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Two-dimensional (2D) materials can take a large amount of mechanical deformation before reaching the fracture limit due to their high Young’s modulus, and this in return, provides a way to tune the properties of 2D materials by strain engineering. Previous works have shown that the optical band gap of transition metal chalcogenides (TMDs) can be modulated by strain, resulting in a drift of photoluminescence (PL) peak position and a decrease (or little change) in PL intensity. Here, we report on a member of post-transition metal chalcogenides (PTMCs), 2D-GaSe sheets, displaying vastly different phenomena under strain. Stained 2D-GaSe emits photons at almost the same wavelength as unstrained parts but appears an order of magnitude brighter. In contrast to GaSe, strained 2D-GaSe sheets can also withstand large amount of strain, thus their properties can be tuned by strain engineering.

Previously, strain-induced changes on the band structure of 2D materials have been demonstrated particularly for group VI-transition metal dichalcogenides (VI-TMDs), such as MoS\textsubscript{2}, and group VII-TMDs (such as ReSe\textsubscript{2}). Generally, photoluminescence (PL) relying on energy-level difference between two electron states, which can reflect transition between excited state and equilibrium state, is in common use as an important probing means for internal mechanism of materials such as impurity, light-emitting mechanism, impurity defect energy level, and so on. Under external stimuli (strain), the band structure of VI-TMDs changes from direct to indirect and the optical band gap value decreases, resulting in much weaker photon emission and a red-shift in PL peak position. Even though VII-TMDs also belong to TMDs family, the extra electron in the outmost orbital of the transition metal atom changes the fundamental understanding of strain-induced changes in their properties. For instance, emission from strained VII-TMDs is red-shifted, similar to MoS\textsubscript{2}, but the PL intensity remains almost the same due to lack of indirect to direct gap transition. Although current strained 2D-materials can provide some new phenomenon, the reduction in the light emission and red-shift in PL peak position limit their applications. Therefore, 2D GaSe, which belongs to another class of material, PTMCs, with emitting photons at the same wavelength without any significant changes under strain and with stronger emission than unstrained one, will be more suited for flexible optoelectronic applications than TMDs.

This work addresses this need by experimental and theoretical studies on the strain-induced changes in the optical-electronic features of few-layer GaSe. Strained few-layer GaSe samples were fabricated by depositing the few-layer GaSe onto flexible pre-strained Gel-film substrates and then releasing the Gel-film strain to create wrinkled (strained) features. In stark contrast to TMDs, strained regions display an order of magnitude larger PL emission intensity that appears to be at almost the same wavelength as unstrained parts. Based on our micro-absorption and UV-VIS measurements, as well as theoretical calculations, we attribute to these effects to much increased photon absorption on wrinkled...
(strained) regions with optically absorbent perpendicular component to the incoming light source due to large optical absorption anisotropy ($\mu_{\parallel} > \mu_{\perp}$) observed in GaSe. The overall result presents the first experimental demonstration of strain-induced changes in PTMCs, and also suggests unique routes to manipulate optical properties of layered materials with large optical absorption coefficient anisotropy.

2 Results and discussion

GaSe crystal with a hexagonal structure is a member of layered PTMCs. In each layer (Se-Ga-Ga-Se), Ga atoms are sandwiched between Se atoms adding up to ~7.98 Å thickness per sheet and these layers are held together by weak van der Waals forces (Figure 1a). Few-layered 2D GaSe were mechanically exfoliated using Scotch-tape from bulk GaSe crystals grown by modified Bridgman technique and the structure was analyzed by using transmission electron microscopy (TEM) (Figure 1b). From the high-resolution TEM (HRTEM) pattern (Figure 1b), it can be observed that distinct and periodic atomic arrangements are obtained for the few-layer GaSe, revealing a high quality crystal characteristic. The corresponding Fast Fourier Transforms (FFT) image (Figure 1c) and the selected area electron diffraction (SAED) image (Figure 1d) both show one set of clear and legible six-fold symmetry diffraction spots, further supporting its high crystallinity and hexagonal symmetry. Prominent (002) XRD reflection peaks, associated with lattice reflections from layers in hexagonal (2H-) phase, were observed on all the synthesized materials, and the average single crystalline domain size was estimated at ~50 nm based on Scherrer’s formula using the (004) peak FWHM value and Cu Kα wavelength (supporting information Figure S1). The chemical compositions of the nanosheets are measured by energy dispersive X-ray spectroscopy (EDX), yielding Ga/Se stoichiometric ratio of ~1:1 (standard deviation ~0.05% see supporting information Figure S1).

To prepare the strained samples, the few-layer GaSe was first mechanically exfoliated from in-house grown GaSe crystals onto a 300 nm thermal oxide on Si substrate (SiO₂/Si). A 200-300 nm thick PMMA film was spin-coated onto the GaSe/SiO₂/Si by a spin coater at 4000 rpm for 1 minute and then was baked at 180°C for 10 minutes on a heating plate to increase adhesion between PMMA with GaSe flakes. After this, the PMMA/GaSe film was decoupled from SiO₂/Si after etching the sacrificial SiO2 layer by immersing the PMMA/GaSe/SiO₂/Si into 5 mol/L aqueous NaOH solution at 60°C for 2 hours. This was followed by cleaning in deionized water. The PMMA/GaSe film was then transferred onto the pre-strained elastomeric Gel-film (a PDMS polymeric film), along the stretching direction with defined tensile pre-strain as $\varepsilon = \Delta L/L$, where $L$ represents the original length of Gel-film and $\Delta L$ is called the elongation after pre-stretching (The schematic diagram of the experimental procedure is showed in supporting information Figure S2-S3). Experiments found that well-defined wrinkles on GaSe sheets correspond to a releasing the 20 % strain as shown in Figure 2a-b. AFM images of wrinkled few-layer GaSe with thickness of 5 nm (about six layers, supporting information Figure S4), displaying a lateral periodicity of ~1.4 μm and an average height of 70 nm as shown in Figure 2c. This observation agrees well with the phase pattern of AFM in Figure 2d, which displays a 40° active phase shift.

![Figure 1](image1.png)

Figure 1 Few-layered GaSe crystal structure and its TEM images. (a) Layered crystal structure of GaSe with each tetra-layer (TL) formed by Se-Ga-Ga-Se atomic sheets. (b) High resolution TEM images from few-layer GaSe. Fast Fourier Transforms (c) and SAED pattern (d).

![Figure 2](image2.png)

Figure 2 Atomic force microscopy measurements on wrinkled GaSe sheets. a. AFM topography and b. AFM phase mode images of few-layer wrinkled GaSe. c-d. The corresponding height profiles of sheets shown in a, b.

The periodicity of the strain-induced wrinkles can be described by:

$$\lambda_{s} = \frac{2\pi h \left( \frac{E}{12\mu(1-\nu)} \right)^{1/3}}{\Lambda},$$

In Eq. (1), $\nu$ and $E$ represent Poisson’s ratio and Young’s modulus of GaSe, respectively. Here we take $\nu = 0.186$, $E = 34$ GPa and $\Lambda=\left[(1+\varepsilon_{pre})^{3}+1/2(1+\varepsilon_{pre})\right]$, where $\varepsilon_{pre}$ refers to the pre-strain amount of Gel-film. As $\mu_{s} \approx 20$ kPa is the shear modulus of the flexible substrate, the value of $\lambda_{0}$ calculated using Eq. (1), is found to be ~317h, where $h$~5 nm is the thickness of GaSe. Using this value, the corresponding wavelength of the strained six-layer GaSe is ~1.5 μm, which is in close agreement with our experimental value (~1.4 microns). Here, we note that these
self-formed wrinkles are always perpendicular to the direction of applied stress due to mismatch between elastic modulus values of GaSe and Gel-film. By applying different pre-strains (from 20% to 100%) and a gradually released process, some representative types of morphologies of the strained few-layer GaSe are exhibited in Figure S3. With increase of the pre-strain, scanning electron microscopy (SEM) images show the evolution from ripple wrinkles (Figure S3a) to standing folds (Figure S3b,c), eventually to collapsed folds (Figure S3d). Since the well-shaped ripple wrinkles are unsustainable when the pre-strain added to a certain degree (>30%), and considering PL well-shaped ripple wrinkles are unsustainable when the pre-strain added to a certain degree (>30%), and considering PL

$$\varepsilon \sim \pi^2 h \delta / \lambda^2 (1 - \nu^2)$$, (2)

where $\lambda$ and $\delta$ denote width and height of wrinkles geometry of the strained few-layer GaSe, which can be characterized by AFM, as shown in Figure 2. According to Eq.(2), local uniaxial strain on the top of wrinkled 2D-GaSe reaches up to 0.3%. In the remainder of this article, ‘strained’ and ‘ wrinkled’ will be used interchangeably to refer to strained GaSe.

Figure 3 Photoluminescence enhancement and lattice vibration of 2D-GaSe by strain engineering a. PL spectra taken from wrinkled and un wrinkled region in Figure S4. b. Optical image of wrinkled GaSe flake formed during the exfoliation process. Region #1 refers to strained and region #2 is flat. Regions are marked. Inset: PL mapping on the highlighted region. c. PL spectra obtained from region #1 and region #2. c. AFM image of the same flake shown in b. e,f. AFM line scan data taken across the wrinkled (blue dotted line) and red dashed region. The latter measurement was performed to estimate the thickness of the overlying flake. g. Raman spectra observed in a region without wrinkles (blue) and with wrinkles (orange) on the same GaSe nanosheets shown in Figure S4.

To understand effects of strain on the optical properties of 2D-GaSe, the PL spectra on strained and flat GaSe regions were measured (Figure 3) for few-layer GaSe with different thickness, different profiles and even different substrates. Interestingly, single scan PL spectra of strained region (Figure 3a) shows that the PL intensity is about 10 folds greater than that of unstrained region, and their emission peaks appear at the same position. These results were reproduced on more than twenty (20) separate sets of samples with PL enhancement factors ranging from half to one and a half orders of magnitude. Similar measurements were also reproduced on another kind of typically strained GaSe sheets (Figure 3b,c) formed by the exfoliation process on the SiO2/Si. Pink regions correspond to the strained ( wrinkled) GaSe (region #1) and lie over the unstrained ( un wrinkled) GaSe sheets (region #2). AFM measurements in Figure 3d show that the wrinkled #1 region lies over the flat region (region #2), which is with 150 nm in height (Figure 3e) and 12 nm in thickness (about 15 layers, Figure 3f). Importantly, our PL mapping measurements (Figure 3b inset) show still that the region #1 (strained region) is nearly an order of magnitude more luminescent compared to flat regions, indicating the PL enhancement is independent of substrate type. Since the 12 nm-thick piece is on top of a 100 nm flake which also contributes to the PL signal, it is hard to evaluate the thickness effect on the PL enhancement only by this experiment. However, the effect of thickness cannot be ruled out based on Eq.(2) and warrants further studies. Consistent with the PL mapping, single scan PL spectra of region #1 (Figure 3c) shows that the PL intensity greater than that of region #2 without peak position drift, further confirming the PL enhancement without peak-shifted emission for different profiles and even different substrates. TMDs have strain-dependent PL emission wavelengths and under strain have much weaker photoluminescence (due to strain induced direct to indirect band gap transition). In this regard, 2D-GaSe sheets are at least an order of magnitude more luminescent and the light emission remains at the same wavelength display stark differences compared to the previous studies on group TMDs.

Considering that the total amount of the material on the wrinkled region is slightly (~10%) more than the un wrinkled parts due to geometrical considerations, this difference can only contribute less than 10% of the PL enhancement, and thus, an additional mechanism is necessary to explain the phenomenon. Before discussion of the mechanism, we have to exclude another possible effect from morphology deformation. As we well know, Raman spectroscopy has been widely used for verifying effect of strain on 2D materials, such as graphene and MoS2.15,20-22 by shifts and shapes of peak corresponding to the phonon modes of the 2D materials, therefore Raman spectroscopy will provide strain-induced information. Our Raman spectroscopy measurements on wrinkled few-layer 2D-GaSe displays three prominent peaks located at 136 cm-1, ~200 cm-1, and 310 cm-1 corresponding to A1g, E1g and A2g modes (Figure 3g and Figure S5a). Obviously, A1g and E1g modes have a slight drift to lower frequencies with respect to unstrained region similar to the observations on MoS2.23 and this is consistent with calculated frequency shifts under 0.3% strain can be up to 5 cm-1 as shown in Figure S5b. Here, we note that the in-plane E2g mode of GaSe shifts by greater amount compared to out-of-plane A1g mode. We attribute this to applied lateral strain which greatly acts on each individual layer instead of greatly changing the interlayer coupling strength (which couples to the A1g). Softening of Raman modes around 200 cm-1 in-plane modes in the wrinkles are not only from softening of E1g mode, but also from the activation of Raman active E2g modes (No.13-16 in Figure S6). These results suggest that strain effects on vibration of Se atoms more than those of Ga atoms in the strain. As analyses above, the strain has...
obviously occurred on top of wrinkled few-layered GaSe flakes and produced an effect on the vibrational modes, further confirming PL enhancement come from strain rather than surface geometry deformation.

Since the PL enhancement is not generated by 10% area increment and surface geometry deformation, an internal mechanism induced by strain should be discussed. Generally, strain can lead to a transition in band-gap of 2D semiconductors, but in our case of PL, peak position drift is negligible (~20 meV) under strain despite of the dramatic increase in integrated PL intensity, which implies that observed effects are not due to the strain induced band renormalization like group VI TMDs. In Figure 4a, b, we present our theoretical simulation results to understand how electronic structure of few-layer (1 and 3) and bulk GaSe are affected via Density Functional Theory (DFT) calculations. Γ-point in the valence band edge is dominated by p atoms and metal. Any lateral strain will not have any effect on charge distribution. Γ-point in the conduction band is a combination of p, and p, orbitals of only chalcogen atoms. As the number of layers in the simulation cell increase, the effect of lateral strain on the direct gap at Γ-point decreases from ~150 meV in monolayer to ~30 meV in the bulk limit under 0.3% applied strain. Since band renormalization results in changes much greater than 20 meV, we eliminate the possibility of strain induced changes in the optical band gap.

Another optical effect is related to the optical absorption coefficient of the overlying material (GaSe or GaS). This is particularly important for layered PTMCs, such as GaS, GaSe, GaTe, where the optical absorption coefficient can be more than an order of magnitude different depending on the polarization conditions. For example, when the absorption coefficient of GaSe crystals probed in the normal incident light is polarized perpendicular flat region- and parallel strained configuration to the c-axis the absorption coefficient ratio reaches to 40 times. This implies that once the wrinkles are formed on the few-layer GaSe, the absorption coefficient will be enhanced and the GaSe sheets absorb (and emit) photons more efficiently as the incident light has a finite perpendicular component to the c-axis. Our micro-absorption measurements performed on the strained GaSe flake / Gel-film confirm that the absorption is much enhanced as shown in Figure 5a (red and blue). Main peak at 2 eV corresponds to the band edge absorption, whereas peak at 3 eV is associated with higher laying electronic bands, which can also be observed in the calculated absorption spectrum in Figure 5b similar to calculated absorption spectrum of monolayer GaSe. (Where the energy values are off by ~0.2 eV due to DFT functional, but theoretical results behave similarly with experiments. We only calculated absorption spectra for monolayer and bulk structures, but not for few layers (in this case 5 nm thick 2D-GaSe consists of ~6 layers) due to extensive computational requirements. The intensity of 2 eV absorption peak is much enhanced for strained regions, implying that the optical absorption coefficient increases rather drastically in agreement with earlier reports on bulk crystals. Consequently, strained regions absorb and emit photons more efficiently (Figure 3) compared to pristine (un-strained) regions due to an increase in the out-of-plane component of the strained sheets and enhanced optical absorption caused by large optical absorption anisotropy coefficient. In accordance with the experimental findings, optical absorption calculations on GaSe thin films performed by density functional theory calculations show that the absorption is enhanced in perpendicular direction with to.
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Conclusions

In summary, strain effects on 2D-GaSe, a member of post-transition metal chalcogenides (PTMCs), were reported for the first time. Strained few-layer GaSe display an order of magnitude stronger light emission (PL) without any change in their light emission peak position (wavelength) for different number of few layers, different profiles, and even different substrates, which is in stark contrast to TMDs materials (MoS$_2$, WS$_2$, WSe$_2$, ReS$_2$ etc.) where the PL intensity and the emission wavelength, both decrease for an increasing strain value. Optical spectroscopy, micro-absorption, and density functional theory calculations show that the strain-induced PL enhancement in few-layer GaSe is related to large optical anisotropy observed in GaSe and associated enhancement in the absorption coefficient. This effect is vastly different from strain effects in TMDs where the strain induced changes occur due to strong band renormalization and associated changes in the excitonic dynamics. Overall result establish the strain-induced effects on GaSe for the first time, providing further insights into strain effects in 2D materials, and enable us to control light-matter interaction at will using optical anisotropy induced by nanoscale strain engineering.

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Notes and references

Notes

These authors contributed equally.

References


