

Large self-defocusing Kerr optical nonlinearity and two-photon absorption in 2D palladium diselenide (PdSe₂) films measured by Z-scan techniques

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Abstract

We report a large third-order nonlinear optical response of palladium diselenide (PdSe₂) films – a two-dimensional (2D) noble metal dichalcogenide material. Both open-aperture (OA) and closed-aperture (CA) Z-scan measurements are performed with a femtosecond pulsed laser at 800 nm to investigate the nonlinear absorption and nonlinear refraction, respectively. In the OA experiment, we observe optical limiting behaviour originating from large two photo absorption (TPA) in the PdSe₂ film of $\beta = 3.26 \times 10^{-8}$ m/W. In the CA experiment, we measure a peak-valley response corresponding to a large and negative Kerr nonlinearity of $n_2 = -1.33 \times 10^{-15}$ m²/W – two orders of magnitude larger than bulk silicon. We also characterize the variation of n_2 as a function of laser intensity, observing that n_2 decreases in magnitude with incident laser intensity, becoming saturated at $n_2 = -9.96 \times 10^{-16}$ m²/W at high intensities. These results verify the large third-order nonlinear optical response of 2D PdSe₂ as well as its strong potential for high performance nonlinear photonic devices.

1. Introduction

With their extraordinary nonlinear optical properties, two-dimensional (2D) layered materials such as graphene [1-4], graphene oxide (GO) [5-9], transition metal dichalcogenides (TMDCs) [10-12], and black phosphorus (BP) [13-15] have attracted a great deal of interest, enabling diverse nonlinear photonic devices with vastly superior performance compared to bulk materials. Amongst them, TMDCs (MX₂, M = transition metal and X = chalcogen), with bandgaps in the near infrared to the visible region, have opened up promising new avenues for photonic and optoelectronic devices. [2, 16]. Previously, the prominent nonlinear optical properties of TMDCs such as MoS₂ [10, 17, 18], WS₂ [18-20] and MoSe₂ [21, 22], including a high Kerr nonlinearity and strong saturable absorption (SA), have been reported. These have provided the basis of many nonlinear photonic devices for applications where, for example, a few mono-layers of MoS₂ and WS₂ have been used as broadband, fast-recovery saturable absorbers for mode locking in pulsed fiber lasers [10, 23, 24]. In addition, nonlinear optical modulators and polarization dependent all-optical switching devices have been realized based on ReSe₂ [25] and SnSe [26].

Palladium diselenide (PdSe₂), a new 2D noble metal dichalcogenide in the TMDC family, has recently attracted significant interest [27-31]. Similar to the puckered structure of BP, it has a puckered pentagonal atomic structure – with one Pd atom bonding to four Se atoms and two adjacent Se atoms covalently bonding with each other. This low-symmetry structure makes PdSe₂ possess unique in-plane anisotropic optical and electronic properties [27, 29], featuring an in-plane noncentrosymmetric structure, in contrast to its cousin PtSe₂. Further, the bandgap of PdSe₂ is layer-dependent, varying from 0 eV (bulk) to 1.3 eV (monolayer) - a property well suited for photonic and optoelectronic applications – in particular, for wavelength tuneable devices [27, 29, 31]. Moreover, PdSe₂ is

highly air-stable, indicating its robustness and potential for practical applications as compared with BP. The high carrier mobility and anisotropic Raman spectroscopy of 2D PdSe₂ layers have been investigated [27, 30] as well as highly-sensitive photodetectors from the visible to mid-infrared wavelengths [31, 32]. Recently, the optical nonlinear absorption of PdSe₂ nanosheets has also been reported in the context of mode-locked laser applications [33-35]. To date, however, its optical Kerr nonlinearity has not been investigated.

Here, we report measurements of the third-order nonlinear optical response of 2D PdSe₂ films. Experimental results using the Z-scan technique with femtosecond optical pulses at 800 nm show that PdSe₂ films exhibit a large and negative (self-defocusing) Kerr nonlinearity (n_2) of $\sim -1.33 \times 10^{-15} \text{ m}^2/\text{W}$, which is two orders of magnitude larger than bulk silicon. Further, we measure a large nonlinear absorption β of $\sim 3.26 \times 10^{-8} \text{ m/W}$, which originates from TPA in the PdSe₂ films. In addition, we investigate the intensity dependence of the nonlinear response of PdSe₂, finding that the absolute magnitude of the Kerr nonlinearity n_2 initially decreases slightly with incident laser intensity, becoming saturated at higher intensities. Our results show that the extraordinary third-order nonlinear optical properties of PdSe₂ have strong potential for high-performance nonlinear photonic devices.

2. Material preparation and characterization

Figure 1(a) illustrates the atomic structure of PdSe₂ crystals. The unique puckered pentagonal structure is different to other TMDCs like MoS₂ and WS₂. The Se-Pd-Se layers stack with weak van der Waals interactions to form a layered structure [27, 36, 37]. In each monolayer, the pentagonal rings are formed with one Pd atom bonding to four Se atoms and two adjacent Se atoms covalently bonding with each other, which is similar to the puckered structure of BP, and yields both anisotropic and non-centrosymmetric properties of PdSe₂ [27, 37]. More importantly, unlike the rapid degradation of BP under ambient conditions, PdSe₂ has significantly better air-stability [29-31]. Together, these properties of PdSe₂ make it promising for high performance photonic and optoelectronic applications.

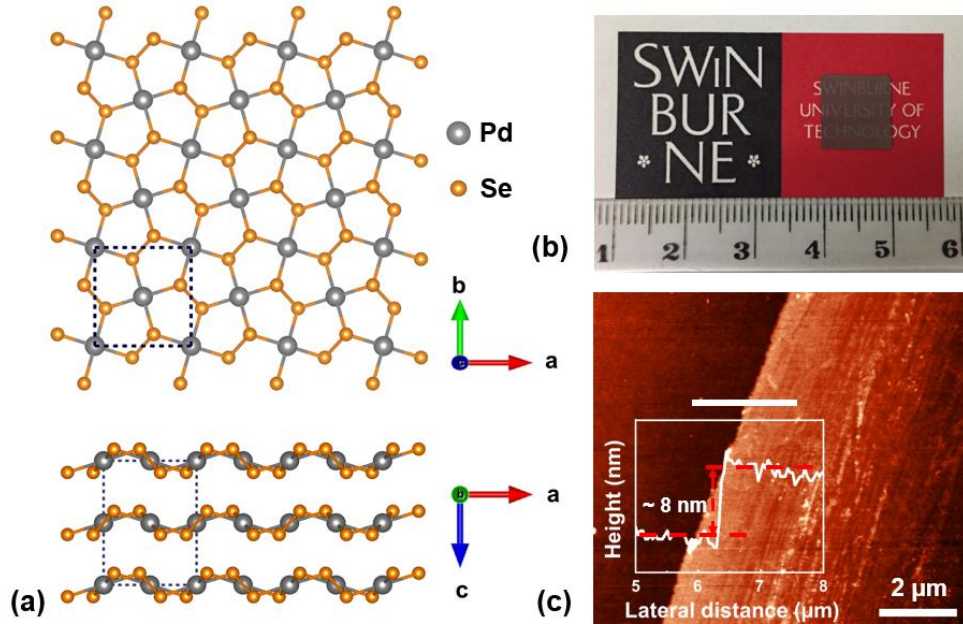


FIG. 1. (a) Crystal structure of PdSe₂. (b) Photograph of prepared multilayer PdSe₂ film. The unit for the numbers on the ruler is centimeter. (c) AFM height profile of the multilayer PdSe₂ film.

Here, we investigated large-area multilayer PdSe₂ films deposited on transparent sapphire substrates. The PdSe₂ films were synthesized via Chemical vapor deposition (CVD) [30, 38]. A three-zone tube furnace was used to grow the PdSe₂ films with palladium chloride (PdCl₂) and selenium (Se) as precursors. Se and PdCl₂ powders were placed at Zone 1 with a heating temperature of 250 °C and Zone 2 heated up to 500 °C, respectively. The evaporated Se and Pd precursors were then transported by the carrier gas of Ar/H₂ to Zone 3 at a high temperature of 600 °C, in which the continuous PdSe₂ films were synthesized on an atomically flat sapphire substrate. The films were polycrystalline, as is typical for CVD synthesized films, with crystal sizes varying from 10's of nanometres up to 100 nm. Because of the polycrystalline nature of the films, the inversion symmetry breaking properties (i.e., non-centrosymmetric) of the single PdSe₂ crystals could not be observed on optical wavelength scales in the macroscopic PdSe₂ continuous films studied in this work. Figure 1(b) shows a photograph of the prepared sample, indicating a high uniformity over the whole substrate. The morphology image and height profile of the prepared PdSe₂ films were characterized by atomic force microscopy (AFM), as illustrated in Fig. 1(c). The film thickness was measured to be ~ 8 nm, which corresponds to ~20 layers of PdSe₂ [27, 30, 36].

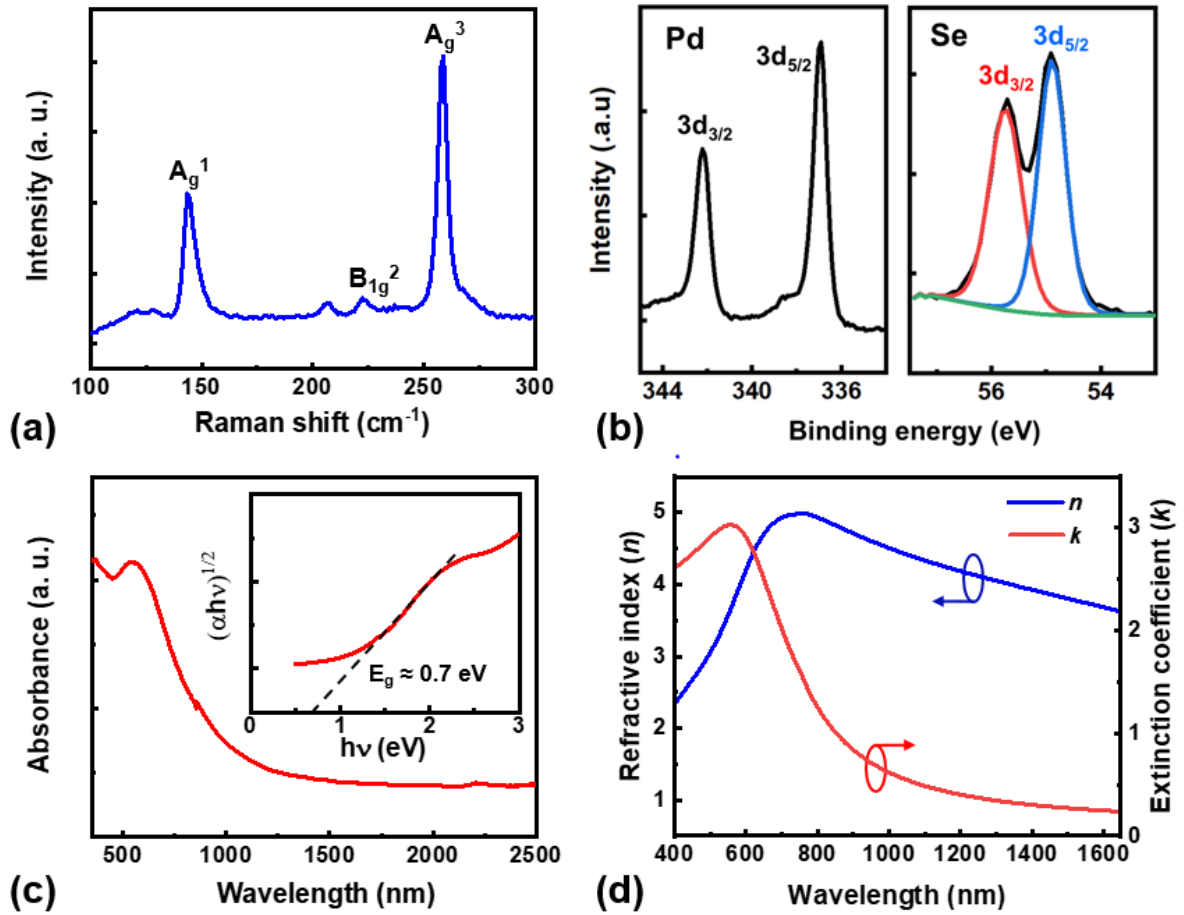


FIG. 2. Characterization of the prepared PdSe₂ film. (a) Raman spectrum excited via a 514-nm laser. (b) X-ray photoelectron spectroscopy (XPS) spectra. (c) UV-vis absorption spectrum. Inset shows the extracted Tauc plot. (d) Measured refractive index (n) and extinction coefficient (k).

Figure 2(a) shows the Raman spectrum of the prepared PdSe₂ film excited with a laser at 514 nm. Three representative phonon modes are observed, including the A_g¹ (~145.5 cm⁻¹) and B_{1g}² (~222.5 cm⁻¹) vibrational modes that correspond to the movement of Se atoms and the A_g³ (~258.8 cm⁻¹) mode that relates to the relative movements between Pd and Se atoms [27, 30, 32]. To further characterize the film quality, X-ray photoelectron

spectroscopy (XPS) was employed to measure the binding energy of PdSe₂. Figure 2 (b) shows the XPS results of Pd 3d and Se 3d core levels for the PdSe₂. The peaks of the fit at ~ 342.2 eV and ~ 336.9 eV are attributed to the Pd 3d_{3/2} and Pd 3d_{5/2}, respectively, whereas the peaks at ~ 55.7 eV and ~ 54.9 eV correspond to Se 3d_{3/2} and 3d_{5/2}, respectively. These results are consistent with previous reports [30, 32] and demonstrate the high quality of our prepared PdSe₂ films.

To characterize the linear absorption and optical bandgap, the optical absorption spectrum (from 400 nm to 2500 nm) of the PdSe₂ film was measured with ultraviolet-visible (UV-vis) spectrometry, as shown in Fig. 2(c). As expected, the linear absorption of the PdSe₂ film increased dramatically from the infrared to visible wavelength regime. The optical bandgap of the PdSe₂ film can be estimated from a Tauc plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ based on the Tauc formula, where α and $h\nu$ represent the optical absorption coefficient and photon energy, respectively.[29, 32, 39] The inset of Fig. 2 (c) shows the Tauc plot extracted from the linear absorption spectrum, where the optical bandgap of the PdSe₂ film is estimated to be ~ 0.7 eV and shows good agreement with the reported values for 20 layers of PdSe₂ in Refs. [29, 32].

We also characterize the in-plane (TE-polarized) refractive index (n) and extinction coefficient (k) of the PdSe₂ film via spectral ellipsometry, as depicted in Fig. 2(d). For the thin PdSe₂ film with a thickness of ~8 nm, the out-of-plane (TM-polarized) response is much weaker. Thus, using spectral ellipsometry we could only measure the in-plane n and k of the PdSe₂ film. It can be seen that the refractive index first increases dramatically with wavelength to reach a peak at ~ 700 nm and then decreases more gradually at longer wavelengths. This trend is similar to that of PtSe₂ – another noble metal dichalcogenide of the TMDC family [40]. The extinction coefficient exhibits a significant decrease from 600 nm to 1200 nm, and then the rate of decrease slows down at longer wavelengths. This shows an agreement with the trend of the UV-vis absorption spectrum in Fig. 2 (c) and further confirms the validity of our ellipsometry measurement. These measurements indicate that the films had a bandgap of about 0.7 eV, residing just below the telecommunications wavelength band.

3. Z-scan measurement

3.1 Experimental setup

To investigate the third-order nonlinear optical properties of PdSe₂, we characterized the nonlinear absorption and refraction of the prepared PdSe₂ film via the Z-scan technique [14, 41, 42] (Fig. 3), where a femtosecond pulsed laser with a centre wavelength at ~800 nm and pulse duration of ~ 140 fs was used to excite the samples. A half-wave plate combined with a linear polarizer was employed to control the power of the incident light. A beam expansion system consisting of a 25-mm concave lens and 150-mm convex lens was used to expand the light beam, which was then focused by an objective lens (10 ×, 0.25 NA) to achieve a low beam waist with a focal spot size of ~1.6 μm. The prepared samples were oriented perpendicular to the beam axis and translated along the Z-axis with a linear motorized stage. A high-definition charge-coupled-device (CCD) imaging system was used to align the light beam to the target sample. Two photodetectors (PDs) were employed to detect the transmitted light power for the signal and reference arms.

The Z-scan measurements were performed in two stages [14, 41] including an open-aperture (OA) and a closed aperture (CA) measurement. The OA measurement was used to characterize the nonlinear absorption of PdSe₂ films where all light transmitted through the sample was collected by a PD. To extract the TPA (β) of PdSe₂, we fit the measured OA results in Fig. 4(a) with [41, 43]:

$$T_{OA}(z) \approx 1 - \frac{1}{2\sqrt{2}} \frac{\beta I_0 L_{\text{eff}}}{\left(1 + \left(\frac{z}{z_0}\right)^2\right)}, \quad (1)$$

where $T_{OA}(z)$ is the normalized optical transmittance; $L_{\text{eff}} = (1 - e^{-\alpha_0 L})/\alpha_0$ is the effective sample thickness; α_0 is the linear absorption coefficient; L is the sample thickness; I_0 is the irradiance intensity at the focus; z is the sample position relative to the focus, and z_0 is the Rayleigh length of the laser beam.

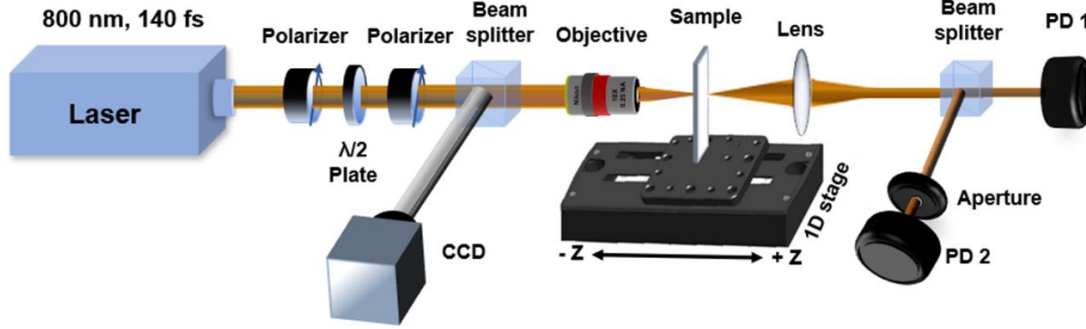


FIG. 3. Schematic illustration of Z-scan experimental setup. PD: power detector.

We also characterized the Kerr nonlinearity of the PdSe₂ film via the CA Z-scan experiment. In the CA measurement, the change in the optical transmission results from both nonlinear absorption and the nonlinear phase shift induced self-defocusing via the Kerr nonlinearity. The value of n_2 for the PdSe₂ films at different laser intensities were extracted by fitting the CA measurement with [41, 42]

$$T_{CA}(z, \Delta\Phi_0) = 1 + \frac{4\Delta\Phi_0\left(\frac{z}{z_0}\right)}{\left[1 + \left(\frac{z}{z_0}\right)^2\right] \left[9 + \left(\frac{z}{z_0}\right)^2\right]}, \quad (2)$$

where $T_{CA}(z, \Delta\Phi_0)$ is the normalized optical transmittance of the CA measurement and $\Delta\Phi_0 = 2\pi n_2 I_0 L_{\text{eff}}/\lambda$ is the nonlinear phase shift, with λ denoting the center wavelength of the femtosecond laser. Therefore, the Kerr nonlinearity of the PdSe₂ film could be extracted from the ratio of the CA result to the OA result in the usual manner [14, 41, 42].

3.2. Results and discussion

We measured the OA curves at different incident laser intensities ranging from 12.08 GW/cm² to 21.32 GW/cm². Figure 4(a) shows the OA Z-scan results for the PdSe₂ film at three representative intensities. A typical optical limiting behaviour was observed in the OA curves, with the transmission decreasing as the PdSe₂ sample was moved through the focal point. We also note that the transmittance dip of the OA curve decreased when the incident laser intensity was increased. Various mechanisms, including nonlinear scattering, reverse saturable absorption (RSA) and two-photon absorption (TPA), may contribute to the observed optical limiting behaviour. The nonlinear scattering mechanism is first excluded since it usually depends on the laser induced microbubble formation for dispersion or solution samples [44, 45]. Usually, RSA is the dominant mechanism for nonlinear absorption under resonant or near resonant excitation, while the TPA dominates under non-resonant excitation [46, 47]. In our case, the incident laser of 800 nm is far from the resonant wavelength (~1771 nm, corresponding to an optical bandgap of 0.7 eV) of the PdSe₂ film. Therefore, the optical limiting behaviour is mainly attributed to TPA. At low laser intensities, the linear absorption is dominant, while as the laser intensity increases, increased

photon population makes TPA possible, resulting in the excitation of electrons from the valence to conduction bands.

To extract the TPA coefficient β of PdSe₂, we fit the measured OA results with Equation (1). The TPA coefficient β for the PdSe₂ film is shown in Fig. 4(b) at different laser intensities. A large $\beta = 3.26 \times 10^{-8}$ m/W is observed, which is comparable to the reported values of graphene, and higher than that of WS₂, highlighting the strong optical limiting effect in PdSe₂ film. In addition, the TPA coefficient β is relatively constant with incident laser intensity, reflecting the fact that we are working in an intensity regime where the material properties of the PdSe₂ films are not changing much. The slight fluctuation in β with laser intensity may arise from light scattering in the PdSe₂ film surface.

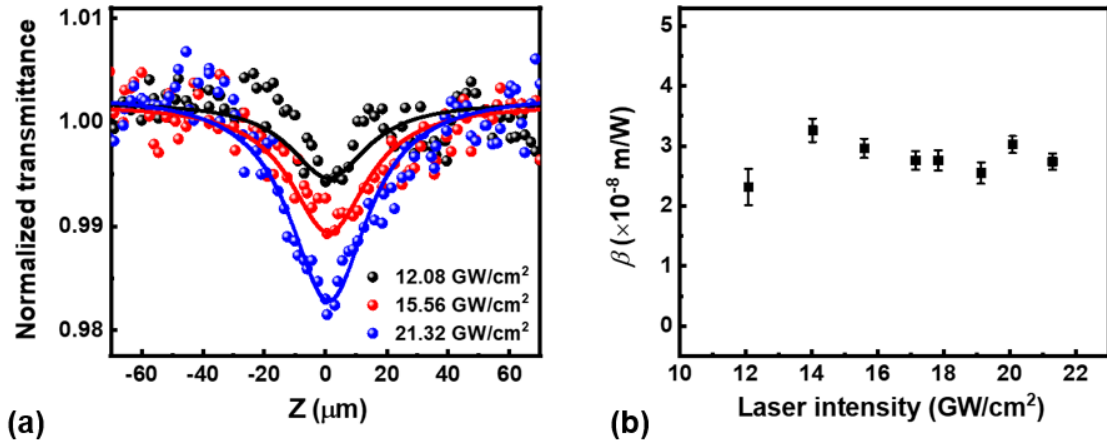


FIG. 4. (a) OA Z-scan results of PdSe₂ film at different intensities. (b) TPA coefficient β of PdSe₂ film versus laser intensity.

To further investigate the nonlinear absorption of the PdSe₂ film, we measured the minimum transmittance with the sample at the focal point of the Z scan setup, for different incident laser intensities. Figure 5(a) shows the transmittance of PdSe₂ at the focal point as a function of laser intensity, where the transmittance fluctuates around a relatively constant value at low intensities and then decreases significantly as the laser intensity increased. The experimental data fits the theory well [45], verifying our assumption of TPA being the dominant process for nonlinear absorption in the PdSe₂ film. The order of the observed nonlinear absorption can also be confirmed by

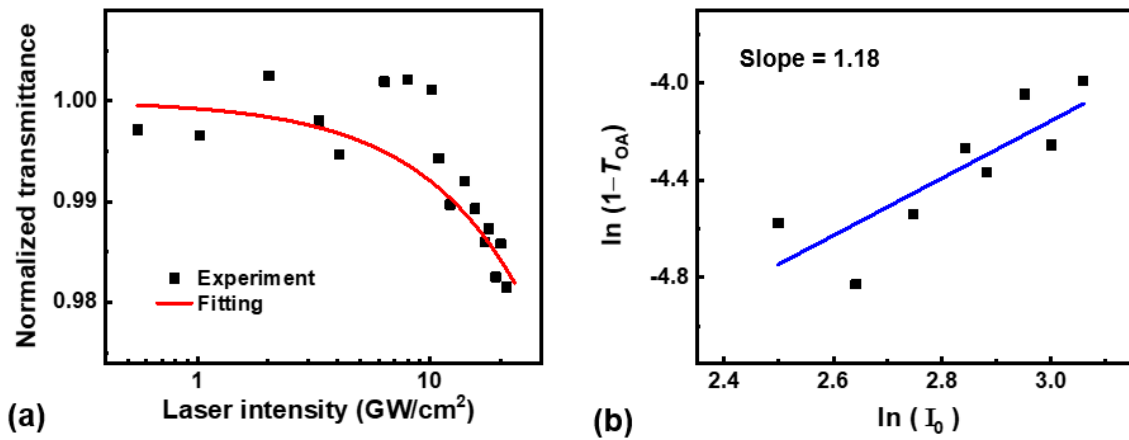


FIG. 5. (a) Normalized transmittance of PdSe₂ film at the focal point as a function of laser intensity. (b) The plot of $\ln(1 - T_{OA})$ versus $\ln(I_0)$ to determine the order of nonlinearity. The measured and fit results are shown by scatter data points and solid lines, respectively.

examining the relation between $\ln(1-T_{OA})$ versus $\ln(I_0)$ [48]:

$$\ln(1 - T_{OA}) = k \ln(I_0) + C, \quad (3)$$

where k is the slope showing the order of the nonlinear absorption and C is a constant. For pure TPA, the slope is equal to 1 [48, 49]. We obtain a slope of 1.18 (Fig. 5(b)), suggesting the observed nonlinear absorption is mainly attributed to TPA in the PdSe₂ film.

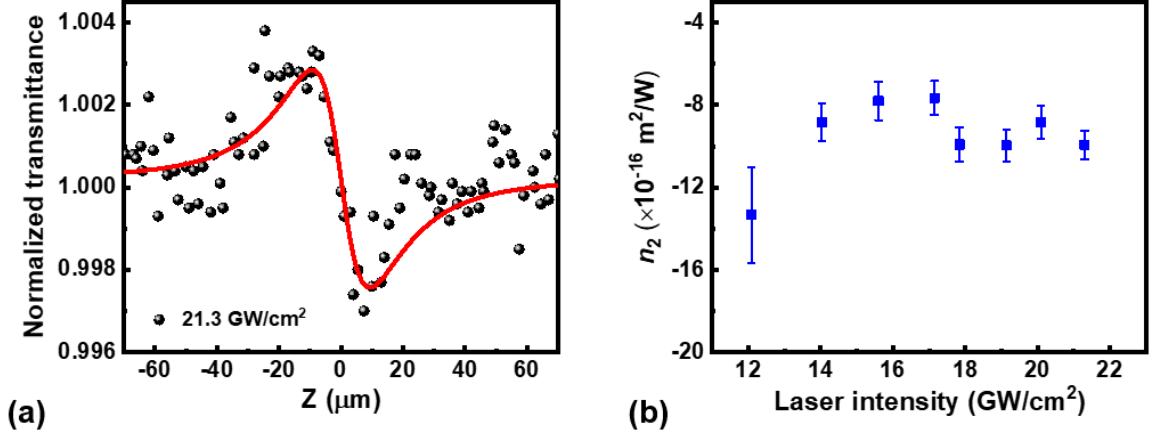


FIG. 6 (a) CA Z-scan result of PdSe₂ film at intensity of 21.32 GW/cm². (b) Kerr coefficient n_2 of PdSe₂ film versus laser intensity.

We also performed CA Z-scan measurements to investigate the Kerr nonlinearity (n_2) of the PdSe₂ films. The values of n_2 for the PdSe₂ film at different laser intensities were extracted by fitting the measured CA results with Equation 2 [41, 42]. Figure 6(a) shows a representative CA result for PdSe₂ at a laser intensity of 21.32 GW/cm². The transmittance of the sample exhibited a transition from peak to valley when the sample passed through the focal plane. Such a peak-valley CA behaviour corresponds to a negative Kerr coefficient n_2 and indicates an optical self-defocusing effect in the PdSe₂ film. As discussed above, TPA results in the transfer of electrons from valence band to conduction band, increasing the free carrier density in the film. Therefore, the observed negative Kerr nonlinearity potentially originates from the TPA-induced free carrier nonlinear refraction and interband blocking [50-52].

Fig. 6(b) shows the measured Kerr coefficient n_2 of PdSe₂ versus laser intensity, showing a large n_2 of $\sim -1.33 \times 10^{-15} \text{ m}^2/\text{W}$. Table 1 compares the β and n_2 of PdSe₂ with other 2D layered materials. As can be seen, the value of n_2 for PdSe₂ is lower than those of graphene and GO, but still more than two orders of magnitude higher than bulk silicon [53, 54]. Such a high n_2 suggests that PdSe₂ is an extremely promising material for self-defocusing based nonlinear photonic applications. For example, a negative Kerr nonlinearity can be used to self-compress ultrashort pulses in the presence of positive group-velocity dispersion [55, 56]. Another application of a negative Kerr nonlinearity is mode locking of lasers using the Kerr mode-locking technique [53, 57] as well as the possibility of achieving net parametric modulational instability gain under normal dispersion conditions [53, 58].

Moreover, as shown in Fig. 6(b), the absolute value of n_2 initially decreases with laser intensity and then saturates at higher intensities. In theory, the optical nonlinear refraction originates mainly from the free-carrier and bound-electron nonlinearities [51, 59, 60]. We assume that both mechanisms exist in PdSe₂ films. The refractive index change in the PdSe₂ film can be expressed by $\Delta n = n_2^* I_0 + \sigma_r N$, where n_2^* is the nonlinear

refraction related to bonding electrons, σ_r is the free carrier refractive coefficient and N is the charge carrier density.[51] Therefore, the effective $n_2 = \Delta n/I_0 = n_2^* + \sigma_r N/I_0$, is an intensity dependent parameter, which can explain the n_2 variation as a function of laser intensity observed in our measurements.

Table 1. Comparison of β and n_2 for various 2D layered materials

Material	Laser parameter	Thickness	β (m/W)	n_2 (m ² /W)	n_2 ($\times n_2$ of Si ¹)	Ref.
Graphene	1150 nm, 100 fs	5-7 layers	3.8×10^{-8}	-5.5×10^{-14}	-1.22×10^4	[61]
GO	800 nm, 100 fs	$\sim 2 \mu\text{m}$	4×10^{-7}	1.25×10^{-13}	2.75×10^4	[62]
MoS ₂	1064 nm, 25 ps	$\sim 25 \mu\text{m}$	$(-3.8 \pm 0.59) \times 10^{-11}$	$(1.88 \pm 0.48) \times 10^{-16}$	41.32	[18]
WS ₂	1040 nm, 340 fs	$\sim 57.9 \text{ nm}$	$(1.81 \pm 0.08) \times 10^{-8}$	$(-3.36 \pm 0.27) \times 10^{-16}$	-73.85	[19]
BP	1030 nm, 140 fs	$\sim 15 \text{ nm}$	5.845×10^{-6}	-1.635×10^{-12}	-3.59×10^5	[14]
PtSe ₂	800 nm, 150 fs	$\sim 4.6 \text{ nm}$	-8.80×10^{-8}	—	—	[63]
PtSe ₂	1030 nm, 340 fs	17 layers	—	$(-3.76 \pm 0.46) \times 10^{-15}$	-8.26×10^2	[48]
PdSe ₂	800 nm, 140 fs	$\sim 8 \text{ nm}$	$(3.26 \pm 0.19) \times 10^{-8}$	$(-1.33 \pm 0.23) \times 10^{-15}$	-2.92×10^2	This work

¹ n_2 for silicon = $4.55 \times 10^{-18} \text{ m}^2/\text{W}$ (ref. [54])

In contrasting the Kerr 3rd order nonlinearity and TPA with other 3rd order effects such as optical third harmonic generation (THG) [64-69] it is interesting to note that unlike THG, both the sign and phase of the Kerr nonlinearity are critically important. The concept of the nonlinear FOM was originally proposed purely in the context of a limitation for n_2 devices having a positive n_2 and TPA. Here, the fact that n_2 for PdSe₂ is negative means that the conventional importance of a large FOM is probably not applicable. Further, TPA has been known to potentially have a positive impact on some signal processing functions [70-72] and so the large TPA of PdSe₂ is a potential advantage to this material. The combination of a large and negative n_2 with a very large TPA makes PdSe₂ a highly interesting material for novel nonlinear processes that can exploit self-defocusing effects.

4. Conclusion

We report a large third-order nonlinear optical response of PdSe₂ films measured with the Z-scan technique. Our results show that PdSe₂ has a strong TPA response with a large β of $\sim 3.26 \times 10^{-8} \text{ m/W}$. We also investigate the Kerr nonlinearity (n_2) of PdSe₂ finding that n_2 is negative, and with an absolute magnitude that is more than two orders of magnitude larger than bulk silicon. Furthermore, the variation in n_2 of PdSe₂ with laser intensity is characterized. We find that n_2 initially increases (decreasing in absolute magnitude) with incident laser intensity and then saturates at higher intensities. These results verify PdSe₂ as a promising 2D material with prominent nonlinear optical properties.

Acknowledgements

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