +K valley is selectively pumped with σ^+ excitation, the resulted PL light emission contain not only σ^+ signal from polarized excitonic transitions in +K valley but also σ^- signal due to intervalley scattering of excitons from +K to -K valley.^[18] The overall circular polarization degree P_c is determined by equation:

$$P_c = P_0 / (1 + 2\tau_0/\tau_v) \quad (2)$$

where P_0 is initial polarization, τ_0 is the valley exciton decay time, and τ_v is the intervalley relaxation time. The term τ_0/τ_v indicates that the value of P_c largely depends on the competition between two processes: radiative recombination of valley polarized excitons ($\sim \tau_0$) and intervalley scattering ($\sim \tau_v$). While τ_v (intervalley scattering dynamics) can be significantly tuned by screening effect induced by carrier doping, which will be discussed in detail later. **Figure 1c** shows PL spectra from a field effect device of exfoliated 1L-WS₂ measured at room temperature (RT) and 80 K. Generally, the PL spectra consists of two

components, where the high/low energy peak corresponds to neutral exciton (A)/negative trion (A^-) emission.^[26] At low temperature the A and A^- peaks present a blue shift which has also been observed in exfoliated MoS₂, MoSe₂ and chemical vapor deposited WS₂ recently.^[37,38] The two exciton peaks are well resolved at various carrier concentration, which enable us to perform the multiple-peak fitting properly and study the evolution of these two exciton species separately.

First part of the article is the results of physical doping induced polarization enhancement. **Figure 2a** shows PL features from a field effect device of exfoliated 1L-WS₂ with the back-gate voltages from -55 V to 55 V at 80 K. Overall, two components A and A^- emission band are well identified. Their corresponding photon energies and spectra dominance change as the voltage sweeps. At gate voltage below -15 V, both A and A^- features are visible. While at higher gate voltage, the integrated intensity of A peak gradually decreases and A^- peak becomes dominated due to the electrostatic doping, resulting in a single peak profile at higher carrier density. In addition, the peak position of A blueshifts and that of A^- redshifts, which leads to the increase of energy difference between A and A^- (i.e. dissociation energy), as can be directly seen in **Figure 2b**. This is attributed to phase space blocking due to Pauli exclusion and many body effects.^[39] As the gate voltage sweeps from negative to positive, the A^- emission energy redshifts by roughly 21 meV. The dissociation energy also monotonically increases to around 50 meV from gate voltage of -55 to -15 V. These behaviors agree well with the previous experimental reports on natively N-doped TMDs like MoS₂ and WS₂.^[26,40,41] The maximum external doping level is estimated as $\Delta n = 7.69 \times 10^{12} \text{ cm}^{-2}$ at 55 V gate voltage compared with -55 V (S1).

Helicity resolved PL spectra from P-type (-45 V) and N-type (+55 V) gated sample are shown in **Figure 2c**. When the WS₂ is negatively gated, A^- shows a low polarization degree of 7%. While, at a positive gate voltage and a higher induced carrier density, the sample exhibits a single A^- peak and a drastically higher polarization degree of 25%. The evolution of

polarization degree as a function of gate voltages is shown in **Figure 2d**. As an indicator of the electron density, the integrated intensity ratio of A^- to A is illustrated at lower carrier concentration regime where the neutral exciton A is visible. The increment of this ratio indicates elevated electron density.^[32,42,43] Obviously, as the voltage is swept from -55 V to +55 V, the polarization of trion is enhanced by more than three-fold. Compared to the previous reports,^[14,44] the overall P_c value especially at lower doping level is relatively low, potentially attributed to a large detuning energy ~ 0.3 eV caused by the off-resonance laser excitation and a temperature far above typical helium cryogenic temperature (4-10 K), which leads to lower initial polarization (P_0).^[18,45] More detailed discussion of P_0 is shown in following parts.

As reported in graphene^[46] and TMDs,^[26] in addition to electrostatic doping, the carrier concentration can also be modified by light excitation, which not only creates electron-hole pairs, but dynamically ionizes the carriers trapped on the donor impurities levels towards conduction band as well.^[51] Here, we studied the influence of excitation laser power on the circularly polarized PL emission of 1L WS₂ at 80 K. **Figure 3a** shows the intensity mapping of PL spectra at various excitation power, in σ^+/σ^+ configuration. Like electrostatic doping case, the overall PL profile evolves from the two-peak (A and A^-) feature into a single peak (A^-) feature at increasing excitation powers. The corresponding photon energies and integrated intensities versus power are depicted in **Figure 3b**. Identical to electrostatic doping case, as power increases within 600 μ W, the A exciton peak slightly blueshifts while the A^- exciton peak redshifts, which are signatures of photoinduced electron doping.^[13,26,45]

With regards to the optical doping dependent valley polarization, as shown in **Figure 3c**, the P_c value of A^- shows great distinction at 1.72 μ W (or 0.219 kW/cm²) and 1754 μ W (or 223.32 kW/cm²) excitation. The corresponding power density at sample surface is calculated in **Figure S6**. In details, three-fold enhancement of P_c from 7% to 22% is achieved with power increasing from 1.72 μ W (or 0.219 kW/cm²) to 3930 μ W (or 500.38 kW/cm²). The

completed power dependence of P_c is plotted in **Figure 3d**. Compared to the gate voltage dependence, there is pronounced fluctuation rather than monotonical increasing, especially at higher powers in mW scale. At both low and high powers, the carrier doping induced screening effect is prominent to influence valley polarization.

Second part of the article is the discussion of mechanism for polarization enhancement. For both electrostatic and optical doping cases, the enhancement of valley polarization obtained in this work is mainly attributed to carrier doping induced suppression on valley relaxation process. The intervalley scattering process of exciton is governed by electron-hole exchange interaction through the Maialle-Silva-Sham mechanism, resulting in short valley lifetime in picosecond scale.^[48-50] In the previous studies by electrically tailoring the doping states in graphene, the intervalley scattering rate was strongly suppressed.^[51] This carrier doping approach was proposed to be applicable to other multivalley systems like TMDs. Furthermore, as indicated by a comprehensive theoretical study on WS₂ recently,^[34] intervalley exciton relaxation time (τ_v) correlates with carrier concentrations and temperatures. This framework is quantitatively compared with our experiment results. In this work we are trying to manipulate the τ_0/τ_v value by tuning electron doping and then to tailor the P_c value consequently. In regards of the electron doping effect on τ_v , the previous mentioned framework suggests in both collisional and thermal broadening regimes, the value of τ_v shows maximum discrepancy (~6-fold) versus carrier concentration at around 70-90 K.^[34] This implies the intervalley scattering process can be effectively suppressed by carrier doping at liquid nitrogen temperature (i.e. 80 K). Compared to τ_v , τ_0 is much less affected by carrier doping, supported by stable linewidth and integrated intensities upon doping,^[43,52] as discussed in **S3 (Figure S1)**. Consequently, the τ_0/τ_v and P_c values are considerably tuned by electrostatic doping, which agrees well with our experimental observations. This is of great importance for the circularly polarized PL study at liquid nitrogen temperature. The physical doping effect is further illustrated by following experiments.

For the optical doping, at low optical excitation ($<532 \mu\text{W}$, corresponding to 67.73 kW/cm^2), the overall effect of photo induced electron doping is clearly demonstrated, which is comparable to our observation in the gate dependent PL measurements. In details, it is noticed that the dissociation energy between A and A⁻ at various power shift in the same manner as the electrostatic gated sample. Under the excitation of $373 \mu\text{W}$ (or 47.49 kW/cm^2), the observed dissociation energy is as large as around 0.05 eV , equivalent to doping effect of 40 V voltage difference (from -55 V to -15 V) and electron density increase is estimated as $2.79 \times 10^{12} \text{ cm}^{-2}$. Importantly, the electron doping effect on valley relaxation is witnessed in the evolution of P_c values. In this regime the P_c value is increased from 7% to 15% . This 2-fold enhancement stay in line with our electrical doping results within 50 V difference and indicates the τ_0/τ_v is effectively tailored.

At higher powers from 532 to $3930 \mu\text{W}$ (67.73 to 500.38 kW/cm^2), however, the P_c value become more diverged with a weak increasing trend up to 22% at $1754 \mu\text{W}$ (or 223.32 kW/cm^2). The power dependence of A⁻ integrated intensity ($I_{\text{Total}} = I_{\sigma^+} + I_{\sigma^-}$) is depicted in **Figure 3f**. The intensity shows linear relationship with excitation power and a slope of ~ 1.05 at power less than $532 \mu\text{W}$ then saturated with a slope of 0.34 . This first slope value presents a symbol of A and A⁻ exciton emission.^[13,26] Noticeably, at higher power the A⁻ peak experiences obvious broadening from 44 to 57 meV caused by excitation induced dephasing effect (**Figure 3e**).^[35] This is in sharp contrast with the electrical doping case where the A⁻ exciton linewidth is relatively unchanged at various gate voltages (**Figure S1c**). Note that the excitonic linewidth is a partial reflector of the coherence lifetime, which is influenced by intervalley scattering.^[53,54] Theoretically, this PL linewidth is proved to be inversely proportional to the τ_v term when temperature and doping level are fixed (S2).^[34,35] As consequences from accelerated intervalley scattering, excitation induced broadening indicates that the further increment of τ_v is hampered. It compromises the enhancement of P_c compared

to electrostatic doping case at similar electron density. We applied previous mentioned framework to estimate the P_c with different electron density and PL peak width and obtained reasonable results which agree well with the experimental data range (S2). Other potential effects like many body effects^[55,56] and intravalley depolarization are also discussed (S3), which are not the focus of this article. Overall, these results indicate a 3-fold enhancement of P_c by pure optical excitation, without requirement for device fabrication. Our findings also serve as a reference to the future TMDs based valley polarized PL or photodetector^[10] studies conducted at different excitation powers.

Unlike the ideal case,^[6] P_0 is less than 1 due to defect assisted exciton trapping^[57] and ultrafast relaxation of hot excitons,^[58] and worth for more detailed discussion. The value of P_0 is mainly dependent on the detuning energy, which is the energy difference between excitation laser and A exciton emission.^[16,18,59,60] It is worth noting that the possibility of P_c enhancement being determined by the change of detuning energy is ruled out, because as the electrical/optical doping increases, the A⁻ emission energy goes through red shift, which enlarges the detuning energy and may slightly reduce P_c rather than increases it.^[16,17] In regards of the P_0 value, while some studies treated P_0 as 1 for simplicity,^[61] previous time resolved PL has measured $P_0 = 0.7 \pm 0.1$ in monolayer WSe₂ system with around 150 meV detuning energy^[35]. As has been theoretically pointed out,^[34] the change of τ_v is around 6 times at 80 K when the carrier concentration is tuned from $8 \times 10^{11} \text{ cm}^{-2}$ to $8 \times 10^{12} \text{ cm}^{-2}$, which relatively corresponds to our previously estimated doping state ($\Delta n = 7.69 \times 10^{12} \text{ cm}^{-2}$). We substitute the experimentally measured P_c and corresponding τ_0/τ_v values at low and high doping into equation (1) to estimate the value of P_0 , which is 51% (S2). Due to the 300 meV detuning energy, the limited value below theoretical limit is consistent with the previous reports.^[14,60] Though, via intentional doping, the measured valley

polarization P_c can be engineered to approach P_0 , yielding an acceptable value even under off-resonance excitation.

Last, we compare our results with the previous reports on tailoring P_c in exfoliated monolayer WS_2 . Recent magneto-PL study has demonstrated valley Zeeman splitting and monotonically increasing P_c of A^- emission with applied magnet field in out of plane direction.^[36] Compared to magnetic methods, electrical/optical control of valley states are more favored for future valleytronic devices operations. As a more practical method to create population imbalance between two valleys, our approaches correspond to a 10 T magnetic field which enhances polarization degree of trion emission from negligible value to about 25% at 4.2 K.^[36] For PL without magnetic field, Cui *et al.* reported $P_c = 40\%$ at near resonance excitation (2.088 eV) and 16% at off-resonance excitation (2.331 eV), measured at 10 K. Korn *et al.* reported 21% for singlet trion and 34% for triplet trion with 2.15 eV laser excitation at 4.5 K.^[44] It is clear that we boost the P_c of monolayer WS_2 to a decent value (25% for electrical doping, 22% for optical doping) comparable to the previous achieved ones with much more demanding facilities (**Figure 4**). The gate voltage dependent circularly polarized PL at room temperature (300 K) is also performed (**Figure S5**), the obtained values are negligible without clear trend compared to the doping dependent data at 80 K. This is attributed to reduced τ_v ^[15] and suppressed tunability by electron doping^[34] at higher temperature range.

Conclusion

In summary, we have studied the valley polarized excitonic emission of monolayer WS_2 . By changing the gate voltage and the excitation power, doping tunable polarization degree in trion emission is achieved. The correlation between electron doping, exciton linewidth and valley polarization are clearly demonstrated in our measurements. In electrical doping case the increasing is mainly attributed to doping induced screening effect, while in optical doping case, especially at higher excitation powers in mW scale, not only the screening but also

excitation induced perturbation is needed to be taken into considerations to explain the spectra features and P_c evolution. These findings serve as a reference for future valleytronic studies using TMD samples with different native or extrinsic doping level. Furthermore, based on our discovery of carrier screening effect, chemical doping or heterostructure formation are also expected to affect the valley polarization of A excitons in TMDs, which is promising for non-degenerate P_c engineering. Such enhanced polarization degree could provide additional degrees of freedom in realizing valley polarized exciton condensation,^[62] exciton-polariton emission^[63,64] and polariton fluid transport.^[65] Our studies develop a simple but practical strategy for electrical and optical control of the valley polarization state, which is a corner stone for future noncryogenic valleytronic operations.

Experimental Section

Sample Preparation and Device Fabrication: Commercial WS₂ crystal (2D semiconductors Inc.) was mechanically exfoliated onto highly doped 300 nm thick SiO₂/Si wafer. For the device fabrication, the drain/source electrodes were made of 5/80 nm of Cr/Au by thermal evaporation and after standard electron beam lithography (Oxford SEM system) and the lift-off process. Before the gated PL measurements, the device was wire bonded to a printed circuit board (PCB).

Photoluminescence Spectroscopy: Micro-PL measurements were performed using a WITec Raman system with excitation wavelengths of 532 nm through 50 × objective lens (1.2 μm laser spot). As for the circular polarization resolved PL, a quarter wave plate was inserted along incident light to convert the linear polarized laser into circular polarized light. Besides a linear polarizer was inserted along the emission light before CCD collection to filter the emission light with left/right helicities. We used 600 lines/mm grating for PL measurements.

For gate-dependent PL measurement the sample was loaded in the Linkam stage and connected with a Keithley 4200-SCS semiconductor characterization system to apply gate voltage between Si substrate and the source/drain electrode, at 80 K in high vacuum (10^{-3} mbar). The excitation power was kept at 40 μ W (5.09 kW/cm²) for gate dependent circularly polarized PL measurement. The sample size is generally larger than 5 μ m for exfoliated monolayer which is larger than laser spot area. Among different samples, we choose the smooth monolayer region at the center of flake to avoid the effect of edge states or metal contacts. Therefore, the difference of pumping/detecting area is minimal among different samples. The accuracy of the circular polarization degree for our setup was no less than 92.0%.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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Figure 1. Monolayer WS₂ based device to explore the doping dependent valley relaxation dynamics. Schematic image of: (a) experimental set up for circularly polarized PL at various

carrier densities, (b) optical selection rules at +K/-K valleys and intervalley scattering process. (c) Polarization resolved PL spectra with σ^+/σ^- configuration at room temperature and 80 K.

Figure 2. Gate voltage dependent circularly polarized PL measurement of monolayer WS₂ at 80 K. All optical excitation is right circularly polarized (σ^+). The exciton species and corresponded polarization degree values are labeled, respectively. (a) PL intensity mapping (color scale in counts) of monolayer WS₂ as a function of gate voltage and photon energy, with σ^+ detection. (b) Corresponding Photon energies of A and A⁻ excitons (left vertical axis) and dissociation energy of A⁻ (right vertical axis) versus gate voltage. (c) Polarization resolved PL spectra of gated WS₂, both with σ^+ (σ^-) detection at 80 K. (d) Intensity ratios I_{A^-}/I_A (left vertical axis) and A⁻ circular polarization degree (left vertical axis) measured in as-exfoliated 1L WS₂ versus gate voltage. The error bars correspond to standard errors of peak heights in multiple-peak fittings.

Figure 3. Power dependent circularly polarized PL measurement of monolayer WS₂ at 80 K. (a) PL intensity mapping (color in counts) of monolayer WS₂ as a function of excitation power and photon energy, with σ⁺ detection. Note that the intensity and power are in log scale. (b) Corresponding photon energies of A and A⁻ excitons (left vertical axis) and dissociation energy of A⁻ (right vertical axis) versus power. (c) Polarization resolved PL spectra of WS₂ pumped at different powers. (d) Circular polarization degree, (e) A⁻ linewidth and (f) integrated intensity of trion peak measured in 1L WS₂ at various excitation power. Solid lines are linear fitting curves on log-log scales and α values correspond to the slopes. The error bars correspond to standard errors of peak heights/widths in multiple-peak fittings.

Figure 4. Comparison with previous report on circularly polarized PL measurement of monolayer WS₂. Black dots denote the previous reported P_c values in Ref.14 and Ref. 36. Red (blue) dots represent P_c from our work with and without physical doping at 80 K (300 K).

Supporting Information

Engineering Valley Polarization of Monolayer WS₂: A Physical Doping Approach

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Figure S1. Additional information from circularly polarized PL measurement of monolayer WS₂ as function of gate voltage. All optical excitation is right circularly polarized (σ^+) with σ^+ and σ^- detection, respectively. The exciton species are labeled. (a) PL intensity ratios of I_{A^-}/I_A for monolayer WS₂ versus gate voltage. (b) Integrated intensity of A^- exciton with σ^+ and σ^- detection versus gate voltage. (c) Full width at half-maximum (PL linewidth) of A and A^- excitons versus gate voltage. (d) Emission energy of A and A^- excitons with σ^+ and σ^- detection versus gate voltage.

Figure S2. Polarization degree of A exciton of monolayer WS_2 as function of doping. (a) P_c of A exciton versus gate voltage. (b) P_c of A exciton versus excitation power. Power is depicted in log scale. The error bars correspond to standard errors in multiple-peak fittings.

Figure S3. Power dependent circularly polarized PL measurement of monolayer WS_2 with estimated data. (a) A^- linewidth at various excitation power and estimated widths. (b) Measured and estimated P_c of trion peak in 1L WS_2 at various excitation power.

Figure S4. Polarization degree of A^- exciton of monolayer WS_2 calculated with different types of PL intensities. (a) Two types of A^- exciton P_c versus gate voltage and (b) excitation power. Power is depicted in log scale.

Figure S5. Gate dependent A^- exciton polarization degree of monolayer WS_2 at 300 K and 80 K.

Figure S6. Excitation power density as a function of excitation power, note that the radius of our laser spot is estimated as 500 nm ($50 \times$ objective lens).

Figure S7. Raman spectra of monolayer WS₂ after laser irradiation, taken at room temperature and 532 nm laser excitation. The major Raman modes are labeled.

Figure S8. Integrated area ratio of trion over exciton versus electrostatic and optical doping means. The PL spectra were taken at 80 K, with σ^+/σ^+ configuration.

S1. The calculation of electron doping density of monolayer WS₂

First, we discuss the electrostatic doping scenario, by converting the gate voltage to the electron doping density ($ne = CV_g$), the back-gate capacitance of is determined by $C = \epsilon_0 \epsilon_r / d$ while $\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$, $\epsilon_r = 3.9$, $e = 1.6 \times 10^{-19} \text{ C}$, $d = 300 \text{ nm}$, then $c = 1.12 \times 10^{-8} \text{ Fcm}^{-2}$, with 110 V voltage difference, we estimated $\Delta n = 7.69 \times 10^{12} \text{ cm}^{-2}$. Electron doping level can be estimated by the tunable Fermi energy $E_F = \hbar^2 \pi n / 2m_e e^2$. The dissociation energy obeys $E_A - E_{A^-} = E_{TB} + E_F$, where E_{TB} is the trion binding energy. It designates that the dissociation energy increases linearly with electron doping Δn , which is proportional to voltage difference or excitation power. As mentioned in main article, the ratio c also reflects the electron density $n \sim I_{A^-} / I_A \times 10^{11} \text{ cm}^{-2}$.^[1, 2] Note that at -55 V gate voltage we estimated the initial carrier density $n_0 \sim 0.5 \times 10^{11} \text{ cm}^{-2}$. In Figure S1, these benchmarks in σ^+ and σ^- emission are identical as the electron density increases.

S2. Estimation of doping dependent valley polarization of monolayer WS₂

First, we refer to previous established framework to estimate the initial polarization P_0 in our measurements. As the valley relaxation time τ_v is dependent on doping and exciton peak linewidth.^[1, 3] In specific at finite doping ($> 0.5 \times 10^{11} \text{ cm}^{-2}$), the τ_v can be simplified as:

$$\tau_v = \frac{\hbar}{AJ^2} \frac{K_{TF}^2}{\Gamma} \quad (\text{S1})$$

where A is a material-dependent constant, J is strength of exchange interaction, $\hbar$ is Planck's constant divided by 2π . While K_{TF} is Thomas–Fermi wave vector which can be further expressed as $K_{TF} = K_0 [1 - \exp(-E_F / K_B T)]$. The magnitude of this term rises along E_F which corresponds to electron doping in WS₂. Γ is the excitonic linewidth, which is inversely proportional to momentum relaxation time. Then tailoring the E_F is a deterministic approach

to alter τ_v . While the Γ evolution also reflects that the intervalley scattering is modified by excitation induced fluctuation of valley relaxation dynamics.

In electrostatic doping case we estimate P_0 by substitute different τ_0/τ_v governed by above mentioned framework into our experimental measured P_c values. Based on:

$$P_c = P_0 / (1 + 2 \tau_0 / \tau_v) \quad (S2)$$

We roughly subtract the $\frac{\tau_0}{\tau_v}$ values at low and high electron densities from Ref. S1 to derive P_0 .

Note that we assume τ_0 does not change significantly with electron doping.

$$\begin{cases} P_0 / (1 + 2 \tau_0 / \tau_{vhigh}) = 25\% \\ P_0 / (1 + 2 \tau_0 / \tau_{vlow}) = 7\% \\ \tau_{vhigh} / \tau_{vlow} \cong 6 \end{cases} \quad (S3)$$

Then P_0 can be calculated as 51.4%. Then we adopted this value to predict P_c with corresponding excitation powers. Compared to the electrostatic doping case, optical excitation yields the lower P_c at comparable doping level. This indicates change in E_F not enough to explain the observed P_c evolution. By comparing experimental change of dissociation energy where 337 μW correspond to 40 voltage difference, we can extrapolate the related power values. Referring the electron density at $n_1 = 8 \times 10^{12} \text{ cm}^{-2}$, $n_2 = 4 \times 10^{12} \text{ cm}^{-2}$, $n_3 = 2 \times 10^{12} \text{ cm}^{-2}$, we select $P_1 = 926 \mu\text{W}$ (117.89 kW/cm²), $P_2 = 463 \mu\text{W}$ (58.95 kW/cm²), $P_3 = 231.5 \mu\text{W}$ (29.47 kW/cm²), respectively. As shown in Figure S3a, the peak widths are also extrapolated as $\Gamma_1 = 0.05484 \text{ eV}$, $\Gamma_2 = 0.05322 \text{ eV}$, $\Gamma_3 = 0.04921 \text{ eV}$. Then we combine equation S1 and S2 to estimate the P_c values upon optical doping. The results are shown in **Figure S3b**, the estimated values are in line with our experimental findings, which means the framework we use based on electron doping and PL linewidth broadening is reasonable.

S3. Disclaimer of valley polarization analysis in monolayer WS₂

Note that in this work the τ_0 values are insensitive to electrical doping, compared to τ_v . Previous theoretical work indicates moderate evolution of τ_0 (~20%) with electron doping at 80 K,^[4] in sharp contrast with τ_v evolution (~600% in theory, proved in experiments). Experimentally the A⁻ linewidth is scattered less than 10% when the gate voltage is swept from -55 to 55 V ($\Delta n = 7.69 \times 10^{12} \text{ cm}^{-2}$). The integrated intensity of A⁻ also shows very limited deviation (~10%) at gate voltages from -25 to 55 V (**Figure S1**), indicating stable τ_0 upon doping.^[2] The more than threefold P_c enhancement is mainly ascribed to the τ_v evolution, which is the focus of this article. Note that the effect of electron capturing speed or trion formation rate is also minor in our work, supported by stable trion intensity from -25 to 55 V (~7% deviation at $5.5 \times 10^{12} \text{ cm}^{-2}$ external doping). Similar argument of doping independent τ_0 has been made in previous chemical doping work.^[2]

For the engineering of τ_0 , BN encapsulation can effectively tailor PL linewidth through coulomb screening effect and quantum confinement, which suppress the nonradiative process and modifies the τ_0 accordingly.^[5,6] This strategy is promising to further promote the P_c value, which shall be investigated in future.

In regards of optical doping, the constant slope at low excitation regime also indicates that the radiative efficiency which is largely dependent on τ_0 is relatively stable at low excitation power. This makes tuning P_c and τ_v by optical excitation feasible.

As the power continues to go up to mW range, beyond the carrier screening effect in valley relaxation process induced by optical gating effect, enhanced many body effects at higher exciton densities like exciton-exciton annihilation may also play a role,^[4,7] supported by a deviation from original slope in power dependence (**Figure 3f**). Specifically, at such high excitation intensity, Auger recombination channel may open, where two excitons interact with each other and fuse to form a higher energy exciton followed by a rapid internal conversion to the lowest energy excited state.^[7] Such process potentially affects exciton

recombination/relaxation dynamics as an effective nonradiative recombination path. Both the Auger recombination and the exchange interaction originate from the strong Coulomb interaction of TMDs. In that sense, the valley dynamics in such strong excitation region provide us a unique physical feature, which deserves future time resolved spectroscopic investigations.

While some previous time resolved spectroscopic studies indicate higher density of excitons are supposed to mediate depolarization by intravalley exciton-exciton exchange interaction.^[8] As consequence of these effects both τ_0 and τ_v decreases at higher power densities, making the evolution of τ_0/τ_v less monotonical. More systems and experimental techniques are required to separate these phenomena from carrier screening effect. Potential heating effect is also excluded. For the estimated time scale of τ_v and τ_0 . Based on **Eq. S1** and derivations in **S2**,^[1-3] the estimated time scale of τ_0 and τ_v are organized, for electrical doping, the τ_v at high (low) doping is estimated as ~50 (8) ps and τ_0 is treated as constant ~50 ps. For the optical doping in weak excitation regime ($\sim 4 \times 10^{12}$), the τ_v at high (low) doping is estimated as 32 (8) ps. As for strong excitation regime, τ_0 might be hampered to be less than 50 ps due to the exciton-exciton interaction, and the τ_v at high doping is ~37 ps, indicting different dynamics between strong optical excitation and electrostatic gating cases.

As the power increases, A exciton peak goes through a blueshift. This presumably excludes the potential laser induced heating which causes the redshift of exciton photon energy. Importantly, as illustrated in **S2**, despite these potential effects that hamper the valley polarization, the carrier screening mechanism with consideration of excitation induced fluctuation (**Eq. S1**) plays a dominate role for polarization in both low and high excitation regimes.

Note that in this study, we focus on intervalley scattering of the bright excitons (trions) between +K and -K valleys. Though dark excitons are reported to preserve robust valley

polarization which may also promote P_C ,^[9] it requires in-plane magnetic field^[10] or light propagation^[11] to effectively visualize these exciton species in PL. For the P_C calculation, as I denotes PL intensity, previous studies have adopted integrated (i.e. exciton peak area)^[1, 12] or absolute (i.e. exciton peak height) PL intensities.^[13-15] For our fitted values for integrated intensity or peak height for $I(\sigma^+)$ and $I(\sigma^-)$, the spectra background are carefully removed. We have calculated the P_C values using both methods, as shown in Figure S4. The overall P_C evolutions with increasing gate voltage or excitation power are identical. In main article we adopt absolute PL intensity for calculation. As for the doping dependence of neutral A exciton, despite very limited data points due to A exciton vanishing with increasing doping, no significant change of P_C has been observed. One possible reason is that the being charges neutral, A is less sensitive to the screening field during intervalley scattering process (**Figure S2**). More system need to be exploited to uncover the valley dynamics of A exciton upon doping in future studies.

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