Tuning Valley Polarization in a WSe_2 Monolayer with a Tiny Magnetic Field

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In monolayers of semiconducting transition metal dichalcogenides, the light helicity (σ^+ or σ^-) is locked to the valley degree of freedom, leading to the possibility of optical initialization of distinct valley populations. However, an extremely rapid valley pseudospin relaxation (at the time scale of picoseconds) occurring for optically bright (electric-dipole active) excitons imposes some limitations on the development of opto-valleytronics. Here, we show that valley pseudospin relaxation of excitons can be significantly suppressed in a WSe_2 monolayer, a direct-gap two-dimensional semiconductor with the exciton ground state being optically dark. We demonstrate that the already inefficient relaxation of the exciton pseudospin in such a system can be suppressed even further by the application of a tiny magnetic field of about 100 mT. Time-resolved spectroscopy reveals the pseudospin dynamics to be a two-step relaxation process. An initial decay of the pseudospin occurs at the level of dark excitons on a time scale of 100 ps, which is tunable with a magnetic field. This decay is followed by even longer decay (>1 ns), once the dark excitons form more complex pseudo-particles allowing for their radiative recombination. Our findings of slow valley pseudospin relaxation easily manipulated by the magnetic field open new prospects for engineering the dynamics of the valley pseudospin in transition metal dichalcogenides.

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Interband excitation of a semiconductor brings up the possibility to transfer the angular momentum of circularly polarized photons to photoexcited carriers, to create a nonequilibrium orientation of their spins and, eventually, to examine the conservation of this orientation in the crystal by probing the polarization degree of the emitted light. This so-called optical orientation has been widely explored in zinc-blende semiconductors with respect to the angular momentum of electronic spins [1,2]. Such studies are now of vivid interest in monolayers of semiconducting transition metal dichalcogenides (S-TMDs) [3–11], in which the circular polarization of light ($\sigma^{\pm}$) is coupled to the valley degree of freedom ($\pm K$). The expected robustness of the valley pseudospin [3,12] (due to strong spin-orbit interaction in S-TMDs) and the possibility of its optical orientation at room temperature [13–15] are promising for designing opto-valleytronic devices. Unfortunately, there exists an efficient mechanism of disorientation of the valley pseudospin. It is due to strong long-range electron-hole exchange interaction [16–20], which is particularly effective when the excited electron-hole pairs occupy the bright excitonic states [8–11]. In the zero approximation, such coupling vanishes for the electric-dipole forbidden (optically dark) excitons. More detailed theoretical treatment reveals finite residual exchange coupling even for the dark excitons [21], yet its strength is still predicted to be orders of magnitude lower than for the bright excitons. As a consequence, the monolayers of S-TMDs with an optically inactive ground state of the neutral exciton are expected to display a significantly suppressed relaxation of the valley pseudospin. In general, such a condition is met in tungsten-based S-TMDs, in contrast to the molybdenum-based dichalcogenides, which exhibit a different order of spin-orbit split bands in the conduction band [18,22] resulting in an optically active ground state.

In the search for inefficient relaxation of the valley pseudospin, we have studied monolayers of tungsten diselenide (WSe_2), which were mechanically exfoliated from bulk crystals and transferred on Si/SiO_2 substrates (for details, see Appendix A 1). Optical orientation experiments have been carried out in continuous-wave (CW) and time-resolved operational modes, at low temperatures ($T = 5$–10 K), and as a function of the magnetic field (for details, see Appendix A 2). We have obtained consistent results for eight different monolayer flakes from various

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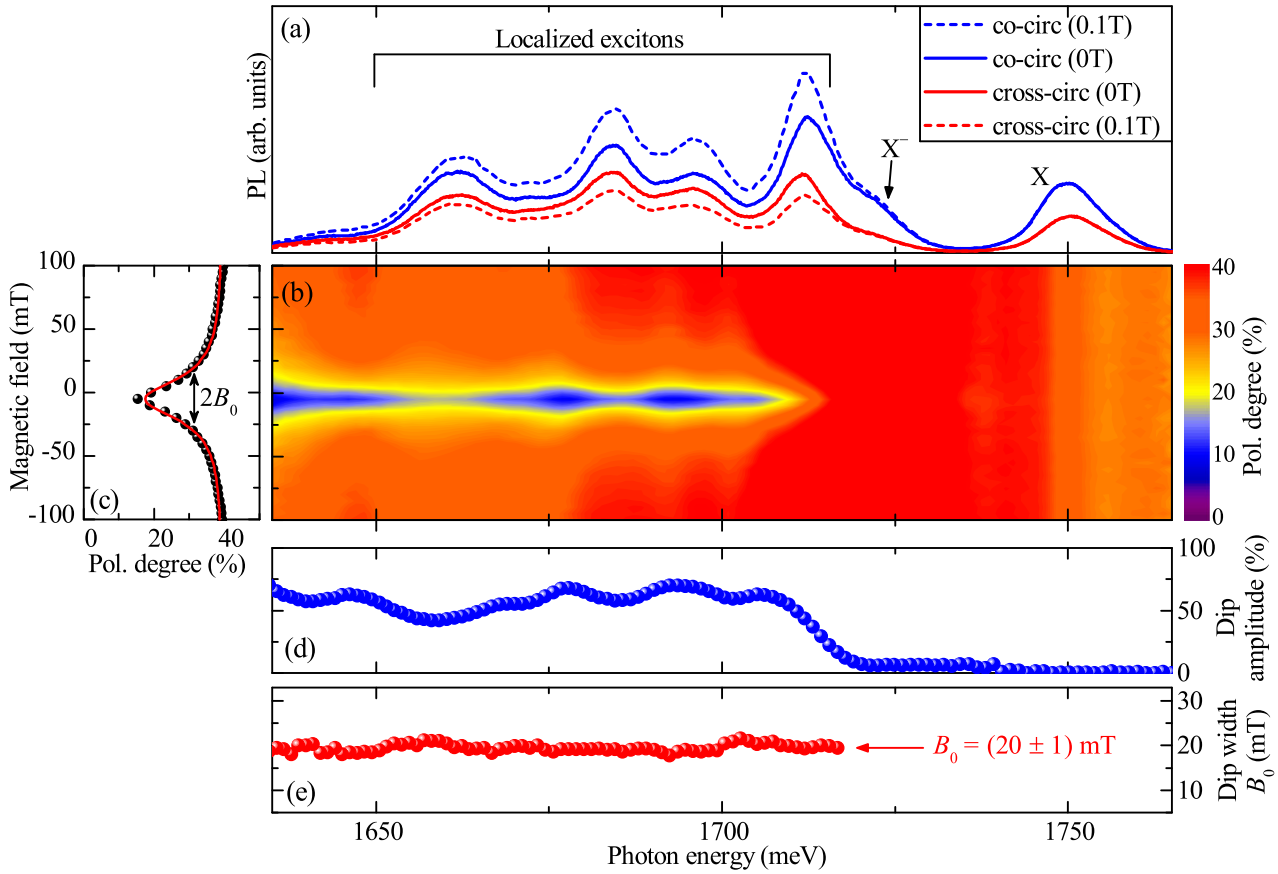

FIG. 1. (a) PL spectra of a representative WSe_2 monolayer (at $T = 6.5$ K) excited with the σ^- polarized light at $E = 1915$ meV. The spectra were measured at zero field (solid lines) and at a magnetic field of 100 mT applied in the Faraday geometry (dashed lines). For each field, the spectra were detected in the two circular polarizations of opposite helicities (as indicated). (b) Color-scale map presenting the circular polarization degree of monolayer WSe_2 PL as a function of magnetic field and emission energy. The plotted degree is obtained as an average of the two polarization degrees determined under the σ^- and σ^+ polarized excitation. A pronounced decrease of the polarization degree at zero field is visible in the energy range corresponding to the emission of localized excitons. (c) Cross section presenting the magnetic-field dependence of the circular polarization degree of the localized excitons PL integrated over the emission energy ranging from $E = 1650$ meV to $E = 1715$ meV. The solid line represents a fit with a formula $\mathcal{P}(B) \propto 1 - \alpha/[1 + (B - B_{\mathrm{rem}})^2/B_0^2]$ accounting for the Lorentzian-like field dependence of the valley pseudospin relaxation rate in line with similar effects observed for real spins in conventional semiconductors [1,23–25]. The parameter α corresponds to the percentage amplitude of the magnetic-field-induced dip in the polarization degree, B_0 represents the HWHM of the dip, while B_{rem} accounts for the remanent field of a superconducting coil. (d,e) The amplitude α (d) and HWHM B_0 (e) of the dip in the polarization degree determined for different emission energies.

samples. A set of our representative data from the CW experiments is presented in Fig. 1. A familiar low-temperature photoluminescence (PL) spectrum of the WSe_2 monolayer can be found in Fig. 1(a). It exhibits a well-established emission pattern [7,10,11,26,27] consisting of several relatively broad (linewidth of about 20 meV) peaks related to the recombination of different excitons. The peak appearing at the highest energy (1750 meV) is attributed to the optically active excitonic resonance (X). This resonance is extremely short-lived (see Ref. [28]) and becomes visible in the spectrum as a hot luminescence since the bright exciton state in a WSe_2 monolayer is energetically higher than the dark exciton ground state. A fast dynamics is also characteristic of the X^- feature (see Ref. [28]), which we attribute to the recombination of the negatively charged complex associated with the excited bright exciton state. In the CW PL spectrum, the X^- peak appears as a small shoulder, which is due to a partial overlap with a stronger low-energy emission band consisting of a few peaks tentatively assigned in the literature to "localized excitons" (LEs) [10,11,29–32]. These peaks decay rather slowly (see Ref. [28]), and we speculate that they indeed may arise from some sort of trapping effects, though involving the dark excitons. These latter excitons hardly recombine alone but presumably can annihilate with the emission of a photon, for example, after forming a more complex excitonic pseudo-particle [18].

Following the approach introduced in earlier studies [4–11], we investigate the pseudospin properties using

polarization-resolved PL measurements. The relevant quantity in such experiments is the circular polarization degree of the emitted light defined as $\mathcal{P} = (I_{co} - I_{cross})/(I_{co} + I_{cross})$, where I_{co} (I_{cross}) is the PL intensity detected in the circular polarization of the same (opposite) helicity as the excitation light. Such a quantity is of principal interest for valleytronics since it directly reflects the degree of pseudospin conservation in S-TMDs monolayers. Figure 1(b) shows the dependence of the PL polarization degree on the magnetic field applied in the Faraday geometry. The data clearly demonstrate the effect of the enhancement of the PL polarization upon application of the magnetic field, which appears in the energy range corresponding to the LE emission band. After switching on either a positive or negative field, the polarization degree of the LEs increases and saturates at a significantly higher level, thus showing a zero-field dip when plotted against the field value [see Fig. 1(c)]. Remarkably, the observed change in the polarization degree is qualitatively distinct from the recently reported changes of the PL polarization at high magnetic fields, mainly caused by different populations of the Zeeman-split excitonic levels [26,29,33]. In contrast, the effect reported here is due to the influence of a small external magnetic field on the efficiency of one of the relevant processes of the pseudospin relaxation in our system. Following a large body of optical orientation studies in conventional semiconductors [1,2], we consider that this particular process of the pseudospin depolarization can be understood in terms of the presence of effective in-plane magnetic fields [25,34], such as those resulting from the electron-hole exchange interaction in S-TMDs monolayers [16,17,20]. The effective depolarization rate (γ_{depol}) related to such effective fields can be suppressed by the application of the external magnetic field directed perpendicularly to the monolayer plane [23,24]. The magnitude B of the field needed for such a suppression is given by the condition $g\mu_B B/\hbar\gamma_{depol} \approx 1$. Setting $B \approx 20$ mT as observed in the experiment [see Figs. 1(b) and 1(c)], we estimate $1/\gamma_{depol}$ to be between 35 ps and 140 ps using g-factor values between $g = 4$ and $g = 12$ that have been reported in the literature for different PL transitions in WSe_2 monolayers [26,27,30,33,35,36]. In any case, the estimated depolarization time significantly exceeds the pseudospin relaxation times of optically active excitons in S-TMDs monolayers that have been reported until now.

As seen in Fig. 1, the field-induced enhancement of the polarization degree occurs only for the localized excitons. The relative amplitude of this enhancement (or, equivalently, the amplitude of the polarization dip at $B = 0$) is slightly different for each LE [Fig. 1(d)]; however, it always exceeds 40%. On the other hand, in spite of different optical responses of each LE peak at high magnetic fields (e.g., different g-factors [30]), the width (HWHM) B_0 of the polarization dip is practically independent of the emission energy and yields about 20 mT for all LEs [Fig. 1(e)]. This finding is of special importance since it directly implies that the field-modulated depolarization of the valley pseudospin occurs at the same level for all transitions. It cannot happen at the energy level at which the carriers are optically injected since we observe the same effect to appear independently of the excitation power or energy, including the laser excitations set either above or below the B-exciton resonance (see Ref. [28] for details). Therefore, the effect must occur at an intermediate state, which we assume to be the dark ground state of the neutral exciton. Such an attribution also explains the low efficiency of the pseudospin relaxation since dark excitons in S-TMDs monolayers should be rather weakly affected by depolarization effects arising because of the electron-hole exchange interaction [17,20,21]. It is noteworthy that the width B_0 of the polarization dip is found to be very similar for all studied monolayer flakes, despite the fact that each of them exhibits slightly different structure and relative intensity of the localized excitons emission band (for details, see Ref. [28]). The mean width of $B_0 = (23 \pm 3)$ mT averaged over the studied flakes might thus be considered as a representative characteristic describing the pseudospin depolarization dynamics of the dark excitons in the investigated material system.

Our interpretation is further supported by the analysis of the orientation of the magnetic field needed to suppress the relaxation. The experimental results from Fig. 2(a)

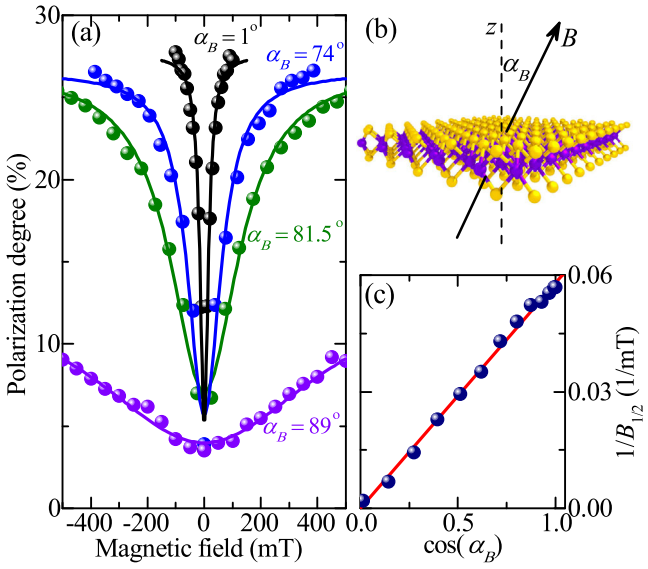

FIG. 2. (a) The circular polarization degree of the WSe_2 monolayer PL measured vs the magnetic field in the energy range between $E = 1650$ meV and $E = 1715$ meV, which corresponds to the emission band of the localized excitons. Each set of data points corresponds to a different orientation of the magnetic field, which is quantified by the angle α_B between the field vector and the out-of-plane direction z [as schematically depicted in (b)]. The angles α_B were determined with an accuracy of less than 2°. (c) The inverse width $1/B_{1/2}$ of the magnetic-field-induced dip in the circular polarization degree as a function of $\cos(\alpha_B)$. The solid line represents the linear fit.

clearly demonstrate that the dip in the polarization degree becomes wider when the magnetic field is applied along a direction tilted by the angle α_B from the out-of-WSe_2-plane direction z. This finding suggests that the observed field modulation of the pseudospin relaxation has a similar magnetic anisotropy as the valley Zeeman effect [26,27], which is sensitive only to the out-of-plane component B_z of the applied magnetic field B owing to the fact that the orbital magnetic moment of a two-dimensional material points out of its plane [27]. In an extreme case of the total magnetic anisotropy of the observed effect, the z component of the magnetic field $B_{1/2}$ at which the polarization degree reaches half of its peak height should be equal to B_0 independently of the angle α_B, i.e., $B_{1/2}\cos(\alpha_B) = B_0$. As such, the inverse HWHM of the polarization dip $1/B_{1/2}$ should scale linearly with $\cos(\alpha_B)$. The data shown in Fig. 2(c) confirm this expectation within our experimental uncertainties, which is consistent with the fact that the polarization enhancement occurs because of the field-induced splitting of the excitonic states in different valleys.

More information on the pseudospin dynamics in our system is provided by time-resolved photoluminescence measurements performed under pulsed σ^+ polarized excitation. Figures 3(a) and 3(b) show representative circular-polarization-resolved PL decay profiles measured at zero magnetic field and a tiny field of 100 mT. These profiles represent the temporal evolution of the PL signal integrated over the entire energy range corresponding to the localized excitons emission. All of the presented time traces exhibit a similar shape featuring a relatively rapid rise followed by a slower, multiexponential decay. Nonetheless, the polarization degrees inferred from the pairs of profiles measured at different fields demonstrate drastically different temporal evolution, as seen in Fig. 3(c). In the absence of the magnetic field, the important loss of the polarization degree is clearly visible on the time scale of about 100 ps after the laser pulse (in a qualitative agreement with the previous studies of the WSe_2 monolayers [10]), and afterwards (> 200 ps), $\mathcal{P}$ sets at practically constant level. Remarkably, the initial loss of the polarization degree is fully suppressed upon the application of a tiny magnetic field ($B = 100$ mT),

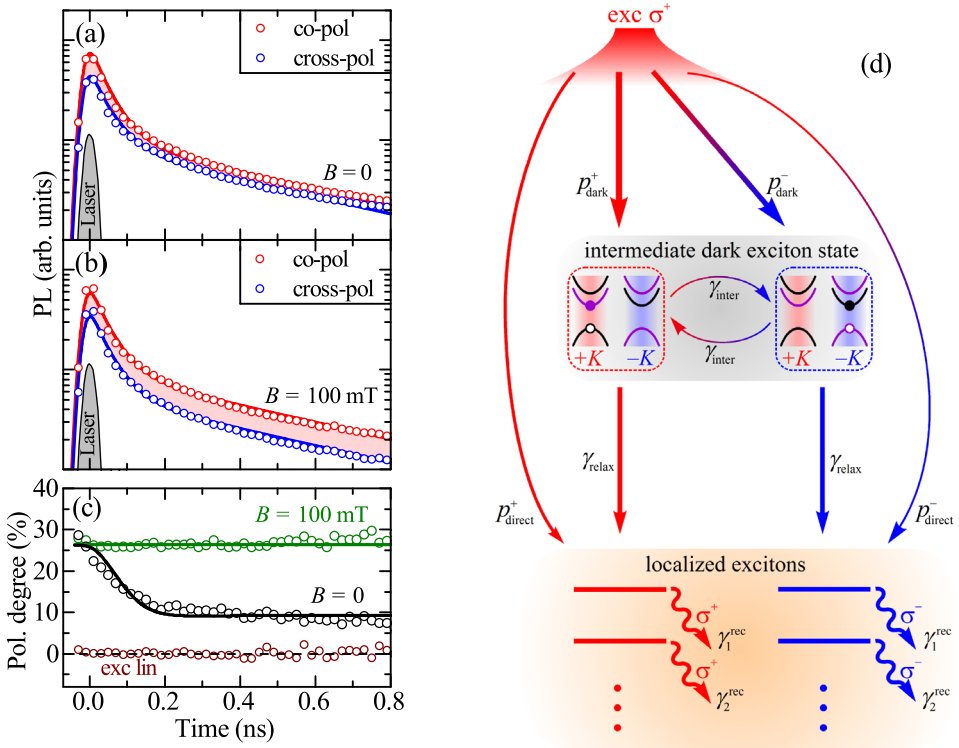

FIG. 3. (a,b) Time-resolved PL of the localized excitons integrated over the emission energy ranging from $E = 1635$ meV to $E = 1710$ meV. The temporal profiles were measured under the σ^+ polarized pulsed excitation at $E = 1915$ meV in two circular polarizations of detection and for two values of the magnetic field: $B = 0$ (a) and $B = 100$ mT (b). The instrument response profile measured using a backscattered laser is shown for reference. (c) The circular polarization degree of the localized excitons emission measured under circularly polarized excitation as a function of time after the laser pulse for $B = 0$ and $B = 100$ mT. The temporal profile of the circular polarization degree showing no observable polarization under linearly polarized excitation is displayed for comparison. The solid lines in (a–c) represent the fit to the experimental data with the rate-equation model described in the text. (d) A scheme of the states and transitions included in the rate-equation model (a quantitative description of the model, together with the list of parameters used, is provided in Ref. [28]). The horizontal lines indicate the states, while the arrows mark the transitions. The color indicates the valley polarization (red: σ^+; blue: σ^-).

when $\mathcal{P}$ remains constant in time but at the significantly higher level.

The scheme of the minimal rate-equation model that accounts for our time-resolved data is presented in Fig. 3(d). We assume that the electron-hole pairs initially photo-created by a σ^+ polarized laser pulse in the $+K$ valley relax instantaneously, in part towards the intermediate dark exciton state and in another part directly towards the LE states. The initial populations of the LE and dark excitonic states are denoted by $p^{\pm}_{\mathrm{direct}}$ and $p^{\pm}_{\mathrm{dark}}$, respectively, where $\pm$ accounts for different $\pm K$ valley occupations. Particularly important are the populations of dark excitonic states, which are crucial for the modeled polarization effects. The initial valley polarization of dark excitons ($p^{+}_{\mathrm{dark}} > p^{-}_{\mathrm{dark}}$ under σ^+ excitation) decays with the rate of γ_{inter} due to the intervalley scattering processes. In parallel, dark excitons relax further towards the localized excitons (and/or form more complex excitonic pseudo-particles) with the rate of γ_{relax}. We assume that the localized excitons are no longer subjected to efficient intervalley scattering, in accordance with previous studies of S-TMDs monolayers [10,37] and in line with negligible decay of the polarization degree on the time scale of 0.5–1 ns in our experiment. For the sake of simplicity, in our model we take into account only two types of localized excitons with different lifetimes. This is a minimal assumption required to account for the nonexponential character of the temporal PL profiles shown in Figs. 3(a) and 3(b). This simplification does not substantially influence the overall character of the calculated transients of the polarization degree due to a suppression of the intervalley scattering at the level of localized excitons. The efficiency γ_{inter} of the valley pseudospin relaxation of the dark excitons is the only parameter assumed to be affected by the magnetic field. Using $1/\gamma_{\mathrm{inter}} = 70$ ps in the absence of the magnetic field and fixing $\gamma_{\mathrm{inter}} = 0$ at $B = 100$ mT, we have well reproduced our time-resolved data [see solid lines in Figs. 3(a)–3(c) and Ref. [28] for more details on the data simulation procedures]. The extracted value of $1/\gamma_{\mathrm{inter}} = 70$ ps is fully consistent with our preliminary conclusions and the estimation of $1/\gamma_{\mathrm{depol}} \approx 35$–$140$ ps for the field-tunable rate of the pseudospin relaxation in a WSe_2 monolayer deduced from the CW PL experiments.

In conclusion, our continuous-wave and time-resolved optical orientation studies uncover a novel channel for the relaxation of the exciton pseudospin in a WSe_2 monolayer. The efficiency of this process is about 2 orders of magnitude weaker than that previously reported for optically active excitons in S-TMDs monolayers. Remarkably, this relaxation process can be completely switched off by the application of a tiny magnetic field of the order of 100 mT. The latter finding invokes an interesting possibility to modulate (at the level of up to 50%) the polarization degree of the emitted light using, for example, the electric microloop wrapped around the WSe_2 monolayer flake. A phenomenological model invoking the role of the dark excitonic state in optical properties of the WSe_2 monolayer is presented to account for the present experimental finding. We believe that these findings will also challenge further investigations towards better understanding and possible practical explorations of the opto-valleytronics concepts in thin layers of S-TMDs.

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APPENDIX: MATERIALS AND METHODS

1. Sample preparation

The samples studied in our experiments were obtained by mechanical exfoliation of bulk WSe_2. In order to fabricate monolayer flakes of high quality and sufficient size for optical probing, we used a two-step approach in which the flakes were first filed down with the help of chemically pure backgrinding tape and then transferred onto a $Si/(90\ \mathrm{nm})$ SiO_2 substrate by means of polydimethylsiloxane-based DGL-X8 elastomeric films from Gel-Pak. To improve the cleanliness and stickiness of the target substrate, we ashed it with oxygen plasma shortly before the final stage of the exfoliation process. The atomic-force-microscopy (AFM) characterization of the samples was performed with the aid of an NSV-VEECO-D3100 microscope operated in tapping mode under ambient conditions.

2. Experimental setup

The polarization-resolved measurements were carried out in a high-resolution μPL setup on a sample placed in helium gas ($T = 5$–10 K) inside a magneto-optical cryostat. The cryostat was equipped with a double split-coil superconducting magnet, which allowed for optical experiments in both Faraday and Voigt geometries. Moreover, simultaneous use of both coils allowed us to apply a magnetic field in an oblique direction with respect to the sample surface. The PL was excited either by a continuous-wave diode lasers (at 488 nm or 647 nm) or by femtosecond pulses from a frequency-doubled tunable optical-parametric-oscillator (OPO) synchronously pumped by a mode-locked Ti:sapphire laser. The laser beam was focalized to a spot of diameter smaller than 2 μm by an aspheric lens immersed in the helium gas together with the sample. The lens was mounted on piezo-electric $x - y - z$ stages, allowing us to scan over the sample surface with a submicrometer precision. The PL signal from the sample was collected by the same lens and dispersed with the monochromator. The PL

spectra were recorded by a charge-coupled device (CCD) camera or, in the case of time-resolved measurements, by a synchroscan Hamamatsu streak camera. The polarization control of both the exciting and detected light was realized with a set of polarization optics (including a linear polarizer, $\lambda/2$ and $\lambda/4$ wave plates) placed either in the laser or the signal beam.

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