Review

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Fine structures of valley-polarized excitonic states in monolayer transitional metal dichalcogenides

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Abstract: Monolayer transitional metal dichalcogenides (TMDCs), a new class of atomically thin semiconductor, respond to optical excitation strongly with robust excitons, which stem from the reduced screening in two dimensions. These excitons also possess a new quantum degree of freedom known as valley spin, which has inspired the field of valleytronics. The strongly enhanced Coulomb interaction allows the exciton to bind with other particles to form new excitonic states. However, despite the discovery of trions, most of the excitonic states in monolayer TMDCs remain elusive until recently, when new light was shed into the fascinating excitonic fine structures with drastically improved sample quality through boron nitride encapsulation. Here, we review the latest research progress on fine structures of excitonic states in monolayer TMDCs, with a focus on tungsten-based TMDCs and related alloy. Many of the new excitonic complexes inherit the valley degree of freedom, and the valley-polarized dark excitonic states are of particular interest because of their long lifetime and possible long valley coherence time. The capability of resolving the excitonic fine structures also enables the investigation of exciton–phonon interactions. The knowledge of the interlayer between excitons and other particles not only advances our understanding of many-body effects

in the monolayer TMDCs but also provides guidance on future applications based on TMDCs.

Keywords: excitonic complexes; exciton–phonon interaction; transition metal dichalcogenides; optoelectronics.

1 Introduction

Since the discovery of graphene from 2004 [1–3], two-dimensional materials (2D materials) have drawn intense attention in the research communities of physics, chemistry, material science, and engineering worldwide [4–13]. Among them, transitional metal dichalcogenides (TMDCs) represent a new class of atomically thin semiconductor that host excitons with large binding energy due to enhanced Coulomb interaction in 2D. These excitons also possess valley contrasting properties, which stem from the combined effects of threefold rotation symmetry and inversion symmetry breaking. However, the lifetime of the excitons is typically short, rendering it difficult to realize valleytronics applications. Because the Coulomb interaction in confined 2D space is strong, is it possible for the exciton to bind with other particles to form new excitonic particles that are both valley-polarized and long-lived? How would the exciton–phonon interaction or other many-body physics affect the new excitonic states? These questions were challenging to address, mostly due to elusive spectra signatures limited by the quality of TMDC devices.

Notably, with the improvement of crystal growth [14–19] and fabrication technique, especially the encapsulation of high-quality hexagonal boron nitride (h-BN) flakes [20–24], high-quality TMDCs devices have been shown to produce rich optical spectroscopy features that are associated with new excitonic complexes. In particular, tungsten-based TMDCs such as tungsten diselenide (WSe₂) and tungsten disulfide (WS₂) possess the unique band structure that hosts spin-forbidden dark exciton, which significantly enriches the library of the excitonic

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quasi-particles. In this article, we review the advances in the understanding of the emerging fine structures of excitonic states in TMDC monolayers, mainly taking WSe_2 as the prototypical example: (i) the resolution of biexciton puzzle by identifying the charge-neutral biexciton and trion–exciton complexes (i.e., charged biexciton) [25–28]; (ii) the verification of the dark exciton and dark trions through the gate voltage–dependent magneto-photoluminescence (PL) and Fourier plane imaging [29–32]; (iii) the exciton–phonon interaction including the chiral phonon replica (E'' chiral phonon at Γ point) of the spin-forbidden dark exciton replica [33, 34], momentum-dark intervalley exciton brightened by the chiral K phonon (E' chiral phonon at K point) [35–38], and the interlayer exciton–phonon coupling in the van der Waals (vdW) heterostructure of monolayer TMDC or alloy ($\text{WS}_{0.6}\text{Se}_{1.4}$) shown in the emerging Raman modes [22, 23, 39, 40]. Improved understanding of the excitonic fine structures in monolayer TMDCs and related alloy will allow us to explore valley-polarized excitonic complexes with long lifetime for valleytronics, to search for excitonic quasi-particle with long valley coherence, and to manipulate the valley spin through interactions such as phonon–exciton interaction. These efforts will greatly advance our understanding of the unique many-body physics in TMDCs and open the door to the novel quantum optoelectronics.

In the review, we only focus on the many-particle excitonic complexes that are not related to defects. For defect-related excitonic physics in monolayer TMDCs, we refer the interested readers to the recent reviews [4, 41].

2 Excitonic states in 2D TMDCs

Transitional metal dichalcogenides have an indirect-to-direct bandgap transition from bulk to single layer [42, 43]. The large spin-orbit coupling (SOC) leads to the splitting both in the valence and conduction bands with the splitting energies of ~ 300 to 400 and ~ 20 to 40 meV, respectively (Figure 1A) [48–51]. Because of the inversion symmetry breaking and threefold rotation symmetry, the excitons in monolayer TMDCs are endowed with the valley degree of freedom, which behaves like a pseudospin [44–46, 52–58]. The valley degree of freedom can be accessed selectively through the circularly polarized light, that is, σ^+ polarized light to selectively excite the K valley, whereas σ^- polarized light to excite the K' valley, which opens up the fascinating field of valleytronics [46, 53, 59–66]. Meanwhile, despite the atomically thin

structure, most of the monolayer TMDCs possess strong light–matter interaction. For instance, the monolayer MoS_2 has $\sim 10\%$ resonant absorption of light (660 nm for A exciton and 615 nm for B exciton) [67]. With the reduced screening effect, the greatly enhanced Coulomb interaction between excited electron and hole results in the formation of extensively studied excitonic complexes [68–71], such as bright exciton [42, 72, 73], dark exciton [31, 32, 74–78], and intravalley and intervalley trions [79–81], as well as positive trion [73, 82], with binding energy orders of magnitude larger than the counterpart in conventional semiconductor such as gallium arsenide [57, 63, 68, 83–86] (Figure 1B–F).

Boron nitride encapsulation has been recently shown to significantly improve the TMDC device quality, which is evidenced by the PL spectra width [87–90] and associated optical spectra. With the significant improvement of the quality of TMDC bulk crystal growth and the optimization of the device fabrication, especially with the high-quality h-BN encapsulation to isolate the monolayer TMDCs from dielectric environment (Figure 2A, B), the PL width of the exciton peak can be reduced to ~ 2 meV, limited by the intrinsic recombination [87–90]. As a result, researchers are able to explore the intrinsic nature of the different excitonic states with the application of different tuning knobs, including electrostatic gating, magneto-PL, polarization, time-resolved PL (TRPL), and so on. Recently, it has been demonstrated that many novel excitonic states will emerge locating both in the hole-doping and electron-doping regimes in h-BN–encapsulated TMDC monolayer. Taking h-BN/ WSe_2 /h-BN structure as an example (Figure 2C), in addition to the well-established bright exciton (X_0), dark exciton (X_D), positive trion (X^+), intervalley trion (X^-), intravalley trion (X_2^-), and the exciton–plasmon (X'^-) [91, 92], we can see several new emerging excitonic states, including the charge-neutral biexciton (XX) and trion–exciton complexes (XX^-), positive dark trion (X_D^+) and negative dark trion (X_D^-), intervalley exciton (X_i), and dark exciton phonon replica (X_D^R) due to the efficient gate tunability, which we describe in detail in the following sections.

3 Biexciton and trion–exciton complexes

The strong Coulomb interaction in monolayer TMDCs would give rise to strong exciton–exciton interaction, and we might expect the easy formation of biexciton. Although the biexciton was experimentally demonstrated as early

Figure 1: Excitonic states in 2D tungsten-based TMDC monolayer.

(A) Valley-dependent optical selection rules for interband transitions in 2D monolayer tungsten-based TMDCs. Both the conduction and valence bands are spin-split due to the strong SOC, resulting in the spin-valley locking. σ^+ polarized light only couples to the K valley, whereas σ^- polarized light only couples to the K' valley. Blue and red stand for spin up and spin down. (B–F) Excitonic configurations of the bright exciton (X_0), dark exciton (X_D), intervalley negative trion (X_1^-), intravalley negative trion (X_2^-), and positive trion (X^+), respectively. The z-component of the total angular momentum for each band, with the Berry phase contribution considered, is labeled in panel B [44–47].

as 2015, however, the theoretical calculations and experimental extracted value of the binding energy of biexciton remain discrepant, calling for unambiguous identification and understanding of the biexciton in TMDCs.

In 2015, You et al. [93] introduced the fluence-dependent PL study and TRPL to demonstrate the presence of a four-body biexciton state in monolayer WSe_2 . They found that under pulsed excitation an emerging state exhibits a superlinear power dependence with the power law of 1.39, which is distinctively different from other excitonic states with linear power dependence (Figure 3A, B). They ascribe this state to be the biexciton state. The TRPL results further indicate that the biexciton has the similar lifetime as the exciton and trion, in contrast to the long decay time

of defect states (Figure 3C). The experimentally extracted binding energy is 52 meV, which is significantly larger than the theoretical prediction of ~ 20 meV. Many other research groups also report similar results both from monolayer WS_2 and WSe_2 [28, 94–101]. However, these results are based on either the devices without gate tunability or the devices with relatively inferior spectral quality, which prevents them from exploring the intrinsic property of biexciton. Yong et al. [102] introduce the pump-probe technique to demonstrate that the driving optical field can couple a hierarchy of excitonic states, and the many-body intervalley biexciton state plays a dominant role in the optical Stark effect in monolayer MoSe_2 . They determine a binding energy of 21 meV for the intervalley

Figure 2: Gate voltage-dependent PL spectra of h-BN sandwiched monolayer WSe₂.

(A) Schematic representing the h-BN sandwiched monolayer WSe₂ device with a top gate. (B) A representative optical image of a top-gated WSe₂ device, in which different flakes are highlighted by different-color dashed lines. (C) Electrostatic doping-dependent color plot of the PL spectra of monolayer WSe₂ at low temperature (4.2 K). Owing to the efficient gate tunability, besides the bright exciton (X_0), dark exciton (X_0^-), positive trion (X^+), intervalley trion (X_1^-), intravalley trion (X_2^-), and exciton-plasmon (X^-), there are several new emerging excitonic states, including the charge-neutral biexciton (XX) and trion-exciton complexes (XX^-), positive dark trion (X_0^+) and negative dark trion (X_0^-), intervalley exciton (X_1), and dark exciton phonon replica (X_0^R).

Figure 3: Excitonic states in monolayer WSe₂.

(A) Photoluminescence spectra for different excitation fluences of 0.8 and 12 $\mu\text{J} \cdot \text{cm}^{-2}$ at 50 K. (B) Logarithmic plot of the XX PL intensity as a function of the PL intensity of exciton. The red line is a power-law fit: $I_{XX} \propto I_X^\alpha$, with $\alpha = 1.39$. The linear relation is shown for a comparison (dashed black line). (C) Time-resolved PL traces for X, X^- , XX, P_1 , and P_2 species and the instrument response function. The decay of XX is similar to that of X and X^- , but it is distinctively different from defect-related P_1 and P_2 , which have decay times >100 ps. The emission lifetimes are 14, 25, and 31 ps for X, X^- , and XX, respectively, with uncertainties of ± 5 ps. (A–C) Adapted from You et al. [93].

biexciton and a transition dipole moment of 9.3 debyes for the exciton-biexciton transition (Figure 4A, B). In addition, Steinhoff et al. [104] and Hao et al. [103] utilize both the polarization-resolved 2D coherent spectroscopy on monolayer MoSe₂ and ultrafast pump-probe measurement on single-layer WSe₂ to reveal the high-order biexciton fine structures (“bright-bright” configuration) (Figure 4C–E). The biexcitons in MoSe₂ and WSe₂ both locate between the exciton and trion with the binding energy of around 20 meV, which is very close to the theoretical

prediction [84, 85, 105–107]. Hence, which one is the real biexciton? What is the binding energy of the biexciton? This is the biexciton puzzle in the research community of 2D materials.

Li et al. [25], along with Ye et al. [28], Chen et al. [27], and Barbone et al. [26], independently report the identification of the neutral biexciton and trion-exciton complexes (or equivalently, negatively charged biexciton) in an h-BN-encapsulated monolayer WSe₂ device. The authors demonstrate the superlinear fluence dependence

Figure 4: Excitonic states in 2D TMDC monolayer.

(A) Transient reflection spectra at $\tau = 0$ ps with different detuning energies. (B) Schematic of the effective coupling between different states upon σ^- -pump radiation. Adapted from Yong et al. [102]. (C) Normalized 2D amplitude spectrum obtained using cross-circular polarization of the first/third fields (σ^+) and second/signal fields (σ^-). The XX is associated with the neutral bound biexciton, whereas the TX^b and XT^b are associated with the charged bound biexciton. Adapted from Hao et al. [103]. (D) Line cut at the excitation energy of ~ 1.648 eV from (C). Peaks XT^b , XX , and X are indicated by the shaded regions with the fitting from Gaussian functions. Adapted from Hao et al. [103]. (E) Differential absorption of WSe_2 pumped at the red wing of its neutral exciton resonance in a pump-probe experiment with cross-polarized (left panel) and cocircularly polarized (right panel) pump and probe pulses. Adapted from Steinhoff et al. [104].

(nearly quadratic power law) for two new excitonic states, XX and XX^- , whereas the bright exciton shows an almost linear behavior. The XX locates between the exciton and the trions with the binding energy of ~ 17 meV, whereas the XX^- lies on the low energy side of the dark exciton with the binding energy of ~ 49 meV, where the binding energy of XX is in excellent agreement with the theoretical prediction of biexciton binding energy, and the binding energy of XX^- is consistent with the result of You et al. [93]. They further employ the efficient electrostatic gating from hole-doping to electron-doping to identify the nature of XX and XX^- (Figure 2C). The XX only brightens up at the charge-neutral region, similar to the dark exciton. However, the XX^- emerges at the slight electron-doping region, and the intensity quickly diminishes with the increase of the electron-doping. Considering the doping dependence and the fluence dependence of the PL, the XX and XX^- are assigned to be charge-neutral biexciton and electron-bound biexciton, respectively. Meanwhile, the valley polarization of the XX and XX^- is higher than that of the bright exciton, which indicates that they are both composed of a bright exciton. Because the XX^- is a five-particle complex, considering the valley polarization and Pauli exclusion, the

lowest energy configuration for XX^- can only be the one shown in the left panel of Figure 5D, which can be viewed as a biexciton bound to a free electron or, equivalently, an intravalley trion bound to a dark exciton. Another interesting observation is that, in contrast to the bright exciton, the PL intensity of XX and XX^- presents an inverse circular polarization under magnetic field, in which the high energy peak has more intense PL intensity than the low energy peak (Figure 5A). This observation is in agreement with the calculated total g factor (contributions from all the constituent particles) of the XX and XX^- with the positive value of 4 and 6, respectively. Therefore, the configuration of the biexciton is also deduced as the one shown in the right panel of Figure 5D, taking into account the valley polarization and the inverted PL intensity behavior, which consists of a bright exciton and a dark exciton. Due to the long lifetime of the dark exciton ($\sim$ hundreds of picoseconds), the bright exciton has high probability to bind with the high density of dark excitons to form the “bright-dark” biexciton, instead of the “bright-bright” biexciton, even at very low excitation power ($\sim \mu\text{W}/\mu\text{m}^2$). Finally, the authors obtain the magneto-PL spectra and extract the spectral g factor for the XX and XX^- with the value of ~ 4.03

Figure 5: Biexciton and trion-exciton complexes in h-BN-encapsulated monolayer WSe_2 .

(A) Polarization-resolved PL spectra of the X_0 , XX , and XX^- states ($B = 17$ T). The XX and XX^- states show the inverse PL intensity of the $\sigma\sigma$ and $\sigma^+\sigma^+$ configurations, compared to the distinctively different behavior of the X_0 . (B) Magneto-PL spectra as a function of the out-of-plane magnetic field. The Zeeman shift of the XX and XX^- is similar to the X_0 with the redshift from -17 to 17 T. It is worth noting that the X_D presents a unique X-pattern, originating from the out-of-plane radiation dipole. (C) The calculated g factor of different excitonic states from the linear fitting of Zeeman splitting between $\sigma\sigma$ and $\sigma^+\sigma^+$ configurations. The g factors of XX and XX^- states are -3.64 and -5.33 , respectively, while the X_D exhibits significantly larger g factor with the value of -9.75 . (D) Schematic configurations of the trion-exciton and biexciton with the calculated total g factor of 6 and 4, respectively, where the solid dots represent the electrons and the empty circles for the holes. Blue color stands for spin up, and red for spin down.

and -5.33 (Figure 5B, C), respectively, which is in excellent agreement with the theoretical expectation from the valley-Zeeman effect [108–111] (Figure 5B, C). Additionally, the dark exciton exhibits a unique X-pattern, originating from the out-of-plane radiation dipole. The g factor of the dark exciton (-9.75) is significantly larger than the bright exciton, which is consistent with the previous report [76].

The advancement of our understanding of the biexciton paves the way for the nonlinear quantum optoelectronics-based TMDCs.

4 Dark trions

Researchers have discovered that the tungsten-based TMDCs, like WSe_2 and WS_2 , have a distinct band structure

with both the splitting in the conduction and valence bands induced by the strong SOC [48–51]. The resulted ground state is a spin-forbidden dark exciton due to the optical selection rule, which prevents it from direct recombination [75, 77, 112–116]. Zhang et al. [32] show that the in-plane magnetic field can brighten the dark excitons in monolayer WSe_2 , which exhibits much-increased emission and valley lifetimes due to the spin-forbidden configuration (Figure 6A, B). Park et al. [74] demonstrate the dramatically enhanced PL emission quantum yield ($\sim 6 \times 10^5$ -fold) of dark exciton through the coupling of the antenna tip to the dark exciton out-of-plane optical dipole moment using the monolayer WSe_2 on a gold substrate at room temperature (Figure 6C). Zhou et al. [31] indicate that by the introduction of near-field coupling to surface plasmon polaritons (SPPs), the dark exciton and

Figure 6: Dark exciton in monolayer WSe₂.

(A) Color plot of the PL spectra as a function of in-plane magnetic field measured from a monolayer WSe₂ at 30 K. (B) Time-resolved PL from the bright exciton and dark trion under the in-plane magnetic field of 17.5 T at 4 K. The lifetime of dark trion is ~ 240 ps, whereas that of the bright exciton is less than 20 ps. (A, B) Adapted from Zhang et al. [32]. (C) Schematic of tip-enhanced PL spectroscopy and electronic band structure of monolayer WSe₂. Selective excitation and probing of the transition dipole moments of dark (out-of-plane) and bright (in-plane) excitons by polarization control (adapted from Park et al. [74]). (D) Schematic of the experimental setup. TMDC monolayer and BN vdW structure is placed on top of single-crystal silver with silver acting as the backgate (V_g). Optical transitions can couple to both near-field SPPs and the FF, while the nanoscale trenches are used to detect the scattering signal into the FF from the coupling to SPPs. (E) Gate voltage-dependent FF-PL of the WSe₂. New peaks of X_D⁺, X_D⁰ and X_D⁻ emerge in the neutral, p-doping, and n-doping regions, respectively. (D, E) Adapted from Zhou et al. [31]. (F) Detection of the PL from the edge of BN-encapsulated WSe₂ sample at 13 K with the different detection polarizations [x is in the monolayer plane (green line), and z is perpendicular to it (red line)]. The schematic of detection method is shown in the inset of panel. Adapted from Wang et al. [78].

dark trions can be probed in monolayer TMDCs. The SPPs selectively couple with the out-of-plane dipole, which enables the enhancement of optical transition that is spin-forbidden. Therefore, when a piece of monolayer WSe₂ is placed on a substrate covered with single-crystal silver film, the emission from near-field-coupled SPPs clearly shows the spectral features that are consistent with the energies and dipole orientations of the dark exciton and dark trions (Figure 6D, E). Wang et al. [78] investigate the optical transitions in monolayer WSe₂, WS₂, and MoSe₂ by the polarization-resolved PL collecting from the edge of the sample. They observe clear signatures of the dark exciton, whose electric field is perpendicular to the monolayer plane, coinciding with the optical selection rules deduced from group theory analysis (Figure 6F).

Nevertheless, is there a more direct way to observe these dark states?

Recently, Li et al. [29] apply the magneto-PL spectroscopy and Fourier plane imaging to investigate a top-gated single-layer WSe₂, which results in unambiguous evidence to reveal the positive dark trion (X_D⁺) and negative dark trion (X_D⁻). In Figure 2C, it clearly presents that the X_D⁺ and X_D⁻ show up with the increases of the hole-doping and electron-doping, respectively, with the binding energy ~ 15 meV. The valley-resolved magneto-PL indicates that the X_D⁺ and X_D⁻ both share the similar “cross” pattern as that of the X_D in Figure 7A and B, respectively. Furthermore, the extracted g factors are approximately -9.8 and -8.6 for the X_D⁺ and X_D⁻, respectively, which are similar to the X_D (Figure 7C). In addition, the brighter branch of the

Figure 7: Positive and negative dark trions in h-BN-encapsulated monolayer WSe₂.

(A, B) Magnetic field dependent PL spectra at the gate voltages of -2 and 1 V, corresponding to the hole-doping and electron-doping, respectively. Both the X_D⁺ and X_D⁻ exhibit the same X-pattern as that of the dark exciton as a function of a magnetic field. (C) Extracted g factors of the X_D⁺ and X_D⁻ from the Zeeman shift. The top panel is for the X_D⁻, while the bottom panel is for X_D⁺. The extracted values are approximately -9.8 and -8.6 for the X_D⁺ and X_D⁻, respectively, which is similar to the X₀. (D) The valley polarization P_B of X_D, X_D⁺, and X_D⁻ under a magnetic field, $P_B = \frac{I(K') - I(K)}{I(K') + I(K)} \sigma(B)$, where $I(K)$ and $I(K')$ are the PL intensities from K and K' valleys, respectively. $\sigma(B)$ is 1 or -1 for positive or negative B field, respectively. (E, F) The schematics of electron and hole recombination for positive dark trion and negative dark trion, respectively.

X_D⁻ (with the PL intensity ratio of ~ 20 between the two branches) is the same as the visible branch of X₀, but the opposite to the brighter branch of the X_D⁺ (with the intensity ratio of ~ 4). It indicates that the dark exciton dressed with a free hole or electron to form the dark trion will emit photon more likely from one valley or the other, granting the valley information to the dark trion. With the quantitative calculation of the valley polarization (P_B) under different magnetic fields, the X_D⁺ shows a negative P_B value, whereas the X_D⁻ has a positive P_B value, which is distinctly different from the X_D with the P_B value close to 0 (Figure 7D). The granted valley polarization from the dressing of the electron or hole can be explained by the intervalley scattering mechanism, where the electron-hole recombination to emit photon is dominated by the optically excited minority carrier (hole for n-doping and electron for hole-doping) under the weak optical excitation. It has been demonstrated that the hole prefers to stay in

the same valley as it is excited [117, 118]. However, for the optically excited electron, it will relax to the lower energy band, either flip spin and relax to the “dark” conduction band in the same valley, or relax to the opposite valley and maintain the same spin. The observation of negative valley polarization of dark p-trion, which is determined by the electron, suggests that electron is more likely to relax to the opposite valley. As a result, the PL of X_D⁻ will exhibit the same valley polarization of the PL from X₀, and the PL emitted from X_D⁺ shows the opposite valley polarization as shown in the schematics in Figure 7E, F.

Considering the complexity of the valley polarization of the dark trions, combined with the weak PL intensity of the negative dark trion, the “cross” pattern is often hard to be resolved. However, the dark trions also radiate through the out-of-plane dipole as the dark exciton, and the radiation pattern of the dark trion should be similar to the dark exciton; direct measurement of the radiation pattern will

provide more direct and unambiguous evidence of the dark trions. It has been proven that the radiation pattern of dark exciton has significantly different features from the bright exciton [28]. Figure 8 is the Fourier plane imaging of different excitonic states. It is distinctively shown that the X_D^+ , X_D , and X_D^- share the same radiation pattern, with the maximum PL intensity locating at the detection degree of $\sim 64^\circ$, distinctively different from the X_0 whose intensity is maximized at 0° .

It is worth noting that a relevant work also reported on the measurement of the dark trions by the continuous tunability of the electrostatic gating from hole-doping to the electron-doping region [30]. The magneto-PL and TRPL reveal that the dark trions have distinct valley optical emission and the lifetime from 0.4 to 1.3 ns.

5 Exciton–phonon interaction

In monolayer TMDCs, the exciton–phonon interaction plays an important role in the relaxation dynamics of excitonic states. Due to the unique band structure of

monolayer TMDCs, the interband transitions of electrons in the intravalley and intervalley processes will involve the absorption or emission of the phonons locating at the Γ and K points, respectively, due to the conservation of momentum. Figure 9A shows the phonon dispersion spectrum of the monolayer WSe₂. Many theoretical and experimental works have contributed to the signature of the strong exciton–phonon interaction in the exciton dynamics [16, 35, 60, 120–126]. For example, double-resonant Raman scattering reveals the preservation of the valley coherence in monolayer WSe₂ [127]; excitons enhance the anti-Stokes shifts in monolayer MoTe₂ [128]; A_1' phonons assist the trion to exciton luminescence upconversion in monolayer WSe₂ [129]. Most importantly, the phonon with helicity has been recently theoretically proposed [31] and experimentally reported [36, 37]. Among them, the E'' mode chiral phonon at the Γ point and the E' mode chiral phonon at the K point are studied extensively in the exciton–phonon interaction (Figure 9B). For the E' (K) phonon, the tungsten atom is stationary, whereas the selenium has a clockwise (or anticlockwise) rotation in K (or K') valley with a $2/3\pi$ phase difference. The E' (K) phonon has been previously

Figure 8: Fourier plane imaging of the different excitonic states.

(A–C) The radiation angle and photon energy–dependent PL spectra color plots of the gate voltages of -2 , 0 , and 1 V, respectively, corresponding to the X_D^+ , X_D , and X_D^- , respectively. (D–F) Linecuts of the PL spectra as a function of the detection angle for the different excitonic states, corresponding to the color plots in A–C. The Fourier plane imaging obviously shows that the X_D^+ , X_D , and X_D^- share the same radiation pattern, with the maximum PL intensity locating at the detection degree of $\sim 64^\circ$, which is distinctively different from the X_0 maximizing at the degree of 0° .

Figure 9: Fourier plane imaging of the different excitonic states.

(A) Phonon dispersion curve for monolayer WSe_2 . Adapted from Yuan et al. [119]. (B) Schematic of E'' mode chiral phonon at the Γ point and the E' mode chiral phonon at the K point. (C) Hole-phonon interaction in the transition between A to B exciton in the monolayer WSe_2 through pump-probe measurement. Adapted from Zhu et al. [36]. (D) E'' (Γ) phonon replicas of the quantum dots in monolayer WSe_2 . The energy spacing between a and b doublets is 21.8 meV, which is consistent with the energy of the E'' (Γ) phonon. Adapted from Chen et al. [34].

observed experimentally by investigating the transition between A and B exciton states with transient infrared (IR) spectroscopy (Figure 9C). The left circularly polarized light pumps holes to move from K to K' valley by creating a LO(K) phonon and simultaneously absorbs an IR probe photon, relaxing to the lower valence band in the opposite valley and emitting right circularly polarized photon [36]. For E'' (Γ) phonon, there are two degenerate modes in which the tungsten atom is stationary, whereas the selenium atoms can vibrate in two orthogonal in-plane directions. The superposition of these two orthogonal linear vibrations results in the left- or right-handed chiral phonon, with the angular momentum of 1 or -1, respectively. Figure 9D reveals the E'' (Γ) phonon replicas of the quantum dots in monolayer WSe_2 [34]. The quantum dots can couple with the E'' (Γ), leading to the

emission of the phonon replica, and the energy spacing is always 21.8 meV, which is the energy of E'' (Γ) mode.

5.1 Dark exciton phonon replica

Tungsten-based monolayer transition metal dichalcogenides host a long-lived “dark” exciton [75, 77, 113–116, 130–132], an electron-hole pair in a spin-triplet configuration. The long lifetime and unique spin properties of the dark exciton provide exciting opportunities to explore light-matter interactions beyond electric dipole transitions. In bright excitons, the in-plane transition dipole in K (or K') valley can selectively couple with the left (or right) circularly polarized light, which empowers us to conveniently access the valley information. However, the valley

selection rule for dark exciton is distinctively different from the bright exciton. The dark exciton with an out-of-plane transition dipole can couple with both left and right circular lights, which make it difficult to distinguish the valley pseudospin of dark states. To overcome this limitation, careful maneuvering of the selection rules through higher-order interactions provides access to the otherwise dark states and reveals additional rich physics.

It has been reported that the coupling of the dark exciton and an optically silent chiral phonon enables the intrinsic PL of the dark-exciton replica in single-layer WSe₂ [33]. The gate voltage-dependent PL spectra reveal that the X_D and X_D^R only have pronounced PL in the charge-neutral region (Figure 2C), which helps to distinguish X_D^R from the charged dark exciton. The valley-resolved

PL spectra illustrate that both the X_D and X_D^R exhibit the same splitting into two peaks, and the splitting increases linearly under the applied out-of-plane magnetic field (Figure 10A), whereas other excitonic states all experience a blue shift. Meanwhile, the higher-energy replica peak is much stronger than the lower-energy one, meaning that the replica PL arising from each valley has finite circular polarization. The extracted g factor values from linearly fitting of the Zeeman splitting are -9.3 and -9.4 for X_D and X_D^R , respectively (Figure 10B). Furthermore, the X_D and X_D^R share the same linear behavior at the low excitation power and sublinear behavior at high excitation power, whereas the bright exciton exhibits linear behavior over the whole regime. Based on these specific features as well as the reproducibility of the X_D^R with the energy difference of

Figure 10: Phonon replica of dark exciton in h-BN-encapsulated monolayer WSe₂.

(A) Valley-resolved PL spectra without magnetic field and with 6-T out-of-plane magnetic field at 4.2 K, using an objective of large numerical aperture (N.A.: ~ 0.60). Both the X_D and X_D^R exhibit a splitting into two peaks with the applied out-of-plane magnetic field. (B) Calculated g factors for different excitonic states from the Zeeman splitting between the two $\sigma\sigma$ and $\sigma^+\sigma^+$ configurations. The extracted g factor values for X_D and X_D^R are -9.3 and -9.4 , respectively. (C) Circular polarized PL spectra of monolayer WSe₂ at 42 K for the detections of σ^- and σ^+ under the σ^- excitation. It clearly shows that the X_D is valley polarized with a valley polarization of $\sim 16.7\%$, whereas the bright exciton possesses a valley polarization of $\sim 39.5\%$. (D) Time-resolved PL spectra (dots) for X_0 , XX , X_1 , X_2 , X_D , and X_D^R . The TRPL data for different excitonic complexes are fitted by the single exponential function $I = Ae^{-t/\tau}$ convolved with the response of the laser as a kernel. The lifetime of X_D and that of X_D^R are 250 ± 20 ps and 230 ± 20 ps, respectively, significantly longer than that of X_0 (15 ps). (E) Phonon coupling and recombination pathway of the K-valley dark exciton. The yellow-shaded area above X_D indicates a quasi-equilibrium population of dark excitons at 4.2 K. The dark exciton phonon replica (X_D^R) state is labeled by a line with alternating blue and yellow color, indicating coupling between X_D and X_D^R . The photon emission by X_D^R is labeled by the black arrow, having an energy $\hbar\omega_D^R$. The emission process from X_D , in the second-order perturbation theory, is illustrated by the purple wavy and blue dashed lines, corresponding to the emission of a chiral E'' phonon ($\hbar\omega_{E''}$) and a circularly polarized photon, respectively. The intermediate state is the bright exciton X_0 .

21.3 meV between X_D and X_D^R , the X_D^R is proposed to be the phonon replica of the dark exciton assisted by the double-degenerate E'' chiral phonon at Γ point with the angular momentum of 1 and -1 , respectively. The theoretical energy of E'' chiral phonon is 21.8 meV (Figure 9B). Therefore, the dark excitons in the K or K' valleys can acquire a finite angular momentum and be brightened up by coupling to one of the chiral combinations (1 for K valley or -1 for K' valley). The E'' phonons are analogous to a fluctuating in-plane effective magnetic field that induces finite coupling between the two conduction bands and hence the bright and dark excitons in the same valley, greatly enhancing the out-of-plane and circularly polarized PL of X_D^R . In addition, a frozen phonon method and a second-order perturbation theory are further introduced to calculate the photon emission probability of the phonon replica X_D^R relative to the bright exciton, resulting in the ratio of photon emission probability between the replica state and the bright state with a relatively large value of ~ 0.04 . Combining the long lifetime of the dark exciton (Figure 10D), the relatively large photon emission probability explains the significant PL emission of replica (Figure 10E). This existence of the X_D^R was further confirmed in another study, which also revealed the same phonon mode could generate the phonon replica of the dark trions [38].

5.2 Intervalley exciton

Not only the spin-forbidden dark exciton can couple with the chiral phonon to emit the phonon replica with circular polarization, but also the momentum-forbidden intervalley dark exciton interacts with the chiral phonon locating at K point, resulting in the emission of circularly polarized light [35]. Assuming the circularly polarized excitation occurring in the K valley, the intervalley exciton consists of one electron in the K' valley and one hole in the K valley. The electron transits to a virtual state in the K valley by emitting a chiral phonon and then recombines with the hole in the valence band of the same valley, emitting a photon with certain helicity (Figure 11A). As shown in Figure 11B, peak X_i always emerges between the X_D^R and XX^- , and the energy difference between X_i and X_D remains 16 meV. Magneto-PL spectra exhibit that X_i is the steepest slope in all of the excitonic states with the extracted g factor of -12.5 , which is consistent with the theoretical calculation of the spectrum g factor of the intervalley exciton (Figure 11C). The valley-resolved PL spectra indicate that the X_i has comparable valley polarization to the bright exciton, 36.7% versus 39.5% (Figure 10C). Furthermore, the lifetime of the X_i is 200 ps from the TRPL line trace,

which is comparable to the dark exciton, but a magnitude order larger than the bright exciton and intervalley trion (Figure 11D). The long-lived intervalley exciton with valley information sheds light on promising routes of realizing excitonic valleytronics, and the coupling of the intervalley exciton with the chiral phonon could inspire future endeavors of exploiting chiral phonon for valley-spin manipulation.

5.3 Interlayer phonon coupling

Emerging phonon mode has also been recently discovered in vdW heterostructure of TMDCs due to strong exciton–phonon interactions. It has been demonstrated that the Raman scattering process between the interface of the WSe_2/SiO_2 and $WSe_2/h-BN$ can enable the Raman scattering with either traditionally inactive or weak; therefore, the PL intensity will be modulated by the exciton–phonon coupling, as the PLE spectra shown in Figure 12A–C [22]. Especially, when the phonon modes are coupled with the A exciton directly or via an A'_1 optical phonon from WSe_2 , the Raman scattering will be enhanced by almost two orders of magnitude. It is worth noting that the h-BN–encapsulated WSe_2 show distinct PLE spectra, which indicates that the exciton–phonon interaction strongly correlates with the coupling strength (Figure 12B, C). Another similar study [23] also shows that two new Raman peaks emerge in the h-BN/ WSe_2 /h-BN sandwiched structure, and their peak positions shift linearly with the excitation laser energy. Moreover, the Raman peaks show strong polarization dependence and completely disappear in the cross-polarization configuration (Figure 12D). Interestingly, the exciton–phonon coupling is a double resonant process, which is resonant not only with the A exciton but also with a new state coinciding with the new resonance peak in the absorption spectra (dashed line highlighted in Figure 12E).

This emerging Raman mode due to strong exciton–phonon interaction has also been found in TMDC alloys, which has tunable optical bandgaps [133–150], such as $WS_{2x}Se_{2(1-x)}$ and $Mo_xW_{1-x}Se_2$. Recently, the high-quality h-BN–encapsulated monolayer $WS_{0.6}Se_{1.4}$ is demonstrated to inherit the superior optical properties of tungsten-based TMDCs [39]. Both the PL and reflection spectra show that both the exciton and trion peaks emerge in monolayer $WS_{0.6}Se_{1.4}$. The trion has the fine structure of the intervalley and intravalley trions with the exchange interaction induced splitting energy of ~ 6 meV (Figure 13A, B), similar to that of WSe_2 or WS_2 . The valley-resolved PL spectra indicate that both the exciton and trion of monolayer $WS_{0.6}Se_{1.4}$

Figure 11: Intervalley exciton in h-BN-encapsulated monolayer WSe₂.

(A) Schematic of the intervalley exciton and chiral phonon coupling. The intervalley exciton consists of one electron and one hole in the different valleys. The electron can transit to a virtual state locating at the hole-sitting valley by emitting a chiral phonon and then recombining with the hole, emitting a circular photon. Inset: schematic representation of the E' chiral phonon mode at the K point. Blue sphere: W atom. Yellow and purple spheres are Se atoms in the equilibrium state and the vibration state, respectively. (B) Photoluminescence spectrum of monolayer WSe₂. Besides the established excitonic states, a novel peak X_i locates between the phonon replica of the dark exciton (X_D^R) and charged biexciton XX^- , with the ~ 16 meV lower than X_D . (C) Extracted g factor for different excitonic states. The g factor of X_i is ~ -12.5 , which is larger than other excitonic states. (D) Time-resolved PL spectra of different excitonic states. The lifetime of X_i is ~ 200 ps, which is comparable to the dark exciton, but a magnitude order larger than the bright exciton and intervalley trion.

possess the gate tunable valley polarization with the value as high as $\sim 60\%$ in the charge-neutral region (Figure 13C). Another interesting phenomenon is that the exciton-phonon coupling in the h-BN/WS_{0.6}Se_{1.4}/h-BN vdW heterostructure can also be tuned by the gate voltage, which renders the optical silent Raman mode visible (Figure 13D). In addition, the reflection contrast and its differential of monolayer WS_{0.6}Se_{1.4} also show an absorption resonance at ~ 1.945 eV, 140 meV above the A exciton energy. This 140 meV is roughly the same as the energy difference between the new resonance and A exciton in WSe₂. Considering the similar dielectric constant between WS_{0.6}Se_{1.4} and WSe₂, the new resonance found in the WS_{0.6}Se_{1.4} is of the same nature of the WSe₂ and is consistent with the reported value of the energy difference between 1s and

2s exciton of WSe₂ [68, 72]. The emerging resonance in the absorption spectra, which corresponds to the second resonance of the exciton-phonon coupling, was then confirmed to be the 2s state of the A exciton (Figure 13E, F). The Raman signals are therefore dramatically enhanced when the excitation is in resonance with the energy of the 2s state of A exciton.

6 Conclusions and perspective

The significant improvement of the sample quality greatly advances our understanding of many-particle excitonic physics in the TMDCs, enabled by the well-resolved and

Figure 12: Interlayer exciton-phonon interaction between h-BN and monolayer WSe₂. (A–C) PLE intensity as a function of the excess energy of the energy difference between the excitation source and emission for WSe₂/SiO₂, h-BN/WSe₂/SiO₂, and h-BN/WSe₂/h-BN/SiO₂ structures, respectively. Adapted from Chow et al. [22]. (D) Photoluminescence emission from h-BN/WSe₂/h-BN sandwiched structure under the excitation energies of 1.849, 1.857, and 1.862 eV. Two Raman peaks (green and orange arrows) emerge, and their peak positions shift linearly with the incident laser energy. (E) Reflection spectroscopy of h-BN/WSe₂/h-BN sandwiched structure (red) and pristine WSe₂ (black) at 77 K. A new peak at 1.85 eV emerges in the sandwiched structure due to the interlayer exciton-phonon coupling. (D, E) Adapted from Jin et al. [23].

tunable optical spectra signatures. The BN-encapsulated TMDC monolayer and associated vdW heterostructure devices therefore provide fascinating platforms to investigate the 2D excitonic physics and many-body interactions. Although many of the excitonic fine features have been revealed in monolayer TMDCs, how would they affect the optical spectra of the twisted bilayer TMDCs? Moiré potential, controlled by the twist angle of the

bilayer, has been shown to significantly modulate the intralayer or interlayer excitons. How would they affect the many-body physics such as the exciton-phonon interactions or exciton-polarons? Is it possible to use any of the many-body interactions to manipulate the valley degree of freedoms? Many intriguing questions remain to be addressed, and we expect to see even more exciting advancement in this field in the near future.

Figure 13: Excitonic states and exciton-phonon coupling in h-BN sandwiched WSe₂.

(A) Light emission of monolayer WS_{0.6}Se_{1.4} as a function of the gate voltage at 14 K. The monolayer alloy clearly shows the emissions of the exciton and trion. The trion also exhibits the fine structure of the intervalley and intravalley trions. (B) Gate voltage-dependent reflection spectroscopy of monolayer WS_{0.6}Se_{1.4}. Similar to the PL spectra, the reflection spectra show the absorption of exciton and trion, which also indicates the intervalley and intravalley trions fine structures. (C) The degree of valley polarization of exciton and trion from valley-resolved PL spectra as a function of the gate voltage. Both the valley polarization of exciton and trion increase with the gate voltage from -2 to 1 V. (D) Color plot of PL spectrum difference between the parallel and cross configuration as a function of the gate voltage at 77 K, which clearly presents the two Raman scattering peaks. (E) Gate voltage-dependent differential reflectance spectra of the monolayer WS_{0.6}Se_{1.4}. (F) Derivative of the differential reflectance spectra of the monolayer WS_{0.6}Se_{1.4} as a function of the gate voltage at 14 K. A new feature X* at ~1.945 eV shows up in the charge-neutral region, corresponding to the 2s state of A exciton.

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