Valley-polarized exciton-polaritons in a monolayer semiconductor

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Single layers of transition metal dichalcogenides are two-dimensional (2D) direct-bandgap semiconductors with degenerate, but inequivalent, ‘valleys’ in the electronic structure that can be selectively excited by polarized light. Coherent superpositions of light and matter, exciton-polaritons, have been observed when these materials are strongly coupled to photons, but these hybrid quasiparticles do not harness the valley sensitivity of the monolayer semiconductors. Here, we observe valley-polarized exciton-polaritons in monolayers of MoS₂ embedded in a dielectric microcavity. These light-matter quasiparticles emit polarized light with spectral Rabi splitting and anticrossing indicative of strongly coupled exciton–polaritons in the topologically separate spin-coupled valleys. The interplay of intervalley depolarization and cavity-modified exciton dynamics in the high-cooperativity regime causes valley-polarized exciton–polaritons to persist at room temperature, distinct from the vanishing polarization in bare monolayers. Achieving polarization-sensitive polaritonic devices operating at room temperature presents a pathway for manipulating novel valley degrees of freedom in coherent states of light and matter.

Confining photons to small volumes, such as between two mirrors, can enhance light–matter interactions and lead to coherent superpositions of light and matter, or polaritons1,2. This framework of cavity quantum electrodynamics (QED) is the foundation for strong, coherent interactions with light in both atoms3 and two-level solid-state systems4–6. Translating this approach to bosonic exciton–polariton quasiparticles in semiconductors7,8 enables new many-body coherent phenomena such as Bose–Einstein condensation in the solid state9, with potential optoelectronic applications in ‘polaritonics’10,11. Although the cavity QED parameter regimes vary greatly across these implementations, they generally share the spectral selectivity of high-quality resonators.

More recently, polarization selectivity has brought a new dimension to cavity QED. For example, accessing specific sublevels using polarized light can merge time-reversal symmetry breaking with chiral photonics12–14. Although individual atoms allow strong coupling in circularly polarized cavity QED15, the degenerate valley-specific excitons of transition metal dichalcogenides (TMDs) are a model material system for achieving polarization selectivity with bosonic exciton–polaritons (Fig. 1a).

TMDs are layered 2D semiconductors that have a direct bandgap in their monolayer form16,17. Inversion asymmetry and strong spin–orbit coupling in TMDs lead to spin–valley locking at the direct bandgap K and K′ valleys. Monolayer TMDs such as MoS₂ or WSe₂ can therefore support two different classes of energy degenerate excitons, identical in most properties, but with opposite Berry curvature and distinct response to light of opposite helicity depending on their valley pseudospin index18 (Fig. 1b). The valley selectivity has been exploited for polarization-dependent optoelectronics19–24, correlated spin–electron motion25, and proposed mechanisms for coherent information processing26–28. Whereas monolayer TMDs can be interfaced with photonic cavities29–33 to enhance radiative coupling, controlling the dynamics of these valley-polarized excitons with polarization-sensitive cavity QED is an exciting possibility not yet explored.

As with excitons in semiconductor quantum wells, strongly coupled 2D exciton–polaritons have been observed in TMDs by embedding monolayers in planar microcavities (MCs)34. The tightly bound excitons and large oscillator strengths in TMDs allow these quasiparticles to persist at room temperature34–37. Marrying strongly coupled light–matter quasiparticles with the valley structure of excitons in TMD monolayers will enable new coupled spin and valley phenomena in polaritonics. Unlike spin-polarized exciton–polaritons in traditional quantum wells34,38,39, the Brillouin zone separation and distinct Berry curvature at the K and K′ valleys of TMDs lead to a regime in which two species of degenerate exciton–polariton quasiparticles can spatially coexist in separate regions of momentum space and can be selectively excited by helical cavity fields. This intrinsic spin–valley structure of TMD microcavity polaritons makes possible exploring more exotic spin and pseudospin-sensitive optical and topological coherent phenomena in 2D semiconductors and their layered heterostructures40–42.

Here, we report the observation of valley-polarized exciton–polaritons in monolayer MoS₂ embedded in a planar microcavity (Fig. 1a). These distinct degenerate light–matter quasiparticles are selectively coupled to circularly polarized cavity modes. In contrast to excitons in bare monolayers, the MC exciton–polaritons preserve valley polarization at room temperature, which is explained by the competition between the exciton valley decay time and the cavity-enhanced total decay rate of the exciton–polaritons in the cavity QED system. The ability to manipulate pseudospin dynamics in hybrid optical devices with 2D materials opens new opportunities for valley-sensitive photonics using engineered chiral light–matter interactions.

Results

The monolayer MoS₂ microcavity (MC-MoS₂) samples consist of a single layer of monolayer MoS₂ embedded in a distributed Bragg reflector (DBR) MC, as illustrated in Fig. 1a. The DBRs are made from alternating silicon dioxide and silicon nitride layers grown
on top of a Si substrate. Separate MCs were fabricated both with the cavity on resonance with and detuned from the MoS$_2$ A-exciton for use in different experiment configurations, as we will describe. The monolayer flakes of MoS$_2$ are synthesized by chemical vapour deposition and transferred on top of the bottom DBR before the top DBR is deposited so that they are at the centre of the inner cavity. Both as-grown and transferred monolayer MoS$_2$ show A-exciton photoluminescence (PL) peak centred at 1.855 eV with an inhomogeneously broadened full-width half-maximum linewidth $\Gamma_{ex} = 64$ meV when collected with a microscope objective. Measured with a lens instead, the A-exciton PL is red-shifted with linewidth of 90 meV due to the increased inhomogeneous broadening of the larger spot and increased relative contribution of low-energy defects and multilayer regions.

We first confirm the presence of strongly coupled light–matter quasiparticles in the MC-MoS$_2$ by observing Rabi splitting and anticrossing in both reflectivity and PL spectra. Our cavity characterization depicted in Fig. 2 is consistent with the results of exciton–polaritons in MC-MoS$_2$ reported previously$^{34}$, demonstrating the strongly coupled quasiparticle eigenstates. In regions of the MC where there is no monolayer MoS$_2$, the reflectivity spectrum shows only a single dip with width $\Gamma_c \approx 10$ meV, which is broadened by the non-zero collection angle from the cavity (Fig. 2a, top). In regions with monolayer MoS$_2$, the MC reflectivity (PL) spectrum shows two dips (peaks) (Fig. 2b). These resonance features are potential signatures of the upper polariton (UP) and lower polariton (LP) quasiparticle eigenstates in the MC.

The strongly coupled exciton–polariton origin of these features at room temperature is verified from an anticrossing in the energy dispersion obtained from angle-resolved white light reflectivity (Fig. 2c). As the angle $\theta$ is swept, the cavity resonance changes energy and detunes from the exciton absorption. For this measurement, the MC is designed to be red detuned from the MoS$_2$ exciton so that the modes are resonant at a non-zero angle ($\theta \approx 13.5^\circ$) and the modified MC-MoS$_2$ dispersion is clearly visible.

For the MC-MoS$_2$ sample shown in Fig. 2d, for $\theta < 13.5^\circ$, the UP energy is nearly constant and the LP energy blue-shifts with increasing angle. For $\theta > 13.5^\circ$, the UP and LP behaviour reverses, but the dispersion curves do not touch. This anticrossing between the UP and LP branches is a feature of the strong light–matter coupling in which the coherent exchange rate dominates the incoherent losses. Under these conditions, a resonant excitation creates exciton–polariton quasiparticles that are nearly equal superpositions of material exciton and cavity photon. The Rabi splitting, $\Omega$, is swept, the cavity resonance changes energy and detunes from the exciton absorption. For this measurement, the MC is designed to be red detuned from the MoS$_2$ exciton so that the modes are resonant at a non-zero angle ($\theta \approx 13.5^\circ$) and the modified MC-MoS$_2$ dispersion is clearly visible.

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between the UP and LP on resonance is $39 \pm 5$ meV (Fig. 2d). The interaction coupling constant, $g$, between 2D excitons and cavity photons was calculated from a two-mode coupled oscillator model as $g = 28 \pm 2$ meV. This room-temperature measurement is consistent with the value reported for strongly coupled monolayer MoS$_2$ exciton–polaritons in a MC.$^{24}$ The dispersion and mode splitting structure verify that the MC at room temperature is populated by exciton–polaritons in a regime dominated by coherent exchange between light and matter excitations.

The polariton energies do not blue-shift at lower temperatures in contrast to excitons in bare MoS$_2$ on thermally grown SiO$_2$. This feature has been explained in previous reports as due to the ratio of the relative exciton relaxation and intervalley scattering rates$^{19,22}$, the combined uncertainty from the sampling standard error and collection spot repeatability. At a temperature of 8 K, both MC-MoS$_2$ and bare MoS$_2$ exhibit significant and comparable polarizations. Increasing to room temperature, $p$ in bare MoS$_2$ decreases close to 0% (Fig. 3e,f). The MC-MoS$_2$, on the other hand, retains a non-zero polarization of 7.5% and 13% for the UP and LP (Fig. 3b,c).

Because emission polarization from valley states is determined by the relative exciton relaxation and intervalley scattering rates$^{19,22}$, the evolution of $p$ with temperature probes valley scattering dynamics. Figure 4a shows the temperature dependence $p(T)$ from both bare MoS$_2$ and MC-MoS$_2$. The measurement was done with constant pump energy ($E_{ph} = 1.938$ eV for MC-MoS$_2$ and $E_{ph} = 1.987$ eV for bare MoS$_2$). In bare MoS$_2$, the low-temperature valley polarization $p$ of A-exciton vanishes quickly as the temperature is raised above 100 K. This behaviour originates from the ratio of the emission, care is taken that the off-resonant circularly polarized excitation from the pump at angle $\theta = 38^\circ$ creates nearly equal $s$- and $p$-linear-polarized electric-field components in the DBR MC so that the circular polarization of the total pumped cavity field is preserved. Additional measurements show that the PL polarization of both bare monolayer and MC-MoS$_2$ is independent of the pump incident angle (Supplementary Information).

To quantify the measurements, the total PL polarization $p$ is defined as

$$ p = \frac{(I_+ - I_-)}{(I_+ + I_-)} $$

where $I_+$ and $I_-$ are the helicity-resolved PL intensities. At 8 K, both UP and LP show significant polarizations of 19 and 29.5%, respectively (Fig. 3a). For bare MoS$_2$ at the same temperature (Fig. 3d), we observe $p = 40\%$ for the A-exciton, a typical MoS$_2$ polarization at cryogenic temperatures$^{20-22}$, at low temperatures, bound defect state luminescence (labelled as D) is present in the bare MoS$_2$ spectrum$^{19,21,46}$. As with previous reports of low-energy defects, this emission does not exhibit polarization$^{19,21,46}$, even when visible in the MC (see examples in the Supplementary Information), confirming that the PL polarization arises from the valley-pumped exciton–polaritons and not measurement bias. The polarization for both UP and LP modes increases for $E_{ph}$ closer to the exciton resonance, following the behaviour of bare MoS$_2$.$^{19,22,24}$ (Supplementary Information).

The emission polarization of the cavity polariton modes in the strong-coupling regime confirms the presence of valley-polarized exciton–polaritons in MC-MoS$_2$. At a temperature of 8 K, both MC-MoS$_2$ and bare MoS$_2$ exhibit significant and comparable polarizations. Increasing to room temperature, $p$ in bare MoS$_2$ decreases close to 0% (Fig. 3e,f). The MC-MoS$_2$, on the other hand, retains a non-zero polarization of 7.5% and 13% for the UP and LP (Fig. 3b,c).

Because emission polarization from valley states is determined by the relative exciton relaxation and intervalley scattering rates$^{19,22}$, the evolution of $p$ with temperature probes valley scattering dynamics. Figure 4a shows the temperature dependence $p(T)$ from both bare MoS$_2$ and MC-MoS$_2$. The measurement was done with constant pump energy ($E_{ph} = 1.938$ eV for MC-MoS$_2$ and $E_{ph} = 1.987$ eV for bare MoS$_2$). In bare MoS$_2$, the low-temperature valley polarization $p$ of A-exciton vanishes quickly as the temperature is raised above 100 K. This behaviour originates from the ratio of the emission, care is taken that the off-resonant circularly polarized excitation from the pump at angle $\theta = 38^\circ$ creates nearly equal $s$- and $p$-linear-polarized electric-field components in the DBR MC so that the circular polarization of the total pumped cavity field is preserved. Additional measurements show that the PL polarization of both bare monolayer and MC-MoS$_2$ is independent of the pump incident angle (Supplementary Information).

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exciton and valley relaxation rates, as predicted by a rate equation model (see Supplementary Information):\(^2\)

\[
P_{\text{bare}} = \frac{A_{\text{bare}}}{1 + \frac{r_v}{\tau_v}}
\]

where \(A_{\text{bare}}\) is a constant depending on optical pumping, \(\Gamma_{ex}\) is the exciton relaxation rate and \(\Gamma_v\) is the intervalley scattering rate (with rates expressed in units of energy). The temperature evolution of \(p\) can therefore be interpreted as a measurement of the ratio \(\Gamma_v/\Gamma_{ex}\). At elevated temperatures, \(\Gamma_v\) increases due to thermally activated phonon-assisted intervalley scattering\(^2,22\) and emission polarization is suppressed. The features are similar if the energy difference \(E_p - E_{ex}\) is held constant across temperature (Supplementary Information).

The temperature-dependent emission polarization for exciton–polaritons in MC-MoS\(_2\) is very different from bare MoS\(_2\). The low-temperature UP and LP polarizations \(p_{\text{UP}}\) and \(p_{\text{LP}}\) are slightly smaller than that in bare MoS\(_2\), which is expected due to the non-perfect circular polarization of the cavity field from oblique incidence (Supplementary Information), the differential shift of the exciton energy with temperature, and the inhomogeneity of the MoS\(_2\) flakes in the collection region of the cavity. At room temperature, the polarizations \(p_{\text{UP}}(T)\) and \(p_{\text{LP}}(T)\) decrease smoothly to 7.5 and 13%, in contrast to the vanishing polarization in bare MoS\(_2\).

We explain this difference using a valley-sensitive cavity rate model accounting for coherent exchange and incoherent scattering (Fig. 4b). Our phenomenological model is a generalization of the standard steady-state master equation approach for interacting boson modes in cavity QED\(^47\), modified to include two distinct MC photon modes (of different polarization) coupled to two distinct exciton modes (for K and K’ valleys). The cavity QED rate equations are augmented with incoherent intervalley scattering (Supplementary Information) and the temperature evolution of \(p\) can therefore be interpreted as a measurement of the ratio \(\Gamma_v/\Gamma_{ex}\). At elevated temperatures, \(\Gamma_v\) increases due to thermally activated phonon-assisted intervalley scattering\(^2,22\) and emission polarization is suppressed. The features are similar if the energy difference \(E_p - E_{ex}\) is held constant across temperature (Supplementary Information).

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\[
P_{\text{MC}} = \frac{A_{\text{MC}}}{1 + \frac{r_v}{\tau_v} + \frac{\Gamma_c}{\Gamma_{ex}}}\tag{3}
\]

This equation has the same structure as equation (2) describing a bare monolayer, but relaxation now occurs equally through both exciton and cavity channels. Importantly, only the excitonic part of the exciton–polariton quasiparticle experiences the intervalley scattering while the polarized photonic amplitudes do not couple for a good cavity with negligible mode mixing. The ratio in the denominator of equation (3) is therefore reduced compared with the bare MoS\(_2\). Radiative decay of the exciton–polaritons through cavity emission occurs before incoherent valley scattering, and the polarization of the output field persists even at elevated temperatures. Additional details of this model are in the Supplementary Information.

This picture is confirmed from the temperature dependence \(p(T)\). Although the homogeneous exciton radiative lifetime is highly temperature dependent\(^38,39\), the total exciton decay time in MoS\(_2\) has been found to be nearly temperature independent \(\tau_{ex} = \hbar/\Gamma_{ex} = 4\) ps (refs 46,50). The intervalley scattering rate is proportional to the phonon thermal population \(\Gamma_v \sim e^{-h\omega_v/T}\) (ref. 20); \(k_B\) is the Boltzmann constant. These assumptions allow \(p_{\text{bare}}\) to be well fit by equation (2) with \(A_{\text{bare}} = 0.413 \pm 0.0098\) and \(E = 35 \pm 4\) meV.

Using these same phonon model parameters as inputs to equation (2) yields a two-parameter fit for \(p_{\text{MC}}\) with the amplitude \(A_{\text{MC}}\) and \(\Gamma_c\) the only free parameters (Fig. 4a). The extracted \(\Gamma_c = 4.2\) meV (UP) and 5.2 meV (LP) are consistent with the intrinsic linewidth (4 meV without angle broadening) of our MC, demonstrating that this valley-sensitive cavity model is a self-consistent description of the exciton–polariton polarization. The good agreement of the valley-sensitive cavity model with the emission polarization verifies the observation of valley-polarized exciton–polaritons with modified dynamics distinct from typical valley excitations in monolayer semiconductors.

By combining the features of exciton–polaritons, including coherent many-body states and strong optical coupling, with the large binding energy, oscillator strength and spin–valley coupling of TMDs, valley-polarized light–matter quasiparticles have the potential to reveal new regimes of polariton physics. The preservation of the polarized emission from light–matter quasiparticles in MoS\(_2\) implies that the two classes of exciton–polariton with distinct valley pseudospin presented in Fig. 1 can be selectively excited. It is therefore necessary to treat the TMD exciton–polariton system as having two classes of exciton–polariton, each with upper and lower branches, residing in topologically distinct regions of momentum space with opposite Berry curvature. The spectral signatures of these valley-polarized exciton–polaritons in MC-MoS\(_2\) are reminiscent of spin-polarized exciton–polaritons explored in GaAs-based semiconductor MCs\(^38,39\). Compared with these spinor gases, which lack the spin–valley locking intrinsic to monolayer TMDs, valley-polarized exciton–polaritons have unique features that can lead to new polaritonic phenomena potentially useful for both valley-based logic and fundamentally new hybrid light–matter states in monolayers\(^40\).

Unlike traditional spinor exciton–polaritons, strongly coupled exciton–polaritons in TMDs can be separated in momentum space with potentially reduced spin interactions. The coherence between these distinct, spatially coexisting polaritonic quasiparticles and their many-body interactions in ensembles and condensates will be determined instead by the dynamics of intervalley scattering. This large-wavevector depolarization mechanism, which is absent from the traditional spin-polarized polariton gas, dominates the valley-polarized exciton–polariton system as evidenced by the analysis of Fig. 4, with potential benefits for long-lived many-body coherent states and valley-based logic compared with those utilized in spin-based polariton logic switches\(^41,42\).

Beyond the modified interactions of momentum-separated quasiparticles, the topologically distinct spin–momentum texture in TMD valleys can be exploited for more exotic optical phenomena. The opposite Berry curvature of the K and K’ valleys manifests as spin and exciton momentum coupling, and the phase-modified optical transitions have been predicted to result in directional light–matter edge modes called topological polaritons\(^40\). Specifically, the valley selectivity of exciton–polaritons in monolayer TMDs can lead to non-trivial topological winding numbers in zero magnetic field. The observation of valley-specific exciton–polaritons is a significant step toward exploring these exotic coherent optical phenomena based on the spin–valley topology.

In summary, we have established the existence of strongly coupled exciton–polaritons with polarized valley pseudospin in a 2D TMD semiconductor. These hybrid light–matter quasiparticles can be selectively pumped and probed in photonic MCs using circularly polarized light. The dynamics of these polarization-sensitive quasiparticles are distinct from valley excitons in TMD monolayers due to the cavity photon, representing ‘half’ of the hybrid quasiparticle, being insensitive to intervalley scattering, resulting in preservation of appreciable exciton–polariton valley polarization at room temperature. The capability to select distinct valley-polarized light–matter quasiparticles in cavity QED with circular polarization makes possible a platform to exploit the intrinsic valley and spin degrees of freedom in 2D semiconductor polaritons\(^38,40\).
**Methods**

**Sample preparation.** The DBR is fabricated by depositing alternating layers of SiO₂ and Si₃N₄ on a silicon wafer substrate using plasma-enhanced chemical vapour deposition (PECVD). Since the reflectivity of the DBR is controlled by the number of alternating layers, the top DBR has fewer pairs than the bottom to favour emission in the detector direction away from the absorptive substrate. The thickness of the inner cavity region of SiO₂ between the DBRs corresponds to \( \lambda/2 \), with \( \lambda \) near the MoS₂ A-exciton transition wavelength and \( n \approx 1.45 \) the index of refraction of SiO₂. Monolayer MoS₂ is grown onto a SiO₂/Si wafer by chemical vapour deposition (CVD) at atmospheric pressure\(^5\). The physical and optical properties of the MoS₂ monolayers are characterized through atomic force microscopy, optical microscopy, Raman spectroscopy and PL measurements (Supplementary Information). The CVD-grown monolayer was transferred using a polycarbonate film\(^5\) onto the bottom DBR, and the system was then encapsulated by growing a top DBR using PECVD. Both as-grown and polycarbonate-transferred monolayer MoS₂ have a direct-gap transition of the A exciton at 1.855 eV with linewidth around 64 meV. Details of CVD procedures, sample structure and characterization can be found in the Supplementary Information.

**Optical measurement.** For the MC-MoS₂, angle-resolved reflectivity measurements were performed using a goniometer with angular resolution of 1°. A stabilized tungsten-halogen light source (Thorlabs) was used as the white light source. The spot size on the sample is estimated at 200 \( \mu \)m. The reflected spectrum was analysed with a fibre-coupled spectrometer and charge-coupled device (Andor). For polarized PL measurements, emission was collected with a lens along the normal direction using the same spectrometer. A tunable continuous-wave dye laser (Matisse 2DR) with linewidth less than 20 MHz was used to pump the sample from 600 to 645 nm with intensity 9.5 W cm\(^{-2}\) over a spot size of \( \sim 200 \mu \)m. The samples were loaded inside an optical cryostat (Advanced Research Systems) capable of reaching 6 K. For all the data shown, the MC is pumped with \( \sigma_+ \) circularly polarized light and the \( \sigma_+ \) and \( \sigma_- \) polarizations are resolved in collection. The same conclusions are achieved by pumping with \( \sigma_- \) light. Reported best-fit parameters are obtained from weighted least-squares fitting with parameter uncertainties estimated using resampling. For polarized PL measurements on the bare MoS₂, pumping and collection were performed using an objective (spot size \( \sim 1 \mu \)m) to minimize the inhomogeneous broadening over the CVD monolayer to obtain the intrinsic polarization of the material.

**Data availability.** The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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