Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Interlayer electron modulation in van der Waals heterostructures assembled by stacking monolayer MoS_2 onto monolayer graphene with different electron transfer ability

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Experimental Section

1. Preparation of Graphene

Monolayer graphene (1L-G) without oxidation: 1L-G flakes were prepared by micromechanical exfoliation and then transferred onto Si/SiO_2 (285 nm) substrates.

Highly oxidized monolayer graphene (1L-oxo-G): Oxo-G flakes were prepared by low-temperature oxidation of graphite based on our previously reported method.[1] The obtained oxo-G was dissolved in methanol/water binary mixtures. Subsequently, the 1L-oxo-G flakes were deposited onto the Si/SiO_2 substrate using the Langmuir–Blodgett technique. The oxo-G with an oxygen degree of approximately 60% was determined in our previous research.[1, 2]

Lowly oxidized monolayer graphene (1L-r-oxo-G): To obtain 1L-r-oxo-G flakes, the 1L-oxo-G flakes on Si/SiO_2 were reduced by the vapor of hydriodic acid (HI) and trifluoroacetic acid (TFA) (1:1, v/v) at 80 °C for 10 min. Subsequently, the 1L-r-oxo-G samples were soaked in double distilled water (Carl Roth) to remove iodine species. Here, the oxygen degree of r-oxo-G (0.1%) was determined on the basis of our previous research.[2]

2. Preparation of G/MoS_2, oxo-G/MoS_2, and r-oxo-G/MoS_2 heterostructures

The 1L-MoS_2 flakes were mechanically exfoliated via polydimethylsiloxane (PDMS, Gel-pack). The 1L-G flakes were mechanically exfoliated from bulk graphite onto Si/SiO_2 substrates. The 1L-oxo-G flakes were deposited onto Si/SiO_2 substrates using the Langmuir–Blodgett technique. The 1L-r-oxo-G flakes were obtained by the reduction of 1L-oxo-G flakes deposited onto the Si/SiO_2 substrate. The 1L-MoS_2 and 1L-graphene layers were identified by optical microscopy, atomic force microscopy (AFM), and Raman spectroscopy. Subsequently, vertically stacked G/MoS_2, oxo-G/MoS_2, and r-oxo-G/MoS_2 heterostructures were produced by stacking 1L-MoS_2 flakes onto three separate Si/SiO_2/G, Si/SiO_2/oxo-G, and Si/SiO_2/r-oxo-G surfaces with PDMS as the carrier. After the transfer, vacuum annealing at 100 °C was performed to eliminate residues and the water layer trapped at the interfaces of these stacked heterostructures.[3] To increase the adhesion of the sample flakes on the SiO_2 surfaces, all the Si/SiO_2 substrates were pre-treated with oxygen plasma prior the transfer process.

3. Characterization

Optical imaging and transfer processes were performed using a Nikon LV100ND microscope. Raman and PL characterizations were conducted using a confocal Raman microscope (Horiba Explorer, 532 nm excitation wavelength, 1200 gratings, 0.045 mW, 100X). KPFM experiments were conducted using a Bruker Icon atomic force microscope (AFM) under ambient conditions with a humidity of approximately 45% (measured with TFA®Digital Professional Thermo-Hygrometer KLIMA BEE). A heavily doped *n*-type Si cantilever with a resonance frequency of 85 kHz and a force constant of 2.7 N/m (SSS-FMR, Nanosensors) was used. The FM-KPFM mode was employed, where the electrostatic force gradient was detected by the frequency shift of the cantilever oscillation. The tip was grounded during the KPFM measurements. The work function of the samples (φ_s) is given by $\varphi_s = eV_{CPD} + \varphi_t$, where V_{CPD} is the contact potential difference measured by the KPFM, and φ_t is the work function of the tip. Prior to these measurements, φ_t was calibrated to be 4.38±0.09 eV

Results

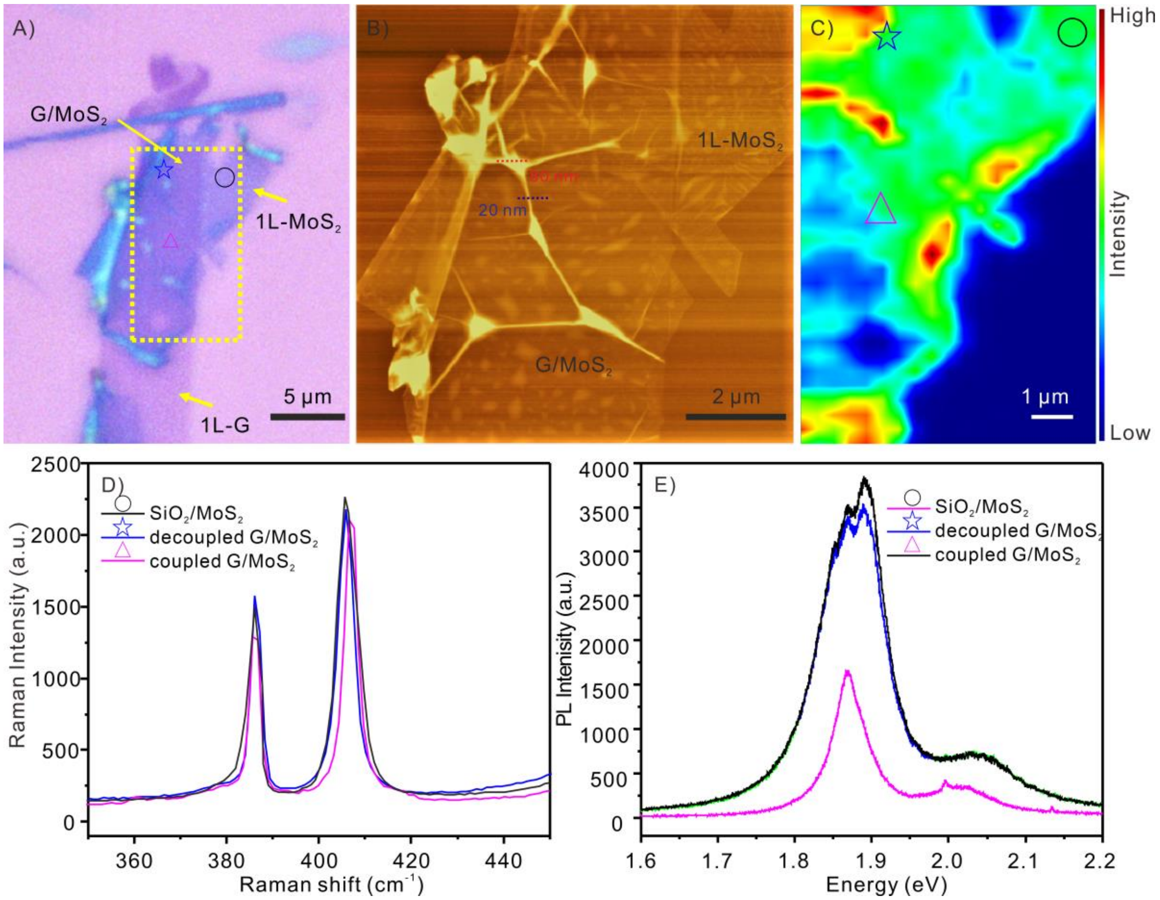

Figure S1. A) An optical image of the G/MoS_2 heterostructure. B) An AFM image of the dotted yellow box in A. C) Raman mapping of the G/MoS_2 heterostructure. D) Raman spectra extracted from the isolated 1L-MoS_2, decoupled G/MoS_2 and coupled G/MoS_2 regions marked by circle, star, and triangle, respectively. E) PL spectra measured from the isolated 1L-MoS_2, decoupled G/MoS_2 and coupled G/MoS_2 regions marked by circle, star, and triangle, respectively.

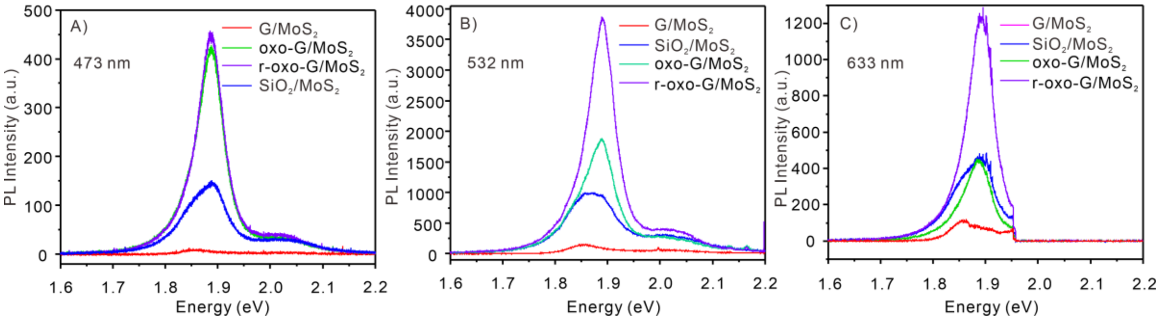

Figure S2. PL spectra of the G/MoS_2, oxo-G/MoS_2 and r-oxo-G/MoS_2 heterostructures under different laser excitation wavelengths.

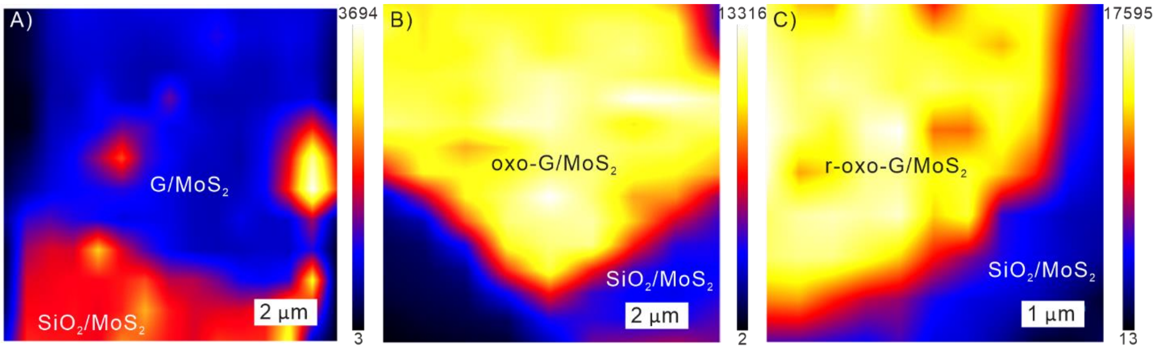

Figure S3. PL mapping images of the G/MoS$_2$, oxo-G/MoS$_2$ and r-oxo-G/MoS$_2$ heterostructures with a 532 laser excitation wavelength.

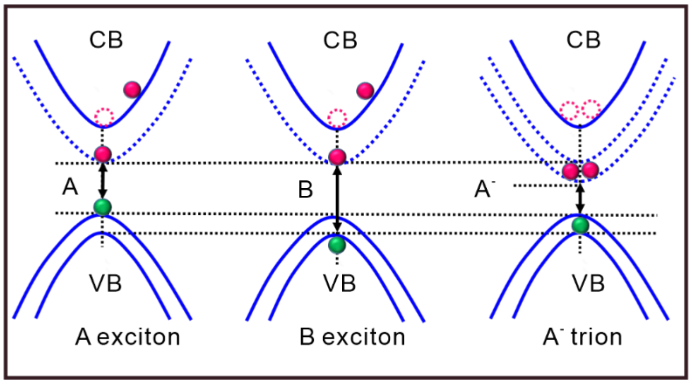

Figure S4. Schematics of the exciton and trion quasi-particles.

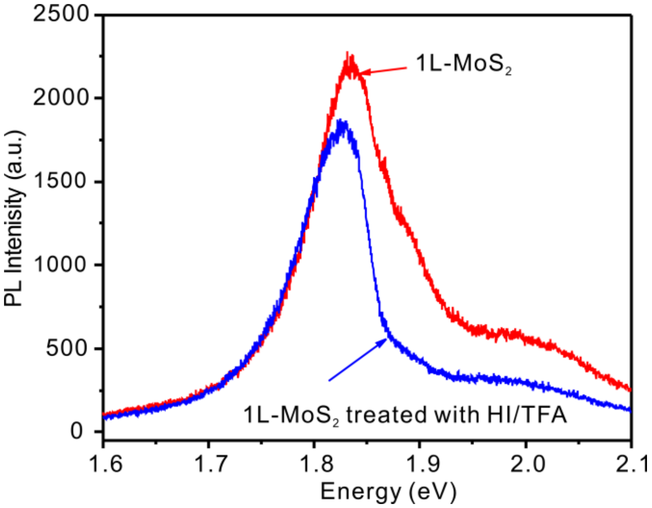

Figure S5. The PL of 1L-MoS$_2$ before and after treatment with the HI/TFA vapor.

Table S1. Parameters about fitted PL peaks by the Lorentz function.

	A^-		A^0		B		Intensity ratio of A^0/A^-
	Position	Intensity	Position	Intensity	Position	Intensity	
SiO_2/MoS_2	1.852	2073.628	1.893	2881.688	2.044	402.038	1.390
G/MoS_2	1.873	1085.793	1.888	559.109	2.020	336.918	0.515
oxo-G/MoS_2	1.863	3700.966	1.897	11010.225	2.053	485.202	2.975
r-oxo-G/MoS_2	1.869	5567.753	1.895	15373.527	2.046	383.357	2.761

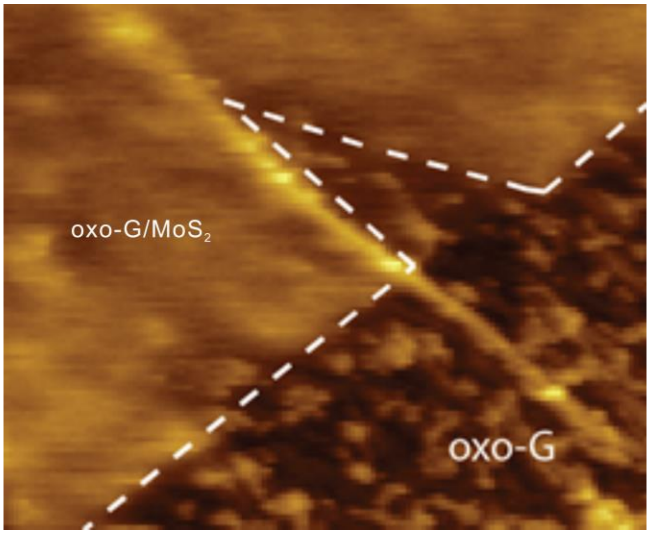

Figure S6. Work function map of the oxo-G/MoS_2.

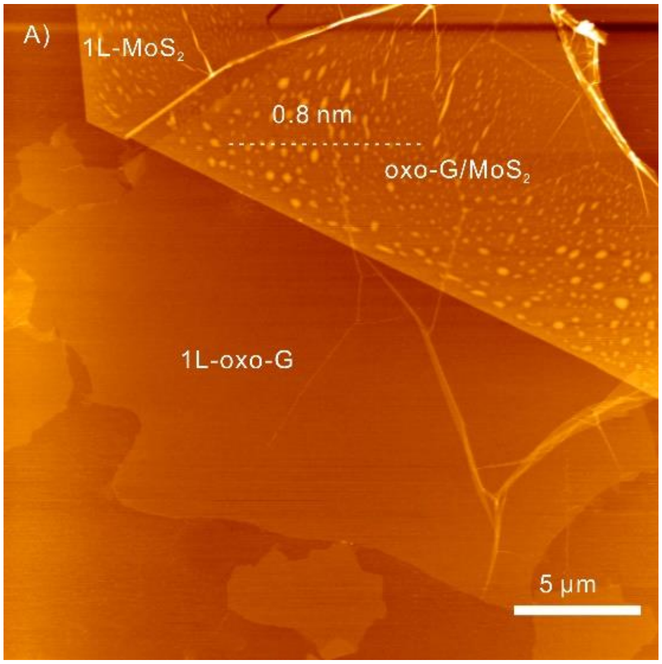

Figure S7. An AFM image of the oxo-G/MoS$_2$ heterostructure.

The G/MoS$_2$ samples were prepared by stacking the exfoliated 1L-MoS$_2$ onto the exfoliated 1L-G layer. There are more contaminants and wrinkles to be formed between the stacked G/MoS$_2$ samples during the tape-peeling and transfer processes. But for the oxo-G/MoS$_2$ and r-oxo-G/MoS$_2$ samples, the oxo-G monolayers were first directly deposited on the substrate surfaces by Langmuir Blodgett technique without polymer contamination (r-oxo-G monolayers were obtained by reduction of these pre-deposited oxo-G monolayers). Then, the exfoliated 1L-MoS$_2$ layers were orderly transferred onto the oxo-G and r-oxo-G by assistance of the PDMS. Therefore, the oxo-G/MoS$_2$ and r-oxo-G/MoS$_2$ samples are well coupled because of cleaner and flatter interfaces.

Reference

1. S. Eigler, M. Enzelberger-Heim, S. Grimm, P. Hofmann, W. Kroener, A. Geworski, C. Dotzer, M. Rockert, J. Xiao, C. Papp, O. Lytken, H. P. Steinruck, P. Muller and A. Hirsch, *Adv. Mater.*, 2013, **25**, 3583-3587.
2. P. Vecera, S. Eigler, M. Kolesnik-Gray, V. Krstic, A. Vierck, J. Maultzsch, R. A. Schafer, F. Hauke and A. Hirsch, *Sci. Rep.* 2017, **7**, 45165-45171.
3. H. C. Diaz, R. Addou and M. Batzill, *Nanoscale*, 2014, **6**, 1071-1078.