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Brightening of Dark Excitons in WS₂ via Tensile Strain-Induced Excitonic Valley Convergence

Tamaghna Chowdhury,^{1,2,*} Sagnik Chatterjee,² Dibyasankar Das,³ Ivan Timokhin,^{1,4} Pablo Díaz Núñez,^{1,4} Gokul M. A.,² Suman Chatterjee,⁵ Kausik Majumdar,⁵ Prasenjit Ghosh,^{2,6} Artem Mishchenko,^{1,4,†} and Atikur Rahman^{2,‡}

¹Department of Physics and Astronomy, University of Manchester, United Kingdom, M13 9PL.

²Department of Physics, Indian Institute of Science Education and Research (IISER), Pune 411008, India.

³Department of Condensed Matter Physics and Material Science, Tata Institute of Fundamental Research, Mumbai 400005, India.

⁴National Graphene Institute, University of Manchester, United Kingdom, M13 9PL.

⁵Department of Electrical Communication Engineering, Indian Institute of Science, Bangalore 560012, India.

⁶Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune 411008, India.

Transition-metal dichalcogenides (TMDs) host tightly bound electron-hole pairs – excitons – which can be either optically bright or dark based on spin and momentum selection rules. In tungsten-based TMDs, a momentum-forbidden dark exciton is the energy ground state, and, therefore, it strongly affects the emission properties. In this work, we brighten the momentum-forbidden dark exciton by placing monolayer tungsten disulphide on top of nanotextured substrates, which imparts tensile strain, modifying its electronic band-structure. This enables phonon-assisted exciton scattering between momentum valleys, thereby brightening momentum-forbidden dark excitons. In addition to offering a tuning knob for light-matter interactions in two-dimensional materials, our results pave the way to designing ultrasensitive strain-sensing devices based on TMDs.

TMDs (*e.g.* MX₂, M = Mo, W, X = S, Se) are known for their novel optical properties [1]. They host excitons - charge neutral electron-hole pairs bound by Coulomb interactions [2–7]. The large spin-orbit coupling in tungsten disulphide (WS₂), due to the heavy mass of the tungsten atom, splits the valance band maxima (VBM) at *K* point and conduction band minima (CBM) at *K*, Λ points in two sub-bands with opposite spin orientations. This results in the formation of ‘bright’ intravalley *KK* excitons with the hole at the upper sub-band of *K* VBM and electron at the upper sub-band of *K* CB minima (CBM+1) [Fig. 1a]. There is also a possibility for the formation of indirect intervalley excitons *K* Λ with the hole at the upper sub-band of *K* VBM and electron at the lower sub-band of Λ CBM as well [Fig. 1a] [8, 9]. But, because of the large momentum mismatch, they require the assistance of phonons to recombine radiatively [10]. The *K* Λ exciton is therefore called momentum-forbidden dark exciton [11]. In the case of W-based monolayer (ML) TMDs, *K* Λ exciton is the excitonic ground state; it has higher binding energy and longer lifetime than the *KK* bright excitons [11–13]. Therefore, *K* Λ plays an important role in the exciton dynamics of the system. Thus, controlling them is essential for designing novel optical devices. The dark exciton can be brightened by exciton-phonon coupling if the energy of the available phonon mode matches the dark-bright exciton energy splitting, which can be effectively tuned by applying strain to ML WS₂ [12, 14, 15]. Therefore, strain acts as a tuning knob for the emission of dark excitons [12, 16, 17].

Recent theoretical and experimental works predict that the dark *K* Λ exciton in WS₂ can be brightened only by applying compressive strain [12, 13]. Conversely, two recent studies [18, 19] reported the existence of dark *K* Λ excitons

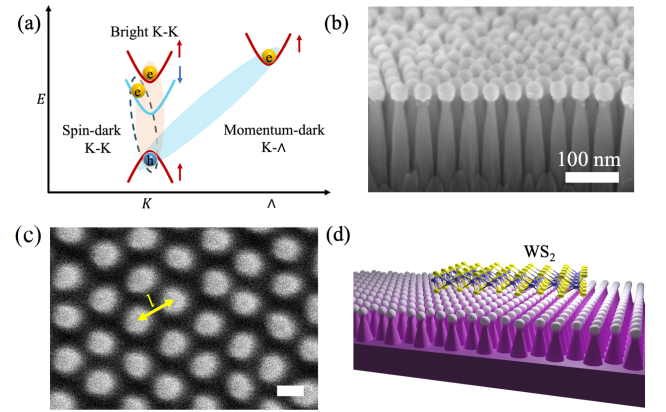


FIG. 1: (a) Schematic showing various excitonic species near the electronic dispersions at *K* and Λ valley. Arrows indicate the spin orientations. (b) Field Emission Scanning Electron Microscope (FESEM) image of the C-99 nanotextured sample (side view). (c) FESEM image of the C-99 substrate as viewed from the top (scale bar is 20 nm). The yellow line shows the interpillar separation *l*. (d) Schematic of the substrate with ML WS₂ placed on top.

in WSe₂ under tensile strain. However, in these works either the mechanism behind the brightening is not addressed [12, 18] or remains elusive due to the various approximations used in its description, such as not taking the binding energy of the *K* Λ exciton into account [13, 19]. It is highly unlikely that two W-based materials will behave differently in terms of strain-mediated brightening of *K* Λ dark excitons, *i.e.*, requiring compressive strain for WS₂ and tensile strain for WSe₂, despite having similar excitonic band structures with *K* Λ dark excitons as the excitonic ground state in W-based TMDs (unlike in Mo-based TMDs) [8]. In this work, we experimentally show that the *K* Λ dark exciton can be

* tamaghna.chowdhury@students.iiserpune.ac.in

† artem.mishchenko@gmail.com

‡ atikur@iiserpune.ac.in

brightened in ML WS₂ by application of tensile strain. We perform temperature-dependent photoluminescence (PL) and Raman measurements on the strained and unstrained ML WS₂ samples. Supported by *ab initio* density functional theory (DFT) based calculations, we put forward a mechanism for the brightening of $K\Lambda$ dark excitons through exciton-phonon coupling upon the application of tensile strain. Here, we apply tensile strain to ML WS₂ by placing them on nanotextured substrates patterned with nanopillars [Fig. 1b, c]. Conically shaped nanopillars of height ‘*h*’ and interpillar separation (centre to centre) ‘*l*’ were made of Si(100) and capped with insulator Al₂O₃ nanospheres 10 nm on top [Fig. 1b, c]. We prepared samples with varied interpillar distances: $l \approx 25$ nm (sample C-48), $l \approx 44$ nm (C-99) and $l \approx 60$ nm (C-132) [20]. By tuning ‘*l*’, we tune the amount of strain applied on ML-WS₂. The latter was grown by chemical vapour deposition (CVD) and was transferred on top of the nanotextured substrates [21] [see schematic Fig. 1d] (see supplementary material Sec. I [22] for details of substrate preparation and transfer process).

The PL measurements were performed using a continuous wave laser of wavelength 514.5 nm (2.41 eV) (see supplementary material Sec. II [22]). In the temperature-dependent PL study of ML WS₂ on C-99 substrate [Fig. 2a], two well-resolved peaks, one at ≈ 2.01 eV (FWHM ≈ 24 meV) and other at ≈ 1.95 eV (FWHM ≈ 32 meV) were observed at 280 K. The peak position and FWHM were extracted from each PL spectrum by fitting with a sum of Gaussian functions (see supplementary material Sec. III [22]). We attribute the peak at 2.01 eV to a bright exciton KK (X^0) and the peak at 1.95 eV to a negatively charged trion (X^-), since ML WS₂ is a n-doped semiconductor. We further confirm this assignment by varying the laser excitation power which alters the exciton density inside the ML WS₂ channel [23] (see supplementary material Sec. XIV [22]). As we lower the temperature both X^0 , X^- blueshift as reported earlier [24]. At around 200 K, a new peak appears at ≈ 1.92 eV. As we further decrease the temperature, the intensity of the new peak increases while that corresponding to X^- and X^0 diminishes, consistent with the earlier proposal by Feierabend et al. for $K\Lambda$ dark exciton brightening [25]. The 1.92 eV peak can be attributed to (a) a biexciton, XX (b) a defect-bound exciton (X^L), or (c) a dark exciton (X^D). The exponent α of the power law dependence (integrated intensity as a function of excitation power) for XX and X^L is known to be superlinear (~ 2.0) and sub-linear (~ 0.5), respectively [24, 26, 27]. From the I vs P plot, we obtain a value of $\alpha \sim 1.0$ for the new peak, typical of an exciton [24, 26, 27] (see Fig. 2d). Also see supplementary material Sec. IV [22] for the excitation power dependence data of X^D for another WS₂/C-99 sample where we extracted $\alpha \sim 1.14$.

Moreover, the new peak shows no blueshift with increasing excitation power, characteristic of X^L because of its broad energy distribution [28, 29]. However, it showed a red shift due to local heating, a behaviour generally seen in excitons [21] (see supplementary material Sec. V [22]). Furthermore, the new peak also shows anisotropy in circular polarization-dependent PL, uncharacteristic of X^L [29, 30] (see supple-

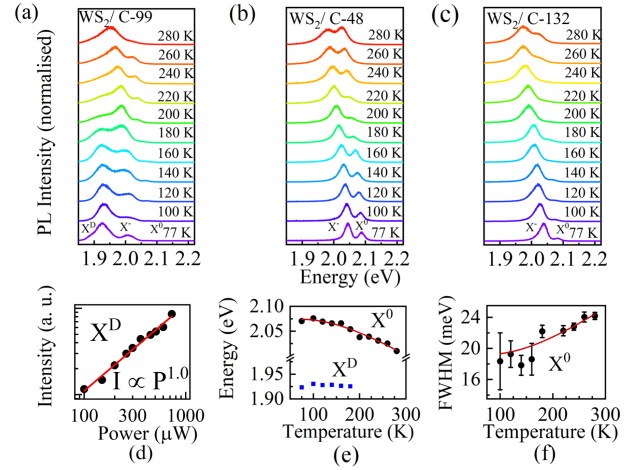


FIG. 2: Temperature dependent PL spectra of ML WS₂ placed on top of (a) C-99 (b) C-48 and (c) C-132 substrates. All the spectra are recorded at an excitation power of ~ 100 μ W. The spectra are shifted along the y-axis for clarity. (d) The integrated intensity (I) of X^0 as a function of excitation power (P) fitted with the relation $I \propto P^\alpha$ where α is the exponent.

(e) Temperature dependence of the peak position of X^0 (black solid circles) and X^D (blue solid squares), the temperature dependence of X^0 is fitted with Eq. 1 (red line). (f) FWHM of X^0 as a function of temperature fitted with Eq. 2.

mentary material Sec. VI [22]). Therefore, the new peak is neither XX nor X^L . The value of α and its peak position is similar to recent reports of observation of $K\Lambda$ dark exciton under compressive strain and strong exciton-phonon coupling [13]. We, therefore, attribute the peak at ~ 1.92 eV as X^D . Temperature-dependent PL data of another ML WS₂/C-99 sample, where we have also observed the X^D peak, is added to the supplementary material Sec. XVI [22]. We performed a similar study on the other two samples, namely, C-48 and C-132 [Fig. 2b and c]. For the C-48 and C-132 samples, we observed X^0 and X^- peaks at every temperature, but no new peaks were observed as we lowered the temperature to 77 K.

The temperature dependence of the peak position of X^0 in the C-99 sample was studied in detail (Fig. 2e). The temperature dependence can be described by the phenomenological model proposed by O’Donnell and Chen [31]:

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

where $E(T)$ is the resonance energy of X^0 at temperature T , S is dimensionless exciton-phonon coupling constant, k_B is Boltzmann constant and $\langle \hbar\omega \rangle$ is the average phonon energy responsible for the coupling. By fitting the experimental data we obtained the parameters, $E(0) = 2.074 \pm 0.003$ eV, $S = 3.65 \pm 0.98$ and $\langle \hbar\omega \rangle = 43 \pm 10$ meV. The value of $\langle \hbar\omega \rangle$ is close to the energy of E' phonon (~ 44 meV) mode of ML WS₂. This suggests that the E' phonon mode is crucial

in the exciton-phonon coupling. Note that the peak position of X^D changes only by ~ 2 meV as we increase the temperature from 77 K to 180 K, whereas, in the same temperature range, the X^0 peak position changes by ~ 20 meV. This observation aligns with our theoretical calculations (see Fig. S13 in supplementary material [22]), which shows that the electronic direct bandgap at the K point changes at a much faster rate with temperature in comparison to the indirect $K - \Lambda$ bandgap.

To determine the strength of exciton-phonon coupling, the evolution of the FWHM of X^0 was fitted by a phonon-induced broadening model, Fig. 2f [32, 33]:

$$\gamma = \gamma_0 + c_1 T + \frac{c_2}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (2)$$

where γ_0 is the intrinsic FWHM, the linear term in T is due to the interaction of acoustic phonon modes and the last term describes the interaction with optical phonon modes. The linear term is negligible compared to the last term, as formulated in [34]. The c_2 is the measure of the exciton-optical phonon coupling strength. The value of $\hbar\omega$ obtained by fitting Eq. 1 was used for fitting Eq. 2. The value of c_2 obtained by fitting Eq. 2 is 26.5 ± 4.6 meV and is significantly higher than the previously reported value of 6.5 for ML WS_2 [32]. This higher value of c_2 further confirms the strong exciton and E' phonon mode coupling in the C-99 substrate. See supplementary material Sec. VII [22] for the above analysis in C-48 and C-132 samples.

We further did a temperature-dependent Raman study on the C-99 sample. The various Raman peaks (E' , 2LA, A_1') were analysed with multiple Lorentzian functions, Fig. 3a [35] (see supplementary material Sec. VIII [22] for fitting details). The E' mode showed unusual blueshift and decreasing linewidth with increasing temperature [see Fig. 3b, c]. This anomalous behaviour of E' phonon mode is related to electron-phonon coupling [36–38]. The Raman linewidth with temperature is generally explained by the anharmonic cubic equation [39, 40]:

$$\gamma_{ph}(T) = \gamma_0 + C \left[1 + 2f_- \left(\frac{\hbar\omega_0}{2k_B T} \right) \right] \quad (3)$$

where $\gamma_{ph}(T)$ is the linewidth at temperature T , γ_0 is the linewidth at $T = 0$ K, $\hbar\omega_0$ is the E' phonon energy, $f_{\pm}(x) = \frac{1}{e^x \pm 1}$ and C is a constant. Eq. 3 is simulated in the inset of Fig. 3c (green curve). The E' phonon modes show an opposite trend which is not explained by Eq. 3, because it takes into account only phonon-phonon interaction (γ_{ph}) and not the electron-phonon interaction (γ_{e-ph}) term [41]. $\gamma_{e-ph}(T)$ is described by the following equation [37]:

$$\gamma_{e-ph}(T) = \gamma_{e-ph}(0) \left[f_+ \left(\frac{-\hbar\omega_0}{2k_B T} \right) - f_+ \left(\frac{\hbar\omega_0}{2k_B T} \right) \right] \quad (4)$$

where, $\gamma_{e-ph}(0)$ is the linewidth at $T = 0$ K due to electron-phonon coupling. In the inset of Fig. 3c, the red curve is simulated with $\gamma(T) = \gamma_{ph} + \gamma_{e-ph}$ and closely resembles the experimental data, thus showing the role of electron-phonon

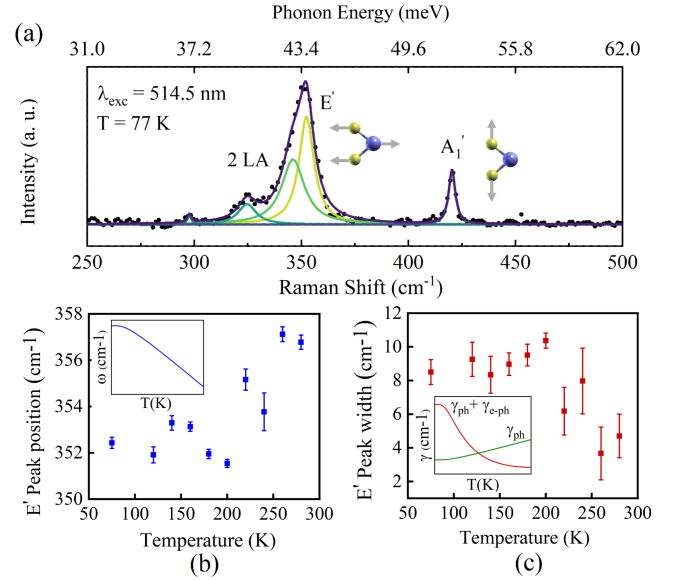


FIG. 3: (a) Raman spectra of ML WS_2 placed on top of C-99 substrate at 77 K. Various peaks are labelled according to ref. [35]. The main vibrational modes E' and A_1' are shown in the schematic. The blue and yellow balls represent tungsten (W) and sulfur (S) atoms respectively. Anomalous behaviour of E' peak (b) position and (c) width as a function of temperature. Simulated ω_{ph} and γ_{ph} are shown in the insets of Fig. 3b (blue curve) and Fig. 3c (green curve) respectively. $\gamma(T) = \gamma_{ph} + \gamma_{e-ph}$ (red curve) is simulated in the inset of Fig. 3c.

coupling. The phonon-phonon interaction term in the Raman frequency, $\omega_{ph}(T) = \omega_0 - D \left[1 + 2f_- \left(\frac{\hbar\omega_0}{2k_B T} \right) \right]$ [41], where ω_0 is the frequency at $T = 0$ K and D is constant, was simulated in the inset of Fig. 3b (blue curve) to show the anomalous behaviour of E' peak position.

To understand the effect of strain on the electronic structure of ML- WS_2 we computed the same within the framework of DFT using full-relativistic norm-conserving pseudopotential with Perdew–Burke–Ernzerhof (PBE) exchange-correlation functionals alongside plane waves, as implemented in Quantum ESPRESSO package [Fig. 4a] [42–51] (see supplementary material Sec. X [22]). With increasing tensile (compressive) strain, the CBM and CBM+1 at K shift down (up), while the CBM at Λ shifts up (down). The K VBM move up (down) on application of tensile (compressive) strain, Fig. 4a. We denote the direct bandgap at K between CBM+1 and VBM as E^{KK} and the indirect bandgap at Λ as $E^{K\Lambda}$. Note that, in the electronic band structure of the unstrained WS_2 , the Λ CBM is at higher energy than the CBM+1 at K by $E^{K\Lambda} - E^{KK} = \Delta E^{K\Lambda} \sim 47$ meV. To get into the exciton picture [Fig. 4b] from the electron-hole picture (as described in ref. [8, 12]), we need to calculate the binding energy E_b of the excitons. To this end, we employed the effective mass model [52]:

$$E_b = \frac{\mu e^4}{2\hbar^2 \epsilon^2 (n - \frac{1}{2})^2}, \quad (5)$$

where $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$ the exciton reduced mass, m_h and m_e are the effective masses of holes and electrons, respectively. ϵ is the dielectric constant of ML WS₂, e is the electron charge, and n is the principal quantum number. Using Eq. 5 we found E_b of X^0 and $X^D \sim 310$ meV and 438 meV respectively (see supplementary material Sec. X and XI [22] for details of calculation). Also, we introduce the center-of-mass momentum $\mathbf{Q} = \mathbf{k}_2 - \mathbf{k}_1$, where $\mathbf{k}_1, \mathbf{k}_2$ are momenta of two bound particles. Now, if we visualize the scenario in the excitonic picture, the bright exciton state is formed at $K - K$, at the energy position $E_{exc}^{KK} = E^{KK} - E_b^{X^0}$ and the dark exciton state is formed at $K - \Lambda$, at the energy position $E_{exc}^{K\Lambda} = E^{K\Lambda} - E_b^{X^D}$ [12]. Our calculations show that, in the unstrained sample, the dark state is below the bright state by energy $E_{exc}^{KK} - E_{exc}^{K\Lambda} = \Delta E_1 \sim 81$ meV. Under tensile (compressive) strain, the excitonic states at $K - K$ and $K - \Lambda$ go down (up) and up (down) respectively. The change of ΔE as a function of strain is plotted in Fig. 4c (the values used to generate this plot can be found in supplementary material Sec. X [22]). The fitting shows $\sim 170 \pm 1.4$ meV change of ΔE with 1% of applied strain. Note that strain has little influence on E_b [12, 53]. As the PBE underestimates the bandgap, we have also calculated the band structure using hybrid functional. The behavior of the band structure with strain remains consistent irrespective of the functional used (see supplementary material Sec. X [22]).

On optically exciting a coherent exciton population at $K - K$, bright excitons are formed. Incoherent excitons are then formed at $K - \Lambda$ by phonon-assisted scattering of excitons from $K - K$, where a phonon compensates for the energy and momentum mismatch [Fig. 4b] [14]. However, in the unstrained case, phonon modes with energy $\Delta E_1 \sim 81$ meV are not available, therefore, excitons are not formed at $K - \Lambda$. On applying tensile strain (theoretically) on the ML WS₂, we observe ΔE decreases and under $\sim 0.21\%$ strain the value of ΔE_1 is reduced to $\Delta E_2 \sim 44$ meV, thereby making the optical phonons accessible to couple with the exciton for phonon-assisted scattering. To estimate the amount of strain on ML WS₂ on top of C-99 substrate due to nanopillars, PL mapping was done and the average peak position of X^- in the C-99 sample was compared with the average X^- peak position in ML WS₂ on top of flat SiO₂/Si (Fig. 4e). Therefore, we can experimentally estimate that ML WS₂ on top of C-99 is under a tensile strain of $\sim 0.15\%$ which is in very close agreement with the theoretical value of $\sim 0.21\%$ (see supplemental material Sec. XII for details of strain determination [22]). In the C-99 sample, phonon-assisted scattering of excitons from $K - K$ to $K - \Lambda$ is possible, thereby forming a population of dark excitons. The scattering process is illustrated in the schematic Fig. 4b. An E' phonon with momentum $K - \Lambda$ and energy ~ 44 meV can make this scattering possible. The calculated phonon density of states shows a large number of phonon states available at ~ 44 meV, thereby making this scattering more favourable [Fig. 4d] (see supplemental material Sec. X for the details of phonon calculation [22]). Note that change of phonon energy with strain is very negligible [54]. To estimate the scattering strength we calculate the electron-phonon matrix element $g_{mn}^\nu(\mathbf{k}, \mathbf{q})$ [Fig. 5a, b] using the for-

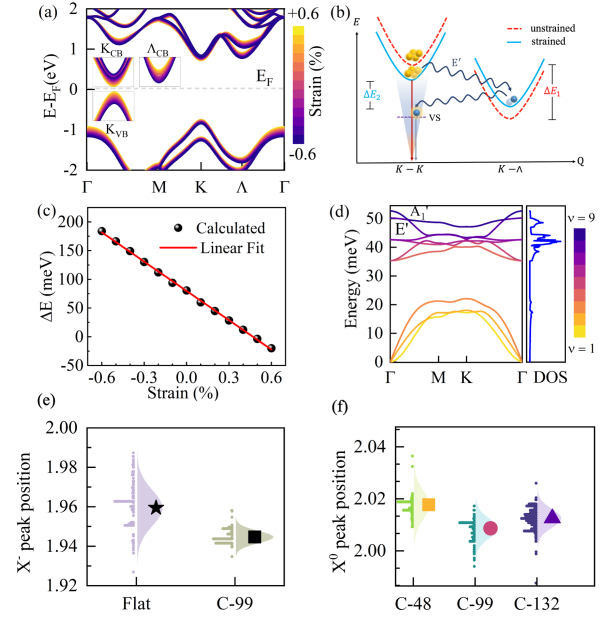


FIG. 4: (a) DFT computed electronic band structure of ML WS₂ with different strain values. (b) Schematic showing the E' phonon mediated scattering of the bright $K - K$ excitons to dark $K - \Lambda$ due to tensile strain. The $K - \Lambda$ excitons then decay to a virtual state (dotted violet line marked as VS) inside the light cone (shaded area) by emitting phonons and finally recombine radiatively from the VS by emitting photons. (c) ΔE as a function of strain on ML WS₂. (d) Phonon dispersion (left panel) and phonon density of states (DOS) (right panel). ν represents the phonon band index. (e) Mean peak position of X^- in ML WS₂ on top of SiO₂/Si (flat) and C-99 extracted from the PL map and (f) Mean peak position of X^0 in ML WS₂ on top of C-48, C-99 and C-132 extracted from the PL map. The normal distribution and the raw data points are also shown.

malism described in ref. [55–57] as,

$$g_{mn}^\nu(\mathbf{k}, \mathbf{q}) = \langle \psi_{m,\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V | \psi_{n\mathbf{k}} \rangle, \quad (6)$$

where $\psi_{n\mathbf{k}}$ is the electronic wavefunction for n^{th} band at $\mathbf{k}$ k-point of the Brillouin zone, ν is phonon band index, $\partial_{\mathbf{q}\nu} V$ the derivative of the self-consistent potential associated with E' phonon of momentum $\mathbf{q}$. Here, we consider the hole to be fixed at the K VBM [Fig. 1a] and take into account the scattering of electrons from CBM+1 at K to Λ CBM with a phonon of momentum $\mathbf{q} = \mathbf{K} - \mathbf{\Lambda}$ and energy value $\Delta E_2 =$ energy of E' phonon mode. Two degenerate E' phonon modes ($\nu = 6, 7$) with momentum $K - \Lambda$ shows significant coupling strength ~ 28 meV for the concerned scattering [Fig. 5c]. We note that this value is comparable with the experimentally estimated exciton-phonon coupling strength reported in the previous paragraphs. The dark excitons at $K - \Lambda$ then can scatter non-radiatively to a virtual state inside the light cone at $K - K$ by emitting phonons. Once inside the light cone, the dark excitons can decay radiatively from the virtual state by emitting

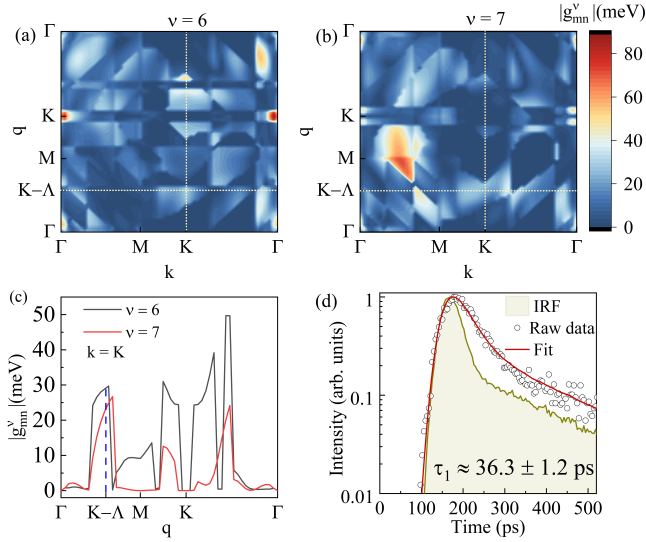


FIG. 5: (a) and (b) Calculated g_{mn}^ν value for two degenerate E' phonon modes with $\nu = 6$ and 7 respectively, responsible for the scattering of electrons from CBM+1 at K to CBM at Λ valley. (c) Line-cut along $k = K$ from (a) and (b) to show the g_{mn}^ν along the phonon momentum (q), $\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma$ direction. The blue dashed line shows the g_{mn}^ν of $q = K - \Lambda$ at $k = K$. (d) TRPL measurement on ML WS_2 at 60 K to determine the lifetime of X^D .

photons, thus leaving its signature in the PL spectra. The X^D peak was not observed in ML WS_2 /C-48 and C-132 samples [Fig. 2b, c] as the imparted tensile strain was $\sim 0.04\%$ and 0.08% respectively (calculated by comparing the average X^0 position in Fig. 4f)(see supplementary material Sec. XII. for details of strain determination [22]). So the ΔE value was not close to the energy of any available phonon mode which can open the scattering channel from $K - K$ to $K - \Lambda$ points. To elucidate the kinetics of X^D , we did time-resolved PL (TRPL) on the ML WS_2 on top of C-99 substrate Fig. 5d). The lifetime τ of X^D is estimated to be $\tau \approx 36.3 \pm 1.2$ ps (see supplementary material Sec. XIII for measurement and fitting

details [22]) which is 30 times larger than the reported decay time of a neutral exciton X^0 ($\tau \sim 1$ ps at $T = 60$ K) [58, 59] as X^D is the excitonic ground state of ML WS_2 [11, 13].

In summary, we have reported the experimental observation of momentum-forbidden $K\Lambda$ dark excitons by applying tensile strain on ML WS_2 using a nanotextured substrate. Our model shows that the $K\Lambda$ dark excitons in both WS_2 and WSe_2 can be brightened by the application of tensile strain, thereby establishing the universality across the W-based TMDs. Also, TMDs are prone to buckling under compressive strain [60] and it is difficult to create at lower temperatures which is necessary for the brightening of $K\Lambda$ dark exciton [13]. Rather they can endure a high tensile strain and are easy to create [61]. Therefore our work paves the way for more application-oriented modulation of the $K\Lambda$ dark exciton, which, being the excitonic ground state, strongly affects exciton dynamics in W-based materials.

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