Supporting Information for Manuscript

Phase-Engineering-Induced Generation and Control of Highly Anisotropic and Robust Excitons in Few-Layer ReS₂

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Experimental Sections

Sample Preparation and Characterization. The single-crystal Td-ReS₂ was produced by the Br₂-assisted chemical vapor transport method described previously.^{S1} A standard mechanical exfoliation method was adopted to isolate the monolayer and few-layer ReS₂ films. The T@Td-ReS₂ nanosheets were prepared by ultrasonic chemical exfoliation as shown in the following. Ten mg of the single crystals of Td-ReS₂ were mixed with 5 mL of 9 M nitric acid in a centrifugal tube and sonicated

for 1 h (100W) at room temperature. The temperature was controlled to be less than 35 °C using an ice bag. The resulting mixture was centrifuged and the supernatant was decanted. The single-crystal Td-ReS₂ was processed for 1, 2, 3, and 4 h, respectively, to obtain T@Td-ReS₂ nanosheets with different T-ReS₂ concentrations. Afterwards, the samples were thoroughly washed with absolute ethanol and water sequentially until neutral and to remove impurities adsorbed on theT@Td-ReS₂ nanosheets. They were then dried in air at 60 °C for 5 h. The samples treated for 1, 2, 3, and 4 h are designated as S1, S2, S3 and S4, respectively. The number of layers can be identified by the color interface of a 285-nm thick SiO₂ wafer and confirmed by measuring the thickness of the flakes using a Bruker Multimode 8 atomic force microscope. Raman scattering JY T64000) was carried out in the backscattering geometry. The incident laser wavelength was 514.5 nm and the illumination power was less than 1 mW to minimize laser heating.

Polarization-resolved PL Measurements. Using the same Raman equipment, the polarized-resolved PL experiments were performed on the ReS₂ nanosheets at an excitation energy of 2.41 eV and spot size of about 1 μ m at room temperature. The excitation laser was linearly polarized. On the detection side, a half-wave plate and linear polarizer were used to select the x and y components of the emitted light. In the PLE measurements, the exciton PL was monitored while the excitation wavelength was scanned from 2.2 to 3.0 eV at a constant excitation power. The excitation source was a Xenon lamp providing tunable wavelengths. Fresh sample areas were selected to minimize the impact of Raman characterization on the samples and all the PL

spectra were corrected for the polarization-dependent response of the measurement system.

Theoretical Calculation. The quasiparticle energies and band gaps were calculated by the many-body perturbation theory (GW approximation)^{S2} based on the generalized gradient approximation Perdew-Burke-Ernzerhof function implemented in the VASP code according to the density-functional theory.^{S3} The GW-BSE calculation was performed with the BERKELEYGE code including the slab Coulomb truncation scheme to mimic the suspended monolayered structure.^{\$4,\$5} The involved unoccupied conduction band number for calculation of the dielectric function and self-energy was about ten times that of the occupied valence band number. In solving the BSE, the kinetic energy cutoff for the plane-wave basis set was 550 eV and the Brillouin zone integration was performed on uniform Monkhorst-Pack of 24×24×1 for the converged excitonic states. The GW-BSE calculation was performed with the BERKELEYGE code including the slab Coulomb truncation scheme to mimic the suspended monolayered structure.⁸⁵ In the optical absorption spectra, the incident light polarized parallel with the plane was considered due to the depolarization effect. The effective region of the "hot" electron distribution at the metal/semiconductor phase interface can be estimated by $R_d = \sqrt{\frac{2\varepsilon_r \varepsilon_0 V_s}{eN_D}} = 25 \text{ nm}$, where $\varepsilon_r = 1.58 \text{ and } \varepsilon_0$ are relative and vacuum dielectric constant. Vs = 0.12 eV is interface potential barrier and $N_D = 3.37 \times 10^{16}$ cm⁻³ is the carrier concentration (ref. S4). The tunneling probability of "hot" electrons can be calculated by Т $\frac{16E(V_s-E)}{V_s}exp\left[-\frac{2l}{\hbar}\sqrt{2m(V_s-E)}\right] = 85\%.$ The "hot" electron kinetic energy is E =

0.02 eV, phase interface width l = 0.47 nm, and *m* is the electron effective mass. The contribution to the quasiparticle band gap is mainly from the screened-exchange interaction which is strongly affected by the spatial localization of electronic stats. This can be seen from its static form (ref. S10):

 $\sum_{SEX}(r,r') = \sum_{nk}^{occ} \phi_{nk}(r) \phi_{nk}^*(r') W(r,r')$, where ϕ_{nk} is the electronic wave function and W is the screened Coulomb interaction. The subscript n is the band index and k is the sampling points in the reciprocal space. When the spatial structure is compressed and stretched, it is equivalent to changes in the "hot" electron concentration per unite area. The overlap between the wave functions and screened Coulomb interactions is regulated correspondingly leading to more reasonable interpretation of the experimental conclusion.



Figure S1. PL spectra of the exfoliated Td-ReS₂ nanosheets varying from monolayer to thick layers. From multilayer to monolayer, the peak energy increases slightly from 1.52 to 1.59 eV due to the direct band gap and interlayer decoupling properties of Td-ReS₂.^{S6}



Figure S2. HR-TEM image of the T@Td-ReS₂ sample showing the T and Td phases in the nanosheet.



Figure S3. XRD patterns acquired from the Td-ReS₂ (Exp-Td) and T@Td-ReS₂ nanosheets (Exp-T@Td). The JCPDS cards and calculated results of the Td-ReS₂ (Cal-Td) and T-ReS₂ (Cal-T) structures are shown for comparison. Compared to the diffraction peaks from the Td-ReS₂ nanosheets, an important difference in T@Td-ReS₂ sample is that two additional diffraction peaks (marked by \bullet) are observed. Based on the literature and our calculation,^{S7} the two peaks (marked by \bullet) originate from T-ReS₂. XRD indicates that the T phase is produced successfully.



Figure S4. XPS spectra of T@Td-ReS₂ nanosheets. The representative experimental spectrum is shown in black and fits are shown in red for the Td phase and green for T phase. The introduced T-ReS₂ peaks appear at around 40.68 and 43.08 eV corresponding to binding energies of the Re⁴⁺ $4f_{5/2}$ and $4f_{7/2}$ electrons. They blue-shift about 0.22eV compared to the pristine Td-ReS₂. This phenomenon is similar to that of the phase-incorporated MoS₂ structure^{S8} and no XPS peaks are observed from impurities or contaminants.



Figure S5. Raman scattering spectra of the exfoliated Td-ReS₂ and T@Td-ReS₂ nanosheets. The Raman spectra show six characteristic peaks (S1-S6) arising from the A_g -like and E_g -like phonon modes in the Td-ReS₂ nanosheets.^{\$9} When the layer thickness and incident polarized angle in theTd-ReS₂ nanosheets are altered, the relative intensities in the Raman spectra change, but no new Raman modes appear.^{\$10} In contrast, for the T@Td-ReS₂ nanosheets, additional peaks (\blacklozenge) appear at 129.5 and 122.2 cm⁻¹ (marked by S) due to the T-ReS₂ phase suggesting that a considerable amount of the T phase is embedded in the Td-ReS₂ host.



Figure S6. (a) Distances between two adjacent T-ReS₂ clusters and (b) sizes of the T phase regions in the T@Td-ReS₂ samples designated as S1, S2, S3, and S4. To obtain

more information on the distribution and the size of the T-phase in the Td-ReS₂ nanosheet matrix, HR-TEM images are acquired from the T@Td-ReS₂ nanosheets to determine the average distance between two adjacent local T-phases and the sizes of the T phase clusters. As shown in Figure S2, some interesting results are obtained from the statistical results. As the treatment time is increased (defined as samples S1-S4), the nearest interspacing distance between two adjacent T-phases becomes smaller and the influence on excitonic emission at the T@Td-ReS₂ interfacial region becomes stronger correspondingly.



Figure S7. IR spectrum of the T@Td ReS₂ nanosheets. The most prominent broad band in the 3500-3300 cm⁻¹ region and that at 1600 cm⁻¹ arise from OH stretching and bending vibration of water molecules, respectively. The bands at 2926 and 2855 cm⁻¹ can be assigned to the stretching vibration of CH₂ in ethanol.^{S11} This is further evidenced by the band at 1044 cm⁻¹ which corresponds to the stretching vibration of C-O. The ethanol molecule is introduced in the washing step during preparation of the T@Td ReS₂ nanosheets but cannot produce PL. Additionally, the T@Td ReS₂ nanosheets show no prominent absorption in the 4000-700 cm⁻¹ range confirming the absence of impurities or contaminants.^{S12}



Figure S8. Calculated band structure of $Td-ReS_2$ with the Re (a) and S (b) defects, respectively. The detailed orbital analysis shows that the band (black lines) originates from the original Re and S atoms and the middle band (blue lines) around the Fermi energy is related to Re or S defects.



Figure S9. PL decay curves acquired from the exfoliated Td-ReS₂ (Td) and T@Td-ReS₂ nanosheets (Sample S2 and S4). By subtracting the spectrometer background signal and fitting the decay transients with two stretched exponential functions, the lifetimes of the exciton emission are obtained to be $\tau_1 = 1.00$ ns, $\tau_2 = 6.67$ ns (Sample Td); $\tau_1 = 2.57$ ns, $\tau_2 = 7.89$ ns (Sample S2); $\tau_1 = 2.88$ ns, $\tau_2 = 10.97$ ns (Sample S4). The difference in the lifetime indicates that the electron transition occurs between T and Td phases ReS₂ and it is consistent with the result from our model.



Figure S10. Measured PL spectra (a) and angle-dependent polarization characteristics (b) of the T@Td-ReS₂ nanosheets (Sample S2) indicating that the excitonic emission shows a similar behavior as Sample S3 (Figure 4).



Figure S11. PL intensity as a function of excitation energy. The data are taken along the vertical black dot line in Figure 4c. Similar to the quasiparticle band edge in the adsorption spectra, the optical band gap in the excited state is defined as the position at which the absorption increase is largest. Using this definition, the optical band gap in the excited state is extracted as 2.45 eV which agrees with the calculated value (2.43 eV in the lower panel of Figure 5b).



Figure S12. Angle-dependent effective masses of electron (m_e) , hole (m_h) , and excition (m) in the Td-ReS₂ monolayer and m_0 is the electron mass.



Figure S13. Measured UV–Vis absorption spectra of the exfoliated Td-ReS₂ and T@Td-ReS₂ nanosheets. After introduction of the T phase clusters, the adsorption peak obviously blueshifts, which is in good agreement with our calculated excitonic absorption in T3 in Figure 5b.

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