Strain control of hybridization between dark and localized excitons in a 2D semiconductor

Mechanical strain is a powerful tuning knob for excitons, Coulomb-bound electron–hole complexes dominating optical properties of two-dimensional semiconductors. While the strain response of bright free excitons is broadly understood, the behaviour of dark free excitons (long-lived excitations that generally do not couple to light due to spin and momentum conservation) or localized excitons related to defects remains mostly unexplored. Here, we study the strain behaviour of these fragile many-body states on pristine suspended WSe₂ kept at cryogenic temperatures. We find that under the application of strain, dark and localized excitons in monolayer WSe₂—a prototypical 2D semiconductor—are brought into energetic resonance, forming a new hybrid state that inherits the properties of the constituent species. The characteristics of the hybridized state, including an order-of-magnitude enhanced light/matter coupling, avoided-crossing energy shifts, and strain tunability of many-body interactions, are all supported by first-principles calculations. The hybridized excitons reported here may play a critical role in the operation of single quantum emitters based on WSe₂. Furthermore, the techniques we developed may be used to fingerprint unidentified excitonic states.

Excitons are responsible for the strong absorption of light by 2D transition metal dichalcogenides (TMDs)⁴⁻⁶, control the valley properties of these materials⁷⁻¹⁰, and condense into various correlated quantum states at low temperatures¹¹⁻¹³. Most early studies focused on “bright” free excitons characterized by large oscillator strength and strong interaction with light fields. More recently, it became clear that other excitonic species may be critical for understanding and exploiting TMDs. First, “dark” excitons interact with light only weakly due to multiple selection rules and momentum conservation⁸⁻¹⁰. For example, the spin selection rules prohibit the radiative recombination of the ground state excitons in TMD systems such as WSe₂ or WS₂ composed of electron and hole wavefunctions in the K valley²,⁸. Other energetically close excitons composed of a hole wavefunction localized in the K valley and an electron in the Q or K’ valleys are dark due to the momentum selection rule. In all cases, dark excitons feature greatly increased charge lifetime, spin lifetime, and diffusion length compared to their bright counterparts¹²⁻¹⁴. These properties caused a surge of interest in such quasiparticles for storing and transporting quantum and classical information¹⁵,¹⁶. The second type of excitonic species arising in TMDs other than bright free excitons are those localized by defects. Spatially localized excitonic states are delocalized in momentum space and are thought to provide the momentum needed for energy relaxation, tunnelling, or emission from TMDs that is momentum-forbidden otherwise¹⁷. In addition, defect-related states function as broadly tunable quantum emitters, one...
of the fundamental building blocks of quantum information technologies allowing the generation of entangled photons\textsuperscript{36–39}. Applying mechanical strain changes the energies and the hierarchy of the excitonic states in TMDs. First-principles calculations reveal that different energy bands as well as the valleys within these bands experience varied rates of energy shift with strain\textsuperscript{24,25}. Excitonic species residing in these valleys inherit the corresponding energy shifts. For example, the conduction/valence band gap at the K/K' valleys decreases at -100 meV/% for uniform biaxial strain\textsuperscript{26}. Correspondingly, all excitonic species associated with these valleys including dark/bright neutral excitons, dark/bright trions, biexcitons, and their phonon replicas redshift at about the same rate. In contrast, excitons from K/Q valleys of e.g., WSe\textsubscript{2} have much weaker strain dependence\textsuperscript{24–26}, while localized excitons associated with defects remain primarily unaffected by strain\textsuperscript{24–26,29}. This suggests the possibility of using the strain response signature to identify excitonic species. Even more interesting, the energy alignment between excitonic species belonging to different valleys becomes strain-dependent. As strain brings the conduction band minima at K and K' into resonance with the localized defect states, we expect hybridization between them\textsuperscript{24–26,30,31}.

The arguments above show that mechanical strain engineering can be used to identify, generate, and tune novel hybridized excitonic states in TMDs. This possibility raises several questions. First, what are the properties of the hybridized states? They are generally expected to combine the traits of underlying excitons before hybridization. This is especially noteworthy in the case of the hybridization between bright defect-related localized excitons and free dark K/K' excitons featuring high oscillator strength and long diffusion length, respectively\textsuperscript{13,30,31}. Second, are there possible applications for the hybridized states? As strain is required for the operation of TMD-based quantum emitters, we believe that the hybridized states may be critical for the operation of these emitters and contribute to their high brightness. More broadly, the ability to manipulate the emission from long-lived dark excitonic states may prove important for various excitonic transport devices\textsuperscript{15}. Finally, how do we realize strain-induced hybridization experimentally? Observing well-separated peaks due to normally faint dark or localized excitonic species via optical spectroscopies requires clean, controllably strained devices operating at cryogenic temperatures. In contrast, most existing strain-engineering techniques either function around the top of the valence band and the bottom of conduction band within one valley or do not allow in situ control of the strain level\textsuperscript{35,36}.

Here we address these questions by implementing an electrostatic-based straining approach capable of straining a pristine suspended WSe\textsubscript{2} monolayer at cryogenic temperatures. We identify two types of excitonic species in addition to the well-known free bright excitons: (i) the free dark excitons localized at K/K' valleys and (ii) a pair of bright localized excitons related to shallow defects states. These two types of excitonic states have starkly different strain dependencies and are brought into energetic resonance at -1% and -2.5% strain (dependent on temperature). At resonance, we observe signatures of the formation of the new hybridized state, including orders-of-magnitude increased photoluminescence of dark excitons and avoided crossing behaviour between dark and localized excitonic species. Our data in combination with first-principles modelling suggests that the hybridized state combines the features of dark and localized excitons. Finally, some signatures of energetic resonance survive up to room temperature allowing us to observe pure defect emission.

**Results**

**Model of exciton strain-dependence**

In WSe\textsubscript{2}, the low-energy physics is determined by the maxima of the valence bands and the minima of two spin-split conduction bands around the K/K' points of the Brillouin zone, Fig. 1a. The lowest-lying excitonic states are dark (X\textsubscript{2}'), since the optical transition between the top of the valence band and the bottom of conduction band within one valley are prohibited by the spin selection rules, while the transition across valleys requires additional momentum. A point defect such as a
Se vacancy in WSe₂ features two strongly localized (spin-degenerate) defect states (D₁ and D₂) within the band gap, slightly below the conduction band minimum. The wavefunctions of excitons associated with these states are largely formed from the valence band hole and an electron localized at the selenium vacancy. As the defect breaks translational invariance, radiative recombination of D₁, D₂ excitons is allowed. Despite the large resulting dipole matrix element, the density of isolated defect states is low. Because of that, neither defect states nor the lowest-lying excitons provide strong photoluminescence in unstrained WSe₂.

This situation changes drastically upon the introduction of strain due to contrasting strain responses of the states X₀² and D₁, D₂. In line with previous literature, our calculations show that while the conduction band at the K and K' minima strongly downshifts with strain, the energy difference of both the valence band hole and the defect states remains almost constant (i.e., valence and defect bands shift at an identical, smaller rate, see Fig. 1b). Therefore, the dark exciton X₀² composed of conduction and valence band Bloch states exhibits a much stronger strain response compared to defect-related excitons D₁, D₂. As a result, X₀² becomes energy-degenerate with D₁ at -1% and with D₂ at -2.5% strain (Fig. 1b, top). Following Fermi’s golden rule, we evaluate the dipole transition matrix element—including contributions from both valleys—to estimate the resulting photoluminescence signal from an optical decay of the different possible excitonic states (see Supplementary Note 2 for technical details). We find that at resonance conditions, the oscillator strength of the dark state X₀² increases by several orders of magnitude. We interpret this striking increase in the oscillator strength as the result of hybridization between dark and defect-related excitons. The hybridized state inherits the bright character of the defect exciton, allowing an efficient de-excitation channel for dark excitons. These theoretical findings imply the possibility of continuously tuning the hybridization between excitonic species as well as their oscillator strength using strain. These phenomena are largely unstudied experimentally mainly due to the difficulties associated with reaching high values of mechanical strain at cryogenic temperatures.

**Straining approach**

We solve the challenges associated with the application of controlled uniform strain to a high-quality WSe₂ device at low temperature by using an electrostatic straining approach. In our technique, the strain is generated by applying a gate voltage \( V_G \) between a suspended monolayer WSe₂ membrane and an electrode below, Fig. 2a. This approach combines several key advantages. First, electrostatic straining functions at cryogenic temperatures, unlike other straining approaches based on, e.g., bending elastic substrates or pressurizing a 2D membrane with gas that only work near room temperature. Second, the approach is capable of large strain values up to a few percent, higher than the limits of other techniques. Such high strain is necessary to reach and surpass the predicted regime in which hybridization between different excitonic species occurs. Third, suspended 2D materials are not affected by substrate-related scattering and therefore feature high optical quality necessary to resolve closely-spaced excitonic states.

Neutral exciton (\( X^0, 1.738 \text{ eV} \)), positively charged trion (\( X^+, 1.713 \text{ eV} \)), negatively charged intervalley trion (\( X^-_f, 1.708 \text{ eV} \)), and negatively charged intravalley trion (\( X^-_c, 1.701 \text{ eV} \)) appear at the energies close to what is reported in literature for high-quality hBN encapsulated devices. Changes in intensity and peak position for \(-70 \text{ V} < V_G < 70 \text{ V} \) closely resemble those in encapsulated devices, showing that charging dominates the device behaviour for this regime. The near-zero \( V_G \) position of the change neutrality point and the disappearance of the X₁² peak outside of the \(-50 \text{ V} < V_G < 10 \text{ V} \) region confirm the good optical quality of our samples.
and to identify the excitonic species, we start by exploring the low gate voltage regime $|V_G| < 80$ V, where changes in the carrier density dominate the optical response of WSe$_2$. For now, we focus on a temperature of 100 K where only the most intense excitons are visible and examine lower and higher temperatures later. Figure 2c,d shows a PL spectral map and spectra at three selected $V_G$. We observe narrow PL peaks corresponding to neutral exciton ($X^0$) and charged trions ($X^+, X^0/C_0$, $X^0/C_S$) at energies close to reported values. The $X^0$ peak width of 7.5 meV is close to the 4–6 meV reported at $T < 5$ K for high-quality WSe$_2$ encapsulated in hBN samples.

**Strain dependence of excitonic peaks**

We now examine the behaviour of our suspended WSe$_2$ in the high voltage regime $|V_G| > 80$ V, where strain effects become dominant. Figure 3a shows the evolution of PL spectra taken with gate voltages up to $V_G = \pm 230$ V with individual spectra shown in Fig. 3b. We observe a redshift in the energetic position of the excitons $X^0$, $X^-$, $X^+$ with increasing gate voltage. The redshift is equal for both polarities of $V_G$. This behaviour is a well-characterized effect of mechanical strain. In general, uniform biaxial strain in WSe$_2$ (see “Methods” discussing this approximation) results in a downshift of all excitonic peaks at a...
rate of 100 meV/%. We use this value to fit the observed peak shifts to Eq. (2) and extract the effective 2D Young’s modulus of 100 N/m, close to previously reported values. We reach strain values of almost 3% in our suspended WS₂ devices.

We now focus on several trends in Fig. 3a, b that are not expected from a simple model based on Eqs. (1 & 2) that only considers spectral redshift due to strain and gating-related redistribution of the oscillator strength between trions and neutral excitons. Our first and most striking observation is the highly non-monotonic evolution of the PL intensity with increasing strain. After the initial intensity drop, cf. Fig. 3a, the PL intensity increases to reach a maximum labelled D1 at $V_G = \pm 160$ V (~0.7% strain) and 1.63 eV, where the integrated PL intensity is a factor 6 higher than the combined intensities of neutral excitons and trion for $V_G = 0$ V. It then drops and peaks again with a maximum (labelled D2) at $V_G = \pm 230$ V (~2.5%), with the peak position at 1.45 eV. The state associated with greatly increased PL intensity emerges 14 meV below the trion state as the trion gradually disappears (Fig. 3c) and dominates the PL when it approaches the energies of D1 and D2. From its energy position, we identify (“Methods”) the state as a dark exciton, $X'_d$. Note that the energetic proximity between dark exciton and trion requires high resolution measurements to resolve the two peaks.

Next, in the region $|V_G| < 100$ V we observe faint lines around 1.6 eV that are largely strain-independent (Fig. 3a, triangles), unlike other brighter excitonic peaks. In addition, these lines exhibit a saturating power dependence that contrasts with the near-linear dependence for neutral excitons and trions (see Supplementary Fig. 3). The saturating power behaviour is characteristic of defect-related states. The near strain-independence suggests that the states do not involve Bloch states in the conduction band (Fig. 1). Finally, the comparison of the energy position of one of these states with our tight-binding calculations allows to unambiguously associate the state with the D1 exciton.

Critically, the strain-independent PL intensity occurs at roughly constant energy for $|V_G| \approx 230$ V (~2.5%) and 1.63 eV, where the integrated PL intensity is a factor 6 higher than the combined intensities of neutral excitons and trions (see Supplementary Fig. 3). The saturating power dependence that contrasts with the near-linear dependence for neutral excitons and trions (see Supplementary Note 1 and Supplementary Fig. 9).

Comparison with theory

Summarizing our discussion so far, the observed strong increase in photoluminescence occurs when a strain-related modification of the energy spectrum brings the dark exciton $X'_d$ into an energetic resonance with defect-related states D1, D2. This behaviour is especially striking since all of these states are either very faint or invisible in unstrained devices. The only explanation consistent with the data in Fig. 3, including changes in the intensity and the appearance of new spectral features, is strain-related hybridization between the dark exciton $X'_d$ and defect-related states D1 and D2, as predicted by our tight-binding model. In Fig. 4, we directly compare the experimental data, now plotted as a function of strain (calculated from the shift of the excionic peaks, see ‘Methods’), to the theoretical modelling. All of the features of the above model are evident in our data, including the linear shift of $X'_d$ with strain, near strain-independence of D1, D2, and an order of magnitude increase in PL intensity when $X'_d$ into resonance with D1 or D2. To confirm our interpretation, we have scrutinized other confounding phenomena that may contribute to our data such as strain-dependent scattering between K- and Q-valleys or interference effects, but find that none of these effects can explain our experimental observation (see Supplementary Note 1 and Supplementary Fig. 9).

Temperature-dependent data

Having understood the strain-dependent hybridization between dark free and bright defect-related excitons, we now want to elucidate the nature of the states undergoing hybridization. For this, we turn to more complex data at temperatures between 10 and 300 K (Fig. 5). First, the strain tunability of the excitonic states (as quantified by their energy shift within our full voltage range) decreases at low temperatures. At $V_G = 200$ V, we generate 2.2% strain at 300 K and only 0.9% at 10 K. This difference is related to temperature-dependent changes in the built-in strain and mechanical constants of WS₂. Second, the strong enhancement in the PL intensity occurs at roughly constant energy for $T = 10, 100,$ and 300 K (dashed lines in Fig. 5) despite a strong temperature-dependent blueshift in the unstrained $X'_d$ and $X'_d^{\infty}$ excitonic peaks with decreasing $T$. As discussed earlier, this behaviour is consistent with near strain-independence of defect-related excitons D1 and D2.
Third, while at 100 and 300 K the state that dominates the photoluminescence after hybridization with either DI or D2 matches the energy position of \( X_D^0 \), we observe a more complex behaviour at 10 K, Fig. 5a (see Supplementary Fig. 4 for individual spectra). A state that lies ~80 meV (~87 meV) below \( X_D^0 \) for p- (n-) doping dominates the spectrum. This state is faint at zero strain, redshifts at the same rate as other excitonic states when the strain is increased, and its intensity reaches a maximum when it is brought into resonance with the defect-related state DI. The energy position of that state is within a band of states related to dark trions \( X_D^- \), \( X_D^0 \), and their phonon replicas. We, therefore, suggest that at low temperatures the strain-driven hybridization between dark trions \( X_D^- \), \( X_D^0 \) on one hand and the defect state DI, on the other hand, dominates the emission in our devices. The fact that such a behaviour is seen only at low temperature is likely due to the increased population of dark trions at low temperatures.

Finally, at 300 K we see a pronounced asymmetry between positive and negative voltages both in the intensity and structure of the PL spectrum, Fig. 5c, that is in contrast to the behaviour at 10 and 100 K (see Supplementary Fig. 5 for other temperatures). As the level of strain in our experimental geometry is independent of the sign of \( V_G \), this asymmetry must arise from changes in the carrier density. For the n-side, the PL intensity of the n-side is about 30 times lower than on the p-side and we do not see any features associated with free excitons with linear strain dependence. We only observe weakly dispersing features at the energies of states \( D_1, \) \( D_2 \) that do not seem to undergo hybridization. We speculate that this behaviour may be related to the small oscillator strength of free excitons seen at room temperature for substrate-supported WSe\(_2\) samples for n-doping. We, therefore, suggest that the features seen on the n-side are the intrinsic contributions from \( D_1 \) and \( D_2 \) localized defect states that are not masked by other much stronger excitons.

**Discussion**

To summarize, we show that mechanical strain brings dark- and localized defect-states into resonance. When that happens, a new hybridized state with large oscillator strength is formed. That state dominates light/matter interactions in WSe\(_2\). We note that the scenario we outline can in principle occur between any pair of excitonic states that have different strain dependencies, including KK and KQ excitons. Point defects other than the Se vacancies discussed here can also be involved, as long as they feature localized defect states sufficiently close to the conduction band edge to result in strain-induced hybridization. Several interesting conclusions can be drawn from our data. First, the hybridized state we observe is likely key for the operation of single quantum emitters in WSe\(_2\). In these devices, highly non-uniform mechanical strain is induced in WSe\(_2\) deposited onto e.g., a bed of pillars. At the point of highest strain, at the pillar’s top, the hybridization conditions are fulfilled and dark excitons effectively release their energy as photons. Around the pillars’ top, the strain gradient “funnels” all excitonic species, including dark, towards the point of highest strain. Since the lifetime of dark excitons is much longer than that of their bright cousins, our work shows that the area from which this funneling process “collects” the energy is much larger than what was thought previously. It is also worth noting that the processes studied here may be contributing to strain-related changes in the PL intensity previously observed in WSe\(_2\) at room temperature. Similar processes may happen in other TMD materials, especially in WS\(_2\), where the ground state is also dark. Second, our results suggest the use of mechanical strain to fingerprint excitonic complexes in TMDs. The data of Fig. 3, for example, shows that free and some defect-related excitons respond to strain very differently allowing their unambiguous identification. Finally, in the future, it will be attractive to use strain engineering to “encode” charge- or spin- information into dark excitons, towards concepts such as excitonic transistors or switches.

**Methods**

**Sample fabrication and measurements**

All devices are fabricated by transferring mechanically exfoliated WSe\(_2\) monolayers onto a circular hole (diameter ~ 5 \( \mu \)m) etched 700 nm into Au/Cr/SiO\(_2\)/Si (70 nm/3 nm/1500 nm/300 \( \mu \)m) substrates (see Supplementary Fig. 10). The large thickness of SiO\(_2\) allows applying voltages of up to \( \pm 280 \) V before the dielectric rupture of the sample, but measurements are typically limited to \( \pm 235 \) V for sample protection. The monolayers are many times larger than the hole to ensure uniform mechanical strain is induced in WSe\(_2\) deposited onto e.g., a bed of pillars. At the point of highest strain, at the pillar’s top, the hybridization conditions are fulfilled and dark excitons effectively release their energy as photons. Around the pillars’ top, the strain gradient “funnels” all excitonic species, including dark, towards the point of highest strain. Since the lifetime of dark excitons is much longer than that of their bright cousins, our work shows that the area from which this funneling process “collects” the energy is much larger than what was thought previously. It is also worth noting that the processes studied here may be contributing to strain-related changes in the PL intensity previously observed in WSe\(_2\) at room temperature. Similar processes may happen in other TMD materials, especially in WS\(_2\), where the ground state is also dark. Second, our results suggest the use of mechanical strain to fingerprint excitonic complexes in TMDs. The data of Fig. 3, for example, shows that free and some defect-related excitons respond to strain very differently allowing their unambiguous identification. Finally, in the future, it will be attractive to use strain engineering to “encode” charge- or spin- information into dark excitons, towards concepts such as excitonic transistors or switches.
device stability. Room temperature PL mapping of the finished device (Fig. 2b, inset) is used to confirm that the monolayer uniformly covers the hole area. The devices are measured in vacuum inside a cryostat with the base temperature of 4 K. To avoid damage to the suspended WSe₂ during pump-down of the cryostat, a pressure relief channel is fabricated in SiO₂. Temperature at the sample is detected via an on-sample thermometer and controlled by tracking the energetic blue-shift and linewidth narrowing of the (bright) neutral exciton (Supplementary Fig. 5). Photoluminescence measurements are carried out in a homebuilt setup using a tightly focused laser (diameter ~1 μm) placed at the centre of the device. We excite the membranes with a linearly polarized, CW laser with λ = 532 nm and power -10 μW (power density 500 W/cm²) and in the range 100 nW–4.5 μW to quantify the character of excitonic states (power densities 5–250 W/cm²). Additionally, from power-dependent measurements we estimate the defect concentration on our samples to be in the order of 10²⁵ cm⁻³ (see Supplementary Fig. 3)⁶⁰. Photoluminescence excitation spectroscopy in the range 570–675 nm with a pulsed laser source (femtosecond Ti:Sa Chameleon Ultra II + OPO-VIS) is used to quantify the contribution of interference effects in our data. The strain generated by applying a gate voltage between suspended WSe₂ and Si is largely uniform, as confirmed by modelling PL linescans across the device (see Supplementary Fig. 6), and high sharpness of excitonic features in strained devices. We ascribe strain values to each spectrum by measuring energetic shifts for excitonic species and assuming the shift rate 95 meV/%⁶¹ for all free excitons. This analysis is confirmed through separate interferometric measurements capable of directly measuring membrane displacement with nanometre resolution (see Supplementary Fig. 7). To identify excitonic species in our PL data, we compare their energy position and the binding energy (measured with respect to the X₀ position) with detailed measurement of excitonic species in high-quality unstrained devices encapsulated in hBN⁶². While the difference in electrostatic screening between suspended and encapsulated devices leads to noticeable changes in the binding energy of the excitons, in most cases the identification is possible.

First-principles calculations
We perform fully spin-polarized (non-collinear), structural and electronic optimization of the pristine cell with the DFT software package VASP⁶³–⁶⁸. Our calculations use the Perdew-Burke-Ernzerhof (PBE) functional, include 35 Å vacuum perpendicular to the membrane and a 25 × 25 × 1 Monkhorst-Pack k-space grid. Plane wave energy cutoff is set to 500 eV and the systems are electronically converged to δE = 10⁻⁵ eV. We find an energetically favourable lattice constant of a₀ = 3.322 Å. We then generate TB parameters based on maximally localized Wannier functions (MLWFs) from a set of DFT calculations of the pristine system and carefully interpolate TB parametrizations for intermediate strain values. Within tight-binding, we build a 17 × 17 supercell, remove a single Se atom, and then calculate Bloch states. We evaluate optical transition amplitudes based on the dipole operator also taken from DFT (see Supplementary Note 2 for technical details).

Data availability
The data that support the findings of this study are available from the authors on reasonable request.

References
1. Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS₂: a new direct-gap semiconductor. Phys. Rev. Lett. 105, 136805 (2010).
2. Wang, G. et al. Colloquium: excitons in atomically thin transition metal dichalcogenides. Rev. Mod. Phys. 90, 021001 (2018).
3. Wang, O. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 7, 699–712 (2012).
4. Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazev, O. V. & Kis, A. 2d transition metal dichalcogenides. Nat. Rev. Mater. 2, 17033 (2017).
5. Schäibley, J. R. et al. Valleytronics in 2d materials. Nat. Rev. Mater. 1, 16055 (2016).
6. Wang, Z. et al. Evidence of high-temperature exciton condensation in two-dimensional atomic double layers. Nature 574, 76–80 (2019).
7. Andrei, E. Y. et al. The marvels of moiré materials. Nat. Rev. Mater. 6, 201–206 (2021).
8. Malic, E. et al. Dark excitons in transition metal dichalcogenides. Phys. Rev. Mater. 2, 014002 (2018).
9. Zhou, Y. et al. Probing dark excitons in atomically thin semiconductors via near-field coupling to surface plasmon polaritons. Nat. Nanotechnol. 12, 856–860 (2017).
10. Li, Z. et al. Direct observation of gate-tunable dark trions in monolayer WSe₂. Nano Lett. 19, 6868–6893 (2019).
11. Zhang, X.-X., You, Y., Zhao, S. Y. F. & Heinz, T. F. Experimental evidence for dark excitons in monolayer WSe₂. Phys. Rev. Lett. 115, 257403 (2015).
12. Zhang, X.-X. et al. Magnetic brightening and control of dark excitons in monolayer WSe₂. Nat. Nanotechnol. 12, 883–888 (2017).
13. Robert, C. et al. Fine structure and lifetime of dark excitons in transition metal dichalcogenide monolayers. Phys. Rev. B 96, 155423 (2017).
14. Erkensten, D. et al. Dark exciton-exciton annihilation in monolayer WSe₂. Phys. Rev. B 104, I241406 (2021).
15. Tang, Y., Mak, K. F. & Shan, J. Long valley lifetime of dark excitons in single-layer WSe₂. Nat. Commun. 10, 4047 (2019).
16. Mapara, V. et al. Bright and dark exciton coherent coupling and hybridization enabled by external magnetic fields. Nano Lett. 22, 1680–1687 (2022).
17. Wu, Z. & Ni, Z. Spectroscopic investigation of defects in two-dimensional materials. Nanophotonics 6, 1219–1237 (2017).
18. Toth, M. & Aharonovich, I. Single photon sources in atomically thin materials. Annu. Rev. Phys. Chem. 70, 123–142 (2019).
19. Wehner, S., Elkouss, D. & Hanson, R. Quantum internet: a vision for the road ahead. Science 362, eaam9288 (2018).
20. Atature, M., Englund, D., Varnavikas, N., Lee, S.-Y. & Wrachtrup, J. Material platforms for spin-based photonic quantum technologies. Nat. Rev. Mater. 3, 38–51 (2018).
21. Baek, H. et al. Highly energy-tunable quantum light from moiré-trapped excitons. Sci. Adv. 6, eaba8526 (2020).
22. Turunen, M. et al. Quantum photonics with layered 2d materials. Nat. Rev. Phys. 4, 219–236 (2022).
23. Dastidar, M. G., Thekkoolen, I., Nayak, P. K. & Bhallamudi, V. P. Quantum emitters and detectors based on 2d van der Waals materials. Nanoscale 14, 5289–5313 (2022).
24. Zhang, C. et al. Probing critical point energies of transition metal dichalcogenides: surprising indirect gap of single layer WSe₂. Nano Lett. 15, 6494–6500 (2015).
25. Aslan, O. B., Deng, M. & Heinz, T. F. Strain tuning of excitons in monolayer WSe₂. Phys. Rev. B 98, 115308 (2018).
26. Lloyd, D. et al. Band gap engineering with ultralarge biaxial strains in suspended monolayer MoS₂. Nano Lett. 16, 5836–5841 (2016).
27. Deilmann, T. & Thysgesen, K. S. Finite-momentum exciton landscape in mono- and bilayer transition metal dichalcogenides. 2D Mater. 6, 035003 (2019).
28. Shi, H., Pan, H., Zhang, Y.-W. & Yakobson, B. I. Quasiparticle band structures and optical properties of strained monolayer MoS₂ and WS₂. Phys. Rev. B 87, 155304 (2013).
29. Khatibi, Z. et al. Impact of strain on the excitonic linewidth in transition metal dichalcogenides. 2D Mater. 6, 015015 (2018).
30. Linhart, L. et al. Localized intervalley defect excitons as single-photon emitters in WSe₂. Phys. Rev. Lett. 123, 146401 (2019).

Article https://doi.org/10.1038/s41467-022-35352-9

Nature Communications | (2022) 13:7691
31. Yang, D., Fan, X., Zhang, F., Hu, Y. & Luo, Z. Electronic and magnetic properties of defected monolayer WSe2 with vacancies. Nanoscale Res. Lett. 14, 192 (2019).
32. Yang, S., Chen, Y. & Jiang, C. Strain engineering of two-dimensional materials: methods, properties, and applications. InfoMat 3, 397–420 (2021).
33. He, K., Poole, C., Mak, K. F. & Shan, J. Experimental demonstration of continuous electronic structure tuning via strain in atomically thin MoS2. Nano Lett. 13, 2931–2936 (2013).
34. Kovalchuk, S. et al. Neutral and charged excitons interplay in non-uniformly strain-engineered WS2. 2D Mater. 7, 035024 (2020).
35. Harats, M. G., Kirchhof, J. N., Qiao, M., Greben, K. & Bolotin, K. I. Dynamics and efficient conversion of excitons to trions in non-uniformly strained monolayer WS2. Nat. Photonics 14, 324–329 (2020).
36. Lee, J. K. et al. Modification of electrical properties of graphene by substrate-induced nanomodulation. Nano Lett. 13, 3494–3500 (2013).
37. Gill, S. T. et al. Mechanical control of graphene on engineered pyramidal strain arrays. ACS Nano 9, 5799–5806 (2015).
38. Khestanova, E., Guinea, F., Fumagalli, L., Geim, A. K. & Grigorieva, I. V. Universal shape and pressure inside bubbles appearing in van der Waals heterostructures. Nat. Commun. 7, 12587 (2016).
39. Branny, A., Kumar, S., Proux, R. & Gerardot, B. D. Deterministic strain-induced arrays of quantum emitters in a two-dimensional semiconductor. Nat. Commun. 8, 13053 (2017).
40. Paro, K., Azzam, S. I., Banerjee, K. & Moody, G. Defect and strain engineering of monolayer WSe2 enables site-controlled single-photon emission up to 150K. Nat. Commun. 12, 3585 (2021).
41. Rivera, P. et al. Intrinsic donor-bound excitons in ultraclean monolayer semiconductors. Nat. Commun. 12, 871 (2021).
42. Aisan, B. et al. Excitons in strained and suspended monolayer WSe2. 2D Mater. 9, 015002 (2021).
43. He, M. et al. Valley phonons and exciton complexes in a monolayer semiconductor. Nat. Commun. 11, 618 (2020).
44. Liu, E. et al. Multipath optical recombination of intervalley dark excitons and trions in monolayer WSe2. Phys. Rev. Lett. 124, 196802 (2020).
45. Kirchhof, J. N. et al. Nanomechanical spectroscopy of 2d materials. Nano Lett. https://doi.org/10.1021/acs.nanolett.2c01289 (2022).
46. Liu, E. et al. Gate tunable dark excitons in monolayer WSe2. Phys. Rev. Lett. 123, 027401 (2019).
47. Conley, H. J. et al. Bandgap engineering of strained monolayer and bilayer MoS2. Nano Lett. 13, 3626–3630 (2013).
48. Noori, K., Cheng, N. L. Q., Xuan, F. & Quek, S. Y. Dielectric screening by 2d substrates. 2D Mater. 6, 035036 (2019).
49. Schmidt, T., Lischka, K. & Züehlner, W. Excitation-power dependence of the near-band-edge photoluminescence of semiconductors. Phys. Rev. B 45, 8989–8994 (1992).
50. Barbone, M. et al. Charge-tunable bie exciton complexes in monolayer WSe2. Nat. Commun. 9, 3721 (2018).
51. Morell, N. et al. High quality factor mechanical resonators based on WSe2 monolayers. Nano Lett. 16, 5102–5108 (2016).
52. Nicholl, R. J. et al. The effect of intrinsic crumpling on the mechanics of free-standing graphene. Nat. Commun. 6, 8789 (2015).
53. Huang, J., Huang, T. B. & Mikkelsen, M. H. Probing the origin of excitonic states in monolayer WSe2. Sci. Rep. 6, 22414 (2016).
54. Arora, A. et al. Dark trions govern the temperature-dependent optical absorption and emission of doped atomically thin semiconductors. Phys. Rev. B 101, 241413 (2020).
55. Shinokita, K. et al. Continuous control and enhancement of excitonic valley polarization in monolayer wse2 by electrostatic doping. Adv. Funct. Mater. 29, 1900260 (2019).
56. Ye, T. et al. Room-temperature exciton-based optoelectronic switch. Small 17, 2005918 (2021).
57. Allain, A. & Kis, A. Electron and hole mobilities in single-layer WSe2. ACS Nano 8, 7180–7185 (2014).
58. Echeverry, J. P., Urbaszek, B., Amand, T., Marie, X. & Gerber, I. C. Splitting between bright and dark excitons in transition metal dichalcogenide monolayers. Phys. Rev. B 93, 121107 (2016).
59. Castellanos-Gomez, A. et al. Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping. 2D Mater. 1, 011002 (2014).
60. Greben, K., Arora, S., Harats, M. G. & Bolotin, K. I. Intrinsic and extrinsic defect-related excitons in TMDCs. Nano Lett. 20, 2544–2550 (2020).
61. Frisenda, R. et al. Biaxial strain tuning of the optical properties of single-layer transition metal dichalcogenides. npj 2D Mater. Appl. 1, 10 (2017).
62. Li, Z. et al. Momentum-dark intervalley exciton in monolayer tungsten diselenide brightened via chiral phonon. ACS Nano 13, 14107–14113 (2019).
63. Liu, E. et al. Valley-selective chiral phonon replicas of dark excitons and trions in monolayer WSe2. Phys. Rev. Res. 1, 032007 (2019).
64. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 1169–1186 (1996).
65. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).
66. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993).
67. Kresse, G. & Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. Phys. Rev. B 49, 14251–14269 (1994).
68. Plechinger, G. et al. Identification of excitons, trions and bie excitons in single-layer WS2. Phys. Status Solidi (RRL) - Rapid Res. Lett. 9, 457–461 (2015).

Acknowledgements
S.K., A.K., D.J.B., J.N.K., B.H., K.G., and K.I.B. acknowledge support by Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) project-ID 449506295 and 328545488, TRR227, SFB951, and ERC Starting grant no. 639739. P.H.L. and S.H. acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) under the Emmy Noether Initiative (project-ID 433878606). C.S. acknowledges support as a recipient of a DOC fellowship of the Austrian Academy of Sciences. Numerical calculations were performed on the Vienna Scientific Cluster VSC4. We acknowledge support by the Open Access Publication Fund of Humboldt-Universität zu Berlin.

Author contributions
P.H.L. and D.J.B. fabricated the samples with support from B.H. and J.K. P.H.L., S.H., D.J.B., A.K., S.K., and D.Y. measured the PL data assisted by K.G. P.H.L., J.N.K., D.J.B., and A.K. performed reflectivity measurements. P.H.L., S.H., and K.I.B. analyzed the experimental data with support from D.J.B. and A.K. L.L., C.S., and F.L. performed the DFT and TB calculations. P.H.L., S.H., C.S., F.L., and K.I.B. co-wrote the paper with input from all authors. S.H. conceived the project. K.I.B. and S.H. supervised the project.

Funding
Open Access funding enabled and organized by Projekt DEAL.

Competing interests
The authors declare no competing interests.
Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-35352-9.

Correspondence and requests for materials should be addressed to Pablo Hernández López, Sebastian Heeg or Kirill I. Bolotin.

Peer review information Nature Communications thanks Runchen Lai and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2022