Research article

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Broadband nonlinear optical response in GeSe nanoplates and its applications in all-optical diode

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Abstract: Germanium selenide nanoplates (GeSe NPs) are considered to have broadband nonlinear optical (NLO) properties and great potential for applications in nanophotonic devices. In this work, we systematically studied the NLO response of GeSe NPs by the open-aperture Z-scan technique. GeSe NPs exhibit strong saturable absorption at wavelengths of 400, 800, and 1064 nm with different pulse durations. Furthermore, we investigated the excited carrier dynamics of GeSe NPs by the non-degenerate pump-probe technique. The fast and slow relaxation times at different wavelengths of 800, 871, 1064, and 1100 nm were components with lifetimes of about 0.54–1.08 and 52.4–167.2 ps, respectively. The significant ultrafast NLO properties of GeSe NPs imply their potential in the development of nanophotonic devices. Here, we designed and fabricated the all-optical diode by means of the GeSe/C₆₀ tandem structure and demonstrated that the saturable absorption behavior of GeSe NPs can be used to fabricate a photonic diode, which exhibits nonreciprocal transmission of light similar to that of an electron diode.

1 Introduction

Nonlinear optics is the branch of modern optics which examines the behavior of light in nonlinear media [1]. Nonlinear optical (NLO) materials play an important role in aspects of photonics and have made possible a variety of currently used photonic devices (e.g. pulsed lasers [2–5], optical switches [6–8], optical modulators [9], etc.). Since the discovery of graphene in 2004, two-dimensional (2D) materials have attracted extensive research due to their unique electric properties and fascinating optical characteristics (e.g. ultrafast broadband optical response [10–12], large optical nonlinearities [13–15], and strong excitonic effects [16]).

In the recent decade, 2D materials, such as graphene [17–20], transition metal dichalcogenides (TMDs) [21–24], and black phosphorus (BP) [25–29], with broadband saturable absorption (SA) behavior and application in different wavebands were proved by experiment. However, the zero band gap of graphene [30]; low carrier mobility, with a relatively large band gap of 1.5–2.5 eV, of TMDs [31]; and the unstable behavior of BP [32] in a way impede their practical applications. Consequently, in order to meet the vigorous development of optoelectronic devices, further explorations of other possible 2D materials with appropriate characteristics including a proper band gap, air stability, high carrier mobility, and low cost are still mandatory. Indeed, while further exploring the new features of these 2D materials, retrieval of the novel 2D materials has been extended recently to comprise the close neighbors of the V-family element, called group IV monochalcogenides MX (M=Ge, Sn; X=S, Se, Te). Among all MX monolayers, only the germanium selenide (GeSe) monolayer had predicted to be a direct gap semiconductor [33], which should exhibit high light-matter interaction and nonlinear absorptions. GeSe has attracted extensive

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study interest for its direct band gap, a relatively high carrier mobility, high environmental stability, low toxicity, high abundance occurrence, unique photoelectric feature, etc.

GeSe, as an important member of the two-dimensional group IV–VI A semiconductor, has a puckered layer structure like that of BP, in which three Se atoms are coordinated to one Ge atom. Due to the low symmetry of the *Pnma* space group, the 2D GeSe shows highly in-plane anisotropic properties and also excellent stability [34]. GeSe owns a large activation energy for the chemisorption of O_2 molecules, which can resist oxidation. Even a low or intermediate content of oxygen atoms chemisorbed on the material surface does not severely degrade its electronic properties [35]. GeSe is a p-type semiconductor with a narrow band gap. And the band-gap shows obvious thickness dependent, it can be changed from an indirect band gap of 0.93 eV (bulk) to a direct band gap of 1.8 eV [36–38]. It overlaps well with the solar spectrum, which makes it a photovoltaic and potential material for photo-detection applications. In addition, GeSe exhibits a high hole mobility [39] ($\sim 128.6 \text{ cm}^2/\text{V} \cdot \text{s}$) and a high absorption coefficient of about 10^5 cm^{-1} in the visible range, rendering it a promising candidate for optics and photo-electronics [40]. For developing viable photonic devices, the investigation of the nonlinear and ultrafast optical properties of 2D materials, such as nonlinear susceptibility, nonlinear refraction and absorption, and carrier relaxation lifetime, is undoubtedly important. But to the best of our knowledge, less literature is available on the NLO properties of GeSe.

In this work, we systematically studied the NLO response of GeSe nanoplate (NP) dispersions by the open-aperture (OA) Z-scan technique and investigated the excited carrier dynamics of GeSe NPs by the non-degenerate pump-probe technique. From the results of our experiments, we found that GeSe NPs exhibited strong SA at a broadband from 400 nm to 1064 nm [$\alpha_{\text{NL}} \sim 10^{-2} \text{ cm/GW}$; $\text{Im}\chi^{(3)} \sim 10^{-14} \text{ esu}$; figure of merit (FOM) $\sim 10^{-15} \text{ esu}$] and showed obvious pulse duration dependence. The ultrafast NLO properties of the layered GeSe imply its potential in the development of nano-photonic devices such as mode lockers and optical switches. In this work, we juxtaposed the dispersions of GeSe NPs and C_{60} to form a double-layer structure composed of SA and reverse saturable absorption (RSA) materials, and demonstrated that the SA behavior of GeSe NPs can be used to produce a photonic diode which exhibits nonreciprocal transmission of light with current flow similar to that of an electron diode.

2 Results and discussion

2.1 Characterization of GeSe NPs

GeSe NPs have been demonstrated to adopt an orthorhombic layered structure like that of BP (see Figure 1A). In the horizontal (or *y-z*) plane, Ge atoms are bonded to Se atoms by covalent bonds, forming a zigzag structure along the *y* direction and an armchair structure along the *z* direction. Along the vertical (or *x*-axis) direction, weak van der Waals interaction enables single layers of GeSe to stack up and ultimately form a multi-layered nanoplate structure. The distance between each layer is $\sim 0.542 \text{ nm}$. In the present work, GeSe NPs were synthesized by the sonication-assisted liquid phase exfoliation method. High-resolution transmission electron microscopy (HRTEM) (Horiba JY, LabRAM HR Evolution, Irvine, CA, USA) and energy dispersive X-ray (EDX) spectroscopy (XFlash6, Bruker, Ettlingen, Germany) were used to characterize the pre-prepared GeSe nanoplates, see Figure 1B and C. The HRTEM image of GeSe NPs in Figure 1B shows a rigid arrangement of the lattice structure where the lattice spacing is $\sim 0.288 \text{ nm}$. This is consistent with those of previously reported (011) planes of GeSe [41–43].

The nature of GeSe NPs is also confirmed by Raman spectra (HORIBA JY LabRAM HR Evolution, Irvine, CA, USA), as shown in Figure S1B in Supporting Information (SI). To determine the size and thickness of GeSe NPs, an atomic force microscopy (Bruker Icon, Ettlingen, Germany) measurement was carried out, see Figure S1C and D in SI. For optical characteristics, GeSe NPs were dispersed in an ethanol-water mixture (1:1). The linear absorption spectrum of the GeSe NPs was measured by a spectrophotometer (UH4150, HITACHI, Tokyo, Japan). As shown in Figure 1D, multi-layered GeSe NPs exhibit broadband optical absorption in the wavelength range from 400 nm to 1200 nm. The band gap of the GeSe NPs was fitted to be around 1.07 eV using the relational expression proposed by Tauc et al. [44]. This value of band gap agrees well with those from previously reported works [43].

2.2 Saturable absorption of GeSe NPs

To investigate the NLO response of GeSe NPs, the OA Z-scan measurement was carried out with a coherent femtosecond laser (center wavelength: 800 nm, pulse duration: 56 fs, and repetition rate: 1 kHz). Figure 2A–C shows the normalized transmittance of GeSe NP dispersions with different pulse laser intensities at 400 nm, 800 nm and 1064 nm, respectively. These curves indicate a broadband SA in GeSe NP

Figure 1: Characterizations of GeSe samples.

(A) Side view and top view of the crystal structure of GeSe; (B) high-resolution TEM images of the GeSe NPs; (C) EDX spectrum of GeSe NPs; (D) the linear absorption spectrum of the multi-layer GeSe NPs and Tauc plot ($n=1/2$, indirect) for GeSe NPs ($E_g=1.07$ eV).

dispersions in which case the GeSe NPs can effectively suppress low-intensity light and allow higher intensity light to pass through. On the other hand, we did not observe any nonlinear response from the solvents. The normalized transmittance $T(z)$ can be fitted by the following equation [45]:

$$T(z) = 1 - \frac{\alpha_s}{1 + \frac{I}{I_s}} - \alpha_{ns} = 1 - \frac{\alpha_s \cdot \left(1 + \frac{Z^2}{Z_0^2}\right)}{1 + \frac{Z^2}{Z_0^2} + \frac{I_0}{I_s}} - \alpha_{ns} \quad (1)$$

Here, α_s denotes SA, which presents the modulation depth (MD) of the sample, α_{ns} denotes non-SA, and the saturable intensity I_s is defined as the optical intensity when T is reduced to half of its unbleached value. As shown in Figure 2D, the experimental results agree very well with the above theoretical model. The fitted I_s and MD are shown in Figure 2E; we found that they have an average

value of 589 ± 31.5 , 294 ± 38.6 , and 120 ± 2.45 GW/cm² for 400, 800, and 1064 nm, respectively. The MD and I_s gradually decreased with the wavelength, which is consistent with its linear absorption spectrum, as shown in Figure 1D.

The imaginary part of the third-order NLO susceptibility $\text{Im}\chi^{(3)} = 10^{-7} c \lambda n^2 \alpha_{NL} / 96 \pi^2$ is calculated to be $-(0.23 \pm 0.02) \times 10^{-14}$, $-(1.81 \pm 0.17) \times 10^{-14}$, and $-(0.79 \pm 0.02) \times 10^{-14}$ esu at 400, 800, and 1064 nm, respectively, as shown in Figure 2F, which were determined by the results of fitting the SA curves (c , λ and n are the speed of light, the wavelength of the incident light, and refractive index, respectively). The value of $\text{Im}\chi^{(3)}$ of GeSe NP dispersions is comparable with some other SA nano-materials, such as graphene [46] ($\sim -0.785 \times 10^{-14}$ esu), BP [46] ($\sim -0.475 \times 10^{-14}$ esu), and MoS₂ [47] ($\sim -0.475 \times 10^{-14}$ esu). The FOM for third-order optical nonlinearity is defined as $\text{FOM} = |\text{Im}\chi^{(3)} / \alpha_0|$, and it is estimated to be $\sim 3 \times 10^{-15}$ esu. We present the NLO parameters of GeSe and

Figure 2: Wavelength dependent nonlinear optical absorption of GeSe NPs.

(A), (B) and (C) Open aperture Z-scan measurements of GeSe NPs dispersions under different intensities at 400, 800, and 1064 nm, respectively; (D) relations of normalized transmittance and input intensity of GeSe NP dispersions at 400, 800, and 1064 nm, respectively; (E) the NLO parameters about GeSe dispersions' saturated intensity I_s and MD; (F) the imaginary part of the third-order susceptibility $\text{Im}\chi^{(3)}$ and the figure of merit (FOM) for the third-order optical nonlinearity of GeSe NPs.

other classic 2D materials in Table 1. It can be indicated that GeSe NPs would possess much larger SA response at a broadband from visible light to near-infrared light. Taking advantages of the SA property, GeSe NPs have great potential for ultrafast nonlinear saturable absorbers and optical diodes [17, 46].

In order to further study the pulse duration dependence on the NLO absorption response of GeSe NPs, we measured OA Z-scan curves with different pulse duration lasers at 1064 nm. The sample was separately excited by a nanosecond (ns) laser (wavelength: 1064 nm; pulse duration: 7 ns; repetition rate: 10 Hz), a picosecond (ps) laser (wavelength: 1064 nm; pulse duration: 10 ps; repetition

rate: 1 kHz), and a femtosecond (fs) laser (wavelength: 1064 nm; pulse duration: 56 fs; repetition rate: 1 kHz). Results of Z-scan measurements at 7 ns, 10 ps, and 56 fs are shown in Figure 3A–C, respectively. Fitting the experimental data with Eq. (1), we obtain the nonlinear absorption coefficients α_{NL} of about $-(51.9 \pm 10.5)$ (the pulse duration: 7 ns), -1.58 (the pulse duration: 10 ps), and $-(0.021 \pm 0.001)$ cm/GW (the pulse duration: 56 fs). Figure 3D–F shows the normalized transmittance as a function of incident intensity for the above-mentioned three laser systems. The saturable fluences are estimated to be 1540, 120, and 6.5 mJ/cm², respectively, and the modulation depths are estimated to be 27%, 15.7%, and

Table 1: Linear and nonlinear optical coefficients of GeSe dispersions measured by the Z-scan technique and femtosecond transient optical absorption spectroscopy.

Sample	λ , nm	Pulse duration	T , %	α_0 , cm ⁻¹	I_{sat} , GW/cm ²	$\text{Im}\chi^{(3)}$, 10^{-14} esu	FOM, 10^{-15} esu	τ_1 , ps	τ_2 , ps
GeSe	400	fs	70.2	3.54	589 ± 31.50	-0.225 ± 0.023	0.637 ± 0.067	–	–
		fs	73.4	3.1	294 ± 38.60	-1.81 ± 0.27	3.64 ± 0.56	0.688	52.4
	1064	fs	78	2.5	120 ± 2.45	-0.79 ± 0.02	3.19 ± 0.94	1.05	167.2
		ps	66.4	4.1	14.1	–67.5	164.7	–	–
		ns	73.5	3.1	0.227 ± 0.047	-2210 ± 600	7200 ± 1560	–	–
MoS ₂ [47]	800	fs	78.9	2.37	413 ± 24	-0.252 ± 0.015	1.06 ± 0.06	–	–
BP [46]	800	fs	42.1	8.7	459	–0.785	0.902	0.016 ± 0.006	0.36 ± 0.071
Graphene [46]	800	fs	38.9	9.4	764	–0.472	0.502	0.047 ± 0.036	0.434 ± 0.155

Figure 3: Pulse duration dependent nonlinear optical absorption of GeSe NPs.

(A), (B) and (C) OA Z-scan measurements of GeSe NP dispersions at 1064 nm with different pulse durations of 7 ns, 10 ps, and 56 fs, respectively; (D), (E) and (F) normalized transmittance and input peak intensity for open aperture Z-scan measurements of GeSe NP dispersions with different pulse durations of 7 ns, 10 ps, and 56 fs, respectively.

6.8%, respectively. This implies that the pulsed laser with a shorter pulse duration time can lead to a lower saturable fluence for NLO response in GeSe NPs.

2.3 The carrier dynamics of GeSe NPs

To further investigate the ultrafast carrier dynamics in GeSe NPs, a non-degenerate pump-probe experiment was performed. In our measurement, a pump beam (wavelength: 400 nm; 0.15 μJ) coming from the optical parametric amplifier (TPR-TOPAS-U, America) was used to excite hot carriers from the ground state in GeSe NPs. A probe super-continuum (750–1400 nm) was generated by delivering the amplified fs pulses into a thin CaF_2 crystal through self-phase modulation. Then, it was used to reveal the carrier relaxation processes by detecting the absorption difference of the sample at different delay times. On the one hand, when the pump beam (400 nm) was focused on GeSe NPs, electrons were excited from the valence band to the conduction band through absorbing photon energy and the excited electrons were heated or cooled with each other by intra-band energy scattering. Then, it reached the dynamic equilibrium in a short period of time, which is referred to as the fast relaxation time of the carrier of GeSe NPs. Over a longer period of time, which is generally

known as slow relaxation time, the thermo carriers were gradually cooled by interaction with optical phonons and the excited electrons gradually relaxed back to the ground state and recombined with holes. The carrier relaxation can be revealed by analyzing the wavelength dependence transient absorption (TA signal: $\Delta A = A - A_0$) of the probe light at different delay times. In general, various mechanisms contributed to the ΔA signal, such as ground state bleaching, excited state absorption, and stimulated emission. For 2D semiconductor materials, the investigation of carrier relaxation dynamics is very important to reveal the mechanism and potential for their practical applications in nano-phonic devices. In Figure 4A, we plot the decay dynamics curves at four probe wavelengths (800 nm, 871 nm, 1064 nm, and 1100 nm).

$$\text{A bi-exponential decay function } \left(\Delta A = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \right)$$

is employed to fit the cooling dynamics of charge carriers, in which A_1 and A_2 are the amplitudes of each component, t is the delay time between the probe light and the pump light, and τ_1 and τ_2 are the fast and slow relaxation time, respectively. The results of fitted τ_1 and τ_2 are shown in Figure 4B; the fast and slow relaxation times at different wavelengths of 800, 871, 1064, and 1100 nm were components with lifetimes of about 0.54–1.08 ps and 52.4–167.2 ps, respectively. It is interesting that the fast and slow relaxation times at

Figure 4: Transient absorption properties of GeSe NPs at different wavelength.

(A) Transient absorption spectra as functions of pump-probe delay time at wavelengths of 800, 871, 1064, and 1100 nm, respectively. (B) Wavelength dependence of the fast and slow relaxation time constants τ_1 and τ_2 , obtained by fitting with the two-exponential function.

1064 nm are 1.05 ps and 167.2 ps, respectively. At 1064 nm and 1100 nm, both fast and slow relaxation times are larger than those at 800 and 871 nm. This might be explained by metastable states at 1064 and 1100 nm as they are near the band gap. It is known that the long relaxation process facilitates the self-starting in passive mode locking, while the short process, to some extent, determines the pulse width of the pulses. Besides, GeSe NPs also have the potential in fast optical modulator applications considering the fast relaxation time. This explains that the pulse duration smaller than these values has a low fluence threshold for SA, as shown in Figure 3, where the rate of exciting electrons is faster than that of relaxation.

2.4 All-optical diode behavior

The significant broadband saturation absorption characteristics facilitate GeSe NPs to be part of an all-optical diode, in which GeSe as a saturable absorber material (SAM) was juxtaposed with a reverse saturable absorber material (RSAM) C_{60} , introducing a nonlinear jump along the beam propagation direction. The OA Z-scan setup, see Figure 5A, was performed to measure the nonlinear transmittance difference of GeSe and C_{60} . In principle, the spatial reciprocity of light is represented by linear and nonlinear light transmission, that is, the transmission of light through materials in the opposite propagation direction is the same. However, due to the axial nonlinear asymmetry, the transport characteristics of the SA/RSAM sandwich structure become nonreciprocal [48]. In the forward bias (SAM followed by RSAM), when light passes through the SAM, the transmittance is initially higher than the linear transmittance, and then attenuates when

passing through RSA. If the SA effect is more pronounced than RSA, the total response will be an increase in the amount of light transmission (Figure 5B), which is similar to the forward bias of the electron diode. The regime of linear transmission (lower input intensity) is equivalent to the knee-voltage regime of the electron diode. When the bias voltage exceeds the knee voltage, current flows through the diode. Similarly, when the input light intensity exceeds a threshold level and which is strong enough to induce saturation in the SAM, the configuration allows increased light transmission in that direction. On the other hand, in the reverse bias structure (RSAM followed by SAM), if the intensity of the light transmitted by RSAM declines below saturation intensity, it will not evoke high transmittance in the SAM, as shown in Figure 5C. Therefore, the overall light transmittance decreases below the linear transmittance of the combined system while at high input intensity, like the reverse bias of the electron diode.

Here, we designed and fabricated the all-optical diode by means of the GeSe/ C_{60} bilayer structure. To demonstrate the behavior of our all-optical diode, we used the GeSe NP dispersions in the 2 mm cuvette and formed a double-layer structure with the cuvette (1 mm) containing fullerene (C_{60}) dispersions. First, we separately measured the OA Z-scan curves of GeSe and C_{60} , as shown in Figure 5D. GeSe and C_{60} showed obvious saturated and reversal saturated absorption behaviors, respectively. The fitted saturation intensity I_s was ~ 15 GW/cm² and the nonlinear absorption coefficient was $\alpha(I) = -1.5 \times 10^{-9}$ cm/W for GeSe. The two-photon absorption coefficient of C_{60} was $\beta = 8.9 \times 10^{-9}$ cm/W. Figure 5E shows the nonreciprocal light transmission >1 GW/cm² with an increasing difference between the forward and reverse transmission characteristics of the GeSe/ C_{60} bilayer structure.

Figure 5: The optical diode of GeSe/C₆₀.

(A) Schematic diagram of the experimental setup; (B), (C) action of an all-optical diode based on asymmetric nonlinear absorption; (B) in forward bias (SA followed by RSA), when light passes through SA, the transmittance is initially higher than the linear transmittance, and then attenuates when passing through RSA. If the SA effect is more pronounced than RSA, the total response will be an increase in the amount of light transmission, which is similar to the forward bias of the electron diode. And (C) is on the contrary. (D) The OA Z-scan curves of the GeSe NP dispersions and C₆₀ dispersions; SA of GeSe NPs in red and RSA of C₆₀ in blue. (E) Optical diode behavior of the GeSe/C₆₀ bilayer structure; the forward bias in red and reverse bias in blue.

The non-reciprocity factor was defined as the gain in $dB = 10 \times \log_{10}(T_{\text{forward}}/T_{\text{reverse}})$, where T_{forward} denotes the nonlinear transmission values for forward and T_{reverse} denotes the values for reverse [49]. As shown in Figure 5E, the non-reciprocity factor of the GeSe/C₆₀ bilayer structure was ~ 3 dB. Most of the optical diodes reported so far are generally based on photonic crystals and magneto-optical isolators. However, the periodicity of photonic crystals will affect the propagation of electromagnetic waves in turn, and the fabrication of photonic crystals is cumbersome. Magneto-optical isolators in fiber coupled lasers are constructed based on Faraday rotators, which need magnetic fields in the system. The optical diodes of GeSe/C₆₀ have the following characteristics: passive, polarization-independent, no phase matching, no need

to satisfy periodic structure and simple structure, good chemical stability and thermal stability, low price, and can withstand high light intensity. This provides the basis and paves a way for the use of broadband optical diodes and optical isolators without bulky components or magnetic fields.

3 Conclusions

In summary, the broadband SA and carrier dynamics of GeSe nanoplates were systematically investigated by the Z-scan and pump-probe technique, respectively. The GeSe NPs show strong SA at wavelengths of 400 nm, 800 nm, and 1064 nm, and exhibit pulse duration-dependent SA

behaviors. The fast and slow relaxation times at different wavelengths of 800, 871, 1064, and 1100 nm were components with a lifetime of about 0.54–1.08 and 52.4–167.2 ps, respectively. Taking the advantage of the ultrafast NLO properties of the GeSe NPs, we designed and fabricated the all-optical diode by means of the GeSe/C₆₀ tandem structure. Our results indicate that the GeSe NP is a potential nonlinear material and pave a way in the development of optical diodes with nano-materials.

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