Optics in Nanosheets

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Layer-Dependent Nonlinear Optical Properties and Stability of Non-Centrosymmetric Modification in Few-Layer GaSe Sheets**

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Abstract: *Gallium selenide, an important second-order nonlinear semiconductor, has received much scientific interest. However, the nonlinear properties in its two-dimensional (2D) form are still unknown. A strong second harmonic generation (SHG) in bilayer and multilayer GaSe sheets is reported. This is also the first observation of SHG on 2D GaSe thin layers. The SHG of multilayer GaSe above five layers shows a quadratic dependence on the thickness; while that of a sheet thinner than five layers shows a cubic dependence. The discrepancy between the two SHG responses is attributed to the weakened stability of non-centrosymmetric GaSe in the atomically thin flakes where a layer–layer stacking order tends to favor centrosymmetric modification. Importantly, two-photon excited fluorescence has also been observed in the GaSe sheets. Our free-energy calculations based on first-principles methods support the observed nonlinear optical phenomena of the atomically thin layers.*

Two-dimensional (2D) layered materials have obtained extensive attention since the first discovery of graphene by the Geim group in 2004.[1] Stimulated by the success of graphene, a simple micromechanical cleavage technique has been expanded to other layered materials,[2] particularly the family of transition-metal dichalcogenides (TMDs).[3] Among the recent advances, 2D gallium selenide (GaSe), a layered III–VI semiconductor, has been receiving lifted attention from electronic and optoelectronic applications.[4] GaSe consists of covalently bonded stacks with top and bottom layers of Se and two layers of Ga ions in the middle, that is, in the sequence of Se-Ga-Ga-Se. There are several different modifications which differ in the stacking sequence, and the three most important classifications are so-called β-GaSe, ε-GaSe, and γ-GaSe.[5] Schematics of β-GaSe in side and top views are shown in Figure 1 a,b, respectively. β-GaSe has two basic layers per unit cell and belongs to the space group D^4_{6h} with an inversion symmetric center because of the stacking sequence. On the other hand, the layered structure of ε-GaSe is generated from one primitive layer by translations, as schematically shown in Figure 1 c,d. Thus, ε-GaSe is non-centrosymmetric and belongs to the space group D^1_{3h}. Both β-GaSe and ε-GaSe show 2H stacking. GaSe crystals possess wide optical transparency ranging from the wavelength of 0.65 to 18 μm, relatively high birefringence, and a high threshold damage value for different laser lines.[6] Note that one of the most important properties of bulk GaSe is the nonlinear optical property because of the absence of an inversion symmetric center.[7] Nonlinear optics has been widely used in many important applications such as integrated optics, optical information communications, biology, and material science as well as imaging techniques.[8]

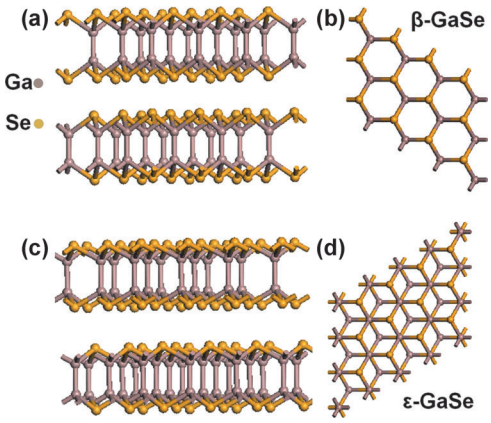

Figure 1. GaSe crystal structure: a) side view and b) top view for β-GaSe; c) side view and d) top view for ε-GaSe.

In comparison with the bulk counterparts of GaSe, the nonlinear optical properties have not been explored in its 2D form. In this work, we report a study on the nonlinear optical properties of few-layer GaSe nanosheets. Our results demonstrate that strong second harmonic generation (SHG) can be observed even when the crystal thins down to a bilayer. In the view of applications, the observation suggests that 2D GaSe sheets can be considered as a promising candidate for future nanophotonic devices.

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Few-layer GaSe nanosheets with different thicknesses can be exfoliated from bulk GaSe crystals, and then the layer number is determined (see Figures S1 and S2 in the Supporting Information). A femtosecond (fs) laser pulse with a wavelength of 800 nm was employed to detect nonlinear optical properties. The inset of Figure 2a shows a strong emission response of a bilayer (2 L) GaSe flake. An emission peak centered at 400 nm is apparently observed, which is exactly at the half wavelength of the incident laser. Such frequency doubling is the so-called second harmonic generation (SHG), giving rise to twice the frequency of the incident light. This implies that the bilayer GaSe sheet is of non-centrosymmetric structure because of the absence of the inversion center, giving rise to strong second-order nonlinearity. Importantly, the presented result differs from the second-order optical nonlinearity recently observed in monolayer TMDs,[9] including edge nonlinear optics from MoS_2.[10,11] 2D TMDs were found to feature second-order optical nonlinearity when decreasing the thickness to single layer because of the absence of an inversion symmetry center. To be more specific, SHG was observed in odd-layered TMDs, while vanished in even layer numbers owing to the restoration of inversion symmetry. The main panel of Figure 2a demonstrates the SHG from GaSe thin flakes with a different layer number. For comparison, the *y* axis (SHG intensity) of the graph is plotted in log scale. When increasing the thickness from a bilayer to a 10-layer (10 L), the SHG intensity is dramatically enhanced. The emission spectra of GaSe layers of different thicknesses further indicate that SHG can be generated regardless of the parity of the layer number of the GaSe sheets, differing from the previously observed phenomena from TMDs layers, the even-layered nanosheets of which showed negligible SHG.

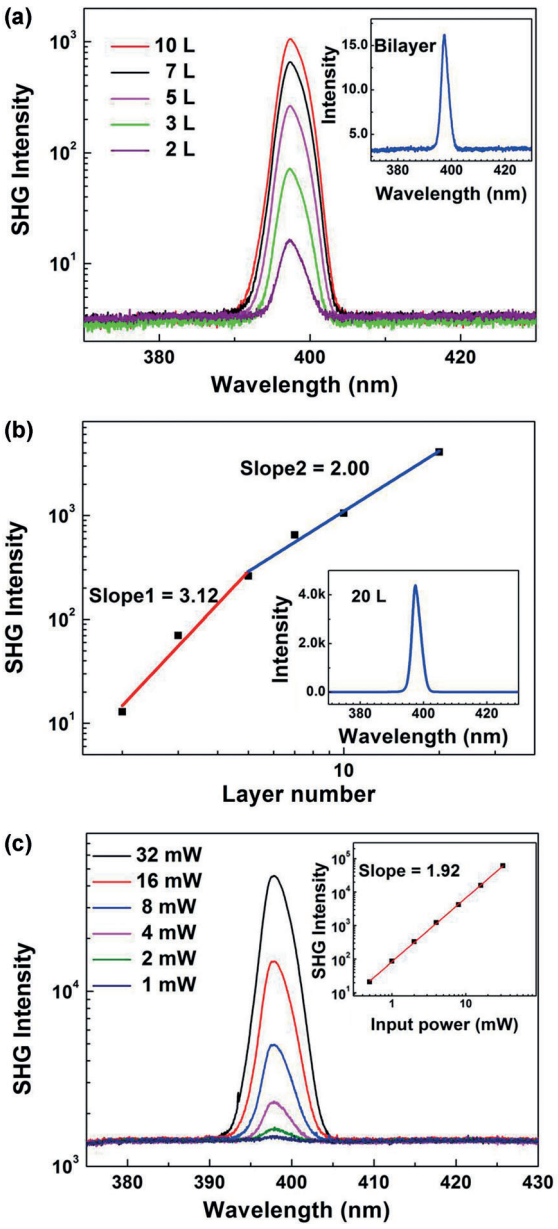

Figure 2. a) Second harmonic generation from GaSe thin layers with different layer number. Inset: SHG spectrum of bilayer GaSe sheet in linear scale. b) The SHG intensity as a function of layer number. SHG spectrum of 20 L GaSe is shown in the inset. c) Spectra of second harmonic generation from GaSe thin layer with different input power. Inset: the input power dependent SHG.

The power-law fitting of the SHG intensity (Figure 2b) yields a slope of 3.14 when the GaSe crystal is thinner than 5 L, indicating an approximately cubic dependence of the SHG intensity on the layer number. On the other hand, when the thickness is beyond 5 L, the fitting shows a quadratic dependence on the thickness of GaSe. In principle, if the sample thickness is much less than the coherence length, the SHG intensity has been reported to possess a quadratic dependence on the thickness of the thin film.[12] Such a discrepancy found in a GaSe crystal thinner than 5 L can be interpreted so that the nonlinear coefficient changed in thinner GaSe nanosheets compared to a bulk crystal. According to the measured SHG intensity, the magnitude of the nonlinear coefficient (d_{eff}) of few-layer GaSe was estimated (see the Supporting Information) by modeling few-layer GaSe as a bulk medium. Since the nonlinear coefficient has a structural origin, it is reasonable that its 20 nm-thick scale value is not distinct from the bulk one. The SHG spectrum of the 20 L GaSe sheet is shown in the inset of Figure 2b. Therefore, d_{eff} is determined to be 30 and 46.3 pm V^{-1} for bilayer and trilayer GaSe, respectively. However, multilayer GaSe sheets possess a d_{eff} comparable to the bulk GaSe when the thickness of GaSe is above 5 L. Nevertheless, the nonlinear coefficient of our few-layer GaSe is relatively high in comparison with some other nonlinear bulk and thin-film materials.[13]

The SHG intensity of GaSe was measured as a function of the excited power, as shown in Figure 2c. When increasing the input power from 1 to 32 mW, the SHG peak is remarkably enhanced. The inset of Figure 2c shows the power-dependent SHG intensity which almost perfectly follows a quadratic dependence as expected in nonlinear optical bulk materials.[11] The measurement can further confirm that the sharp and strong peak at 400 nm is the second harmonic response in nature.

The above results have shown SHG signals from the local spot of a laser beam, which irradiated the GaSe nanosheets of varied thicknesses under different pumping power. It is

interesting to characterize the second harmonic response for the overall GaSe flakes. Thus, confocal laser scanning microscopy (CLSM) was employed. Taking into account that the signal detected by CLSM is transmissive, another set of GaSe flakes was prepared on a transparent glass substrate. The emission spectrum is shown in Figure S3. Similar to the above result of the nanosheet pumped at 800 nm, the SHG effect can also be observed in our few-layer GaSe sheets under fs laser irradiation at wavelengths varied from 900 to 1080 nm (Figure S3). Figure 3a shows a representative bright

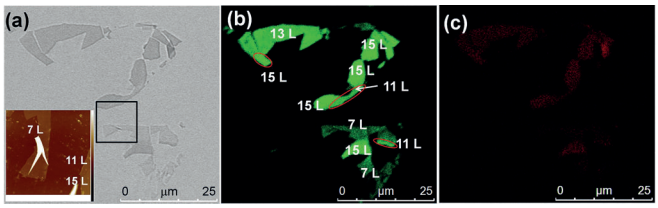

Figure 3. Confocal laser scanning microscope image of layered GaSe flakes on transparent glass substrate. a) Bright-field image, b) the SHG image with emission filter ranging from 450 to 500 nm excited by 976 nm fs laser light, and c) the fluorescent image with emission filter ranging from 600 to 700 nm.

field image of few-layer GaSe sheets. In addition, atomic force microscopy (AFM) was used to verify the layer thickness. The inset of Figure 3a shows the AFM image of 7 L, 11 L, and 15 L GaSe flakes. Under excitation at 976 nm, a strong and eminent emission (488 nm) can be observed on the GaSe flakes with different thicknesses. The SHG image with an emission filter from 450 to 500 nm clearly shows the thickness-dependent optical contrast, as marked in Figure 3b. The overlay of a bright-field image and a SHG image (Figure S4a) further indicates that the GaSe nanosheets can generate second-order nonlinearity regardless of the parity of the layer number.

In addition to the above SHG signal, photoluminescence emission originating from two-photon excited fluorescence (TPEF) can be obtained, as shown in Figure 3c, where the excitation is far below the band gap of the GaSe flakes. The overlay of a bright-field image and a fluorescent image for GaSe flakes is shown in Figure S4b. The emission intensity also varies with the layer number of the GaSe sheets. In theory, SHG involves that two photons interact simultaneously with the nonlinear material with no absorption process, which is essentially a scattering process. However, TPEF is a third-order optical process, involving simultaneous absorption of the two photons and carrier relaxation followed by radiative emission from the band edges. In this process, two-photon absorption (TPA) is the simultaneous absorption of two photons, which usually takes place under intense excitation. In particular, TPA is a nonlinear optical process several orders of magnitude weaker than linear absorption, that is, one photon absorption (OPA).[14]

To evaluate the TPEF of 2D GaSe sheets, the linear (one-photon) photoluminescence (PL) of bulk GaSe samples was measured. The spectrum (Figure 4a) excited by 488 nm continuous-wave (cw) laser light shows a peak at about

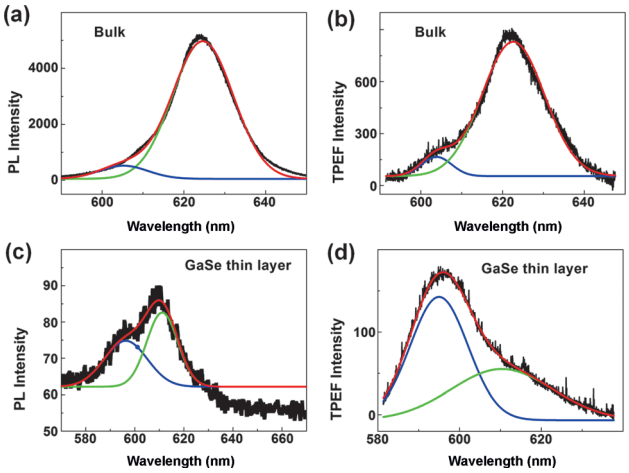

Figure 4. Photoluminescence spectra excited by 488 nm cw laser light for a) bulk and c) several-layer GaSe samples, respectively. Two-photon excited fluorescence spectra excited by 800 nm fs laser light for b) bulk and d) several-layer GaSe samples, respectively.

620 nm, indicating an optical band gap of about 2.0 eV. There is a significant shoulder peak at the red band of the feature peak. As a consequence, this peak can be well described by a superposition (red line) of two Gauss peaks, which are centered at 605 (blue line) and 624 nm (green line), corresponding to photon energies of 2.051 and 1.989 eV, respectively. Furthermore, the spectrum (Figure 4b) excited by 800 nm fs laser light exhibits a peak at about 620 nm, which can be fitted by two peaks with center positions at 605 and 620 nm. This may be attributed to the two different modifications of β- and ε-GaSe which have slightly different band gaps. At 300 K, the band gap of β- and ε-GaSe is about 2.046 and 1.996 eV, respectively.[15] The later peak shows relatively strong PL peak compared to the former, indicating the main modification of the GaSe crystal is non-centrosymmetric ε-GaSe.

Next, we examined the luminescence properties of few-layer GaSe sheets. The PL peak (Figure 4c) can be divided into two peaks, which are centered at 596 and 611 nm, respectively. On the other hand, the TPEF of 2D GaSe layer, as demonstrated in Figure 4d, can also be described by a superposition of two peaks (centered at 595 and 610 nm). The blue shift of the two peaks indicates a larger band gap (2.082 eV and 2.031 eV) compared with their bulk counterparts. Such a slight increase of 30 meV has been achieved by cleaving GaSe to few-atomic-layer sheets. This small blue shift is possibly due to the modification of band gap structure caused by the decrease in the thickness of GaSe layers as well as the quantum confinement effect.[16] Notably, another difference between bulk and its 2D form in the spectra is the intensity ratio of two emission peaks centered at 595 nm and 610 nm corresponding to β-GaSe and ε-GaSe, respectively. This observation suggests that the amount of non-centrosymmetric ε-GaSe may be reduced in its 2D layers by considering the majority is ε-polytype in bulk.

The shift of TPEF and the SHG response may be related to the energy stability of stacking sequence in 2D GaSe sheets. There are two stacking orders for GaSe in our

experiments, which can be determined by the PL and TPEF measurements. The detailed stacking manner can also be detected by high-resolution transmission electron microscope reported by other groups.[4b,d,e,16] In bulk, both β- and ε-GaSe are stable with an interlayer coupling effect by van der Waals force. However, their coupling energies should be different because of distinct stacking sequence and the impact of such discrepancy may be more remarkable in low dimension. Specifically, despite of the identical interlayer distances in both modifications, the spacing between a Ga and the nearest Se in the adjacent layer is distinct. The spacing in ε-GaSe is larger than in β-GaSe, resulting in a weaker interlayer coupling energy. External perturbations, such as thermal excitation and photoexcitation, may modify the stacking order at atomically thin films from ε-GaSe to β-GaSe, which consequently gives rise to the trend of centrosymmetry of the whole sample. To verify this hypothesis, the free-energy calculation for bulk and 2D layered ε- and β-GaSe was performed using first-principles method with the CASTEP package.[17] The final lowest energy of each modification is obtained after a geometry optimization to their structures, as shown in Table 1. In our calculation, the unit cell in bulk contains two basic layers by considering the periodicity, while bilayer and trilayer GaSe consists of two and three basic layers, respectively, with breaking the periodicity on the z axis. The lattice parameters of ε- and β-GaSe have the same values ($a = b = 3.750$ Å, $c = 15.94$ Å) so that their stacking sequences can be compared. In bulk, the energies of β- and ε-GaSe are very similar with a difference of -0.00327 eV. However, the energy of ε-GaSe is higher than that of β-GaSe in the bilayer, indicating that bilayer ε-GaSe is less stable than β-GaSe. Similar energy difference between β- and ε-GaSe can also be obtained for trilayer GaSe. The energy calculation implies that both β- and ε-GaSe are stable in bulk with small energy difference. However, in the atomically thin flakes, larger energy difference between the two materials suggests that the layer–layer stacking order tends to favor the existence of β-modification. The calculation results can address the measured nonlinear properties of atomically thin GaSe sheets detected in our experiments by considering that centrosymmetric β-GaSe is not capable of generating SHG.

Table 1: The calculated free-energy of bulk, bilayer, and trilayer β- and ε-GaSe and the energy difference between the two types.

GaSe	ε-GaSe [eV]	β-GaSe [eV]	Δ [eV]
bulk	−9262.109265509	−9262.105992214	−0.00327
bilayer	−9261.252611656	−9261.997738663	0.745127
trilayer	−13891.76899318	−13893.05227135	1.283278

In summary, we have observed layer-dependent nonlinear properties of SHG and TPEF in few-layer GaSe sheets. Especially, bilayer GaSe sheet is capable of demonstrating second harmonic response when excited by a fs pulse laser. The SHG response of GaSe nanosheets smaller than 5 L shows a nearly cubic dependence on the layer number, differing from the quadratic dependence of GaSe sheets with the thickness beyond 5 L. The observation can be attributed to the weakened stability of ε-GaSe in the atomically thin flakes. First-principles calculations indicate that the stacking order at atomically thin films tends to form β-GaSe modification with centrosymmetric structure which is not capable of possessing nonlinear optical properties. SHG and TPEF have also simultaneously been observed in few-layer GaSe sheets. At any rate, our results firstly provide an experimental evidence that the intrinsic nonlinear optical properties can be maintained even when the thickness of GaSe is decreased to bilayer. In the view of applications, the observation in this work suggests that 2D layered GaSe sheets with strong second harmonic response can be considered as a promising candidate for future nanophotonic devices.

Experimental Section

2H-GaSe crystals were purchased from 2D Semiconductors. Few-layer GaSe sheets were cleaved and adhered to the subsequent 300 nm SiO_2 coated Si and transparent glass substrates by micromechanical exfoliation method. Atomic force microscopy (AFM, DI Nanoscope 8) combined with optical microscope (OM, Olympus DX51) was employed to perform the surface morphology characterization and determine the thickness of GaSe layers. The photoluminescence measurements were performed in the micro-Raman system (HORIBA, HR800) with PL mode by using 488 nm laser. A Ti:sapphire fs laser (repetition rate: 80 MHz, pulse duration: 100 fs) with the wavelength of 800 nm was used to examine the nonlinear optical properties of GaSe sheets on SiO_2/Si substrates. The spot size of the fs laser is about 1 μm. Additionally, a confocal laser scanning microscope (Leica TCS SP5) equipped with a fs Ti:sapphire laser (Libra II, Coherent) with the wavelength ranging from 680 to 1080 nm was employed to characterize the overall GaSe flakes.

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