Supporting Information for

Interface charge-transfer induced intralayer excited-state biexciton in graphene/WS_2 van der Waals heterostructures

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Note 1. Steady-state and time-resolved PL measurements

Low-temperature and temperature dependent PL measurements of the heterostructures were carried out by a Renishaw Invia micro-Raman system in a Janus cryostat with laser excitation wavelength of 532 nm. Helicity-resolved PL measurements were performed by a home-built micro PL setup with laser excitation wavelength of 566 nm. The time resolved PL measurements were performed by utilizing a streak camera (Hamamatsu C4742) under excitation of a 400 nm frequency-doubled Ti:sapphire femtosecond laser with a pulse width of ~150 fs and a repetition rate of 76 MHz. The response time of our low temperature TRPL measurement setup was measured to be ~ 4 ps. The sample was in an Oxford cryostat mounted under the home-built microscope for low temperature PL measurements.

Note 2. DFT calculations of charge transfer at the graphene/WS_2 interface

Charge transfer calculations. The charge densities were computed using density functional theory (DFT) calculations with plane-wave basis sets, employing the PBE exchange-correlation functional with Grimme's D2 correction [1,2]. Norm-conserving pseudopotentials (ONCV) were used [3,4]. All calculations were performed using the

Quantum ESPRESSO software [5,6]. A supercell consisting of 3×3 WS_2 unit cells on top of 4×4 graphene unit cells was constructed. The Brillouin zone was sampled with a 4×4×1 Monkhorst-Pack *k*-point mesh [7]. The supercell was relaxed with a kinetic energy plane-wave cutoff of 150 Ry. The resulting in-plane lattice constant was 9.77 Å. The distances between the graphene layer and the closest S atoms in WS_2 were 3.2~3.3 Å. With periodic boundary conditions, the vacuum separating the heterostructure and its replica was at least 13 Å.

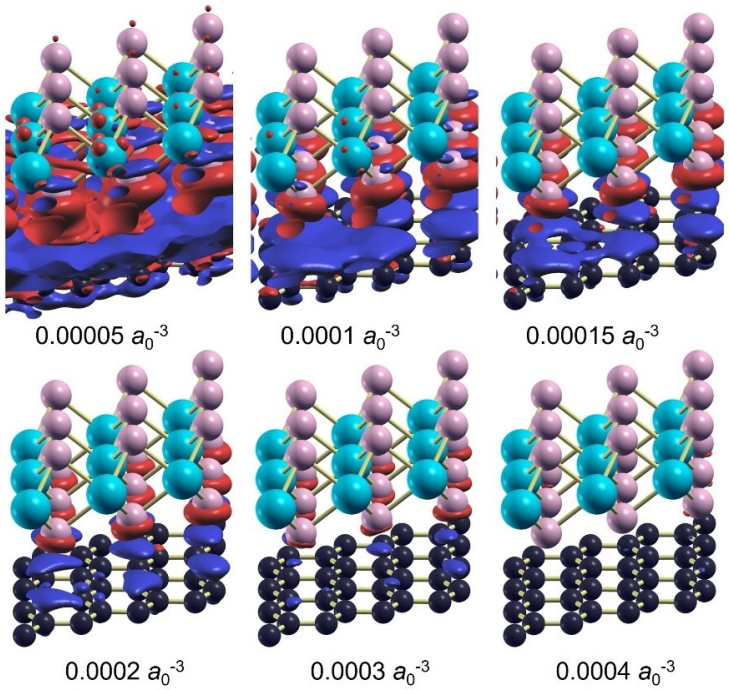

Figure S1. Changes in the electronic charge densities ($\Delta\rho = \rho_{heterostructure} - \rho_{graphene} - \rho_{WS_2}$) of graphene and WS_2 upon formation of the heterostructure. The red and blue isosurfaces correspond to charge increase and decrease, respectively. From left to right and top to bottom, the isosurface values are 0.00005, 0.0001, 0.00015, 0.0002, 0.0003 and 0.0004 $Bohr^{-3}$. When forming the graphene/WS_2 heterostructure, the charge transfers from graphene to WS_2.

Note 3. Calculation of the excited-state biexciton binding energy

The environment dielectric screening is expected to affect the binding energy of excitonic complexes [8-13]. The interaction potential between quasiparticles in a 2D TMDC layer is given by [14]

$$V(r_{ij}) = \frac{q_i q_j \pi}{\kappa r_0 2}\left[H_0\left(\frac{r_{ij}}{r_0}\right) - Y_0\left(\frac{r_{ij}}{r_0}\right)\right]. \quad (1)$$

Here q_i is the charge on the ith particle, r_{ij} is the distance between the ith and jth particles, H_0 is the Struve function, and Y_0 is the Bessel function of the second kind. The average dielectric constant outside the TMDC layer, κ, is given by $\kappa = (\varepsilon_a + \varepsilon_b)/2$, where ε_a and ε_b are the dielectric constants above and below the TMDC layer, respectively. The screening distance in the 2D system is r_0, and depends on the 2D layer polarizability χ_{2D} according to $r_0 = 2\pi\chi_{2D}/\kappa$. The binding energy is a function of r_0 and the electron-hole effective mass ratio σ. For WS_2, χ_{2D} was calculated to be 6.03 Å [15]. The σ value obtained by the $scGW_0$ calculation is used here ($\sigma = 0.84$) [16]. We assume the binding energy of excitonic complexes, E_b^x, has the same form as Eq. (1):

$$E_b^x(r_0) = \frac{1}{\kappa r_0} F^x(r_0),$$

where $F^x(r_0)$ is given by $a_1^x(H_0(a_2^x/r_0) - Y_0(a_2^x/r_0))$, and a_1^x and a_2^x are two parameters. The superscript x denotes the excitonic complex of interest: $x = t$ for trions and $x = b^*$ for excited biexcitons. The binding energies of trions and biexcitons in single-layer WS_2 in vacuum ($\kappa = 1$) have been computed with multiple values of r_0 and σ in Ref. [13]. The binding energies at $\sigma=0.84$ can be obtained by the interpolation with cubic splines. We used the binding energies of trions, $E_{b,}^t$ to obtain $F^t(r_0)$ by fitting the parameters a_1^t and a_2^t in $F^t(r_0) = E_b^t \cdot r_0$ with $\kappa = 1$. Similarly, the parameters a_1^{b*} and a_2^{b*} can also be fitted by using the binding energies of excited biexcitons with the orbital angular momentum $L = 0$.

Having obtained $F^t(r_0)$, we used the experimental value of E_b^t to calculate the effective screening distance r_0^{heter} in the graphene/WS_2/BN heterostructure. Using the obtained r_0^{heter}, we can also estimate the environment dielectric constant κ^{heter}. The binding energy of excited biexcitons in the graphene/WS_2/BN heterostructure can be calculated by substituting $r_0 = r_0^{heter}$ into the expression $E_b^{b*} = F^{b*}(r_0)/(2\pi\chi_{2D})$. Hence, using the experimental trion binding energy, we can calcuate the binding energy of

excited biexitons, which is shown in Table 1. There is good agreement between the calculated and experimental E_b^* in the graphene/WS_2/BN heterostructure.

Table 1: The excited biexciton binding energy and environment dielectric constant in the raphene/WS_2/BN heterostructure calculated by using the measured trion binding energy. Energies are in meV.

Experimental average trion binding energy	Calculated environmental dielectric constant	Calculated excited biexciton binding energy (L = 0)	Experimental excited biexciton binding energy
38.6	2.4	79.5	78

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