

Letter

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Harnessing in-plane optical anisotropy in WS_2 through ReS_2 crystal

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Abstract: In this work, we explore how the optical properties of isotropic materials can be modulated by adjacent anisotropic materials, providing new insights into anisotropic light-matter interactions in van der Waals heterostructures. Using a WS_2/ReS_2 heterostructure, we systematically investigated the excitation angle-dependent photoluminescence (PL), differential reflectance, time-resolved PL, and power-dependent PL anisotropy of WS_2 . Our findings reveal that the anisotropic optical response of WS_2 , influenced by the crystallographically low symmetry and unique dielectric environment of ReS_2 , significantly impacts both the optical and temporal behavior of WS_2 . We observed that the emission anisotropy increases with optical power density, highlighting that anisotropic localization of photo-generated carriers and subsequent charge transfer dynamics are key contributors to the polarization-sensitive optical response. These findings provide a framework for leveraging optical density-sensitive anisotropy mirroring to design advanced anisotropic optoelectronic and photonic devices.

Keywords: transition metal dichalcogenides; anisotropy; photoluminescence; charge transfer

1 Introduction

Two-dimensional (2D) group VI transition metal dichalcogenides (TMDs) exhibit direct bandgaps in their monolayer

(1L) [1], [2] with near-unity quantum yield [3], even at high pump powers [4] and valley selective excitation at band edges [5]–[8]. In their optical properties, excitons, quasiparticles consisting of electron-hole pairs, play a key role due to the reduced dielectric screening of Coulomb interactions, which allows a large exciton binding energy with excitonic states even at room temperature [9], [10], long diffusion length [11], [12], and formation of the various exciton species [13], [14]. Owing to the 3-fold rotational symmetry, group VI TMDs exhibit in-plane isotropic physical properties [15].

Anisotropic 2D materials can serve as templates for isotropic group VI TMDs to induce anisotropy in their physical properties [16]. Low-symmetry 2D materials, such as black phosphorus (BP) and transition metal monochalcogenides (TMMs), show anisotropy in their physical properties due to structural anisotropy from in-plane atom arrangement [17], [18]. However, these materials struggle with degradation under ambient conditions for BP [19] or low exfoliation yield for TMMs [20]. Group VII TMDs, such as ReS_2 , exhibit anisotropic physical properties arising from distorted 1T structure, characterized by Re–Re atoms in a zig-zag chain-like geometry along the b -axis. This unique arrangement leading to triclinic symmetry and the stability even under ambient conditions positions ReS_2 as a promising 2D materials for harnessing polarization-sensitive optical excitation and emission [21], [22].

Furthermore, ReS_2 can form type-II heterojunctions with most group VI TMDs [23], which are widely applied in optoelectronic devices [24]–[27], memristors [28], and radiation enhancement [29] through efficient fast charge transfer between them [30]. While most studies focus on device applications leveraging efficient charge separation in type-II heterojunctions, the understanding of induced anisotropy of group VI TMDs remains limited. As ReS_2 exhibits a limited quantum yield due to its indirect bandgap, integrating ReS_2 with group VI TMD monolayers with direct bandgap enables the mirroring of its anisotropic optical responses while benefiting from the high quantum yield of the group VI materials [31].

In-plane anisotropic optical responses in ReS_2 are attributed to its anisotropic optical oscillator strength relative to the excitation polarization, which leads to

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polarization-dependent photoemission, an anisotropic dielectric function, and a directional absorption coefficient [32]. Building on these anisotropic optical properties of ReS₂, the anisotropic response of WSe₂ on ReS₂ has been explained by directional dielectric screening, which induces exciton localization due to the underlying ReS₂ [33]. Additionally, although it has been suggested that the polarization behaviors of WS₂ PL induced by ReS₂ was due to anisotropic moiré potential leading to anisotropic absorption of bright excitons [34], previous work has primarily focused on demonstrating the anisotropy in photoluminescence (PL) and Raman scattering without systematic studies of the mechanisms of anisotropic optical responses.

In this work, we unveil the underlying mechanisms that explain how an isotropic material adjacent to anisotropic material can exhibit anisotropic optical properties. To comprehensively investigate the optical responses of individual WS₂ and ReS₂ layers, as well as their heterostructure regions, we employ PL, differential reflectance (dR), and time-resolved PL (TRPL) measurements at room temperature. Furthermore, under various optical pumping conditions, we track the optical anisotropy of WS₂ on ReS₂ and seek to understand how the optical anisotropy in the isotropic material emerges from the anisotropic material, particularly in terms of photo-generated charge carrier behaviors. This comprehensive analysis allows us to explore the role of optical excitation in inducing the optical anisotropy in WS₂, originating from underlying ReS₂ with intrinsic structural nonsymmetry.

2 Results and discussion

To investigate the optical response of WS₂ influenced by adjacent anisotropic materials, we prepared a heterostructure consisting of monolayer WS₂ on multilayer ReS₂. Figure 1(a) illustrates a schematic of the fabricated WS₂/ReS₂ sample on a SiO₂/Si substrate, along with the configuration of the optical anisotropy measurement setup. The excitation angle (θ) is defined to be the angle between electric field of incident linearly polarized light and the *b*-axis of ReS₂. Figure 1(b) shows the optical microscope image of fabricated WS₂/ReS₂ heterostructure. It was prepared by mechanical exfoliation of ReS₂ flake onto SiO₂/Si, followed by the dry transfer of an exfoliated WS₂ flake on polydimethylsiloxane (PDMS) onto ReS₂. As the natural cleavage axis of ReS₂ corresponds to the *b*-axis during the mechanical exfoliation [22], [26], we could determine the *b*-axis, as illustrated in a white arrow.

To confirm the formation of the monolayer WS₂ and multilayer ReS₂ heterostructure, Raman spectroscopy was conducted (Supplementary Information, 1). In the WS₂ region, the monolayer was identified by the Raman frequency difference (65 cm⁻¹) between the in-plane E_{2g}^1 mode at 349 cm⁻¹ and the out-of-plane A_{1g} mode at 414 cm⁻¹ [35]. In contrast, the multilayer ReS₂ region exhibited multiple Raman peaks in the range of 100–250 cm⁻¹, including E_g modes and an A_g – like mode. The peak position difference between Mode III (146 cm⁻¹) and Mode I (134 cm⁻¹), corresponding to 13 cm⁻¹, indicates the presence of more than four layers of bulk ReS₂. This is consistent with our atomic force microscopy (AFM) topography scan and height profiles showing 134 nm in the ReS₂-only region and 136 nm in the WS₂/ReS₂ region (Supplementary Information, 2). In the overlapping WS₂/ReS₂ region, Raman spectra displayed characteristic peaks of both WS₂ and ReS₂ layers. A slight redshift of the ReS₂ A_g – like mode (0.4 cm⁻¹) in the heterostructure compared to the ReS₂-only region suggests charge transfer induced by interlayer coupling [27], [36]. In the WS₂/ReS₂ heterostructure, the A_{1g} mode of WS₂ was significantly suppressed due to its intrinsically low vibrational intensity and hybridization with the Raman modes of bulk ReS₂ offering enhanced dielectric environment. The crystallographic orientation of ReS₂, aligned along the *b*-axis, was confirmed by the enhanced ReS₂ A_g – like mode *V* at 210 cm⁻¹ under linearly polarized excitation light parallel to the *b*-axis (0°), compared to the excitation light perpendicular to the *b*-axis (90°).

We then investigated the anisotropic optical response of ReS₂ and WS₂ through excitation angle-dependent PL spectroscopy. The measurements were performed by rotating the sample while maintaining a fixed linear polarizer in the incident beam path and an analyzer in the collection beam path with cross-polarization configuration. At a θ of 0°, parallel to the *b*-axis (Figure 1(c)), the PL spectrum revealed dominant intralayer exciton resonance peaks from both WS₂ and ReS₂ layers.

The PL spectrum of WS₂ was deconvoluted into two peaks: a neutral exciton at 615 nm and a trion at 630 nm, corresponding to the intrinsic n-type characteristics of WS₂, with a trion binding energy of 42 meV [37]. Similarly, the PL spectrum of ReS₂ exhibited two neutral exciton peaks at 780 nm and 817 nm, which result from the splitting of spin-degenerate exciton states [33], [38]. The indirect exciton states in ReS₂ showed significantly lower PL intensities compared to the direct bandgap excitons of monolayer WS₂, due to nonradiative recombination dominated by phonon-assisted scattering processes outside the light cone at room temperature. In the WS₂/ReS₂ heterostructure,

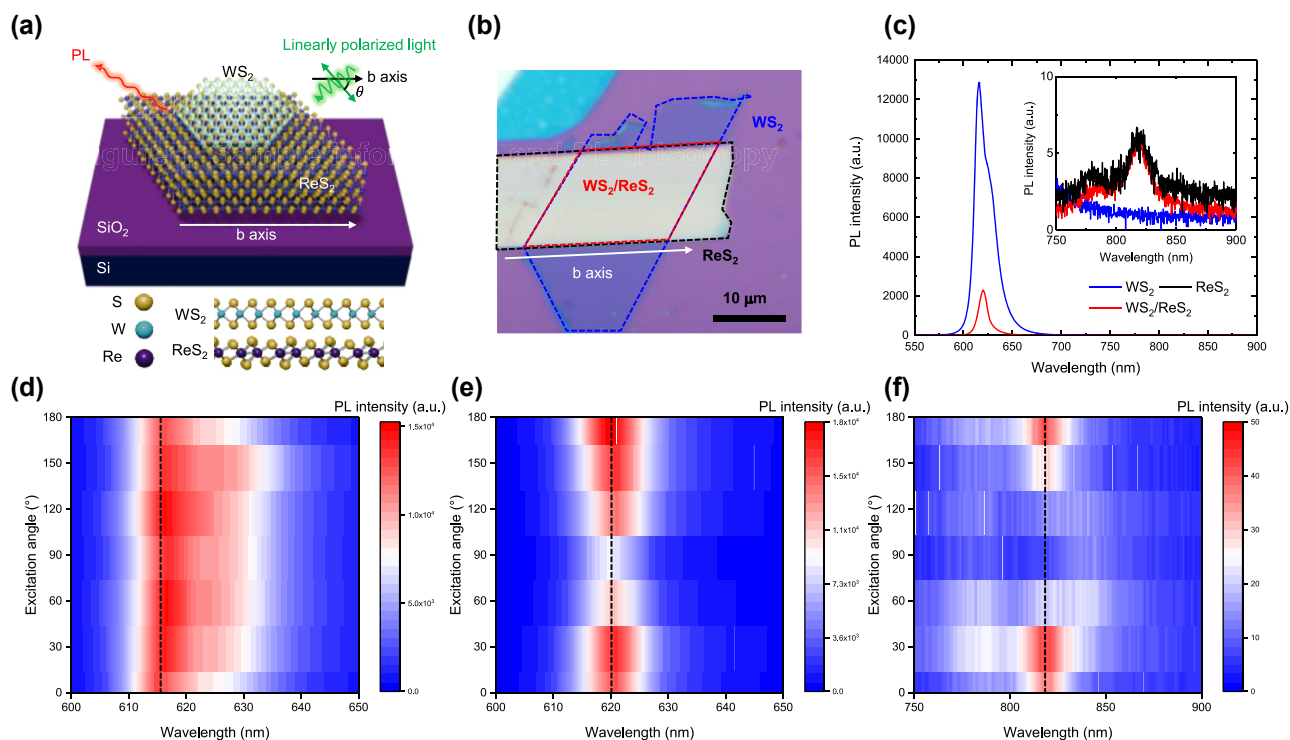


Figure 1: Structural Illustration and PL Characterization of WS₂/ReS₂ Heterostructure. (a) Schematic of fabricated WS₂/ReS₂ heterostructure and the side view of each layer. Linearly polarized light was excited with an excitation angle (θ), which is determined by the sample rotation. (b) Optical image of WS₂/ReS₂ heterostructure. (c) PL spectrum of WS₂ (blue), ReS₂ (black), and WS₂/ReS₂ (red) at excitation angle of 0°, with an inset showing magnified spectrum in the range of ReS₂ emission. Excitation angle-dependent PL spectra of (d) WS₂ and WS₂/ReS₂ in the ranges of (e) WS₂ emission and (f) ReS₂ emission.

excitons from both layers remained present, including red-shifted WS₂ neutral exciton peak from 615 nm to 620 nm due to the dielectric screening effect of ReS₂ [30], [33]. The intensities of intralayer excitons in heterostructure were noticeably suppressed, accompanied by a reduction in the trion PL intensity of WS₂, suggesting charge transfer between the two layers [30]. The interlayer exciton, an electron–hole pair spatially separated in individual layers, was not observed due to the valley mismatch between the monolayer WS₂ and ReS₂ layers, which prevents the simultaneous transition required for an efficient interlayer exciton formation [39].

Interestingly, we observed that the excitonic species of WS₂ at 620 nm, typically isotropic in nature exhibited anisotropic polarization-dependent PL intensity within the WS₂/ReS₂ heterostructure (Figure 1(d) and (e)). The highest PL intensities of WS₂ and ReS₂ at an excitation angle of 0°, along with their suppression at 90°, indicate that the distorted structure of ReS₂ in contact with WS₂ induces this anisotropic optical response (Figure 1(f)). By comparing the excitation angle-dependent PL intensities in individual WS₂ and ReS₂ layers, we confirmed that the isotropic emission of WS₂ was modulated by the anisotropic optical response of ReS₂ (Supplementary Information, 3).

To further substantiate our findings of anisotropic optical response of WS₂ in the heterostructure region, we performed reflectance measurements using a broadband halogen lamp with linearly polarized white light and collected the reflected light intensities using a confocal optical microscope. The configuration was identical to that used for PL measurements, utilizing a linear polarizer and analyzer with sample rotation to change the excitation angle. The differential reflectance ($\Delta R/R_0$) was plotted, where R and R_0 represent the reflectance spectra from the sample and the SiO₂/Si substrate, respectively (Figure 2). As shown in Figure 2(a), the $\Delta R/R_0$ spectrum of WS₂/ReS₂ under an excitation angle of 0° exhibits a local minimum at 620 nm corresponding to WS₂ exciton absorption resonance, which closely aligns with the PL peak position (Figure 1(c)). Additionally, heterostructure shows local minima at 690, 804, and 824 nm corresponding to the dips of ReS₂.

From the excitation angle-dependent $\Delta R/R_0$ spectrum in the 600–640 nm range (Figure 2(b)), we observed that the WS₂ exciton resonance dip feature at 620 nm displays periodicity at 90° intervals in WS₂/ReS₂. Notably, at 0°, the WS₂ dip closely resembles that of ReS₂, whereas at 90°, the dip resembles the dip from isotropic monolayer WS₂ of which intrinsic dips lack the excitation angle dependence.

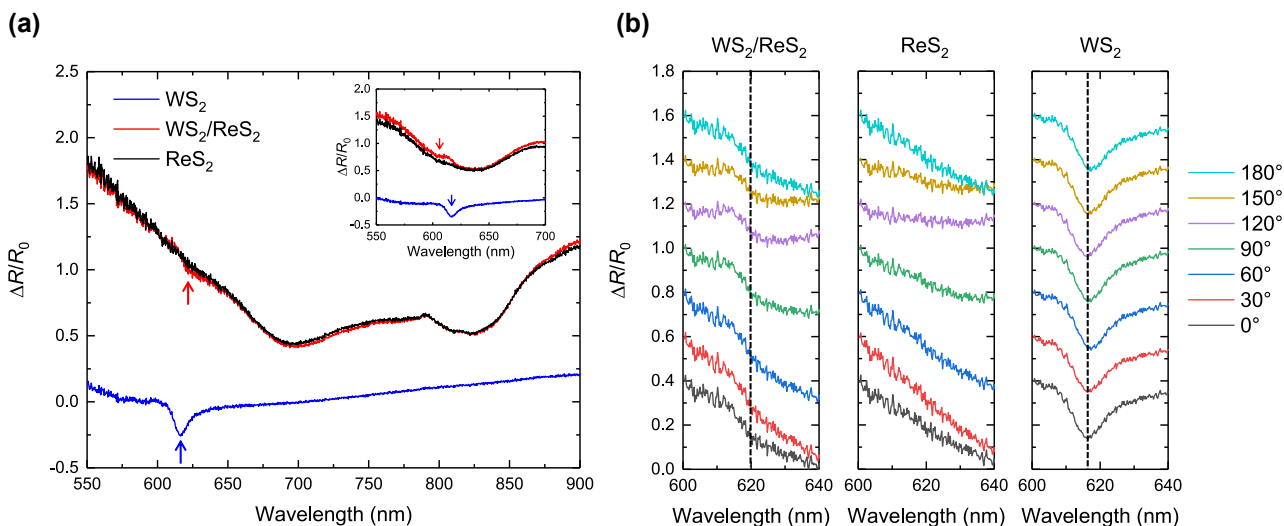


Figure 2: Differential Reflectance Characterization of WS₂/ReS₂ Heterostructure. (a) Differential reflectance of WS₂ (blue), ReS₂ (black), and WS₂/ReS₂ (red) at an excitation angle of 0°. The inset highlights the differential reflectance of each region in the wavelength range of 550–700 nm at an excitation angle of 90°. (b) Excitation angle-dependent differential reflectance spectra of WS₂/ReS₂, ReS₂, and WS₂ in the range of WS₂ absorption.

Assuming the dielectric contribution is dominated by the resonances of bound excitons, the broadening of the WS₂ dip at 0° is attributed to strong exciton resonance hybridization resulting from crystallographic orientation-dependent dielectric constant of ReS₂ as indicated by excitation angle-dependent $\Delta R/R_0$ spectrum (Supplementary Information, 4). Comparing the $\Delta R/R_0$ spectrum at an excitation angle of 90° to that at 0°, we observe a notable difference in the behavior of the WS₂/ReS₂ heterostructure, as illustrated in Figure 2(a) and its inset. At 0°, the dip in the $\Delta R/R_0$ spectrum of the heterostructure shows a smaller intensity than that of the individual ReS₂ layer, indicating enhanced absorption of WS₂ excitons. In contrast, at an excitation angle of 90°, the $\Delta R/R_0$ spectrum of ReS₂ undergoes a general blue shift of its reflectance dip compared to excitation angle of 0°, leading to the dip of ReS₂ in the WS₂/ReS₂ heterostructure moving closer to that of WS₂. This results in an increase in its optical transition energy and a slight blue shift of WS₂, along with higher intensity of $\Delta R/R_0$ indicating reduced absorption of WS₂ excitons than under excitation at 0°. These observations suggest that the anisotropic dielectric environment of ReS₂ significantly influences the WS₂ exciton resonance in the heterostructure.

The PL spectra primarily reflect both direct and indirect transitions and are more sensitive to radiative recombination during transitions to the lowest energy state. In contrast, the $\Delta R/R_0$ spectrum, which resonates with direct transitions, provides more comprehensive information about charge transitions. This allows us to uncover the dielectric environment mirroring effect in WS₂/ReS₂, which is not as apparent in the PL spectra.

To investigate the relationship between the optical anisotropy in temporal behaviors of excitons, we performed time-resolved photoluminescence (TRPL) measurements on WS₂/ReS₂ and WS₂ using a time-correlated single photon counting (TCSPC) system, coupled with the same cross-polarization setup used in PL measurements. A bandpass filter (610 nm ± 10 nm) was placed in the light path of the TCSPC to isolate the radiative recombination of neutral WS₂ excitons. In Figure 3(a), we compare the lifetime decay characteristics of WS₂ and WS₂/ReS₂ under an excitation angle of 0°.

To ensure accurate analysis of the decay curve and precise determination of the PL lifetime, the decay curves for each region were normalized to their highest PL intensities and fitted with an exponential decay equation, $I = I_0 e^{-t/\tau}$, to extract the exciton lifetime values, τ . Additionally, the time point where the normalized PL intensity equals to unity was used as the starting point for the decay analysis. The extracted lifetimes were $\tau_{\text{WS}_2/\text{ReS}_2} = 0.33 \pm 0.003$ ns, $\tau_{\text{WS}_2} = 0.32 \pm 0.004$ ns, indicating negligible differences. Interestingly, lifetime decay characteristics at excitation angle of 90° reveal $\tau_{\text{WS}_2/\text{ReS}_2}$ increases to 0.38 ± 0.004 ns, in contrast to $\tau_{\text{WS}_2} = 0.32 \pm 0.004$ ns, as shown in Figure 3(b) and (c) and Supplementary Information, 5. The previously reported PL lifetime of WS₂ and transient absorption decay in ReS₂/WS₂ heterostructures, which were observed to be shorter than those of monolayer WS₂ (within the 10–100 ps range) [26], [28], were not evident in our case.

Anisotropic lifetime of WS₂ in the heterostructure region can be attributed to band anisotropy in combination with the electron–phonon scattering [40], [41], as well

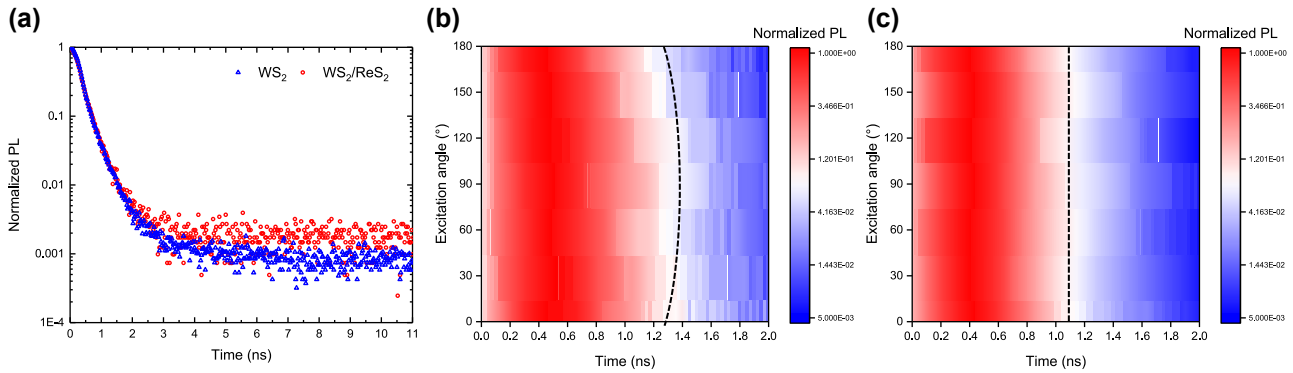


Figure 3: Time-Resolved PL Characterization of WS₂/ReS₂ Heterostructure. (a) Time-resolved PL decay characteristics in WS₂ (blue) and WS₂/ReS₂ (red) at an excitation angle of 0°. Excitation angle-dependent decay characteristics in (b) WS₂/ReS₂ and (c) WS₂.

as more efficient charge mobility and exciton diffusion coefficient along the *b*-axis of ReS₂. While more photocarriers are generated along the *b*-axis compared to the *a*-axis of ReS₂ [40], [42], as indicated by higher PL intensities and absorption at 620 nm at an excitation angle of 0°, the enhanced charge transport efficiency along the *b*-axis results in faster charge recombination in WS₂ on ReS₂. Consequently, slightly shorter lifetime is justified to cool hot electrons via electron–phonon coupling along the *b*-axis. This observation aligns with angle-dependent relaxation times previously reported in SnS and BP, which exhibits optical anisotropy induced by orthorhombic structures [43], [44].

In addition, our observed lifetime anisotropy of WS₂ in the WS₂/ReS₂ heterostructure region is consistent with previous time-resolved photoelectron emission microscopy results for WSe₂ on ReS₂ under controlled probe polarization [45]. In particular, the strong anisotropy of time constant suggests that interlayer charge transfer process is faster along the *b*-axis, due to faster evolution of excited electron distribution. The anisotropic lifetime of WS₂ in the WS₂/ReS₂ suggests that the crystal orientation of ReS₂ along the *a*- and *b*-axes may lead to variations in the band structure, including band dispersion flattening and the electron hopping behaviors [41], which can influence excitonic recombination lifetimes.

Lastly, we analyzed the power-dependent PL anisotropy by tracking the anisotropy parameter (*A*) defined as $(I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$, as a function of laser power. $I_{\max}$ and $I_{\min}$ represent the PL peak intensity at 0° and 90°, respectively, with $I_{\max}$ showing the maximum intensity at 0° and $I_{\min}$ corresponding to the minimum intensity at 90°. First, as shown in Figure 4(a), the PL intensity contrast at different excitation angles increases with higher laser power. Figure 4(b) and (c) present the PL spectra at various laser powers for excitation angles of 0° and 90°,

and the corresponding calculated *A* values, respectively. The anisotropy parameter *A* increases within the laser power range of 4–15 μW, while at a low power of 2 μW, the PL intensities decrease significantly due to insufficient optical excitation (Supplementary Information, 6 and 7). However, at the highest laser power of 47 μW, anisotropy parameter declines back to values observed in the 4 μW range, which implies the optical anisotropy influenced by optical densities of the photons.

The increase in *A* within the 4–15 μW laser power range can be attributed to not only the greater absorption of incident light enhancing the number of photo-generated carriers but also disparity in the amounts of the photo-generated carriers along the crystallographic axes. Specifically, at higher powers, the abundance of photo-generated carriers along the *b*-axis with excessive energy enhances wavefunction overlap, facilitating charge transfer from WS₂ to ReS₂ along the type-II band alignment [26], [28]. This effect is particularly pronounced when optical excitation occurs along the *b*-axis of ReS₂ (0°), where optical oscillator strength is strongest originating from anisotropic electronic band structure. In this case, the effective charge transfer and separation of photocarriers become more significant, leading to stronger interlayer coupling between WS₂ and ReS₂. This coupling, combined with the inherent anisotropy of ReS₂ due to its crystallographic axes, amplifies the optical anisotropy of WS₂ at high optical densities.

The enhanced anisotropy of WS₂ at high optical densities, resulting from an increased disparity in the amounts of photogenerated carriers depending on the optical excitation direction, is further supported by data in Supplementary Information, 8, where the integrated PL areas at 620 nm and 630 nm are compared. Each wavelength of the PL peak indicates radiative recombination of neutral exciton (620 nm) and trion (630 nm) [33], [37]. At an excitation angle of 0°, the proportion of the 630 nm area is higher

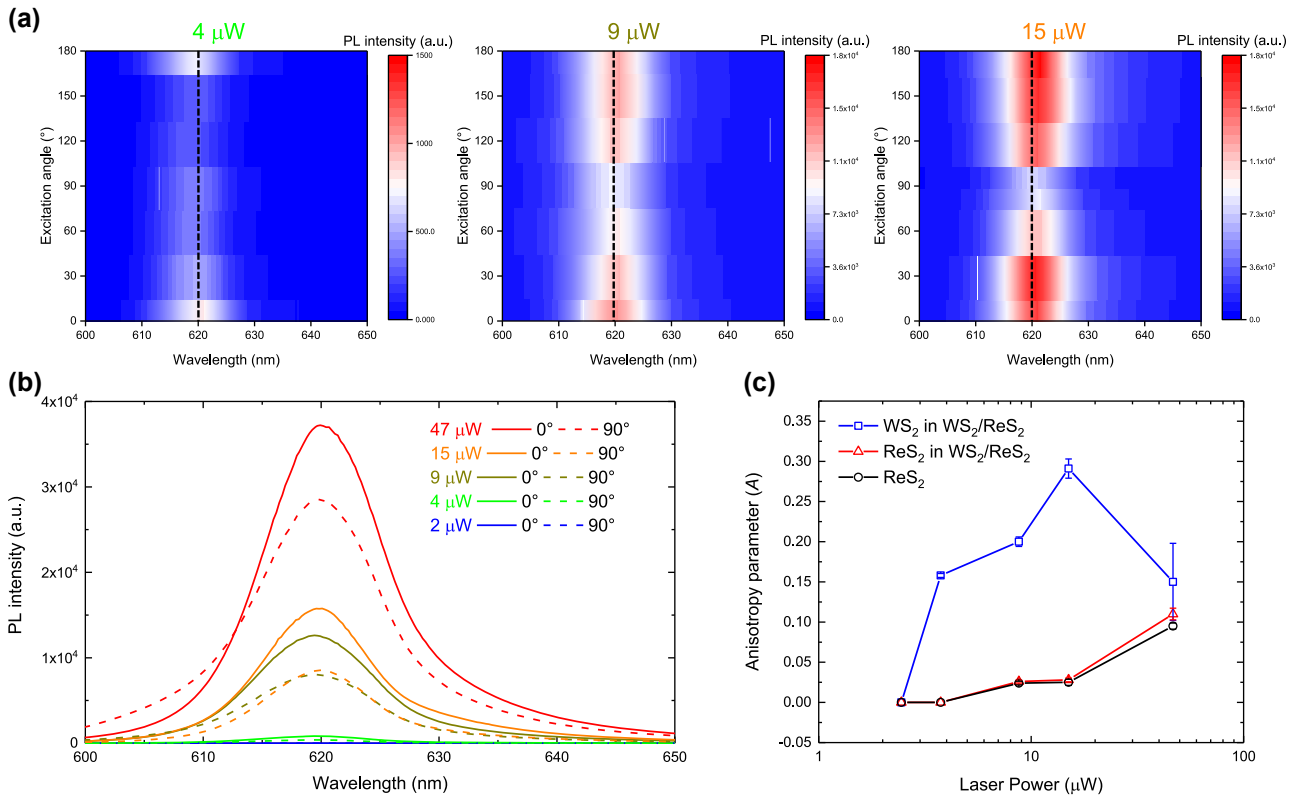


Figure 4: Laser Power-Dependent PL Characterization of WS₂/ReS₂ Heterostructure. (a) Excitation angle-dependent PL spectra of WS₂/ReS₂ in the WS₂ emission range at laser powers of 4 μW, 9 μW, and 15 μW. (b) Power-dependent PL spectra at excitation angles of 0° and 90°, with laser power varying from 2 μW to 47 μW. (c) Anisotropy parameter of WS₂ emission in WS₂/ReS₂ (blue), ReS₂ emission in WS₂/ReS₂ (red), and ReS₂ emission in ReS₂ itself (black), as a function of laser power.

at 15 μW than at 4 μW, suggesting an increase in trion population due to a higher optical doping carrier density. Additionally, as the excitation angle changes from 90° to 0°, the integrated area at 630 nm increases, indicating that the radiative recombination path of trions become more prominent due to anisotropically enhanced localizations of photo-generated carriers along the *b*-axis. The faster decay of WS₂ neutral exciton in WS₂/ReS₂ at an excitation angle of 0° further supports the reduction in the integrated PL area of neutral excitons at the same angle.

On the other hand, the abnormal decrease in anisotropy at 47 μW can be explained by the increased role of electron–phonon coupling due to excessive thermal energy. Under these high power conditions, the trion population no longer increases as it did at 15 μW. Instead, the integrated 630 nm area remains comparable to that observed at 15 μW at excitation angle of 0°. The excessive thermal energy increases the likelihood of charge carriers being excited to higher energy states far from band edges, accompanied by phonon scattering. In heterostructures, enhanced electron–phonon coupling can lead to phonon softening, which induces weakening of interlayer coupling

caused by an increased interlayer distance [46]–[48]. When the photon density of the laser exceeds the critical range, the increased interlayer distance impedes the efficient wavefunction overlap between the layers [49], [50], causing WS₂ on ReS₂ to lose its anisotropic optical response.

Furthermore, in contrast to the decrease in the anisotropy parameter of WS₂ in the WS₂/ReS₂ heterostructure at the 47 μW, the anisotropy parameter of ReS₂ in the heterostructure and ReS₂ itself steadily increases. Therefore, we hypothesize that the anisotropic optical response of WS₂, particularly induced by ReS₂, arises from optical excitation, which generates photocarriers whose amounts vary with the optical excitation angle. At higher optical densities, disparity in population of localized photogenerated carriers increases, thereby enhancing the optical anisotropy in WS₂ on ReS₂.

3 Conclusions

In this study, we investigated how an isotropic material, WS₂, adjacent to an anisotropic material, ReS₂, can

exhibit anisotropic optical responses. Through excitation angle-dependent PL, differential reflectance, time-resolved PL, and power-dependent PL anisotropy analyses, we demonstrated that the isotropic emission response of WS₂ is influenced by the anisotropic optical properties of ReS₂, which has crystallographically low symmetry. By comparing the excitation angle-dependent PL intensities of WS₂ on ReS₂ with those of individual WS₂ and ReS₂ layers, we confirmed that the anisotropic optical response of ReS₂ modulates the optical behavior of WS₂. In differential reflectance measurements, we observed that the anisotropic dielectric environment of ReS₂ influences the WS₂ exciton resonance. The shorter emission lifetime anisotropy in the WS₂/ReS₂ under excitation parallel to the *b*-axis indicates that the efficient charge mobility along the *b*-axis of ReS₂ facilitates faster charge transfer. We identified that anisotropic charge transport originating from band structure anisotropy, along with electron–phonon scattering, should be carefully considered when interpreting the optical and temporal dynamics of WS₂ excitons in WS₂/ReS₂ heterostructure.

The increasing anisotropy at higher optical photon densities suggests that the enhanced population of photo-generated carriers along the *b*-axis, along with their disparity, plays a key role in optical anisotropy. These results highlight the importance of carefully considering optical excitation, in conjunction with structural anisotropy, when interpreting optical responses in heterostructures consisting of isotropic and anisotropic material. This work provides valuable insights into harnessing anisotropic exciton states for the development of advanced anisotropic optoelectronic and photonic devices by symmetry breaking in 2D materials.

4 Materials and methods

4.1 Fabrication of WS₂/ReS₂ heterostructure

To assemble the WS₂/ReS₂ heterostructure, we used mechanical exfoliation and dry transfer. Multilayer ReS₂ and monolayer WS₂ were exfoliated from their bulk crystals (2D Semiconductors and HQ Graphene) with mechanical exfoliation (the Scotch tape method) onto SiO₂/Si substrate and PDMS (Gel-Pak X4), respectively. We prepared WS₂ with a cleaved edge along the isotropic crystallographic direction, exhibiting 60° angles at the corners, and ReS₂ with a clearly defined *b*-axis along the anisotropic crystallographic direction. We stacked monolayer WS₂ onto multilayer ReS₂ on SiO₂/Si with aligning the crystal axes, utilizing a rotation stage (Zaber XL5M025A) having an angular accuracy of up to 80 millidegrees (0.08°) to

minimize atomic reconstruction between two layers. We used a transfer stage (Newport XYZ-PPP) inside a humidity-controlled glovebox to reduce the effects of adsorbates, contaminants, and oxidation of sample during transfer.

4.2 Optical and topographical characterizations

PL/Raman spectroscopy, differential reflectance spectroscopy, and time-resolved PL measurements were conducted using a customized confocal Raman microscope (NanoBase XPER Raman system) at room temperature. For PL/differential reflectance and Raman measurements, gratings with 300 lines per mm (lpmm) and 1800 lpmm were used, respectively, providing spectral resolutions of 0.9 nm and 4.3 cm^{−1}. For excitation angle-dependent microscopic investigations, a linear polarizer was incorporated in the incident laser path to align the laser polarization direction with the *b*-axis of ReS₂. An analyzer in a cross-polarization configuration was added, and the sample was manually rotated in 30° increments to adjust the excitation angle. Area mapping of optical responses was performed with lower than 1 μm spatial resolution using a galvo-mirror scanner, and area-averaged spectra were extracted to minimize discrepancies caused by surface roughness in single-point spectra.

For PL/Raman spectroscopy, a continuous-wave 532 nm green laser (Cobolt Tor) was used as the excitation source and emitted and scattered light was collected by the detector. Laser power was controlled using a continuous neutral density filter. For reflectance measurements, a broadband halogen lamp (U-LH100L-3) served as the excitation source. The sample was globally illuminated with white light, and the reflectance signal from the target area (selected via a galvo mirror) was collected using a confocal setup with 300 lpmm grating. Charge-coupled device camera (iVac 316, Andor) was employed for detection of PL/Raman and reflectance signals.

TRPL measurements were performed using a time-correlated single photon counting (TCSPC) system, consisting of a single-photon avalanche detector (PDM series, PicoQuant) and time-tagging electronics (TimeHarp 260, PicoQuant) with a timing resolution of 30 ps and 25 ps, respectively. A 510 nm ps pulsed diode laser (PDL 800D, PicoQuant) operating at an 80 MHz repetition rate was used for excitation. To isolate 510 nm excitation light and emission signals from neutral WS₂ excitons, a 510 ± 10 nm bandpass filter was placed in the excitation path, and a 610 ± 10 nm bandpass filter was positioned before the detector.

Atomic force microscopy (AFM) (Vista One, Molecular Vista) was used for surface topography imaging and roughness analysis. A gold-coated silicon tip with a <35 nm radius (Q:NSC15/Cr-Au, MikroMasch) was employed for non-contact mode AFM scans. The scanning covered the sample area with a resolution of 512 pixels and a scan speed of 8 $\mu\text{m/s}$.

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Author contributions: All authors have accepted responsibility for the entire content of this manuscript and consented to its submission to the journal, reviewed all the results, and approved the final version of the manuscript. SK, TY, PJM, and SN initiated the research and wrote the manuscript. SK and SN designed the experiments. SK, TY, and PJM conducted all experiments.

Conflict of interest: Authors state no conflict of interest.

Data availability: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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