

Supporting Information

Engineering Ultrafast Charge Transfer in Bismuthene/ Perovskite Nanohybrid

Yingwei Wang^{a,†}, Keqiang Chen^{a,†}, Hao Huang^a, Guannan Yu^a, Bowen Zeng^b, Hui Wang^b, Feng Zhang^a,
Leiming Wu^c, Jianqing Li^c, Si Xiao^b, Jun He^b, Yupeng Zhang^{a,*}, Han Zhang^{a,*}.

^aKey Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Electronic Science and Technology and college of optoelectronic Engineering, Shenzhen University, Shenzhen 518060, People's Republic of China. ypzhang@szu.edu.cn or hzhang@szu.edu.cn

^bInstitute of Super-Microstructure and Ultrafast Process in Advanced Materials, School of Physics and Electronics, Central South University, 932 South Lushan Road, Changsha, Hunan 410083, People's Republic of China

^cFaculty of Information Technology, Macau University of Science and Technology, Macao 519020, P. R. China

Y. Wang, and K. Chen contributed equally to this work

Experimental Section

Chemicals: Lead iodide (PbBr_2 , 99.999% metals basis), cesium acetate (CsAc , $\text{C}_2\text{H}_3\text{CsO}_2$, 99.9% metals basis), 1-octadecene (ODE, $\text{C}_{18}\text{H}_{36}$, technical grade, 90%), oleylamine (OLA, $\text{C}_{18}\text{H}_{37}\text{N}$, 80-90%), oleic acid (OA, $\text{C}_{18}\text{H}_{34}\text{O}_2$, AR), *t*-butanol ($\text{C}_4\text{H}_{10}\text{O}$, AR, $\geq 99.0\%$), hexane (C_6H_{14} , 98%), bismuth (Bi, 99.99% metals basis), and isopropyl alcohol (IPA, $\text{C}_3\text{H}_8\text{O}$, anhydrous, 99.5%) were purchased from Aladdin. All chemicals were used without any further purification.

Preparation of few-layer Bismuthene: A sonochemical exfoliation method was carried out for the preparation of bismuthene nanosheets. Briefly, bulk bismuth was crushed into bismuth powder using a mortar and pestle. To avoid oxidation, the bismuth was immersed in isopropyl alcohol during the trituration. Then, the bismuth powder mixture was added into a flask with large amount of isopropyl alcohol and kept under ice-bath sonication for several hours. Thereafter, the above solution was centrifuged at 6000 rpm for 20 min to remove by-products.

Preparation of CsPbBr_3 QDs: The Cs-OA solution was pre-prepared by mixing 0.192 g (1 mmol) CsAc and 2 mL OA and heated to 120 °C under atmosphere. 0.110 g (0.3 mmol) PbBr_2 was added into the 50 mL three-neck flask containing 20 mL ODE and heated to 120 °C under Ar atmosphere. Then, 0.5 mL OA and OLA were added at this temperature. The solution temperature was raised to 150 °C after 20-30 min. Subsequently, the above mentioned Cs-OA solution (0.4 mL) mixed with ODE (1 mL) was swiftly injected into the reaction solution. The reaction was stopped after 5s. 1 mL of the crude solution was mixed with 3 mL *t*-butanol and centrifuged at 9000 rpm for 6 min. The suspension was discarded and the precipitate was re-dispersed by hexane for another centrifugal process to remove the by-product.

Preparation of Bi / CsPbBr_3 QDs nanohybrid: 1 mL of the pre-prepared bismuthene solution was centrifuged at 13000 rpm for 20 min. Then, the suspension was discarded and 1 mL hexane was employed to disperse the bismuthene precipitate by ultrasonics. The bismuthene-hexane solution was centrifuged and re-dispersed in hexane again. This process was repeated for several times to make sure that all of the IPA had been removed. Finally, the bismuthene was dispersed in hexane and mixed with CsPbBr_3 QDs (dispersed in hexane). The mixture was kept under ice-bath sonication to promote the self-assembling of QDs on the layered bismuthene.

Characterization: The microstructures of bismuthene, CsPbBr_3 QDs, and CsPbBr_3 QDs/Bi nanohybrid were collected by TEM (JEM-3100, JEOL, Japan). Raman spectra was obtained by the HORIBA JY LabRAM HR Evolution confocal Raman microscope equipped with the excitation wavelength of 532 nm. X-ray diffraction (XRD) was performed on a BRUKER D8 ADVANCE XRD system. Their optical absorption properties were measured by UV-vis spectrophotometer (Cary60, Agilent). The steady-state photoluminescence (PL) were recorded by RF-5301PC (excited by a 365 nm laser, Shimadzu, Japan) and a fluorescence spectrometer (FLS 980, 400 nm laser),

respectively. AFM images were collected by ScanAsyst in air mode (Dimension Icon, Veeco Instruments/Bruker, Germany) with samples dispersed on mica substrates.

Transient absorption experimental: The pump pulses are generated from the double frequency of a regenerative amplified Ti: sapphire laser (Central wavelength: 800 nm, repetition rate: 1 kHz, pulse width: 100 fs). The visible probe continuum is generated by injecting the femtosecond pulse into a thin sapphire crystal. They overlap in the sample, where the diameter of the pump and probe light are measured to be 330 μm and 120 μm . After excitation, the absorption change (ΔA) of the probe light can be detected by the spectrometer, revealing the photo-induced species.

Time-resolved PL: A picosecond lasers (Advanced Laser Diode System, the repetition frequency 40MHz) was used as a laser source to obtain the time-resolved PL spectroscopies. The time-correlated single-photon counting (TCSPC) device can collect a series of information of the number of photoluminescent photons of the sample, which is the attenuation function curve related to time.

DFT calculations: Our calculations are performed with density functional theory (DFT) via the Vienna ab initio simulation package (VASP) ¹. We adopt the generalized gradient approximation (GGA) ² with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation potential including the spin orbit coupling (SOC). The projector-augmented wave (PAW) ³ is used to represent electron-ion interactions with a cut-off energy of 300 eV for the plane wave basis set. The criterion of convergence for structure relaxation is that the change of total energy is less than 10^{-7} eV and the residual force on the atom is less than 0.01 eV \AA^{-1} . The BZ is sampled by $11 \times 11 \times 1$ k-points for structural relaxation. The vacuum space between two neighbouring nanostructures is set to greater than 10 \AA to decrease the interactive effect.

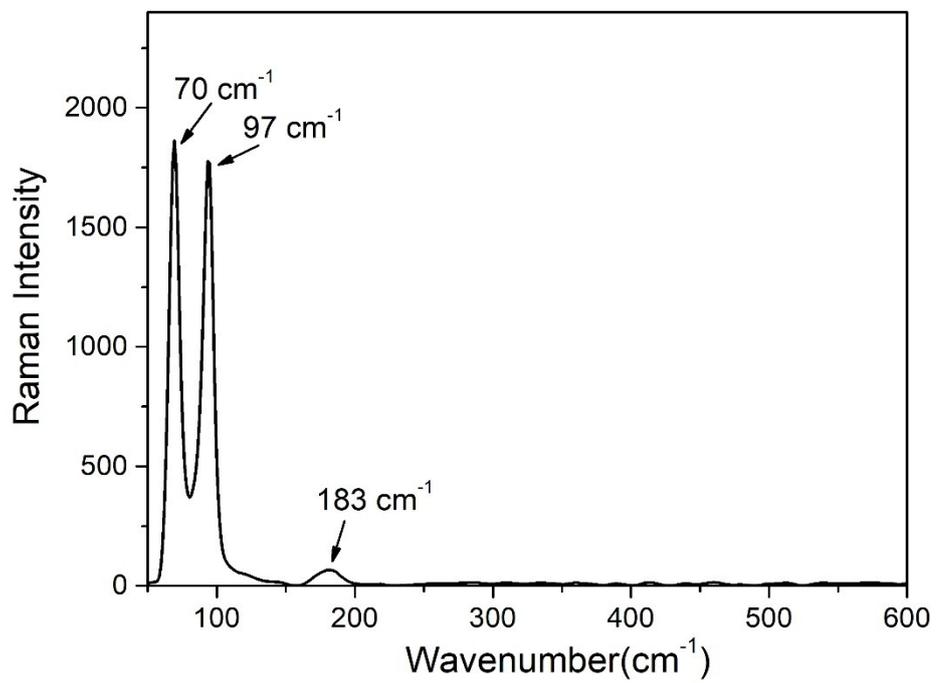


Figure S1. The Raman spectra of few-layer Bimuthene

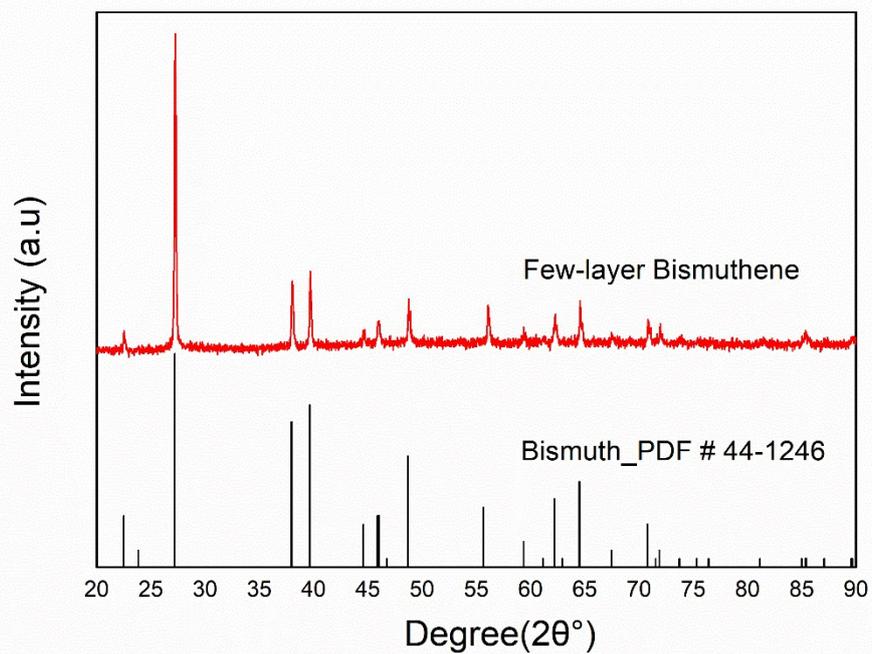


Figure S2 XRD pattern of as-synthesized few-layer Bimuthene and standard XRD spectra of Bismuth (JCPDS No. 44-1246).

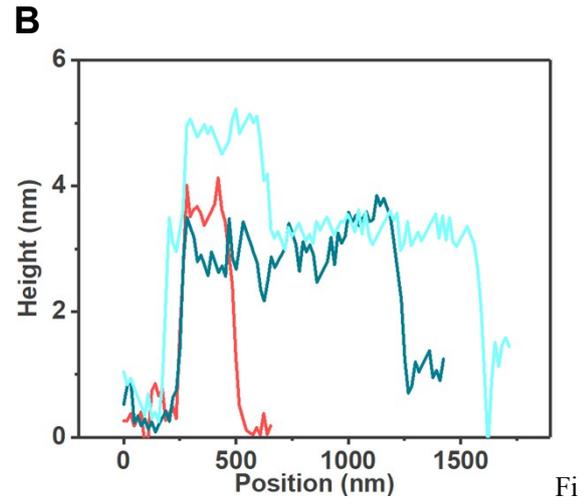
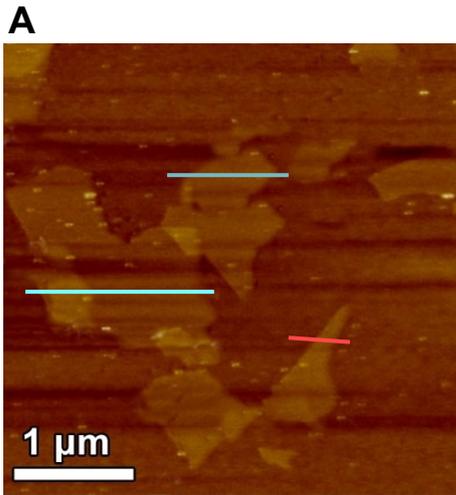


Figure S3. (A) AFM images of Bi nanosheets. (B) The height profile measured at the corresponding color solid line in (A).

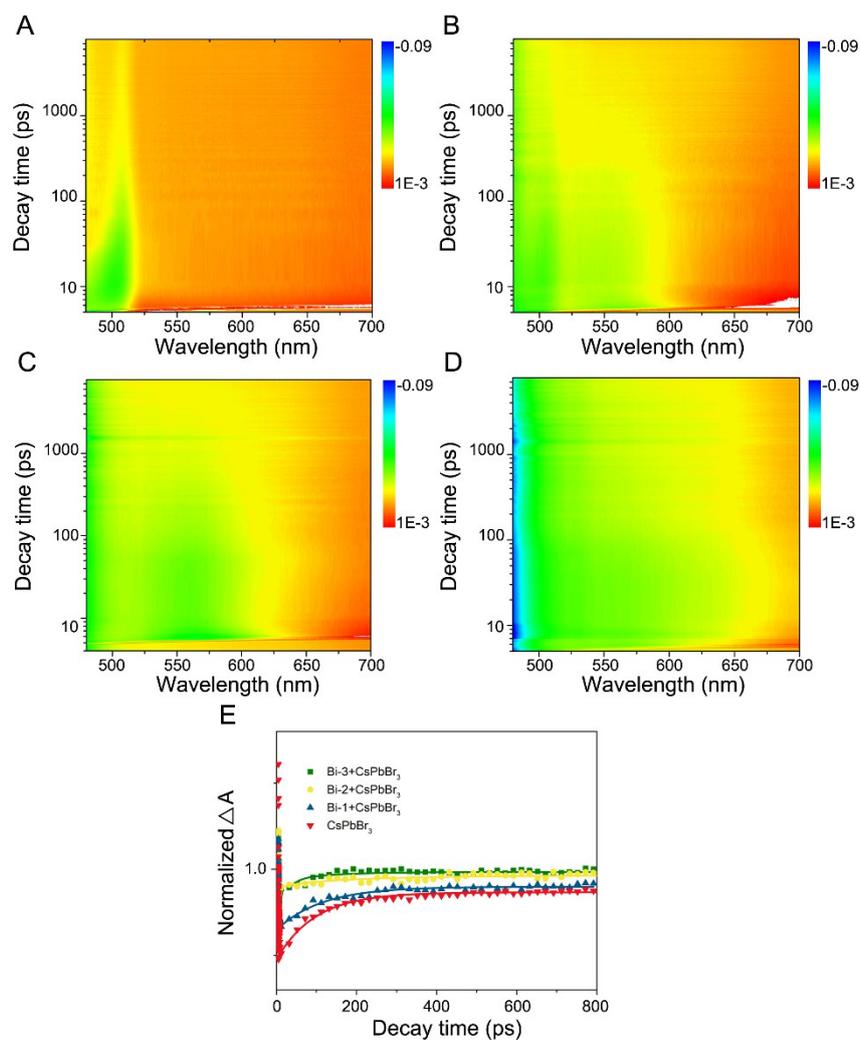


Figure S4. Transient absorption spectra of CsPbBr₃ (A), Bi-1+CsPbBr₃ (B), Bi-2+CsPbBr₃ (C), Bi-3+CsPbBr₃ (D). (E) Transient absorption spectra for different sample.

Table S1 Fitting results of TA spectra of different samples.

Sample	Fitting formula	τ_1 (ps)	τ_2 (ps)
CsPbBr ₃	$y = A_1 e^{-(x-x_0)/\tau_1} + A_2 e^{-(x-x_0)/\tau_2}$	63	596
Bi-1+ CsPbBr ₃		62	339
Bi-2+ CsPbBr ₃		29	217
Bi-3+ CsPbBr ₃		23	132

References

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