Ultrafast Carrier Dynamics and Bandgap Renormalization in Layered PtSe₂


Carrier interactions in 2D nanostructures are of central importance not only in condensed-matter physics but also for a wide range of optoelectronic and photonic applications. Here, new insights into the behavior of photoinduced carriers in layered platinum diselenide (PtSe₂) through ultrafast time-resolved pump–probe and nonlinear optical measurements are presented. The measurements reveal the temporal evolution of carrier relaxation, chemical potential and bandgap renormalization in PtSe₂. These results imply that few-layer PtSe₂ has a semiconductor-like carrier relaxation instead of a metal-like one. The relaxation follows a triple-exponential decay process and exhibits thickness-dependent relaxation times. This occurs along with a band-filling effect, which can be controlled based on the number of layers and may be applied in saturable absorption for generating ultrafast laser pulses. The findings may provide means to study many-body physics in 2D materials as well as potentially leading to applications in the field of optoelectronics and ultrafast photonics.

Atomically thin 2D layered crystalline materials are currently attracting much attention in the field of optoelectronics, photonics, and condensed matter physics due to their uniquely controllable properties.[1–3] By tuning the layer number and stacking sequence/angles, quantum confinement and interlayer coupling can be modified, resulting in massive changes of the electronic and optical responses of such materials. This tunability suggests that 2D layered materials are an ideal platform for developing novel devices such as spintronics[3–5] and valleytronics,[6,7] as well as studying many-body phenomena such as charge density waves and superconductivity.[1,8,9] Among the 2D material family, platinum diselenide (PtSe₂), a noble metal dichalcogenide, has emerged as a promising material for investigating quasiparticle interactions and for developing mid-infrared devices.[10,11] The unique properties of PtSe₂ not only include a layer-dependent bandgap (bulk has zero bandgap, while mono- and bilayer have 1.2 and 0.21 eV) but also potential phase transitions from a type-II Dirac semimetal to a topological insulator or Weyl semimetal in its bulk crystalline form.[12,13] Recent studies have shown some intriguing properties of PtSe₂, such as high charge-carrier mobility,[14] intrinsic patterning,[15] piezoresistivity,[16] and spin-layer locking.[17] Moreover, PtSe₂ exhibits great potential in electronic and optoelectronic devices, for example, field effect transistors (FETs),[14,18] spintronics,[17] mid-infrared photodetectors,[10,19] gas sensors,[20] valleytronics,[12] and optical modulators.[21,22] Despite a number of reports addressing the synthesis,[11,23] electrical properties,[12,17,18] and prototype devices,[10,11,14,21] there is still a lack of understanding regarding the carrier dynamics in layered PtSe₂ on an ultrafast time scale.

Understanding ultrafast dynamical processes in 2D materials is essential for exploring many-body phenomena...
and light–matter coupling from a fundamental physics point of view. Many interesting effects, such as excitonic quasi-particle interactions, hot carrier transport, Mott transition, valley selective optical Stark effect, bandgap renormalization, and charge density waves, can be probed with ultrafast carrier dynamics.\[8,9,24–28\] Moreover, it is possible to engineer the material’s response through carrier injection by ultrafast laser pulses.\[24,25,29\] Thus, investigation of carrier dynamics is of importance as it provides an insight into the feasibility of utilizing the novel features of 2D systems in optoelectronic and photonic applications.

Here, we investigate the carrier dynamics of PtSe\(_2\) of various thicknesses by pump–probe spectroscopy with ultrafast laser pulses. We show that separate electron and hole distributions are established within a few hundred femtoseconds after photocarrier injection, implying semiconductor- rather than metal-like carrier dynamics.\[24,25,29\] Thus, investigation of carrier dynamics is of importance as it provides an insight into the feasibility of utilizing the novel features of 2D systems in optoelectronic and photonic applications.

Figure 1. Structure and characterization of layered PtSe\(_2\) films synthesized by the thermally assisted conversion method. a) Side- and top-view of 1T-type octahedral PtSe\(_2\) crystal structures. Dark balls represent Pt atoms while red ones indicate Se atoms. b) TEM image of the cross-section of the PtSe\(_2\) [0.5 nm] film grown on SiO\(_2\) substrate. [0.5 nm] represents the PtSe\(_2\) was selenized from an initially 0.5 nm thick Pt metallic film and so forth. The white scale bar is 4 nm. c) STEM and d) HRTEM images of the crystalline grains in a sample of 3 nm starting thickness. e) X-ray photoelectron spectroscopy of [3 nm] sample, indicating atomic percentages of Pt and Se to be about 30.3% and 69.7%, respectively. f) Raman spectra of PtSe\(_2\) grown from different initial Pt thicknesses. g) Transmission and absorption spectra of the PtSe\(_2\) films from visible to mid-infrared. The dashed line indicates the noise region associated with switching of photodetectors. h) Real and imaginary part of the refractive index of PtSe\(_2\) from ellipsometry measurement.

Platinum diselenide has a 1T-type layered crystal structure as presented in Figure 1a. As the side-view image shows, the neighboring layers are bonded by van der Waals forces with \(\approx 5.4\) Å pitch.\[11\] To obtain layered PtSe\(_2\) thin films, we employed the method of thermally assisted conversion as previously reported\[10,23\] (see in the Experimental Section). In this synthesis process, a platinum film was deposited onto a fused quartz substrate and then selenized to form PtSe\(_2\). During this selenization, the film thickness can expand \(\approx 4\) times comparing to that of the starting metal films.\[30\] According to the starting Pt metallic film thickness, we named these samples as [3], [1], and [0.5 nm]. In order to confirm the quality of the films for later measurements, we characterized them using a variety of techniques. Figure 1b shows the cross-section transmission electron microscope (TEM) image of an as-synthesized [0.5 nm] film on fused quartz, where we can count \(\approx 6\) layers in the film and a total film thickness of \(\approx 3\) nm. This \(\approx 0.5\) nm layer pitch agrees well with the experimental values reported in the literature.\[10,11\] In Figure 1c, a scanning transmission electron microscope (STEM) image displays the top-view geometry of a typical PtSe\(_2\) crystal in [3 nm] sample, where the lattice lines are clearly seen. To confirm the 1T-type structure of our PtSe\(_2\) film, we performed high-resolution transmission electron microscope (HRTEM) measurements and a typical image is shown in
Figure 1d. The octahedral structure of PtSe₂ can clearly be seen with an average lattice constant of ≈3.8 Å, corresponding well to the reported experimental value.[¹¹]

The chemical state and quality of the PtSe₂ thin film was further investigated by X-ray photoelectron spectroscopy (XPS) in Figure 1e.[¹²,¹³] The Pt 4f spectra (72–80 eV) are dominated by a doublet peak at ≈73.6 eV. This dominant Pt signal is ascribed to Pt covalently bound to Se. This peak accounts for 92% of the identified Pt, implying that the majority of the Pt has bonded to Se resulting in the formation of PtSe₂. A small amount of residual Pt, attributed to Pt oxides, is shown as the gray doublet at ≈75.2 eV. The Se 3d spectra are composed of two overlapping doublets, the main doublet located at 54.9 eV is attributed to PtSe₂ and the second, smaller doublet likely originates from undercoordinated Se, potentially from grain boundaries and edges (PtSeₓ/Se–Se). Based on the above analysis, the atomic percentage of Pt and Se in our film contributing to PtSe₂ was calculated to be about 30.3% and 69.7%, respectively. Energy dispersive X-ray spectroscopy (EDS) was also carried out to study the constitution of the PtSe₂ films.[¹¹]

The Pt and Se EDS peaks are presented in Figure S1 in the Supporting Information. We obtained the atomic ratio of Pt/Se to be ≈30.2/69.8%, which agrees well with our XPS results. These atomic ratios of Pt/Se obtained by EDS and XPS also indicate the presence of undercoordinated Se.

We also performed Raman and UV–vis–IR spectroscopy on our PtSe₂ films. The obvious dependence of the position of Raman peaks on the thickness of PtSe₂ thin film made it possible to identify the number of layers.[¹⁴,¹⁵] In Figure 1f, the characteristic in-plane E₂ mode (≈175 cm⁻¹) and out-of-plane A₁g mode (≈205 cm⁻¹) were observed in all three specimens.[¹³] As the thickness of the initial Pt thin film was increased from 0.5 to 3 nm, a slight redshift/broadening (noticeable when zoom in) in E₂ peak and an increase in the relative intensity of the A₁g peak were observed. These results are in line with previous reports, where the A₁g peak intensity can be attributed to a stronger out-of-plane van der Waals interaction in samples with a greater number of layers.[¹³] To understand the linear optical properties of PtSe₂, we show the transmission and absorption of PtSe₂ thin films on fused quartz in Figure 1g. These measurements were carried out in an integrating sphere where the reflection and scattering were considered. As expected, thicker samples transmit less light. All PtSe₂ thin films exhibited broadband ground-state absorption from near-UV 354.3 nm (3.5 eV) to mid-infrared 2000 nm (0.62 eV). This broadband absorption is due to the semimetallic property of few-layered PtSe₂. More discussions about Raman spectroscopy and linear optical absorption of PtSe₂ can be seen in our previous works.[¹⁶]

The complex refractive index is a fundamental property of a material that not only determines its optical responses, but also directly connects to its complex permittivity and dielectric constant. We determined the real and imaginary part of the refractive index n and k (the latter also known as the extinction coefficient) of the PtSe₂ [3 nm] sample by spectroscopic ellipsometry in the wavelength range from 200 to 900 nm (see in the Experimental Section). The resulting refractive index and extinction coefficient are presented in Figure 1h. The real refractive index increased from 1.5 to 4.5 as the photon energy changed from 4 to 1.38 eV, while the extinction coefficient is relatively flat around 2.4. This refractive index is important for analyzing our transient spectroscopy results in later sections.

To obtain carrier relaxation times from experimental results, we analyzed the DT spectrum along the temporal axis by employing a triple-phase decay equation, which has taken into account the convolution of the pump and probe pulses (see Section 3 in the Supporting Information). As shown in Figure 2 and Figure S2 in the Supporting Information, this triple-phase model provides satisfying fitting results (solid lines). To provide a general idea about the relaxation times in PtSe₂, we summarized the time constants obtained from the integrated spectra (Figure 2g–i) in Table S1 in the Supporting Information.

In a pump–probe experiment, carriers generally experience initial excitation, rapid thermalization, cooling, and recombination. The optical pulses excite a large number of carriers into a nonequilibrium distribution at time-zero. This nonequilibrium regime cannot be described by any thermal distribution, e.g., Maxwell–Boltzmann or Fermi–Dirac (FD) functions.[²⁹] The carriers then dephase to a quasiequilibrium thermal regime via carrier–carrier scattering and/or emission of phonons in a...
few tens of femtoseconds, which is beyond our temporal resolution. These carriers are subsequently cooled via intraband scattering paths. The lifetimes of this intraband scattering in Figure 2g–i are calculated to be 0.65, 1.09, and 1.71 ps for PtSe₂ sample with [0.5], [1], and [3 nm] starting thickness. The state filling by a large amount of electron–hole pairs introduces the shrinkage of the bandgap, i.e., band renormalization, leading to the negative signal in Figure 2. The time constants related to this BGR are measured to be 0.91, 1.3, and 1.8 ps for [0.5], [1], and [3 nm] samples. The electrons in the lower excited states finally recombine with corresponding holes via the assistance of trap states (Shockley–Read–Hall recombination). These trap states may originate from excess Se atoms in the samples implied by the XPS and EDS results in Figure 1e and Figure S1 in the Supporting Information, respectively. The recombination time constants correspond to 27.3, 80.7, and 256.5 ps for [0.5], [1], and [3 nm] PtSe₂ thin films, respectively, as seen in Table S1 in the Supporting Information, showing a dramatic increase with increasing film thickness. This difference in recombination rate may be attributed to a variable defect density, where more defects are present in thinner films because of unreacted selenium and/or surface states.

We applied a quasiequilibrium carrier distribution model to quantify the contribution of BGR \( dE \), carrier temperature \( T_c \), chemical potential \( \mu \). The changes of the imaginary part of permittivity after optical excitation are

\[
\Delta \varepsilon'' = \varepsilon''(E + dE) - \varepsilon''(E) - 2\varepsilon''(E + dE)f\left(\frac{E + dE}{2}, T_c\right) \tag{1}
\]

where \( \varepsilon'' \) is the imaginary part of the complex permittivity \( \varepsilon \) at photon energy \( E \). The complex permittivity \( \varepsilon = \varepsilon' - i\varepsilon'' \) is connected to the complex refractive index \( n \) by relationship \( \varepsilon = n^2 = (n - ik)^2 \), where \( n \) and \( k \) can be interpolated from the complex refractive index measurement in Figure 1h. \( dE \) is the bandgap shift from BGR. For simplicity, we evaluated the
average behavior of electrons and holes and assumed that they behave equivalently, so the Fermi–Dirac distribution of carriers becomes \( f(E, T) = \frac{1}{1 + \exp[(E - \mu)/kT]} \). We specified two situations for chemical potential \( (\mu \neq 0 \text{ and } \mu = 0) \) because they correspond to different hot-carrier equilibration processes after optical excitation as Figure 3b shows. For \( \mu \neq 0 \), the electrons and holes establish a separate FD distribution in the conduction and valence bands if the intraband carrier scattering is much faster than the interband one. For \( \mu = 0 \), in contrast, the interband and intraband scattering rate are similar, leading to a distribution that can be described by a single FD distribution.[29,33]

Thus, by fitting for both cases, it is possible to ascertain which type of carrier dynamics dominates in layered PtSe₂.

To accurately calculate the variation in DT, changes of the PtSe₂ surface reflection and the effect from the fused quartz substrate should be also taken into account. To this end, a characteristic matrix method was employed to calculate the total transmission \( T \) for our PtSe₂ sample on fused quartz (see Section 4 in the Supporting Information). Figure 3c,d displays fits to the DT spectra by nonlinear regression using Equation (1) and Equations (S2) and (S3) in the Supporting Information. For DT spectra of PtSe₂ [3 nm] in Figure 3c, fits to the experimental results using separate FD distributions \( \mu \neq 0 \) (solid line) are much better than those using a single FD distribution \( \mu = 0 \) (dash line) for all delay times. This phenomenon implies that, like graphite, the carrier dynamics of PtSe₂ [3 nm] is more similar to that of a semiconductor than that of a metal.[29,33] For DT spectra of PtSe₂ [1 nm] in Figure 3d, both distributions \( (\mu \neq 0 \text{ and } \mu = 0) \) show indistinguishable behavior for 0.2 and 0.6 ps delay time. For a delay time above 1 ps, however, the fitting using \( \mu \neq 0 \) is still better than for \( \mu = 0 \). More details about the chemical potential as a function of delay time can be found in Figure 3f,g. The time-dependent BGR for both samples, \( dE \), can be found in Figure 3e. The BGR in PtSe₂ has a similar starting value of \( \approx 10 \text{ meV} \) at the first picosecond after the carrier injection for all PtSe₂ films, while the thicker ones show a slower relaxation. The BGR almost fully decays after \( \approx 2.6, \approx 1.2, \text{ and } \approx 1 \text{ ps} \) for the [3], [1], and [0.5 nm] samples, respectively.

The carrier temperature of PtSe₂ samples are also extracted from the fits as seen in Figure 3f,g, nicely showing carrier cooling. In PtSe₂ [3 nm], carriers cooled from about 2500 to 500 K over 4 ps nearly exponentially. However, in PtSe₂ [1 nm] the carrier temperature appears to linearly decrease from 1850 to 1750 K in the first picosecond, and then exponentially cools to \( \approx 400 \text{ K} \) after 2.5 ps. The fitted chemical potentials in Figure 3f,g also show similar behavior with temperature. These differences in temperature and chemical potential may be due to the fact that the carrier intraband equilibration after optical interband excitation in PtSe₂ [1 nm] is much slower than that in PtSe₂ [3 nm], where the latter looks “instantaneous” because of our \( \approx 200 \text{ fs} \) temporal resolution.

From the DT spectra of PtSe₂, we observed obvious optically induced bleaching with photon energy from 1.72 eV (720 nm) to 2.64 eV (470 nm) due to band filling. This effect implies a saturable absorption response in PtSe₂, which is important for broad applications working at a single wavelength,
such as optical-switching and mode-locking. Thus degenerate pump–probe experiments, where the pump and probe pulses have the same wavelength, is both an effective and appropriate technique to reveal the carrier dynamics of ground and excited states for such applications. We carried out degenerate pump–probe experiments at 800 nm for the three samples with pump fluence from 10 to 40 nJ (see Figure 4). Every 10 nJ corresponds to an excitation density of $7.90 \times 10^{14}$, $4.37 \times 10^{14}$, and $3.23 \times 10^{14}$ cm$^{-2}$ for [3], [1], and [0.5 nm] starting Pt thickness, respectively. The measurements in Figure 4a–c range from −1.8 to 6.5 ps, showing details of electron states near time-zero and longer delay times in Figure 4d–f corresponding to carrier recombination.

Positive DT signals were observed in all the three PtSe$_2$ samples immediately after excitation, which were attributed to the photoinduced bleaching that is caused by Pauli-blocking.[29] Upon irradiation by the pump, electrons are promoted from the ground to excited states. This band filling will reduce the probability of absorption of probe photons and results in positive changes in DT $\Delta T/T_0$ as seen in Figure 4a–c. Then the electron/holes cooled to thermal regime via carrier–phonon scattering, exhibiting a decrease in DT. After around 2 ps, $\Delta T/T_0$ was observed to increase slightly for all samples, similar to the DT spectra in Figure 2. Turning points are more obvious in Figure 4d–f, where there appears to be dips resulting in negative DT in [1] and [0.5 nm] samples. These negative DT signals in Figure 4 may be contributed to by two mechanisms: 1) structural changes induced by coupling of the excited carriers to coherent phonons taking place in hundreds of fs because of the infrared pump (800 nm) pulses;[31,32] or 2) red shifting of interband absorption from BGR.[29,33] Further studies using fs-electron energy loss spectroscopy (FEELS) could help to clarify such processes.[31,32] After ≈10 ps, electron–hole recombination dominates the optical response for all samples and the details are shown in Figure 4d–f. The time constants related to the above carrier relaxations were also obtained by fitting with the triple-phase decay model Equation (S1) in the Supporting Information. We determined the decay times of carrier–phonon scattering $\tau_c$ to be 0.52, 0.9, and 1.29 ps for [3], [1], and [3 nm] samples, respectively, and that of the negative signal $\tau_N$ to be 1.54, 1.73, and 2.63 ps. The electron–hole recombination times $\tau_r$ are in the range of 81.2–316.4 ps (see Table S2 in the Supporting Information). These decay times are approximately equal to those in Table S1 in the Supporting Information which we obtained from transient absorption spectroscopy and also imply that carrier relaxation is faster in thinner samples.

To further study the band-filling effect and obtain potentially thickness-dependent NLO coefficients for PtSe$_2$, we performed a series of open-aperture z-scan measurements using a single femtosecond laser beam. These measurements were based on 800 nm pulses laser with an ≈100 fs pulse duration at room temperature. In the open-aperture z-scan measurement, the sample transmission is recorded as a function of its position along the focused laser beam propagation direction (z-axis). Figure 5a–c presents z-scan results for the three PtSe$_2$ samples at 800 nm, where the normalized transmission increases when the sample moves toward the focused point ($z = 0$) and peaks at $z = 0$. This is saying the optical transmission of PtSe$_2$ increases with the laser irradiance intensity. Such response is known as saturable absorption, which is caused by Pauli-blocking. Under
Figure 5. Nonlinear optical response of PtSe2 thin films from z-scan, showing saturable absorption, i.e., transmission increases with the incident intensity. a–c) Open-aperture z-scan traces using 800 nm femtosecond laser pulses. d–f) Transmission as a function of laser fluence for PtSe2 samples obtained from the fittings employing the modified Frantz–Nodvik equation. Insets: nonlinear absorption coefficient \(\beta_{NL}\) and imaginary part of the third-order NLO susceptibility \(\text{Im}(\chi^{(3)})\) versus on-focused intensity \(I_0\).

Intense laser irradiation, electrons are pumped to fill the excited states and the excited state cannot accept more incoming electrons because of the Pauli-exclusion principle. This allows the majority of intense light to pass through and blocks the light with low intensity. This photoinduced response of PtSe2 can be exploited as a saturable absorber for passive mode-locking to generate femtosecond laser pulses, especially in mid-infrared range because of its small bandgap. [21, 22, 35]

Small \(\approx\) 2019 92.3, and 187.5 GW cm\(^{-2}\) for [3], [1], and [0.5 nm] samples respectively, implying easier saturation for thicker samples. The imaginary part of the third-order NLO susceptibility for the PtSe2 thin films is on the order of \(\times 10^{-3}\) esu, which is \(\times 10\) times larger than that \(\times 10^{-3}\) esu of few-layer MoSe2 and WS2 saturable absorbers. [38] The modulation depth of the film was observed to be dependent on thickness with corresponding values of 25.61%, 8.04%, and 4.25% for [3], [1], and [0.5 nm] films, respectively. The absorption cross-sections of the ground state for the three films are calculated to be \(2.25 \times 10^{-16}\), \(2.08 \times 10^{-16}\), and \(1.87 \times 10^{-16}\) cm\(^2\), while those of the excited states are found to be \(1.74 \times 10^{-16}\), \(1.47 \times 10^{-16}\), and \(0.92 \times 10^{-16}\) cm\(^2\), respectively, showing a decrease with increasing thickness (see Table S3 in the Supporting Information). This implies that nonlinear absorption in PtSe2, such as modulation depth, can be tuned by modifying the film thickness, offering a degree of flexibility in designing saturable absorbers.

In summary, ultrafast bandgap renormalization, carrier dynamics, and Pauli-blocking induced saturable absorption were observed in layered PtSe2 thin films with transient absorptive spectroscopy, degenerate pump–probe spectroscopy, and open-aperture z-scan measurements. The relaxation of excited carriers follows a triple exponential decay with thickness-dependent characteristic times of \(\approx 0.6–1.7\), \(\approx 2–3\), and \(\approx 27–250\) ps, which originate from carrier–phonon scattering, bandgap renormalization and electron–hole recombination, respectively. The analysis of the chemical potential evolution

\[ T(F) = T_0 + \frac{T_{\text{max}} - T_0}{1 - T_0} \left( T_{\text{max}} - T_0 \right) \]

where \(T_0 = \exp(-\sigma_e k)\) is the linear transmission and \(T_{\text{max}} = \exp(-\sigma_e k)\) is the maximum transmission at relative high intensity. \(T_\text{fit} = \ln(1 + q_0) / q_0\) is the fitted transmission at relative intensity. \(\sigma_e\) and \(\sigma_g\) are the excited-state and ground-state cross-section, and \(F\) is the laser-pulse fluence. \(k = N L\) is the absorber density per unit area, in which \(N\) is the atom density of the absorber and \(L\) is the optical path inside the sample.

The fitting results based on Equation (2) were plotted in Figure 5d–f and the fitted parameters are listed in Table S3 in the Supporting Information. We obtained a saturated intensity of 75.0, 92.3, and 187.5 GW cm\(^{-2}\) for [3], [1], and [0.5 nm] samples respectively. This imaginary part of the third-order NLO susceptibility for the PtSe2 thin films is on the order of \(\times 10^{-3}\) esu, which is \(\times 10\) times larger than that \(\times 10^{-3}\) esu of few-layer MoSe2 and WS2 saturable absorbers. [38] The modulation depth of the film was observed to be dependent on thickness with corresponding values of 25.61%, 8.04%, and 4.25% for [3], [1], and [0.5 nm] films, respectively. The absorption cross-sections of the ground state for the three films are calculated to be \(2.25 \times 10^{-16}\), \(2.08 \times 10^{-16}\), and \(1.87 \times 10^{-16}\) cm\(^2\), while those of the excited states are found to be \(1.74 \times 10^{-16}\), \(1.47 \times 10^{-16}\), and \(0.92 \times 10^{-16}\) cm\(^2\), respectively, showing a decrease with increasing thickness (see Table S3 in the Supporting Information). This implies that nonlinear absorption in PtSe2, such as modulation depth, can be tuned by modifying the film thickness, offering a degree of flexibility in designing saturable absorbers.

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strongly implies that carrier dynamics in few-layered PtSe₂ follow semiconducting behavior instead of metallic behavior. The amplitude of bandgap renormalization is estimated to be \( \approx 10 \) meV. Pauli-blocking of electrons in excited states leads to a band-filling effect, i.e., saturable absorption, with increasing NLO modulation depth as the number of layers increases. Strong thickness-dependent saturation intensities of 75.0, 92.3, and 187.5 GW cm\(^{-2}\) were measured for the [3], [1], and [0.5 nm] films, respectively. The results will benefit the development of novel optoelectronic devices based on layered PtSe₂, particularly for mid-infrared optical modulators and photodetectors, and give a view toward potential applications in monowavelength photonic devices.

**Experimental Section**

**Materials:** PtSe₂ films were synthesized by thermally assisted conversion of platinum films as previously reported.\(^{[9,11]}\) Briefly, platinum was deposited onto fused quartz substrates via sputtering using a Gatan precision etching and coating system. A quartz-crystal microbalance was used to monitor the deposition process. The Pt-deposited substrates were then placed in a quartz-tube vacuum furnace and heated up to 450 °C. Se powder was heated to 220 °C in an independently controlled heating zone upstream of the Pt samples and its vapor was carried to the Pt films under a 150 sccm flow of forming gas (10% H₂/Ar). A dwell time of 2 h was used for complete selenization.

**Characterization:** The TEM specimens were prepared by transferring the PtSe₂ film onto a holey-carbon TEM grid. The PtSe₂ film used was grown on a SiO₂ coated silicon wafer under the same conditions as other samples. Then, the SiO₂ layer was etched away by floating the sample on 2 m NaOH solution. After etching the substrate, the PtSe₂ film remained floating on the surface. The PtSe₂ film was then transferred to deionized water and then fished onto a holey-carbon TEM grid and dried before TEM measurements. The lamella for cross-section TEM imaging was prepared by the standard technique with focused ion beam. More morphological information and thickness of the Pt and converted PtSe₂ films can be found in the previous reports.\(^{[20,21]}\)

A confocal Raman spectrometer (Witec Alpha 300 R, 1800 lines mm\(^{-1}\) spectral grating) was employed to characterize the thin films with 512 nm excitation wavelength. To measure absorption and reflection spectra, the samples were grown on a SiO₂ coated silicon wafer under the same conditions as the [1 nm] samples. A spectrophotometer (Perkin Elmer Lambda 900) equipped with an integrating sphere was used.

**Ellipsometry:** The complex refractive index of the PtSe₂ thin films was measured on a SOPRA GESP5 rotating polarizer Spectroscopic ellipsometer. Spectra were taken from 200 to 900 nm at a resolution of 5 nm and under multiple angles of incidence of 72°, 75°, and 78° for each sample. The data was then fitted using a dispersion law model based on four Lorentzian oscillators.

**Transient Spectroscopy:** The 800 nm pulses with an \( \approx 100 \) fs pulse width were generated by a mode-locked Ti:sapphire laser (Coherent RegA 9000, repetition rate 100 kHz). Then, the beam was split into two such that one beam went into a beta barium borate (BBO) crystal to generate 400 nm femtosecond pulses for pumping. This pump beam was then modulated by an optical chopper. The other beam was focused onto a 3 mm thick sapphire to obtain a supercontinuum white light source for probing. These pulses were then filtered by a 750 nm short-pass (\( \approx 480-750 \) nm) filter to remove 800 nm fundamental wavelength and then delayed by a motorized stage. Both pump and probe were combined collinearly by a dichroic mirror (450 nm) and focused onto the samples by an \( f = 10 \) cm convex lens with the same polarization. The 400 nm pump was then blocked by a 425 nm long-pass filter. The transmitted light was collected by a charge-coupled device (CCD) spectrometer and then the differential transmission signals at the frequency of the optical chopper were extracted via a home-developed computer program.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

2D platinum diselenide, bandgap renormalization, carrier dynamics, noble metal dichalcogenides, saturable absorption

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