We use time- and angle-resolved photoemission spectroscopy (tr-ARPES) to investigate ultrafast charge transfer in an epitaxial heterostructure made of monolayer WS$_2$ and graphene. This heterostructure combines the benefits of a direct-gap semiconductor with strong spin-orbit coupling and strong light-matter interaction with those of a semimetal hosting massless carriers with extremely high mobility and long spin lifetimes. We find that, after photoexcitation at resonance to the A-exciton in WS$_2$, the photoexcited holes rapidly transfer into the graphene layer while the photoexcited electrons remain in the WS$_2$ layer. The resulting charge-separated transient state is found to have a lifetime of $\sim 1$ ps. We attribute our findings to differences in scattering phase space caused by the relative alignment of WS$_2$ and graphene bands as revealed by high-resolution ARPES. In combination with spin-selective optical excitation, the investigated WS$_2$/graphene heterostructure might provide a platform for efficient optical spin injection into graphene.

**RESULTS**

Figure 1A shows a high-resolution ARPES measurement obtained with a helium lamp of the band structure along the $\Gamma$K-direction of the epitaxial WS$_2$/graphene heterostructure. The Dirac cone is found to be hole-doped with the Dirac point located $\sim 0.3$ eV above the equilibrium chemical potential. The top of the spin-split WS$_2$ valence band is found to be $\sim 1.2$ eV below the equilibrium chemical potential.

Figure 1B shows a tr-ARPES snapshot of the band structure close to the WS$_2$ and graphene K-points measured with 100-fs extreme ultraviolet pulses at 26-eV photon energy at negative pump-probe delay before the arrival of the pump pulse. Here, the spin splitting is not resolved because of sample degradation and the presence of the 2-eV pump pulse that causes space charge broadening of the spectral features. Figure 1C shows the pump-induced changes of the photocurrent with respect to Fig. 1B at a pump-probe delay of 200 fs where the pump-probe signal reaches its maximum. Red and blue colors indicate gain and loss of photoelectrons, respectively.

To analyze this rich dynamics in more detail, we first determine the transient peak positions of the WS$_2$ valence band and the
Fig. 1. Equilibrium band structure and photocarrier dynamics of WS2/graphene heterostructure. (A) Equilibrium photocurrent measured along the ΓK-direction with an unpolarized helium lamp. (B) Photocurrent for negative pump-probe delay measured with p-polarized extreme ultraviolet pulses at 26-eV photon energy. Dashed gray and red lines mark the position of the line profiles used to extract the transient peak positions in Fig. 2. (C) Pump-induced changes of the photocurrent 200 fs after photoexcitation at a pump photon energy of 2 eV with a pump fluence of 2 mJ/cm². Gain and loss of photoelectrons are shown in red and blue, respectively. The boxes indicate the area of integration for the pump-probe traces displayed in Fig. 3.

Next, we integrate the pump-probe signal over the areas indicated by the colored boxes in Fig. 1C and plot the resulting counts as a function of pump-probe delay in Fig. 3. Curve 1 in Fig. 3 shows the dynamics of the photoexcited carriers close to the bottom of the conduction band of the WS2 layer with a lifetime of 1.1 ± 0.1 ps obtained from an exponential fit to the data (see the Supplementary Materials).

In curves 2 and 3 of Fig. 3, we show the pump-probe signal of the graphene π-band. We find that the gain of electrons above the equilibrium chemical potential (curve 2 in Fig. 3) has a much shorter lifetime (180 ± 20 fs) compared to the loss of electrons below the equilibrium chemical potential (1.8 ± 0.2 ps in curve 3 Fig. 3). Further, the initial gain of the photocurrent in curve 2 of Fig. 3 is found to turn into loss at t = 400 fs with a lifetime of ~2 ps. The asymmetry between gain and loss is found to be absent in the pump-probe signal of uncovered monolayer graphene (see fig. S5 in the Supplementary Materials), indicating that the asymmetry is a consequence of interlayer coupling in the WS2/graphene heterostructure. The observation of a short-lived gain and long-lived loss above and below the equilibrium chemical potential, respectively, indicates that electrons are efficiently removed from the graphene layer upon photoexcitation of the heterostructure. As a result, the graphene layer becomes positively charged, which is consistent with the increase in binding energy of the π-band found in Fig. 2B. The downshift of the π-band removes the high-energy tail of the equilibrium Fermi-Dirac distribution from above the equilibrium chemical potential, which partly explains the change of sign of the pump-probe signal in curve 2 of Fig. 3. We will show below that this effect is further enhanced by the transient loss of electrons in the π-band.

This scenario is supported by the net pump-probe signal of the WS2 valence band in curve 4 of Fig. 3. These data were obtained by integrating the counts over the area given by the black box in Fig. 1B that captures the electrons photomitted from the valence band at all pump-probe delays. Within the experimental error bars, we find no indication for the presence of holes in the valence band of WS2 for any pump-probe delay. This indicates that, after photoexcitation, these holes are rapidly refilled on a time scale short compared to our temporal resolution.

To provide final proof for our hypothesis of ultrafast charge separation in the WS2/graphene heterostructure, we determine the number of holes transferred to the graphene layer as described in detail in the Supplementary Materials. In short, the transient electronic distribution of the π-band was fitted with a Fermi-Dirac distribution. The number of holes was then calculated from the resulting values for the transient chemical potential and electronic temperature. The result is shown in Fig. 4. We find that a total...
The photoexcited electrons in the conduction band of WS₂ are refilled by electrons originating from the graphene but considerably less efficiently. The photoexcited holes in the valence band of WS₂ are transferred from WS₂ to graphene with a lifetime of 1.5 ± 0.2 ps.

In the transient state, the photoexcited electrons reside in the conduction band of WS₂ while the photoexcited holes are located in the π-band of graphene (Fig. 5C). This means that the WS₂ layer is negatively charged and the graphene layer is positively charged. This accounts for the transient peak shifts (Fig. 2), the asymmetry of the graphene pump-probe signal (curves 2 and 3 of Fig. 3), the absence of holes in the valence band of WS₂ (curve 4 Fig. 3), as well as the additional holes in the graphene π-band (Fig. 4). The lifetime of this charge-separated state is ∼1 ps (curve 1 Fig. 3).

Similar charge-separated transient states have been observed in related van der Waals heterostructures made out of two direct-gap semiconductors with type II band alignment and staggered bandgap (27–32). After photoexcitation, the electrons and holes were found to rapidly move to the bottom of the conduction band and to the top of the valence band, respectively, that are located in different layers of the heterostructure (27–32).

In the case of our WS₂/graphene heterostructure, the energetically most favorable location for both electrons and holes is at the Fermi level in the metallic graphene layer. Therefore, one would expect that both electrons and holes rapidly transfer to the graphene π-band. However, our measurements clearly show that hole transfer (<200 fs) is much more efficient than electron transfer (∼1 ps). We attribute this to the relative energetic alignment of the WS₂ and the graphene bands as revealed in Fig. 1A that offers a larger number of available final states for hole transfer compared to electron transfer as recently anticipated by (14, 15). In the present case, assuming a ∼2 eV WS₂ bandgap, the graphene Dirac point and equilibrium chemical potential are located ∼0.5 and ∼0.2 eV above the middle of the WS₂ bandgap, respectively, breaking electron-hole symmetry. We find that the number of available final states for hole transfer is ∼6 times larger than for electron transfer (see the Supplementary Materials), which is why hole transfer is expected to be faster than electron transfer.

A complete microscopic picture of the observed ultrafast asymmetric charge transfer should, however, also consider the overlap between the orbitals that constitute the A-exciton wave function in WS₂ and the graphene π-band, respectively, different electron-electron and electron-phonon scattering channels including the constraints imposed by momentum, energy, spin, and pseudospin conservation, the influence of plasma oscillations (33), as well as the role of a
found that, when excited at resonance to the A-exciton of WS\textsubscript{2} at 2 eV, the conduction band of WS\textsubscript{2}. The corresponding holes in the valence band of WS\textsubscript{2} spin polarization.

be used for efficient optical spin injection into graphene resulting in transient state was found to be larger than for electron transfer. The lifetime of the charge-separated fer. In this case, the investigated WS\textsubscript{2}/graphene heterostructure might mediate the charge transfer (34–35, 37). Also, one might speculate whether the observed charge transfer state consists of charge transfer excitons or free electron-hole pairs (see the Supplementary Materials). Further theoretical investigations that go beyond the scope of the present paper are required to clarify these issues.

In summary, we have used tr-ARPES to study ultrafast interlayer charge transfer in an epitaxial WS\textsubscript{2}/graphene heterostructure. We found that, when excited at resonance to the A-exciton of WS\textsubscript{2} at 2 eV, the photoexcited holes rapidly transfer into the graphene layer while the photoexcited electrons in WS\textsubscript{2} and the corresponding holes in graphene are expected to show opposite spin polarization.

possible displacive excitation of coherent phonon oscillations that might mediate the charge transfer (34, 35). Also, one might speculate whether the observed charge transfer state consists of charge transfer excitons or free electron-hole pairs (see the Supplementary Materials). Further theoretical investigations that go beyond the scope of the present paper are required to clarify these issues.

In summary, we have used tr-ARPES to study ultrafast interlayer charge transfer in an epitaxial WS\textsubscript{2}/graphene heterostructure. We found that, when excited at resonance to the A-exciton of WS\textsubscript{2} at 2 eV, the photoexcited holes rapidly transfer into the graphene layer while the photoexcited electrons remain in the WS\textsubscript{2} layer. We attributed this to the fact that the number of available final states for hole transfer is larger than for electron transfer. The lifetime of the charge-separated transient state was found to be 1 ps. In combination with spin-selective optical excitation using circularly polarized light (22–25), the observed ultrafast charge transfer might be accompanied by spin transfer. In this case, the investigated WS\textsubscript{2}/graphene heterostructure might be used for efficient optical spin injection into graphene resulting in novel optospintronic devices.

**MATERIALS AND METHODS**

**Sample fabrication**

The graphene samples were grown on commercial semiconducting 6H-SiC(0001) wafers from SiCrystal GmbH. The N-doped wafers were on-axis with a miscut below 0.5°. The SiC substrate was hydrogen-etched to remove scratches and obtain regular flat terraces. The clean and atomically flat Si-terminated surface was then graphitized by annealing the sample in Ar atmosphere at 1300°C for 8 min (36). This way, we obtained a single carbon layer where every third carbon atom formed a covalent bond to the SiC substrate (37). This layer was then turned into completely sp\textsuperscript{2}-hybridized quasi free-standing hole-doped graphene via hydrogen intercalation (38). These samples are referred to as graphene/H-SiC(0001). The whole process was carried out in a commercial Black Magic growth chamber from Aixtron. The WS\textsubscript{2} growth was carried out in a standard hot-wall reactor by low-pressure chemical vapor deposition (39, 40) using WO\textsubscript{3} and S powders with a mass ratio of 1:100 as precursors. The WO\textsubscript{3} and S powders were kept at 900 and 200°C, respectively. The WO\textsubscript{3} powder was placed close to the substrate. Argon was used as carrier gas with a flow of 8 sccm. The pressure in the reactor was kept at 0.5 mbar. The samples were characterized with secondary electron microscopy, atomic force microscopy, Raman, and photo-luminescence spectroscopy, as well as low-energy electron diffraction. These measurements revealed two different WS\textsubscript{2} single-crystalline domains where either the ΓK- or the ΓK’-direction is aligned with the ΓK-direction of the graphene layer. Domain side lengths varied between 300 and 700 nm, and the total WS\textsubscript{2} coverage was approximated to ~40%, suitable for the ARPES analysis.

**High-resolution ARPES**

The static ARPES experiments were performed with a hemispherical analyzer (SPECS PHOIBOS 150) using a charge-coupled device—detector system for two-dimensional detection of electron energy and momentum. Unpolarized, monochromatic He I\textsubscript{α} radiation (21.2 eV) of a high-flux He discharge source (VG Scienta VUV5000) was used for all photoemission experiments. The energy and angular resolution in our experiments were better than 30 meV and 0.3° (corresponding to 0.01 Å\textsuperscript{−1}), respectively. All experiments were conducted at room temperature. ARPES is an extremely surface-sensitive technique. To eject photoelectrons from both the WS\textsubscript{2} and the graphene layer, samples with an incomplete WS\textsubscript{2} coverage of ~40% were used.

**Tr-ARPES**

The tr-ARPES setup was based on a 1-kHz Titanium:Sapphire amplifier (Coherent Legend Elite Duo). 2 mJ of output power was used for high harmonics generation in argon. The resulting extreme ultraviolet light passed through a grating monochromator producing 100-fs probe pulses at 26-eV photon energy. 8 mJ of amplifier output power was sent into an optical parametric amplifier (HE-TOPAS from Light Conversion). The signal beam at 1-eV photon energy was frequency-doubled in a beta barium borate crystal to obtain the 2-eV pump pulses. The tr-ARPES measurements were performed with a hemispherical analyzer (SPECS PHOIBOS 100). The overall energy and temporal resolution was 240 meV and 200 fs, respectively.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/20/eaay0761/DC1

**REFERENCES AND NOTES**


Please refer to the original paper for the complete list of references and acknowledgments.
Direct evidence for efficient ultrafast charge separation in epitaxial WS$_2$/graphene heterostructures

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