Supporting Information for

Tuning the sharing modes and composition in a tetrahedral GeX_2 (X=S, Se) system via one-dimensional confinement

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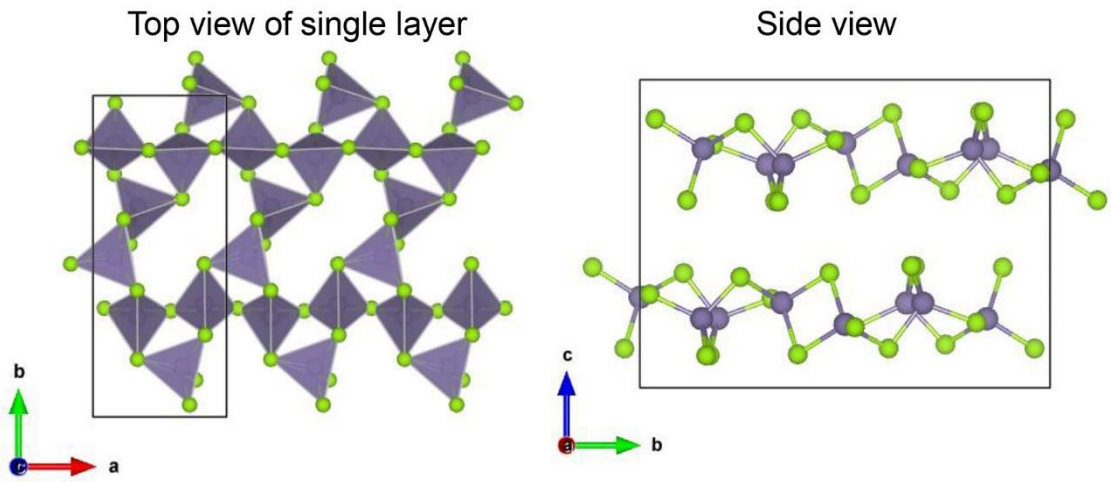
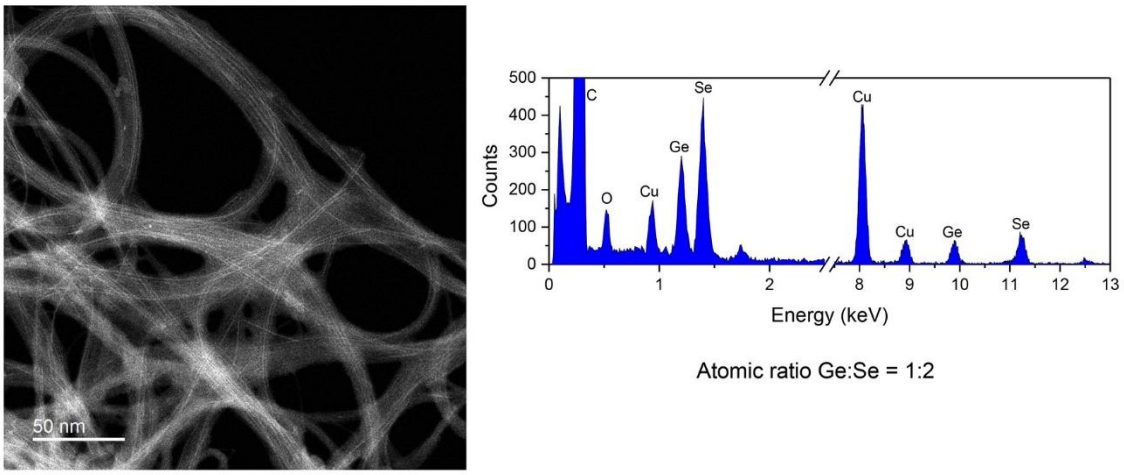
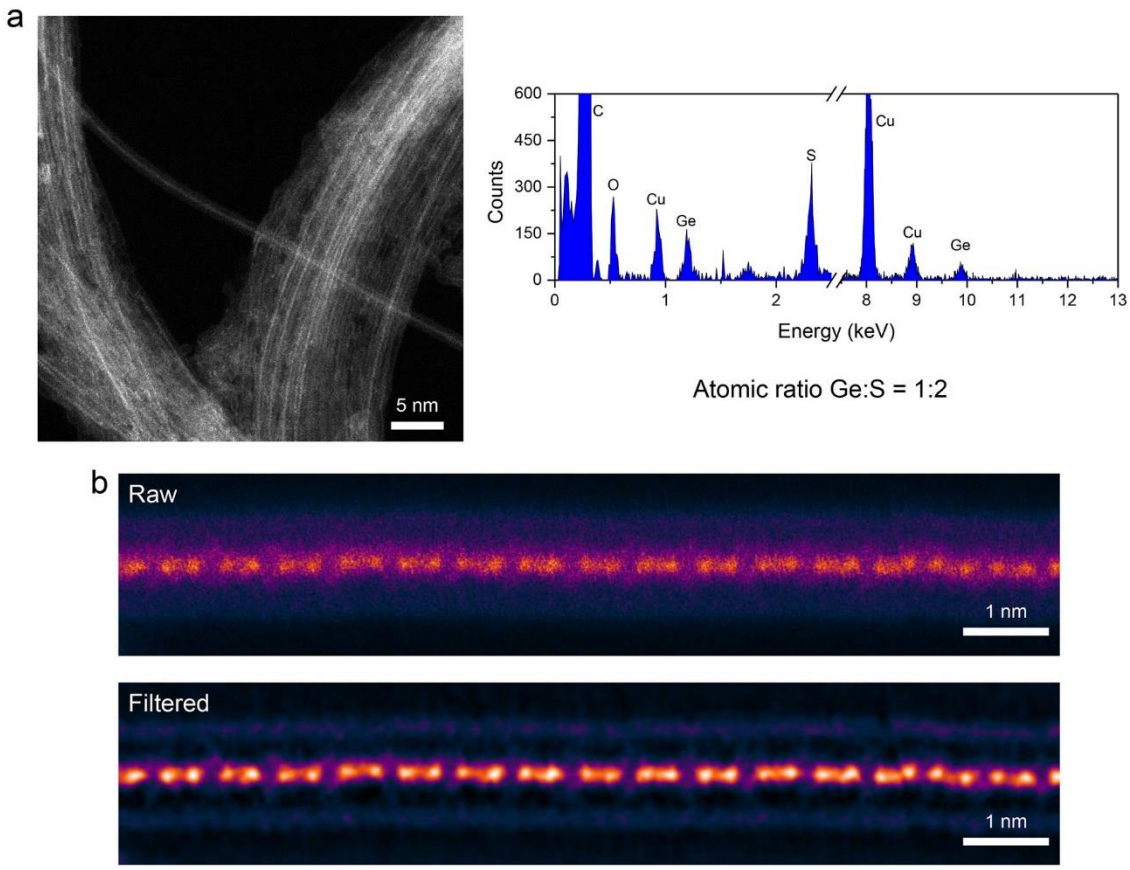


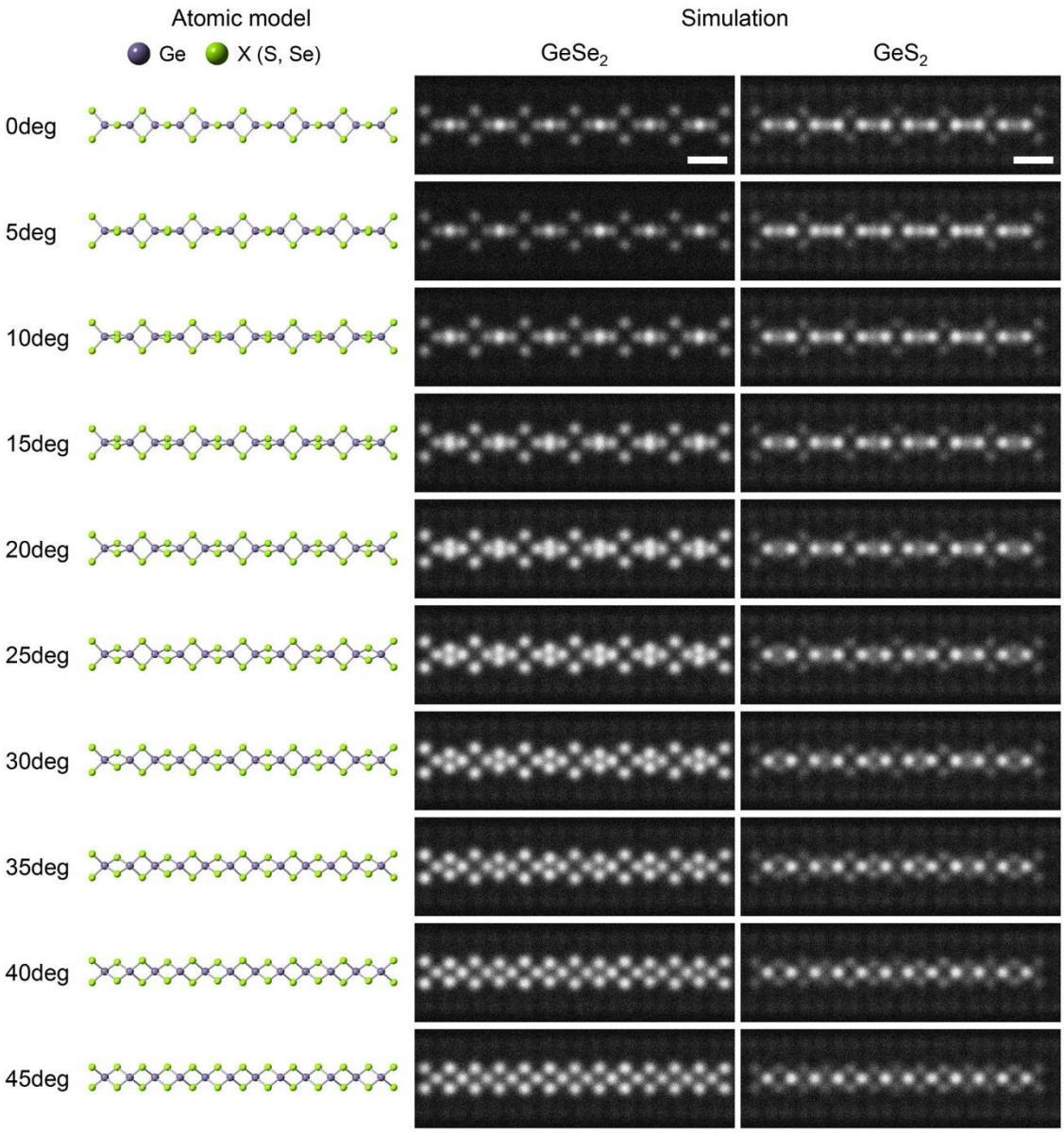
Supporting Figure S1. Crystal structure of bulk GeX_2 (X= S, Se).



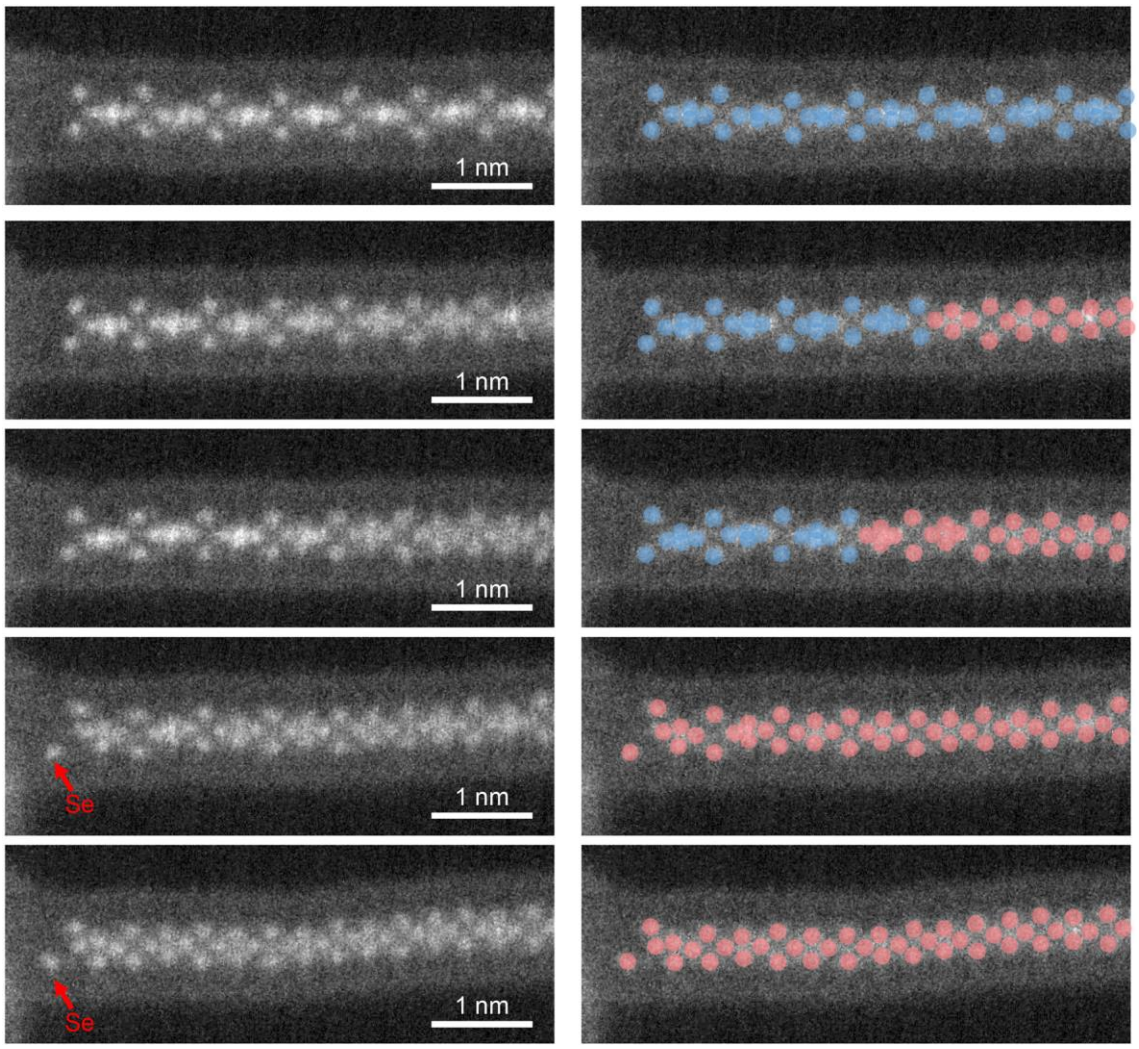
Supporting Figure S2. $GeSe_2$ inside a nanotube. EDS spectrum showing Ge and Se L- and K-edge peaks (Cu signals are from the TEM grid). The quantification based on the Ge and Se K-edges yields an atomic ratio of approximately 1 Ge:2 Se.



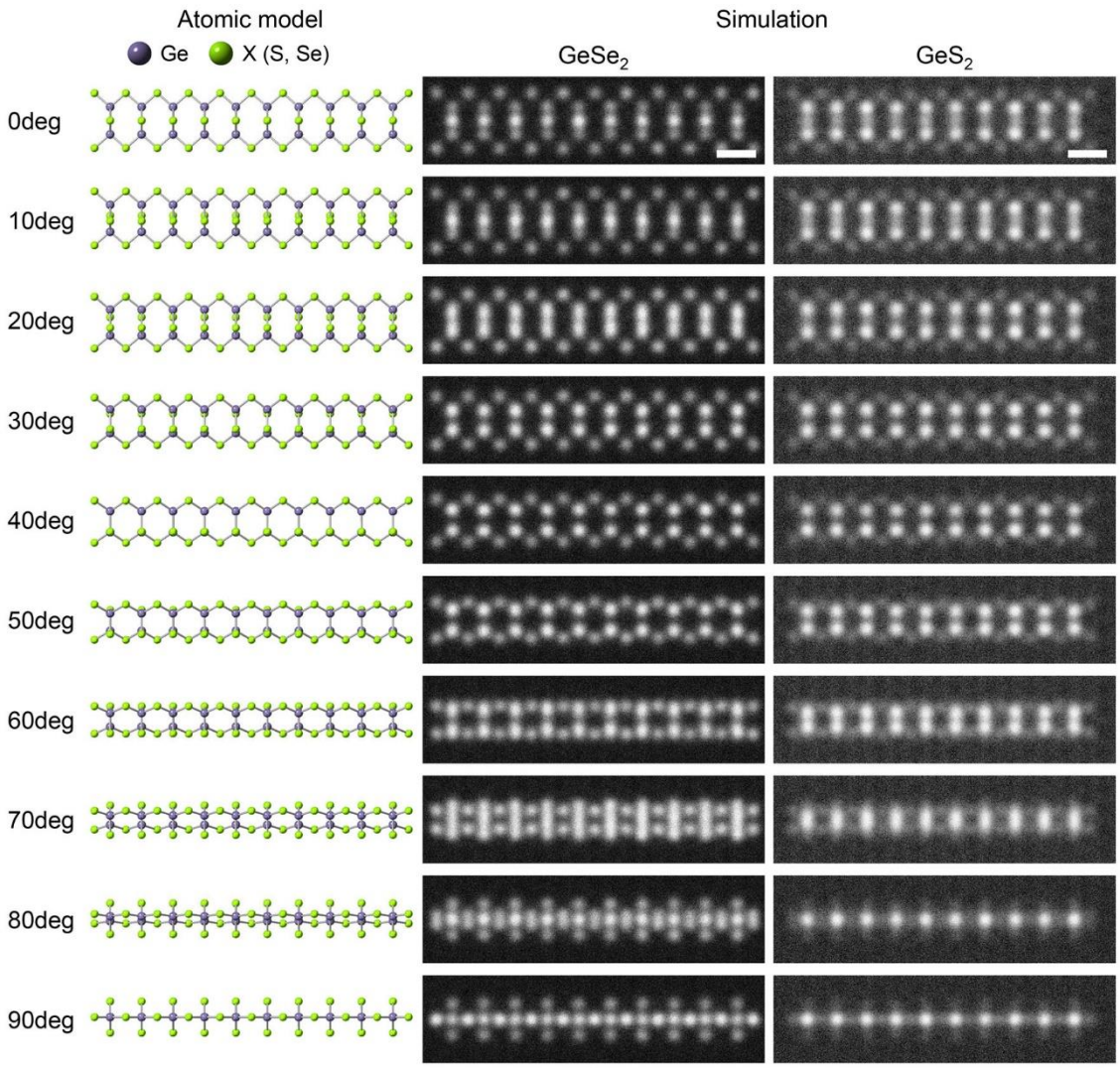
Supporting Figure S3. Type-1 1D GeS_2 chain inside a nanotube. (a) Low-magnification STEM image of GeS_2 inside nanotubes and EDS spectrum. The quantification based on Ge and S yields an atomic ratio of approximately 1 Ge:2 S. (b) Atomic-resolution image of the type-1 1D GeS_2 chain inside a nanotube.



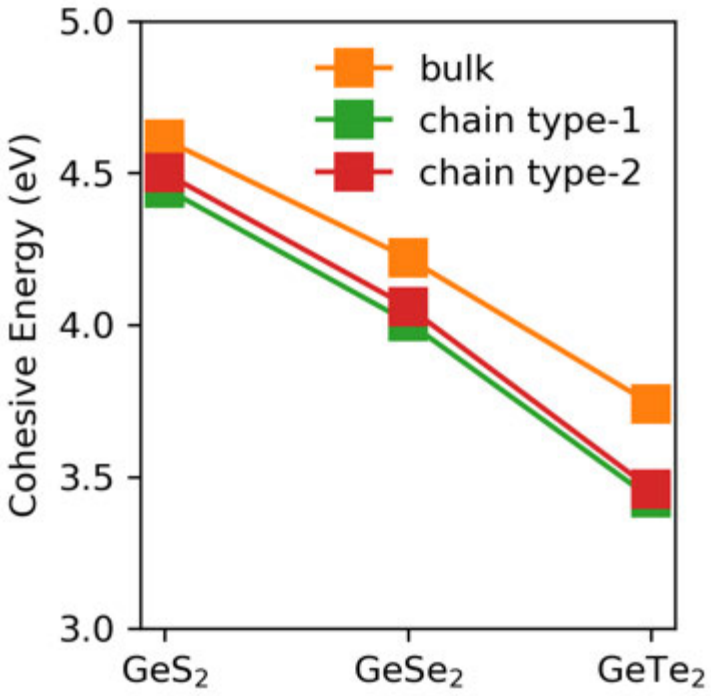
Supporting Figure S4. Simulated STEM images of type-1 $GeSe_2$ and GeS_2 with various rotation angles. Scale bar: 0.5 nm.



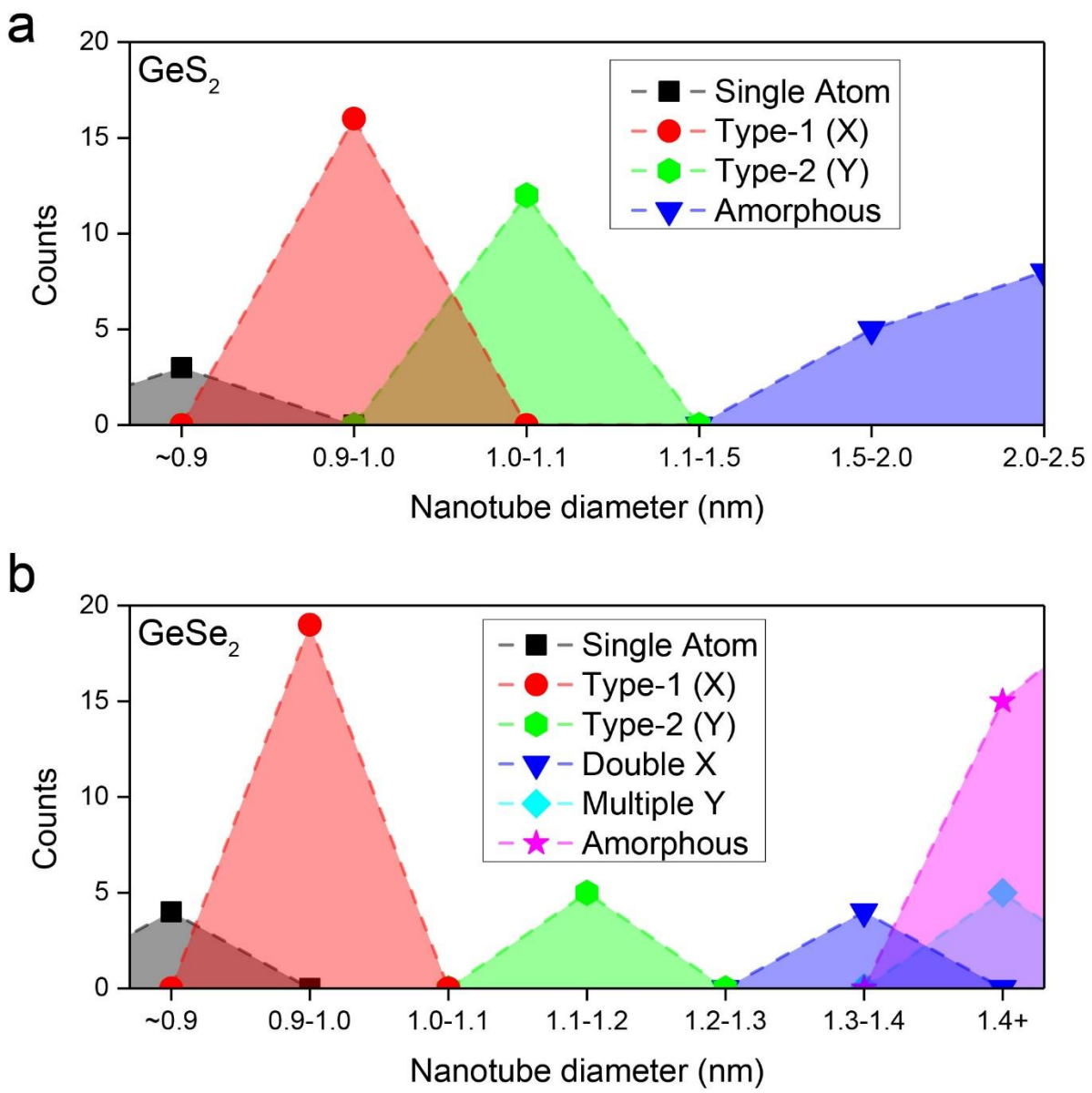
Supporting Figure S5. Sequential atomic-resolution STEM images of a type-1 1D $GeSe_2$ chain inside a nanotube. The 0° initial chain is in blue, and the 45° rotated chain is in red, with a color overlay to help distinguish the two.



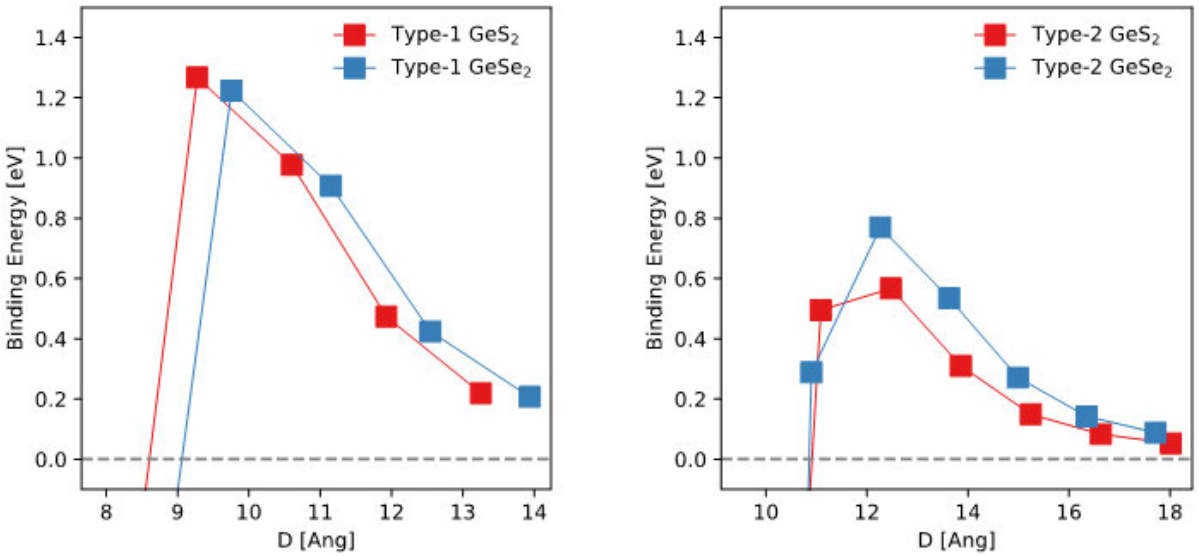
Supporting Figure S6. STEM image simulation of type-2 1D $GeSe_2$ and GeS_2 chains with various rotation angles. Scale bar: 0.5 nm.



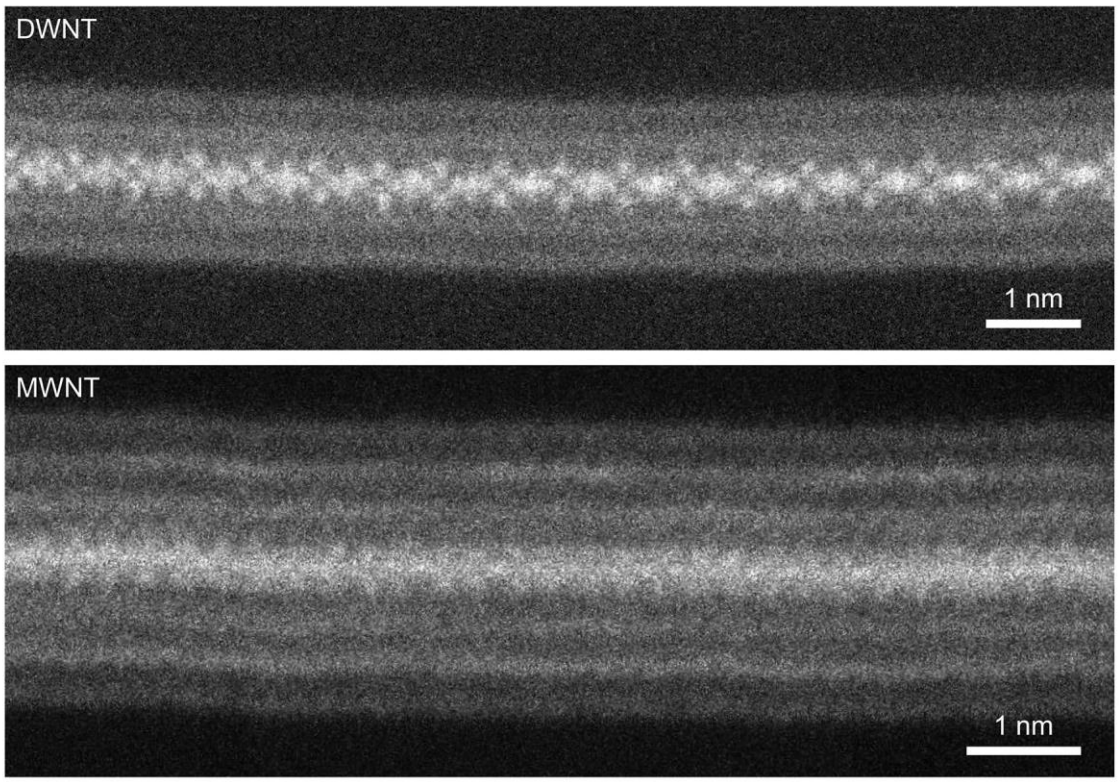
Supporting Figure S7. Calculated cohesive energy per formula unit of bulk, type-1, and type-2 GeX_2 (S, Se, Te) chain structures. The cohesive energy is calculated as $E_{\mathrm{coh}} = E_{\mathrm{Ge}} + 2 * E_{\mathrm{X}} - E_{\mathrm{GeX_2}}$, where E_{Ge} and E_{X} are the total energies of a single Ge atom and a single X atom, respectively, and $E_{\mathrm{GeX_2}}$ is the total energy per formula unit of the isolated chain.



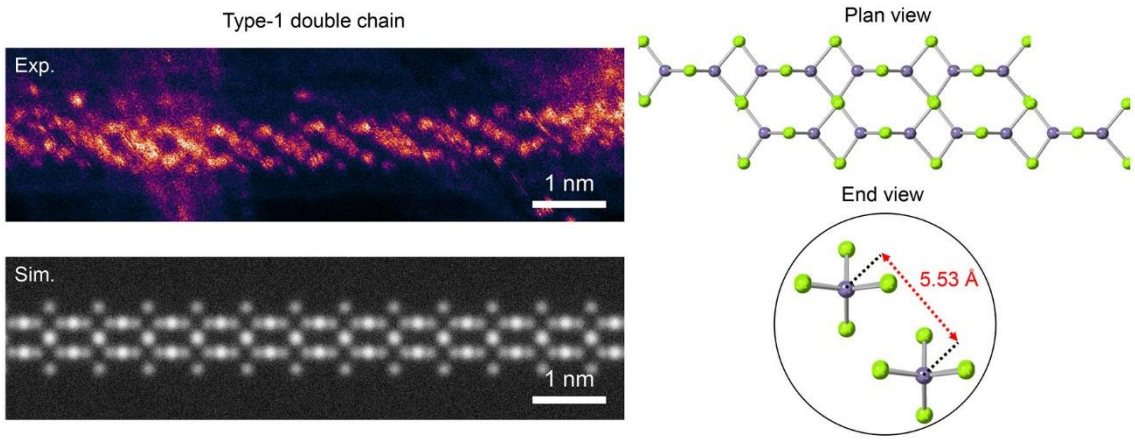
Supporting Figure S8. Occurrences of the different nanostructures as a function of the nanotube diameter for (a) GeS_2 and (b) $GeSe_2$.



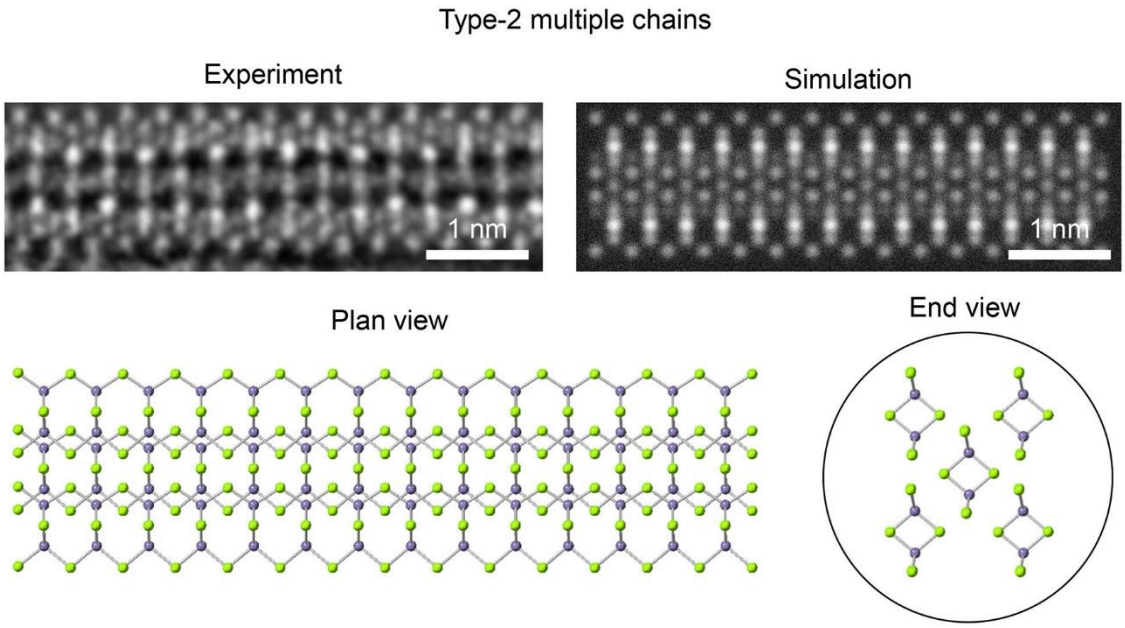
Supporting Figure S9. Calculated binding energy per formula unit of GeS_2 and $GeSe_2$. The binding energy is calculated as $E_b = E_{GeX_2} + E_{CNT} - E_{GeX_2+CNT}$, where E_{GeX_2}, E_{CNT}, and E_{GeX_2+CNT} are the total energies of the isolated GeX_2 chain, isolated CNT, and combined system, respectively.



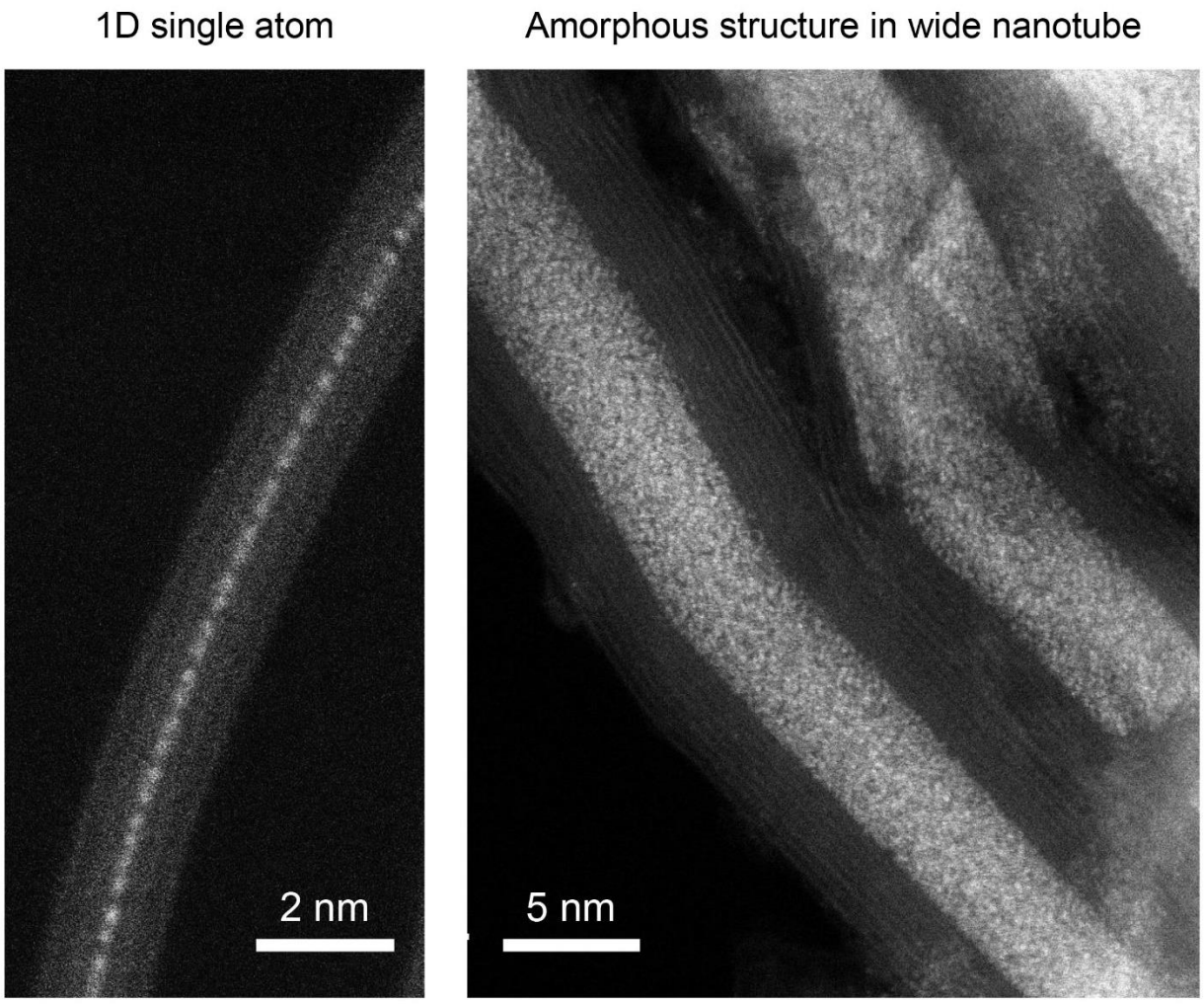
Supporting Figure S10. Type-1 1D $GeSe_2$ chains inside double-walled and multiwalled nanotubes.



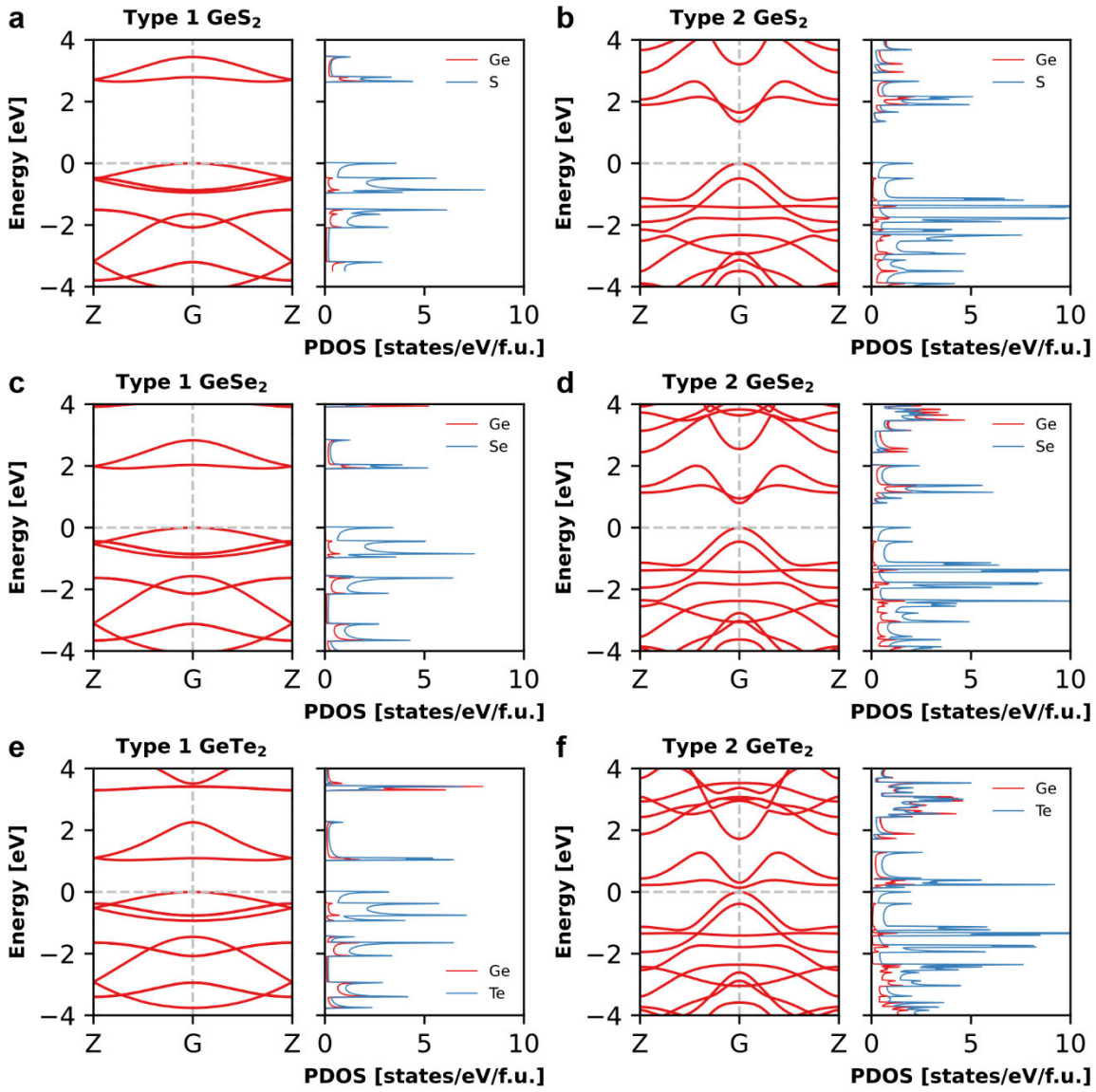
Supporting Figure S11. Type-1 $GeSe_2$ double chain inside a nanotube.



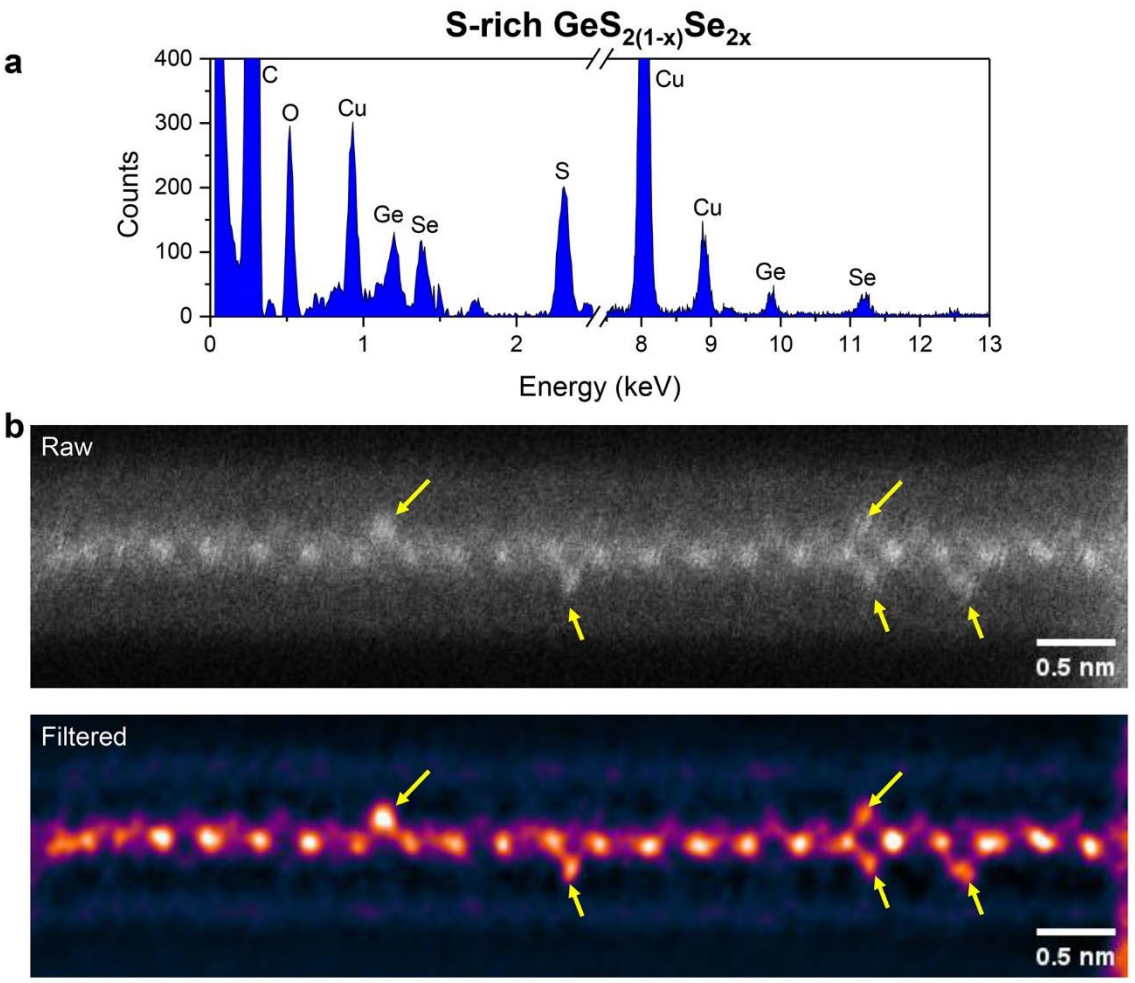
Supporting Figure S12. Multiple type-2 $GeSe_2$ chains inside a nanotube.



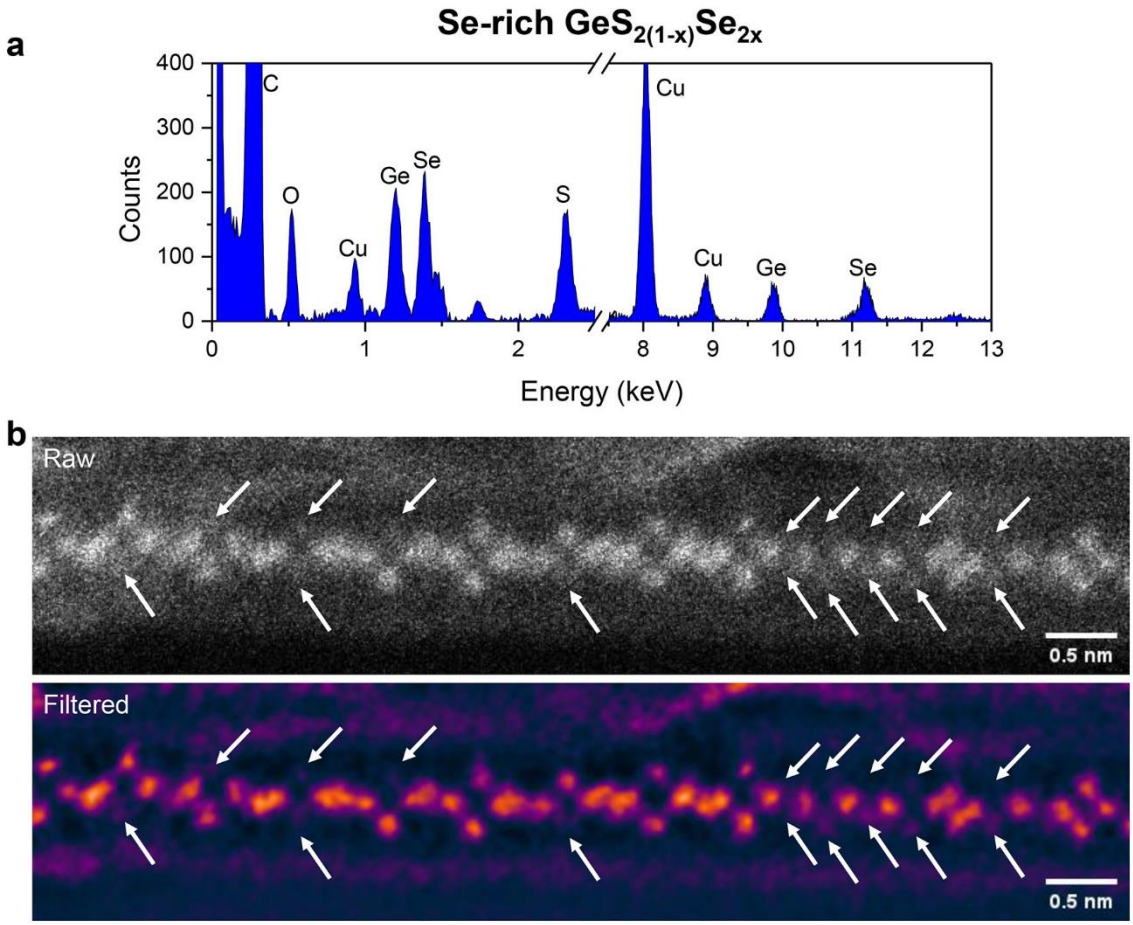
Supporting Figure S13. 1D single atomic chain inside a narrow nanotube (~0.9 nm) and amorphous structure inside wide nanotubes.



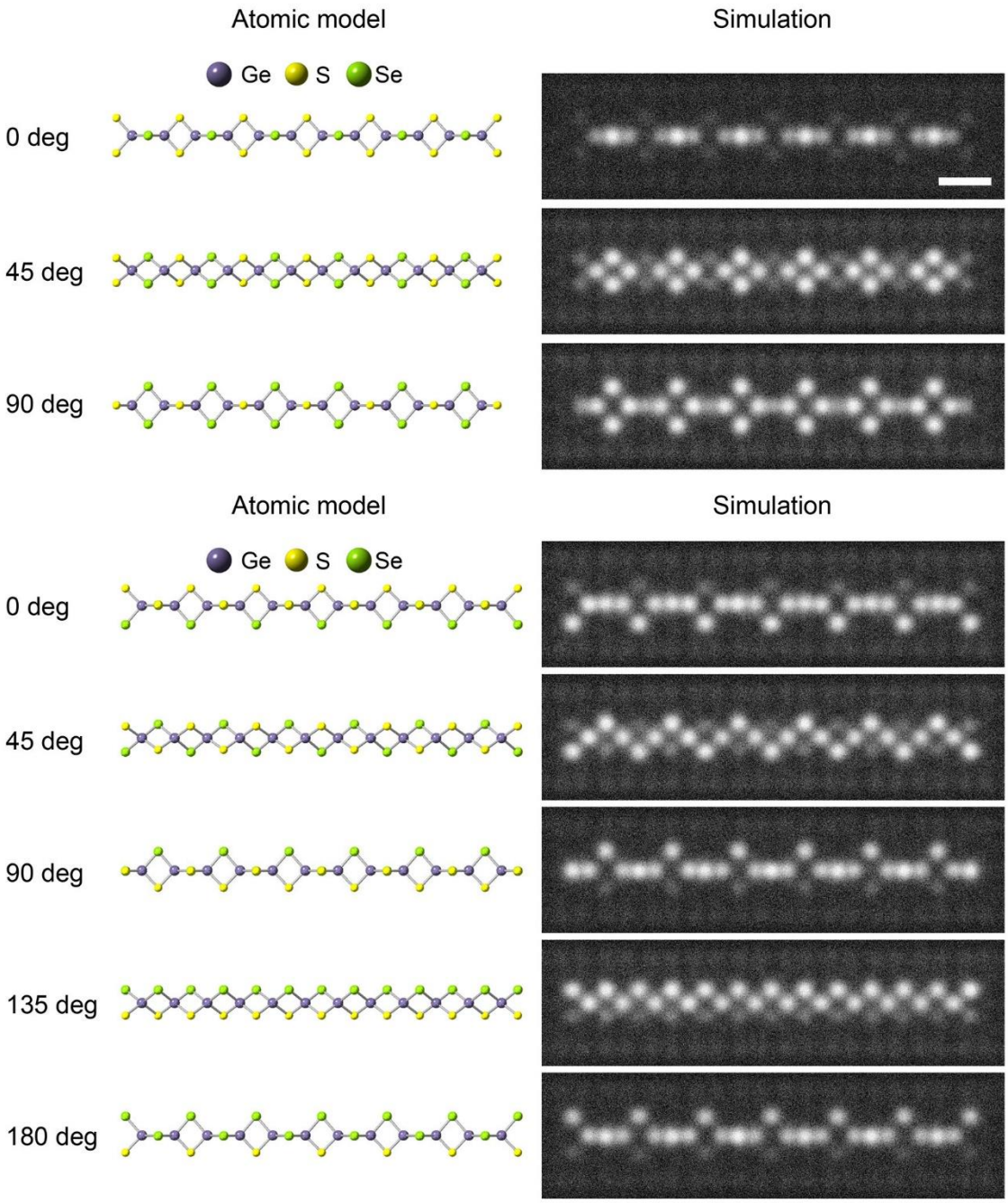
Supporting Figure S14. Calculated electronic structures of isolated single-chain GeX_2 (X=S, Se, Te). Band structure and PDOS for isolated single-chain (a) type-1 GeS_2, (b) type-2 GeS_2, (c) type-1 $GeSe_2$, (d) type-2 $GeSe_2$, (e) type-1 $GeTe_2$, and (f) type-2 $GeTe_2$. The Fermi level is set to zero energy and marked with a horizontal dashed line.



Supporting Figure S15. Atomic-resolution image of a type-1 1D S-rich $GeS_{2(1-x)}Se_{2x}$ chain inside a nanotube. (a) EDS spectrum of the 1D S-rich $GeS_{2(1-x)}Se_{2x}$ chain. The quantification based on Ge, S, and Se yields an atomic ratio of approximately 1 Ge:1.4 S: 0.6 Se. (b) Atomic-resolution image of the 1D S-rich $GeS_{2(1-x)}Se_{2x}$ chain inside a nanotube. Se atom positions are marked by yellow arrows.



Supporting Figure S16. Atomic-resolution image of a type-1 1D Se-rich $GeS_{2(1-x)}Se_{2x}$ chain inside a nanotube. (a) EDS spectrum of the 1D Se-rich $GeS_{2(1-x)}Se_{2x}$ chain. The quantification based on Ge, S, and Se yields an atomic ratio of approximately 1 Ge:0.8 S: 1.2 Se. (b) Atomic-resolution image of the 1D Se-rich $GeS_{2(1-x)}Se_{2x}$ chain inside a nanotube. S atom positions are marked by white arrows.



Supporting Figure S17. Simulated STEM images of a type-1 1D $GeS_{2(1-x)}Se_{2x}$ chain inside a nanotube. Two different atomic models with x=0.5 were used for the simulations. Scale bar: 0.5 nm.