(Supporting Information)

Enhanced excitonic features in anisotropic ReS_2/WSe_2 heterostructure

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Figures S1-S4.

Table 1: Parameters to calculate trion binding energy.

Note 1: Theoretical model and DFT input for calculation of exciton binding energy and wavefunction.

Note 2: Raman spectroscopy.

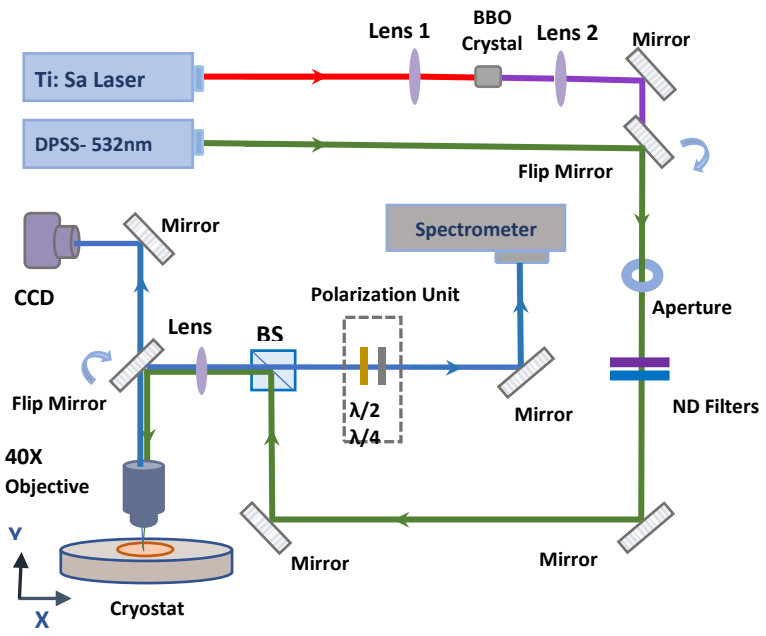

Figure S1: Schematic of PL and Polarization resolved measurement setup

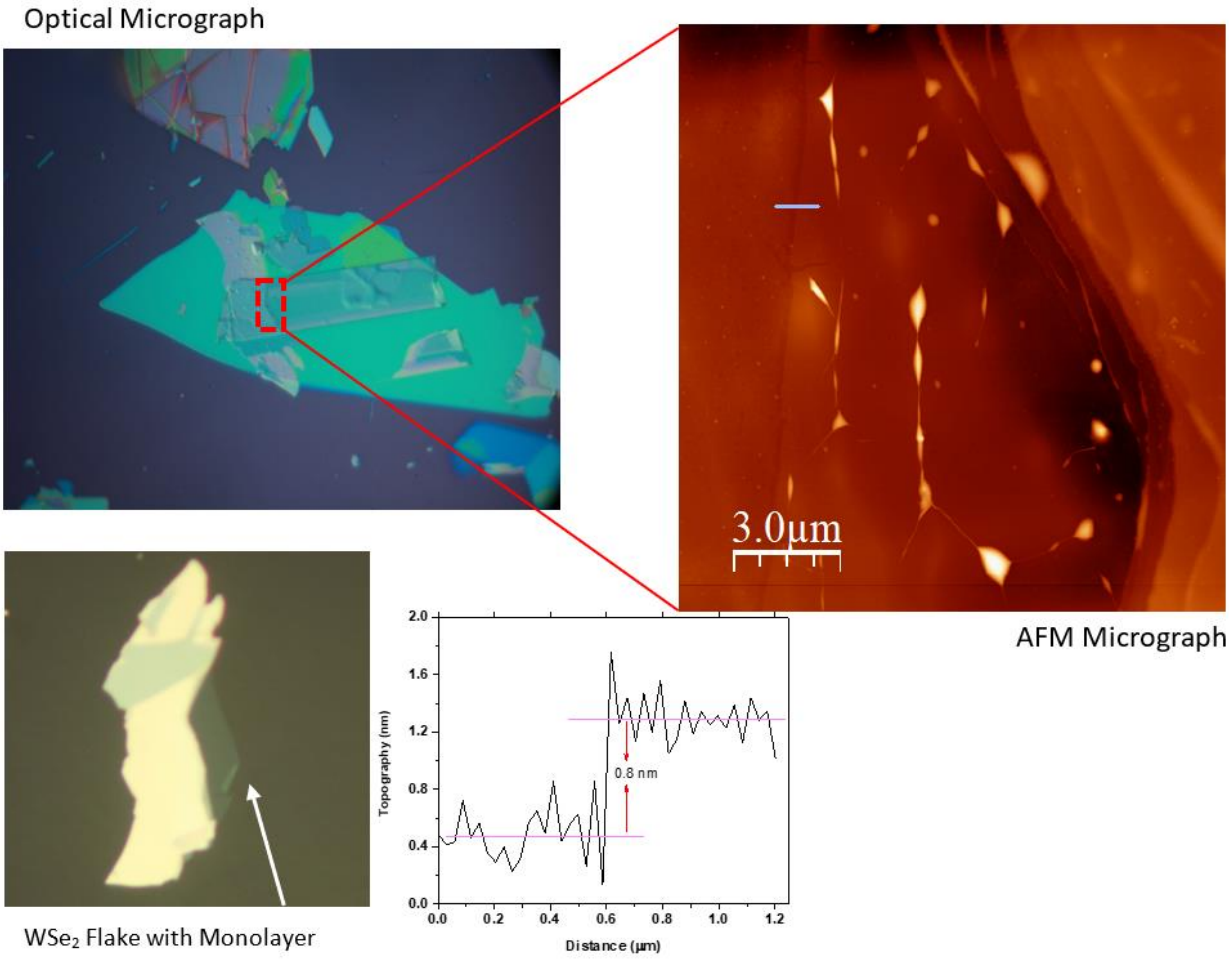

Figure S2: Optical and AFM micrograph of heterostructure along with line profile**.**

Table T1: Parameters used to calculate trion binding energy

C_o	-0.42 [1]
C_1	158 [1]
C_2	-1330 [1]
C_3	3113 [1]
C_4	-2640 [1]
µ	0.59
ε	6.8, 7.2 [2]

N1- Theoretical model and DFT input for calculation of exciton binding energy and wavefunction

In this section we outline the theoretical method and DFT data to calculate the excitonic binding energy and wavefunctions.

We use DFT data to extract the effective mass, dielectric constant and crystal structure. DFT calculations were performed using the QUANTUM ESPRESSO [3] software, with scalar relativistic LDA pseudopotentials from the PSLibrary [4]. These pseudopotentials used the Perdew-Zunger parametrisation of the exchange-correlation energy [5] and were used with the projector augmented wave (PAW) method [6, 7]. The valence of Re was taken as 15, and no van der Waals' corrections were included. Initial atomic coordinates were taken from the Chemical Database Service [8] for monolayer ReS2. The kinetic energy cutoff was 60 Ry (816 eV) and Monkhorst-Pack [9] k-point meshes of 20x20x1 were used.

The lattice constant of monolayer ReS_2 is approximately 0.63 nm which comes from previous experimental works and ab initio calculations [10]. We use the calculated DFT electronic dispersion to find the effective mass of the anisotropic band structure. We extract the effective mass in the directions parallel to (x) and perpendicular to (y) the Re-chains in the monolayer.

For the conduction band we obtain

$m_c^x = 0.59 m_o$
$m_c^y = 1.66 m_o$

For the valence band we obtain

$m_v^x = -2.42 m_o$
$m_v^y = -14.9 m_o$

These values reflect the 1D-nature of the electronic motion along the Re-chains (b-axis) in the monolayer.

We were also provided with DFT data for the dielectric constant in ReS_2 which we expect to be anisotropic in the plane. Eliminating the vacuum contribution, we obtain the tensor

$$\epsilon = \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix} = \begin{pmatrix} 14.06 & 0 & 0 \\ 0 & 13.29 & 0 \\ 0 & 0 & 4.61 \end{pmatrix}$$

where x lies along the Re chains in the monolayer, and z is out of plane. We use the Wannier equation to obtain the binding energies, modified to consider the band anisotropy and anisotropic dielectric screening in the TMD.

We rely on the assumption that around the band gap, the valence band maximum and conduction band minimum are approximately parabolic. From this we can employ the Wannier equation to calculate the excitonic binding energy.

$$\frac{\hbar^2(k_x^2+k_y^2)}{2m_r^{xy}}\varphi^n_{k_x,k_y}+\sum_{q_x,q_y}V_{Kel}(k_x+q_x,k_y+q_y)\varphi^n_{q_x,q_y}=E_b^n\varphi^n_{k_x,k_y}$$

Here, E_b^n denotes the exciton binding energy with energy level n, V_{Kel} is the screened Keldysh Coulomb interaction, $\varphi^n_{k_x,k_y}$ the excitonic wavefunction, and m_r^{xy} the reduced mass which varies due to the anisotropy.

The calculation presented here is for freestanding ReS_2, the presence of substrates (especially hBN encapsulation) should reduce the magnitude of the binding energy.

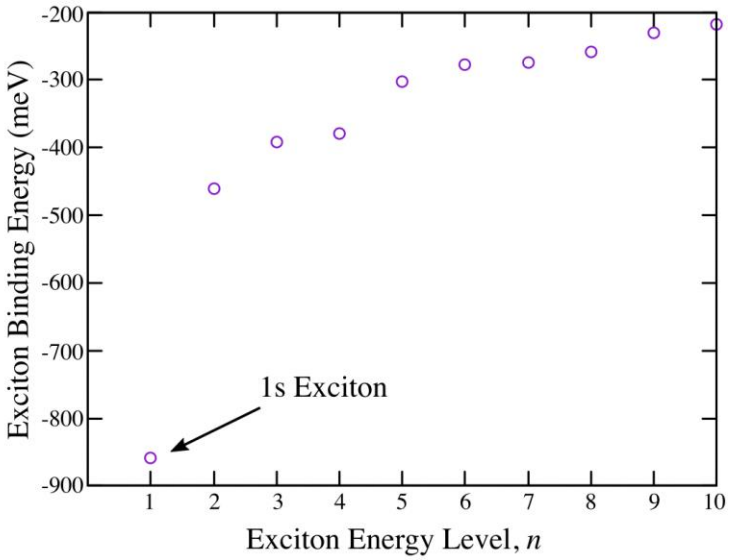

Figure S3: Binding energies, E_b^n for ReS_2. The 1s-exciton has a binding energy of 859 meV.

N2- Raman Spectroscopy

In ReS_2 the spectral position of the Raman peak depends on the number of monolayers [11]. To determine the number of monolayers, present in our sample we performed a Raman spectroscopic analysis in back scattered geometry. It is carried out under ambient conditions using an Argon Ion laser (514 nm) which is focused onto the heterostructure with a 100x objective. The spectral resolution of the Raman setup is 0.04 cm^{-1}. Figure S4, shows characteristic vibrational spectra obtained for the monolayer as well as for the corresponding heterostructure. The spectra reveal the characteristic A^1_g mode of WSe_2 along with the 2nd order longitudinal phonon mode.

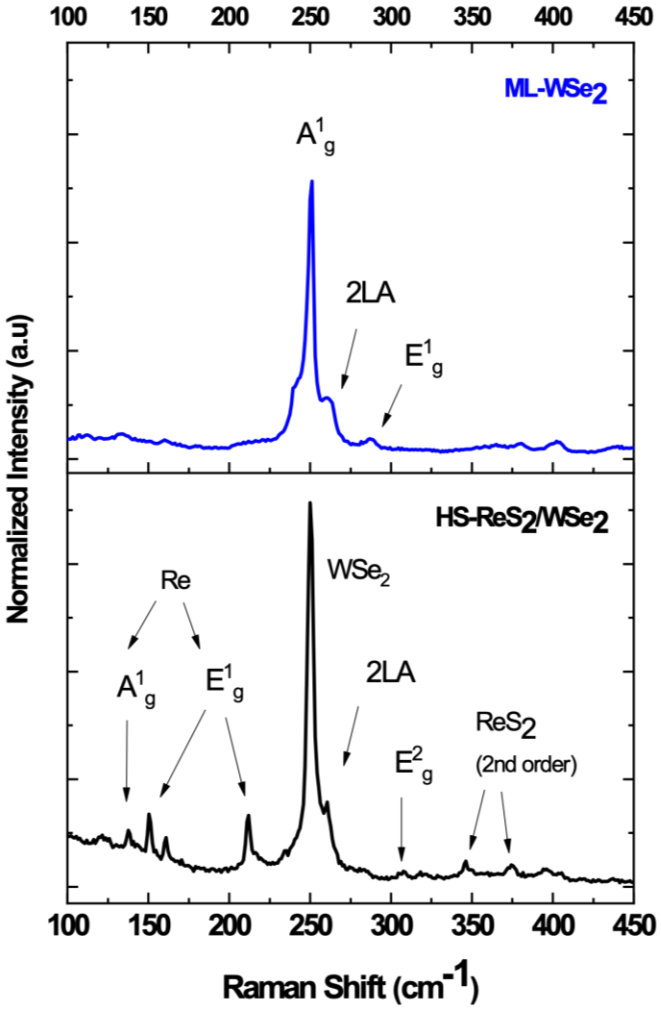

Figure S4: Raman spectra of the WSe_2 monolayer and the corresponding heterostructure with FL- ReS_2

These phonon modes are also visible in the heterostructure alongside with the ReS_2 berating mode at 260 cm^{-1}. The distinct A^1_g mode of ReS_2 corresponds to out-of-plane vibrations of Re atoms. The phonon distribution in few layer ReS_2 seems to be nearly identical to that of bulk [12, 13]. This indicates

electronic and vibrational isolation of this material with respect to the number of layers. The in-plane vibrational mode of Re and S atoms can be seen at 160 cm^{-1}, 212 cm^{-1} and 308 cm^{-1}, respectively. It is also noticeable that the breathing mode is stronger than the shear mode in ReS_2, whereas the shear mode is dominating in conventional 2D materials [14, 15]. We could also quantify the number of ReS_2 layers by analyzing the peak positions [16]. The peak at 136 cm^{-1} indicates that there are 4-layers of ReS_2 in our heterostructure. When the Raman frequency increases the vibrational atomic weights of Re and S atoms changes due to intrinsic difference of their atomic weights, this leads to variable Re-Re dimers and thus changes the bond charge polarization and generates different intensities [17].

References:

1. Thilagam A, *Physical Review B*, 1997, **56,** 4665.
2. Ankur Sharma, Han Yan, Linglong Zhang, Xueqian Sun, Boqing Liu, Yuerui Lu, *Accounts of Chemical Research*, 2018, **51**(5), 1164–1173.
3. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., *J. Phys.: Condens. Matter.,* 2009, **21**, 395502.
4. A. Dal Corso, *Comput. Mater. Sci.,* 2014, 95, 337.
5. J. P. Perdew; A. Zunger, *Physical Review B,* 1981, **23**, 5048.
6. P. E. Blöchl., *Physical Review B.* 1994, **50**, 17953.
7. G. Kresse; D. Joubert, *Physical Review B*, 1999, **59**, 1758.
8. D. A. Fletcher; R. F. McMeeking; D. Parkin, *Journal of Chemical Information and Computer Sciences*. 1996, **36**, 746.
9. H. J. Monkhorst, J. D. Pack, *Physical Review B,* 1976, **13**, 5188.
10. S. M. Gunasekera. D. Wolverson; L. S. Hart, M. Mucha-Kruczyński, *J. Electron. Mater*. 2018, **47**, 4314−430.
11. Daniel A. Chenet, O. Burak Aslan, Pinshane Y. Huang, Chris Fan, Arend M. van der Zande, Tony F. Heinz, James C. Hone, *Nano Letters*, 2015, **15**, 5667−5672.
12. Yanqing Feng, Wei Zhou, Yaojia Wang, Jian Zhou, Erfu Liu, Yajun Fu, Zhenhua Ni, Xinglong Wu, Hongtao Yuan, Feng Miao, Baigeng Wang, Xiangang Wan, Dingyu Xing, *Physical Review B*, 2015, **92**, 054110.
13. Naktal Al-Dulaimi, David J. Lewis, Xiang Li Zhong, M. Azad Malik, Paul O'Brien, *Journal of Material Chemistry C*, 2016, **4**, 2312.
14. Takeshi Fujita, Yoshikazu Ito, Yongwen Tan, Hisato Yamaguchi, Daisuke Hojo, Akihiko Hirata, Damien Voiry, Manish Chhowalla, Mingwei Chen, *Nanoscale*, 2014, **6**, 12458-12462.
15. Etienne Lorchat, Guillaume Froehlicher, Stéphane Berciaud, *ACS Nano*, 2016, **10**, 2752–2760.
16. A. McCreary, J. R. Simpson, Y.Wang, D. Rhodes, K. Fujisawa, L. Balicas, M. Dubey, V. H. Crespi, M. Terrones, A. R. Hight Walker, *Nano Letters*, 2017, **17**, 5897.
17. Xiancui Su, Baitao Zhang, Yiran Wang, Guanbai He, Guoru Li, Na Lin, Kejian Yang, Jingliang He, Shande Liu, *Photonics Research*, 2018, **6**, 498-505.