Ultrafast Charge Separation in Bilayer WS$_2$/Graphene Heterostructure Revealed by Time- and Angle-Resolved Photoemission Spectroscopy

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Efficient light harvesting devices need to combine strong absorption in the visible spectral range with efficient ultrafast charge separation. These features commonly occur in novel ultimately thin van der Waals heterostructures with type II band alignment. Recently, ultrafast charge separation was also observed in monolayer WS$_2$/graphene heterostructures with type I band alignment. Here we use time- and angle-resolved photoemission spectroscopy to show that ultrafast charge separation also occurs at the interface between bilayer WS$_2$ and graphene indicating that the indirect band gap of bilayer WS$_2$ does not affect the charge transfer to the graphene layer. The microscopic insights gained in the present study will turn out to be useful for the design of novel optoelectronic devices.

Keywords: TMD, graphene, van der Waals heterostructures, tr-ARPES, ultrafast charge transfer, photovoltaics

1. INTRODUCTION

Solar energy conversion plays an important role in satisfying mankind's ever-increasing energy usage in an environmentally friendly way. Despite several decades of optimization Silicon solar cells still lack efficiency. On the other hand, highly efficient III-V multijunction solar cells are expensive and not sustainable [1, 2]. Recently, van der Waals (vdW) heterostructures made of different monolayer (ML) transition metal dichalcogenides (TMDs) have emerged as a promising new solar cell platform due to their strong excitonic absorption in the visible spectral range [3, 4] followed by efficient ultrafast charge separation due to type II band alignment [5–10] (see **Figure 1A**). Interestingly, ultrafast charge separation was also found to occur in ML WS$_2$/graphene heterostructures despite the type I band alignment [11–13] (see **Figure 1B**). These heterostructures combine the benefits of a direct gap semiconductor with strong spin-orbit coupling [14, 15] and a semimetal with high-mobility carriers and long spin lifetimes [16] with great potential for novel optoelectronic and optospintronic applications [17].

FIGURE 1 | Influence of band alignment on ultrafast charge transfer in different van der Waals heterostructures. **(A)** Example of a heterostructure with type II band alignment favoring electron transfer. **(B)** Type I band alignment of a heterostructure made of monolayer WS_2 and monolayer graphene. Both electrons and holes are found to transfer to the graphene layer albeit at different rates resulting in ultrafast charge separation. **(C)** Band alignment of a heterostructure made of bilayer WS_2 and monolayer graphene. The influence of the indirect band gap on the microscopic scattering channels mediating ultrafast charge transfer remains unexplored.

One simple way to improve the efficiency of WS_2/graphene-based light harvesting devices might be to enhance the thickness and therefore the absorption of the WS_2 layer [18–20]. It is not *a priori* clear, however, if ultrafast charge separation survives when direct-gap monolayer WS_2 is replaced by thicker WS_2 layers with an indirect band gap (**Figure 1C**). In this work we address this issue by exciting carriers across the direct gap at the K-point of BL WS_2 in an epitaxial BL WS_2/graphene heterostructure on SiC(0001) and tracing the relaxation of the photogenerated electron-hole pairs as a function of time, energy, and momentum using time- and angle-resolved photoemission spectroscopy (tr-ARPES). We find that photoexcited holes in BL WS_2 are transferred to the graphene layer within 100 fs. The photoexcited electrons are found to remain in the conduction band of BL WS_2 for 420 fs resulting in the formation of a charge separated transient state with a lifetime of 770 fs. These timescales are consistent with the microscopic charge transfer model recently proposed for ML WS_2/graphene heterostructures [13] indicating that also in the case of BL WS_2 on graphene the timescale for charge separation is determined by direct tunneling at the points in the Brillouin zone where WS_2 and graphene bands intersect.

2. METHODS

2.1. Sample Preparation and Characterization

Commercial N-doped 6H-SiC(0001) wafers from SiCrystal GmbH were etched in hydrogen atmosphere and then graphitized by annealing at 1,300°C in argon atmosphere for 8 min [21]. The resulting carbon buffer layer was decoupled from the substrate by hydrogen intercalation at 800°C yielding a completely sp²-hybridized quasi free-standing hole-doped graphene monolayer [22]. WS_2 was grown on top of this graphene layer by low pressure chemical vapor deposition (LPCVD) in a standard hot-wall reactor at a pressure of 1 mbar [23, 24]. Argon served as carrier gas with a flow of 80 sccm. WO_3 and S precursors with a mass ratio of 1:100 were kept at

900 and 120°C, respectively. The WO_3 powder was placed close to the substrate. After growth, the sample was characterized with secondary electron microscopy (SEM), Raman and photoluminescence (PL) spectroscopy, as well angle-resolved photoemission spectroscopy (ARPES).

The SEM picture in **Figure 2A** shows dark triangular WS_2 islands that cover $\sim 80\%$ of the graphene layer. The orientation of the triangles reveals the presence of two rotational domains with an angle of 60° between them. From previous low energy electron diffraction measurements on similar samples [11] we deduce that either the ΓK- or the $\Gamma K'$-direction of the WS_2 islands are aligned with the ΓK-direction of graphene. Further, the topological contrast reveals that $\sim 90\%$ of the islands consist of bilayer WS_2. This is consistent with the Raman spectrum shown in **Figure 2B** where the energy of the A_{1g} peak at 417 cm^{-1} and the intensity ratio between the central peak at 351 cm^{-1} ($2LA + E_{2g}$) and the A_{1g} peak of ~ 6 are indicative of bilayer WS_2 [25]. From the PL spectrum in **Figure 2C** we find a quenched A-exciton resonance at 635 nm (1.95 eV) which confirms the presence of bilayer WS_2 [26]. The ARPES spectrum in **Figure 2D** was taken along the along the ΓK-direction. We find that the band structure of the heterostructure is a superposition of the band structures of the constituting materials that are indicated by the white dashed lines [15, 27]. The Dirac cone of graphene is found to be hole-doped with the Dirac-point 300 meV above the Fermi level, E_F. As expected for bilayer WS_2 [15] the maximum of the WS_2 valence band is found to be located at the Γ-point.

2.2. Tr-ARPES

Tr-ARPES experiments were performed at the Artemis user facility at the Rutherford Appleton Laboratory in Harwell, UK. We used a Ti:Sa amplifier with a central wavelength of 795 nm, a repetition rate of 1 kHz, 30 fs pulse duration, and 12 mJ pulse energy to generate visible pump and extreme ultraviolet (XUV) probe pulses. Two mJ of output energy were focused into an Argon gas jet for high harmonics generation. A single harmonic at $\hbar\omega_{\mathrm{probe}} = 31.8$ eV was selected with a time-preserving grating

FIGURE 2 | Sample characterization: **(A)** Secondary electron micrograph revealing triangular WS$_2$ islands with two different rotational domains. The picture was obtained with *in lens* mode with an accelerating voltage of 5 keV and a beam current of 96 pA. **(B)** Raman spectrum. Arrows indicate the phonon modes that were used to determine the layer thickness. **(C)** Photoluminescence (PL) spectrum. Raman and PL measurements were carried out with 1 mW laser excitation at $\lambda = 532$ nm at room temperature. **(D)** ARPES spectrum revealing the occupied part of the band structure of the heterostructure. Orange and red lines indicate the two energy distribution curves (EDCs) that were chosen for the time-resolved measurements in **Figure 3**. White dashed lines denote theoretical band positions of graphene [27] and bilayer WS$_2$ [15]. A rigid band shift of +0.3 eV was applied to graphene bands to account for the observed p-doping. WS$_2$ CB and VB were rigidly shifted by -0.81 and -1.19 eV, respectively, to match the experimental dispersion. The thin white line marks the position of the Fermi level, E_F. At an emission angle of $\sim 23°$ the laser beam was directly reflected into the Time-of-Flight analyzer dazzling the detector and leading to a dark corridor at ~ 0.8 Å^{-1}.

monochromator [28] to be used as the probe. Ten mJ of output power were used to seed an optical parametric amplifier. The signal beam with a photon energy of 1 eV was frequency doubled yielding 2 eV pump pulses matching the A-exciton resonance in WS$_2$. The kinetic energy of the photoelectrons emitted from the sample by the XUV probe pulse were measured with a home-built Time-of-Flight analyzer with an angular acceptance of 2° [29]. The static ARPES spectrum in **Figure 2D** was obtained by rotating the sample. We measured the energy dependence of the photocurrent at two different emission angles (energy distribution curves, EDCs) as a function of pump-probe delay. The energy and temporal resolution of the experiment were 450 meV and 66 fs, respectively.

3. RESULTS

To investigate ultrafast charge transfer in our BL WS$_2$/graphene heterostructure we excited carriers across the direct band gap

at the K-point of BL WS$_2$ using 2 eV pump pulses and probed the response of the heterostructure using tr-ARPES. In detail, we investigated the time dependence of two representative energy distributions curves (EDC 1 and EDC 2 in **Figure 2D**) to obtain the population and band structure dynamics of the WS$_2$ conduction and valence band (CB and VB) and the graphene Dirac cone, respectively. The pump fluence was 6.6 mJ/cm^2 for EDC 1 (WS$_2$) and 9.1 mJ/cm^2 for EDC 2 (graphene).

Figures 3A,B show EDC 1 and EDC 2, respectively, as a function of pump-probe delay. The corresponding pump-induced changes obtained by subtracting the respective EDC at negative pump-probe delay from the transient EDCs are shown in **Figures 3C,D**. Upon arrival of the pump pulse the WS$_2$ VB is found to shift toward the Fermi level in **Figure 3A**. This up-shift is responsible for the strong gain (red) and loss (blue) signal around -2 eV in **Figure 3C**. **Figure 3C** also reveals a transient gain of photoelectrons in the CB of WS$_2$ around $+1$ eV following photoexcitation. The graphene π-band in **Figure 3B** is found to

FIGURE 3 | Time- and angle-resolved photoemission spectroscopy (tr-ARPES). **(A,B)** Time-resolved EDCs measured along the orange (EDC 1) and red lines (EDC 2), respectively, in **Figure 2D** as a function of pump-probe delay after photoexcitation at $\hbar\omega_{pump} = 2$ eV. **(C,D)** Pump-induced changes of EDC 1 and EDC 2, respectively, obtained by subtracting the equilibrium EDC taken at negative pump-probe delay from all transient EDCs. Red and blue correspond to gain and loss of photoelectrons with respect to negative pump-probe delay, respectively. Colored brackets indicate the integration ranges for the data presented in **Figure 4**.

broaden and to shift down which—together with the up-shift of the WS$_2$ VB at lower energy—produces the gain-loss-gain signal in the energy range between $+1$ and -2 eV in **Figure 3D**.

To analyze the transient population dynamics of the individual bands we integrated the EDCs in **Figure 3** over the energy range indicated by the colored brackets yielding the pump-probe traces in **Figure 4**. Panel A shows the transient population of the WS$_2$ VB and CB in green and orange, respectively. The population of the WS$_2$ VB is found to be unaffected by the photoexcitation within the experimental signal-to-noise ratio. The WS$_2$ CB on the other hand exhibits a clear gain of electrons. An exponential fit to the data yields a lifetime of the electrons in the WS$_2$ CB of $\tau = 420 \pm 20$ fs. **Figure 4B** shows the gain above and the loss below the Fermi level in graphene. We find a short-lived gain ($\tau = 97 \pm 3$ fs) and a long-lived loss ($\tau = 840 \pm 30$ fs). The transient up-shift of the WS$_2$ VB gives rise to a gain of photoelectrons above its equilibrium position that is plotted as a function of pump-probe delay in **Figure 4C**. An exponential fit to the data yields a lifetime of $\tau = 770 \pm 30$ fs.

In agreement with Aeschlimann et al. [11] and Krause et al. [13], we interpret these timescales as follows: The absence of holes in the WS$_2$ VB together with the short-lived gain in graphene indicates that the photogenerated holes in the WS$_2$ VB are rapidly (within ~ 100 fs) refilled by electrons from the Dirac

cone. The photoexcited electrons are found to remain in the WS$_2$ CB for ~ 400 fs, indicating the formation of a charge-separated transient state where the holes reside in the graphene layer and the electrons reside in the WS$_2$ layer. This charge-separated state is expected to decrease the binding energy of the WS$_2$ states and to increase the binding energy of the graphene states [11, 13].

Figures 5A,B illustrate the fitting procedure used to determine the transient peak positions of the WS$_2$ VB and CB and the graphene Dirac cone, respectively. Details are provided in the figure caption. The transient positions of the WS$_2$ CB and VB are shown in **Figures 5C,D**, respectively. We find that the WS$_2$ VB shifts up by ~ 110 meV with a lifetime of $\tau = 600 \pm 20$ fs (**Figure 5D**). The transient WS$_2$ band gap at $k \approx 1.1$ Å^{-1} obtained by subtracting the transient position of the VB from the transient position of the CB is displayed in **Figure 5E**. An exponential fit yields a transient band gap reduction of ~ 230 meV with a lifetime of $\tau = 140 \pm 40$ fs. Note that the equilibrium gap size of 2.7 eV at $k \approx 1.1$ Å^{-1} is bigger than the direct band gap at the K-point [13, 30]. In good agreement with Chernikov et al. [31], Liu et al. [32], Ulstrup et al. [33], and Pogna et al. [34], we attribute this band gap renormalization to the presence of photoexcited carriers that screen the Coulomb interaction.
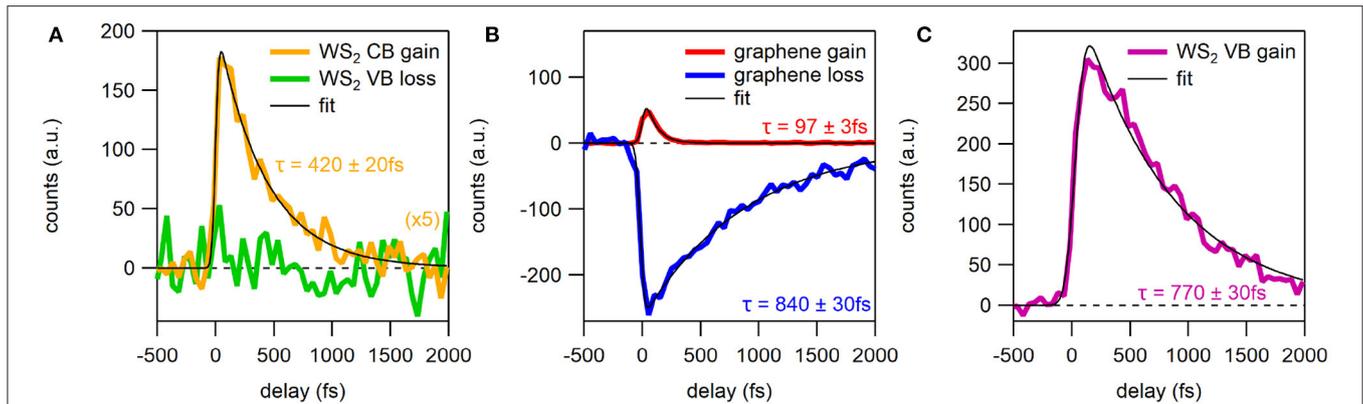
FIGURE 4 | Population dynamics of WS$_2$ and graphene states. **(A)** Transient occupation of WS$_2$ conduction band (CB, orange) and valence band (VB, green). The curves were obtained by integrating the photocurrent over the energy range marked by the orange and green brackets in **Figure 3A** for CB and VB, respectively. **(B)** Transient photocarrier dynamics of graphene. The curves were obtained by integrating the photocurrent over the energy range marked by the red and blue brackets in **Figure 3B** corresponding to the gain above E_F and the loss below E_F, respectively. **(C)** Photocurrent integrated over the energy range marked by the purple bracket in **Figure 3C** as a function of pump-probe delay. Black lines are exponential fits to data.
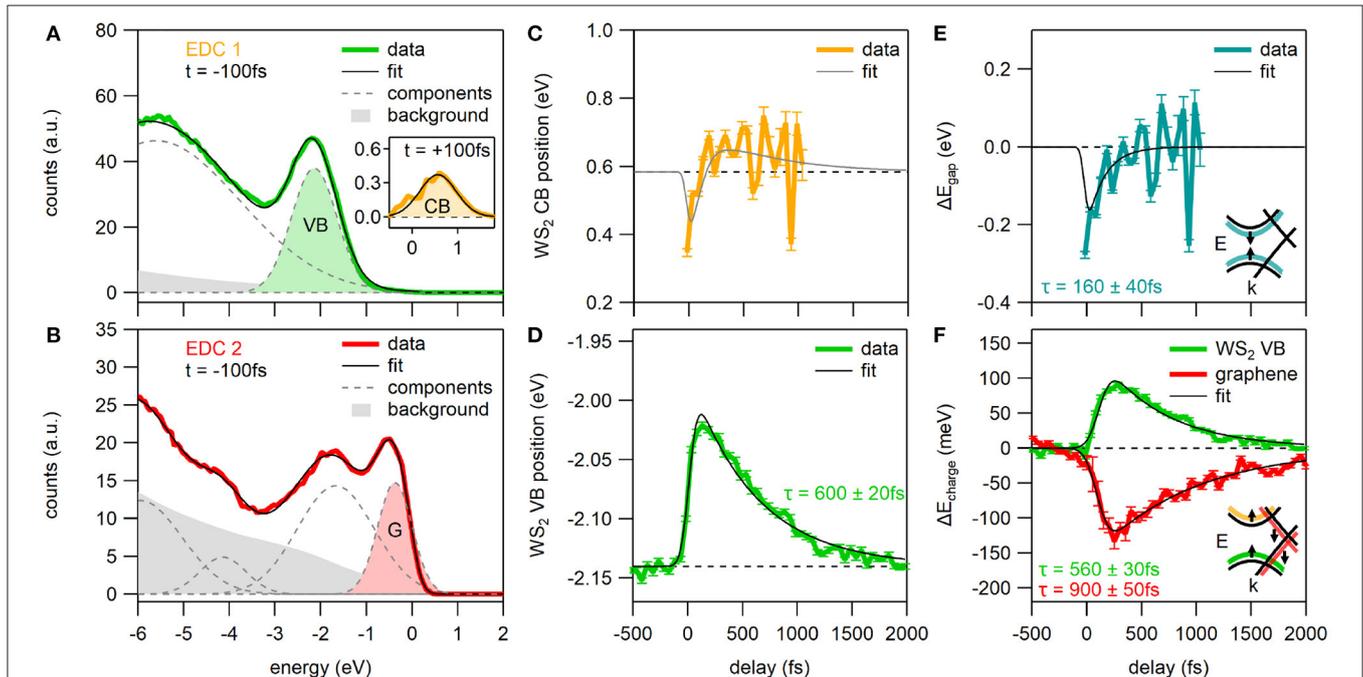
FIGURE 5 | Transient band shifts. **(A)** EDC 1 at negative pump-probe delay together with Gaussian fit. The inset shows the difference EDC 1 at the peak of the pump-probe signal used to fit the binding energy of the WS$_2$ CB with a single Gaussian. **(B)** EDC 2 at negative pump-probe delay together with Gaussian fit. Fit components and Shirley background are displayed as dashed gray lines and gray-shaded areas, respectively, in **(A,B)**. The peaks that were used to determine the transients peak positions in **(C,D,F)** are shaded in the respective colors in **(A,B)**. **(C)** Transient position of WS$_2$ CB. **(D)** Transient position of WS$_2$ VB. **(E)** Transient changes of WS$_2$ band gap calculated by subtracting **(D)** from **(C)**. **(F)** Charging shifts of WS$_2$ VB and graphene Dirac cone as a function of pump-probe delay. Black lines are exponential fits to the data.

The transient band gap renormalization results in shifts of the WS$_2$ VB and CB that are symmetric with respect to the center of the WS$_2$ band gap (see inset of **Figure 5E**). By subtracting $|\Delta E_{gap}|/2$ from the transient position of the WS$_2$ VB we obtain the transient VB shift shown in green in **Figure 5F** that shows a remaining up-shift of $\sim$ 90 meV with a lifetime of $\tau = 560\pm30$ fs.

At the same time the π-bands of graphene shown in red in **Figure 5F** shift down by $\sim$ 110 meV with a lifetime of $\tau = 900 \pm 50$ fs. As discussed previously, these shifts are a direct consequence of the transient charge-separated state where excess negative charge on the WS$_2$ layer decreases the binding energy of the WS$_2$ states and the corresponding excess positive charge on

FIGURE 6 | Sketch of microscopic charge transfer model. Thick yellow and red arrows indicate direct tunneling of electrons and holes, respectively, through the crossing points of the respective bands. Green arrows indicate defect-assisted tunneling of electrons via S vacancies inside the WS$_2$ layer.
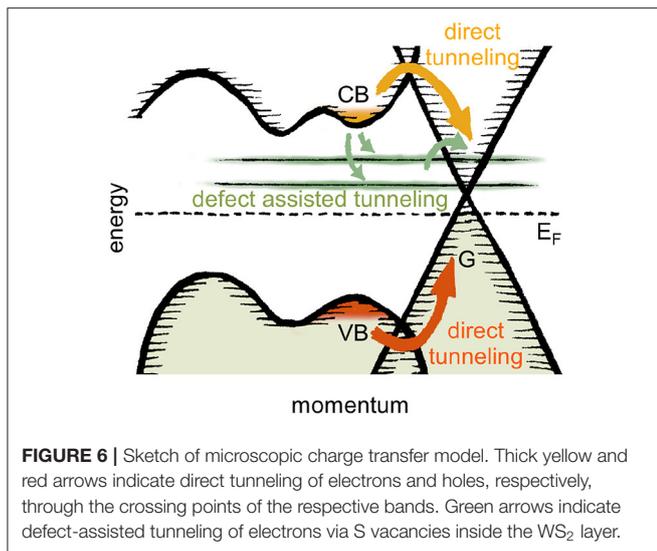
the graphene layer increases the binding energy of the graphene states. These charging shifts are sketched in the inset of **Figure 5F**. At this point we are able to attribute the pump-probe signal in **Figure 4C** to the transient up-shift of the WS$_2$ layer the lifetime of which is linked to the lifetime of the charge-separated state [13]. Also, the dynamics of the WS$_2$ CB shown in **Figure 5C** can now be explained by the combined effect of band gap renormalization that increases the binding energy of the WS$_2$ CB on the timescale of the photoexcitation and charging that decreases the binding energy of the WS$_2$ CB on the timescale of the hole transfer.

All things considered, our data reveals a detailed picture of the ultrafast charge separation following photoexcitation of the WS$_2$/graphene heterostructure. We find that (1) hole transfer from WS$_2$ to graphene occurs within $\sim$ 100 fs, (2) photoexcited electrons remain inside the WS$_2$ CB for $\sim$ 400 fs, and (3) the charge-separated state decays within $\sim$ 800 fs (This number corresponds to the average of the lifetimes of the graphene loss in **Figure 4B**, the WS$_2$ VB gain in **Figure 4C** and the charging shifts in **Figure 4F**).

4. DISCUSSION

The observed lifetimes for electron and hole transfer are in good agreement with previous tr-ARPES [11, 13] and time-resolved optical techniques [12] on similar WS$_2$/graphene heterostructures. Next we will discuss if the microscopic model for ultrafast charge separation across the interface between monolayer WS$_2$ and monolayer graphene [13] also applies to heterostructures made of bilayer WS$_2$ and monolayer graphene. In this model [13], the timescale for ultrafast charge separation in the heterostructure is determined by direct tunneling of hot carriers from WS$_2$ to graphene at those points in the Brillouin zone where the respective bands intersect. The associated energy barrier is smaller for holes than for electrons which, combined with a larger tunneling matrix element and a larger scattering phase space, results in hole transfer being faster than electron

transfer. The lifetime of the charge separated state, on the other hand, is determined by defect-assisted tunneling via in-gap states originating from S vacancies inside the WS$_2$ layer. This decay channel is extremely sensitive to the number of S vacancies in the sample, resulting in lifetimes of the transient charge-separated state between $\sim$ 1 ps in high-quality epitaxial samples [11, 13] and > 1 ns in commercial manually assembled heterostructures [12]. In this model ultrafast charge transfer occurs close to the K-point of WS$_2$ where the WS$_2$ VB maximum and CB minimum are located.

It is not *a priori* clear whether this model also applies to heterostructures made of bilayer WS$_2$ and monolayer graphene because, in this case, the maximum of the WS$_2$ VB and the minimum of the WS$_2$ CB are located at Γ and Σ (in between Γ and K), respectively. The observed timescales for hole transfer from WS$_2$ to graphene within $\sim$ 100 fs and a lifetime of the electrons inside the WS$_2$ CB at K of $\sim$ 400 fs are perfectly consistent with direct tunneling via band intersections close to the K-point. The lifetime of the charge-separated transient state of $\sim$ 800 fs observed in the present heterostructure is consistent with defect-assisted tunneling via S vacancies in similar high-quality epitaxial samples [11, 13]. Therefore, we conclude that, despite the band structure differences, the microscopic model for ultrafast charge transfer developed for the interface between monolayer WS$_2$ and monolayer graphene [13] also applies for heterostructures made of bilayer WS$_2$ and monolayer graphene (see sketch in **Figure 6**).

In summary, we have shown that ultrafast charge separation also occurs at the interface between bilayer WS$_2$ and monolayer graphene. Together with the enhanced absorption in the visible spectral range compared to monolayer WS$_2$ our findings provide important insights that will guide the design of novel optoelectronic applications.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors upon request.

AUTHOR CONTRIBUTIONS

FUNDING

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