## **Supplementary Information**

## Strain-engineering on GeSe: Raman spectroscopy study



Figure S1. (a) The AFM and (b) height image of the GeSe nanoflake with strain loaded along AC direction. (c) The AFM and (d) height image of the GeSe nanoflake with strain loaded along ZZ direction.



Figure S2. Raman spectra of GeSe when the strain is loaded along the middle direction of AC and ZZ.



Figure S3. Strain dependence of polarization of monolayer GeSe



Figure S4. The calculated polar plots of Ag<sub>1/2</sub> mode with different parameters of |c/b| and  $\phi_{cb}$  according to eqn (1) in the main text.

## **METHODS**

**Sample Preparations:** GeSe films are mechanically peeled from GeSe single crystals using Scotch tape, and then the peeled samples are transferred to the Polyimide (PI) substrate using (polydimethylsiloxane) PDMS. Before deposition, the PI substrate is ultrasonic treated to reduce the surface roughness of the substrate, which can ensure good adhesion of GeSe to the PI. For unstrained sample experiments,  $SiO_2$  was employed as the substrate. The thickness and initial size of the samples were characterized by atomic force microscope (AFM) and optical microscope.

**Tensile Strain Loading**: A homemade stretching fixture was used for the tensile strain loading, in which the long stripe-shaped PI substrate was mounted across the two clamps of the stretcher.

**XRD measurements:** X-ray diffraction data for GeSe crystals were collected on a Bruker D8 Discover using Cu radiation operating at 40 kV and 40 mA.

**Raman Characterization**: Raman spectra were measured in a back-scattering configuration using a commercial Renishaw inVia micro-Raman system and a 532 nm wavelength laser. The temperature-dependent Raman spectrum are collected from 80 K to 873 K with a step of 50 K, where the laser output intensity was set to 25  $\mu$ W with 10 × 5 s exposure time. The angle-dependent Raman spectrum are collected by rotate the sample every 15<sup>0</sup> in the plane by rotating the table horizontally. By inserting a vertical or horizontal polarizer into the entrance of the monochromator, the scattering signal along the vertical or horizontal polarization is selected.

**Theoretical calculation**: First-principles calculations were carried by employing QUANTUM-ESPRESSO (QE) package within the framework of density of functional theory (DFT) and density functional perturbation theory (DFPT) to study the structural, electric and phonon frequency. The exchange-correlation potential was adopted in Perdew-Zunger form of the local density approximation (LDA). We token account of the van der Waals (vdW) correction by using DFT-D method of Grimme6. The energy cutoff and vacuum spacing was set to 60 Ry and 15 Å to guarantee the stable structure we obtained. We employed 9×9×3 k-point samplings for bulk structure. We optimized the structure until the total Hellmann-Feynman forces is below 10<sup>-7</sup> Ry/Bohr. To simulate the strain effect of bulk structure, we changed the lattice parameters of armchair and zigzag direction from 0% to 2%.