Supporting Information for

Interface charge-transfer induced intralayer excited-state biexciton in graphene/WS₂ 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/WS₂ 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 $3 \times 3$ WS$_2$ unit cells on top of $4 \times 4$ graphene unit cells was constructed. The Brillouin zone was sampled with a $4 \times 4 \times 1$ 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](image)

**Figure S1.** Changes in the electronic charge densities ($\Delta \rho = \rho_{\text{heterostructure}} - \rho_{\text{graphene}} - \rho_{\text{WS}_2}$) 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]
\[ V(r_{ij}) = \frac{q_i q_j \pi}{\kappa r_0^2} \left[ H_0 \left( \frac{r_{ij}}{r_0} \right) - Y_0 \left( \frac{r_{ij}}{r_0} \right) \right]. \]  

(1)

Here \( q_i \) is the charge on the \( i \)th particle, \( r_{ij} \) is the distance between the \( i \)th and \( j \)th 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, \( \kappa \), is given by \( \kappa = (\varepsilon_a + \varepsilon_b)/2 \), where \( \varepsilon_a \) and \( \varepsilon_b \) 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 \( \chi_{2D} \) 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 \( \sigma \). For WS\(_2\), \( \chi_{2D} \) was calculated to be 6.03 Å [15]. The \( \sigma \) value obtained by the \textit{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 \( a_{1x} H_0(a_{2x}/r_0) - Y_0(a_{2x}/r_0) \), and \( a_{1x} \) and \( a_{2x} \) 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 \( \sigma \) 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 \( a_{1t} \) and \( a_{2t} \) in \( F^t(r_0) = E_{b,t} \cdot r_0 \) with \( \kappa = 1 \). Similarly, the parameters \( a_{1b^*} \) and \( a_{2b^*} \) 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 \( r_{0,\text{heter}} \) in the graphene/WS\(_2\)/BN heterostructure. Using the obtained \( r_{0,\text{heter}} \), we can also estimate the environment dielectric constant \( \kappa_{\text{heter}} \). The binding energy of excited biexcitons in the graphene/WS\(_2\)/BN heterostructure can be calculated by substituting \( r_0 = r_{0,\text{heter}} \) into the expression \( E_{b^*} = F_{b^*}^*(r_0)/(2\pi \chi_{2D}) \). Hence, using the experimental trion binding energy, we can calculate the binding energy of
excited biexcitons, 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 graphene/WS$_2$/BN heterostructure calculated by using the measured trion binding energy. Energies are in meV.

<table>
<thead>
<tr>
<th>Experimental average trion binding energy</th>
<th>Calculated environmental dielectric constant</th>
<th>Calculated excited biexciton binding energy ($L = 0$)</th>
<th>Experimental excited biexciton binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.6</td>
<td>2.4</td>
<td>79.5</td>
<td>78</td>
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</table>

**References**


[12] Florian M et al 2018 The dielectric impact of layer distances on exciton and trion binding energies in van der Waals heterostructures *Nano Letters* **18** 2725-2732