Influence of substrate on ultrafast interfacial charge transfer and dynamical interlayer excitons in monolayer WSe₂/graphene heterostructures

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1. Sample preparation

1.1 Preparation of graphene

Large-area monolayer (ML) graphene grown by CVD on copper foils¹ and transferred onto a sapphire substrate using a polymethyl methacrylate (PMMA)mediated transfer method.² Large-area ML graphene was grown on copper foils at 1000° C by a CVD method using 200 sccm argon and 20 sccm hydrogen as the growth cleaning gas, 10 sccm methane as the carbon source as reported elsewhere.¹

1.2 Preparation of WSe₂

The continuous WSe₂ ML were direct growth on a sapphire substrate by CVD system.³ High purity WO₃ was placed in a ceramic boat at the heating center of the furnace. WO₃ was heated by heating tape (1000 $^{\circ}$ C), and Se powder was heated by heating tape (250 $^{\circ}$ C) and carried by Ar and H₂ (Ar=200sccm, H₂=20sccm) to the furnace heating center. A sapphire substrate was placed in the downstream side 150 mm away from the ceramic boat (about 850 $^{\circ}$ C), and the growth time was 20 minutes.

1.3 Preparation of WSe₂/Gr heterostructures

To stack the WSe₂ ML on graphene, First, Large-area ML graphene was grown on copper foils, and then transferred onto a sapphire substrate using a PMMA-mediated transfer method. ² After that, a layer of PMMA thin film was coated on the WSe₂/sapphire as a transfer supporting layer. After the wet etching of sapphire by KOH solution, the PMMA-supported WSe₂ film was transferred to the top of the graphene/sapphire substrate, followed by the removal of PMMA using acetone.

1.4 Preparation of Gr /WSe₂ heterostructures

To stack the graphene ML on WSe₂, a layer of PMMA thin film was coated on the graphene/Cu foil as a transfer supporting layer. After the wet etching of Cu by an aqueous solution containing Fe^{3+} ions, the PMMA-supported graphene film was transferred to the top of the as-grown WSe₂ ML film, followed by the removal of PMMA using acetone.

2. The Raman parameters of graphene and the two stack heterostructures



Figure S1 The Raman spectra of G band and 2D band in the graphene, WSe₂/Gr heterostructure and Gr/WSe₂ heterostructure.

heterostructures					
	Peak(G	FWHM(cm ⁻¹)	Peak(2D	FWHM(cm ⁻¹)	
	band)		band)		
Graphene/sapphire	1588	20	2687	33.2	
WSe ₂ /Gr/sapphire	1587	27	2688.8	36.3	
Gr/ WSe ₂ /sapphire	1590	19.6	2687.9	36.9	

Table S1 The fitting parameters of Raman spectra of graphene and the two stack

Figure S1 shows the Raman spectra of G band and 2D band in the graphene, WSe₂/Gr heterostructure and Gr/WSe₂ heterostructure. Table S1 shows the Raman parameters (the position of the G and 2D peaks, and the FWHM of the G and 2D peak) of the three samples. In contrast to the position of the G-band peak in ML graphene (located at 1588 cm⁻¹), the position of the G-band peak in the WSe₂/Gr (Gr/WSe₂) heterostructure was blue shifted by ~1 cm⁻¹ (red shifted by ~2 cm⁻¹), indicating that the charge transfer between WSe₂ and graphene was different in the two heterostructures. Normally, pristine CVD-grown ML graphene is hole doped. ^{4, 5}. Thus, compared with the pristine graphene, following photoexcitation by the Raman laser, the blue shift of the G-band peak in the WSe₂/Gr heterostructure indicates that the ML graphene accepted electrons from the ML WSe₂, while the red shift of the G-band in the Gr/WSe₂ heterostructure indicates that the ML graphene donated

electrons to the ML WSe₂.⁶ We also contrast the FWHM of G peak in the three samples. The increase in the FWHM of the G peak for WSe₂/ Gr heterostructure indicate that the graphene accepted electrons, and the decrease in the FWHM of the G peak for Gr /WSe₂ heterostructure indicate that the graphene donated electrons. The results of both the Raman position shift of G band and the FWHM of G band display the same conclusion. We also excluded the contribution from the strain state effect. If the strain effect dominates the Raman spectra shift, the position of 2D band must show blue-shift the same as the G band in WSe₂/Gr heterostructure. ^{7, 8} However, in contrast with the ML graphene, the position of 2D band is redshifted 2cm⁻¹ while the G band is blueshifted 1cm⁻¹ in WSe₂/Gr heterostructure. And also the FWHM of the G band are random variation with the effect of strain.



FigureS2 The Raman spectra of A_{1g} band in the monolayer WSe₂ and the two heterostructures

	Peak(A _{1g}	FWHM(cm ⁻¹)	
	band)		
WSe ₂ /sapphire	252.1	14.1	
WSe ₂ /Gr/sapphire	252.1	14.5	
Gr/ WSe ₂ /sapphire	252.4	14.7	

Table S2 The fitting parameters of A_{1g} band in monolayer WSe_2 and the two stack heterostructures

After repeated Raman spectroscopy testing, we found that the position of A_{1g} lines shows no shift among the three samples. The Raman spectra of A_{1g} band in the monolayer WSe₂ and the two heterostructures are shown in Fig.S2. The fitting parameters of the A_{1g} band are shown in Table S2.

3. The contrast dynamics of photoinduced THz conductivities ($\Delta\sigma$) of the WSe₂/Gr, Gr/WSe₂ heterostructures and its constituent monolayers between the photo energy of 1.55eV and 3.1 eV



Figure S3 The contrast of photoinduced terahertz conductivity ($\Delta \sigma$) of the two stacks of heterostructures and its constituent monolayers with the pump energy of 3.1 eV and 1.55 eV.

Figure S3(a)-(d) show the normalized photoinduced THz conductivities ($\Delta\sigma$) of the two heterostructures and its constituent monolayers as a function of optical pump-THz probe delay, with the optical pump fluence fixed at $30\mu J/cm^2$. If the heterostructures are pumped with the photo energy of 1.55 eV, only electron-holes of the graphene layer can be excited, while WSe₂ layer remains unexcited due to the lower pump energy than the energy band gap of WSe₂. Both Gr/WSe₂ and WSe₂/Gr heterostructures displayed the THz signal of graphene under photoexcitation of 1.55 eV. Hence, It should be noted that photoexcitation with photoenergy of 3.1 eV can excite the electron-hole pairs of both the top and bottom layers of the heterostructures. For monolayer graphene, the THz signal of both 400nm pump and 800 nm pump are the same. For both the heterostructures, the WSe₂ is used as light absorption material when photoexcited with 3.1 eV. The results of photoinduced THz conductivity of the samples with 3.1 eV are discussed in the text.

4. Typical transient absorption spectra (TAS)of the two heterostructures and ML WSe₂ collected at several delay times



Figure S4 (a)-(c) display the transient absorption spectra of the two heterostructures and ML WSe₂ collected at several delay times with the pump fluence of $80\mu J/cm^2$, respectively.

Typical TAS of the two heterostructure types and ML WSe₂ collected at several delay times under 400nm excitation (pump density of $80\mu J/cm^2$) are shown in Figure S4. These spectra represent the pump-induced absorption changes observed in the samples, namely the differential optical density with and without pump light excitation ($\Delta OD = OD_{pump} - OD_0$). A broad photobleaching signal are clearly seen, and the bleaching signal peaked around 750nm and 500nm are indicated as "A1" "A2", and "C1" "C2" in Figure 1(b), which are corresponding to the A-exciton, and C-exciton transition of WSe₂ ML. The positive peaks for atomically thin vdW heterostructures are usually attributed to peak shift and broading of A/C exciton states,^{9, 10} excited-state absorption and/or the absorption of new generated transient species, for example, the effect of charges at high pump conditions^{11, 12}.

5. The fast components (τ_1) and slow components (τ_2) and (τ_3) of the



A exciton dynamics as a function of the pump fluence

FigureS5 The fast components τ_1 (a) and slow components τ_2 (b) and τ_3 (c) of the A exciton dynamics as a function of the pump fluence.

Figure S5 displays the fast components ($^{\tau}$ 1) and slow components ($^{\tau}$ 2) and ($^{\tau}$ 3) of the A exciton dynamics as a function of the pump fluence, respectively. In WSe₂, the fast component $^{\tau}$ 1 (2~3 ps) decrease as the pump fluence increases in the two heterostructures and ML WSe₂, which display the process of Auger-assisted trapping of carriers in defects¹³⁻¹⁵. The slow component $^{\tau}$ 2 (20ps~50ps) is not affected on the pump fluence or increases as the pump fluence in both the heterostructures and individual WSe₂, which indicates that the exciton-phonon scattering process plays a dominated role in this process.^{16, 17} The component $^{\tau}$ 3 (hundreds of ps) are independent of the excitation fluence, which indicates that $^{\tau}$ 3 comes from the electron-hole recombination.¹⁵ In the heterostructures, the hot carrier redistribution ($^{\tau}$ sr) is maintained by efficient carrier-carrier thermalization, accompanied with the process of charge transfer. Then the process of Auger-assisted trapping in defects ($^{\tau}$ as) removes the energy from the high-energy tail of the hot-carrier distribution.

Thus, τ_1 can be given by $1/\tau_{1=}1/\tau_{sr} + 1/\tau_{as}$. In heterostructures, the slow component (τ_2) and (τ_3) exhibited the same process as in ML WSe₂.

6. The calculation methods of the average exciton lifetime

The triexponential function mentioned above can be described as:

$$\sum_{\mathbf{l}(\mathbf{t})=-i} \alpha_i \exp^{i\omega}(-t/\tau_i)$$
 Eq. (1)

Here, τ_i is the decay time, α_i represents the amplitude at t=0, and i stands for the number of decay channels.

The average lifetime is given by

$$\bar{\tau} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3}$$
 Eq. (2)

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