

Giant valley polarization splitting and circular dichroism response in $\text{WS}_2/\text{CrBr}_3$ heterostructure via ultrafast spin-charge transfer

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ABSTRACT: Manipulation of exciton dynamics is a fundamental approach for exploiting the valley degree of freedom in two-dimensional van der Waals (vdWs) heterostructures and developing high-performance valleytronic devices. Herein, we report a method for controlling interlayer spin-charge transfer in $\text{WS}_2/\text{CrBr}_3$ vdWs heterostructure through graphene proximity coupling and achieve a giant chirality-dependent valley polarization splitting. Theoretical and experimental findings reveal that the $\text{WS}_2/\text{CrBr}_3$ vdWs heterostructure retains its initial large conduction band offset under light irradiation when it is coupled with a few-layered graphene in the bottom. The interlayer spin-charge transfer time is significantly reduced from 17.3 to 1.3 ps, leading to a remarkable improvement in the valley polarization. The degree of valley polarization and polarization splitting of trion excitons in WS_2 are enhanced by 32% and 261%, respectively. Moreover, a highly sensitive circularly polarized photodetector was developed by using the $\text{WS}_2/\text{CrBr}_3/\text{graphene}$ heterostructure. This work pioneers a route to efficiently manipulate the transport behavior of excitons in vdWs heterostructures and also offers a novel idea for designing high-performance spintronic devices.

KEYWORDS: exciton dynamics, valley polarization, graphene proximity coupling, conduction band offset, spin-charge transfer

1 Introduction

Manipulation of the valley degree of freedom has recently emerged as a significant research area due to its promising applications in advanced valleytronic devices [1–3]. Two-dimensional (2D) transition metal dichalcogenides (TMDs), such as WS_2 and MoS_2 , provide an ideal platform for investigating valleytronics owing to their unique physical properties, including intrinsic broken inversion symmetry and strong spin-orbit coupling [4, 5]. Nevertheless, for practical implementations, it requires breaking the

energy degeneracy between the two inequivalent valleys and ensuring that carriers can be distinguished and manipulated for each defined valley. In principle, it can be achieved by controlling the dynamics process of spin electrons within or between valleys based on the spin-valley locking effect in monolayer TMDs. Accordingly, diverse manipulation methods, such as strain engineering [6], applying an external electric field or magnetic field [7, 8], or stacking heterostructures [9], have been proposed, which reduce the intervalley scattering of spin electrons and induce the inequivalence in spin-electron population of k and k' valleys, thereby enhancing the valley polarization. Nevertheless, none of these methods can completely suppress the scattering behavior of spin-electrons, and thus the enhancement magnitude of valley polarization is restricted.

Recently, a novel method of constructing type-II heterostructures of TMDs/2D magnet (such as CrI_3 , CrBr_3) has been developed

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[10–12]. It can regulate the electron population with a given spin orientation within the TMDs through an interlayer spin-selective charge transfer, thereby improving the valley polarization. In our previous work, we found that this method can also be utilized to manipulate the valley polarization of interlayer excitons in TMD-based van der Waals (vdWs) heterostructures [13]. From the perspective of exciton dynamics, both the radiative recombination of excitons and the depolarization of spin-electrons require a certain amount of time, and spin-selective charge transfer rate will affect the valley polarization [10]. As reported, the exciton lifetimes in monolayer TMDs (such as WS_2 , MoS_2) are typically in the range of a few picoseconds to several tens of picoseconds [14–16], while the electron transfer times in TMDs-based vdWs heterostructures are of this order of magnitude [17–19]. For this reason, modulating the exciton dynamics within heterostructures to accelerate spin-charge transfer rate is the key to enhancing the valley polarization.

In this work, we introduce a proximate coupling strategy to indirectly regulate the interlayer charge transfer dynamics in TMDs/2D magnet heterostructures, and observe significantly enhanced valley polarization in $\text{WS}_2/\text{CrBr}_3/\text{graphene}$ (Gr) heterostructure. By taking advantage of the characteristic of ultrafast charge transfer between graphene and CrBr_3 , the spin-charge transfer time between WS_2 and CrBr_3 is shortened from 17.3 to 1.3 ps. As a result, the maximal degree of valley polarization (DOP) and polarization splitting of trion excitons in WS_2 reach 59.8% and 37.9%, respectively, which correspond to the enhancements of 32% and 261%. Moreover, we fabricate circularly-polarized photodetectors by using $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures. The $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ photodetector exhibits a circular anisotropy ratio as high as 88% (@10 V, 1500 Gs), which is a 76% enhancement compared to that of the $\text{WS}_2/\text{CrBr}_3$ photodetector. Furthermore, its photoresponsivity is significantly

improved by 370%. This work provides a new means of regulating exciton dynamics and demonstrates great potential for the development of next-generation electronic devices.

2 Results and discussion

In our experiments, monolayer WS_2 , few-layered CrBr_3 and graphene are firstly mechanically exfoliated and then stacked on a SiO_2/Si substrate by an alignment transfer technique. As shown in Fig. 1(a), three kinds of samples are fabricated and labelled as I, II and III, respectively. Their structures are identified by the measurements of Raman spectrum. As for sample I, only two characteristic peaks are observed at 344.9 and 414.5 cm^{-1} (see Fig. 1(b)), corresponding to the in-plane vibrational mode and the out-of-plane vibrational mode of monolayer WS_2 , respectively. The wavenumber difference between these two peaks is found to be less than 60 cm^{-1} , indicating a monolayer characteristic of the sample I [20]. For the sample II, as shown in Fig. 1(c), besides the characteristic peaks of monolayer WS_2 , Raman peaks associated with the CrBr_3 are also detected, which located at 152.3, 171.3, and 210.7 cm^{-1} , respectively. Compared to that of sample II, as shown in Fig. 1(d), the Raman spectrum of sample III additionally exhibits the G peak (1586.7 cm^{-1}) and the 2D peak (2721.6 cm^{-1}) of graphene [21, 22]. These results indicate that the $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures are successfully constructed for sample II and III, respectively. Figure 1(e) displays the low-temperature photoluminescence (PL) spectra for different samples. To identify the emission peaks, their spectra are fitted by Gaussian functions with the results shown in Figs. 1(f)–1(h). The emission spectra of different samples exhibit the similar shape, which are composed of three emission peaks at approximately 1.94, 1.98, and 2.05 eV, corresponding to the biexciton (XX), trion exciton (X^T),

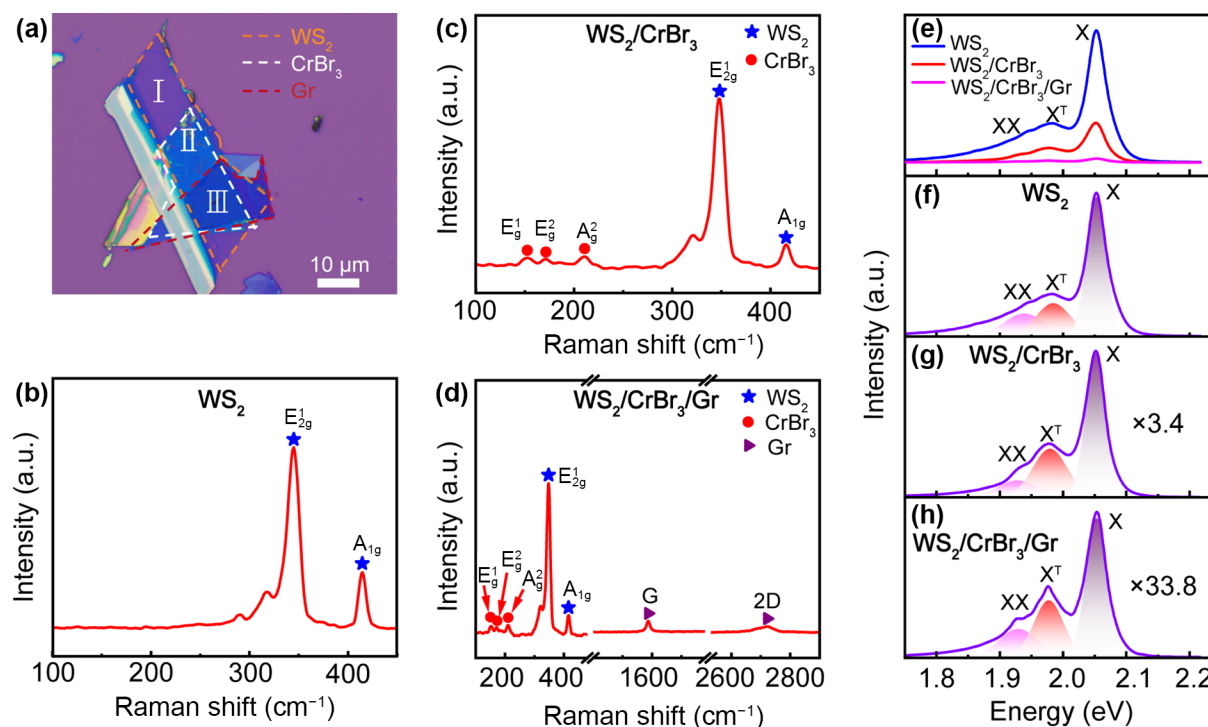


Figure 1 Characterizations of monolayer WS_2 , $\text{WS}_2/\text{CrBr}_3$, and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures. (a) Optical microscope image of the stacked sample, where the dashed outlines in different colors indicate the edges of different materials, and the three kinds of samples are labelled with I, II and III, respectively. (b)–(d) Raman spectra of sample I, II, and III, respectively. (e) PL spectra of different samples at 9 K. (f)–(h) Enlarged PL spectra of sample I, II, and III, respectively. Each spectrum is fitted by using Gaussian functions.

and neutral exciton (X) emissions of monolayer WS₂, respectively [23–25]. It is worth noting that the PL intensity of WS₂ material is significantly weakened after the formation of heterostructure, and the intensity of X peak in WS₂/CrBr₃/Gr heterostructure is only 1/33.8 of that in monolayer WS₂ (see Fig. 1(e)). This phenomenon is primarily related to the exciton dynamics, which will be discussed in detail later.

To investigate the exciton valley characteristics in different heterostructures, their circularly polarized PL spectra are measured under external magnetic fields. Figures 2(a) and 2(b) show the PL spectra of the WS₂/CrBr₃ heterostructure under the magnetic field of +1500 Gs and −1500 Gs, respectively. Herein, σ^+ and σ^- represent left- and right-handed chirality, respectively. Clearly, the PL intensity of the co-polarized spectra is significantly higher than that of the cross-polarized ones, exhibiting a valley polarization property. Under σ^+ (or σ^-) excitation, the DOP (ρ) can be calculated by Eq. (1)

$$\rho = \frac{I(\sigma^{+/-}) - I(\sigma^{-/+})}{I(\sigma^{+/-}) + I(\sigma^{-/+})} \quad (1)$$

where $I(\sigma^{+/-})$ represent the PL intensities of left- and right-handed circularly polarized emission, respectively [26]. Figures 2(c)–2(e) show the temperature dependence of the DOP for X, XX, and X^T excitons in the WS₂ layer of the WS₂/CrBr₃ heterostructure under external magnetic fields, respectively. Initially, the DOPs of all three kinds of excitons increase slightly as the temperature decreases. Notably, a significant splitting emerges in the curves when the temperature is lower than ~ 36 K, indicating a chirality-dependent valley polarization. The similar splitting behavior is also observed in our previous work about the valley polarization in WS₂/MoSe₂/CrBr₃ heterostructure [13]. The splitting values of DOP at 9 K for the X, XX, and X^T excitons are 9.8%, 8.7%, and 10.5%, respectively. The CrBr₃ crystal undergoes a transition from a

paramagnetic state to a ferromagnetic state when the temperature is lower than the Curie temperature (~ 36 K) [27, 28], and the spin-selective charge transfer occurs between the WS₂ and CrBr₃ layers [13]. As a result, the difference in number between the spin-up and spin-down electrons varies with the chirality of circularly polarized light or the direction of magnetic moment in CrBr₃, which contributes to the chirality-dependent valley polarization. To confirm the contribution of CrBr₃, valley polarization in monolayer WS₂ is also characterized under different temperatures and magnetic fields, while no polarization splitting is observed (see Fig. S1 in the Electronic Supplementary Material (ESM)).

Similarly, we characterize the properties of exciton valley polarization in the WS₂/CrBr₃/Gr heterostructure. Figures 3(a) and 3(b) show its polarization-resolved PL spectra under the magnetic field of +1500 and −1500 Gs, respectively, and Figs. 3(c)–3(e) plot the temperature dependence of the DOP for X, XX, and X^T excitons in WS₂. Similar to the WS₂/CrBr₃ heterostructure, the WS₂/CrBr₃/Gr heterostructure also exhibits chirality-dependent valley polarizations at low temperature. Interestingly, the polarization splitting is significantly enhanced. The maximal splitting of 37.9% is obtained for the X^T exciton, which is enhanced by 261% compared with that in WS₂/CrBr₃. Meanwhile, the maximal DOP of the X^T exciton increases to 59.8%, reflecting a 50% enhancement compared with that in monolayer WS₂ (see Fig. S1 in the ESM). Besides, Fig. 3(f) illustrates the magnetic field dependence of the DOP for X^T exciton under σ^+ and σ^- light excitation (the data of X and XX excitons is shown in Fig. S2 in the ESM). The hysteresis-like shape strongly reconfirms that the chirality-dependent valley polarization is associated with the magnetism evolution of CrBr₃. This behavior also indicates that the valley polarization in TMDs/2D magnet vdWs heterostructures can be manipulated by an external magnetic field, which provides a new route towards the design of advanced valleytronic devices.

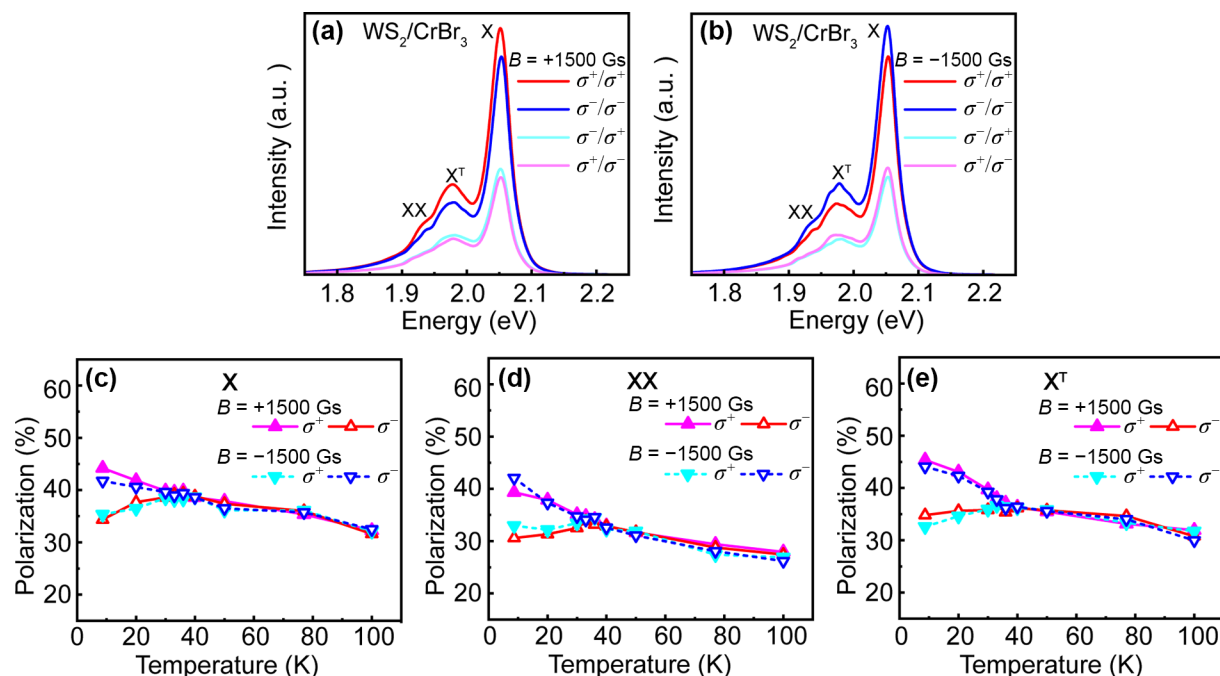


Figure 2 PL spectra and valley polarization of the WS₂/CrBr₃ heterostructure. (a) and (b) Polarization-resolved PL spectra of the WS₂/CrBr₃ heterostructure at 9 K under an external magnetic field of +1500 and −1500 Gs (taking the direction perpendicular to the sample surface toward the bottom as the positive direction). (c)–(e) Temperature-dependent DOP under an external magnetic field (+1500 or −1500 Gs) for X, XX, and X^T excitons in WS₂ layer of the WS₂/CrBr₃ heterostructure, respectively.

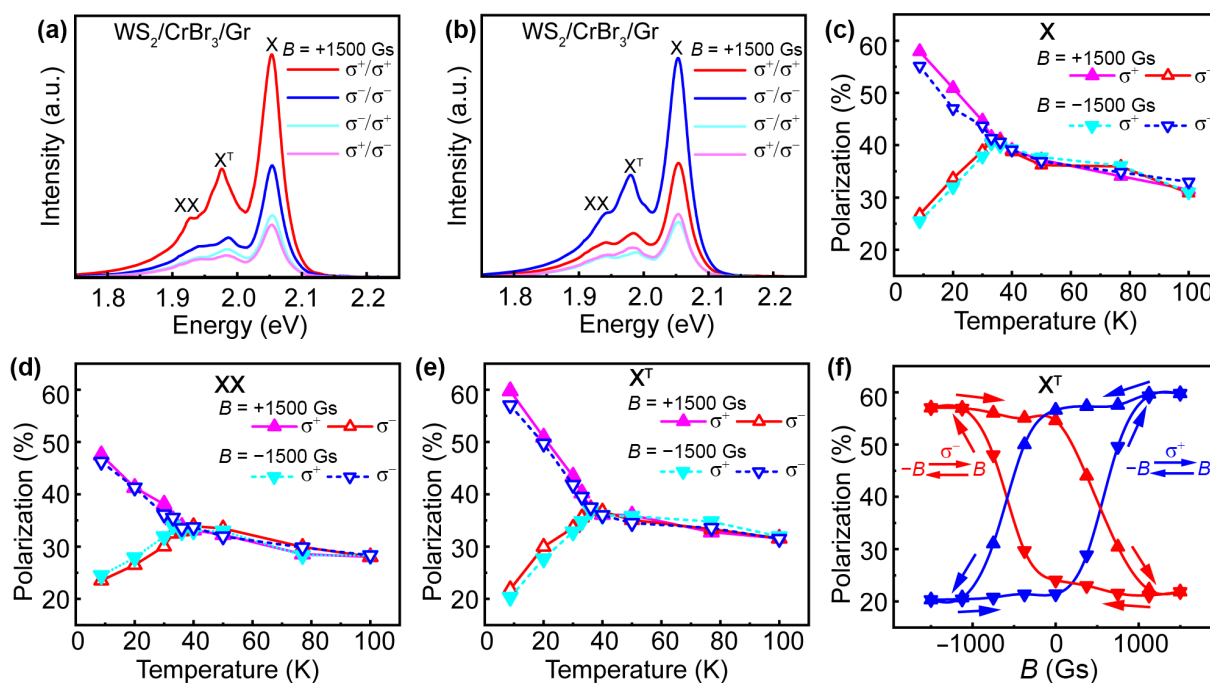


Figure 3 PL spectra and valley polarization of the WS₂/CrBr₃/Gr heterostructure. (a) and (b) Polarization-resolved PL spectra of the WS₂/CrBr₃/Gr heterostructure at 9 K under an external magnetic field of +1500 and -1500 Gs, respectively. (c)–(e) Temperature-dependent DOP under an external magnetic field (+1500 or -1500 Gs) for X, XX, and XT excitons in WS₂, respectively. (f) DOP of XT exciton as a function of the magnetic field (ranging from -1500 to +1500 Gs) at 9 K.

In principle, as the sample is irradiated by σ^+ (or σ^-) light, electrons in the valence band of the k (or k') valley can be excited to the conduction band of the same valley due to the optical selection rule. Subsequently, electrons transit back to the valence band and recombine with the holes, accompanied by a light emission. Ideally, the material only emits σ^+ (or σ^-) light after being excited by σ^+ (or σ^-) light, which corresponds to a DOP of 100%. However, spin-electrons at k or k' valley inevitably undergo an intervalley scattering due to the lattice vibrations [29], impurity or defect scattering [30], or Coulomb interactions [31], resulting in a suppressed DOP value. It is assumed that the intensity of σ^+ and σ^- light emission is proportional to the electron populations in the k and k' valleys, respectively. According to Eq. (1), the DOP significantly depends on the difference in population of spin-electrons in the two valleys, where a larger value is in favor of a higher DOP. Unlike most of previous works, where the valley polarizations were generally enhanced by suppressing the intervalley scattering of spin-electrons [32–34], the high valley polarization here should be attributed to the selective transfer of the scattered spin-electrons to 2D ferromagnetic material. Since the exciton radiative recombination takes a certain amount of time, the spin-electron transfer rate will inevitably have a great impact on the valley polarization.

To analyze the differences in the spin-electron transfer rate between the two heterostructures, we calculated their band structures using first-principles calculations. The stacking configurations are firstly optimized with the results depicted in Figs. S3 and S4 in the ESM. As shown in Figs. 4(a) and 4(b), both heterostructures form a type-II band alignment, where the conduction band minimum (CBM) and valence band maximum (VBM) are located in CrBr₃ and WS₂, respectively. Figure 4(e) presents a schematic of the band structures of the two heterostructures, with representing the conduction band offset between WS₂ and CrBr₃. It can be seen from Fig. 4(a) that the

conduction band offset of WS₂/CrBr₃ heterostructure is 0.92 eV. As for the WS₂/CrBr₃/Gr heterostructure, the conduction band of CrBr₃ shifts downward due to the coupling effect of graphene, so that its increases to 0.99 eV, which is slightly larger than that of the WS₂/CrBr₃ heterostructure. Meanwhile, with the aim of simulating the impact of light irradiation on the electronic structure of the heterostructure, we carry out the calculations with varying concentrations of electron doping. The electronic structures of the WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures with a doping concentration of 0.2 e/u.c. are shown in Figs. 4(c) and 4(d), respectively, while those with other doping concentrations are given in Fig. S5 in the ESM. Figure 4 summarizes the electronic band structures of the two kinds of heterostructures with different electron-doping concentrations. As the doping concentration increases, the conduction band offset of WS₂/CrBr₃ heterostructure quickly decreases, while that of WS₂/CrBr₃/Gr heterostructure only has a slight change. In the case of the WS₂/CrBr₃ heterostructure, the conduction band offset rapidly decreases from 0.92 to 0.43 eV upon an electron-doping with a concentration of 0.2 e/u.c. By contrast, for the WS₂/CrBr₃/Gr heterostructure, it decreases by merely 0.08 eV under the same doping condition. This is because the injected charges rapidly transfer to the graphene, which leads to a reduction in the charge accumulation within WS₂. Consequently, the Fermi level only experiences a slight shift (see Fig. 4(d)), thereby giving rise to a minor change in conduction band offset. As is known, a large band offset in the heterostructure boosts the charge transfer [35, 36], which means that the WS₂/CrBr₃/Gr heterostructure possesses a faster spin-charge transfer rate. The exciton lifetimes of XT exciton in monolayer WS₂, WS₂/CrBr₃ heterostructure and WS₂/CrBr₃/Gr heterostructure are obtained to be 41.5, 37.4, and 21.5 ps, respectively, by the measurement of time-resolved PL spectra (see Fig. 4(g)). Obviously, the exciton lifetime of XT exciton in the WS₂/CrBr₃/Gr heterostructure is substantially shorter than that in the WS₂/CrBr₃ heterostructure, which indicates

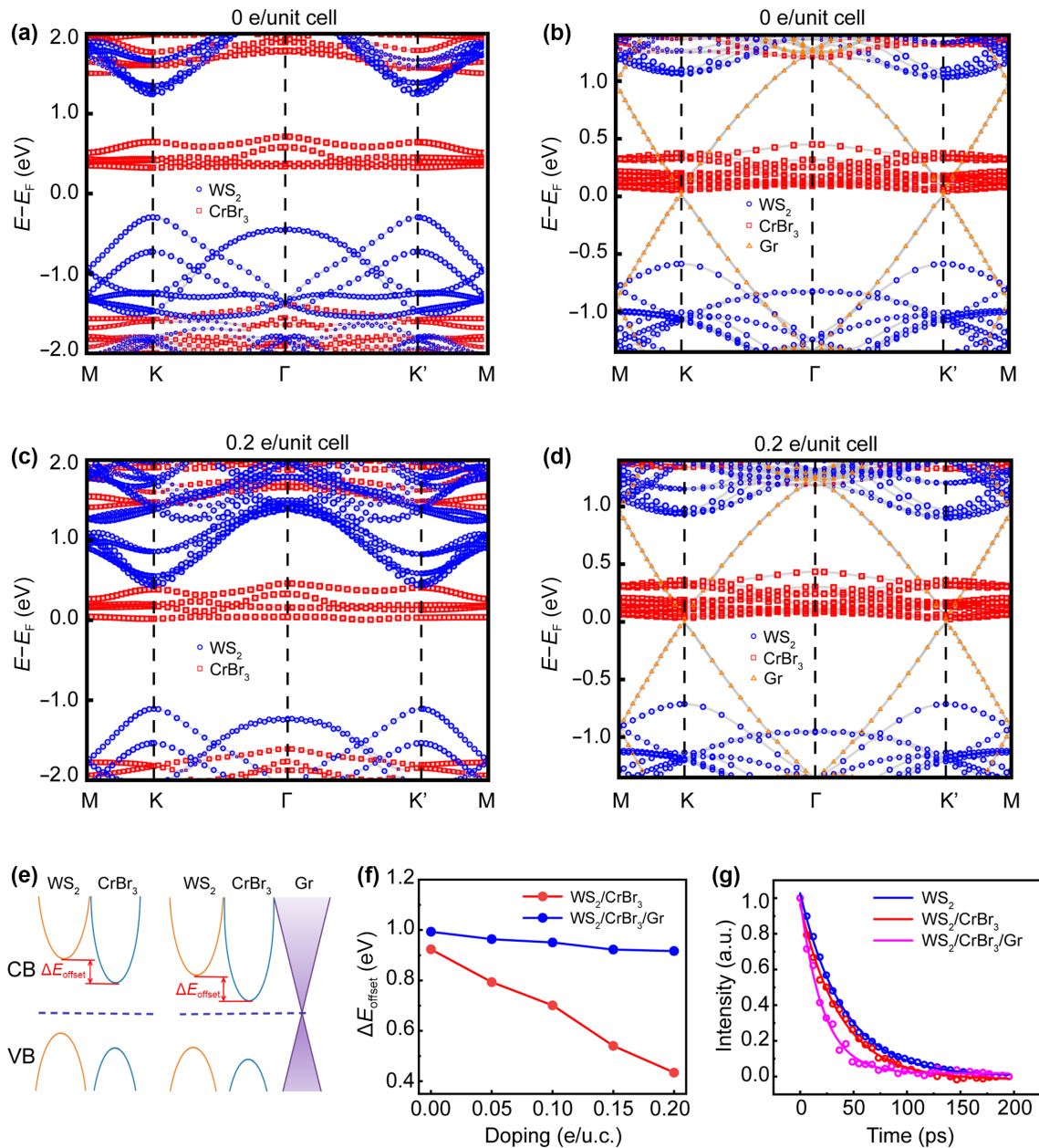


Figure 4 Electronic band structures of WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures. (a) and (b) Band structures of WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures, respectively. Different colors represent the contributions from different materials. (c) and (d) Band structures of the WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures with a 0.2 e/u.c. electron doping, respectively. (e) Schematic diagrams of the band structure for WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures. (f) Conduction band offset of WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures under different electron-doping concentrations. (g) Time-resolved PL spectra of the X^T exciton in monolayer WS₂, WS₂/CrBr₃, and WS₂/CrBr₃/Gr heterostructures.

that the charge transfer rate between WS₂ and CrBr₃ is significantly enhanced, thereby leading to a sharp decrease in the PL intensity. To further quantify the transfer rate in the two kinds of heterostructures, we calculate the interlayer charge transfer time τ_{CT} by using Eq. (2) [19]

$$QY = (1/\tau_{CT}) / (1/\tau_{CT} + 1/\tau_0) \quad (2)$$

where τ_0 and QY are the exciton lifetime of X^T exciton in monolayer WS₂ and the interlayer charge transfer quantum yield, respectively. As shown in Fig. 1(e), the PL intensity of the WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures is only 1/3.4 and 1/33.8 of that of the monolayer WS₂, respectively, and correspondingly, the

interlayer charge transfer quantum yield QY are estimated to be 2.4/3.4 and 32.8/33.8, respectively. According to Eq. (2), the interlayer charge transfer times τ_{CT} for the WS₂/CrBr₃ and WS₂/CrBr₃/Gr heterostructures are calculated to be approximately 17.3 and 1.3 ps, respectively. In previous reports, TMDC/Gr heterostructures, exemplified by WS₂/Gr, MoS₂/Gr, have been demonstrated to exhibit the characteristic of ultrafast charge transfer, with the electron transfer time being the order of picosecond [37–39], which is almost consistent with that in our WS₂/CrBr₃/Gr heterostructure. This finding suggests that ultrafast charge transfer between CrBr₃ and graphene can effectively promote spin-charge transfer between WS₂ and CrBr₃, which is consistent with the above theoretical analysis in Fig. 4(f).

Based on the above analysis, we have drawn a schematic diagram illustrating the mechanism of the enhanced chirality-dependent valley polarization. Figures 5(a) and 5(b) show the dynamics process of spin-selective charge transfer in the $\text{WS}_2/\text{CrBr}_3$ heterostructure after being excited by σ^+ and σ^- light, respectively, under a downward saturated magnetic field. Under a σ^+ (or σ^-) light excitation, the spin-up (or spin-down) electrons in the k (or k') valley of WS_2 are excited to their conduction band, and then some of the spin-up (or spin-down) electrons relax to spin-down (or spin-up) electrons by intervalley scattering or spin-flip. In the case of σ^+ light excitation, as shown in Fig. 5(a), a part of spin-down electrons is transferred to CrBr_3 due to the spin-selective charge transfer between WS_2 and CrBr_3 , which increases the concentration difference between the spin-up and spin-down electrons in the conduction band of WS_2 , thus enhances the valley polarization (see Figs. 2(c)–2(e)). Meanwhile, for the case of σ^- light excitation, as shown in Fig. 5(b), the predominant spin-down charges in the conduction band of WS_2 are partially transferred to CrBr_3 , which instead reduces the concentration difference between the spin-up and spin-down electrons and thus its valley polarization (see Figs. 2(c)–2(e)). The different variation trends of valley polarization under σ^+ and σ^- light excitations give rise to the valley polarization splitting, namely, chirality-dependent valley polarization. Nevertheless, due to the relatively long charge transfer time (13.8 ps), a part of the flipped electrons still accumulates in the

opposite valley, rendering only a moderate valley polarization splitting. When a few-layered graphene is coupled with the $\text{WS}_2/\text{CrBr}_3$ heterostructure, the dynamics process of interlayer charge transfer experiences a significant change. As shown in Fig. 5(c), under a σ^+ light excitation, a part of spin-down electrons in WS_2 is transferred to CrBr_3 , similar to that happened in $\text{WS}_2/\text{CrBr}_3$ heterostructure. Remarkably, due to the coupling with graphene, ultrafast transfer of the spin-down electrons happens from CrBr_3 to graphene. As a result, a large ΔE_{offset} is still maintained between WS_2 and CrBr_3 , in line with the theoretical prediction illustrated in Fig. 4 and effectively shortens the interlayer spin-charge transfer time from 17.3 to 1.3 ps. Since the transfer time is significantly shorter than the exciton lifetime in the $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure, there will be a larger concentration difference between spin-up and spin-down electrons compared to that in $\text{WS}_2/\text{CrBr}_3$ heterostructure, thus the valley polarizations are further enhanced remarkably. Besides, under a σ^- light excitation, as depicted in Fig. 5(d), due to the ultrafast spin-charge transfer between WS_2 and CrBr_3 in $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure, the concentration difference between spin-up and spin-down electrons in WS_2 is further decreased compared with that in $\text{WS}_2/\text{CrBr}_3$ heterostructure, which then leads to the reduction of valley polarization. The synergy of these effects results in the giant valley polarization splitting of up to 37.9%.

Inspired by the aforementioned mechanism, we fabricated metal-

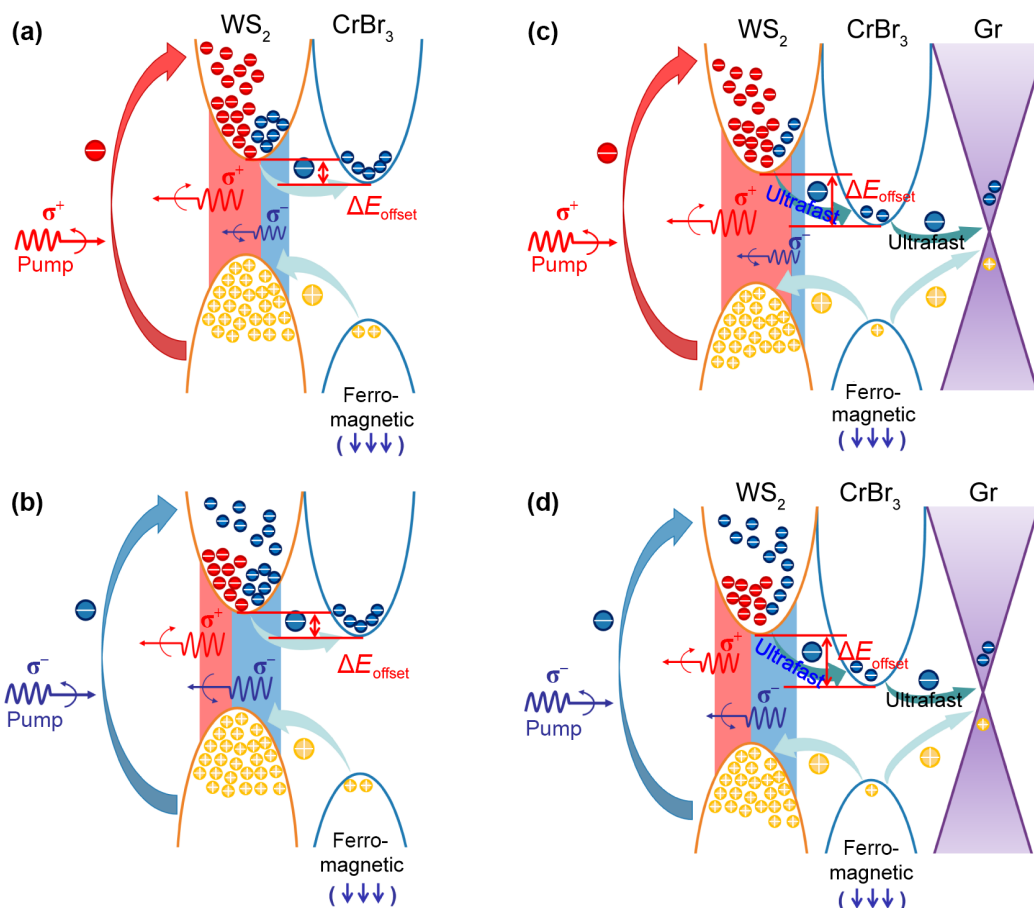


Figure 5 Mechanism of enhanced chirality-dependent valley polarization. (a) and (b) Schematic diagram of interlayer spin-selective charge transfer in the $\text{WS}_2/\text{CrBr}_3$ heterostructure under σ^+ and σ^- light excitation, respectively. (c) and (d) Schematic diagram of interlayer spin-selective charge transfer in the $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure under σ^+ and σ^- light excitation, respectively. The saturation magnetization direction of CrBr_3 is downward. The red and blue wide arrows represent the transition process of photogenerated carriers under σ^+ and σ^- light excitation, respectively. The red and blue small spheres in the conduction band represent the spin-up and spin-down electrons, respectively, while the yellow spheres in the valence band represent the holes.

semiconductor-metal (MSM)-type circularly-polarized-light photodetectors based on the two different heterojunctions (see Figs. 6(a) and 6(b)). Figures 6(c) and 6(d) show their I - V characteristic curves in response to circularly polarized light under different magnetic fields. We calculated their circular anisotropy ratio (CAR) by the following Eq. (3) [40]

$$\text{CAR} = 2 \frac{i(\sigma^{+/-}) - i(\sigma^{-/+})}{i(\sigma^{+/-}) + i(\sigma^{-/+})} \quad (3)$$

where $i(\sigma^{+/-})$ represents the photocurrent under σ^+ and σ^- light excitation, respectively.

The CAR of the $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ photodetector is improved by 76% compared with the $\text{WS}_2/\text{CrBr}_3$ detector, i.e. from 50% and 46% to 88% and 78% at a bias voltage of 10 V under the magnetic fields of ± 1500 Gs, respectively. Meanwhile, the responsivity of the $\text{WS}_2/\text{CrBr}_3$ photodetector is 1.0×10^{-4} A/W under an incident optical power of 0.5 mW, while that of the $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ photodetector increases to 4.7×10^{-4} A/W, corresponding to an enhancement of approximately 370%. This indicates that, with the interfacial coupling of graphene, the polarization response is greatly improved due to the ultrafast transfer of spin carriers. This result not only confirms the significant potential of $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure for achieving high-sensitivity circularly polarized detection but also highlights the effectiveness of regulating exciton dynamics regulation through proximity coupling engineering to optimize optoelectronic device performance.

3 Conclusions

In summary, we demonstrate a method of controlling exciton dynamics through the proximity coupling effect and achieve an enhanced valley polarization in $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure. It has been discovered that the spin-charge transfer rate between WS_2 and CrBr_3 is highly dependent on the conduction band offset in vdWs heterostructure. Compared with the $\text{WS}_2/\text{CrBr}_3$ heterostructure, the $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure maintains a larger conduction band offset under light irradiation due to the

graphene-assisted charge extraction effect, which leads to a much faster interlayer spin-charge transfer process. This unique property leads to a significant reduction in the spin-charge transfer time between WS_2 and CrBr_3 from 17.3 to 1.3 ps, which is substantially lower than the exciton recombination lifetime in WS_2 . Accordingly, the concentration difference between spin-up and spin-down electrons greatly increases, leading to a remarkable improvement in the valley polarization. The degree of valley polarization and polarization splitting of X^τ exciton in WS_2 are enhanced by 32% and 261%, respectively. Following this idea, circularly-polarized photodetectors were developed, showing remarkably improved circular dichroism and polarization response. This work paves a novel way to efficiently manipulate the valley degree of freedom in vdWs heterostructures, holding a great potential for the development of next-generation valleytronic devices.

4 Experiments and calculations

4.1 Sample fabrication

Monolayer WS_2 , few-layered CrBr_3 , and graphene were exfoliated from bulk crystals using adhesive tape and polydimethylsiloxane (PDMS) and then stacked on a SiO_2/Si substrate by an alignment transfer technique. Monolayer graphene was used in our experiments. The thickness of CrBr_3 flakes was controlled to be below 8 nm. The CrBr_3 and graphene layers were stacked with a twist angle of $\sim 0^\circ$ [41]. The samples were annealed for 3 h at 120 $^\circ\text{C}$ in an atmosphere of 200 sccm Ar and 10 sccm H_2 .

4.2 Characterization

Raman spectra of different samples were acquired using a Raman spectrometer with a 532 nm excitation laser. Circularly polarized PL spectra were measured by using a custom-built confocal spectroscopy system, which was equipped with a 532 nm steady-state laser. Exciton lifetime measurements were performed by using a transient fluorescence spectroscopy system with a 515 nm femtosecond laser. Precise temperature control down to 9 K was

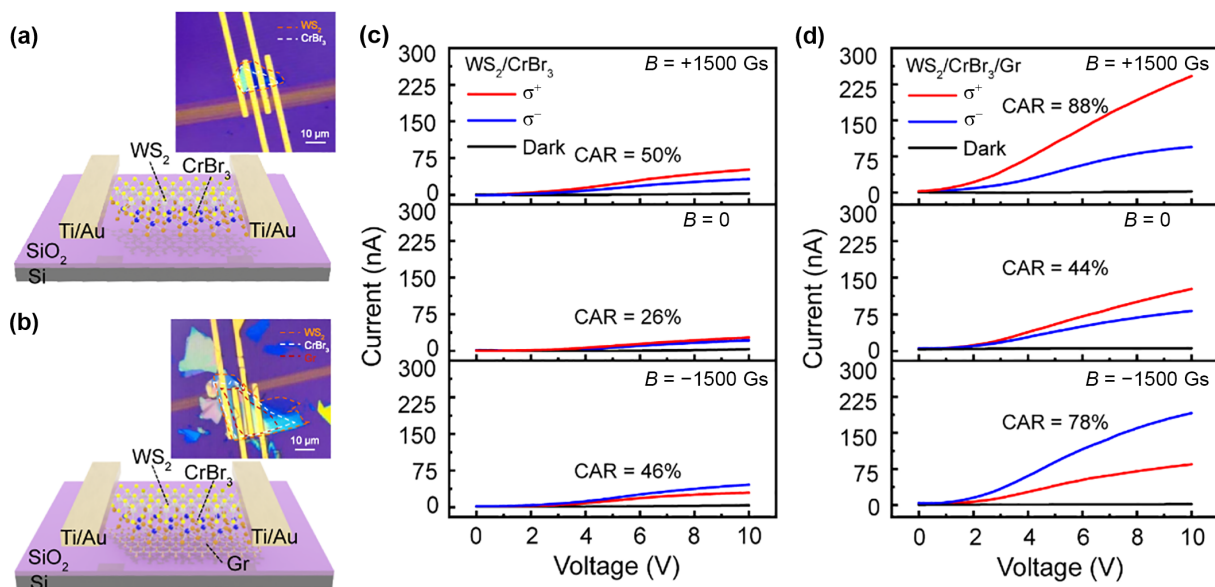


Figure 6 Circular-polarization-response of the photodetectors. (a) and (b) Schematic diagram of the circular-polarization-response photodetector based on $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures, respectively. The insets are the optical microscope images. (c) and (d) Circular photocurrent curves under different magnetic fields for $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ photodetectors, respectively. The measurement temperature was 9 K.

achieved using a closed-loop cryostat that was integrated with a temperature controller.

4.3 Devices fabrication and characterization

The structure of photodetector was patterned via direct-write laser photolithography (TuoTuo Technology, TTT-07-UV Litho-ACA). Ti/Au electrodes were deposited using electron-beam evaporation. Photocurrent measurements were conducted in a cryostat integrated with an electromagnet, and the signals were detected by a semiconductor parameter analyzer (Agilent B2901A). A 532-nm laser was used as the light source, and the left and right circularly polarized lights were generated by linear polarizers and quarter-wave plates. The measurement temperature was 9 K.

4.4 First-principles calculations

The electronic band structures of $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures were calculated by using Vienna *ab initio* simulation package. A $2 \times 2 \times 1$ WS_2 supercell and a $1 \times 1 \times 1$ CrBr_3 unit cell are constructed for the $\text{WS}_2/\text{CrBr}_3$ heterostructure, while a $4 \times 4 \times 1$ WS_2 supercell, a $2 \times 2 \times 1$ CrBr_3 supercell, and a $5 \times 5 \times 1$ Gr supercell were constructed for the $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure. A vacuum thickness of 20 Å along the z axis was used to isolate the interactions caused by periodic extensions. Generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof was employed to describe exchange–correlation function. In order to include the effective on-site Coulomb interactions of Cr atom, the DFT+U method with Hubbard parameter $U_{\text{eff}} = 2.1$ eV was employed. The DFT-D3 method was considered for the longer-ranged correlation in evaluating vdWs interaction for multi-layered 2D materials. For the $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure, we employed a $3 \times 3 \times 1$ Monkhorst-Pack k-point grid to sample the Brillouin zone and used a plane-wave cutoff energy of 400 eV. And for the $\text{WS}_2/\text{CrBr}_3$ heterostructure, we employed a $5 \times 5 \times 1$ Monkhorst-Pack k-point grid to sample the Brillouin zone and use a plane-wave cutoff energy of 500 eV. The conjugate-gradient algorithm was used for structural relaxation until the Hellmann–Feynman force on each atom was less than 0.01 eV/Å and the energy was less than 1×10^{-5} eV.

Electronic Supplementary Material: Supplementary material (PL spectra and valley polarization of monolayer WS_2 , valley polarization of $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructure, theoretical models of $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures, binding energy of $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures with different stacking configurations, and electronic band structures of $\text{WS}_2/\text{CrBr}_3$ and $\text{WS}_2/\text{CrBr}_3/\text{Gr}$ heterostructures with different doping levels) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908802>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. Y.: Data curation, project administration, validation, writing manuscript, experimental design. M. Y. L.: Data curation, project administration, validation, experimental design. J. H.: Data curation, project administration, validation, experimental design. J. W. G.: Project administration, experimental design. Y. X. Z.: Project administration, validation. W. W.: Project administration, validation. J. P. Z.: Project administration, validation. B. Y. Z.: Project administration, validation. C. H. Z.: Project administration, validation. X. L. Z.: Project administration, funding acquisition, writing manuscript. X. L.: Project administration, funding acquisition, writing manuscript. Y. P. W.: Project administration, funding acquisition, writing manuscript. Z. M. W.: Project administration, funding acquisition, writing manuscript. J. Y. K.: Project administration, funding acquisition, writing manuscript. All authors have approved the final manuscript.

Use of AI statement

None.

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