Control of light–valley interactions in 2D transition metal dichalcogenides with nanophotonic structures

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Electronic valley in two-dimensional transition-metal dichalcogenides (2D TMDCs) offers a new degree of freedom for information storage and processing. The valley pseudospin can be optically encoded by photons with specific helicity, enabling the construction of electronic information devices with both high performance and low power consumption. Robust detection, manipulation and transport of the valley pseudospins at room temperature are still challenging because of the short lifetime of valley-polarized carriers and excitons. Integrating 2D TMDCs with nanophotonic objects such as plasmonic nanostructures provides a competitive solution to address the challenge. The research in this field is of practical interest and can also present rich physics of light–matter interactions. In this minireview, recent progress on using nanophotonic strategies to enhance the valley polarization degree, especially at room temperature, is highlighted. Open questions, major challenges, and interesting future developments in manipulating the valley information in 2D semiconductors with the help of nanophotonic structures will also be discussed.

1. Introduction

The prosperity of modern information science and technology relies on the continued scaling in silicon-based complementary metal–oxide–semiconductor (CMOS) technologies. In such devices, electron charge serves as the information carrier. As the minimum feature size goes down to the sub-5 nm regime, the continued scaling of integrated-circuit technologies approaches the quantum mechanical limit and faces great challenges in cost, reliability, and power consumption. To meet the demands of further development of the semiconductor industry, research has been conducted on exploiting novel low-dimensional materials and new degrees of freedom (DoFs) of electrons. Besides charge, spin and valley are other DoFs of semiconductor electrons. In recent years, the discovery of two inequivalent valleys in two-dimensional (2D) materials that lack inversion symmetry, such as monolayer transition-metal dichalcogenides (TMDCs) and biased graphene bilayer, has attracted interest in the field of valleytronics, that is, exploiting the valley DoF for future electronics.

Valleys refer to the multiple degenerate energy extrema in the conduction or valence bands of a crystalline structure. In analogy to spin, a valley in a crystalline structure is also a binary DoF and could be regarded as valley pseudospin. Studies on the valley pseudospin of electrons have been performed in conventional material systems for years, including Si, AlAs quantum wells, diamond and bismuth. Manipulating the valley pseudospin in these materials is challenging because of the lack of valley-dependent physical quantities. In 2D semiconductors with hexagonal lattices, there are two energy-degenerate valleys at the corners of the first Brillouin zone, i.e. $K$ and $K'$ $(−K)$ points. When the spatial inversion symmetry of the lattice is broken, the electron orbital magnetic moment $m$ and the Berry curvature $Ω$ are nonzero and of opposite signs at the $K$ and $K'$ valleys, giving rise to a ‘valley’ index that can be detected independent of spin. The valley pseudospin in 2D materials was firstly demonstrated in graphene systems with a broken inversion symmetry, but it received much more interest when it comes to 2D TMDCs, which belong to semiconductors naturally with bandgaps in the range of visible light. The interband transition in monolayer TMDCs follows valley-contrast optical selection rules because of the broken spatial inversion symmetry. The 2D TMDCs also exhibit valley excitons...
with a large binding energy. Another interesting property of the monolayer TMDCs is that their spin index is locked with their valley index, which comes from the strong spin–orbit coupling of electrons. The electrons or holes have opposite spin orientations around $K$ and $K'$ points. Moreover, the opposite Berry curvatures and valley-contrasting optical selection rules combined with spin-valley locking offer more access to encode and manipulate the valley and spin DoFs by external fields. The valley addressability makes the 2D TMDCs promising for valleytronics that uses the momentum state of electrons, holes, or excitons for information processing.

Various techniques have been employed to address the valley pseudospin in TMDCs. For example, valley contrasting electron occupancy, i.e. valley polarization, in TMDCs can be introduced by spin injection or optical excitation with circularly polarized light. Besides the encoding methods, the valley information can be read out through the valley Hall effect or circularly polarized photoluminescence (PL) measurements. However, the valley contrast signals of single layer TMDCs are severely weakened by phonon-assisted intervalley scattering as the temperature increases and vanish at room temperature. To suppress the intervalley scattering, a low working temperature, resonant optical excitation and an out-of-plane magnetic field have been usually applied to achieve better valley contrast. So far, robust detection, manipulation and transport of the valley information at room temperature are still challenging.

Integrating 2D TMDCs with nanophotonic structures such as plasmonic nanostructures offers a competitive solution to address the challenge in constructing room-temperature valleytronic devices. Nanophotonic structures that support resonant interactions with light have been widely pursued for enhancing the coupling between photons and excitons in 2D TMDCs. In recent years, more and more efforts have been made to selectively couple light to certain valleys and spatially route the valley exciton emission through nanophotonic approaches. High valley contrast has been demonstrated at room temperature. Therefore, research in this field is very important for making high performance optoelectronic and valleytronic devices.

Several previous review articles have summarized the studies on various aspects of the interaction between nanophotonic structures and excitons in 2D TMDCs, including the modulation of photoluminescence, strong light–matter interaction, and chiral routing of valley-polarized excitons. These review articles provide an excellent foundation for our discussion of the very recent progress in manipulating the valley pseudospin in TMDCs with the help of nanophotonic structures in this review. We will start with an introduction of the valley pseudospin in 2D TMDCs and the depolarization process of valley carriers or excitons due to the intervalley scattering. This background knowledge is important for understanding the effects of plasmonic and other nanophotonic structures in modulating valley excitation. We will then highlight the recent experimental advances in using the nanophotonic structures, especially plasmonic structures, to control light–valley interactions in TMDCs. Finally, we will discuss the phenomena and physical processes that have not been understood clearly and provide perspectives on the important issues for future research.

2. Light–valley interactions in TMDCs

2.1 Valley pseudospin in 2D TMDCs

The most investigated 2D TMDCs have the chemical composition of $MX_2$, where $M$ represents the transition metal element Mo or W and $X$ represents the chalcogen element S or Se. The bulk TMDCs are layered materials where layers are linked by van der Waals interaction. Monolayer 2H-TMDCs have been intensively studied for valleytronics. They consist of a layer of transition metal atoms ($M$) between two layers of chalcogen atoms ($X$) in a trigonal prismatic structure, forming a quasi-2D hexagonal lattice (Fig. 1A). The corresponding first Brillouin zone is a hexagon with $K$ and $K'$ points at the corners. These two points are related to each other by time reversal symmetry. The TMDCs typically exhibit indirect-to-direct bandgap transition when the materials change from bulk to the monolayer. Benefiting from the direct optical band-gap, photoluminescence (PL) emission from monolayer structures is much stronger than that from bilayer and multilayer TMDCs.

The valley of energy–momentum dispersion can be seen at the $K$ ($K'$) point from a typical schematic band structure of the monolayer $MX_2$ (Fig. 1B). Because the spatial inversion symmetry in the monolayer $MX_2$ lattice breaks while the time-reversal symmetry still holds for all the electronic states, the electron orbital magnetic moment $m$ and the Berry curvature $\mathbf{\Omega}$ in the two degenerate yet inequivalent valleys ($K$ and $K'$) are nonzero and of opposite signs. In addition, the strong spin–orbit coupling of d orbital electrons of the transition metal leads to large energy splitting at the top of the TMDC valence band ($\sim$0.2 eV for MoX$_2$ and $\sim$0.4 eV for WX$_2$) (Fig. 1C). In contrast, the energy splitting in the conduction band is two orders of magnitudes smaller. The constraint of time-reversal symmetry requires that the spin splitting at $K$ and $K'$ valleys must be opposite. As a result, the combination of the strong spin–orbit interaction with a broken inversion symmetry results in the locking of the valley pseudospin and the real electron spin at $K$ and $K'$ points (Fig. 1C). The electrons or holes have opposite spin orientations around $K$ and $K'$ points. Such energy and spin splitting gives rise to two types of excitons, i.e. the low-energy A exciton and the high-energy B exciton, in the visible range, accounting for the two obvious peaks in the absorption spectra. The PL emission intensity of the B exciton is much weaker than that of the A exciton since most excitons will relax to the lower energy state through a fast intravalley scattering process.

The broken inversion symmetry in 2D TMDCs endows the interband transition with valley-contrasting optical selection rules. Similar to the cases in atoms, the optical transition selection rules in 2D TMDCs are determined by orbital mag-
Valley pseudospin in two-dimensional (2D) transition-metal dichalcogenides (TMDCs) and approaches to address the valley information. (A) Schematic showing the hexagonal crystal structure of a monolayer 2H-TMDC material. The red and blue arrows show the paths of valley carriers with opposite Berry curvatures ($\Omega$) driven by an in-plane electric field. A side view of the unit cell (top right) with $M$ representing the transition metal element Mo or W and $X$ representing the chalcogen element S or Se. The corresponding hexagonal Brillouin zone is shown at the bottom right. The energy–momentum dispersion is usually obtained along the $\Gamma$–$K$–$M$–$\Gamma$ line in the Brillouin zone. (B) Band structure of a monolayer $\text{MX}_2$. Remarkable energy splitting occurs at the valence-band maximum because of the strong spin–orbit coupling. The energy splitting at the conduction-band minimum is much smaller. Adapted from ref. 23 with permission from American Physical Society, 2012. (C) Optical selection rules for the A exciton at the two inequivalent valleys in a monolayer $\text{MX}_2$. The order of the conduction band splitting is reversed when the metal is changed. (D) Schematic of the circularly polarized photoluminescence (PL) measurement setup. 

Besides, the nonzero Berry curvature $\Omega$ acts as a magnetic field in momentum space in the effective quantum Hamiltonian. The Berry curvatures have opposite signs for the $K$ ($K'$) valley. Near the $K$ or $K'$ valley, the signs of $\Omega(k)$ for the valence band and the conduction band are also opposite. As a result, carriers (electrons and holes) at these two valleys possess anomalous velocities in opposite transverse directions under an in-plane electric field $E$ (Fig. 1A), leading to the valley Hall effect.

The valley-dependent physical quantities in TMDCs open the path for manipulating and controlling the valley pseudospin. The encoding of valley pseudospin has been achieved by spin injection via a diluted ferromagnetic semiconductor or by optical excitation through the optical selection rules. Such information could be further modulated using an out-of-plane magnetic field (the valley Zeeman effect) or electrical gating. The valley pseudospin can be read out by measuring the valley-dependent Hall voltage or observing the circular polarization of the PL emission. Fig. 1D shows the schematic of a polarization-resolved PL measurement setup, in which the intensities of the left- and right-handed components of the PL are measured when applying a circularly polarized excitation light.

2.2 Methods to improve the valley polarization

The valley polarization can be characterized by the degree of circular polarization of the PL, $P = [I(\sigma+) - I(\sigma-)]/[I(\sigma+) + I(\sigma-)]$. Here, $I(\sigma+)$ and $I(\sigma-)$ are the intensities of PL with $\sigma^+$ and $\sigma^-$ polarizations, respectively. Ideally, $P$ equals to 1 and the PL helicity follows that of the excitation light. However, the strong intervalley electron–hole exchange interaction leads to fast valley depolarization. Three characteristic time constants, the valley coherence time ($\tau_c$), the valley lifetime ($\tau_v$), and the exciton lifetime ($\tau_e$), are used to describe the depolarization process. The valley coherence time $\tau_c$ characterizes the lifetime of the coherent superposition of the $K$ and $K'$ excitons generated by a linearly polarized excitation. $\tau_c$ is found to be in the order of tens to hundreds of fs. The valley lifetime $\tau_v$ is the time carriers or excitons maintain their valley pseudospin. It is a few ps at low temperature and decreases dramatically at elevated temperatures. The radiative lifetime of excitons in TMDCs is about several ps at low temperature and a few ns at...
room temperature.\textsuperscript{62,63} Since the valley lifetime becomes much shorter than the exciton lifetime when temperature increases, the monolayer TMDCs have a poor degree of valley polarization (DVP) at room temperature.\textsuperscript{19,33} In addition, off-resonance excitation populates both valleys simultaneously, making the PL emission unpolarized. As a result, low temperature and resonant excitation are usually required to achieve better valley contrast in monolayer TMDCs.\textsuperscript{8,19,27}

In contrast to the monolayer structure, bilayer and multilayer TMDCs could have much higher DVP (\(P > 60\%\)) even at room temperature because of the coupling of spin, layer, and valley degrees of freedom.\textsuperscript{33,44,64} Interlayer excitons with a longer valley lifetime (tens of ns or even longer) in van der Waals heterostructures have been demonstrated to possess high and electrically tunable DVP (\(P > 30\%\)).\textsuperscript{55,65} The DVP can also be improved by introducing ternary monolayer TMDCs. The ternary monolayer Mo\((\text{S}_{1-x}\text{Se}_{x})_2\) with a designed S to Se atom ratio can modulate the intra- and inter-valley dynamics of excitons and reduce the valley-pseudospin mixing induced by the electron-hole exchange interaction through the thermal-mixing of bright-dark exciton wavefunctions and carrier screening. As a result, room temperature valley polarization up to \(\sim 50\%\) in such a structure has been achieved.\textsuperscript{66}

In addition to material engineering, integrating 2D TMDCs with optical cavities or nanophotonic structures is promising for further increasing the valley contrast and therefore promoting valley-polarized photonic and polaritonic devices working at room temperature. Various photonic effects, including chiral Purcell effects, strong coupling, chiral coupling with the spin–orbit interaction of light, and hot carrier injection, have been exploited for both enhanced valley polarization and spatial separation of valley exciton emissions. These nanophotonic strategies offer high flexibility for developing high-performance optoelectronic and valleytronic devices and will be discussed in detail in the next section.

3. Control of light–valley interactions with plasmonic and other nanophotonic structures

Nanophotonic structures can confine light to the nanoscale and significantly enhance the light–matter interaction.\textsuperscript{67} They can be designed to modulate the electromagnetic field distribution and tailor light propagation.\textsuperscript{68} The coupling between nanophotonic structures and valley pseudospin brings about rich physics and may lead to new breakthroughs in optoelectronic applications. In this section, we will discuss the use of plasmonic and other nanophotonic structures in enhancing the valley contrast.

3.1 Valley-polarized photoluminescence mediated by a plasmonic nearfield

The emission process of an emitter is influenced by the photonic local density of states (LDOS), which can be tailored by the plasmonic nearfield. Chiral plasmonic nanostructures have been employed to mediate the valley-polarized PL emission of TMDCs. Such structures, whose mirror images cannot be superimposed onto themselves, have been widely studied for enhancing the chiroptical response of molecules.\textsuperscript{69} They can provide large optical chirality, which is defined as \(C(r) = \frac{\mathbf{r}_0 \mathbf{E}(r) \times \mathbf{E}(r) + 1\mu_0 \mathbf{B}(r) \times \mathbf{B}(r)}{2. \mathbf{E}(r) \times \mathbf{B}(r)}\), where \(\mathbf{E}(r)\) and \(\mathbf{B}(r)\) are the electric and magnetic fields, respectively.\textsuperscript{70,71} The optical chirality enhancement is defined as \(C(r)/C_0\), with \(C_0\) the optical chirality value obtained for circularly polarized light in the absence of any plasmonic nanostructures. The optical chirality is an important quantity to quantify the enhancement of chiroptical effects. It is correlated to the excitation rate of a chiral molecule.\textsuperscript{70} Chiral plasmonic nanostructures can generate a superchiral nearfield with greater chiral asymmetry than that of circularly polarized light, giving rise to much higher enantioselectivity.\textsuperscript{70–72} Recently, the super-chiral nearfield of plasmonic nanostructures has also been applied to improve the PL valley polarization in monolayer TMDCs.\textsuperscript{39,40}

The chiral plasmonic nanostructures that exhibit enhanced chirality-dependent optical effects include asymmetric assembles of metal nanoparticles,\textsuperscript{41,73} chiral metamaterials,\textsuperscript{74,75} and chemically synthesized chiral nanocrystals.\textsuperscript{76,77} The chiral plasmonic nanostructures offer both large local optical field enhancement and chirality asymmetry. The plasmonic nearfield with a large local optical chirality enhancement selectively interacts with TMDC excitons with different valley indexes, giving rise to remarkably enhanced valley polarization. It is also important that the largely enhanced optical chirality occurs in the wavelength range matching the exciton energy of different TMDCs. For instance, a chiral plasmonic antenna was constructed by assembling two stacked gold nanorods to form a dimer with different intersection angles \(\text{via}\) atomic force microscopy (AFM) manipulation (Fig. 2A).\textsuperscript{41} The monolayer MoS\(_2\) was sandwiched inside the nanogap between the two nanorods to enable the strong interaction between the localized surface plasmon and excitons. The broken mirror symmetry in the structure leads to large optical chirality enhancement. The DVP of the hybrid at room temperature reached up to \(\sim 47\%\) under the excitation with matched polarization (Fig. 2B), much higher than that (\(\sim 18\%\)) of the pristine MoS\(_2\). The value of DVP decreased to \(11\%\) under the excitation by polarization of opposite handedness with the antenna structure.

In addition to the assembled nanostructures with chiral configuration, chiral metamaterials made by micro-fabrication processes have been used to enhance the valley-polarized emission. Such metamaterials were constructed from arrays of chiral unit cells. For example, a metamaterial with its chiral unit of four coupled Au nanorods arranged in C\(_4\) symmetry exhibited a distinct chiral optical response (Fig. 2C). To strengthen the interaction between the plasmonic chiral metamaterial and the valley excitons, the MoS\(_2\) monolayer was sandwiched between the chiral nanostructure array and an Au reflection layer.\textsuperscript{39} The absolute value of DVP in MoS\(_2\) was increased from \(25\% \pm 2\%\) to \(43\% \pm 2\%\) under \(\sigma–\) excitation at
When combined with the plasmonic metamaterial. In contrast, it decreased to 20% ± 2% under σ+ excitation. Moreover, valley-polarized emission could be observed even under linearly polarized excitation (Fig. 2D). Simulation results showed that the plasmonic metamaterial supports the super-chiral nearfield ($C/C_0 > 1$). The distribution of the super-chiral nearfield strongly depends on the excitation polarization (σ+ or σ−) (Fig. 2E). The modulation of DVP could be partially contributed by the far-field chiral response of the plasmonic structure, which is reflected by the circular dichroism (CD) in the extinction. In some experimental studies, the circular polarization asymmetry of the PL emission was found to be larger than that of the extinction CD, implying the coupling between valley exciton in 2D TMDCs and the plasmon resonance in the chiral metal nanostructure.78 The enhanced valley polarization of MoS2 integrated with chiral plasmonic nanostructures. (A and B) Hybrid structure of chiral plasmonic antenna and the MoS2 monolayer.41 The monolayer MoS2 was sandwiched in the nanogap between two Au nanorods stacked in a chiral configuration (A). Circularly polarized PL spectra of the left-handed antenna–MoS2 hybrid structure were measured under the excitation of σ−polarized light (B). Adapted from ref. 41 with permission from American Association for the Advancement of Science, 2020. (C–E) Hybrid structure of the plasmonic chiral metamaterial and MoS2 monolayer.39 The MoS2 monolayer was sandwiched between the chiral metamaterial composed of a unit of four coupled Au nanorods arranged in C4 symmetry and an Au film (C). σ+ (red) and σ− (blue) polarized PL spectra of the MoS2–metamaterial hybrid were measured under the excitation of a linearly polarized 633 nm laser (D). The super-chiral field around the four coupled Au nanorods at the PL emission wavelength was calculated (E). The valley exciton emission was modulated by the chiral nearfield (F). Reproduced from ref. 39 with permission from Wiley-VCH, 2018.

87 K when combined with the plasmonic metamaterial. In contrast, it decreased to 20% ± 2% under σ+ excitation. Moreover, valley-polarized emission could be observed even under linearly polarized excitation (Fig. 2D). Simulation results showed that the plasmonic metamaterial supports the super-chiral nearfield ($C/C_0 > 1$). The distribution of the super-chiral nearfield strongly depends on the excitation polarization (σ+ or σ−) (Fig. 2E). The modulation of DVP could be partially contributed by the far-field chiral response of the plasmonic structure, which is reflected by the circular dichroism (CD) in the extinction. In some experimental studies, the circular polarization asymmetry of the PL emission was found to be larger than that of the extinction CD, implying the coupling between valley exciton in 2D TMDCs and the plasmon resonance in the chiral metal nanostructure.78 The enhanced valley polarization of MoS2 integrated with chiral plasmonic nanostructures. As a result, the TMDC excitons in different valleys are generated at different rates because of the asymmetric optical nearfield (Fig. 2F). In addition, the spontaneous decay rate of excitons can be modulated by the increased LDOS via the Purcell effect. In intrinsic TMDCs, the DVP ($\propto 1/(1 + 2\Gamma_{ff}/\Gamma_0)$) is strongly affected by the competition between the intervalley scattering rate ($\Gamma_{ff}$) and the exciton decay rate ($\Gamma_0$).41,79 A larger radiative decay rate will help to maintain the valley helicity of the exciton emission. The valley helicity can be further amplified by the plasmonic chiral effect, for the decay rates of different valley excitons will be altered differently. To reflect the plasmonic chiral effect, a newly defined quantity called the chiral Purcell factor ($F_{ch}$) is used to describe the modified spontaneous decay rates of excitons at different valleys.80 The chiral Purcell factor is given by $F_{ch} = (1/4\pi^2)(\lambda_0/n)^3(Q/V_C)$ and has a similar form to the conventional Purcell factor $F_p = (3/4\pi^2)(\lambda_0/n)^3(Q/V)$. Herein, $\lambda_0$, $n$ and $Q$ are the resonant wavelength, the refractive index, and the quality factor of the cavity, respectively. $V$ and $V_C$ are the mode volume and chiral mode volume, respectively. Differently from $V_C$, $V_C$ is given by the ratio between the total energy of the resonator ($U$) and the maximum local optical chirality ($C$). $U$ is related to the local electric field ($E$). Large asymmetry in the decay rate of different valleys can be obtained by optimizing the nearfield and optical chirality distribution. As a result, the selective enhancements of both exciton generation and
emission in one specific valley contribute to significant valley-polarized PL.

Various chiral plasmonic nanostructures have been designed for enhancing the PL valley polarization of monolayer TMDCs other than MoS$_2$, such as MoSe$_2$, WS$_2$, and WSe$_2$. The employed chiral nanostructures include a metamaterial made up of arrays of asymmetric n-shaped Au nanoantenna,$^{81}$ colloidal chiral Au nanocrystals,$^{43}$ and the moiré chiral metamaterials formed by two periodic Au nanohole arrays stacked with an in-plane rotation angle.$^{40}$ The largest DVP measured from the monolayer TMDCs reached up to $\sim$50% at room temperature under the excitation of circularly polarized light.$^{41,43}$ With the modulation of the chiral plasmonic structures, the DVP of monolayer TMDCs is comparable to that from their bi- and multi-layer counterparts at the same temperature.

In addition to the chiral plasmonic nanostructures, it has been recently proposed that the achiral nanocube on the mirror (NCOM) structure (Fig. 3A) also possesses local optical chirality asymmetry when the mirror symmetry of the system is eliminated.$^{42}$ The NCOM structure exhibits degenerated radiative circularly polarized LDOS when the high-quality Ag nanocube is placed horizontally on an ultrasmooth Au film (Fig. 3A). However, when an imperfection is introduced by slightly tilting the nanocube, the mirror symmetry breaks and the NCOM becomes an intrinsic chiral structure (Fig. 3B). The left-handed ($\sigma^-$) components of PL emission from A excitons of the MoS$_2$ monolayer placed in the gap between the tilted cube and the Au mirror were found to be stronger than the right-handed ($\sigma^+$) components, for both $\sigma^+$ and $\sigma^-$ laser excitation (Fig. 3B and C). The PL valley polarization can be attributed to the chiral Purcell effect resulting from the uneven spatial distribution and lifted degeneracy of the $\sigma^-$ and $\sigma^+$ LDOS (Fig. 3D and E). The decay rate of the excitons in $K$ and $K'$ valleys can therefore be separately manipulated at different locations. The relatively high room temperature DVP (48.7%) obtained in such a structure provides new possibilities for addressing the valley-polarized emission beyond the conventional chiral nanostructures.

### 3.2 Strong coupling-induced excitation of valley-polarized excitons

The chiral Purcell effect we discussed in the previous section belongs to the weak coupling regime, where the interaction rate between the excitons and the photonic/polaritonic modes is slower than their average dissipation rates. When the interaction rate is higher than the average dissipation rates, one enters the strong coupling regime, forming the half-light, half-matter bosonic quasiparticles.$^{82}$ Benefiting from the large exciton binding energy, strong coupling could be observed in 2D TMDCs at room temperature, leading to the formation of exciton–polaritons.$^{58,83–91}$ Interestingly, the excitons–polaritons have been recently found to preserve the valley properties of their excitonic component, opening a new path for manipulating the valley pseudospin.$^{58,83–91}$

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**Fig. 3** Enhanced photoluminescence valley polarization by a tilted achiral Ag nanocube on the Au film.$^{42}$ (A) Schematic showing the MoS$_2$ monolayer inserted in the Ag nanocube–Au film nanocavity. The circularly polarized radiative LDOS acquired in the middle plane of the MoS$_2$ exhibits a non-chiral LDOS mapping. (B–E) Circularly polarized emission of valley-polarized excitons modified by the tilted achiral nanocube. (B) and (C) are circularly polarized PL of the MoS$_2$ monolayer under the $\sigma^+$ and $\sigma^-$ excitation, respectively. The schematic of the hybrid structure is shown in the inset of (B) and the nanocube has a tilted angle of $4^\circ$ with the Au film. (D) and (E) are the simulated $\sigma^-$ and $\sigma^+$ radiative LDOS of the Ag nanocube–Au film structure. The $\sigma^-$ LDOS had a maximum value at the bottom-right corner of the cube while the $\sigma^+$ LDOS was more uniform at the four corners. Reproduced from ref. 42 with permission from American Chemical Society, 2020.
Valley-polarized exciton–polaritons in the strong coupling regime have been firstly demonstrated by coupling the 2D TMDCs with optical microcavities having ultrahigh quality factors. The lifetimes of the photons inside the cavity are very long. For example, a TMDC-cavity system can be constructed by placing the TMDC monolayer between the distributed Bragg reflector (DBR) mirrors. The cavity resonance was designed to be close to the exciton energy. When detuning the cavity resonance, the characteristic anti-crossing behaviour with two pronounced modes associated with the lower polariton branch (LPB) and upper polariton branch (UPB) can be observed in the reflectivity or PL spectra, indicating the strong coupling between the cavity optical resonance and the TMDC excitons. Under circularly polarized excitation, both UPB and LPB in the PL spectra show a remarkable degree of circular polarization. The polarization can be maintained over a wide detuning and temperature range. It can survive at room temperature while the PL valley polarization of A excitons of the bare TMDC almost disappears (Fig. 4B). These results clearly show that the valley pseudospin of the exciton component is imprinted onto the hybrid polariton state, which can be addressed directly via their photonic component. To give a clear picture of the coupling, the two different exciton modes corresponding to the K and K’ valley can be understood to couple with the two cavity modes resulting from the left- and right-handed circular polarizations, respectively, forming two types of exciton–polaritons with opposite valley pseudospin (Fig. 4C). Such a hybrid system in the strong coupling regime features ultrafast energy transfer dynamics and offers an extra cavity channel for radiative decay. Importantly, the photonic part of the exciton–polaritons is barely affected by the intervalley scattering and has a relatively long valley lifetime.

Fig. 4 Valley-polarized exciton–polaritons in the strong coupling regime. (A–C) Valley-polarized exciton–polaritons in a DBR microcavity. In the strong coupling regime, excitons in the K valley couple to a certain cavity mode under the pumping of σ+ polarized light at an incident angle of θ, forming the exciton–polaritons (A). The degree of circular polarization of the PL emission from both bare MoS2 and microcavity-MoS2 hybrid deceases with temperature in different manners under the excitation of 1.938 eV photons (B). The dynamics of the two types of exciton–polaritons with opposite valley pseudospin was discussed (C). Reproduced from ref. 85 with permission from Nature Publishing Group, 2017. (D–I) Room-temperature valley-polarized exciton–polaritons in a plasmonic resonator supporting optical spin–orbit (OSO) interaction. The monolayer WSe2–plasmonic metasurface hybrid was employed (D). The metasurface consists of a plasmonic hole array with rectangular nanoapertures rotated stepwise along the x-axis by an angle of π/6. The two plasmon polariton modes with spin–momentum locked properties couple with the σ+ and σ– valley excitons separately, as the energy level diagram shows (E). The angle-resolved absorption spectrum of the hybrid under white light excitation was analysed in σ+ (F) and σ– (G) circular polarizations. The horizontally aligned dotted lines indicate the exciton energy. The dispersive dotted line shows the OSO mode of the plasmonic resonator. The differential PL dispersion spectrum for left and right circularly polarized excitations (H) and the differential angle-resolved reflection spectrum for left and right circularly polarized light (I) show the net flows of chiralitons with spin-determined momenta. Reproduced from ref. 90 with permission from American Chemical Society, 2018.
Large valley polarization can thus be retained. Moreover, the valley-decoherence-free decay path allows the detection of valley-coherent exciton–polaritons.\(^5,8,89\) The degree of valley coherence of the quasiparticles exceeded 90% when the exciton–polariton states were excited quasi-resonantly close to their ground state by a two-photon absorption process.\(^89\)

Different from the microcavity, the plasmonic cavities do not have ultrahigh quality factors but provide ultra-small mode volumes. They also facilitate a strong coupling with TMDCs.\(^92–94\) The valley-polarized exciton–polaritons have been verified in a plasmonic resonator (Fig. 4D).\(^90\) Similar to the physical picture given above when discussing the coupling between valley excitons and microcavity resonances, excitons from \(K\) and \(K'\) valleys can selectively couple to the plasmon modes with different polarization properties. In the plasmonic resonator supporting optical spin–orbit (OSO) interaction shown in Fig. 4D, two plasmon OSO modes are launched in counter-propagating directions when excited by light with opposite spins. The two plasmon polariton modes with spin–momentum locked properties couple with the \(\sigma^+\) and \(\sigma^-\) valley excitons separately, leading to remarkable energy splitting (\(\Delta E_0\)) (Fig. 4E). The valley-index-determined strong coupling was confirmed by the anti-crossing behaviour in the dispersion diagrams of the angle-resolved absorption spectrum (Fig. 4F and G) that was analysed in left and right circular polarizations. The spin-momentum locked polaritonic states resulting from the coupling between plasmon OSO modes and the valley excitons are referred to as chiralitons because of the chiral nature of the interaction. The net flows of chiralitons with spin-determined momenta were observed from both PL (Fig. 4H) and reflectivity spectra (Fig. 4I).

Except for the neutral exciton, the photonic modes have been designed to couple with trions and dark excitons as well.\(^84,86,88,95\) These charged and dark excitons allow a much longer valley lifetime than the bright neutral ones. They therefore can contribute to a higher valley contrast. However, the insufficient oscillator strengths of such excitons still hinder their strong coupling with the photonic states, especially at room temperature.\(^84,86,95\)

3.3 Routing valley exciton emissions

Photons carry spin angular momentum (associated with the polarization) and orbit angular momentum (associated with the phase). In recent years, the spin–orbit interaction (SOI) of light in the nanophotonic structure, where the light energy is confined in the subwavelength scales and its phase is tailored by the structured optical fields, has gained enormous interest.\(^68\) The strong coupling between the spin and orbit angular momentum of light gives rise to rich possibilities in spin-controlled intensity distribution and propagation paths of light. The SOI of light in nanophotonic structures has been performed in routing the valley exciton emissions.\(^44–47,96\) Routing the valley emissions at optical interfaces or in the free space enables the spatially separated transport and readout of valley emissions, which are very important for the on-chip integration of valleytronic devices. In this section, we will discuss the significant progress in routing valley emission via the structured optical fields and the spin–momentum locking effect of surface plasmon polaritons (SPPs). More details about the SOI of light can be found in ref. 68.

Structured materials have been widely used to modify the optical field distribution of light. Such a field distribution can be spin-dependent when the spin angular momentum of light is coupled with the coordinate frame rotations or tailored by anisotropic structures such as metamaterials.\(^68\) Correspondingly, the propagation path of light is helicity-dependent as a result of the far-field interference of different optical modes. 2D TMDCs integrated with the plasmonic nanoantenna have been demonstrated to show a valley-dependent unidirectional emission effect.\(^41,96\) As an example, an asymmetric Au nanostructure dimer constructed by two Au nanobars with a designed size and orientation was employed as an antenna to direct the emission of valley excitons (Fig. 5A).\(^96\) The two Au nanobars support electric dipole and quadrupole modes with engineered amplitudes and phases. Under the excitation of different circular-polarized light, the phase difference has a \(\pi/2\) to \(-\pi/2\) transformation. The scattering direction of the antenna therefore is spin locked. Since the different valleys in TMDCs can be addressed optically by light of different circular polarizations, the emissions from different valley excitons are predicted by calculation to be directed into different directions when the TMDC monolayer is placed in the vicinity of the plasmonic antenna (Fig. 5B).

Artificial anisotropic arrays in the 2D plane are also promising candidates that can modulate the phase gradient and thus the propagation of light.\(^46,47,96,97,98\) All-dielectric photonic crystal (PhC) slabs without in-plane inversion symmetry (C2 symmetry) were employed for routing valley emissions from a WS\(_4\) monolayer at room temperature (Fig. 5C).\(^47\) The broken symmetry in such PhC slabs gives rise to circularly polarized photonic Bloch modes, which couple with the valley-polarized emitted photons and lead to efficient separation of valley-polarized PL in the far-field (Fig. 5D). The angle- resolved PL experimental results show that the degree of valley polarization can reach up to 88%.

As we have discussed in the end of Section 3.2, plasmonic metamaterials with space-variant rectangular nanoholes are able to impose a spin-related geometric phase to light and separate the emission with opposite helicities.\(^99\) The formation of the spin-momentum locked SPP can be used to direct the valley-polarized emission into different directions (Fig. 4D–I).\(^90\) In addition, such types of plasmonic metamaterials are capable of enhancing and routing the nonlinear signals of second-harmonic generation (SHG) from the TMDCs besides the neutral A exciton emission (Fig. 5E–G).\(^46,90,98,100\) The plasmonic metamaterials mainly play two roles in the process. First, the plasmonic metamaterials provide large local electric nearfields to enhance the nonlinear process, leading to a high second-harmonic conversion efficiency of 10\(^6\).\(^98\) Second, the plasmonic metamaterials modify the phase gradient of the fundamental-frequency light. The gradient further pumps the coherent SHG process and steers the paths of the nonlinear
The metasurface consists of an array of rectangular nanoholes with the spatially varied rotation angle as shown in (E).

Routing the valley emission of TMDCs with structured optical fields. (A and B) The routing of σ+ and σ− PL by using the asymmetric Au nanobar dimer.96 The schematic of the system is shown in (A). The corresponding polar plots of the total radiated power in the far field were calculated (B). An obvious spatial separation of the σ+ and σ− PL can be seen. Reproduced from ref. 96 with permission from Beilstein Institute for the Advancement of Chemical Sciences, 2018. (C and D) Routing valley emissions from a WS2 monolayer on the photonic crystal slab without in-plane inversion symmetry.47 The schematic of the system is shown in (C). The σ+ (red) and σ− (blue) polarized emission light at 615 nm were measured at different emission angles (D). Reproduced from ref. 47 with permission from Nature Publishing Group, 2020. (E–G) Metamaterial-assisted routing of the valley polarized nonlinear signals.46 The metasurface consists of an array of rectangular nanoholes with the spatially varied rotation angle as shown in (E). The mechanism of the directional propagation of valley polarized SHG emissions from the TMDCs is schematically shown in (F). (G) The experimentally measured differential energy distribution and evolution of the SHG signal along the propagation direction (z, in μm). Reproduced from ref. 46 with permission from Nature Publishing Group, 2019.

chiral photons (Fig. 5G).46 The use of these plasmonic metamaterials is promising in addressing valley information with multiple excitonic degrees and has been demonstrated for chirality-selected second-harmonic holography.98

In contrast to the structured metal or dielectric metamaterial that can modulate the phase gradient and thus the propagation direction of polaritons, a much simpler platform employing the propagating modes in waveguide or on metal surface can also separate different circular polarizations with near-100% polarization directionality.101,102 Such a spin-direction locking effect is correlated to the transverse optical spin of evanescent waves.103 The transverse spin, unlike the conventional longitudinal spin of light, has a direction perpendicular to the propagating direction of light. It can be regarded as a product of the SOI of light. The transverse optical spin angular momentum (t-OSAM) is written as \( S_{t-OSAM} = (Re k \times Im k)/(Re k)^2 \), where \( k = k_x i + \alpha \) is the complex wavevector and \( \alpha \) is the decay constant. The direction of the t-OSAM is locked with the propagation direction of the evanescent wave. Benefiting from the characteristic spin-direction locking effect, routing the valley emission of TMDCs with coupled propagating SPP modes has attracted intense interest.44,45,104 For example, when a Ag nanowire is placed on a two dimensional WS\(_2\), the plasmonic eigenstate in the Ag nanowire couples to the valley-polarized exciton of WS\(_2\) with the same handedness of its local transverse optical spin. The SPP-exciton hybridized mode thus transports in a certain direction, indicating the valley-direction coupling (Fig. 6A).44 Simulation results clearly showed that the sign (handedness) of the transverse optical spin on either side of the nanowire is opposite, and will be reversed when the propagation direction changes (Fig. 6B). The handedness of the coupled emission showed the same dependence (Fig. 6C). Such phenomena were further verified by fluorescence imaging (Fig. 6D and E). It is noted that the directionality of the chiral coupling is determined not only by the helicity of the valley emission but also by the excitation/emission position. The measured directional coupling efficiency in such a system was \( \sim 40\% \) because of the finite DVP of WS\(_2\) and the experimental limitations in finite excitation spot size and background noise. By considering the above effects, the effective directional coupling efficiency was calculated to be \( \sim 90\% \), showing robust coupling between the valley pseudospin of WS\(_2\) and the propagation direction of the nanowire SPP. High-fidelity chiral coupling was further demonstrated for TMDCs placed on an array of subwavelength asymmetric grooves (Fig. 6F).45 By breaking the mirror symmetry, spin and direction were uniquely locked regardless of the excitation laser position, as demonstrated by the calculated electric field distribution (Fig. 6G). The spatial profile of the PL from the MoS\(_2\) monolayer on the asymmetric grooves showed that the spatial separation efficiency of emission photons with different handedness was close to 1
confirming the robust unidirectional transport of valley-polarized emissions.

### 3.4 Plasmon-enabled injection of valley-polarized carriers

In addition to the near-field effect, plasmon excitation in metallic nanostructures also generates energetic charge carriers through nonradiative decay, including hot electrons and hot holes.\(^{105}\) Hot carriers with energy well above the Fermi level can overcome energy barriers and be injected to the semiconductors within an ultrashort time (hundreds of fs).\(^{106}\) Such an effect offers an approach for the injection of energetic electrons into the semiconductor conduction band even when the excitation photons have an energy below the bandgap. The plasmon-induced hot carriers therefore have important applications in photodetection, solar energy harvesting and catalysis.\(^{105,107-110}\) By using chiral nanostructures, the plasmon-enabled injection of valley-polarized carriers becomes possible.

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**(Fig. 6H)**, confirming the robust unidirectional transport of valley-polarized emissions.
nic hot carrier generation is polarization-dependent\textsuperscript{111,112} and has high potential for enantioselective photocatalysis.\textsuperscript{113} Very recently, it was observed that plasmon-induced hot electrons could selectively inject into the valleys in TMDCs, forming valley-polarized carriers (Fig. 7A–C).\textsuperscript{114} An array of chiral nano-crescent plasmonic antennae were fabricated on the MoS\textsubscript{2} monolayer (Fig. 7A). When resonantly pumped by a linearly polarized infrared laser (1550 nm) with the photon energy far below the MoS\textsubscript{2} bandgap, the chiral antennae showed distinct super-chiral nearfields (Fig. 7B) and circular-polarization-dependent absorption. More importantly, since the chiral nanoantenna interacts with the $\sigma^+$ and $\sigma^-$ components of light differently, the generation of hot electrons by plasmon-decay has different efficiencies when the nanostructure is excited by the $\sigma^+$ and $\sigma^-$ components of the infrared light. As a result, it is possible to selectively occupy one valley since the energy barrier at the Au/MoS\textsubscript{2} interface naturally filters out the hot carriers in the low absorption valley (Fig. 7C). In experiments, both the circular-polarization-resolved PL and the valley Hall effect measurements verified the valley polarization in the Au/MoS\textsubscript{2} device excited by the 1550 nm laser. The experimental results showed that the valley Hall voltage changed its sign with the excitation helicity while no Hall signal was obtained under the illumination of 532 nm laser (Fig. 7D), indicating that the plasmonic hot carriers played important roles in generating the valley polarization. More interestingly, the valley Hall voltage was nonzero even without the in-plane electric field (Fig. 7E), which was attributed to the diffusion of the valley carriers (electrons). The valley Hall voltage was further shown to be tunable by applying a gate voltage to the MoS\textsubscript{2} field effect transistor. The generated valley carriers by hot electron injection sustained a quite high DVP around 85\% at room temperature, opening a new path for manipulating the valley polarization beyond the conventional excitonic approach. The detailed mechanism of the valley-selective injection of plasmonic hot carriers is still unclear and requires further study.

4. Conclusion and outlook

2D TMDCs possess unique valley properties and allow the robust manipulation of valley DoFs via external fields. They show high potential for constructing high-performance optoelectronic and valleytronic devices. The related research has attracted enormous interest. Despite the exciting progress in this field, manipulating the valley pseudospin is still challenging especially at room temperature because of the fast inter-valley scattering. Integrating TMDCs with nanophotonic structures has been studied to address this challenge. Here, we have reviewed nanophotonic approaches to facilitate the manipulation of valley polarization, including the valley-polar-
ized photoluminescence mediated by surface plasmon resonance, the valley-polarized plasmon/photon-exciton polaritons generated through strong coupling, the spatial separation of valley-polarized information by nanophotonic modes, and the valley polarization of excitons or carriers achieved by plasmon-enabled hot carrier injection. First, chiral plasmonic nanostructures have been used to enhance both the excitation and the spontaneous decay rate of the valley excitons, leading to improved valley contrast at room temperature even under the linearly polarized excitation. Second, strong coupling between photonic modes and the valley excitons offers another important approach to increase the valley polarization because of the long valley lifetime of the photonic part of the exciton–polaritons. Third, nanophotonic structures provide a useful platform for spatially routing the valley emission, which is promising for transporting and reading the valley pseudospin at the on-chip level. Moreover, the valley-selective injection of plasmon-induced hot carriers opens a new path for controlling the valley pseudospin. In this review, we have highlighted the important research progress in the above fields. We would further like to compare the time scales of different processes in the nanophotonic/plasmonic structure–TMDC system to help understand their mechanisms (Fig. 8).\textsuperscript{31,106,115–119} As we have discussed, the introduction of nanophotonic structures can either modulate the decay rate of valley excitons by their nearfield or alleviate the effect from intervalley scattering through the strong coupling interaction, which results in a modified exciton radiative lifetime and valley lifetime. Additionally, the plasmon decay and the subsequent processes of hot carrier generation and injection appear at an ultrashort timescale (<1 ps), which is comparable to the valley lifetime of monolayer TMDCs.\textsuperscript{59–61} The ultrafast plasmonic processes\textsuperscript{120} enable the manipulation of the valley pseudospin before valley depolarization. In addition, it is possible to maintain the spin of carriers during the hot carrier injection process because of the long electron spin relaxation time (∼ps) in metal.\textsuperscript{117–119}

Despite the remarkable advances achieved, research in this emerging field is still in its infancy and more efforts are needed to achieve a full understanding of the mechanisms and realize robust manipulation of the valley pseudospin in TMDCs. First, the existing nanophotonic techniques can be improved to obtain a better control of the valley polarization. For example, the maximum PL DVP of monolayer TMDCs with the help of nanophotonic structures is around 50%.\textsuperscript{41,43} There is still room for further improving the valley contrast by applying nanophotonic structures with higher optical chirality and coupling efficiency with the valley excitons. Enhancing the routing efficiency of the valley emission will also benefit the processing of valley information. Second, the mechanisms for the valley manipulation in some processes (e.g. the plasmon-enabled injection of valley-polarized carriers) are still not clear. Improving our understanding of such processes is not only of fundamental interest, but it also may open a new way for building valleytron devices. In addition, reliable and scalable fabrication of the hybrid system is of vital importance for practical applications. So far, the powerful nanofabrication process has enabled the preparation of structured systems with complicated morphologies.\textsuperscript{46,90} However, the nanofabrication process suffers from high cost when preparing various different samples and the fabrication is quite time-consuming, slowing down the investigations in this field. A more cost-effective and facile preparation process (e.g. bottom-up chemical synthesis and Fig. 8 Several important processes discussed in this review and their related characteristic time scales.
assembly) could be complementary in some specific applications and is still less studied. Besides, it is worthwhile exploring more possibilities with nanophotonic structures for better valley polarization control. TMDCs can support different types of excitons such as the neutral A excitons, charged excitons, dark excitons, localized excitons, and interlayer excitons in heterostructures. In contrast to the bright A excitons, others are less affected by the intervalley scattering and have much longer lifetimes (>ns).\textsuperscript{121,122} They are promising in achieving high valley polarization. Although such excitons usually have a low quantum efficiency and some of them possess out-of-plane dipole moments,\textsuperscript{123,124} which makes them hard to be excited and detected by the commonly used PL measurement setup, these excitons could be coupled effectively with nanophotonic structures with well-designed resonance properties. Furthermore, exploring pseudospin polarization in 2D semiconductors beyond TMDCs and van der Waals heterostructures will help to uncover new functions and expand potential applications.\textsuperscript{35,125} Recent studies show that chiral plasmons can appear in moiré superlattices constructed by van der Waals heterostructures.\textsuperscript{126} The chiral plasmons may be coupled with the excitons and provide new phenomena. Last but not least, it is important to develop nanophotonic–valleytronic device structures. According to the existing studies, various device structures have been demonstrated for encoding, transporting, and reading valley information. For example, a chiral light emitting transistor constructed using van der Waals heterostructures has been shown to have electrically tunable circularly polarized emission, which is promising for writing the valley information.\textsuperscript{127} Spin injection \textit{via} a diluted ferromagnetic semiconductor can also act as a writing unit in integrated devices. As for the transporting and reading process, optical means through the Ag nanowire or structured plasmonic systems and electrical means based on the valley Hall effects have been presented.\textsuperscript{44–47,96,114} Based on the progress, it will be a good idea to further develop a functional valleytronic circuit. Recently, some interesting studies on the theoretical design of valleytronic devices such as logic gates have been reported.\textsuperscript{128,129} However, the experimental demonstration of such devices is still challenging and calls for efforts on achieving high quality valley-polarized signals and their robust manipulation using less-complicated structures.

In all, we believe that further research into this field will bring not only significant understanding in physical mechanisms but also new opportunities in optoelectronic and valleytronic applications.

Conflicts of interest

There are no conflicts to declare.

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