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

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ABSTRACT

The packing and connectivity of tetrahedral units are central themes in the structural and electronic properties of a host of solids. Here, we report one-dimensional (1D) chains of GeX_2 ($\text{X} = \text{S}$ or Se) with modification of the tetrahedral connectivity at the single-chain limit. Precise tuning of the edge- and corner-sharing modes between GeX_2 blocks is achieved by diameter-dependent 1D confinement inside a carbon nanotube. Atomic-resolution scanning transmission electron microscopy directly confirms the existence of two distinct types of GeX_2 chains. Density functional theory calculations corroborate the diameter-dependent stability of the system and reveal intriguing electronic structure that sensitively depends on tetrahedral connectivity and composition. $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ compound chains are also realized, which demonstrate the tunability of the system's semiconducting properties through composition engineering.

KEYWORDS: One-dimensional materials, Germanium dichalcogenide, Atomic chain, Nanotubes, Transmission electron microscopy

INTRODUCTION

The packing and connectivity of tetrahedra in solids play essential roles in various fields of research and industrial applications.¹⁻³ In particular, tetrahedral systems with the AX_2 stoichiometry (A=Si, Ge; X = O, S, Se) are interesting systems with tunable connectivity between tetrahedra and have played an important role in materials science, especially in semiconductor technologies.^{4, 5} In these systems, the short-range atomic ordering is often described by structural units of $A(X_{1/2})_4$ tetrahedra, and the edge/corner sharing between these building blocks determines the long-range ordering with various structural phases and complexities.⁶⁻¹³ For example, SiO_2 displays oxygen-corner-sharing modes between SiO_4 tetrahedra, and a slight modification of its connectivity results in several distinct crystalline phases of quartz or silica glass networks.¹⁴ In addition, the tetrahedral connectivity can also be substantially altered by changing the atomic constituents or adjusting the temperature and pressure.¹⁵⁻¹⁸ Therefore, the connectivity between tetrahedral building blocks serves as a key parameter to understand the structural complexity.

One way to tune the connectivity between tetrahedra and the packing is through the dimension-reduction effect induced by geometrical confinement. For example, previous studies have indicated that silica can be stabilized in the two-dimensional (2D) limit.^{19, 20} Similarly, one-dimensional (1D) confinement inside carbon nanotubes (CNTs) or boron nitride nanotubes (BNNTs) may be utilized to pack tetrahedral building blocks and realize crystalline phases with modified connectivity. Previous studies have indeed demonstrated the synthesis and stabilization of various materials inside nanotubes, including carbon nanomaterials, pnictogens (P, As, and Sb), halides, and transition metal chalcogenides.²¹⁻³² Although these studies have shown interesting quasi-1D nanostructures and physical properties,^{24, 27, 29, 31, 33-35} packing of tetrahedral

building blocks has yet to be reported. Transition metal chalcogenides with octahedral building blocks have been encapsulated in nanotubes^{30, 36}, but the tuning of the octahedral connectivity is limited due to the isotropic bonding nature.

Here, we report the discovery of crystalline phases of 1D tetrahedral chains of GeX_2 ($\text{X}=\text{S}, \text{Se}$) with modified tetrahedral connectivity in the single-chain limit. GeX_2 , as an archetype member of the tetrahedral AX_2 family, was chosen to explore the tunable connectivity between tetrahedra in the confined space of a CNT. Atomic-resolution scanning transmission electron microscopy (STEM) imaging and simulation clearly identify different chain structures. The identified type-1 GeX_2 chain structure is a tetrahedral chain structure composed solely of edge-sharing modes, and the type-2 chain shows both edge and corner-sharing modes. Precise tuning of the edge- and corner-sharing modes of GeX_2 is achieved by the diameter-dependent 1D confinement effect. Density functional theory (DFT) calculations support the stability of the system and predict that electronic structures of GeX_2 chains are also strongly affected by its tetrahedral connectivity and composition. Additionally, we demonstrate synthesis of 1D $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ ternary chains with a controllable alloy composition without compromising the modified tetrahedral connectivity. First-principles calculations support the stability of the system and the widely tunable electrical properties of the 1D tetrahedral GeX_2 chains via the control of the tetrahedral connectivity and substitution.

RESULTS AND DISCUSSION

Bulk crystalline GeSe_2 and GeS_2 are known to form a 2D layered structure with a relatively complex structure due to the local connectivity between tetrahedra (the crystal structures are shown in Supporting Fig. S1).^{13,14} Each layer is composed of repeated corner- and edge-sharing

GeX₄ tetrahedra. In each layer, the ratio of edge-shared and only-corner-shared tetrahedra is 1:1. The ratio of corner- and edge-sharing tetrahedra plays a critical role in the GeX₂ structure, such as the formation of an amorphous network structure.¹² For our experiments, GeX₂ chains are synthesized by vacuum annealing GeX₂ precursors in the presence of open-ended nanotubes at temperatures close to the melting point of the precursors (see the Methods section for more details). The samples are examined using transmission electron microscopy (TEM) to confirm that the target material was successfully filled inside the nanotubes. Upon examination, approximately 90% of the nanotubes are filled, with the total length of the chains ranging from 100 nm to over 1 μm (Supporting Fig. S2). Chemical analysis of the encapsulated GeSe₂ chains using energy-dispersive spectroscopy (EDS) confirms a composition of 34.4 ± 1.2 atomic percent (at%) Ge and 65.6 ± 1.8 at% Se. The atomic structure of the filled material is further investigated using aberration-corrected STEM with an annular dark field (ADF) detector.

Figure 1a shows an atomic-resolution ADF-STEM image of a GeSe₂ chain encapsulated within a nanotube with an inner diameter of 1.0 nm. In the ADF-STEM image, the contrast is proportional to the atomic number (Z-contrast); thus, Se (Z=34) exhibits a slightly higher signal than Ge (Z=32). The same atomic ratio and structure are also observed for GeS₂ encapsulated within a nanotube (Supporting Fig. S3), in which Ge appears brighter than S because S (Z = 16) has a lower atomic number than Ge (Z = 32).

Based on the observed STEM images (Figs. 1b and 1c), GeX₂ tetrahedral building blocks share edges to form a chain within a nanotube, which we refer to as the type-1 structure. Figure 1b illustrates the overall structure of the 1D GeX₂ chain within the nanotube, while Figure 1c shows a detailed view of the edge-sharing GeX₂ tetrahedral unit cell. The lattice constant of the GeX₂ tetrahedral block (motif) varies depending on the chalcogen element (S or Se) due to differences

in the bond length between Ge and the chalcogen. The measured lattice constants are 6.3 Å (x-axis) and 3.6 Å (y-axis) for GeSe₂ and 6.0 Å (x-axis) and 3.4 Å (y-axis) for GeS₂, which are in good agreement with the relaxed structure obtained through density functional theory (DFT) calculations. The optimized lattice parameters are 6.01 Å and 3.52 Å for GeS₂ and 6.32 Å and 3.71 Å for GeSe₂. The bond length is 2.28 Å for Ge-S and 2.42 Å for Ge-Se. The STEM images simulated based on our DFT calculations are in good agreement with the experimental STEM images, as seen in Fig. 1d and Fig. 1e.

During TEM/STEM imaging, electron-beam stimulation can cause the chains inside the tube to rotate or move axially along the core of the tube.³² This motion can be used to great advantage. The rotated chains facilitate three-dimensional (3D) structural analysis by providing various projection images without the need to tilt the entire sample. We simulate STEM images with different rotation angles of the type-1 1D chain structure inside the nanotube, as shown in Supporting Fig. S4. Sequential STEM images are captured, showing the type-1 1D GeSe₂ chains freely rotating inside the nanotubes (Supporting Fig. S5), in which the tetrahedral GeSe₂ chain structure initially at 0° is rotated by 45° during the imaging. Despite the rotation caused by the electron beam, the chain structure itself is observed to remain constant, with the end of the chain still terminating in Se. Figures 1g-i show representative examples of the 45° rotated type-1 GeSe₂ and GeS₂ chain structures within nanotubes, which well match the simulated STEM images.

The confinement effect of the nanotube diameter can modify the tetrahedral connectivity, yielding a different chain structure. Inside a CNT with a slightly larger diameter (1.0~1.2 nm), another form of the chain structure, which we name type-2, is formed. In type-2, the building blocks are connected along the perpendicular direction compared to type-1, resulting in a chain structure with edge and corner-sharing. Figures 2a and 2b show the atomic model and an STEM

image of the type-2 GeX_2 single chain. The type-2 GeX_2 chain is made up of a 1D chain composed of edge-sharing GeX_4 tetrahedral units (motifs) connected through corner sharing (y-direction in Fig. 1c). A comparison of Figures 2c and 2d shows good agreement between the experimental and simulation results. The type-2 chain can also easily rotate inside the nanotube during STEM imaging, and the projected atomic-resolution STEM images show significant differences as a function of the rotation angle (Supporting Fig. S6). Experimental STEM images and simulated images along different projection directions show excellent agreement, confirming the three-dimensional structure of type-2 GeSe_2 and GeS_2 single chains inside the nanotubes. We find that the type-2 GeX_2 chains can be stabilized within nanotubes 1.0~1.2 nm in diameter, highlighting the significant impact of geometrical confinement on the tetrahedral connectivity.

To the best of our knowledge, the observed type-1 and type-2 1D GeX_2 single-chain structures have not been previously reported. Our calculations reveal that both the type-1 and type-2 chain structures exhibit similar structural stability compared to that of the bulk structure (Supporting Fig. S7). We also note that the edge-sharing type-1 tetrahedral chain structure has been reported in SiX_2 compounds; however, the isolation of a 1D SiX_2 in the single-chain limit has yet to be reported. Considering the poor air stability of SiX_2 ,³⁷ encapsulation in a CNT may be a good way to synthesize 1D structures protected from environmental instability.

As the diameter of the nanotube plays a crucial role in determining the structure within it induced by geometrical confinement, we evaluated the frequency of experimental observation of the various phases of GeS_2 and GeSe_2 as a function of the nanotube diameter (Supporting Fig. S8). We also calculate the binding energy of single-chain GeX_2 with the encapsulating nanotube as

$$E_b = E_{iX_2} + E_{CNT} - E_{iX_2+CNT}, \quad (1)$$

where E_{GeX_2} , E_{CNT} , and $E_{\text{GeX}_2+\text{CNT}}$ are the total energies of the isolated GeX₂ chain, isolated CNT, and combined system, respectively. Supporting Fig. S9 shows the calculated binding energy as a function of the nanotube diameter. We find that type-1 chains are most stable within approximately 0.9 nm nanotubes, while type-2 chains are most stable within 1.2 nm nanotubes. In our calculations, there is no charge transfer between GeX₂ chain and nanotube, indicating that the interaction between the chain and nanotube is mostly of van der Waals character. Our calculations are in line with experimental evidence that shows the appearance of different chains depending on the diameter of the nanotube. This is consistent with previous studies^{24-26, 31, 33, 34, 38-40}, which indicate that the nanotube diameter is the primary factor in determining the confined structure, rather than the number of walls. Supporting Fig. S10 illustrates that identical type-1 GeSe₂ chains can be found inside double-walled and multiwalled nanotubes with an inner diameter of approximately 1.0 nm.

Furthermore, we observe various structural variations that correlate with the nanotube diameter, which agrees with prior research^{24-26, 31, 33, 34, 38-40}. For ultranarrow nanotubes with an inner diameter less than 0.9 nm, we observe the presence of 1D single atomic chains, as reported in several previous studies^{24-26, 31, 33-35, 38-40}. The stacking structure of multiple type-1 or type-2 chains can be stabilized within larger diameter nanotubes, as shown in Supporting Fig. S11 and Fig. S12. Inside relatively wide nanotubes (typically larger than 1.2 nm), amorphous-type structures are found, as shown in Supporting Fig. S13. The formation of amorphous structures in large-diameter nanotubes can be attributed to the variation in the ratio of corner-sharing and edge-sharing GeX₄ tetrahedra.¹² As the number of corner-sharing tetrahedra increases, the network becomes more flexible and forms an amorphous structure.¹⁶ GeX₂ encapsulated within a

nanotube is therefore considered an ideal system for studying Ge-chalcogenide amorphous structures. Further microscopic studies, such as directly observing the change in the ratio of corner-sharing and edge-sharing tetrahedra under external stimuli (e.g., in situ heating), are needed.

We investigate the electrical properties of isolated GeX_2 chains and those encapsulated within CNTs by first-principles calculations. Supporting Fig. S14 shows the electronic structures of isolated single-chain GeX_2 . All the chains are semiconducting, and type-1 (type-2) chains have an indirect (direct) band gap. DFT band gaps are 2.64 (1.35), 1.92 (0.79), and 1.03 (0.13) eV for type-1 (type-2) GeS_2 , GeSe_2 , and GeTe_2 chains, respectively. For both types of chains, the size of the band gap is the largest for GeS_2 and decreases when changing to Se and then Te. The projected density of states (PDOS) shows that the valence bands mostly consist of chalcogen atomic orbitals, whereas the conduction bands have contributions from both Ge and chalcogen atoms.

For single-chain GeX_2 encapsulated within the CNT system, we construct appropriate supercells to match the periodicity of the GeX_2 chain and CNT along the chain direction with less than 3% strain applied to the CNT. We use an (8,8) CNT for type-1 and a (9,9) CNT for type-2. Then, the atomic positions of GeX_2 are relaxed while those of the CNT are fixed. Figure 3 shows the band structure, PDOS, and conduction/valence band wavefunctions of single-chain GeX_2 encapsulated within CNTs. We find that encapsulation does not significantly alter the atomic and electronic structures, with no charge transfer between the GeX_2 chain and CNT. All the GeX_2 states remain semiconducting. When we compare GeS_2 and GeSe_2 , the conduction band energies relative to the Dirac point of the CNT are nearly the same, but the valence bands are higher in energy for GeSe_2 than GeS_2 for both chain types.

Type-1 chains are indirect-band-gap semiconductors with large effective masses (Table 1). The valence band wavefunction of the type-1 chain has no contribution from Ge atoms and consists of only Se $4p$ orbitals pointing in the transverse direction relative to the chain axis (Fig. 3d). In the conduction band state of the type-1 chain, the two Ge $4s$ orbitals within a primitive unit cell of GeX_2 have opposite phases, and the Se $4p$ orbitals are directed toward the chain axis (Fig. 3c). In this case, the direct hopping between Ge $4s$ orbitals and the indirect hopping mediated by Se $4p$ orbitals destructively interfere, resulting in a very narrow conduction bandwidth. In contrast, Figures 3e and 3f show that type-2 GeX_2 chains have direct band gaps and highly dispersive band-edge states with small effective masses (Table 1). The valence band states are composed of p orbitals of the inner Se atoms, and the conduction band states are from Ge and the outer Se atoms (Figs. 3g and 3h).

Manipulating the alloy composition of semiconductor materials is crucial for tuning their optical and electronic properties. We also synthesize $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ ternary single chains inside nanotubes with a controllable alloy composition, as shown in Figure 4. We successfully tuned the atomic ratio of S and Se by varying the precursor ratio during synthesis. For example, a 1.4:0.6 ratio for the S-rich sample ($x=0.3$) and a 0.8:1.2 ratio for the Se-rich sample ($x=0.6$) are confirmed by EDS quantitative analysis (Supporting Figs. S15 and S16). Figures 4a and 4b show atomic-resolution STEM images and atomic models of type-1 $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ single chains with different S/Se ratios in nanotubes. The contrast between Se and S atoms is clearly visible in the ADF-STEM images, with the brighter Se atoms being distinguishable from the darker S atoms. The STEM image simulation of the type-1 $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ single chain also clearly displays a distinguishable image contrast, as shown in Supporting Fig. S17. As expected from our synthesis

method were S and Se are simultaneously present in the reaction vessel, the distribution of S and Se along the chains is random.

Finally, we calculate the composition-dependent electronic structures of $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ based on the virtual crystal approximation (VCA). To account for the structural changes as a function of the composition, we linearly interpolate the lattice parameters and atomic positions between those of isolated GeS_2 and GeSe_2 chain structures at a given mixing ratio. Then, the VCA potential is generated by mixing the pseudopotentials of S and Se. Figure 4c shows the calculated band gap with respect to the composition. For both type-1 and type-2 chains, the band gap linearly decreases as the Se concentration increases, and it reaches the band gap of GeSe_2 . This result demonstrates that the band gap of the 1D germanium chalcogenide ternary single chain can be tuned by controlling the alloy composition.

CONCLUSIONS

In conclusion, we report the discovery of 1D tetrahedral GeX_2 single-chain structures with a sharing mode modified by encapsulation within nanotubes. Our findings reveal that the inner diameter of the encapsulating nanotube is the determining factor for forcing a connectivity between GeX_2 tetrahedral building blocks. We also demonstrate the possibility of synthesizing and controlling the composition of the $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ ternary chain, leading to the potential for wide tunability of the semiconducting properties through structural and composition engineering. Our study provides further groundwork for the study of low-dimensional tetrahedral systems and confinement-stabilized materials in nanotubes, offering opportunities for future research and applications in various fields.

METHODS

Material Synthesis: CNTs were purchased from Sigma–Aldrich (single-walled: 704113, multiwalled: 698849) and CheapTubes (90% SW-DW CNTs). The nanotubes were annealed in air at 510 °C for 10~30 minutes to open the end caps before the filling step.²⁷ GeS₂ and GeSe₂ powders were purchased from Ossila. The as-prepared CNTs (~3 mg) together with precursor materials (~30 mg) were sealed under high vacuum (~10⁻⁶ torr) in a 6 mm diameter and 15 cm long quartz ampoule. The sealed ampoule was kept at 600~700 °C in a single zone box furnace for 2 days and then cooled to room temperature over 1 day. The as-synthesized materials were dispersed in isopropanol by a bath sonicator for 15 minutes and then drop-cast onto lacey carbon TEM grids for TEM/STEM characterization.

TEM/STEM Imaging and Simulations: Preliminary sample screening was performed using a JEOL 2010 microscope operated at 80 kV. Atomic-resolution ADF-STEM images were acquired by the double spherical (Cs) aberration-corrected JEOL ARM-200F and TEAM 0.5 at the National Center for Electron Microscopy (NCEM). The JEOL ARM-200F was operated at 80 kV with a 23 mrad convergence angle and collection semiangles from 40 to 160 mrad. The TEAM 0.5 was operated at 80 kV with a semiconvergence angle of 30 mrad and collection semiangles from 37 to 187 mrad.

STEM image simulations were performed using MacTempas software, which implements multislice calculations for high-resolution (HR)-STEM imaging. STEM simulation parameters similar to the parameters in the experiments (i.e., a probe semiangle of 23 mrad or 30 mrad, 0.05 Å/pixel sampling, and 10 frozen phonon calculations) were used for each simulation. Image analysis and processing were performed using ImageJ software. The average-cell calculation was performed with the template matching technique to increase the signal-to-noise ratio and quality of the STEM image.⁴¹

Calculations: We perform first-principles DFT calculations as implemented in SIESTA.⁴² We use the Perdew-Burke-Ernzerhof (PBE) functional⁴³, norm-conserving pseudopotentials⁴⁴, and a localized pseudoatomic orbital basis. Van der Waals interactions are included within the Grimme-D2 scheme.⁴⁵ A real-space mesh cutoff of 500 Ry is used. We use a 25 Å thick cell along the transverse vacuum direction. The primitive Brillouin zone of isolated GeX₂ chains is sampled by 8 k points, and the number of k points is proportionally reduced in supercell

calculations. The atomic positions of GeX₂ chains are optimized with a force threshold of 0.01 eV/Å, while carbon atoms in encapsulating CNTs are fixed.

To calculate the unfolded band structure, we calculate the unfolding weight $w_{nk}^{unfold} = \sum_{G_{PUC}} |(k+G_{PUC}|\psi_{nk})|^2$, where ψ_{nk} is a Bloch state obtained from a supercell calculation, which contains both GeX₂ and CNT, and G_{PUC} is a reciprocal lattice vector for the primitive unit cell of either GeX₂ or CNT. Then, to distinguish GeX₂ and CNT states, we multiply the unfolding weight by the orbital projection weight $w_{nk}^X = \sum_{i \in X} \sum_j S_{ij}(k) c_{nk,i}^i c_{nk,j}$, where $S_{ij}(k)$ is the overlap matrix, $c_{nk,i}$ is the wavefunction coefficient for the i th orbital, and X refers to a subsystem that is either GeX₂ or CNT.

We use the virtual crystal approximation (VCA) to calculate the electronic structure of GeS_{2(1-x)Se_{2x}} chains. For a given mixing ratio x , we linearly mix both local and non-local part of the pseudopotentials of S and Se: $V_{S_{1-x}Se_x} = (1-x)V_S + xV_{Se}$, where V_S and V_{Se} are the pseudopotentials of S and Se, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/...>

Crystal structure of bulk GeX₂, extra experimental STEM characterizations of samples including atomic-resolution images, EDX spectra and sequential STEM images, simulated STEM images with various rotation angles, histogram of the different nanostructures as a function of the nanotube diameter, and DFT-calculations including cohesive energy, binding energy, and electronic structures. (PDF)

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Author Contributions

†Y.L. and Y.W.C. contributed equally to this work.

Author Contributions

Y.L. and A.Z. conceived the idea; Y.L. synthesized the materials; Y.L., K.L., C.S. and P.E. performed transmission electron microscopy data acquisition, image simulation, and analysis. Y.W.C. and M.L.C. carried out density functional calculations. Y.L., Y.W.C., M.L.C., K.K, and A.Z. wrote the manuscript with input from all authors.

Notes

The authors declare no competing interests.

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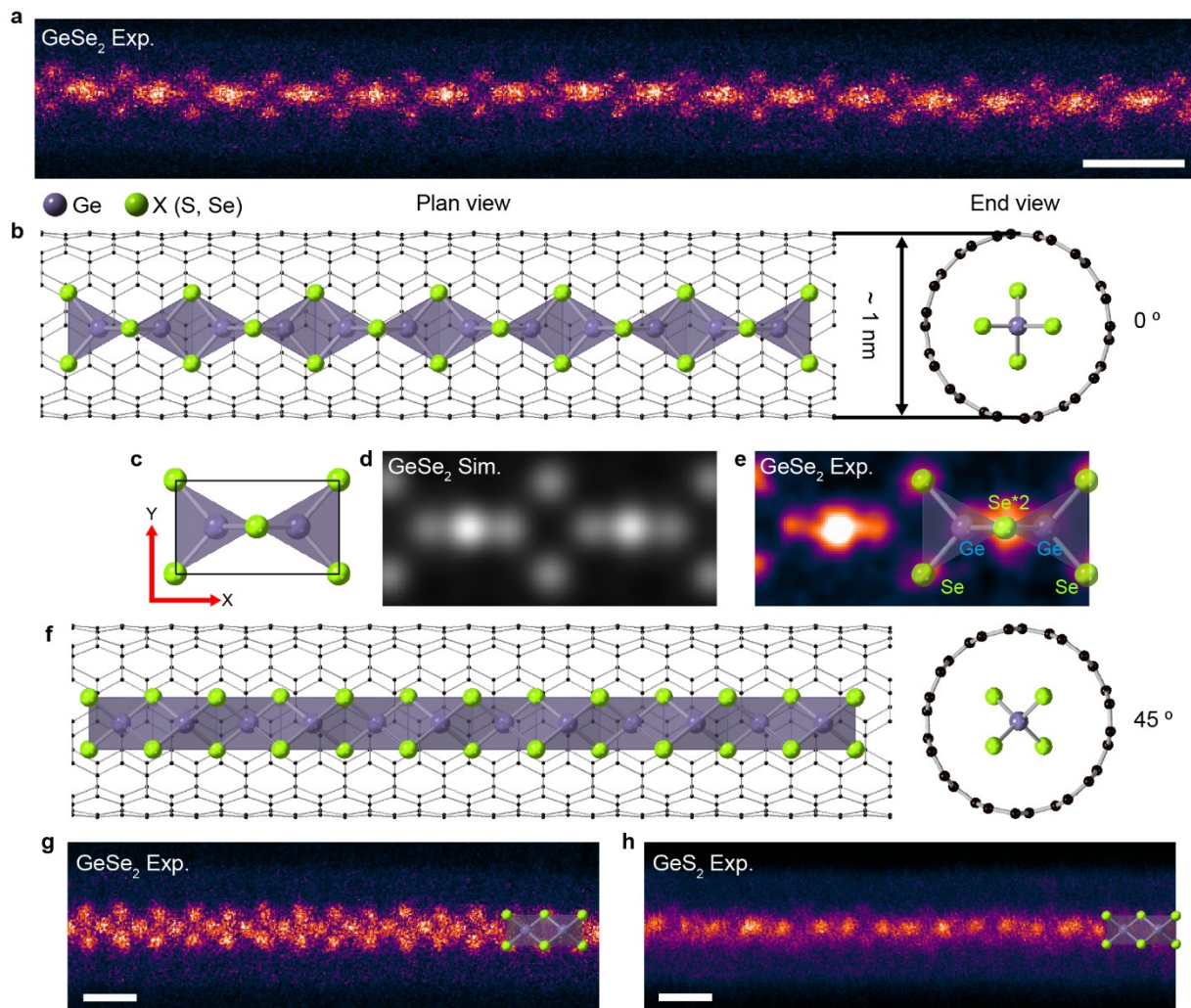


Figure 1. Type-1 1D tetrahedral GeX_2 single chain inside a nanotube. (a) Aberration-corrected ADF-STEM image of a type-1 tetrahedral GeSe_2 single chain encapsulated within a single-walled CNT. Scale bar: 1 nm. (b) Atomic model of the type-1 tetrahedral GeX_2 single chain inside a nanotube. (c) Edge-sharing GeX_2 tetrahedral building block unit. (d) Simulated and (e) experimental ADF-STEM image of the edge-sharing GeSe_2 tetrahedral building block. (f) Atomic model of a 45° rotated type-1 tetrahedral GeX_2 single chain. (g), (h) Experimentally observed atomic-resolution STEM images of 45° rotated type-1 1D tetrahedral (g) GeSe_2 and (h) GeS_2 single chains encapsulated inside nanotubes. Scale bar: 0.5 nm.

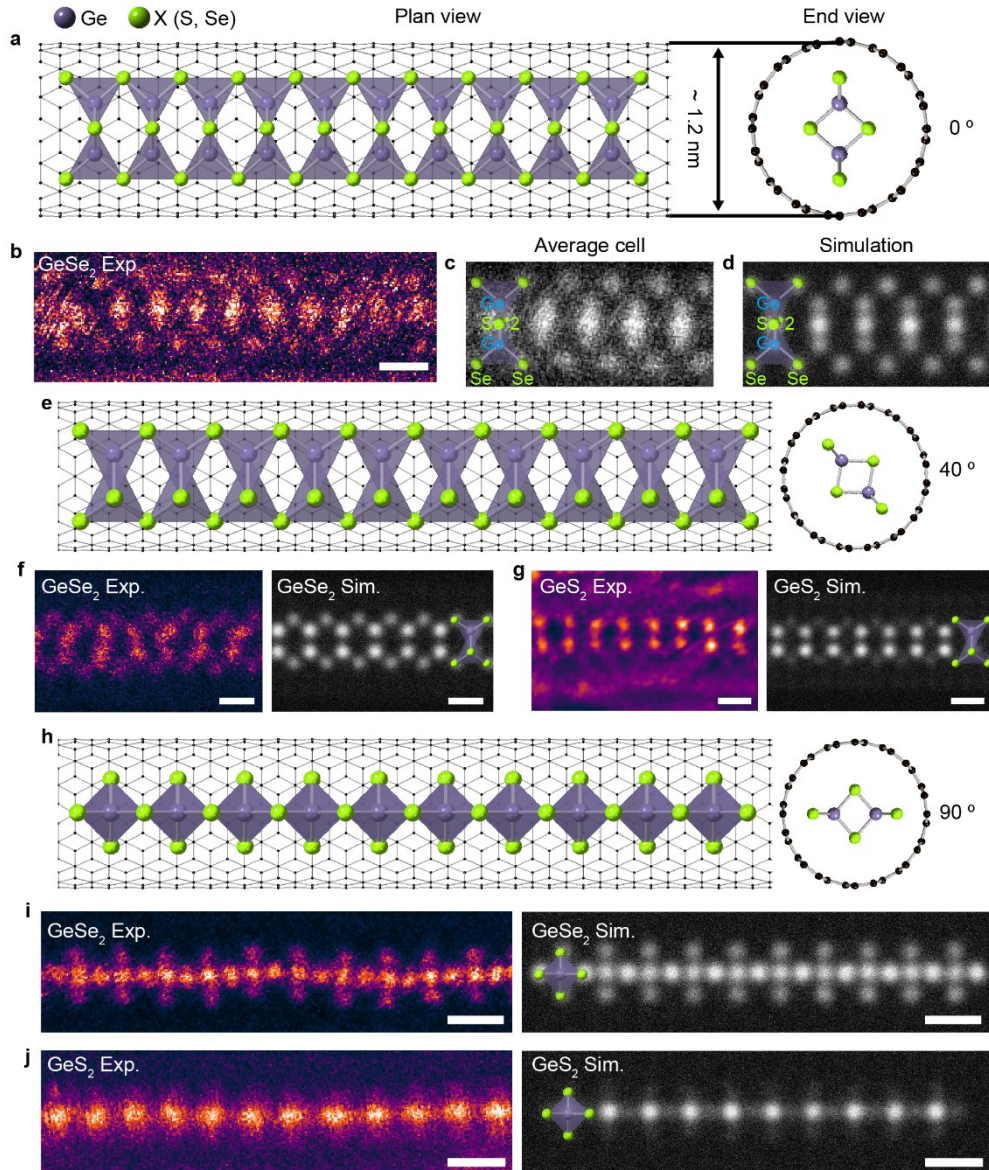


Figure 2. Type-2 1D tetrahedral GeX_2 single chain inside a nanotube. (a) Atomic model of a type-2 tetrahedral GeX_2 single chain inside a nanotube. (b) Atomic-resolution STEM image of a type-2 GeSe_2 single chain inside a nanotube. (c) Composite STEM image generated by averaging experimentally collected orientationally similar single segments (average cell). (d) Simulated STEM image produced using the proposed type-2 GeSe_2 atomic structure. (e) Atomic model of a 40° rotated type-2 1D GeX_2 single chain. (f), (g) Experimentally observed and simulated STEM images of 40° rotated type-2 1D (f) GeSe_2 and (g) GeS_2 single chains. (h) Atomic model of a 90° rotated type-2 1D GeX_2 single chain. (i), (j) Experimentally observed and simulated STEM images of 90° rotated type-2 (i) GeSe_2 and (j) GeS_2 single chains. (Scale bar: 0.5 nm.)

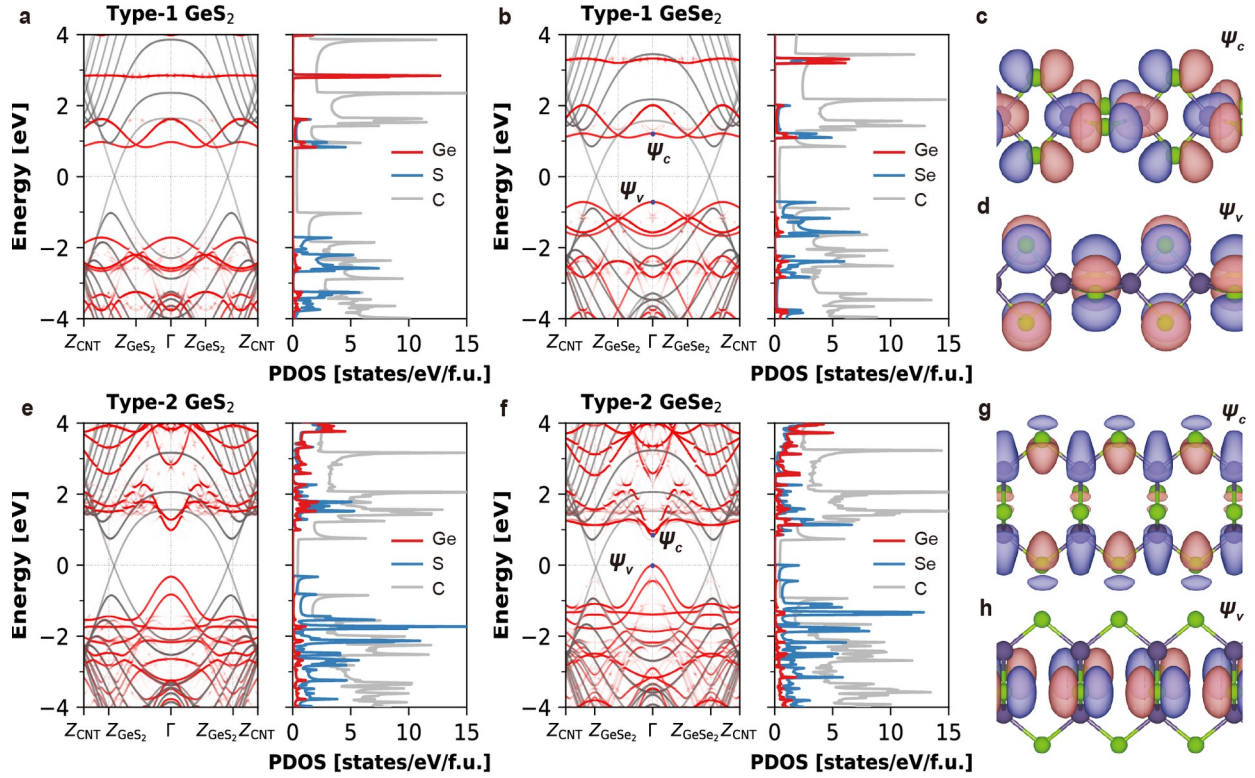


Figure 3. Calculated electronic structures of single-chain GeX_2 ($X = \text{S}$ and Se) encapsulated in CNTs. Band structure and PDOS for (a) type-1 GeS_2 and (b) type-1 GeSe_2 in (8,8) CNTs. (c) Conduction and (d) valence band wavefunctions at the Γ point for type-1 GeSe_2 . Band structure and PDOS of (e) type-2 GeS_2 (f) and type-2 GeSe_2 in (9,9) CNTs. (g) Conduction and (h) valence band wavefunctions at the Γ point for type-2 GeSe_2 . In the band structures, the zero energy is set to the Fermi level. Red and gray lines represent projected and unfolded electronic states for the GeX_2 chain and CNT, respectively. $Z_{\square_{iX_2}}$ ($Z_{\square_{CNT}}$) denotes the primitive Brillouin zone boundary for the GeX_2 chain (CNT). The PDOSs for Ge, X ($X=\text{S}$ and Se), and C atoms are represented by red, blue, and gray lines, respectively. In the wavefunction plots, carbon atoms are not displayed for clarity.

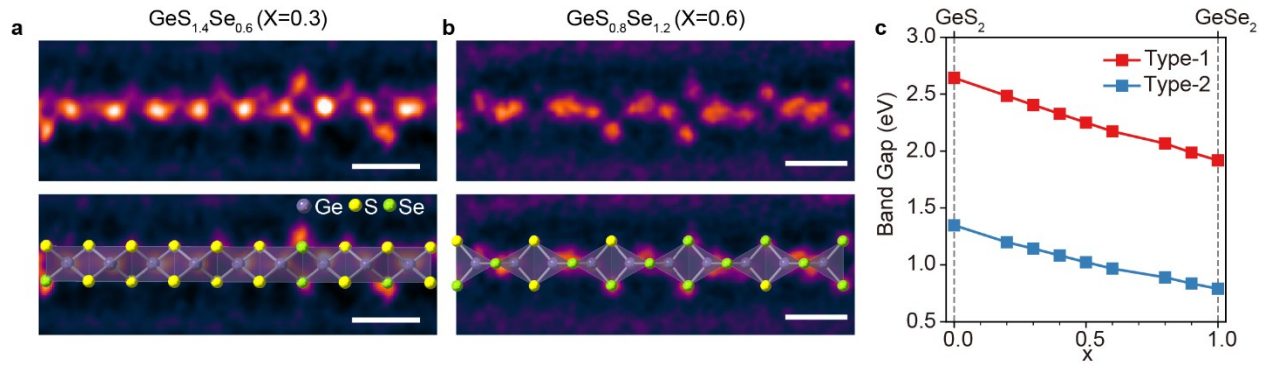


Figure 4. 1D $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ ternary single chain inside a nanotube with a controllable alloy composition. (a), (b) Atomic-resolution STEM images of $\text{GeS}_{2(1-x)}\text{Se}_{2x}$ single chains with different S/Se ratios, (a) $x=0.3$ and (b) $x=0.6$, respectively. Atomic models are overlaid on the images (Ge: purple, S: yellow, Se: green). Scale bar: 0.5 nm. (c) Composition-dependent band gap of single-chain $\text{GeS}_{2(1-x)}\text{Se}_{2x}$. At $0 < x < 1$, atomic positions and lattice parameters are linearly interpolated between those of the GeS_2 ($x=0$) and GeSe_2 ($x=1$) structures. For a given composition, the band gap is obtained by mixing S and Se pseudopotentials under the VCA.

	Type-1		Type-2	
	GeS ₂	GeSe ₂	GeS ₂	GeSe ₂
m_e^{Γ}	1.30	1.34	0.17	0.15
m_h^{Γ}	1.43	1.25	0.42	0.35
$E_g^{PBE} (eV)$	2.64	1.91	1.35	0.79

Table 1. Effective masses and band gaps of single-chain GeX₂. The electron and hole effective masses are calculated from parabolic fitting near the conduction and valence band edges, respectively. Type-1 chains have an indirect band gap while type-2 chains have a direct band gap at Γ .

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