Optical dispersion of valley-hybridised coherent excitons with momentum-dependent valley polarisation in monolayer semiconductor

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Keywords: optical exciton dispersion, pseudo-spin texture, 2D exciton fine-structure, hBN-encapsulated WSe2 monolayer

Abstract

2D excitons in transition-metal dichalcogenides (TMDCs) offer interesting effects related to the valley pseudo-spin degree of freedom and long-range exchange interactions, as well as the coupling with light states. Several theoretical predictions have claimed that the neutral exciton of TMDCs splits into a transversal and longitudinal exciton branch, with the longitudinal one, which is the upper branch, exhibiting an extraordinary strong dispersion in the meV range within the light cone. Historically, this was linked for semiconductor quantum wells to strong far-field optical dipole coupling, or strong electronic long-range exchange interactions. Recently, experiments utilizing Fourier-space spectroscopy have shown that the exciton (exciton–polariton) dispersion can indeed be measured for high-quality hexagonal-BN-encapsulated WSe2 monolayer samples and can confirm the energy scale. Here, the exciton fine-structure’s pseudo-spin and the valley polarisation are investigated as a function of the centre-of-mass-momentum and excitation-laser detuning. For quasi-resonant excitation, a strong dispersion featuring a pronounced momentum-dependent helicity is observed. By increasing the excitation energy step-wise towards and then above the electronic band gap and the B-exciton level, the dispersion and the helicity systematically decrease due to contributions of incoherent excitons and emission from plasma. The decline of the helicity with centre-of-mass momentum can be phenomenologically modelled by the Maialle–Silva–Sham mechanism using the exciton splitting as the source of an effective magnetic field. By contributing to a better understanding of valley decoherence effects and the role of hybridised states in the optoelectronic properties, polarisation-sensitive Fourier-space investigations can support the development of future ‘optical-valleytronic’ devices.

1. Introduction

Light–matter interactions are of fundamental importance and great interest to various research communities, and similarly, the abundance of quasiparticles and many-body complexes in monolayer semiconductors have attracted considerable attention in recent years. The favourable opto-electronic properties of this unique material class of transition-metal dichalcogenides (TMDCs) are strongly influenced by the 2D excitons, which have been widely studied in the science community as a consequence of their remarkably large binding energy [1–3], high oscillator strength [2, 4] and spin-valley locking [5], to name but a few (also see ref. [6]). In this context, it has become clear that h-BN encapsulation is an essential tool to obtain a narrow linewidth close to the homogenous linewidth and an increased excitonic emission [7–9]. This positive role of h-BN in 2D stacks has been attributed to its mitigation of the influence of external effects compared to the situation for monolayers on bare substrate material (e.g. SiO2) [10], e.g. by reducing the amount of adsorbates, strain (due surface roughness) [11], and charge disorder [12, 13]. Thus, h-BN encapsulation allows the excitonic properties to be better probed...
including the observation of their dispersion [16], multi-particle states across valleys [33, 34], selection rules and radiation patterns. While this has opened the path to the exploration of a variety of different application scenarios [18–21], it has also changed the charge-carrier screening important to many fundamental investigations.

Theoretical work has shown that the carrier screening in these 2D semiconductors and metals is indeed very different from that of their 3D counterparts [22–26]. The renormalisation of Coulomb energies is not scale invariant [22], but the tiny height of the material introduces a characteristic length scale; or if speaking in terms of the reciprocal space, the dielectric function is (linearly) dependent on the momentum. This means that for the case of a suspended layer [22] for small distances the screening creates effectively a Rytova-Keldysh potential [27, 28], while for distances between hole and electron larger than the characteristic length of that system, the effective potential behaves like the unscreened 3D-Coulomb potential. This change of screening could be proven by the observation of a non-hydrogenic Rydberg series [1, 2].

Caused by this reduced screening, the single-layer material features comparably strong Coulomb interactions especially for long-range interactions. Furthermore, the free-standing monolayer in vacuum also exhibits—additionally affected by the strong localisation of charge carriers in the spatial domain onto the sub-nm-thick layer of transition metals (i.e. their in-plane d-orbital bonds)—a comparably large exciton binding energy for (Wannier-like) crystal excitons, not far from that of (Frenkel-like) molecule excitons. It is clear that, when the monolayer is transferred onto a substrate or encapsulated with a dielectric such as h-BN, changes to the screening model [23, 29–31] have to be applied owing to the induction of mirror charges in the environment. Nonetheless, the fundamental difference between the 2D material and the 3D crystals in terms of a momentum-dependent screening stays valid even when encapsulated as long as the permittivity contrast between the 2D material and the surrounding is significant. In fact, recent measurements show that excitons in h-BN encapsulated WSe$_2$ behave like a hypothetical hydrogenic Rydberg series in the fractal dimension of dimensionality 2.834 [32]. Thus, encapsulated samples feature physics between the 2D and the 3D case.

The reduced screening enhances not only the effects by the direct Coulomb term but also by those related to its exchange interaction. Therefore, Yu et al [33] and other scientists [34–37] rediscovered the concept of an enhanced or even linear dispersion of the longitudinal exciton branch caused by the long-range exchange interactions already proposed for quantum-well (exciton–)polaritons in III–V semiconductors [38, 39]. While in III/V quantum wells the effect is negligible (about 80 µeV) and smaller than the usual quadratic dispersion, in 2D materials, where the interaction strength is about two orders of magnitude stronger, it has been predicted to be on the order of 1–2 meV within the light cone, i.e. the energy–momentum range in which a photon can exist in free space.

Here, Yu et al [33], Wu et al [34] and Qiu et al [35] predicted a linear slope of the dispersion relation around zero centre-of-mass momentum, as they use a strictly 2D-Coulomb potential, whereas Deilmann et al [37] claimed merely an increased curvature of the underlying parabolic dispersion by using a 3D-Coulomb potential. The authors argued that for realistic samples on a substrate or encapsulated monolayers a strict 2D treatment is not valid anymore. The aforementioned measurements [32], claiming physics between the 2D and 3D case, makes this reasoning believable.

Furthermore, Refs. [33–35] reported that the longitudinal (upper) and transversal (lower) branch have to be considered as coherent superpositions of both valleys, with the energetic separation between the hybridised states resembling the Rabi oscillations between the Rabi-split states, i.e. a periodic transfer of excitation takes place between both valleys due to the exchange interaction. Thus, the valley pseudo-spin is necessarily linked with the centre-of-mass motion and a measurement of the splitting can give insights into the dephasing mechanism of the valley pseudo-spin by exchange interactions or decoherence.

Recently, the WSe$_2$ exciton (exciton–polariton) dispersion within the light cone was measured successfully both in white-light reflection and in photoluminescence by optical Fourier-space spectroscopy [16] on high-quality h-BN encapsulated samples. Indeed, a measurable dispersion in the meV range could be experimentally demonstrated, giving access to intriguing studies of light–matter interactions and exciton physics in 2D materials. To leap one crucial step further, here, we investigate the phase-space-dependent pseudo-spin texture of the rich exciton fine-structure in such encapsulated WSe$_2$ monolayer by optical helicity measurements and reveal the polarisation- and excitation-energy dependence of the neutral exciton (exciton–polariton) dispersion branch as a function of the in-plane momentum. A systematic decrease is evidenced due to contributions of incoherent excitons and emission from plasma when moving the excitation energy step-wise above the electronic band gap. Our findings indicate—in accordance with the strong dispersion feature and valley-polarisation degree—an ultra-light species of delocalised and hybridised quasi-particles in the valley (pseudo-spin) landscape of the WSe$_2$ monolayer’s 2D lattice. Remarkably, high-quality 2D stacks offer these highly-mobile correlated electron–hole pairs with pronounced helicity, strong in-plane long-range dipole interactions and macroscopic polarisation.
2. Experiment

Generally, when a light beam is incident onto a monolayer under an angle $\alpha$ with respect to the plane’s normal, the electric field (polarisation) of the light wave can be decomposed into a longitudinal (oriented in the plane of incidence parallel to the monolayer), a transversal (orthogonal to the propagation direction and in the plane of the monolayer) and an out-of-plane component (cf figure 1 (a)). These different field components couple to the different branches of the exciton fine structure [35, 36]. The longitudinal component couples to the upper branch of the bright exciton with non-analytic dispersion, the transversal part to the lower branch and the out-of-plane projection to the $z$-mode, which is often also called a dark exciton [34–36, 40, 41] (cf schematic in figure 1(b)).

The underlying parabolic free-exciton dispersion of all three species is in theory only strongly modified by the coupling to the longitudinal polarisation in the case of the upper bright branch, rendering it indistinguishable from the lower bright branch at exact zero momentum (normal incidence) due to the maximum induced energy shift (the two polarisations in the plane become indistinguishable at $\alpha = 0^\circ$). The modified dispersion recovers to the uncoupled curve at angles approaching $90^\circ$, corresponding to a vanishing longitudinal field component.

To analyse the valley pseudo-spin of these branches, polarisation-resolved PL spectra with $k_F$-space resolution [16] (for detailed information on the experimental technique see the supporting information (available online at https://stacks.iop.org/2DM/8/015009/mmedia)) have been acquired using different excitation energies under continuous-wave (cw) pumping. The sample is a high-quality h-BN-encapsulated WSe$_2$ monolayer employed in a cryostat and measured optically using a $\mu$-PL setup with a 4-f geometry [16]. The used excitation energies are 1.784 eV, 1.810 eV, 1.952 eV and 2.330 eV and cover distinct detunings (that is the energy difference between the A-exciton resonance and the excitation energy) from quasi-resonant (A$_{1h}$) over continuum excitation (above the electronic band gap, where an unbound correlated electron–hole pair resembles the A exciton in its ionised state, but below the B exciton) to excitation even above the B exciton. Note that the reference energies for A and B exciton resonances in the h-BN-encapsulated monolayer correspond to those in ref. [32] and are according to the dielectric environment significantly different from that of free-standing or merely substrate-supported WSe$_2$. The excitation power was kept constant at 0.4 mW for all situations. All situations are in the linear regime resulting in an approximate carrier density of about $10^{10}$ cm$^{-2}$. From former studies [42, 43], the non-linear regimes of exciton–exciton annihilation and the Mott transition are expected to be around a density of $10^{13}$ cm$^{-2}$. The charge-carrier density has been estimated by solving the steady state of a simple differential equation (see Supporting Information for details). A schematic energy–momentum diagram indicating the relative pump levels with respect to the excitonic states in WSe$_2$ according to refs. [35, 44] is shown in figure 1(c).

The experimentally obtained Fourier-space-resolved spectra (energy vs. in-plane-momentum plot; short: far-field [FF] spectrum) at 10 K are shown in figures 2(a)–(d) and have been recorded without selecting a particular polarisation of the emitted light.
Figure 2. PL Fourier-space-resolved spectra for different excitation detunings. (a)–(d) Logarithmic false-colour contour plots of the total intensity under right-circular-polarised pumping for different excitation energies (labelled Ex.) and fixed low photon flux at 10 K. The signal was not detected with polarisation sensitivity. The line spectra displayed as insets represent angle-integrated data. The different excitonic features are labelled in (d) similar to Refs. [15, 17, 45–47] (X0 for the neutral excitons, X− for trions, XX for biexcitons and PSB for phonon sidebands). (e) Neutral exciton’s extracted peak positions as a function of the in-plane momentum for average effective mass estimations using parabolic dispersion fits. The error bars denote the 1-sigma confidence interval of extraction by the automatic fitting routine. The energies are vertically offset by 1 meV for better visibility.

Momentum-integrated line spectra are displayed onto the FF spectra for comparison (the polarisation-resolved spectra are shown in the Supporting Information on a logarithmic scale). Remarkably, a curved—i.e. measurable—dispersion of the neutral exciton can be measured via FF spectroscopy for quasi-resonant pumping on the meV scale as known from [16]. For an overview reflection contrast FF spectrum, which also exhibits a visibly curved dispersion (a noticeable one for the 1 s and very subtle signs for the 2 s resonance), see the Supporting Information. In contrast to differently-detuned quasi-resonant excitations of the A exciton, only a flat line is obtained for off-resonant pumping, i.e. a non-resolvable dispersion is measured. The former case, i.e. the behaviour obtained for quasi-resonant excitation, is expected by the discussed theories [34, 35, 37].

In contrast, for off-resonant excitation, the coherence times are expected to be very low. Thus, macroscopic polarisation is quickly transformed into microscopic polarisation due to decoherence. The long-range interaction, which in a simplified picture can be understood as the backaction (feedback) of the electric field from the induced polarisation—induced by the dipole of the exciton—on the exciton itself [6, 38, 39], is therefore lower due to the loss of a macroscopic dipole when compared to a case with long coherence time. In this picture, such long-range interaction between excitations in different valleys is very similar to the formation of exciton–polaritons, i.e. dipole–dipole coupling via a macroscopic polarisation takes place. In the case of weak interaction at off-resonant pumping above the B-exciton, the separate valleys can be still seen as the (uncoupled) eigenstates of the system and no hybridisation occurs. However, in the other extreme, a purely coherent long-lasting excitation in both valleys would strongly interact and hybridise the eigenstates.

In between these two cases, when pumping the 2D crystal shortly above its quasi-particle gap (figure 2(c)) of the neutral exciton but below the B-exciton, it seems as if the observation exhibits a mixture of, both, a strong dispersion from coherent excitonic, hybridised valley states, as well as a flat dispersion arising from non-coherent contributions, i.e. free carriers. The observation of a vanishing curvature can be understood as a decreasing fraction of excitons. This becomes clearer when existing knowledge concerning traditional semiconductors is considered. Full many-body calculations for GaAs quantum wells [48] showed that at increased detuning (even if just above the 2 s state) the population fraction of excitons in the 1 s state drops dramatically, namely from about 80% at a resonant condition to 20% when pumping the 2 s state resonantly, and to only 3% when pumping the system above the quasi-particle band gap (into continuum states), while the counter fraction (i.e. the rest) corresponds to an uncorrelated electron–hole plasma. Our experimental observations for monolayer-TMDC excitons are in qualitative agreement with these calculations.

The extracted dispersion relations from figures 2(a) to (d) are shown in figure 2(e). Although a number of theories predict a linear slope [33–35],
we have followed the argument of Deilmann et al [37] and extracted the effective mass by parabolic fits to the extracted position of the neutral exciton as it describes the data well and allows for easy comparison with polariton systems. The bright exciton’s average effective mass gets heavier starting from $1 \times 10^{-4} m_0$ at quasi-resonant pumping to more than $1 \times 10^{-3} m_0$ with increased detuning until finally no parabolic fit is applicable when the system is pumped into the continuum. Note that the change of effective mass is attributed to the mixture of coherent and incoherent components in the FF spectra which affect the extraction of dispersion curves, whereas the underlying curvatures of the different emitters is not necessarily altered. The small tilt in figure 2(e) visible for the actually flat dispersion is caused by a slightly tilted orientation of the imaging monochromator’s CCD camera (rotation of 0.5°).

Interestingly, while for quasi-resonant pumping, the spectrum indicates equidistantly separated replicas of the exciton mode attributed to phonon sidebands (PSBs), the higher the chosen pump energy, the more exciton complexes become visible in the spectrum. When comparing the spectra, one can see that the emission from trions ($X^\pm\pm$, ± sign indicating the excess charge) and biexcitons ($XX$) increases significantly when the excitation energy is raised above the quasi-energy band gap of the A-exciton. While the emission from (acoustic/optical) phonon sidebands of dark exciton states ($X_d$ ac/op-PSB, respectively) [45, 47, 49, 50] from 1.65 eV to 1.67 eV and from z-mode excitons (also among the dark states, $X_d$) [40, 41, 45] around 1.69 eV is weaker at quasi-resonant conditions, it can be measured at all excitation conditions studied here. Logarithmically-scaled, angle-integrated intensity spectra for every case can be found in the Supporting Information.

Ultimately, to study the helicity, i.e. the degree of circular polarisation, for the different excitation conditions, FF spectra with a selected circular polarisation under circularly polarised pumping have been acquired. The amount of helicity is calculated using the common formula $\rho = (I^{\sigma^+} - I^{\sigma^-}) / (I^{\sigma^+} + I^{\sigma^-})$ and is plotted in figures 3(a)–(d). Here, $I^{\sigma^\pm}$ denotes the intensity of detected light in $\sigma^\pm$ polarisation. For the quasi-resonant 1 s excitation cases, a pronounced helicity of about 40% is obtained for the neutral exciton. When exciting above the 2 s resonance and A-continuum edge, the helicity is reduced but still clearly visible in comparison to the case when the system is excited well above its quasi-particle band and above the B-exciton, where it is almost absent similar to previous characterisations without angle resolution [51–53]. Remarkably, these helicity maps for FF spectra all indicate the considerable amount of the circular-polarisation degree for various exciton complexes as expected, clearly highlighting the valley-excitonic nature (in contrast to defect state emission) with the valley-selective excitation and detection scheme. For clarity, these four false-colour contour maps share the same helicity scale and are, thus, directly comparable.

In order to analyse the momentum dependence of the helicity for the neutral exciton species, the maximum measured helicity value in the relevant energy
range of 1.725 eV and 1.733 eV has been extracted along the momentum axis for all different excitation energies (see figure 4(a)). For the quasi-resonant excitation cases, one can see a drop of helicity with increasing in-plane momentum. In the intermediate case only a small variation in helicity is obtained, which is only slightly bigger than the noise. However, in the case of continuum excitation, no correlation between the centre-of-mass momentum and helicity can be found, as expected. As Yu et al. [33] explained that the splitting between the states of the bright exciton resembles their Rabi oscillation, it is not surprising that a smaller helicity is evidenced at larger centre-of-mass momentum and correspondingly larger energetic splitting between the branches, as a stronger interaction will lead to a faster depolarisation.

3. Discussion

The strong dispersion observed here has its origin in the lifting of the degeneracy between a longitudinal and transversal exciton–polariton branch due to long-range exchange interaction and the additional energy due to the long-range exchange interaction and \( \phi_k \) the orientational in-plane angle of the centre-of-mass momentum. In such a scenario, where excitons polarised in two perpendicular in-plane directions have different energies, it is established knowledge that this leads to spin and valley decoherence [36, 55]. This is easily understood, as the interaction leads to a mixing of the pure valley states [36]. This spin-decoherence is normally modelled by introducing an effective magnetic field \( \Omega_{\text{eff}}(k) \) and has been used to model classical semiconductors [56], angle-integrated helicity of excitons in 2D-monolayers [36] as well as the angle-resolved helicity found for valley cavity–polaritons based on TMDC [54, 57].

The dynamics of the valley pseudospin \( S_k \) then follows the following equation:

\[
\frac{\partial S_k}{\partial t} = Q \{ S_k \} - S_k \times \Omega_{\text{eff}}(k). \tag{2}
\]

Here, \( Q \) is the collisional integral, which describes other decoherence pathways such as scattering with phonons and other excitons. In case of excitons in TMDCs, the effective magnetic field can be denoted as follows [34, 35, 54] with the excitonic Hopfield coefficient \( |X_k|^2 \) and the energetic splitting of the exciton branches \( \Omega_{\text{ex}}(k) \):

\[
\Omega_{\text{eff}}(k)|X_k|^2\Omega_{\text{ex}}(k) = |X_k|^22\hbar k (\cos(2\phi_k) + \sin(2\phi_k) / 2)/h = |X_k|^22\hbar k (\cos(2\phi_k), \sin(2\phi_k), 0) / h \tag{3}
\]

The effective field vanishes at zero momentum. \( A \) denotes the strength of the in-plane interactions. Under the assumption that the collisional integral
dependence on the momentum is negligible within the light cone, the resulting decoherence time $\tau_{\text{deco}}$ can be decomposed into a momentum-independent part $\tau_{\text{deco},k=0}$ and the $k$-dependent decoherence part due to exchange interactions $\tau_{\text{deco},E_{I,I}}$. If one assumes further that the spin decoherence happens by the Maialle-Silva-Sham mechanism [58] (for more details on the model see the Supporting Information) similar to previous reports on cavity–polaritons in TMDs [54, 57], the spin-decoherence time can be written as follows with the momentum relaxation time $\tau_{\text{relax}}$:

$$
\frac{1}{\tau_{\text{deco}(k)}} = \frac{1}{\tau_{\text{deco},k=0}} + \frac{1}{\tau_{\text{deco},E_{I,I}(k)}} = \frac{1}{\tau_{\text{deco},k=0}} + \frac{\Omega_{\text{eff}||}^2(k)}{\tau_{\text{relax}}}. \tag{4}
$$

Note that Glazov et al. [36] assumed a Dyakonov-Perel type mechanism instead. As in both cases motional narrowing results in the spin decoherence, this will not change equation (4). As the long-range part does not contribute to the decoherence at zero momentum, the momentum-independent pseudo-spin decoherence time can be directly estimated using the following formula (after [36]):

$$
\rho_c = \rho_0 \left(1 + \frac{\tau_{\text{rel}}}{\tau_{\text{deco},k=0}}\right). \tag{5}
$$

Assuming strict selection rules ($\rho_0 = 100\%$), a recombination time of $\tau_{\text{rel}} = 5.0 \pm 0.5 \text{ps}$ similar to previous reports [14, 36, 54] and the experimentally measured degree of circular polarisation $\rho_{c,\text{max}}$ (figure 4(c)), one can determine the $k$-independent decoherence time (figure 4(d)).

In order to extract the effective magnetic field, the energy derivatives of the Fourier-space spectra were plotted and the approximated splitting for distinct $k$ values was manually extracted (figure 4(b)). Two example derivative spectra are shown in the Supporting Information. The resulting energy splitting was fitted with a line to extract the slope $2A$ of the linear branch (see figures 4(b), (c)). Note that, while the linear fits suggest a large splitting at the light cone edge, Qiu et al. [35] predicted a saturation towards the edge such that a maximum splitting of 2.0 to 2.7 meV at the edge can be expected from this experimental data set. For the cases with measurable dispersion, the underlying plausible value of 2.5 meV is used (figure 4(d)).

Finally, if a pure exciton gas ($|X_k|^2 = 1$) and a momentum relaxation time of 241 fs ($2h/\Gamma$) (using a linewidth of 6 meV) is assumed, the decoherence time can be calculated using equation (4) and the polarisation using equation (5). The resulting predictions for all detuning cases are shown together with the experimental helicity in figure 4(a) which is in good agreement with the experimental observations.

The model shows that the decaying helicity is indeed most likely arising from the $k$-dependent long-range exchange interaction. Similarly, the valley decoherence due to other processes is strongly enhanced at increased detuning, as expected. The model is general enough such that a similar momentum-dependent helicity can be expected for other TMDs, although the effect may be smaller due to the weaker Coulomb interaction—particularly for molybdenum-based monolayers.

4. Conclusion

To summarise, we observe a dispersion of the neutral exciton emission under quasi-resonant circularly-polarised cw excitation conditions attributed to coherent mixing of the excitonic states at the $K$ and $K'$ valley in qualitative agreement with the predictions for monolayer TMDs [33–36, 38]. Remarkably, but not surprisingly, the curved dispersion is gradually vanishing if the excitation detuning is increased with respect to the neutral exciton resonance. This is understood when taking into account a faster decoherence of the coherently mixed exciton states with increasing detuning. In the case of quasi-resonant excitation, where strong coherence is expected, a decline of the mode’s helicity with increasing angle is observed compared to normal incidence. A phenomenological model based on the Maialle-Silva-Sham mechanism [58] on the basis of the extracted energy splitting shows good agreement with the observations. Accordingly, the increased long-range exchange interaction towards higher in-plane momenta facilitates depolarisation. This effect also reduces with increased detuning, for instance as noticeable for pumping higher excitonic states quasi-resonantly. However, in the case of well-above continuum excitation, where basically only plasma and an incoherent exciton population occur [6], no correlation between centre-of-mass momentum and helicity is found, as expected. Revealing that there is a complex locking between valley pseudo-spin and centre-of-mass momentum present, our study encourages further investigations of angle-resolved polarisation anisotropy in exciton-complexes-rich 2D semiconductors. In particular, time-resolved Fourier-space mapping may further shed light on valley decoherence mechanisms as function of the centre-of-mass momentum.

5. Methods

Sample preparation. The here employed high-quality stack of monolayer tungsten diselenide (WSe$_2$) encapsulated between thin h-BN flakes was achieved with a pick-and-lift technique. The base material for monolayer exfoliation was a bulk single crystal grown in an excess selenium flux (defect density: $5 \times 10^{10} \text{cm}^{-2}$) [59]. First, h-BN flakes and the WSe$_2$ monolayer were exfoliated from bulk single crystals and isolated on SiO$_2$. An O$_2$ plasma treatment of the SiO$_2$ substrate preceded the exfoliation.
for WSe$_2$. All flakes were identified under a microscope using optical contrast. Using an established dry stacking technique with polypropylene carbonate (PPC) on polydimethylsiloxane (PDMS), individual flakes were sequentially picked up to form the h-BN/WSe$_2$/h-BN stack, first a top layer of h-BN (at 48 °C), then WSe$_2$, and at last the bottom layer of h-BN. To re-smoothen the PPC and ensure a clean wave front, the PPC was briefly heated to 90 degrees C after each h-BN pickup. Note that the whole stack was then released onto the target substrate, which had been first heated up (75 °C) before establishing a contact with the stack. To achieve the clean release, the stack was gradually heated to 120 °C. Consecutively, the PPC/PDMS was lifted and the substrate immersed in chloroform. Then it was rinsed with IPA to remove polymer residue from the sample. The total stack thickness of about 40 nm was confirmed by atomic-force microscopy, showing an ≈10 nm bottom and 30 nm top h-BN sheet.

**Optical measurement.** Angle-resolved microphotoluminescence (µ-PL) measurements were performed using a self-built confocal optical microscope with Fourier-space imaging capabilities (similar to ref. [16]; the technique is further detailed in the Supporting Information). For the experiments at 10 K, the sample was mounted in an evacuated (≈10$^{-7}$ mbar) helium-flow cryostat, which was placed under the 40x microscope objective of the µ-PL setup. For quasi-resonant excitation, a continuous-wave-operated titanium-sapphire laser (SpectraPhysics Tsunami) was used, emitting light at about 695 or 685 nm. A high aspect-ratio long-pass filter with specified edge at 700 nm was used to block the laser light. Also, higher-detuning pumping was achieved with continuous-wave lasers. For detection, a nitrogen-cooled charge-coupled device (CCD) behind an imaging monochromator (Princeton Instruments Acton SP2300) was employed, using two-dimensional chip read-out. Fourier-space spectra that are intensity (counts per integration time) over wavelength (long axis) over momentum (short axis) were recorded via the exposed CCD area, from which optical dispersion curves were extracted. All data shown are time-integrated spectra. For k-space-resolved spectroscopy, the Fourier-space image of the sample’s emission was projected onto the monochromator entrance slit via a set of lenses (cf Supporting Information). The light cone in the medium (vacuum) amounts to $|k_0| ∼ 34 (8.7) \mu m^{-1}$, the maximum detectable angle of ±37° for the used objective (NA 0.6) corresponds to $|k_0| ∼ 5.2 \mu m^{-1}$ in WSe$_2$. Relative effective-mass fit certainty is about 5%–10%. Detection of the µ-PL signal from the sample took place behind a spatially-filtering aperture in the real-space projection plane of the confocal microscope, which selects a spot of about 1 µm diameter. The laser-spot diameter amounts to approximately 2 µm. The evaluation procedure follows that of ref. [16].

**Visualisation.** The schematic depiction of the WSe$_2$ monolayer in figure 1(a) is based on crystallographic data provided by the Materials Project [60] and drawn by the tool *Mercury* [61].

**Acknowledgments**

The authors acknowledge financial support by the German Research Foundation (DFG: SFB1083—Project-ID 223848855—and RA2841/5-1), by the Philips-Universität Marburg, and the German Academic Exchange Service (DAAD). Synthesis of WSe$_2$ and heterostructure assembly are supported by the NSF MRSEC program through Columbia in the Center for Precision Assembly of Superstatic and Superatomic Solids (DMR-1420634).

**Authors’ contributions**

A R-I conceived the experiment and initiated the study on 2D-exciton-dispersion measurements in 2015. A R-I guided the joint work together with J C H High-quality WSe$_2$ synthesis and heterostructure assembly were achieved by S S E, D A R, K B and J C H The setup was established by L M S and A R-I, and the structures were measured by L M S The results were interpreted, discussed and summarised in a manuscript by L M S and A R-I with the support of all co-authors.

**Authors’ statement/Competing interests**

The authors declare no conflict of interest.

**Additional information**

Supplementary Information accompanies this paper.

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