Probing momentum-indirect excitons by near-resonance photoluminescence excitation spectroscopy in WS$_2$ monolayer

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Keywords: transition metal dichalcogenides, monolayer, near-resonant photoluminescence excitation spectroscopy, light absorption, exciton-phonon interaction, momentum-indirect excitons

Supplementary material for this article is available online

Abstract

Coulomb-bound electron-hole pairs (excitons) dominate the optical response of atomically-thin transition metal dichalcogenides (TMDs) semiconductors. The photoluminescence spectrum in W-based TMDs monolayers (i.e. WS$_2$ and WSe$_2$) at low temperature exhibits much richer features than Mo-based TMDs monolayers, whose origin is currently not well understood. Herein, by using near-resonant photoluminescence excitation spectroscopy, we probe the scattering events between excitons and phonons with large $k$-momentum, which provides strong evidence for the momentum-indirect nature of the optical bandgap in monolayer WS$_2$. The scattering between carriers and zone-edge phonons creates excitons at different valleys, among which, the lowest-energy is momentum-indirect. Our findings highlight that more efforts are required to solve the current debate on the inherent bandgap nature of TMD monolayers and the complex photoluminescence spectrum reported on W-based compounds.

1. Introduction

Atomically thin layers of group-VI transition metal dichalcogenides (TMDs) such as MX$_2$ (M = Mo, W; X = S, Se) and hexagonal lattice feature prominent exciton properties and spin-valley physics. As a result of strong quantum- and dielectric confinement in single atomic layer of TMD materials, the photoexcited electrons and holes are tightly bound via Coulomb interaction to form excitons with the binding energy of hundreds meV$^{[1–6]}$. The large exciton binding energies reinforce the stability of exciton complexes such as charged excitons (trions)$^{[7–10]}$ and biexcitons$^{[10–12]}$ that offers great opportunities to study many-body physics. In addition, the inversion symmetry breaking in TMDs monolayers gives rise to the energy-degenerate but non-equivalent $K/K'$ valleys, which are coupled with electron spins$^{[13]}$. This unique spin-valley coupling enables the use of light helicity to selectively excite valley excitons at $K$ or $K'$ valley$^{[13]}$, making TMD monolayers ideal candidates for opto-valleytronic applications$^{[13–15]}$.

The presence of neutral excitons and trions has been widely observed in previous optical studies on TMD monolayers$^{[7, 8, 16]}$. The substitution of the metal element M, e.g. W into Mo, reverses the energetic order of the optically allowed (bright) and optically forbidden (dark) states at the $K/K'$ valley$^{[17]}$. In particular, W-based monolayers harness the dark exciton band lying at lower energy than the bright band, leading to the poor emission efficiency at low temperature$^{[11]}$. Instead, the photoluminescence spectrum of WX$_2$ monolayer is dominated by several features arising at the low-energy side of the exciton energies, which is currently under intense debate among defects, bound excitons and biexcitons$^{[10, 11]}$. For example, the strongest peak that lies below the charged exciton (trion) was previously assigned to biexciton emission$^{[10, 11]}$. However, the discrepancy lies in that the PL intensity of that peak
shows a sub-quadratic increase with excitation power and the binding energy (∼52 meV) \cite{11} is much larger than the theoretically predicted value ∼20 meV \cite{18–22}. In addition, the energies of lower energy features in WX\textsubscript{2} monolayers coincidently match the calculated momentum-indirect exciton transitions, which arises from the recombination of electrons and holes in different valleys \cite{23–29}, suggesting the more complicated nature of these low-energy peaks. Therefore, a detailed investigation on the exciton dynamics of WX\textsubscript{2} material is needed.

In this work, by using photoluminescence excitation spectroscopy, we probe the momentum-indirect transition in WX\textsubscript{2} monolayers that could explain for the low-energy features in the photoluminescence spectrum of W-based compounds. Under near-resonant excitation condition, multiple scattering processes between excitons and phonons carrying non-zero wavevector are revealed, indicating the presence of indirect excitons whose constituent electrons and holes locate at different valleys, beside the well-understood direct excitons with their electrons and holes located at the same valley. Furthermore, we find that phonon scattering contributes to valley depolarization during hot exciton relaxation. Our results advance non-trivially the fundamental understanding of the photoluminescence spectra of W-based monolayers that can shed light to intrinsic exciton properties in TMD monolayer semiconductors.

2. Results and discussion

Sample and Optical Characterization of WX\textsubscript{2} Monolayer. The high-quality monolayers of WX\textsubscript{2} were prepared by mechanical exfoliation onto a Si/SiO\textsubscript{2} substrate and extensively characterized by optical spectroscopy at cryogenic temperatures (T = 20 K). Figure 1(a) shows the reflectance-contrast spectrum, in which, three sharp resonances are clearly resolved. Specifically, the features arising at ∼2.09 eV and ∼2.50 eV are attributed to A-exciton (\(X_A\)) and B-exciton (\(X_B\)) whose constituent electrons and holes are excited at K or \(K'\) valleys in the Brillouin zone \cite{1, 14, 16, 30}. The energy splitting of ∼400 meV between A and B originates from the spin-splitting of the valence band at K and \(K'\) points \cite{1, 14, 30}. In addition, the energy structure observed at ∼2.06 eV is ascribed to a charged exciton state (trion), which is formed by the neutral A-exciton and a free charge (electron or hole) \cite{7–10}.

A schematic of the energy structure of WX\textsubscript{2} monolayer is illustrated in figure 1(b). The energy positions of A-exciton and B-exciton are taken from the reflectance measurement. The continuum band of A-exciton is located at ∼2.44 eV \cite{3}, which is close to the energy of B-exciton. The existence of different electronic states around the energy of A-exciton and B-exciton suggests nontrivial exciton behaviors, especially under near-resonant excitation conditions. For example, with excitation energies of ∼2.5 eV (see the black arrows in figure 1(b)), excitons can be directly generated at B resonance or free-carriers are created at the continuum of A. In the first case, B-excitons can either radiatively recombine in a so-called hot luminescence process \cite{16, 31–33}, or relax non-radiatively to \(X_B^0\) (A-exciton with zero center-of-mass momentum). On the other hand, when free carriers are generated at the continuum of A, an electron and a hole can relax and later bind together to form exciton at A to result in photoluminescence. Alternatively, when the excitation energy is well below 2.45 eV (see the red, green, orange arrows in figure 1(b)), \(X_A^0\) excitons are directly generated and later radiatively recombine. Here the exciton formation, relaxation and recombination processes in WX\textsubscript{2} are intensively investigated by varying the excitation energy across the resonances.

Figure 1(c) presents the low-temperature photoluminescence spectrum under \(h\omega_{\text{exc}} = 2.707\) eV excitation. Several optical features are resolved, including the radiative recombination of the neutral A-exciton (∼2.09 eV) and the charged state trion (∼2.06 eV). The energy positions are in good agreement with the reflectance contrast spectrum shown in figure 1(a). Interestingly, the PL spectrum is dominated by very intense features (\(P_1\)) at the low-energy side of the trion, where the light-absorption is negligible. The origin of the peaks \(P_1\) (especially \(P_1\) and \(P_2\)) is currently under debate, which will be discussed later in this work. On the other hand, when the excitation energy is tuned close to the resonance A (\(h\omega_{\text{exc}} = 2.103\) eV), additional sharp features are resolved on top of A-exciton with the linewidth of ∼0.4 meV. The behaviors of these emission features are carefully monitored while varying the excitation energy from 2.103 to 2.707 eV across the A and B resonances. In the case of the A resonance, up to eighteen excitation energies from a continuous tunable laser ranging from 2.103 to 2.173 eV (see Supporting Information figure S1 (stacks.iop.org/TDM/7/031002/mmedia)) are used to excite the WX\textsubscript{2} monolayer.

Identification of Exciton-Phonon Scattering Processes Under Near-Resonant Excitation of A-Excitons. Figure 2(a) shows PL spectra acquired with selected excitation energies of 2.103 eV, 2.111 eV, 2.125 eV and 2.136 eV. All the spectra are plotted relative to the energy position of the zero phonon line of \(X_A^0\) (ZPL \(X_A^0\)), which corresponds to the direct transition of excitons with zero center-of-mass momentum and is independent of excitation energy. On the other hand, the narrow features clearly shift while changing the excitation conditions. For instance, while changing \(h\omega_{\text{exc}}\) closer to the A resonance, from 2.136 eV (top panel) to 2.111 eV (middle panel), the peak marked by blue arrow (later identified as 2\(LA(M)\)) shifts in
Figure 1. Optical characterization of WS$_2$ monolayer. (a) Reflectance contrast spectrum. Three resonances corresponding to trion, A-exciton and B-exciton are clearly resolved. (b) Schematic energy diagram illustrating the absorption energy positions of A-exciton, B-exciton and continuum of A. The photo-generated carriers/excitons can relax to the lower-energy states via phonon scattering (wavy arrow) or directly recombine (straight arrows). The exciton formation, relaxation and recombination were monitored by varying the laser-excitation energy across the electronic bands (coloured arrows). Representative photoluminescence spectra taken with the excitation energies of (c) (off-resonance) 2.707 eV and (d) (near-resonance) 2.103 eV.
Figure 2. Photoluminescence excitation spectroscopy near A resonance in WS$_2$ monolayer. (a) Selected low-temperature ($T = 20$ K) PL spectra obtained with different excitation energy. The sharp features are labelled according to the energies of the different phonon modes that are involved in the exciton-phonon scattering event. The dashed-line illustrates the evolution of the 2LA(M) mode as the excitation energy varies, taken as a representative example. In the bottom panel, a illustrative fitting procedure to the PL lineshape (black solid-line) is shown. Voigt functions are used to model each of the different peaks, where the blue solid-curve centred at zero represents the ZPL $E_1^T (0)$. Green solid-lines indicate scattering events between excitons and phonons, while red solid-curve is the cumulative fitting of all curves. (b) The identified phonon energies and their maximum amplitude of the resonant-scattering event, $\hbar \omega_{\text{ZPL}}$, responding to an exciton radiative lifetime of $2.125$ eV, which is in excellent agreement with experiments and theoretical calculations [43, 44]. Moreover, the strongest scattering intensity among different phonon modes comes from the scattering with zone-edge phonons (M-point) (see figure 2(b)). Therefore, we highlight that most of the scattering features resolved in our optical spectra involve zone-edge phonons, suggesting that they originate from the collisions between real excitonic states and phonons.

**Evidences of Indirect Excitons in WS$_2$ Monolayer.** Figure 3(a) demonstrates the exciton-phonon scattering processes in single-particle (left panel) and exciton (right panel) representations. Excitons are composed of electrons and holes, both of which can be scattered by phonons. The exciton momentum is defined by center-of-mass momentum $\hat{Q}_X$ given by the momentum difference between the electrons and holes $\hat{Q}_X = \hat{k}_e - \hat{k}_h$, while the phonon momentum is $\hat{q}_{\text{ph}}$ (i corresponds to the position in the Brillouin zone). During the events of exciton-phonon (light absorption) and exciton-phonon collisions,
In monolayers TMDs, direct photoexcitation of electron and holes takes place at $K$ and $K'$ valleys, generating $Q_X^k$ excitons (see figure 3). In the following, the generated carriers are scattered by phonons, involving the zone-center (the $\Gamma$-point, $\hat{q}_{\text{ph}}^\Gamma \sim 0$) and the zone-edge (the $M$-point, $\hat{q}_{\text{ph}}^M \neq 0$) of the Brillouin phonon zone (see blue hexagon at figure 3(a)). Phonons at $\Gamma$-point ($\hat{q}_{\text{ph}}^\Gamma \sim 0$) scatter the electron-hole pairs generated at the light cone into the zone-centre ($\Gamma$-point) of exciton dispersion (see orange symbol and parabola at figure 3(b) and (c)). When only a single phonon mode is involved in the collision, either an electron or a hole is scattered after the photoexcitation. As both electrons and holes have similar effective masses ($m \sim 0.42m_e$) [45, 46], their first-order phonon-scattering probability is likely comparable, in clear contrast to conventional semiconductors such as II-VI and III-V, where exciton scattering is normally dominated by lighter electrons [34]. More interestingly, phonons at the $M$-point have non-zero momentum ($\hat{q}_{\text{ph}}^M \neq 0$), which implies that the virtually generated excitons are scattered out of the light cone to their dispersion at other high-symmetry points in their Brillouin zone to satisfy the momentum conservation $\Delta \hat{q}_{\text{ph}}^M \sim -Q_X$ (see bluish parabolas at figure 3(c)).

Figure 3. Exciton dispersion, formation, relaxation and recombination processes in WS$_2$ monolayer. (a) Electron-hole picture involving the scattering with $M$-point phonon. The black hexagon represents the free-particle Brillouin zone. The blue hexagon represents the phonon lattice. It has been shifted to match with the electronic $K$’-valley, where direct photoexcitation takes place in WS$_2$ monolayer. With the assistance of $M$-point phonons, photoexcited electrons at $K$ ($K'$) valley can be scattered into $\Lambda$ or $K$ ($K'$) valleys, to bind with a scattered (or residing) hole at respectively $K$ ($K'$) or $K'$ ($K$) valley to form excitons with nonzero wavevector ($Q_X^k$ or $Q_X^M$). (b) The hexagonal Brillouin zone of excitons. The wavevectors for each band are indicated. The coloured legend indicates the valley from where carriers originate to form excitons. (c) Exciton dispersion as a function of its center-of-mass momentum $Q_X$. Exciton formation and relaxation are mediated by exciton-phonon scattering. In the electron-electron representation, the dashed curves represent the spin-forbidden (dark) excitons consisting of electrons and holes with opposite spin. Green curved arrows indicate for intervalley scattering and formation of excitons. Black curved arrows indicated for intra-valley relaxation. Broken orange arrow represents the optically direct transition from $\Gamma$-point exciton band. Broken purple arrow represents the optically indirect transition from $\Lambda$-point exciton states. The indirect transition from $K$-point excitons has been omitted for clarity.

momentum is conserved and obeys the relationship $\hat{k}_{\text{photon}} = Q_X^k + \hat{q}_{\text{ph}}^k$.
is satisfied $k^K_e - k^\Lambda_e = \tilde{a}_{ph}^M$ (and $\tilde{k}^K_e - \tilde{k}^\Lambda_e = \tilde{a}_{ph}^M$).
Furthermore, since $\Lambda$-valley is an energy minimal [47], the electrons preferentially reside on this band. In other way, the $M$-phonon could scatter the electron from $K$ ($K'$) to the $K$ ($K$) valley. In this case, $\tilde{k}$-momentum is not strictly satisfied, lowering the probabilities for this scattering channel. For photoexcited holes at $K$ ($K$)-valleys, the situation is slightly different. By considering just momentum, they could be scattered to the $\Lambda$ ($\Lambda$)-valley. However, this valley-extrema is hundreds of meV lower in energy that the $K$ ($K$)-valence band maxima. Therefore, in our near-resonant excitation conditions, this event is unlikely to take place. Most probably, $M$-point phonon modes scatter holes from $K$ ($K$) to the $K$ ($K$) valley. Scattering events via $M$-point phonon modes have been proposed as being responsible for valley depolarization in TMDs [48]. Nonetheless, no direct experimental evidence was yet reported, while the sharp features we observed in figure 2 provide strong evidence for the scattering between exciton and $M$-point phonons.

Exciton Formation Pathways in WS$_2$ Monolayer. Following near resonant photoexcitation and subsequent phonon-scattering by $\Gamma$- or $M$-modes, electrons in monolayer WS$_2$ can reside at $K$-, $K'$- and $\Lambda$-valleys, while holes can locate mostly at $K$- and $K$-valleys. After scattering by zone-center ($\Gamma$-point) phonons, tightly bound $A$-excitons are formed at the $\Gamma$-point ($X^A, Q^A_{\Gamma} = \Gamma, \ast$), as depicted in figure 2(a) from photoexcited electrons and holes at the same $K$ or $K$-valley. On the other hand, owing to strong electrostatic interactions between electron and holes in monolayer TMDS, whose large reciprocal Bohr radius $r_{ph} \sim 0.8$ nm$^{-1}$ is about one third of a typical lattice wavevector $k_L \sim 3$ nm$^{-1}$, electron and holes wavefunctions located at different valleys can spatially overlap to form excitons at $\Lambda$-point. For example, after scattering by zone-edge ($M$-point) phonons, electrons at $\Lambda$-valleys bind with holes at the momentum-nearest $K$-valley to form momentum-indirect excitons at the $\Lambda$-point ($X^A, Q^A_{\Lambda} = -\Lambda$). Moreover, electrons at the $K$-valley could bind with holes at the $K$-valley to form momentum-indirect excitons at the $K$-point ($X^K, Q^K_{\Lambda} = K$).

Light Emission from Momentum-Indirect Transitions in WS$_2$. Figure 3(c) shows a schematic structure of the lowest-energy exciton bands as a function of the center-of-mass momentum $Q_X$. The location of the excitonic valleys, the dispersion of the parabolas and relative energies are reproduced from calculations for excitons in TMD monolayers [27, 28] and from our scattering features with phonons of non-zero wavevector (see figure 2). In W-based monolayers, for $Q_X = \Gamma$, two kinds of exciton branches exist due to different spin configuration of electron and holes. When the electron and hole own the same spin orientation, the resultant exciton transition is spin-allowed (orange solid parabola). In contrast, the opposite spin orientation of the constituent carriers gives rise to the spin-forbidden exciton band (grey dash parabola). For $Q_X = K$ ($K$-valley), the spin configuration is opposite to the exciton at the $\Gamma$-valley. Specifically, the spin-forbidden band of $X^K$ energetically lies above the spin-allowed branch. The energy splitting between allowed and forbidden spin-states ($\Delta E_{\pm}^{X^A} - E_{\pm}^{X^K}$) so-called (spin) bright-dark splitting varies for different compounds, being $\sim 50$ meV as recently reported for W-based monolayers. [27, 49–52] The spin order of each band is reversed in Mo-based monolayers. [17, 49–53] For $Q^A_X$ ($\Lambda$-valley), the calculated lowest-energy exciton branch is spin-allowed. Interestingly, the momentum-indirect exciton $X^A$ lies energetically below the momentum-direct $X^\Lambda$, which is due to the larger exciton effective mass at $\Lambda$-valley[27].

The energy separation between spin-allowed excitons at $\Gamma$- and $\Lambda$ valleys ($\Delta E_{\pm}^{X^A} - E_{\pm}^{X^K}$) in WS$_2$ monolayer has been calculated in the range of 70 to 100 meV [23, 27]. The formation of the excitons at $\Lambda$-valley is elucidated by the observation of first-order intervalley scattering events assisted by $M$-point phonons in our near-resonance experiments.

The spin-allowed $X^A$ branch possesses a giant oscillator-strength that allows for a transient decay (~1 ps) of excitons. At the same time, the excitons decay into spin- or momentum-forbidden branches at lower energies of $\sim 50$ meV [27, 49–52] and $\sim 70$ meV[27] respectively, from which the luminescence is nominally forbidden. The complexity of the excitonic landscape determines the light emission properties of two-dimensional W-based semiconductors. The lineshape of the PL spectrum in figure 4 has been fitted by using Voigt functions to model each of the different peaks, where blue solid-lines refer to excitonic resonances, green solid-lines indicate scattering events between excitons and phonons, while red solid-curve is the cumulative fitting of all curves. The parameters obtained from the fitting to the PL spectrum are listed in table S2 in the Supporting Information. The PL spectrum exhibits several features whose origin is currently under intense debate. An overall consensus exists on the high-energy structures, attributed to radiative recombination of the neutral $X^A$ (~2.09 eV) and its charge state trion $T^+_A$ (~2.06 eV), whose energy separation is $\Delta E_{\pm}^{X^A} - E_{\pm}^{T^+_A} \sim 30$ meV. However, the largest contribution to the PL spectrum comes from the energy structures lying 50–100 meV below $A$-exciton ($P_3$, $A$), at which the light absorption is negligible. They have been attributed to biexciton luminescence [10, 11, 54] and to localized exciton states [55–57]. Similar PL structures have been resolved in boron nitride encapsulated WS$_2$ (and WS$_2$) monolayers, while only excitons and trions are present in MoS$_2$ (and MoSe$_2$) monolayers[54, 58] that strongly suggests the contribution of intrinsic exciton-states emission into the energy features below the A-exciton.
Our PLE experimental results, otherwise, provide evidence for the indirect nature of the optical transition from $P_1$ to $P_4$. At low temperature, most of the exciton population resides at the lowest-energy and momentum-indirect exciton at the A-point. This is confirmed by the observation of i) first-order scattering events with non-zero wavevector phonons and of ii) weak light emission from the zero-phonon-line $X^A_\Gamma$ ($ZPL_{X^A_\Gamma}$) in our near-resonant excitation experiments. For radiative recombination to take place from the indirect-$X^A_\Gamma$, the assistance of phonons, carrier doping or disorder scattering might provide additional momentum to the optical transition. For phonon-assisted recombination, different types and combinations of lattice vibrations might contribute [59], leading to various phonon-assisted features. As a result, several lines are expected at energies $\Delta E_{n-\Lambda} \sim 70$ meV below the $ZPL_{X^A_\Gamma}$. A peak at energy $\sim \Delta E_{n-\Lambda} - n\Delta_p$ below the $ZPL_{X^A_\Gamma}$, where $n\Delta_p$ is the energy of the n-phonon mode ($n = 1, 2,...$) assisting the optical transition.

For light emission arising from the indirect-$X^A_\Gamma$, the constituent electrons of these indirect excitons located at the A-points (see figure 3(a)) need to be scattered into the light cone at K- or K'-valleys. There could be two possible scenarios. Firstly, with the assistance of zone-edge phonons, electrons at A-valleys can be scattered to K'-valleys and then recombine with K'-valley holes. Due to strong exciton-(zone-edge)-phonon coupling, it might give rise to several phonon replicas. Interestingly, the energy $\Delta E_1 = E_{P_2} - E_{P_1}$ and $\Delta E_2 = E_{P_3} - E_{P_4}$ is $\sim 26$ meV (1LA(M) $\sim 26$ meV) as can be observed in figure 4, suggesting evidences for the phonon-assisted processes. Secondly, it is also possible that electrons at A-valleys are scattered to the nearest K-valley to recombine with resident K-valley holes.

![Figure 4](image_url)

**Figure 4. Multicomponent fitting of the low-temperature ($T = 20$ K) PL spectrum in WS$_2$ monolayer after near-resonant excitation.** The PL energy is plotted relative to $ZPL_{X^A_\Gamma}$. The raw PL spectrum is shown by the black solid-line, while the red-solid line is the global fitting by using multiple peaks with Voigt lineshapes, indicating for exciton-like (blue solid-lines) and exciton-phonon (green solid-line) scattering processes. The inset shows the relative energy of excitonic-like peaks with respect to the $ZPL_{X^A_\Gamma}$. As obtained from the fitting, the height of the color bars indicates the relative contribution of each line to the total PL spectrum.
dynamics might alter the spectral weights of the phonon-assisted resonances.

On the other hand, electrostatic doping might lead to the formation of a negatively charge state of the indirect $\Lambda$-exciton or intervalley $\Lambda$-trion ($T^\Lambda$). In a simple scenario, the additional charge would locate at either $K$ or $K'$, depending on the spin-valley configuration ($K$ or $K'$) of the hole to which the $\Lambda$ electron is bounded. The additional electron will lead to intervalley Coulomb scattering between carriers providing additional momentum and turn the optical transition brighter. The associated peak will appear at the energy of $\sim \Delta P_{\alpha}^{A} - \Delta T_{\alpha}$ below the ZPL$_{X^\Lambda}$. The binding energy $\Delta T_{\alpha}$ of the intervalley $\Lambda$-trion will be smaller than that of $T_{4}^A$, as the the $k$-overlap between $T_{4}^A$ carriers might be smaller.

Therefore, besides the features below ZPL$_{X^\Lambda}$ that have been attributed to luminescence from biexciton and localized states, we argue that a multitude of available radiative recombination pathways of the lowest-energy and indirect-exciton $X^\Lambda$, might contribute to the low-energy peaks ($P_1$ to $P_4$) in the photoluminescence spectrum of WS$_2$ monolayer. We highlight that multiple phonon-scattering processes could contribute into lines with similar energies, leading to super-linear power-dependencies that are often observed in literature\cite{11,54}. Biexciton emission with a nonquadratic power-dependence ($I_{\text{PL}} \sim P^\alpha$, $\alpha \sim 1.4$) in WS$_2$ monolayers at energies of $\sim 50$ meV below ZPL$_{X^\Lambda}$, which largely deviates from theoretical predictions\cite{69}, might be reconsidered.

A superlinear emission with excitation power could also be attributed to the increase of the PL quantum efficiency with the increase of excitation power. It is due to the coexistence of nonradiative decay pathways and a non-linear increase of the radiative recombination efficiency. The non-linearity could result from the increase of the relaxation rates or from the saturation of the nonradiative channels\cite{70}. Within the drawn picture, it is very likely that the non-linearity appears due to the saturation of the nonradiative recombination channel of the indirect-exciton $X^\Lambda$. We believe that future power-dependent time-resolved PL experiments could distinguish the origin of the non-linearity in the power law of the low-energy structures ($P_1$–$P_4$).

**Exciton Relaxation and Valley Depolarization Under Near-Resonant Excitation of $B$-Excitons.** Besides the excitation near $A$-exciton, we also investigated the relaxation processes of excitons after resonantly creating $B$-excitons (see details in Supporting Information). We found that the relaxation from $B$ to $A$ is quite efficient and the lack of valley polarization (see figure S6) during fast cooling of $B$- to $A$-excitons suggests that intra-valley and inter-valley relaxation are equally probable, of which the latter causes the valley-pseudospin depolarization of the PL emission. Therefore, the scattering of hot excitons with zone-edge phonons should be considered as a valley depolarization channel in addition to electron-hole exchange interaction\cite{59}.

**3. Conclusion**

In summary, by using near-resonant excitation experiments, we prove exciton-phonon scattering events with non-zero wavevector that provide strong evidences for the momentum indirect nature of the optical bandgap in WS$_2$ monolayer. The scattering between carriers and zone-edge phonons creates excitons at different valleys, among which, the lowest-energy band is momentum indirect. Our findings advance the understanding on the inherent bandgap nature of TMD monolayers and highlight that more efforts are required for a complete understanding of the complex photoluminescence spectrum reported on W-based compounds. In addition to biexciton and localized states, the low-energy emission features observed at low temperature could arise from momentum indirect transitions. Moreover, future experiments might be considered on high-quality hBN-encapsulated TMD monolayers. We believe such samples will benefit the clear identification of the different PL resonances. Furthermore, by using a backgate the charge density could be tuned to clearly distinguish between charge- and phonon-assisted recombination pathways for momentum indirect excitons. Furthermore, photoluminescence excitation across the whole spectral range in combination with polarization-dependent experiments could provide further evidences on the formation and polarization properties of momentum indirect excitons. Finally, one could use magneto-optical spectroscopy to obtain $g$-factors that might vary across different valley excitons. These further experiments will shed light on the origin of the low-energy features observed in the low-temperature PL spectrum in W-based monolayer semiconductors.

**4. Methods**

Monolayer WS$_2$ was obtained by mechanical exfoliation of a high-quality bulk crystal. The thin WS$_2$ flakes were first exfoliated by polydimethylsiloxane (PDMS) stamp attached onto glass slides. The monolayers were identified under an optical microscope by the optical contrast with the substrate and by fluorescent measurements at room temperature. After, the samples were transferred onto a Si/(300 nm)SiO$_2$ substrate. For low-temperature ($T = 20$ K) photoluminescence excitation spectroscopy (PLE) studies, the monolayer was loaded and cooled in a liquid He continuous-flow optical cryostat. For PLE measurements on $A$-excitons, a very narrow excitation source ($\leq 0.08$ nm FWHM) was achieved, using a tunable jet-stream dye (Rhodamine 6G) laser with lines ranging from $2.103$ eV till $2.173$ eV that was filtered by a $600$ gr/mm single grazing grating spectrometer.
with 300 mm focal length. The output monochromatic beam was directed to the cryostat and focused on the sample by using a microscope objective (N.A 0.45). The photoluminescence, collected by the same objective (so-called back-scattering configuration), was dispersed by a triple-grating spectrometer operating in the subtractive mode. The near-resonant PL emission was dispersed by the final stage, a 640 mm focal length spectrometer and by using a 1800 gr/mm grating and finally detected by a liquid nitrogen cooled CCD camera. Additionally, for polarization-resolved PLE measurements on B-excitons, all the lines (2.707 eV, 2.627 eV, 2.605 eV, 2.541 eV, 2.499 eV, 2.470 eV and 2.412 eV) of an Argon-Ion laser were used. The PL signal was dispersed by using a 600 gr/mm single grating spectrometer with 800 mm focal length and finally detected by a liquid nitrogen cooled CCD camera.

5. Author information

5.1. Author contribution

QX and AGDA, started the project, conceived and designed the experiments. SL prepared the TMD micro-sized semiconductor layers. AGDA and DB performed the optical measurements. TTGD and JP intensively discussed on the data and the manuscript. DB and AGDA analyzed, interpreted the data and wrote the manuscript with input from all co-authors. DB and AGDA contributed equally to this work.

Acknowledgment

QX gratefully acknowledges financial support from Singapore National Research Foundation through an NRF-ANR joint programme (NRF2017-NRF-ANR005 2D CHIRAL), Singapore Ministry of Education via AcRF Tier 3 Programme "Geometrical Quantum Materials" (MOE2018-T3-1-002) and Tier 2 grant (MOE2017-T2-1-I040) and two Tier1 grants (RG 113/16 and RG 194/17). AGDA gratefully acknowledges the financial support of the Presidential Postdoctoral Fellowship program of the Nanyang Technological University.

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At exponentially large interlayer separations, the electronic states of the two layers become delocalized, and the interlayer coupling becomes weak. In this limit, the low-energy excitations consist of excitons localized in one layer and delocalized in the other layer. The excitonic properties of the monolayer MoS$_2$ and WS$_2$ are determined by the interlayer coupling and the electronic structure of the layers.

Exciton formation in monolayer MoS$_2$ and WS$_2$ can be studied by resonance Raman scattering spectroscopy. The Raman spectrum of monolayer MoS$_2$ shows a single peak at $\approx 300$ cm$^{-1}$, which corresponds to the in-plane optical phonon mode of the MoS$_2$ layer. This peak is much broader than the peak in the Raman spectrum of bulk MoS$_2$, indicating a change in the electronic structure due to the formation of excitons.

In conclusion, the study of excitonic properties in monolayer MoS$_2$ and WS$_2$ provides a new platform for exploring the fundamental physics of strongly correlated materials and for developing new electronic and optoelectronic devices.