

Metallic NbS₂ one-dimensional van der Waals heterostructures

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ABSTRACT: This study presents the experimental demonstration of metallic NbS₂-based one-dimensional van der Waals heterostructures using a modified NaCl-assisted chemical vapor deposition strategy. By employing a "remote salt" strategy, we achieved precise control of the NaCl supply, enabling the growth of high-quality coaxial NbS₂ nanotubes on single-walled carbon nanotube–boron nitride nanotube (SWCNT-BNNT) templates. Using this remote salt strategy, the morphologies of as-synthesized NbS₂ could be tuned from 1D nanotubes to suspended 2D flakes. Structural characterization via high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) confirmed the formation of crystalline NbS₂ nanotubes, revealing a distinct bi-layer preference compared to monolayer-dominated behavior of semiconducting transition metal dichalcogenide analogs. Optical analyses using UV-vis-NIR and FTIR spectroscopy highlighted the metallic nature of NbS₂. Raman-based oxidation studies demonstrated a relatively higher degradation rate of 1D NbS₂ under ambient conditions. Density functional theory (DFT) calculations further clarified the stabilization mechanism of bi-layer NbS₂ nanotubes, emphasizing interlayer charge transfer and Coulomb interactions. This work establishes a robust framework for synthesizing metallic 1D vdW heterostructures, supporting their potential applications in optoelectronics and nanodevices.

Introduction

Over the past decade, a wide variety of van der Waals (vdW) heterostructures have been developed based on two-dimensional (2D) materials, including graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDCs).¹ These heterostructures are typically constructed via mechanical stacking or chemical synthesis.²⁻⁴ 2D TMDCs, with their diverse and unique physical properties, have played a critical role in the exceptional characteristics of vdW heterostructures.^{5, 6} The concept of one-dimensional (1D) TMDCs was proposed as early as the 1990s.⁷ Isolated TMDC nanotubes and nanostructures coated with TMDC 1D layers have been synthesized via approaches such as chemical transport reactions and template-assisted CVD methods since the early 2000s.⁸⁻¹⁰ These pioneering studies laid the groundwork for constructing 1D hybrid nanostructures. However, such structures were generally not regarded as 1D vdW heterostructures, as they often involved mixed phases containing Nb oxides or lacked high crystallinity. The experimental realization of high-quality 1D vdW heterostructures with single-crystal sheet was first demonstrated in 2020, through the sequential assembly of single-walled carbon nanotubes (SWCNTs), boron nitride nanotubes (BNNTs), and molybdenum disulfide nanotubes (MoS₂ NTs).¹² This 1D tubular hybrid crystal represents a new class of materials featuring clean coaxial vdW interfaces and programmable shell architectures, which exhibit unique optical and electronic properties, making them promising candidates for applications such as optical detectors and field-effect transistors with 1D geometrical features.^{13,}

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Since 1D TMDCs can be regarded as counterparts of their 2D analogs, it is expected that most of the TMDCs can be rolled into a tubular shape and incorporated into 1D vdW heterostructures.^{7,10,17} To date, experiments have successfully demonstrated coaxial 1D TMDC

vdW heterostructures based on various TMDCs such as MoS₂, WS₂, MoSe₂, and WSe₂,^{16,17} all of which are semiconductors. Metallic TMDCs, e.g., niobium disulfide (NbS₂), stand out as another group of important candidates as they can serve as electrode materials in 1D tubular devices.^{9,15,16} Meanwhile, NbS₂ also possesses additional unique properties such as superconductivity and spintronic behavior.¹⁸⁻²¹ Therefore, the incorporation of metallic TMDCs such as NbS₂ into 1D vdW systems provides opportunities for designing and fabricating more complex 1D heterostructures and devices with unique functionalities. However, the fabrication of 1D vdW heterostructures differs significantly from their 2D counterparts in terms of synthetic approach. Unlike 2D vdW heterostructures, which can often be assembled through mechanical stacking, 1D structures require a layer-by-layer chemical vapor deposition (CVD) process with nucleation and extension processes over highly curved surfaces.¹⁷ Although previous studies have investigated the synthesis of 2D NbS₂,²³⁻²⁵ and NbS₂ nanotubes,⁷⁻¹⁰ the fabrication of high-quality and single-crystal 1D NbS₂ with well-controlled vdW interfaces in a 1D vdW heterostructure system remains challenging due to its narrow growth window and distinct growth mechanism. In addition, previous nanostructures are usually thick, while TMDC nanotubes with small diameters (sub-10 nm) are rarely demonstrated. Moreover, NbS₂ undergoes oxidation in the ambient atmosphere, complicating the study of its intrinsic properties arising from its 1D nature.²⁶⁻²⁹

In this study, we demonstrate the fabrication of NbS₂ 1D vdW heterostructures using a modified NaCl-assisted CVD synthesis strategy. TEM and STEM analysis confirm the formation of well-defined coaxial NbS₂ nanotubes wrapping around the SWCNT–BNNT templates. By adjusting the synthesis parameters, we modulated the morphology of NbS₂ from coaxial 1D nanotubes to suspended 2D flakes. To investigate the intrinsic optical properties of the fabricated NbS₂ 1D vdW heterostructures, we employed an argon gas-assisted storage and optical

characterization protocol. The optical behavior of these heterostructures was evaluated using Raman spectroscopy, UV-vis-NIR absorption spectroscopy, and Fourier-transform infrared (FT-IR) spectroscopy, while their oxidation processes were studied via Raman analysis. A statistical investigation of structural characterization revealed a surprising bilayer preference in the synthesized NbS₂ 1D nanotubes outside the 1D template backbone, unlike other semiconducting 1D TMDCs, which typically prefer a monolayer. Additionally, density functional theory (DFT) calculations provided insight into the stabilization mechanisms underlying the formation of coaxial NbS₂ nanotubes, offering a theoretical explanation for the experimentally observed layer-number preference in NbS₂ 1D vdW heterostructures.

Results and Discussion

Synthesis and structural characterization of NbS₂ based vdW heterostructure

In our previous research, we demonstrated a bottom-up CVD synthesis process for fabricating coaxial structures consisting of SWCNT, BNNT, and 1D MoS₂.^{7,17} In this study, we extend this approach to synthesize NbS₂ nanotubes using a NaCl-assisted CVD process. Structural characterization revealed highly crystalline coaxial NbS₂ nanotubes wrapping around the SWCNT–BNNT templates. The overall scheme of the synthesized SWCNT–BNNT–NbS₂ 1D vdW heterostructures is shown in Figure 1A. The fabricated heterostructure comprises three types of materials: SWCNTs, BNNTs, and NbS₂. The synthesis method is similar to our previous works, which applied a layer-by-layer CVD process, starting with BNNT synthesis over the SWCNT template to form the SWCNT-BNNT heterostructure, followed by deposition of the desired TMDC layer in a subsequent CVD step.^{12,22,30}

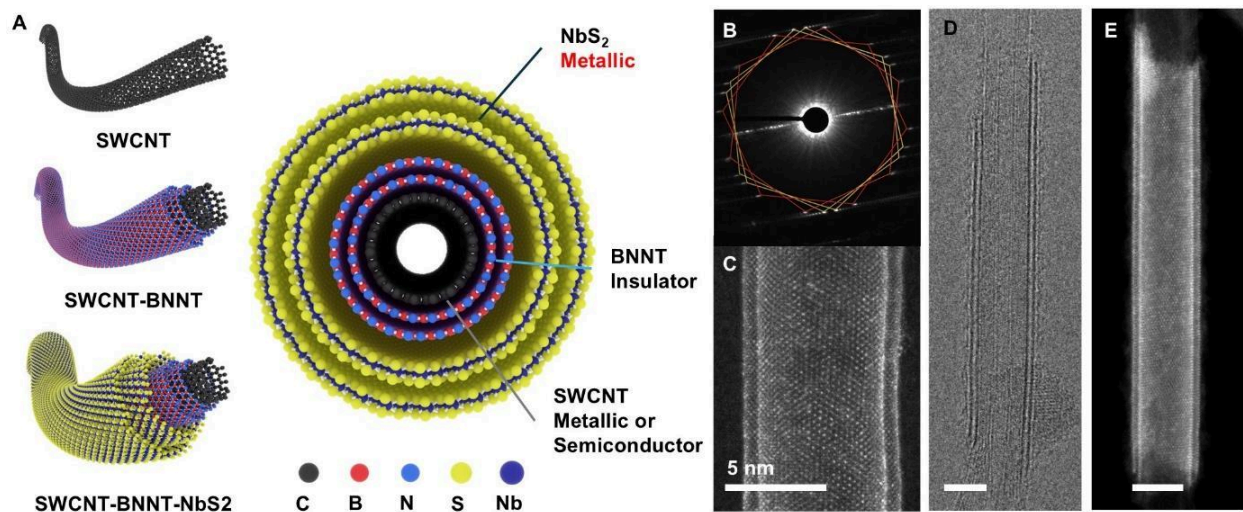
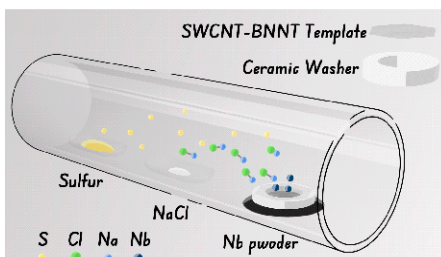


Figure 1. (A) Schematic illustration of SWCNT–BNNT–NbS₂ 1D vdW heterostructure. (B) SAED pattern of bilayer NbS₂ nanotubes @ SWCNT–BNNT (C) STEM image of bilayer NbS₂ nanotubes @ SWCNT–BNNT (D) HRTEM image of 1D heterostructure comprising bilayer NbS₂ nanotubes, five-layer BNNTs, and SWCNT. (E) STEM of bilayer NbS₂ @ SWCNT-BNNT. Scale bar: 5 nm

High-resolution transmission electron microscopy (HRTEM) and STEM were employed to characterize the structures. Annular dark field (ADF) STEM images clearly showed the coaxial wrapping of NbS₂ nanotubes, where the bright spots corresponded to heavier atoms, specifically Nb atoms, in this heterostructure. (Figure 1C, E) The typical structure of SWCNT-BNNT-NbS₂ 1D vdW heterostructures consists of a SWCNT core wrapped by 3-6 BNNT layers and bilayer NbS₂ nanotubes forming the outermost shells. A typical diameter for this coaxial 1D vdW heterostructure is around 8 to 10 nm, with a length ranging from 50 to 150 nm. Selected-area electron diffraction (SAED) patterns of 1D vdW heterostructures were used to visualize the crystal orientation of NbS₂ nanotube layers. The diffraction pattern shown in Figure 1B is from a 1D vdW heterostructure with two layers of NbS₂ nanotubes over a SWCNT-BNNT template. The

orange and red SAED pattern groups represent two layers of NbS₂, with a relatively small chiral angle difference of approximately 13.5°. The diffraction pattern indicated a strong interlayer coupling between the chiral angles of the inner and outer NbS₂ nanotubes.³¹ As shown in Figure 1D, the HRTEM image reveals a coaxial structure comprising a SWCNT, five layers of BNNT, and two layers of NbS₂ nanotubes, with an interlayer spacing of approximately 0.7 nm. A lower-magnification ADF image is shown in Figure S1, where a high coverage rate of NbS₂ was observed over the SWCNT–BNNT template. Energy dispersive spectroscopy (EDS) mapping also confirmed the wide distribution of NbS₂ nanotubes, as illustrated in Figure S2, validating the successful formation of coaxial NbS₂ nanotubes with a relatively high yield.

The synthesis of NbS₂ over SWCNT-BNNT templates utilized a modified NaCl-assisted CVD process, with the setup illustrated in Figure 2A. Unlike conventional methods that mix NaCl directly with metal precursors for 2D TMDC synthesis, this study separated NaCl into a different temperature zone and treated NaCl as an independent variable, enabling precise control over its contribution and further developing NaCl-assisted TMDC synthesis strategies.^{18,32} This configuration, which we call the “remote salt strategy”, was critical for the growth of NbS₂ 1D vdW heterostructures, because a precise control over NaCl supply was confirmed to determine the final morphology of NbS₂ in 1D vdW heterostructures. The SWCNT–BNNT template, prepared following our previous methods, was suspended over a ceramic washer with a 2.5 mm inner diameter hole.^{22,35} Using a dry transfer technique, the SWCNT film was positioned on the ceramic washer. Subsequent BNNT synthesis via low-pressure CVD employed ammonia borane as precursor, yielding three to six BNNT layers on the SWCNT template. The increased diameter of SWCNT–BNNT templates was found to reduce the curvature-induced strain effect in TMDC



200 nm diameter

layers, facilitating the synthesis of 1D TMDCs.²² The resulting SWCNT-BNNT heterostructures served as templates for the subsequent synthesis of NbS₂. For NbS₂ synthesis, a three-zone CVD system was employed, utilizing Nb metal powder as the precursor and gaseous sulfur with the assistance of NaCl. With optimized temperature setups of these three zones, successful wrapping of NbS₂ over the templates was achieved. Adjusting the NaCl temperature allowed control over the morphology of the as-synthesized NbS₂, ranging from coaxial 1D nanotubes to suspended 2D flakes over the SWCNT–BNNT templates. As the NaCl temperature increased, the morphology evolved from coaxial 1D NbS₂ nanotubes to suspended 2D NbS₂ flakes, as shown in Figure 2B. SEM images revealed the progressive appearance of suspended 2D flakes with higher NaCl temperatures. While the precise mechanism of the NaCl-assisted synthesis process remains unclear, it is evident that NaCl significantly lowers the reaction barriers, possibly by facilitating the formation of volatile metal oxychloride gaseous intermediates.^{33,34} This hypothesis is supported by previous reports on NaCl-assisted synthesis of NbS₂ based on Nb₂O₅ precursors, as well as by our remote NaCl promotion results.

Figure 2. (A) Scheme illustration of NaCl-assisted synthesis process of NbS₂. Exploded view of the SWCNT-BNNT template suspended on a ceramic washer is illustrated upright. (B) Evolution of NbS₂ morphologies with NaCl temperature change. (C) Picture of SWCNT, SWCNT-BNNT, SWCNT-BNNT-NbS₂ film suspended on ceramic washer. (D) Raman spectra of 1D and 2D NbS₂ @ SWCNT-BNNT (E) Absorbance of SWCNT, SWCNT-BNNT, SWCNT-BNNT-MoS₂, SWCNT-BNNT-1D NbS₂, and SWCNT-BNNT-2D NbS₂ as a function of energy (F) Absorbance of WCNT, SWCNT-BNNT, SWCNT-BNNT-1D NbS₂, and SWCNT-BNNT-2D NbS₂ to different wavelengths.

2.2 Optical characterization of NbS₂

Noticeable color changes after the synthesis of each type of nanotubes suggest significant modifications in the optical properties, as illustrated in Figure 2C. These color variations correspond to the optical absorption characteristics of the resulting 1D vdW heterostructures in the visible range.¹² The Raman and UV–vis–NIR absorbance spectra of the as-synthesized SWCNT–BNNT–NbS₂ heterostructures were investigated, revealing distinct optical behaviors of NbS₂-based vdW heterostructures compared to other TMDC-based 1D vdW heterostructures.

Raman spectroscopy is widely regarded as an effective method for characterizing TMDC materials³⁶⁻³⁸. A conventional Raman spectrum of NbS₂ includes E_{1g}, E_{2g}, A_{1g}, and A_{2g} modes²³⁻²⁵. However, the Raman spectrum of monolayer NbS₂ has not been thoroughly studied due to several challenges. First, NbS₂ is difficult to exfoliate into few-layer or monolayer forms, as it tends to fragment into small pieces rather than forming continuous thin layers.³⁹ In addition, synthesizing monolayer NbS₂ is inherently challenging. Although previous studies have demonstrated that Nb chlorides can be used as a precursor for the CVD synthesis of few-layer NbS₂ nanotubes,⁸ these compounds are susceptible to hydrolysis under ambient conditions, which complicates the handling process.²⁴ In contrast, our remote NaCl-assisted method provides a more robust approach for synthesizing high-quality, small-diameter 1D NbS₂ nanotubes, where a finer control is critical. Moreover, NbS₂ is highly prone to oxidation when exposed to air, further complicating its Raman characterization.²⁶⁻²⁹

In this study, the SWCNT-BNNT-NbS₂ heterostructures were preserved in an argon (Ar) atmosphere throughout transportation and storage processes to minimize oxidation. (Figure S3) Before optical measurements, the sample's exposure to air was limited to less than 15 seconds. Furthermore, to prevent NbS₂ oxidation accelerated by laser-induced heating, the samples were placed in an Ar-filled chamber during Raman measurements. During the measurement process, a

continuous Ar gas flow was maintained, and the laser power was kept below 0.3 mW to minimize heating effects.

The Raman spectra of the synthesized heterostructures were found to depend on the morphology of NbS₂. As shown in expanded Figure 2D, four distinct Raman modes emerged following NbS₂ CVD synthesis. Figure 2D presents a comparative Raman spectrum of 1D and suspended 2D NbS₂ obtained from the same SWCNT–BNNT template batch. For the SWCNT–BNNT–NbS₂ 1D vdW heterostructures, the Raman peaks corresponding to NbS₂ were observed at 271.64 cm⁻¹ (E_{1g}), 337.47 cm⁻¹ (E_{2g}), 378.29 cm⁻¹ (A_{1g}), and 450.91 cm⁻¹ (A_{2g}). The Raman spectra of suspended 2D NbS₂ on SWCNT–BNNT templates exhibited peaks at 284.82 cm⁻¹ (E_{1g}), 342.89 cm⁻¹ (E_{2g}), 378.02 cm⁻¹ (A_{1g}), and 449.02 cm⁻¹ (A_{2g}), respectively. These data of suspended 2D NbS₂ flakes are consistent with measurements from 2D NbS₂ flakes synthesized on Si/SiO₂ substrates (Figure S6), confirming that the Raman measurements in the Ar atmosphere reliably revealed the intrinsic vibration response of NbS₂-based vdW heterostructures. Additionally, a noticeable minor peak around 800 cm⁻¹ was observed in both 1D and 2D results, which may correspond to the Raman-active modes of trace amounts of Nb-O-related species formed through surface oxidation.⁴⁰ A notable difference between 1D and 2D NbS₂ is the considerable downshift of the E_{2g} and A_{1g} modes in 1D NbS₂, suggesting significant strain effects induced by the curvature of NbS₂ nanotubes.⁴⁴

The absorbance spectra of SWCNT–BNNT–NbS₂ heterostructures, along with SWCNT, SWCNT–BNNT, and SWCNT–BNNT–MoS₂ 1D vdW heterostructures, are presented in Figure 2E and F. These spectra of SWCNT–BNNT–NbS₂ 1D vdW heterostructures were sequentially acquired from the same sample before and after each step of the CVD synthesis process. All the heterostructures were prepared using the same batch of SWCNT–BNNT templates. After BNNT

synthesis, a characteristic absorption peak appeared at approximately 205 nm, as reported in our prior studies.¹² As shown in Figure 2E, SWCNT–BNNT–MoS₂ exhibited three distinct absorption peaks at 1.879 eV, 2.023 eV, and 2.850 eV, corresponding to the A, B, and C excitonic transitions associated with the MoS₂.^{13,14} As a semiconductor, MoS₂-based 1D vdW heterostructures display multiple absorption features within the visible range, which correspond to their interband transmissions. In comparison, SWCNT–BNNT–NbS₂ 1D vdW heterostructures only exhibit a single broad absorption peak at approximately 420 nm, consistent with the metallic nature of NbS₂ and attributed to metallic interband transitions.⁴¹

Additionally, the UV-vis-NIR absorbance results revealed enhanced absorption in the NIR region for the synthesized SWCNT–BNNT–NbS₂ vdW heterostructures. To further investigate this enhancement, FT-IR measurements were conducted. The transmittance spectra of the vdW heterostructures were converted to absorbance values, and the combined UV-vis-NIR and IR spectra of various samples were plotted (Figure 2E). A good overlap was observed between the FT-IR and UV-vis-NIR data, demonstrating good consistency with each other. Characteristic peaks of SWCNT and SWCNT-BNNT were easily identified, while a noise signal near ~2350 cm⁻¹ (4255 nm) corresponded to atmospheric CO₂. For the SWCNT template, plasmonic, metallic, and semiconducting modes in the absorption spectrum were reported.^{42,43} After BNNT synthesis, a new peak at ~205 nm appeared, which can be assigned to the band gap of BNNT.⁴³ Another distinctive peak at ~7300 nm (~1370 cm⁻¹) was observed in the IR range, which can be assigned to the longitudinal vibration of BNNT along its axis.⁴⁴ Following NbS₂ synthesis, two prominent features appeared in the absorption spectrum: a broad peak at ~420 nm and an enhanced absorption region in the NIR and IR ranges. The enhancement near ~2600 nm is likely

associated with the plasmonic peaks of NbS₂, suggesting that the synthesized NbS₂ vdW heterostructures exhibit metallic behavior.

Stability of NbS₂ 1D vdW heterostructures in ambient atmosphere

As discussed above, 2D NbS₂ is known to oxidize readily when exposed to air. Upon full atmospheric exposure, the formation of a layer of Nb oxide on the surface of the synthesized NbS₂ flakes is often reported,^{28,29} although the timescale and detailed atomic structure remain poorly understood. Here, we performed a systematic microscopic and spectroscopic analysis of our NbS₂ 1D vdW heterostructures. As shown in Fig. 3A, STEM observation confirmed that the crystal structure of 1D NbS₂ @ SWCNT–BNNT remained intact after short-term (~15 min) exposure. However, the crystal structure was severely degraded after approximately 24 hours of exposure to the air. EDS mapping of oxidized NbS₂ nanotubes revealed the presence of oxygen atoms on their outer surfaces (Fig. S4). These results from STEM and EDS clearly demonstrate the high susceptibility of 1D NbS₂ to oxidation in ambient conditions.

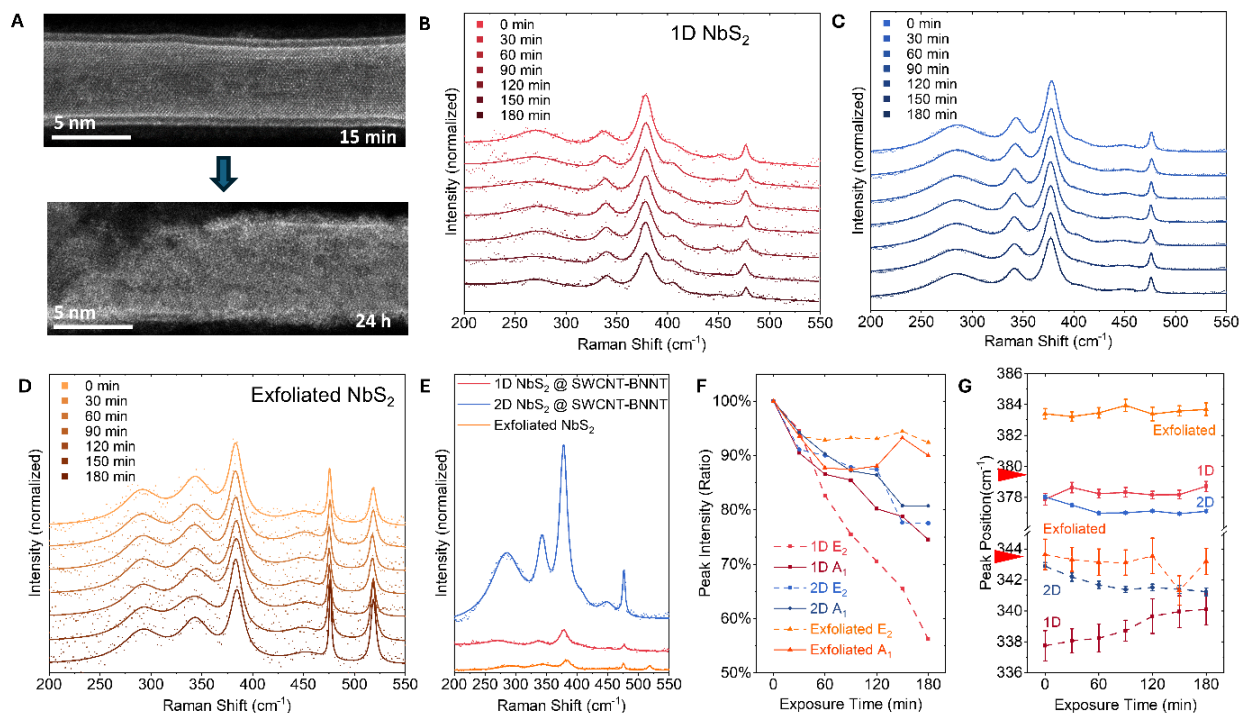


Figure 3. (A) STEM image of bi-layer NbS₂ nanotubes after exposure to ambient atmosphere for a few minutes and for 24 hours, severe degradation of atomic structures could be observed in the 24-hour exposed samples. (B-D) Raman spectra of as-synthesized 1D (B), suspended 2D (C) NbS₂ @ SWCNT-BNNT, and exfoliated NbS₂ on a Si/SiO₂ substrate (D). (E) Comparative Raman spectra of as-synthesized 1D, suspended 2D NbS₂ @ SWCNT-BNNT, and exfoliated 2D NbS₂. (F) Peak intensity decay as a function of each sample to exposure time in air, normalized to 100% at the initial time point. (G) Time-dependent Raman peak positions of each sample upon atmospheric exposure.

In this study, Raman spectroscopy was employed as a sensitive tool to monitor the atmospheric degradation of 1D NbS₂, leveraging its capability in layer-number and quality identification of TMDCs.^{23,24,29} To perform the time-dependent Raman measurements, a custom-designed gas exchange system was used. Building upon the Ar-filled Raman chamber employed for initial measurements, this system enabled controlled switching between Ar and ambient air by adjusting the gas valves. During Raman measurements, the initial Raman spectrum was acquired while the chamber was purged with Ar gas and maintained under continuous Ar flow. Subsequent air exposure intervals of 30 minutes were followed by Ar flushing and another Raman measurement. This cycle was repeated until a total exposure time of 180 minutes was reached. All spectra were collected from the exact sample location to ensure consistency. By comparing Raman spectra at different exposure times, the degradation behavior of NbS₂ with different morphologies was systematically evaluated.

Figure 3E presents a comparison of the Raman spectra of as-synthesized 1D NbS₂ nanotubes, suspended 2D NbS₂ flakes @ SWCNT-BNNT, and exfoliated 2D NbS₂ @ Si/SiO₂ substrate as a reference. The initial Raman peak position of exfoliated NbS₂ are 290.37 cm⁻¹ (E_{1g}), 320.7 cm⁻¹ (E_{2g}), 383.41 cm⁻¹ (A_{1g}), and 450.83 cm⁻¹ (A_{2g}). Figure 3B–D display the time-resolved Raman spectra for each sample type, recorded after stepwise air exposure. Spectra were collected at 30-minute intervals, allowing detailed tracking of time-dependent shifts in both peak positions and intensities. Among these NbS₂ Raman modes, the E_{2g} and A_{1g} modes were used as representative indicators to monitor the oxidation process, which are commonly applied in previous studies to estimate the layer number of 2D NbS₂ flakes.^{23,25}

The intensity decay of each Raman mode is summarized in Figure 3F, with initial intensities normalized to 100%. After 180 minutes of air exposure, the E_{2g} intensity of 1D NbS₂ decreased to 56.2%, and the A_{1g} intensity decreased to 74.5%. In contrast, the E_{2g} and A_{1g} intensities of suspended 2D NbS₂ decreased to 77.5% and 80.7% respectively. Exfoliated 2D NbS₂ flakes exhibited the smallest reduction, with both modes retaining approximately 90% of their initial intensities. These results highlight the faster degradation of 1D NbS₂ on SWCNT-BNNT compared to suspended 2D NbS₂ and exfoliated flakes. Notably, the E_{2g} mode in 1D NbS₂ exhibited a more pronounced intensity loss, which is likely due to the strain induced by the curvature of the nanotubes, a factor also known to cause downshifts in specific Raman modes of TMDCs.^{47,48}

The shifts in Raman peak positions for each sample are summarized in Figure 3G. Initially, the Raman peak positions of 1D, suspended 2D, and exfoliated NbS₂ exhibited distinct peak positions, with the SWCNT–BNNT–NbS₂ 1D vdW heterostructure showing a significantly different starting profile. After 180 minutes of air exposure, the E_{2g} peak of 1D NbS₂ @

SWCNT-BNNT upshifted from 337.73 cm^{-1} to 340.09 cm^{-1} , while the corresponding peak for suspended 2D NbS₂ @ SWCNT-BNNT downshifted from 342.89 cm^{-1} to 341.22 cm^{-1} . The A_{1g} peak for 1D NbS₂ upshifted from 377.88 cm^{-1} to 378.71 cm^{-1} , and that of suspended 2D NbS₂ @ SWCNT-BNNT downshifted from 378.02 cm^{-1} to 377.10 cm^{-1} . Compared to the E_{2g} mode, the A_{1g} mode exhibited less pronounced shifts in both structures. For 1D NbS₂ @ SWCNT-BNNT, the E_{2g} peak gradually approached the value of suspended 2D NbS₂ @ SWCNT-BNNT, suggesting partial strain release during oxidation. This trend can be attributed to the structural degradation of the tubal crystal structure, which reduced curvature-induced strain. Previous studies on 2D TMDCs, such as MoS₂ and WS₂, have shown that curvature strain primarily affects the E_{2g} mode, leading to downshifts under tensile strain.^{45,46} In the case of 1D NbS₂, the observed upshift of the E_{2g} mode thus implies that strain is relieved as the oxidation progresses. The final oxidation state of 1D NbS₂ may resemble fragmented 2D NbS₂ domains attached to the SWCNT-BNNT template. For suspended 2D NbS₂ @ SWCNT-BNNT, smaller peak shifts were observed. The nearly constant E_{2g}-A_{1g} peak separation (Δ) suggests negligible variations in layer thickness during oxidation, while the peak position shifts may indicate the oxidation-induced doping effects. Similar behavior was also observed in as-synthesized 2D NbS₂ flakes (Figure S6).

Based on the Raman intensity decay and peak position shifts, the oxidation behavior of as-synthesized NbS₂ vdW heterostructures was systematically investigated. The initial Raman features of suspended 2D NbS₂ @ SWCNT-BNNT showed good agreement with those of as-synthesized 2D NbS₂ flakes on Si/SiO₂ substrates (Figure S5, S6). The initial Raman peak positions of 1D NbS₂ @ SWCNT-BNNT differed notably from those of 2D NbS₂, which can be attributed to curvature-induced strain effects. This strain may also account for the faster Raman

intensity decay observed in 1D NbS₂ compared to its 2D counterparts. As oxidation progressed, the Raman spectra of 1D NbS₂ gradually approached those of 2D NbS₂, indicating a progressive strain release as the crystal structure degraded.

2.4 Bi-layer preference of NbS₂

Based on STEM/TEM results, a statistical analysis was conducted on a database of 207 individual NbS₂ nanotubes, revealing a predominant formation of double-walled nanotubes (DWNTs). Representative STEM/TEM images are shown in Figure S7. The statistical results are presented in Figure 4A, where the distribution of nanotube layer numbers is expressed by the total accumulated length per category, reflecting the relative abundance of each configuration. All nanotubes included in the analysis were synthesized using an identical CVD setup. This pronounced preference for double-walled configurations is noteworthy, suggesting an intrinsic stability or energetic favorability in NbS₂ vdW heterostructures that distinguishes it from other semiconducting TMDC 1D vdW heterostructures, which exhibit monolayer structural tendencies.^{12,16,17} The combination of structural characterization and statistical analysis underscores the need for deeper insight into the formation mechanism behind this double-walled preference.

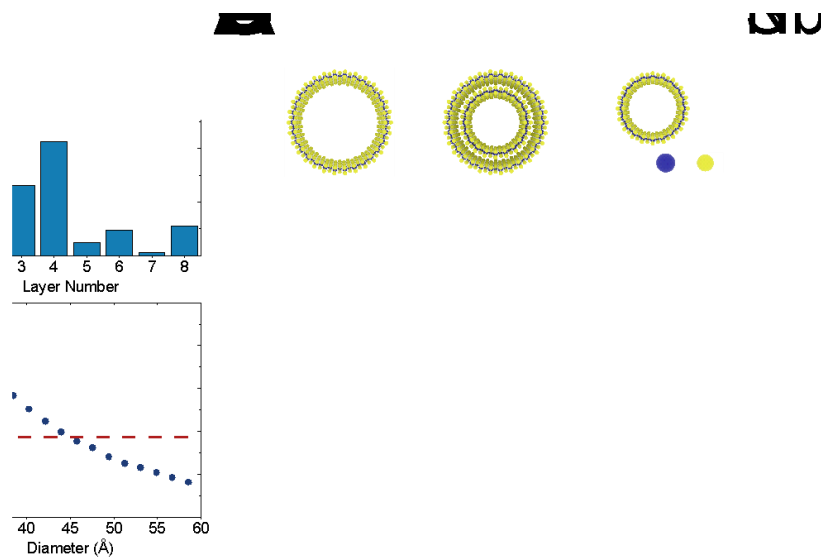


Figure 4. (A) Layer-number distribution of 207 NbS₂ nanotubes based on statistical analysis. (B) Total energy of NbS₂ nanotubes as a function of diameter, relative to that of an isolated monolayer NbS₂ sheet. The red dashed horizontal line indicates the total energy of the (20,20) @ (30,30) double-walled nanotube. (C) Electronic band structures near the Fermi level of (30,30), (20,20) @ (30,30), and (20,20) nanotubes. The energy scale is measured from the vacuum level. The red horizontal line in each panel marks the Fermi level energy. (D) DFT-calculated Fermi level energies of single-walled NbS₂ nanotubes as a function of diameter. The red dashed horizontal line indicates the Fermi level energy of the (20,20) @ (30,30) double-walled nanotube.

To explore the underlying mechanism behind this bi-layer preference, density functional theory (DFT) calculations were conducted on armchair-configured NbS₂ nanotubes with varying diameters. The total energy of a single-walled NbS₂ nanotube decreases with increasing diameter and asymptotically approaches the energy of an isolated flat NbS₂ sheet (Fig. 4B). To evaluate the energetic favorability of the double-walled configuration, we calculated the formation energy of a coaxially arranged (20,20) @ (30,30) double-walled NbS₂ nanotube. The calculated formation energy is -63 meV per unit length. This energy gain is ascribed to inter-wall Coulomb interactions, which arise from the charge transfer between inner and outer walls, as the orbital hybridization in the double-walled NbS₂ nanotubes is negligible at an inter-wall spacing of 0.61 nm. The electronic energy bands of (20,20)@(30,30), (20,20), and (30,30) nanotubes further support this charge transfer (Fig. 4C): The Fermi level energy of (20,20) nanotube is shallower than that of (30,30) nanotube, indicating a potential charge redistribution between the shells and subsequent Fermi level alignment during the formation of the double-walled structure. Indeed,

the Fermi level of a (20,20) @ (30,30) nanotube is located in the middle of those of (20,20) and (30,30) nanotubes. As shown in Figure 4D, the Fermi level energy of a single-walled NbS₂ nanotube shifts deeper (work function increases) with increasing diameter. This trend suggests that a double-walled NbS₂ nanotube comprising an appropriate pair of constituent nanotubes may be stabilized by the inter-wall Coulomb interactions arising from charge transfer between the nanotubes.

The DFT calculations provide a possible explanatory framework for the observed bilayer preference in NbS₂ nanotubes. This preference may originate from interactions between metallic layers. A simple model for the mechanical stability of multiwall systems, which takes into account charge transfer, elastic, and van der Waals interactions between walls, predicts charge transfer-induced asymmetries in the wall-to-wall distance distribution and interlayer Coulomb coupling, both of which should collectively stabilize the bilayer configuration. The full details of this model will be presented elsewhere. Investigations of bilayer 2D NbS₂ systems further underscore the intrinsic properties of NbS₂ that contribute to this bilayer preference. Although more detailed calculations, such as density of states, are currently limited by platform capabilities, the present DFT results offer valuable insights into the bilayer preference of NbS₂ nanotubes. These findings contribute to a deeper understanding of metallic nanotube growth via CVD and support the future development of metallic TMDC-based 1D vdW heterostructures.

3. Conclusion

In summary, we have demonstrated the experimental synthesis of NbS₂-based 1D vdW heterostructures. This study developed a modified NaCl-assisted CVD method, which is referred to as the “remote salt strategy”, to fabricate high-quality 1D metallic NbS₂ vdW heterostructures

on SWCNT–BNNT templates. Structural analysis using HRTEM and STEM confirmed the formation of crystalline, coaxial NbS₂ nanotubes with relatively high coverage over the templates. Moreover, the use of NaCl as an individually controlled parameter in this synthesis strategy enabled precise modulation of the final NbS₂ morphology, which could be tuned from coaxial 1D wrapping to suspended 2D flakes. Absorption spectroscopy revealed distinct optical features of NbS₂ compared to other TMDCs, notably the absence of visible-range band gap modes, indicating its metallic nature. Raman spectroscopy identified the characteristic Raman vibration modes of NbS₂ in both 1D and 2D NbS₂ @ SWCNT–BNNT configurations. The oxidation behavior of as-synthesized NbS₂ vdW heterostructures was systematically investigated via time-dependent Raman intensity decay and peak shifts. The 1D NbS₂ exhibited a distinct initial Raman peak position and a higher decay rate, which can be attributed to curvature-induced strain effects. Statistical analysis of STEM/TEM images of as-synthesized NbS₂ nanotubes revealed a bi-layer preference, contrasting with the monolayer-dominated tendencies of semiconducting TMDC nanotubes. DFT calculations further elucidated a lowered Fermi level in double-walled NbS₂ nanotubes compared to their single-walled counterparts, suggesting that interlayer charge transfer contributes to the energetic stabilization of the bi-layer configuration.

These findings provide critical insights into the synthesis and optical behavior of NbS₂, establishing a foundation for the development of more advanced vdW heterostructures and enabling their potential applications in optoelectronics, spintronics, and nanoscale devices.

Methods

Synthesis of NbS₂ based vdW heterostructures

The template SWCNT film used in this study was synthesized by the aerosol CVD method. Typically, ferrocene was used as the catalyst precursor, and CO was used as the carbon source.⁴⁹ The growth temperature was 880 °C. The SWCNTs were formed in the gas phase and collected onto a filter paper, forming SWCNT films for further synthesis. The SWCNT films used in this study exhibited a typical optical transmittance of 97.5%, ensuring low nanotube density for effective TEM and STEM characterization.

The SWCNT-BNNT structures were synthesized via a low-pressure CVD process, using ammonia borane (H_3NBH_3) as the precursor.³⁵ Approximately 38mg of ammonia borane was placed upstream in the reaction system. SWCNT films suspended on ceramic washers were placed at the center of the furnace to serve as templates for BNNT growth. The high-temperature CVD synthesis process was performed with the BN precursor heated to 70-90 °C, while the reaction temperature was maintained at 1150-1250 °C with a 300 sccm Ar/3% H_2 carrier gas flow. The reaction time served as the main parameter governing the number of BNNT layers. In this study, synthesis durations of 15 minutes to 1 hour typically resulted in BNNT coverage of 3–6 layers.

The SWCNT–BNNT– NbS_2 heterostructures were synthesized using the SWCNT–BNNT templates acquired in the previous steps. NbS_2 was synthesized via a low-pressure NaCl-assisted CVD process. Sulfur powder placed upstream served as the sulfur source, heated to 160–220 °C. NaCl, heated to 500–600 °C, acted as a promoter for NbS_2 formation. Nb powder served as the Nb source, and the SWCNT–BNNT films suspended over ceramic washers were directly placed over the Nb powder. The reaction temperature was maintained between 530–600 °C. During the synthesis, a 50 sccm Ar carrier gas was introduced into the chamber, and the pressure was maintained between 34–50 Pa throughout the entire synthesis process. The reaction time ranged

from 15 to 90 minutes, depending on the reaction temperature. By increasing the NaCl temperature, the NbS₂ morphology could be tuned from coaxial 1D nanotubes to suspended 2D flakes on the SWCNT–BNNT templates. After the synthesis, the samples were immediately transferred to a home-made Ar gas-filled chamber to prevent possible oxidation. The further preparation of TEM samples was performed in a glove box with a dry transfer method onto Si/SiO₂ TEM grids.²²

SEM and TEM Characterizations

The SEM images were obtained by Hitachi-4800, operating at an acceleration voltage of 1.0 kV.

The HRTEM images were acquired using a JEM-ARM200F operated at an acceleration voltage of 200kV. The STEM images were taken by a JEM-ARM200F ColdFE with an acceleration voltage of 80 and 200 kV. In this case, a near parallel beam is used together with a small convergence lens aperture (10 μm in diameter) to obtain a small-area electron beam size (~10 nm in diameter). Additionally, the samples were heated to 300 °C during the measurement to avoid carbon contamination using a heating holder (EM-31670SHTH) and a controller unit (EM-08170HCU). HAADF- and BF-STEM images, along with EDS mapping of SWCNT–BNNT–NbS₂ heterostructures were obtained in the same ARM STEM operating at 80 kV.

Spectroscopic Characterizations

UV-vis-NIR absorbance spectra were measured using a UV-vis-NIR spectrophotometer (Shimadzu UV-3150). The FT-IR spectra were acquired with a Fourier-transform infrared spectrophotometer (Shimadzu IRPrestige-21). Both measurements were performed directly on the

as-synthesized samples suspended on ceramic washers, without any transfer or post-treatment, to ensure that the optical response reflects the intact, free-standing membrane as formed.

Raman spectra were acquired using a Renishaw inVia Raman spectrometer equipped with 1800 and 2400 grooves/mm gratings. Excitation wavelengths of 488 nm and 532 nm were employed. All measurements were conducted in a backscattering geometry utilizing a 50 $\times$ long-working-distance objective lens (NA = 0.5). During the Raman measurement process, the samples were maintained under an Ar atmosphere using Linkam's CCR1000 stage, as shown in Figure S3. To avoid laser-induced heating of the heterostructures, the excitation laser power was set to less than 0.3 mW. For oxidation measurements, after each Raman acquisition, continuous ambient air would be introduced via a gas supplement system driven by a pump. After 30 minutes of air exposure, the chamber would be purged with Ar gas (3min at 150 sccm), followed by a continuous flow of 30 sccm during Raman acquisition. All Raman signals were collected at the same position on each sample.

DFT Calculations

The geometric and electronic structures of NbS₂ nanotubes were calculated using the density functional theory^{50,51} implemented in the STATE program package.⁵² The exchange-correlation potential energy between the interacting electrons was treated using the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional.⁵³ Interactions between valence electrons and nuclei were treated by the ultrasoft pseudopotentials.⁵⁴ The valence wave function and deficit charge density were expanded in terms of the plane-wave basis set with the cutoff energies of 25 and 225 Ry, respectively. Structural optimizations were carried out until the force acting on each atom is less than 1.33×10^{-3}

Hartree/bohr under the fixed lattice parameter $c = 0.332$ nm along the tube axis, which corresponds to the optimized lateral lattice parameter of an isolated monolayer NbS₂ sheet. To investigate the physical properties of an isolated nanotube, the nanotube was separated by 1 nm vacuum spacing from those in the adjacent imaging cells, excluding unintentional inter-tube interactions. The Brillouin zone integration was carried out with the use of 5 k points along the tube axis.

ASSOCIATED CONTENT

Supporting Information.

- S1. Low-magnification ADF imaging of SWCNT-BNNT-NbS₂ heterostructures and 2D NbS₂ flakes on SWCNT-BNNT template.
- S2. Elemental mapping of SWCNT-BNNT-NbS₂ heterostructures via EDS analysis.
- S3. Scheme of Raman measurement setup for NbS₂ heterostructures and comparison of Raman spectra results with/without Ar protection.
- S4. HAADF imaging and EDS mapping of SWCNT-BNNT-NbS₂ heterostructures under varying atmospheric exposure durations.
- S5. Liquid precursor-based synthesis process and layer statistics of 2D NbS₂ flakes.
- S6. Layer-dependent Raman peak shifts in synthesized 2D NbS₂ under argon-protected conditions.
- S7. Representative TEM/STEM images of NbS₂ nanotubes with labeled layer numbers.

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REFERENCES

1. Geim, A. K.; Grigorieva, I. V. Van der Waals Heterostructures. *Nature* **2013**, *499*, 419–425.
2. Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H. 2D Materials and van der Waals Heterostructures. *Science* **2016**, *353*, aac9439.
3. Withers, F.; Del Pozo–Zamudio, O.; Mishchenko, A.; Rooney, A. P.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S. J.; Geim, A. K.; Tartakovskii, A. I.; Novoselov, K. S. Light-emitting diodes by band-structure engineering in van der Waals heterostructures. *Nat. Mater.* **2015**, *14*, 301–306.
4. Zhou, Z.; Hou, F.; Huang, X.; Wang, G.; Fu, Z.; Liu, W.; Yuan, G.; Xi, X.; Xu, J.; Lin, J.; Gao, L. Stack Growth of Wafer-Scale van der Waals Superconductor Heterostructures. *Nature* **2023**, *621*, 499–505.
5. Li, J.; Yang, X.; Liu, Y.; Huang, B.; Wu, R.; Zhang, Z.; Zhao, B.; Ma, H.; Dang, W.; Wei, Z.; Wang, K.; Lin, Z.; Yan, X.; Sun, M.; Li, B.; Pan, X.; Luo, J.; Zhang, G.; Liu, Y.; Huang, Y.; Duan, X.; Duan, X. General Synthesis of Two-Dimensional van der Waals Heterostructure Arrays. *Nature* **2020**, *579*, 368–374.
6. Zhang, J.; Wang, J.; Chen, P.; Sun, Y.; Wu, S.; Jia, Z.; Lu, X.; Yu, H.; Chen, W.; Zhu, J.; Xie, G.; Yang, R.; Shi, D.; Xu, X.; Xiang, J.; Liu, K.; Zhang, G. Observation of strong interlayer coupling in MoS₂/WS₂ heterostructures. *Adv. Mater.* **2015**, *28*, 1950–1956.
7. Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. Polyhedral and Cylindrical Structures of Tungsten Disulphide. *Nature* **1992**, *360*, 444–446.

8. Schuffenhauer, C.; Popovitz-Biro, R.; Tenne, R. Synthesis of NbS₂ Nanoparticles with (Nested) Fullerene-like Structure (IF). *J. Mater. Chem.* **2002**, 12, 1587–1591.
9. Zhu, Y. Q.; Hsu, W. K.; Kroto, H. W.; Walton, D. R. M. An Alternative Route to NbS₂ Nanotubes. *J. Phys. Chem. B* **2002**, 106, 7623–7626.
10. Tenne, R.; Rao, C. N. R. Inorganic Nanotubes. *Philos. Trans. R. Soc. A* **2004**, 362, 2099-2125.
11. M. Remskar; A. Mrzel; A. Jesih; F. Lévy. Metal-Alloyed NbS₂ Nanotubes Synthesized by the Self-Assembly of Nanoparticles. *Adv. Mater.* **2002**, 14, 680–684.
12. Xiang, R.; Inoue, T.; Zheng, Y.; Kumamoto, A.; Qian, Y.; Sato, Y.; Liu, M.; Tang, D.; Gokhale, D.; Guo, J.; Hisama, K.; Yotsumoto, S.; Ogamoto, T.; Arai, H.; Kobayashi, Y.; Zhang, H.; Hou, B.; Anisimov, A.; Maruyama, M.; Miyata, Y.; Okada, S.; Chiashi, S.; Li, Y.; Kong, J.; Kauppinen, E. I.; Ikuhara, Y.; Suenaga, K.; Maruyama, S. One-dimensional van der Waals heterostructures. *Science* **2020**, 367, 537–542.
13. Liu, M.; Hisama, K.; Zheng, Y.; Maruyama, M.; Seo, S.; Anisimov, A.; Inoue, T.; Kauppinen, E. I.; Okada, S.; Chiashi, S.; Xiang, R.; Maruyama, S. Photoluminescence from Single-Walled MoS₂ Nanotubes Coaxially Grown on Boron Nitride Nanotubes. *ACS Nano* **2021**, 15, 8418–8426.
14. Burdanova, M. G.; Kashtiban, R. J.; Zheng, Y.; Xiang, R.; Chiashi, S.; Woolley, J. M.; Staniforth, M.; Sakamoto–Rablah, E.; Xie, X.; Broome, M.; Sloan, J.; Anisimov, A.; Kauppinen, E. I.; Maruyama, S.; Lloyd–Hughes, J. Ultrafast Optoelectronic Processes in 1D

- Radial van der Waals Heterostructures: Carbon, Boron Nitride, and MoS₂ Nanotubes with Coexisting Excitons and Highly Mobile Charges. *Nano Lett.* **2020**, *20*, 3560–3567.
15. Feng, Y.; Li, H.; Inoue, T.; Chiashi, S.; Rotkin, S. V.; Xiang, R.; Maruyama, S. One-Dimensional van der Waals Heterojunction Diode. *ACS Nano* **2021**, *15*, 5600–5609.
16. Cambré, S.; Liu, M.; Levshov, D.; Otsuka, K.; Maruyama, S.; Xiang, R. Nanotube-Based 1D Heterostructures Coupled by van der Waals Forces. *Small* **2021**, *17* (38).
17. Xiang, R.; Maruyama, S.; Li, Y. Building Blocks for One-Dimensional van der Waals Heterostructures. *Nat. Sci. Open* **2022**, *1*, 20220016.
18. Seifert, G.; Terrones, H.; Terrones, M.; Frauenheim, T. Novel NbS₂ Metallic Nanotubes. *Solid State Commun.* **2000**, *115* (12), 635–638.
19. Martino, E.; Putzke, C.; König, M.; Philip, Berger, H.; LeBoeuf, D.; Leroux, M.; Proust, C.; Akrap, A.; Kirmse, H.; Koch, C.; Zhang, S.; Wu, Q.; Yazyev, O. V.; László Forró; Semeniuk, K. Unidirectional Kondo Scattering in Layered NbS₂. *npj 2D Mater. Appl.* **2021**, *5*.
20. Wang, Z.; Cheon, C.-Y.; Tripathi, M.; Guilherme Migliato Marega; Zhao, Y.; Ji, H. G.; Macha, M.; Aleksandra Radenovic; Kis, A. Superconducting 2D NbS₂ Grown Epitaxially by Chemical Vapor Deposition. *ACS Nano* **2021**, *15*, 18403–18410.
21. I. Guillamon; H. Suderow; Vieira, S.; Cario, L.; Diener, P.; P. Rodiere. Superconducting Density of States and Vortex Cores of 2H-NbS₂. *Phys. Rev. Lett.* **2008**, *101*.
22. Zheng, Y.; Kumamoto, A.; Kaoru Hisama; Otsuka, K.; Wickerson, G.; Sato, Y.; Liu, M.; Inoue, T.; Shohei Chiashi; Dai Ming Tang; Zhang, Q.; Anisimov, A.; Kauppinen, E. I.; Li, Y.;

- Suenaga, K.; Yuichi Ikuhara; Maruyama, S.; Xiang, R. One-Dimensional van Der Waals Heterostructures: Growth Mechanism and Handedness Correlation Revealed by Nondestructive TEM. *Proc. Natl. Acad. Sci. U.S.A.* **2021**, *118*, 2107295118.
23. Fu, Q.; Wang, X.; Zhou, J.; Xia, J.; Zeng, Q.; Danhui Lv; Zhu, C.; Wang, X.; Shen, Y.; Li, X.; Hua, Y.; Liu, F.; Shen, Z.; Jin, C.; Liu, Z. One-Step Synthesis of Metal/Semiconductor Heterostructure NbS₂/MoS₂. *Chem. Mater.* **2018**, *30*, 4001–4007.
24. Wang, Z.; Cheon, C.-Y.; Tripathi, M.; Guilherme Migliato Marega; Zhao, Y.; Ji, H. G.; Macha, M.; Aleksandra Radenovic; Kis, A. Superconducting 2D NbS₂ Grown Epitaxially by Chemical Vapor Deposition. *ACS Nano* **2021**, *15*, 18403–18410.
25. Zhao, S.; Hotta, T.; Koretsune, T.; Watanabe, K.; Taniguchi, T.; Sugawara, K.; Takahashi, T.; Shinohara, H.; Kitaura, R. Two-Dimensional Metallic NbS₂ : Growth, Optical Identification and Transport Properties. *2D Mater.* **2016**, *3*, 025027.
26. Li, Z.; Yang, W.; Yaroslav Losovyj; Chen, J.; Xu, E.; Liu, H.; Madilynn Werbianskyj; Fertig, H. A.; Ye, X.; Zhang, S. Large-Size Niobium Disulfide Nanoflakes down to Bilayers Grown by Sulfurization. *Nano Res.* **2018**, *11* (11), 5978–5988.
27. Nagaoka, D. A.; Grasseschi, D.; Cadore, A. R.; Fonsaca, J. E. S.; Jawaaid, A. M.; Vaia, R. A.; De Matos, C. J. S. Redox Exfoliated NbS₂: Characterization, Stability, and Oxidation. *Phys. Chem. Chem. Phys.* **2023**, *25*, 9559–9568.
28. Yan, R.; Khalsa, G.; Schaefer, B. T.; Jarjour, A.; Rouvimov, S.; Nowack, K. C.; Xing, H. G.; Jena, D. Thickness Dependence of Superconductivity in Ultrathin NbS₂. *Appl. Phys. Express* **2019**, *12*, 023008.

29. Wang, B.; Luo, H.; Wang, X.; Wang, E.; Sun, Y.; Tsai, Y. -C.; Zhu, H.; Liu, P.; Jiang, K.; Liu, K. Bifunctional NbS₂-Based Asymmetric Heterostructure for Lateral and Vertical Electronic Devices. *ACS Nano* **2019**, *14*, 175–184.
30. Wang, S.; Levshov, D. I.; Otsuka, K.; Zhang, B.-W.; Zheng, Y.; Feng, Y.; Liu, M.; Kauppinen, E. I.; Xiang, R.; Chiashi, S.; Wenseleers, W.; Cambré, S.; Maruyama, S. Evaluating the efficiency of boron nitride coating in Single-Walled Carbon-Nanotube-Based 1D heterostructure films by optical spectroscopy. *ACS Nano* **2024**, *18*, 9917–9928.
31. Gao, M.; Zuo, J. M.; Twisten, R. D.; Petrov, I.; Nagahara, L. A.; Zhang, R. Structure determination of individual single-wall carbon nanotubes by nano area electron diffraction. *Appl. Phys. Lett.* **2003**, *82*, 2703–2705.
32. Zhou, J.; Lin, J.; Huang, X.; Zhou, Y.; Chen, Y.; Xia, J.; Wang, H.; Xie, Y.; Yu, H.; Lei, J.; Wu, D.; Liu, F.; Fu, Q.; Zeng, Q.; Hsu, C.-H.; Yang, C.; Lu, L.; Yu, T.; Shen, Z.; Lin, H.; Yakobson, B. I.; Liu, Q.; Suenaga, K.; Liu, G.; Liu, Z. A library of atomically thin metal chalcogenides. *Nature* **2018**, *556*, 355–359.
33. Lei, J.; Xie, Y.; Kutana, A.; Bets, K. V.; Yakobson, B. I. Salt-Assisted MoS₂ Growth: Molecular Mechanisms from the First Principles. *J. Am. Chem. Soc.* **2022**, *144*, 7497–7503.
34. Li, S.; Lin, Y.-C.; Zhao, W.; Wu, J.; Wang, Z.; Hu, Z.; Shen, Y.; Tang, D.-M.; Wang, J.; Zhang, Q.; Zhu, H.; Chu, L.; Zhao, W.; Liu, C.; Sun, Z.; Taniguchi, T.; Osada, M.; Chen, W.; Xu, Q.-H.; Wee, A. T. S.; Suenaga, K.; Ding, F.; Eda, G. Vapour–liquid–solid growth of monolayer MoS₂ nanoribbons. *Nat. Mater.* **2018**, *17*, 535–542.

35. Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From bulk to Monolayer MoS₂: Evolution of Raman Scattering. *Adv. Func. Mater.* **2012**, *22*, 1385–1390.
36. Zhou, K.-G.; Withers, F.; Cao, Y.; Hu, S.; Yu, G.; Casiraghi, C. Raman Modes of MoS₂ Used as Fingerprint of van der Waals Interactions in 2-D Crystal-Based Heterostructures. *ACS Nano* **2014**, *8*, 9914–9924.
37. Zhang, X.; Qiao, X.-F.; Shi, W.; Wu, J.-B.; Jiang, D.-S.; Tan, P.-H. Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material. *Chem. Soc. Rev.* **2015**, *44*, 2757–2785.
38. Benameur, M. M.; Radisavljevic, B.; Héron, J. S.; Sahoo, S.; Berger, H.; Kis, A. Visibility of Dichalcogenide Nanolayers. *Nanotechnology* **2011**, *22*, 125706.
39. Sun, X.; Shi, B.; Wang, H.; Lin, N.; Liu, S.; Yang, K.; Zhang, B.; He, J. Optical Properties of 2D 3R Phase Niobium Disulfide and Its Applications as a Saturable Absorber. *Adv. Opt. Mater.* **2019**, *8*, 1901181.
40. Jehng, J. M.; Wachs, I. E. Structural Chemistry and Raman Spectra of Niobium Oxides. *Chem. Mater.* **1991**, *3*, 100–107.
41. Miyata, Y.; Yanagi, K.; Maniwa, Y.; Kataura, H. Optical Evaluation of the Metal-to-Semiconductor Ratio of Single-Wall Carbon Nanotubes. *J. Phys. Chem. C* **2008**, *112*, 13187–13191.

42. Jiang, S.; Hou, P.-X.; Chen, M.-L.; Wang, B.-W.; Sun, D.-M.; Tang, D.-M.; Jin, Q.; Guo, Q.-X.; Zhang, D.-D.; Du, J.-H.; Tai, K.-P.; Tan, J.; Kauppinen, E. I.; Liu, C.; Cheng, H.-M. Ultrahigh-performance transparent conductive films of carbon-welded isolated single-wall carbon nanotubes. *Sci. Adv.* **2018**, *4*, eaap9264.
43. Chopra, N. G.; Luyken, R. J.; Cherrey, K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. Boron nitride nanotubes. *Science* **1995**, *269*, 966–967.
44. Lee, C. H.; Wang, J.; Kayatsha, V. K.; Huang, J. Y.; Yap, Y. K. Effective growth of boron nitride nanotubes by thermal chemical vapor deposition. *Nanotechnology* **2008**, *19*, 455605–455605.
45. Wang, Y.; Cong, C.; Qiu, C.; Yu, T. Raman Spectroscopy Study of Lattice Vibration and Crystallographic Orientation of Monolayer MoS₂ under Uniaxial Strain. *Small* **2013**, *9*, 2857–2861.
46. Dadgar, A. M.; Scullion, D.; Kang, K.; Esposito, D.; Yang, E. H.; Herman, I. P.; Pimenta, M. A.; Santos, E. -j. G.; Pasupathy, A. N. Strain Engineering and Raman Spectroscopy of Monolayer Transition Metal Dichalcogenides. *Chem. Mater.* **2018**, *30*, 5148–5155.
47. Liu, Z.; Amani, M.; Najmaei, S.; Xu, Q.; Zou, X.; Zhou, W.; Yu, T.; Qiu, C.; Birdwell, A. G.; Crowne, F. J.; Vajtai, R.; Yakobson, B. I.; Xia, Z.; Dubey, M.; Ajayan, P. M.; Lou, J. Strain and structure heterogeneity in MoS₂ atomic layers grown by chemical vapour deposition. *Nat. Commun.* **2014**, *5*, 5246.
48. Longo, R. C.; Addou, R.; Kc, S.; Noh, J.-Y.; Smyth, C. M.; Barrera, D.; Zhang, C.; Hsu, J. W. P.; Wallace, R. M.; Cho, K. Intrinsic air stability mechanisms of two-dimensional

transition metal dichalcogenide surfaces: basal versus edge oxidation. *2D Mater.* **2017**, *4*, 025050.

49. Kaskela, A.; Nasibulin, A. G.; Timmermans, M. Y.; Aitchison, B.; Papadimitratos, A.; Tian, Y.; Zhu, Z.; Jiang, H.; Brown, D. P.; Zakhidov, A.; Kauppinen, E. I. Aerosol-Synthesized SWCNT Networks with Tunable Conductivity and Transparency by a Dry Transfer Technique. *Nano Lett.* **2010**, *10*, 4349–4355.
50. Hohenberg, P.; Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* **1964**, *136*, B864–B871.
51. Kohn, W.; Sham, L. J. Self-Consistent equations including exchange and correlation effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.
52. Morikawa, Y.; Iwata, K.; Terakura, K. Theoretical study of hydrogenation process of formate on clean and Zn deposited Cu(1 1 1) surfaces. *Appl. Surf. Sci.* **2001**, *169–170*, 11–15.
53. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
54. Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* **1990**, *41*, 7892–7895.