

Plasmonic nanocavity induced valley manipulation in monolayer transition metal dichalcogenides: A phenomenological description

Jiawei Sun^{1,2,*}, Zhiwei Hu^{3,*}, Wen Chen³, Yang Li^{1,†}, Huatian Hu^{4,‡}, and Hongxing Xu^{5,6}

¹State Key Laboratory of Radio Frequency Heterogeneous Integration, *Shenzhen University*, Shenzhen 518060, China

²Institute of Nanoscience and Applications, *Southern University of Science and Technology*, Shenzhen 518055, China

³State Key Laboratory of Precision Spectroscopy, *East China Normal University*, Shanghai 200241, China

⁴Center for Biomolecular Nanotechnologies, *Istituto Italiano di Tecnologia*, via Barsanti 14, 73010 Arnesano, Italy

⁵School of Physics and Technology, Center for Nanoscience and Nanotechnology,

and Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education, *Wuhan University*, Wuhan 430072, China

⁶*Henan Academy of Sciences*, Zhengzhou, Henan 450046, China



(Received 2 August 2025; revised 12 December 2025; accepted 4 February 2026; published 11 March 2026)

Manipulating the valley degree of freedom in monolayer transition metal dichalcogenides (TMDs) is essential for advancing valleytronics-based information processing and transport. However, significant intervalley scattering causes valley signals to vanish at room temperature, posing a major challenge. To mitigate this, strategies involving magnetic fields, intense circularly polarized light, and in-plane electric fields have been explored to enhance valley polarization. Recently, increasing the excitons lifetimes using photonic nanostructures has emerged as a promising approach. In this work, we present a phenomenological model based on rate equations that describes and regulates the valley depolarization process in TMDs embedded within engineered photonic environments. Our findings demonstrate the potential to achieve near-unity valley polarization and enable negative valley polarization of dark excitons. Additionally, we identify extrinsically chiral nanocavities as effective platforms for generating chiral emission and spatially separating valley states. This research offers valuable insights for the nanophotonic design of devices with enhanced valley control, including manipulation of valley-polarized dark excitons, and paves the way for the development of advanced integrated valleytronic systems.

DOI: [10.1103/1355-mgqs](https://doi.org/10.1103/1355-mgqs)

I. INTRODUCTION

Valley selection rules in monolayer transition metal dichalcogenides (TMDs) require that the right (left) circularly polarized light couples to the electronic transition in K ($-K$) valleys [1,2]. The spin angular momentum of the light can be transferred to the valley-polarized excitons in monolayer TMDs. As a readout, the photoluminescence (PL) emitted will possess the same circular polarization as the excitation light or can be guided to propagate in the waveguides, making them be potential materials for building up low-dimensional devices in information storage and processing [3–8]. However, the significant phonon-assisted intervalley scattering at room temperature will destroy the fidelity of the valley signals and result in a low-valley polarization [4,9]. To enhance and manipulate the valley polarization, external magnetic

fields [10–13] and intense circularly polarized light [14,15] can be introduced to accumulate population in a single valley, effectively lifting the valley degeneracy. Additionally, methods like applying an in-plane electric field [16] and electrostatic doping [17] have also been shown to enhance the valley polarization by effectively suppressing the intervalley scattering.

According to the rate equations model, the degree of valley polarization depends on the ratio between the rates of intervalley scattering and radiative decay. Thus, the valley polarization can be manipulated through modifying radiative decay rates by tailoring the photonic environment [18–21]. To be specific, suppression of valley depolarization via phonon-assisted intervalley scattering requires that the radiative decay rates exceeds the intervalley scattering rates, thereby preserving valley-polarized emission. Plasmonic nanocavities with strongly enhanced local fields have demonstrated significant Purcell enhancement to accelerate the radiative decay rate of TMDs, showing the ability to achieve high-valley polarization at room temperature [18,22,23]. Therefore, a theoretical framework based on the rate equations model is essential for guiding the design of nanocavities to control the valley polarization of excitons in various TMDs.

In addition, the conduction band spin splitting in monolayer TMDs gives rise to two types of excitons: spin-allowed (bright) states and spin-forbidden (dark) states [2]. While

*These authors contributed equally to this work.

†Contact Author: yang.li@szu.edu.cn

‡Contact Author: Huatian.hu@iit.it

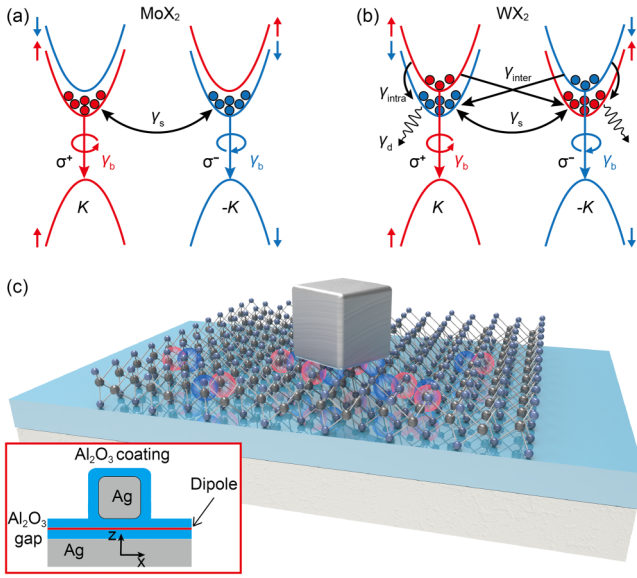


FIG. 1. (a), (b) The valley depolarization processes for monolayers (a) MoX₂ and (b) WX₂. (c) The schematic of nanocube-over-mirror (NCOM) nanocavity coupled with monolayer TMDs. In the simulation, the dipole is situated in the middle height (marked as red line) of the gap region in simulation as shown in the inset.

valley-polarized emission from bright excitons has been extensively studied, the decay mechanisms of valley-polarized dark excitons remain largely unexplored. This is primarily due to their weak emission in conventional spectroscopy methods, as their out-of-plane transition dipole moments make detection challenging [24–27]. However, the strong out-of-plane field enhancement and antenna effect provided by plasmonic nanocavities can significantly brighten dark excitons and enable their emission into the far field [28]. Therefore, it is crucial to clarify the decay dynamics and valley polarization mechanisms of dark excitons in plasmonic nanocavities.

In this work, we develop a phenomenological model based on rate equations to guide the manipulation of valley depolarization processes in monolayer TMDs. Using this model, we investigate the influence of Purcell enhancement—engineered through nanocavity design—on valley polarization and demonstrate the possibility of achieving near-unity valley polarization. Remarkably, our results also reveal that the valley polarization of dark excitons can be reversed, potentially explaining the negative valley polarization observed in previous experiments. Furthermore, we calculate the valley polarization in chiral nanocavities and show that these structures can serve as promising platforms for generating chiral emission and enabling spatial valley separation.

II. THEORETICAL FRAMEWORK

A. Rate equation models

The conduction band order in MoX₂ (MoS₂, MoSe₂) and WX₂ (WS₂, WSe₂) exhibits a contrasting diagram. The dark state of MoX₂ stays in the higher-energy band, whereas that of WX₂ stays at the lower-energy band [2]. The schematic of the energy band of MoX₂ and WX₂ is shown in Fig. 1. Consequently, valley-polarized excitons in monolayer MoX₂

and WX₂ undergo different depolarization processes. These processes significantly impact the observed valley polarization in PL spectra. According to the rate equation model, the valley polarization of bright excitons P_b in monolayer MoX₂ can be expressed as [3]

$$P_b = \frac{1}{1 + 2\gamma_s/\gamma_b}, \quad (1)$$

where γ_s and γ_b are the intervalley scattering rate and decay rate of bright excitons, respectively. The valley polarization depends on the competition between the two parameters γ_s and γ_b , as shown in Fig. 1(a). At low temperature, the decay rate of bright excitons exceeds the intervalley scattering rate, resulting in a high-valley polarization [3,4]. However, low-valley polarization is typically observed at room temperature, as phonon-assisted intervalley scattering is significantly enhanced with increasing temperature [3,9]. To achieve high-valley polarization at room temperature, controlling the radiative decay rate (γ_b) turns out to be an effective strategy.

As for the WX₂, the depolarization process is illustrated in Fig. 1(b). After the excitation, the valley-polarized excitons in the higher-energy band will decay into the lower-energy band through two channels: (i) intravalley decay (γ_{intra}) with spin-flip from bright state to dark state within the same valley; (ii) intervalley decay (γ_{inter}) with spin-conserved from one valley to another valley [29]. Except for the intervalley scattering and decay of bright excitons, the dark excitons can also decay through relaxation to localized excitons with the timescale of 0.5 ~ 1 ns, much slower than the radiative decay of bright excitons [13]. However, the out-of-plane nature of dark excitons' transition dipole moments restricts the emission to far-field, leading to the decay rate of dark excitons (γ_d) being only 10⁻² to 10⁻³ times that of bright excitons. All the detailed discussions on these parameters and their references are shown in the Supplementary Material (SM) [30] (see also Refs. [31–34] therein). The rate equations of WS₂ monolayers with excitation rate g_b can be expressed as

$$\begin{aligned} \frac{dn_b^K}{dt} &= g_b^K + \gamma_s n_b^{-K} - (\gamma_b + \gamma_{intra} + \gamma_{inter} + \gamma_s) n_b^K, \\ \frac{dn_b^{-K}}{dt} &= g_b^{-K} + \gamma_s n_b^K - (\gamma_b + \gamma_{intra} + \gamma_{inter} + \gamma_s) n_b^{-K}, \\ \frac{dn_d^K}{dt} &= \gamma_{intra} n_b^K + \gamma_{inter} n_b^{-K} + \gamma_s n_d^{-K} - (\gamma_s + \gamma_d) n_d^K, \\ \frac{dn_d^{-K}}{dt} &= \gamma_{intra} n_b^{-K} + \gamma_{inter} n_b^K + \gamma_s n_d^K - (\gamma_s + \gamma_d) n_d^{-K}, \end{aligned} \quad (2)$$

n_b and n_d represent the populations of the bright and dark excitons, respectively. The superscripts “K” and “-K” denote the corresponding parameters in the K and -K valleys. By solving the rate equations, we calculate the valley polarization of the bright (P_b) and dark (P_d) excitons

$$\begin{aligned} P_b &= \frac{n_b^K - n_b^{-K}}{n_b^K + n_b^{-K}} = \frac{1}{1 + \frac{2\gamma_s}{\Gamma}}, \\ P_d &= \frac{n_d^K - n_d^{-K}}{n_d^K + n_d^{-K}} = \frac{1}{1 + \frac{2\gamma_s}{\gamma_d}} \times \frac{1}{1 + \frac{2\gamma_s}{\Gamma}} \times \frac{\gamma_{intra} - \gamma_{inter}}{\gamma_{intra} + \gamma_{inter}}, \end{aligned} \quad (3)$$

where $\Gamma = \gamma_b + \gamma_{\text{intra}} + \gamma_{\text{inter}}$. The spin-conserved intervalley decay rate is significantly larger than the spin-flipped intravalley decay rate, i.e., $\gamma_{\text{inter}} \gg \gamma_{\text{intra}}$ [32]. Therefore, we can derive a simplified relation, $\frac{\gamma_{\text{intra}} - \gamma_{\text{inter}}}{\gamma_{\text{intra}} + \gamma_{\text{inter}}} \approx -1$. This indicates that the valley polarization of dark excitons is negative, which is consistent with the previous experimental results [25].

Since valley polarization is strongly influenced by the decay rates, which can be engineered through the photonic local density of states (LDOS), we demonstrate the use of a nanocube-over-mirror (NCOM) nanocavity to enhance the valley polarization of both bright and dark excitons. The nanocavity is constructed by placing the silver nanocube over the silver film, as shown in Fig. 1(c). The plasmonic resonance of NCOM nanocavity could be easily tuned by particle size, gap size, and extra coating thickness, providing more freedom to modulate the excitonic decay rates [35,36]. In this study, the Ag nanocubes, each with a length of 80 nm (unless otherwise specified), are positioned on a silver film coated with 8 nm Al_2O_3 . The gap between the silver nanocube and the silver film is spaced with Al_2O_3 layers, and one electric dipole is positioned at the middle height of the gap region (highlighted by the red line). On top of the NCOM nanocavity, extra Al_2O_3 layers could be coated as a capping layer to tune the resonance of the plasmonic modes and protect the silver nanoparticle from oxidation.

B. Methods on simulation

According to Fermi's golden rule, the spontaneous decay rate is proportional to the LDOS ρ as $\gamma = \frac{2\omega}{3\hbar\epsilon_0} |\mathbf{p}|^2 \rho(\omega)$, where ω is the transition frequency of the emitter. Therefore, the spontaneous decay rate of emitters can be manipulated through engineering the LDOS within photonic cavities [37,38]. We can calculate the enhancements of the decay rate, which is proportional to the enhancement of LDOS, i.e., $\frac{\rho}{\rho_0} = \frac{\gamma}{\gamma_0}$. The transition dipole moment of dark excitons is out-of-plane, while that of bright excitons is in-plane. So, the spontaneous decay rate enhancement of dark excitons (γ_d/γ_d^0) and bright excitons (γ_b/γ_b^0) can be attributed to the out-of-plane LDOS and in-plane LDOS enhancement, i.e., $\frac{\rho_{\text{in}}}{\rho_0} = \frac{\gamma_b}{\gamma_b^0}$ and $\frac{\rho_{\text{out}}}{\rho_0} = \frac{\gamma_d}{\gamma_d^0}$. In general, to calculate the LDOS enhancement, commercial software comsol multiphysics was employed for full-wave simulation. The refractive indices of the cube and the Ag substrate were derived from the Johnson and Christy data [39], while the refractive index of Al_2O_3 , serving as the gap layer and coating, was set to 1.5. The in-plane and out-of-plane LDOS enhancement is calculated following the relation $\frac{\rho_{\text{in,out}}}{\rho_0} = \frac{\gamma_{\text{in,out}}}{\gamma_0} = \frac{P_{\text{in,out}}^{\text{tot}}}{P_0}$, where the total emission power $P_{\text{in,out}}^{\text{tot}}$ is obtained by performing a closed-surface integral of the Poynting vector of the total field around the dipole in the nanojunction. Here, $P_0 = \frac{|\mu|^2}{4\pi\epsilon_0\epsilon} \frac{n^3\omega^4}{3c^3}$ means the radiation power of the dipole in a vacuum. The in-plane LDOS enhancement was achieved by placing the dipole in the central plane of the gap region as the excitation source, and the dipole moment oriented along the in-plane direction. By positioning the dipole at different locations to compute the LDOS enhancement ($P_{\text{tot}}^{\text{in}}/P_0$) at each point, the in-plane LDOS mapping in the nanocavity can be obtained. As for the

simulation of the out-of-plane LDOS, the dipole orientation of the dipole was simply changed to the out-of-plane direction.

The asymmetric nanocavities can generate chiral LDOS and lead to the chiral Purcell effect [18]. Monolayer TMDs embedded into such chiral nanocavities can be an ideal platform to generate chiral spontaneous emission. We can further investigate whether the system formed by integrating monolayer materials into chiral nanocavities can construct a tunable and efficient chiral light source. Such a problem can be attributed to the calculation of circularly polarized radiative LDOS. In the simulation, the circularly polarized dipole is centered in the gap layer with moments defined as $(\mu_x, \mu_y, \mu_z) = (1, j, 0)$ for σ^- and $(1, -j, 0)$ for σ^+ polarization, respectively. The far-field Poynting vector is decomposed into left-handed ($\mathbf{p}_{\text{rad}}^- = |\mathbf{E}_\theta - i\mathbf{E}_\phi|^2/4Z_0$) and right-handed ($\mathbf{p}_{\text{rad}}^+ = |\mathbf{E}_\theta + i\mathbf{E}_\phi|^2/4Z_0$) components, where Z_0 represents the free-space impedance and $\mathbf{E}_\theta, \mathbf{E}_\phi$ are the spherical field components in the far field. The circularly polarized radiative LDOS is calculated by summing contributions from both dipoles: left-handed radiative LDOS from the superposition of P_{rad}^-/P_0 from σ^- and σ^+ sources; right-handed radiative LDOS from the superposition of $P_{\text{rad}}^{+,-}/P_0$ from both sources. Here $P_{\text{rad}}^{+,-} = \int \mathbf{p}_{\text{rad}}^{+,-} \cdot d\mathbf{S}$ is the chiral far-field emission power, and P_0 is the free-space dipole radiation power. We should note that the quantum efficiencies do not change dramatically, such that the enhancement of the radiative decay rate can present the enhancement of the total decay rate. So we can deduce the decay rate of excitons in chiral nanocavities by calculating the radiative LDOS.

III. RESULTS AND DISCUSSION

A. Near-unity valley polarization in MoX_2

To calculate the valley polarization of monolayers in nanocavities, we could estimate the unknowns in the Eqs. (1) and (3) using experimental results. For bare monolayer MoS_2 without nanocavities, the typical valley polarization with moderate quality at room temperature is 0.05 [4]. γ_b^0 is the decay rate of bright excitons in bare monolayer MoS_2 , and γ_s the intervalley scattering rate. So, we can obtain the relation $2\gamma_s/\gamma_b^0 = 19$ according to Eq. (10). When the monolayer MoS_2 is coupled to nanocavities, we should notice that γ_s is an intrinsic property related to the temperature that is assumed to remain unchanged when modifying the photonic environment with nanocavities. Furthermore, nanocavities can enhance the decay rate of excitons due to the Purcell effect and the enhancement factor is $F_b = \gamma_b/\gamma_b^0$. Consequently, the nanocavity-enhanced valley polarization of bright excitons in MoS_2 P_b can be calculated as $P_b = \frac{1}{1+2\gamma_s/\gamma_b} = \frac{1}{1+19/F_b}$. Therefore, we can obtain the valley polarization only after we simulate the Purcell enhancement factor $F_b = \gamma_b/\gamma_b^0$.

The enhancements of the in-plane and out-of-plane LDOS, i.e., ρ_{in}/ρ_0 and ρ_{out}/ρ_0 , are directly proportional to the enhancement of the decay rates, as expressed by the equations $\frac{\rho_{\text{in}}}{\rho_0} = \frac{\gamma_b}{\gamma_b^0}$ and $\frac{\rho_{\text{out}}}{\rho_0} = \frac{\gamma_d}{\gamma_d^0}$. By simulating the LDOS in the gap region, we can determine the enhancement of valley polarization facilitated by the nanocavity according to the Eqs. (1) and (3). The simulated in-plane LDOS enhancement (at 675 nm) is shown in Fig. 2(a). We should note that the dark

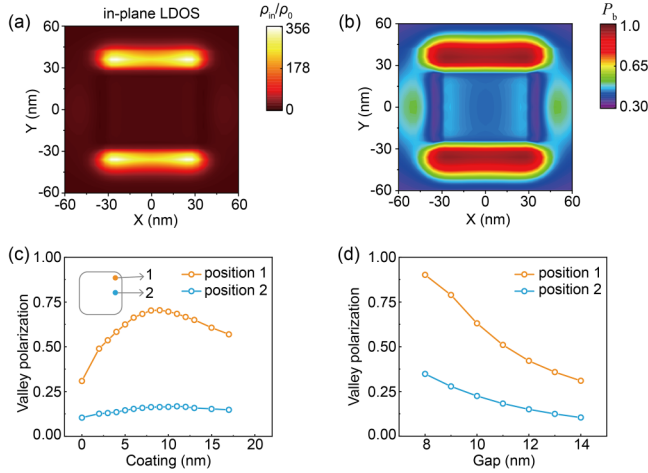


FIG. 2. (a) The simulated mapping of in-plane LDOS enhancement (at 675 nm). (b) The calculated mapping of valley polarization. (c) and (d) are the dependance of valley polarization in positions 1 and 2 against the coating thickness and gap thickness, respectively.

and bright excitons will have slight energy splitting due to the lifting degenerate of spins in conductive bands [2]. To simplify, we calculate the out-of-plane and in-plane LDOS at the same wavelength because the energy splitting only slightly influences our results. Then, the nanocavity-enhanced valley polarization of bright excitons in MoS₂ P_b can be calculated according to the Purcell enhancement of the bright excitons. (details are shown in the SM Sec. 1) Therefore, the mapping of the valley polarization is shown in Fig. 2(d), where we can find that the maximum of the valley polarization is nearly unity (up to 0.95), which is enhanced by 19 times compared to the bare MoS₂ whose polarization is 0.05.

Furthermore, the valley polarization of MoS₂ can be tuned by engineering the LDOS through geometric modifications, such as varying the gap thickness and the coating thickness. (details are shown in the SM Secs. 2 and 3) As shown in Figs. 2(e) and 2(f), we calculate the valley polarization at two representative positions within the nanocavity (denoted as “1” and “2”) by adjusting the Al₂O₃ coating thickness and the gap thickness, respectively. Figure 2(e) reveals that the valley polarization initially increases and then decreases with increasing Al₂O₃ coating thickness with a fixed gap thickness at 14 nm. A maximum valley polarization of 0.70 is achieved when the nanocavity plasmon is resonant with the exciton transition under an 8 nm Al₂O₃ coating. Additionally, the valley polarization and its tunability are significantly higher near the corner of the nanocube (position 1) compared to the center of the nanocube edge (position 2). This is attributed to the strong localization of the nanocavity mode near the nanocube corners, where LDOS enhancement is maximized. The dependance of valley polarization against varying gap thickness but without Al₂O₃ coating are illustrated in Fig. 2(f). It shows that increasing the gap thickness from 8 to 14 nm leads to a reduction in valley polarization from 0.90 to 0.31 at position 1 and from 0.35 to 0.10 at position 2. This trend is consistent with the understanding that a smaller gap results in stronger confinement of the nanocavity mode, thereby producing higher LDOS and enhanced valley polarization.

B. Reverse the valley populations for dark excitons in WX₂

Likewise, we can investigate the manipulation of valley polarization in monolayer WX₂ through the engineered LDOS in NCOM nanocavity. The gap layer is modified from the previous 8 nm [Figs. 2(b) and 2(c)] to 12 nm to shift the plasmon resonance to 620 nm, corresponding to the bright excitons in WS₂. We should note that increasing the gap layer results in a significant decrease in LDOS compared to the previous configuration, and this can be attributed to the impact of reduced local field enhancement. The simulated in-plane and out-of-plane LDOS at 620 nm are illustrated in Figs. 3(a) and 3(b), respectively. The maximum out-of-plane LDOS is enhanced by a factor of 2580 times, which is much higher than the in-plane LDOS. This indicates that the NCOM nanocavity is a promising structure to brighten the dark excitons with the out-of-plane transition dipole moment.

To calculate the valley polarization of WX₂ monolayers according to Eq. (3), we need to make clear the value of parameters including γ_s/Γ and γ_s/γ_d . The intervalley depolarization process (spin-conserved) is significantly larger than the intravalley one (spin-flip), which reads $\gamma_{inter} \gg \gamma_{intra}$ [25,40]. This is so o we can have a simplification $\frac{\gamma_{intra} - \gamma_{inter}}{\gamma_{intra} + \gamma_{inter}} \approx -1$. Furthermore, the Boltzmann distribution requires that the monolayer WX₂ with 30 meV bright-dark splitting follows the following relation at room temperature ($T = 300$ K) [24]

$$\frac{n_d^K + n_d^{-K}}{n_b^K + n_b^{-K}} = \frac{\gamma_{intra} + \gamma_{inter}}{\gamma_d} = \frac{1}{\exp(-\Delta/k_B T)} \approx 3. \quad (4)$$

Based on these two relations, the valley polarization for monolayer WX₂ can be simplified to

$$P_b = \frac{1}{1 + \frac{2\gamma_s}{\gamma_b} + 3\gamma_d}, \quad P_d = \frac{-P_b}{1 + \frac{2\gamma_s}{\gamma_d}}. \quad (5)$$

Let's take WS₂ as an example. The valley polarization for bright excitons is normally less than 0.05 according to the experimental results, and the decay lifetime of dark excitons is more than 100 times larger than that of bright excitons [41]. We can estimate the decay rate relationship $\gamma_s \approx 10\gamma_b^0$ and $\gamma_b^0 \approx 100\gamma_d^0$ where γ_b^0 and γ_d^0 represent the decay rate of bright and dark excitons in bare monolayer WS₂, meanwhile, the intervalley scattering rate γ_s remains unchanged within nanocavities. By inserting these relations into the equations above, we can calculate the valley polarization of both bright and dark excitons as $P_b = \frac{1}{1+20/(F_b+0.03F_d)}$ and $P_d = \frac{-P_b}{1+2000/F_d}$ where $F_b = \gamma_b/\gamma_b^0$ and $F_d = \gamma_d/\gamma_d^0$ are the Purcell enhancement of bright and dark excitons, and they are simulated as shown in the LDOS results in Figs. 3(a) and 3(b), respectively.

Figure 3(c) shows the mapping of the nanocavity-enhanced valley polarization for bright excitons, significantly surpassing the bare monolayer WS₂. Figure 3(d) displays the nanocavity-enhanced valley polarization for dark excitons, revealing a negative valley polarization of up to -0.47 . This reversal sign suggests a change in the valley selection rule for dark excitons in WS₂. The underlying mechanism is that electrons in the bright state formatted in one valley can be scattered to the dark state in another valley with spin conservation [25]. The ultraslow decay process of the dark states

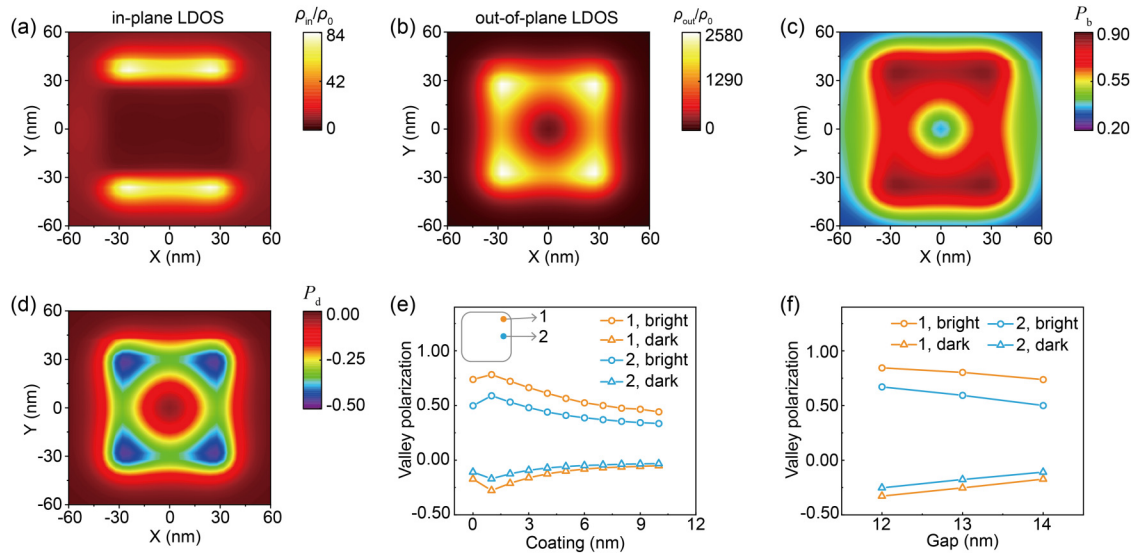


FIG. 3. (a) and (b) are the simulated mapping of LDOS enhancement (at 620 nm) in and out of the plane, respectively. The calculated mapping of valley polarization for (c) bright and (d) dark excitons. (e) and (f) are the dependance of valley polarization in positions 1 and 2 against the coating thickness and gap thickness, respectively.

causes the population to be accumulated in the valley opposite to the excitation, leading to the inversion of valley population inversion and a negative degree of valley polarization.

Furthermore, we systematically varied both the gap thickness and coating thickness of the NCOM nanocavities to modulate valley polarization in monolayer WS_2 for both bright and dark excitons. As illustrated in Figs. 3(e) and 3(f), valley polarization was calculated at two distinct positions: near the nanocube corner (designated as position 1) and at its center (position 2). At the corner region (position 1), the valley polarization of bright excitons demonstrates a decrease from 0.78 to 0.44 as the coating thickness increases from 0 to 10 nm, while dark excitons exhibit a corresponding decrease, but with a negative sign. Meanwhile, at the central region (position 2), valley polarization of bright excitons is controlled from 0.53 to 0.33, with dark excitons showing a moderate reducing but with a negative sign. Notably, gap thickness emerges as another critical parameter governing valley polarization. Enhanced gap thickness reduces field confinement effects, leading to decreased valley polarization. Specifically, corner-positioned bright excitons display a slightly valley polarization decreasing from 0.84 to 0.74 with increasing gap thickness, while dark excitons exhibit a reducing but with a negative sign [Fig. 3(f)]. A parallel trend, though less pronounced in magnitude, is observed at the nanocube center (position 2).

C. Circularly polarized emission coupled with chiral nanocavities

Integrating monolayer TMDs into chiral nanocavities presents a highly promising platform for creating tunable, high-performance chiral light sources [20]. This geometry leverages the intrinsic valley selection rule of the monolayer TMDs as chiral emission sources and the cavity's ability to strongly enhance light-matter interaction via the chiral Purcell effect, selectively boosting emission of one circular

polarization over the other. Next, we further investigate whether the hybrid system constructed by embedding monolayer MoS_2 into chiral nanocavities can build up tunable and efficient chiral emission sources. Since the excitons in K and $-K$ valleys can only couple with specific circularly polarized light, using a chiral nanostructure may separately modulate the decay rate in different valleys [18]. If the edge lengths on the x and y directions are different, i.e., the nanocubes have nonequal edge lengths in the xy -plane, the $\sigma+$ and $\sigma-$ LDOS will distribute along either diagonal of the rectangular cube due to the extrinsic chirality [as shown in Figs. 4(a) and 4(b)] [18,31,42]. Though this kind of rectangular cube is intrinsically achiral, the dipole excitation in such system will

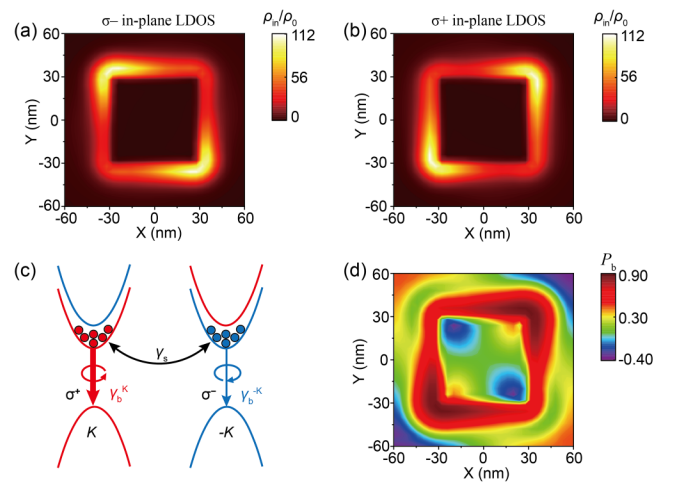


FIG. 4. (a) and (b) are the simulated mapping of left and right circularly polarized LDOS enhancements (at 675 nm) in plane, respectively. (c) The energy band sketch of monolayer MoS_2 coupled with a chiral nanocavity. (d) The calculated mapping of valley polarization for bright excitons in monolayer MoS_2 within the chiral nanocavity.

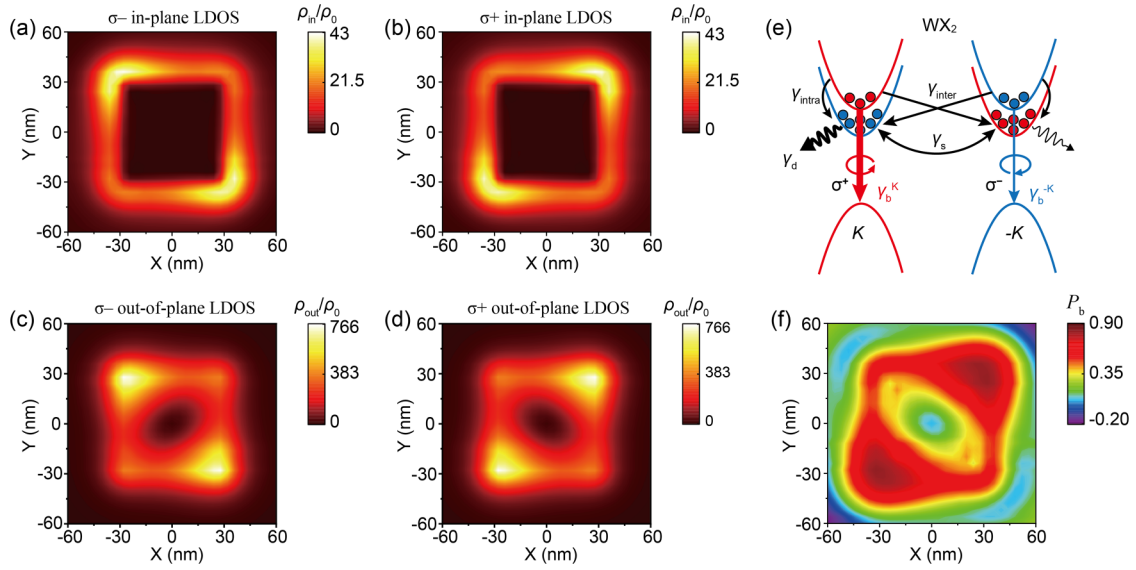


FIG. 5. (a) and (b) are the simulated mapping of left and right circularly polarized LDOS enhancements (at 620 nm) in plane, respectively. (c) and (d) are the simulated mapping of left and right circularly polarized LDOS enhancements (at 620 nm) out of plane, respectively. (e) The energy band sketch of monolayer WS₂ coupled with chiral nanocavity. (f) The calculated mapping of valley polarization for bright excitons in monolayer WS₂ within the chiral nanocavity.

break the symmetry and arouse extrinsic chirality and makes the overall system chiral [18]. Hereafter, we call this extrinsic chiral nanocavity as chiral cavity for simplification. The gap layer is 8 nm and the size of the nanocube is $80 \times 78 \times 80$ nm to make sure that the plasmon resonances of the nanocavity is near resonant with the excitons in monolayer MoS₂. Due to the unequal edge length in xy -plane of the cube, the distribution of $\sigma+$ and $\sigma-$ radiation LDOS in Figs. 4(a) and 4(b) exhibits local chirality features.

For the hybrid structures constructed by a chiral nanocavity and monolayer MoS₂, the degeneration of the $\sigma+$ and $\sigma-$ LDOS will modify the valley polarization [as shown in Fig. 4(c)]. The valley polarization of bright excitons can be represented by [20]

$$P_b = \frac{\gamma_s \gamma_b^K + \gamma_b^K \gamma_b^{-K} - \gamma_s \gamma_b^{-K}}{\gamma_s \gamma_b^K + \gamma_b^K \gamma_b^{-K} + \gamma_s \gamma_b^{-K}} = \frac{\tau_s + \tau^{-K} - \tau^K}{\tau_s + \tau^{-K} + \tau^K}, \quad (6)$$

γ_b^K and γ_b^{-K} stand for the decay rate of bright excitons in K and $-K$ valleys, respectively. τ_s represents the lifetime of intervalley scattering. τ^K and τ^{-K} are the lifetime of the excitons' decay in the K and $-K$ valleys, respectively. Figure 4(d) shows the distribution of the valley polarization from -0.36 to 0.87 , exhibiting the distribution from negative to positive in the real space within a single nanocavity. This demonstrates that chiral nanocavities can spatially separate the valley-polarized excitons in K and $-K$ valleys at nanoscale, indicating a significant future for on-chip information encoding and logical nanophotonic circuits.

Then we turn to the valley polarization when monolayer WS₂ is coupled with chiral nanocavity. The gap is set to be 12 nm to make sure that the nanocavity mode is resonant at 620 nm. The simulated chiral LDOS (at 620 nm) is shown in Figs. 5(a)–5(d). Among them, Figs. 5(a)–5(c) show the left and right circularly polarized LDOS in plane, respectively. The degenerated chiral LDOS is distributed on either diagonal

of the rectangular nanocube. In addition, the chiral LDOS out of plane exhibits a similar distribution as shown in Figs. 5(b) and 5(d). For the hybrid structures constructed by a chiral nanocavity and monolayer WS₂, the degeneration of the $\sigma+$ and $\sigma-$ LDOS will modify the valley polarization [as shown in Fig. 5(e)]. The rate equations, as illustrated in Eq. (2) need to be modified, and then we can get the valley polarization of bright excitons in WS₂ (details are shown in the SM Sec. 4)

$$P_b = \frac{\gamma_b^K (\gamma_{intra} + \gamma_{inter}) + \gamma_s \gamma_b^K + \gamma_b^K \gamma_b^{-K} - \gamma_s \gamma_b^{-K}}{\gamma_b^K (\gamma_{intra} + \gamma_{inter}) + \gamma_s \gamma_b^K + \gamma_b^K \gamma_b^{-K} + \gamma_s \gamma_b^{-K}}. \quad (7)$$

Therefore, we can calculate the valley polarization of bright excitons as shown in Fig. 5(f). The valley polarization can be modified by the chiral nanocavity from -0.18 to 0.83 , meanwhile exhibiting the spatial separation of valley-polarized excitons in K and $-K$ valleys.

The separation of valley-polarized free carriers or excitons serves as fundamental conditions to construct valleytronic devices. Some earlier research achieved the valley separation based on the unidirectional SPPs propagation on metasurface [43–45]. As shown in Figs. 4 and 5, we demonstrate that chiral nanocavities are ideal platforms to spatially separate the valley-polarized excitons. Owing to the huge local field enhancements, chiral nanocavities we construct can simultaneously achieve huge valley polarization and spatial valley separation. We should note that we only investigated the manipulation of valley polarization in the near field of nanocavities. However, the degree of circular polarization of photons will be influenced by the spin-orbit coupling when the light is coupled outside to the far-field through the nanocavity plasmons [46].

IV. CONCLUSION

In summary, we systematically investigated how to manipulate the valley polarization of both bright and dark excitons

in monolayer TMDs by engineering the photonics LDOS with plasmonic nanocavities. We came up with a phenomenological model to describe the valley depolarization process based on the rate equations for monolayer TMDs coupled with nanocavities. Combined with the simulation, we revealed that the near-unity valley polarization of bright excitons and reversed valley populations of dark excitons are realized owing to the huge LDOS enhancement in nanocavities. Furthermore, by coupling with a chiral LDOS-degenerated nanocavity, the bright excitons exhibit the distribution of valley polarization from negative to positive in real space. Therefore, our results can give guidance for future research on manipulating valley polarized response with nanocavities.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (Grants No. 12204315, No. 12104317, and No. 62475071), Shenzhen Science and Technology Program (No. ZDSYS20220527171201003).

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

- [1] D. Xiao, G. B. Liu, W. Feng, X. Xu, and W. Yao, Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides, *Phys. Rev. Lett.* **108**, 196802 (2012).
- [2] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, *Colloquium* : Excitons in atomically thin transition metal dichalcogenides, *Rev. Mod. Phys.* **90**, 021001 (2018).
- [3] K. F. Mak, K. He, J. Shan, and T. F. Heinz, Control of valley polarization in monolayer MoS₂ by optical helicity, *Nat. Nanotechnol.* **7**, 494 (2012).
- [4] H. Zeng, J. Dai, W. Yao, D. Xiao, and X. Cui, Valley polarization in MoS₂ monolayers by optical pumping, *Nat. Nanotechnol.* **7**, 490 (2012).
- [5] T. Cao, G. Wang, W. P. Han, H. Q. Ye, C. R. Zhu, J. R. Shi, Q. Niu, P. H. Tan, E. Wang, B. L. Liu, *et al.*, Valley-selective circular dichroism of monolayer molybdenum disulphide, *Nat. Commun.* **3**, 887 (2012).
- [6] S. H. Gong, F. Alpeggiani, B. Sciacca, E. C. Garnett, and L. Kuipers, Nanoscale chiral valley-photon interface through optical spin-orbit coupling, *Science* **359**, 443 (2018).
- [7] Z. Li, X.-Y. Zhang, R. Ma, T. Fu, Y. Zeng, C. Hu, Y. Cheng, C. Wang, Y. Wang, Y. Feng, *et al.*, Versatile optical manipulation of trions, dark excitons and biexcitons through contrasting exciton-photon coupling, *Light Sci. Appl.* **12**, 295 (2023).
- [8] L. Zheng, Z. Dang, D. Ding, Z. Liu, Y. Dai, J. Lu, and Z. Fang, Electron-induced chirality-selective routing of valley photons via metallic nanostructure, *Adv. Mater.* **35**, 2204908 (2023).
- [9] G. Kioseoglou, A. T. Hanbicki, M. Currie, A. L. Friedman, D. Gunlycke, and B. T. Jonker, Valley polarization and intervalley scattering in monolayer MoS₂, *Appl. Phys. Lett.* **101**, 221907 (2012).
- [10] G. Aivazian, Z. R. Gong, A. M. Jones, R. L. Chu, J. Yan, D. G. Mandrus, C. W. Zhang, D. Cobden, W. Yao, and X. Xu, Magnetic control of valley pseudospin in monolayer WSe₂, *Nat. Phys.* **11**, 148 (2015).
- [11] A. Srivastava, M. Sidler, A. V. Allain, D. S. Lembke, A. Kis, and A. Imamoglu, Valley Zeeman effect in elementary optical excitations of monolayer WSe₂, *Nat. Phys.* **11**, 141 (2015).
- [12] R. Schmidt, A. Arora, G. Plechinger, P. Nagler, A. Granados del Águila, M. V. Ballottin, P. C. M. Christianen, S. Michaelis de Vasconcellos, C. Schüller, T. Korn, *et al.*, Magnetic-field-induced rotation of polarized light emission from monolayer WS₂, *Phys. Rev. Lett.* **117**, 077402 (2016).
- [13] T. Smoleński, M. Goryca, M. Koperski, C. Faugeras, T. Kazimierczuk, A. Bogucki, K. Nogajewski, P. Kossacki, and M. Potemski, Tuning valley polarization in a WSe₂ monolayer with a tiny magnetic field, *Phys. Rev. X* **6**, 021024 (2016).
- [14] E. J. Sie, J. W. McIver, Y.-H. Lee, L. Fu, J. Kong, and N. Gedik, Valley-selective optical Stark effect in monolayer WS₂, *Nat. Mater.* **14**, 290 (2014).
- [15] T. LaMountain, H. Bergeron, I. Balla, T. K. Stanev, M. C. Hersam, and N. P. Stern, Valley-selective optical Stark effect probed by Kerr rotation, *Phys. Rev. B* **97**, 045307 (2018).
- [16] F. Liu, J. Zhou, C. Zhu, and Z. Liu, Electric field effect in two-dimensional transition metal dichalcogenides, *Adv. Funct. Mater.* **27**, 1602404 (2016).
- [17] K. Shinokita, X. F. Wang, Y. Miyauchi, K. Watanabe, T. Taniguchi, and K. Matsuda, Continuous control and enhancement of excitonic valley polarization in monolayer WSe₂ by electrostatic doping, *Adv. Funct. Mater.* **29**, 1900260 (2019).
- [18] J. Sun, H. Hu, D. Pan, S. Zhang, and H. Xu, Selectively depopulating valley-polarized excitons in monolayer MoS₂ by local chirality in single plasmonic nanocavity, *Nano Lett.* **20**, 4953 (2020).
- [19] S. W. Zhao, X. X. Li, B. J. Dong, H. D. Wang, H. W. Wang, Y. P. Zhang, Z. Han, and H. Zhang, Valley manipulation in monolayer transition metal dichalcogenides and their hybrid systems: Status and challenges, *Rep. Prog. Phys.* **84**, 026401 (2021).
- [20] Z. Wu, J. Li, X. Zhang, J. M. Redwing, and Y. Zheng, Room-temperature active modulation of valley dynamics in a monolayer semiconductor through chiral Purcell effects, *Adv. Mater.* **31**, 1904132 (2019).
- [21] Z. W. Li, C. X. Liu, X. Rong, Y. Luo, H. T. Cheng, L. H. Zheng, F. Lin, B. Shen, Y. J. Gong, S. Zhang, *et al.*, Tailoring MoS₂ valley-polarized photoluminescence with super chiral near-field, *Adv. Mater.* **30**, 1801908 (2018).
- [22] S. Kim, Y. C. Lim, R. M. Kim, J. E. Fröch, T. N. Tran, K. T. Nam, and I. Aharonovich, A single chiral nanoparticle induced valley polarization enhancement, *Small* **16**, 2003005 (2020).
- [23] T. Wen, W. Zhang, S. Liu, A. Hu, J. Zhao, Y. Ye, Y. Chen, C. W. Qiu, Q. Gong, and G. Lu, Steering valley-polarized emission of monolayer MoS₂ sandwiched in plasmonic antennas, *Sci. Adv.* **6**, eaao0019 (2020).
- [24] X. X. Zhang, Y. You, S. Y. F. Zhao, and T. F. Heinz, Experimental evidence for dark excitons in monolayer WSe₂, *Phys. Rev. Lett.* **115**, 257403 (2015).

- [25] X. X. Zhang, T. Cao, Z. Lu, Y. C. Lin, F. Zhang, Y. Wang, Z. Li, J. C. Hone, J. A. Robinson, D. Smirnov, *et al.*, Magnetic brightening and control of dark excitons in monolayer WSe₂, *Nat. Nanotechnol.* **12**, 883 (2017).
- [26] G. Wang, C. Robert, M. M. Glazov, F. Cadiz, E. Courtade, T. Amand, D. Lagarde, T. Taniguchi, K. Watanabe, B. Urbaszek, *et al.*, In-plane propagation of light in transition metal dichalcogenide monolayers: Optical selection rules, *Phys. Rev. Lett.* **119**, 047401 (2017).
- [27] Y. Zhou, G. Scuri, D. S. Wild, A. A. High, A. Dibos, L. A. Jauregui, C. Shu, K. De Greve, K. Pistunova, A. Y. Joe, *et al.*, Probing dark excitons in atomically thin semiconductors via near-field coupling to surface plasmon polaritons, *Nat. Nanotechnol.* **12**, 856 (2017).
- [28] T. W. Lo, X. Chen, Z. Zhang, Q. Zhang, C. W. Leung, A. V. Zayats, and D. Lei, Plasmonic nanocavity induced coupling and boost of dark excitons in monolayer WSe₂ at room temperature, *Nano Lett.* **22**, 1915 (2022).
- [29] J. Ye, Y. Li, T. Yan, G. Zhai, and X. Zhang, Ultrafast dynamics of spin generation and relaxation in layered WSe₂, *J. Phys. Chem. Lett.* **10**, 2963 (2019).
- [30] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/1355-mgqs> for methods, LDOS against coating thickness in nanocavities, LDOS against gap thickness in nanocavities, and rate equations in chiral nanocavities, which includes Refs. [31–34].
- [31] J. Yang, H. T. Hu, Q. F. Zhang, S. Zu, W. Chen, and H. X. Xu, Manipulating chiral photon generation from plasmonic nanocavity-emitter hybrid systems: From weak to strong coupling, *Nanophotonics* **13**, 357 (2024).
- [32] T. Yu and M. W. Wu, Valley depolarization due to intervalley and intravalley electron-hole exchange interactions in monolayer MoS₂, *Phys. Rev. B* **89**, 205303 (2014).
- [33] T. B. Hoang, G. M. Akselrod, C. Argyropoulos, J. Huang, D. R. Smith, and M. H. Mikkelsen, Ultrafast spontaneous emission source using plasmonic nanoantennas, *Nat. Commun.* **6**, 7788 (2015).
- [34] K. D. Park, T. Jiang, G. Clark, X. Xu, and M. B. Raschke, Radiative control of dark excitons at room temperature by nano-optical antenna-tip Purcell effect, *Nat. Nanotechnol.* **13**, 59 (2018).
- [35] J. B. Lassiter, F. McGuire, J. J. Mock, C. Ciraci, R. T. Hill, B. J. Wiley, A. Chilkoti, and D. R. Smith, Plasmonic waveguide modes of film-coupled metallic nanocubes, *Nano Lett.* **13**, 5866 (2013).
- [36] J. Sun, H. Hu, D. Zheng, D. Zhang, Q. Deng, S. Zhang, and H. Xu, Light-emitting plexciton: Exploiting plasmon-exciton interaction in the intermediate coupling regime, *ACS Nano* **12**, 10393 (2018).
- [37] E. M. Purcell, Spontaneous emission probabilities at radio frequencies, *Phys. Rev.* **69**, 681 (1946).
- [38] P. Anger, P. Bharadwaj, and L. Novotny, Enhancement and quenching of single-molecule fluorescence, *Phys. Rev. Lett.* **96**, 113002 (2006).
- [39] P. B. Johnson and R. W. Christy, Optical constants of the noble metals, *Phys. Rev. B* **6**, 4370 (1972).
- [40] M. He, P. Rivera, D. Van Tuan, N. P. Wilson, M. Yang, T. Taniguchi, K. Watanabe, J. Yan, D. G. Mandrus, H. Yu, *et al.*, Valley phonons and exciton complexes in a monolayer semiconductor, *Nat. Commun.* **11**, 618 (2020).
- [41] A. O. Slobodeniuk and D. M. Basko, Spin-flip processes and radiative decay of dark intravalley excitons in transition metal dichalcogenide monolayers, *2D Mater.* **3**, 035009 (2016).
- [42] H. Hu, W. Chen, X. Han, K. Wang, and P. Lu, Plasmonic nanobar-on-mirror antenna with giant local chirality: A new platform for ultrafast chiral single-photon emission, *Nanoscale* **14**, 2287 (2022).
- [43] L. Sun, C.-Y. Wang, A. Krasnok, J. Choi, J. Shi, J. S. Gomez-Diaz, A. Zepeda, S. Gwo, C.-K. Shih, A. Alù, *et al.*, Separation of valley excitons in a MoS₂ monolayer using a subwavelength asymmetric groove array, *Nat. Photon.* **13**, 180 (2019).
- [44] X. Wen, Y. Zhou, S. Chen, W. Yao, and D. Li, Room-temperature unidirectional routing of valley excitons of monolayer WSe₂ via plasmonic near-field interference in symmetric nano-slits, *Nanophotonics* **12**, 3529 (2023).
- [45] T. Chervy, S. Azzini, E. Lorchat, S. Wang, Y. Gorodetski, J. A. Hutchison, S. Berciaud, T. W. Ebbesen, and C. Genet, Room temperature chiral coupling of valley excitons with spin-momentum locked surface plasmons, *ACS Photonics* **5**, 1281 (2018).
- [46] D. Pan, H. Wei, L. Gao, and H. X. Xu, Strong spin-orbit interaction of light in plasmonic nanostructures and nanocircuits, *Phys. Rev. Lett.* **117**, 166803 (2016).