Supporting Information

Van der Waals Epitaxial Growth of Two-Dimensional Single-Crystalline GaSe Domains on Graphene

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1. DFT simulation of GaSe/graphene supercells

Our first-principles calculations use plane wave functions as a basis set, where calculational systems consist of an infinitely repeating three-dimensional periodic unit (supercell). Our supercell represents periodic units of experimentally observed 2D GaSe on graphene. We confirmed that our cell size along the stacking direction is large enough and no artificial inter-cell interactions affect total energies of the system under periodic boundary conditions. The in-planar dimension of a supercell is constructed to accommodate GaSe and graphene of different lattice constants, with computationally tractable sizes of systems containing less than 2000 atoms, allowing for a relative rotation between them and possibly for some small strain ε (due to lattice mismatch) in GaSe layer. This corresponds to assuming that interlayer interactions (van der Waals interactions) are sufficiently strong to enforce commensurability between GaSe and the underlying graphene. As the lattices of both GaSe and graphene are hexagonal, the GaSe/graphene supercell is also hexagonal with a primitive lattice vector **C** that can be written as

$$\mathbf{C}=n_1\mathbf{a_1} + n_2\mathbf{a_2}=(1 + \varepsilon)\, R_\theta(m_1\mathbf{b_1}+m_2\mathbf{b_2}) \quad (1).$$

In our simulations, we only find several specific angles with relatively small sizes of GaSe/graphene supercell that can have ε <1% and satisfy the equation (1), as shown in Figure 2d and Figure S7, and the strains are plotted in Figure 2c as well. Among these rotation angles, the 10.9° rotation results in the smallest supercell and strain.

2. Supporting figures

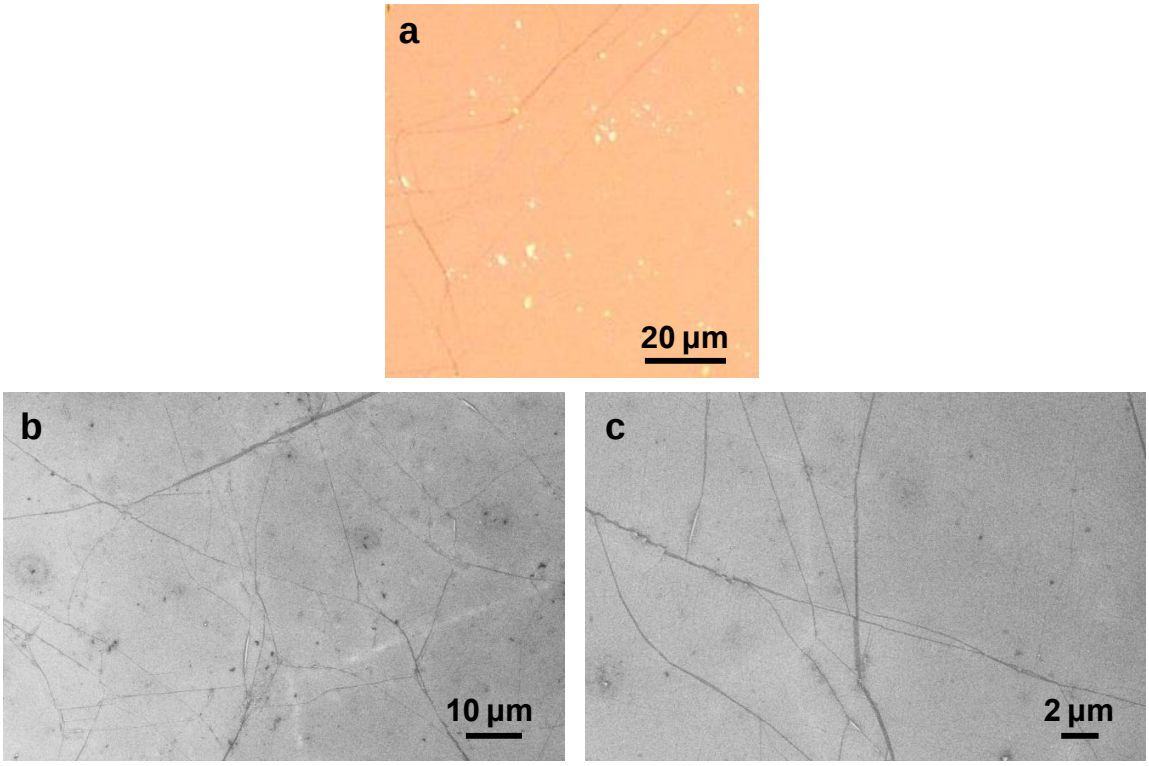

Figure S1. (**a**) Optical image and (**b**−**c**) SEM images of 1L CVD-grown graphene transferred onto a SiO_2/Si substrate. Wrinkles are clearly shown on graphene.

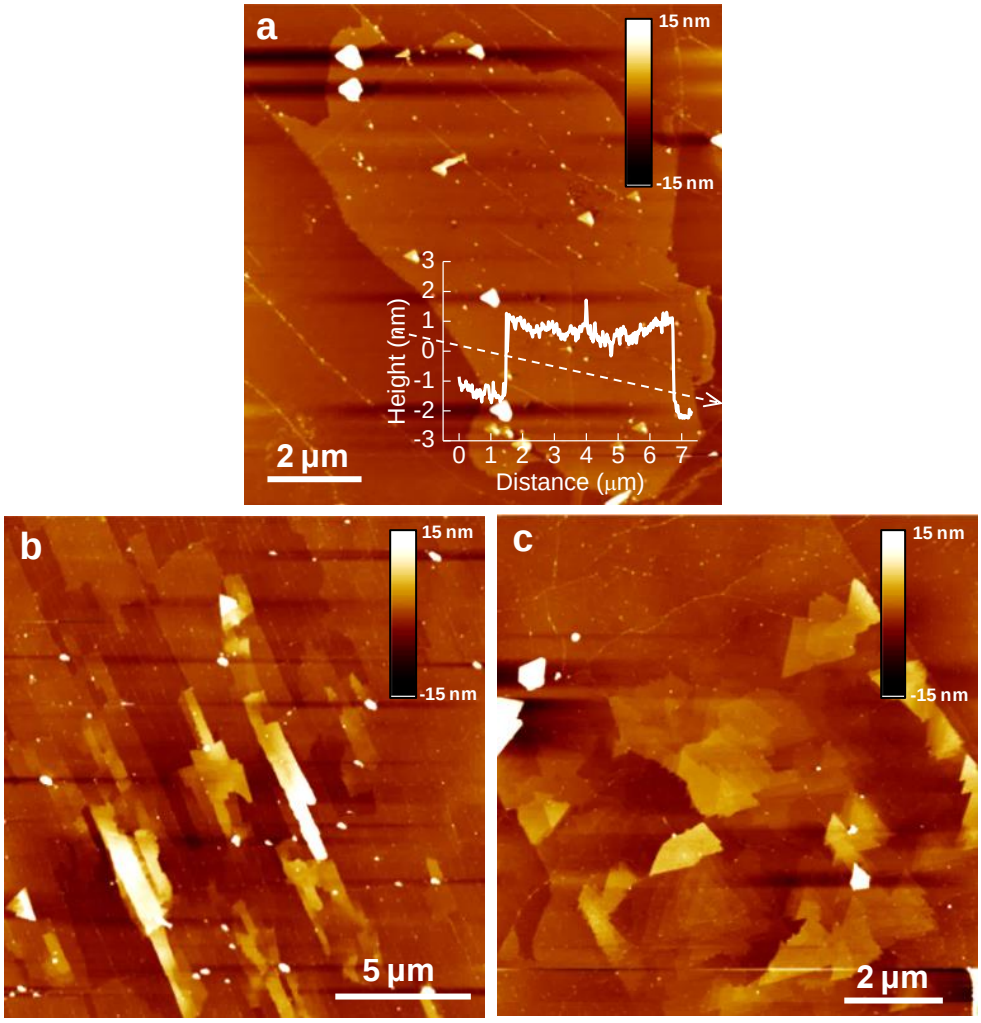

Figure S2. AFM images showing multi-layer vdW epitaxial GaSe crystals on graphene. (**a**) 2L. (**b**−**c**) Thicker crystals.

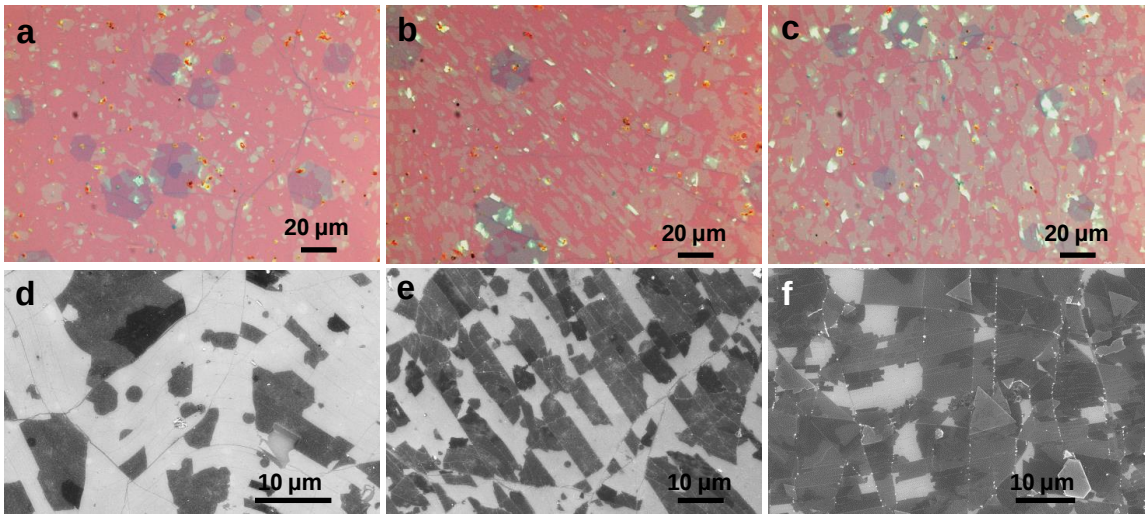

Figure S3. Optical micrographs and SEM images of vdW epitaxial GaSe crystals grown for longer times on graphene. (**a**, **d**) 2 min. (**b**, **e**) 3 min. (**c**, **f**) 4 min. In the optical micrographs, the irregularly-shaped islands in light gray color are monolayer GaSe, while those in much brighter greenish color are thicker GaSe crystals. The purple hexagons are occasionally grown multi-layer graphene. The images indicate that a longer growth time resulted in larger size of monolayer GaSe islands, as well as more thicker GaSe crystals.

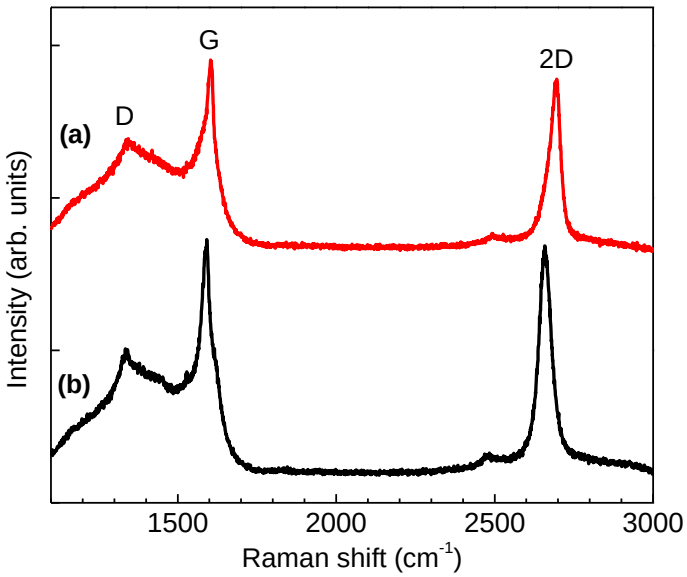

Figure S4. Raman spectra showing graphene features after GaSe growth. (**a**) Obtained from the graphene beneath 1L GaSe epilayer. (**b**) Obtained from graphene area without GaSe grown on it.

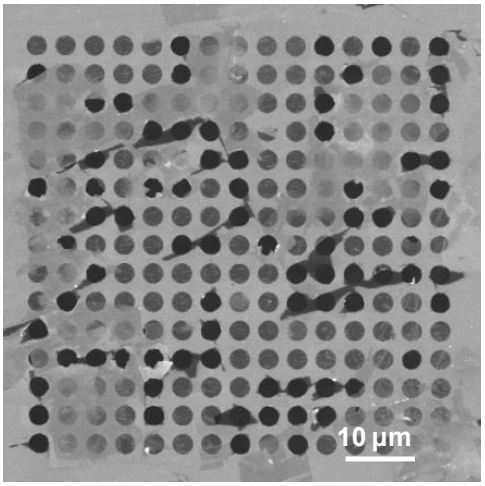

Figure S5. SEM image showing GaSe epilayer on graphene that was transferred onto a Si TEM grid covered with 5 nm-thick porous (pore size: 2 μm) SiN films.

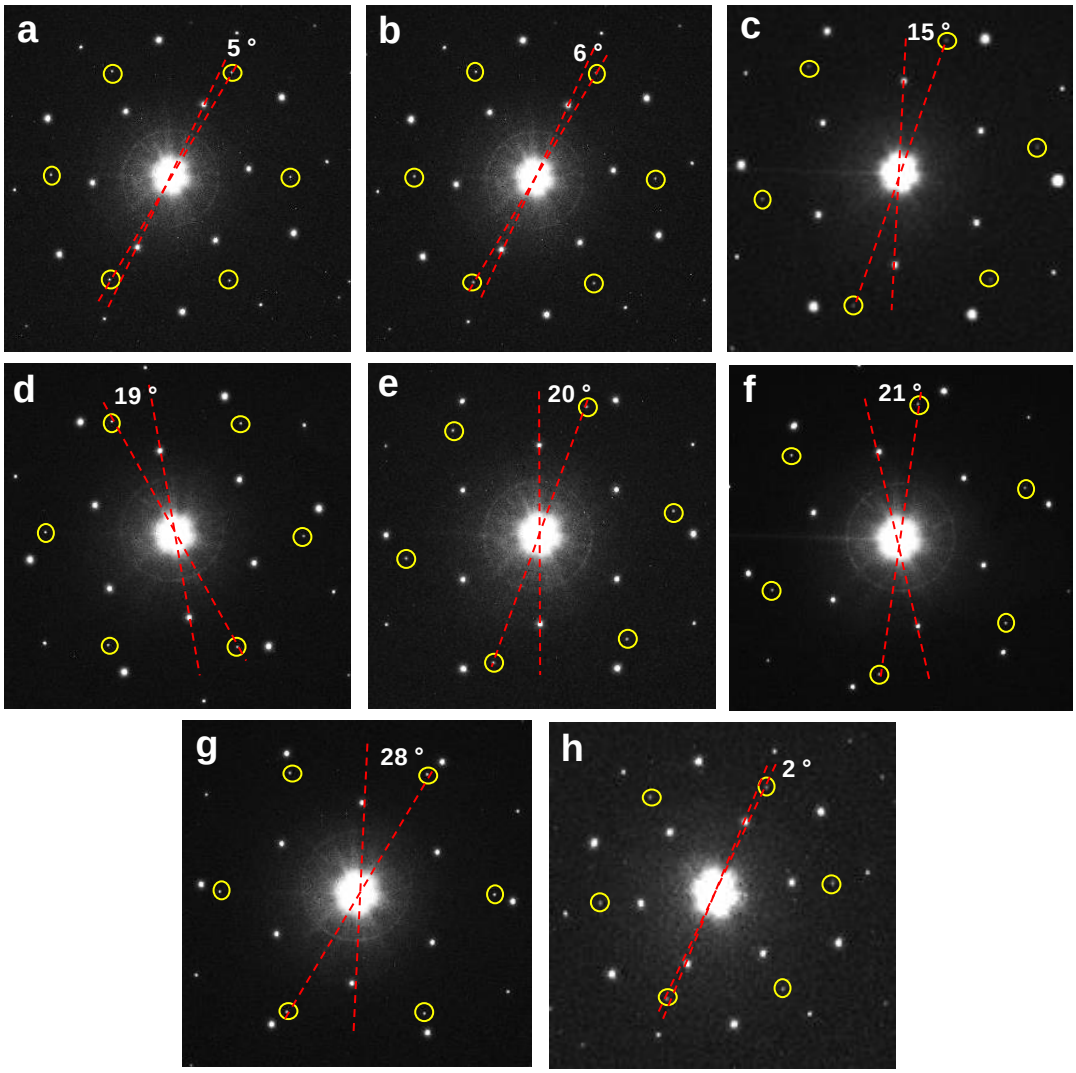

Figure S6. SAED patterns obtained from a variety vdW epitaxial GaSe islands on graphene, showing different interlayer lattice rotation angles.

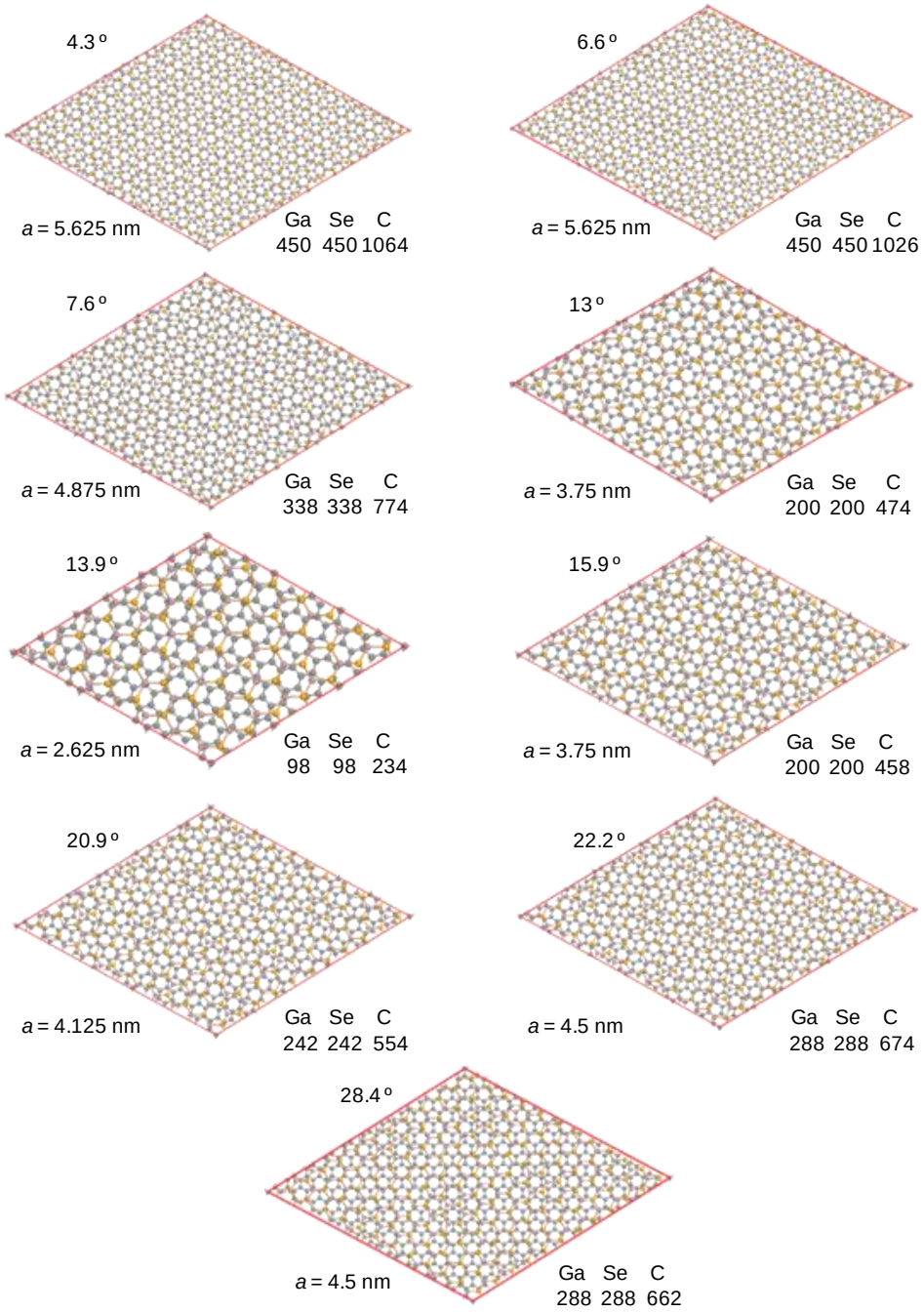

Figure S7. Schematic illustrations of vdW heterostructure unit cells (supercells) constructed by 1L GaSe epitaxy on 1L graphene with interlayer lattice rotation angles of 4.3, 6.6, 7.6, 13, 13.9, 15.9, 20.9, 22.2, and 28.4° .

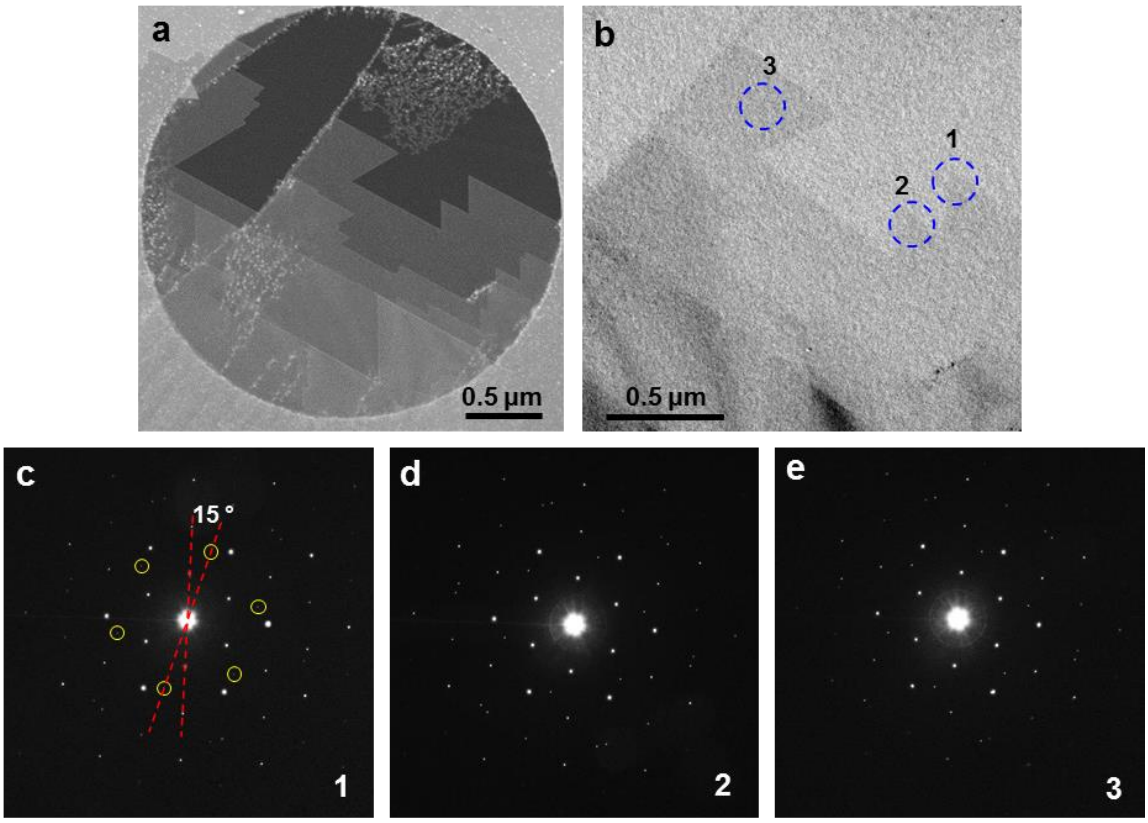

Figure S8. Epitaxy of single-crystalline GaSe on graphene. (**a**–**b**) SEM and TEM images showing the area near the edge of vdW epitaxial GaSe islands on graphene. (**c**–**e**) SAED patterns obtained from regions 1, 2, and 3 included in the dashed circles in (b). The three regions show the exact same SAED patterns, in which the patterns from GaSe rotate by 15º with respect to those from graphene, indicating a 15º rotation between GaSe and graphene lattices.

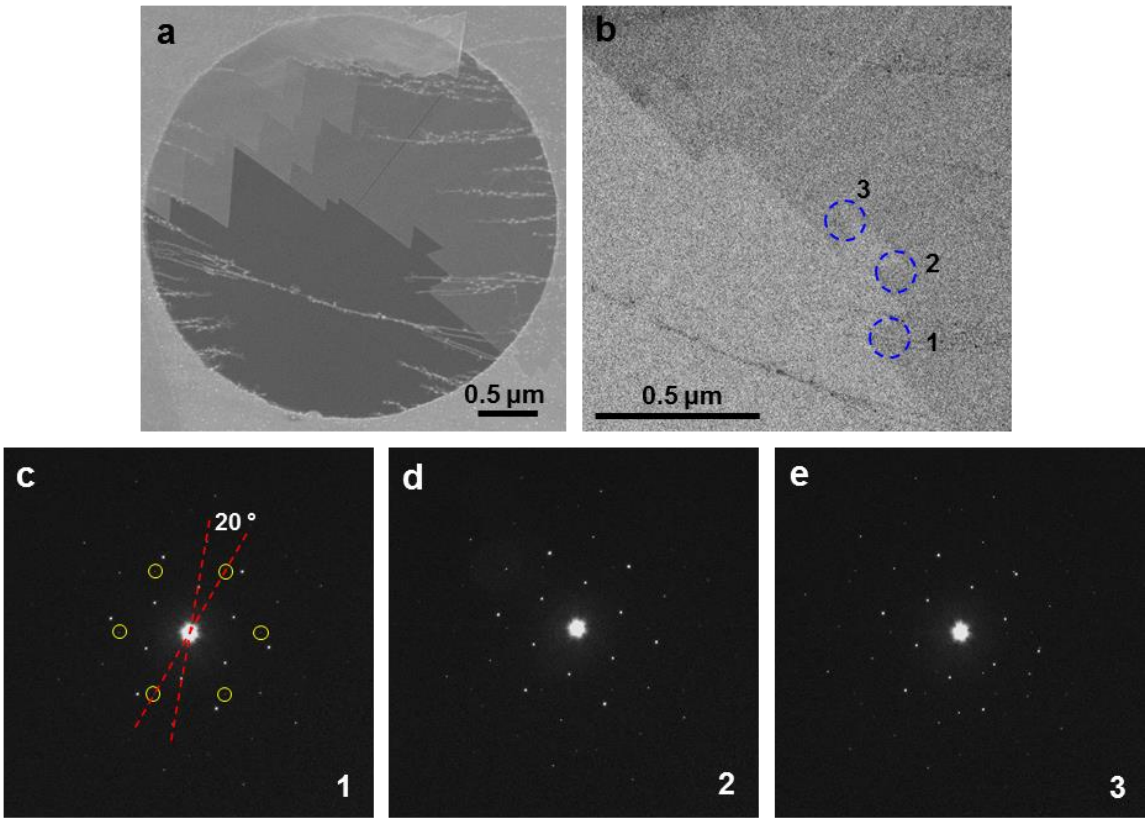

Figure S9. Epitaxy of single-crystalline GaSe on graphene. (**a**–**b**) SEM and TEM images showing the area near the edge of vdW epitaxial GaSe islands on graphene. (**c**–**e**) SAED patterns obtained from regions 1, 2, and 3 included in the dashed circles in (b). The three regions show the exact same SAED patterns, in which the patterns from GaSe rotate by 20º with respect to those from graphene, indicating a 20º rotation between GaSe and graphene lattices.

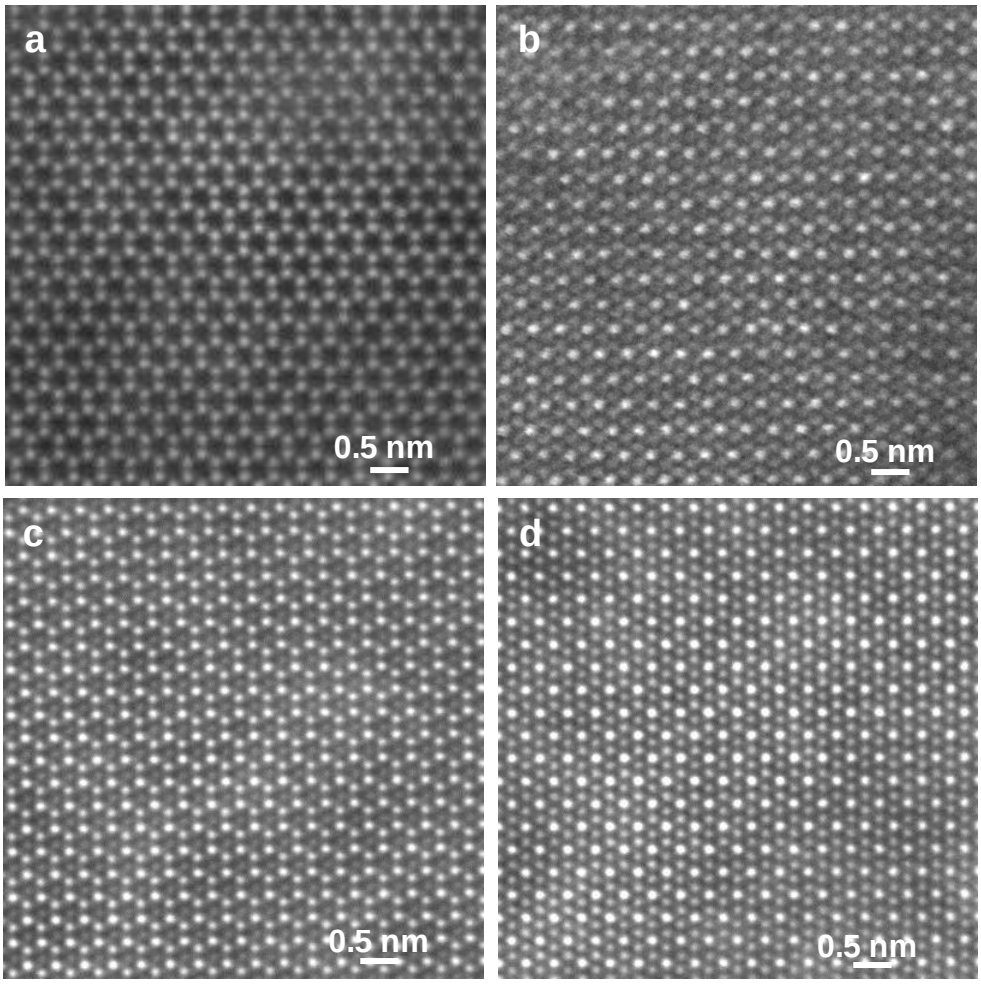

Figure S10. Atomic resolution ADF-STEM images showing bilayer and trilayer GaSe with different stacking modes on graphene. (**a**) 2L, 2H-stacking (β-GaSe). (**b**) 2L, 2R-stacking (ε-GaSe). (**c**) 3L, 2H-2R-stacking (δ-GaSe). (**d**) 3L, 3R-stacking (γ-GaSe).