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ISBN

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Author

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Publication Date

2026-09-02

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UNIVERSITY OF CALIFORNIA,
IRVINE

Anisotropy-Driven Morphological and Dimensional Control of One-Dimensional van der Waals
Nanocrystals from Vapor-Phase Routes

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Diana Lopez

Dissertation Committee:
Associate Professor Maxx Q. Arguilla, Chair
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Professor Joseph P. Patterson

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ACKNOWLEDGMENTS

My deepest gratitude goes to my committee chair, Professor Maxx Q. Arguilla, who welcomed me into his laboratory with exceptional warmth and support. Even before I officially joined his research group or the university, he took the time to meet with me and share his work, making me feel valued and inspired from the very beginning. His passion for science was immediately evident and truly contagious. Throughout my graduate career, Professor Arguilla played a central role in my development as an independent researcher, providing guidance, encouragement, and unwavering support at every stage. His mentorship was instrumental in the successful completion of this dissertation, and I am deeply grateful for the opportunities he provided and the confidence he placed in me.

I am also sincerely grateful to my committee members, Professor Matt Law and Professor Joe Patterson, whose expertise helped shape my scientific training. The research of Professor Matt Law on semiconducting nanowires, together with his lectures in inorganic chemistry, greatly influenced my understanding of the field and provided a strong foundation for my own research. The lectures of Professor Joe Patterson in microscopy and his seminar highlighting his scientific achievements broadened my understanding of advanced characterization techniques and provided valuable insight into the process of scientific research. I am thankful to both of them for their guidance, for serving on my dissertation committee, and for their careful review of this dissertation.

I would also like to thank Professor Dmitri Leo Mesoza Cordova of Michigan State University and Doctor Kaleolani Shinnosuke Ogura for their exceptional mentorship and friendship. Their guidance, encouragement, and friendship made my graduate education both productive and enjoyable. I am grateful to the former and current members of the Maxx Lab, including Doctor M. Griffin Milligan, Kaitlyn G. Dold, Angela Gotingo, Meherin Hossain, Lyra Macek, Kenneth Chua, Doctor Ze-Fan Yao, Doctor Steven Allison, and Maran Sardoni, for fostering a collaborative, supportive, and engaging research environment. I also thank the members of the Ardoña Lab, especially Harrison Jeong and Sheng Wei Tang, for their kindness and support throughout my graduate studies.

This work was made possible through the contributions of many talented scientists and the use of outstanding shared research facilities. I sincerely thank Professor Ruqian Wu, Professor Yinong Zhou, and Doctor Jatin Kumar Bidika for performing the computational studies that supported two of the publications arising from this work. I also thank Professor Maxim R. Shcherbakov and Sakib Alam Mashnoon for their calculations and simulations, and Ron Synowicki of Woollam Co. for generously performing the ellipsometry measurements. I am also grateful to the staff of the UC Irvine Materials Research Institute (IMRI) and the UC Irvine Department of Chemistry Laser Spectroscopy Laboratories for their technical assistance, training, and support with the instrumentation throughout my graduate research.

Financial support for this research was provided by the National Science Foundation (NSF) under Award No. DMR-2340918 and through the NSF Graduate Research Fellowship Program.

Finally, I thank my family and friends outside of academia whose unwavering love, encouragement, and friendship sustained me throughout every stage of my graduate journey.

Chapter 2 was adapted from the following publication: Lopez, D.; Zhou, Y.; Cordova, D. L. M.; Milligan, G. M.; Ogura, K. S.; Wu, R.; and Arguilla, M. Q. Bonding-Directed Crystallization of Ultra-Long One-Dimensional NbS₃ van der Waals Nanowires, *J. Am. Chem. Soc.*, **2024**; *146* (33), 22863–22868. DOI: 10.1021/jacs.4c05730. This work is licensed under a Creative Commons CC-BY-NC-ND 4.0 license and is reproduced with appropriate attribution.

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PUBLICATIONS

- [1] Lopez, D.; Dold, K. G.; Ogura, K. S.; Cordova, D. L. M.; Milligan, G. M.; Sardoni, M. R.; Arguilla, M. Q. Bottom-Up Crystallization of Long and Highly Anisotropic Nanowires Based on a Dimerized 1D van der Waals Transition Metal Trihalide. *Chem. Mater.*, **2026**. *Under review*.
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ABSTRACT OF THE DISSERTATION

Anisotropy-Driven Morphological and Dimensional Control of One-Dimensional van der Waals Nanocrystals from Vapor-Phase Routes

by

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Doctor of Philosophy in Chemistry

University of California, Irvine, 2026

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One-dimensional (1D) van der Waals (vdW) materials provide a unique platform that enables the understanding of how anisotropic bonding governs crystal growth and enables access to complex morphologies and emergent physical states. However, predictive synthetic strategies for directing their crystallization remain underdeveloped. This work establishes chemical design principles for directing the bottom-up crystallization of 1D vdW materials by controlling directional bonding, composition, and defect-mediated growth. Using modified chemical vapor transport, strong intra-chain bonding—particularly Peierls-like metal dimerization—is shown to promote catalyst-free growth of ultralong, high-aspect-ratio nanowires in NbS₃-I and MoI₃. Building on this framework, compositional alloying and chalcogen deficiency emerge as complementary chemical design parameters that modify lattice flexibility and growth pathways that enable the formation of self-coiled nanorings and screw-dislocation-mediated spiral hillocks while preserving the intrinsic anisotropic properties of the parent crystals. Microscopy, spectroscopy, and first-principles calculations collectively reveal the interplay between bonding anisotropy, lattice perturbations, and crystal growth. Together, these studies establish generalizable chemical design principles for programming crystal growth in burgeoning classes of 1D vdW materials and provide new synthetic routes to structurally complex crystals that serve as platforms for exploring structure–property relationships and emergent physical phenomena.

CHAPTER 1: Growth and Morphological Control of High-Aspect-Ratio One-Dimensional Nanostructures

1.1 Definition and Significance of One-Dimensional Nanostructures

One-dimensional (1D) nanostructures comprise a broad class of materials characterized by high aspect ratios, in which two dimensions are confined to the nanoscale regime while the third extends over much larger length scales.¹⁻⁴ Conventionally, the nanoscale is defined as dimensions ranging from approximately 1–100 nm.¹⁻⁴ These nanostructures can originate from materials with different bonding dimensionalities. The bonding network may extend predominantly through one, two, or three dimensions, defined by strong bonding interactions such as covalent, ionic, or metallic.⁵ In 1D materials, strong bonding, usually covalent in nature, occurs primarily along a single crystallographic axis, resulting in chain-like motifs.⁵ In two-dimensional (2D) materials, strong bonding extends along two crystallographic axes, forming sheets or planes that are held together by weaker van der Waals (vdW) interactions.⁵ In three-dimensional (3D) materials, strong bonding extends along three crystallographic directions, resulting in a fully interconnected bonding network throughout the crystal.⁵ Regardless of the bonding-imposed dimensionality of the parent material, the resulting nanostructures may adopt a variety of morphologies (**Figure 1.1.1**).

Based on their geometry and dimensions, 1D nanostructures are commonly categorized as nanorods, nanowires, nanoribbons, and nanotubes. Nanorods typically possess circular, hexagonal, or square cross sections, with aspect ratios (length/width) between ~ 1 and 25.^{6,7} Structures with higher aspect ratios are generally classified as nanowires, although the distinction between nanorods and nanowires is not universally defined. While nanoribbons and nanotubes may exhibit similar aspect ratios to nanowires, they are distinguished by their specific cross-sectional geometries. Nanoribbons, sometimes referred to as nanobelts, exhibit rectangular cross sections and are characterized by width, length, and a nanoscale thickness or height.^{2,3,8-10} Nanotubes are distinguished by their hollow cylindrical (ring-like) cross sections with nanoscale diameters.¹¹⁻¹⁵ Beyond these conventional morphologies, 1D nanostructures can adopt a diverse range of architectures, including zigzag, helical, coiled, and other structurally complex forms.^{1,3,8,10,16-24} Among these various morphologies, nanowires and nanoribbons have emerged as two of the most

extensively studied 1D nanostructures owing to their synthetic accessibility and structural versatility.

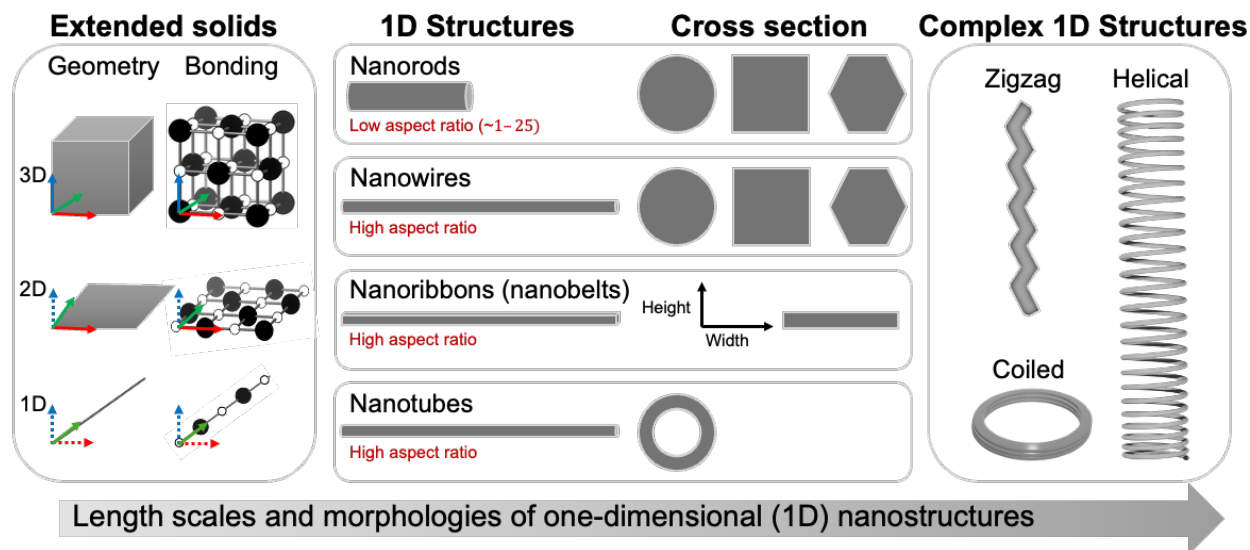


Figure 1.1.1. Schematic illustration of representative bonding dimensionalities and morphologies of 1D nanostructures. 1D nanostructures can originate from materials with different bonding dimensionalities, represented by geometric shapes such as a 3D cube, a 2D plane, and a 1D line (left). Conventional 1D nanostructures include nanorods, nanowires, nanoribbons (nanobelts), and nanotubes, which are distinguished by their characteristic aspect ratios and cross-sectional geometries (middle). Beyond these conventional morphologies, 1D nanostructures can adopt more complex architectures, including zigzag, helical, and coiled structures (right). Structures are schematic and not drawn to scale.

Semiconducting nanowires and nanoribbons exhibit tunable charge transport and light–matter interactions, enabling their use as active components in next-generation electronic, optoelectronic, and sensing devices.^{4,25–44} Such tunability can be achieved through control of composition, doping, crystal structure, and size.^{4,25–44} Their elongated geometries facilitate integration into miniaturized devices, particularly as nanoscale interconnects.^{34,45–49} Depending on their intrinsic mechanical properties, some 1D nanostructures can also support flexible device architectures.^{41,45,46,50–56} As dimensions approach the atomic scale, quantum confinement effects can emerge, leading to tunable electronic and optical properties.^{2,8,30,34,49,57–61} The combination of high aspect ratios and anisotropic crystal structures can further give rise to direction-dependent physical properties and support direction-dependent electronic and optical transport.^{42,44,46,51,62–64} In addition, the large surface-to-volume ratios characteristic of 1D nanostructures enhance surface-mediated processes, making them attractive for sensing applications.^{41,45,46,50–52}

Beyond conventional high-aspect-ratio nanostructures, structurally complex morphologies such as coiled structures, nanorings, helices, and other defect-induced morphologies have attracted increasing interest because they introduce additional degrees of structural complexity, enabling further tunability of physical properties. Curvature, twisting, and crystallographic defects can modify local symmetry, strain distributions, and local electronic structure, giving rise to mechanical, optical, and electronic phenomena that are not typically accessible in conventional straight morphologies.^{65–72} As a result, considerable efforts have been devoted to developing synthetic strategies that provide greater control over morphology. However, many complex architectures emerge through crystallization pathways that are highly sensitive to growth conditions, limiting the reproducibility and predictability of their synthesis. These challenges continue to motivate the development of new synthetic approaches. **This chapter** provides an overview of semiconducting nanowires and nanoribbons, including their material diversity, applications, synthesis, and the challenges and limitations of conventional approaches for accessing high-aspect-ratio and structurally complex 1D nanostructures.

1.2 Physical Properties and Applications of One-Dimensional Nanostructures at the Atomic Scale

In electronic device applications, semiconducting nanowires such as Si and III-V materials including InAs, GaN, and InP have been extensively investigated as field-effect transistors (FETs) and logic devices that exploit gate-tunable charge transport (**Figure 1.2.1**).^{27,42,47,49,63,73–75} Similarly, semiconducting oxide nanoribbons, such as ZnO, exhibit anisotropic charge transport and have been explored in FETs and sensing applications.^{8,10,31,76–78} In these systems, charge transport is governed by the interplay between reduced dimensionality, crystal structure, and carrier confinement. These characteristics establish semiconducting nanowires and nanoribbons as versatile components for next-generation nanoscale electronic technologies.

Nanowires and nanoribbons have also been widely explored in optoelectronics owing to their ability to generate, guide, manipulate, and detect light at the nanoscale (**Figure 1.2.1**). III-V materials, such as GaN, InP, and GaAs, are commonly used in light-emitting devices, including nanowire lasers and light-emitting diodes, because of their direct band gaps and high radiative efficiency.^{27,30,38,42,44,74} II-VI semiconductors and metal oxides, such as CdS and ZnO, have served as model systems for nanoscale photonics, demonstrating lasing, waveguiding, and ultraviolet

photodetection.^{30,35,43,44,51,79} Si nanowires are primarily utilized for photodetection and solar energy conversion, as their indirect band gap suppresses radiative recombination and favors light absorption.^{44,80–83} More recently, halide perovskite nanowires have emerged as high-performance materials for tunable light emission and detection.^{32,44,84,85} Together, these material systems demonstrate the versatility of 1D nanostructures for light generation, manipulation, and detection across a broad range of optoelectronic technologies.

Beyond electronic and optoelectronic functionalities, nanowires and nanoribbons have also been extensively investigated for sensing applications because their high surface-to-volume ratios enhance sensitivity to changes in the surrounding environment (**Figure 1.2.1**). In particular, metal oxide nanowires, such as ZnO, SnO₂, TiO₂, and WO₃, represent one of the most widely studied classes of nanowire-based sensors, in which surface adsorption of gas molecules modulates electrical conductivity.^{86–94} Silicon nanowires have also been widely employed as sensing elements, particularly in FET configurations, where surface charge interactions influence channel conductance, enabling highly sensitive detection of chemical and biological species.^{26,28,95–98} In addition, III-V semiconductor nanowires, such as InAs and GaN, have been investigated for chemical and biological sensing owing to their high carrier mobility and surface sensitivity.^{26,29,99–105} Surface-mediated interactions therefore play a central role in governing the sensing performance of 1D nanostructures.

In addition to surface-mediated phenomena, reducing the dimensions of nanowires and nanoribbons can fundamentally alter their electronic structure through quantum confinement (**Figure 1.2.1**). Silicon nanowires represent one of the most extensively studied systems, where reduced dimensions can lead to band-gap widening, with strong confinement effects emerging at diameters below ~5 nm and bulk-like behavior being recovered above ~10 nm.^{25,39,106,107} Similarly, III-V semiconductor nanowires, such as InAs and GaAs, can exhibit quantized transport and subband formation as dimensions approach the quantum confinement regime.^{36,108–110} In II-VI semiconductors, including CdS and CdSe, quantum confinement leads to pronounced changes in optical properties, such as size-dependent photoluminescence and tunable emission wavelengths.^{3,111–114} Metal oxide nanowires, such as ZnO, also exhibit confinement-induced optical behavior, particularly in the ultraviolet region.^{33,115–117} These examples demonstrate how quantum confinement provides an additional mechanism for tailoring the electronic and optical

properties of 1D nanostructures beyond conventional control through composition and crystal structure.

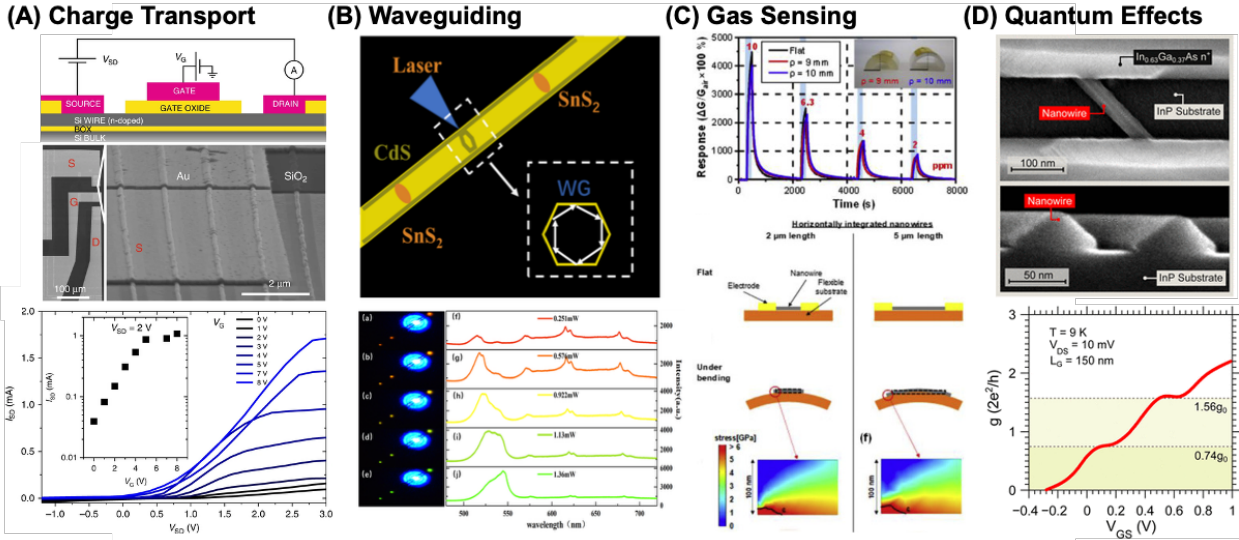


Figure 2.2.1. Representative functionalities enabled by 1D nanostructures. (A) A silicon nanowire field-effect transistor (FET) illustrating gate-tunable charge transport and the integration of 1D nanostructures into nanoelectronic devices (adapted from Ref. 46). (B) A Sn-doped CdS nanowire exhibiting excitation-power-dependent color tuning (adapted from Ref. 114). (C) A Pd-decorated ZnO/ZnS core-shell nanowire gas sensor demonstrating sensitive H_2S detection under mechanical deformation, highlighting the suitability of 1D nanostructures for flexible sensing applications (adapted from Ref. 94). (D) An InGaAs nanowire demonstrating quantized conductance, a hallmark of electronic quantum confinement in 1D systems (adapted from Ref. 108). These examples highlight the diverse electronic, optoelectronic, sensing, and quantum functionalities that emerge from the reduced dimensionality of 1D nanostructures.

Beyond tuning through composition, crystal structure, and dimensional confinement, structurally complex nanostructures can give rise to morphology-dependent physical phenomena (**Figure 1.2.2**). An intriguing example is provided by the semiconducting and piezoelectric ZnO nanoribbons, where polar-surface-driven growth enables the spontaneous formation of helical nanostructures.^{10,17,21,23,118,119} The resulting helical structures introduce periodic curvature, chirality, and spring-like mechanical flexibility, enabling reversible elastic deformation and electromechanical coupling.^{10,17,21,23,118,119} As a result, these structures have been proposed as promising architectures for nanoscale resonators, transducers, sensors, and other electromechanically responsive nanodevices.^{21,23,119,120} Ring-shaped semiconductor nanostructures can modify optical confinement and resonant cavity behavior relative to conventional linear nanostructures.^{22,121–124} For example, GaN nanorings have been explored as

photonic ring resonators and nanolasers, where circulating optical modes and whispering-gallery-mode confinement enable tunable lasing and geometry-dependent optical resonances.^{40,121,125}

Extending beyond curvature-induced phenomena, defect-mediated structures involving screw dislocations can drive spiral crystal growth and, in sufficiently thin crystals, induce strain-driven crystallographic twisting, thereby modifying local crystal structure and/or physical properties.^{65–68,71,126–131} For example, GeS nanowires have been shown to grow around axial screw dislocations and exhibit Eshelby twisting, producing continuously rotated vdW layers and tunable moiré superstructures.^{67,69,71} This progressive interlayer twist can modify interlayer coupling and electronic structure while introducing chirality and local symmetry breaking, providing potential opportunities for twistonic applications.^{67,69,71,132,133} Taken together, these studies highlight how structural complexity provides an additional degree of freedom for engineering crystal architectures and the associated physical properties of 1D nanostructures beyond conventional control through composition, crystal structure, and dimensional confinement, further expanding opportunities for both fundamental studies and technological applications.

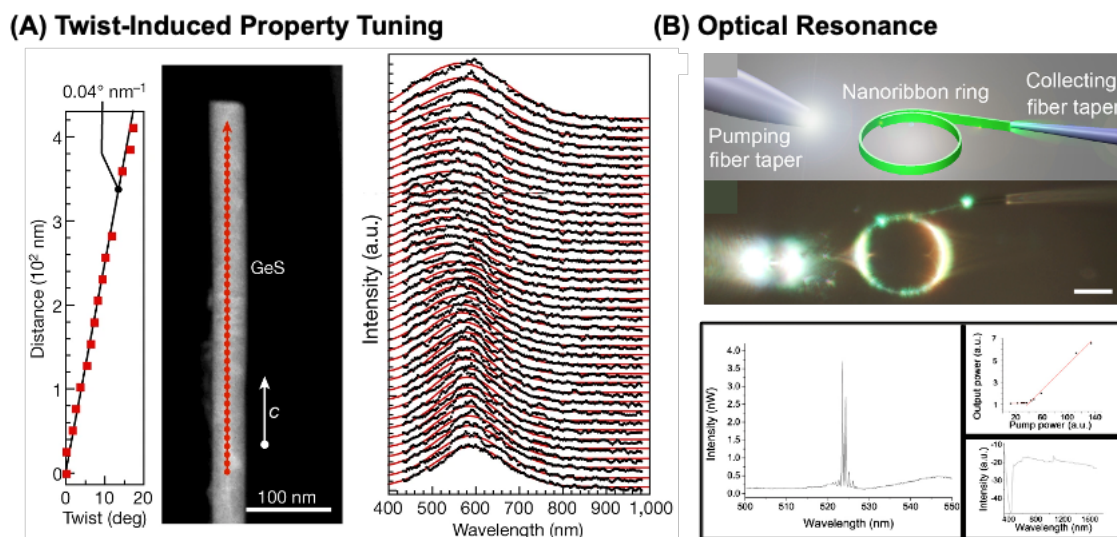


Figure 3.2.2. Representative functionalities enabled by complex 1D nanostructures. (A) A GeS nanowire exhibiting a twisted crystal structure and twist-induced modulation of photoluminescence, as evidenced by variations in wavelength, intensity, and linewidth along the nanowire axis (adapted from Ref. 67). (B) A ring-shaped CdS nanoribbon laser demonstrating optical resonance within a closed-loop cavity geometry (adapted from Ref. 120). These examples highlight how twisted crystal structures and curved morphologies can be exploited to tailor the physical properties of 1D nanostructures.

1.3 Growth Mechanisms and Methods for Nanowires and Nanoribbons

The ability to experimentally synthesize nanowires and nanoribbons with desired structural and functional properties depends critically on control over their crystal structure, dimensions, and morphology. Synthesis of these nanostructures is generally achieved through two primary approaches: top-down fabrication and bottom-up growth. Top-down methods include lithography, etching, and exfoliation from bulk crystals.^{2,49,134} Although lithography and etching can provide precise geometric patterning and dimensional control, they may introduce surface damage, defects, and structural disorder, particularly at the nanoscale.^{135–138} Exfoliation approaches also present limitations. For example, mechanical exfoliation often yields materials with nonuniform lateral dimensions and limited control over thickness and length, while liquid-phase exfoliation can introduce surface contamination and structural degradation.^{57,139–146} Consequently, bottom-up growth strategies are frequently pursued to enable direct crystallization of nanostructures with controlled composition, crystallinity, morphology, and dimensionality.

Bottom-up growth methods include solution-phase and vapor-phase synthesis, which can be combined with catalyst-assisted mechanisms or template-assisted growth strategies.^{2,3,65,147–150} These approaches offer a route towards controlling crystal structure, dimensions, and morphology while often yielding high-quality single-crystalline materials. Among solution-phase methods, hydrothermal and solvothermal synthesis are the most widely employed (**Figure 1.3.1**).^{2,3,116,118,151,152} Both processes are conducted in sealed autoclaves under elevated temperature and pressure; however, hydrothermal synthesis uses water as the solvent, whereas solvothermal synthesis uses organic solvents.^{151,153–156} The solvent plays a critical role in determining precursor solubility, reaction pathways, nucleation kinetics, and crystal growth behavior. Hydrothermal methods are particularly effective for metal oxides such as ZnO, TiO₂, WO₃, and Fe₂O₃ because aqueous precursor chemistry facilitates oxide formation.^{151,153,155–165} In contrast, solvothermal approaches are widely used for metal chalcogenides including CdS, ZnS, and Bi₂S₃, where organic solvents provide greater flexibility in precursor selection and growth conditions.^{156,166–170} For materials that do not intrinsically favor anisotropic growth, or when additional control over nanowire dimensions and morphology is desired, surfactants or ligands may be introduced as capping or structure-directing agents.^{3,156,165–167} These species selectively adsorb onto specific crystal facets, modifying relative growth rates and promoting the formation of targeted morphologies.^{154,156,165,166} They can also influence nucleation behavior and suppress particle

aggregation during growth.^{154,156,165,166} Despite these advantages, solution-phase growth methods remain largely limited to materials whose precursors possess sufficient solubility and reactivity within the chosen solvent environment to enable controlled crystallization of the desired phase, motivating the widespread use of vapor-phase growth strategies for many materials.^{3,156,165,171}

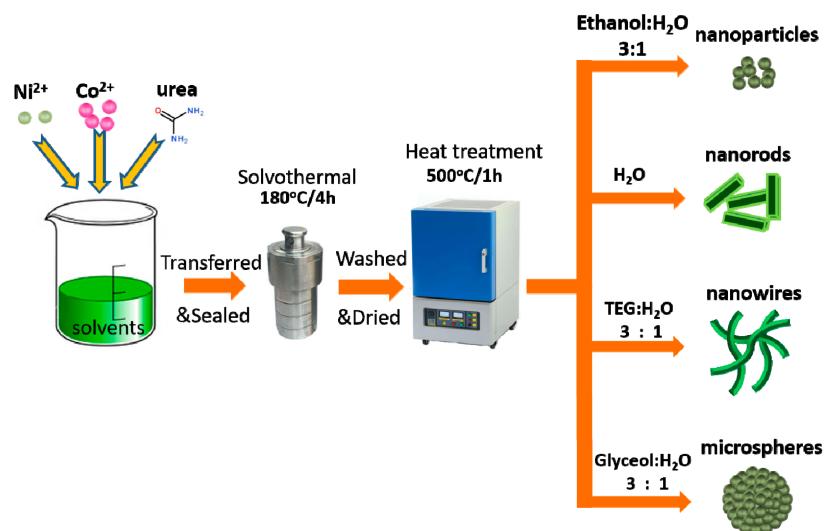


Figure 4.3.1. Representative solution-phase growth method for nanostructures. Schematic illustration of the solvothermal synthesis of nickel cobaltite (NiCo_2O_4) nanostructures, highlighting the role of solvent composition in directing morphology evolution toward nanoparticles, nanorods, nanowires, or microspheres. Adapted from Ref. 152.

Common bottom-up vapor-phase methods include chemical vapor deposition (CVD) and chemical vapor transport (CVT) (**Figure 1.3.2**). CVD is widely employed for the direct growth of thin films and low-dimensional nanostructures.^{57,128,172–176} CVT, on the other hand, is traditionally used for the synthesis of high-quality bulk single crystals.^{139,177–189} In CVD, volatile precursor species are generated in the vapor phase and transported by a carrier gas to a substrate, where they undergo surface reactions that drive nucleation and crystal growth.^{57,128,172–176} The ability to independently control precursor delivery, substrate temperature, and growth environment makes CVD a versatile method for engineering crystal structure, morphology, and dimensionality. By contrast, CVT relies on the transport of volatile species between spatially separated temperature zones. In a typical CVT process, precursor materials are exposed to a temperature gradient, generating gaseous transport species that diffuse from a high-temperature source region to a lower-temperature growth region where crystallization occurs.^{139,177–189} Owing to its ability to produce

large, high-quality single crystals, CVT remains one of the most widely used methods for preparing bulk materials for subsequent characterization and exfoliation.^{139,177–187}

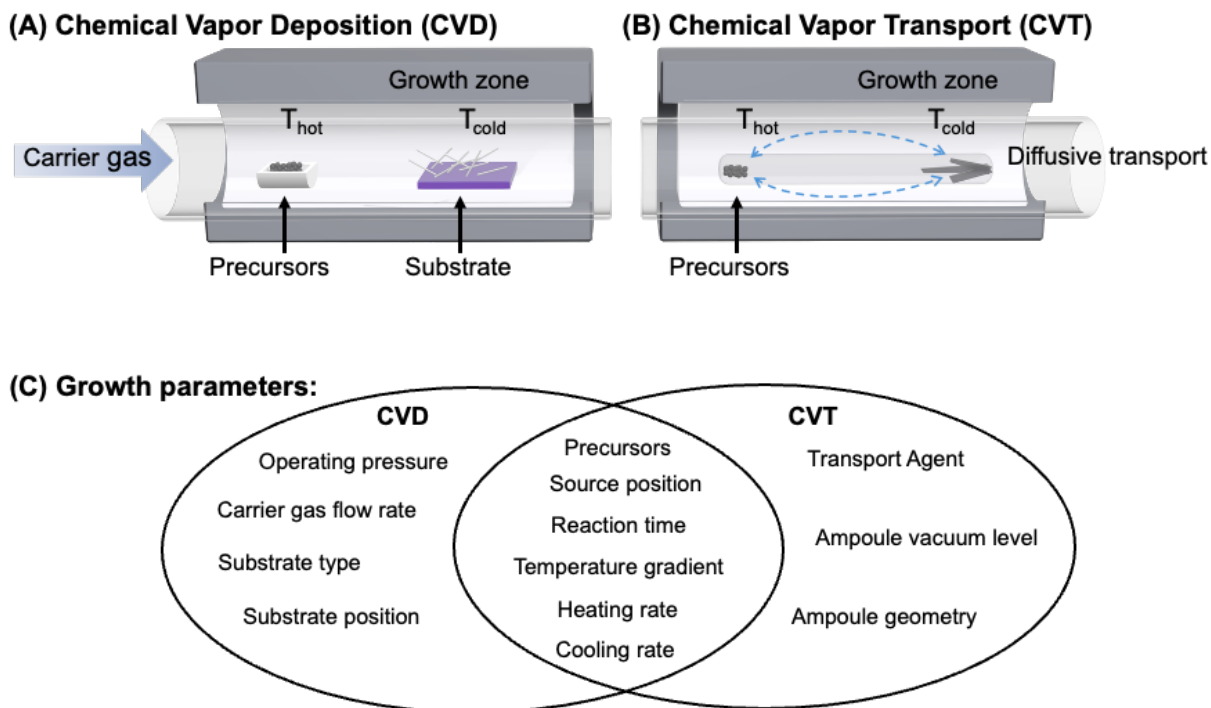


Figure 5.3.2. Comparison of typical experimental configurations used for CVD and CVT. (A) Representative CVD setup, where precursor species are transported by a carrier gas to a substrate positioned within the growth zone. (B) Conventional CVT setup for bulk crystal growth, where vapor species are transported by diffusion from the source region (hot zone, T_{hot}) to the growth region (cold zone, T_{cold}) under an applied temperature gradient. (C) Growth parameters unique to CVD and CVT, together with parameters common to both techniques.

Although vapor-phase methods can directly produce thin films and nanostructures, catalyst-assisted mechanisms and template-assisted growth strategies are often employed to promote anisotropic nanowire or nanoribbon growth. One of the most widely used catalyst-assisted mechanisms is vapor-liquid-solid (VLS) growth, in which vapor-phase precursor species dissolve into a liquid metal catalyst droplet to form a eutectic alloy.^{69,148,176,190–192} Continued precursor incorporation increases the concentration of the growth species until supersaturation is reached, driving crystallization at the liquid-solid interface and resulting in anisotropic nanowire growth. Because VLS growth relies on eutectic alloy formation, the catalyst and precursor materials must be chemically compatible. Template-assisted growth provides an alternative route for controlling nanowire morphology by using patterned substrates or confined growth geometries to direct nucleation and crystal growth.^{47,159,192–194} Such templates are commonly fabricated through

lithographic patterning or substrate etching techniques and can provide enhanced control over nanowire dimensions, alignment, and spatial organization.^{47,159,192–194} In some systems, catalyst-assisted and template-assisted approaches are combined to achieve exceptional aspect ratios and growth control. For example, millimeter-scale GaN nanowires have been synthesized by CVD using a combination of VLS and template-assisted growth strategies.¹⁹²

Despite significant advances in bottom-up nanowire and nanoribbon growth, many conventional synthesis approaches continue to rely on exfoliation, catalyst-assisted growth, or template-assisted growth strategies. As a result, achievable dimensions, morphology, and structural uniformity are often influenced by external factors such as catalyst size, eutectic compatibility, template geometry, lithographically defined features, or the stochastic nature of exfoliation processes. These constraints become critical as the dimensions approach the sub-10 nm and atomic scale regimes, where many predicted low-dimensional phenomena are expected to emerge most strongly. 1D vdW materials provide an alternative route for accessing 1D nanostructures by leveraging their intrinsic anisotropic bonding.^{57,140,173} In these materials, strong covalent bonding along one crystallographic direction with comparatively weak vdW interactions along the remaining directions promote preferential 1D growth, often resulting in needle-like crystal morphologies.^{186,187} Furthermore, as the material dimensions approach the atomic limit and the surface-to-volume ratio increases, ideal 1D vdW materials exhibit fewer exposed dangling-bond sites than 2D or 3D materials (**Figure 1.3.3**). In 2D vdW materials such as graphene and MoS₂, covalent bonding extends within a plane, with weak vdW interactions perpendicular to the plane, giving rise to layered sheet-like structures.¹⁹⁵ Consequently, dangling bonds are primarily located along the sheet edges, whereas in ideal 1D vdW materials they are largely confined to the terminal chain ends. In contrast, 3D materials such as silicon possess strong covalent bonding along all three crystallographic directions. As their dimensions are reduced, the increasing surface-to-volume ratio results in a larger fraction of surface dangling bonds, leading to enhanced surface reactivity compared to 2D and 1D materials.¹⁹⁶ Therefore, the unique geometry of 1D vdW materials, combined with their highly anisotropic bonding, makes them attractive platforms for exploring confinement effects and emergent low-dimensional phenomena.

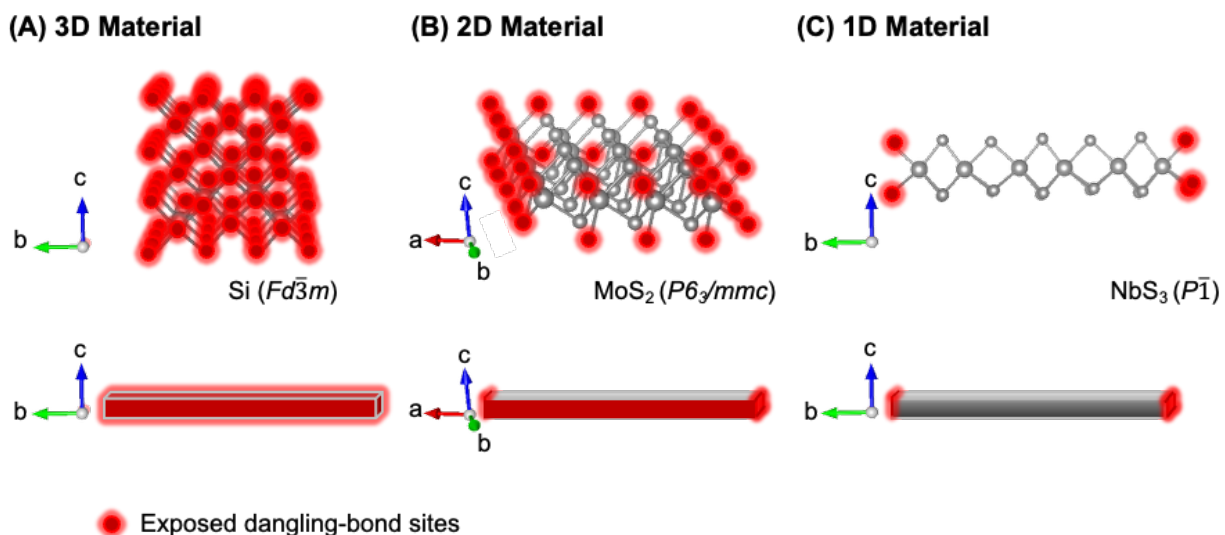


Figure 6.3.3. Comparison of bonding dimensionality and exposed dangling-bond sites in representative 3D, 2D, and 1D materials. (A) Silicon (Si), a 3D material with dangling-bond sites present on exposed surfaces. (B) MoS₂, a 2D vdW material with strong in-plane covalent bonding and dangling-bond sites primarily confined to sheet edges. (C) NbS₃, a 1D vdW material consisting of covalently bonded chains with dangling-bond sites largely confined to chain termini. Red highlighting indicates exposed dangling-bond sites, while the lower schematics illustrate the corresponding crystal morphologies and locations of these sites.

To date, most 1D vdW materials have been synthesized as bulk crystals through conventional CVT and solid-state synthesis followed by mechanical or liquid-phase exfoliation, whereas comparatively few studies have reported the direct bottom-up growth of nanostructures.^{57,140,173,186,187,197–199} Existing bottom-up approaches have primarily relied on CVD, which typically employs volatile chloride- or oxide-derived precursor species together with continuous carrier-gas flow to facilitate vapor-phase transport of refractory transition metals.^{57,173,197} Beyond CVD, modified CVT has also been explored for the growth of nanostructures, although primarily in 2D vdW systems.^{140,188,189,200,201} In contrast to conventional CVT, the reaction ampoule is typically modified by narrowing the tube near its midpoint (necking) and introducing a substrate in the growth zone (**Figure 1.3.4**).^{140,188,189,200,201} Necking reduces precursor flux and supersaturation at the deposition site by restricting mass transport, thereby slowing growth kinetics.^{177,188,201,202} This behavior is consistent with diffusion-limited transport models, in which the transport rate is proportional to the cross-sectional area of the diffusion path and inversely proportional to its length.^{188,201} Consequently, reducing the effective diffusion-path cross section through necking lowers precursor transport to the growth zone, promoting slower and more controlled crystal growth. Combined with other growth parameters, including the

temperature profile, reaction time, and precursor composition, these modified transport conditions can facilitate the direct growth of nanostructures with controlled size and morphology.^{140,188,189,200,201} Despite receiving considerably less attention than CVD, modified CVT is a promising route for accessing morphologies that remain difficult to obtain through conventional exfoliation or CVD methods.^{140,188,189,200,201}

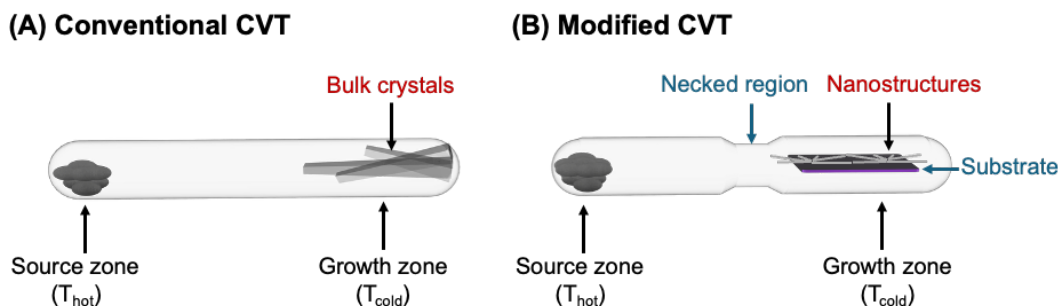


Figure 7.3.4. Illustration comparing conventional and modified CVT. (A) Conventional CVT typically employs a uniform ampoule and is commonly used for the growth of bulk crystals. (B) Modified CVT incorporates a necked ampoule and a substrate in the growth zone to alter vapor transport conditions for the direct growth of low-dimensional nanostructures.

1.4 Distinct Structure and Significance of Emergent One-Dimensional van der Waals Materials

1.4.1 One-Dimensional and Quasi-One-Dimensional van der Waals Materials

1D vdW materials represent a unique class of low-dimensional solids composed of anisotropic chain-like structural motifs that promote preferential crystal growth along a single crystallographic direction. Within this class, materials are commonly categorized as either “true”-1D vdW or quasi-1D vdW materials based on the strength of the interactions between neighboring chains.^{187,203} “True”-1D vdW materials exhibit strong covalent bonding along the chain direction, while neighboring chains interact exclusively through weak vdW forces. In contrast, quasi-1D vdW materials exhibit strong covalent bonding along the chain axis with appreciable interchain interactions, often resulting in layered assemblies of chains separated by larger vdW gaps. Consequently, quasi-1D materials are frequently described as 2D assemblies of 1D chains,

whereas “true”-1D materials consist of more isolated chains. Examples of “true”-1D materials include Nb_2Se_9 and MoI_3 , while examples of quasi-1D materials include NbS_3 and ZrS_3 .

The strong anisotropic bonding in 1D vdW materials dictates their morphology and exfoliation behavior. Variations in interchain coupling can give rise to needle-like or ribbon-like crystal morphologies, while the presence of weak vdW interactions enables mechanical or chemical exfoliation into nanowires, nanoribbons, and, depending on the bonding hierarchy, nanosheets, or even individual atomic chains. Access to these reduced-dimensional structures has been instrumental for probing the fundamental physical properties that emerge at the nanoscale. A growing number of 1D vdW materials have been experimentally realized across a broad range of chemical compositions and crystal structures (**Figure 1.4.1**). Representative material families include pnictogen chalcogenides, V-VI-VII compounds, bismuth halides, III-VI-VII compounds, transition metal halides, and transition metal trichalcogenides. Although these families share a common 1D structural motif, they exhibit distinct bonding hierarchies, crystal structures, phase stabilities, and physical properties, giving rise to a broad range of electronic, optical, magnetic, and collective phenomena.

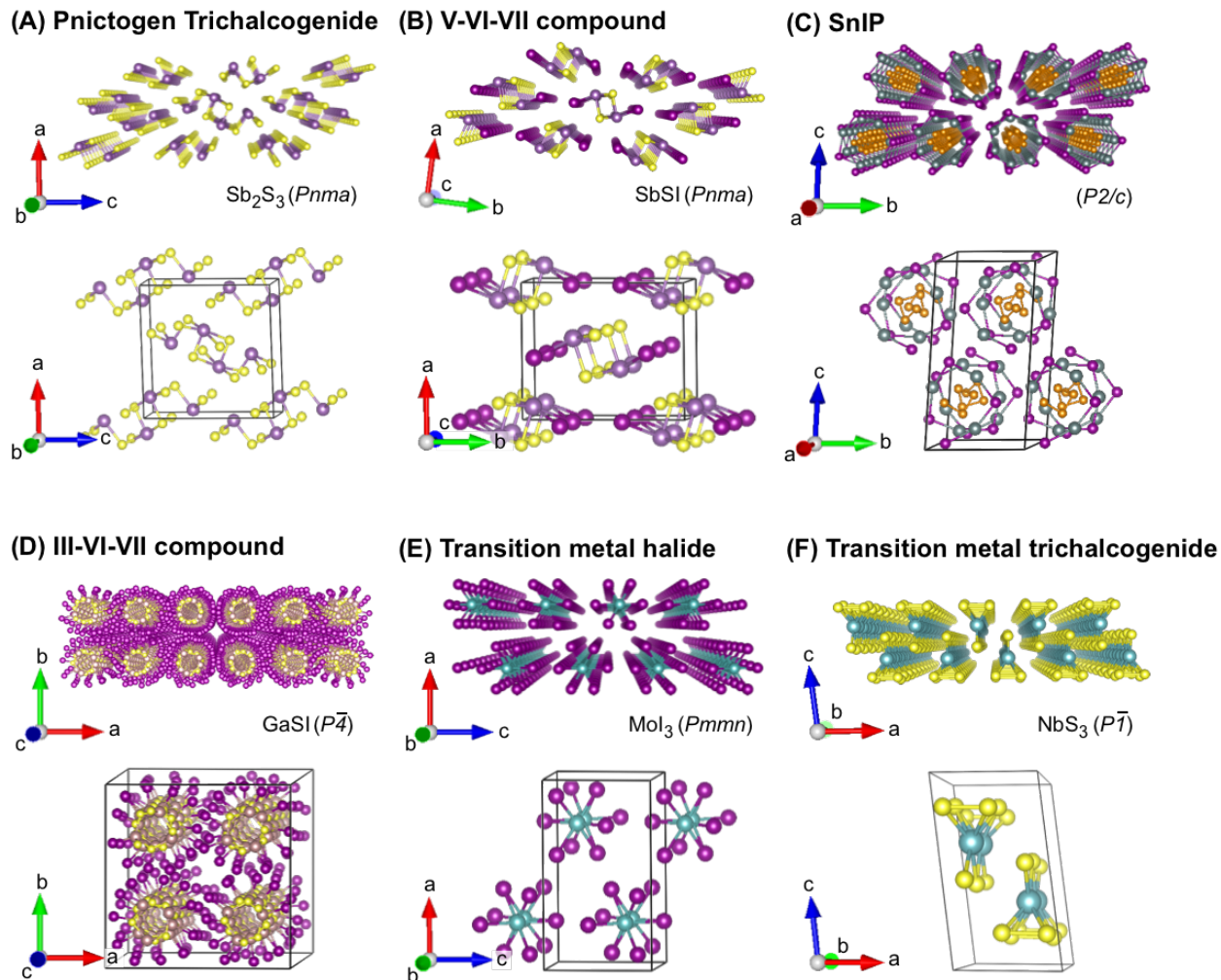


Figure 8.4.1. Representative crystal structures of major “true”-1D and quasi-1D vdW material families. (A) Pnictogen trichalcogenides, (B) V-VI-VII compounds, (C) SnIP, (D) III-VI-VII compounds, (E) transition metal halides, and (F) transition metal trichalcogenides. The upper panels show the isolated 1D structural motifs viewed along the chain axis, while the lower panels show the corresponding unit cell.

1.4.2 Pnictogen Chalcogenides

Pnictogen chalcogenides comprise a prominent family of quasi-1D vdW materials composed of pnictogen elements (Pn = Sb or Bi) and chalcogen elements (Ch = S or Se), with the general formula Pn_2Ch_3 . Representative members include Sb_2Se_3 , Sb_2S_3 , and Bi_2S_3 , which crystallize in the orthorhombic $Pnma$ structure.^{57,204–207} These semiconductors exhibit suitable band gaps and strong visible-light absorption, making them attractive candidates for thin-film photovoltaic applications.^{204,206,207} Beyond their optoelectronic properties, studies of Sb_2S_3 have demonstrated how anisotropic intra- and interchain interactions can be leveraged to direct bottom-up crystallization. Using CVD growth, rather than conventional bulk crystal growth methods such

as CVT, prior studies have achieved controlled synthesis of dimensionally distinct nanostructures, including nanowires, nanoribbons, and quasi-2D nanosheets, by tuning the growth environment and vapor composition.⁵⁷ These findings established Sb_2S_3 as an important model system for understanding morphology control and structure-directed crystallization in 1D vdW materials.

1.4.3 Ternary Sb-based V-VI-VII Materials

Antimony chalcogenides, SbChX , constitute a family of quasi-1D vdW materials composed of antimony (Sb), a chalcogen elements (Ch = S or Se), and halogen element (X = Br or I).^{208–211} Representative members include SbSeI , SbSI , and SbSBr , which crystallize in the orthorhombic *Pnma* structure.^{209–211} Notably, SbSI undergoes a ferroelectric phase transition at a Curie temperature of approximately 295 K, lowering its symmetry to the non-centrosymmetric *Pna2₁* space group.^{209,210} The coexistence of semiconducting and ferroelectric behavior has made SbSI a model ferroelectric semiconductor, while the broader SbChX family has attracted considerable interest for photovoltaic and optoelectronic applications owing to their high dielectric permittivity, chemical stability, and suitable band gaps.^{209–211} To date, SbChX materials have primarily been investigated as bulk crystals and polycrystalline powders obtained through solid-state and vapor-phase synthetic routes.^{208–211}

1.4.4 Bismuth Halides

Bismuth halides, including Bi_4Br_4 and Bi_4I_4 , have emerged as a prominent family of quasi-1D vdW materials owing to their non-trivial topological electronic states.^{212–217} Bi_4I_4 is particularly notable because it undergoes a temperature-dependent phase transition, exhibiting the high-temperature β -phase above room temperature and the low-temperature α -phase below room temperature.^{212,213,215–217} The β -phase has been identified as a topological insulator, whereas the α -phase exhibits a higher-order topological insulator behavior.^{212,213,215–217} Both phases of Bi_4I_4 , as well as Bi_4Br_4 , crystallize in the monoclinic crystal system with space group *C2/m*.^{212–217} Historically, bismuth halides have been synthesized primarily through CVT, and investigated as bulk single crystals.^{212–217} More recently, controlled bottom-up growth approaches have begun to emerge, including CVD and molecular beam epitaxy (MBE). CVD enabled the selective formation of Bi_4I_4 nanowires and quasi-2D nanosheets through VLS growth.¹⁹⁹ MBE enabled the epitaxial

growth of Bi₄I₄ nanoribbons on Bi (111)/graphene/SiC substrates, providing a platform for direct visualization of 1D topological edge states by scanning tunneling microscopy (STM).²¹⁸

1.4.5 SnIP and SnBrP

Another important class of quasi-1D vdW materials comprises compounds that exhibit atomic-scale double-helical structures.^{219–221} SnIP and SnBrP consist of double-helical strands running along the chain direction, giving rise to left- and right-handed enantiomeric forms within the crystal structure.^{219–223} These materials are typically synthesized as needle-like bulk single crystals by CVT and can be exfoliated into nanorods and nanowires.^{219–223} Among these materials, SnIP is the most extensively studied and was the first reported inorganic material with an atomic-scale double-helical structure.^{221–224} SnIP crystallizes in the monoclinic *P2/c* space group and exhibits exceptional mechanical flexibility together with a band gap within the visible range, making it a promising candidate for flexible electronic and optoelectronic applications.^{220–224}

1.4.6 Ternary III-VI-VII Materials

Another important family of quasi-1D vdW materials exhibiting helical motifs are the III-VI-VII compounds, which are formed from Group III (Al, Ga, In), Group VI (S, Se, Te), and Group VII (Cl, Br, I) elements.^{225–236} Examples include InSeI, GaSI, GaSeI, and AlSeI. III-VI-VII materials consist of helical covalent chains constructed from corner-sharing quasi-tetrahedral [(III)(VI)₃(VII)]_n building units that propagate through crystallographic screw symmetry.^{225,226,233–236} To date, most III-VI-VII compounds have been synthesized as needle-like bulk single crystals through CVT and related vapor-phase growth methods, reflecting the strong anisotropy of the chain structures.^{225–229,231–236} Most III-VI-VII compounds are semiconductors with composition-dependent band gaps spanning the visible to ultraviolet spectral regions.^{225–229,231–236} Reported band gaps range from approximately 2.45 eV for InSeI, 2.85 eV for GaSeI, 3.69 eV for GaSI, and 3.9 eV for AlSeI.^{225–229,231–236}

Among the currently known helical III-VI-VII phases, InSeI is unique in being centrosymmetric, crystallizing in the tetragonal *I4₁/a* space group.^{225,230–232,235} Its structure consists of a periodic tetrahelix generated by a 4₁ screw axis, producing a 135° rotation between consecutive tetrahedral vertices and translational periodicity every four atomic layers.^{225,230–232} In

contrast, GaSI crystallizes in the non-centrosymmetric tetragonal P-4 space group and exhibits a distinctive squircular helical cross-section.^{226,235,236} The absence of inversion symmetry gives rise to second-harmonic generation, making GaSI a promising nonlinear optical material.^{226,235,236} GaSeI and AlSeI crystallize in the non-centrosymmetric Cc space group and are composed of racemically packed helices.^{226,235,236} Their structures adopt Boerdijk-Coxeter (B-C) tetrahelical motifs characterized by an irrational twist angle of approximately 131.81° , resulting in the absence of true translational periodicity along the chain direction.^{226,235,236} The combination of helical crystal structures, non-centrosymmetric ordering in several members, and tunable electronic properties has attracted interest in these materials as a platform for studying anisotropic optical phenomena, nonlinear optical responses, and low-dimensional structure-property relationships.^{225–229,231–236}

1.4.7 Nb₂Se₉ and V₂Se₉

Nb₂Se₉ and V₂Se₉ are representative “true”-1D vdW semiconductors. Nb₂Se₉ crystallizes in the triclinic $P\bar{1}$ space group and is commonly synthesized by selenium flux methods,^{237,238} although direct growth of Nb₂Se₉ nanoribbons by CVD has also been demonstrated.²³⁹ V₂Se₉ adopts the monoclinic $C2/c$ crystal structure and is generally synthesized through solid-state reactions.^{238,240} Theoretical studies predict an indirect-to-direct band-gap transition upon dimensional reduction in both materials, highlighting their potential for optoelectronic and nanoelectronic applications.²³⁸

1.4.8 Transition Metal Halides

Transition metal halides are composed of transition metal and halogen elements (Cl, Br, or I). The niobium tetrahalides NbX₄ (X = Cl, Br, or I) form another family of “true”-1D vdW materials consisting of chains of edge-sharing NbX₆ octahedra.^{241–244} Typically, these materials are synthesized through vapor-phase halide reactions.^{241–244} Their structures exhibit alternating short and long Nb–Nb distances along the chain direction, reflecting Nb–Nb bonding.^{241–244} The Nb⁴⁺ (d¹) ions undergo electron localization within these Nb–Nb dimers, giving rise to

semiconducting behavior.^{241–245} This alternating bond distance is characteristic of a Peierls instability in a 1D chain.²⁴⁶

MoI₃, also a “true”-1D vdW transition metal halide, crystallizes in the orthorhombic *Pmmn* space group and similarly exhibits alternating Mo–Mo distances along the chain direction attributed to Peierls distortion.^{139,247–250} Unlike the niobium tetrahalides, recent theoretical and spectroscopic studies suggest that MoI₃ may also host magnetic ordering, with an easy-plane antiferromagnetic ground state composed of alternating spins along the dimerized chains and noncollinear helical magnetic order between neighboring chains.^{139,247–249} These properties make MoI₃ a promising platform for probing magnetic phenomena as materials approach the atomic-chain limit. To date, the synthesis of MoI₃ has largely been limited to bulk crystal growth by CVT, with mechanical and liquid exfoliation subsequently employed to access nanowires and approach the atomic-chain limit.^{139,247} As discussed in **Chapter 3**, modified CVT growth strategies have demonstrated the direct growth of MoI₃ nanowires on Si/SiO₂ substrates, providing a route towards controlled bottom-up synthesis of MoI₃ nanowires.

1.4.9 Transition Metal Trichalcogenides

Among known 1D vdW materials, transition metal trichalcogenides (TMTCs) constitute one of the most chemically, structurally, and electronically diverse material families. TMTCs possess the general formula MCh₃, where M is a Group IVB or VB transition metal (Ti, Zr, Hf, V, Nb, or Ta) and Ch is a chalcogen (S, Se, or Te).^{178,179,182,183,185–187,203} Their diversity arises from the ability of many compositions to adopt multiple crystallographic phases, resulting in a broad range of electronic behaviors that span semiconducting, metallic, charge-density-wave (CDW), and superconducting states.^{178,179,182,183,185–187,203}

A defining characteristic of the TMTc family is the occurrence of multiple crystallographic phases arising from polymorphism.^{178,182,183,185,187,203} In the literature, the terms polymorph and polytype are sometimes used interchangeably for TMTCs, although they describe distinct structural relationships. Strictly, polymorphism refers to the existence of multiple crystal structures with identical chemical composition but different atomic arrangements, whereas polytypism describes structures that differ in the stacking sequence or relative arrangement of otherwise equivalent structural units.²⁵¹ Because the phases discussed here generally involve distinct crystal structures rather than stacking variants, the term polymorph is used throughout unless referring

directly to prior literature. These structural variations strongly influence interchain interactions, electronic band structures, lattice dynamics, and resulting optical and transport properties.^{203,251} The formation of specific polymorphs is highly sensitive to synthesis conditions, including reaction temperature and the choice of transport agent.^{178,185,203}

The Group IVB transition-metal trisulfides, TiS_3 , ZrS_3 , and HfS_3 , constitute an important subclass of the MCh_3 family that crystallize in the monoclinic $P2_1/m$ space group.^{182,183,186,252} Group IVB trisulfides are semiconductors with band gaps that increase systematically with increasing atomic number of the transition metal. TiS_3 possesses a band gap of approximately 1–1.4 eV^{253,254}, ZrS_3 exhibits a band gap of approximately 2.0–2.5 eV^{255–259}, and HfS_3 displays the widest gap, typically reported between 2.0 and 3.1 eV^{256,260,261} depending on the measurement technique. Consequently, the optical absorption window shifts from the visible and near-infrared regions in TiS_3 toward the visible and ultraviolet regions in HfS_3 . All three compounds exhibit strong photoresponse and polarization-sensitive optoelectronic behavior.^{182,183,186,252} Among the Group IVB transition-metal sulfides, ZrS_3 has attracted considerable attention because of its exceptional optical anisotropy, manifested through pronounced linear dichroism, large birefringence, and strong polarization-dependent third-harmonic generation (THG).^{180,181,257,262,263} These characteristics have positioned ZrS_3 as a promising material for polarization-sensitive photonics, nonlinear optics, and integrated optoelectronic applications.

The Group IVB transition-metal trisulfides have traditionally been synthesized as bulk crystals by CVT. However, alternative bottom-up growth approaches have also been explored. For example, the direct growth of ZrS_3 nanoribbons has been demonstrated by CVD.¹⁹⁷ In addition, defect-mediated growth mechanisms can provide further control over crystal morphology. As discussed in **Chapter 5**, a sulfur-deficient modified CVT growth was used to promote screw-dislocation-driven crystallization.

Group IVB transition metal selenides TiSe_3 , ZrSe_3 , and HfSe_3 are semiconducting TMTCs that crystallize in the monoclinic $P2_1/m$ space group and exhibit pronounced anisotropy in their electrical, optical, vibrational, and transport properties.^{179,262,264–266} These characteristics make them attractive candidates for polarization-sensitive electrical and optoelectronic devices and nonlinear optical applications.^{179,262,264–266} While ZrSe_3 and HfSe_3 can be synthesized using

conventional CVT methods, TiSe_3 has only been recently synthesized under high-pressure conditions (~ 6 GPa).^{179,262,264–266}

Group IVB transition metal tritellurides ZrTe_3 and HfTe_3 are metallic TMTCs that crystallize in the monoclinic $P2_1/m$ space group.^{267–275} Upon cooling, both materials undergo CDW transitions, followed by the emergence of superconductivity at lower temperatures, making them model systems for investigating the interplay and competition between these collective electronic states.^{267–275} Bulk crystals are typically synthesized by CVT,^{267–275} whereas ZrTe_3 nanoribbons have been grown directly on SiO_2 substrates through CVD.^{276,277} TiTe_3 , together with the Group VB transition metal tritellurides VTe_3 and NbTe_3 , has not been realized as a stable bulk crystal phase. However, these materials have been successfully stabilized through nanoconfined growth within carbon nanotubes, enabling their synthesis and characterization in the few- and single-chain limits.²⁷⁸ Density functional theory calculations indicate that nanotube encapsulation induces semiconducting behavior in these tellurides.²⁷⁸

The Group VB transition metal trisulfides, comprising VS_3 , NbS_3 , and TaS_3 , demonstrate exceptional structural and electronic diversity. VS_3 is a semiconductor that crystallizes in the monoclinic $P2_1/m$ space group,²⁷⁹ whereas TaS_3 is metallic and crystallizes in monoclinic $P2_1/m$ and $C2/m$ structures and exhibits CDW behavior.^{280–282} NbS_3 exhibits one of the most complex structural phase spaces among the TMTCs, with at least seven experimentally reported phases (**Table 1.4.1**). Semiconducting behavior has been observed for NbS_3 -I (triclinic $P\bar{1}$),²⁸³ NbS_3 -IV (monoclinic $P2_1/c$),¹⁸⁵ and the high-pressure polymorph NbS_3 -HP (monoclinic $P2_1/m$),²⁸⁴ whereas NbS_3 -II (monoclinic $P2_1/m$)^{285–288} exhibits metallic behavior accompanied by CDW transitions. NbS_3 -V (monoclinic $P2_1/m$)¹⁸⁵ is predicted to be metallic based on its crystal structure, while the electronic properties of NbS_3 -VI (monoclinic Pm)¹⁷⁸ remain largely unexplored. NbS_3 -III exhibits a CDW transition near 155 K and has been proposed to be a subphase of NbS_3 -II, although its crystal structure has not been resolved.^{203,288} The rich polymorphism gives rise to a remarkable diversity of electronic behaviors, making NbS_3 a model system for investigating structure-property relationships in quasi-1D materials. NbS_3 -I is a particularly intriguing case because it exhibits a Peierls-like dimerized crystal structure with alternating Nb–Nb bond distances.²⁸³ However, thermoelectric measurements reveal the behavior to be inconsistent with a conventional Peierls semiconductor, suggesting that carrier localization and electron-correlation effects may play an important role in its electronic structure.²⁸⁹ In addition to its unusual electronic properties, NbS_3 -I

has attracted considerable interest as a low-dimensional semiconductor due to its air stability, mechanical flexibility, narrow band gap, and pronounced anisotropy.^{52,290–292} These characteristics highlight its potential for polarization-sensitive photodetectors, broadband photodetection, and other nano-optoelectronic technologies.^{52,290–292} The synthesis of bulk Group VB trisulfides has traditionally been achieved through CVT,^{185,203} apart from NbS₃-HP, which is accessible only through high-pressure synthesis.²⁸⁴ In addition, modified CVT approaches have enabled the growth of ultra-long NbS₃-I nanowires¹⁴⁰ and unusual ring-like morphologies through compositional alloying, as discussed in **Chapters 2 and 4**.

Table 1.4.1. Structural motifs and electronic characteristics of NbS₃ polymorphs. Electronic behavior is summarized from experimental reports where available; predicted and unresolved properties are indicated accordingly.

Structural Feature	Phases	Electronic Behavior
Dimerized Nb chains	I, IV	Semiconducting
Undimerized Nb chains	II, V, HP	Metallic/CDW behavior observed for II; metallic behavior predicted for V; semiconducting behavior reported for HP
Mixed dimerized and undimerized chains	VI	Electronic properties unresolved
Unresolved structure	III	CDW transition (~155 K) reported for III; transport consistent with a Peierls insulating state below the transition

Group VB transition metal triselenides NbSe₃ and TaSe₃ are metallic materials that crystallize in the monoclinic $P2_1/m$ space group and are commonly synthesized as bulk crystals by CVT.^{293–295} NbSe₃ undergoes two CDW transitions at approximately 145 and 59 K, making it a prototypical system for investigating CDW formation, transport, and collective electronic phenomena.^{293,296} Its highly anisotropic electronic properties have attracted interest in neuromorphic memory and nanoelectronics applications.²⁹⁷ In contrast, TaSe₃ does not exhibit CDW ordering but remains metallic down to low temperatures and becomes superconducting

below $\sim 2\text{K}$. In addition to conventional CVT growth, TaSe_3 nanowires have also been synthesized by CVD.¹⁷³

These studies demonstrate the remarkable diversity of 1D vdW materials, spanning semiconducting, metallic, superconducting, and CDW systems. Their intrinsically anisotropic structures, often coupled with direction-dependent physical properties, enable the study of a wide range of physical phenomena in confined 1D structures. Furthermore, their accessibility as 1D nanostructures has facilitated the exploration of emerging applications in nanoelectronics, optoelectronics, and quantum materials research.

1.5 Research Gap and Scientific Rationale

The intrinsically anisotropic bonding of 1D vdW materials provides a unique opportunity to direct crystal growth along specific crystallographic directions. However, despite this potential, the controlled bottom-up growth of these materials remains in its early stages. Consequently, most studies have focused on the development of vapor-phase growth techniques, with CVD emerging as the predominant synthetic route. Among 1D vdW materials, transition metal trichalcogenides, such as TaSe_3 , ZrTe_3 , and ZrS_3 , have been successfully synthesized by CVD.^{173,197,277}

The following are specific examples and morphologies that have been experimentally realized in the literature: In TaSe_3 , reaction time was shown to influence nanowire dimensions, with nanowire lengths increasing initially before reaching an optimum size in the minutes time scale and decreasing with longer growth times.¹⁷³ The resulting nanowires exhibited cross-sectional dimensions in the sub-10 nm range and lengths ranging from hundreds of nanometers to several micrometers.¹⁷³ These findings demonstrated that reaction time is an important parameter for influencing crystal dimensions, but also highlighted that longer growth durations do not necessarily promote continued axial crystal growth.

Similarly, ZrTe_3 has been synthesized by CVD as high-aspect-ratio nanoribbons, with crystal dimensions controlled by growth temperature and reaction time.²⁷⁷ Ribbon lengths exceeding 100 μm have been reported,²⁷⁷ while related CVD approach also produced trapezoidal ZrTe_3 crystals with lengths of several tens of micrometers.²⁷⁶ Together, these studies demonstrated that CVD enables controlled growth of ZrTe_3 crystals with diverse morphologies and dimensions; however, the resulting structures remained confined to the micrometer length scale.

ZrS₃ nanoribbons have also been synthesized by CVD, with crystal dimensions controlled primarily by growth temperature.¹⁹⁷ Nanoribbons with lengths of approximately 10 μm, widths below 3 μm, and thicknesses in the 5 to 100 nm range were obtained.¹⁹⁷ Higher growth temperatures favored larger ribbon structures through thermodynamically driven growth, whereas lower temperatures promoted thinner nanoribbons by enhancing the influence of edge energetics and molecular diffusion.¹⁹⁷ These results demonstrated that crystal dimensions could be systematically tuned by varying the growth temperature, although the resulting structures remained limited to micrometer-scale nanoribbons.

Beyond transition metal trichalcogenides, Nb₂Se₉, Bi₄I₄, and Sb₂S₃ have also been synthesized through bottom-up vapor-phase growth methods. Nb₂Se₉ nanoribbons were grown by liquid precursor-assisted CVD, with ribbon dimensions systematically controlled by varying the precursor and growth-promoter concentrations.²³⁹ The average ribbon lengths reached approximately 30 μm under optimized growth conditions.²³⁹ These results demonstrated that precursor chemistry provided an effective means of controlling crystal dimensions, although the resulting structures remained confined to the micrometer length scale.

Bi₄I₄ has been synthesized through both MBE and CVD.^{199,218} MBE growth produced segmented nanoribbons with widths of approximately 5–8 nm, demonstrating that bottom-up growth can generate morphologically complex 1D structures.¹⁹⁹ In contrast, CVD produced Bi₄I₄ nanowires with lengths of tens of micrometers, while the introduction of Au nanoparticles redirected crystal growth toward the formation of 2D nanosheets.¹⁹⁹ The authors attributed this morphological transition to a change in the dominant crystallization pathway, in which Au nanoparticles modified the nucleation kinetics and favored lateral crystal growth over preferential 1D growth.¹⁹⁹ These studies demonstrated that modifying the nucleation pathway can fundamentally redirect crystal growth, enabling 1D and 2D morphologies.

A more recent study on the controlled bottom-up growth of 1D vdW materials was reported by Cordova *et al.*, which studied how sulfur availability governed the competition between covalent chain growth and interchain vdW growth in Sb₂S₃.⁵⁷ The authors proposed two distinct growth pathways in which sulfur availability determined the dominant crystallization mode, producing nanowires, nanoribbons, or 2D nanosheets.⁵⁷ Under high sulfur flux, crystal growth was directed along the covalently bonded chain direction, yielding nanowires with thicknesses in the 10 nm range and lengths of up to 15 μm.⁵⁷ In contrast, reduced sulfur availability promoted

interchain vdW stacking, resulting in the formation of nanoribbons and nanosheets.⁵⁷ In addition to sulfur transport, temperature also influenced morphology, with higher temperatures favoring bulk crystal growth and lower temperatures promoting dimensionally resolved nanostructures.⁵⁷ This study established one of the first mechanistic frameworks for understanding how competing growth pathways can be manipulated to direct crystal morphology in 1D vdW materials.

Taken together, these examples demonstrate that the intrinsic bonding anisotropy unique to 1D vdW materials can be exploited to direct crystal growth along the covalently bonded chain direction, enabling the bottom-up synthesis of nanowires and nanoribbons. However, despite these advances, bottom-up vapor-phase growth has remained largely limited to micrometer-scale structures, with reported crystal lengths typically ranging from several micrometers to, at most, approximately 100 μm .^{57,173,197,199,239,276,277} Furthermore, in many reported systems, increases in crystal length were accompanied by increases in cross-sectional dimensions, indicating that the growth conditions promoting axial extension did not fully suppress competing interchain vdW growth. As a result, crystal growth proceeded through simultaneous axial and lateral growth rather than selective extension along the covalently bonded chain direction. These limitations suggest that achieving substantially longer 1D crystals may require alternative approaches for controlling crystal growth pathways. In this context, **Chapter 2** demonstrates the growth of NbS₃-I nanowires reaching lengths of up to 8 mm, representing a substantial increase in length compared with previous bottom-up studies of 1D vdW materials.

A second challenge lies in accessing structurally complex morphologies beyond conventional nanowires and nanoribbons. Although several studies have demonstrated control over crystal dimensions and morphology in 1D vdW materials, the accessible structures remain largely limited to variations in nanowire and nanoribbon geometries. Sb₂S₃ represents a notable exception, in which sulfur availability was used to tune crystal morphology between nanowires, nanoribbons, and 2D nanosheets.⁵⁷ Nevertheless, these studies primarily controlled the balance between growth along the covalently bonded chain direction and growth through interchain vdW stacking. More complex crystal architectures, including curved, coiled, and ring-shaped morphologies, as well as defect-driven crystallization processes that generate new crystal morphologies, remain largely unexplored in bottom-up vapor-phase growth of 1D vdW materials.

To date, most bottom-up studies of 1D vdW materials have relied on CVD, suggesting that overcoming the current limitations may require alternative vapor-phase growth strategies. The

following chapters investigate this possibility through modified CVT. **Chapter 2** demonstrates the growth of NbS₃-I nanowires with lengths of up to 8 mm, extending the characteristic length scale of bottom-up grown 1D vdW crystals from the micrometer to the millimeter regime.¹⁴⁰ **Chapter 3** extends the modified CVT approach to the first reported bottom-up growth of MoI₃ nanowires. **Chapter 4**, on the other hand, demonstrates how compositional heterogeneity in Ta-alloyed NbS₃-I gives rise to ring-shaped morphologies.²⁹⁸ Lastly, **Chapter 5** investigates how sulfur deficiency promotes screw-dislocation-driven crystallization in ZrS₃, providing mechanistic insight into the formation of spiral hillocks that are increasingly rare in 1D vdW crystals. Together, these studies demonstrate that modified CVT provides a versatile platform for achieving anisotropy-driven control over crystal dimensions, morphology, and defect-mediated crystallization in 1D vdW materials.

1.6 Objectives and Scope of the Present Work

This dissertation addresses the current limitations of conventional CVD approaches for the bottom-up growth of 1D vdW materials by developing synthetic strategies capable of accessing structurally complex morphologies and previously unattainable nanowire dimensions. Specifically, this work focuses on the growth of ultra-long nanowires,¹⁴⁰ ring-shaped structures,²⁹⁸ and spiral hillocks. To achieve this, a modified CVT approach was developed based on a method previously employed for the growth of 2D vdW materials but relatively underexplored for 1D vdW systems.^{140,188,189,200,201} Through systematic optimization of the reaction ampoule design, determination of specific chemical cues, and precise tuning of growth conditions, the method was developed and tailored to promote controlled anisotropic crystal growth specific to 1D vdW materials. The overarching objective was to realize novel 1D vdW structures at the nanoscale without the use of catalysts or templated substrates, while providing new insights into the growth mechanisms governing crystal morphology evolution.

1.6.1 Chapter 2. Bonding-Directed Crystallization of Ultra-Long One-Dimensional NbS₃ van der Waals Nanowires

Chapter 2 establishes NbS₃-I as a model system for investigating the controlled growth of 1D vdW materials and demonstrates the bottom-up synthesis of nanowires with lengths of up to 7.9 mm,¹⁴⁰ extending the characteristic length scale of bottom-up grown 1D vdW crystals from the

micrometer to the millimeter regime. Using a modified CVT approach, preferential crystallization along the covalently bonded chain direction was achieved through systematic optimization of the growth conditions, enabling sustained axial growth over extended reaction times. The chapter further demonstrates that crystal morphology can be tuned without altering the precursor composition or overall growth configuration. By modifying only the temperature program to reduce sulfur availability during growth, crystallization shifted toward interchain vdW stacking, producing wide ribbon-shaped morphologies rather than nanowires. This behavior parallels the growth mechanism previously reported for Sb_2S_3 ,⁵⁷ and demonstrates that sulfur availability provides a general strategy for directing morphology in anisotropic 1D vdW materials.

1.6.2 Chapter 3. Bottom-Up Crystallization of Long and Highly Anisotropic Nanowires Based on a Dimerized 1D van der Waals Transition Metal Trihalide

Because Nb–Nb dimerization appeared to play a critical role in the preferential axial growth observed in NbS_3 -I, **Chapter 3** extends the leveraging of such motif in the growth of 1D vdW nanostructures through the investigation of another dimerized 1D vdW material, MoI_3 , and demonstrate its first reported bottom-up crystallization. Similar to NbS_3 -I, MoI_3 was synthesized directly from elemental precursors and exhibited a strong tendency toward anisotropic crystal growth. However, unlike NbS_3 -I, reaction time was not an effective parameter for independently controlling nanowire dimensions, as shorter reaction times primarily reduced nanowire length rather than cross-sectional area. To overcome this limitation, bulk MoI_3 was employed as the precursor source to reduce precursor diffusion during growth, enabling improved control over crystal dimensions and the synthesis of thinner nanowires. Together, these results demonstrate that modified CVT can be extended beyond transition metal trichalcogenides to dimerized transition metal trihalides and further support the role of metal–metal dimerization in promoting highly anisotropic crystal growth in 1D vdW materials.

1.6.3 Chapter 4. Compositional Heterogeneity Drives Nanoscale Ring Formation in Optically Active One-Dimensional van der Waals Crystals

Chapter 4 builds upon the ultra-long nanowires developed in **Chapter 2** to address the limited morphological diversity of bottom-up grown 1D vdW materials. Although ultra-long

NbS₃-I nanowires occasionally exhibited spontaneous self-coiling into ring-shaped structures, this behavior occurred only rarely and without experimental control. This observation motivated the hypothesis that compositional heterogeneity could be used to deliberately promote self-coiling during crystal growth. To test this idea, **Chapter 4** investigates Ta-alloyed NbS₃-I, where Ta incorporation was used to modify the crystal lattice and promote ring formation. These studies demonstrate that compositional heterogeneity provides an effective strategy for controlling crystal morphology beyond conventional nanowires and nanoribbons while providing mechanistic insight into the role of lattice perturbations in self-coiling during vapor-phase crystallization.

1.6.4 Chapter 5. Deficiency-Induced Concentric Spiral Hillocks in Anisotropic One-Dimensional van der Waals Crystals

Elemental analysis by energy-dispersive X-ray spectroscopy (EDS) revealed that the ring-shaped structures discussed in **Chapter 4** exhibited a sulfur deficiency relative to stoichiometric NbS₃. This observation motivated a broader investigation of the role of sulfur deficiency in directing crystal growth, which is explored in **Chapter 5** using ZrS₃ as a model system. Unlike the preceding chapters, which focus on bottom-up nanostructures grown by modified CVT, **Chapter 5** employs conventional CVT to investigate crystal growth at the bulk scale. By systematically introducing sulfur deficiency during CVT growth, **Chapter 5** demonstrates that sulfur deficiency promotes screw-dislocation-driven crystallization and the formation of concentric spiral hillocks. These studies provide insight into how compositional deficiency influences defect-mediated crystal growth and morphology evolution in anisotropic 1D vdW materials.

In conclusion, these investigations advance the fundamental understanding and control of crystal growth in 1D vdW materials. The results demonstrate that crystal morphology and dimensional evolution are governed by the interplay among crystal bonding, composition, mass transport, and defect formation. By systematically manipulating these factors, these studies establish new strategies for engineering ultra-long nanowires, ring-shaped structures, and spiral hillocks. Furthermore, this work shows that the accessible morphological landscape of 1D vdW materials is substantially broader than previously recognized.

1.7 References

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CHAPTER 2: Bonding-Directed Crystallization of Ultra-Long One-Dimensional NbS₃ van der Waals Nanowires

2.1 Abstract

The rediscovery of one-dimensional (1D) and quasi-1D (q-1D) van der Waals (vdW) crystals ushered the realization of nascent physical properties in 1D that are suitable for applications in photonics, electronics, and sensing. However, despite renewed interest in the creation and understanding of the physical properties of 1D and q-1D vdW crystals, the lack of accessible synthetic pathways for growing well-defined nanostructures that extend across several length scales remains. Using the highly anisotropic 1D vdW NbS₃-I crystal as a model phase, we present a catalyst-free and bottom-up synthetic approach to access ultralong nanowires, with lengths reaching up to 7.9 mm and with uniform thicknesses ranging from 13 to 160 nm between individual nanowires. Control over the synthetic parameters enabled the modulation of intra- and inter-chain growth modalities to selectively yield only 1D nanowires or quasi-2D nanoribbons. Comparative synthetic and density functional theory (DFT) studies with a closely related nondimerized phase, ZrS₃, show that the unusual preferential growth along 1D can be correlated to the strongly anisotropic bonding and dimeric nature of NbS₃-I.

2.2 Introduction

Physical properties of low-dimensional materials are significantly influenced by their size, composition, and crystal structure.^{1–8} Low-dimensional materials, such as graphene and transition metal dichalcogenides (TMDCs, MCh₂; M = Mo, W, Nb, Ti, etc.; Ch = S, Se, Te) have gained widespread interest owing to inherently strong covalent in-plane bonds that form confined 2D layers that are held together by weak van der Waals (vdW) forces.^{1,9} Due to their anisotropic bonding nature at the monolayer limit, 2D vdW materials display unique physical properties that are often drastically altered upon exfoliation down to length scales that approach the single-atom-thick regime.^{1,9–11} In lower dimensionalities, recent efforts have demonstrated the observation of nascent physical properties in one-dimensional (1D) and quasi-one-dimensional (q-1D) dimensional analogues of 2D vdW solids.^{12–22} Unlike nanosheet-forming 2D materials, 1D vdW materials exfoliate into nanowires and nanoribbons, which often display anisotropic electronic and optical properties.^{5–7,23}

Of these, the modular class of 1D vdW MCh₃ (M = Ti, Zr, Hf, Nb, Ta; Ch = S, Se) crystals which exhibit strong anisotropy due to covalent bonding along only one crystallographic axis has served as a reliable platform to understand the properties of sub-nanometer-thick 1D chains held by vdW forces.^{7,23} Like TMDCs, MCh₃ crystals exhibit unique properties based on their sub-unit structure and packing.^{3,24–28} The polymorph-rich NbS₃ phase, for example, shows electronic properties that range from semiconducting (Types I, IV, VI) to metallic (Types II, III, V).^{24,25} It also hosts unusual properties, including near-room temperature charge density wave states with exceptional coherence,²⁹ field-effect responsive sliding,³⁰ and highly polarized optoelectronic properties.²³ The more stable NbS₃-I polymorph has a triclinic structure (P1̄ space group),³¹ which arises from the in-chain dimerization of Nb atoms (Fig. 1A).²⁵ NbS₃-I is an air-stable and mechanically robust semiconducting material^{23,32,26} which displays ultra-broadband photodetection from UV (375 nm) to THz (118.8 μm), making it ideal for use in optoelectronic nanodevices.^{23,32} While heavily studied in the bulk,^{3,25} efforts to understand emergent properties and applications of NbS₃-I and related MCh₃ phases from quantum confinement are hampered by the stochasticity of top-down exfoliation which result in a distribution of nanowires, nanoribbons, and nanosheets (**Fig. S1**). Here, we sought to understand the role of anisotropic bonding and intra-chain dimerization in the growth of MCh₃ crystals and investigate whether these can be leveraged to grow ultra-long nanowires with high aspect ratios. We present a catalyst-free, bottom-up, and controllable vapor-phase approach to grow record-long nanowires of the MCh₃ model phase NbS₃-I, obviating the need for top-down exfoliation. Using dark-field scattering, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), Raman spectroscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM), we confirmed the polytype and dimensions of the resulting nanowires, which reached unusually long lengths up to 7.9 mm. We rationalize this growth behavior using a DFT-guided assessment of the anisotropic intra- and inter-chain bonding which highlights the pronounced role of phase stability and intra-chain dimerization in distinctly promoting in-chain growth.

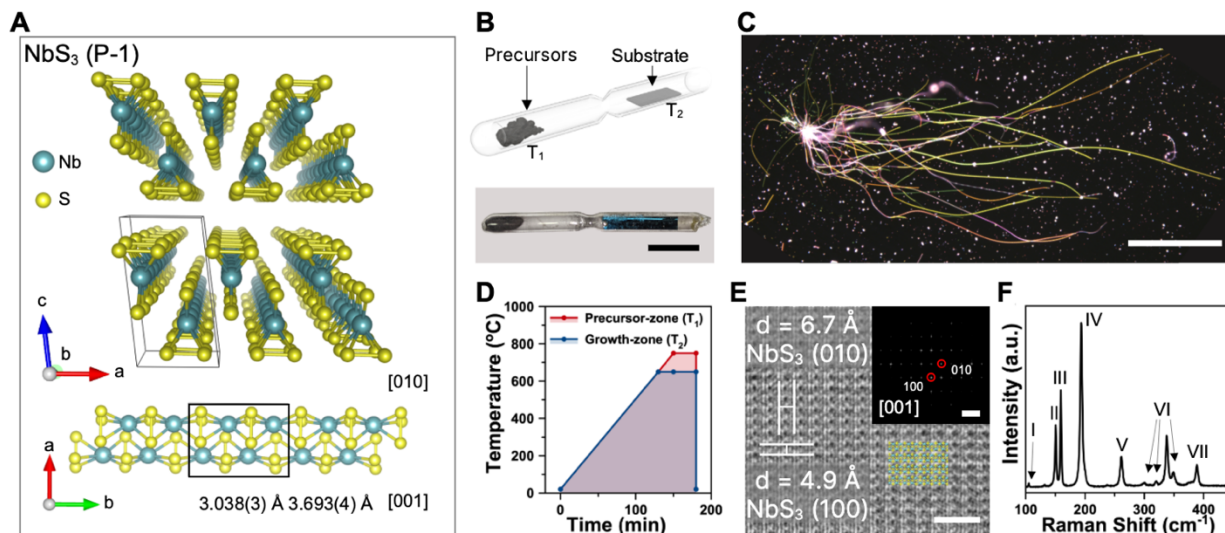


Figure 1. Crystal structure and characterization of NbS₃-I. (A) Crystal structure of NbS₃-I and projection of parallel ([010] zone axis) and perpendicular ([001] zone axis) to the chain direction.³¹ (B) Graphical representation (top) and actual ampoule post-reaction (bottom) used to synthesize NbS₃-I nanowires. The two regions are labeled as T₁ and T₂. Scale bar, 3 cm. (C) Dark-field optical micrograph of NbS₃-I nanowires on Si/SiO₂ substrate. Scale bar, 245 μm. (D) Corresponding CVT furnace temperature program at the high (T₁) and low (T₂) temperature regions used to grow nanowires in C. (E) TEM image of a NbS₃-I nanowire from C with an overlaid [001]-oriented crystal model of NbS₃-I. Scale bar, 2 nm. Corresponding FFT and zone axis assignment are inset. Scale bar, 0.5 Å⁻¹. (F) Raman spectrum of an isolated NbS₃-I nanowire from C (532 nm excitation).

2.3 Experimental Section

2.3.1 Supplementary text: Promoting the lateral growth of NbS₃ into nanoribbons

We established that the optimal program to grow wide quasi-2D nanoribbons characterized by laterally assembled 1D chains involved: (1) positioning the substrate furthest away from T₁, (2) heating the growth zone to 800 °C for one minute to increase the sulfur vapor concentration, (3) applying the temperature gradient (T₁ = 750 °C to T₂ = 650 °C) for 30 minutes to initiate the deposition, and (4) slow cooling at a rate of 0.25 °C/min to room temperature.

2.3.2 Supplementary text: Distinction between intra- (nanowire) and inter-chain (nanoribbon) growth routes

The nanowire growth route was optimized to promote the thermodynamically favored 1D morphology and uniform growth across the substrate (**Fig. S7**). This thermodynamic preference is

due to the strong bonding along the covalent b-axis (long-chain axis), which is further enhanced by the dimerization of Nb atoms. In contrast, the nanoribbon growth route promoted growth along the a-axis (perpendicular to the long-axis), resulting in quasi-2D nanoribbons. This route involves more sulfur atoms and is promoted by a high sulfur environment implemented in the growth program. Due to overlap in the methods, it was possible to obtain a mixture of nanowires and nanoribbons in some areas of the substrate (**Fig. S14**). However, the nanoribbon method results in nanoribbons with widths that are not achieved using the nanowire growth method.

2.3.3 Reagents and Substrates

Niobium powders (99.8%), zirconium powders (99.5%), sulfur powders (sublimed; 99+%; Strem Chemicals, Inc.), and Si/SiO₂ substrates (300 nm wet thermal oxide; University Wafer, Inc.) were used in this study.

2.3.4 Growth of NbS₃ Nanowires

NbS₃ nanowires were grown on Si/SiO₂ wafers via a modified CVT method. In a typical synthetic experiment, Nb and S powders were lightly ground and mixed in a stoichiometric Nb:S ratio of 1:4 using an agate mortar and pestle. A 14.5 cm-long (10 mm inner diameter (I.D.) 12 mm outer diameter (O.D.)) quartz reaction tube was modified by necking the center of the tube 6 cm from the sealed end. The outer circumference at the narrowed region of the ampoule is between 2.8–3 cm. The powders, positioned on the left side of the tube (T_1), along with a Si/SiO₂ wafer (positioned on the right side of the tube (T_2); 50 mm × 9 mm), were encapsulated in the quartz tube and vacuum-sealed (~15 mTorr). The resulting ampoule was placed in a two-zone furnace (OTF-1200X, MTI Corporation), and a temperature gradient of 100°C ($T_1 = 750\text{ }^{\circ}\text{C}$; $T_2 = 650\text{ }^{\circ}\text{C}$) was applied through a ramp-up rate of 5 min/°C. The 100°C temperature gradient was maintained for 30 min or 3 days, depending on the desired length of the resulting nanowires. Once the reaction was complete the furnace was turned off and allowed to reach room temperature naturally. To grow wide nanoribbons, a 15 cm- long quartz reaction tube and the substrate is positioned away from the T_1 zone. The growth zone was first heated to 800°C for one minute before applying the temperature gradient of 750–650°C followed by a significantly slower cooling rate of 0.25°C/min to room temperature.

2.3.5 Growth of ZrS₃ Nanowires

ZrS₃ nanowires were grown on Si/SiO₂ wafers using a similar modified CVT approach described for the synthesis of NbS₃ nanowires. In a typical synthetic experiment, Zr and S powders were lightly ground and mixed in a stoichiometric Zr:S ratio of 1:4 using an agate mortar and pestle. A 14.5 cm-long (10 mm inner diameter (I.D.) 12 mm outer diameter (O.D.)) quartz reaction tube was modified by necking the center of the tube 6 cm from the sealed end. The powders, positioned on the left side of the tube (T_1), along with a Si/SiO₂ wafer (positioned on the right side of the tube (T_2); 50 mm × 9 mm), were encapsulated in the quartz tube and vacuum-sealed (~15 mTorr). The resulting ampoule was placed in a two-zone furnace (OTF-1200X, MTI Corporation), and an optimized temperature gradient of 130 °C ($T_1 = 650$ °C; $T_2 = 520$ °C) was applied through a ramp-up rate of 5 min/ °C. The 130 °C temperature gradient was maintained for 30 min or 5 days, depending on the desired length of the resulting nanowires. Once the reaction was complete the furnace was turned off and allowed to reach room temperature naturally or at a slow cooldown rate of 0.25 °C/min.

2.3.6 Optical Microscopy and Dark-Field Scattering Spectroscopy

Dark-field microscopy imaging and spectroscopic scattering measurements were performed using a modified Olympus BX-43F microscope equipped with a Cytoviva hyperspectral system (automated stage, grating, and a CCD detector capable of measurements from 450 nm to 1000 nm) and a high-resolution imaging camera. The scattering spectra were obtained in dark-field mode which was measured using the Cytoviva spectrometer. The resulting spectra were normalized with respect to the illuminating light source by taking the intensity of the nanowire measured in the dark-field minus the intensity of the background and dividing this by the intensity of the light source.

2.3.7 Atomic Force Microscopy (AFM)

The heights and topographies of the resulting nanowires were obtained using an Anton Paar Tosca AFM with ARROW-NCR Al-coated tips (resonance frequency of 285 kHz and force constant of 42 N/m) (NanoWorld). The background was corrected and processed using Gwyddion® software.

2.3.8 Raman Spectroscopy

Raman spectra of the resulting nanostructures on Si/SiO₂ substrates were taken using a HORIBA LabRAM HR Evolution confocal Raman microscope with a 532 nm excitation laser. From the NbS₃ Raman spectra, the following phonon peaks are assignable: the 109 cm⁻¹ peak (labeled as I) from the lattice deformation mode along the Nb-Nb chain; the 154 cm⁻¹ peak (II) from the lattice compression along the chain (T'y mode); 163 cm⁻¹ peak (III) from the $\nu(\text{Nb-Nb})$ stretching; the 197 cm⁻¹ peak (IV) from the $\nu\text{Nb}-(\text{S}^2)$ mode; 264 cm⁻¹ peak (V) from the symmetrical valence of the Nb-S vibrations (from the rigid sublattice); the 303 cm⁻¹, 323 cm⁻¹, 341 cm⁻¹, and 352 cm⁻¹ peaks (VI) from the $\nu(\text{Nb-S})$ intra-chain vibration; and 375 cm⁻¹ and 392 cm⁻¹ peaks (VII) from the (Nb-S) interchain vibration.

2.3.9 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS)

The SEM images and chemical compositions of the resulting nanostructures were obtained using an FEI Magellan XHR SEM and EDS (Oxford Silicon Drift Detector, 80 mm²). The resulting EDS data were analyzed using the built-in Aztec software.

2.3.10 Transmission Electron Microscopy (TEM) and Sample Preparation

The samples were prepared for TEM imaging by dry transferring of the nanowires onto a lacey carbon grid (400 mesh; Ted Pella Inc.) by smearing the carbon side of the grid onto the growth substrate. TEM was performed at 200 kV on a JEOL JEM-2800 equipped with a Gatan OneView camera. Processing of raw (.dm4) images was done in DigitalMicrograph. Fast Fourier transformations (FFTs) of the images were produced in ImageJ. Indexing of FFTs was performed in SingleCrystal (CrystalMaker software).

2.3.11 Density Functional Theory Calculations of Intra-and inter-chain Interactions in NbS₃ and ZrS₃

First-principles calculations were performed using the projector-augmented wave pseudopotentials^{1,2} and the generalized gradient approximation of Perdew-Burke-Ernzerhof³ using Vienna Ab initio Simulation Package (VASP) code.⁴ An energy cutoff of 450 eV and the

Monkhorst-Pack k-point grid⁵ are $8 \times 14 \times 6$ for bulk ZrS_3 and $\text{NbS}_3\text{-V}$, $8 \times 8 \times 6$ for bulk $\text{NbS}_3\text{-I}$. The structure is optimized until the atomic forces are smaller than $0.01 \text{ eV/\AA}$. For the vdW corrections, we used the DFT-D3 method.⁶ The lattice constants for ZrS_3 are $a = 5.117 \text{ \AA}$, $b = 3.632 \text{ \AA}$, $c = 9.067 \text{ \AA}$, $\beta = 96.897^\circ$; for $\text{NbS}_3\text{-V}$ are $a = 4.864 \text{ \AA}$, $b = 3.328 \text{ \AA}$, $c = 9.104 \text{ \AA}$, $\beta = 96.649^\circ$; for $\text{NbS}_3\text{-I}$ are $a = 4.939 \text{ \AA}$, $b = 6.743 \text{ \AA}$, $c = 9.188 \text{ \AA}$, $\beta = 96.644^\circ$.

2.3.12 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) spectra were measured using a Kratos Analytical Axis Supra spectrometer. The resulting spectra were corrected with the binding energy of the adventitious C *1s* peak. High resolution spectra for each elemental line were modeled with Lorentzian Asymmetric (LA) line shapes with CasaXPS software.

2.3.13 Experimental Section References

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2.4 Results, Discussion, and Conclusion

NbS₃-I nanowires were grown using a modified chemical vapor transport (CVT) method previously reported by Hu et al. for 2D vdW crystals, where the reaction ampoule was narrowed near the center to grow thin nanoscale structures on a suitable substrate.³³ Here, we significantly modified several parameters, including the reaction ampoule dimensions, substrate, and temperature profile, to precisely grow NbS₃-I nanostructures (**Fig. 1B, D**). For all syntheses, elemental Nb and S powder loadings followed an optimized Nb:S ratio of 1:4, as we found that excess sulfur acts as a transport agent and suppresses the growth of the competing 2D phase, NbS₂ (**Fig. S2, 3**). Necking the center of the ampoule tuned the precursor flux to the substrate (**Fig. S4**). Reports on the CVT synthesis of bulk NbS₃-I were able to use close-to-stoichiometric ratios because of longer reaction times of 5 days to 2 weeks,^{3,23,24,32,34} which facilitate complete reaction and precursor mixing. However, when growing nanostructures at shorter reaction timescales (30 min to 3 days), higher sulfur partial pressures are necessary to grow the target sulfur-rich NbS₃. Bulk, needle-like crystals with smooth facets formed on the inner top surface of the quartz ampoule, whereas the targeted nanowires were deposited on the Si/SiO₂ substrate (**Fig. S5-7**). Generally, we observed that thin nanowires grew radially from localized nucleation spots and along the substrate edges, resulting in comparable cross-sections across the substrate (**Fig. 1C; Fig. S7, Table S1**).

TEM, EDS, and Raman spectroscopy demonstrated that bulk crystals and nanowires belong to the NbS₃-I polytype (**Fig. 1E, F; Fig. S6, 8**). For all nanowires in **Fig. 1C**, EDS analysis confirmed the composition of single, isolated nanowires composed of Nb and S elements with an Nb:S average ratio of $\approx 1:3$. EDS mapping showed a uniform distribution of Nb and S across the nanowires (**Fig. S8**). Dark-field optical images of the substrate showed nanowires with high aspect ratios emerging from few nucleation spots (**Fig. 1C**). TEM imaging shows the high crystallinity of the nanowires with d-spacing matching that of NbS₃-I and their flexibility (**Fig. 1E; Fig. S6, 9**). The fast Fourier transform (FFT) was indexed as the NbS₃-I [001] zone axis (**Fig. 1E**). Peaks in the Raman spectrum of the nanowires in **Fig. 1C** (**Fig. 1F**) are consistent with the NbS₃-I polytype.^{28,35} X-ray photoelectron spectroscopy (XPS) of bulk crystals showed peaks corresponding to the 3d_{3/2} and 3d_{5/2} states of Nb, and the S' 2p_{1/2}, S' 2p_{3/2}, and S 2p_{1/2}, S 2p_{3/2} states of S (**Fig. S10**). Assignments of Raman peaks I to VII are in the Supplementary Information.

We systematically varied the duration of the reactions from 30 min to 3 d at a fixed temperature gradient ($T_1 = 750\text{ }^{\circ}\text{C}$ to $T_2 = 650\text{ }^{\circ}\text{C}$) to further understand the effect of time on the growth of NbS₃-I. Generally, the growth of NbS₃-I nanowires was observed at all reaction times used in this study. If the reaction is quenched using an ice bath, the nanowires would be shorter than the naturally cooled analogues. Nanowires from a quenched 30-minute reaction reached lengths of up to ~ 1 mm, with most nanowires having lengths between 30 and 249 μm and heights ranging from 13 nm to 100 nm (**Fig. 1C**). In contrast, a 30-minute reaction with natural cooling yielded nanowires with lengths up to ~ 2.5 mm, with most lengths between 69 and 728 μm and with comparable heights from 24 nm to 100 nm (**Fig. S7**). Intriguingly, a three-day reaction time with natural cooling yielded ultra-long nanowires of up to ~ 7.9 mm in length, with most lengths ranging from 251 μm to 2.2 mm and heights of 40 nm to 160 nm (**Fig. 2A-E**). Our ability to grow well-defined NbS₃-I nanowires enabled us to measure their thickness-dependent optical scattering properties (**Fig. 2F,G**). From dark-field hyperspectral imaging and spectroscopy, we found thickness-dependent spectral features in nanowires that are ~ 40 to 120 nm-thick, illustrating that the frequency distribution of scattered light can be systematically modulated by controlling the nanowire thickness (**Fig. 2F**). Generally, nanowires that were sub-100 nm thick appeared green-blue, whereas thicker nanowires (>100 nm) appeared yellow-white in the dark-field micrographs (**Fig. 2G**).

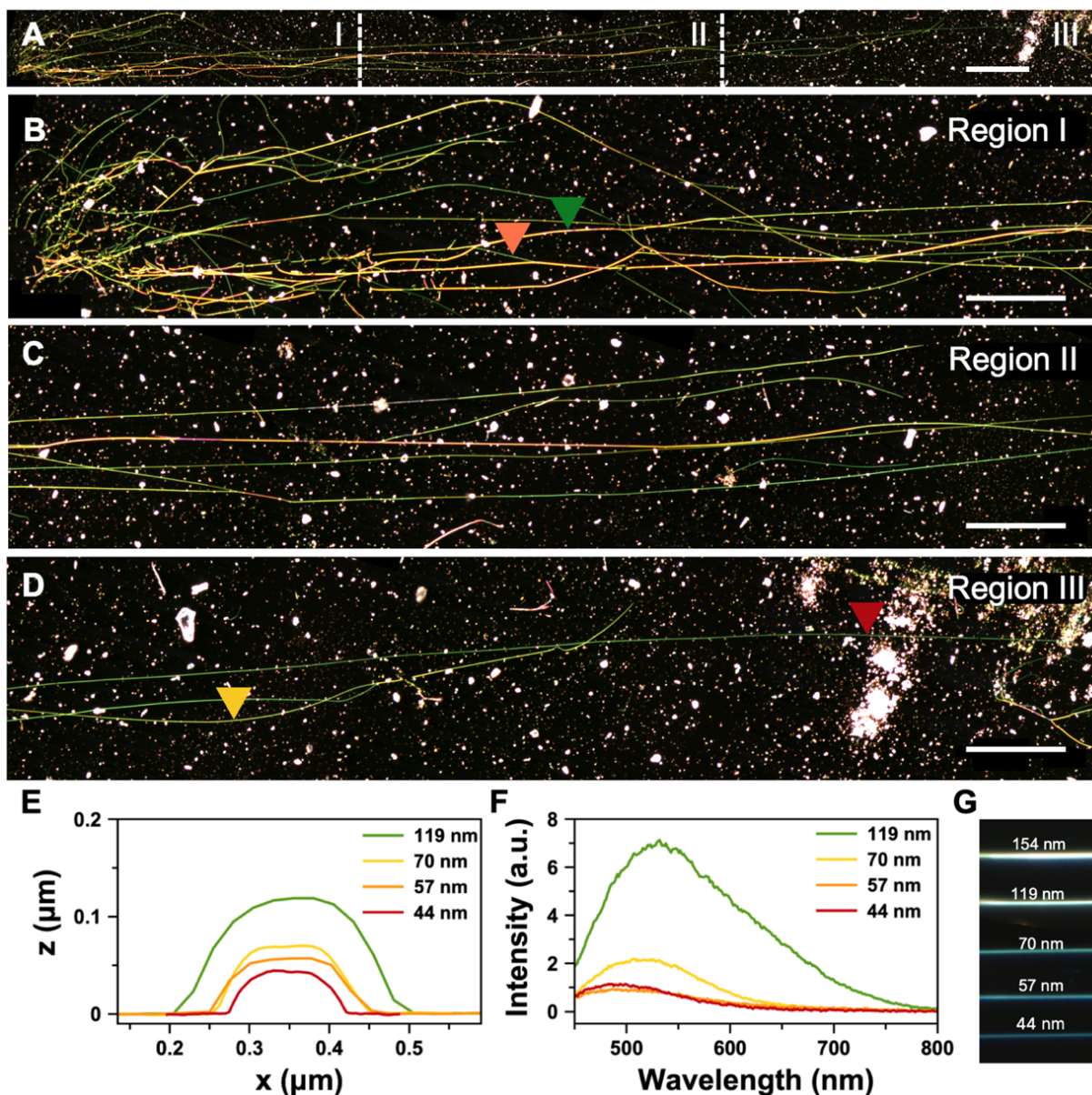


Figure 2. Thickness-dependent light scattering of NbS₃-I (A) Dark-field optical micrographs of NbS₃-I nanowires on a Si/SiO₂ substrate after a 3-day vapor-phase synthesis, divided into three regions: I, II, and III. Scale bar, 490 μm . (B, C, D) High-magnification micrographs corresponding to regions I, II, and III in A, respectively. Triangles point to the location where AFM and optical scattering spectroscopy measurements were taken, colors correspond to measurements in E and F. (E) AFM height profiles of the NbS₃-I nanowires from A. (F) Corresponding thickness-dependent dark-field optical scattering spectra of NbS₃-I nanowires in A. (G) Dark-field optical micrographs of nanowires of various thicknesses taken at 50 $\times$ objective magnification.

We found that the morphology of the NbS₃-I nanostructures could also be modulated by adjusting the temperature and duration of the synthetic steps to promote a sulfur-rich environment (**Fig. S11, 12; Supplementary Text**). We observed that this program promoted lateral growth of the chains along the a-axis (vdW direction), which uniquely yielded the wide nanoribbon analogues of NbS₃-I (**Fig. S13, 14**). Peaks in the Raman spectra of the nanoribbons, like the nanowires, agreed well with NbS₃-I phonon modes (**Fig. S15**). Nanoribbons crystallized into long and thin structures with dimensions ranging from 88 nm × 10 μm × 640 μm to 91 nm × 37 μm × 1200 μm (**Fig. S13, 14, 16, 17**). Nanoribbons display shorter lengths compared to nanowires (**Fig. S17**). EDS analysis confirmed a Nb/S ratio of $\approx 1:3$, and like the nanowires, mapping showed an even distribution of Nb and S throughout the crystal (**Fig. S18**). The distinction between nanowire and nanoribbon growths is discussed in the Supplementary Text.

To understand the unusual growth behavior of NbS₃-I, we directly applied the methods used to grow NbS₃-I to a closely related MCh₃ phase, ZrS₃. ZrS₃ displays the same trigonal prismatic coordination environment along the chain and strong covalent bonding along the b-axis, but without the in-chain metal-metal dimerization (**Fig. S19**). Crystals found on the substrate were nanoribbons significantly shorter than NbS₃-I. The nanoribbons had thicknesses ranging from ~ 6 to 200 nm and lengths ranging from 0.056 to 1.8 μm, which are at least three orders of magnitude shorter than NbS₃-I nanowires (**Fig. S20**). Raman spectroscopy (**Fig. S21**), and TEM (**Fig. S22**) confirmed that the crystal structure of the nanocrystals is consistent with that of ZrS₃.

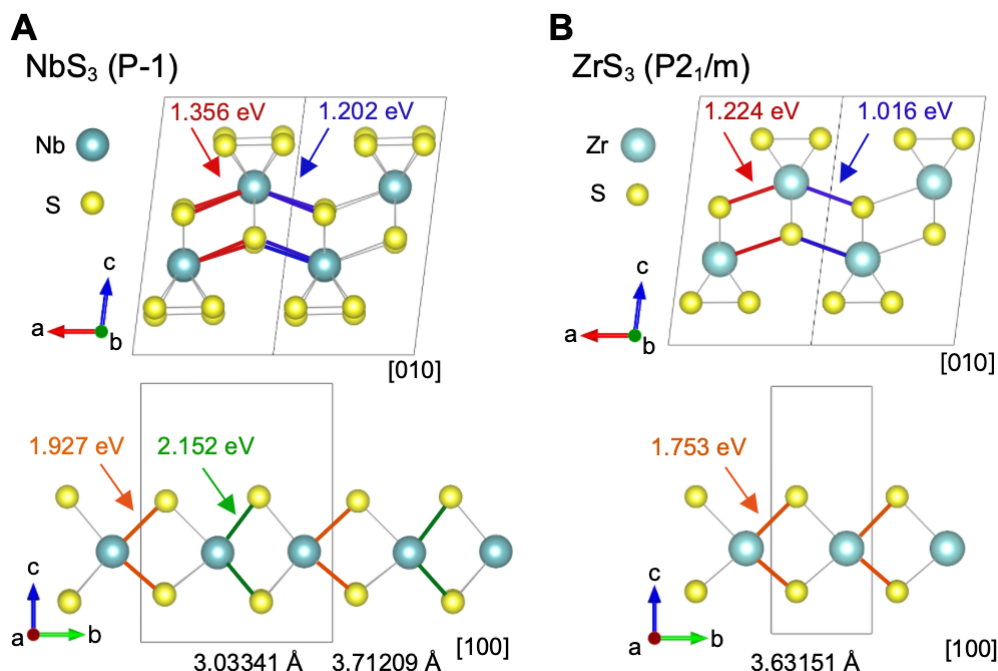


Figure 3. Bonding energies of NbS₃-I and ZrS₃. (A, top) DFT-calculated inter-chain bonding energies of NbS₃-I within (red) and across (blue) the unit cell along a-axis. (A, bottom) DFT-calculated bonding energies of the covalent intra-chain interactions in NbS₃-I. There are two bonding energies (orange and green bonds) corresponding to the non-equivalent intra-chain interactions arising from Nb-Nb dimerization along b-axis. (B, top) DFT-calculated inter-chain bonding energies of ZrS₃ within (red) and across (blue) the unit cell along a-axis. (B, bottom) DFT-calculated bonding energies corresponding to the covalent intra-chain interactions in ZrS₃ (orange).

We performed density functional theory (DFT) calculations to analytically compare bond strengths of NbS₃-I and ZrS₃ across multiple crystallographic directions and rationalize the disparity between the growth of ultra-long NbS₃-I nanowires versus the significantly shorter ZrS₃ nanoribbons (**Fig. 3**; **Fig. S23-30**; **Table S2**). Partial filling of the d-orbital bands in NbS₃ (d¹), as opposed to ZrS₃ (d⁰), leads to in-chain Nb-Nb interactions, which split the band and decrease the overall energy (**Fig. S29, 30**).³⁶ This is evidenced by the overall stronger bonding in NbS₃-I (**Fig. 3**). For NbS₃-I, calculated intra-chain bonding strengths of 1.927 eV (orange; **Fig. 3A**) and 2.152 eV (green; **Fig. 3A**) were significantly higher than calculated intra-chain bonding strength of 1.753 eV in ZrS₃ (orange; **Fig. 3B**). Enhancement of the intra-chain bonding strength reaches 0.4 eV and is significantly higher than the enhancement along other directions (<0.2 eV; **Table S2**). This increase in covalent intra-chain bonding strength is primarily attributable to in-chain dimerization of Nb atoms. Calculations were also performed to understand the origin of the dimerization and stability of NbS₃-I. We constructed the NbS₃-V polytype,^{3,25} a metastable P2₁/m polymorph with a non-dimerized structure like ZrS₃ (**Fig. S29B**). The additional electron in Nb, compared to Zr,

introduce two extra electrons per unit cell. This lifts the Fermi level, leading to a metallic state in NbS₃-V (**Fig. S29D, E**). Comparing NbS₃-I to NbS₃-V, we found that: (1) dimerization in NbS₃-I lowers the total energy (E) of the system by 0.18 eV, calculated as $2[E(\text{NbS}_3\text{-V}) - E(\text{NbS}_3\text{-I})]$; and (2) dimerization, reminiscent of Peierls-induced transition,²⁵ opens an indirect band gap in NbS₃-I (**Fig. S29F**).^{26,27} We posit that the stable in-chain dimerization likely influences the preferential bottom-up growth of NbS₃-I nanocrystals along the chain direction

2.4 References

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CHAPTER 3: Bottom-Up Crystallization of Long and High Anisotropic Nanowires Based on a Dimerized 1D van der Waals Transition Metal Trihalide

3.1 Abstract

Owing to their atomic precision and intrinsic chain structure, one-dimensional (1D) van der Waals (vdW) crystals have emerged as promising building blocks for device integration approaching the sub-nanometer limit. However, while there have been significant advances in the discovery of new and more complex analogues of 1D vdW crystals, current pathways to access their nanoscale morphologies are still limited to the stochastic process of mechanical exfoliation. Compared to their 2D counterparts, the controlled bottom-up synthesis of 1D vdW nanostructures, together with the chemical and structural factors governing anisotropic crystal growth, remains largely unexplored. Here, we investigate the emerging concept of intra-chain dimerization as a structural motif to preferentially confine the crystallization of 1D vdW crystals only into one direction and drive their crystallization into nanowires without the need of a catalyst. Using MoI_3 as a model system, our results support the hypothesis that the pronounced intra-chain Mo—Mo dimerization promotes preferential crystal growth along the chain direction, yielding ultrathin, high-aspect-ratio nanowires with widths down to ~ 4 nm and lengths of up to 0.5 mm. Through their synthesis into well-defined nanowires, we demonstrate the structural anisotropy arising from the bundling of MoI_3 chains through orientation-dependent Raman spectroscopy. Using single-nanowire hyperspectral microscopy, we further demonstrate pronounced optical anisotropy through orientation-dependent light scattering and polarization-dependent absorption. Taken together, these results support intra-chain dimerization as a useful structural motif for directing anisotropic crystal growth in 1D vdW materials and provide a rational route toward high-aspect-ratio nanostructures approaching the single-chain limit.

3.2 Introduction

Semiconducting one-dimensional (1D) nanostructures with high aspect ratios have become particularly attractive for device integration, as their geometry enables their use as nanoscale interconnects while supporting well-defined optical states, high-fidelity photonic modes, and

directional charge transport.^{1–10} In particular, advances in the discovery and fabrication of emergent low-dimensional materials have pushed the boundaries of 1D confinement down to the sub-nanometer range, including nanowires, nanoribbons, nanotubes, and single chains.^{10–13} With the advent of two-dimensional (2D) van der Waals (vdW) solids comprised of non-covalently bound sheets, top-down (e.g., micromechanical and liquid-phase exfoliation) and bottom-up (e.g., vapor deposition and nanotube encapsulation) routes have further scaled down the sizes of 1D and quasi-1D nanostructures beyond the size regimes and aspect ratios realizable through the well-established catalyzed, vapor-liquid-solid growth pathway for nanowire structures. While such approaches yield nanowires and nanoribbons with thicknesses that approach the atomic limit, they still face specific and longstanding constraints: the stochastic nature of top-down exfoliation, especially the reliance of this approach on 2D vdW crystals that have quasi-1D sub-motifs to access 1D nanostructures; the limited long-range order of structures confined within nanotubes; and the lack of intrinsic crystallographic anisotropy, which necessitates the use of bespoke substrates or catalysts to drive bottom-up 1D growth.

Alternatively, the intrinsic structural anisotropies arising from the directional and dimensionally localized bonding in 1D, which are inherent to several classes of vdW and ionic crystals, provide an opportune materials design motif and synthetic approach to intrinsically promote the directed crystallization of ultrathin and high-aspect-ratio 1D nanostructures.^{3,12–17} Specifically, the unidirectional growth of materials with preferential bonding along a specific crystallographic axis is facilitated by differences in surface and bonding energies. In these cases, the system minimizes its overall energy by favoring growth along a particular crystallographic orientation while suppressing growth in orthogonal directions, coinciding with axis-specific covalency or strong directional bonding interactions.^{3,12–14} Still, while demonstrations of the effectiveness of 1D structural anisotropy in driving unidirectional, nanowire growth exist, the generalizable bonding motifs, coordination geometries, and chemical cues that contribute to this specific growth modality have remained largely underexplored.

Among highly anisotropic materials that exhibit strong uniaxial covalency, 1D and quasi-1D vdW crystals have gained recent interest as platforms for catalyst-free nanowire growth along the covalent chain axis.^{12,14} They are characterized by atomically precise chain structures that are held together by weak, non-covalent bonding in the bulk,^{8,12–16} as well as size-, polymorph-, and anisotropy-driven physical states.^{8,12–16,18} Due to their intrinsic chain structure and vdW bonding,

these crystals have been demonstrated to be exfoliable into few-to-single chain structures, although the process remains random, occurs at very low yields, and results in a variety of morphologies (e.g., nanowires, nanoribbons, and nanosheets).^{8,19–21} Alternatively, bottom-up vapor-phase growth routes have been pursued to selectively control the crystallization of 1D and quasi-1D vdW materials into well-defined and predictable nanocrystal structures. However, given the nascency of these materials, the distinct chemical cues, structural motifs, and materials design parameters that direct the crystallization of 1D and quasi-1D vdW materials remain largely underexplored. To this end, our previous studies demonstrated that 1D vdW transition metal trichalcogenides (TMTCs) with specific chain structures and packing motifs, such as NbS₃ Type-I, can be grown as record-long, ultra-thin, and high-aspect-ratio nanowires under appropriate vapor-phase conditions without the need for catalysts or templated substrates.^{14,16,22–24} Based on the specific structural signatures and comparing with other TMTCs, the formation of these nanowires strongly correlates with the pronounced anisotropic bonding arising from their 1D nature, combined with the uniquely strong Nb–Nb covalent bonding in the intra-chain direction associated with dimerization reminiscent of Peierls distortion.

We sought to probe the generality of this emergent approach that capitalizes on the strong covalency imparted by intra-chain dimerization to crystallize 1D and quasi-1D vdW crystals into nanowires. We approached this study by examining a closely related system in the form of a transition metal trihalide, MoI₃, which also exhibits intra-chain Mo–Mo dimerization with distinct alternating Mo–Mo bond lengths of 2.84 Å and 3.57 Å. MoI₃ crystallizes in the orthorhombic *Pmmn* space group, forming chains of dimerized Mo³⁺, each coordinated by six I[−] ions in linear chains of face-sharing MoI₆ octahedra (**Figure 1A,B**).^{19,25–28} Beyond its 1D dimerized structure and vdW nature, MoI₃ has attracted interest for its semiconducting behavior and distinct magnetic states, characterized by easy-plane antiferromagnetic ordering with alternating spins along the dimerized Mo chains and predicted non-collinear helical magnetic order between neighboring chains.^{26,27} Exfoliation strategies have been explored to access nanoscale crystals, but they have yielded only a limited number of thin structures with sub-nanometer thicknesses.^{19,25} Furthermore, micromechanical and liquid phase exfoliation have resulted in non-uniform morphologies and, as expected from top-down routes, comparatively short nanowires.^{19,25} Therefore, in this study, we experimentally demonstrate that the intra-chain dimerization intrinsic to MoI₃ drives the catalyst-free crystallization of very long nanowires—up to about 1 mm—from a closed-system vapor-phase

route. Owing to the well-defined and highly anisotropic nanowires obtained using this synthetic approach, we further demonstrate the strong structural, morphological, and optical anisotropy of MoI_3 .

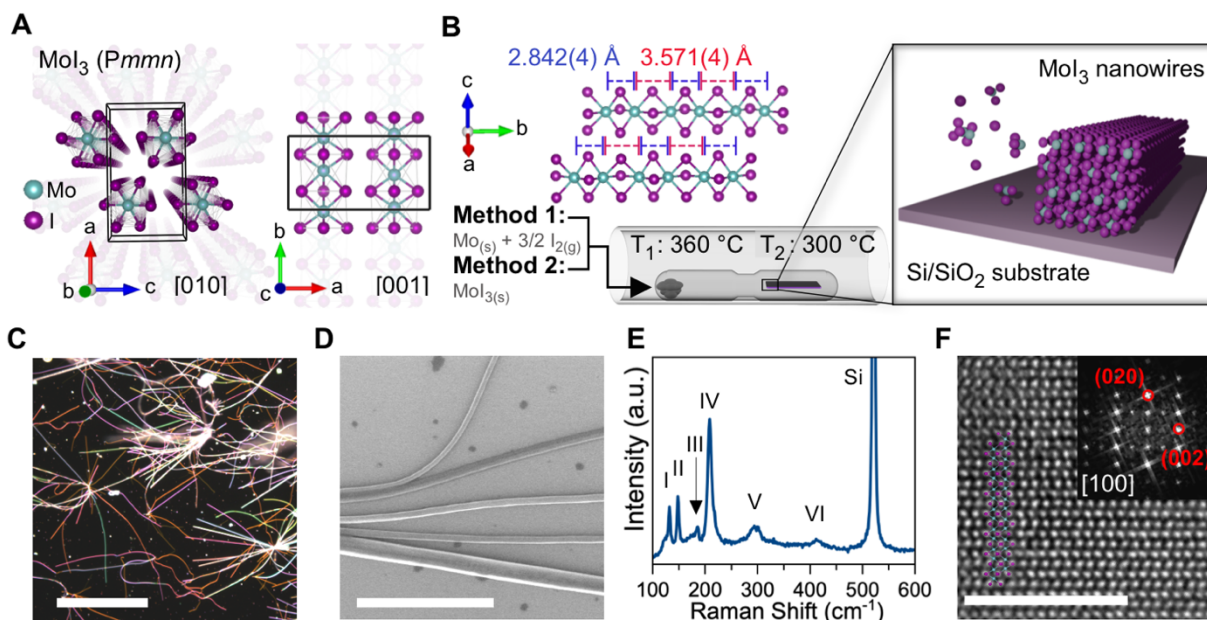


Figure 1. Structurally driven crystallization of well-defined MoI_3 nanowires. (A) Crystal structure of MoI_3 projected along the [010] and [001] crystallographic directions. (B) Schematic illustration of the alternating Mo–Mo bond distances and the synthetic conditions used for vapor-phase nanowire growth. (C) Dark-field optical micrograph of MoI_3 nanowires grown on a Si/SiO₂ substrate. Scale bar, 245 μm. (D) SEM image of representative as-grown MoI_3 nanowires on Si/SiO₂. Scale bar, 1 μm. (E) Representative Raman spectrum of an isolated MoI_3 nanowire on Si/SiO₂. (F) HRTEM image of a MoI_3 nanowire overlaid with a [100]-oriented crystal model. Inset shows the corresponding FFT and indexed diffraction spots. Scale bar, 5 nm.

3.3 Experimental Section

3.3.1 Reagents and Substrates

Molybdenum powders (99.95%, Strem Chemicals, Inc.), resublimed iodine crystals (99.8-100.5%, Spectrum Chemical Mfg. Corp.), and Si/SiO₂ substrates (300 nm wet thermal oxide; University Wafer, Inc.) were used in this study.

3.3.2 Growth of MoI_3 Nanowires

MoI_3 crystals were synthesized on Si/SiO₂ substrates via a modified chemical vapor transport (CVT) method. For Method 1, which produced predominantly bulk crystals, Mo and I₂

powders were combined in a stoichiometric Mo:I = 1:3.05. For Method 2, which produced nanowires, 1.4 g of pre-synthesized MoI₃ crystals were used as precursors. Reactions were carried out in a 13 cm-long quartz tube (10 mm inner diameter, 12 mm outer diameter) that was necked 6 cm from the sealed end. The precursor was placed in the high-temperature zone (T_1), while a Si/SiO₂ substrate (50 mm × 9 mm) was positioned downstream in the low-temperature zone (T_2). The tube was evacuated (~15 mTorr) and placed in a two-zone furnace (OTF-1200X, MTI Corporation). A temperature gradient of $T_1 = 360$ °C and $T_2 = 300$ °C was applied. The furnace was heated at 1.4 °C/min and cooled to room temperature at 1 °C/min after completion of the reaction.

3.3.3 Optical Microscopy, Dark-Field Scattering Spectroscopy, and Optical Absorbance Measurements

Dark-field microscopy imaging, spectroscopic scattering measurements, and transmission measurements were performed using a modified Olympus BX-43F microscope equipped with a Cytoviva hyperspectral imaging system (automated stage, diffraction grating, and CCD detector capable of measurements over the 450–1000 nm spectral range) and a high-resolution imaging camera. Scattering spectra were obtained in dark-field mode using a Cytoviva spectrometer.

Atomic Force Microscopy (AFM). Nanowire topography and height were obtained using an Anton Paar Tosca AFM with ARROW-NCR Al-coated tips (resonance frequency of 285 kHz and force constant of 42 N/m) (NanoWorld). Data were processed and background corrected using Gwyddion® software.

3.3.4 Raman Spectroscopy

Raman spectra were acquired using an InVia microscope by Renishaw Inc. A 532 nm excitation laser and a 2400 lines/mm grating were used. A laser power of 1% and a 30 s exposure time was used. Linear fitting of peak positions was done using MagicPlot 3.0.1 software.

3.3.5 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Morphology and elemental composition of the nanostructures were characterized using an FEI Magellan XHR SEM equipped with an Oxford silicon drift detector (80 mm²). EDS data were analyzed using built-in Aztec software.

3.3.6 Transmission Electron Microscopy (TEM) and Sample Preparation

Samples for TEM were prepared by dry transfer of the nanowires onto a lacey carbon grid (400 mesh; Ted Pella Inc.) by gently contacting the carbon side of the grid with the growth substrate. TEM imaging was performed at 200 kV on a JEOL JEM-2800 equipped with a Gatan OneView camera. Processing of raw (.dm4) images was processed in DigitalMicrograph. Fast Fourier transformations (FFT) of the images were generated in ImageJ. FFTs were indexed using SingleCrystal (CrystalMaker software).

3.3.7 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction was measured using a Rigaku Smartlab X-ray diffractometer equipped with a Cu K α source and a 1D D/teX silicon strip detector. The diffraction pattern was Le Bail fitted using Profex.

3.3.8 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron measurements were performed on MoI₃ crystals grown on Si/SiO₂ substrates. Data were collected on a Kratos Analytical Axis Supra surface science instrument equipped with an Al/Ag X-ray monochromatic source and charge neutralization capabilities. The spectra were energy calibrated using the adventitious sp³ C 1s peak at 284.8 eV. All peaks were fitted with asymmetric Lorentzian functions using CasaXPS software.

3.3.9 Diffuse reflectance spectroscopy (DRS) Measurements

Diffuse reflectance spectra were collected using a Jasco V-670 spectrometer equipped with a 60 mm integrating sphere (Jasco ISN-923), operating over a working range of 190–2500 nm.

Single crystals were ground and dispersed in KBr, and the resulting mixture was loaded into a custom-made holder with a transparent quartz window.

3.3.10 Thermogravimetric analysis (TGA)

Thermogravimetric measurements of bulk MoI₃ crystals were performed using a TA Instruments Q500 thermogravimetric analyzer. During analysis, samples were loaded onto a Pt sample pan and purged with nitrogen gas throughout the measurement.

3.4 Results and Discussion

To understand the parameters that drive the crystallization of MoI₃ nanowires, we first investigated the influence of precursor selection on growth behavior to evaluate the potential for structurally driven unidirectional crystallization in MoI₃ (**Figure 2**). Here, we employed two growth approaches. Method 1 used elemental Mo and I₂ powders in a 1:3.05 molar ratio as precursors, with a slight excess of I₂ to prevent the crystallization of MoI₂. Method 2 used bulk MoI₃ crystals as precursors to further control the flux and nature of the precursor species entering the deposition zone. Both methods generated excess iodine, which re-deposited as I₂ and was subsequently removed by applying a reverse temperature gradient with one end of the ampoule positioned outside of the furnace. Post-synthesis, Method 1 predominantly produced large, needle-like MoI₃ crystals that formed in a radial growth pattern and resembled bulk crystals. The crystals were localized on the upper inner surface of the quartz ampoule and over a significant portion (~3 cm) of the substrate nearest the hotter, T_1 zone (**Figure 2A,B**). Optical microscopy and SEM images further show that Method 1 yields predominantly bulk MoI₃ crystals with only a small fraction of nanowires (**Figure 2C**), as expected from the high material flux generated from elemental precursors. Second, to evaluate the influence of reaction time, we found that an 8-day reaction produced crystals with lengths ranging from approximately 0.01 to 1 mm (average length 0.29 ± 0.22 mm, measured from optical images; $n = 500$) and widths ranging from approximately 50 to 3×10^3 nm (average width 700 ± 500 nm, measured from SEM images; $n = 100$). Reducing the reaction time to 1 day yielded slightly shorter and wider structures with lengths ranging from approximately 3×10^{-3} to 0.9 mm (average length 0.23 ± 0.15 mm, measured from optical images; $n = 500$) and widths ranging from approximately 90 to 5×10^3 nm (average width $1 \times 10^3 \pm 700$ nm, measured from SEM images; $n = 100$) (**Figure 2C,D,F; Figure S1**). While subtle, the effect

of growth time highlights an important growth parameter that can be tuned to minimize crystal width and thereby increase the aspect ratio of the resulting MoI₃ crystals.

Based on these considerations, we devised Method 2 to determine whether reducing the material flux using bulk MoI₃ crystal precursors and optimizing the growth time would produce thinner, longer, and more uniform nanowires. The bulk MoI₃ crystals used as precursors for Method 2 were obtained using Method 1. Le Bail refinement of the powder X-ray diffraction (PXRD) pattern confirmed agreement with the reported *Pmmn* crystal structure of MoI₃ (**Figure S2**).²⁸ Energy-dispersive X-ray spectroscopy (EDS) confirmed a Mo:I atomic ratio of 1:3 and a uniform distribution of Mo and I in the elemental maps (**Figure S3**; **Table S1**). X-ray photoelectron spectroscopy (XPS) measurements of the bulk crystals confirmed the presence of Mo and I, with binding energies corresponding to Mo³⁺ and I⁻ species (**Figure S4**). The weaker and broader peaks corresponding to Mo⁶⁺ are attributed to the inevitable surface oxidation of the crystals upon exposure to ambient air. Collectively, these results confirm the phase purity and composition of the bulk MoI₃ crystals used as precursors for Method 2.

To assess the thermal suitability of the selected Method 2 growth conditions, we performed thermogravimetric analysis and derivative thermogravimetry (TGA/DTG) on as-synthesized bulk MoI₃ crystals before applying the reverse temperature gradient used to remove excess I₂ (**Figure S5**). The TGA profile exhibited three distinct mass-loss steps: (1) a first smaller step from approximately 25 to 80 °C, attributed to the evaporation of residual or unreacted I₂; (2) a second step commencing at approximately 474.5 °C, corresponding to the decomposition of MoI₃ to MoI₂ ($MoI_3 \rightarrow MoI_2 + \frac{1}{2} MoI_2$); and (3) a third step beginning at 686.9 °C, corresponding to the further decomposition of MoI₂ to elemental Mo ($MoI_2 \rightarrow Mo + I_2$). The 360–300 °C temperature gradient used for Method 2 lay below the onset of the first major decomposition event, indicating that vapor-phase growth occurs under conditions that limit pronounced bulk thermal decomposition of MoI₃.

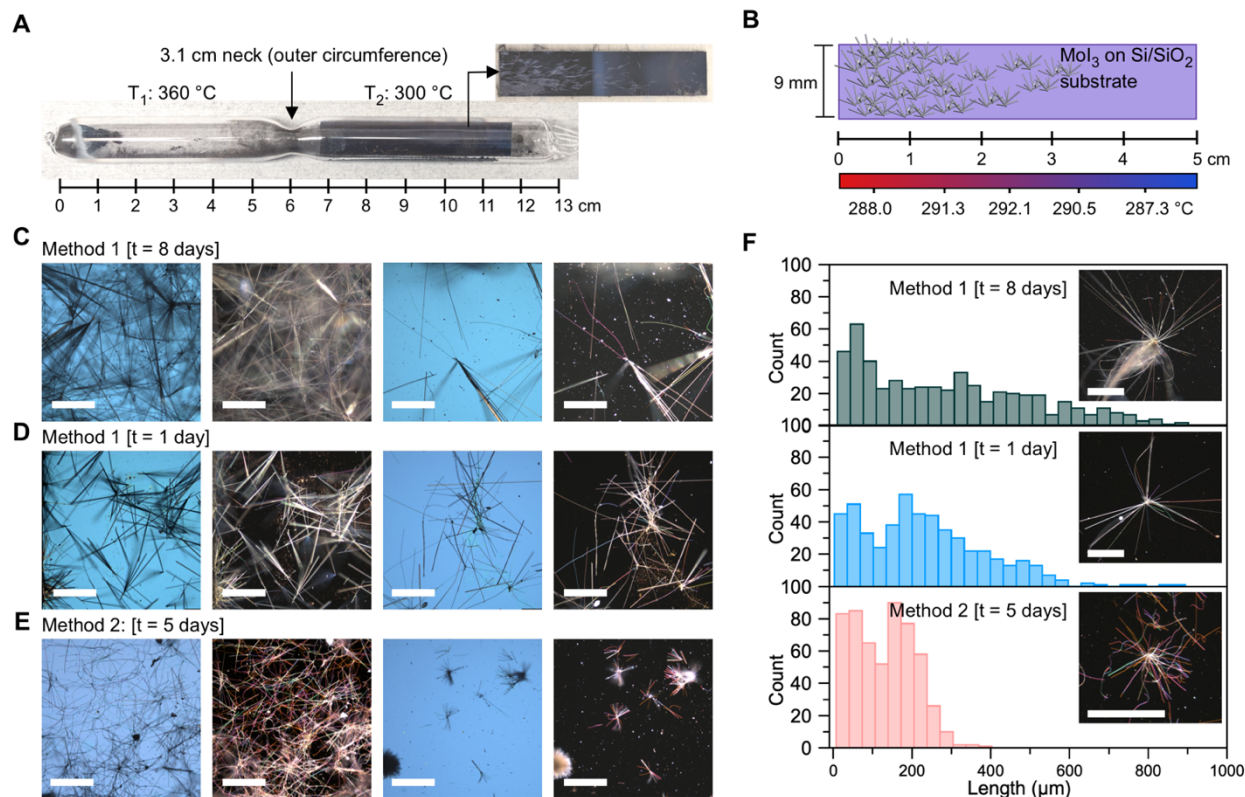


Figure 2. Bottom-up growth of MoI₃ nanowires. (A) Representative post-reaction ampoule and the corresponding growth substrate. (B) Graphical representation of MoI₃ crystal growth via CVT on a Si/SiO₂ substrate, showing the measured temperature profile at 1 cm intervals along the 360–300 °C temperature gradient with an external thermocouple probe. (C,D) Representative bright-field (left) and dark-field (right) optical micrographs from Method 1 after 8-day (C) and 1-day (D) reactions using elemental precursors. Scale bars, 245 μm. (E) Representative bright-field (left) and dark-field (right) optical micrographs from Method 2 after a 5-day reaction using bulk MoI₃ crystals as precursors. Scale bars, 245 μm. (F) Histograms of crystal lengths for each reaction condition shown in (C), (D), and (E). Representative dark-field micrographs to each histogram are shown in the insets. Scale bars, 245 μm.

Post-synthesis characterization by bright- and dark-field optical microscopy, SEM, and HRTEM (**Figure 2E**; **Figure S6**) showed that Method 2, using a 5-day reaction time, produced nanowires with lengths ranging from approximately 7×10^{-3} to 0.4 mm (average length 0.13 ± 0.08 mm, measured from optical images; $n = 500$). SEM analysis further revealed widths ranging from approximately 15 to 520 nm (average width $110 \text{ nm} \pm 80 \text{ nm}$; $n = 100$). Representative HRTEM images further showed that individual nanowires can reach widths as small as approximately 4 nm (range 4–255 nm; average width $95 \pm 80 \text{ nm}$; $n = 8$) (Figure S6,7). Similar to Method 1, EDS measurements of nanowires by Method 2 confirmed a Mo:I atomic ratio of 1:3, with the elemental maps showing a homogeneous spatial distribution of Mo and I (Figure S8; Table S2). These results demonstrate that the 5-day reaction time yields a high density of long,

thin nanowires, whereas a 1-day reaction produced only sparse population of nanowires on the substrate which produced less than five identifiable nanowires.

Taken together, the results from Methods 1 and 2 (**Figure 2C-F**) suggest that, in addition to the intrinsic influence of intra-chain Mo–Mo dimerization, growth conditions that favor a lower supersaturation, such as the use of bulk MoI₃ precursors in Method 2, promote growth along the intra-chain direction and yield significantly longer and thinner nanowires. In contrast, the powdered elemental precursors used in Method 1 provide a substantially larger reactive surface area, which likely increases the generation and transport of vapor-phase precursor species and produces higher supersaturation. Consistent with conventional crystal-growth behavior, the resulting higher supersaturation likely favors the formation of the bulkier crystals observed in Method 1. We note that these observations may not extend to other 1D and quasi-1D vdW materials because, in some systems, competing phases form under conditions similar to those required for the target phase.^{14,29}

The long, thin, and well-defined bulk crystals and nanowires enabled Raman spectroscopy to probe the lattice vibrational modes of MoI₃ and demonstrate the pronounced structural anisotropy arising from its intra-chain covalent bonding (**Figure 3A-C**). The representative Raman spectra in **Figure 3A** display prominent peaks at 123.9 cm⁻¹ (I), 146.8 cm⁻¹ (II), 184.6 cm⁻¹ (III), 208.7 cm⁻¹ (IV, known as B_{3g} symmetry in the literature),²⁶ 293.7 cm⁻¹ (V), and 415.4 cm⁻¹ (VI). Together with the temperature-dependent measurements, these are consistent with the previously reported phonon modes and signatures of magnetic ordering of the *Pmmn* phase of MoI₃ (**Figure S9**).²⁶ Systematic rotation of the bulk single crystal revealed a non-monotonic, with Raman mode intensities varying significantly with rotation angle (**Figure 3A,B**). In these measurements, 0° and 90° correspond to conditions where the long axis (crystallographic b-axis) of MoI₃ is parallel and perpendicular, respectively, to the polarization of the incident laser. These measurements highlight the pronounced anisotropic behavior of MoI₃, most clearly demonstrated by the strong intensity of modes I, IV, V and VI when the incident laser polarization is parallel (0°) to the crystal long axis, which is substantially reduced when the polarization is rotated to the perpendicular orientation (90°). An opposite behavior is observed for mode II. Based on their polarization dependence and the well-established anisotropic Raman response of 1D crystals,^{18,30–33} modes I, IV, V and VI are consistent with predominantly intra-chain vibrations, whereas mode II is consistent with an inter-chain vibration. Because the larger bulk crystal provided higher signal-to-noise ratios than

individual nanowires, it was used as a reference for orientation-dependent Raman measurements (**Figure 3A,B**). Similar orientation-dependent behavior was observed across several nanowires (**Figure S10**). Representative Raman spectra from two nanowires (Nano 1 and Nano 2), measured at orientations corresponding to those of the bulk crystal in **Figure 3A**, are shown in **Figure 3C**. The close agreement between the Raman response of the Method 2 nanowires and the Method 1 bulk crystal demonstrates that the anisotropic lattice vibrational characteristics of MoI₃ are preserved in the nanowires.

Beyond the structural anisotropy revealed by the orientation-dependent Raman measurements, we next investigated the optical anisotropy of MoI₃ using orientation-dependent transmittance measurements on single crystals (**Figure 3E,F**). To establish a reference absorbance spectrum for bulk MoI₃, we characterized an ensemble of Method 1 crystals using room-temperature diffuse reflectance spectroscopy (DRS), with the spectrum converted using the Kubelka-Munk (K-M) function, $F(R_{\infty})$ (**Figure 3D**). The K-M absorbance spectrum exhibited an absorption edge corresponding to an extrapolated optical band gap of ~ 1.36 eV for bulk MoI₃ (**Figure 3D, inset**), which is also consistent with the transmittance experiments (**Figure 3E,F**) and prior reports based on bulk crystals.²⁵ The absorbance spectrum revealed a maximum near 550 nm together with two well-defined peaks at approximately 700 nm and 780 nm. The presence of multiple absorption features is qualitatively consistent with first-principles calculations of isolated MoI₃ chains, which predict several closely spaced Mo *4d*-derived electronic states near the band edges that give rise to multiple inter-band optical transitions.^{34,35} Having established the ensemble spectrum, we next measured the transmittance spectrum of a representative Method 1 single crystal, which was subsequently converted to absorbance. The resulting spectrum closely matched the DRS spectrum, including the three distinct absorption features (**Figure 3D**). Polarization-dependent absorbance spectra were then acquired from a different Method 1 single crystal and a Method 2 nanowire using linearly polarized incident light oriented parallel and perpendicular to their long axes, enabling direct comparison of their optical anisotropy (**Figure 3E,F**). Comparison of the parallel- and perpendicular-polarized spectra with the corresponding unpolarized spectrum revealed pronounced linear dichroism in both the bulk crystals and nanowires, consistent with the behavior of highly anisotropic low-dimensional materials.^{18,33,36} This polarization dependence is manifested as a redistribution of spectral weight, with the broad absorption centered near 650 nm enhanced for light polarized parallel to the crystal long axis, while the longer-wavelength feature

near 825 nm is relatively enhanced for perpendicular polarization. The unpolarized spectrum closely matches the combined response of the two orthogonal polarization directions, consistent with the expected averaging of the polarization-dependent optical response.

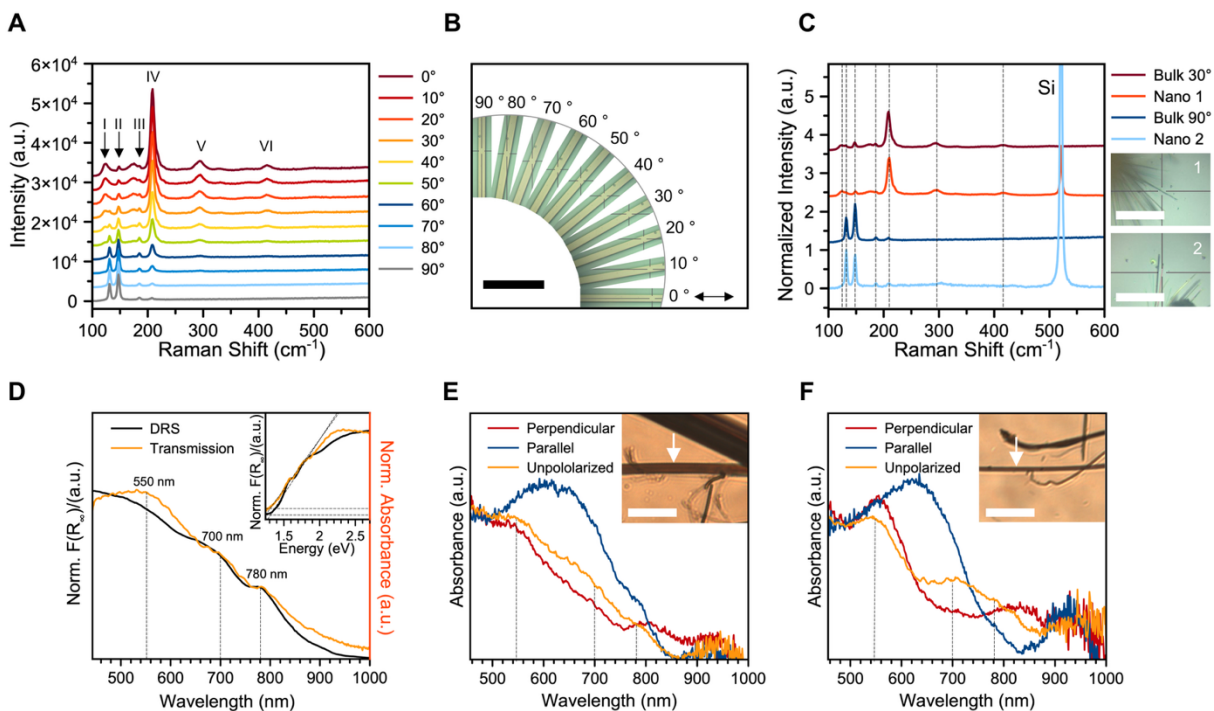


Figure 3. Structural and electronic anisotropy of MoI₃ nanowires. (A) Orientation-dependent Raman spectra of a bulk MoI₃ crystal (shown in B) rotated from 0° to 90° relative to the polarization of the incident 532 nm laser. Scale bar, 80 μ m. (C) Raman spectra of two representative MoI₃ nanowires (Nano 1 and Nano 2), shown in images 1 and 2, together with the spectra of the bulk crystal at 30° and 90° (Bulk 30° and Bulk 90°) from (A) for direct comparison. Scale bars, 40 μ m. (D) DRS and absorbance spectra obtained from transmittance measurements of bulk MoI₃. (E) Absorbance spectra obtained from transmittance measurements of a representative MoI₃ bulk crystal grown by Method 1 using parallel (blue), perpendicular (red), and unpolarized (yellow) light relative to the crystal long axis. Inset: transmission optical image of the measured crystal. Scale bar, 10 μ m. (F) Absorbance spectra from transmittance measurements of a representative MoI₃ nanowire grown by Method 2 using parallel (red), perpendicular (blue), and unpolarized (yellow) light relative to the long axis. Inset: transmission optical image of the measured nanowire. Scale bar, 10 μ m.

To further investigate the optical properties of MoI₃ nanowires, we performed dark-field scattering measurements, which revealed size-dependent scattering from as-grown MoI₃ nanowires on a Si/SiO₂ substrate (**Figure 4A,B**; **Figure S11**). Nanowires with heights ranging from 38–93 nm, as measured by atomic force microscopy (AFM), exhibit increased scattering intensity and redshifted scattering peaks with increasing thickness, whereas thinner nanowires exhibit lower scattering intensity and blue-shifted peaks, consistent with Mie-like scattering

behavior. Polarization-dependent scattering measurements further demonstrate the highly anisotropic nature of MoI₃ nanowires through orientation-dependent light scattering (**Figure 4C,D**). For a representative nanowire (approximately ~90 nm in height and width, as probed by AFM and SEM, respectively), the scattering intensity is maximized when the long axis is oriented parallel to the linear polarizer, whereas it decreases when the long axis is oriented perpendicular to the polarizer (parallel to the a-axis). This anisotropic optical response is further supported by angle-dependent reflection measurements acquired under crossed-polarizer conditions (**Figure 4E-G**). Under crossed-polarizer conditions (**Figure 4E**), the reflected intensity exhibits a strong angular dependence, with pronounced extinction when the nanowire is oriented parallel (0°) or perpendicular (90°) to the polarizer. This behavior is further illustrated in the polar plot (**Figure 4F**) and crossed-polarizer bright-field images (**Figure 4G**), where the nanowire, indicated by the arrow, appears dark at these orientations. These results indicate that the optical response is highly sensitive to the alignment of the incident electric field relative to the crystallographic axes of the nanowire. This behavior is consistent with the polarization-dependent light-matter interactions reported for anisotropic semiconducting and low-dimensional dielectric materials,^{18,33,36–39} and highlights the strong coupling between crystallographic orientation and the optical response in MoI₃.

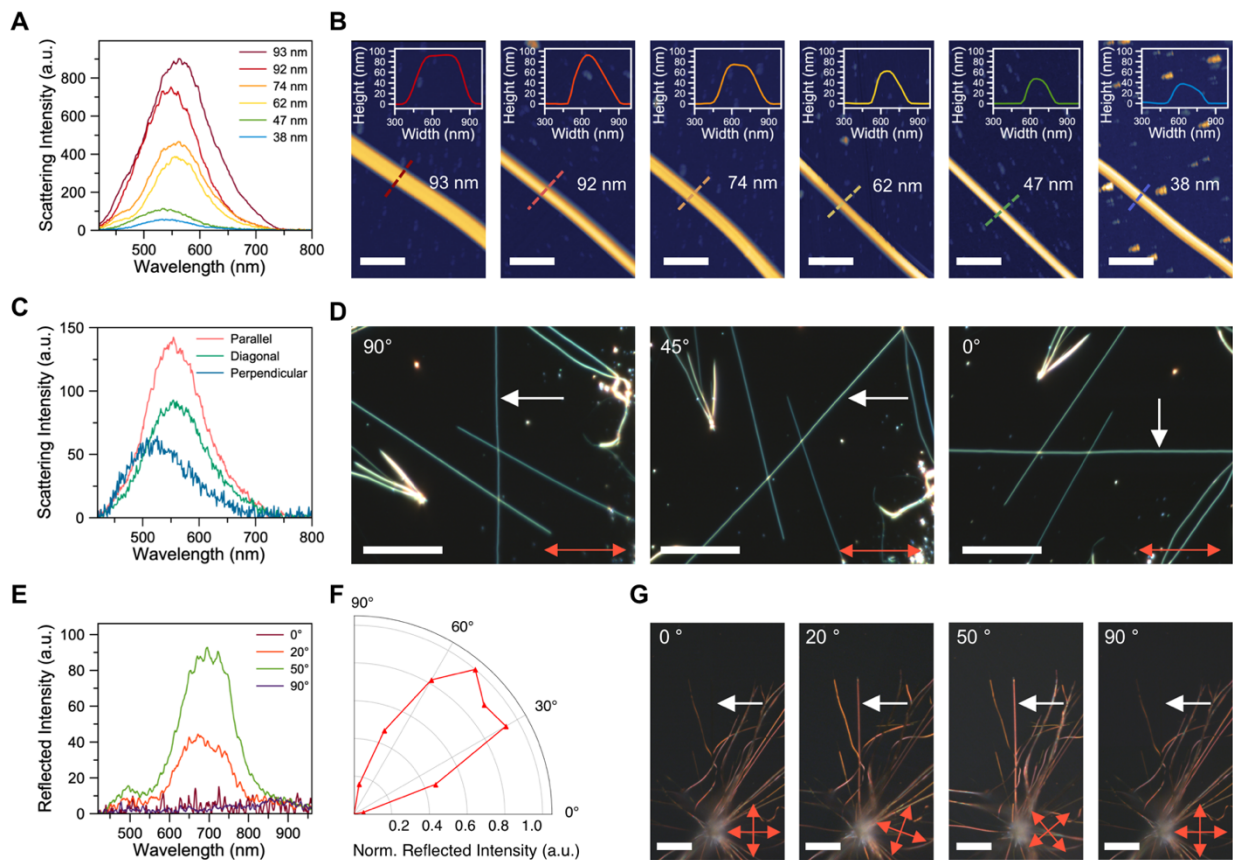


Figure 4. Anisotropic light-scattering properties of MoI_3 nanowires. (A) Size-dependent dark-field scattering spectra of MoI_3 nanowires. (B) AFM images and corresponding height profiles of the nanowires shown in (A). Scale bars, 2 μm . (C) Angle-dependent dark-field scattering spectra of a representative MoI_3 nanowire (height and width ~ 90 nm) measured with linearly polarized incident light, showing intensity variations with nanowire orientation relative to the polarization direction. (D) Dark-field optical micrographs of the nanowire measured in (C) at orientations of 90° (perpendicular), 45° , and 0° (parallel) relative to the polarization direction. Scale bars, 25 μm . (E) Angle-dependent reflection spectra acquired under crossed-polarizer conditions from the representative nanowire indicated in (G). (F) Polar plot of the normalized reflected intensity at 700 nm extracted from (E), illustrating the angular dependence. (G) Bright-field reflection images of the representative nanowire measured in (E), acquired under crossed-polarizer conditions at different sample orientations. The white arrow indicates the measured nanowire. Scale bars, 20 μm .

3.4 Conclusion

In summary, we demonstrate a catalyst-free, bottom-up synthesis of high-aspect-ratio MoI_3 nanowires via a modified CVT method. By controlling precursor chemistry and growth conditions, our results support extending the previously proposed hypothesis that Peierls-distorted chain structures promote preferential crystal growth along the intrachain direction, enabling the formation of high-aspect-ratio nanowires in dimerized 1D vdW materials such as MoI_3 . The resulting nanowires enabled direct characterization of the pronounced structural and optical anisotropy of MoI_3 through polarization- and orientation-dependent optical spectroscopy,

including Raman, absorption, scattering, and reflection measurements. The realization of crystalline nanoscale MoI_3 nanowires provides a platform for future investigations of the predicted low-dimensional magnetic properties of MoI_3 , including possible magnetic confinement effects, either as stand-alone nanostructures, when interfaced with other 1D and 2D vdW materials, or under photonic stimulation. Taken together, these results advance the understanding of the chemical origins of anisotropic crystallization in 1D and quasi-1D vdW crystals and open new opportunities for accessing functional nanostructures approaching the atomic scale.

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CHAPTER 4: Compositional Heterogeneity Drives Nanoscale Ring Formation in Optically Active One-Dimensional van der Waals Crystals

4.1 Abstract

While ubiquitous in nature, synthetic nanostructures that form ring- or spiral-like structures have remained particularly elusive. This has been especially the case for all-inorganic systems, which despite their potential to manifest distinct long-range physical states arising from twisting and inversion symmetry breaking, are generally devoid of twist-inducing interactions such as hydrogen bonding, π -stacking, and disulfide bridging. Here, leveraging the non-covalently bound and one-dimensional (1D) van der Waals (vdW) nature of transition metal trichalcogenides, we demonstrate the compositionally driven formation of well-defined spiral nanorings from NbS₃ Type I (NbS₃-I) chains that spontaneously self-coil through deliberate Ta alloying and S vacancy formation, forming Nb_{1-x}Ta_xS_{3- δ} during vapor-phase crystallization. The spiraled nanorings displayed an average circumference of 18 ± 10 μ m, with average cross-sectional heights from ~ 550 nm down to ~ 20 nm, and widths ~ 620 nm down to ~ 40 nm, respectively. We reconcile the compositionally driven spiraling of the chains into nanorings using density functional theory (DFT) calculations on idealized model structures, which revealed that Ta incorporation disrupts the intra-chain Nb–Nb dimerization, weakens the inter-chain bonding, lowers the Young’s modulus by a factor of ~ 5.6 relative to pristine NbS₃-I, and renders the chains more susceptible to spiraling and self-coiling into nanorings during vapor-phase growth. Owing to their high refractive index and nanoscale dimensions, these nanorings exhibit strong optical activity and size-dependent dipolar photonic signatures reminiscent of confined Mie-type resonance. Their nanoring geometry and structural anisotropy further give rise to polarization-dependent light scattering. These findings establish a deliberate and predictable synthetic route to access atypical nanoscale ring morphologies in 1D vdW solids, highlighting the potential of programmed spiraling and twisting of extended lattice nanostructures to realize optically active nanoscale platforms and collective states arising from curved and twisted structures.

4.2 Introduction

Low-dimensional materials exhibit emergent and tunable physical properties through the precise control of their composition, size, crystal structure, and morphology.^{1–9} Nanoscale morphologies with curved motifs that often break inversion symmetry at the atomic scale, such as tubes, coils, rings, helices, and twisted structures, provide a platform for dense integration into miniaturized functional devices while introducing structural complexity, quantum confinement, and unusual physical states arising from their non-native symmetries.^{10–16} Often, when realized in all-inorganic systems with long-range order, these complex structures display diverse properties: functioning as inductors and antennas with localized magnetic states; manifesting non-linear optical signatures, confined photonic states,^{17–20} and chiral signatures;^{21–24} and hosting non-conventional photovoltaic mechanisms such as the bulk photovoltaic effect and shift-current generation.^{10–16} Beyond their physical properties, nanoscale structures with curved motifs offer a powerful platform for strain-induced property modulation because their curved geometries impart mechanical robustness by resisting buckling and torsional deformation and, in some cases, by exhibiting spring-like mechanical behavior.^{10–16,25} However, while these motifs present exciting materials opportunities, experimentally demonstrated inorganic micro- to nanoscale systems remain relatively rare. Reported examples have primarily relied on selective etching, imposed boundary constraints for growth, or the less common and more heuristic approach of synthetically induced electrostatic self-coiling mechanisms, such as in the unusual case of ZnO twisted nanobelts.^{10,11,26–28} More commonly observed in nature and engineered organic materials,^{29–36} helical and chiral nanostructures typically arise from ultrathin chain-like structures, such as organic polymers and peptide chains, which can contort into such complex motifs without physically breaking.

Structurally reminiscent of polymeric, supramolecular, and biomacromolecular systems, one-dimensional (1D) van der Waals (vdW) transition metal trichalcogenides (MCh_3 , where $M = Ti, Zr, Hf, Nb, Ta$; $Ch = S, Se$) constitute an intriguing class of materials capable of crystallizing into curved motifs and spiral self-coiled nanostructures.^{9,37–41} These crystals consist of sub-nanometer-thin chains that are covalently bonded along one crystallographic axis and held together by weak, non-covalent interactions.^{3,8,42–46} Such a 1D motif results in highly anisotropic crystal structures that lead to strongly axis-dependent physical states and mechanical properties.^{3,8,9,42–49} Owing to the 1D chain-like nature and the weak inter-chain coupling, these materials exhibit

substantial structural and compositional diversity, making them a suitable platform for exploring how chain structure and composition influence nanoscale morphology during bottom-up vapor-phase growth. Thus, variations in composition, chain structure, and crystal packing give rise to numerous polymorphs (e.g., NbS₃ Types I to VI; denoted herein as NbS₃-I to VI) and electronic behavior, including semiconducting NbS₃-I/-IV/-VI, ZrS₃, and TiS₃ phases, as well as metallic NbS₃-II/-III/-V and TaSe₃ phases with charge-density-wave (CDW) transitions and field-effect modulation of CDW transport.^{3,8,9,42–51}

Under very specific, heuristically determined, and unpredictable growth conditions, certain MCh₃ phases that are metallic (e.g., TaS₃, TaSe₃, NbSe₃) exhibit spontaneous self-coiling to form nanoscale structures that resemble rings, cylinders, and even Möbius-strip morphologies.^{9,37–41} Although nanoring formation was initially posited to arise from the coiling of the nanostructures around chalcogen droplets that eventually vaporize, this mechanism is supported by limited evidence and is contradicted by the formation of larger tubular structures in related compositional analogues. Consequently, the origin of these curved nanostructures and specific synthetic parameters responsible for their often-stochastic formation remain elusive. Among the known 1D transition metal trichalcogenides that can be employed to systematically demonstrate the deliberate triggering of nanoring formation, NbS₃-I has emerged as the most stable phase, crystallizing in a triclinic ($P\bar{1}$) structure characterized by alternating intra-chain Nb—Nb distances.^{9,42,43,48,49,52,53} Its combination of air stability, flexibility, semiconducting properties, ultra-broadband and polarization-sensitive photodetection behavior^{9,42,43,48,49,52,53} makes it a highly promising candidate for future optoelectronic applications.

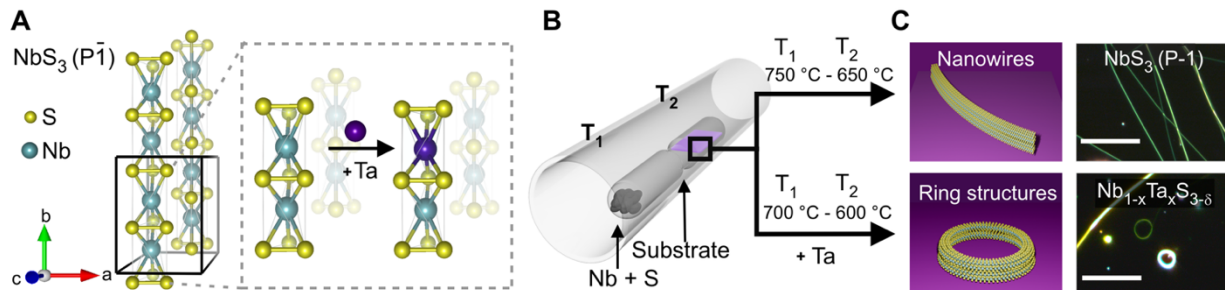


Figure 1. Synthetic pathways to $\text{NbS}_3\text{-I}$ nanowires and $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings. (A) Crystal structure of $\text{NbS}_3\text{-I}$ and target site occupation of Ta. (B) Schematic of the reaction setup and temperature gradients used to synthesize $\text{NbS}_3\text{-I}$ nanowires and $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring structures. (C) Graphical representation of nanowires and nanoring structures (left) and dark-field optical micrographs of $\text{NbS}_3\text{-I}$ nanowires and $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring structures (right). Scale bars, 25 μm .

Here, we report the deliberate, predictable, and reproducible synthesis of the first example of nanoring structures based on the $\text{NbS}_3\text{-I}$ model phase through the spiral growth of nanowires systematically triggered by the alloying of Ta atoms in the system (**Figure 1**). Grown via a modified bottom-up chemical vapor transport (CVT) method, the nanorings preserve the native triclinic structure of $\text{NbS}_3\text{-I}$ as confirmed by electron microscopy and Raman spectroscopy despite the incorporation of $\sim 18\%$ Ta and the concerted formation of S vacancies. Based on a series of control experiments, electron microscopy imaging of nanorings across various conditions and samples, and first-principles calculations, we propose in this study that the reliable growth of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings arises from the predicted lowering of the Young's modulus of the chains upon the inclusion of S vacancies and Ta. This, we posit, leads to intra-chain flexibility and deformability, which increase the propensity of the nanowires to twist and spiral back onto the leading growth edge, ultimately forming nanorings. Owing to their substantially high refractive indices and well-defined structure, the nanorings show emergent optical activity and photonic resonant states with strong polarization dependence in the visible range. Our results highlight the potential of 1D vdW crystals to form complex nanoscale structures that behave similarly to their organic counterparts and underscore their potential to host emergent photophysical states (anticipated to arise from spiraling) at length scales approaching the atomic scale either as stand-alone nanostructures or when heterostructured with other nanomaterials.

4.3 Experimental Section

4.3.1 Materials

Niobium powders (99.8%), tantalum powders (99.98%), sulfur powders (sublimed; 99+%; Strem Chemicals, Inc.), Si/SiO₂ substrates (300 nm wet thermal oxide; University Wafer, Inc.), and quartz tubes with 10 mm inner diameter and 12 mm outer diameter were used in this study. An OTF-1200X, MTI Corporation two-zone furnace was used to run reactions.

4.3.2 Nanoring synthesis

In a typical synthesis, conditions involve the following: (1) elemental powders were ground using a mortar and pestle and sealed in a 14 cm long quartz tube. The ampule was necked (3.0–3.2 mm outer tube circumference) positioned 6 cm from the sealed end to enabled control of precursor flux to the substrate (Figure S1). The precursors were positioned on the left side of the tube (T_1) and a substrate (5 cm × 9 mm) was positioned on the right side of the tube (T_2) and vacuum-sealed (~15 mTorr) (Figure 1B). A temperature gradient of $T_1 = 700$ °C and $T_2 = 600$ °C was applied at a ramp-up heating rate of 5°C/minute. The temperature gradient was maintained for 30 minutes, resulting in both nanowires and nanoring structures (**Figure 1C, S2-5**). Once the reaction was complete, the furnace was turned off and allowed to reach room temperature naturally.

4.3.3 Optical Microscopy and Dark-Field Scattering Spectroscopy.

Dark-field microscopy and light scattering measurements were conducted using an Olympus BX-43F microscope equipped with a Cytoviva hyperspectral system, which includes an automated stage, diffraction grating, CCD detector (covering 450 nm to 1000 nm), and a high-resolution imaging camera. Scattering spectra were collected in dark-field mode using the Cytoviva spectrometer.

4.3.4 Atomic Force Microscopy (AFM)

Topographical images of the nanostructures were acquired using an Anton Paar Tosca AFM with ARROW-NCR Al-coated tips (resonance frequency: 285 kHz; force constant: 42 N/m) (NanoWorld). The data were subsequently background-corrected and processed using Gwyddion® software.

4.3.5 Raman Spectroscopy

Raman spectra were collected using a InVia confocal Raman spectro-microscope by Renishaw Inc. Measurements were performed with a 532 nm excitation laser and a 2400 lines mm⁻¹ grating.

4.3.6 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Samples were dry transferred onto Cu substrate by gently sliding the substrate across the Si/SiO₂ substrate containing the as-grown Nb_{1-x}Ta_xS_{3-δ} nanorings to minimize signal overlap between the Ta M-shell emission and the Si K α peak. SEM images and EDS elemental compositions were acquired using an FEI Magellan XHR SEM and EDS with an Oxford Silicon Drift Detector (80 mm²). The resulting EDS data were analyzed using the built-in Aztec software.

4.3.7 High-Resolution Transmission Electron Microscopy (HRTEM)

The samples obtained from the study were dry-transferred onto a lacey carbon grid (400 mesh; Ted Pella Inc.) by gently smearing the carbon-coated side of the grid across the growth substrate. TEM imaging was carried out at 200 kV on a JEOL JEM-2800 equipped with a Gatan OneView camera. Processing of raw (.dm4) images was done in DigitalMicrograph and Fast Fourier transformations (FFTs) were generated in ImageJ. FFT indexing was performed using the SingleCrystal module of CrystalMaker software.

4.3.8 Refractive Index Measurements

Data used to extract the refractive index of NbS₃ were acquired using a J.A. Woollam RC2XF small spot ellipsometer with a focused beam elliptical spot size of 25 × 60 microns. The spot was positioned along the length of the NbS₃ nanoribbon stripes for different samples of different thicknesses. Data were acquired at an angle of incidence of 65° over the spectral range from 193 nm to 1500 nm. The experimental data were analyzed using an isotropic optical model using a combination of one or two Sellmeier dispersion functions for the real part of the refractive index $n(\lambda)$, and between 11 and 21 Gaussian absorptions for the imaginary part of the refractive index $k(\lambda)$ versus wavelength. For the thickest sample, a model including uniaxial

birefringence improved the data fits significantly, suggesting the thicker NbS₃ films show birefringence effects.

4.3.9 DFT Calculation of Bond Distances and Mechanical Properties

The first principles calculations were performed within the framework of the density functional theory by using the projector-augmented wave^{1,2} pseudopotentials and generalized gradient approximation of Perdew-Burke-Ernzerhof³ as implemented in the Vienna Ab initio Simulation Package⁴ code. The plane wave energy cut-off was set to 600 eV and a $1 \times 8 \times 1$ Monkhorst–Pack k-point grid⁵ was considered for the Brillouin zone integration. For the vdW correction, the DFT-D3 method⁶ is adopted. The convergence criterion for force and total energy was set to 10^{-3} eV/Å and 10^{-6} eV, respectively. A vacuum layer of 15 Å was added along the x-, z- axes to avoid interactions due to periodic boundary conditions. The calculations were performed by using $1 \times 3 \times 1$ supercell structure of pristine NbS₃-I and 16.7% Ta-alloyed NbS₃-I chains.

The elastic stiffness constants (C_{ij}) are estimated by using the finite difference method and stress-strain relationship.⁷ For this purpose, we have considered ISIF = 3, IBRION = 6, and POTIM = 0.015 in the calculations, which results in six finite distortions of the lattice and calculates the elastic stiffness constants from the corresponding stress.

4.3.10 Finite-Difference Time-Domain (FDTD) Simulations of Nanorings

We performed full-wave electromagnetic simulations using a finite-difference time-domain (FDTD) method with commercially available Ansys Lumerical FDTD software to calculate the scattering spectra and the associated electric field distributions in the NbS₃-I circular-shaped nanoring resonators. A total-field scattered-field (TFSF) setup is used to excite the simulated nanoring resonators on a silica-on-silicon (Si/SiO₂) substrate where the silica layer thickness is 300 nm. We calculated the E-field distributions in two different nanorings geometries (as shown in **Figures 6D and 6H**). The incident plane wave is transverse-magnetic polarized at an angle, $\theta = 0^\circ$ with respect to the x-axis of the nanorings. The 3D simulation region is calculated with a uniform mesh size of 5 nm in the x-, y- and z- directions. The boundary conditions along the x-, y- and z-directions are set with perfectly matched layers. We note that in our scattering experiments, the broadband white light passes through a linear polarizer for illuminating the target nanorings. During FDTD simulations, the use of a TFSF source excitation mechanism allows us

to model the scattering spectra and collection scheme in a more realistic manner. Additionally, tabulated data were used to model the optical properties of NbS₃, silica (SiO₂), and silicon.⁸ We record the electric field strength and intensity profiles from the interface surface of the NbS₃ nanorings with frequency-domain field and power monitors and we collect the scattering intensity with frequency-dependent time monitors.

4.3.11 Experimental Section References

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4.4 Results and Discussion

The modular nature of transition metal trichalcogenides has endowed us with a suitable phase space to fundamentally probe the influence of intra-chain compositional heterogeneity on the nanoscale morphologies of bottom-up grown nanostructures. With the aim of utilizing the highly stable NbS₃-I phase as a platform to demonstrate how deliberate changes to its intra-chain composition could induce nanoscale nanoring formation, we probed whether nanoscale analogues of this phase could be obtained when systematically alloyed with Ta and how the morphologies of the nanostructures would evolve with varying amounts of the alloyant (**Figure 1A**). Tantalum, which shares the same d¹ electronic configuration and has a comparable ionic radius to niobium (0.68 Å for both Ta⁴⁺ and Nb⁴⁺ in six-coordinate environments),⁵⁴ was chosen as an isovalent alloyant to incorporate at the transition-metal site in Nb_{1-x}Ta_xS₃ alloys. Despite their similar ionic radii, substitution of Nb by Ta introduces a chemically distinct 5d transition-metal site into the NbS₃-I chains, providing a means of perturbing the local bonding environment while maintaining the underlying NbS₃-I crystal structure.

To investigate whether size and compositional variations along the chain direction perturb bottom-up crystallization, Ta-alloyed NbS₃-I nanostructures were synthesized using a modified CVT method previously optimized for the growth of NbS₃-I nanowires on Si/SiO₂ substrates (**Figure 1B,C**).⁵⁷ Interestingly, we found that nanoscale ring morphologies (referred to as nanorings throughout the manuscript) that distinctly deviate from the long, nanowire morphologies of pure NbS₃-I nanostructures emerge at certain Ta contents (**Figure 1C**). Using carefully controlled Ta loading, we systematically probed the evolution of the Raman-active modes (**Figure S1A**) and morphologies (**Figure S1B**) of the nanostructures grown from the vapor-phase, which display phonon modes consistent with the NbS₃-I structure and form thin nanowires and curled nanostructures and nanorings at lower Ta loading and manifest distorted NbS₃-I-like Raman peaks and straighter, thicker nanowires at higher Ta loading. When key parameters such as Ta loading, ampoule length, ampoule neck circumference (to control vapor flux), substrate positioning, and temperature gradient were systematically tuned and optimized, the yield of nanorings is maximized and is on the order of ~180 nanorings per reaction substrate (**Figures S2-4**). We also observed that Ta introduction and alloying within the structure led to the formation of fuzzy, hair-like protrusions from the bulk crystals on both the top inner surface of the ampoule and the substrate (**Figure S5**), with some exhibiting very curled ends (**Figure S6**). Under the optimal conditions, we found that

the highest yield of nanorings results from reactions that involve the elemental loading ratio (as loaded) of Nb:Ta:S = 0.92:0.08:4 (note that the actual elemental ratios in the nanorings are different, as will be discussed in the subsequent sections) with excess sulfur acting as the vapor-phase transport agent and suppressing the formation of the two-dimensional NbS₂ phase.⁵⁷

Based on several optimization reactions, we were able to narrow down the conditions that specifically yielded the highest number of nanorings (**Figure 1**). Compared to the synthesis of pure NbS₃-I, nanorings were reliably obtained when Ta was introduced, the ampoule neck was the widest (~3.0 to 3.2 mm outer tube circumference) and slightly lower source (T_1 ; 700 °C) and deposition (T_2 ; 600 °C) temperatures were used while maintaining the same 100 °C temperature gradient (**Figure 1B,C**). After maximizing the nanoring yield, we mapped the substrate post-synthesis to highlight the temperature-dependence (based on calibrated, position-dependent furnace temperatures) and spatial positioning of the nanorings (**Figure S3**). Based on our mapping, the highest density of nanorings was located on the hottest end of the substrate (~620 °C during synthesis) and along the sides of the 9 mm-wide substrate extending up to about 4 cm of its length. Optical imaging showed that ring formation predominantly occurred 1 mm from the edges of the substrate, with occasional rings observed closer to the center of the substrate, which was dominated by the growth of nanowires and bulk crystals (**Figure S3**).

The resulting nanorings, based on optical micrographs and scanning electron microscopy (SEM), appear as flat rings that crystallize parallel to the substrate surface and are often isolated or, in some cases, in the vicinity of a dense growth of nanowires (**Figure S4**). To establish the extended structure of the nanorings, we used high-resolution transmission electron microscopy (HRTEM) to confirm that the nanorings generally maintained the NbS₃-I crystal structure (**Figure 2A-C**). Complementarily, elemental mapping based on SEM energy dispersive X-ray spectroscopy (EDS) and TEM-EDS showed a uniform distribution of Nb, Ta, and S elements throughout the nanoring structures (**Figures 2B, S7**). SEM-EDS gave an average composition of Nb_{0.82(3)}Ta_{0.18(3)}S_{2.4(2)} for the nanorings and Nb_{0.83(1)}Ta_{0.17(1)}S_{2.70(4)} for the structurally curled nanowires that crystallize alongside the nanorings (**Figures S8-9; Tables S1-4**). Thus, based on our experimental results, we are denoting the nanorings from here on as Nb_{1-x}Ta_xS_{3-δ} to highlight that the incorporation of Ta also induces the formation of a sulfur-deficient structure. We further note that the incorporation of ~18% of Ta with respect to the Nb site (Nb:Ta = 0.82:0.18) is significantly higher than the as-loaded precursor amount of ~8% (Nb:Ta = 0.92:0.08).

Nonetheless, although the SEM-EDS showed sulfur deficiencies, TEM imaging confirmed the high crystallinity of the nanorings, with the image contrast corresponding to the chain structure and lattice fringes directly matching the d-spacing of the NbS₃-I phase (**Figure 2C**). Additionally, the corresponding fast Fourier transform (FFT) pattern was squarely indexable to the [001] zone axis of the triclinic NbS₃-I structure (**Figure 2C**).

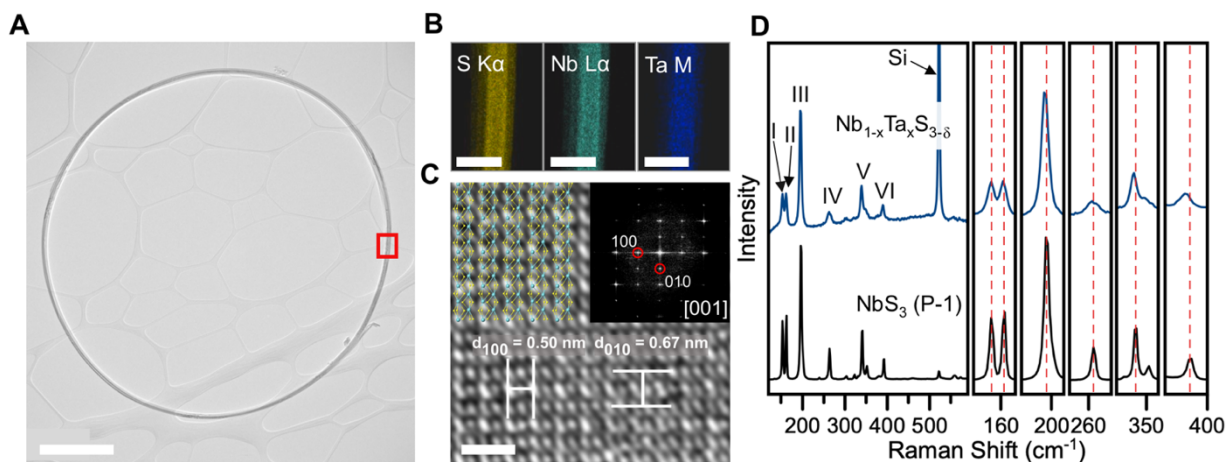


Figure 2. Structural and compositional characterization of Nb_{1-x}Ta_xS_{3-δ} nanorings. (A) Representative HRTEM image of a Nb_{1-x}Ta_xS_{3-δ} nanoring structure. Scale bar, 1 μm. (B) EDS elemental map of the boxed region in (A). Scale bars, 100 nm. (C) HRTEM image of (A) with an overlaid [001]-oriented crystal model of NbS₃-I. Scale bar, 1 nm. Inset: corresponding FFT indexed [001]. (D) Raman spectra of a representative Nb_{1-x}Ta_xS_{3-δ} nanoring (top) and NbS₃-I (bottom) measured with 532 nm excitation.

To further ascertain the long-range order and crystallization of the Ta-alloyed nanorings into the NbS₃-I polymorph, Raman spectroscopy performed on individual nanorings revealed phase-pure spectra with all observed vibrational modes consistent with those of the NbS₃-I polymorph (**Figures 2D, S10, S11**).^{291,299} Using a 532 nm excitation wavelength, intense and well-defined Raman peaks were observed and are assignable to the established NbS₃-I phonon modes: (I) the 152 cm⁻¹ peak corresponding to lattice compression along the chains (*T'*_y mode); (II) the 160 cm⁻¹ peak corresponding to Nb—Nb stretching vibrations; (III) the 194 cm⁻¹ peak corresponding to Nb—S₂ vibrations; (IV) the 262 cm⁻¹ peak corresponding to the symmetric Nb—S stretching vibration associated with the rigid sublattice; (V) the 338 cm⁻¹ and 348 cm⁻¹ peaks corresponding to Nb—S intra-chain vibrations; and (VI) the 388 cm⁻¹ peak corresponding to Nb—S inter-chain vibrations. Compared to pure NbS₃-I nanostructures and bulk crystals, the Raman spectra of the Nb_{1-x}Ta_xS_{3-δ} nanorings and the alloyed bulk structures systematically exhibit slight

peak broadening and a consistent red shift (**Figures S11-14**). The red shift and the observed peak broadening are attributable to the softening of the phonon modes and the introduction of local and extended lattice distortions arising from the incorporation of the larger Ta atom into the Nb site. These results are consistent with our complementary characterization results and establish the alloying of Ta into the nanoring lattice. However, we cannot exclude that the sulfur vacancies introduced during Ta incorporation also contribute to the observed Raman peak shifts and band broadening.

We further evaluated the influence of reaction time on nanoring formation, dimensions, and morphology by conducting syntheses at a fixed temperature gradient of 700 to 600 °C for representative reaction times ranging from 10 to 60 min (**Figure 3A**). Nanorings formed under all conditions; however, the highest yields were observed at 30 min reaction time, producing over ~180 nanorings per substrate. Shorter reaction times resulted in lower yields, with ~130 nanorings formed at 20 min and ~60 nanorings at 10 min. We note that increasing the reaction time beyond 30 min did not further enhance the nanoring yield. Regardless of synthesis time, the nanorings consistently exhibited an average circumference below ~21 μm . The average circumferences were 12 ± 4 , 19 ± 13 , 18 ± 10 , and 21 ± 12 μm for the 10, 20, 30, and 60 min reactions, respectively. For the 30 min reaction, the nanorings exhibited average cross-sectional heights of ~20 to 550 nm (Average = 170 nm; based on 20 nanorings) and widths of ~40 to 620 nm (Average = 190 nm; based on 52 nanorings) (**Figures 3B, S4**). Moreover, we find that reactions targeting pure NbS₃-I and NbS₃-V can also produce nanoring structures associated with sulfur-deficient compositions, NbS_{3- δ} , albeit occurring randomly and with very low yields as expected from the stochastic nature of S vacancy formation. Under the previously reported growth conditions for NbS₃-I nanowires,¹⁴⁰ nanorings form only sporadically, typically yielding only 1-2 nanorings per reaction (**Figure S15**). In contrast, reactions following previous synthetic conditions targeting NbS₃-V crystals¹⁸⁵ produce bulk-like cylindrical morphologies that resemble overgrown nanorings that form alongside bulk needle-like crystals (**Figure S16**). Notably, EDS analysis of these pure, non-alloyed polytypes further confirms sulfur deficiency within these structures, with an average S/Nb ratio of 2.7 ± 0.5 for NbS₃-I and 2.3 ± 0.6 for NbS₃-V (**Tables S5-6**). These observations indicate that we cannot discount the contributions of S vacancies in inducing nanoring formation, albeit to a much smaller extent.

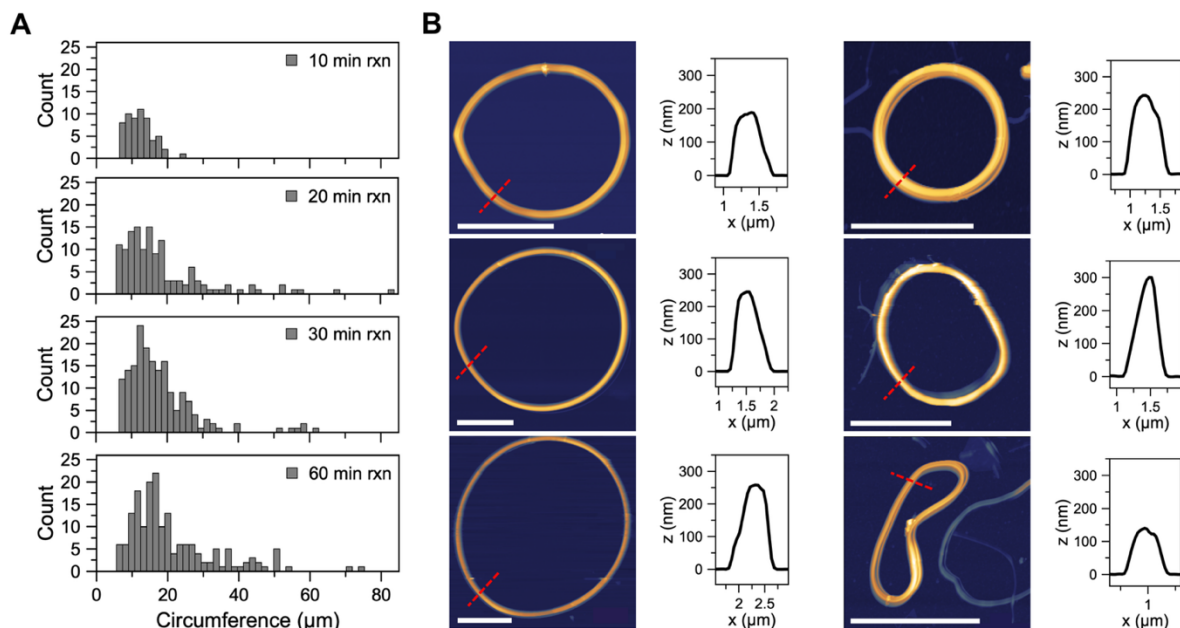


Figure 3. Size distributions and AFM profiles of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring structures. (A) Histograms of the circumference of the nanoring structures grown under four different reaction times. (B) AFM images and height profiles of representative nanorings. Scale bars, 5 μm . The red lines indicate where the height profile was taken.

To understand how Ta alloying facilitates the nanoring formation and to provide a possible mode of growth, we performed first principles density functional theory (DFT) calculations on a model structure that reasonably represents the extended lattice structure of our experimental nanoring system (Figure 4). For these calculations, we considered a hypothetical $1 \times 3 \times 1$ supercell of pristine and 16.7% Ta-alloyed “ $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3$ ” Type-I (based on a fractional occupancy of 1/6 the Nb site, the closest fractional equivalent of our experimental composition) and show the relaxed structures and corresponding bond lengths in Figure 4A. While we considered incorporating S vacancies, the random positioning of these vacancies and the resulting reduction in symmetry increased the computational cost and hindered our efforts; hence, the “ $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3$ ” notation. The pristine NbS_3 -I structure shows intra-chain dimerization of Nb atoms, featuring the alternating intra-chain Nb–Nb distances that repeat periodically. As is known, the inversion symmetry is broken in these chains since the Nb–S₂ triangle motifs are staggered along the b-axis (**Figure S17B**). This, in the model structure, results in asymmetry between the two chains, where one chain alternates between 3.42 Å and 3.33 Å, whereas the other alternates between 3.82 Å and 2.93 Å.

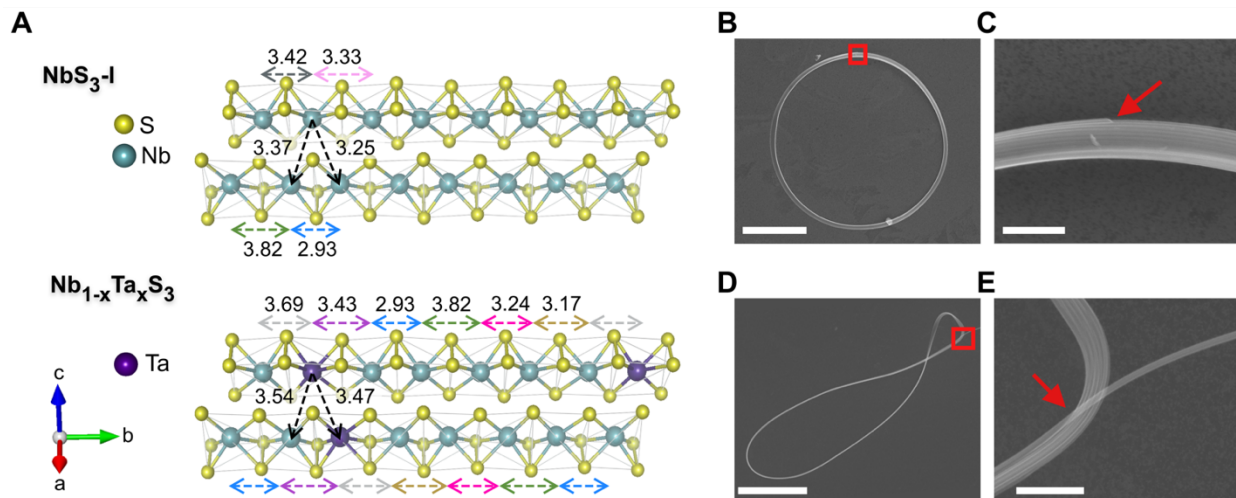


Figure 4. The DFT-calculated bond lengths and SEM images of self-coiled $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings. (A) The relaxed structures of pristine $\text{NbS}_3\text{-I}$ (top) and alloyed “ $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3$ ” (bottom; $x = 0.167$) chains, showing the Nb–Nb and Nb–Ta bond lengths in Å units along the long-axis. (B, D) SEM images of representative $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings that show self-coiling behavior. Scale bars, 4 μm. (C, E) Magnified areas of the boxed regions in (B) and (D), respectively, highlighting nanowire tails extending from the nanorings. Scale bars, 500 nm.

Looking into the alloyed model structure, in which 1/6 of the Nb sites (16.7%) are occupied by Ta, we evaluated different alloying configurations and identified the most stable structure (**Figure S18**). Based on our calculations, we found that the structure in **Figure 4A** (bottom) corresponds to the lowest-energy configuration that preserves the inversion symmetry between the two chains. Intriguingly, we found that Ta alloying disrupts the Nb–Nb dimerization and introduces distortions, affecting not only the Nb–S₂ triangle motifs but also the site positioning of the Nb and Ta atoms (**Figure S17C**). This structural perturbation resulted in intra-chain bond lengths of 3.69, 3.43, 2.93, 3.82, 3.24, and 3.17 Å that alternate periodically, with the same sequence repeating in the second chain with a two-position shift. Likewise, upon Ta alloying, the inter-chain distances increase from 3.37 Å and 3.25 Å (inter-chain Nb–Nb distances) in the pristine $\text{NbS}_3\text{-I}$ to 3.54 Å and 3.47 Å (inter-chain Ta–Nb and Ta–Ta distances) in the alloyed structure. These atomic-scale distortions are also consistent with the Raman spectra of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings, which exhibit slight peak broadening and a red shift relative to pristine $\text{NbS}_3\text{-I}$ (**Figures S11-14**). Morphologically, these distortions support the observed nanowire bending into nearly perfect nanoscale circles, ellipses, lemniscates, and nanorings with visible tails (**Figures 4B-E, S4**). Therefore, the results support a mode of growth in which Ta-induced bond-length distortions weaken chain rigidity, enabling spontaneous self-coiling of nanowires. As observed in other vdW

systems, once an initial loop is formed, vdW interactions likely drive continued coiling into complete nanorings.^{19,20}

From the observed growth behavior of the nanorings and the calculated structural distortions that perturb the chain structure, we posited that the compositional heterogeneity introduced by Ta alloying modulates the flexibility of the constituent $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ chains to form a curved, nanoring structure instead of a straight, 1D nanowire. To investigate the mechanical behavior of pure and alloyed NbS_3 -I nanostructures, we estimated their elastic stiffness constants using DFT within the framework of the generalized Hooke's law, expressed as $\sigma_i = \sum_{j=1}^6 C_{ij} \varepsilon_j$. Here, the stress (σ) and strain (ε) are represented as vectors with six independent components, and C_{ij} is the second-order elastic stiffness tensor expressed as a 6×6 matrix. The elastic stiffness constants C_{ij} are obtained using the finite difference method and the stress-strain relationship.⁵² Since the pure and alloyed nanowires are stable in the triclinic symmetry based on our calculations, these structures can be assumed to have 21 independent C_{ij} terms (**Table S7**). As the chain structure of the pure and alloyed nanostructures shown in **Figure 4A** are aligned along the crystallographic b -axis, the elastic stiffness constant $C_{22} = \sigma_2 / \varepsilon_2$ can be used to computationally assess the Young's modulus of these chains. Based on our results, Ta alloying significantly reduces the Young's modulus from 1.74 GPa for the pristine NbS_3 -I to 0.31 GPa for the Ta-alloyed phase, corresponding to an approximately 5.6-fold reduction.

Qualitatively, the smaller modulus suggests that the Ta-alloyed system is expected to yield chains that are more compressible, stretchable, and mechanically flexible. Based on our calculations, we postulate that this mechanical response arises from the substantial tensile lattice strain induced by the larger Ta atoms, which weakens inter-chain bonding and lowers the overall stiffness, thereby explaining the growth modality of the nanorings that we observed herein. These qualitatively assessed structural characteristics are also evident in the microscopy of bulk structures of NbS_3 -I (**Figure S5A**) and $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ (**Figures S5B, S6**): NbS_3 -I forms straight, uniform, needle-like crystals, whereas $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ forms similar needle-like crystals but with curly nanowires that splinter away from the main structure. Taken together, these calculations show that the enhanced deformability introduced by Ta alloying creates the conditions necessary for coiling into nanoring structures, a morphology not accessible in the more rigid pristine NbS_3 -I. Thus, these mechanical trends strongly support the experimental observations that tensile strain from Ta substitution is the key factor enabling nanoring formation.

The unique curved morphology of the $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings provides an opportunity to investigate anisotropic resonant optical responses in a quasi-1D crystal system (**Figure 5**). Polarization-dependent dark-field scattering measurements of the $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings reveal pronounced anisotropic optical responses. Bright-field optical images show the as-grown nanorings on the Si/SiO₂ substrate (**Figure 5A,F**), while the corresponding dark-field images reveal size-dependent scattering behavior (**Figure 5B,G**). SEM and AFM analyses show that nanoring from **Figure 5A** has average height of ~ 173 nm, width of ~ 171 nm, and inner circumference of ~ 46 μm (**Figure 5C,D,E; Table S8**), whereas the nanoring from **Figure 5F** has an average height of ~ 105 nm, width of ~ 606 nm, and inner circumference of ~ 18 μm (**Figure 5H,I,J; Table S9**). Hyperspectral dark-field images acquired under co-polarization conditions show enhanced scattering from nanoring segments aligned parallel to the polarizer (P) direction (Region A), while segments oriented perpendicular to the polarization direction (Region B) exhibit substantially weaker scattering (**Figure 5L,M,N,O,P**). The scattering spectra acquired from Region A exhibit two dominant resonances centered near ~ 550 nm and ~ 700 nm (**Figure 5M,P**), with Region B showing substantially weaker scattering across the measured spectral range. The angular dependence of these resonances presents a strongly anisotropic behavior, with maximum intensities observed when the nanoring segment is aligned parallel to the incident polarization and minima occurring near the perpendicular orientation (**Figure 5N**). The polar plots further demonstrate a two-lobed response characteristic of linearly polarized anisotropic scattering.

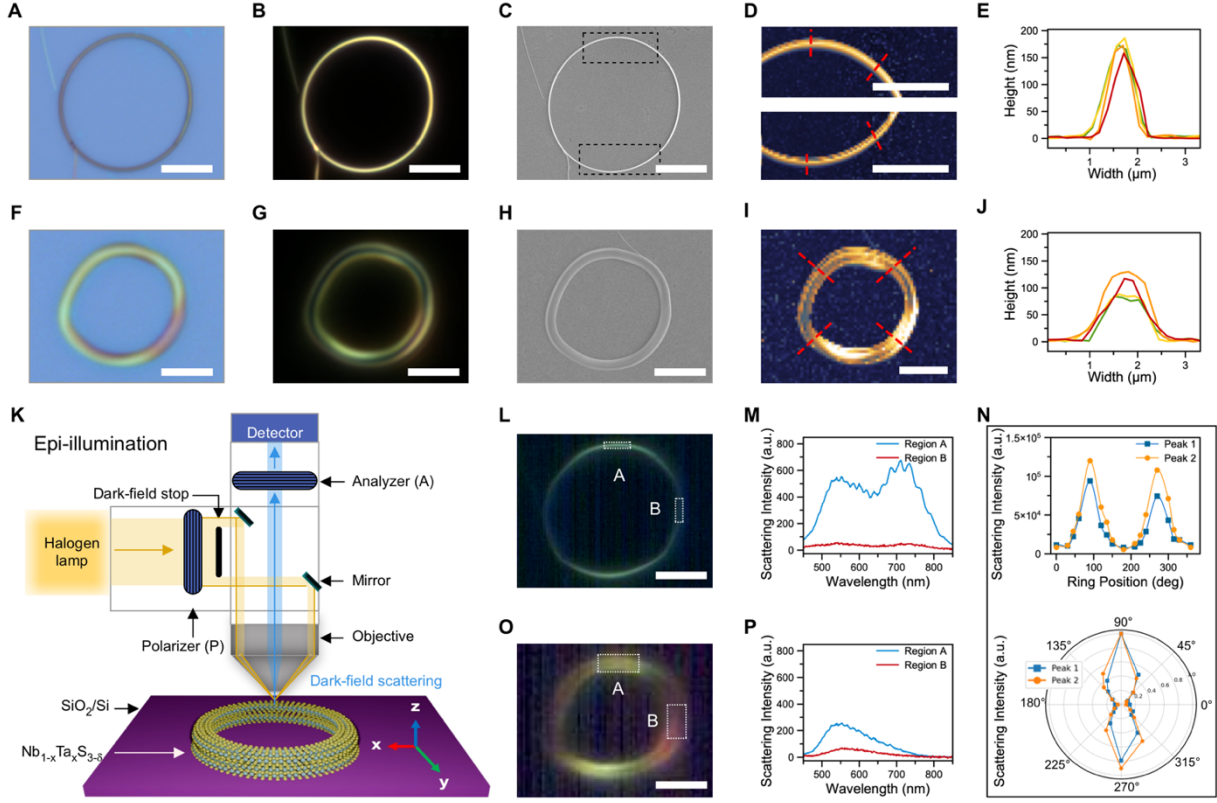


Figure 5. Characterization and Polarization-dependent scattering spectra of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings. (A,F) Bright-field optical images of two representative $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings. (B,G) Corresponding dark-field optical images. (C,H) SEM images of the nanorings. Boxed regions in (C) indicate the locations where AFM scans were collected. (D,I) AFM images of the nanorings. The red dashed lines correspond to the height-profiles directions. Scale bars, 6 μm (A-D) and 3 μm (F-I). (E,J) AFM height profiles of the marked regions in (D,I). (K) Schematic illustration of the polarization-dependent dark-field scattering measurement setup used for the $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings. (L,O) Hyperspectral images of the nanorings acquired with the polarizer (P) and analyzer (A) in the co-polarization configuration. Regions A and B correspond to ring segments oriented parallel and perpendicular to the polarization direction, respectively. Scale bars, 6 μm (L) and 3 μm (O). (M,P) Scattering spectra from Regions A and B in (L,O). (N) Dependence of the scattering intensity of the two characteristic spectral peaks in (M) on position around the nanoring. Peak 1 corresponds to the feature near ~ 550 nm, and Peak 2 corresponds to the feature near ~ 700 nm. The top panel shows the extracted peak intensities as a function of nanoring position, while the bottom panel presents the corresponding normalized intensities in polar coordinates

To further probe the anisotropic response, hyperspectral dark-field measurements were performed in the cross-polarized configuration, where the analyzer polarization was oriented perpendicular to the incident polarization (**Figure S19**). Under these conditions, the overall scattering intensity decreases relative to the co-polarized measurements, consistent with suppression of the co-polarized scattering component. Despite the reduced intensity, the nanorings continue to exhibit pronounced orientation-dependent scattering behavior. Regions perpendicular to the incident polarization direction (Region B) display enhanced scattering compared to parallel-

oriented regions (Region A), particularly for the broad resonance centered near $\sim 550\text{--}700$ nm (**Figure S19B,D**). This behavior contrasts with the co-polarized measurements, where parallel-oriented regions exhibited the strongest scattering responses. The persistence of polarization-dependent scattering indicates that the optical response is governed not only by the nanoring morphology, but also by the intrinsic anisotropic optical properties of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$.

We then performed finite-difference time-domain (FDTD) simulations of the nanoring structures to verify and further understand the photonic origin of the resonant scattering modes observed in the nanorings (**Figure 6**). Ensuring the closest correspondence between the experimental measurements and simulations, the polarized dark-field scattering experiments were modified to adopt a simplified configuration that could be more readily implemented in the FDTD model (**Figure 6A**). Using only an incident linear polarizer in the experimental configuration, we observed similar anisotropic scattering behavior and spectral characteristics in the representative nanorings, including the two distinct resonant features centered around ~ 550 and ~ 700 nm for the larger nanoring (**Figure 6B,C**) and a dominant resonance near ~ 550 nm for the smaller nanoring (**Figure 6F,G**). To simulate scattering response of the nanorings, we first experimentally determined the optical constants of bulk, pristine $\text{NbS}_3\text{-I}$, which to our knowledge have not previously been reported in the literature (**Figure S20**). Spectroscopic ellipsometry measurements performed on a bulk, pristine $\text{NbS}_3\text{-I}$ crystal with ribbon-like morphology (width of $65\text{ }\mu\text{m}$, thickness of $4.2\text{ }\mu\text{m}$, and length exceeding 1 mm) yielded large anisotropic refractive indices across the visible spectral range, with values comparable to and, in portions of the visible range, exceeding those of crystalline Si.⁵⁸ For comparison, at 546 nm , crystalline Si exhibits optical constants of $n \approx 4.10$ and $k \approx 0.04$, whereas $\text{NbS}_3\text{-I}$ exhibits $n_{\parallel b} \approx 4.46$, $k_{\parallel b} \approx 2.20$, and $n_{\perp b} \approx 5.95$, $k_{\perp b} \approx 2.20$. Similarly, at 633 nm , crystalline Si exhibits $n \approx 3.88$ and $k \approx 0.02$, while $\text{NbS}_3\text{-I}$ exhibits $n_{\parallel b} \approx 5.23$, $k_{\parallel b} \approx 1.11$, and $n_{\perp b} \approx 6.71$, $k_{\perp b} \approx 1.11$. These experimentally extracted optical constants were subsequently used as input parameters for the FDTD simulations.

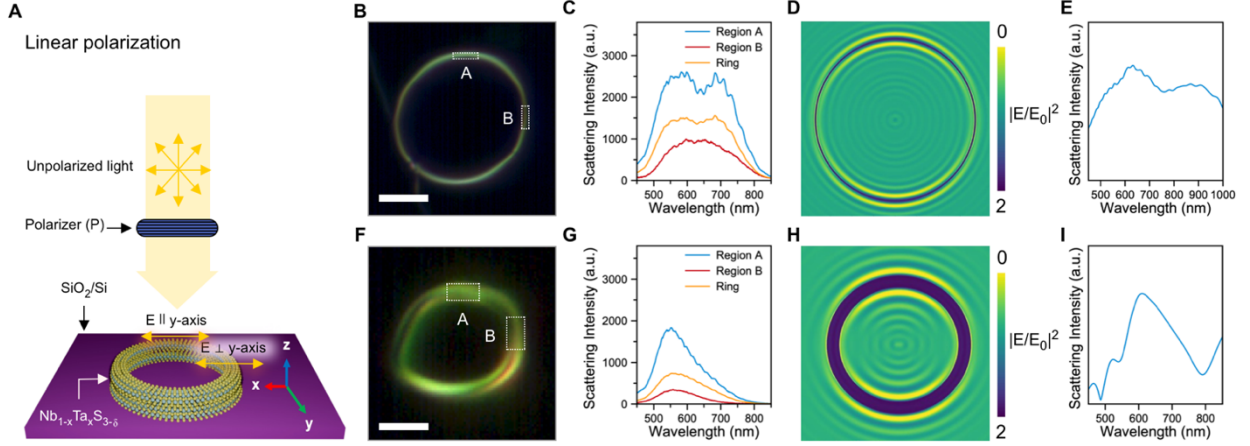


Figure 6. Polarization-dependent scattering spectra of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings and electric field intensities. (A) Illustration of the polarization-dependent scattering configuration used for the FDTD electric field simulations. (B,F) Dark-field optical images of two representative $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings acquired with the polarizer (P) and no analyzer (A). Regions A and B correspond to nanoring segments oriented parallel and perpendicular to the polarization direction, respectively. Scale bars, $6\ \mu\text{m}$ (B) and $3\ \mu\text{m}$ (F). (C,G) Scattering spectra from Regions A, B, and the whole nanoring in (B,F). (D,H) Simulated near-field maps from FDTD showing the computed electric field intensities $|E/E_0|^2$ in pristine NbS_3 -I rings with the dimensions of (B,F). (E,I) Corresponding scattering spectra of a region parallel (region A) to the polarization direction.

With the experimental setup configured and the refractive index determined, FDTD simulations were performed to generate near-field maps of the electric-field intensity, $|E/E_0|^2$, in the plane of the nanoring for two nanoring resonator sizes at a wavelength of 625 nm (**Figure 6D,H**). For the smaller nanoring (**Figure 6F-H**), the field is strongly localized at the wire cross section, with the nanowire acting as a strong optical scatterer whose evanescent field generates a standing-wave pattern bounded by the nanowire. Our experimental results and simulations reveal anisotropic scattering behavior arising from strong field confinement at the nanoring walls and consistent with resonant optical confinement. We posit that this behavior arises from the highly anisotropic quasi-1D chain structure of the nanoring and its axis-dependent refractive index, which is maximized along the direction perpendicular to the chain long axis (parallel to our measurement geometry). In contrast, for the larger nanoring (**Figure 6B-D**), a similar field morphology is observed, but with additional field maxima and more complex field distributions consistent with higher-order resonant behavior supported by the larger nanoring cross section.

Looking more closely at the simulations, the computed scattering intensity spectra correspond to FDTD calculations for resonators of varying geometries and sizes (**Figure 6E,I**). Both spectra display a common spectral envelope, with a dominant peak near 600 nm followed by a broader scattering feature extending toward 900 nm. Moreover, the simulated spectra spanning

450-900 nm qualitatively resemble the key spectral features measured experimentally in **Figures 6C,G**, including a minimum below 500 nm, a sharp rise to a dominant peak in the 500-600 nm region, and an additional scattering feature at longer wavelengths. This qualitative agreement between the simulated and experimental spectra, particularly for Region A identified in **Figure 6B,F**, provides further support for the FDTD model geometry and the dielectric function employed for the simulations. Minor deviations and spectral shifts are expected because the simulations utilize the dielectric function of pristine NbS₃-I rather than the alloyed Nb_{1-x}Ta_xS_{3-δ} nanorings investigated experimentally. Additional discrepancies may arise from small differences between the simulated and experimental nanoring dimensions, as well as the presence of sub-micron grooves produced by the spiraled growth of the nanorings (**Figure 4B-E**), which were approximated as smooth nanoring slabs for the purposes of our simulations.

For dielectric nanoresonators with sufficiently high refractive indices, such as the Ta-alloyed NbS₃-I nanorings, the observed anisotropic resonant scattering behavior is consistent with Mie-like dielectric resonances supported within the curved nanoring geometry.^{17,59} The nanoring cross-sections and geometries reported herein provide suitable dimensions for sustaining resonant optical confinement within the nanoring diameter. As observed experimentally and supported by FDTD simulations, these resonant features are associated with strong near-field enhancement and dominate the scattering response at specific wavelengths. In particular, the dominant scattering feature observed in the 500-600 nm region is consistent with low-order Mie-like resonant behavior associated with the nanoring cross-section. The curved nanoring geometry further suggests that geometric discontinuities, such as gaps, junctions, or significant diameter variations, could potentially support localized Fabry-Perot-like resonances along segments of the nanoring.

Altogether, the experimental dark-field spectra and FDTD calculations demonstrate that nanoring resonators based on Ta-alloyed NbS₃-I are strongly polarization-anisotropic optical scatterers whose response is dominated by a primary resonance in the visible 500-700 nm spectral window, with secondary features extending into the near-IR. The experimentally measured and FDTD-simulated scattering profiles qualitatively converge to show optical field confinement localized to curved-arc segments where the orientation of the constituent chains of the nanoring is parallel to the excitation polarization. Such a structure comprising chains that form the nanorings produces the characteristic electric-field intensity distribution in a crescent-shaped bright zone, as

was observed in dark-field imaging, establishing a self-consistent optical model for this class of quasi-1D transition metal trichalcogenide nanoring resonators.

4.5 Conclusion

In this work, we have shown that alloying $\text{NbS}_3\text{-I}$ with Ta enables the reproducible formation of nanoring structures through a spontaneous self-coiling growth modality. The resulting nanorings exhibit morphologies ranging from nearly perfect circles and ellipses to lemniscate-like structures, with Raman spectroscopy and HRTEM FFT analysis confirming the preservation of the general triclinic $\text{NbS}_3\text{-I}$ crystal structure despite local lattice distortions introduced by Ta incorporation and sulfur deficiency. Combined electron microscopy, Raman spectroscopy, and first-principles DFT calculations indicate that Ta alloying disrupts the native chain bonding and lowers the mechanical rigidity of the constituent chains, thereby increasing their propensity to bend, twist, and self-coil into curved nanostructures during vapor-phase crystallization. Beyond enabling nanoscale nanoring morphologies, the semiconducting and high-refractive-index $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ exhibits pronounced polarization-dependent optical scattering and supports size-, orientation-, and geometry-dependent resonant photonic responses. Combined experimental and computational analyses reveal strongly anisotropic optical behavior arising from the curved nanoring geometry and the underlying quasi-1D crystal structure—features that are unique to this class of transition metal trichalcogenides. More broadly, this work establishes alloying-induced coiled nanoring architectures in quasi-1D vdW systems, opening pathways to accessing distinct physical states that emerge from curved and spiraled morphologies—either as stand-alone nanostructures or when coupled with other nanomaterials and low-dimensional crystals in close proximity.

4.6 References

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CHAPTER 5: Deficiency-Induced Concentric Spiral Hillocks in Anisotropic One-Dimensional van der Waals Crystals

5.1 Abstract

Screw dislocations are defects generally deemed detrimental to the form and function of crystalline materials. In nanomaterials, however, the deterministic control over their formation results in complex geometries like spiral hillocks and Eshelby twisting, both associated with nascent properties. Broadening this phase space, we demonstrate the formation of spiraled surface terraces in one-dimensional (1D) van der Waals (vdW) crystals using ZrS_3 as a model phase. Here, we deliberately triggered the consistent growth of dislocation-mediated “super”-spiral hillocks via sub-stoichiometric sulfur loading. These left- and right-handed structures comprise atypically concentric and interlaced nanoscale spirals emerging from a common origin and propagating parallel to the $[001]$ direction. Coexisting with the surface features, the structure, anisotropy, and orientation-specific bandgap of bulk ZrS_3 are preserved. These results represent a route towards unusual motifs in 1D vdW crystals and enable a platform to explore physical states arising from extrinsic symmetry breaking at the nanoscale.

5.2 Introduction

Screw dislocations are integral structural features that govern crystal growth and influence the physical properties of low-dimensional materials.^{1–6} Under low-supersaturation conditions, screw dislocations provide self-perpetuating step edges that enable continuous spiral step-flow growth, as described by the Burton-Cabrera-Frank (BCF) theory.^{1,4,5} In this growth regime, the formation of new two-dimensional (2D) nuclei becomes energetically unfavorable, and crystal growth proceeds primarily through the propagation of existing dislocation-mediated steps.^{1,4,5} Such dislocations are well studied in molecular and three-dimensional (3D) crystals and are often considered as imperfections that impede the intrinsic physical properties sought in their pristine form. Yet, when the occurrence of such dislocations is carefully controlled and confined to the nanoscale regime, screw dislocations provide a means to access complex, hierarchical crystal geometries^{7,8} and, owing to their non-centrosymmetric and spiral nature, a pathway to program chiral motifs and physical states.^{9–12}

In highly anisotropic low-dimensional crystals comprised of 2D layered sheets, one-dimensional (1D) nanocrystals, or non-covalently bound 1D, chain-like building units, the directional bonding and crystallographic anisotropy present an opportunity to directly, discretely, and deterministically influence the step propagation, terrace evolution, and spiral morphology.^{3,5,6,13} Of these, the emergence of 1D spiral growth arising from Eshelby twist has recently gained interest as a rational means to endow achiral materials including 3D lattices (e.g. PbSe₈ and PbS₁₄) and 2D van der Waals (vdW) crystals (e.g. transition metal dichalcogenides,^{2,15} triel chalcogenides,^{16,17} antimonene¹⁸), with extended lattice chirality. Screw dislocations also introduce localized strain fields, distorted atomic registry, and symmetry breaking that can modify the electronic structure and influence optical, electronic, and thermal behavior.^{2,6} As a result, properties including electronic band structure, optical absorption, charge-carrier transport, and nonlinear optical response can be tuned through defect and dislocation engineering.^{6,13} In layered materials, screw dislocations can additionally influence interlayer stacking symmetry and electronic coupling through the formation of well-defined spiral growth hillocks,^{2,3} enabling the emergence of novel optical and quantum phenomena and chiral collective states.¹⁰ However, while the emergence of programmable screw-dislocation-driven geometrical motifs in nanoscale 3D lattices and 2D vdW crystals has been extensively studied in recent years, the manifestation of such motifs has been rarely, let alone predictably, observed in their 1D vdW counterparts comprised of non-covalently bound all-inorganic chains that have attracted considerable interest because of their composition-, structure-, and packing-driven physical properties,^{19–26} sub-nanometer dimensions,^{27–29} and complex chiral and helical motifs.^{30–35}

Transition metal trichalcogenides (TMTCs) are a structurally unique class of 1D vdW crystals comprised of ultrathin chains with trigonal prismatic coordination.^{36–38} With a general formula of MCh₃ (M = Ti, Zr, Hf, Nb, Ta; Ch = S, Se, Te), these materials exhibit a wide range of electronic behavior, from semiconducting to metallic, that is strongly governed by their structural anisotropy and broad polymorphic phase space.^{36–39} Owing to their sub-nanometer-thin chain structure and mechanical flexibility, these crystals provide an ideal platform for developing synthetic routes to reliably realize screw-dislocation-driven morphological features at the nanoscale. Among these phases, ZrS₃, which consists of Zr⁴⁺ cations coordinated by both sulfide (S²⁻) and disulfide (S₂²⁻) units to form chains extending along the *b*-axis, serves as a suitable model structure for directly visualizing dislocation-driven hillocks because of its slightly stronger

interchain coupling which enables the growth of crystals with close to millimeter-scale surface areas (**Figure 1A**).^{38–41} Moreover, the pronounced structural anisotropy in ZrS_3 gives rise to strong birefringence, linear dichroism, and highly anisotropic optical and optoelectronic responses that could potentially be modified by the extrinsic symmetry breaking introduced by dislocation-driven structural features at the nanoscale.^{38,42–49}

In this letter, through the model ZrS_3 phase, we present a direct synthetic pathway to deliberately induce the formation of well-defined spiral hillock structures composed of nanoscale terraces through screw-dislocation-mediated growth. Reliably driven by intentional non-stoichiometric sulfur loading to introduce sulfur vacancies, we demonstrate the achievable geometries, unusual spiral motifs, and handedness of the hillocks through a survey of as-grown crystals. We establish their composition and structure to be consistent with the parent ZrS_3 phase while containing sulfur vacancies, thereby preserving the visible-range band gap and revealing that screw-dislocation-mediated spiral features can coexist with the intrinsically strong anisotropic optical behavior sought after in ZrS_3 .

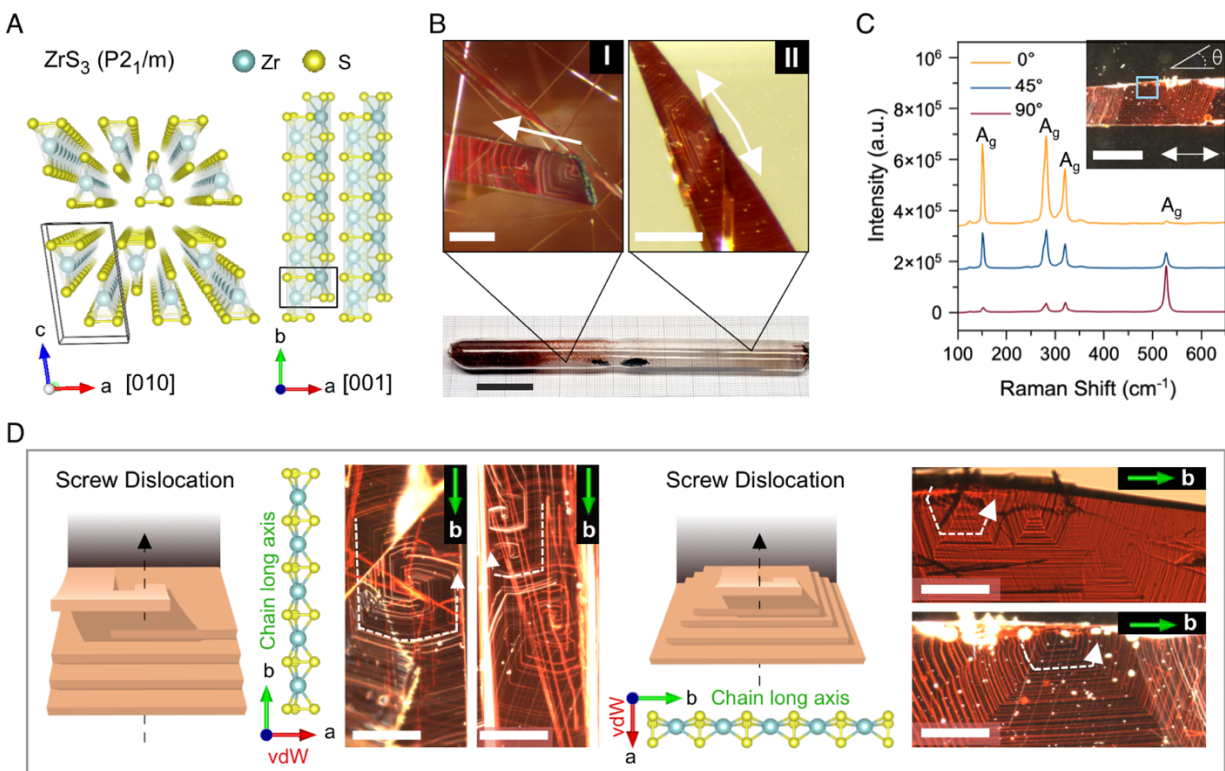


Figure 1. Structure and unusual spiral hillock formation in $\text{ZrS}_{3-\delta}$ crystals. (A) Crystal structure of pristine ZrS_3 ($P2_1/m$) projected along the $[010]$ and $[001]$ zone axes. (B) Post-reaction ampoule showing the domains of crystal growth. Scale bar, 2 cm. Insets I and II highlight representative crystals that present surface hillocks, with arrows denoting the long-axis (b -axis) growth direction. Scale bars, 2 mm. (C) Orientation-dependent Raman spectra collected at 0° , 45° , and 90° relative to the polarization direction of the incident laser. The boxed region indicates the position of the 532 nm incident laser spot. Scale bar, 245 μm . (D) Schematic illustration of screw-dislocation-mediated growth of the surface hillocks with the corresponding optical micrographs that experimentally show the spiral hillocks. The spiral propagation directions relative to the long axis for the growth directions parallel (B(I)) and perpendicular (B(II)) to the long axis are highlighted. Scale bars, 100 μm .

5.3 Experimental Section

5.3.1 Reagents and substrates

Zirconium powder (99.95 %); Strem Chemicals, Inc.), sulfur powder (sublimed, 99+%; Strem Chemicals, Inc.), iodine crystals (resublimed; Spectrum Chemical Mfg. Corp.), and 650 μm -thick sapphire substrates with one side-epi-polished ($R_a < 02 \text{ nm}$) and the opposite side fine-ground ($R_a = 0.6 - 1 \text{ um}$) (UniversityWafer, Inc.) were used in this study.

5.3.2 Growth of ZrS_3 Crystals. ZrS_3 crystals were synthesized via chemical vapor transport (CVT) method

A metal-to-sulfur ratio of $\text{Zr}:\text{S} = 1:4$ was used, and the precursors were pelletized. Iodine (10 wt% relative to total precursor mass) was added as the transport agent. Reactions were performed in fused quartz ampoules of two different geometries. The first consisted of a 14 cm long tube with a 10 mm inner diameter, a 12 mm outer diameter, and a necked region near the midpoint with an outer circumference of 3 cm. The second consisted of a 14.5 cm long tube with a 15 mm inner diameter, an 18 mm outer diameter, and a necked region near the midpoint with an outer circumference of 4.9 cm. Each ampoule was evacuated to approximately 15 mTorr and placed in a two-zone furnace (OTF-1200X, MTI Corporation), with the precursors positioned in the high-temperature zone (T_1) and a sapphire substrate placed in the low-temperature zone (T_2). A $5\text{ cm} \times 9\text{ mm}$ sapphire substrate was used with the smaller ampoule, whereas a $5\text{ cm} \times 1.5\text{ cm}$ substrate was used with the larger ampoule. In both cases, the polish side of the substrate was faced upward. The reactions were conducted using a temperature gradient of $T_1 = 750\text{ }^\circ\text{C}$ and $T_2 = 700\text{ }^\circ\text{C}$ for 7 days. The furnace was heated at $3\text{ }^\circ\text{C}/\text{min}$ and cooled to room temperature at $0.25\text{ }^\circ\text{C}/\text{min}$.

5.3.3 Growth of $\text{ZrS}_{3.8}$ Crystals

$\text{ZrS}_{3.8}$ crystals were synthesized via chemical vapor transport (CVT) method. A metal-to-sulfur ratio of $\text{Zr}:\text{S} = 1:2.8$ was used, and the precursors were pelletized. Iodine (10 wt% relative to total precursor mass) was added as the transport agent. Reactions were performed in a 13 cm long fused quartz tube with a 10 mm inner diameter and a 12 mm outer diameter. The tube was evacuated to approximately 15 mTorr and placed in a two-zone furnace (OTF-1200X, MTI Corporation), with the precursor pellet positioned in the high-temperature zone (T_1). A temperature gradient of $T_1 = 750^\circ\text{C}$ and $T_2 = 700^\circ\text{C}$ was applied for 1 day. The furnace was heated at $3\text{ }^\circ\text{C}/\text{min}$ and cooled to room temperature at $0.25^\circ\text{C}/\text{min}$.

5.3.4 Optical Absorbance Measurements

Transmission absorbance measurements were performed using a modified Olympus BX-43F microscope equipped with a Cytoviva hyperspectral imaging system, consisting of an

automated stage, diffraction grating, and CCD detector capable of measurements from 450 nm to 1000 nm, with a high-resolution imaging camera.

5.3.5 Atomic Force Microscopy (AFM)

Crystal topography and height measurements were obtained using an Anton Paar Tosca AFM with ARROW-NCR Al-coated tips (resonance frequency: 285 kHz; force constant: 42 N/m; NanoWorld). The data were processed and background corrected using Gwyddion® software.

4.3.6 Raman Spectroscopy. Raman spectra were acquired using an inVia Raman microscope (Renishaw Inc.). Measurements were performed using a 532 nm excitation laser and a 2,400 lines mm⁻¹ grating. A laser power of 1 % and an exposure time of 30 s were used. Linear fitting of the Raman peak positions was performed using MagicPlot version 3.0.1.

5.3.7 Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy (SEM-EDS)

The morphology and elemental composition of the structures were characterized using an FEI Magellan XHR scanning electron microscope equipped with an Oxford 80 mm² silicon drift detector. Energy-dispersive X-ray spectroscopy data were analyzed using the built-in Aztec software.

5.3.8 Transmission Electron Microscopy (TEM) and Sample Preparation

Samples for TEM were prepared by dry transfer of the crystals onto a lacey carbon grid (400 mesh; Ted Pella, Inc.) by gently contacting the carbon side of the grid with the growth substrate. TEM imaging was performed at an accelerating voltage of 200 kV using a JEOL JEM-2100F equipped with a Gatan OneView camera. Raw (.dm4) images were processed using DigitalMicrograph. Fast Fourier transformation (FFT) was generated using ImageJ. FFTs were indexed using a SingleCrystal (CrystalMaker Software Ltd.).

5.3.9 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns were collected using a benchtop Rigaku MiniFlex X-ray diffractometer equipped with a monochromatic X-ray source and a D/teX Ultra 1D silicon strip detector. The patterns were fitted using Le Bail method in Profex.

5.4 Results and Discussion

The model phase, ZrS_3 , is well known to form highly anisotropic ribbon-like crystals with large, smooth surfaces when grown via chemical vapor transport (CVT; iodine transport agent) under stoichiometric or sulfur-rich conditions, as shown in **Figure S1**. Reports of screw-dislocation-mediated growth in this material system, however, remain scarce and often stochastic in nature, with their chemical and synthetic origins unknown.^{50–52} Beyond ZrS_3 , to our knowledge, there has been no report of screw-dislocation-induced spiral hillocks in the broader class of 1D vdW TMTCs. Positing that slightly lower, non-stoichiometric amounts of the coordinating sulfur atoms within the chains would perturb the crystal growth behavior of ZrS_3 , potentially promoting interchain crystallization,⁵³ introducing lattice strain, and altering the mechanical characteristics of the chains,^{54,55} we sought to use this synthetic strategy to trigger the formation of screw-dislocation-mediated nanoscale hillocks on the surface of bulk crystals. By using a controlled Zr:S ratio optimized to 1:2.8 (in contrast to the stoichiometric ratio of 1:3), while holding all the other synthetic parameters constant (temperature program, ampoule size, temperature gradient, etc.; **Figure S2**), we consistently found that sulfur-deficient $\text{ZrS}_{3-\delta}$ crystals exhibited synthetically imposed spiral growth hillocks on the surfaces of the bulk crystals (Figure 1B). Consistent with the BCF theory, we found that the controlled slow cooling is critical for the formation of the surface spiral hillocks as our results suggest that slow cooling (over the course of two days) maintains a low-supersaturation regime during the late stages of CVT growth, which favors screw-dislocation-mediated step propagation to form the spiral hillocks over rapid 2D nucleation.^{1,4,5} In contrast, rapid or natural cooling does not produce spiral hillocks, suggesting that sustained near-equilibrium growth conditions are necessary for the development of well-defined spiral growth features.

Generally, we found that crystal growth occurs preferentially on the inner surface of the growth ampoule, with a higher yield near the hot zone, $T_1 = 750^\circ\text{C}$ (**Figure 1B**). The resulting crystals have average lengths of 1–2 cm, widths of 100–200 μm , and thicknesses of 3–16 μm

(**Figure S3, and S4**). The spiral hillocks are found either at or near the crystal nucleation point, where they radiate outward in the direction of the crystal growth, or at various locations along the length of the crystal. The spiral hillocks extend along a well-defined long axis and exhibit two distinct directional growth behaviors originating from localized growth centers: (I) spiral hillocks that extend outward along the crystal long axis, corresponding to the covalent intrachain direction; and (II) spiral hillocks that originate from the crystal nucleation point and propagate along the axis perpendicular to the chain direction (the weak, non-covalent interchain direction), as indicated by the arrows in **Figure 1B**.

To assess the crystalline order of the crystals, we used Raman spectroscopy to confirm that the phonon modes are consistent with the pristine, monoclinic structure of ZrS_3 ($P2_1/m$),^{40,43} with characteristic peaks observed at 151 cm^{-1} (Ag, rigid chain mode), 281 cm^{-1} , 319 cm^{-1} (Ag, internal modes), and 528 cm^{-1} (Ag, S—S stretching mode) (**Figure 1C**). Beyond the characteristic phonon modes, orientation-dependent Raman spectroscopy, where the polarization angle is defined such that 0° corresponds to the crystal b-axis (long-axis) aligned with the incident polarization and 90° corresponds to the perpendicular orientation, revealed the pronounced structural anisotropy of the crystals. The Ag modes at 281 and 319 cm^{-1} exhibit maximum intensity when the b-axis is aligned with the polarization direction (0°), consistent with the anisotropic, 1D chain-like structure of ZrS_3 with strong covalency. In contrast, the S—S stretching mode at 528 cm^{-1} becomes more prominent when the polarization is perpendicular to the b-axis (90°). This polarization-dependent Raman response is preserved both at and away from the spiral hillock features, indicating that screw-dislocation-mediated growth does not significantly disrupt the underlying atomic order, crystalline structure, and anisotropic behavior of the parent phase (**Figure S5**). Complementary powder X-ray diffraction (PXRD) analysis showed that the sulfur-deficient crystals exhibit diffraction peaks consistent with the monoclinic ZrS_3 ($P2_1/m$) crystal structure (**Figure S6**).

Although Raman spectroscopy confirms the retention of the monoclinic ZrS_3 structure, compositional analysis of the resulting crystals with spiral hillocks reveals deviations from the ideal stoichiometric ratio that were intentionally introduced through our synthetic methodology. Energy-dispersive spectroscopy (EDS) measurements indicate that regions containing spiral hillocks exhibit an average composition of approximately $\text{Zr}:\text{S} \approx 1:2.5$ (**Table S1**), corresponding approximately to $\text{ZrS}_{3-\delta}$ ($\delta \approx 0.5$), which is lower than the loading ratio of $\text{Zr}:\text{S} \approx 1:2.8$. In contrast, regions away from the spiral hillocks exhibit compositions closer to the stoichiometric ratio of

Zr:S $\approx$ 1:3 (**Table S2**), strongly suggesting that sulfur deficiency is localized at the spiral hillocks. In addition, we observed that the non-stoichiometric loading of sulfur results in a secondary phase that crystallized alongside the $\text{ZrS}_{3-\delta}$ crystals localized in the hot/source zone (T_1) appearing as silver-colored, two-dimensional plates, which are visually distinct from the characteristic ribbon-like reddish appearance of ZrS_3 and $\text{ZrS}_{3-\delta}$. Raman spectroscopy of this secondary phase shows vibrational modes consistent with the 2D ZrS_2 phase (**Figure S7**). The coexistence of these phases, together with the measured composition, indicates that the system lies within a regime of competing phase formation between ZrS_3 and ZrS_2 during the growth process.

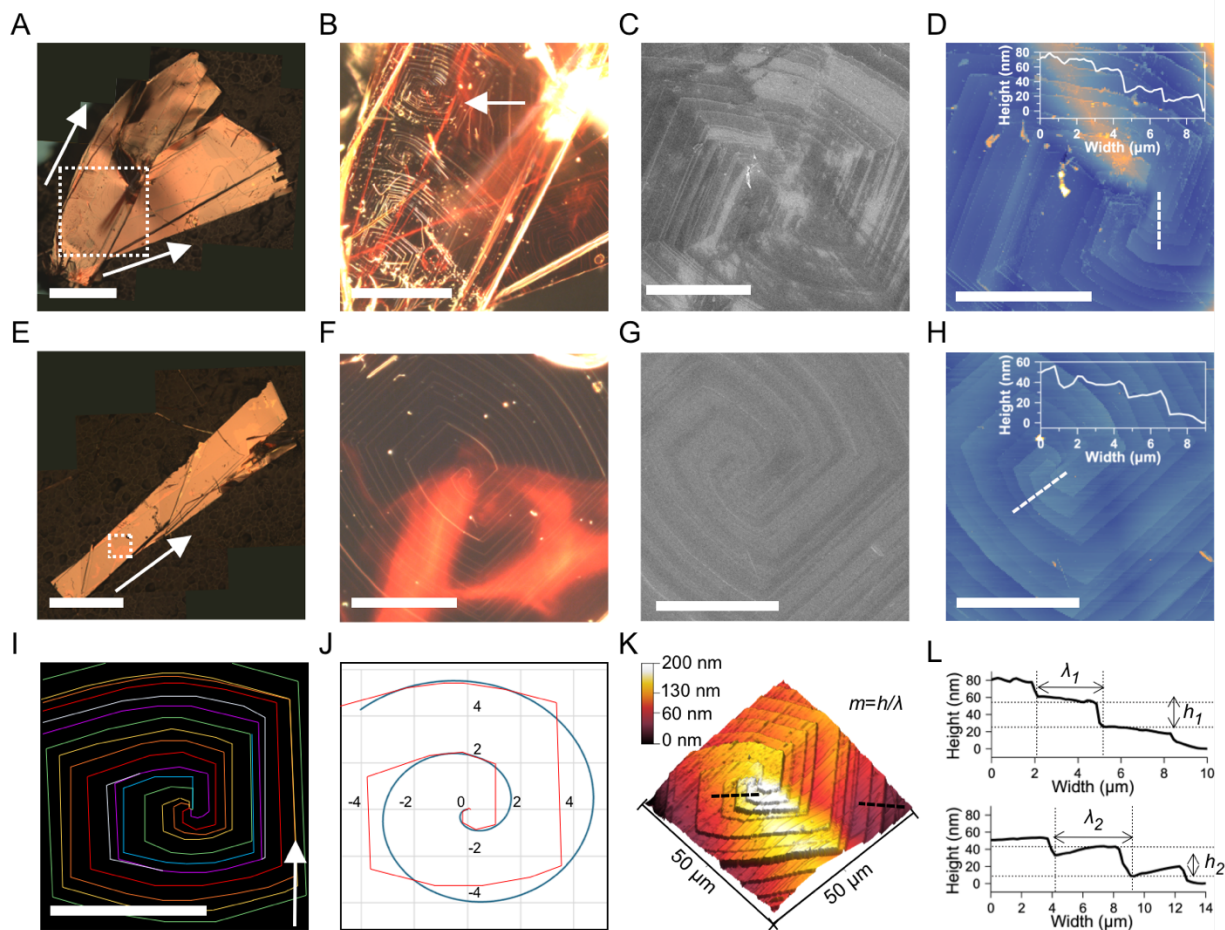


Figure 2. Characterization of spiral hillocks in $\text{ZrS}_{3-\delta}$ crystals. (A,E) Bright-field (BF) optical images showing the ribbon-like morphology of $\text{ZrS}_{3-\delta}$ crystals. Arrows indicate the crystal growth direction and b-axis direction. Scale bars, 500 μm . (B,F) Dark-field optical images of the boxed regions in (A,E), highlighting polygonized spiral hillocks on the crystal surfaces. Scale bars, 245 μm . (C,G) SEM images of the spiral hillocks highlighted in (B,F). Scale bars, 25 μm . (D,H) AFM topography images corresponding to (C,G) with line profiles along the dashed lines, showing discrete terrace steps. Scale bars, 25 μm . (I) Terrace-tracing analysis of the spiral hillock in (G), illustrating nested polygonized spiral terraces relative to the b-axis denoted by the arrow. Scale bar, 50 μm . (J) Single spiral (red) extracted from (I) overlaid with an ideal Archimedean spiral (blue). (K) Three-dimensional AFM topography of the spiral hillock shown in (G). (L) AFM line profiles extracted from (K), showing representative terrace widths and heights measured near (λ_1 , h_1) and away from the spiral center (λ_2 , h_2).

Morphological characterization of the crystals and the hillocks formed on their surfaces further supports the presence of screw-dislocation-mediated growth associated with local compositional inhomogeneity. Representative optical and electron microscopy images reveal that $\text{ZrS}_{3-\delta}$ crystals display either a single spiral hillock or, more commonly, multiple spiral hillocks within a single crystal. **Figure 2** highlights two representative growth morphologies: one consisting of multiple ribbon-like crystals originating from a common nucleation site and radiating outward in a growth morphology commonly observed for 1D crystals (**Figure 2A-D**); and another

representing a single monolithic crystal (**Figure 2E-H**). AFM measurements further confirm the step-like nature of the spiral terraces. Height profiles reveal discrete periodic steps ranging from 15–33 nm, corresponding to approximately 17–37 layers based on an interlayer spacing of ~ 0.898 nm (8.98 Å). Terrace widths (interstep spacing) in the marked regions range from 1.6 to 3.5 μm , consistent with layer-by-layer propagation around a localized screw dislocation (**Figure 2D,H**).

Across several representative spiral hillocks, we found both left- and right-handed rotational senses, occurring either as isolated spiral hillocks or as multiple hillocks on the same crystal surface (**Figures 1D, 2, S8, and S9**). Based on the representative crystals imaged, we observed that the spirals are not racemic but rather exhibit a preference for right-handedness. Examining the geometry of the hillocks, which resemble pyramidal structures, we correlate the approximate hillock angles along the [001] direction with the Zr—Zr—Zr bond angles oriented either parallel ($\sim 109.5^\circ$; intrachain) or perpendicular ($\sim 70.5^\circ$; interchain) to the crystal long axis ([0k0]), reinforcing the notion that the underlying crystal structure influences the hillock geometry (**Figure S10**). Intriguingly, based on several representative crystals, we found that, rather than forming a single propagating spiral, the hillocks are usually composed of more than two concentric, interlaced spirals, with some emerging from a localized spot suggestive of dislocation migration in a linear trajectory parallel to the crystal growth direction and long-axis.⁵⁶ These complex hillocks, commonly referred to as “super”-spirals, are rare and have only been observed in calcite,^{57,58} SiC,⁵⁹ and L-cysteine^{60,61}.

To further understand the nature of the “super”-spiral hillocks in ZrS_{3-8} we traced the spiral terraces from AFM topography images of hillocks consisting of multiple polygonized terraces winding around localized dislocation centers. **Figure 2I** shows terrace-tracing analysis of a representative spiral hillock, revealing that it is composed of seven distinguishable spirals propagating outward from the center. Extracting a single spiral near the center enabled us to compare it with an Archimedean spiral, a motif commonly observed in spiral hillocks (**Figure 2J**). We found that the spiral generally conforms to an Archimedean spiral and as expected, agrees more closely with the ideal geometry near the center of the hillock. The deviation becomes increasingly pronounced as the “super”-spiral morphology causes lateral expansion of the spiral during successive rotations, particularly after several turns. Linear fitting of the representative spiral within the image frame yielded an R^2 of 0.86 for an ideal Archimedean spiral. This value

increases to 0.99 near the center of the spiral and contrasts with the logarithmic spiral fit, which yielded an R^2 of 0.81 (**Figure S11**).

The “super”-spiral nature of the hillocks and their slight deviation from an ideal Archimedean spiral are further supported by the AFM line profiles acquired near and away from the spiral core (**Figure 2K,L**). These measurements reveal discrete terrace steps with average heights of approximately $h_1 \approx 30$ nm and $h_2 \approx 33$ nm, and terrace widths of $\lambda_1 \approx 3$ μ m near the core and $\lambda_2 \approx 5$ μ m at larger radial distances. The measured step heights are significantly larger than the single-layer step height expected for typical spiral hillocks in vdW materials.^{2,15,62} The resulting local hillock slopes, estimated as $m = h/\lambda$, decrease from $m_1 \approx 1.0 \times 10^{-2}$ to $m_2 \approx 6.6 \times 10^{-3}$, indicating progressive terrace broadening during outward spiral propagation. The progressive terrace broadening and corresponding decrease in hillock slope are consistent with dislocation-mediated step-flow growth under low supersaturation conditions.⁵

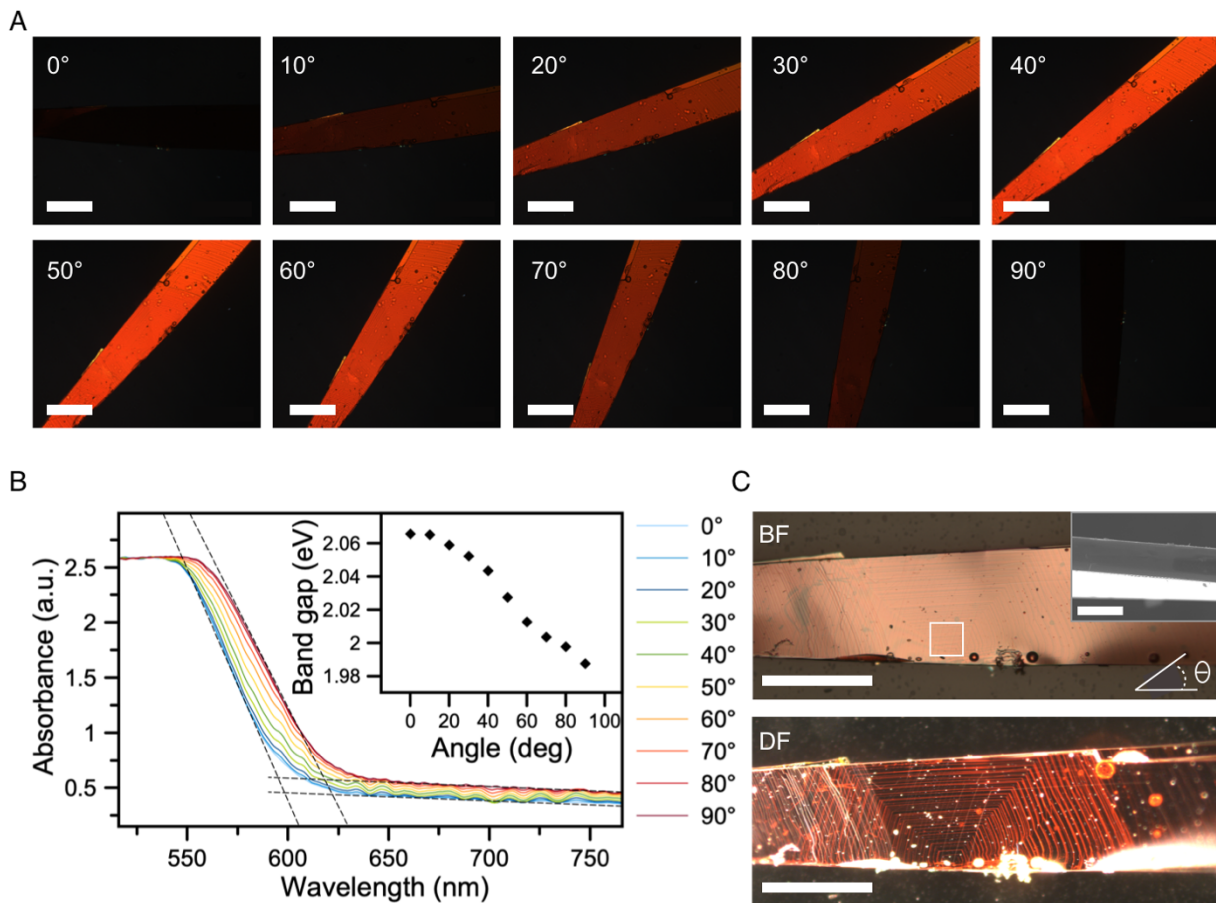


Figure 3. Polarization-dependent optical response of $\text{ZrS}_{3-\delta}$ crystals. (A) Transmission optical images under crossed polarizers as the crystal is rotated from 0° to 90° . Scale bars, $245\ \mu\text{m}$. (B) Polarization-dependent absorbance spectra collected by rotating the crystal relative to the incident polarization direction. Inset shows the angular dependence (with respect to the incident polarization) of the band gap. (C) Bright-field (BF, top) and dark-field (DF, bottom) optical micrographs of the corresponding crystal. Scale bars, $245\ \mu\text{m}$. Inset shows the side-view of the crystal. Scale bar, $10\ \mu\text{m}$.

Beyond the structural characteristics observed in these crystals, polarization-resolved optical measurements also revealed a pronounced anisotropic optical response in $\text{ZrS}_{3-\delta}$ crystals. Under crossed polarization, the transmitted intensity varies systematically as the crystal is rotated from 0° to 90° (**Figure 3A**), exhibiting periodic extinction every 90° . This angular dependence is consistent with the intrinsic quasi-1D crystal structure and anisotropic optical response previously reported to arise from the anisotropic electronic structure and birefringent behavior in ZrS_3 .⁴⁵ Moreover, the polarization-dependent absorption spectra (**Figure 3B**) of the crystal in **Figure 3A,C** further reveal anisotropic optical absorption, with the absorption edge exhibiting changes in both intensity and onset as the crystal is rotated relative to the incident polarization direction.

Linear extrapolation of the absorption edge yields an estimated optical bandgap of approximately 2.0 eV when the crystal is oriented parallel to the polarization direction, which increases by about 0.1 eV when the crystal is rotated by 90° and oriented perpendicular to the polarization direction (inset, **Figure 3B**). Similar behavior is consistently observed across various crystals (**Figure S12**). The polarization-dependent absorption behavior agrees with previous experimental and theoretical studies of ZrS_3 , which attribute the anisotropic optical response to the strong covalency along the chain direction (*b*-axis).⁴³

5.5 Conclusion

In summary, we demonstrate that sulfur-deficient growth conditions enable the predictable and deliberate formation of screw-dislocation-mediated spiral hillocks in $\text{ZrS}_{3-\delta}$ crystals. Taken together, our results suggest that sulfur-deficient growth conditions promote defect formation and local structural and geometric perturbation, while low-supersaturation growth enables the sustained development of screw-dislocation-mediated spiral hillocks in $\text{ZrS}_{3-\delta}$. Specific to $\text{ZrS}_{3-\delta}$ and TMTCs, we posit that these hillocks emerge from the preferential interchain growth induced by low sulfur content (in contrast to high sulfur concentrations that promote 1D growth in TMTCs), together with the anisotropic growth behavior of these materials⁵³ along which the screw dislocation preferentially propagates. Coupled with the weak, non-covalent interactions that hold the flexible chains together, these structural perturbations are more readily accommodated during crystal growth, thereby making it more favorable for extrinsic lattice strain to develop and induce screw dislocations that drive spiral hillock formation.

5.6 References

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CHAPTER 6: Conclusions and Outlook

The work presented in this dissertation establishes a unified framework for understanding and controlling crystal growth in 1D vdW materials through the interplay of crystal bonding, composition, mass transport, and defect formation. By integrating modified and conventional CVT with systematic control of crystal chemistry and growth conditions, this work demonstrates that anisotropic crystal growth can be rationally directed to achieve previously inaccessible crystal dimensions and complex morphologies. Collectively, these studies provide new design principles for the vapor-phase synthesis of 1D vdW materials.

The growth strategies developed in this dissertation establish a foundation for the rational synthesis of increasingly complex 1D vdW materials and raising several important questions for future investigation. Although the design principles identified here were demonstrated using NbS₃-I, MoI₃, and ZrS₃, determining the extent to which these principles apply across other 1D vdW systems remains an important direction for future research. Extending these studies to the growing classes of transition metal trichalcogenides and related low-dimensional materials will help determine whether these parameters are broadly applicable design principles for anisotropic crystal growth in phases that have underlying 1D motifs.

The findings herein instigate future efforts focused on understanding how controlled crystal dimensions, morphology, and defect structures influence the emergent physical properties of 1D vdW materials. In particular, progressively reducing nanowire dimensions toward the atomic scale, investigating the magnetic behavior of highly anisotropic 1D systems such as MoI₃, and exploring the unique properties associated with ring-shaped nanostructures and spiral hillocks represent promising directions for future research. Establishing these structure–property relationships will be essential for translating advances in crystal growth into functional low-dimensional materials and future device applications.

APPENDIX A: Supplementary Data and Results

A.1 Supplementary Figures and Tables for Chapter 2

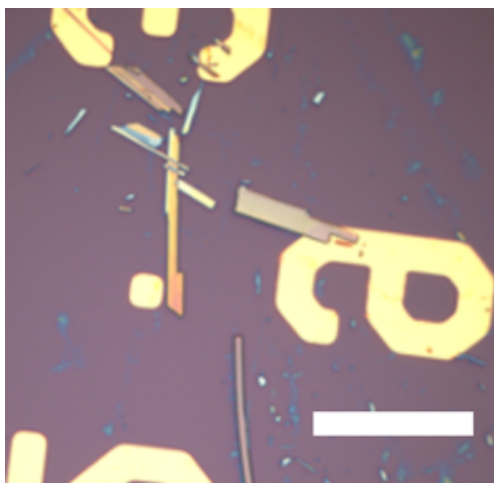


Figure S1. Exfoliated NbS₃-I. Bright-field optical micrograph of nanostructures resulting from micro-mechanically exfoliated bulk NbS₃. Scale bar, 25 μ m

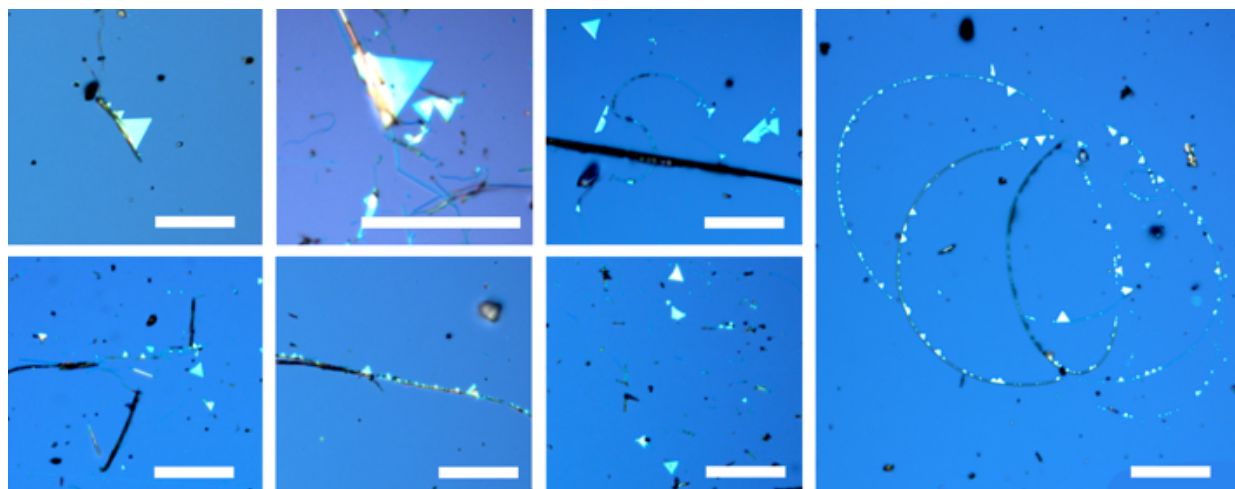


Figure S2. Optical images of NbS₂. Bright-field optical micrographs of triangular-shaped NbS₂ nanosheets that grow from NbS₃ nanowires. Scale bars, 25 μm .

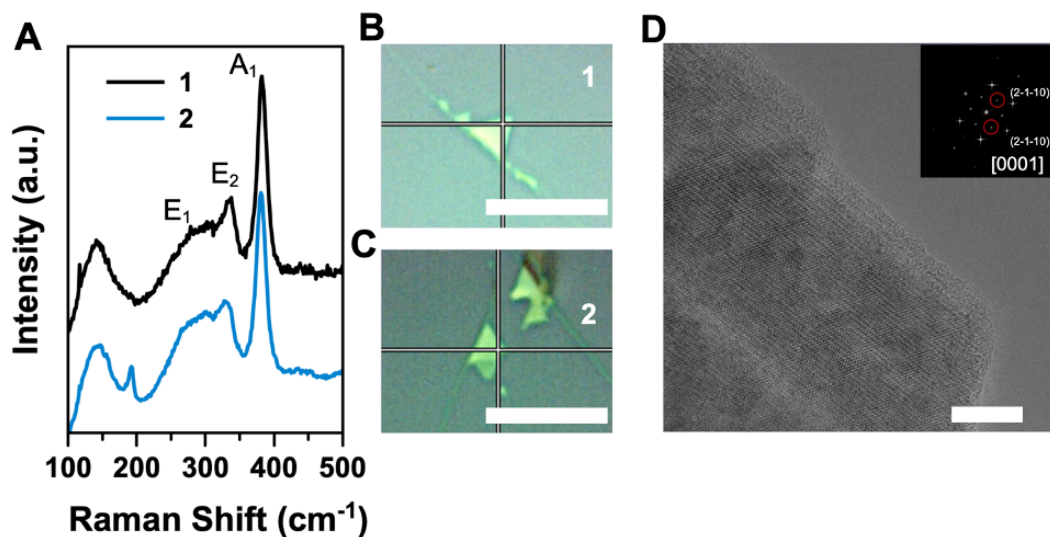


Figure S3. Raman spectroscopy and electron microscopy of NbS₂ nanosheets. (A) Representative Raman spectra of NbS₂ nanosheets which crystallized from NbS₃ nanowires, as seen in Figure S₂. The in-plane (E₁ and E₂) and out-of-plane (A₁) phonon modes are labeled for easier visualization. (B and C) Corresponding micrographs of the NbS₂ nanosheets from which the Raman spectra in A were taken from. (D) Representative TEM image of NbS₂ nanosheet with the corresponding FFT as inset. Scale bars, 20 μ m (B), 10 μ m (C), and 10 nm (D).

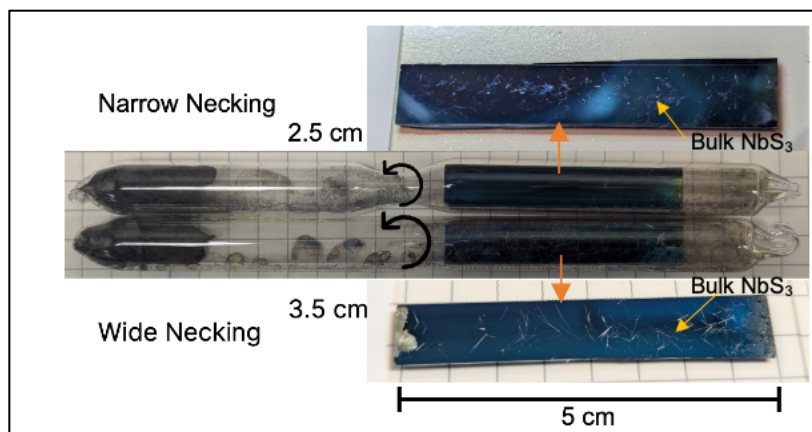


Figure S4. Images of two reaction ampoules: the top with narrow necking (2.5 cm outer circumference) and the bottom wide necking (3.5 cm outer circumference). The top ampoule results in a combination of bulk crystals before the narrowed region and induces the growth environment of smaller bulk crystals and nanowires, whereas the bottom ampoule results in mostly bulk crystal growth on the substrate. The outer circumference of the quartz tube without narrowing is 4 cm. We note that with the substrate positioned in the middle of zone T_2 , the center of the growth ampoules must be narrowed sufficiently to prevent the predominant growth of bulk crystals on the substrate, but not too small for bulk crystals to accumulate before the narrowed area and interrupt the transport of the precursors to the substrate.

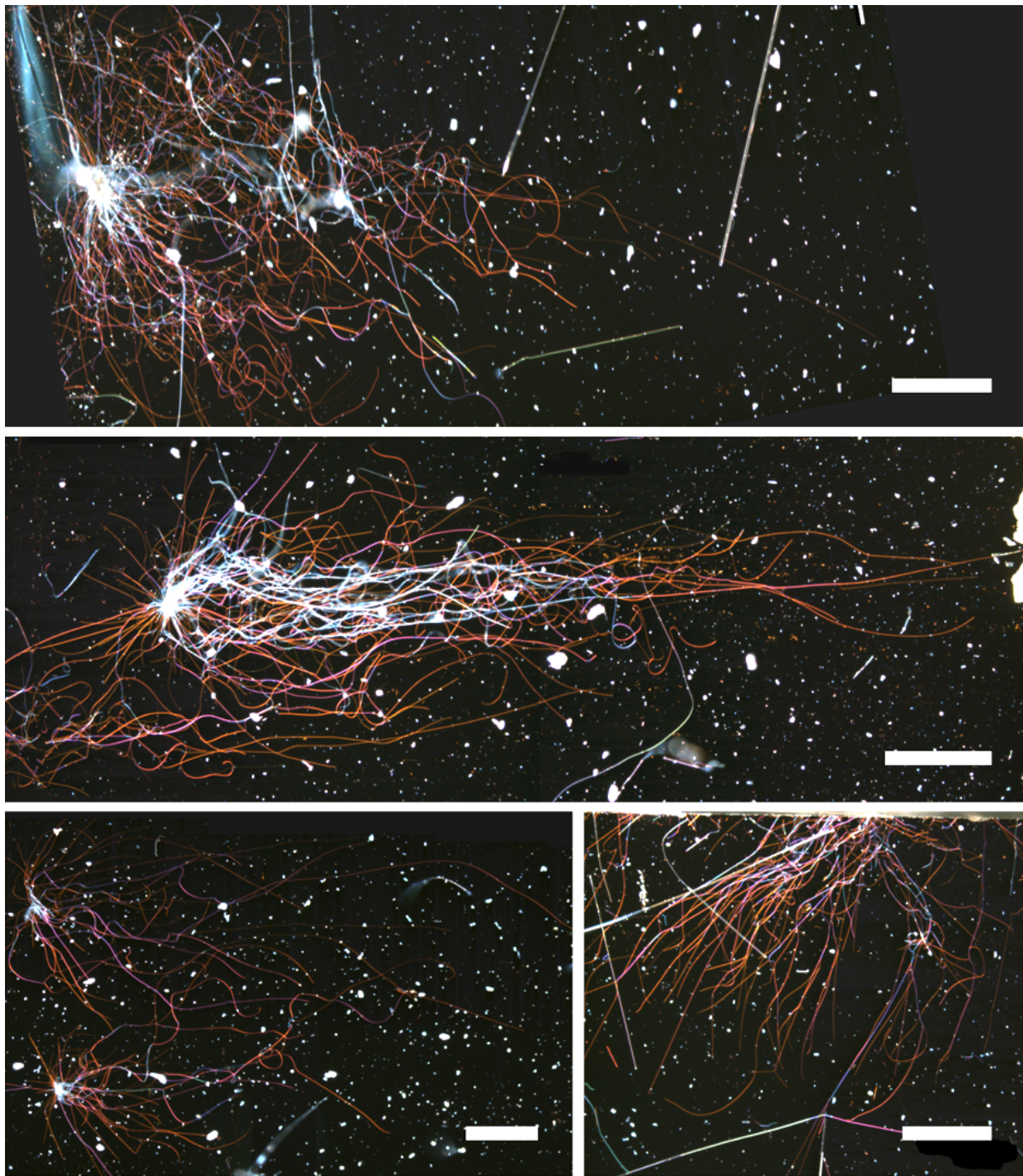


Figure S5. Dark-field images of NbS₃-I nanowires. (A-D) Representative dark-field optical micrographs of NbS₃ nanowires on Si/SiO₂ substrates. Scale bars, 245 μm.

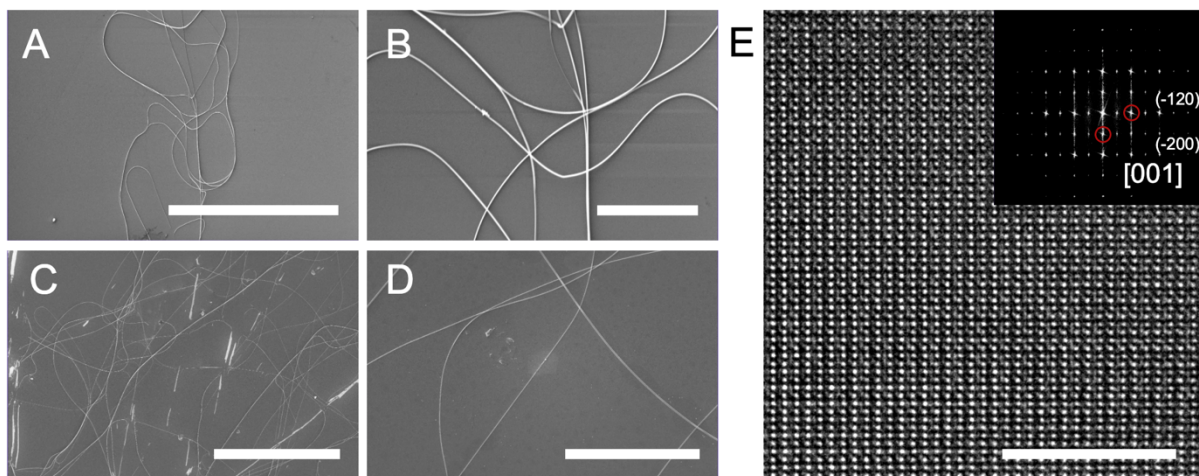


Figure S6. SEM and TEM micrographs of NbS_3 nanowires. (A-D) Representative SEM images of NbS_3 nanowires on Si/SiO_2 substrates. (E) Representative TEM image of a NbS_3 nanowire with the corresponding FFT as inset. Scale bars, 40 μm (A), 5 μm (B), 50 μm (C), 10 μm (D), and 5 nm in (E).

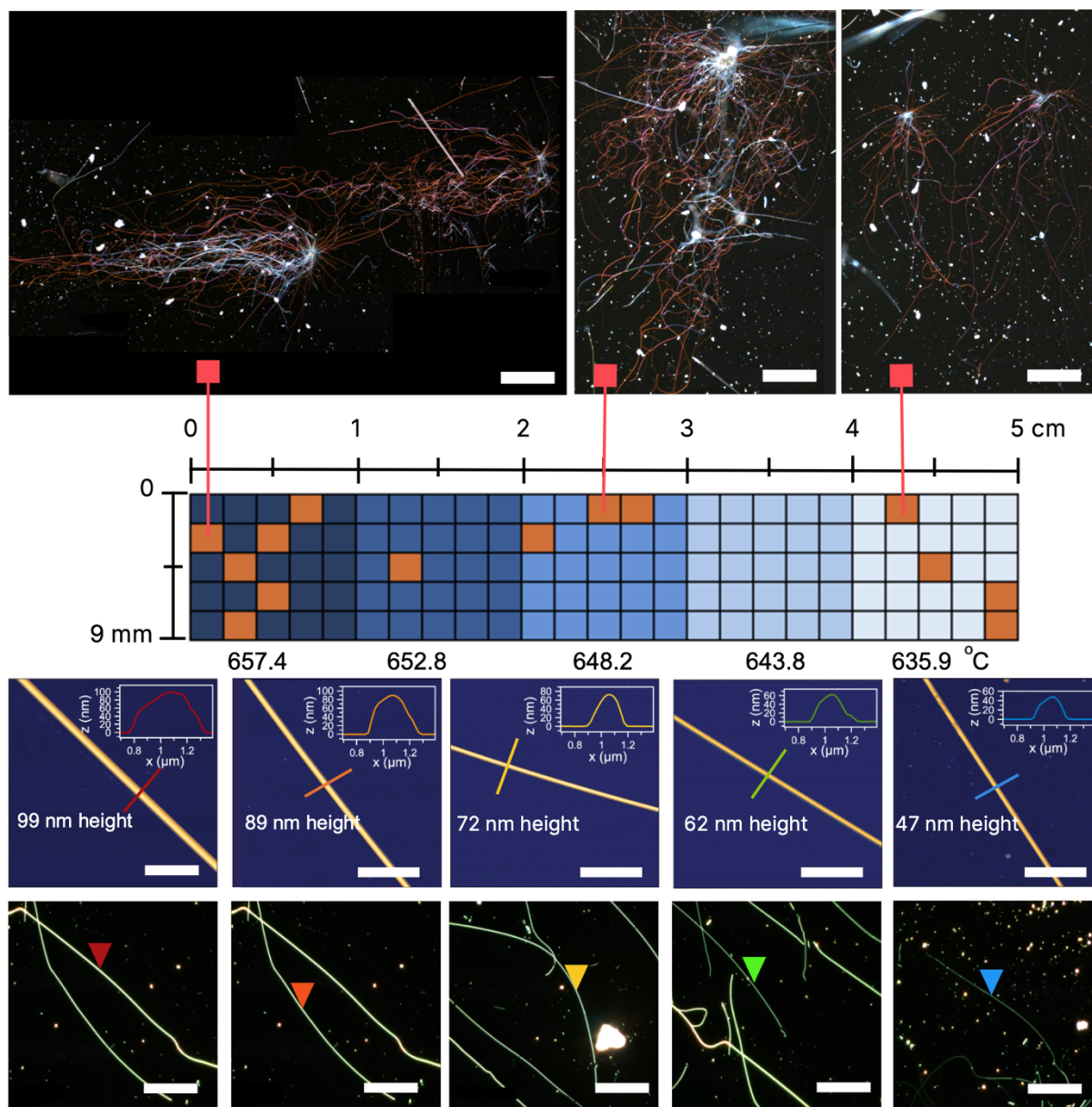


Figure S7. Mapped substrate with AFM and dark-field images of NbS₃ nanowires from a 30-min reaction. (A) Representative dark-field images of the as-grown NbS₃ nanowires on different regions of the Si/SiO₂ substrates. Scale bars, 245 μm. Below the substrate map are the calibrated temperatures of each substrate region, measured using an external probe, during the reaction at the fixed temperature gradient programmed at $T_1 = 750$ °C and $T_2 = 650$ °C. The orange boxes represent the regions where nanowires were found. (B) AFM images of various nanowires from A with their corresponding height profiles as the inset and dark-field image at 50x magnification (C). Scale bars: 3 (B) and 50 μm (C).

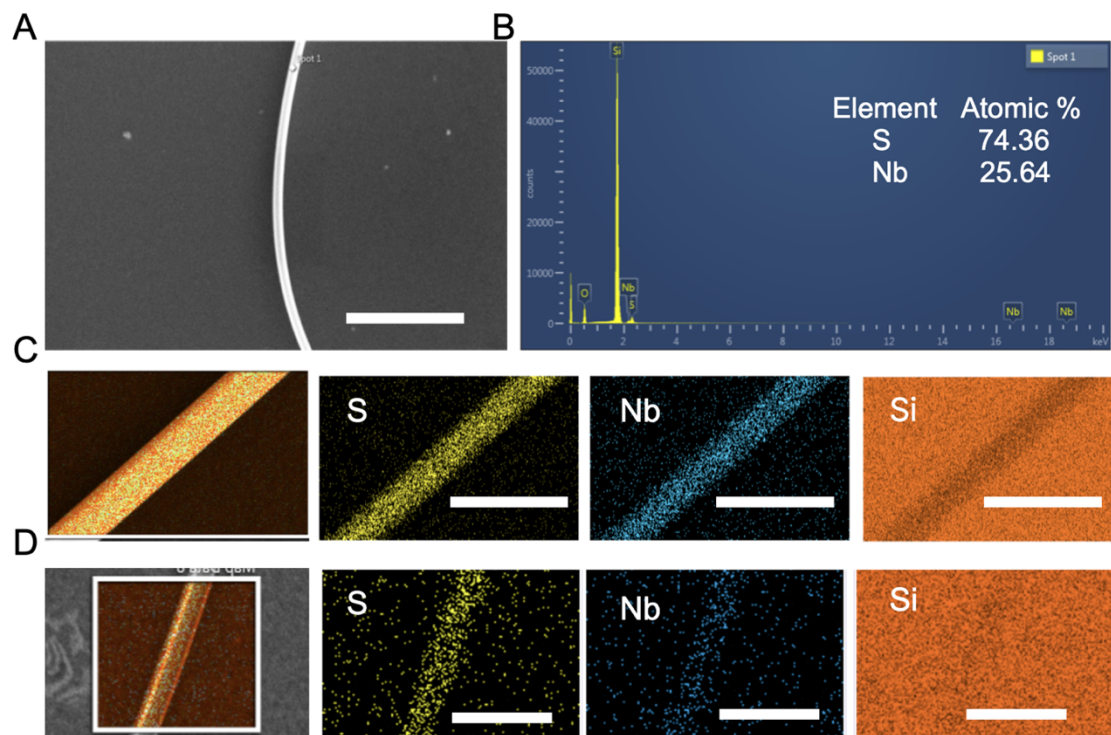


Figure S8. SEM-EDS of NbS_3 nanowires from a 30-min reaction. (A) Representative SEM image of a NbS_3 nanowire on the Si/SiO_2 substrate from Figure S5 with its corresponding EDS spectrum (B). Scale bar, $1\ \mu\text{m}$ (A). Representative EDS elemental maps of the NbS_3 nanowires shown in Figure S5. Scale bars: $1\ \mu\text{m}$ (C) and $500\ \text{nm}$ (D).

Table S1. Atomic percentages of Nb and S in individual nanowires as derived from the SEM-EDS analysis.

Sample	Atomic %	
	Nb	S
1	24.41	75.59
2	25.57	74.43
3	25.56	74.44
4	26.06	73.94
5	25.51	74.49
6	25.32	74.68
7	25.38	74.62
8	25.94	74.06
9	25.4	74.6
10	25.45	74.55
Average:	25.46	74.54
Average Ratio		
S/Nb:	2.93	

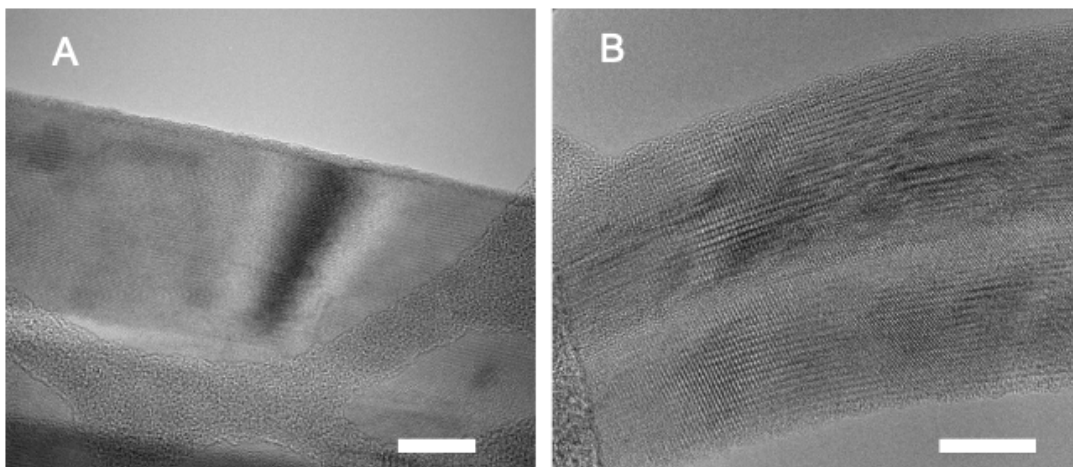


Figure S9. Representative TEM images of NbS₃ nanowires displaying folds and curves due to growth on substrate and/or external strain. Scale bars: 20 nm (A) and 10 nm (B).

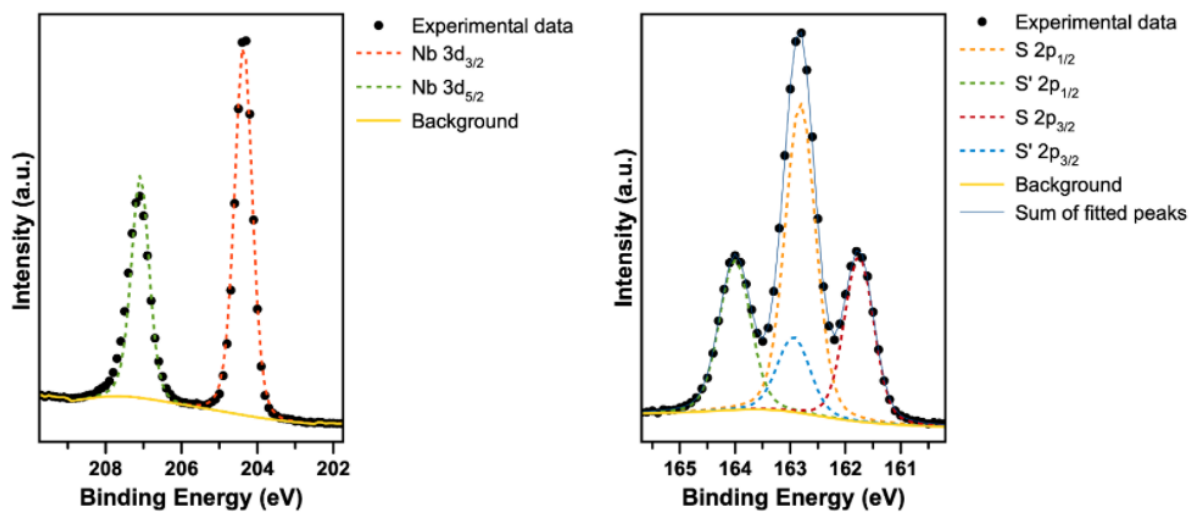


Figure S10. XPS peak parameters of bulk NbS₃ crystals. The XPS peaks correspond to the 3d_{3/2} and 3d_{5/2} states of Nb, and the S' 2p_{1/2}, S' 2p_{3/2}, and S 2p_{1/2}, S 2p_{3/2} states of S.

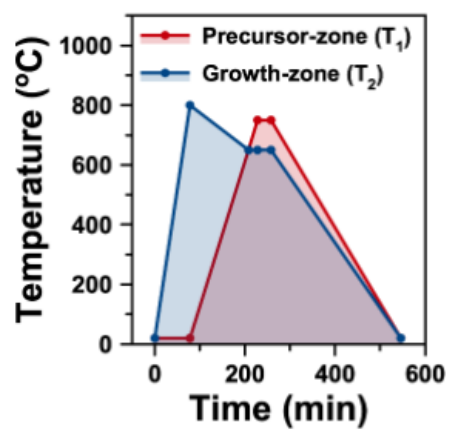


Figure S11. CVT temperature program used for the growth of NbS₃ nanoribbons shown in Figure S13.

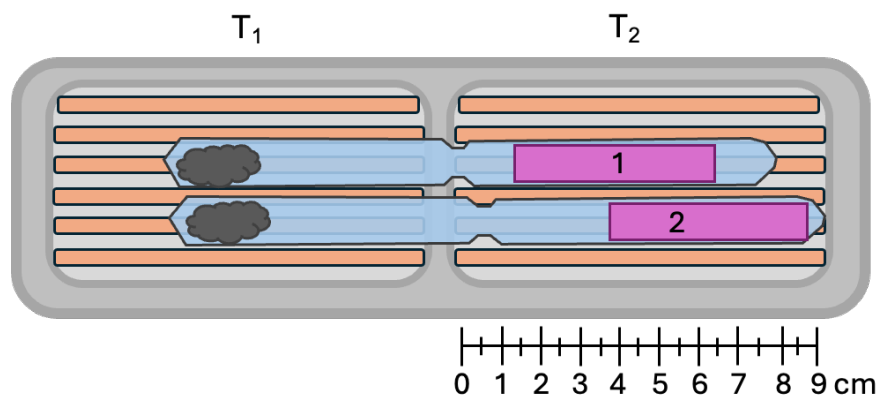


Figure S12. Substrate position placement inside the two-zone furnace. Substrate 1 was used for nanowire growth, whereas substrate 2 was used for nanoribbon growth.

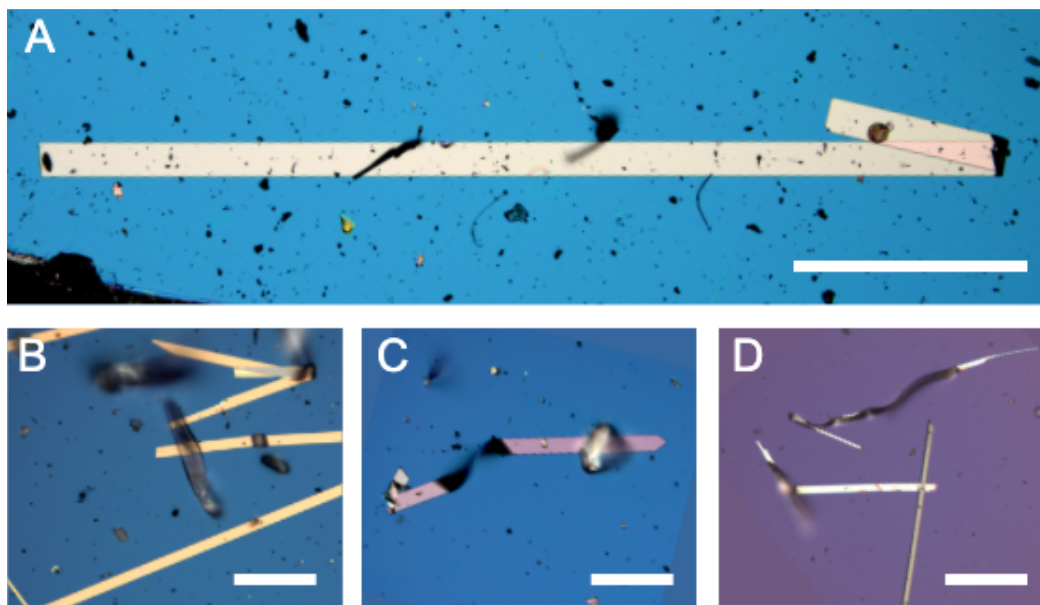


Figure S13. Optical micrographs of NbS₃ nanoribbons. (A-D) Bright-field optical micrographs of NbS₃ nanoribbons on Si/SiO₂ substrates. Scale bars, 245 μ m and 50 μ m (B-D).

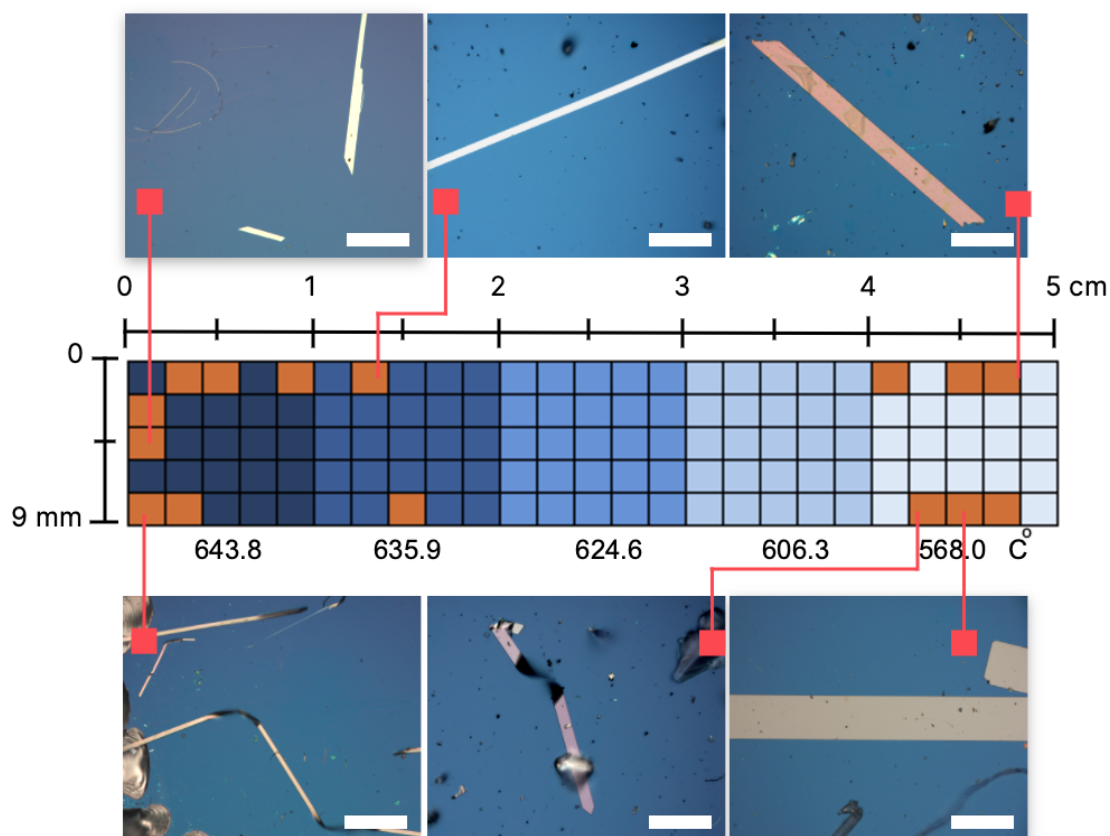


Figure S14. Representative bright-field images of the as-grown NbS_3 nanoribbons on different regions of the Si/SiO_2 substrates. Scale bars, 50 μm . The calibrated temperatures of each substrate region were measured using an external probe during the reaction at the fixed temperature gradient programmed at $T_1 = 750\text{ }^\circ\text{C}$ and $T_2 = 650\text{ }^\circ\text{C}$. The orange boxes represent the regions where the nanoribbons were found.

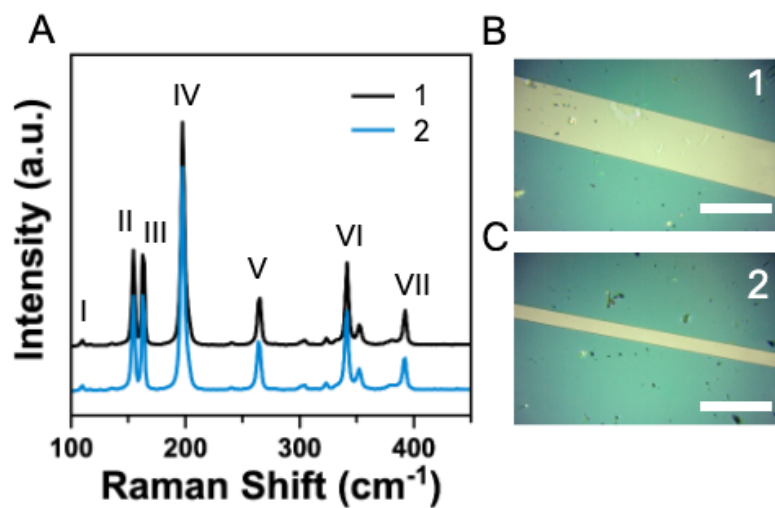


Figure S15. Representative Raman spectra of NbS₃ nanoribbons as shown in Figure S13. The phonon modes corresponding to the designation in the main manuscript is labeled for easier visualization. (B,C) Corresponding micrographs of the NbS₃ nanoribbons from which the Raman spectra in A were taken from. Scale bars, 50 μm (B,C).

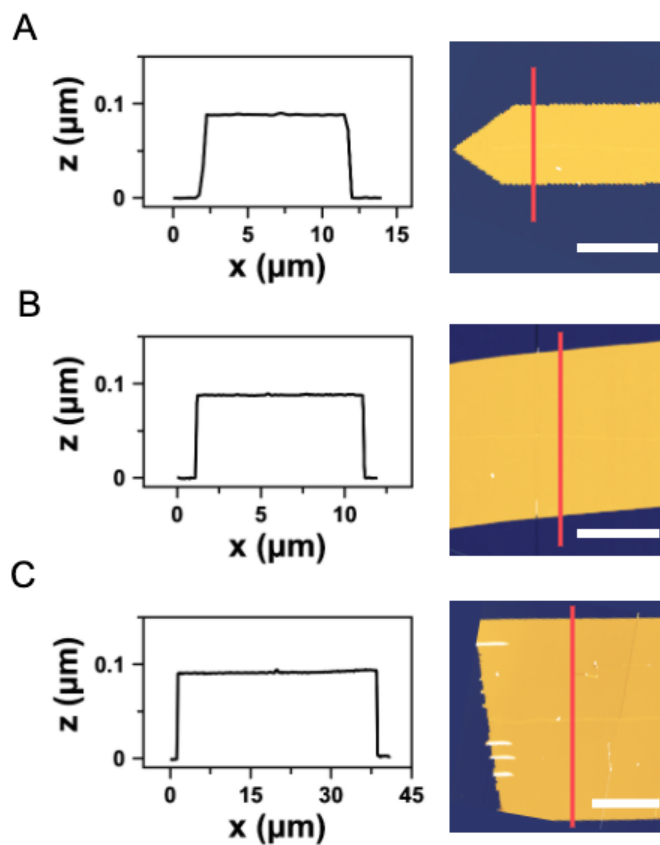


Figure S16. Representative AFM images of NbS_3 nanoribbons as shown in Figure S13. The red line indicates the region from which the height profile was taken. (A) Nanoribbon from Figure S13C with a height of 88 nm and width of 10 μm . Scale bar, 10 μm . (B) A nanoribbon with a height of 88 nm and width of 10 μm . Scale bar, 5 μm . (C) Nanoribbon from Figure S13A with a height of 91 nm and width of 37 μm . Scale bar, 12 μm .

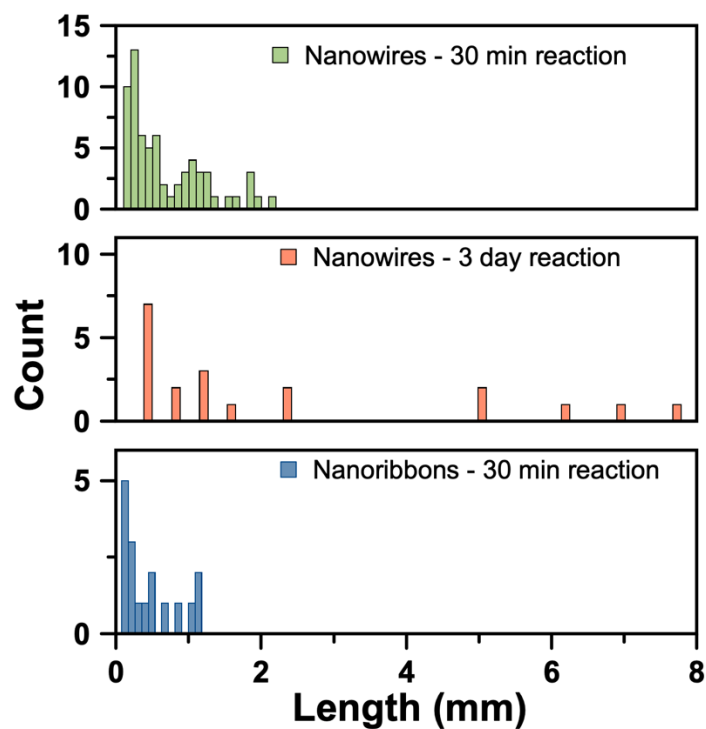


Figure S17. Histograms of the lengths of nanostructures grown under three different growth conditions. The top histogram in green shows the lengths of nanowires growing from a single nucleation spot, from Figure S5B. The middle histogram in orange shows the lengths of nanowires from the 3-day nanowire growth from Figure 2A. The bottom histogram in blue shows the lengths of the various nanoribbons from Figure S14.

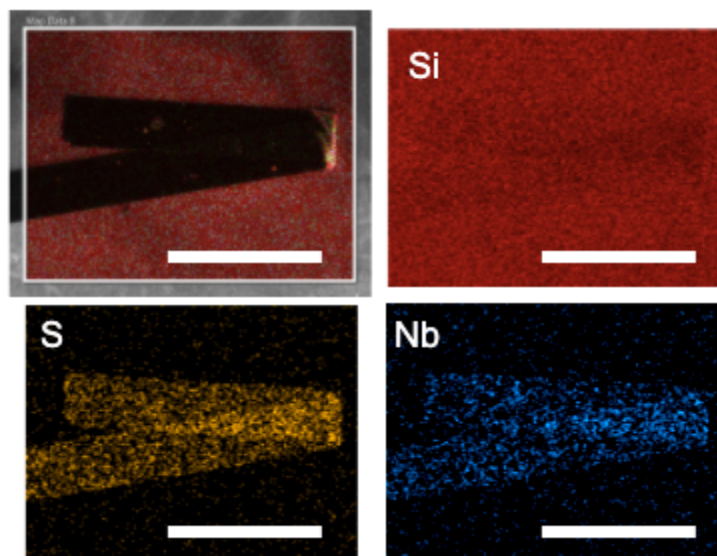


Figure S18. Representative EDS elemental maps of the NbS_3 nanoribbon shown in Figure S13A. Scale bars, 100 μm .

ZrS_3 ($P2_1/m$)

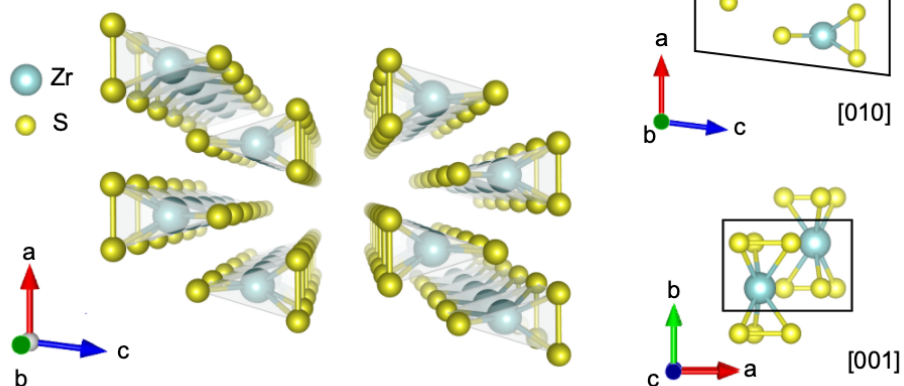


Figure S19. (left) Crystal structure of ZrS_3 which crystallizes in the $P2_1/m$ space group. (right) The unit cell is depicted by the black solid outline box in two different projections: $[010]$ zone axis parallel to the chains (top) and $[001]$ zone axis perpendicular to the chains (bottom). Zr atoms are depicted in blue and S atoms are depicted in yellow.

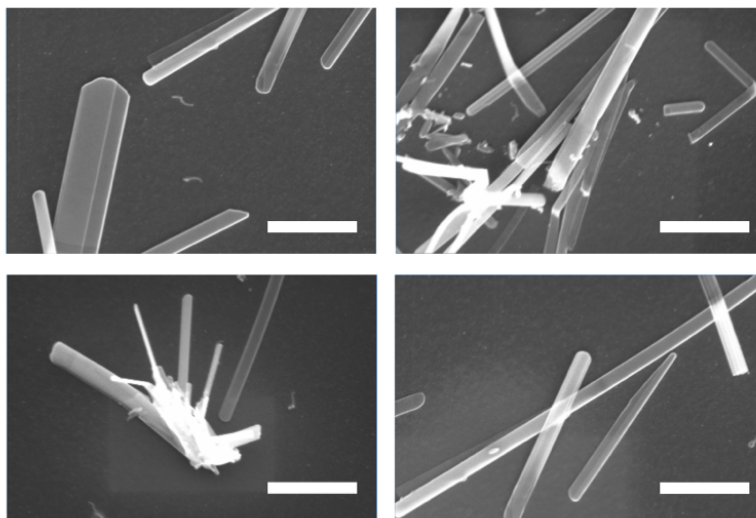


Figure S20. Representative SEM images of ZrS₃ nanoribbon structures on Si/SiO₂. Scale bars, 1 μm.

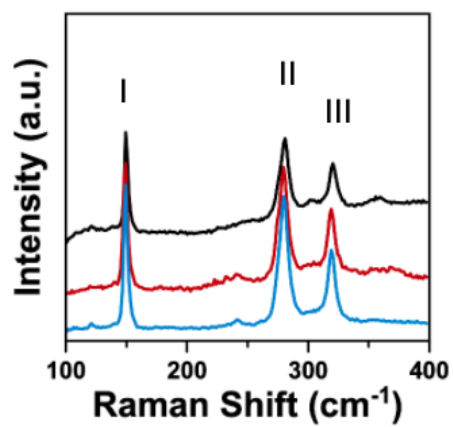


Figure S21. Three representative Raman spectra of ZrS_3 nanosheets as shown in Figure S20. The phonon modes corresponding to the designation in the main manuscript is labeled for easier visualization.

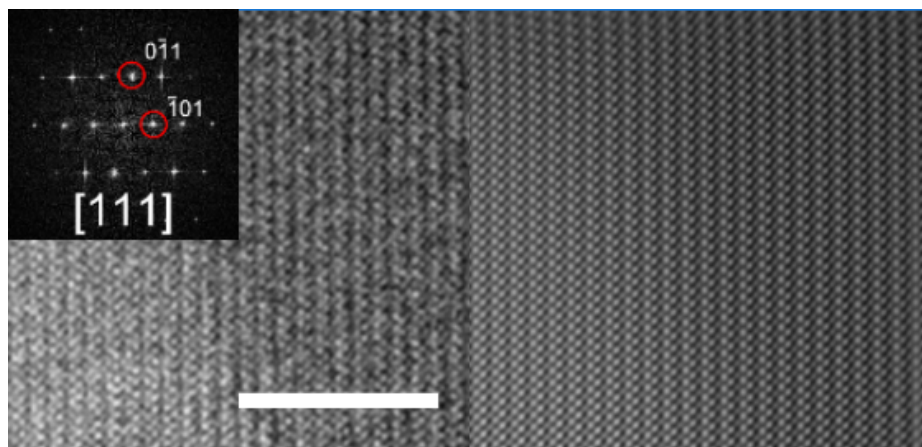


Figure S22. Representative HRTEM image of a ZrS_3 nanoribbon. Scale bar, 5 nm. The inset is a fast-Fourier transform image that is indexable to the $[111]$ zone axis. On the right is the corresponding Fourier-filtered micrograph. Fourier filtering was performed in ImageJ by excluding all but the most intense points of the Fourier transform of the image by adjusting the color map, then taking the inverse Fourier transform.

Table S2. Comparative DFT bonding strengths of ZrS_3 and NbS_3 across various crystallographic directions with respect to the chain orientations. The corresponding structures from which these calculations were based on are shown in Figures S23-28.

	ZrS_3 ($\text{P2}_1/\text{m}$)	NbS_3 (P-1)			
	Bond strength (eV)	Bond strength (eV)		Difference (eV)	
Inter-layer	0.193	0.384		0.191	
Inter-chain (1)	1.016	1.202		0.186	
Inter-chain (2)	1.224	1.356		0.132	
		<i>Covalent</i>	<i>Covalent</i>	<i>Covalent</i>	<i>Covalent</i>
		<i>bond (1)</i>	<i>bond (2)</i>	<i>bond (1)</i>	<i>bond (2)</i>
Intra-chain	1.753	1.927	2.152	0.173	0.399

$$\text{Inter-layer} = |\text{bulk} - \text{monolayer}|$$

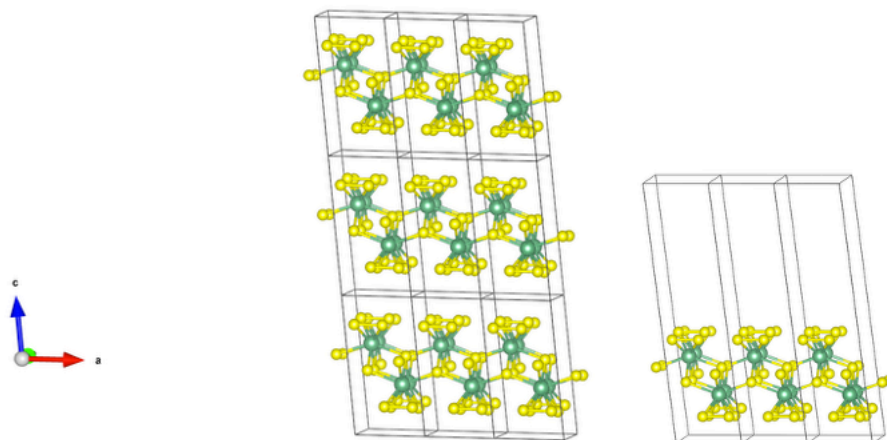


Figure S23. Bulk and quasi-2D monolayer crystal models that were used as the basis for the DFT calculation and comparison of the inter-layer bonding strength (along c-axis) between NbS₃ and ZrS₃.

$$\text{Inter-chain (1)} = |\text{monolayer} - \text{bichain in adjacent unit cell}|$$

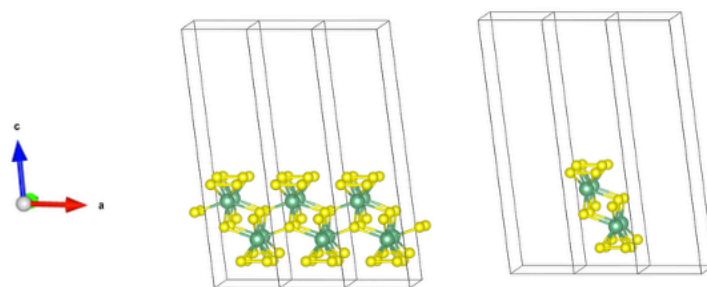


Figure S24. *Quasi-2D monolayer and the bi-chain crystal models that were used as the basis for the DFT calculation and comparison of the inter-chain (1) bonding strength (along a-axis and across the unit cell) between NbS₃ and ZrS₃.*

$$\text{Inter-chain (2)} = |\text{monolayer} - \text{interchain}|$$

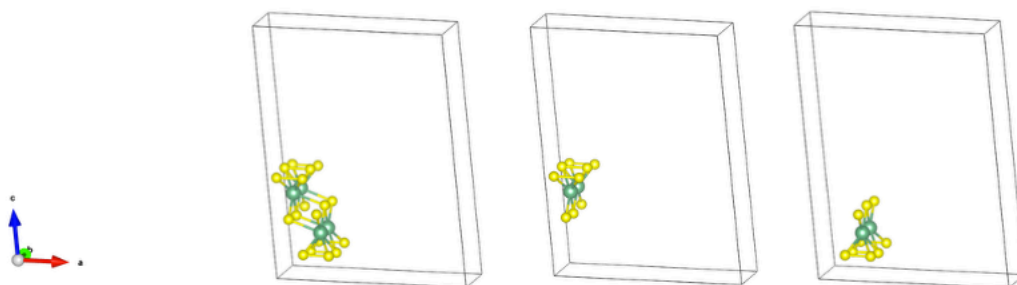


Figure S25. Bi-chain and single chain crystal models that were used as the basis for the DFT calculation and comparison of the inter-chain (2) bonding strength (along *a*-axis and within the unit cell) between NbS₃ and ZrS₃.

$$\text{Intra-chain} = |\text{chain} - \text{bond to adjacent unit cell}|$$

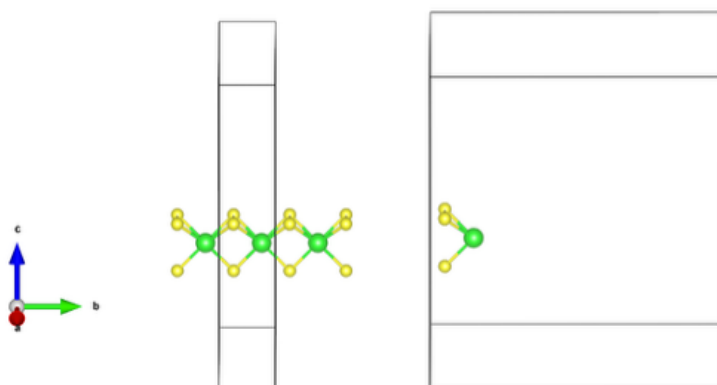


Figure S26. Single chain crystal structure models that were used as the basis for the DFT calculation of the intra-chain bonding strength (along *b*-axis) in ZrS₃.

$$\textit{Intra-chain} = |\textit{chain} - \textit{bond to adjacent unit cell}|$$

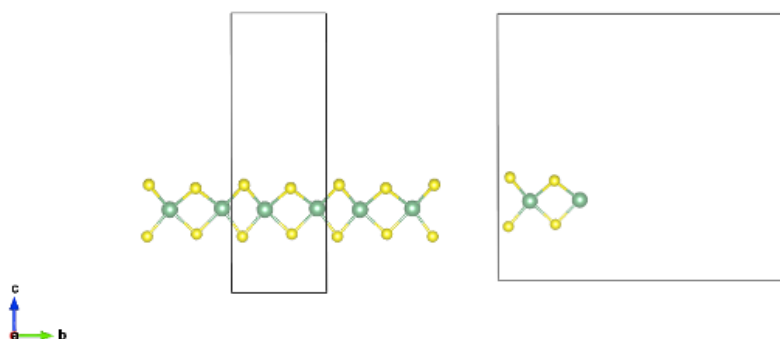


Figure S27. Single chain crystal structure models that were used as the basis for the DFT calculation of the intra-chain bonding strength (along *b*-axis, denoted as Covalent bond (2)) in NbS₃.

$$\textit{Intra-chain} = |\textit{chain} - \textit{bond to adjacent unit cell}|$$

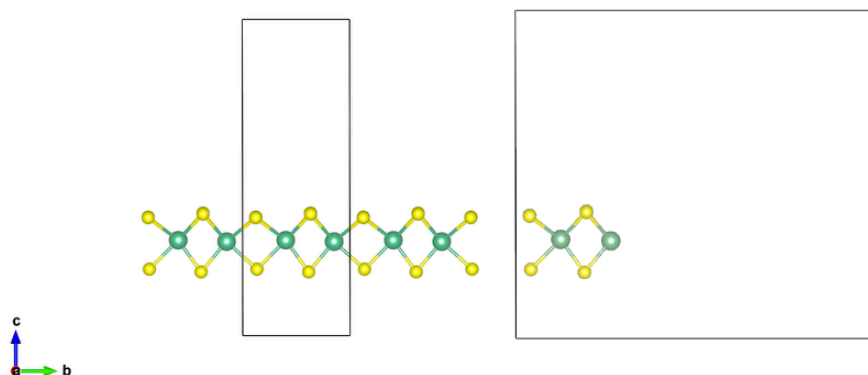


Figure S28. Single chain crystal structure models that were used as the basis for the DFT calculation of the intra-chain bonding strength (along *b*-axis, denoted as Covalent bond (1)) in NbS₃.

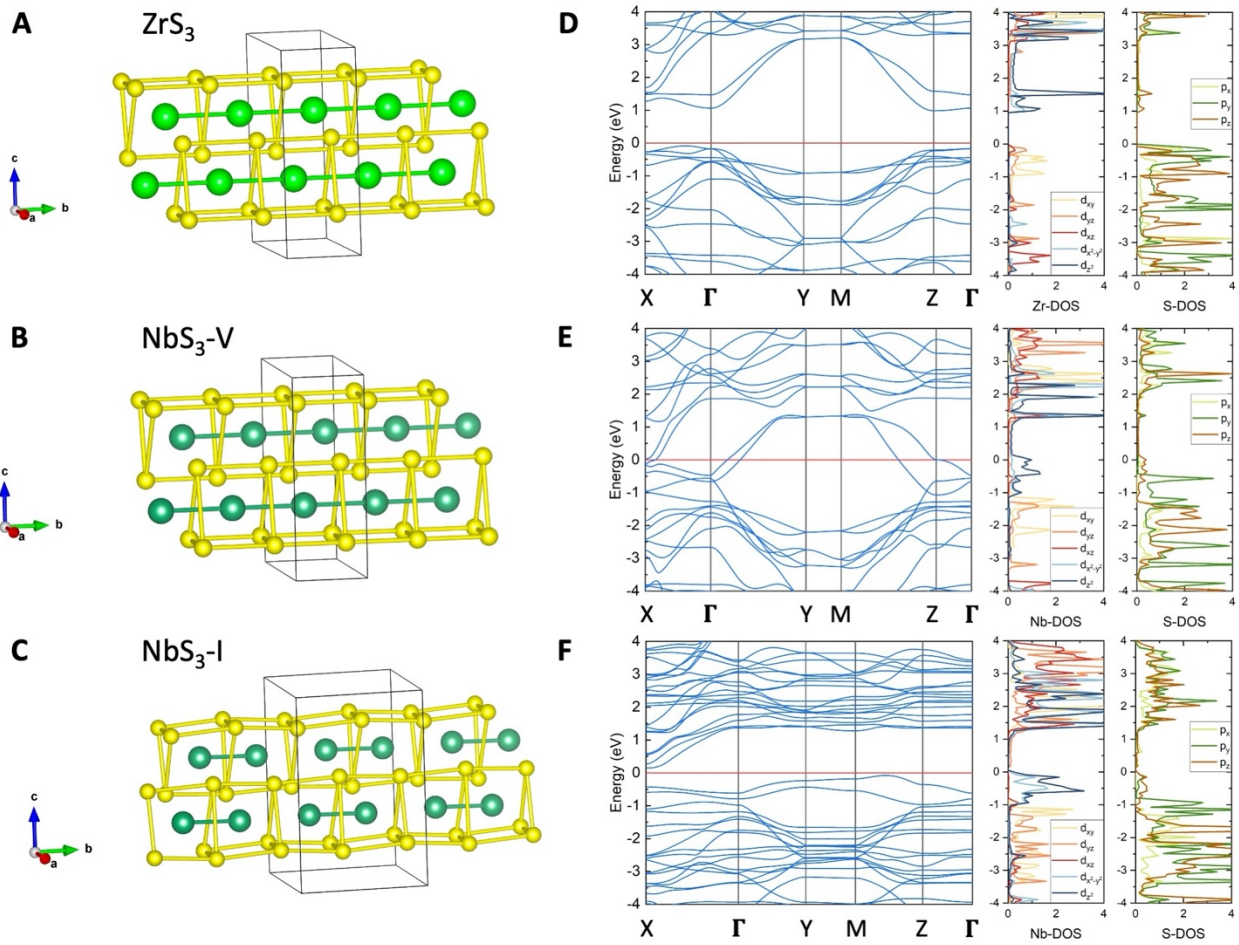


Figure S29. Lattice structures (A-C) and electronic band structures and projected density of states (pDOS) (D-F) of ZrS₃, NbS₃-V, and NbS₃-I, respectively. The high symmetry points in D-F are labeled as $X=[0.5, 0, 0]$, $\Gamma=[0, 0, 0]$, $Y=[0, 0.5, 0]$, $M=[0, 0.5, 0.5]$, $Z=[0, 0, 0.5]$ in the monoclinic reciprocal lattice. The pDOS are projected to Zr/Nb-d and S-p orbitals, respectively.

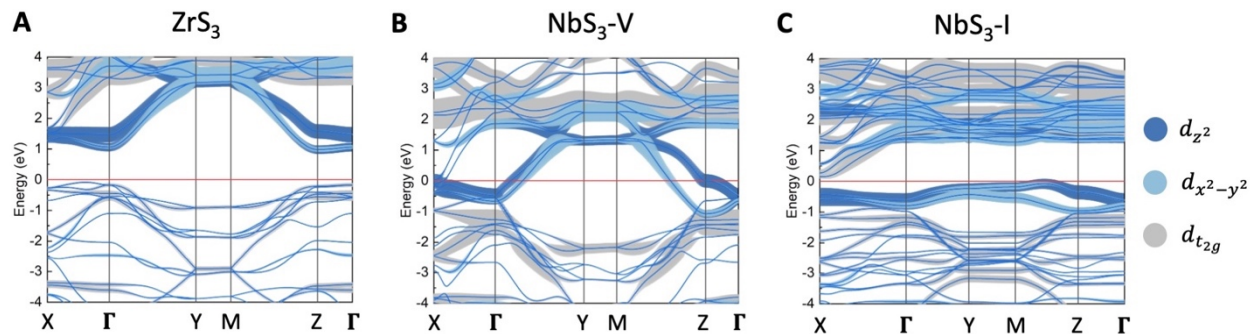


Figure S30. Electronic band structures projected to d_{eg} (d_{z^2} and $d_{x^2-y^2}$) and d_{t2g} orbital contributions of Zr/Nb atoms of (A) ZrS_3 , (B) $\text{NbS}_3\text{-V}$, and (C) $\text{NbS}_3\text{-I}$, respectively. B and C illustrates the opening of the gap from the lowering in energy of the bonding d_{z^2} and $d_{x^2-y^2}$ states in the dimerized $\text{NbS}_3\text{-I}$ phase. This stabilization of the bonding states arises due to the more pronounced orbital overlap as a consequence of the in-chain dimerization.

A.2 Supplementary Figures and Tables for Chapter 3

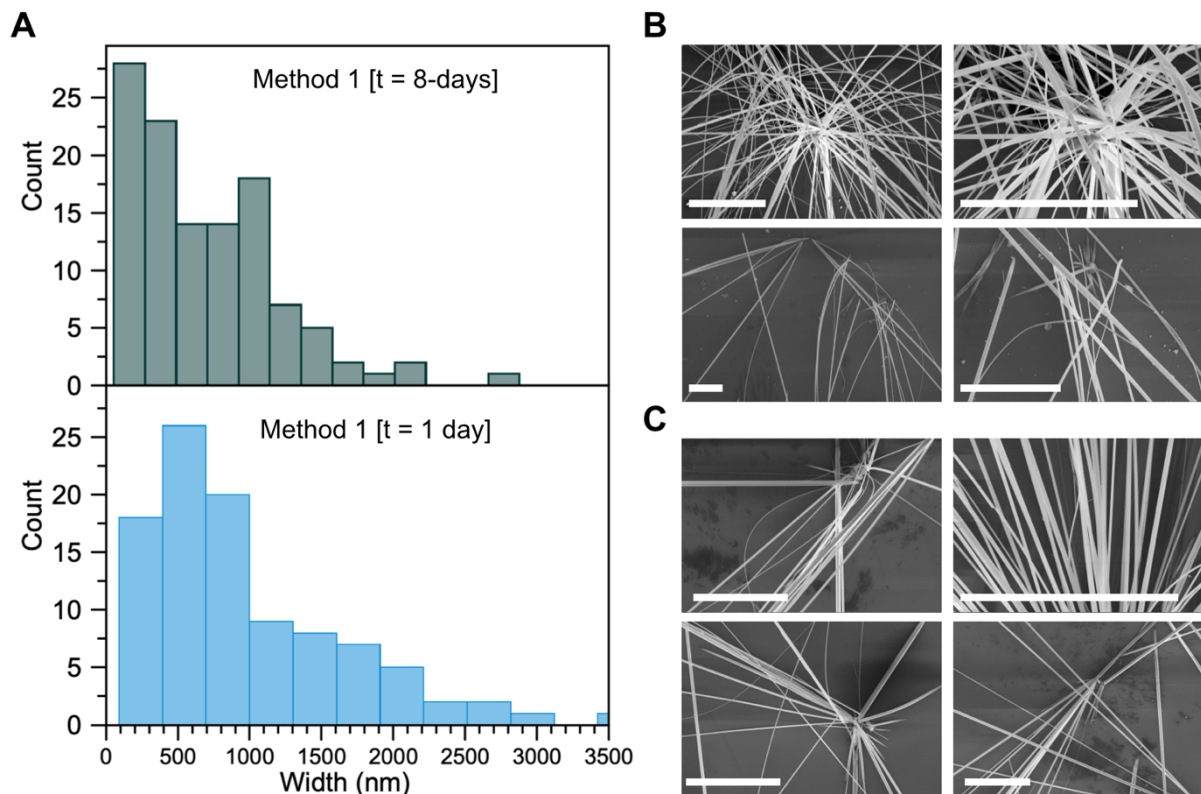


Figure S1. Width distribution and morphology of MoI_3 crystals. (A) Histograms of crystal widths from 8-day and 1-day reactions using elemental Mo and I precursors. (B) Representative SEM images of MoI_3 crystals as grown on Si/SiO₂ substrates from an 8-day reaction and (C) a 1-day reaction. Scale bars, 40 μm (B). Scale bars, 50 μm (C).

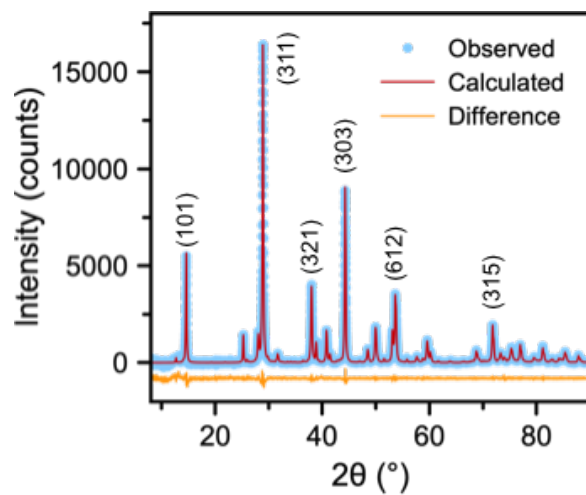


Figure S2. Le Bail refinement of the PXRD pattern of bulk MoI_3 crystals. Powder X-ray diffraction pattern fitted using the Pmmn structural model. Fit quality parameters: $R_{wp} = 3.36$, $R_{exp} = 2.76$, $\chi^2 = 1.48$ and goodness-of-fit = 1.22.

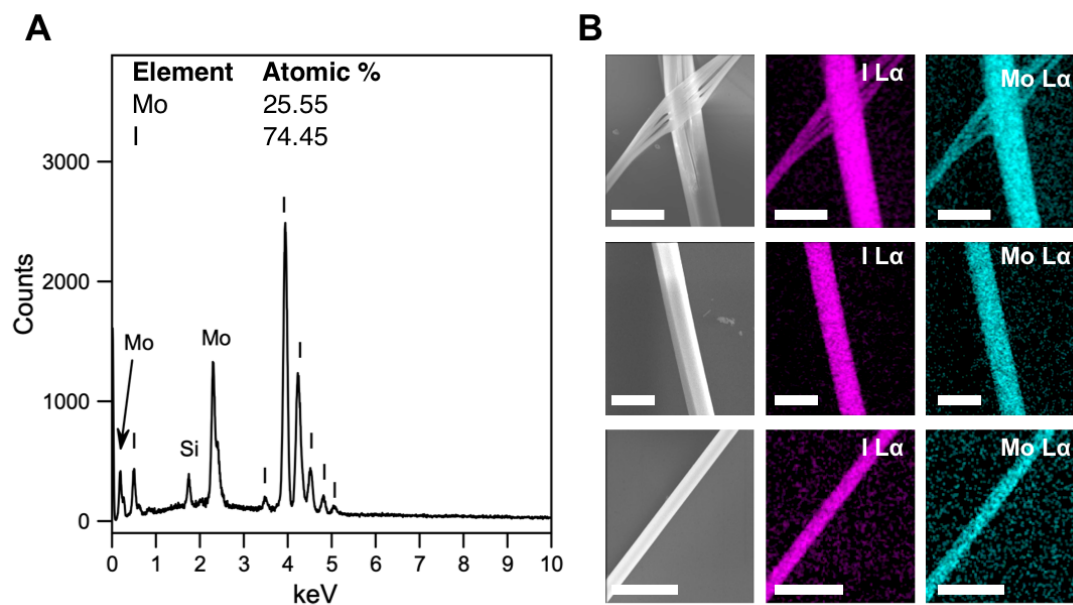


Figure S3. EDS analysis of bulk MoI_3 crystals. (A) Representative EDS spectrum of MoI_3 crystals obtained from bulk growth, showing the Mo and I atomic composition. (B) Corresponding SEM images and EDS elemental maps showing the uniform distribution of Mo and I. Scale bars, 5 μm .

Table S1. Atomic composition of bulk MoI_3 crystals shown in Figure S3. Atomic percentages of Mo and I determined by SEM-EDS.

Crystal	Atomic %	
	Mo	I
1	25.55	74.45
2	24.15	75.85
3	24.30	75.70
4	25.50	74.50

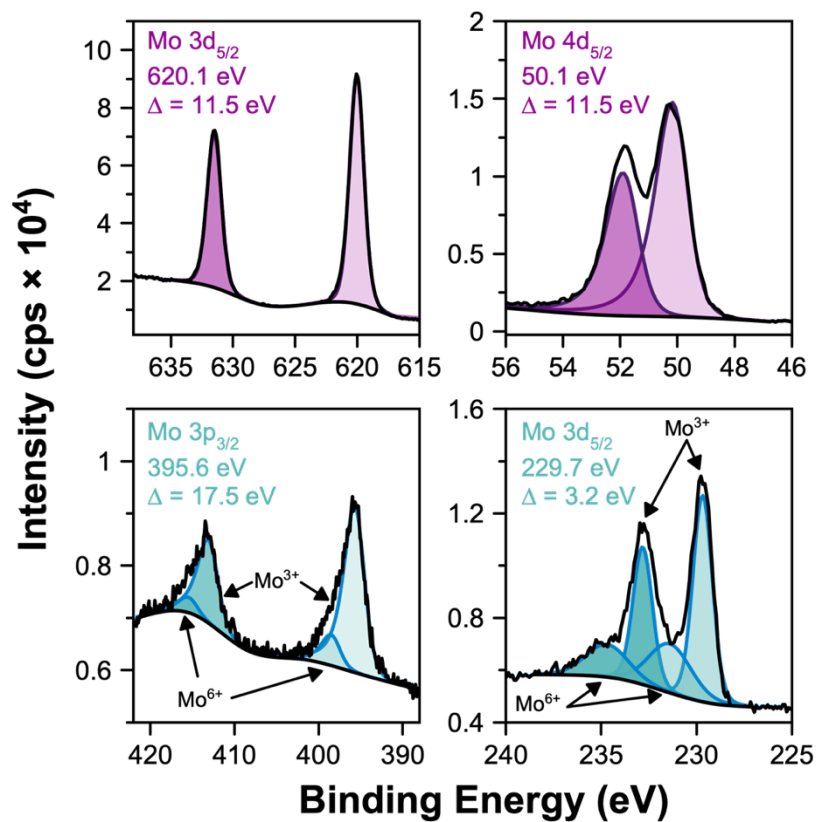


Figure S4. XPS analysis of bulk MoI_3 . XPS spectra of the I 3d, I 4d, Mo 3p, and Mo 3d regions with their corresponding peak-fitting profiles.

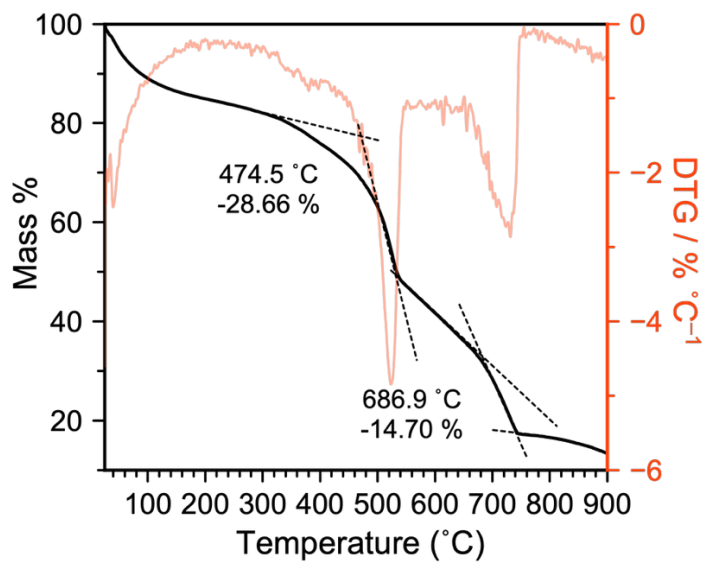


Figure S5. Thermogravimetric analysis of bulk MoI_3 crystals. TGA (black) and derivative thermogravimetric (DTG, orange) curves showing two major mass-loss steps at 474.5 $^{\circ}\text{C}$ and 686.9 $^{\circ}\text{C}$.

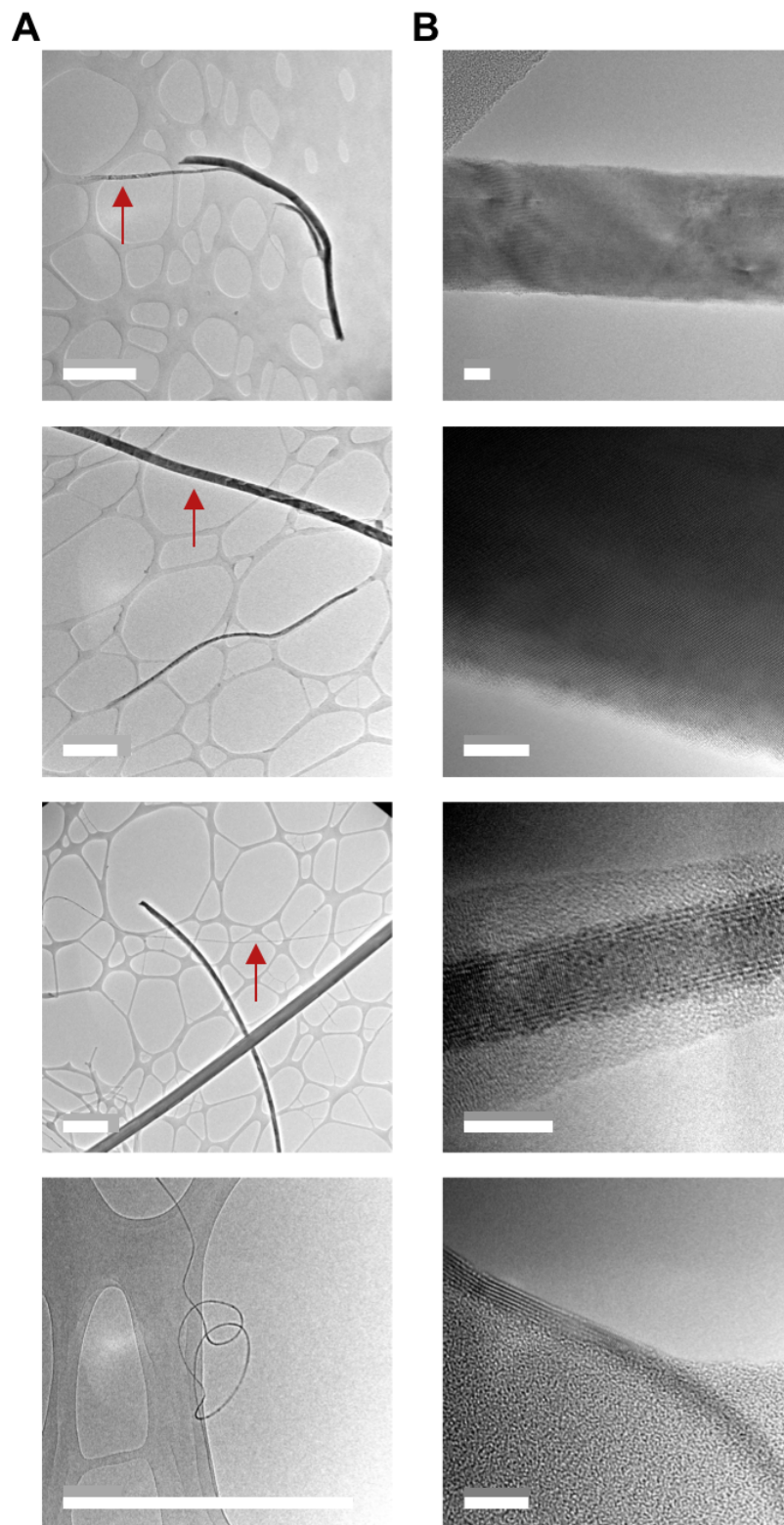


Figure S6. HRTEM images of MoI_3 nanowires. (A) Low-magnification HRTEM images. Scale bars, 800 nm. (B) High-magnification HRTEM images of the nanowires indicated by the red arrows in (A). Scale bars, 10 nm.

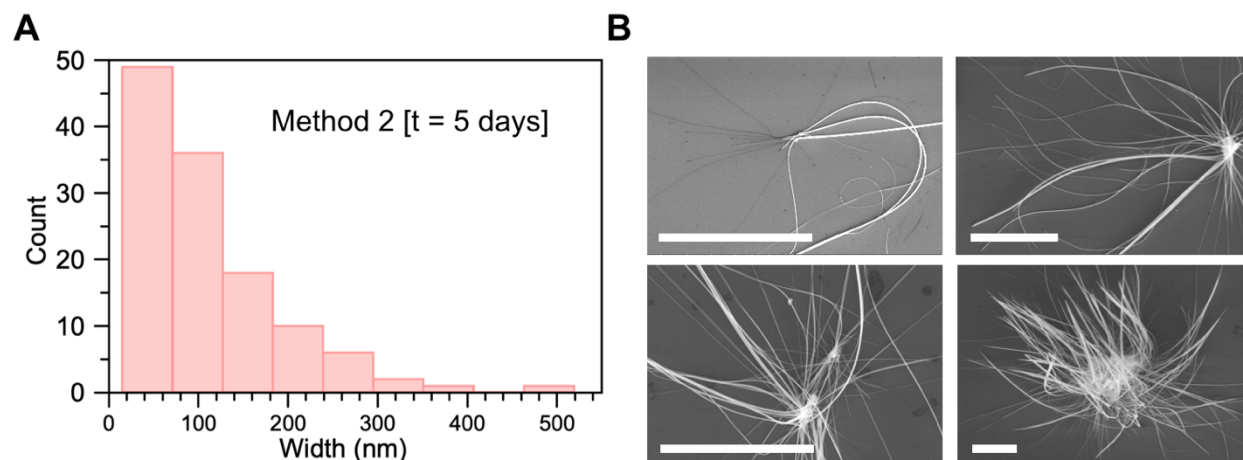


Figure S7. Width distribution and morphology of MoI_3 nanowires grown from bulk MoI_3 precursors. (A) Histogram of nanowire widths obtained from a 5-day reaction using bulk MoI_3 as precursors. (B) Representative SEM images of MoI_3 nanowires as grown on Si/SiO_2 substrates. Scale bars, 30 μm .

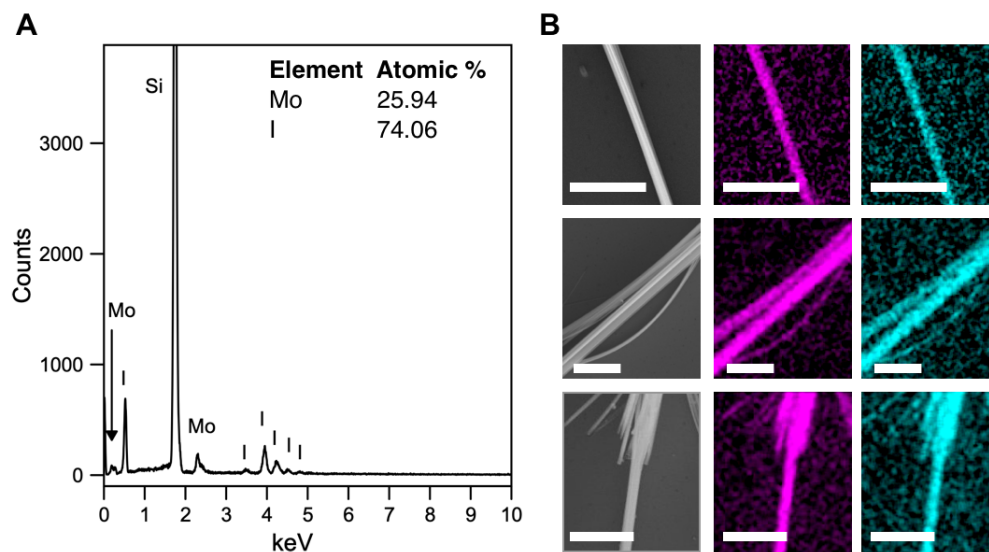


Figure S8. EDS analysis of MoI_3 nanowires. (A) Representative EDS spectrum of MoI_3 nanowires, showing the Mo and I atomic compositions. (B) Corresponding SEM images and EDS elemental maps showing the uniform distribution of Mo and I. Scale bars, 3 μm .

Table S2. Atomic composition of MoI_3 nanowires shown in Figure S8. Atomic percentages of Mo and I determined by SEM-EDS.

Crystal	Atomic %	
	Mo	I
1	25.95	74.06
2	25.07	74.93
3	24.70	75.28
4	25.65	74.35

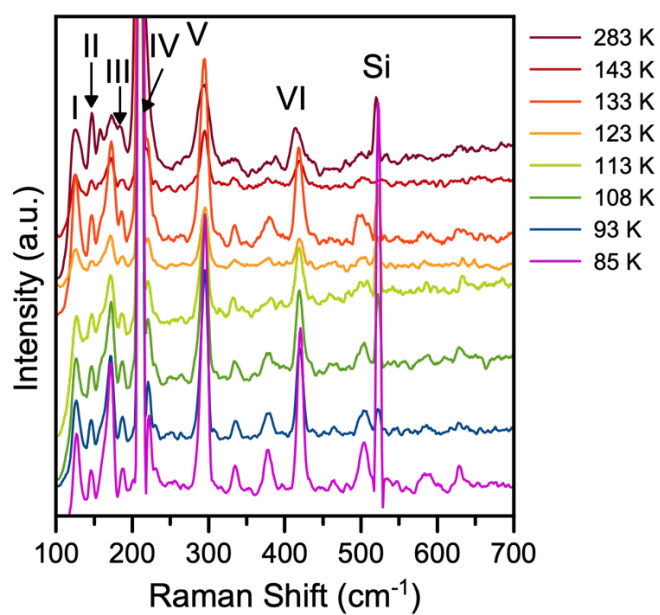


Figure S9. Temperature-dependent Raman characterization of a representative bulk MoI_3 crystal. Raman spectra of a MoI_3 crystal grown using Method 1.

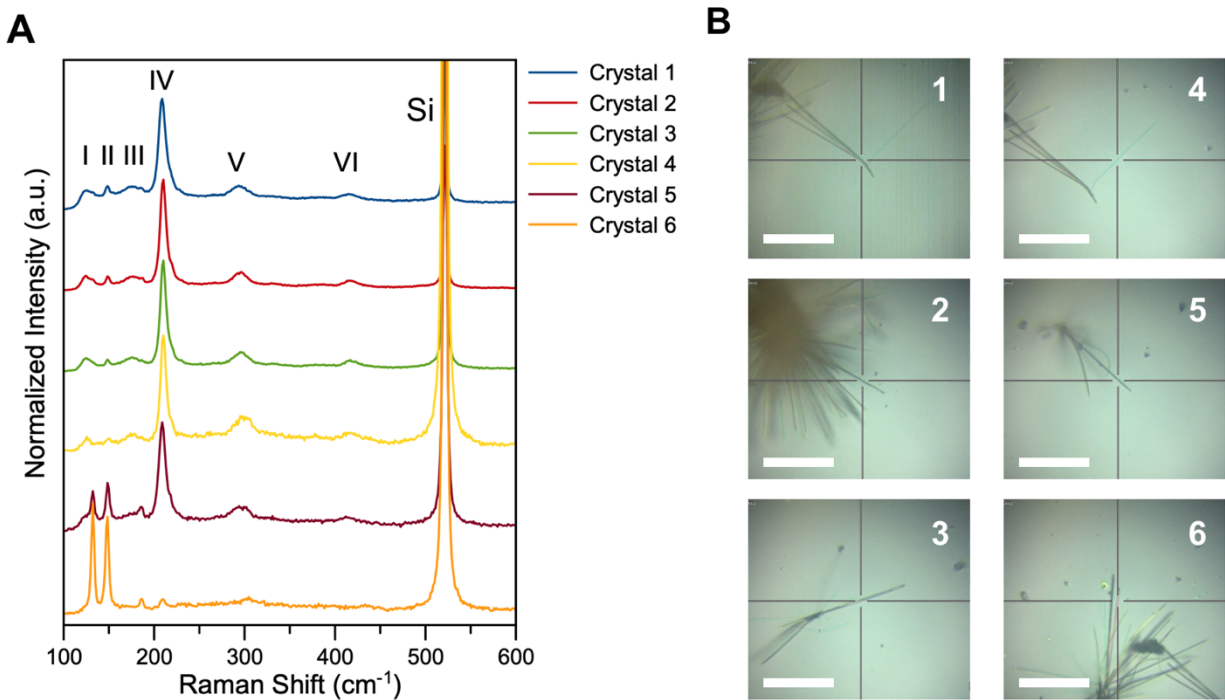


Figure S10. Raman characterization of MoI₃ nanowires. (A) Normalized Raman spectra of six representative MoI₃ nanowires grown using Method 2. (B) Corresponding optical microscopy images of the nanowires labeled 1-6 in (A). Scale bars, 40 μ m.

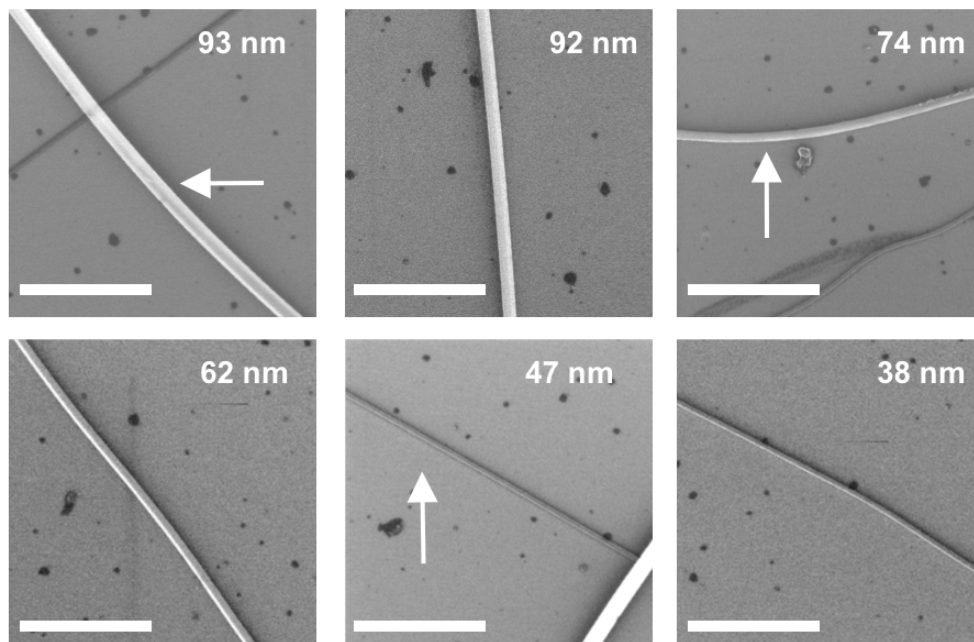


Figure S11. SEM images of MoI_3 nanowires used for optical scattering measurements. SEM images of the nanowires analyzed in Figure 4A–D, with the indicated heights measured by AFM. Scale bars, 1 μm .

A.3 Supplementary Figures and Tables for Chapter 4

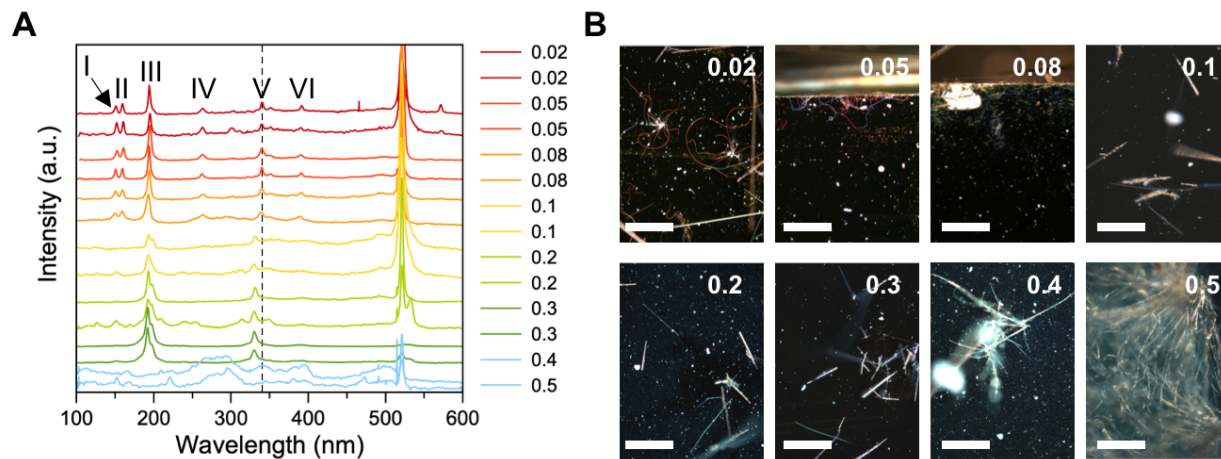


Figure S1. Influence of Ta alloying on the nanocrystal structure and morphology of vapor-phase grown NbS₃-I. (A) Representative Raman spectra of Ta-alloyed nanocrystals of NbS₃-I at various Ta loading conditions (as loaded x in Nb_{1-x}Ta_xS₃ from $x = 0.02$ to 0.5). (B) Representative dark field optical micrographs of the nanocrystals grown on Si/SiO₂ substrates at various Ta loading. Scale bar, 245 μm.

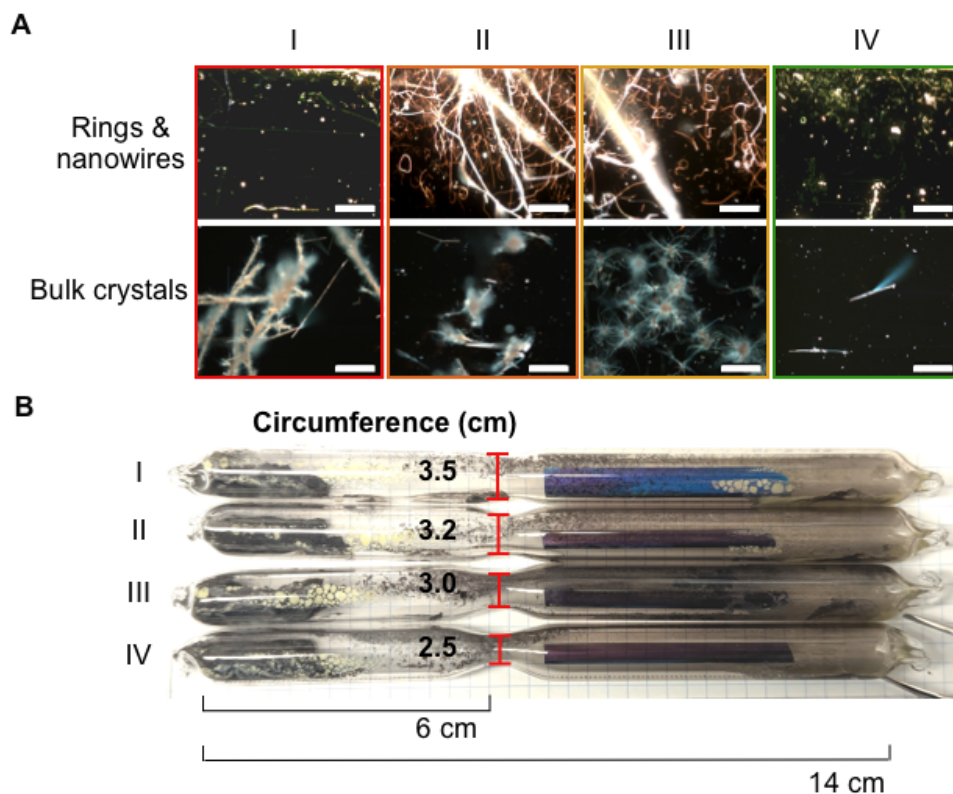


Figure S2. Effect of necking circumference on the growth of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3-\delta$ nanostructures. (A) Representative dark-field optical micrographs of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3-\delta$ nanostructures (top row: nanorings and nanowires) and bulk structures (bottom row) as-grown on Si/SiO_2 substrates from the corresponding ampoules shown in B. Scale bars, 50 μm (top row) and 245 μm (bottom row). (B) Image of four reaction ampoules (I–IV) with progressively narrowed outer circumferences (3.5, 3.2, 3.0, and 2.5 cm) of the necked region while all other growth parameters were held constant. Necking the ampoule between 3.0–3.2 cm (ampoule II and III) targeted higher density of nanostructure growth on the substrates.

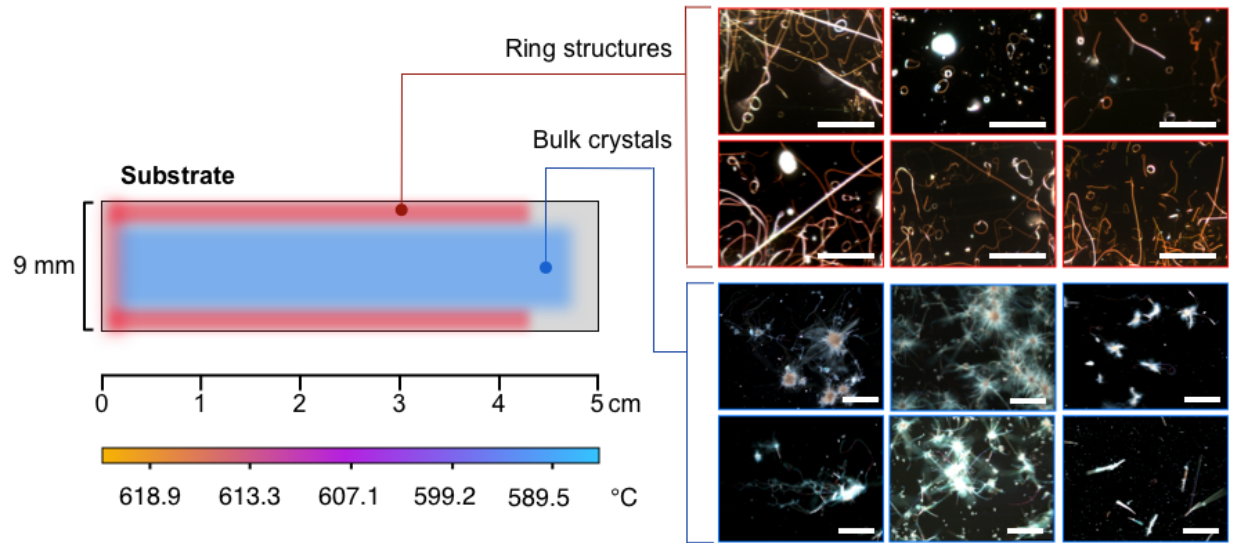


Figure S3. Substrate mapping of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring structures. Graphical illustration of the substrate, with red regions marking where nanoring and nanowire structures are concentrated and the blue region marking the area where bulk crystals dominate. On the right are the representative dark-field macrographs. Nanoring structures scale bars, 50 μm. Bulk crystals scale bars, 245 μm. Nanowires and nanoring structures are found at higher concentrations ~1 mm from the edges of the substrate. Below the substrate are the calibrated temperatures at each substrate region, measured using an external probe, during the 700-600 °C temperature gradient.

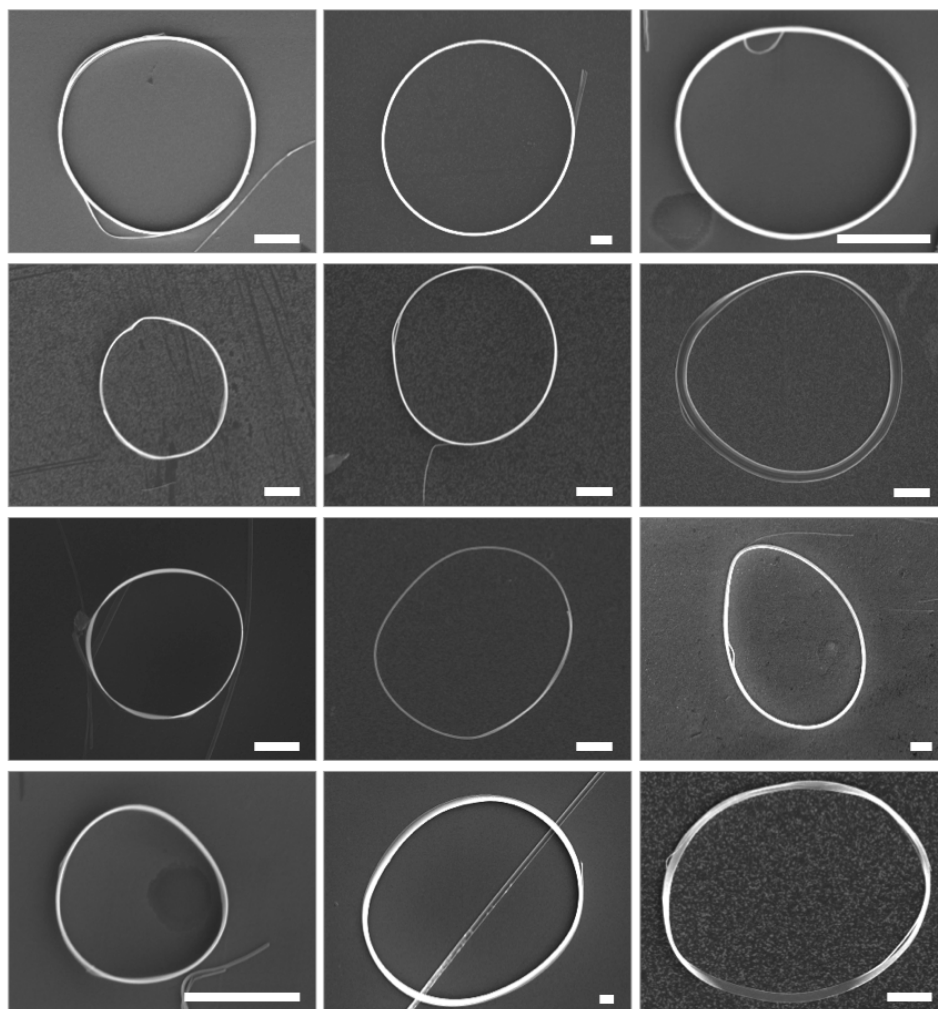


Figure S4. Representative SEM images of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring structures. SEM images of the as-grown nanoring structures on Si/SiO₂. Scale bars, 1 μm .

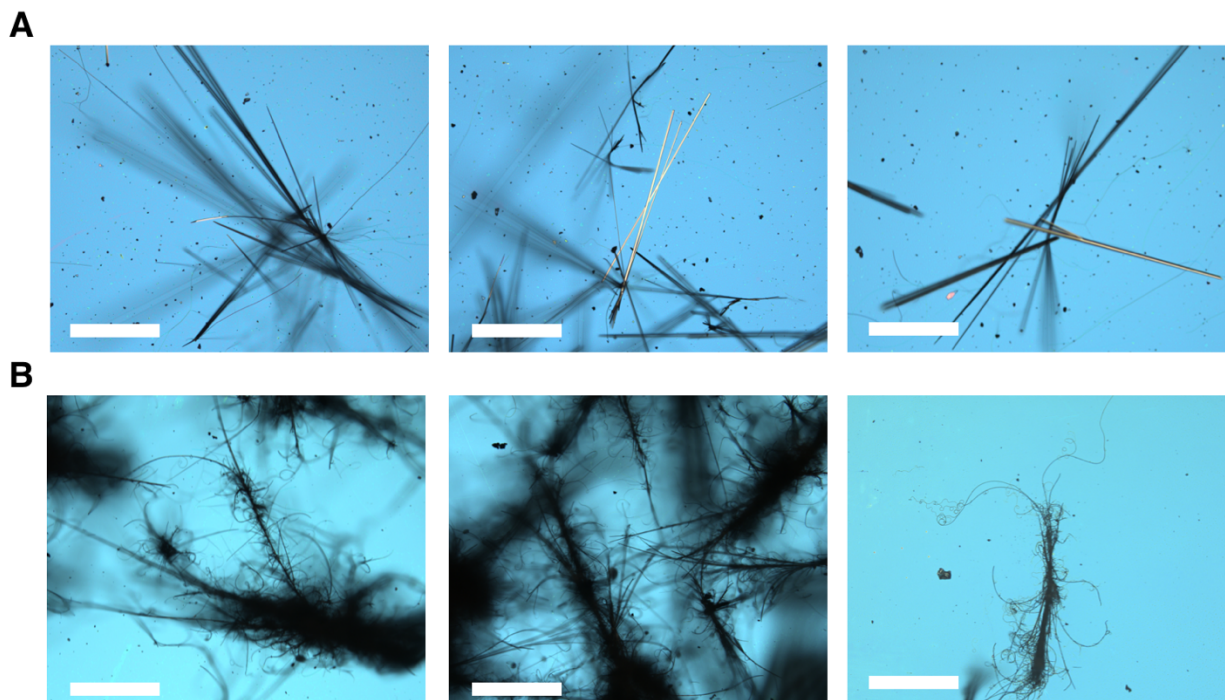


Figure S5. Bulk $\text{NbS}_3\text{-I}$ and $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ crystals grown on Si/SiO_2 substrates. (A) $\text{NbS}_3\text{-I}$ forms straight, uniform, needle-like crystals radiating from a nucleation spot. Scale bars, 245 μm . (B) $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ exhibits similar needle-like structures but with nanowires that splinter away from the main structure. Scale bars, 245 μm .

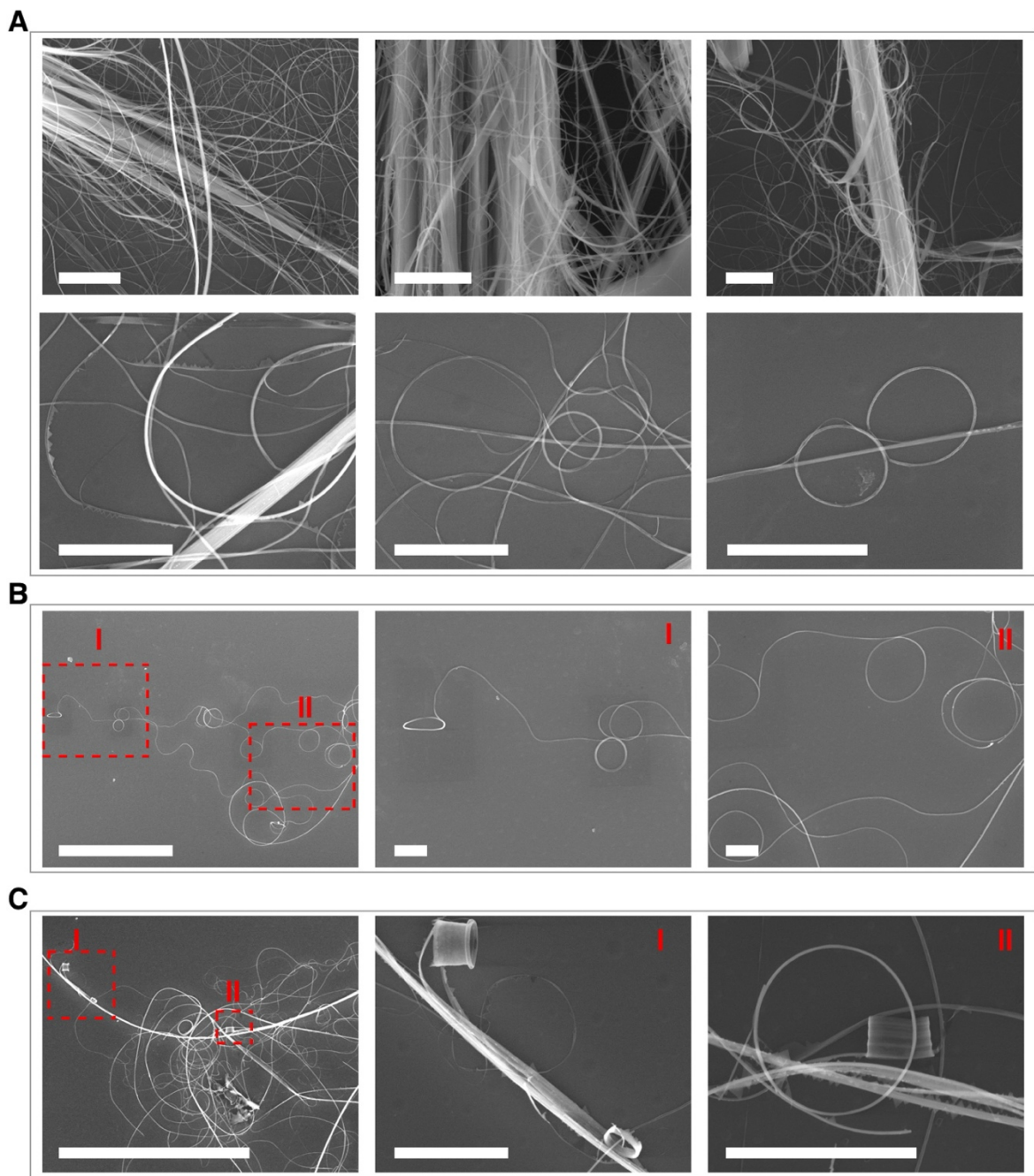


Figure S6. Bulk $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ crystals grown on Si/SiO_2 substrates. (A) SEM images showing different regions of the bulk crystal structures. Scale bars, 5 μm . (B,C) SEM images highlighting two regions showing the ends of the bulk structures forming ring-like morphologies. The boxed regions labeled I and II are enlarged and shown to the right. Scale bars, 50 μm (left) and 5 μm (panels I and II).

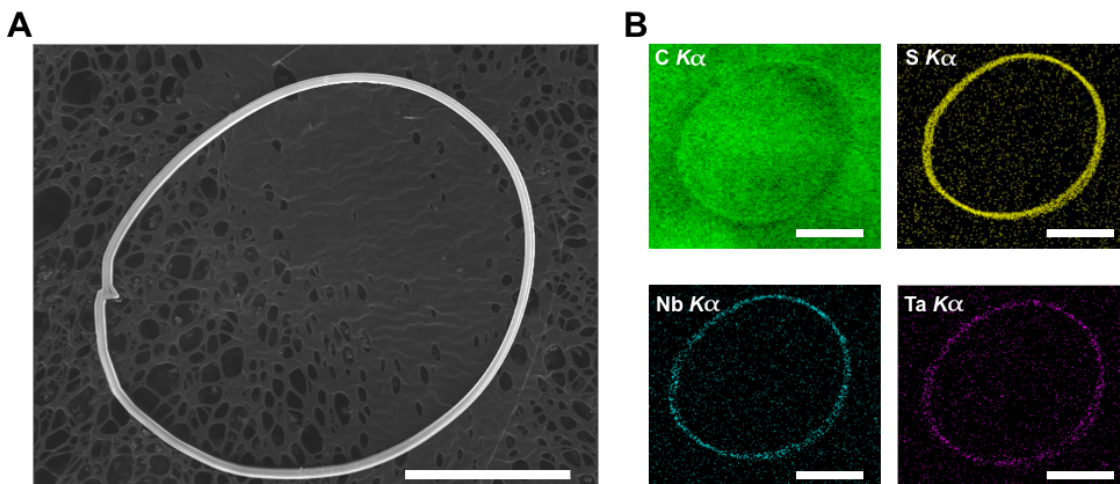


Figure S7. Representative SEM image and SEM-EDS elemental maps of an $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3\text{-}\delta$ nanoring. (A) SEM image of a transferred nanoring onto a lacey carbon TEM grid and (B) its corresponding SEM-EDS elemental maps. Scale bars, 5 μm .

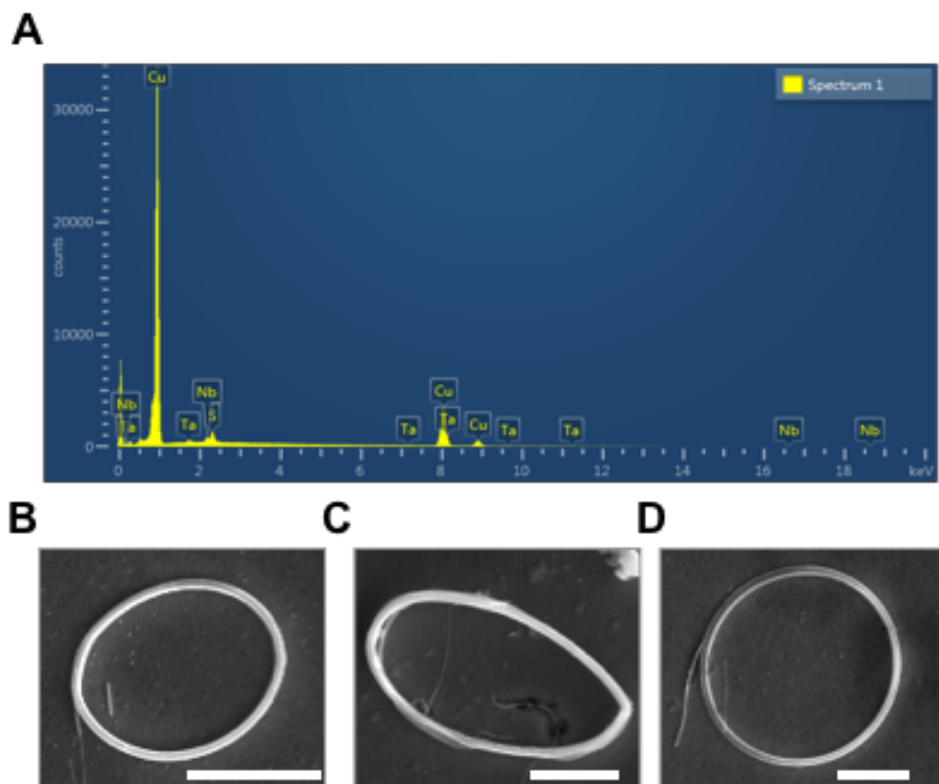


Figure S8. SEM-EDS spectrum and SEM images of $Nb_{1-x}Ta_xS_{3-\delta}$ nanoring structures. (A) Representative SEM-EDS spectrum showing the elemental composition of $Nb_{1-x}Ta_xS_{3-\delta}$ nanorings. (B-D) SEM images of transferred nanorings onto a copper substrate for SEM-EDS analysis. Scale bars, 2 μm .

Table S1. Atomic composition of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring in Figure S8B. Atomic percentages of S, Nb, and Ta of the nanorings shown in Figure S8B as derived from the SEM-EDS analysis. Eight measurements were done at different spots around the nanoring structure.

Spot	S K	Nb L	Ta L
1	71.88	22.94	5.19
2	70.48	24.55	4.98
3	71.76	23.72	4.53
4	69.78	24.94	5.28
5	72.21	23.1	4.69
6	71.97	23.95	4.08
7	70.51	24.25	5.24
8	72.72	23.18	4.1
Avg.	71.41	23.83	4.76

Table S2. Atomic composition of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring in Figure S8C. Atomic percentages of S, Nb, and Ta of the nanorings shown in Figure S8C as derived from the SEM-EDS analysis. Eight measurements were done at different spots around the nanoring structure.

Spot	S K	Nb L	Ta L
1	71.27	23.64	5.09
2	71.17	23.07	5.76
3	71.33	22.72	5.95
4	68.7	25.08	6.22
5	72.71	22.06	5.23
6	72.32	21.86	5.83
7	71.55	22.87	5.57
8	72.06	22.70	5.24
Avg.	71.39	23.00	5.61

Table S3. Atomic composition of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring in Figure S8D. Atomic percentages of S, Nb, and Ta of the nanorings shown in Figure S8D as derived from the SEM-EDS analysis. Eight measurements were done at different spots around the nanoring structure.

Spot	S K	Nb L	Ta L
1	67.73	24.49	7.78
2	70.74	23.79	5.47
3	68.61	26.05	5.34
4	66.59	27.49	5.92
5	69.67	24.93	5.4
6	71.03	23.91	5.06
7	68.18	27.46	4.36
8	70.68	22.09	7.23
Avg.	69.16	25.03	5.82

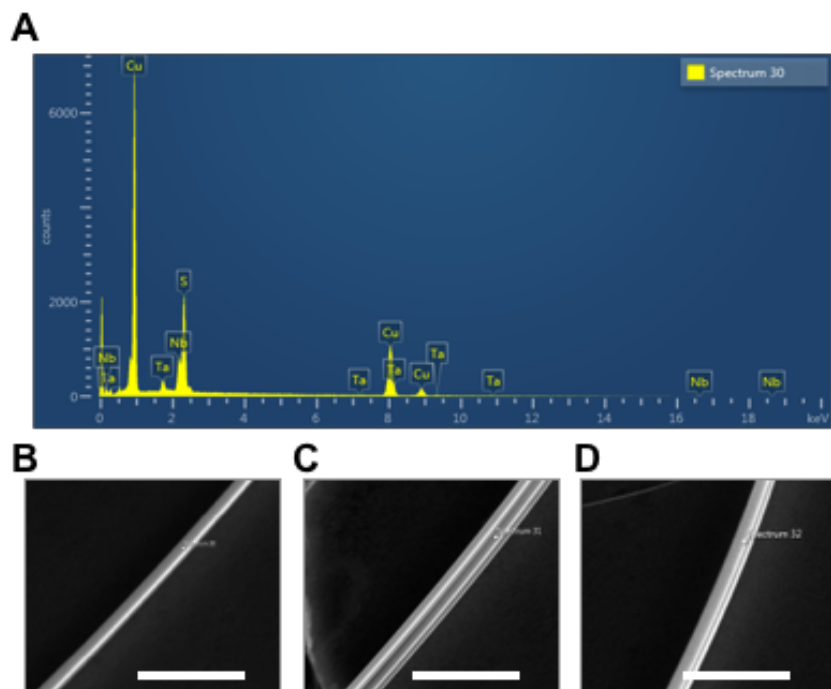


Figure S9. SEM-EDS spectrum and SEM images of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanowires. (A) Representative SEM-EDS spectrum showing the elemental composition of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanowires. (B–D) SEM images of transferred nanowires onto a copper substrate for SEM-EDS analysis. Scale bar, 2 μm .

Table S4. Atomic composition of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanowires in Figure S9B-D. Atomic percentages of S, Nb, and Ta of the nanowires shown in Figure S9B-D as derived from the SEM-EDS analysis.

Sample	S K	Nb L	Ta L
B	73.19	22.02	4.79
C	72.6	22.66	4.73
D	73.04	22.58	4.39
Avg.	72.94	22.42	4.64

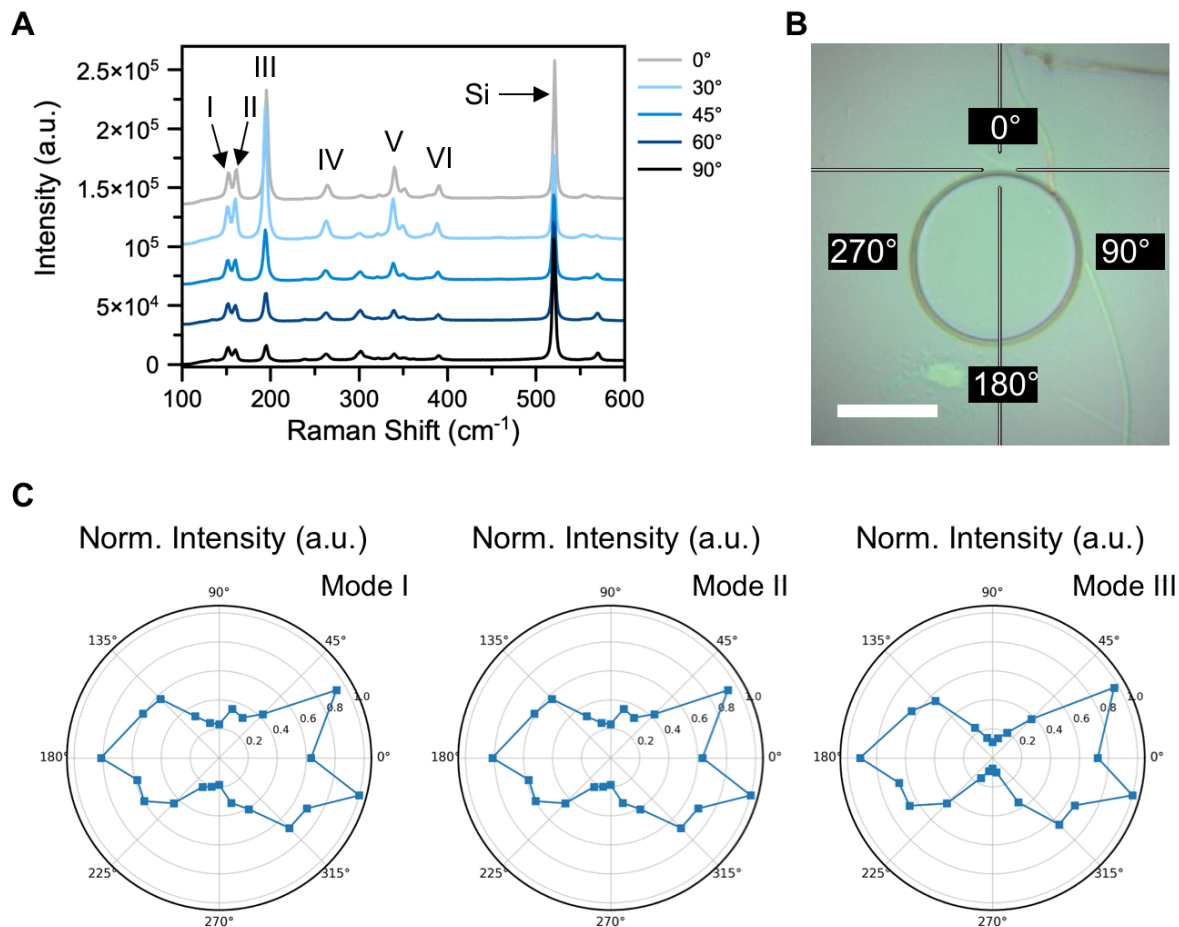


Figure S10. Polarization-resolved Raman spectroscopy of representative $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring. (A) Raman spectra collected at different positions around a single nanoring where, 0° corresponds to the ring segment parallel to the polarization direction of the 532 nm laser and 90° corresponds to the perpendicular orientation. (B). Image of corresponding $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanoring indicating the angular measurement positions. Scale bar, 10 μm . (C) Polar plots of the normalized Raman intensities for modes I, II, and III demonstrating the polarization-dependent Raman response of the nanoring.

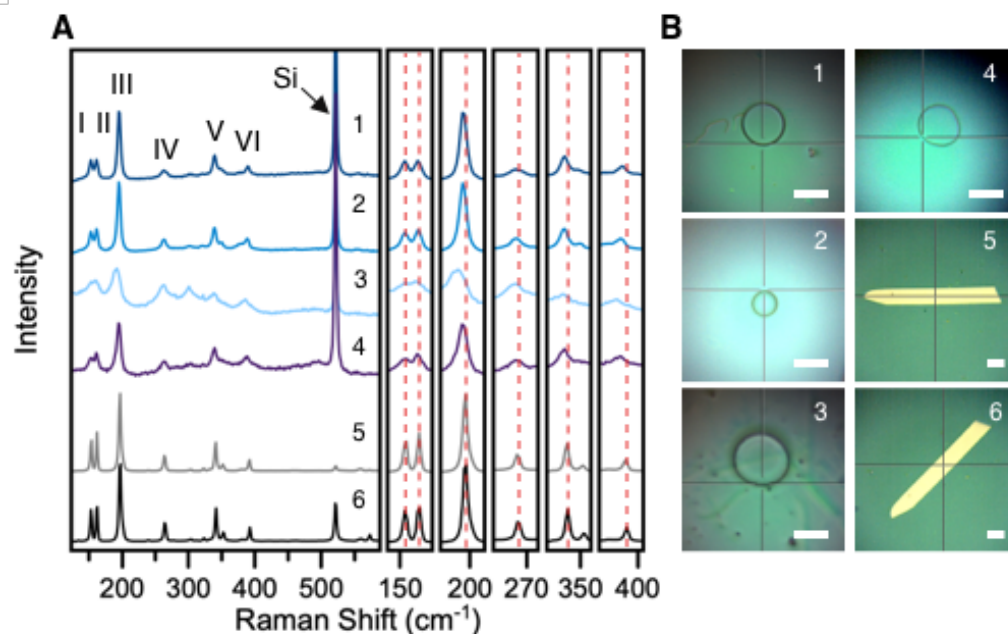


Figure S11. Comparison of Raman spectra of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings to $\text{NbS}_3\text{-I}$ crystal. (A) Raman spectra of six samples shown in (B). Spectra 1–4 correspond to different $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings, while spectra 5–6 correspond to $\text{NbS}_3\text{-I}$. (B) Optical images of four different nanorings (1–4) as-grown on Si/SiO₂ substrates and $\text{NbS}_3\text{-I}$ (5–6) matching the orientation used for the Raman measurements compared with the nanoring structures. Scale bars, 10 μm.

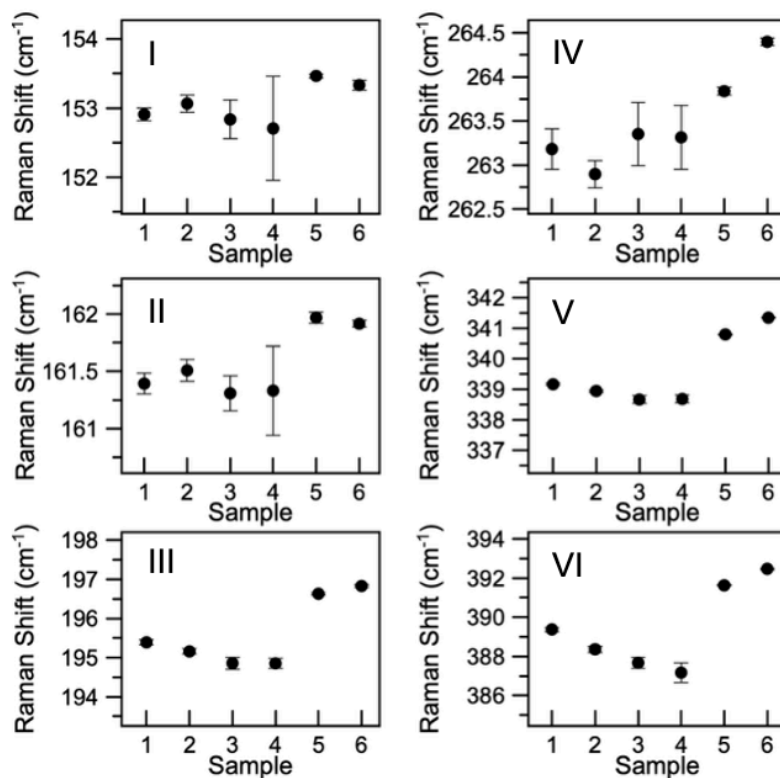


Figure S12. Vibrational mode shifts in the Raman spectra from Figure S11. Raman shifts of six vibrational modes (I–VI) are plotted for each sample (1–6) corresponding to those shown in Figure S11. Raman peaks were fitted using Lorentzian functions. Samples 1–4 ($\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings) red shift compared to samples 5–6 (NbS_3 -I).

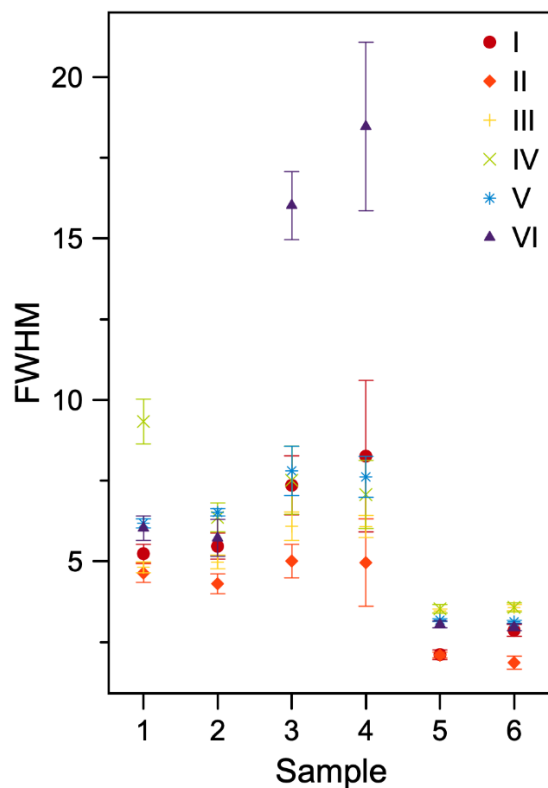


Figure S13. Full width at half maximum (FWHM) of Raman modes I–VI from Figure S11. FWHM values are plotted for each vibrational mode (I–VI) across the six samples shown in Figure S11. Raman peaks were fitted using Lorentzian functions. Samples 1–4 ($\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings) exhibit broader modes compared to samples 5–6 (NbS_3 -I).

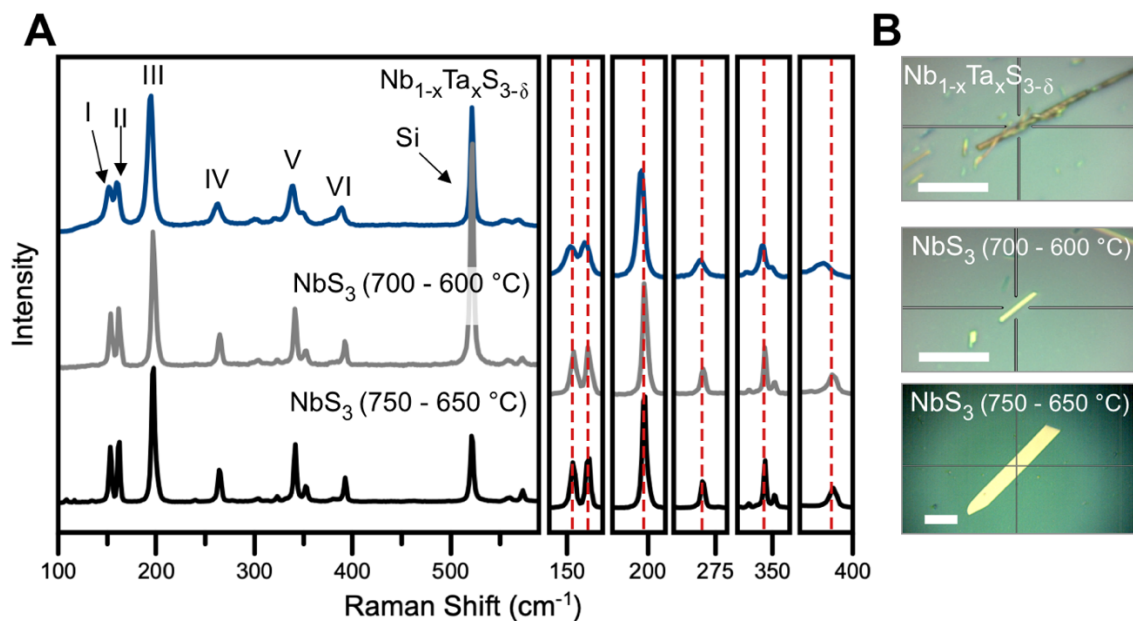


Figure S14. Raman spectra of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ bulk crystals compared with $\text{NbS}_3\text{-I}$. (A) Raman spectra of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ bulk crystals (blue) and $\text{NbS}_3\text{-I}$ crystals grown at 700-600 °C (gray) and 750-650 °C (black). Characteristic modes (I–VI) are highlighted for comparison. (B) Optical images of the corresponding samples from panel (A). Scale bars, 10 μm . NbS_3 grown at both temperature ranges (700-600 °C and 750-650 °C) yields Raman peaks consistent with $\text{NbS}_3\text{-I}$. $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ bulk crystals show a red shift in the Raman modes, similar to that observed for the nanoring structures.

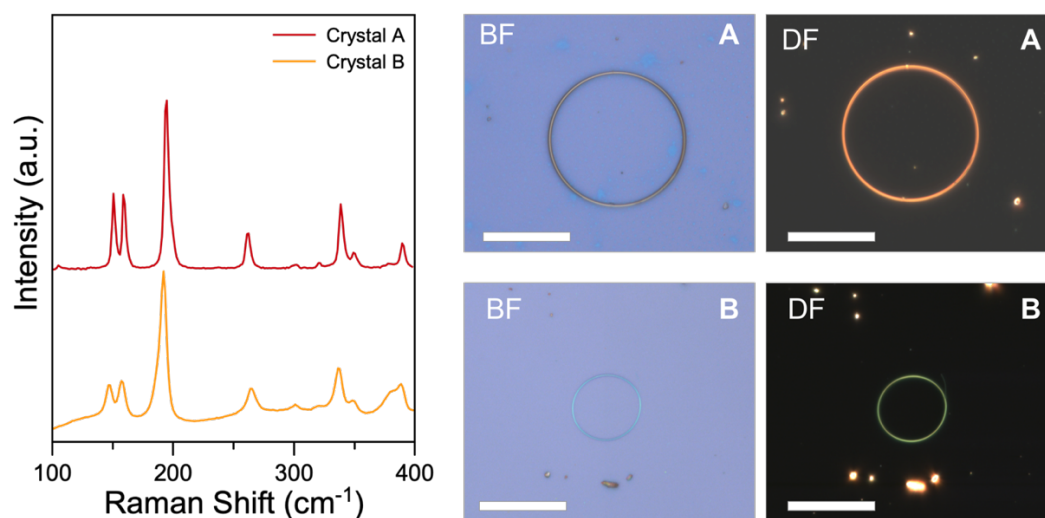


Figure S15. Raman spectra of representative $\text{NbS}_3\text{-I}$ rings. Raman spectra collected from two individual rings (Crystal A and Crystal B) are shown alongside the corresponding bright-field and dark-field optical images. Scale bars, 25 μm .

Table S5. Atomic composition of NbS₃-I rings in Figure S15. Atomic percentages of S and Nb of the rings shown in **Figure S15** as derived from the SEM-EDS analysis. Several measurements were done at different spots around the rings Crystal A and Crystal B.

	Atomic %	
	S K	Nb L
Ring A	72.74	27.26
	72.53	27.47
	73.44	26.56
	74.3	25.7
	72.72	27.28
Ring B	67.98	32.02
	75.48	24.52
	77.14	22.86
	64.49	35.51
	75.52	24.48
Avg.	72.63	27.37

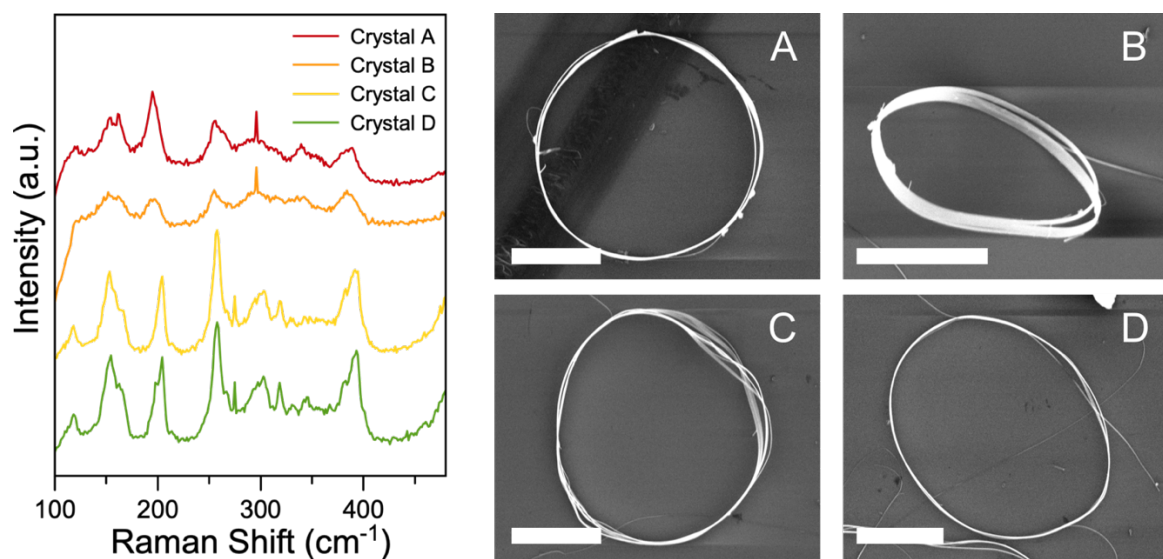


Figure S16. Raman spectra of representative NbS₃-V rings. Raman spectra collected from four individual rings (Crystal A, B, C, and D) are shown alongside the corresponding SEM images. Scale bars, 10 μm.

Table S6. Atomic composition of NbS₃-V rings in Figure S16. Atomic percentages of S and Nb of the rings shown in Figure S16 as derived from the SEM-EDS analysis. Several measurements were done at different spots around the rings Crystal A, B, C, and D.

	Atomic %	
	S K	Nb L
A	67.27	32.73
	65.93	34.07
	70.27	29.73
	70.04	29.96
B	70.55	29.45
	66.49	33.51
	73.54	26.46
	70.13	29.87
C	68.78	31.22
	69.33	30.67
	69.78	30.22
	70.64	29.36
D	73.24	26.76
	64.6	35.4
	71.43	28.57
	70.12	29.88
Avg.	69.51	30.49

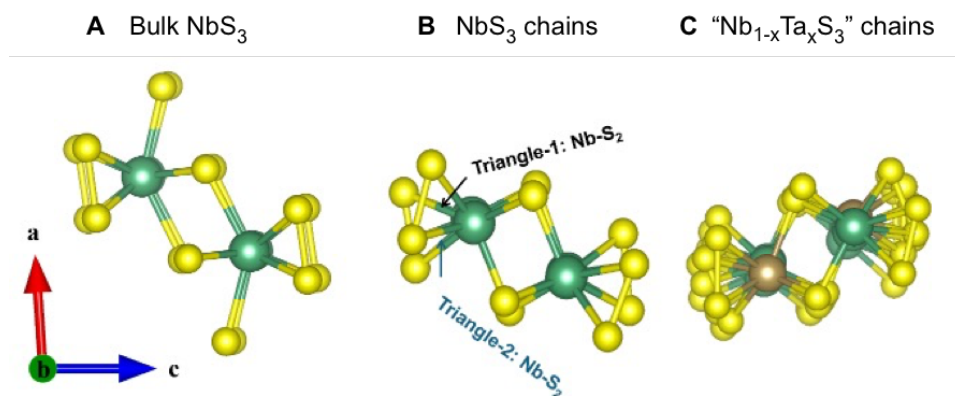


Figure S17. Computed structural distortion in pristine and Ta-alloyed NbS₃ chains. Side views along the [010] orientation for the (A) bulk, (B) pristine NbS₃-I chains, and (C) “Nb_{1-x}Ta_xS₃” chains with $x = 0.167$. The pristine NbS₃-I nanowire exhibits two triangular motifs (Triangle-1 and Triangle-2, where S₂ is bonded to Nb atoms). Triangle-1 and Triangle-2 are staggered along the nanowire direction. In addition to the distortion of triangular motifs, Ta doping introduces a misalignment of the Nb and Ta atoms along the nanowire direction.

Table S7. Independent elastic stiffness constants C_{ij} of NbS_3 -I and “ $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3$ ” chains.

Elastic stiffness constant C_{ij} (GPa)	NbS_3-I	“$\text{Nb}_{1-x}\text{Ta}_x\text{S}_3$”
C_{11}	0.45	-0.68
C_{12}	-0.04	-0.22
C_{13}	0.50	-0.49
C_{14}	-0.01	0.45
C_{15}	-0.14	-0.05
C_{16}	0.17	-0.08
C_{22}	15.17	6.47
C_{23}	-0.48	-0.53
C_{24}	1.18	0.80
C_{25}	0.12	0.05
C_{26}	0.08	-0.18
C_{33}	-0.93	-1.13
C_{34}	1.36	1.01
C_{35}	0.10	0.06
C_{36}	-0.03	-0.60
C_{44}	-0.51	-1.91
C_{45}	-0.30	-0.11
C_{46}	0.14	0.81
C_{55}	-0.08	-0.03
C_{56}	-0.04	-0.03
C_{66}	-0.17	-0.78

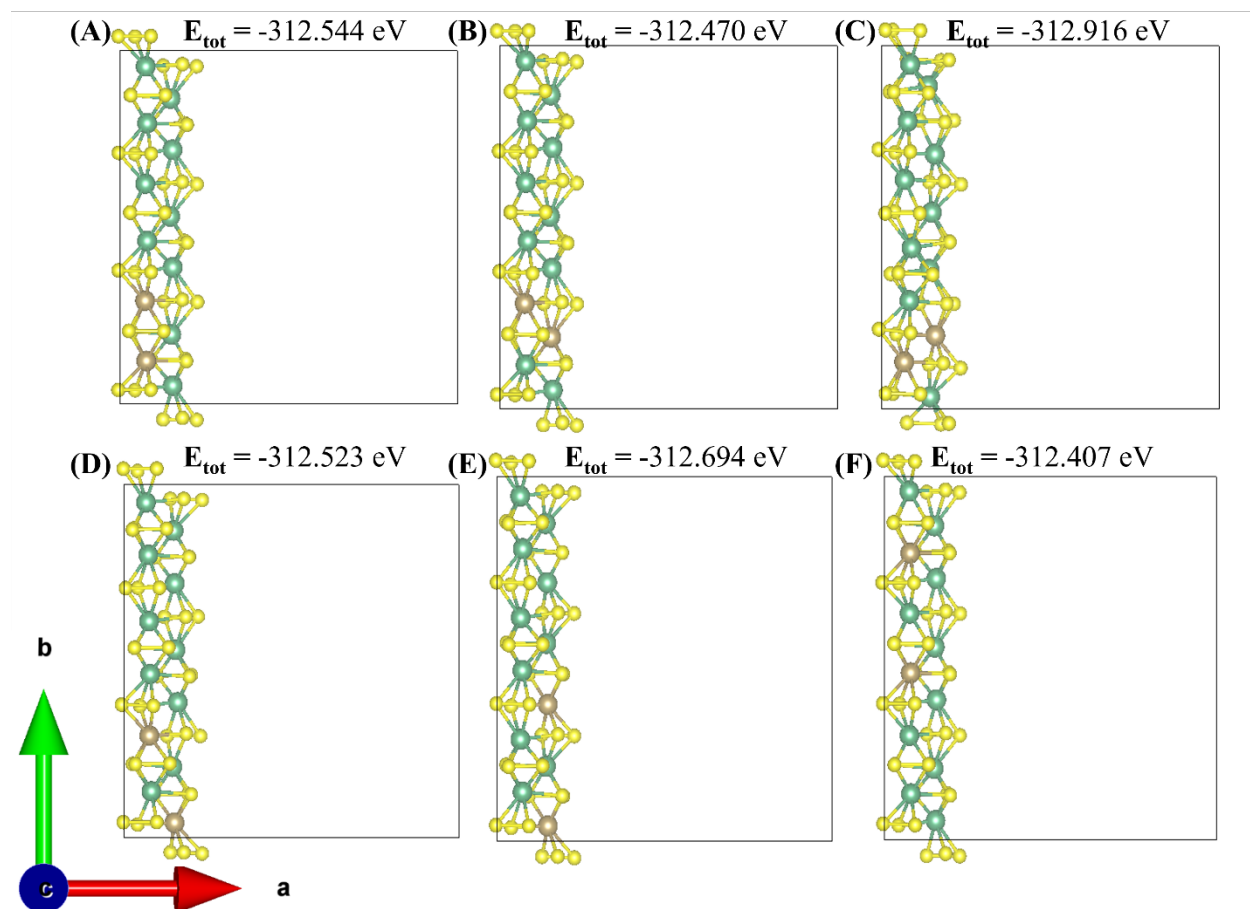


Figure S18. Different alloying configurations for 16.7% Ta-alloyed “ $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3$ ” chains. The total energy of “ $\text{Nb}_{1-x}\text{Ta}_x\text{S}_3$ ” chain is lowest for the configuration in (C).

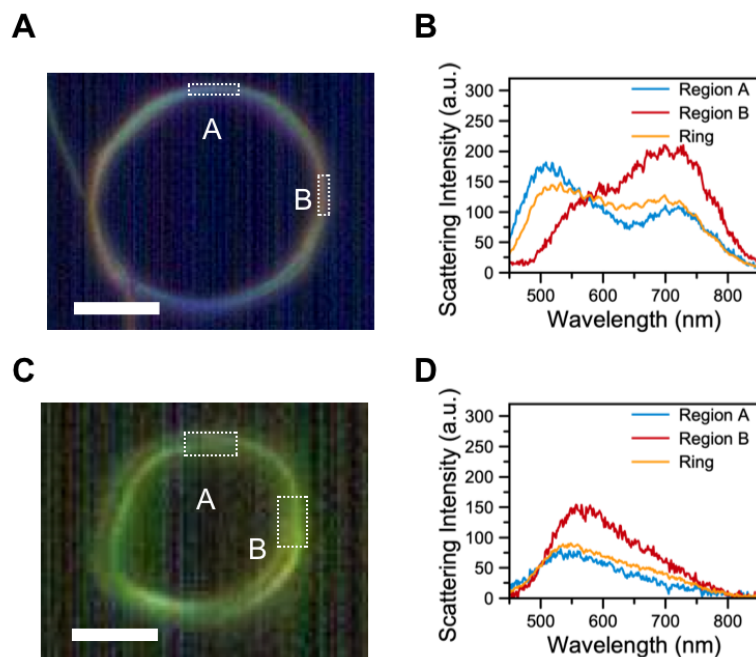


Figure S19. Polarization-dependent scattering spectra of $\text{Nb}_{1-x}\text{Ta}_x\text{S}_{3-\delta}$ nanorings. (A,C) Hyperspectral images of the nanorings from Figure 5A,F acquired with the polarizer (P) and analyzer (A) in the cross-polarization configuration. Regions A and B correspond to ring segments oriented parallel and perpendicular to the polarization direction, respectively. Scale bars, 6 μm (A) and 3 μm (C). (B,D) Scattering spectra from Regions A and B in (A,C).

Table S8. Dimensions of the nanoring structure from Figure 5A. Width and circumference values were obtained from ImageJ analysis of SEM image Figure 5C. Height values were determined from the maximum of the height profiles shown in Figure 5E. Reported averages represent measurements across distinct spots around the nanoring.

Spot	Width (nm)	Height (nm)	Inner Circumference (μm)	Outer Circumference (μm)
1	155	173.74	45.98	47.2
2	155	186.15		
3	166	172.67		
4	184	157.94		
5	178			
6	165			
7	197			
8	165			
Avg.	171	172.63		

Table S9. Dimensions of the nanoring structure from Figure 5F. Width and circumference values were obtained from ImageJ analysis of SEM image Figure 5H. Height values were determined from the maximum of the height profiles shown in Figure 5J. Reported averages represent measurements across distinct spots around the nanoring.

Spot	Width (nm)	Height (nm)	Inner Circumference (μm)	Outer Circumference (μm)
1	550	129.9	18.02	21.83
2	613	117.17		
3	631	84.46		
4	622	88.27		
5	615			
6	612			
7	582			
8	619			
Avg.	606	104.95		

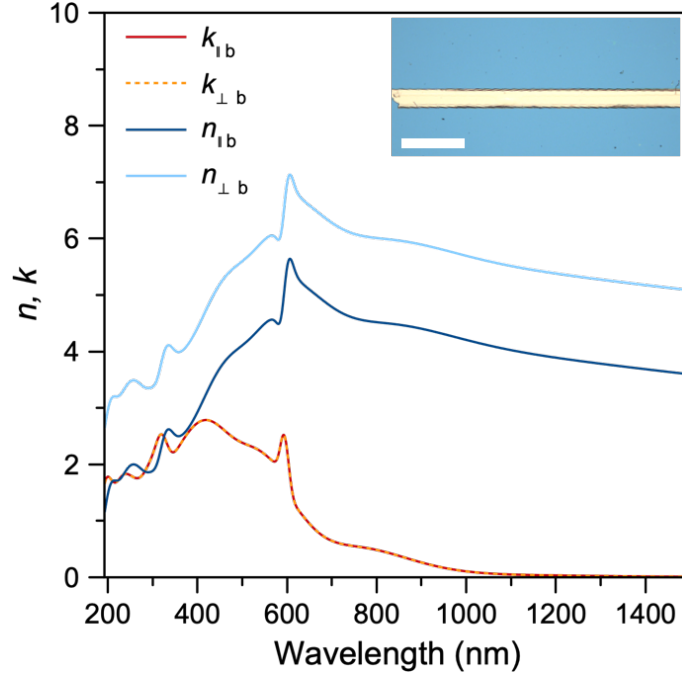


Figure S20. Effective optical constants of bulk NbS₃-I crystal extracted from spectroscopic ellipsometry using uniaxial birefringence model. The measured NbS₃-I ribbon has a cross-sectional width of 65 μm , thickness of 4175 nm, and length exceeding 1 mm. Wavelength-dependent refractive indices and extinction coefficients measured parallel ($n_{\parallel b}$, $k_{\parallel b}$) and perpendicular ($n_{\perp b}$, $k_{\perp b}$) to the crystallographic b -axis are shown over the spectral range of 193-1500 nm. Inset shows the corresponding NbS₃-I crystal used for the ellipsometry measurements. Scale bar, 245 μm .

A.4 Supplementary Figures and Tables for Chapter 5

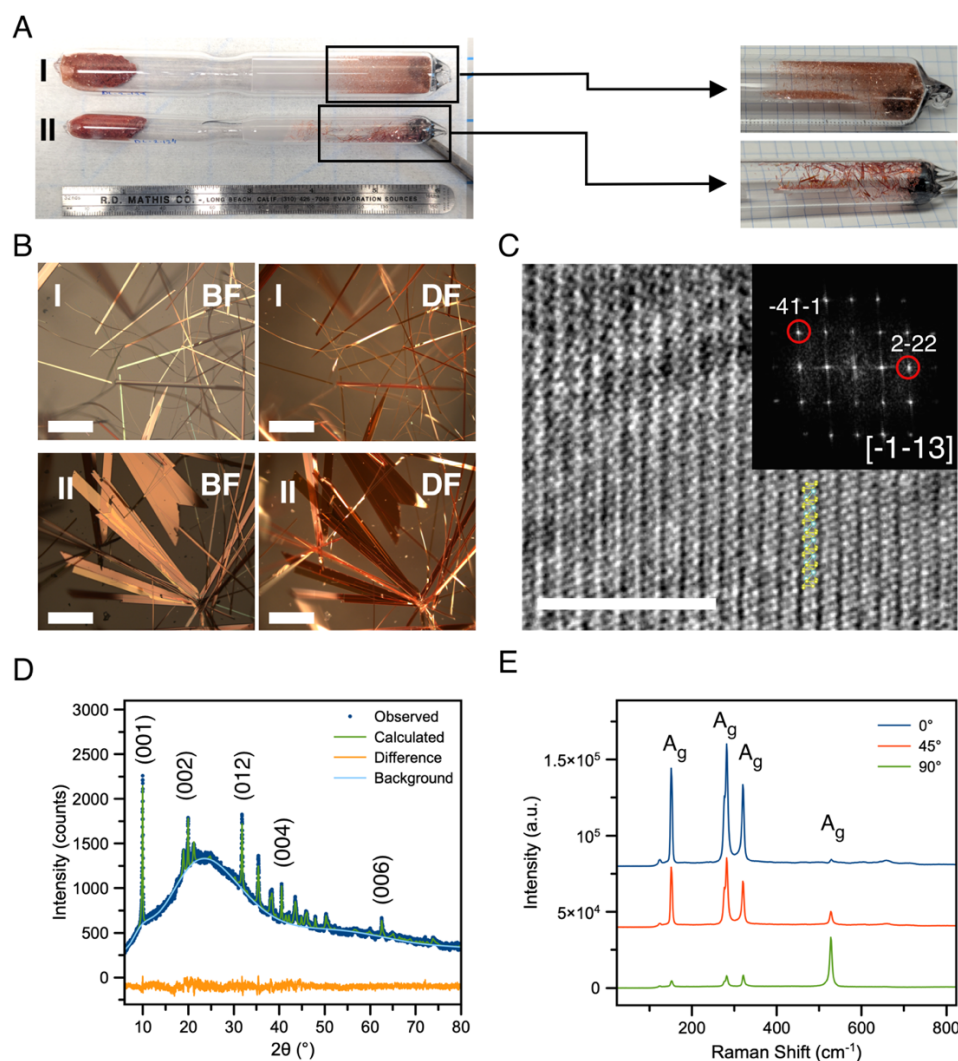


Figure S1. Synthesis and characterization of pristine ZrS_3 . (A) Images of fused quartz ampoules after CVT growth of ZrS_3 using two reaction conditions: (I) 0.34 g total precursor mass in a larger ampoule and (II) 0.48 g total mass in a smaller ampoule. (B) Representative bright-field (BF) and dark-field (DF) optical images of ZrS_3 crystals grown on sapphire substrates from the reactions shown in (A). Scale bars, 245 μm . (C) Representative TEM image with the corresponding FFT inset indexed along the $[-1-13]$ zone axis. Scale bar, 5 nm. (D) Representative PXRD pattern of the product from reaction A(II), fitted using Le Bail method to the monoclinic ZrS_3 ($P2_1/m$) crystal structure ($\chi^2 = 0.78$). (E) Orientation-dependent Raman spectra of a rotated ZrS_3 crystal measured from 0 to 90° relative to the polarization direction of the 532 nm excitation laser.

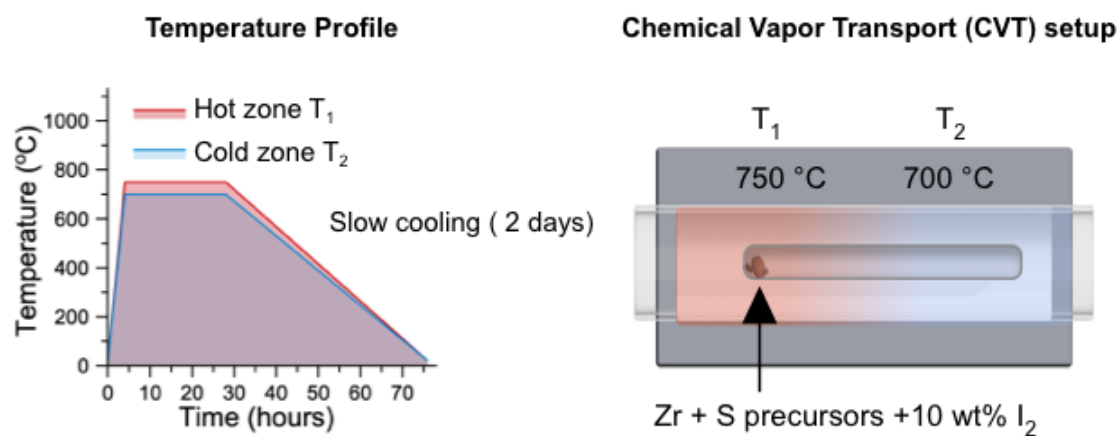


Figure S2. Temperature profile and schematic of chemical vapor transport (CVT) setup. (Left) Temperature profile used for CVT growth, consisting of an isothermal dwell followed by controlled slow cooling to room temperature over 2 days. (Right) Schematic of the two-zone furnace used for CVT growth. The precursor pellet was vacuum sealed in a fused quartz ampoule and positioned in the high-temperature (T_1) zone.

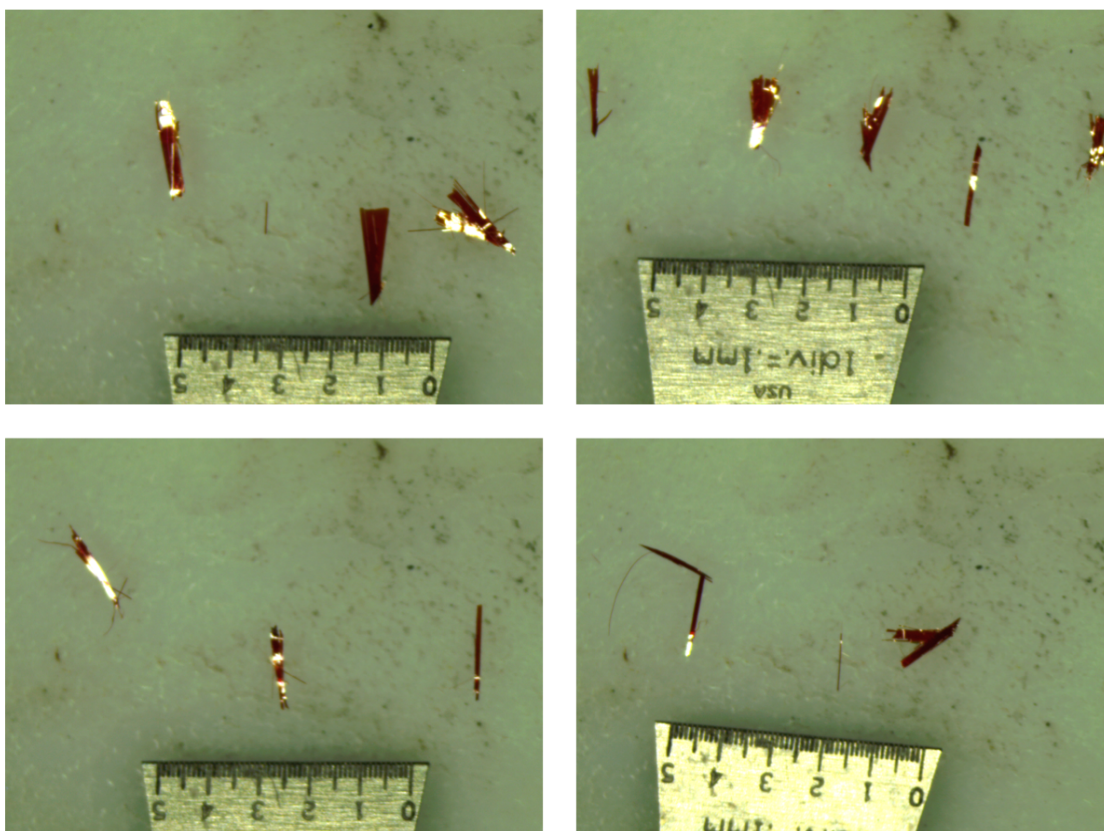


Figure S3. Optical images of representative $\text{ZrS}_{3-\delta}$ crystals. Each division on the ruler corresponds to 1 mm.

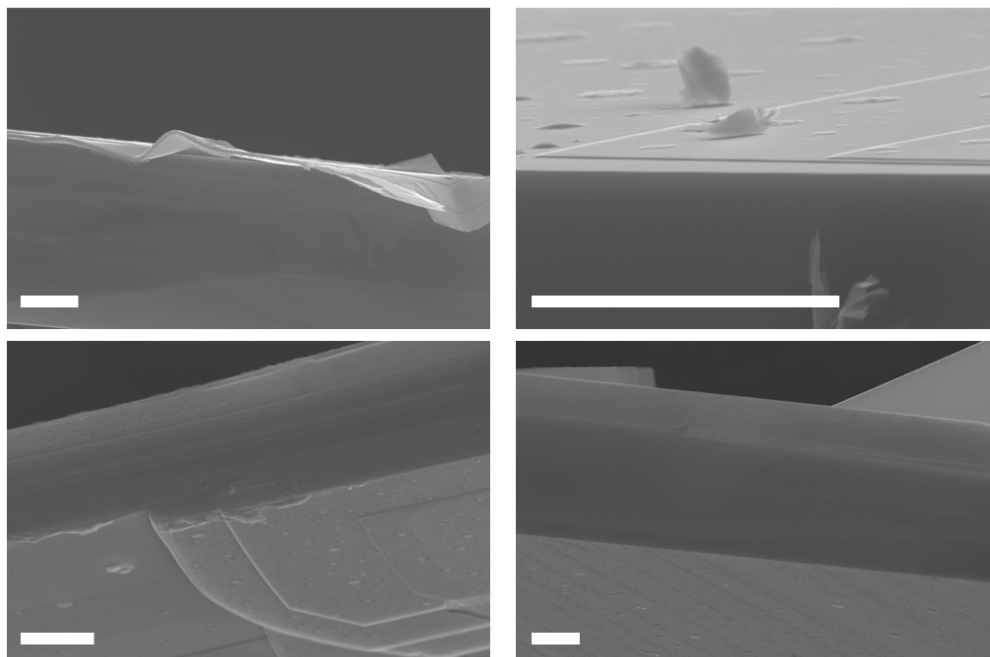


Figure S4. SEM side-view images of layered $\text{ZrS}_{3-\delta}$ crystals. Representative SEM images showing side views of $\text{ZrS}_{3-\delta}$ crystals, revealing the layered crystal morphology. Scale bars, 2 μm .

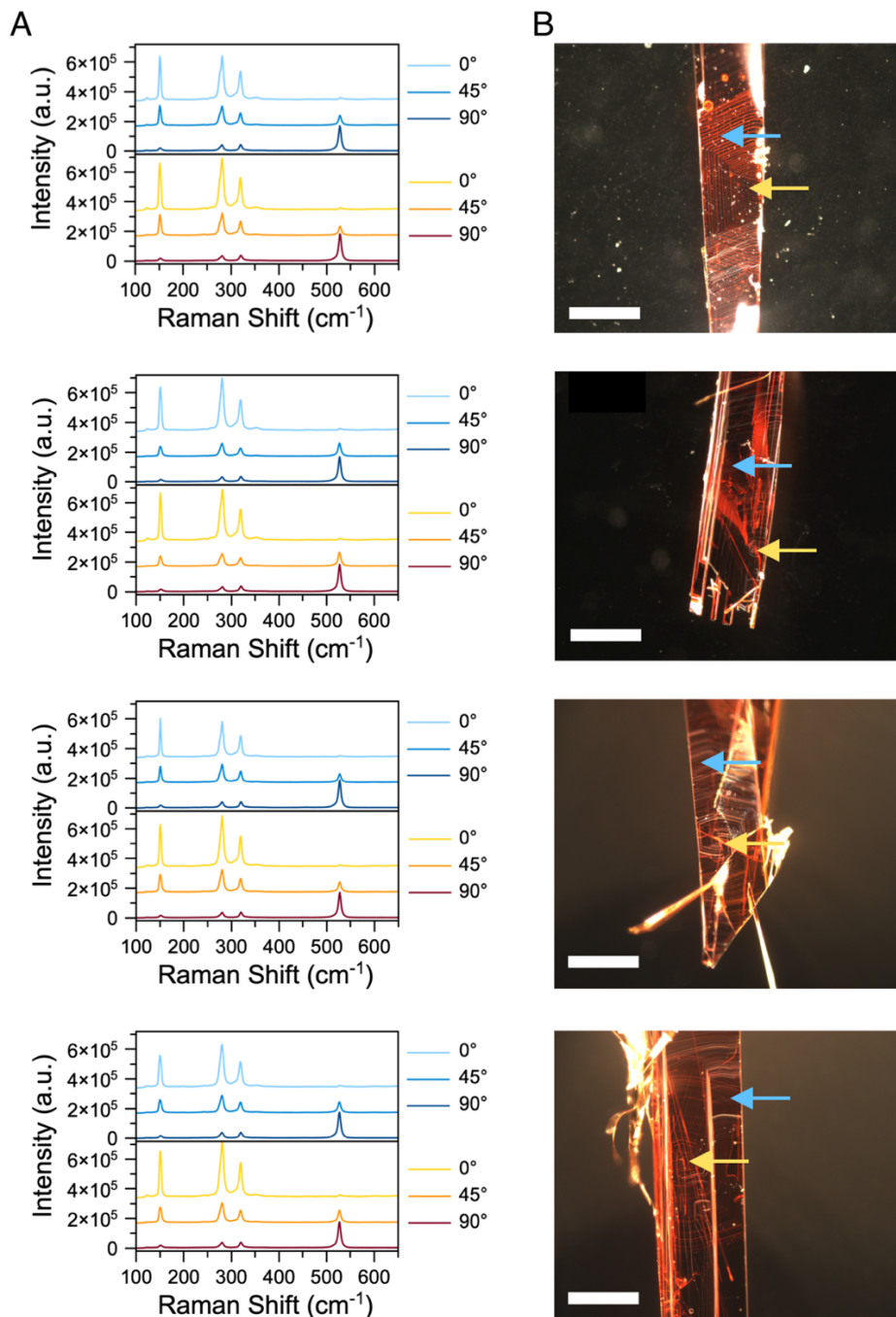


Figure S5. Polarization-dependent Raman spectroscopy of $\text{ZrS}_{3-\delta}$ crystals. (A) Raman spectra collected from regions containing spiral hillocks (red to yellow spectra) and from adjacent flat crystal regions away from the spiral hillocks (light to dark blue spectra), measured at polarization angles of 0°, 45° and 90°. (B) Corresponding optical images of the crystals. Blue arrows indicate the measurement locations on flat crystal regions, and yellow arrows indicate the locations containing spiral hillocks. Scale bars, 245 μm .

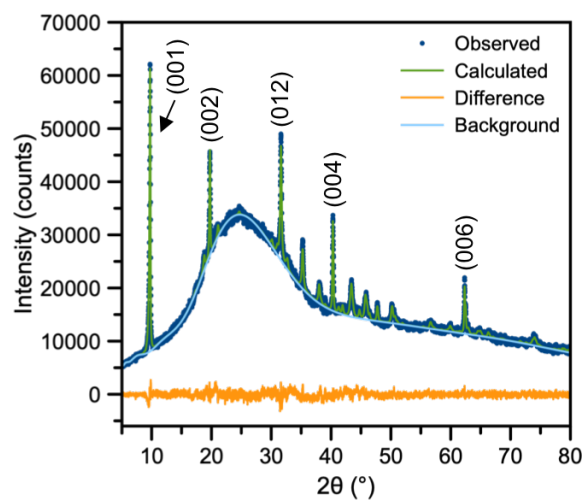


Figure S6. Representative PXRD pattern of $\text{ZrS}_{3-\delta}$ crystals. PXRD pattern of $\text{ZrS}_{3-\delta}$ crystals ground into a powder and mixed with glass powder to reduce preferred orientation, fitted using the Le Bail method to the monoclinic ZrS_3 ($P2_1/m$) crystal structure ($\chi^2=12.0$).

Table S1. Elemental composition of regions containing spiral hillocks. Atomic percentages of Zr and S determined by SEM-EDS analysis from four selected regions containing a spiral hillock. The measurements correspond to the same four crystals analyzed in Table S2.

Crystal	Atomic %	
	S K	Zr L
1	70.55	29.45
2	71.60	28.40
3	70.50	29.50
4	72.16	27.84
Standard deviation	0.82	0.82
Average	71.20	28.80

Table S2. Elemental composition of flat crystal regions. Atomic percentages of Zr and S determined by SEM-EDS analysis from four selected flat regions away from spiral hillocks. The measurements corresponded to the same four crystals analyzed in Table S1.

Crystal	Atomic %	
	S <i>K</i>	Zr <i>L</i>
1	74.73	25.27
2	78.40	21.60
3	76.98	23.02
4	71.46	28.45
Standard deviation	3.03	2.99
Average	75.39	24.59

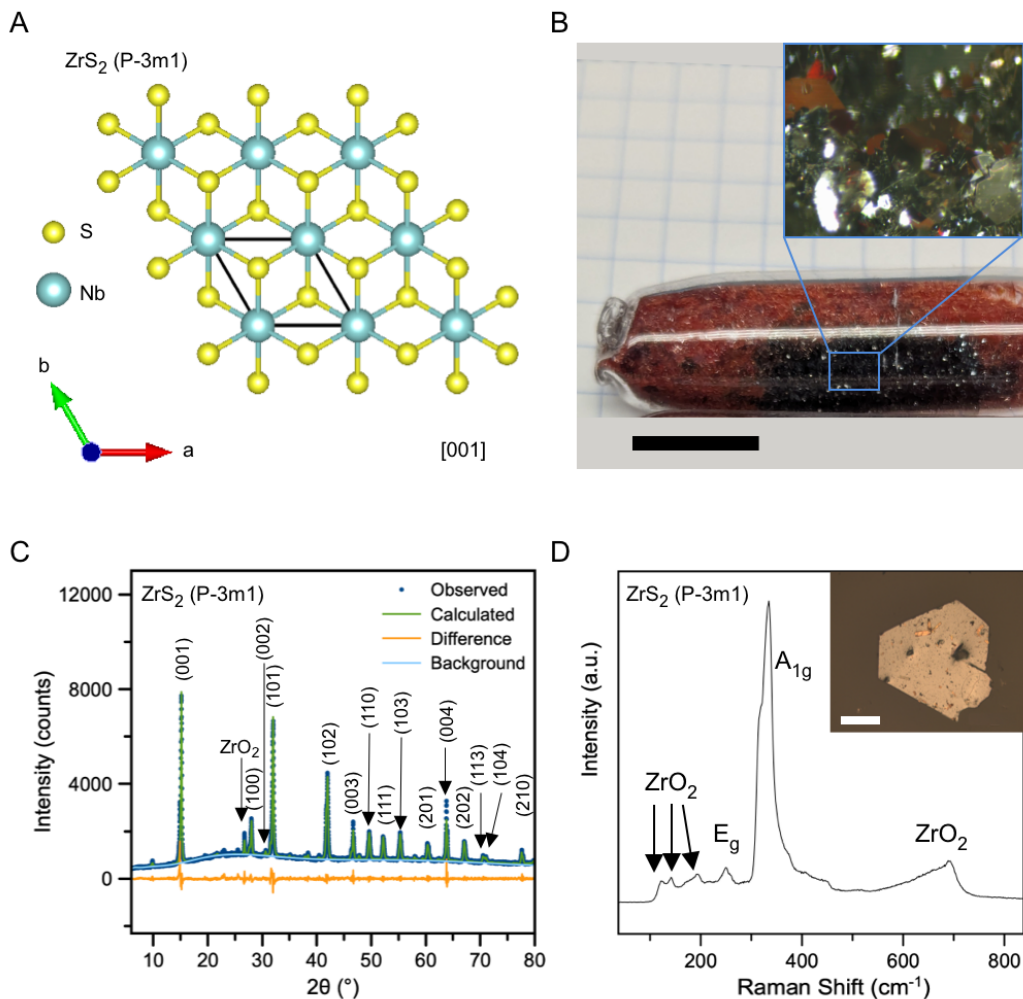


Figure S7. Formation of ZrS_2 side products on the hot/source zone (T1). (A) Crystal structure of ZrS_2 (P-3m1). (B) Optical image of the ZrS_2 side product localized at the hot/source zone (T1) following the reaction. Scale bar, 1 cm. (C) Representative PXRD pattern of the side product, fitted using the Le Bail method to the ZrS_2 (P-3m1) crystal structure ($\chi^2=1.9$). The peak corresponding to ZrO_2 is labeled. (D) Representative Raman spectrum of the side product showing vibrational modes consistent with ZrS_2 and ZrO_2 . The inset shows the corresponding crystal. Scale bar, 245 μm .

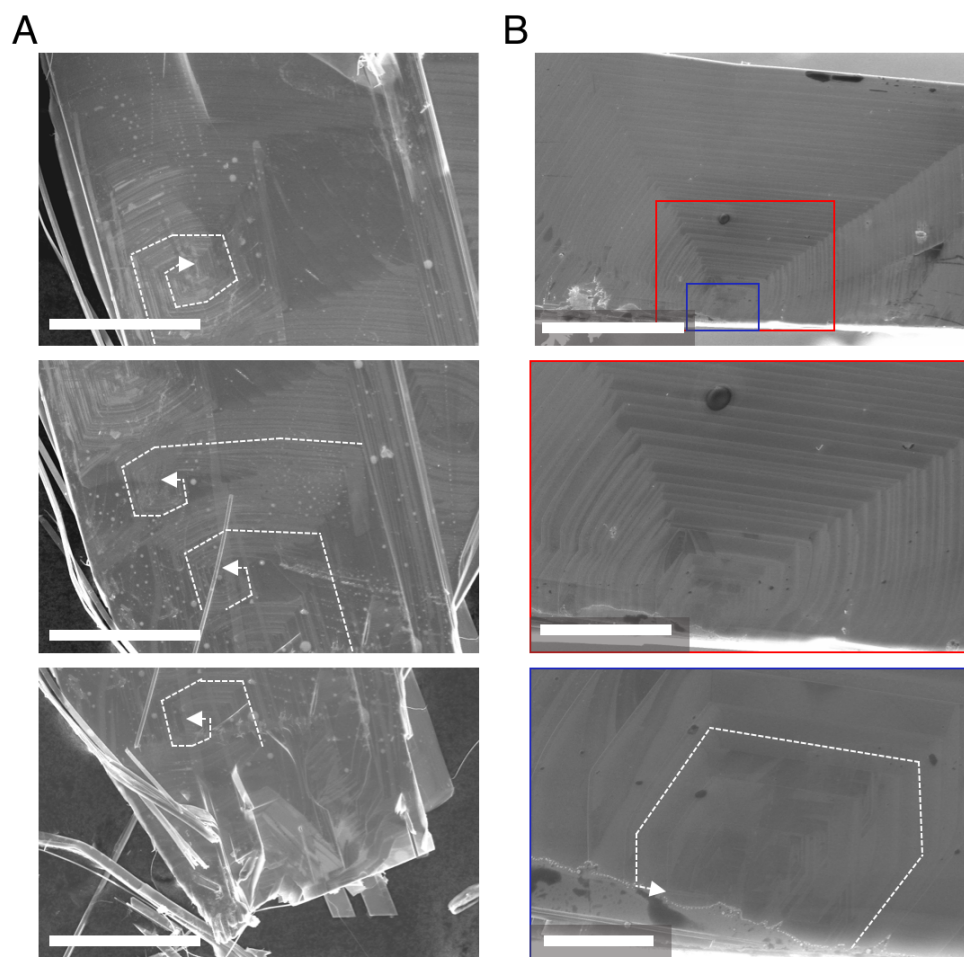


Figure S8. SEM images of spiral hillocks in $\text{ZrS}_{3-\delta}$ crystals. (A) SEM images of a single crystal showing multiple spiral hillocks (outlined by dashed lines). Scale bars, 200 μm . (B) SEM image with magnified views of the boxed regions highlighting a spiral hillock originating from the crystal edge. Scale bars, from top to bottom: 100 μm , 40 μm , and 10 μm .

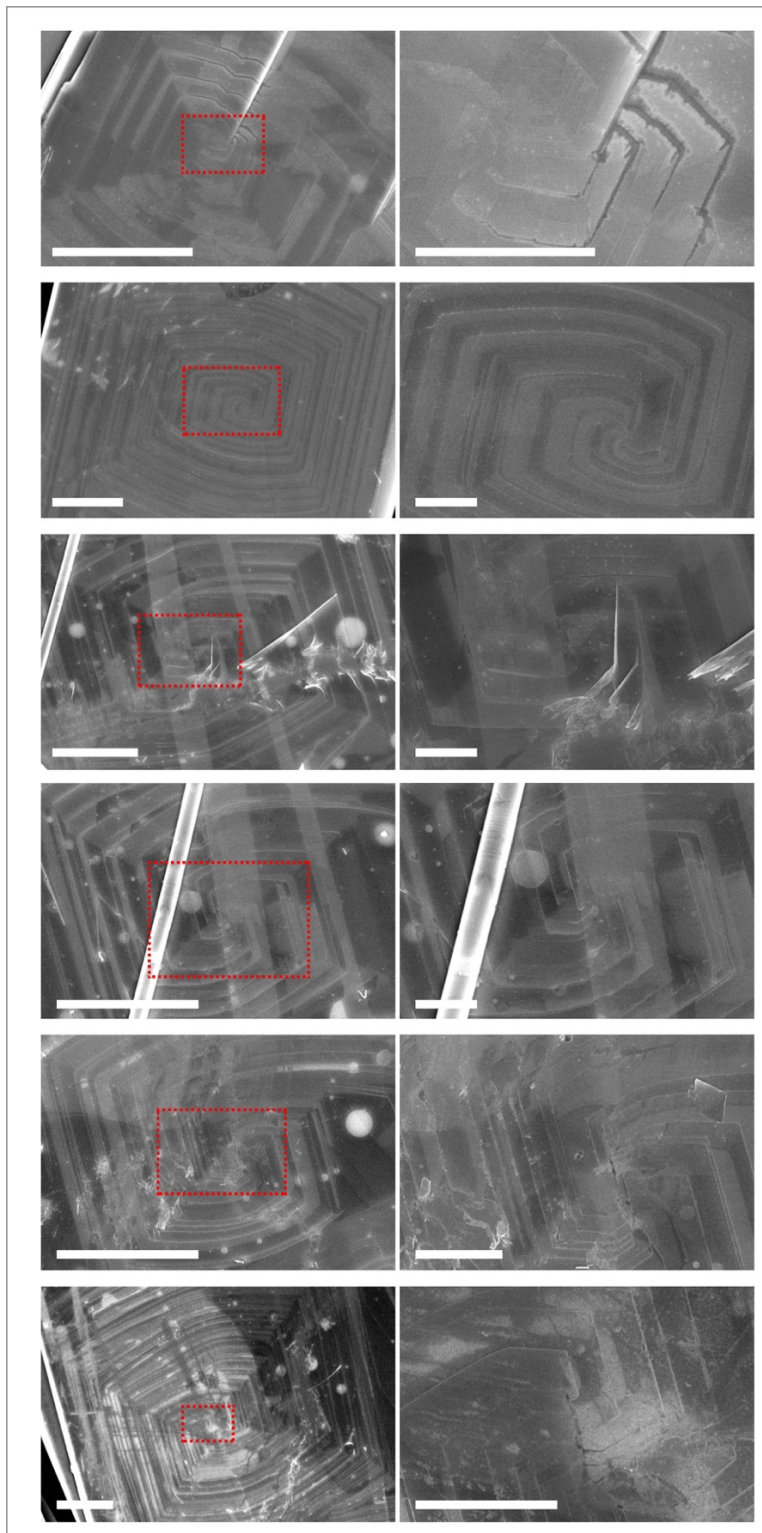


Figure S9. SEM images of spiral hillocks on $\text{ZrS}_{3-\delta}$ crystals. (Left) Representative SEM images showing spiral hillocks on the surface of $\text{ZrS}_{3-\delta}$ crystals. (Right) Corresponding magnified views of the regions outlined by the red boxes. Scale bars, 40 μm (left) and 10 μm (right).

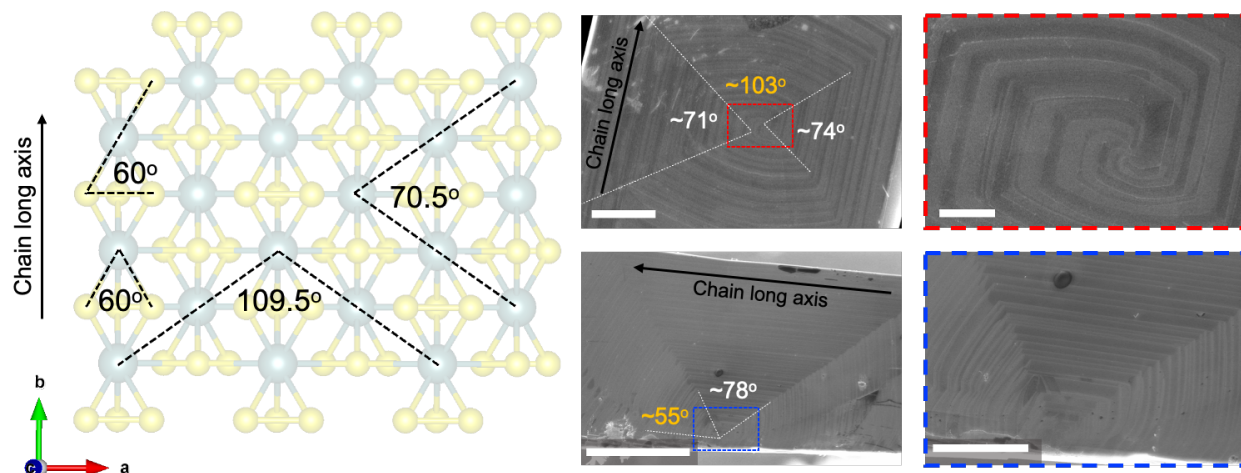


Figure S10. Comparison of crystallographic and spiral hillock angles in ZrS_3 . (Left) Selected Zr—Zr—Zr, S—S—S, and S—Zr—S angles projected onto the a/b plane of the ZrS_3 crystal structure. (Right) Representative spiral hillocks illustrating measured interior angles that closely match the Zr—Zr—Zr angles projected parallel and perpendicular to the crystal long axis (b -axis). Scale bars: 40 μm (top, left), 10 μm (top, right), 100 μm (bottom, left), and 40 μm (bottom, right).

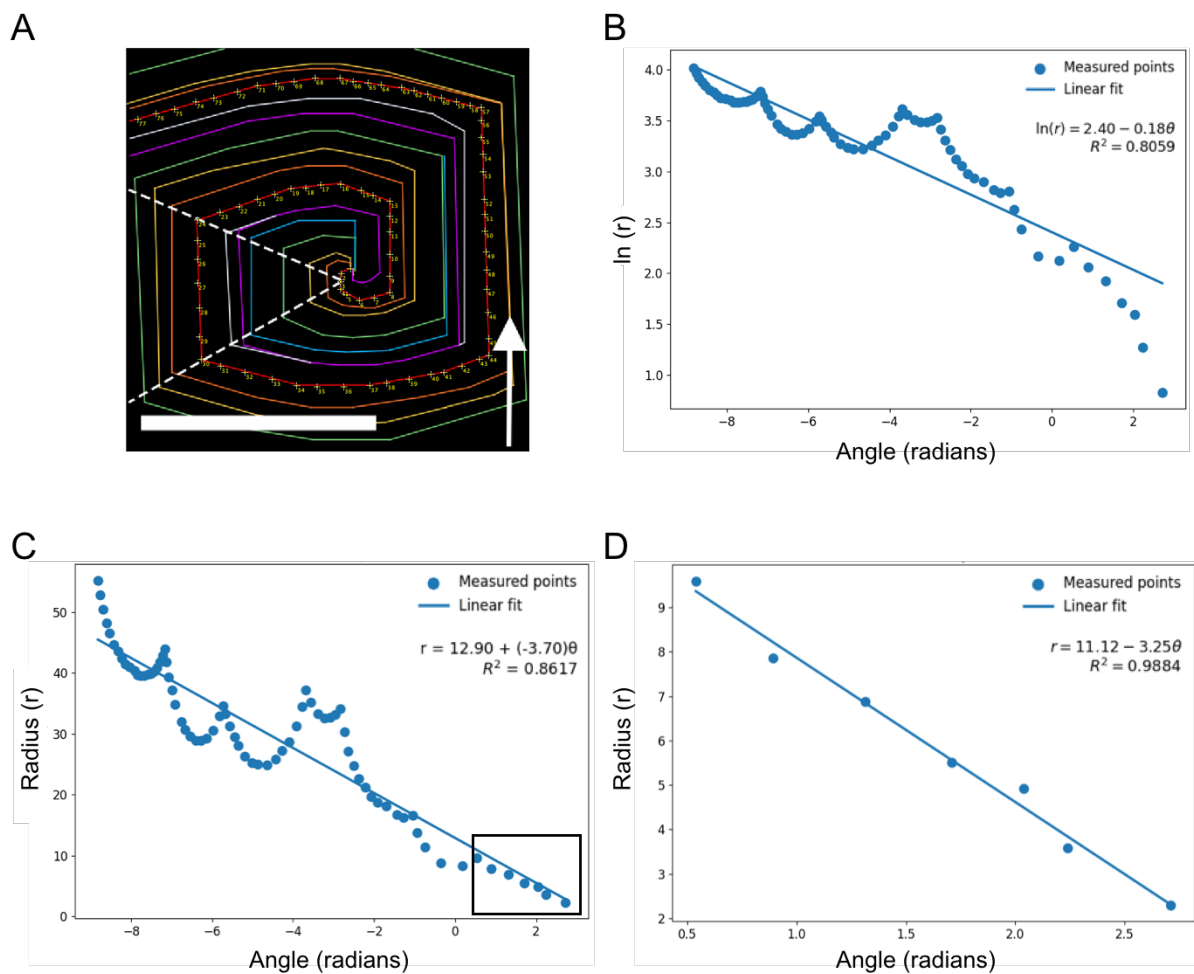


Figure S11. Geometric analysis of a representative spiral hillock in $\text{ZrS}_{3-\delta}$. (A) Tracing of a representative "super"-spiral hillock in Figure 2E-H using ImageJ. Colored lines represent successive spiral turns, and red points denote the coordinates extracted for the geometric analysis. Scale bar, 50 μm . (B) Linear fit of $\ln(r)$ versus angle (radians), where r is the radial distance from the spiral center, for comparison with an ideal logarithmic spiral. (C) Linear fit of radius (r) versus angle for comparison with an ideal Archimedean spiral. (D) Linear fit to a subset of points near the spiral center (boxed region in (C)) to evaluate the local Archimedean behavior of the spiral.

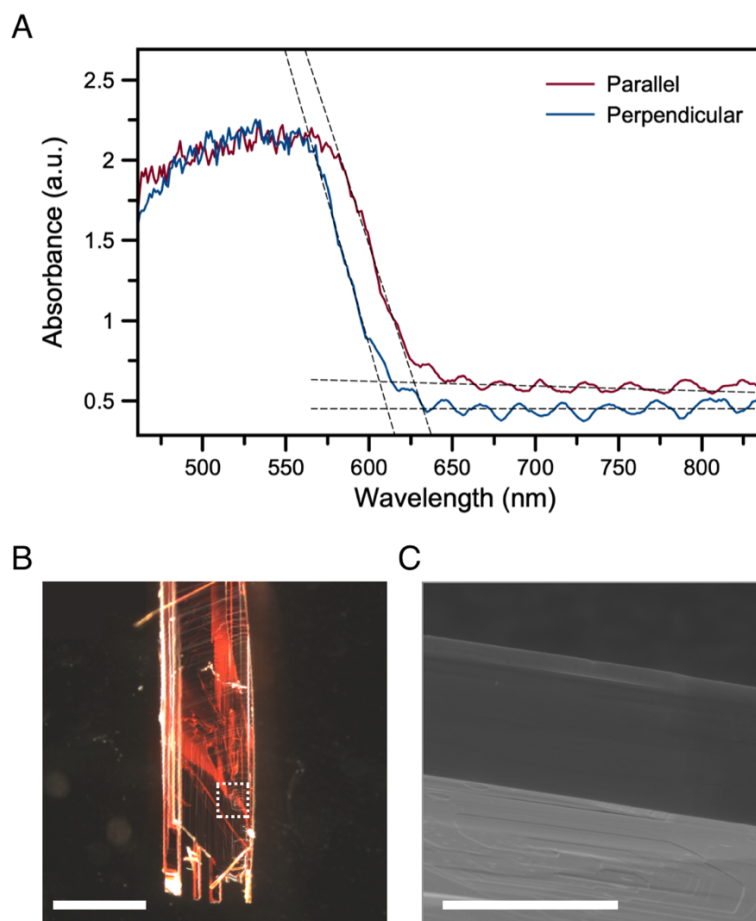


Figure S12. Polarization-dependent absorbance spectroscopy of a $\text{ZrS}_{3-\delta}$ crystal. (A) Absorbance spectra obtained from transmission measurements with the incident polarization oriented parallel and perpendicular to the crystal long axis, showing a polarization-dependent absorption edge. (B) Optical micrograph of the crystal, with the boxed region indicating the area analyzed in (A). Scale bar, 245 μm . (C) SEM side-view image of the corresponding crystal region showing a crystal thickness of 15.8 μm . Scale bar, 20 μm .