Role of the *Direct to Indirect* Bandgap Crossover in the '*Reverse*' Energy Transfer Process

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Van der Waals (vdW) heterostructures (HSs), composed of layered materials, have demonstrated significant potential for advancing (opto)electronic applications [1]. In the type-II transition metal dichalcogenide (TMDC) HSs, long-range energy transfer (ET) happens via the dipole-dipole coupling (Förster type). Traditionally, the ET process happens from the higher energy bandgap materials (donor) to the lower energy bandgap materials (acceptor), i.e., thermodynamically favorable. However, in some cases a reverse ET happens from the acceptor to donor materials due to the resonant overlaping between the high-lying absorption states [2]. To investigate this, we studied a HS made by the 1L of tungsten disulfide (WS_2) and 1L-5Ls of molybdenum disulfide (MoS_2), with hexagonal boron nitride (hBN) as a charge-blocking interlayer (Fig. a), using differential reflection contrast (RC), photoluminescence (PL), photoluminescence excitation (PLE) and time resolved PL (TR-PL), complemented by the density functional theory (DFT) calculations. At room temperature, PL enhancement has been observed in the neutral exciton of WS_2 (Fig. c) in the 1L WS_2-hBN-1L MoS_2 (1L HS) and 1L WS_2-hBN-2L MoS_2 (2L HS) regions compared to isolated WS_2 emission, but with further increasing the layer thickness this enhancement destroys. This enhancement confirms an efficient ET from the MoS_2 B excitonic level to the WS_2 A excitonic level. The increase in layer number changes the MoS_2 bandgap from direct to indirect, promoting more immediate carrier scattering from the K valley. Consequently, carrier population decreases and ET becomes less effective. Our results also prove that this reverse ET happens at a faster timescale than the intervalley scattering (K+ ↔ K-). Overall, this work helps to understand the competing interlayer processes for better development of the TMDC-based next-generation (opto)electronic device applications.

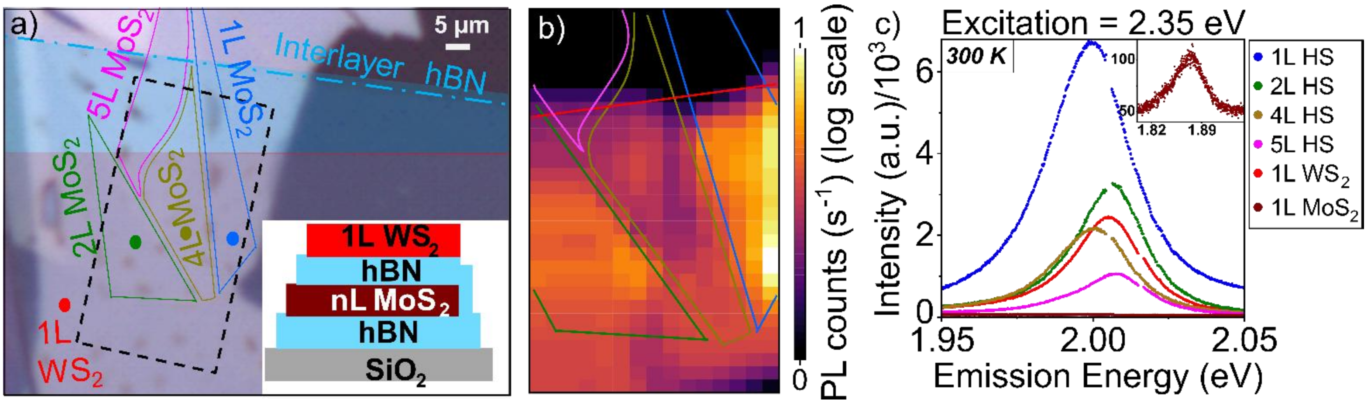

Figure 1: a) Optical image of the sample with schematic illustration of the cross-sectional view of the HS as an inset in which different areas of the sample are depicted in various colours. The dashed black box indicates the region selected for PL mapping. b) PL intensity mapping of the black box region at 300 K with excitation energy 2.35 eV, shows the change of enhancement due to the ET process in the multilayer regions of HS. c) PL spectra of all regions measured at room temperature, with the inset showing the PL spectrum from the 1L MoS_2 region, which clearly shows the enhancement in the intensity of the WS_2 neutral exciton in the 1L HS and 2L HS region compared to the 1L WS_2. This confirms the energy transfer from MoS_2 to WS_2.

References

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