Supporting Information

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Exciton Rate Equation

If a circularly polarized light pumps K valley only, the evolution of the density of excitons (N_K and $N_{K'}$ on K and K′ valleys) can be described by the following rate equations as $\frac{dN_K}{dt} = -\frac{N_K}{\tau} - \left(\frac{N_K}{\tau_K} - \frac{N_{K'}}{\tau_K}\right) + A = 0$ and $\frac{dN_{K'}}{dt} = -\frac{N_{K'}}{\tau} + \left(\frac{N_K}{\tau_K} - \frac{N_{K'}}{\tau_K}\right) = 0$, where τ is the exciton life time at both K and K′ valley, τ_K^{-1} is the $K \leftrightarrow K'$ intervalley scattering rate, and A is the exciton generation rate. The degree of photoluminescence polarization P depends on the steady values of the density of excitons N_K and $N_{K'}$ as $P = \frac{N_K - N_{K'}}{N_K + N_{K'}} = \frac{P_0}{1 + 2\tau/_{\tau_k}}$.

Carrier Lifetime in Monolayer and Bilayers

The carrier dynamics measurement was carried out using the time-resolved pump-probe technique. A passive mode-lock Ti:sapphire laser, with 150-fs pulses and an 80-MHz repetition rate, is used to pump a fiber crystal so as to generate the pulse white laser. The output light with the 580-nm wavelength selected by a bandpass filter is used as the pump pulse, and almost resonates to the A exaction transition. After passing the delay line, it is focused on the sample surface by using a 50x microscope objective. The probe pulse with wavelength of 630 nm is combined with the pump pulse by a dichromic beamsplitter, and focused on the sample with normal incidence. The reflection of probe pulse is collected and detected by photodiode. The output photocurrent is detected by a lock-in amplifier, which modulates the pump pulse with the frequency of 100 kHz generated by a photoelastic modulator chopper. All of the measurements were performed under ambient conditions. The curve of ΔR/R as a function of delay time is shown in Fig. S1. After fitting by the exponential equation, we get three carriers lifetime for monolayer and bilayer WS_2 shown in Table S1.

Exchange Interaction

The bright exciton basis states assume the form

$$\left|B_{K(K')}\right\rangle \equiv \left|\mu_e, \nu_h, q, K(K')\right\rangle = \Psi_{\mu_e}^{K(K')}(r_e)\Psi_{\nu_h}^{K(K')}(r_h)\varphi_{1s}^{2D}(\rho)e^{ik\cdot R}$$

at K (K′) valley, where $\Psi_{\mu_e}^{K}(r_e)$ and $\Psi_{\nu_h}^{K}(r_h)$ are electron and hole Bloch wave functions with electron spin state μ_e and hole spin state ν_h at K valley. $\varphi_{1s}^{2D}(\rho)$ is the ground state of 2D exciton envelop function with the relative coordinate $\rho = r_e - r_h$; $\mathbf{k} = k(\cos\theta, \sin\theta)$ and R denote the exciton center-of-mass wavevector with angular θ and its center-of-mass position, respectively.

The exchange coupling J_{ex}^{intra} between the radiative electrons and holes in the same valley has the form (1)

$$J_{ex}^{intra} \approx f_{eh}\int dr_1 dr_2 \Psi_{\downarrow_e}^{K} * (r_1)\Psi_{\uparrow_h}^{K}(r_1)V(r_1 - r_2)\Psi_{\downarrow_e}^{K}(r_2)\Psi_{\uparrow_h}^{K} * (r_2),$$

which is independent of valley index and thus does not contribute to the depolarization. Here, f_{eh} corresponds to the modulus square of the envelope function of the electron–hole relative motion evaluated at zero distance.

The depolarization of exciton actually results from the intervalley electrons and holes exchange coupling, which is described as the coupling between the two valley configurations of the bright excitons as $H_{ex} = J_{eh}^{inter}|B_K\rangle\langle B_{K'}| + h.c.$ Here the coupling strength is (2)

$$J_{eh}^{inter} = \sum_G \frac{V(G+k)}{A}\left(\sum_q \varphi(-q)\left\langle u_{\downarrow_h}^{K'+q-\frac{k}{2}}\middle|e^{-iGr}\middle|u_{\downarrow_e}^{K'+q+\frac{k}{2}}\right\rangle\right) \times \left(\sum_{q'} \varphi(q')\left\langle u_{\uparrow_e}^{K+q'+\frac{k}{2}}\middle|e^{iGr}\middle|u_{\uparrow_h}^{K+q'-\frac{k}{2}}\right\rangle\right),$$

where $V(\mathbf{k}) = \int V(\mathbf{r})e^{i\mathbf{k}\bullet\mathbf{r}}d\mathbf{r}$ denotes the Coulomb interaction in $\mathbf{k}$ space, A is the area of the 2D plane, $\mathbf{G}$ are reciprocal lattice vectors, $\varphi(\mathbf{q}) = \int \varphi_{1s}^{2D}(\boldsymbol{\rho})e^{i\mathbf{q}\bullet\boldsymbol{\rho}}d\boldsymbol{\rho}$ is the wavefunction for relative motion in momentum space, and $u_{\mu_e}^{K(K')}(r_e)$ and $u_{\nu_h}^{K(K')}(r_h)$ are the periodic parts of the electron and hole Bloch wave functions $\Psi_{\mu_e}^{K(K')}(r_e)$ and $\Psi_{\nu_h}^{K(K')}(r_h)$. Because we have $V(\mathbf{G}+\mathbf{k}) << V(\mathbf{k})$ from $\mathbf{k} << \mathbf{G}$, the short range part of the exchange interaction is negligible.

For the long-range exchange interaction, by using the kp expansion and assuming the periodic parts of Bloch wave functions can be replaced by the ones at Dirac points as $u_{\mu_e(\nu_h)}^{K+q} \approx u_{\mu_e(\nu_h)}^{K}$, the exchange interaction strength is simplified as

$$J_{eh}^{inter} = -\left|\varphi_{1s}^{2D}(\rho = 0)\right|^2 \frac{a^2t^2}{\Delta^2}V(\mathbf{k})k^2e^{-2i\theta},$$

where a is the lattice constant of monolayer transition metal dichalcogenides, t is the hopping amplitude, and Δ is the band gap. Here, $\left|\varphi_{1s}^{2D}(\rho = 0)\right|^2$ corresponds to the probability density of finding the electron and hole to spatially overlap, which is $1/a_B^2 \sim E_B^2$ with the exciton Bohr radius a_B and binding energy E_B. Therefore, the exchange interaction is proportional to the square of the exciton-binding energy.

1. Pikus GE, Bir GL (1971) Exchange interaction in excitons in semiconductors. *Zh Eksp Teor Fiz* 60:195.

2. Yu H, Liu GB, Gong P, Xu X, Yao W (2014) Dirac cones and Dirac saddle points of bright excitons in monolayer transition metal dichalcogenides. *Nat Commun* 5:3876.

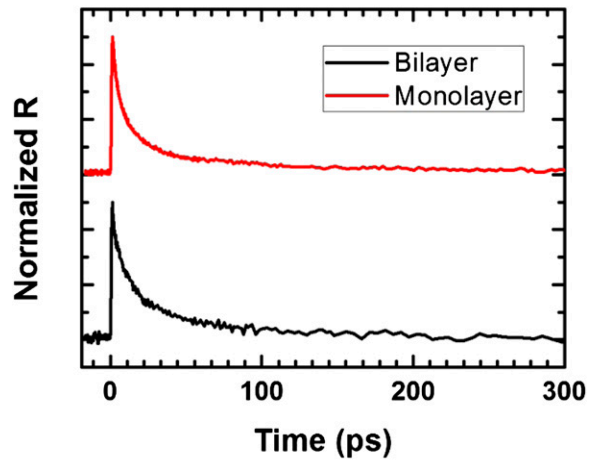

Fig. S1. Carrier lifetime measurements. Here, $\Delta R/R$ is a function of the delay time for monolayer (red curve) and bilayer (black curve) WS_2.

Table S1. The lifetime for monolayer and bilayer WS_2 sample

Carrier lifetime	Monolayer (ps)	Bilayer (ps)
T1	3	0.6
T2	14	12.0
T3	118	89.0