Supporting Information

Direct Observation of Gate-Tunable Dark Trions in Monolayer WSe$_2$

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Supplementary Note 1. Gate-voltage dependent PL spectra of the second and third WSe$_2$ devices

Here we show the color plots of PL spectra as a function of the gate voltage for the second and third BN encapsulated WSe$_2$ devices in Fig. S1a and S1c, and the corresponding line cuts at specific gate voltages in Fig. S1b and S1d. The gate-dependence behavior of these two devices is similar to what is shown in the Fig. 1b of the main text. They all show well-resolved fine excitonic structure, including the X$_0$, XX, XX$^-$, X$^+$, X$_T$, X$_2$, X$_D$ and X$_D^R$. Most importantly, it also exhibits the emergence of X$_D^+$ and X$_D^-$. It is worth noting that the PL shown in the main text from the first device was collected with an extremely large NA objective (0.9) while the PL shown in the SI were measured with another objective (NA, ~ 0.6), which is the main reason that we can see the cross pattern for both positive and negative dark trions in the device shown in the main text while we only see it for the positive dark trion for the second and third devices.
Figure S1. PL spectra of the second and third WSe$_2$ devices. (a,c) Color plots of the PL spectra of the second and third BN encapsulated monolayer WSe$_2$ devices as a function of the gate voltage at 4.2 K, with the continuous-wave (CW) laser excitation centered at 1.959 eV (40 µW). The color represents the PL intensity. (b,d) PL spectra at the specific gate voltages of electron-doped WSe$_2$, charge-neutral WSe$_2$ hole-doped WSe$_2$, corresponding to the different dash lines in (a) and (c).

Supplementary Note 2. g-factor extracted from the Zeeman shift of different excitonic complexes

Fig. S2 shows the valley-resolved PL spectra as a function of the out-of-plane magnetic field at the gate voltage of 0 V and the extracted g-factors for different excitonic states through linear fitting of the Zeeman shift as magnetic field. It can be seen all the excitonic states show a blue shift from -17 T to 17 T, except for the dark exciton, which exhibits a unique cross pattern.
Figure S2. Valley-resolved magneto-PL spectra of the charge-neutral WSe$_2$ for the first device. (a) Color plot of the PL spectra as a function of the out-of-plane magnetic field at the gate voltage of 0 V for the ($\sigma^-$, $\sigma^-$) and ($\sigma^+$, $\sigma^+$) configurations at 4.2 K, respectively. The excitation is a continuous-wave (CW) laser centered at 1.879 eV (100 $\mu$W). (b) The $g$-factors for different excitonic states extracted from the Zeeman shift corresponding to (a).

Fig. S3-5 are the valley-resolved PL spectra as a function of the out-of-plane magnetic field for ($\sigma^-$, $\sigma^-$) and ($\sigma^+$, $\sigma^+$) configurations at the gate voltage of -4.5 V, 0 V and 2.5 V, respectively. All the bright excitonic complexes in the ($\sigma^-$, $\sigma^-$) or ($\sigma^+$, $\sigma^+$) configuration exhibit either a linear blueshift or redshift as a function of the magnetic field. However, both the $X_D^-$ and $X_D^+$ exhibit a “cross” pattern either in ($\sigma^-$, $\sigma^-$) or ($\sigma^+$, $\sigma^+$) configuration. It is worth noting that no obvious change in the valley polarization was observed with the different excitation photon energy (1.879 eV and 1.956 eV).

Here, we also extract the g-factor through the fitting of the individual Zeeman shift of each valley ($\Delta E_{K'} = -\frac{1}{2}\mu_B g B$ and $\Delta E_{K} = \frac{1}{2}\mu_B g B$) as a function of the magnetic field for the second device, and the values for different excitonic complexes are shown in Fig. S3b and S3d, Fig. S4b and S4d and Fig. S5b and S5d, which are consistent with the values shown in the Fig. 3.
Figure S3. Valley-resolved magneto-PL spectra of the hole-doped WSe$_2$. (a,c) Color plots of the PL spectra as a function of the out-of-plane magnetic field at the gate voltage of -4.5 V for the ($\sigma^-\sigma^-$) and ($\sigma^+\sigma^+$) configurations at 4.2 K, respectively. The excitation is a continuous-wave (CW) laser centered at 1.959 eV (100 $\mu$W). The color represents the PL intensity. The dash lines act as the eye guide for the energy shift of different peaks. It is worth noting that the cross pattern from the dark exciton, although weak in the p-doped WSe$_2$, is also feasible. (b,d) The $g$-factors for bright exciton and positive dark trion extracted from the Zeeman shift corresponding to (a) and (c), respectively.
Figure S4. Valley-resolved magneto-PL spectra of the charge neutral WSe$_2$. (a,c) Color plots of the PL spectra as a function of the out-of-plane magnetic field at the gate voltage of 0 V for the ($\sigma^-\sigma^-$) and ($\sigma^+\sigma^+$) configurations at 4.2 K, respectively. The excitation is a continuous-wave (CW) laser centered at 1.959 eV (100 µW), and the color represents the PL intensity. The dash lines act as the eye guide for the energy shift of different peaks. (b,d) $g$-factors for $X_0$ and $X_D$ extracted from the Zeeman shift corresponding to (a) and (c), respectively.
Figure S5. Valley-resolved magneto-PL spectra of the electron-doped WSe$_2$. (a,c) Color plots of the PL spectra as a function of the out-of-plane magnetic field at the gate voltage of 2.5 V for the ($\sigma^-$-$\sigma^-$) and ($\sigma^+$-$\sigma^+$) configurations at 4.2 K, respectively. The excitation is a continuous-wave (CW) laser centered at 1.959 eV (100 µW), and the color represents the PL intensity. The dash lines act as the eye guide for the energy shift of different peaks. (b,d) $g$-factors for $X_0$ and $X_D$ extracted from the Zeeman shift corresponding to a and c, respectively.
Supplementary Note 3. Valley-resolved magneto-PL spectra of the third WSe$_2$ device
**Figure S6. Valley-resolved magneto-PL spectra of the second WSe$_2$ device.** (a,b) Color plots of the PL spectra as a function of the out-of-plane magnetic field at the gate voltage of -2 V (hole-doped) for the ($\sigma^-$,$\sigma^-$) and ($\sigma^+$$\sigma^+$) configurations at 4.2 K, respectively. (c,d) Color plots of the PL spectra as a function of the out-of-plane magnetic field at the gate voltage of -0.27 V (charge neutral) for the ($\sigma^-$,$\sigma^-$) and ($\sigma^+$$\sigma^+$) configurations at 4.2 K, respectively. (e,f) Color plots of the PL spectra as a function of the out-of-plane magnetic field at the gate voltage of 0.5 V (electron-doped) for the ($\sigma^-$,$\sigma^-$) and ($\sigma^+$$\sigma^+$) configurations at 4.2 K, respectively. The excitation is a continuous-wave (CW) laser centered at 1.959 eV (100 µW), and the color represents the PL intensity. The dash lines act as the eye guide for the energy shift of different peaks.

We also show the valley-resolved magneto-PL spectra of the third device for both the ($\sigma^-$,$\sigma^-$) and ($\sigma^+$$\sigma^+$) configurations in Fig. S6, for the gate voltage of -2.0 V, -0.27 V and 0.5 V. The B field dependence of the valley-resolved spectra for the second and third devices both exhibit the “cross” pattern for the XD and XD$^+$ in both the ($\sigma^-$,$\sigma^-$) and ($\sigma^+$$\sigma^+$) configurations.

**Supplementary Note 4. PL spectra at specific radiation angles**

Fig. S7a shows the schematic of the back focal plane PL setup under the out-of-plane magnetic field. A continuous-wave laser centered at 1.879 eV is focused on the sample with a large N.A. objective (~ 0.9). The emission PL is collected with the same objective and the back focal plane is converted into collimated light by the lens 1 and then refocused on the long slit before the monochromator by the lens 2. The size of the back focal plane image before the slit is ~ 6 mm. Here we use the long slit (width ~200 µm) to select the central part of the back focal plane image and disperse it by the spectrometer. The spectrum information of the PL is resolved with the horizontal array of the pixels of the silicon charge-coupled device (CCD), while the vertical array is utilized to resolve the radiation angle, defined here as the angle from the normal.

Fig. S7b-7d exhibit the PL spectra at different detected angles for hole-doping, charge-neutral and electron-doping WSe$_2$, respectively, corresponding to the Fig. 3 in the main text. It can be seen that the positive dark trion, dark exciton and negative dark trion all have the strongest PL intensity with the largest radiation angle (limited by NA), while the bright excitonic states have the strongest PL intensity at 0º.
Figure S7. Back focal plane PL spectra. (a) Schematic of the back focal plane PL setup. (b-d) PL spectra at different detected angles at the gate voltages of -2.0 V (b), 0 V (c) and 1.0 V (d), respectively.

Supplementary Note 5. Lifetime for different gate voltages

Fig. S8a shows the instrumental response function (IRF) with the pulse laser excitation at 1.908 eV that we use as the kernel for the convolution to extract the lifetimes of positive bright trion and positive dark trion. Fig. S8b and S8c are the fitting results of the positive dark trion as a function of gate voltage, which we obtain by using a biexponential function $I = A_1 e^{-t_1/\tau_1} + A_2 e^{-t_2/\tau_2}$ to convolute with the IRF. $A_1$ and $A_2$ are the weight of the fast and slow exponential decay. As discussed in the main text, the lifetime of $X_D^+$ is described by $\tau_1$, which decreases with the increase of the doping density. Fig. S8d includes the fitting results of the gate voltages of -0.5 V and -3.0 V, respectively, which indicates the good fitting quality of the convolution method.
Figure S8. Lifetime of the positive dark trion at different gate voltages. (a) The IRF of the pulsed laser excitation at 1.908 eV that is used as a kernel for the convolution. (b) Extracted lifetime for the positive dark trion as a function of the gate voltage, including the fast component (blue) and slow component (magenta). (c) The weight of the fast (blue) and slow (magenta) components as a function of the gate voltage, which indicates that the fast component dominates TRPL spectra of the positive dark trion for the first hundreds of picoseconds, which is the time range that we are interested. (d) Comparison of the fitting results of lifetime for the gate voltages of -0.5 V and -3.0 V to show the fitting quality of the convolution method.