

Exciton Dynamics in Janus WSSe Driven by Structural Asymmetry

Ufuk Erkilic^{1,2}, Shengnan Wang¹, Yoshiaki Sekine¹, Takashi Taniguchi³, Kenji Watanabe⁴ and Yoshitaka Taniyasu¹*

¹NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan

²Nanoscale Quantum Photonics Laboratory, RIKEN Pioneering Research Institute, Wako, Saitama 351-0198, Japan

³Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, Namiki, Tsukuba 305-0044, Japan

⁴Research Center for Electronic and Optical Materials, National Institute for Materials Science, Namiki, Tsukuba 305-0044, Japan

*Correspondence to: ufuk.erkilic@riken.jp

KEYWORDS: transition metal dichalcogenides, Janus, WSSe, exciton, dipole

ABSTRACT

Artificially engineered Janus transition metal dichalcogenides (TMDCs) feature distinct chalcogen atoms on their top and bottom layers that break mirror symmetry, which is expected to alter exciton dynamics and exciton–phonon interactions. Here, we present direct experimental evidence for the dipolar nature of excitons in high-quality Janus WSSe monolayers. Spatial imaging of exciton emission reveals that the exciton diffusion length in Janus WSSe is almost twice that of WS₂, which is attributed to electron–hole spatial separation induced by the intrinsic out-of-plane electric field. Furthermore, temperature-dependent photoluminescence measurements indicate significantly enhanced excitonic linewidth broadening of WSSe above 100 K, arising from stronger exciton–phonon scattering via additional optical phonons. These findings highlight the pivotal role of intrinsic structural asymmetry in governing radiative and non-radiative processes in Janus TMDCs and offer insights into their potential for excitonic device applications.

INTRODUCTION

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) with strong confinement and reduced Coulomb screening host bound electron-hole pairs (excitons) with large binding energies exceeding 500 meV, making them stable even at room-temperature^{1,2}. These intralayer excitons govern optical responses in TMDC monolayers, play a crucial role in determining light–matter interactions and carrier transport, and hold great potential for excitonic devices including light-emitting diodes and lasers.^{3–5} In TMDC heterostructures with type-II band alignment, on the other hand, spatially separated electron-hole pairs form electrically tunable interlayer

excitons with permanent out-of-plane dipole moments.⁶ Compared to intralayer excitons, these interlayer excitons have longer radiative recombination lifetime, diffusion length, and valley depolarization lifetime.^{7,8}

Artificially engineered Janus TMDCs, such as WSSe, introduce an additional degree of freedom to conventional TMDCs by incorporating structural asymmetry, which gives rise to an intrinsic electric field and modifies the phonon modes—which are predicted to significantly influence exciton dynamics and exciton–phonon interactions. In particular, the presence of an out-of-plane electric field is expected to alter the electron-hole wave function overlap and create dipolar intralayer excitons.^{9–12} Recent studies have shown longer exciton radiative recombination lifetimes in Janus TMDCs compared to conventional symmetric TMDCs, supporting previous theoretical predictions.^{13,14} These dipolar intralayer excitons can be considered as analogous to the interlayer excitons in TMDC heterostructures but benefit from a simpler monolayer structure that avoids moiré potential traps known to be detrimental to interlayer excitons.^{15–17} In this context, Janus TMDCs offer an appealing platform for applications requiring long exciton diffusion lengths combined with strong light absorption. However, due to challenges in growing high-quality and large-area Janus monolayers, a comprehensive assessment of the effect of structural asymmetry on the excitonic properties remains largely unexplored.

Here, we report the growth of high-quality Janus WSSe via a fully chemical vapor deposition (CVD)-based approach using a parent WS₂ monolayer. The CVD-grown WSSe and WS₂ monolayers are sandwiched between hBN layers. We then investigate the effect of intrinsic electric field on the excitonic properties of Janus WSSe by direct comparison with WS₂. The spatial extent of exciton diffusion is directly captured by using a spatially resolved photoluminescence (PL) imaging technique. We demonstrate that excitons in WSSe propagate

farther away from the excitation spot, creating a significantly wider exciton cloud compared to WS_2 excitons. This effect is attributed to the intrinsic electric field in Janus WSSe , which spatially separates electrons and holes, leading to the formation of dipolar excitons. This observation is further corroborated by the increased exciton diffusion length of WSSe at higher excitation densities, resulting from the repulsive interactions between dipolar excitons. Additionally, exciton linewidths in Janus WSSe exhibit a much stronger dependence on increasing temperature. The linewidth broadening is attributed to enhanced exciton-phonon interactions driven by additional scattering channels introduced by optical phonons due to the inherent out-of-plane asymmetry.

RESULTS AND DISCUSSION

Preparing high-quality hBN-encapsulated WSSe and WS_2 monolayers. Figure 1(a) illustrates the fabrication steps starting from the growth of the parent TMDC (WS_2) to encapsulation of TMDCs with hBN layers. First, WS_2 monolayer is grown on sapphire substrate by CVD. Subsequent selenization is performed in another chamber by exposing WS_2 to Se vapor under controlled temperatures (see Fig. S1 for details). Temperatures lower than 870°C typically do not lead to Janus structure but instead cause random selenization around the edges or grain domains. Substrate temperatures higher than 900°C typically cause complete conversion of WS_2 into WSe_2 with some randomly alloyed domains. A substrate temperature window of $870\text{--}900^\circ\text{C}$ was identified to achieve the Janus WSSe structure in our CVD reactor. In this range, we observe Janus WSSe formation and its progress, which starts from the edges of the monolayer or from the grain boundaries in the case of merged monolayers.

The transformation from WS₂ to Janus WSSe was confirmed by Raman spectroscopy as shown in Fig. 1(b). The Raman spectrum of WS₂ features typical 2LA+E_{2g} and A_{1g} modes at ~353 cm⁻¹ and ~418 cm⁻¹, respectively.¹⁸ After selenization, we observed the ¹A₁ mode at ~284 cm⁻¹, E² at ~329 cm⁻¹, and ²A₁ at ~420 cm⁻¹, which are characteristic of Janus WSSe.^{19,20} The absence of Raman modes related to WS₂, as well as the emergence of new Raman modes after selenization, confirms the formation of the Janus structure.

The Janus WSSe structure is further confirmed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) [Fig. 1(c)]. As S and Se atoms are aligned in the out-of-plane direction, the sample is tilted ~15° in X-Y plane to observe S and Se atomic contrasts. The inset is an enlarged STEM image with an overlapped WSSe atomic model. From the image, W, Se, and S atomic contrasts are clearly observed. In addition, we did not observe any chalcogenide defects within the scanned areas, which confirms that the parent WS₂ already has low defect density and that sample heating during the selenization process does not introduce defects to the bottom chalcogenide layer. In 0° tilt STEM images of WSSe and WS₂ (see Fig. S2), S₂ and S+Se atomic contrasts are also clearly distinguished from the line profiles.

To minimize the substrate induced doping and environment-related effects on the optical properties, WS₂ and WSSe monolayers are encapsulated between hBN layers, which provide a flat surface and protect the TMDCs from the environment.²¹ An optical image of a hBN/WSSe/hBN stack on SiO₂/Si substrate is shown in Fig. 1(d). To create this stack, we developed a delamination and transfer method, which enables the formation of clean interfaces without contamination (see Methods in SI). The PL spectra of hBN-encapsulated WS₂ and WSSe measured at RT are shown in Fig. 1(e) (see Figure S3 for the PL spectrum of as-grown samples). The WSSe PL emission energy is around 1.87 eV and that of WS₂ is around 1.99 eV. The PL

spectrum of both WSSe and WS₂ are well-fitted by two Voigt profiles, where we assign high energy peaks to neutral exciton (X^0) and low energy peaks to trion (X^T) emissions (see Fig. S4).^{22–24} From Voigt fitting we also determined the neutral exciton linewidths and peak position energies. Figure 1(f) compares exciton linewidths and peak position distributions obtained from large-area PL mapping (see Fig. S5) on as-grown and hBN encapsulated monolayers. Compared to the as-grown samples, linewidths in encapsulated samples are considerably narrower and show a very uniform distribution. For as-grown WSSe (WS₂), the average exciton linewidth is ~63 meV (~45 meV). For encapsulated WSSe, the average exciton linewidth is ~51 meV, while it is ~26 meV for encapsulated WS₂. The exciton linewidth of encapsulated WS₂ is comparable with those of exfoliated flakes (23–25 meV).²¹ This confirms the high quality of our as-grown WS₂, which we consider to be crucial for achieving high-quality Janus samples, as chalcogenide defects at the bottom layer and transition metal defects are inherited from WS₂. Further, the average linewidth of ~51 meV in encapsulated WSSe is one of the best values reported among all-CVD-grown Janus TMDCs and comparable to those synthesized using exfoliated TMDCs.^{25–27} We attribute this to the high crystal quality of the parent WS₂ and sequential selenization process that minimized defect formation (see Fig. S6).

Exciton diffusion in Janus WSSe. To investigate the effect of the intrinsic electric field induced by the out-of-plane asymmetry on the excitonic properties of Janus WSSe, we performed spatially resolved PL mapping, as it is a direct method to visualize the extent of exciton diffusion. Spatially resolved PL images of WS₂ and WSSe taken at 77 K are shown in Fig. 2(a) along with an intensity distribution of a 532-nm excitation laser as a reference. The data were acquired from an area of WSSe grain where PL intensity is strong and linewidth that corresponds to the overall average to minimize the effect of local inhomogeneities (see Fig. S4).

The spatially resolved PL images from WS₂ are comparable to that of the laser; there is only a slight widening of the emission from the excitation spot. For WSSe, however, PL emission extends significantly farther away from the excitation spot. We note that the PL emission of WSSe is slightly elongated along the y-axis, likely due to the measurement spot being positioned near the flake edge, which restricted exciton diffusion along the x-direction closer to the edge. Figure 2(b) shows the emission intensities as a function of radial distance (r), which were extracted by averaging PL line profiles along the x and y -axis from the spatial images acquired at 5- μ W excitation power. From the radial profiles, it becomes clear that WSSe PL emission comes from a broader area compared to WS₂, suggesting increased diffusivity of excitons. The exciton diffusion length (L_D) in a 2D system can be calculated by using the relation,^{28,29}

$$L_D = \sqrt{\sigma^2 - \sigma_{\text{Laser}}^2} \quad (1)$$

where σ and σ_{Laser} are Gaussian covariances that fit the line profiles of the TMDC PL intensity and the laser profile, respectively. We fitted each profile in Fig. 2(b) with a Gaussian function and extracted the profile widths as the variance. From the fits, we found diffusion lengths of ~ 0.6 μm for WS₂ and ~ 1.1 μm for WSSe. The diffusion length of excitons in WS₂ agrees well with the previously reported values,^{30–32}

The radiative recombination rate, hence the exciton diffusion length, of a monolayer TMDC is proportional to the square of the electron-hole wavefunction overlap probability, $|\phi^{e,h}(r=0)|^2$ (r is the relative distance).^{33,34} We note that the L_D is determined by the recombination lifetime and the diffusion coefficient, which are affected by radiative recombination process and non-radiative recombination processes such as exciton-phonon scattering.³⁵ Since the diffusion length measurements are conducted at 77 K—where exciton-phonon interactions are significantly

suppressed in both WS₂ and WSSe as discussed below—we attribute the difference in diffusion length primarily to the intrinsic out-of-plane electric field in Janus WSSe. As illustrated in Fig. 2(c), electron (ψ^e) and hole (ψ^h) wavefunctions in monolayer TMDCs overlap, causing short exciton lifetimes and diffusion lengths. On the other hand, excitons in Janus WSSe monolayers resemble the interlayer excitons in TMDC heterostructures.³⁶ We consider that the intrinsic electric field caused by structural asymmetry in Janus WSSe spatially separates electron and hole of exciton as it pushes the carriers to opposite directions within the monolayer and reduces the spatial overlap of ψ^e and ψ^h as shown in Fig. 2(d). In the case of Janus TMDCs, the separation of electrons and holes lowers the radiative recombination rate by decreasing $|\phi^{e,h}(r=0)|^2$ and giving relatively weaker oscillator strengths. This leads to a longer exciton lifetime, allowing excitons to diffuse farther into the Janus TMDC lattice [Figure 2(a) and (b)].¹⁴

We now turn our attention to the excitation power dependence of exciton diffusion, which provides insights into exciton–exciton interactions. Representative spatial PL images taken at excitation powers of 5 μW and 88 μW are shown in Fig. 3(a) and (b), respectively. At the highest excitation density, the PL signal from WSSe expands significantly farther from the excitation spot, while no noticeable change is observed in the PL signal of WS₂. Figure 3(c) shows the PL line profiles of WSSe at various excitation powers (see Fig. S7 for WS₂ line profiles). The extracted diffusion lengths from line profiles are plotted Fig. 3(d) as a function of excitation power. L_D of WS₂ does not show any clear excitation power dependence with an average value of $\sim 0.6 \mu\text{m}$. In contrast, while the L_D of WSSe exhibits small variation at lower excitation powers, it shows a significant increase at higher excitation densities, reaching approximately $1.6 \mu\text{m}$ at 88 μW , where exciton–exciton interactions become dominant. This further confirms the dipolar nature of excitons in WSSe, as repulsive dipole interactions result in

longer diffusion lengths with increasing exciton density.^{36–38} Although a clear increase in exciton diffusion length was observed in WSSe with increasing excitation power—consistent with exciton–exciton repulsion—the PL spectra did not exhibit a noticeable blue shift (see Fig. S8). This behavior may be attributed to band renormalization in WSSe that compensates the blue shift due to stronger exciton–phonon coupling as discussed below, and/or dominant trion emission at higher excitation powers, where trion emission shows a super-linear power dependence (see Fig. S4).

Exciton-phonon interactions. The structural asymmetry not only affects the radiative recombination but also non-radiative recombination processes such as phonon scattering, as it introduces new Raman modes that excitons can scatter. The exciton linewidth, in this context, is an important parameter to understand exciton dynamics as it is directly related to the intrinsic features of the exciton and its interactions with the phonons.³⁹ We performed temperature-dependent PL measurements and investigated the evolution of exciton linewidth and exciton energy with temperature. In Fig. 4(a) and (b), we plot the PL spectra at various temperatures ranging from 4 K to room temperature for encapsulated WS₂ and WSSe, respectively. The X⁰ linewidth is as narrow as 23 meV for WSSe at 4K (see Fig. S9) with a clear red shift of its emission energy with increasing temperature. Figure 4(c) and (d) plot the temperature dependence of X⁰ emission energies and linewidths for WS₂ and WSSe, respectively. The temperature dependence of the X⁰ emission energy is fitted by the semiempirical formula given by,⁴⁰

$$E_g = E_g(0) - S\langle\hbar\omega\rangle\left[\coth\left(\frac{\langle\hbar\omega\rangle}{2k_B T}\right) - 1\right] \quad (2)$$

where $E_g(0)$ is the PL peak energy at 0 K, S is a dimensionless coupling constant related to the strength of exciton-phonon coupling, $\langle\hbar\omega\rangle$ is the average phonon energy, k_B is the Boltzmann constant, and T is temperature. For WS_2 , the fit gives $E_g(0) = 2.05$ eV, $S = 1.7$, and $\langle\hbar\omega\rangle = 0.0128$ eV. For WSSe , it gives $E_g(0) = 1.932$ eV, $S = 1.9$, and $\langle\hbar\omega\rangle = 0.0186$ eV (see Table S1). The higher value of S for WSSe indicates a stronger exciton-phonon interaction in WSSe compared to WS_2 .

For both WS_2 and WSSe , linewidth broadens with increasing temperature, which is caused by the exciton scattering through phonons. In the case of WSSe , linewidth broadening above 100 K is much more drastic than at WS_2 . The linewidth broadening due to exciton-phonon scattering can be described by the following relation,^{41,42}

$$\Gamma = \Gamma_0 + AT + \frac{B}{\exp\left(\frac{\langle\hbar\omega\rangle}{k_B T}\right) - 1} \quad (3)$$

where Γ_0 is the temperature-independent contribution to the linewidth broadening, and A and B are the exciton-phonon coupling constants for the acoustic and optical phonons, respectively. From the fitting, we extract the values for WS_2 as $\Gamma_0 = 11.5$ meV, $A = 0.021$ meV/K, and $B = 5.8$ meV. For WSSe , the extracted values are $\Gamma_0 = 23.5$ meV, $A = 0.024$ meV/K, and $B = 26.02$ meV. We note that the Γ_0 of WSSe is much larger than that of WS_2 . Although we were able to achieve a significantly narrower linewidth in Janus WSSe through hBN encapsulation and defect reduction via a sequential selenization process, compared to previous reports, we consider that the defect density in Janus WSSe is higher than parent material WS_2 . As a result, the temperature-independent linewidth component (Γ_0) in Janus WSSe is larger, attributed to inhomogeneous broadening caused by residual defects.^{41,43} Using the values obtained from the

fitting, we calculated the contribution of acoustic and optical phonon scattering to the linewidth broadening at room temperature, and we compare the results for WSSe and WS₂ in Fig. 4(e). Here, it becomes clear that linewidth broadening through optical phonons is much more prominent in Janus WSSe. In WS₂ monolayer, carrier scattering at elevated temperatures (>100 K) takes places through longitudinal (LO) phonons via the Fröhlich interaction.^{44,45} In the case of Janus WSSe, we consider that enhanced phonon coupling might be due to the additional scattering channels introduced by the emergence of new Raman modes arising from out-of-plane symmetry breaking. In Janus WSSe, we observe two out-of-plane Raman modes, namely ¹A₁ (ZO₁) and ²A₁ (ZO₂) (Fig. 1(b) and Fig. S10). A recent theoretical study on Janus MoSSe has shown significantly large carrier scattering rates originating in zone-center optical phonons (the ZO₁ mode in particular) compared to those of MoS₂.⁴⁶ In addition, exciton formation time in Janus TMDCs has been found to be 30% faster than their conventional counterparts,¹³ which can be attributed to enhanced phonon scattering.⁴⁷ As illustrated in Fig. 4(f), in addition to LO phonons, extra scattering channels from ZO phonon modes may lead to enhanced exciton-phonon scattering, causing significantly broader linewidths of WSSe at room temperature compared to its parent WS₂.

In summary, we experimentally demonstrated the dipolar nature of excitons in Janus WSSe monolayers. The intrinsic electric field reduces the overlap of electron-hole wavefunctions, allowing excitons to diffuse over greater distances. As a result, the exciton diffusion length in Janus WSSe is significantly larger compared to WS₂. At higher excitation densities, the exciton diffusion length increases further due to enhanced interactions between dipolar excitons in Janus WSSe. Additionally, the enhanced exciton-phonon coupling observed in WSSe likely originate from the crystal asymmetry, which reshape phonon scattering dynamics. Our findings provide

direct experimental evidence supporting theoretical predictions that Janus TMDCs host dipolar excitons with distinct transport and recombination characteristics arising from their distinctive structural asymmetry. These unique features of Janus excitons position them between the strongly bound intralayer excitons in conventional TMDCs and the interlayer excitons in TMDC heterostructures, where moiré potentials localize excitons, effectively shortening their diffusion length despite their substantially longer lifetimes compared to intralayer excitons.¹⁵ In contrast, the monolayer structure of Janus TMDCs provides a uniform potential landscape for excitons while retaining the benefits of an intrinsic dipole. In this context, dipolar excitons in Janus TMDCs can be ideal for photodetectors and photovoltaic applications where long exciton diffusion and high absorption efficiency are needed.⁴⁸ As recently suggested by theoretical calculations, by stacking a few layers of Janus TMDCs, electron and hole separation can be further enhanced and even lead to the creation of intrinsic p-n junctions.⁴⁹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at

Detailed experimental methods; CVD setup schematic; large area STEM images and ADF intensity profiles of WS₂ and WS_{Se}; PL spectra of as-grown samples; power dependent PL spectra at room temperature; details of the PL mapping; details of the selenization process; power dependent PL line profiles of WS₂; power dependent PL spectra at 4 K; PL spectra of WS_{Se} and WS₂ at 4 K; circularly polarized Raman spectra; summary of fitting parameters

(PDF).

AUTHOR INFORMATION

Corresponding Author

Ufuk Erkılıç – NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan; Nanoscale Quantum Photonics Laboratory, RIKEN Pioneering Research Institute, Wako, Saitama 351-0198, Japan

Email: ufuk.erkilic@riken.jp

Author Contributions

The manuscript was written through contributions of all authors. All authors approved the final version of the manuscript.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGEMENTS

We thank Y. Krockenberger and Y. Endo for the help with low temperature PL measurements and fruitful discussions. T.T. and K.W. acknowledge support from the JSPS KAKENHI (Grant Numbers 21H05233 and 23H02052), the CREST (JPMJCR24A5), JST and World Premier International Research Center Initiative (WPI), MEXT, Japan.

REFERENCES

- (1) Zhu, B.; Chen, X.; Cui, X. Exciton Binding Energy of Monolayer WS₂. *Sci. Rep.* **2015**, *5* (1), 9218. <https://doi.org/10.1038/srep09218>.
- (2) Cheiwchanchamnangij, T.; Lambrecht, W. R. L. Quasiparticle Band Structure Calculation of Monolayer, Bilayer, and Bulk MoS₂. *Phys. Rev. B* **2012**, *85*, 205302. <https://doi.org/10.1103/PhysRevB.85.205302>.
- (3) Schneider, C.; Glazov, M. M.; Korn, T.; Höfling, S.; Urbaszek, B. Two-Dimensional Semiconductors in the Regime of Strong Light-Matter Coupling. *Nat. Commun.* **2018**, *9*, 2695. <https://doi.org/10.1038/s41467-018-04866-6>.
- (4) Britnell, L.; Ribeiro, R. M.; Eckmann, A.; Jalil, R.; Belle, B. D.; Mishchenko, A.; Kim, Y.-J.; Gorbachev, R. V.; Georgiou, T.; Morozov, S. V.; Grigorenko, A. N.; Geim, A. K.; Casiraghi, C.; Neto, A. H. C.; Novoselov, K. S. Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films. *Science* **2013**, *340* (6138), 1311–1314. <https://doi.org/10.1126/science.1235547>.
- (5) Ye, Y.; Wong, Z. J.; Lu, X.; Ni, X.; Zhu, H.; Chen, X.; Wang, Y.; Zhang, X. Monolayer Excitonic Laser. *Nat. Photonics* **2015**, *9*, 733–737. <https://doi.org/10.1038/nphoton.2015.197>.
- (6) Jin, C.; Ma, E. Y.; Karni, O.; Regan, E. C.; Wang, F.; Heinz, T. F. Ultrafast Dynamics in van Der Waals Heterostructures. *Nat. Nanotechnol.* **2018**, *13*, 994–1003. <https://doi.org/10.1038/s41565-018-0298-5>.
- (7) Rivera, P.; Schaibley, J. R.; Jones, A. M.; Ross, J. S.; Wu, S.; Aivazian, G.; Klement, P.; Seyler, K.; Clark, G.; Ghimire, N. J.; Yan, J.; Mandrus, D. G.; Yao, W.; Xu, X. Observation of Long-Lived Interlayer Excitons in Monolayer MoSe₂–WSe₂ Heterostructures. *Nat. Commun.* **2015**, *6*, 6242. <https://doi.org/10.1038/ncomms7242>.
- (8) Jin, C.; Kim, J.; Iqbal Bakti Utama, M.; Regan, E. C.; Kleemann, H.; Cai, H.; Shen, Y.; Shinner, M. J.; Sengupta, A.; Watanabe, K.; Taniguchi, T.; Tongay, S.; Zettl, A.; Wang, F. Imaging of Pure Spin-Valley Diffusion Current in WS₂-WSe₂ Heterostructures. *Science* **2018**, *360* (6391), 893–896. <https://doi.org/10.1126/science.aao3503>.

- (9) Lu, A. Y.; Zhu, H.; Xiao, J.; Chuu, C. P.; Han, Y.; Chiu, M. H.; Cheng, C. C.; Yang, C. W.; Wei, K. H.; Yang, Y.; Wang, Y.; Sokaras, D.; Nordlund, D.; Yang, P.; Muller, D. A.; Chou, M. Y.; Zhang, X.; Li, L. J. Janus Monolayers of Transition Metal Dichalcogenides. *Nat. Nanotechnol.* **2017**, *12*, 744–749. <https://doi.org/10.1038/nnano.2017.100>.
- (10) Riis-Jensen, A. C.; Deilmann, T.; Olsen, T.; Thygesen, K. S. Classifying the Electronic and Optical Properties of Janus Monolayers. *ACS Nano* **2019**, *13*, 13354–13364. <https://doi.org/10.1021/acsnano.9b06698>.
- (11) Xia, C.; Xiong, W.; Du, J.; Wang, T.; Peng, Y.; Li, J. Universality of Electronic Characteristics and Photocatalyst Applications in the Two-Dimensional Janus Transition Metal Dichalcogenides. *Phys. Rev. B* **2018**, *98*, 165424. <https://doi.org/10.1103/PhysRevB.98.165424>.
- (12) Li, F.; Wei, W.; Wang, H.; Huang, B.; Dai, Y.; Jacob, T. Intrinsic Electric Field-Induced Properties in Janus MoSSe van Der Waals Structures. *J. Phys. Chem. Lett.* **2019**, *10*, 559–565. <https://doi.org/10.1021/acs.jpcclett.8b03463>
- (13) Zheng, T.; Lin, Y.-C.; Yu, Y.; Valencia-Acuna, P.; Puretzky, A. A.; Torsi, R.; Liu, C.; Ivanov, I. N.; Duscher, G.; Geohegan, D. B.; Ni, Z.; Xiao, K.; Zhao, H. Excitonic Dynamics in Janus MoSSe and WSSe Monolayers. *Nano Lett.* **2021**, *21*, 931–937. <https://doi.org/10.1021/acs.nanolett.0c03412>.
- (14) Jin, H.; Wang, T.; Gong, Z. R.; Long, C.; Dai, Y. Prediction of an Extremely Long Exciton Lifetime in a Janus-MoSTe Monolayer. *Nanoscale* **2018**, *10*, 19310–19315. <https://doi.org/10.1039/c8nr04568b>.
- (15) Choi, J.; Hsu, W.-T.; Lu, L.-S.; Sun, L.; Cheng, H.-Y.; Lee, M.-H.; Quan, J.; Tran, K.; Wang, C.-Y.; Staab, M.; Jones, K.; Taniguchi, T.; Watanabe, K.; Chu, M.-W.; Gwo, S.; Kim, S.; Shih, C.-K.; Li, X.; Chang, W.-H. Moiré Potential Impedes Interlayer Exciton Diffusion in van Der Waals Heterostructures. *Sci. Adv.* **2020**, *6*, eaba8866. <https://doi.org/10.1126/sciadv.aba8866>.
- (16) Yuan, L.; Zheng, B.; Kunstmann, J.; Brumme, T.; Kuc, A. B.; Ma, C.; Deng, S.; Blach, D.; Pan, A.; Huang, L. Twist-Angle-Dependent Interlayer Exciton Diffusion in WS₂-WSe₂ Heterobilayers. *Nat. Mater.* **2020**, *19*, 617–623. <https://doi.org/10.1038/s41563-020-0670-3>.

- (17) Lu, X.; Li, X.; Yang, L. Modulated Interlayer Exciton Properties in a Two-Dimensional Moiré Crystal. *Phys. Rev. B* **2019**, *100* (15), 155416. <https://doi.org/10.1103/PhysRevB.100.155416>.
- (18) Berkdemir, A.; Gutiérrez, H. R.; Botello-Méndez, A. R.; Perea-López, N.; Elías, A. L.; Chia, C.-I.; Wang, B.; Crespi, V. H.; López-Urías, F.; Charlier, J.-C.; Terrones, H.; Terrones, M. Identification of Individual and Few Layers of WS₂ Using Raman Spectroscopy. *Sci. Rep.* **2013**, *3*, 1755. <https://doi.org/10.1038/srep01755>.
- (19) Petrić, M. M.; Kremser, M.; Barbone, M.; Qin, Y.; Sayyad, Y.; Shen, Y.; Tongay, S.; Finley, J. J.; Botello-Méndez, A. R.; Müller, K. Raman Spectrum of Janus Transition Metal Dichalcogenide Monolayers WSSe and MoSSe. *Phys. Rev. B* **2021**, *103* (3), 035414. <https://doi.org/10.1103/PhysRevB.103.035414>.
- (20) Lin, Y.-C.; Liu, C.; Yu, Y.; Zarkadoula, E.; Yoon, M.; Puretzky, A. A.; Liang, L.; Kong, X.; Gu, Y.; Strasser, A.; Meyer, H. M.; Lorenz, M.; Chisholm, M. F.; Ivanov, I. N.; Rouleau, C. M.; Duscher, G.; Xiao, K.; Geohegan, D. B. Low Energy Implantation into Transition-Metal Dichalcogenide Monolayers to Form Janus Structures. *ACS Nano* **2020**, *14*, 3896–3906. <https://doi.org/10.1021/acsnano.9b10196>.
- (21) Cadiz, F.; Courtade, E.; Robert, C.; Wang, G.; Shen, Y.; Cai, H.; Taniguchi, T.; Watanabe, K.; Carrere, H.; Lagarde, D.; Manca, M.; Amand, T.; Renucci, P.; Tongay, S.; Marie, X.; Urbaszek, B. Excitonic Linewidth Approaching the Homogeneous Limit in MoS₂-Based van Der Waals Heterostructures. *Phys. Rev. X* **2017**, *7* (2), 021026. <https://doi.org/10.1103/PhysRevX.7.021026>.
- (22) Sebait, R.; Biswas, C.; Song, B.; Seo, C.; Lee, Y. H. Identifying Defect-Induced Trion in Monolayer WS₂ via Carrier Screening Engineering. *ACS Nano* **2021**, *15* (2), 2849–2857. <https://doi.org/10.1021/acsnano.0c08828>.
- (23) Plechinger, G.; Nagler, P.; Kraus, J.; Paradiso, N.; Strunk, C.; Schüller, C.; Korn, T. Identification of Excitons, Trions and Biexcitons in Single-Layer WS₂. *Phys. Status Solidi RRL* **2013**, *9* (8), 457–461. <https://doi.org/10.1002/pssr.201510224>.

(24) Shang, J.; Shen, X.; Cong, C.; Peimyoo, N.; Cao, B.; Eginligil, M.; Yu, T. Observation of Excitonic Fine Structure in a 2D Transition-Metal Dichalcogenide Semiconductor. *ACS Nano* **2015**, *9* (1), 647–655. <https://doi.org/10.1021/nn5059908>.

(25) Trivedi, D. B.; Turgut, G.; Qin, Y.; Sayyad, M. Y.; Hajra, D.; Howell, M.; Liu, L.; Yang, S.; Patoary, N. H.; Li, H.; Petrić, M. M.; Meyer, M.; Kremser, M.; Barbone, M.; Soavi, G.; Stier, A. V.; Müller, K.; Yang, S.; Esqueda, I. S.; Zhuang, H.; Finley, J. J.; Tongay, S. Room-Temperature Synthesis of 2D Janus Crystals and Their Heterostructures. *Adv. Mater* **2020**, *32*, 2006320. <https://doi.org/10.1002/adma.202006320>.

(26) Qin, Y.; Sayyad, M.; R-P Montblanch, A.; G Feuer, M. S.; Dey, D.; Blei, M.; Sailus, R.; Kara, D. M.; Shen, Y.; Yang, S.; Botana, A. S.; Atature, M.; Tongay, S.; Qin, Y.; Sayyad, M.; Blei, M.; Sailus, R.; Shen, Y.; Yang, S.; Tongay, S.; R-P Montblanch, A.; G Feuer, M. S.; Kara, D. M.; Atature, M.; Dey, D.; Botana, A. S. Reaching Excitonic Limit in 2D Janus Monolayers by In-Situ Deterministic Growth. *Adv. Mater.* **2021**, 2106222. <https://doi.org/10.1002/ADMA.202106222>.

(27) Gan, Z.; Paradisanos, I.; Estrada-Real, A.; Picker, J.; Najafidehaghani, E.; Davies, F.; Neumann, C.; Robert, C.; Wiecha, P.; Watanabe, K.; Taniguchi, T.; Marie, X.; Biskupek, J.; Mundszinger, M.; Leiter, R.; Kaiser, U.; Krasheninnikov, A. V.; Urbaszek, B.; George, A.; Turchanin, A. Chemical Vapor Deposition of High-Optical-Quality Large-Area Monolayer Janus Transition Metal Dichalcogenides. *Adv. Mater.* **2022**, 2205226. <https://doi.org/10.1002/ADMA.202205226>.

(28) Penzo, E.; Loiudice, A.; Barnard, E. S.; Borys, N. J.; Jurow, M. J.; Lorenzon, M.; Rajzbaum, I.; Wong, E. K.; Liu, Y.; Schwartzberg, A. M.; Cabrini, S.; Whitelam, S.; Buonsanti, R.; Weber-Bargioni, A. Long-Range Exciton Diffusion in Two-Dimensional Assemblies of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* **2020**, *14*, 6999–7007. <https://doi.org/10.1021/acsnano.0c01536>.

(29) Rossi, A.; Zipfel, J.; Maity, I.; Lorenzon, M.; Dandu, M.; Barré, E.; Francaviglia, L.; Regan, E. C.; Zhang, Z.; Nie, J. H.; Barnard, E. S.; Watanabe, K.; Taniguchi, T.; Rotenberg, E.; Wang, F.; Lischner, J.; Raja, A.; Weber-Bargioni, A. Anomalous Interlayer Exciton Diffusion in

WS₂/WSe₂ Moiré Heterostructure. *ACS Nano* **2024**, *18*, 18202–18210. <https://doi.org/10.1021/acsnano.4c00015>.

(30) Uddin, S. Z.; Higashitarumizu, N.; Kim, H.; Yi, J.; Zhang, X.; Chrzan, D.; Javey, A. Enhanced Neutral Exciton Diffusion in Monolayer WS₂ by Exciton-Exciton Annihilation. *ACS Nano* **2022**, *16*, 8005–8011. <https://doi.org/10.1021/acsnano.2c00956>.

(31) Kulig, M.; Zipfel, J.; Nagler, P.; Blanter, S.; Schüller, C.; Korn, T.; Paradiso, N.; Glazov, M. M.; Chernikov, A. Exciton Diffusion and Halo Effects in Monolayer Semiconductors. *Phys. Rev. Lett.* **2018**, *120* (20), 207401. <https://doi.org/10.1103/PhysRevLett.120.207401>.

(32) Zipfel, J.; Kulig, M.; Perea-Causín, R.; Brem, S.; Ziegler, J. D.; Rosati, R.; Taniguchi, T.; Watanabe, K.; Glazov, M. M.; Malic, E.; Chernikov, A. Exciton Diffusion in Monolayer Semiconductors with Suppressed Disorder. *Phys. Rev. B* **2020**, *101* (11), 115430. <https://doi.org/10.1103/PhysRevB.101.115430>.

(33) Leppenen, N. V.; Golub, L. E.; Ivchenko, E. L. Exciton Oscillator Strength in Two-Dimensional Dirac Materials. *Phys. Rev. B* **2020**, *102* (15), 155305. <https://doi.org/10.1103/PhysRevB.102.155305>.

(34) Rosati, R.; Paradisanos, I.; Huang, L.; Gan, Z.; George, A.; Watanabe, K.; Taniguchi, T.; Lombez, L.; Renucci, P.; Turchanin, A.; Urbaszek, B.; Malic, E. Interface Engineering of Charge-Transfer Excitons in 2D Lateral Heterostructures. *Nat. Commun.* **2023**, *14*, 2438. <https://doi.org/10.1038/s41467-023-37889-9>.

(35) Li, J.; Yang, R.; Li, R.; Grigoropoulos, C. P. Exciton Dynamics in 2D Transition Metal Dichalcogenides. *Adv. Opt. Mater.* **2025**, *13*, 2403137. <https://doi.org/10.1002/adom.202403137>.

(36) Jauregui, L. A.; Joe, A. Y.; Pistunova, K.; Wild, D. S.; High, A. A.; Zhou, Y.; Scuri, G.; de Greve, K.; Sushko, A.; Yu, C. H.; Taniguchi, T.; Watanabe, K.; Needleman, D. J.; Lukin, M. D.; Park, H.; Kim, P. Electrical Control of Interlayer Exciton Dynamics in Atomically Thin Heterostructures. *Science* **2019**, *366*, 870–875. <https://doi.org/10.1126/science.aaw4194>.

(37) Chand, S. B.; Woods, J. M.; Quan, J.; Mejia, E.; Taniguchi, T.; Watanabe, K.; Alù, A.; Grosso, G. Interaction-Driven Transport of Dark Excitons in 2D Semiconductors with Phonon-

Mediated Optical Readout. *Nat. Commun.* **2023**, *14*, 3712. <https://doi.org/10.1038/s41467-023-39339-y>.

(38) Javey, A.; Uddin, S. Z.; Kim, H.; Lorenzon, M.; Yeh, M.; Lien, D. H.; Barnard, E. S.; Htoon, H.; Weber-Bargioni, A. Neutral Exciton Diffusion in Monolayer MoS₂. *ACS Nano* **2020**, *14*, 13433–13440. <https://doi.org/10.1021/acsnano.0c05305>.

(39) Raja, A.; Selig, M.; Bergha, G.; Yu, J.; Hill, H. M.; Rigosi, A. F.; Brus, L. E.; Knorr, A.; Heinz, T. F.; Malic, E.; Chernikov, A. Enhancement of Exciton–Phonon Scattering from Monolayer to Bilayer WS₂. *Nano Lett.* **2018**, *18*, 6135–6143. <https://doi.org/10.1021/acs.nanolett.8b01793>.

(40) O'Donnell, K. P.; Chen, X. Temperature Dependence of Semiconductor Band Gaps. *Appl. Phys. Lett.* **1991**, *58* (25), 2924–2926. <https://doi.org/10.1063/1.104723>.

(41) Selig, M.; Berghäuser, G.; Raja, A.; Nagler, P.; Schüller, C.; Heinz, T. F.; Korn, T.; Chernikov, A.; Malic, E.; Knorr, A. Excitonic Linewidth and Coherence Lifetime in Monolayer Transition Metal Dichalcogenides. *Nat. Commun.* **2016**, *7*, 13279. <https://doi.org/10.1038/ncomms13279>.

(42) Selig, M.; Berghäuser, G.; Richter, M.; Bratschitsch, R.; Knorr, A.; Malic, E. Dark and Bright Exciton Formation, Thermalization, and Photoluminescence in Monolayer Transition Metal Dichalcogenides. *2D Mater.* **2018**, *5*, 035017. <https://doi.org/10.1088/2053-1583/aabea3>.

(43) Moody, G.; Kavir Dass, C.; Hao, K.; Chen, C.-H.; Li, L.-J.; Singh, A.; Tran, K.; Clark, G.; Xu, X.; Berghäuser, G.; Malic, E.; Knorr, A.; Li, X. Intrinsic Homogeneous Linewidth and Broadening Mechanisms of Excitons in Monolayer Transition Metal Dichalcogenides. *Nat. Commun.* **2015**, *6* (1), 8315. <https://doi.org/10.1038/ncomms9315>.

(44) Miller, B.; Lindlau, J.; Bommert, M.; Neumann, A.; Yamaguchi, H.; Holleitner, A.; Högele, A.; Wurstbauer, U. Tuning the Fröhlich Exciton-Phonon Scattering in Monolayer MoS₂. *Nat. Commun.* **2019**, *10*, 807. <https://doi.org/10.1038/s41467-019-08764-3>.

- (45) Thilagam, A. Exciton Formation Assisted by Longitudinal Optical Phonons in Monolayer Transition Metal Dichalcogenides. *J. Appl. Phys.* **2016**, *120* (12), 124306. <https://doi.org/10.1063/1.4963123>.
- (46) Guo, R.; Bu, X.; Wang, S.; Zhao, G. Enhanced Electron–Phonon Scattering in Janus MoSSe. *New. J. Phys.* **2019**, *21*, 113040. <https://doi.org/10.1088/1367-2630/ab54a6>.
- (47) Trovatiello, C.; Katsch, F.; Borys, N. J.; Selig, M.; Yao, K.; Borrego-Varillas, R.; Scotognella, F.; Kriegel, I.; Yan, A.; Zettl, A.; Schuck, P. J.; Knorr, A.; Cerullo, G.; Conte, S. D. The Ultrafast Onset of Exciton Formation in 2D Semiconductors. *Nat. Commun.* **2020**, *11*, 5277. <https://doi.org/10.1038/s41467-020-18835-5>.
- (48) Liu, C.; Liang, T.; Sui, X.; Du, L.; Guo, Q.; Xue, G.; Huang, C.; You, Y.; Yao, G.; Zhao, M.; Yin, J.; Sun, Z.; Hong, H.; Wang, E.; Liu, K. Anomalous Photovoltaics in Janus MoSSe Monolayers. *Nat. Commun.* **2025**, *16*, 544. <https://doi.org/10.1038/s41467-024-55623-x>.
- (49) Palsgaard, M.; Gunst, T.; Markussen, T.; Thygesen, K. S.; Brandbyge, M. Stacked Janus Device Concepts: Abrupt pn-Junctions and Cross-Plane Channels. *Nano Lett.* **2018**, *18*, 7275–7281. <https://doi.org/10.1021/acs.nanolett.8b03474>.

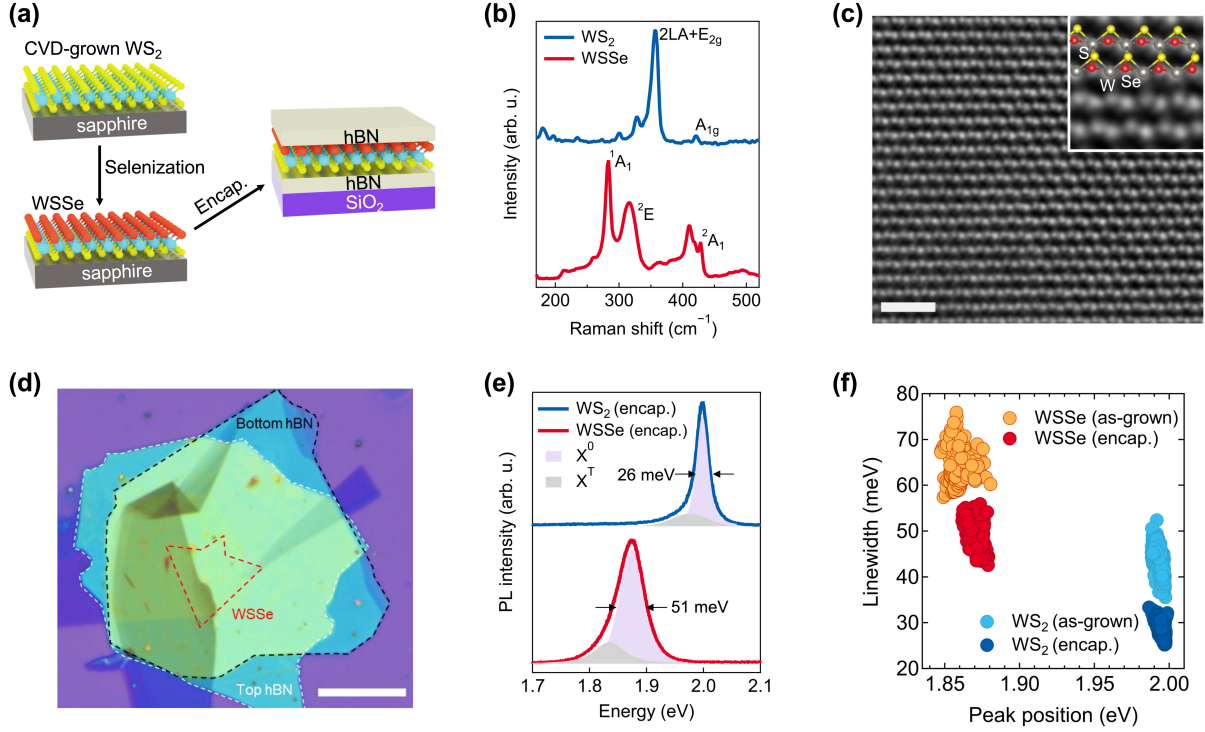


Figure 1. CVD growth and optical quality of Janus WSe₂. (a) An illustration of the steps involved for growing Janus WSe₂ and hBN encapsulation. (b) Raman spectra of as-grown monolayer WS₂ (blue) and WSe₂ (red). (c) Tilted HAADF-STEM image of WSe₂. The inset is an enlarged image and an atomic model of WSe₂ overlaid on the image. Scale bar is 1 nm. (d) Optical micrograph of WSe₂ encapsulated by hBN layers on SiO₂/Si substrate. Black and white dashed lines highlight the bottom and top hBN layers, respectively. The red dashed line marks the WSe₂ monolayer. Scale bar is 10 μ m. (e) PL spectra of hBN encapsulated WS₂ (blue) and WSe₂ (red). Both PL spectra are fitted with two Voigt functions. The low-energy and high-energy peaks are assigned to trion (X^T) and exciton (X⁰) emissions, respectively. (f) X⁰ peak position and linewidth distribution of hBN encapsulated WS₂ and WSe₂ in comparison with as-grown samples. The data were extracted from large area PL maps.

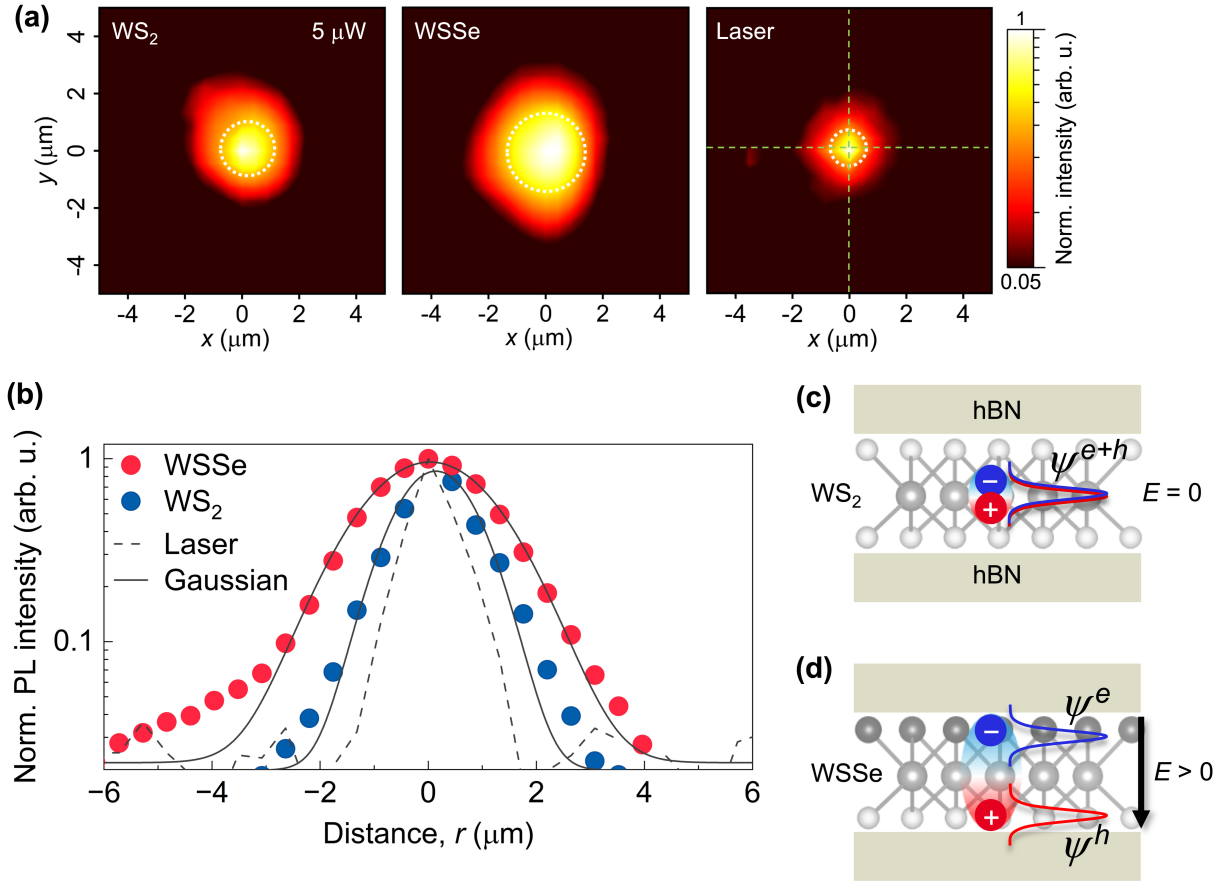


Figure 2. Spatial PL imaging. (a) Spatial PL images of the encapsulated WS₂ and WSe captured by a CCD camera at 77 K. All PL images were acquired with an excitation power of 5 μW. White dashed circles correspond to $\sim 1/e$ of the maximum PL intensity. (b) Normalized PL intensity profile of WS₂ (blue dots) and WSe (red dots). The laser profile is shown by grey dashed line. PL profiles extracted from the PL images given by averaging radial profiles along the x and y axis as shown by the green dashed lines in panel (a). PL profiles are fitted by a Gaussian function to extract diffusion lengths according to Eq. (2). (c) and (d) Atomic model illustrations of hBN encapsulated WS₂ and WSe monolayers, respectively. Wavefunctions of electrons (ψ^e) and holes (ψ^h) are overlapped in WS₂, while for WSe, the intrinsic electric field (E) pointing from Se to S atoms separates the electrons and holes.

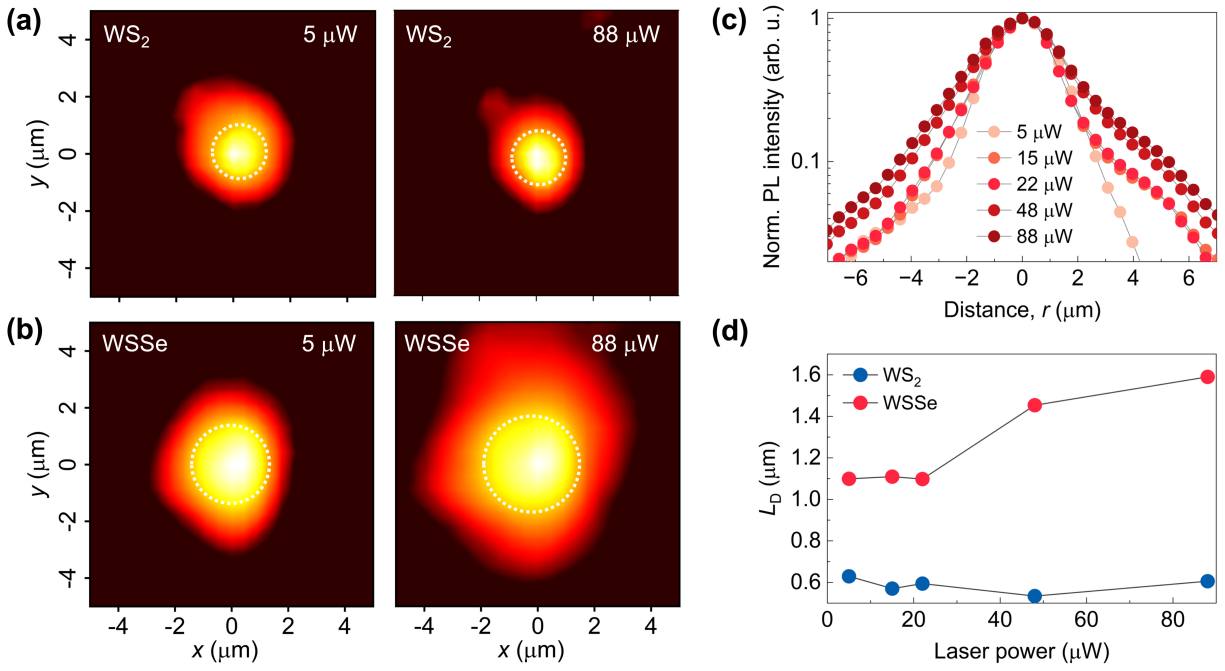


Figure 3. Excitation power dependence of diffusion length. (a) and (b) Spatial PL images of WS₂ and WSSe obtained at 5 and 88 μW, respectively. For WSSe, the exciton cloud becomes noticeably wider at 88 μW, whereas no significant change is observed in WS₂. (c) PL line profiles at various excitation powers for WSSe. (d) Excitation power dependence of diffusion length (L_D) for WS₂ (blue dots) and WSSe (red dots).

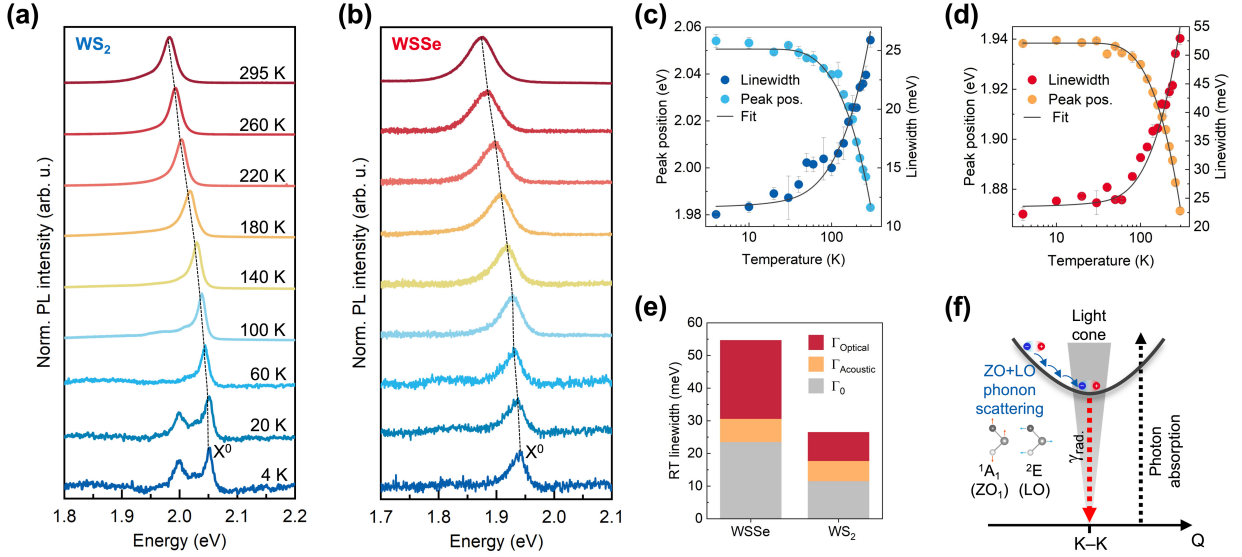


Figure 4. Effect of structural asymmetry on exciton-phonon interactions. (a) and (b) Temperature dependent PL spectra of WS₂ and WSe₂, respectively. Dashed lines highlight the blue shift of the X⁰ peak with decreasing temperature. (c) and (d) Plots of peak position and linewidth of X⁰ as a function of temperature for WS₂ and WSe₂, respectively. The solid lines are fits to the data. (e) Histogram comparing the contributions from optical (Γ_{Optical}) and acoustic (Γ_{Acoustic}) phonon scatterings to linewidth broadening at room temperature (RT). (f) Schematic of exciton dynamics in WSe₂ at RT. Photon absorption upon off-resonance excitation forms hot excitons in the monolayer. Then, these excitons scatter through ZO and LO phonons. Scattering through optical phonons cause nonradiative broadening of exciton linewidth. Finally, excitons inside the light cone recombine radiatively (γ_{rad}).

Graphical TOC

