

Enhancing Light Emission Efficiency without Color Change in Post-Transition Metal Chalcogenides

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METHODS

Sample preparation and methods. GaSe nanosheets on a 300 nm SiO₂/Si substrate were prepared by mechanical exfoliation from GaSe crystals with Scotch tape. Following this, the thickness of GaSe sheets was measured by using the optical microscope (LEICA DM2500M supplemented with an LEICA DFC425 digital camera) and a 3D laser scanning confocal microscopy (Olympus LEXT OLS4000) through the different optical contact between the nanosheets and SiO₂/Si substrate. The nanosheets were then transferred using PMMA (polymethyl methacrylate 950K) as a medium for dry transfer method,¹ onto a pre-strained elastomeric substrate (Gel-PAK Film® WF-40-X4). Gel-PAK film is a common commercial elastomeric substrate which is a polysiloxane-based material similar to poly-dimethylsiloxane (PDMS). GaSe crystals were grown using modified Bridgman growth technique.

Optical spectroscopy measurements. A micro-Raman spectrometer (Renishaw inVia plus) was used in a backscattering configuration with a laser excitation at 532 and 488 nm. Micro-Raman spectra were measured with a 100× objective lens at a low power of 0.5 mW to avoiding the heat-induced damage to the samples. Micro-photoluminescence (PL) spectra were measured with the same instrument (Renishaw inVia plus) to study the evolution of the optical and band structure of the wrinkled GaSe. Optical absorption measurements were performed by home-made optical setup using deuterium lamp in the back illumination geometry and the signal was collected using Ocean Optics detector.

Atomic force microscopy measurements. Topography of the wrinkled GaSe was observed by atomic force microscopy (AFM). AFM was performed by Dimension 3100 scanning probe microscopy. The height of Gel-film measured by AFM was larger than that measured value on SiO₂/Si, due to the different tip-sample interaction between substrate-tip and MoS₂-tip.²

TEM measurements. The TEM and selected area electron diffraction (SAED) patterns were observed by using a FEI Tecnai G2 F20 U-TWIN at a voltage of 200 KV. The ultrathin layered GaSe nanosheets were mechanically exfoliated from bulk GaSe crystals onto SiO₂/Si and then transferred to the micro TEM grid through PMMA.

Density Functional Theory Calculations. Our predictions are based on first-principles density functional theory (DFT) using projector augmented wave potentials.³ The exchange correlation potential has been represented by the Generalized Gradient Approximation and HSE06 Hybrid functional⁴ characterized by Perdew-Burke-Ernzerhof⁵ including van der Waals correction (vdW)⁶ both for spin-polarized and spin-unpolarized cases. Effects of spin-orbit coupling and non-collinear magnetism are not taken into account. Supercell size, kinetic energy cut-off, Brillouin zone (BZ) samplings of the calculations have been determined after

extensive convergence analysis. A large spacing of ~ 15 Å between 2D single layers is taken to prevent interlayer interactions. A plane-wave basis set with kinetic energy cut-off of 370 eV is used. In the self-consistent field potential and total energy calculations BZ is sampled by special $\mathbf{k}$ -points. The numbers of these $\mathbf{k}$ -points are (18x18x1) and (12x12x3) for the primitive monolayer and bulk ϵ -GaSe unit cell and are scaled according to the size of the super cells. All atomic positions and lattice constants are optimized by using the conjugate gradient method, where the total energy and atomic forces are minimized. The convergence for energy is chosen as 10^{-6} eV between two consecutive steps, and the maximum Hellmann-Feynman forces acting on each atom is less than 0.01 eV/Å upon ionic relaxation. The pressure in the unit cell is kept below 5 kBar in each lattice vectors. For hybrid calculations, wavefunction, charge density and relaxed atomic structures are initially generated using GGA functional and further optimized by HSE06⁴. Numerical calculations have been performed by using VASP software.⁷ Frequencies of phonon modes are calculated using small displacement method (SDM)⁸ in terms of forces calculated from first-principles. Optical spectrum calculations⁹ are conducted by taking at least 8 times more the required number of bands for each simulation cell and (20x20x1) and (20x20x4) $\mathbf{k}$ -points are used for monolayer and bulk GaSe structures. In order to have more accurate absorption spectrum with DFT, one needs to consider using GW¹⁰ and BSE¹⁰ approximations.

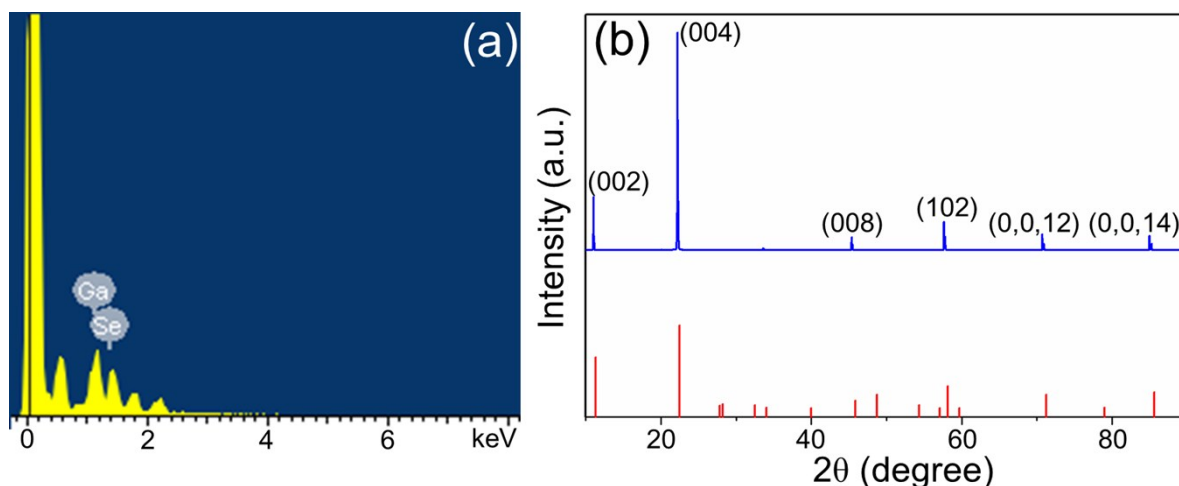


Figure S1. a. The energy dispersive X-Ray spectroscopy (EDX). **b.** XRD patterns; the black lines give the corresponding standard pattern of JCPDS card no. 37-0931.

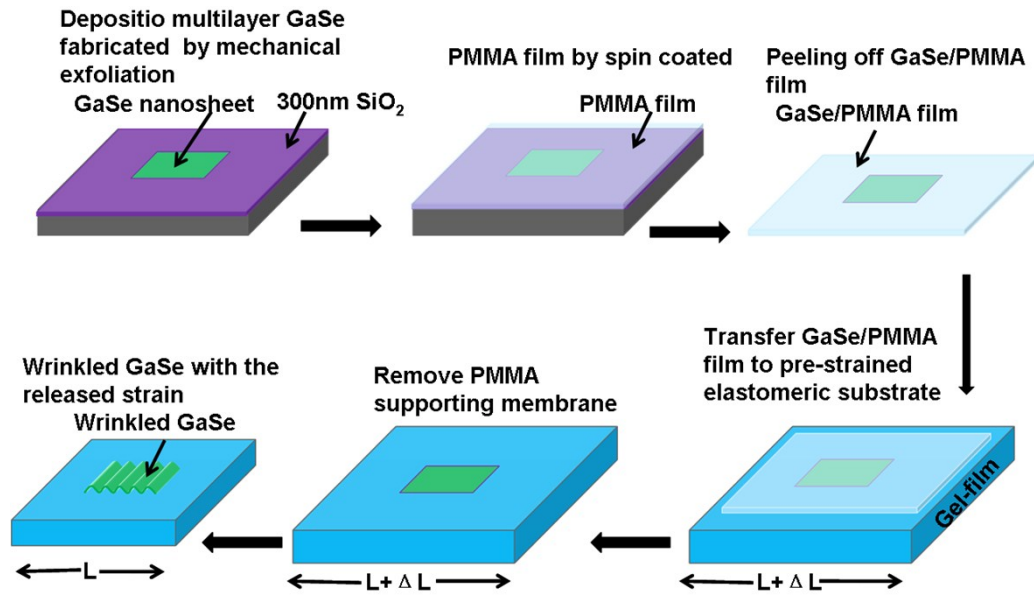


Figure S2. Schematic diagram of wrinkled GaSe fabrication on Gel-film substrate. The GaSe nanosheets on SiO₂/Si were fabricated by mechanical exfoliation method, then a thin PMMA film was spin-coated on GaSe nanosheets. The PMMA/GaSe film was peeled off from SiO₂/Si substrate through wet etching and transferred to a pre-strained Gel-film, and then the PMMA was removed. When the pre-strained elastomeric substrate was released, GaSe wrinkles perpendicular to the initial strain axis were produced.

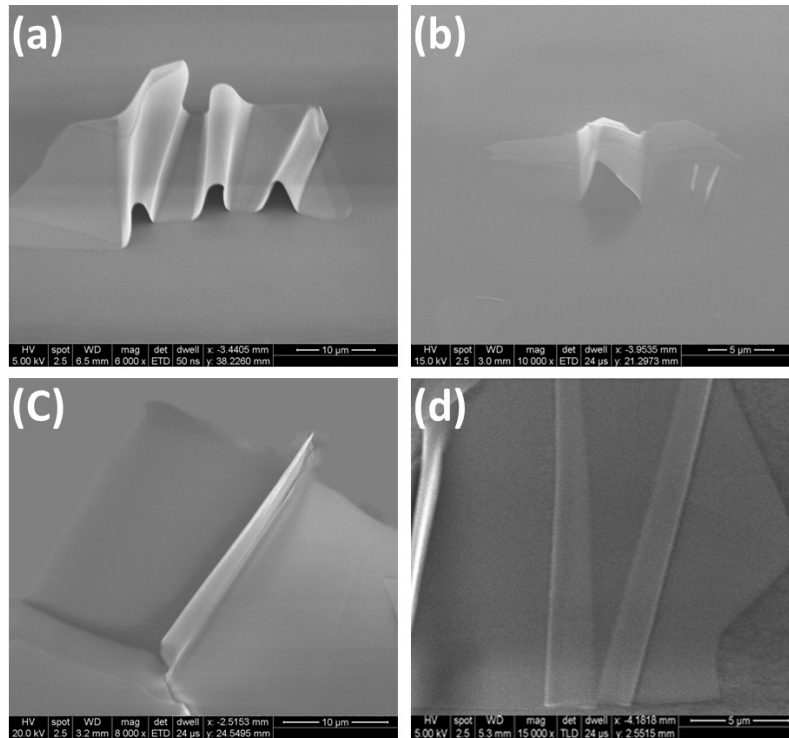


Figure S3. The SEM images of four typical types of morphologies of wrinkled GaSe. The geometry of GaSe wrinkles depends on the compressing strain after releasing pre-strain. By applying different pre-strains and gradually released process, four representative types of morphologies of wrinkled GaSe with different thick are exhibited in **Figure S3**. Scanning electron microscopy (SEM) images show the evolution process of wrinkles. **Figure S3a** shows the typical ripple geometry of the few-layer sample by applying 20 % pre-strain; when adding the pre-strain up to 30 %, ripple type wrinkles will be squeezed into triangle geometry (**Figure S3b**). Wrinkles will evolve to a wall type after applying a 50 % pre-strain, and this structure still remains stable (**Figure S3c**). Figure **S3d** shows that the wall type will collapse to folded wrinkle after releasing the 100 % pre-strain. Summarily, it can be seen that the wrinkles characteristics are closely related to strain, and it is a simple method for designing the wrinkle type by tuning the strain.

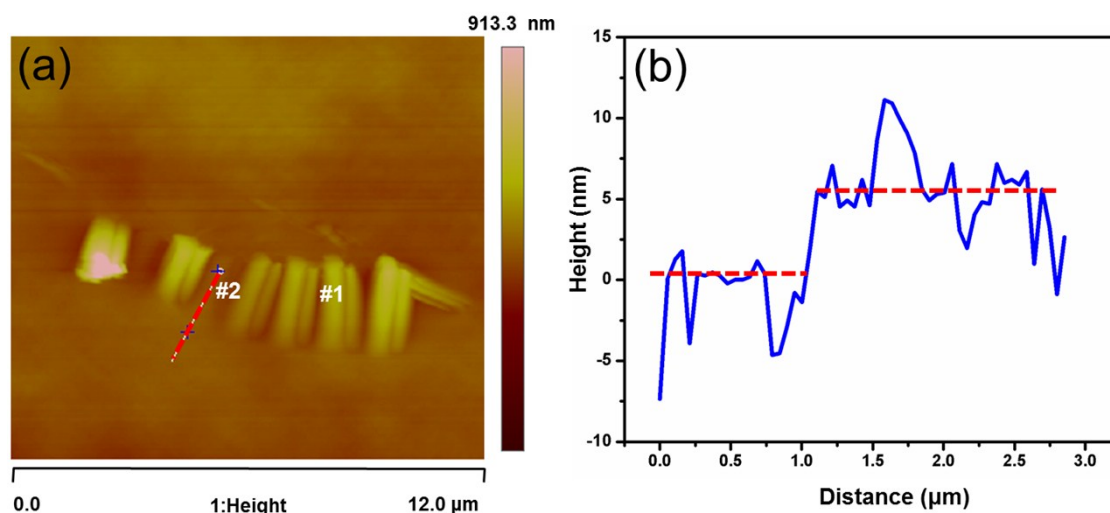


Figure S4. Atomic force microscopy measurements on wrinkled GaSe flakes. **a.** AFM topography images of wrinkled few-layer GaSe. **b.** The corresponding height profiles of the flakes.

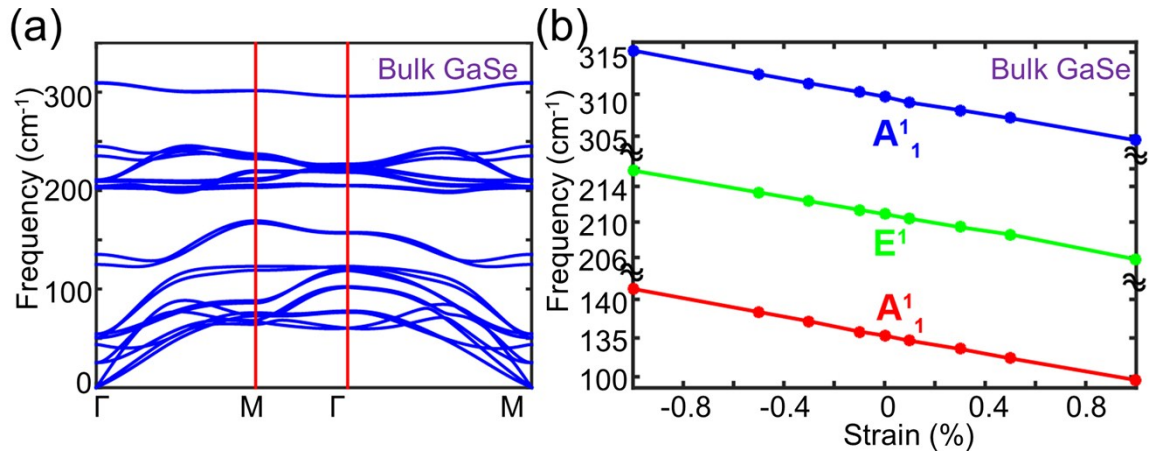


Figure S5. Strain induced changes in lattice vibration of 2D-GaSe **a.** Calculated vibrational spectrum of bulk GaSe and **b.** changes in the vibrational mode frequency for different strain values.

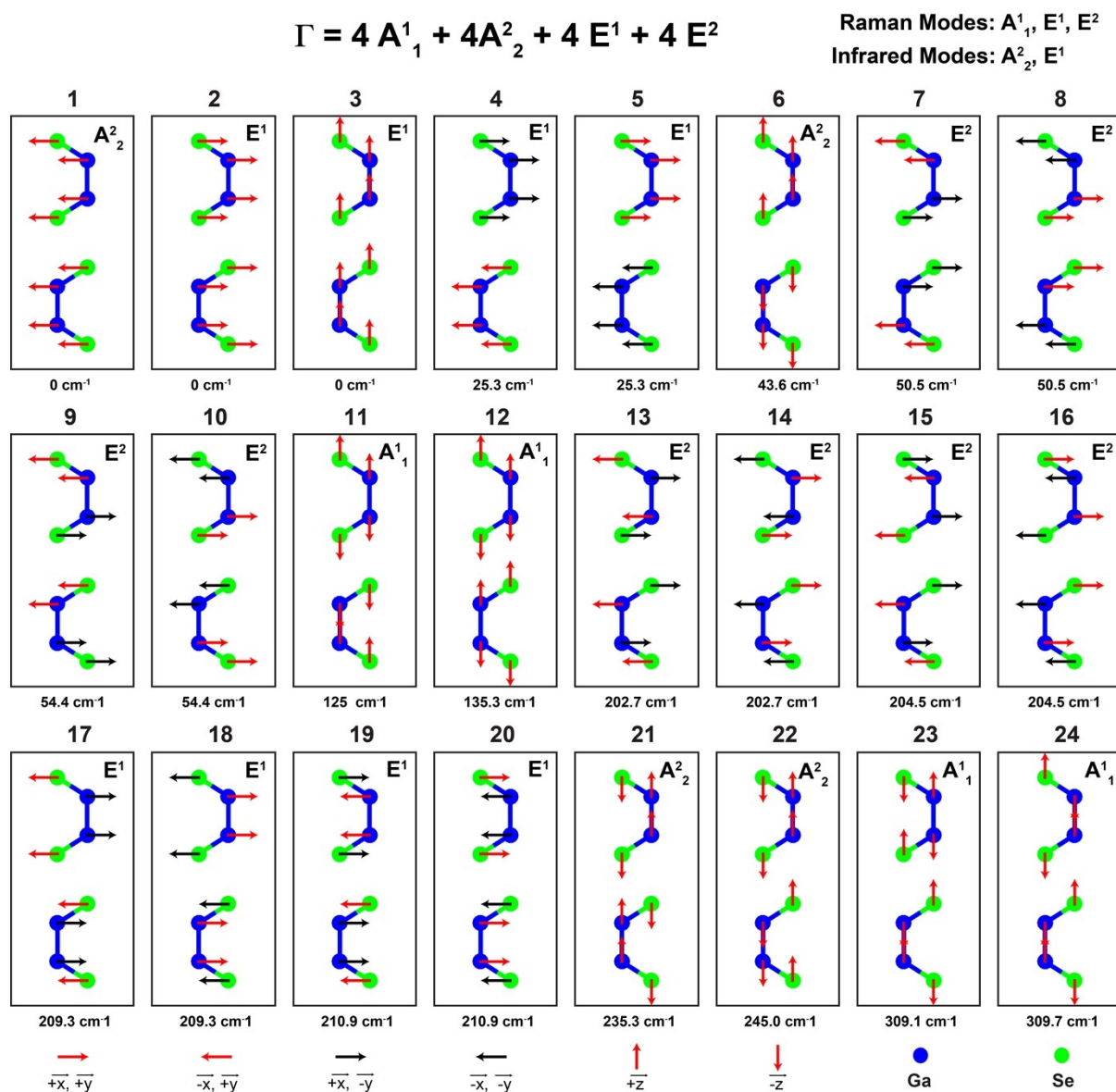


Figure S6. Schematic illustration of phonon modes in first-order: First row indicates which modes contribute at Γ -point and are Raman and Infrared active. The direction of atomic vibrations and vibration frequencies of 24 modes are shown. Last row shows the notation of the different color and direction of arrows.

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