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SUPPLEMENTARY INFORMATION

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Radiative control of dark excitons at room temperature by nano-optical antenna-tip Purcell effect

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Supplementary Information to: Radiative control of dark excitons at room temperature by nano-optical antenna-tip Purcell effect

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TEPL SPECTRA OF THE BRIGHT AND DARK EXCITONS

In Fig. 2a of the main text, we show TEPL spectra of WSe_2 monolayer at 1 nm tip-sample distance with excitation polarization oriented parallel or perpendicular with respect to the sample surface. We perform Lorentzian line fit analysis of the bright (blue) and dark (orange) excitons of Fig. 2a to compare the peak energy and spectral linewidth of them as shown in Fig. S1a and b. Lorentzian functions provide for a better line fit for both spectra compared to Gaussian function due to the homogeneous broadening likely dominated by phonon scattering.

The dark exciton state is found at ∼46 meV below the bright exciton associated with the energy splitting in the conduction band. While the bright exciton peak shows Lorentzian shape to good approximation, the dark exciton is asymmetric with a shoulder at 780 nm. This shoulder is possibly due to a lifting of the valley degeneracy [1], a Fano resonance resulting from the exciton-plasmon coupling [2], or the dark trions [3, 4].

The observed TEPL linewidth of the dark exciton emission is more narrow than that of the bright exciton in agreement with recent observation based on surface plasmon polaritons (SPP)-device based probing [3]. On the other hand, the dark exciton emission induced by the Zeeman effect showed the same linewidth as the bright excitons [4, 5]. We believe this feature is attributed to the different (intrinsic vs. extrinsic) spin flip mechanisms of the dark excitons as discussed in the main text.

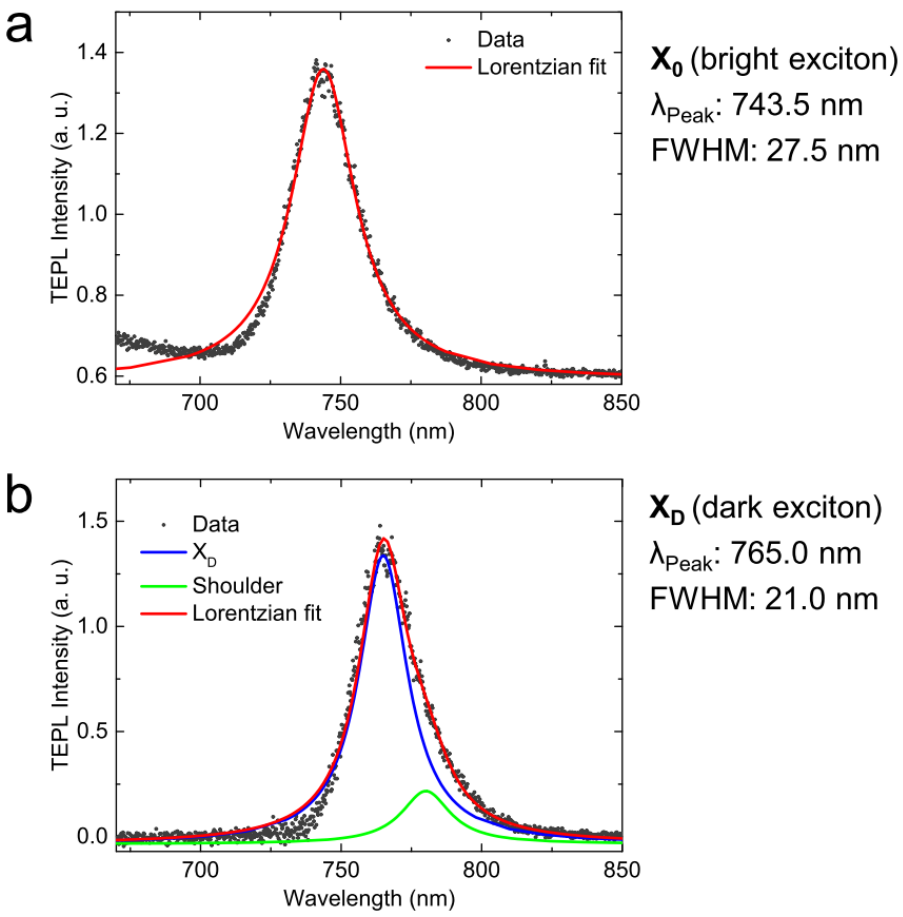

Figure S1. TEPL spectra of the bright (a) and dark (b) excitons of WSe_2 monolayer transferred onto the Au substrate with Lorentzian line fit analysis, derived from Fig. 2a.

FDTD SIMULATION OF PURCELL ENHANCEMENT FACTOR

We use a commercial finite-difference time domain (FDTD) simulation software (Lumerical Solutions) to estimate the Purcell enhancement (radiative decay rate enhancement) factor of the dark excitons, $\gamma_{PF} = \gamma/\gamma_0$. For the geometry of Au tip (with 5 nm apex radius) in close proximity to the Au substrate, we model the dark exciton of a monolayer WSe_2 as a monochromatic fluorescent emitter (electric dipole, $\lambda = 765$ nm) as shown in Fig. S2a. The position of the emitter is fixed at 0.3 nm above the Au substrate. For simulation of the distance dependent Purcell enhancement factor (Fig. 3d), the distance (d) between the Au tip and the Au substrate is controlled by moving the tip position. The orientation of the emitter is set between 0° and 90° to simulate the angle dependent Purcell factor (Fig. S2b) as well as the dark and bright excitons.

In FDTD simulations, the Purcell factor is calculated by the ratio of the emission intensity radiated by an electric dipole in the nano-structured environment and in free space emission. Specifically, the Purcell factor is determined by the polarizability of the near-field coupled Au-Au nano-gap, the local density of states of the system defined by the Green's function, and the vector magnitude of the dipole moment.

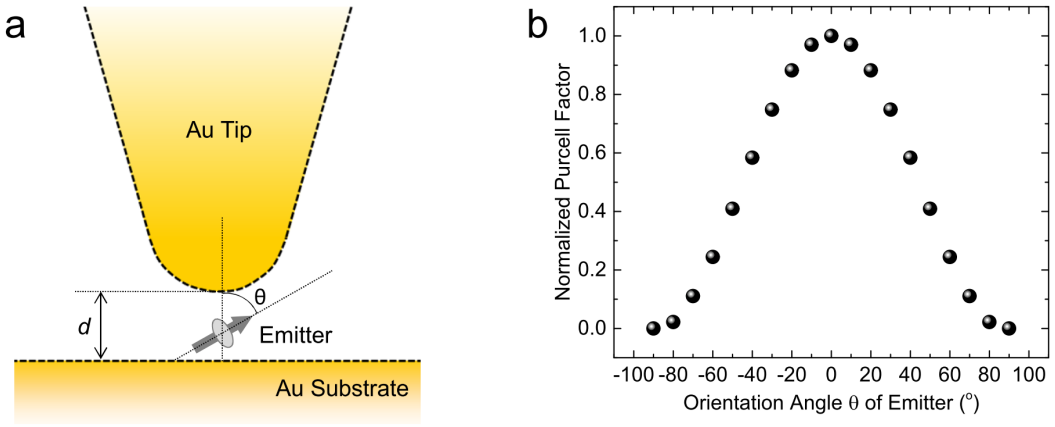

Figure S2. (a) Illustration of the computational design of Au tip, Au substrate, and fluorescent emitter (electric dipole) for finite-difference time domain (FDTD) simulation of Purcell enhancement factor. (b) Normalized Purcell enhancement factor of the fluorescent emitter with respect to the orientation angle.

SCREENING EFFECT OF THE AU SUBSTRATE

We note that the Au substrate primarily serves the purpose to allow for the formation of the *out-of-plane* plasmonic nano-cavity by the Au tip inducing a near-field coupled image dipole in the substrate. This nanocavity with ≤ 1.5 nm gap gives rise to large Purcell factor ($> 2{,}000$) compared to dielectric substrates, which is responsible for the enhancement of the dark exciton emission. With regards to the screening effect, the energy of bright and dark exciton emission is only minimally perturbed by the Au substrate due to the tightly bound exciton within the monolayer. In literature, a slight modification in peak energy has been observed for TMD monolayers using a gold substrate/nanoparticle as results of several effects, e.g., hot-electron induced structural phase transition [6] and n-doping [7] effects. However, these hot-electron induced effects are very weak in our case due to the lower excitation energy as explained in [8].

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