Electrically controlled emission from triplet charged excitons in atomically thin heterostructures

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Excitons are composite bosons that can feature spin singlet and triplet states. In usual semiconductors, without an additional spin-flip mechanism, triplet excitons are extremely inefficient optical emitters. Large spin-orbit coupling in transition metal dichalcogenides (TMDs) couples circularly polarized light to excitons with selecteive valley and spin¹–⁴. Here, we demonstrate electrically controlled brightening of spin-triplet interlayer excitons in a MoSe₂/WSe₂ TMD van der Waals (vdW) heterostructure. The atomic registry of vdW layers in TMD heterostructures provides a quasi-angular momentum to interlayer excitons⁵,⁶, enabling emission from otherwise dark spin-triplet excitons. Employing magnetic field, we show that photons emitted by triplet and singlet excitons in the same valley have opposite chirality. We also measure effective exciton g-factors, presenting direct and quantitative evidence of triplet interlayer excitons. We further demonstrate gate tuning of the relative photoluminescence intensity between singlet and triplet charged excitons. Electrically controlled emission between singlet and triplet excitons enables a route for optoelectronic devices that can configure excitonic chiral, spin, and valley quantum states.

Inefficient light emission from triplet excitons is known to be a major bottleneck for many optoelectronic devices, such as e.g. organic LEDs, where a significant portion of randomly generated excitons are in spin-triplet states⁷. The search for highly emissive “bright” triplet excitons generally involves materials with strong spin-orbit coupling (SOC)⁸ that also provide such spin-flip mechanisms with altered optical selection rules. Electronic band structure engineering in van der Waals (vdW) heterostructures of transition metal dichalcogenides (TMDs) with strong SOC may produce a unique material platform to realize emissive triplet excitons.

Semiconducting TMDs exhibit extraordinary excitonic effects when reduced to the two-dimensional limit⁹–¹¹. Monolayer TMDs have large exciton binding energies¹² and spin-valley locking¹³,¹⁴, which can be harnessed for optoelectronic¹⁵,¹⁶ and valleytronic¹⁴ applications. When monolayer TMDs are stacked together to form heterobilayers such as WSe₂/MoS₂¹–⁴,¹⁷–²¹, MoSe₂/MoS₂²²,²³, or WS₂/MoS₂²⁴–²⁶, interlayer excitons (IEs) can form across the atomically sharp
interfaces owing to their type-II band alignment and ultrafast charge transfer between the layers. The resulting IEs have long lifetimes, a permanent out-of-plane dipole moment, and modified optical selection rules due to the electrons and holes residing in separate layers. When the heterostructures are electron or hole doped, the IEs bind with free carriers to form charged interlayer excitons (CIEs).

Our experiments employ h-BN encapsulated WSe₂/MoSe₂ devices with top and bottom gates, and electrically transparent contacts (Fig. 1a left inset and Supplementary Fig. 1), as described in the previous work. We use a dual-gating scheme where the top-gate voltage (Vtg) and the back-gate voltage (Vbg) have the same polarity, achieving higher carrier densities than in previous IE studies (details in Supplementary Section 1).

Figure 1a shows the photoluminescence (PL) spectrum as a function of Vtg = αVbg, where α = 0.617 (based on top and bottom h-BN thicknesses measured...
measurements. We perform polarization under the interlayer excitons observed in our experiments to understand the component angular momenta of valley, spin, and magnetic. 

Surprisingly, the excitons in TMD materials have a binding energy between regions I/II and I/III that is significantly higher than the typical lifetime of neutral or charged excitons. We spectrally isolate the exciton feature in intensity with increasing applied voltage (Supplementary Fig. 2). Since the excitons in TMD materials are dark triplet excitons in monolayers, unlike dark triplet excitons in monolayers, we verify the PL under magnetic fields to establish the effective Zeeman splitting of the exciton, $\Delta E = g \mu_B B$, where $g$ is the effective $g$-factor and $\mu_B$ is the Bohr magneton. From the slope of measured relation between $\Delta E$ and $B$, we obtain the effective $g$-factors for $X^0$, $X^-_1$, and $X^-_2$: $g_0 = 6.99 \pm 0.35$, $g_1 = 6.06 \pm 0.58$, and $g_2 = -10.6 \pm 1.0$, respectively. 

Interestingly, the $g$-factor for $X^-_2$ is greater than and has the opposite sign of $g_0$ and $g_1$, implying $X^-_2$ has an additional Zeeman splitting contribution and that the chiral light coupling to the K valleys is flipped compared to $X^0$ or $X^-_1$.

To explain the emergence of $X^-_2$ and its unexpected $g$-factor, we consider the well-established band alignment diagram of a 0-degree aligned WSe$_2$/MoSe$_2$ heterostructure with spin-valley locking. The observation of a higher energy emission in region IV suggests that transitions between the highest WSe$_2$ K-valley valence band and both spin-split MoSe$_2$ K-valley conduction bands are allowed. This would indicate that the higher energy peak is an emissive triplet transition with an in-plane dipole moment, unlike dark triplet excitons in monolayers. 

Modified selection rules arise from the space group symmetry of the atomic configuration of WSe$_2$/MoSe$_2$ heterostructures – as opposed to being purely determined by the symmetry of any individual, constituent layer. It was theoretically and experimentally shown that for WSe$_2$/MoSe$_2$ heterostructures, the lowest energy atomic stacking registry is $R^X_{h}$, representing an $R$-type stacking (0-degree aligned) with the $X$ site of the top MoSe$_2$ layer above the $h$ site of the bottom WSe$_2$ layer (Supplementary Fig. 4). In this stacking configuration, the optical selection rules for interlayer recombination involve the phase difference from the translation of the Bloch wave function between the two...
rotation sites, \( h \) and \( X \), in addition to the orbital angular momentum quantum number (Supplementary Section 4). This induced phase from the atomic registry translation can be regarded as an additional quasi-angular momentum in the optical transition, altering the resulting selection rules (Supplementary Table 1). These selection rules show that a transition from CB2 is optically allowed, consistent with our experimental observations. Moreover, they predict spin-singlet and spin-triplet IEs that have opposite circular light polarization coupling to the K valleys (Supplementary Fig. 5a).

Evidence for the singlet and triplet states and opposite circular polarization coupling is revealed by calculating the expected exciton g-factors. Using the single electron band picture\(^{17,33}\), theoretically expected values for the g-factor can be determined based on the band alignment of the 0-degree aligned MoSe\(_2\)/WSe\(_2\) heterostructure. The g-factor can be broken into the Zeeman shift of each electron band (Fig. 2e), which has contributions from the spin (\( \mu_s \)), the atomic orbitals (\( \mu_l \)), and the valley magnetic moment (\( \mu_{\pm K} \)) (further details in Supplementary Section 5). The exciton g-factor can then be determined as the relative shift of the conduction and valence bands for each circularly polarized transition. From these arguments, we calculate the singlet g-factor to be \( g_{\text{singlet}}^{\text{theory}} \approx 7.1 \), with contributions from only the atomic orbitals and
the valley magnetic moments of the bands. The triplet g-factor, however, is $g_{\text{triplet}}^\text{theory} \approx -11.1$, with an additional contribution from the spins and the opposite sign due to the flipped circular polarized light coupling. These calculated g-factors are in excellent agreement with experimentally observed values both in terms of sign and magnitude, confirming spin singlet and triplet assignments for $X_1^+$ and $X_2^-$. We note that unlike the traditional picture of singlet and triplet states, the degeneracy of interlayer exciton singlet and triplet states is already broken due to spin-orbit coupling. These states split differently under magnetic field as shown in Figure 2f in the exciton particle picture. We also remark that the observed g-factors in our experiment are inconsistent with a 60-degree aligned sample (Supplementary Section 7). Thus, we confirm the $R_h^X$ stacking configuration for our heterostructure and demonstrate direct evidence of spin-singlet and triplet excitons.

From these measurements, we can now assign the peaks as either singlet or triplet states. In regions I-III, $X^0$, $X^+$, and $X_1^-$, all have transitions from CB1, allowing us to assign them as singlet neutral or singlet charged excitons. In region IV, the $X_2^-$ peak is a transition from CB2 in the presence of free carriers and is therefore a triplet charged exciton. The emergence of $X_2^-$ only after sufficient band filling can be explained by relative dipole strength, and PL being dominated by the lowest energy transition. Our lifetime measurements of $X_1^+$ and $X_2^-$ showed that $\tau_1 \approx \tau_2$, suggesting the optical dipole strength of the two exciton species are similar, consistent with theoretical calculations\(^5\). Therefore, although the triplet transition is allowed, we only observe $X_2^-$ once the inter-conduction band relaxation rates are quenched by Pauli blocking (further discussion in Supplementary Section 9).

Understanding the spin-state of the excitons allows us to control the optical behavior of charged excitons in regions II and III under magnetic field. Figures 3a-b show polarization-resolved PL measurements at $B = 15$ T in the band filling regimes corresponding to $p$-, neutral and $n$-doped singlet excitons. To minimize the induced vertical electric field, we apply $V_{bg}$ ($V_{bg}$) for negative (positive) voltages so that the electric field is screened and remains constant once the WSe$_2$ (MoSe$_2$) layer is doped\(^9\). Using the same cross-polarization measurement scheme described above, we observe the $\sigma^+$ ($\sigma^-$) emission intensity to be larger for the $X^+$ ($X_1^-$). Figure 3d shows the normalized difference in PL peak intensity, $\Delta PL_{\text{norm}} = (I_{PL}^{\sigma^+} - I_{PL}^{\sigma^-})/(I_{PL}^{\sigma^+} + I_{PL}^{\sigma^-})$, as a function of gate voltage for $B = -15, 0$, and 15 T. Without magnetic field, $\Delta PL_{\text{norm}}$ stays nearly constant, indicating excitons with opposite chirality are nearly degenerate. At $B = 15$ T, $\Delta PL_{\text{norm}}$ is positive (negative) for the $X^+$ ($X_1^-$), while the effect is reversed for $B = -15$ T.

Assuming $\Delta PL_{\text{norm}}$ is proportional to the percentage of charged exciton density imbalance towards $\sigma^+$ circular polarization, our experimental observations imply a magnetic field induced imbalance in CIE density between the two valleys due to Zeeman splitting of the bands. CIEs ($X^+$ and $X_1^-$), at low doping, can only bind to a free carrier from the opposite valley due to the Pauli exclusion principle. Therefore, for the $\sigma^+$ exciton, the hole (electron) must come from the +K valley (Fig. 3c). Taking $X^+$, the hole density is expected to be larger in the +K valley than in the −K valley for $B > 0$ (Fig. 3d left inset). Since the emitting exciton binds with a hole from the opposite valley, higher hole density in the +K valley induces higher emission of $\sigma^+$ (−K valley) $X^+$ for $B > 0$, in agreement with our experimental results. Similarly, in the conduction band (Fig. 3d right inset), we expect a higher density of $\sigma^-$ for $X_1^-$ when $B > 0$, in agreement with the experiment.

Increasing gate voltage further into region IV under magnetic fields, we now can demonstrate gate tunable singlet-triplet CIE transitions inducing electrically tunable chiral optical response in our devices. Figures 4a-b shows the doping-dependent polarization-resolved PL in the singlet-triplet transition regime at $B = 15$ T. Here, we apply a dual-gating scheme $V_{bg} = \alpha V_{bg}$, reaching $n_{2D} \sim 10^{13}$ cm$^2$, sweeping through regions III to IV in Fig. 1a. Figures 4c-d compare the $X_2^-$ and $X_1^-$ PL intensity as a
function of the gate at \( B = 0 \) and 15 T and we observe \( X_2^- \) overtake \( X_1^- \) in PL intensity with carrier density.

Quantitative understanding of the gate dependent PL spectra can be made considering the band filling of both CB1 and CB2 as a function of \( n_{2D} \), controlled by both gates. Figure 4c shows that the transition from \( X_1^- \) to \( X_2^- \) occurs at \( n_{2D}^* \approx 1.3 \times 10^{13} \text{ cm}^2 \) (density calculated from capacitor model in Supplementary Section 1), where the PL emission is overtaken by \( X_2^- \). Taking the effective mass of CB1 to be \( m_{e}^{(1)} = 0.8 \, m_0 \)\(^{34}\) in units of bare electron mass \( (m_0) \), the \( n_{2D}^* \) value obtained above allows us to estimate the energy separation between the spin-split MoSe\(_2\) conduction band minima: \( \Delta E_{CB} = \frac{2\pi \, n_{2D}^* \, h^2}{\nu \, m_e^{(1)}} \approx 39 \text{ meV} \), where we use \( \nu = 2 \) for the K-valley degeneracy factor. The estimated \( \Delta E_{CB} \) value is consistent with previous experimental values\(^{34}\), but larger than theoretically calculated values\(^{32,35}\). We note that we use the effective mass from recent transport studies\(^{34}\) for all calculations, which suggest a systematic underestimate of the effective mass in DFT calculations\(^{35}\).

Applying a magnetic field in the singlet-triplet transition regime, we demonstrate a flip in the dominant polarized light and tuning of the transition due to the Zeeman splitting of CB2. Figure 4d shows the polarization-resolved PL intensities for \( X_1^- \) and \( X_2^- \) across the transition at \( B = 15 \) T. First, we find that the difference in polarized PL intensity is opposite for \( X_1^- \) and \( X_2^- \). In the band filling model mentioned above, the \( X_2^- \) population is controlled by Pauli blocking rather than free carrier density. For \( X_2^- \), when the...
Fermi energy reaches CB2, the +K valley is reached before the –K valley, resulting in a higher $s^+$ emission intensity, consistent with our experimental results. Second, comparing the $X_1^-$ to $X_2^-$ transition for $s^+$ and $s^-$ emission, we see the transition for $s^+$ occurs at a density $\Delta n_{2D} \sim 3.4 \times 10^{11} \text{ cm}^{-2}$ lower than for $s^-$, corresponding to a Zeeman splitting of 1.6 meV. This value is also consistent with the expected Zeeman spin splitting at $B = 15 \text{ T}$ of $\Delta E = 2\mu_B B = 1.7 \text{ meV}$, further supporting $X_2^-$ emission with sufficient band filling. Finally, the difference in PL intensity for $X_2^-$ and $X_1^-$ is larger for $s^+$ than for $s^-$, allowing us to enhance the ratio of $X_2^-$ to $X_1^-$ PL emission under the magnetic field.

Our capability of gate tuning to access the higher conduction band with opposite spin allows us to create charged excitons with singlet and triplet spin configurations and opposite chiral light coupling. By combining long lifetime with local gate engineering, bright triplet charged interlayer excitons in vdW heterostructures provides a new scheme to control chiral, valley, and spin quantum states and can pave the way towards the realization of electrically controlled valleytronic devices with multiple quantum degrees of freedom.

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