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Nonlinear Optical Signatures of Transition from Semiconductor to Semimetal in PtSe₂

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ABSTRACT

The demand for an ultrabroad optical material with a bandgap tunable from zero to at least 1~2 eV has been one of the driving forces for exploring new two-dimensional (2D) materials since the emergence of graphene, transition metal dichalcogenides and black phosphorus. As an ultra-broadband 2D material with energy bandgap ranging from 0 to 1.2 eV, PtSe₂ shows much better air stability than its analogue, black phosphorous. In this work, the superior nonlinear optical performance, ultrafast dynamics of layered PtSe₂ and signatures of transition from semiconductor to semimetal have been systematically studied. Combining with rate equations, first principle calculation and electrical measurements, we provided a comprehensive understanding about the evolution of nonlinear absorption and carrier dynamics with increasing layer thickness, indicating its promising potential in nanophotonic devices such as infrared detector, optical switches and saturable absorber.

1. Introduction

The conventional ideology of nanoscience and nanotechnology has been revolutionized since the emergence of two-dimensional (2D) materials provides a novel platform for fabricating optoelectronic and nanophotonic devices with atomical thickness.^[1-3] In the last decade, researchers have invested tremendous enthusiasm into the extending of 2D materials family and the exploration of their exceptional properties.^[4, 5] Graphene and its analogue black phosphorus (BP), have attracted enormous attention owing to their extraordinary properties such as high carrier mobility and broadband optical responses.^[6, 7] While the low absorption coefficient of gapless graphene constrains its application in optoelectronic field,^[8] the poor air stability and 0.3 eV bandgap of bulk black phosphorus (BP) mean that it is too difficult to be used in photodetectors or modulators beyond 4.1 μm .^[8-10] PtSe₂, a rising member of the group-10 transition metal dichalcogenides (TMDC) family, has been demonstrated with a strong interlayer interaction and undergoes a unique evolution from semiconductor to semimetal with

increasing layer thickness.^[10-14] It possesses many intriguing properties including an indirect energy bandgap ranging from 0 to 1.2 eV, high carrier mobility and good environmental stability, which suggests that beyond graphene and BP,^[8, 10-12] PtSe₂ can be used as a good candidate in electronic devices,^[15-17] wide spectral response photodetector and photodiodes,^[8, 18, 19] optical switches and saturable absorbers,^[20-22] *etc.* However, the evolution of nonlinear optical (NLO) properties and ultrafast dynamics with layer thickness, which is crucial for developing high performance photonic devices, has been rarely reported to date. Moreover, the exact transition layer from semiconductor to semimetal is still in controversy though the angle-resolved photoemission spectroscopy (ARPES) technique and field-effect transistor electrical measurements have been used to investigate the band structure and the nature of conductivity of PtSe₂.^[8,10-13]

In our work, the superior NLO performance and ultrafast dynamics of layered PtSe₂ were revealed systematically. The free carrier absorption cross section, the inter- and intraband relaxation time of excited carriers were determined by using a four level rate equation model. The evolution of nonlinear absorption and ultrafast carrier dynamics with increasing layer thickness were discussed in detail. Meanwhile, our results provided a viewpoint to characterize the semiconductor to semimetal transition from the perspectives of nonlinear optics and ultrafast dynamics based on a systematic investigation of films with different thicknesses. Comparing with conventional electrical methods, the NLO method can be utilized as a qualitative method to investigate the distinction of relaxation dynamics of excited carriers between semiconductor and semimetal.

2. Results and Discussion

2.1. Materials and Characterization

The PtSe₂ thin films of different thicknesses were synthesized by a thermally assisted conversion process.^[15, 23-25] Photographs of four synthesized PtSe₂ films with initial Pt thickness

of 0.5, 1, 3 and 5 nm are shown in Fig. 1a. Figure 1b demonstrates the 1T crystal structure of PtSe₂, a sublayer of Pt atoms sandwiched between two layers of Se atoms, where the gray spots represent Pt atoms and the green spots represent Se atoms.

Figure 1. (a) Photographs of the PtSe₂ films with different thicknesses. 0.5, 1, 3 and 5 nm represent the initial deposition thickness of Pt. (b) The crystal structure of PtSe₂ from top view and side view. (c) - (d) Cross sectional TEM and surface AFM images of the thinnest PtSe₂ film. Inset shows the height profile. (e) - (f) XPS for Pt 4f region and Se 3d region of the thinnest PtSe₂ film. (g) Raman spectra of the PtSe₂ films with different layer numbers, (h) thickness dependent behavior of E_g, A_{1g} and longitudinal optical (LO) phonon peaks, (i) transmission, reflection, and absorption spectra of 4 L PtSe₂ film, (j) Tauc plots of four PtSe₂ films.

The bandgaps of most 2D materials, including many TMDCs, depend strongly on their thickness. In order to identify the layer number of PtSe₂ films, we carried out cross-sectional

transmission electron microscopy (TEM) for the thin films with initial Pt thicknesses of 0.5 and 1 nm and made atomic force microscopy (AFM) measurements for all. The cross-sectional TEM images for the two thinner films are shown in Fig. 1c and Fig. S1a in Supporting Information (SI). The thicknesses of these two films after selenization are about 2.3 and 4.8 nm, respectively. This is in good agreement with the height profiles measured by AFM, about 2.3 ± 0.3 nm and 4.5 ± 1.6 nm as shown in Fig. 1d and Fig. S1b-d. The monolayer thickness of PtSe₂ grown by molecular beam epitaxy was reported to be 0.59 nm,^[13] which suggests that our layer numbers here are about 4 ± 1 and 7 ± 3 , respectively. The AFM results manifest the homogeneity of the film and the sharp film edge demonstrates the characteristics of 2D layered structure.^[11] The AFM results of films with initial Pt thickness of 3 nm and 5 nm can be found in SI and the layer numbers for these two films were determined to be 17 ± 5 and 55 ± 12 , respectively. Table 1 summarizes the film thicknesses before and after selenization, and the real numbers of layers for PtSe₂.

Table 1. Number of layers in four PtSe₂ films

	Initial nominal Pt (nm)	Thickness after selenization (nm)	Layer number (L)
PtSe ₂	0.5	2.3 ± 0.3	4 ± 1
	1	4.5 ± 1.6	7 ± 3
	3	10.2 ± 2.8	17 ± 5
	5	32.2 ± 7.3	55 ± 12

X-ray photoelectron spectroscopy (XPS) was carried out to measure the binding energy and to verify the quality of PtSe₂ films. Figure 1e and 1f are the XPS results of Pt 4f and Se 3d core level for 4 L PtSe₂ film. The fitted peak positions are 76.30, 72.98 eV for Pt 4f and 54.33, 55.18 eV for Se 3d, which are consistent with previous reports.^[11, 26] Hardly any oxides, unreacted Pt metal or Se substance was found in the Pt 4f and Se 3d core levels, indicating the good quality and complete selenization of 4 L PtSe₂ film. Additional XPS spectra acquired from thicker PtSe₂ are presented in Fig. S2.

Raman spectra of PtSe₂ films with laser excitation at 633 nm are shown in Fig. 1g. All the four films exhibit two prominent peaks at $\sim 174\text{ cm}^{-1}$ and $\sim 203.4\text{ cm}^{-1}$, corresponding to E_g (in plane) and A_{1g} (out of plane) vibrations of Se atoms. And for the 4 L and 7 L PtSe₂ films, a weak longitudinal optical (LO) mode is located at $\sim 230\text{ cm}^{-1}$, corresponding to the combination of the E_u (in plane) and A_{2u} (out of plane) vibrations of Pt and Se atoms, which is similar to those observed in HfS₂, ZrS₂ and CdI₂.^[27, 28] A red shift with the increase of the layer number is observed for both E_g and A_{1g} mode (Fig. 1h), while the shift is less prominent for A_{1g} mode than that for E_g one. The positions of all Raman peaks and the tendency of Raman shifts are in accordance with previous results.^[13, 15, 23]

Optical absorption spectra from 350 to 2000 nm were investigated to obtain the linear absorption coefficients and to determine the bandgaps of PtSe₂ films. Figure 1i and S3 demonstrate the linear transmission (T), reflection (R) and absorption (A) spectra of PtSe₂ films with different thicknesses, while the absorption spectra were obtained from the formula $A = 1 - R - T$ similar to previous studies on MoS₂ and WS₂.^[29] Both absorption and reflection increase with increasing thickness in the visible and infrared range. As shown in Fig. 1j, the layer-dependent Tauc plots acquired from the linear optical absorption spectra demonstrate the indirect bandgaps of PtSe₂. A red shift of the absorption edge with increasing layer number is observed, in good agreement with previous reports on mechanically-exfoliated PtSe₂ flakes^[10] and films.^[16] The three thinner films, 4 L, 7 L and 17 L, show a sizeable bandgap which are 0.87, 0.59 and 0.33 eV respectively, while for the 55 L films, the extracted bandgap is zero which suggests that the thickest film is a semimetal, just like the bulk.

2.2. Nonlinear Optical Absorption

The third order NLO properties of the PtSe₂ films were investigated using an open-aperture (OA) and closed-aperture (CA) Z-scan system with a mode-locked fiber laser (1030 nm and its

second harmonic generation 515 nm, 340 fs, 100 Hz). The precision of this system was confirmed by testing graphene/PVA films, MoS₂ nanoflake dispersions, BP nanoflake dispersions and WS₂ films.^[29-34] The beam waists at the focus point were 27 ± 2 μm and 15 ± 1.5 μm for 1030 nm and 515 nm, respectively. Figure 2a and 2b illustrate the OA signal of PtSe₂ films at 1030 nm and 515 nm, respectively. As the sample moved along the z direction, the OA signals of 4 L and 7 L PtSe₂ exhibit two small peaks near the symmetrical valley at 1030 nm, indicating the OA signals consist of both saturable absorption (SA) and two-photon absorption (TPA) response, similar to the previous reports of graphene and MoS₂.^[35, 36] As reported previously,^[37-39] the order of NLO response can be distinguished by the relationship between the normalized transmission T_{Norm} and the incident beam intensity I , and the formula can be written as:

$$\ln(1 - T_{Norm}) = k \times \ln(I) + C_0 \quad (1)$$

where k is the slope showing the order of nonlinearity and C_0 is a constant. For pure TPA process, k is equal to 1. Figure 2c demonstrates the plots of $\ln(1 - T_{Norm})$ versus $\ln(I)$ of 4 L and 7 L PtSe₂ films. The solid lines represent the linear fitting of the experimental data. As we can see, the slopes for 4 L and 7 L are 0.97 and 1.14, respectively, indicating TPA is still the dominant NLO response in our incident intensity range at 1030 nm. This conclusion was further verified in the following pump probe experiments. On the contrary, the 17 L and 55 L films exhibit pure SA response at 1030 nm. On the basis of our findings, it can be concluded that the bandgaps of all PtSe₂ films are less than the excitation photon energy (1.20 eV), in consistency with the linear Tauc plot results. As shown in Fig. 2b and Fig. S5, all PtSe₂ films with different thicknesses exhibited SA response at 515 nm and the SA amplitude increases with the enhancement of incident pulse energy. The damage thresholds for all four films at both 1030 nm and 515 nm were also studied and listed in Table 2.

Figure 2. Open-aperture Z-scan results of 4 L, 7 L, 17 L and 55 L PtSe₂ films at (a) 1030 nm and (b) 515 nm femtosecond pulse excitation, respectively. (c) Plots of $\ln(1-T_{\text{Norm}})$ vs $\ln(I)$ to determine the order of nonlinearity. (d) The saturation irradiance and (e) nonlinear refractive index of 4 L, 7 L, 17 L and 55 L PtSe₂ films at both 1030 nm and 515 nm.

Figure 3. Close-aperture Z-scan results of 4 L, 7 L, 17 L and 55 L PtSe₂ films at (a)-(d) 1030 nm and (e)-(h) 515 nm femtosecond pulse excitation, respectively.

In order to quantitatively describe the NLO properties of PtSe₂ films, we fitted the Z-scan results with the nonlinear propagation equation,

$$\frac{dI}{dz} = -\frac{\alpha_0 I}{1+I/I_{sat}} - \beta I^2 \quad (2)$$

where I is the beam irradiance, z is the propagation distance in the sample, α_0 is the linear absorption coefficient, I_{sat} is the saturation irradiance and β is the TPA coefficient. For the coexistence of SA and TPA response, β is positive, while for pure SA process, β is zero. To obtain a precise value of the linear absorption α_0 , we have taken the reflection of the films into account. Thereby we should multiply the incident beam irradiance I by $(1-R)$ when we solve the propagation equation numerically. The imaginary part of the third-order NLO susceptibility $\text{Im}\chi^{(3)}$ can be deduced from $\text{Im}\chi^{(3)} = \frac{10^{-7}c\lambda n^2}{96\pi^2}\beta$, where c is the velocity of light, λ is the wavelength of incident laser and n is the refractive index. The figure of merit (FOM), which is defined to eliminate the discrepancy caused by different linear absorption coefficients, can be calculated from $\text{FOM}_{\text{Im}} = |\text{Im}\chi^{(3)}/\alpha_0|$.

Table 2. Linear and NLO parameters of PtSe₂ films obtained by Z-scan technique

λ (nm)	Layer number (L)	T_0 (%)	R_0 (%)	α_0 ($\times 10^5$ cm ⁻¹)	β ($\times 10^4$ cm GW ⁻¹)	I_{sat} (GW cm ⁻²)	$\text{Im}\chi^{(3)}$ ($\times 10^{-10}$ esu)	FOM_{Im} ($\times 10^{-15}$ esu cm)	n_2 ($\times 10^{-11}$ cm ² W ⁻¹)	$\text{Re}\chi^3$ ($\times 10^{-9}$ esu)	FOM_{Re} ($\times 10^{-14}$ esu cm)	Damage threshold (GW cm ⁻²)
1030	4	79.5	9.0	5.87	2.96±0.05	14.5±1	147.1±5.5	25.1±0.13	-1.73±0.48	-6.72±1.86	1.14±0.32	12.48
	7	68.7	14.1	4.97	1.64±0.09	20±3.2	81.2±0.8	16.4±0.16	-2.59±0.03	-10.1±0.1	2.03±0.02	10.89
	17	41.1	32.4	4.87	-	53±8.5	-	-	-3.76±0.46	-14.6±1.7	2.99±0.35	10.28
	55	24.5	46.2	2.44	-	23.7±1.9	-	-	-1.23±0.07	-4.77±0.28	1.95±0.012	11.56
515	4	60.8	12.6	15.8	-	54.4±11	-	-	-	-	-	6.24
	7	49.7	18.4	11.1	-	84.7±4.5	-	-	-	-	-	6.24
	17	30.6	31.4	7.91	-	104.5±7.5	-	-	-0.36±0.08	-1.39±0.07	0.18±0.02	8.33
	55	18.6	39.6	3.66	-	92.1±6.5	-	-	-0.20±0.04	-0.77±0.15	0.21±0.04	10.41

Table 2 summarizes all the linear and NLO parameters for PtSe₂ films in the Z-scan measurement. The TPA coefficient β for 4 L PtSe₂ film is larger than that of 7 L at 1030 nm, while it is about 4 orders of magnitude larger than that of bulk ZnTe, GaAs and ZnO and three times larger than that of monolayer MoS₂.^[29, 40, 41] Figure 2d plots the layer dependence of the saturation irradiance I_{sat} at different wavelengths. As we can see, the magnitude of the I_{sat} is larger at 515 nm, indicating that PtSe₂ films possess lower saturation intensity in near-infrared range than that in visible range as a saturable absorber.

The real part of the third order nonlinear susceptibility $\text{Re}\chi^{(3)}$, corresponding to nonlinear refractive index n_2 , has also been studied by the CA Z-scan system. The n_2 listed in Table 2 was obtained by fitting the CA Z-scan data using the model reported previously.^[42] $\text{Re}\chi^{(3)}$ and FOM_{Re} can be derived through the equations $\text{Re}\chi^{(3)}(\text{esu}) = \frac{n_0^2 c}{12\pi^2} n_2 \times 10^{-7} (\text{cm}^2 \text{ W}^{-1})$ and $\text{FOM}_{\text{Re}} = |\text{Re}\chi^{(3)} / \alpha_0|$, respectively. As depicted in Fig. 3, all four PtSe₂ films of different thicknesses have a peak-valley type signal at 1030 nm, indicating a self-defocusing effect with a negative n_2 . When the excitation wavelength is 515 nm, no CA signal is detected for 4 L, 7 L films, while 17 L and 55 L still exhibit a peak-valley signal. The layer dependence of the nonlinear refractive index n_2 is plotted in Fig. 2e. The value of n_2 is comparable to graphene and other TMDCs such as MoS₂, WS₂ and WSe₂ and considerably larger than many conventional NLO crystals, such as LiNbO₃:MgO, KTiOAsO₄, KTiOPO₄, β -BaB₂O₄, and LiB₃O₅.^[30, 43, 44] Such a large n_2 indicates its great potential as a self-defocusing material in integrated NLO devices.

2.3. Excited Carrier Dynamics

Degenerate time-resolved pump-probe measurements were carried out in order to further explore the nonlinear absorption and the excited carrier dynamics. Figures 4a, 4b and 4c show

the dynamics for 4 L, 7 L, 17 L and 55 L PtSe₂ films at 1040 nm with the same pump intensity $I=3.72$ GW/cm² at room temperature. It is obvious that for the two thin films, the sign of the initial $\Delta T/T_0$ is opposite to the two thicker ones, which implies the mechanisms of the NLO response are totally different. For the 4 L, 7 L PtSe₂ films, transient dynamics show a photoinduced absorption (negative $\Delta T/T$) with a slow recovery process which lasts for more than a hundred picoseconds. Conversely, 17 L and 55 L PtSe₂ show an initial SA response followed by a photoinduced absorption process which results in the rapid decrease of the transmission signal and the extended negative transient dynamics. The overall transient behavior of 17 L and 55 L PtSe₂ is analogous to what has been reported in BP.^[45] The insets in Figs. 3a and 3b show the values of $\Delta T/T_0$ at time zero as a function of pump intensity. For 4 L and 7 L films, the linear dependence confirmed TPA was the dominant NLO response.^[46] While for the 17 L and 55 L ones, the differential transmission signals saturate upon increasing pump intensity and show a large modulation depth. Figure 4c shows a direct comparison of dynamic processes in the first ten picoseconds. It is noteworthy that there remains a time shift among four transient dynamics. The transmission minimum for 4 L, 7 L PtSe₂ films appears at 0.47 ps and 0.86 ps, respectively. Figure 4d shows a comparison between the transient transmission and reflection spectra obtained simultaneously for 4 L film. The orange region represents the overlapping zone of pump and probe pulse. A symmetric valley signal with a timescale less than 1 ps is observed in the transient reflection. This instantaneous process is similar to the previously reported TPA process in GaAs.^[46] It indicates that the initial decrease in the transient dynamics of 4 L, 7 L PtSe₂ is due to the TPA between the pump and the probe pulse, in accordance with the preceding Z-scan results at 1030 nm. The transient transmission decreases further after the overlapping zone (more obvious for 7 L film), indicating that the ultrafast dynamics contains another absorption process after the TPA.

Figure 4. (a)-(b) Transient transmission dynamics of 4 L, 7 L, 17 L and 55 L PtSe₂ films at 1040 nm with a pump intensity of 3.72 GW cm⁻², while the solid lines represent the fitting using a four-level rate equation model. The insets show $\Delta T/T_0$ versus the pump intensity at zero time delay. (c) The first ten picoseconds of the transient dynamics of four PtSe₂ films which are marked by dashed rectangle in (a) and (b). A temporal delay of 0.47 ps for 4 L PtSe₂ and 0.86 ps for 7 L PtSe₂ was observed. (d) Transient reflection and transmission dynamics of 4 L PtSe₂ film at 1040 nm pulse excitation. The orange region indicates the overlapping region of the pump and probe pulse.

For the dynamics of 4 L, 7 L PtSe₂ films, the ground state electrons in the valence band will be excited *via* TPA and create a large number of free carriers in the conduction band. The generated free carriers can absorb photons from the probe beam after the overlapping of the pump and probe pulses. It will lead to a further decrease of the probe signal as shown in Fig. 3c. As for the positive $\Delta T/T_0$ of 17 L and 55 L PtSe₂ films, it is due to the Pauli blocking just

the same as Z-scan results. The negative transmission part can also be attributed to the free carrier absorption (FCA) like BP and graphene.^[45, 47]

Figure 5. (a)-(b) Normalized transient transmission of 4 L PtSe₂ film at different pump intensities. (b) Transient transmission dynamics of 17 L PtSe₂ film at probe intensities of 0.13 and 0.26 GW cm⁻². (c) Temperature-dependent transient transmission dynamics of 4 L PtSe₂ film. The solid lines represent the fitting by the rate equation model. (d) Schematic illustration of the four-level system. The coexistence of SA and TPA will change to only SA when the band

gap decreases. (e) The layer-dependent intraband relaxation time τ_{32} and τ_{21} and (f) interband relaxation time τ_{10} at 300 K. (g) The temperature-dependent relaxation time τ_{32} and τ_{21} of 4 L PtSe₂ film.

To determine whether the phonon emission accompanies carrier relaxation, the normalized transient transmission of 4 L PtSe₂ films at different pump intensities are illustrated in Fig. 5a. It shows that the carrier relaxation is independent on the pump intensity, suggesting that the hot phonon effect is not significant for this pump intensity range in our experiments.^[48] To verify the FCA process in the relaxation dynamics, we performed the pump-probe experiments at different probe intensities and temperatures. Figure 5b shows the transient transmission dynamics of 17 L PtSe₂ films at different probe intensities with the same pump intensity at about 5.58 GW/cm². Since the total free carrier population is mainly generated by the pump pulse due to the large pump/probe intensity ratio (>20:1), the number of photons which can be absorbed during the FCA process is almost fixed. When we increase the intensity of probe pulse, the number of the photons absorbed by free carriers remains the same, leading to an increase of the transient transmission. We verified this trend experimentally, as shown by the red arrow in Fig. 5b. On the other side, the FCA mainly contributes to the absorption of probe light here, and typically shows a strong dependence on temperature since the stronger electron-phonon scattering will result in a larger relaxation rate at high temperature.^[49] Figure 5c and S6 plot the temperature-dependent transient transmission signals of four PtSe₂ films at 1040 nm. It is obvious that our near-infrared transients exhibit remarkable temperature dependence of both signal amplitude and relaxation time, which suggests that the Auger process during the carrier recombination process can be excluded.^[50-52] As shown in Fig. S6, the signal amplitude increases when the temperature is decreased from 300 K to 200 K, while it remains nearly unchanged from 78 K to 200 K.

To better understand the dynamics, we proposed a four-level rate equation model to simulate the results numerically. As illustrated in Fig. 4d, for 4 L and 7 L PtSe₂, besides the dominant TPA process, the electrons in the ground state E₀ can also jump to conduction band minimum (CBM) E₁ by absorbing one photon and emitting one phonon. With the increasing of layer thickness, the energy bandgap decreases and ground state electrons can jump to E₂ directly by one photon absorption for 17 L and 55 L PtSe₂. The free carriers in E₂ will relax to the CBM E₁ through the electron-phonon interaction with a relaxation time of τ_{21} . After the overlapping of the pump and probe pulse, the free carriers in E₁ and E₂ can still absorb photons from the probe beam and jump to a higher energy band E₃, which represents the FCA in the conduction band. Once in E₃, they relax to E₂ via carrier-phonon interaction with a decay time τ_{32} , which strongly depends on temperature.⁵³ The excited carriers in E₁ will slowly decay to the ground state E₀ with time τ_{10} , which represents the lifetime of E₁. Thus, the rate equations consisting of SA, TPA and FCA processes in 4 L, 7 L PtSe₂ films are:

$$\begin{cases} \frac{dn_3}{dt} = \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_1 - n_3) + \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_2 - n_3) - \frac{n_3}{\tau_{32}} \\ \frac{dn_2}{dt} = \frac{\sigma_{tpa} \cdot (I_{pump}^2 + I_{pump} \cdot I_{pr})}{2\hbar\omega} (n_0 - n_2) - \frac{n_2}{\tau_{21}} - \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_2 - n_3) + \frac{n_3}{\tau_{32}} \\ \frac{dn_1}{dt} = \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_{10}} - \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_1 - n_3) + \frac{\sigma_0 \cdot (I_{pump} + I_{pr})}{\hbar\omega} (n_0 - n_1) \end{cases} \quad (3)$$

and for 17 L and 55 L films with only SA and FCA processes are:

$$\begin{cases} \frac{dn_3}{dt} = \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_1 - n_3) + \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_2 - n_3) - \frac{n_3}{\tau_{32}} \\ \frac{dn_2}{dt} = \frac{\sigma_0 \cdot (I_{pump} + I_{pr})}{\hbar\omega} (n_0 - n_2) - \frac{n_2}{\tau_{21}} - \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_2 - n_3) + \frac{n_3}{\tau_{32}} \\ \frac{dn_1}{dt} = \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_{10}} - \frac{\sigma_{fca} \cdot I_{pr}}{\hbar\omega} (n_1 - n_3) \end{cases} \quad (4)$$

where n_0 , n_1 , n_2 and n_3 refer to the populations of carriers in ground state E₀, CBM E₁, photoexcited state E₂ and FCA energy state E₃, respectively. σ_{fca} , σ_{tpa} and σ_0 are the FCA, TPA and ground state absorption cross sections. I_{pump} and I_{pr} are the pump and probe pulse intensities with temporal Gaussian profiles of $I = I_0 \exp(t^2/\tau_p^2)$, where τ_p is the laser pulse

duration. Since the temporal transient transmission signal $\Delta T/T$ mainly originates from the nonlinear absorption, for 4 L, 7 L PtSe₂ films, it can be written as:

$$\Delta T = [\sigma_0 * (N - n_0 + n_1) - \sigma_{tpa} * I_{pump} * (n_0 - n_2) - \sigma_{fca} * (n_1 + n_2 - 2n_3)] \quad (5)$$

while for 17 L, 55 L films, it can be written as:

$$\Delta T = [\sigma_0 * (N - n_0 + n_2) * I_{pr} - \sigma_{fca} * (n_1 + n_2 - 2n_3) * I_{pr}] / I_{pr} \quad (6)$$

The TPA cross section can be obtained by $\sigma_{tpa} = \beta/N$, where the TPA coefficient β can be deduced from the fitting results of Z-scan measurements. $N = n_0 + n_1 + n_2 + n_3$ represents the total population of electrons in the four levels. For convenience we used the areal density in the fitting ($N_0 = N \times d$, where d is the monolayer thickness). We fit the transient transmission signal only by tuning the value of the σ_{fca} and the lifetime of each state at different pump intensities and temperatures. The optimized fitting parameters are summarized in Figs. 5e-g and Table S1. As we can see, the time τ_{32} and τ_{21} of all films are several picoseconds, corresponding to intraband relaxation processes. The time τ_{10} for 4 L, 7 L and 17 L PtSe₂ films is about 100~200 ps, which corresponds to the typical interband relaxation time in semiconductors. However, for 55 L PtSe₂ film, the τ_{10} decreases dramatically by an order of magnitude to only ~13 ps. It is worth noting that in semimetals, the excited carriers can relax fast to the equilibrium state near the Fermi level *via* intraband processes like electron-electron and electron-phonon scattering. The relaxation time around Fermi surface is only about several picoseconds for semimetals like graphene (4~11 ps) and Cd₃As₂ (~4 ps).^[53, 54] Therefore, in our case, it is reasonable to deduce that the sudden drop of the interband relaxation time indicates the disappearing of the slow interband relaxation process and thus the transition from semiconductor to semimetal. The time shift of transmission minimum between 4 L and 7 L PtSe₂ in Fig. 4c is probable due to their different FCA cross sections (1.35×10^{-17} cm² for 4 L and 1.15×10^{-16} cm² for 7 L) and densities of states, which are layer-dependent in 2D materials.^[55-58] As shown in Fig. 5g and Table S1, the lifetime (τ_{32} and τ_{21}) and the FCA cross section of each

state in the conduction band are larger at lower temperature, while they almost stay the same below 200 K. This is different from the FCA caused by thermal free carriers.^[59, 60] Here most of the free carriers in E₂ state are optically induced ($\sim 10^{22} \text{ cm}^{-3}$), which are one or two orders of magnitude more than the intrinsic thermal free carriers measured by Hall effect ($10^{20}\sim 10^{21} \text{ cm}^{-3}$). Since the excitation of thermal phonon becomes less at low temperature, the excited carriers are more difficult to decay due to the weaker carrier-phonon interaction. This results in a larger FCA cross section and a longer intraband relaxation time at low temperature.

2.4. Layer-dependent Electrical Characteristics

Figure 6. (a) The resistance and conductivity of 4 L, 7 L, 17 L and 55 L PtSe₂ films at 300 K, (b) temperature dependence of 2D conductivities of PtSe₂ films.

To further verify the layer-dependent semiconductor-to-semimetal evolution, we measured the electrical characteristics of PtSe₂ films. Details for the electrical characteristics measurements were shown in Methods and Note S4 in SI. Figure 6a plots the results of the electrical measurements of all four PtSe₂ films. The conductivities σ of 4, 7, 17 L are about 2.92×10^3 , 3.55×10^4 , $7.33 \times 10^4 \text{ S m}^{-1}$ and lie in the range of semiconductors ($10^{-6}\sim 10^4 \text{ S m}^{-1}$).^[61] For 55 L film, it is about $1.41 \times 10^5 \text{ S m}^{-1}$, on the same order of magnitude with metal manganese

($6.94 \times 10^5 \text{ S m}^{-1}$) and semimetallic bulk PtSe₂ ($6.20 \times 10^5 \text{ S m}^{-1}$).^[10] The conductivities of our films (7 L and 17 L) are relatively larger than the mechanically exfoliated ones,^[10] which may be due to the tiny unreacted Pt residual during selenization process.

It is known that the empirical temperature dependence of conductivity for semiconductors is opposite to that for metals. As shown in Fig. 6b, the distinct dependencies of the 2D conductivity on temperature reveal that 4 L PtSe₂ is a semiconductor and 55 L PtSe₂ is a semimetal. However, for 7 L and 17 L films in the vicinity of semiconductor-semimetal transition point, we found that this empirical rule failed. As reported previously, the conductivity of 8-nm-thick and 11-nm-thick PtSe₂ prepared by mechanical exfoliation does not follow a monotonical trend with increasing temperature.^[10] This is in consistency with our 7 L and 10 L films prepared by Pt selenization method. Therefore, it can be concluded that the temperature dependent conductivity of layered PtSe₂ does not obey the empirical monotonical rule of common semiconductors when it is close to the transition point from semiconductor to semimetal. The semiconducting properties of 7 L and 17 L films can be determined from our Hall electrical measurements, which is consistent with Tauc plots, Z-scan and ultrafast dynamics results.

2.5. DFT Calculation

The first-principles calculations are based on the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP),^[62] where planewaves are used as basis set and projector-augmented wave (PAW) potentials are used to represent ion cores (see details in Methods).^[63] The calculated indirect band gap using the SCAN+rVV10 functional, as shown in Figs. 7a-d, is significantly different from the previous DFT calculations using LDA or PBE functionals, which predicts that PtSe₂ of three-layer thickness is already metallic.^[8, 10, 11] In our calculations, PtSe₂ films with a thickness up to 15 L still exhibits a tiny

band gap (~ 0.07 eV). Meanwhile, we calculate the density of states (DOS) of 4 L and bulk sample shown in Fig. 7a and 7b, respectively. As we can see, for 1040 nm (1.19 eV) excitation, the DOS corresponding to one photon absorption (1PA) transition is very low. Most electrons go up to E_2 through two photon absorption (2PA). After the overlapping of the pump and probe pulse, the free carriers in E_1 and E_2 can still absorb photons from the probe beam and jump to a higher energy band E_3 , which represents the free carrier absorption (FCA) in the conduction band. Here for 1040 nm excitation, E_0 is the ground state in the valance band, E_1 is the conduction band minima, E_2 represents the 2PA (for 4 L and 7 L) and 1PA (for 17 L and 55 L) energy level with a large DOS and E_3 is the FCA level, as marked in Fig. 7a and 7b. The calculated bandgap of layer-dependent PtSe₂ with and without spin-orbit coupling (SOC) effect are shown in Fig. 7e. The SOC effect can be neglected for thicker layers. According to our DFT calculations, only monolayer has a sizable bandgap. When layer number increases, the bandgap decreases dramatically. We also made a comparison between the Tauc plot and DFT calculations, as shown in Table S2. Although the bandgaps calculated are still smaller, the newly developed SCAN functional we used is fully constrained for the bulk and it is more reasonable for the thicker layers than LDA one.^[64] For 4 L and 7 L films, the bandgaps are smaller than 1.2 eV, resulting saturable absorption in the NLO measurements. In Fig. 7e, it can be seen that for 55 L PtSe₂, the bandgap is negative, indicating that it is a semimetal. The variation trend and the transition point from semiconductor to semimetal are in good consistence with Tauc plot, Z-scan, carrier dynamics results and electrical measurements.

Figure 7. The band-structures of (a) 4 L, (b) bulk, (c) 7 L and (d) 15 L PtSe₂. (e) The calculated bandgaps of layer-dependent PtSe₂ with and without spin-orbit coupling (SOC).

3. Conclusion

In summary, the wavelength-dependent NLO properties of few-layer PtSe₂ films were studied through the open/closed aperture Z-scan method and degenerate pump probe technique. The 4 L and 7 L PtSe₂ films exhibit a giant TPA coefficient of $(2.96 \pm 0.05) \times 10^4$ and $(1.64 \pm 0.09) \times 10^4$ cm GW⁻¹, respectively. The carrier dynamics for 4 L and 7 L films consists of SA, TPA and FCA processes at 1040 nm excitation. It changes to only SA and FCA processes for 17 L

and 55 L PtSe₂ films due to the decrease of energy bandgap. The excited carrier dynamics can be well fitted using a four level rate equation model. The interband relaxation time drops dramatically from hundreds of picoseconds to just several picoseconds when the layer thickness increases from 17 L to 55 L, indicating the disappearance of the bandgap and the transition from semiconductor to semimetal. The layer-dependent FCA cross section was determined to be on the order of 10^{-17} cm² quantitatively. Electrical characterization and DFT calculations further confirmed the layer-dependent semiconductor to semimetal evolution of the layered PtSe₂. Our results manifested the mechanism of carrier dynamics and significant ultrafast NLO properties of layered PtSe₂ films. We provided an optical nonlinear method to reveal the evolution between semiconductor and semimetal, which holds enormous potential for the development of nanophotonic devices.

Methods

Sample preparation. The sample preparation process involved first sputtering thin films of Pt onto substrates (fused quartz) and subsequently converting these films into PtSe₂ by exposing them to Se vapor in a two-zone quartz tube furnace. In this two-zone furnace the Se precursor (Se pellets, Sigma Aldrich) was placed in the upstream zone and heated to 250 °C. The Pt substrates, in the downstream zone of the furnace, were heated to 450 °C. Ar/H₂ (9:1) was used as the carrier gas to transport the Se vapor from the upstream zone to the downstream zone where it converted the Pt films. A dwell time of 2 hours was used to ensure complete conversion, in line with previous reports.^[15]

Materials characterization. The height profile of each PtSe₂ film was measured on a FM-Nanoview 6800 in tapping mode. The XPS spectra were acquired on a VG Scientific ESCA lab MkII system using Al K α X-rays with an analyzer pass energy of 20 eV. Raman characterization of PtSe₂ films were carried out using a confocal microscopy system (LabRAM HR Evolution)

excited by 633 nm cw laser. The optical transmission, reflection and absorption spectra of PtSe₂ films were measured using a PerkinElmer Lambda 950 instrument.

Time-resolved pump probe technique. The transient transmission measurements were performed through 380 fs pulses at 1040 nm with a repetition rate of 1000 Hz. The pump and probe pulses were split from the laser source by an ultrafast beamsplitter, while the energy of pump pulse is always one order of magnitude larger than probe pulse to avoid the self-induced nonlinearities of the probe pulse.^[46] The polarization of probe pulse was rotated to be perpendicular to the pump pulse, which could minimize the coherent artefacts.^[56] To analyze the temperature-dependent carrier relaxation dynamics, the differential-transmission signal $\Delta T/T_0$ was measured in a vacuum cryostat.

Electrical characterization. The measurements were carried out in a physical property measurement system (PPMS-9). The temperature was set at 300 K with a stabilization which is better than 0.01%. The temperature dependent 2D conductivity σ_{2D} calculated by $\sigma_{2D} = \sigma * d$. The 3D conductivity σ can be calculated by $\sigma = \ln 2 / \pi R d$ approximately, where R is the resistance of the films and d is the sample thickness. The Hall coefficient (K_H) can be calculated by $K_H = \frac{V_H}{IB} = \frac{1}{nqd}$, where V_H is the Hall voltage, n is the 2D charge carrier density, q is the charge of the carrier and d is the thickness of the film. By measuring the V_H and I at different magnetic field B , we can easily calculate the value of K_H . Since the sample thickness is far less than the sample size, the conductivity σ can be calculated by $\sigma = \frac{\ln 2}{\pi R d}$ approximately, where R is the resistance of the films.

DFT calculation. Our first-principles calculations were based on the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP),^[62] where planewaves are used as the basis set and projector-augmented wave (PAW) potentials^[63] are used to represent ion cores. We used the strongly constrained and appropriately normed (SCAN) exchange-correlation functional,^[65] which is further amended by the rVV10 functional

to describe the weak interlayer van der Waals interaction.^[66] Structural optimizations, including the lattice constants, were carried out until the force on each atom was smaller than 0.05 mRy/Bohr. The kinetic cutoff energy for the planewave basis set was set to 30 Ry. The Brillouin zone (BZ) was sampled by a $11 \times 11 \times 1$ k -point grid. To calculate the band structure, the high symmetry points in the BZ were included in a self-consistent calculation while setting their weights to 0. The effect of spin-orbit coupling (SOC) on the band structure was considered up to a thickness of seven layers.

Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's website.

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Conflict of Interest

The authors declare no competing financial interest.

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References

- [1] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
- [2] F. Bonaccorso, Z. Sun, T. Hasan, A. C. Ferrari, *Nat. Photonics* **2010**, *4*, 611.
- [3] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, V. Pellegrini, *Science* **2015**, *347*, 6217.
- [4] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10451.
- [5] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* **2012**, *7*, 699.
- [6] P. A. George, J. Strait, J. Dawlaty, S. Shivaraman, M. Chandrashekhar, F. Rana, M. G. Spencer, *Nano Lett.* **2008**, *8*, 4248.
- [7] F. Xia, H. Wang, Y. Jia, *Nat. Commun.* **2014**, *5*, 4458.
- [8] X. Yu, P. Yu, D. Wu, B. Singh, Q. Zeng, H. Lin, W. Zhou, J. Lin, K. Suenaga, Z. Liu, Q. J. Wang, *Nat. Commun.* **2018**, *9*, 1545.
- [9] A. Castellanos-Gomez, L. Vicarelli, E. Prada, J. O. Island, K. L. Narasimha-Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. V. Alvarez, H. W. Zandbergen, J. J. Palacios, H. S. J. van der Zant, *2D Mater.* **2014**, *1*, 025001.
- [10] Y. Zhao, J. Qiao, Z. Yu, P. Yu, K. Xu, S. P. Lau, W. Zhou, Z. Liu, X. Wang, W. Ji, Y. Chai, *Adv. Mater.* **2017**, *29*, 1604230..
- [11] Y. Wang, L. Li, W. Yao, S. Song, J. T. Sun, J. Pan, X. Ren, C. Li, E. Okunishi, Y. -Q. Wang, E. Wang, Y. Shao, Y. Y. Zhang, H. Yang, E. F. Schwier, H. Iwasawa, K. Shimada, M. Taniguchi, Z. Cheng, S. Zhou, S. Du, S. J. Pennycook, S. T. Pantelides, H. -J. Gao, *Nano Lett.* **2015**, *15*, 4013.
- [12] A. Ciarrocchi, A. Avsar, D. Ovchinnikov, A. Kis, *Nat. Commun.* **2018**, *9*, 919.

- [13] M. Yan, E. Wang, X. Zhou, G. Zhang, H. Zhang, K. Zhang, W. Yao, N. Lu, S. Yang, S. Wu, T. Yoshikawa, K. Miyamoto, T. Okuda, Y. Wu, P. Yu, W. Duan, S. Zhou, *2D Mater.* **2017**, *4*, 045015.
- [14] Y. Zhao, J. Qiao, P. Yu, Z. Hu, Z. Lin, S. P. Lau, Z. Liu, W. Ji, Y. Chai, *Adv. Mater.* **2016**, *28*, 2399.
- [15] C. Yim, K. Lee, N. McEvoy, M. O'Brien, S. Riazimehr, N. C. Berner, C. P. Cullen, J. Kotakoski, J. C. Meyer, M. C. Lemme, G. S. Duesberg, *ACS Nano* **2016**, *10*, 9550.
- [16] C. Yim, V. Passi, M. C. Lemme, G. S. Duesberg, C. Ó. Coileáin, E. Pallecchi, D. Fadil, N. McEvoy, *NPJ 2D Mater. Appl.* **2018**, *2*, 5.
- [17] L. Li, K. Xiong, R. J. Marstell, A. Madjar, N. C. Strandwitz, J. C. M. Hwang, N. McEvoy, J. B. McManus, G. S. Duesberg, A. Göritz, M. Wietstruck, M. Kaynak, *IEEE T. Electron Dev.* **2018**, *65*, 4102.
- [18] C. Yim, N. McEvoy, S. Riazimehr, D. S. Schneider, F. Gity, S. Monaghan, P. K. Hurley, M. C. Lemme, G. S. Duesberg, *Nano Lett.* **2018**, *18*, 1794.
- [19] Z. -X. Zhang, L. -H. Zeng, X. -W. Tong, Y. Gao, C. Xie, Y. H. Tsang, L. -B. Luo, Y. -C. Wu, *J. Phys. Chem. Lett.* **2018**, *9*, 1185.
- [20] J. Yuan, H. Mu, L. Li, Y. Chen, W. Yu, K. Zhang, B. Sun, S. Lin, S. Li, Q. Bao, *ACS Appl. Mater. Interfaces* **2018**, *10*, 21534.
- [21] L. Tao, X. Huang, J. He, Y. Lou, L. Zeng, Y. Li, H. Long, J. Li, L. Zhang, Y. H. Tsang, *Photon. Res.* **2018**, *6*, 750.
- [22] K. Zhang, M. Feng, Y. Ren, F. Liu, X. Chen, J. Yang, X. -Q. Yan, F. Song, J. Tian, *Photon. Res.* **2018**, *6*, 893.
- [23] M. O'Brien, N. McEvoy, C. Motta, J. Zheng, N. C. Berner, J. Kotakoski, K. Elibol, T. J. Pennycook, J. C. Meyer, C. Yim, M. Abid, T. Hallam, J. F. Donegan, S. Sanvito, G. S. Duesberg, *2D Mater.* **2016**, *3*, 021004.

- [24] J. -K. Huang, J. Pu, C. -L. Hsu, M. -H. Chiu, Z. -Y. Juang, Y. -H. Chang, W. -H. Chang, Y. Iwasa, T. Takenobu, L. -J. Li, *ACS nano* **2013**, 8, 923.
- [25] L. -H. Zeng, S. -H. Lin, Z. -J. Li, Z. -X. Zhang, C. Xie, C. -H. Mak, Y. Chai, S. P. Lau, L. -B. Luo, Y. H. Tsang, *Adv. Funct. Mater.* **2018**, 28, 1705970.
- [26] Z. Wang, Q. Li, F. Besenbacher, M. Dong, *Adv Mater* **2016**, 28, 10224.
- [27] A. Cingolani, M. Ferrara, M. Lugara, F. Levy, *Solid State Commun.* **1984**, 50, 911.
- [28] L. Roubi, C. Carlone, *Phys. Rev. B* **1988**, 37, 6808.
- [29] S. Zhang, N. Dong, N. McEvoy, M. O'Brien, S. Winters, N. C. Berner, C. Yim, Y. Li, X. Zhang, Z. Chen, L. Zhang, G. S. Duesberg, J. Wang, *ACS Nano* **2015**, 9, 7142.
- [30] N. Dong, Y. Li, Y. Feng, S. Zhang, X. Zhang, C. Chang, J. Fan, L. Zhang, J. Wang, *Sci. Rep.* **2015**, 5, 14646.
- [31] K. Wang, Y. Feng, C. Chang, J. Zhan, C. Wang, Q. Zhao, J. N. Coleman, L. Zhang, W. J. Blau, J. Wang, *Nanoscale* **2014**, 6, 10530.
- [32] Y. Feng, N. Dong, G. Wang, Y. Li, S. Zhang, K. Wang, L. Zhang, W. J. Blau, J. Wang, *Opt Express* **2015**, 23, 559.
- [33] F. Zhou, J. H. Kua, S. Lu, W. Ji, *Optics Express* **2018**, 26, 16093.
- [34] J. Huang, N. Dong, S. Zhang, Z. Sun, W. Zhang, J. Wang, *ACS Photonics* **2017**, 4, 3063.
- [35] H. Yang, X. Feng, Q. Wang, H. Huang, W. Chen, A. T. S. Wee, W. Ji, *Nano lett.* **2011**, 11, 2622.
- [36] X. Zhang, S. Zhang, Y. Xie, J. Huang, L. Wang, Y. Cui, J. Wang, *Nanoscale* **2018**, 10, 17924.
- [37] J. He, Y. L. Qu, H. P. Li, J. Mi, W. Ji, *Opt. Express* **2005**, 13, 9235.
- [38] R. Li, N. Dong, F. Ren, H. Amekura, J. Wang, F. Chen, *Sci. Rep.* **2018**, 8, 1977.
- [39] R. Li, N. Dong, C. Cheng, F. Ren, R. Hübner, J. Wang, S. Zhou, F. Chen, *ACS Omega* **2017**, 2, 1279.

- [40] J. H. Bechtel, W. L. Smith, *Phys. Rev. B* **1976**, *13*, 3515.
- [41] E. W. Van Stryland, H. Vanherzeele, M. A. Woodall, M. J. Soileau, A. L. Smirl, S. Guha, T. F. Boggess, *Opt. Eng.* **1985**, *24*, 613.
- [42] C. H. Kwak, Y. L. Lee, S. G. Kim, *J. Opt. Soc. Am. B.* **1999**, *16*, 600.
- [43] N. Dong, Y. Li, S. Zhang, N. McEvoy, X. Zhang, Y. Cui, L. Zhang, G. S. Duesberg, J. Wang, *Opt. Lett.* **2016**, *41*, 3936.
- [44] H. P. Li, C. H. Kam, Y. L. Lam, W. Ji, *Opt. Mater.* **2001**, *15*, 237.
- [45] R. J. Suess, M. M. Jadidi, T. E. Murphy, M. Mittendorff, *Appl. Phys. Lett.* **2015**, *107*, 081103.
- [46] M. Reichert, A. L. Smirl, G. Salamo, D. J. Hagan, E. W. Van Stryland, *Phys. Rev. Lett.* **2016**, *117*, 5.
- [47] F. Wendler, A. Knorr, E. Malic, *Nanophotonics* **2015**, *4*, 224.
- [48] J. Shah, *Superlattices Microst.* **1989**, *6*, 293.
- [49] S. Cha, J. H. Sung, S. Sim, J. Park, H. Heo, M. -H. Jo, H. Choi, *Nat. Commun.* **2016**, *7*, 10768.
- [50] H. Wang, C. Zhang, F. Rana, *Nano Lett.* **2015**, *15*, 339.
- [51] F. A. Riddoch, M. Jaros, *J. Phys. C: Solid State Phys.* **1980**, *13*, 6181
- [52] D. J. Robbins, P. T. Landsberg, *J. Phys. C: Solid State Phys.* **1980**, *13*, 2425..
- [53] D. Sun, Z. K. Wu, C. Divin, X. Li, C. Berger, W. A. de Heer, T. B. Norris, *Phys. Rev. Lett.* **2008**, *101*, 157402.
- [54] W. Lu, S. Ge, X. Liu, H. Lu, C. Li, J. Lai, C. Zhao, Z. Liao, S. Jia, D. Sun, *Phys. Rev. B* **2017**, *95*, 024303.
- [55] S. Lebegue, O. Eriksson, *Phys. Rev. B* **2009**, *79*, 115409.
- [56] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. -Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, *10*, 1271.

- [57] L. Li, J. Kim, C. Jin, G. J. Ye, D. Y. Qiu, F. H. da Jornada, Z. Shi, L. Chen, Z. Zhang, F. Yang, K. Watanabe, T. Taniguchi, W. Ren, S. G. Louie, X. H. Chen, Y. Zhang, F. Wang, *Nat. Nanotechnol.* **2017**, *12*, 21.
- [58] A. Carvalho, M. Wang, X. Zhu, A. S. Rodin, H. Su, A. H. Castro Neto, *Nat. Rev. Mater.* **2016**, *1*, 16061.
- [59] T. Korn, S. Heydrich, M. Hirmer, J. Schmutzler, C. Schueller, *Appl. Phys. Lett.* **2011**, *99*, 102109.
- [60] P. D. Olszak, C. M. Cirloganu, S. Webster, L. A. Padilha, S. Guha, L. P. Gonzalez, S. Krishnamurthy, D. J. Hagan, E. W. Van Stryland, *Phys. Rev. B* **2010**, *82*, 235207.
- [61] R. A. Serway, *Principles of Physics* (2nd ed.). Saunders College Pub: London, **1998**; p. 602.
- [62] G. Kresse, J. Furthmuller, *Comp. Mater. Sci.* **1996**, *6*, 15.
- [63] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
- [64] W. Zhang, J. Qin, Z. Huang, W. Zhang, *J. Appl. Phys.* **2017**, *122*, 205701.
- [65] J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein, J. P. Perdew, *Nat. Chem.* **2016**, *8*, 831.
- [66] H. Peng, Z.-H. Yang, J. P. Perdew, J. Sun, *Phys. Rev. X* **2016**, *6*, 041005.

Graphical Abstract