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Manipulating charge and energy transfer between 2D atomic layers via heterostructure engineering

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Abstract:

Two-dimensional (2D) van der Waals heterostructures have attracted enormous research interests due to their emergent electrical and optical properties. The comprehensive understanding and efficient control of interlayer couplings in such devices are crucial for realizing their functionalities, as well as improving their performance. Here, we report a successful manipulation of interlayer charge transfer between 2D materials by varying different stacking layers consisting of graphene, hexagonal boron nitride, and tungsten disulfide. Under visible light excitation, despite being separated by few-layer boron nitride, the graphene and tungsten disulfide exhibit clear modulation of their doping level, *i.e.*, a change of the Fermi level in graphene as large as 120 meV and a net electron accumulation in WS₂. By using a combination of micro Raman and photoluminescence spectroscopy, we demonstrate that the modulation is originated from simultaneous manipulation of charge and/or energy transfer between each two adjacent layers.

KEYWORDS: *2D materials, van der Waals heterostructure, Raman and photoluminescence spectroscopy, interlayer charge and energy transfer, band engineering*

Charge and energy transfer (CT and ET) play crucial roles in nanoscale solid-state systems, especially in hetero-interfaces formed between 2D atomically thin layers.¹⁻¹¹ Continuous research effort has been conducted mainly based on van der Waals heterostructures built by semiconducting transition metal dichalcogenide (TMD) 2D layers, so as to reveal their fundamental physical pictures as interplayed with their unique properties, *i.e.*, tunable electronic structure, ultimate proximity, and rich excitonic states.^{12,13} Between these 2D semiconductors, type-II band alignment is usually formed, which makes the electron/hole transfer more efficient or even dominated.^{1-3,5} In addition, different types of ET, including shorter range Dexter-type^{6,14} and longer range Föster-type^{7,15} are expected to play an important role as well in 2D heterostructures. Moreover, in Graphene/TMD heterostructure, the ET mechanisms are even dominated as proposed in a recent study.¹⁶ On the other hand, as the rapid

growth of 2D library with variety of properties, careful design and selection of materials provide an extraordinary platform to explore new concepts in CT and ET at 2D limit. Thus, in order to further promote their practical applications in next-generation low dimensional optoelectronic devices, the successful detection and efficient modulation of CT and ET in such a unique system are highly advantageous.

Here, we propose an efficient manipulation of CT and/or ET between 2D systems, referring to as heterostructure engineering. Based on delicate designing of band alignments and offsets between different 2D layers, including bottom graphene (conductor), middle h-BN (insulator), and top WS₂ (semiconductor), we have observed clear photoluminescence quenching in WS₂ and energy shift of Raman-active modes in both graphene and WS₂. The corresponding changes of their charge carrier density and photo-induced charge flow direction have been determined by using combined micro-Raman and photoluminescence spectroscopy together with photocurrent characterizations. Furthermore, by using power-dependent Raman studies, we have revealed photo-induced hole transfer between WS₂ and h-BN, as well as an effective energy transfer between h-BN and graphene, processes of which can be effectively manipulated by the bottom graphene and top WS₂ respectively. These observations indicate simultaneously modulations of the CT and/or ET between each two adjacent layers by simply staking selected 2D materials. Our study unravels the importance of band engineering in manipulating CT and ET in 2D heterostructures, which is of great importance for the fundamental understanding and efficient controlling of the working performance of such optoelectronic devices.

Figure 1a schematically shows the heterostructure configuration. From bottom to top, atomically thin 2D layers including graphene (Gr), few-layer (5-8 nm) h-BN, and monolayer tungsten disulfide (WS₂) have been exfoliated and stacked together in inert environment, so as to form heterostructure with three different regions, labeled as Gr/h-BN, Gr/h-BN/WS₂, and h-BN/WS₂. Figure 1b shows the optical image of one typical sample as prepared, in which different layers and overlapping regions can be clearly distinguished. Then, we performed steady-state optical spectroscopy characterizations, including Raman and photoluminescence measurements under 2.33 eV excitation (532 nm solid state laser). For the graphene layer, we focused on its Raman G -mode ω_G ¹⁷⁻²⁰ measured at selected spots from different regions, including the pristine Gr on SiO₂, Gr/h-BN, and Gr/h-BN/WS₂. The $2D$ -mode ω_{2D} on Gr/h-BN region has also been carefully studied which will be discussed later, while on Gr/h-BN/WS₂ region the Raman features are generally masked by a strong WS₂ PL background under this excitation. As shown in Figure 1c, the ω_G peak of pristine Gr on SiO₂ substrate is near 1582.6 cm⁻¹ with a full width at half maximum (FWHM) around 10 cm⁻¹, which indicates a nearly charge neutral status of the original Gr layer.^{18,19,21} Then, a clear redshift by ~5.6 cm⁻¹ and narrowing down by ~1.7 cm⁻¹ can be observed when measured at the Gr/h-BN region (detailed lineshape analysis can be found as Supplementary Figure S1). It is well established that the G -Raman mode in Gr can be used as clear indicator of its doping level due to the strong electron phonon coupling.^{18,19,21} Here, we can exclude other possible reasons such as temperature, defects, and strain (see Supplementary Information Note 1).^{22,23} Then, the ω_G redshift and narrowing as measured in Gr and h-BN heterostructure suggests a prominent carrier doping in Gr. The sign of net transferred charge flow will be determined later. Furthermore, when the top WS₂ layer is added, the ω_G peak blueshifts back by ~4.3 cm⁻¹ and becomes broadened by ~3.5

cm^{-1} , indicating a suppressed doping effect in the bottom Gr. In other words, the top WS_2 layer has a clear modulation to the bottom Gr or the Gr/h-BN under optical excitation, which is surprising since the middle-layer h-BN is normally considered as a perfect insulator, which behaves as a barrier to block any charge transfer.

In TMD mono- and few-layers, the Raman spectra are closely correlated to their intrinsic properties, including the basic lattice vibrations, interlayer coupling, spin-orbit splitting, *etc.*, which have been extensively investigated.²⁴⁻²⁸ In addition, their Raman-active modes exhibit sufficient sensitivity to external perturbations. For example, the out-of-plane A_{1g} mode in TMD monolayer is sensitive to its charge carrier density,^{29,30} while the E_{2g} mode is believed to be more sensitive to the strain or stress.^{28,31} Then, the extracted parameters of A_{1g} mode including peak position and FWHM can be used as clear readout of the relative doping level. In our heterostructures, we observed a distinctive shift for the A_{1g} mode in WS_2 from different regions, referring to as a blueshift by $\sim 2.5 \text{ cm}^{-1}$ in Gr/h-BN/ WS_2 as compared to h-BN/ WS_2 as shown in Figure 1d. This distinctive blueshift as well as broadening of A_{1g} peak (by approximately 21%) happens at all excitation powers (see Supplementary Figure S2), which indicates a net electron accumulation in the WS_2 layer.³⁰ As a comparison, the E_{2g} mode as measured in these two regions stays consistent, which also confirm a negligible strain effect in our heterostructures (see supplementary Figure S2).^{28,31} Since we choose relatively thick (10 - 20 number of layers) h-BN flake, the direct tunneling through h-BN potential barrier without any assistance of bias is negligible.³²⁻³⁵ So, a charge transfer mechanism, either electron or hole transfer between WS_2 and h-BN, may be considered as the origin for the electron accumulation in WS_2 .

Then, we measured the WS_2 PL spectra at different regions, as shown by Figure 1e and 1f. At room temperature, the intensities of the measured exciton (X) near 2.01 eV and trion (X^-) near 1.96 eV at the Gr/h-BN/ WS_2 region all get quenched by a factor of 2 to 3 times as compared to that from h-BN/ WS_2 region. At lower temperature $\sim 77 \text{ K}$, we observed better resolved X and X^- peaks with even stronger PL quenching, especially for the exciton peak which exhibits about 15 times difference between these two regions. This significant PL quenching together with the Raman A_{1g} mode modulation in Gr/h-BN/ WS_2 region clearly imply a modification of the charge carrier density of the top WS_2 .^{1,16} Thus, although separated by few-layer h-BN, the bottom Gr has a significant influence on the top WS_2 , and vice versa. Therefore, we believe that an efficient manipulation of the charge or energy transfer can be realized by applying different hetero-stacking structures between 2D atomic layers.

Before we look into more detailed analysis, let us first discuss the band diagram in order to tentatively understand the designing of our heterostructure. It is worth noting that the h-BN defect states have been carefully studied,³⁶ which plays an important role in our case. Firstly, as shown by Figure 2a, the existence of h-BN defect states enables photoinduced electron doping in Gr/h-BN heterojunction, which makes the Gr n-doped as we observed. Indeed, the electron doping of Gr by photoexcited defect states in h-BN has been observed by using transport measurements.³⁷ Here, we can also locate the h-BN defect levels by measuring its defect emission, which exhibits a broaden peak centered at $\sim 2.0 \text{ eV}$ with a few narrow peaks observed, as shown by Supplementary Figure S3. Thus, under 2.33 eV green laser excitation, the defect states can be effectively excited. From previous theoretical and experimental reports,³⁶ this defect state may come from a ground-to-excited state transition, for which the

defect ground (DG) and defect excited (DE) states locate at 1.95 eV and 3.9 eV above the valence band respectively.³⁶ Then, the DG and DE states will form a type-II band alignment with the top WS₂ layer as indicated by Figure 2b. Since the DE state holds larger energy difference between Gr Fermi level than the WS₂ conduction band, the excited electrons will keep transferring to Gr side. On the other hand, the DG state locates in-between the Gr Fermi level and WS₂ valence band, which enables the hole transfer from WS₂ to h-BN. In this case, the accumulated holes in h-BN will further transfer to Gr since a type-I band alignment is formed between h-BN defect states and Gr. In addition, the stimulated hole transfer is further confirmed to be balanced with the electron transfer which we will discuss in more details. Thus, there exists no net charge flow from h-BN to Gr, which is in agreement with effective interlayer energy transfer between h-BN and Gr led by the balanced charge flow. Indeed, similar effect has been reported between Gr and TMD monolayer.¹⁶ Since we are working on atomically close interfaces, this energy transfer can possibly rely on either electron exchange (Dexter type) or dipole-dipole couplings (Föster-type), which we cannot distinguish based on our current experiments. More importantly, in order to confirm the photo-induced hole transfer from WS₂ to Gr, we have performed photocurrent characterizations based on another Gr/h-BN/WS₂ heterostructure device with fabricated electric contacts (see Supplementary Figure S7 for device structure, optical and electrical characterizations). As shown in Figure 2c, we have observed a finite negative short circuit current I_{SC} between bottom Gr and top WS₂ layer upon optical excitation, whose magnitude increases almost linearly upon increasing excitation power. More details can be found in Supplementary Information Note 2 and Supplementary Figure S7.

To comprehensively understand and confirm the mechanism, we performed the spatial photoluminescence mapping based on the heterostructure. Figure 3a-c show the integrated intensities of WS₂ exciton I_X , trion I_{X^-} , and their ratio I_X/I_{X^-} at room temperature. All three maps allow us to distinctively identify the Gr/h-BN/WS₂ regions and confirm the PL quenching trend observed on selected spots. From our Raman spectra analysis, a net electron accumulation has been observed in the Gr/h-BN/WS₂ region, which is in agreement with the exciton quenching.³⁸⁻⁴⁰ In addition, the reduced trion intensity indicates no extra electrons accumulated but additional channel for losing holes instead.³⁸⁻⁴⁰ Indeed, this is also consistent with the band alignment in Figure 2b. At first, the electrons in h-BN excited states would prefer to transfer to Gr side which possesses a larger potential difference than the WS₂ side. In addition, the h-BN DG state just reside at an energy level between Gr Fermi level and WS₂ valence band maximum³⁶, which act as an intermediate level for the hole transfer from WS₂ to Gr.

In order to further understand the carrier dynamics in WS₂, we performed the time-resolved photoluminescence (TRPL) studies at room temperature. Figure 3d shows the normalized TRPL spectra for the exciton (X) measured at different regions. From our observations, the rising processes are similar by reaching maximum within 100 ps, while the decay processes differ significantly. We first employed a double exponential fitting to check the decay processes, as shown in Supplementary Figure S5. The spectra measured at h-BN/WS₂ region clearly show two distinct time scales, *i.e.*, a fast decay component $\tau_1 \sim 56.3 \pm 0.9$ ps and a slow decay component $\tau_2 \sim 460 \pm 15$ ps. For the Gr/h-BN/WS₂ region, the fast decay component τ_1 is around 60% longer ($\sim 94 \pm 1.0$ ps) and the slow decay component τ_2 stays almost unchanged $\sim 500 \pm 14$ ps. In addition, the τ_1 process has a clear dependence on the pump fluence (directly

linked to the initial exciton population), while the latter τ_2 stays constant (see Supplementary Figure S5). Therefore, the τ_1 process can be attributed to non-radiative decay process which is correlated to exciton-exciton annihilation (EEA), and the τ_2 process corresponds to the radiative decay process which reflects the direct electron-hole recombination.⁴¹⁻⁴³ Then, we focus on the analysis of τ_1 process since it significantly differs at these two regions, which is supposed to follow the bi-molecular dynamics.^{42, 43} The rate equation of PL decay by including the EEA term can be described as

$$\frac{dn}{dt} = -\frac{n}{\tau} - \gamma n^2 \quad (1)$$

where n is the exciton population, τ is the exciton lifetime without annihilation, and γ is the annihilation rate constant. The solution to equation (1) is

$$n(t) = \frac{N_0 \exp(-\frac{t}{\tau})}{1 + \gamma \tau N_0 [1 - \exp(-\frac{t}{\tau})]} \quad (2)$$

where N_0 is the initial exciton population. Assuming that every pump photon absorbed creates one exciton, the N_0 can be estimated using an absorption cross-section of $5 \times 10^5 \text{ cm}^{-1}$.⁴⁴ So the reciprocal of $n(t)$ is linearly dependent on $\exp(t/\tau)$ as

$$\frac{1}{n(t)} = \left(\frac{1}{N_0} + \gamma \tau \right) \exp\left(\frac{t}{\tau}\right) - \gamma \tau \quad (3)$$

with a slope determined by the N_0 , γ , and τ .⁴³ In order to get the EEA rate γ for different overlapping regions, including h-BN/WS₂ (without Gr) and Gr/h-BN/WS₂ (with Gr), we have replotted the PL decays under different N_0 from $2.64 \times 10^{11} \text{ cm}^{-2}$ to $1.06 \times 10^{12} \text{ cm}^{-2}$ as shown in Figure 3e and 3f. By applying a global fit to the whole data set, we have observed clear different EEA rates in h-BN/WS₂ and Gr/h-BN/WS₂ regions of $\gamma_1 = (3.1 \pm 0.4) \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and $\gamma_2 = (2.1 \pm 0.3) \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, respectively. The slower EEA rate in the three-layer overlapping region suggests a suppressed EEA process when an extra hole transfer channel opens up between WS₂ and h-BN.

At last, to reveal the degree of charge transfer between the layers, we quantitatively determine the Gr Fermi energy evolution by studying the Raman modes dependence on the incident photon flux ϕ_{ph} . Firstly, as shown by Figure 4a and 4b, the ω_G position spatial mapping in the selected area (green rectangular area as shown in Figure 4a) indicates a good uniformity and consistency of the ω_G redshift. Figure 4c and 4d show the ω_G and full width at half maximum Γ_G dependence on ϕ_{ph} as measured from different spots, blue from Gr/h-BN region and red from Gr/h-BN/WS₂ region. In Gr/h-BN region, with an increasing ϕ_{ph} , the ω_G keeps rising, whereas Γ_G decreases. It is worth noting that the ω_{2D} and ω_G display a linear correlation with a slope ~ 0.34 , and their intensity ratio drops significantly under higher ϕ_{ph} , as shown by Supplementary Figure S5. These features allow us to determine the direction of the charge flow between Gr and h-BN, which is photo-induced electron transfer from h-BN to Gr.²² However, with the top WS₂ layer, the ω_G and Γ_G stay nearly constant at all measured ϕ_{ph} . The totally different evolution of Raman G-mode of Gr with increasing ϕ_{ph} , as summarized in Figure 4e, indicates that the net electron doping in Gr has been clearly suppressed when adding the top WS₂. According to our previous analysis, the existence of Gr on the bottom has stimulated the hole transfer from WS₂ to h-BN defect ground state. Given that the Gr Fermi level still lies above the h-BN defect ground state, the holes as transferred

from WS₂ will continue to transfer to Gr. Together with the photo-induced electron transfer from h-BN excited defect state, an effective energy transfer between h-BN and Gr has been enabled, referring to as both electron and hole transfer from h-BN to Gr. In this scenario, there shows nearly balanced charge flow between them, and the doping level in Gr remains unchanged.

As a consequence of the strong coupling between low-energy electronic excitations and the zone-center optical phonons, an anomalous doping dependence of the *G*-mode can be described using the phonon self-energy, whose real part is equal to ω_G and the imaginary part to Γ_G .^{16,19} As shown by the solid lines in Figure 4f, the evolutions of ω_G and Γ_G along with the correlated Fermi energy are due to *G* phonon interactions with electron-hole pairs and the decay of *G* phonon into an electron-hole pair respectively (see methods for theoretical modeling equations). Therefore, by comparing our experimental results (scattered dots in Figure 4f) with the theoretical calculations, we can estimate the correlated Fermi energy of graphene relative to the charge neutrality point as manipulated by the photo-induced charge doping. From our observations, the initial doping level of the Gr as achieved at low ϕ_{ph} is ~100 meV, corresponding to a slightly n-doped initial state. Then, as the ϕ_{ph} increases, the Fermi energy keeps increasing monotonically, and finally reaches a saturation around 220 meV. The saturation behavior and saturation energy level as measured from different samples show good consistency (see Supplementary Note 2). In order to explain this phenomenon, we should consider the relative position of band structure as determined by the offsets between graphene Dirac point and defect levels in h-BN.¹⁶ As sketched in the band diagram in Figure 2a, since the graphene Dirac point lies closer to the defect ground state in h-BN, the photo-induced electron transfer rate should exceed the hole transfer rate immediately after light-on. With an increasing photon flux, the effective Fermi energy of graphene will rise up efficiently due to the small density of states of graphene near the Dirac point. Assuming the transfer rate is mainly determined by the energy difference between the defect levels in h-BN and effective Fermi energy in Gr, a balanced electron and hole transfer will be finally satisfied, resulting in vanished net electron transfer.

In conclusion, we have demonstrated effective heterostructure engineering approaches to prominently manipulate the charge/energy transfer between 2D atomic layers in Gr/h-BN/WS₂ heterostructures. Combined both Raman and photoluminescence spectroscopy, we unravel that the effective photo-induced electron transfer from the defect states in h-BN to Gr can give a clear change of the Fermi energy of Gr by ~120 meV. On the contrary, the photo-induced hole transfer from WS₂ to h-BN defect ground state stimulates an effective energy transfer between h-BN and graphene, which eventually neutralizes the rising of Fermi energy. Our findings pave a new way for understanding and manipulating the microscopic charge and energy transfer mechanisms in emerging van der Waals heterostructure platforms. The simple and effective hetero-stacking engineering between different 2D interfaces are expected to promote further developments not only in light matter interactions manipulations, but also in promising applications in modern photonic and optoelectronic devices.

Methods

Sample Preparation.

Heterostructures formed by graphene, few-layer h-BN, and monolayer WS₂ were fabricated by standard dry transfer technique in a N₂ purified glove box. Each flake was exfoliated mechanically from the bulk crystal and carefully aligned to form Gr/h-BN, Gr/h-BN/WS₂, and h-BN/WS₂ regions. The as transferred heterostructures were thermally annealed at 120°C at high vacuum to clean the surface and enhance the interlayer coupling.

Optical Raman and Photoluminescence Measurements.

The micro Raman and steady-state photoluminescence spectroscopy was conducted by using a Horiba HR800 spectrometer equipped with a liquid nitrogen cooled charge-coupled device (CCD). A 532 nm solid state laser was used as the excitation source, and the power was changed from a few microwatts to above 5 mW. The 1800 grooves/mm and 300 grooves/mm gratings were chosen for Raman and PL spectra dispersions respectively.

Time-resolved Photoluminescence Measurements.

The excitation pulsed laser at 400 nm was obtained from a frequency-doubling of the Ti:sapphire 800 nm laser with a BBO crystal (100 fs pulse duration and 80 MHz repetition rate). The PL emission is first spectrally filtered with the spectrometer, and then detected with an avalanche single photon detector (APD) connected to a single photon counting module (PicoHarp 300). The overall temporal resolution of our setup for the range of wavelengths under investigation is measured to be about 40 ps. We use an 1800 grooves/mm grating and proper entrance slit width to reduce the bandpass range to ~2 nm.

Theoretical Modelling of Graphene G-mode Evolution.

Firstly, the variation of Γ_G is due to the decay of the G phonon into electron-hole pairs,^{18,19} which is given by:

$$\Delta\Gamma_G = \frac{\lambda_\Gamma}{4} \omega_G^0 \left[f\left(-\frac{\hbar\omega_G^0}{2} - E_F\right) - f\left(\frac{\hbar\omega_G^0}{2} - E_F\right) \right],$$

where ω_G^0 is the phonon frequency at $E_F = 0$, $f(E) = [1 + \exp(E/k_B T)]^{-1}$, which is the Fermi-Dirac distribution at temperature T , and λ_Γ corresponds to the electron-phonon coupling strength which is a dimensionless coefficient. Secondly, the frequency shift is the sum of adiabatic and non-adiabatic terms as

$$\Delta\omega_G = \Delta\omega_G^A + \Delta\omega_G^{NA},$$

in which, the adiabatic term $\Delta\omega_G^A$ is correlated to the equilibrium lattice parameter, and the non-adiabatic term $\Delta\omega_G^{NA}$ is corresponding to the renormalization of the G-mode phonon energy due to interactions with electron-hole pairs, as

$$\Delta\omega_G^{NA} = \frac{\lambda_\Gamma}{2\pi\hbar} P \int_{-\infty}^{+\infty} \frac{[f(E-E_F) - f(E)]E^2 \text{sgn}(E)}{E^2 - (\hbar\omega_G^0)^2/4} dE,$$

where P is the principle part.^{18,19} It is worth noting that when $|E_F| < 1$ eV (moderate doping range), the adiabatic contribution only provides a minor correction to the non-adiabatic term and does not affect Γ_G . In our calculations, we applied $\lambda_\Gamma = 0.03$ and $\omega_G^0 = 1582.5$ cm⁻¹ to these two equations, yielding the best matching with our experimental results, which is also consistent with previous reports.²¹

Author Contributions

X.L. and Q.X. conceived the idea. X.L., Z.H., and C.Y. prepared the heterostructures. X.L., J.P., S.L., M.R.A., and W.Z. performed the micro-spectroscopy experiments. K.W. and T.T. provided the h-BN bulk crystals. X.L. wrote the manuscript with input from all authors. Q.X. supervised the whole project.

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Figures and Captions

Figure 1| Heterostructure fabrication and spectroscopy characterizations. **a**, Schematic drawing of Gr/h-BN/WS₂ heterostructure fabricated by dry transfer technique. **b**, Optical image of one typical as-fabricated sample. Black, purple, and red dashed lines indicate graphene, few-layer h-BN, and monolayer WS₂ flakes respectively. **c**, Room temperature Raman spectra of graphene G-mode as measured in different regions including pristine graphene, Gr/h-BN, and Gr/h-BN/WS₂. The spectra are vertically shifted for clarity. **d**, Raman spectra of monolayer WS₂ as measured in Gr/h-BN/WS₂ and h-BN/WS₂ regions. Steady-state photoluminescence spectra of WS₂ as measured in Gr/h-BN/WS₂ (black lines) and h-BN/WS₂ (red lines) at **e**) 300K and **f**) 77K. The exciton and trion peaks of WS₂ are denoted as X and X⁻.

Figure 2| Band diagram and interlayer charge transfer analysis of our heterostructure design. Band alignment and charge transfer between **a)** Gr/h-BN and **b)** Gr/h-BN/WS₂ interfaces. The h-BN defect ground state (DGS) and defect excited state (DES) are located at 1.95 eV and 3.90 eV above the valence band respectively. Red and blue arrows represent interlayer electron and hole transfer respectively. Note, with the existence of top WS₂, the simultaneous electron and hole transfer from h-BN to graphene is in agreement with an effective energy transfer. **c)** Determination of the photo-induced hole movement from Gr to WS₂ by using photo-induced electrical characterizations. Note 1, the top WS₂ is grounded and a bias V_{DS} is applied between Gr (drain) and WS₂ (source). Note 2, more device details are provided in the supplementary information. Inset, excitation power dependent short circuit current I_{SC} .

Figure 3| Steady-state and time-resolved photoluminescence spectroscopies study of WS₂. Contour mapping of **a)** exciton intensity I_X , **b)** trion intensity I_{X^-} , and **c)** I_X/I_{X^-} ratio as measured at room temperature for heterostructure sample in Figure 1b. Black dashed lines indicate Gr/h-BN/WS₂ regions. **d**, Normalized time-resolved photoluminescence spectra of WS₂ exciton in Gr/h-BN/WS₂ (black) and h-BN/WS₂ (red) regions at $2.64 \times 10^{11} \text{ cm}^{-2}$ initial exciton population. Note, gray dashed line represents instrument response function. The linearized form by using equation (3) for WS₂ exciton PL decay at different initial exciton populations N_0 as measured at **e)** h-BN/WS₂ (without Gr) and **f)** Gr/h-BN/WS₂ (with Gr), respectively. Note, the solid lines represent the linear fit to the data.

Figure 4| Determination of graphene Fermi level by Raman spectroscopy. **a**, Optical image of the heterostructure sample with green rectangular indicating the Raman spatial mapping region. **b**, Spatial mapping of the Raman G -mode position ω_G in graphene. Photon flux dependent Raman G -mode **c**) peak position ω_G and **d**) full width at half maximum Γ_G measured at selected spots in (a). Red denotes Gr/h-BN/WS₂ region, blue denotes Gr/h-BN region. **e**, Evolution of the Raman G -mode upon increasing photon flux in different regions. **f**, Determination of the graphene Fermi level in Gr/h-BN region. Note, scattered dots represent experimental results and solid lines represent fitting results.

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