Anomalous valley Hall effect in antiferromagnetic monolayers
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Anomalous valley Hall (AVH) effect is a fundamental transport phenomenon in the field of condensed-matter physics. Usually, the research on AVH effect is mainly focused on 2D lattices with ferromagnetic order. Here, by means of model analysis, we present a general design principle for realizing AVH effect in antiferromagnetic monolayers, which involves the introduction of nonuniform potentials to break of PT symmetry. Using first-principles calculations, we further demonstrate this design principle by stacking antiferromagnetic monolayer MnPSe3 on ferroelectric monolayer Sc2CO2 and achieve the AVH effect. The AVH effect can be well controlled by modulating the stacking pattern. In addition, by reversing the ferroelectric polarization of Sc2CO2 via electric field, the AVH effect in monolayer MnPSe3 can be readily switched on or off. The underlying physics are revealed in detail. Our findings open up a new direction of research on exploring AVH effect.

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INTRODUCTION
Valley, characterizing energy extrema of conduction or valence band, is an emerging degree of freedom of carriers in condensed-matter materials1,2. Benefiting from the large separation in momentum space, the valley degree of freedom is particularly stable against low-energy phonons and smooth deformations3–5. Analogous to charge and spin, the valley degree can be utilized to encode information and perform logic operations, leading to the concept of valleytronics6–9. Early interest in valley dates back to the works in 1970s on silicon inversion layer8,9. In recent years, following the discoveries of intrinsic physical properties associated with valley occupancy in two-dimensional (2D) lattices10,11, rapid experimental and theoretical progress12–46 has been made in the field of valleytronics at both the fundamental and applied levels.

As a new piece of puzzle in the Hall family, the anomalous valley Hall (AVH) effect in valley-polarized materials lies at the heart of valleytronics. In principle, polarized light is able to induce AVH effect in valley-polarized monolayers, however, it is a dynamic process and subjected to the life time of carriers, which is not applicable for practical valleytronics27,28. Physically, there are two essential ingredients for realizing stable AVH effect: one is magnetism and the other is spin-orbital coupling (SOC), which, respectively, plays the role of breaking the time-reversal symmetry and giving rise to coupled spin and valley physics. The former can be either intrinsic magnetism29–36 or extrinsic magnetism caused by magnetic doping37–40, magnetic field41,42 and magnetic proximity effect43–46, while the latter is related to the chemical compositions. The past years have seen impressive progress for identifying such AVH effect in single-layer materials27–46. In all the prior studies, there is one default assumption, namely, the magnetism must be ferromagnetic. Compared with ferromagnetism, antiferromagnetic materials have great potential in the next generation of valleytronics and spintronics applications thanks to the intrinsic advantages such as robustness against magnetic field perturbation, ultrafast dynamics, stray field-free operation47,48. However, to our knowledge, it is still unclear how to realize stable AVH effect in single-layer materials with an antiferromagnetic order.

In the present work, we show by model analysis that the realization of stable AVH effect can be extended to single-layer materials with an antiferromagnetic order. The proposed general design principle for this extension correlates with the introduction of nonuniform potentials to break the PT symmetry (invariance under the combined operation of spatial inversion (P) and time reversal (T)). Based on first-principles calculations, we further demonstrate this design principle by stacking antiferromagnetic monolayer MnPSe3 on ferroelectric monolayer Sc2CO2 and realize the AVH effect. Such AVH effect is shown to exhibit a tantalizing stacking pattern depended character. Moreover, we reveal that the AVH effect in monolayer MnPSe3 can be switched on or off by reversing the ferroelectric polarization of monolayer Sc2CO2. This extension of AVH effect to single-layer materials with an antiferromagnetic order is of great significance from both fundamental perspective and for potential use in devices.

RESULTS AND DISCUSSION
Introducing nonuniform potentials to break PT symmetry
Our proposed design principle for realizing AVH effect in single-layer materials with an antiferromagnetic order is schematically illustrated in Fig. 1. Without losing the generality, we take monolayer MnPSe3 as an example to discuss the scheme by considering the fact that monolayer MnPSe3 is known as a typical Néel antiferromagnetic semiconductor with spontaneous valley polarization. Monolayer MnPSe3 exhibits a hexagonal lattice with the space group of D3d (see Supplementary Fig. 1a). Without considering exchange interaction, its structure hosts the inversion symmetry P. In monolayer MnPSe3, the Mn atoms constitute two sublattices, which are referred to as A and B sublattices. Although the A and B sublattices are structurally equivalent, their spin orientations are opposite. In this regard, neither inversion symmetry (P) nor time-reversal symmetry (T) is preserved. However, it shows invariance under the simultaneous time reversal and spatial inversion, namely, PT symmetry. Because of the PT symmetry, the spin and valley polarization occur spontaneously in such antiferromagnetic monolayers, as schematically shown in Fig. 1a. Also protected by the PT symmetry, the valley spin splitting is prohibited, yielding the spin degeneracy for the K and K′ valleys. Such spin degeneracy in antiferromagnetic monolayers forbids the realization of AVH effect. For example, upon shifting Fermi level between the K and K′ valleys in the

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conduction bands, the spin-up and spin-down electrons from the K’ valley would accumulate at opposite edges of the sample in the presence of an in-plane electric field, preventing the AVH effect.

If we introduce nonuniform potentials to neighboring Mn atoms, the equivalence of the A and B sublattices is deformed, which will break the PT symmetry. Without the protection of PT symmetry, the valley spin splitting at the K and K’ valleys would be achieved (see Fig. 1b), rendering the observation of AVH effect. Such valley spin splitting is different from the case in nonmagnetic materials, where the valley spin splitting relates to Zeeman splitting. To preserve the valley physics, the nonuniform potentials introduced here should be regular. More importantly, it is natural to expect that the spin orders at both the K and K’ valleys can be reversed by reversing the nonuniform potentials introduced to A and B sublattices (Fig. 1c), which would enrich the AVH effect in antiferromagnetic monolayers.

Given the proposed design principle, we construct a k·p model to verify it. The spin-full Hamiltonian with excluding SOC for low-energy quasiparticles near the K(K’) valley of a honeycomb lattice can be expressed as:

$$H' = v_p \tau_0 \sigma_x p_x + v_s \tau_0 \sigma_y p_y + m \tau_0 \sigma_z$$

(1)

Here, $p$ and $v$ represent the momentum operator and the massless Fermi velocity, respectively. $\tau_0 \sigma_x$ and $\tau_0 \sigma_y$ are the Pauli matrices for the valley, isospin, and spin degree of freedom, respectively. The mass term ($m$), referring to an AFM perturbation, creates a band gap of $E_g = 2m$ for both spins, preserving the spin and energy degeneracy. When taking SOC into account, the Hamiltonian for SOC is introduced as:

$$H_{SOC} = \delta \tau_z \sigma_z$$

(2)

where $\delta$ is the SOC parameter. In the presence of SOC, the band gap is enlarged by $2\delta$ at the K valley and reduced by $2\delta$ at the K’ valley. As a result, the energetic degeneracy of the K and K’ valleys is lifted, but the spin degeneracy is preserved due to the invariance of the $H' + H_{SOC}$ under simultaneous time reversal and spatial inversion. The term for the nonuniform potential between two sublattices can be written as:

$$H_{ex} = \frac{\zeta}{2} \sigma_z$$

(3)

where $\zeta$ represents the strength of the nonuniform potential. In this case, the $H' + H_{SOC} + H_{ex}$ would not be invariance under simultaneous time reversal and spatial inversion. This drives the bands from one sublattice to shift upward with respect to those from the other, resulting in a valley spin splitting of $\zeta$ at the K and K’ valleys. According to the total Hamiltonian $H = H' + H_{SOC} + H_{ex}$, the eigenvalues of the highest valence bands are estimated to be $(m - \delta - \frac{\zeta}{2})$ and $(m - \delta + \frac{\zeta}{2})$ for spin-up and spin-down at the K valley, respectively, and $(m + \delta - \frac{\zeta}{2})$ and $(m + \delta + \frac{\zeta}{2})$ for spin-up and spin-down at the K’ valley. And the eigenvalues of the lowest conduction bands are found to be $(m + \delta + \frac{\zeta}{2})$ and $(m + \delta - \frac{\zeta}{2})$ for spin-up and spin-down at the K valley, respectively, and $(m - \delta + \frac{\zeta}{2})$ and $(m - \delta - \frac{\zeta}{2})$ for spin-up and spin-down at the K’ valley. When reversing the nonuniform potential between two sublattices, the sign of $H_{ex}$ is reversed, leading to the opposite valley spin splitting at the K and K’ valleys. These results firmly indicate that the proposed design principle for realizing AVH effect in antiferromagnetic monolayers is feasible physically.

Stacking-dependent AVH effect in MnPSe3/Sc2CO2

Having established the feasibility of the proposed design principle, next we discuss its realization in real materials. The proximity effect is proposed here to introduce nonuniform potentials on the A and B sites regularly. For detail, we consider monolayer Sc2CO2 as the substrate to induce the proximity effect in monolayer MnPSe3. The crystal structure of monolayer Sc2CO2 is shown in Supplementary Fig. 1b. It exhibits a hexagonal lattice with the space group P3m1. Due to the asymmetric displacement of inner C atomic layer with respect to Sc atoms, it hosts intrinsic ferroelectricity with out-of-plane polarization. The band structure shown in Supplementary Fig. 1d suggests that monolayer Sc2CO2 is a semiconductor with an indirect band gap of $1.79 \text{ eV}$. Concerning the stacking between monolayer MnPSe3 and Sc2CO2, a $2 \times 2$ supercell of Sc2CO2 is adopted to match the unit cell of MnPSe3. This results in a compressive strain of about 6% for Sc2CO2 layer, which is in an accessible range in experiments. It should be noted that when two van der Waals (vdW) materials are brought into contact, the lattice would undergo relaxation, while could result in lattice reconstructions as well as strain. To reveal strain effect on AVH physics, we also investigate the band structures of MnPSe3/Sc2CO2 under different tensile strain, and similar results are obtained (see Supplementary Fig. 2). According to the previous works, three typical stacking patterns (i.e., h-I↓, h-II↓, and h-III↓, as shown in Fig. 2a) with the polarization of Sc2CO2 pointing away from the interface are considered for the stacking between monolayer MnPSe3 and Sc2CO2. These three patterns can induce three distinct proximity effects on MnPSe3. In h-I↓ pattern, the Mn1 atoms sit above the top-O sites of Sc2CO2, and the Mn2 atoms are right above the Sc atoms in the second layer of Sc2CO2. In h-II↓ pattern, the Mn1 atoms lie above the C atoms in the middle layer, and the Mn2 atoms are right above the top-O atoms. In h-III↓ pattern, the Mn1 atoms sit above the Sc atoms in the second layer, and Mn2 atoms...
lie above the C atom in the middle layer of Sc$_2$CO$_2$. Concerning other stacking patterns, the proximity effect is expected to be similar to or in between the cases of h-I/II/III configurations. Taking the configuration with Mn atom sitting above the center of Sc-O-C triangle as an example, we calculate its band structure. As shown in Supplementary Fig. 3, the scenario is similar to that of h-III configuration.

In h-I configuration, the Mn$_1$ atoms would experience an extra interaction due to their proximity to the top-O sites of Sc$_2$CO$_2$, while the Mn$_2$ atoms would endure with a relatively small interaction as they lie farther. This can be described by the scenario illustrated in Fig. 1b, which introduces nonuniform potentials into the two sublattices of Mn atoms. The band structure of h-I configuration without considering SOC is shown in Fig. 2b and Supplementary Fig. 4a. The conduction band minimum (CBM) and valence band maximum (VBM) are contributed by monolayer Sc$_2$CO$_2$ and MnPSe$_3$, respectively, forming a type-II band alignment. The degenerate valleys of MnPSe$_3$ in both the conduction and valence bands located at the K and K' points are preserved after stacking on Sc$_2$CO$_2$. However, as shown in Fig. 2b, the interesting valley spin splitting occurs in both the bottom conduction and top valence bands of MnPSe$_3$ at the K/K' point, which correlates to the nonuniform potentials induced by stacking. Although the valleys of MnPSe$_3$ in the conduction bands submerge in the bands of Sc$_2$CO$_2$, they are still investigated for comparison. The valley spin splitting in the valence bands ($\zeta^\downarrow = \zeta^\uparrow$) and conduction bands ($\zeta^\downarrow = \zeta^\uparrow$) are estimated to be 28.5 and 16.7 meV, respectively. Such sizeable valley spin splitting stands in sharp contrast to the valley spin splitting in nonmagnetic materials which are induced by SOC and P breaking.

When taking SOC into account, as shown in Fig. 2c, the character of valley spin splitting of MnPSe$_3$ is maintained at both the K and K' valleys, but the values of valley splitting at K and K' valleys are no longer equal; see Supplementary Table 1. In this case, the energetic degeneracy of the K and K' valleys in MnPSe$_3$ is lifted, leading to the spontaneous valley polarization. Particularly, the valley polarization in the valence band is as large as 24.6 meV. The coexistence of valley spin splitting and valley polarization would ensure the observation of AVH effect in antiferromagnetic monolayer of MnPSe$_3$, as we will show later.

As discussed above, the valley spin splitting relates to the nonuniform potentials induced by the proximity effect. Therefore, by engineering the stacking pattern, the valley spin splitting can be modulated. In h-II configuration, the Mn$_1$ atoms experience an extra interaction due to their proximity to the top-O sites of Sc$_2$CO$_2$, while the Mn$_2$ atoms endure with a relatively small interaction as they lie farther. This corresponds to the scenario illustrated in Fig. 1c. Accordingly, the nonuniform potentials introduced to Mn$_1$ and Mn$_2$ atoms in h-II configuration is reversed with respect to those in h-I configuration. The band structure of h-II configuration with considering SOC is presented in Fig. 2d. It shares similar features to the band structure of h-I. The interesting valley spin splitting and spontaneous valley polarization are observed at the K and K' valleys of MnPSe$_3$, and the magnitudes are comparable to that in h-I configurations. However, the sign of the valley spin splitting is opposite to that of h-I configurations, which is consistent with the proposed design principle. Such simultaneous existence of valley spin splitting and valley polarization would facilitate the AVH effect as well.

Different from the cases of h-I and h-II configurations, both the Mn$_1$ and Mn$_2$ atoms in h-III configuration experience a weak extra interaction since they lie far away from the atoms of Sc$_2$CO$_2$. Thus, the nonuniform potentials introduced to Mn$_1$ and Mn$_2$ atoms by the proximity effect would be rather weak. According to the proposed design principle, the valley spin splitting of MnPSe$_3$ in h-III configuration would be tiny. The band structure of h-III configuration with considering SOC is displayed in Fig. 2e. As expected, the valley spin splitting is as small as 2.3 meV (2.6 meV) at the K (K') valley in the valence band, while it is even 1 meV (1 meV) in the conduction band of MnPSe$_3$, although large
The nonuniform potentials introduced to Mn1 and Mn2 atoms by the proximity effect for all these three stacking patterns can also be straightforwardly reflected by the variation of magnetic moments. For freestanding MnPSe3, the magnetic moments on Mn1 and Mn2 atoms are found to be 4.52 and −4.52 μB, respectively, which is protected by the PT symmetry. When stacking MnPSe3 on Sc2CO2 to form the h-I configuration, the magnetic moment on Mn1 atom changes to 4.508 μB, while the magnetic moment on Mn2 atom experiences with a relatively slight change (−4.513 μB). This suggests the nonuniform potentials on the Mn1 and Mn2 atoms. As compared with h-I configuration, the absolute values of the magnetic moments on Mn1 and Mn2 atoms in h-II configuration are exchanged, but the signs of the magnetic moments remain the same. Namely, the magnetic moments on Mn1 and Mn2 atoms in h-II configuration are found to be 4.513 and −4.508 μB, respectively. This can be easily understood by recalling the reversal of the atomic environments for Mn1 and Mn2 atoms in h-I and h-II configurations. For h-III configuration, the magnetic moments on Mn1 and Mn2 atoms slightly change to 4.514 and −4.514 μB, respectively. The preservation of identical absolute values of the magnetic moments on Mn1 and Mn2 atoms in h-III configuration relates to the weak extra interactions on both Mn atoms.

In 2D hexagonal lattices with inversion symmetry breaking, the K and K′ valleys will exhibit a nonzero Berry curvature along the out-of-plane direction. The Berry curvature is defined as

$$\Omega(k) = -\sum_n \sum_{n' \neq n} f_n \left( 2im \left| \psi_{nk}^* \right| v_x \psi_{nk} \right) \left( \psi_{nk}^* \right| v_y \psi_{nk} \right) \left( E_n - E_{n'} \right)^2$$

(4)

Here, fn is the Fermi-Dirac distribution function, ψnk is the Bloch wave function with eigenvalue En, and vx, vy is the velocity operator along x/y direction. The calculated Berry curvatures of the spin-up and spin-down channels over the 2D Brillouin zone for monolayer MnPSe3 are shown in Fig. 3a. Obviously, the Berry curvatures for the same spin state around the K and K′ valleys are opposite, and the Berry curvatures for spin-up and spin-down states at the same valley are opposite as well. Note that under a longitudinal in-plane electric field, the Bloch carriers will acquire an anomalous transverse velocity proportional to the Berry curvature: vx ~ E × Ω(k). In monolayer MnPSe3, when shifting the Fermi level between the K and K′ valleys in the valence band, protected by the PT symmetry, the spin-down and spin-up holes from the K′ valley will gather to opposite edges of the sample in the presence of an in-plane electric field, see Fig. 3b. In this regard, a net spin current is generated, which results in the spin Hall effect, however, the AVH effect is absent. In h-I configuration, because of the additional valley spin splitting, the spin degeneracy is lifted. When shifting the Fermi level between the K and K′ valleys in the valence band, only the spin-down holes from the K′ valley move to the bottom boundary of the sample under an in-plane electric field; see Fig. 3c. This gives rise to the long sought AVH effect in antiferromagnetic monolayers. In addition, the accumulated spin-down holes will result in a net charge/spin current. Similar to the case of h-I configuration, when shifting the Fermi level between the K and K′ valleys in the valence band of the h-II configuration, the spin-up holes from the K′ valley will accumulate at the top edge of the sample (Fig. 3d), which results into the AVH effect as well.

**Ferroelectrically controllable AVH effect**

Note that monolayer Sc2CO2 is a 2D ferroelectric crystal with an out-of-plane polarization, its polarization direction can be reversed under a short-term out-of-plane electric field. Note that the reversed polarized state will be retained when the external electric field is removed. Such ferroelectric switching might affect the electronic properties of the MnPSe3/Sc2CO2. In the following, we investigate the properties of the three typical stacking patterns with switching the ferroelectric polarization of Sc2CO2 from downward to upward, which are referred to as h-I, h-II, h-III, respectively, see Supplementary Fig. 5. Figure 4a presents the band structures of h-I, h-II and h-III, configurations with considering SOC. The band structures of all these three configurations share similar characters. In all these three configurations, the Fermi level crosses the bottom of the conduction band and top of the valence band, yielding a metallic nature. More interestingly, the valleys of MnPSe3 in both the conduction and valence bands are submerged in the trivial bands of Sc2CO2, restricting any potential utilization of these valleys. In other word, under the ferroelectric switching, all these three configurations undergo a semiconductor-to-metal transition. Such transition is also accompanied with the disappearance of valley physics as well as the AVH effect. Accordingly, the AVH effect in h-I, and h-II, configurations is ferroelectrically controllable, benefiting for developing controllable valleytronic devices.

To understand the underlying mechanism of the ferroelectric-polarization-dependent properties, we calculate the plane-average electrostatic potentials of monolayer MnPSe3, monolayer Sc2CO2, h-I, and h-II (Fig. 4b and Supplementary Fig. 6). It can be seen that arising from the asymmetric structure, intrinsic polarization occurs along the out-of-plane direction, leading to the different work functions at the two sides of monolayer Sc2CO2. Accordingly, upon contacting monolayer MnPSe3 with Sc2CO2 in different polarized states, the distinctly different band alignments forms, as shown in Fig. 4c. When the polarization of monolayer Sc2CO2 points away from the interface, the CBM of Sc2CO2 locates above the VBM of MnPSe3, inhibiting the transfer of electrons between Sc2CO2 and MnPSe3. The valley feature in the valence band from MnPSe3 is reserved. In contrast, when the polarization pointing to the interface, the CBM of MnPSe3 shifts below the VBM of Sc2CO2, prompting the electron transfer from Sc2CO2 to MnPSe3, leading to the metallic nature. By comparing Supplementary Figs. 1c, d and 4, it can be seen that the bands from the constituent layers are roughly similar to the corresponding free-standing ones, which indicates the weak hybridization between them for both the upward-polarization and down-polarization cases. The polarization reversal only changes the band alignment and gives rise to different band contributions around the Fermi level, leading to the submersion of valleys in the trivial bands or not. The charge transfer character between Sc2CO2 to MnPSe3 in h-I, h-II, and h-III configurations is also confirmed by the charge density differences shown in Supplementary Fig. 7. While for h-I, h-II, and h-III configurations, the charge redistribution occurs around the interface. The charge transfer caused by polarization reversal could lead to semiconductor-to-metal transition. Such transition is accompanied with the submersion of valleys in the trivial bands and thus deforms the valley physics. While for the case under hole doping, it will not lead to the submersion of valleys in the trivial bands, which could preserve the valley physics. With these results in hand, we can understand the polarization dependent behaviors in MnPSe3/Sc2CO2.

To summarize, through model analysis, a general design principle for realizing stable AVH effect in antiferromagnetic monolayers is proposed, which involves the introduction of nonuniform potentials to Mn1 and Mn2 atoms to break the PT symmetry.
first-principles calculations, the proposed design principle is further demonstrated by stacking antiferromagnetic monolayer MnPSe$_3$ on ferroelectric monolayer Sc$_2$CO$_2$. The realized AVH effect hosts the stacking pattern depended character. In addition, the AVH effect in MnPSe$_3$/Sc$_2$CO$_2$ can be switched on or off under ferroelectric switching of monolayer Sc$_2$CO$_2$.

**METHODS**

**Density functional theory calculations**

Our first-principles calculations are performed based on density functional theory (DFT) methods as implemented in the Vienna ab initio simulation package (VASP)$^{62,63}$. The generalized gradient approximation (GGA) in form of Perdew-Burke-Ernzerhof (PBE) functional is used to describe the exchange-correlation interaction$^{64}$. The cutoff energy is set to 500 eV. Crystal structures are fully relaxed with the convergence criteria of $10^{-5}$ eV and $0.01$ eVÅ$^{-1}$ for energy and force, respectively. The Brillouin zone is sampled with Monkhorst–Pack grids of $9 \times 9 \times 1$. To avoid interactions between adjacent periodical structures, the vacuum space along the z direction is set to 30 Å. The zero damping DFT-D3 method is utilized to treat the vdW interaction$^{65}$. To describe the strong correlation effects, the effective on-site Hubbard term of $U = 4$ eV is set for the 3d electrons of the Mn atom, as this value is employed in previous works$^{64,66,67}$. Berry curvature is calculated using the maximally localized Wannier function method as implemented in the WANNIER90 package$^{68}$.
DATA AVAILABILITY
The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files.

CODE AVAILABILITY
The central codes used in this paper are VASP and WANNIER90. Detailed information related to the license and user guide are available at http://www.wannier.org and https://www.vasp.at.

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REFERENCES
1. Xiao, D., Yao, W. & Niu, Q. Valley-contrastings physics in graphene: magnetic moment and topological transport. Phys. Rev. Lett. 99, 236809 (2007).
2. Yao, W., Xiao, D. & Niu, Q. Valley-dependent optoelectronics from inversion symmetry breaking. Phys. Rev. B 77, 235406 (2008).
3. Berkelbach, T., Hybertsen, M. & Reichman, D. Theory of neutral and charged excitons in monolayer transition metal dichalcogenides. Phys. Rev. B 88, 045318 (2013).
4. Lu, H., Yao, W., Xiao, D. & Shen, S. Intervalley scattering and localization behaviors of spin-valley coupled dirac fermions. Phys. Rev. Lett. 110, 016806 (2013).
5. Sanchez, O., Owchinnikov, D., Misra, S., Allain, A. & Kis, A. Valley polarization by spin injection in a light-emitting van der Waals heterojunction. Nano Lett. 16, 5792 (2016).
6. Schablitz, J. R. et al. Valleytronics in 2D materials. Nat. Rev. Mater. 1, 16055 (2016).
7. Vitale, S. A. et al. Valleytronics: opportunities, challenges, and paths forward. Small 14, 1801483 (2018).
8. Sham, L. J., Allen, S. J. Jr., Kamgar, A. & Tsui, D. C. Valley-valley splitting in inversion layers on a high-index surface of silicon. Phys. Rev. Lett. 40, 472 (1978).
9. Ohkawa, F. J. & Uemura, Y. Theory of valley splitting in an N-channel (100) inversion layer of Si I. Formulation by extended zone effective mass theory. J. Phys. Soc. Jpn 43, 907 (1977).
10. Ryceker, A., Tvorzydzik, J. & Beenakker, C. W. J. Valley filter and valley valve in graphene. Nat. Phys. 3, 172 (2007).
11. Akhmerov, A. R. & Beenakker, C. W. J. Detection of valley polarization in graphene by a superconducting contact. Phys. Rev. Lett. 98, 157003 (2007).
12. Wu, S. et al. Electrical tuning of valley magnetic moment through symmetry control in bilayer MoS2. Nat. Phys. 9, 149 (2013).
13. Sie, E. J. et al. Valley-selective optical Stark effect in monolayer WS2. Nat. Mater. 14, 290 (2015).
14. Zhu, Z. Y., Cheng, Y. C. & Schwingenschlögl, U. Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors. Phys. Rev. B 84, 153402 (2011).
15. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS2 and other Group-VI dichalcogenides. Phys. Rev. Lett. 108, 196802 (2012).
16. Li, X., Cao, T., Niu, Q., Shi, J. & Feng, J. Coupling the valley degree of freedom in bilayer MoS2. npj Quant. Mater. 2, 47 (2017).
17. Xu, L. et al. Large valley splitting in monolayer WS2 by proximity coupling to an insulating antiferromagnetic substrate. Phys. Rev. B 97, 041405 (2018).
18. Ma, Y. et al. Conduction-band valley spin splitting in single-layer H-TiLO. Phys. Rev. B 97, 035444 (2018).
19. Ke, C. et al. Large and controllable spin-valley splitting in two-dimensional WS2/h-BN heterostructure. Phys. Rev. B 100, 195435 (2019).
20. Hu, H., Tong, K.-Y., Shen, Y.-H. & Du, C.-G. Electrical control of the valley degree of freedom in 2D ferroelectric/antiferromagnetic heterostructures. J. Mater. Chem. C. B, 0809 (2020).
21. Hu et al. Tunable valley splitting and anomalous valley Hall effect in VTe2/SiC heterostructures. J. Mater. Chem. C. 8, 14985 (2020).
22. Li, S. et al. Valley-dependent properties of monolayer MoS2, WSe2, and MoS2As2. Phys. Rev. B 102, 235433 (2020).
23. Yang, C., Song, Z., Sun, X. & Lu, J. Valley pseudospin in monolayer MoS2 and MoS2As2. Phys. Rev. B 103, 035308 (2021).
24. Dou, K. & Lu, J. Promising valleytronics materials with strong spin-valley coupling in two-dimensional MNX2 (M = Mo, W; X = F, H). Appl. Phys. Lett. 117, 172405 (2020).
25. Lei, C. et al. Nonvolatile controlling valleytronics by ferroelectricity in 2H-VSe2/-SC4C08 van der Waals heterostructure. J. Phys. Chem. C. 125, 2802 (2021).
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AUTHOR CONTRIBUTIONS

W.D. executed calculations. W.D., R.P. and Z.H. performed data analysis. Y.M. supervised the project. W.D. and Y.M. co-wrote the paper. All authors discussed the results and commented on the manuscript at all stages.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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