Phase-Engineering-Induced Generation and Control of Highly Anisotropic and Robust Excitons in Few-Layer ReS$_2$

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Supporting Information

ABSTRACT: The anisotropic exciton behavior in two-dimensional materials induced by spin–orbit coupling or anisotropic spatial confinement has been exploited in imaging applications. Herein, we propose a new strategy to generate high-energy and robust anisotropic excitons in few-layer ReS$_2$ nanosheets by phase engineering. This approach overcomes the limitation imposed by the layer thickness, enabling production of visible polarized photoluminescence at room temperature. Ultrasonic chemical exfoliation is implemented to introduce the metallic T phase of ReS$_2$ into the few-layer semiconducting Td nanosheets. In this configuration, light excitation can readily produce “hot” electrons to tunnel to the Td phase via the metal–semiconductor interface to enhance the overlap between the wave functions and screened Coulomb interactions. Owing to the strong electron–hole interaction, significant increase in the optical band gap is observed. Highly anisotropic and tightly bound excitons with visible light emission (1.5–2.25 eV) are produced and can be controlled by tailoring the T phase concentration. This novel strategy allows manipulation of polarized optical information and has great potential in optoelectronic devices.

Current optoelectronic devices composed of two-dimensional (2D) materials are mainly based on the band gap as the optical response to encode electronic information in which photoluminescence (PL) and absorption are two important spectroscopic techniques to realize this goal. More efficient devices for optical information storage and processing can be produced if the degree of freedom of PL polarization is also introduced. Such an optical device requires the generation and control of PL polarization. That is, the PL needs to display polarized characteristics and is in the visible region. For example, because of the absence of the inversion symmetry in the monolayered MoS$_2$ structure, valley polarization induced by the spin–orbit coupling effect is adopted to obtain circularly polarized PL in the visible region. However, this performance is strongly related to the MoS$_2$ layer thickness because of the crossover from the direct band gap of the monolayer to the indirect band gap of the multilayer. To overcome this difficulty, linearly polarized light has been used to directly excite anisotropic 2D materials to generate excitons with particular spatial confinement and to manipulate the PL behavior. Although this polarization strategy slightly depends on the thickness of the few-layer materials, the PL energies deviate from the visible region.

With regard to 2D transition-metal dichalcogenide semiconductors (TMDCSs) with a considerable band gap ($E_g \sim 1$ to $2$ eV), the symmetric hexagonal structure cannot produce anisotropic excitonic emission by anisotropic quantum confinement. Although monolayered black phosphorus has an anisotropic symmetry, the polarization-resolved PL from anisotropic bright exciton (1.3 eV) is beyond the visible range because of the relatively small band gap. Unlike hexagonal 2D TMDCSs, layered ReS$_2$ crystallizes from the distorted 1T diamond-chain structure (Td phase) with a triclinic symmetry as a result of charge decoupling from an extra valence electron of the Re atom. The structural distortion gives rise to much weaker interlayer coupling; hence, band renormalization is absent, and bulk ReS$_2$ behaves as an electronically and vibrationally decoupled monolayer.

The vanishing interlayer coupling is advantageous to controlling the exciton emission behavior by regulating the carrier interaction in the excited states. A schematic of the PL mechanism in the Td phase ReS$_2$ structure is presented in Figure 1a. Absorption of the laser pulse promotes the transition of electrons from the valence band (VB) to conduction band (CB), followed by relaxation to

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the exciton binding energy ($E_b$) level via a nonradiative recombination process to generate $\sim 1.5$ eV excitonic emission ($E_o = E_g - E_b$). However, this emission is still in the nonvisible region and cannot be easily controlled by changing the Td ReS$_2$ layer number because of weak interlayer coupling (Figure S1). If external electrons are intentionally implanted to adjust the electron–electron (e–e) and electron–hole (e–h) interactions, the electron effects will enlarge the band gap producing excited-state properties. Therefore, the incorporated T-ReS$_2$ not only provides the necessary excited-state electrons but also generates a built-in electric field to adjust the electron–hole (exciton) recombination process. When the T-ReS$_2$ concentration is increased, more robust anisotropic excitons can be produced and controlled by implanting more external electrons and constructing a stronger built-in electric field to enhance the anisotropic quantum confinement effect. Consequently, excitonic recombination can produce angle-dependent visible PL (Figure 1c).

The T phase incorporated Td-ReS$_2$ nanosheets are prepared by the ultrasonic chemical exfoliation method (see Sample Preparation and Characterization in the Supporting Information). The critical step is to control the T-ReS$_2$ nanocrystal concentration in the Td-ReS$_2$ matrix. The initial Td-ReS$_2$ single crystals are produced by the Br$_2$-assisted chemical vapor transport method. The Td-ReS$_2$ crystals are sonicated in nitric acid at room temperature for several hours to introduce the desired Re vacancies which act as distortion sites. At the same time, the thermal energy produced facilitates the formation of the metastable states. Finally, Peierls distortion in which local neighboring Re atoms move away from a lozenge

![Figure 1](image-url)  
**Figure 1.** Scheme for phase engineering and detection of visible polarized excitonic emission. (a) Diagrammatic representation of the PL mechanism in the Td-ReS$_2$ nanosheets. (b) T phase incorporation strategy to achieve a larger band gap in the T@Td-ReS$_2$ interfacial region. The pink arrows show the built-in electric field direction. (c) Anisotropic wave function of the exciton and detection of polarization-resolved PL with the red arrows showing the emission intensity.

![Figure 2](image-url)  
**Figure 2.** Characterization of the T@Td-ReS$_2$ nanosheets. (a) SEM image. (b) AFM image. Inset: Height profile along the white arrow indicating the layer thickness. (c) HR-TEM image. (d) Atomic structural model at the phase interface. The images consisting of blue and red balls indicate the symmetry of the Td and T phases, and the yellow and green balls represent the S and Re atoms, respectively.
of four atoms into the metal sites of the octahedral T structure occurs.

Figure 2a displays the scanning electron microscopy (SEM) image of the T@Td-ReS$_2$ nanosheets which are rectangular and have a planar size of 4.5–13.5 μm. Figure 2b shows the typical atomic force microscopy (AFM) image disclosing changes in the thickness. The inset reveals that the thickness of the edge of a T@Td-ReS$_2$ nanosheet is about 0.9 nm (monolayer) to 1.7 nm (bilayer). Generally, the nanosheet thickness varies from 0.8 to 8 nm (1–10 layers with an interlayer spacing of ~0.75 nm). High-resolution transmission electron microscopy (HR-TEM) reveals that the T and Td phases can coexist in a nanosheet (Figure S2), and Figure 2c clearly shows the interfacial region between the two phases. The lattice fringes of 0.285 and 0.296 nm can be indexed to the (100) planes of T-ReS$_2$ and Td-ReS$_2$, respectively, suggesting formation of a lateral interfacial heterostructure in the Td-ReS$_2$ nanosheet. X-ray diffraction, X-ray photoemission, and Raman scattering corroborate the conclusion (Figures S3–S5). The interfacial structure composed of the T and Td phases is also theoretically simulated, as shown in Figure 2d (please refer to the calculation details in the Supporting Information). Different from the
hexagonal symmetrical structure, Td-ReS₂ shows a distorted T structure with clustering of Re₄ units forming parallel metal chains along the van der Waals plane⁵ consistent with the HR-TEM results.

The room-temperature PL spectra in Figure 3a provide information about generation of excitonic emission from the T@Td-ReS₂ nanosheets. Compared to the PL (peaked at 1.51 eV) of the pristine Td-ReS₂ nanosheet (Figure S1), the PL peaks blue-shift significantly to 2.05 eV (visible region). The peak positions depend slightly on the layer number (Figure 3b), which is consistent with previous results obtained from few-layer ReS₂ flakes (Exp-Td).¹⁷ The large blueshift from 1.51 to 2.05 eV (Exp-T@Td) indicates that the introduced T-ReS₂ plays a critical role in the excitonic emission energy. To explain the large PL blueshift, we theoretically calculate the e−e and e−e−e interactions in the excited states by the many-body perturbation theory (Cal-GW) based on the density functional theory (Cal-DFT) (see the calculation details in the Supporting Information) and find that the blueshift can indeed occur in the T@Td-ReS₂ heterostructure (Figure 3b).

To determine the role of T-ReS₂ in the excitonic behavior, PL spectra for different T phase concentrations (changing the average distance between the T-ReS₂ regions and T-ReS₂ phase sizes as discussed in Sample Preparation and Characterization and Figure S6a,b in Supporting Information) are obtained as shown in Figure 3c. When some Td phases are converted into the T phase to form T@Td-ReS₂ (sample S1), the emission peak begins to blue-shift from 1.51 (pristine Td-ReS₂) to 1.63 eV. As the T-ReS₂ concentration is increased further, the emission peaks expand into the visible region (1.77 eV for sample S2; 2.06 eV for sample S3; 2.25 eV for sample S4). Obviously, this cannot be attributed to impurities and contaminants, because there is no related PL from the nitric acid solution (see the IR spectrum in Figure S7). In addition, it is known that the vacancies and impurities can only produce red-shifts in the PL peak (Figure S8).

To investigate the excitonic feature, the polarized PL spectra of the T@Td-ReS₂ nanosheets are depicted in Figure 4a,b (samples S3 as an example). The polarization-resolved PL measurements are described in the Supporting Information. The excitation (marked by E) and detection (marked by D) polarizations are selectively oriented along either the x or y axis corresponding to the shortest and second-shortest axes in the basal plane (marked by black arrows on the left side of Figure 2d). The four different measurements all show a single peak at 2.05 eV; therefore, the peak position is independent of excitation or detection polarization. However, the largest PL intensity is observed when both excitation and detection polarization are aligned with the x direction (E-x; D-x). When it changes to the y direction, the PL intensity (E-x; D-y) is obviously attenuated by more than 70% compared to that along the x direction (E-x; D-x) regardless of the excitation light polarization. To show the polarized feature more clearly, the angle-dependent PL intensity is shown in Figure 4b in which the excitation polarization is arranged along the x and y directions. Because the wave function is strongly extended along the 0° and 180° (x) direction, observation of highly polarized emission indicates an anisotropic excitonic nature. The excited electrons and holes are preferentially dispersed along the x band direction, and the isotropic Coulomb interaction leads to stronger binding effects of e−h in the y direction. Furthermore, in the T@Td-ReS₂ interfacial region, the exciton recombination process is adjusted by the built-in electric field induced by the incorporated T-ReS₂. Without considering excitation light polarization, higher-energy photons will first generate “hot” electrons in T-ReS₂ and free electrons and holes in Td-ReS₂, and then the “hot” electrons are transferred to Td-ReS₂ to control the e−h interaction in which anisotropic excitons form to produce highly polarized light emission (Figure S9). Thus, regardless of the excitation polarization, the emitted light is strongly angle-dependent because the PL always originates from recombination of these anisotropic excitons. Similar polarized features are observed from the samples with different T-ReS₂ concentrations (Figure S10). These results showing strongly polarized PL are consistent with our theoretical prediction (Figure 1) that shows that excited states are dominated by anisotropic excitons as a result of the structural symmetry and screening effect.

Two-dimensional mapping of the PL excitation (PLE) spectra as functions of both excitation and emission photon energies is shown in Figure 4c (see Sample Preparation and Characterization in the Supporting Information). The strongest PL occurs at an excitation energy of 2.45 eV (white dotted lines), which is four times stronger than that at an excitation energy of 2.14 eV. The PL intensity as a function of excitation energy (the black dotted line) is plotted in Figure S11. The optical band gap in the excited state increases as 2.45 eV. To reveal the anisotropy of the PLE spectra, the exciton Bohr radius is calculated (Figure 4d) to show the electron wave function distribution (see Figure S12 for calculated effective mass). The asymmetrical distribution in the wave function implies that the recombination probability of excited electrons and holes depends on spatial confinement which causes the observed anisotropic emission of excitons.

The schematic presentation of the “hot” electron-transfer process based on the interfacial band structure is shown in Figure 5a. The difference in the work function between the metallic T-ReS₂ and semiconducting Td-ReS₂ is only 0.12 eV thereby causing a small potential barrier in the phase interface. During light excitation, many excited “hot” electrons (free electrons) of T-ReS₂ can readily penetrate the Td-ReS₂ region by tunneling with a transmission coefficient of about 85% (see the Supporting Information for calculation details). Electron accumulation in the Td-ReS₂ produces the many-electron effect and excited-state properties, which not only increase the optical band gap but also modify the PL process with the built-in electric field. The metal–semiconductor contact increases the effective transfer range of “hot” electrons to reach 25 nm (see the Supporting Information for calculation details). Because the average distance between the T-ReS₂ phase regions is about 9 nm (see the HR-TEM image in Figure S2), electron transfer occurs easily.

To determine the exciton binding energy, the quasiparticle absorption spectrum and differential results (Dif) are derived and shown in the lower panel of Figure 5b. In general, the maximum in the differential absorption spectrum is the quasiparticle band gap. According to our experiments, the optical band gap in the excited state can be extracted as 2.45 eV (marked by red shaded line in Figure S11), which is in accordance with the calculated quasiparticle band gap (2.43 eV in the lower panel of Figure 5b). After considering the excitonic effect by solving the GW–Bethe–Salpeter equation, the absorption peak shifts to 1.98 eV (T³, which is consistent with the measured absorption spectra of T@Td ReS₂ in Figure S13) leading to an exciton binding energy of 0.45 eV. However, two minor factors need to be considered when comparing the
on the ReS$_2$ thickness, thereby allowing us to probe the PL of 2D-like systems without the need to prepare large-area, single-crystal monolayers. This idea can be generalized to other 2D materials to tune optical properties.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01029.

Sample preparation and characterization; PL and polarization-resolved PL measurements; theoretical calculations; HR-TEM images; XRD patterns; XPS, Raman spectra, and IR spectra; calculated band structures; PL decay curves; angle-dependent polarized characteristics; PL intensity as a function of exciton energy; angle-dependent effective masses of electron, hole, and excitation (PDF)

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Notes

The authors declare no competing financial interest.

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Figure 5. “Hot” electron-transfer mechanism and calculation of exciton binding energy. (a) Schematic representation of the “hot” electron-transfer process based on the calculated results. (b) Top: Calculated excitonic absorption with e−h interactions in the different deformed structures (T1, compressed 2%; T2, original structure; T3, stretched 2%). Bottom: Calculation quasiparticle absorption and differential curves for the T2 structure. The estimated quasiparticle band edge is indicated by the shaded region (theoretical) and red line (experimental).
Spectra of Monolayer, Few-Layer, and Bulk ReSe$_2$

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Integrated Digital Inverters Based on Two-Dimensional Anisotropic


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