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SUPPLEMENTARY INFORMATION

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Interlayer electron–phonon coupling in WSe_2/hBN heterostructures

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1. Raman selection rules of the emerging Raman modes in WSe_2/hBN heterostructure

Hexagonal hBN has a space group of D_{6h}^4 ($P6_3/mmc$). The vibrational normal modes near Γ point can be divided into E_{1u} mode (infrared active, 1370cm^{-1}), A_{2u} mode (infrared active, 780 cm^{-1}), E_{2g} mode (Raman active, 1370cm^{-1}) and B_{1g} (ZO) mode (820cm^{-1}, optically silent)[1,2]. The only Raman active mode with in-plane electric field is the E_{2g} mode around 1367cm^{-1}, consistent with the Raman spectra we measure from pristine hBN (Fig. 2b in the text). The interaction between WSe_2 and hBN layers lowers the symmetry of the heterostructure, and the WSe_2/hBN interface has a reduced symmetry of C_3. The original B_{1g} (ZO) mode of hBN thereby becomes A mode in the combined system, which is Raman active with in-plane electric field when incident and outgoing light polarization are parallel. Therefore, the hBN ZO mode not only emerges in the heterostructure (mode I), but also shows well-defined linear polarization selection rule.

Similarly, the WSe_2 A_{1g} mode (250cm^{-1}) also becomes A mode in the heterostructure. Since the product of two A representations is still A representation; the combinatorial hBN ZO + WSe_2 A_{1g} mode will show the same polarization dependence as the hBN ZO mode, consistent with our observation of mode II. On the other hand, the hBN ZO + WSe_2 E_{2g} mode, though also have energy around 1070cm^{-1}, will break the polarization selection rule. Therefore the perfect selection rule of mode II suggests that the contribution from hBN ZO + WSe_2 E_{2g} mode is negligible. This is consistent with the fact that E_{2g} mode is in-plane phonon mode and will not interact as strongly with the other layer.

2. Photoluminescence excitation (PLE) spectroscopy of WSe_2/hBN heterostructure

Figure S1 shows the PLE spectroscopy of WSe_2/hBN heterostructure (red) and pristine WSe_2 (black), where horizontal and vertical axis are photoexcitation energy and A exciton PL intensity, respectively. As excitation energy is scanned from 1.8 to 1.89 eV, the PL intensity dramatically increases when excitation energy is resonant at X peak (labeled with blue dashed line). In comparison, no obvious excitation energy dependence is observed in the PLE of pristine WSe_2 (black circles). The dramatic enhancement of WSe_2 A exciton PL with optical excitation

at X peak energy indicates that X peak state can efficiently relax to WSe_2 A exciton state to emit light. Therefore, the origin the X peak state cannot be localized defects/impurities deep in hBN which has inefficient relaxation channel to WSe_2. Instead, the optical response of WSe_2 itself is strongly modified from interlayer interaction with hBN.

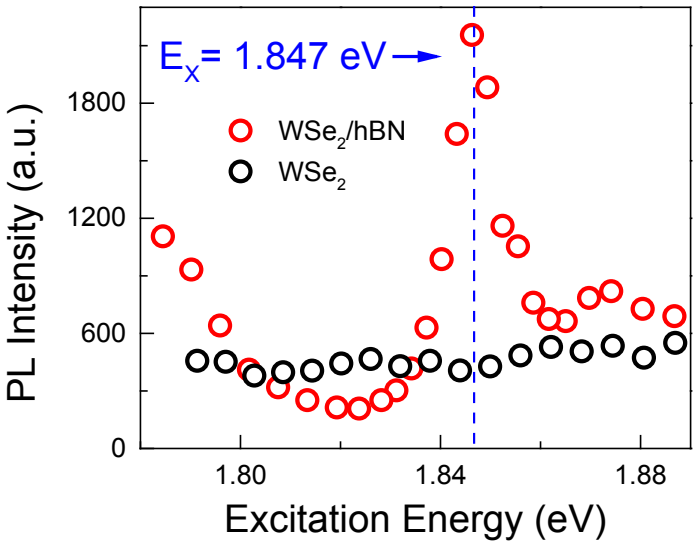

Figure S1. **PLE spectroscopy of WSe_2/hBN heterostructure (Red) and pristine WSe_2 (black).** Horizontal and vertical axes are photoexcitation energy and A exciton PL intensity, respectively. The heterostructure shows a dramatic PL intensity increase with excitation at X peak, confirming that optical response of WSe_2 is strongly modified from interlayer interaction.

3. Potential mechanisms giving rise to the X peak in absorption

The interlayer interaction can change the electronic structure in vdW heterostructure in general. There are three commonly observed effects: Firstly, a direct hybridization between interlayer electronic states, which will be most significant when the electronic states from two layers match in both energy and momentum, i.e. degenerate coupling[3,4]. Secondly, an effective Moire potential when the two layers form a superlattice, as is observed in graphene/hBN system with Moire pattern[5-10]. Thirdly, a dielectric screening effect due to change of dielectric

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environment, which could lead to change of quasiparticle bandgap and exciton binding energy[11,12].

However, none of the above mechanisms can account for the new transition we observe in this study. Firstly, the direct hybridization will be weak since electronic states of hBN and WSe2 does not match in our spectral range due to hBN's large band gap. Secondly, the periodicity of effective Moire potential depends sensitively on the rotation angle between layers, so does the energy of the induced new optical transitions[8]. However, we find that the X peak energy is independent of twist angle between WSe2 and hBN. Thirdly, the dielectric screening effect can induce shift of exciton resonance energy, but not new optical transitions. Given the above reasons, the origin of X peak cannot be easily explained by the established mechanisms. So far, we have not been able to account for this X peak theoretically, as stated in the manuscript, and we hope further theoretical studies can explain this new resonance.

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