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Nonlinear Optical Signatures of Transition from Semiconductor to Semimetal in PtSe$_2$

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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, PtSe$_2$ shows much better air stability than its analogue, black phosphorous. In this work, the superior nonlinear optical performance, ultrafast dynamics of layered PtSe$_2$ 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.$^{[8-10]}$ PtSe$_2$, 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.\textsuperscript{[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,\textsuperscript{[8, 10-12]} PtSe\textsubscript{2} can be used as a good candidate in electronic devices,\textsuperscript{[15-17]} wide spectral response photodetector and photodiodes,\textsuperscript{[8, 18, 19]} optical switches and saturable absorbers,\textsuperscript{[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 PtSe\textsubscript{2}.\textsuperscript{[8,10-13]}

In our work, the superior NLO performance and ultrafast dynamics of layered PtSe\textsubscript{2} 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 PtSe\textsubscript{2} thin films of different thicknesses were synthesized by a thermally assisted conversion process.\textsuperscript{[15, 23-25]} Photographs of four synthesized PtSe\textsubscript{2} 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 PtSe$_2$, 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 PtSe$_2$ films with different thicknesses. 0.5, 1, 3 and 5 nm represent the initial deposition thickness of Pt. (b) The crystal structure of PtSe$_2$ from top view and side view. (c) - (d) Cross sectional TEM and surface AFM images of the thinnest PtSe$_2$ film. Inset shows the height profile. (e) - (f) XPS for Pt 4f region and Se 3d region of the thinnest PtSe$_2$ film. (g) Raman spectra of the PtSe$_2$ films with different layer numbers, (h) thickness dependent behavior of E$_{1g}$, A$_{1g}$ and longitudinal optical (LO) phonon peaks, (i) transmission, reflection, and absorption spectra of 4 L PtSe$_2$ film, (j) Tauc plots of four PtSe$_2$ films.

The bandgaps of most 2D materials, including many TMDCs, depend strongly on their thickness. In order to identify the layer number of PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$.

**Table 1.** Number of layers in four PtSe$_2$ films

<table>
<thead>
<tr>
<th>Initial nominal Pt (nm)</th>
<th>Thickness after selenization (nm)</th>
<th>Layer number (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSe$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2.3±0.3</td>
<td>4±1</td>
</tr>
<tr>
<td>1</td>
<td>4.5±1.6</td>
<td>7±3</td>
</tr>
<tr>
<td>3</td>
<td>10.2±2.8</td>
<td>17±5</td>
</tr>
<tr>
<td>5</td>
<td>32.2±7.3</td>
<td>55±12</td>
</tr>
</tbody>
</table>

X-ray photoelectron spectroscopy (XPS) was carried out to measure the binding energy and to verify the quality of PtSe$_2$ films. Figure 1e and 1f are the XPS results of Pt 4f and Se 3d core level for 4 L PtSe$_2$ 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 PtSe$_2$ film. Additional XPS spectra acquired from thicker PtSe$_2$ are presented in Fig. S2.
Raman spectra of PtSe\(_2\) films with laser excitation at 633 nm are shown in Fig. 1g. All the four films exhibit two prominent peaks at \(\sim 174\) cm\(^{-1}\) and \(\sim 203.4\) 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 PtSe\(_2\) films, a weak longitudinal optical (LO) mode is located at \(\sim 230\) 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 HfS\(_2\), ZrS\(_2\) and CdI\(_2\).[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 PtSe\(_2\) films. Figure 1i and S3 demonstrate the linear transmission (T), reflection (R) and absorption (A) spectra of PtSe\(_2\) films with different thicknesses, while the absorption spectra were obtained from the formula \(A=1–R–T\) similar to previous studies on MoS\(_2\) and WS\(_2\).[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 PtSe\(_2\). A red shift of the absorption edge with increasing layer number is observed, in good agreement with previous reports on mechanically-exfoliated PtSe\(_2\) 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 PtSe\(_2\) 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, MoS$_2$ nanoflake dispersions, BP nanoflake dispersions and WS$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 MoS$_2$.$^{[35,36]}$ As reported previously,$^{[37-39]}$ the order of NLO response can be distinguished by the relationship between the normalized transmission $T_{\text{Norm}}$ and the incident beam intensity $I$, and the formula can be written as:

$$\ln(1 - T_{\text{Norm}}) = k \times \ln(I) + C_0$$  \hspace{1cm} (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 $\ln(1-T_{\text{Norm}})$ versus $\ln(I)$ of 4 L and 7 L PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe\textsubscript{2} films at (a)-(d) 1030 nm and (e)-(h) 515 nm femtosecond pulse excitation, respectively.

In order to quantitatively describe the NLO properties of PtSe\textsubscript{2} films, we fitted the Z-scan results with the nonlinear propagation equation,

\[
\frac{dl}{dz} = - \frac{\alpha_0 I}{1 + I/I_{\text{sat}}} - \beta I^2
\]

where \(I\) is the beam irradiance, \(z\) is the propagation distance in the sample, \(\alpha_0\) is the linear absorption coefficient, \(I_{\text{sat}}\) is the saturation irradiance and \(\beta\) is the TPA coefficient. For the coexistence of SA and TPA response, \(\beta\) is positive, while for pure SA process, \(\beta\) is zero. To obtain a precise value of the linear absorption \(\alpha_0\), 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, \(\lambda\) 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 PtSe\textsubscript{2} films obtained by Z-scan technique

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>Layer numbe</th>
<th>(T_0) (%)</th>
<th>(R_0) (%)</th>
<th>(a_0) ((\times 10^4) cm(^{-1}) (\text{cm GW}^{-1}))</th>
<th>(\beta) ((\times 10^4) cm GW(^{-3}))</th>
<th>(I_{\text{sat}}) ((\text{GW cm}^2))</th>
<th>(\text{Im}\chi^{(3)}) ((\times 10^{-15}) esu cm))</th>
<th>(\text{FOM}_{\text{im}}) ((\times 10^{15}) esu cm))</th>
<th>(n_2) ((\times 10^{-11}) cm(^2) W(^{-1}))</th>
<th>(\text{Re}\chi^{(3)}) ((\times 10^{-9}) esu))</th>
<th>(\text{FOM}_{\text{re}}) ((\times 10^{14}) esu cm))</th>
<th>Damage threshold ((\text{GW cm}^2))</th>
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<td>1030</td>
<td>4</td>
<td>79.5</td>
<td>9.0</td>
<td>5.87</td>
<td>2.96±0.05</td>
<td>14.5±1</td>
<td>147.1±5.5</td>
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<td>14.1</td>
<td>4.97</td>
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<td>20±3.2</td>
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<tr>
<td>515</td>
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<td>12.6</td>
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<td>-0.77±0.15</td>
<td>0.21±0.04</td>
<td>10.41</td>
</tr>
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</table>
Table 2 summarizes all the linear and NLO parameters for PtSe$_2$ films in the Z-scan measurement. The TPA coefficient $\beta$ for 4 L PtSe$_2$ 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 MoS$_2$.$^{[29,40,41]}$ 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 PtSe$_2$ 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 $\text{Re}\chi^{(3)} (\text{esu}) = \frac{n_2^2 c}{12\pi^2} n_2 \times 10^{-7}$ (cm$^2$ W$^{-1}$) and $\text{FOM}_{Re} = |\text{Re}\chi^{(3)}/\omega_0|$, respectively. As depicted in Fig. 3, all four PtSe$_2$ 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 MoS$_2$, WS$_2$ and WSe$_2$ and considerably larger than many conventional NLO crystals, such as LiNbO$_3$:MgO, KTiOAsO$_4$, KTiOPO$_4$, $\beta$-BaB$_2$O$_4$, and LiB$_4$O$_5$. 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 PtSe$_2$ films at 1040 nm with the same pump intensity $I=3.72$ GW/cm$^2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ films which are marked by dashed rectangle in (a) and (b). A temporal delay of 0.47 ps for 4 L PtSe$_2$ and 0.86 ps for 7 L PtSe$_2$ was observed. (d) Transient reflection and transmission dynamics of 4 L PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ 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 PtSe$_2$ film at different pump intensities. (b) Transient transmission dynamics of 17 L PtSe$_2$ film at probe intensities of 0.13 and 0.26 GW cm$^{-2}$. (c) Temperature-dependent transient transmission dynamics of 4 L PtSe$_2$ 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 $\tau_{32}$ and $\tau_{21}$ and (f) interband relaxation time $\tau_{310}$ at 300 K. (g) The temperature-dependent relaxation time $\tau_{32}$ and $\tau_{21}$ of 4 L PtSe$_2$ film.

To determine whether the phonon emission accompanies carrier relaxation, the normalized transient transmission of 4 L PtSe$_2$ 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 PtSe$_2$ films at different probe intensities with the same pump intensity at about 5.58 GW/cm$^2$. 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 PtSe$_2$ 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 PtSe$_2$, besides the dominant TPA process, the electrons in the ground state E$_0$ can also jump to conduction band minimum (CBM) E$_1$ 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 E$_2$ directly by one photon absorption for 17 L and 55 L PtSe$_2$. The free carriers in E$_2$ will relax to the CBM E$_1$ through the electron-phonon interaction with a relaxation time of $\tau_{21}$. 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 FCA in the conduction band. Once in E$_3$, they relax to E$_2$ via carrier-phonon interaction with a decay time $\tau_{32}$, which strongly depends on temperature. The excited carriers in E$_1$ will slowly decay to the ground state E$_0$ with time $\tau_{10}$, which represents the lifetime of E$_1$. Thus, the rate equations consisting of SA, TPA and FCA processes in 4 L, 7 L PtSe$_2$ films are:

\[
\begin{align*}
\frac{dn_3}{dt} &= \sigma_{fca}^{1pr} \frac{I_{pump}^2 + I_{pump} I_{pr}}{h\omega} (n_1 - n_3) + \sigma_{fca}^{1pr} \frac{I_{pump}}{h\omega} (n_2 - n_3) - \frac{n_3}{\tau_{32}} \\
\frac{dn_2}{dt} &= \sigma_{tpa} \frac{I_{pump}^2 + I_{pump} I_{pr}}{2h\omega} (n_0 - n_2) - \frac{n_2}{\tau_{21}} - \sigma_{fca} \frac{I_{pump}}{h\omega} (n_2 - n_3) + \frac{n_3}{\tau_{32}} \\
\frac{dn_1}{dt} &= \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_{10}} - \frac{\sigma_{fca}^{1pr}}{h\omega} (n_1 - n_3) + \frac{\sigma_0 (I_{pump} + I_{pr})}{h\omega} (n_0 - n_1)
\end{align*}
\]

(3)

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

\[
\begin{align*}
\frac{dn_3}{dt} &= \sigma_{fca} \frac{I_{pump}}{h\omega} (n_1 - n_3) + \sigma_{fca} \frac{I_{pump}}{h\omega} (n_2 - n_3) - \frac{n_3}{\tau_{32}} \\
\frac{dn_2}{dt} &= \sigma_0 \frac{I_{pump}}{h\omega} (n_0 - n_2) - \frac{n_2}{\tau_{21}} - \sigma_{fca} \frac{I_{pump}}{h\omega} (n_2 - n_3) + \frac{n_3}{\tau_{32}} \\
\frac{dn_1}{dt} &= \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_{10}} - \frac{\sigma_{fca}}{h\omega} (n_1 - n_3)
\end{align*}
\]

(4)

where $n_0$, $n_1$, $n_2$ and $n_3$ refer to the populations of carriers in ground state E$_0$, CBM E$_1$, photoexcited state E$_2$ and FCA energy state E$_3$, respectively. $\sigma_{fca}$, $\sigma_{tpa}$ and $\sigma_0$ 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 $I = I_0 \exp \left( t^2 / \tau_p^2 \right)$, where $\tau_p$ 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 PtSe$_2$ films, it can be written as:

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

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

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

The TPA cross section can be obtained by $\sigma_{tpa} = \beta / N$, where the TPA coefficient $\beta$ 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 $\sigma_{fca}$ 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 $\tau_{32}$ and $\tau_{21}$ of all films are several picoseconds, corresponding to intraband relaxation processes. The time $\tau_{10}$ for 4 L, 7 L and 17 L PtSe$_2$ films is about 100~200 ps, which corresponds to the typical interband relaxation time in semiconductors. However, for 55 L PtSe$_2$ film, the $\tau_{10}$ decreases dramatically by an order of magnitude to only $\sim 13$ 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 Cd$_3$As$_2$ (~4 ps).\cite{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 PtSe$_2$ in Fig. 4c is probable due to their different FCA cross sections ($1.35 \times 10^{-17}$ cm$^2$ for 4 L and $1.15 \times 10^{-16}$ cm$^2$ for 7 L) and densities of states, which are layer-dependent in 2D materials.\cite{55-58}

As shown in Fig. 5g and Table S1, the lifetime ($\tau_{32}$ and $\tau_{21}$) 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. Here most of the free carriers in E₂ state are optically induced (~10²² cm⁻³), which are one or two orders of magnitude more than the intrinsic thermal free carriers measured by Hall effect (10²⁰–10²¹ 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 2.92×10³, 3.55×10⁴, 7.33×10⁴ S m⁻¹ and lie in the range of semiconductors (10⁻⁶~10⁴ S m⁻¹). For 55 L film, it is about 1.41×10⁵ S m⁻¹, on the same order of magnitude with metal manganese.
(6.94×10⁵ S m⁻¹) and semimetallic bulk PtSe₂ (6.20×10⁵ S m⁻¹). The conductivities of our films (7 L and 17 L) are relatively larger than the mechanically exfoliated ones, 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. 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), where planewaves are used as basis set and projector-augmented wave (PAW) potentials are used to represent ion cores (see details in Methods). 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. 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 E₂ through two photon absorption (2PA). 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 free carrier absorption (FCA) in the conduction band. Here for 1040 nm excitation, E₀ is the ground state in the valance band, E₁ is the conduction band minima, E₂ represents the 2PA (for 4 L and 7 L) and 1PA (for 17 L and 55 L) energy level with a large DOS and E₃ 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 PtSe$_2$. (e) The calculated bandgaps of layer-dependent PtSe$_2$ with and without spin-orbit coupling (SOC).

3. Conclusion
In summary, the wavelength-dependent NLO properties of few-layer PtSe$_2$ films were studied through the open/closed aperture Z-scan method and degenerate pump probe technique. The 4 L and 7 L PtSe$_2$ films exhibit a giant TPA coefficient of $(2.96\pm0.05) \times 10^4$ and $(1.64\pm0.09) \times 10^4$ 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 ESCAland Mkll system using Al Ka 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 PtSe$_2$ 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 $\sigma_{2D}$ calculated by $\sigma_{2D} = \sigma \ast d$. The 3D conductivity $\sigma$ can be calculated by $\sigma = \frac{\ln 2}{\pi R d}$ 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 $\sigma$ 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.

**Keywords:** layered PtSe$_2$, nonlinear optical absorption, carrier dynamics, damage threshold

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