

One-Dimensional van der Waals Heterostructures: A Perspective

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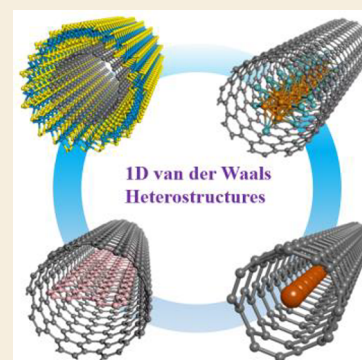


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ABSTRACT: As a new frontier in low-dimensional material research, van der Waals (vdW) heterostructures, represented by 2D heterostructures, have attracted tremendous attention due to their unique properties and potential applications. The emerging 1D heterostructures open new possibilities for the field with expectant unconventional properties and yet more challenging preparation pathways. This Perspective aims to give an overall understanding of the state-of-the-art growth strategies and fantastic properties of the 1D heterostructures and provide an outlook for further development based on the controlled preparation, which will bring up a variety of applications in high-performance electronic, optoelectronic, magnetic, and energy storage devices. A quick rise of the fundamentals and application study of 1D heterostructures is anticipated.



KEYWORDS: one-dimensional van der Waals heterostructures, chemical vapor deposition, properties

INTRODUCTION

van der Waals (vdW) heterostructures composed of stacked atomically thin two-dimensional (2D) materials have generated great interest owing to their novel and fascinating properties such as gate tunability, valley effects, and moiré physics as well as the potential applications in the electronic and optoelectronic devices.^{1,2} The integration of both structural and electronic variety in vdW layered materials exceeds the restriction of lattice symmetry and lattice constants and does not rely on chemical bonds. In principle, the bond-free integration strategy can be extended beyond 2D materials and create a sequence of artificial heterostructures and superlattices with dangling-bond-free surfaces and electronically sharp interfaces.^{3,4} For instance, the one-dimensional (1D) vdW heterostructures coaxially stacking different kinds of 1D counterparts in a chosen sequence (Figure 1) open up an entirely new realm and provide a distinctive platform for fundamental scientific studies and applications.^{5,6} Compared with 2D vdW heterostructures, 1D vdW heterostructures exhibit a high aspect ratio associated with the highly constrained radial size. The resulting quantum confinement effects boost intriguing 1D physics in heterostructure properties such as electron or photon transport along the radial direction. Besides, the curvature of noncovalent bonding heterointerfaces leads to a strong light–matter interaction, which may be used to build new 1D devices.⁷ However, the preparation of high-quality 1D vdW heterostructures is still at its humble beginnings.

In this Perspective, we start with the fundamental concepts of the 1D vdW heterostructures and the current 1D building blocks. Next, we outline the early efforts to synthesize state-of-

the-art 1D vdW heterostructures and then discuss potential opportunities and challenges arising in the synthesis strategies to achieve well-crystallized structures of large-area uniformity, controllable layer thickness, high purity, and low defects with a considerable yield and growth rate. Further, we summarize the electronic, optical, and thermal properties of a 1D vdW heterostructure and discuss the future directions and applications based on high-quality growth, dispersion, and transfer. Overall, we hope to highlight the arising 1D heterostructure family that can impart coaxial freedom to integrate distinct materials beyond the limits of traditional synthesis approaches, opening up new opportunities for fundamental studies and enabling unprecedented physical and chemical properties beyond the existing materials.

DEFINITION AND TYPES OF ONE-DIMENSIONAL VAN DER WAALS HETEROSTRUCTURES

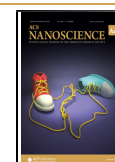
It is instructive to review the existing library of 1D crystal nanotubes before explaining how to define and classify 1D vdW heterostructures. Building blocks of 1D vdW heterostructures comprise various kinds of nanotubes, covering a very broad range of intrinsic properties. These individual nanotube components should survive ambient conditions without

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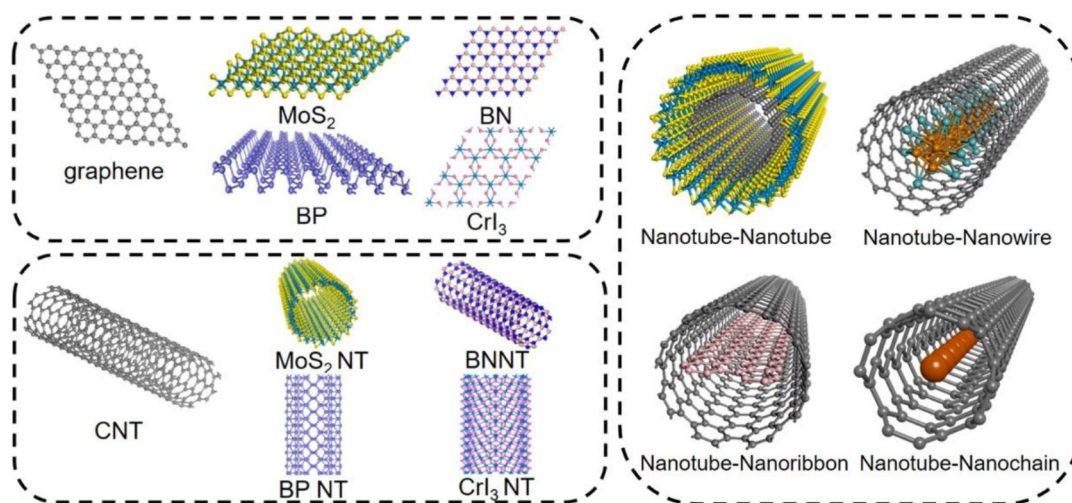


Figure 1. Schematic illustrations of prototypical 1D and 2D materials and one-dimensional van der Waals (vdW) heterostructures including nanotube–nanotube, nanotube–nanowire, nanotube–nanoribbon, and nanotube–chain.

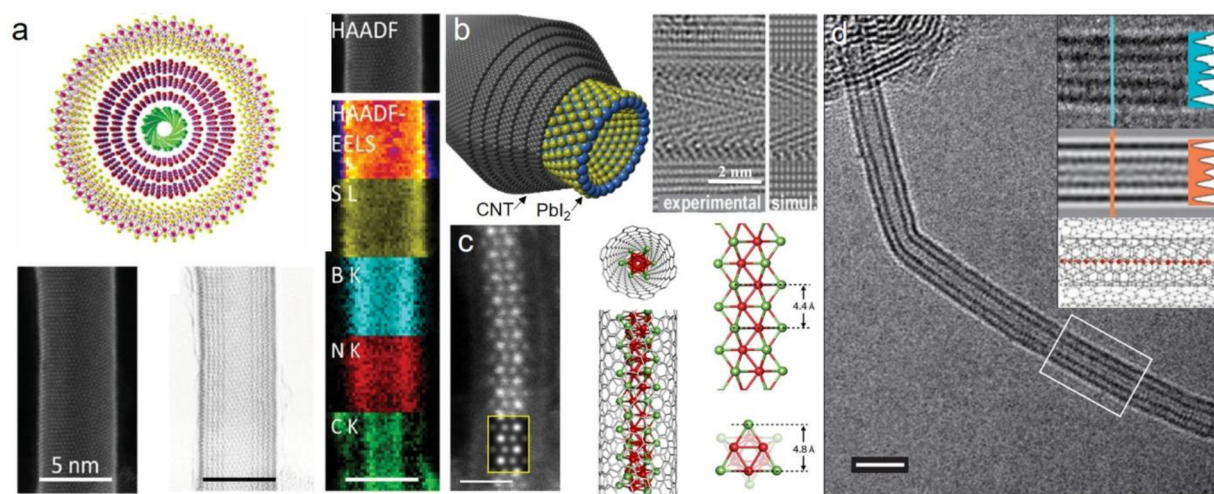


Figure 2. Multiple one-dimensional vdW heterostructures. (a) Ternary SWCNT–BNNT–MoS₂ nanotube vdW heterostructure. Reproduced with permission from ref 5. Copyright 2020 The Authors. (b) Single-layered PbI₂ nanotubes encapsulated within CNTs. Reproduced from with permission from ref 15. Copyright 2013 Wiley-VCH. (c) Arrangement of MoTe nanowires inside a CNT. Reproduced from ref 16. Copyright 2019 American Chemical Society. (d) An ultralong linear carbon chain enclosed in a double-walled CNT. Reproduced from with permission from ref 17. Copyright 2016 Springer Nature.

hybridization, corrosion, decomposition, and segregation. The most involved one-dimensional material is the carbon nanotube (CNT).⁸ The CNT has emerged as one of the most promising materials with a hollow structure, a dangling-bond-free surface, and sp² carbon atoms with hexagonal arrangements, which are described by a pair of chiral indices. A single-walled CNT (SWCNT) can be viewed as a cylinder rolled up from monolayer graphene following a chiral vector, whose electronic structure is classified into semiconducting and metallic. A multiwalled CNT (MWCNT) consists of several concentric cylinders held together by a vdW interaction, generally exhibiting metallic properties. In MWCNTs, a relative freedom in a rotational disorder between neighboring carbon shells allows assembly of a wide variety of helicities. Another representative example is a boron nitride nanotube (BNNT),⁹ where carbon atoms are fully substituted by nitrogen and boron atoms. It is a very close analogue of the CNT in structure, presenting excellent chemical and thermal

stability, thermal conductivity, and mechanical robustness. However, BNNTs are electrically insulating with a bandgap of ~6 eV. In contrast to multiwalled CNTs, of which the outer layer helical angle is hardly related with the inner layer, the arrangement of walls in a multiwalled BNNT is governed by the strong tendency to have the atomically perfect B–N-stacked consecutive layers, leading to grouped selective helical angles within a tube.⁹

Transition-metal dichalcogenide (TMD) compounds, which are combined by groups IV, V, VI, VII, IX, or X transition metals and chalcogens (S, Se, or Te), can also present 2D layered or 1D tubular structures.¹⁰ Such TMD nanotubes possess a wide spectrum of electronic properties acting as metals, semimetals, semiconductors with various bandgaps, or insulators. In parallel with the rapid development of research on CNTs in the 1990s, Tenne and other researchers made great efforts on inorganic nanotubes, which were commenced with the discovery of multiwalled WS₂ and MoS₂ nano-

tubes.^{11,12} From theoretical calculations, the electronic properties of single-walled WS₂ NTs mainly depend on their chirality. Multiwalled WS₂ NTs are exclusively semiconductors with a well-defined bandgap, depending on their diameters. WS₂ nanotubes exhibit excellent optoelectrical properties such as a bulk photovoltaic effect, which is greatly enhanced by reducing the crystal symmetry and inducing a polar crystal structure.¹³ Compared to WS₂ nanotubes, MoS₂ nanotubes are expected to show higher mechanical strength and stronger light emission, which gives a strong stimulus to develop elaborate synthetic strategies.¹⁴

One-dimensional crystalline nanotubes can be coaxially assembled into heterostructures, where the individual nanotubes are held together by vdW forces. Considering that many nanotubes with various compositions and structures currently available, it should be possible to create a substantial variety of 1D heterostructures with different combinations. The assembly strategy currently in use is templated layer-by-layer synthesis. Based on the primary nanotube template, there are two different routes: vdW epitaxy on the surface (Figure 2a) and encapsulation inside the nanotubes (Figure 2b). The former one requires the host nanotube to have a clean surface facilitating the templated growth of a guest nanotube.¹⁸ The latter one needs to first open the ends of the nanotube template and then introduce the precursors of the filler into the cavity to form a tubular structure. As a further step toward expanding the 1D heterostructure library, multiple vdW heterostructures composed of more than two kinds of nanotubes can be constructed.⁵ This approach can lead to a higher integration of different 1D components with well-designed properties.

The preparation of CNTs filled with foreign nanowires with a very narrow diameter and high aspect ratio has been reported.^{19–21} The long and continuous nanowires of nitrides,²² carbides,²³ halides,²⁴ and sulfides²⁵ have been prepared. With the encapsulation in CNTs, which have mechanical stability and electronic activity, the nanowires of chemically active materials may encounter a rearrangement of the crystal structure along with the passivation of dangling bonds, resulting in a unique crystal phase and properties.²⁶ The optical and transport properties of host nanotubes can also be modulated by the charge transfer and other interactions with the filled nanowires.^{27,28} For example, transition-metal monochalcogenide MoTe nanowires were synthesized by using CNTs as molds as shown in Figure 2c.¹⁴ CNTs can also be used as a one-dimensional chemical reactor for the formation of nanoribbons such as graphene and MoS₂.^{29,30} Interestingly, the graphene nanoribbon enclosed into the CNT display a helical configuration under the vdW potential well and the π - π stacking interaction. The templated synthesis process needs the involvement of suitable carbon precursors to transform into the sp²-hybridized carbon allotrope and additive atoms like sulfur to terminate the edges, further determining the metallic or semiconducting properties of the obtained graphene nanoribbon.

Besides, various endohedral linear chains such as sulfur chain, carbon chain, phosphorus chain, and tellurium chain, etc., can also be prepared within the inner cavities of CNTs.^{17,31–33} However, the study on the property of the inner linear chains is restricted by their short length. A breakthrough in this field is attributed to the synthesis of ultralong linear carbon chains with up to 6000 contiguous carbon atoms arranged in the core space of double-walled

CNTs synthesized at high temperature and high vacuum in an annealing process (Figure 2d).³² The inner diameter and chirality of the nanotube template handle the fine-tuning of optical and vibrational properties of the encapsulated chains. The carbon chains can be further extracted and separated from the inner cavities of CNTs by applying a combined tip ultrasonication and density gradient ultracentrifugation process.³⁴ It is worth noting that theoretical calculation predicted that the high-density hydrogen confined in a (8,0) SWNT under a pressure of 163.5 GPa becomes metallic and superconductive.³⁵ Meanwhile, water confined inside SWNTs is expected to exhibit at least nine different ice phases depending on the diameter of the tubes and the temperature.³⁶

■ PREPARATION OF ONE-DIMENSIONAL VAN DER WAALS HETEROSTRUCTURES

Synthesis and assembly of vdW heterostructures for 2D materials in desired stacking order follow the top-down and bottom-up strategies. Especially, the alignment transfer method has been widely used for creating complex heterostructures.³⁷ However, to form 1D vdW heterostructures, a class of nanotubes or nanotubes and other 1D nanomaterials needs to be coaxially stacked. It is much more difficult to realize via physical routes. A feasible strategy is to directly grow heterostructures by using nanotubes as templates through either coating or filling processes.

Several methods, which can be used to directly synthesize 1D vdW heterostructures, are shown in Figure 3. A wet

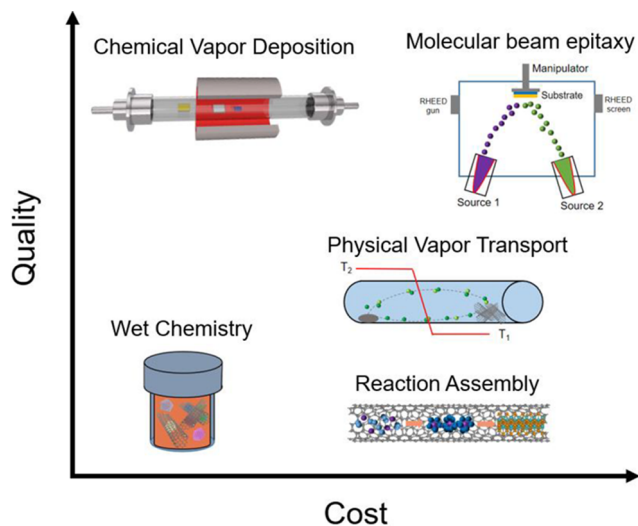


Figure 3. Comparison of the current experimental methods for preparing one-dimensional vdW heterostructures in terms of quality and cost.

chemistry pathway and vapor phase growth are commonly adopted methods for preparing 1D vdW heterostructures. Early efforts to coat or fill nanotube templates with heteromaterials focused on the wet chemistry method.^{38,39} For example, Wang and co-workers use CNTs as a template to grow multiwalled MoS₂ sheets around every individual CNT in a conformal way by the solvothermal method.⁴⁰ However, the grown layers on the existing templates are typically amorphous, disordered, or polycrystalline, and the resultant heterostructure interfaces are usually plagued by unavoidable reaction-induced defects and rich chemical disorders that dictate the interface

properties, which are known to play a critical role in the extensive decline of device properties. In addition, it is difficult to control the number of layers and uniformity using this technique. On the other hand, the vapor-phase-based direct growth approaches, especially chemical vapor deposition (CVD), provide a scalable and controllable way to grow high-quality 1D heterostructures.

The layer-by-layer growth of 1D vdW heterostructures on the outer surface of primary nanotubes includes three steps: (I) the precursors first nucleate on the template, (II) active species are continuously added to the edge of the outer nanotubes, and (III) extended conformal growth to increase the length. As a landmark example, Xiang et al. reported the ternary 1D vdW heterostructures of SWCNT@BNNT@MoS₂NT with single crystallinity, which consists of a core SWCNT, a middle three walls of BNNTs, and an outer single layer of a MoS₂ NT using a noncatalytic CVD process.⁵

There are a few important issues for using CNTs as the templates for growing heterogeneous nanotubes on the outer surfaces. First, the appropriate assembly morphology of CNTs is essential for obtaining high-quality 1D vdW heterostructures. Due to their great flexibility and high surface energy, CNTs tend to aggregate into large bundles, making it difficult to act as ideal templates. This is a serious hurdle in the synthesis of 1D heterostructures. Therefore, CNT assemblies of non-bundled CNTs are preferred, for example, the horizontally aligned arrays.^{41,42} The self-supporting SWCNT networks prepared from the floating catalytic CVD can also be a choice, because part of the tubes is not bundled.⁴³ Second, surface cleanness of the host CNTs is another key issue for the growth of outside nanotubes to form high-quality 1D vdW heterostructures.¹⁸ The contaminations on the surface of the nanotubes can be categorized as⁴⁴ (1) the amorphous carbon formed during the CVD growth of CNTs; (2) the polymer and other residues from the dispersion process; (3) the airborne contaminants. The formation of intrinsic contamination during the CVD process can be suppressed by introducing etching gas treatment during the growth process. Other postgrowth treatments including the annealing and plasma etching can also be used to remove the surface contaminations. Third, the CNTs need to have appropriate diameters. When the inorganic compound with a layered structure folds into a nanotube, it is inevitably strained. For a single-walled TMD nanotube with three atomic layers, reducing the diameter beyond a critical size will result in a sharp increase of the strain energy,⁴⁵ consequently, TMD nanotubes normally present larger diameters than SWCNTs.⁵ Therefore, an adequate diameter of the CNTs is an essential factor to construct coaxial heterostructures with TMD nanotubes.

The 1D vdW heterostructures can also be made by filling the inner cavity of nanotubes. The cavities of nanotubes, especially CNTs, being mechanically stable conductors, can serve as powerful protecting layers of the inner guest materials against oxidation. On the other hand, the guest fillers can strengthen and dope the CNTs. The ends of CNTs need to be opened before the filling procedure. Under some harsh conditions such as arc discharge, the filling can be done simultaneously with the formation of CNTs, resulting in filled CNTs with ends closed at both sides.⁴⁶ Besides the cavity diameter of nanotubes, the physical properties of the filler materials such as the melting point, boiling point, solubility, and decomposition temperature are also very important for the successful filling. Meanwhile, the redox potential, surface tension, and viscosity of the liquid

fillers are presumably significant for the capillarity/wetting-driven filling process.⁴⁷ Using a physical vapor transport (PVT) technique, Qin et al. synthesized Te nanowires down to a single atomic chain or a few chains limited by the sizes of the cavities of CNTs and BNNTs,³³ respectively. Nakanishi et al. used ammonia borane complexes as a precursor to synthesize single-walled BNNTs inside the SWCNTs.⁴⁸ In some cases, CNTs can donate electrons to activate the reactants, leading to a series of reactions inside the tubes. A new polymeric phase of molybdenum iodide [Mo₆I₁₂]_n and nanoribbons of molybdenum/tungsten disulfide [MS₂]_n were so prepared within CNTs.⁴⁹

In general, 1D vdW heterostructures have been prepared by bottom-up growth methods including wet chemical pathways, CVD, PVD, and PVT, etc. CVD-based vapor phase growth methods are powerful in preparing high-quality 1D materials with scale-up capability. They can offer special freedom for rational design and careful tuning of the growth process to control the morphology, phase, interfaces, and crystallinity. Therefore, it is important to find out the general parameters that affect mass transport, interface reactions, and the nucleation and growth of the heterostructures. It is worth noting that MBE method has the potential to achieve better layer control, high purity, and high uniformity of single-crystal 1D vdW heterostructures.

Intrinsic disorder arising from crystalline imperfections from the synthesis process have negative effects on electrical, thermal, and mechanical properties of 1D heterostructures.⁵⁰ For example, grain boundaries and defects cause the carrier scattering, which seriously impairs the mobility. To achieve the growth of heterostructures with high crystallinity, a general strategy is to decrease the nucleation density. Though the nucleation and growth mechanism of guest nanotubes on the surface of CNTs is still not very clear, we can imagine that defects will be introduced when two domains extend to merge along the tube axis. Using the *ex situ* TEM approach, the growth processes of BNNTs on SWCNT templates are investigated.¹⁸ Another promising strategy of increasing crystal size is to maintain the reaction activity for the 1D material growth over a long time. For this purpose, introducing catalysts or additives to decrease the energy barrier for the surface reaction should be effective.

In 2D vdW heterojunctions, the important properties such as bandgap are tunable by controlling the number of layers and the twisted angle between layers.⁵¹ Therefore, precisely tunable wall numbers and the twisted angles between stacked walls achieved by CVD growth are desirable for manipulating the properties of 1D vdW heterostructures. The growth conditions such as the concentrations of precursors, temperature, and pressure may influence the wall numbers of the resultant heterojunctions. The rational tuning of the twist angle during the synthesis process is still very challenging.

At present, the formation of outer or inner 1D materials on or in the nanotube template is rather inefficient due to lack of a catalyst and limited feeding of precursors from the gas phase. According to the experimental results, the growth rate of hexagonal BN nanotubes on the CNT is about 10 nm/min.⁵² The filling of most 1D nanocrystal materials enclosed into the nanotubes needs long-time reactions. Therefore, improvement of the growth kinetics is essential for realizing the final goal of ultralong and perfect 1D heterostructures. On the other hand, the CVD approach holds appealing potentials in the mass production of a 1D heterostructure with an excellent balance of

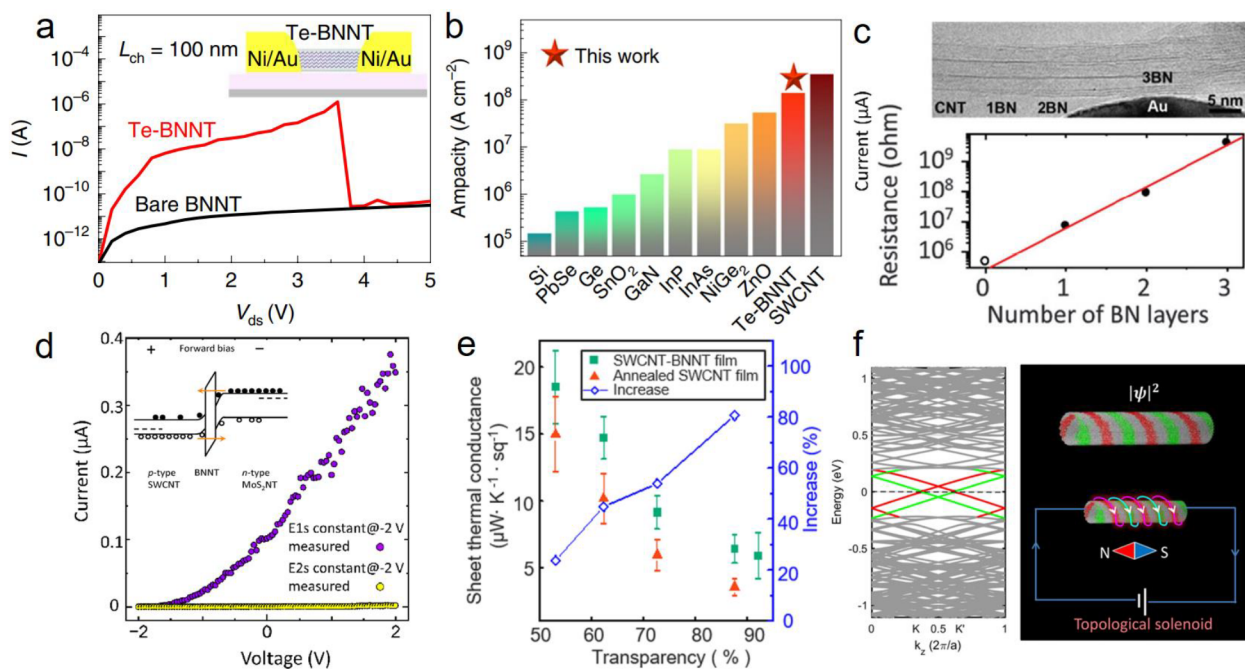


Figure 4. Properties of one-dimensional vdW heterostructures. (a) I - V curves of Te NWs encapsulated in BNNTs with a 100 nm channel length compared with the empty BNNT device with the same configuration. Reproduced with permission from ref 33. Copyright 2020 The Authors. (b) Comparison of the ampacity of Te NW-BNNTs and other semiconductor NWs. Reproduced with permission from ref 33. Copyright 2020 The Authors. (c) TEM images of SWCNT-BNNT heterostructures and resistance versus zero, one, two, and three layers of BNNTs. Reproduced with permission from ref 5. Copyright 2020 The Authors. (d) Electrical characteristic of an SWCNT-BNNT-MoS₂ nanotube vdW heterojunction diode. The inset is the corresponding energy band diagram. Reproduced from ref 53. Copyright 2021 American Chemical Society. (e) Comparison of sheet thermal conductance with SWCNT-BNNT films and annealed SWCNT films. Reproduced from ref 54. Copyright 2020 American Chemical Society. (f) Band structure of the spiral topological 1D heterostructures composed of a coaxial CNT inside BNNT and schematic demonstration of a topological solenoid or nanomagnet. Reproduced from ref 55. Copyright 2019 American Chemical Society.

quality, controllability, cost, and scalability. However, there are still some key issues to be resolved before the real production, such as the uniformity and yield of coating or filling materials.

■ PROPERTIES OF 1D VDW HETEROSTRUCTURES

With the developing availability of numerous 1D materials, it is prospective to combine different counterparts into heterostructures by the template-assisted growth method. Integrating 1D crystals with different properties can produce vdW-bonded stacks with novel functionalities, which open up a new dimension for engineering the electronic, optical, thermal, and magnetic properties of 1D materials at the atomic level.

Electronic and Optoelectronic Property

The internal encapsulation and external coating at the nanoscale allow tuning the properties of both guest species and the host nanotubes. Guest species can undergo modifications of their space configuration, crystalline structure, or the atomic ratio of their constituting elements, while the hosts' electronic and optical properties will also be modulated by the interaction between the foreign material and the walls of the nanotubes.

The early study of filling with iodine nanowires into CNTs reveals that the electric resistance of the nanotubes decreases dramatically, and Raman spectroscopy evidences the charge transfer of CNTs due to the doping effect.⁵⁶ Another pioneering effort in creating a helical single-atomic tellurium chain shielded in BNNTs shows that a Te-BNNT heterostructure has a high current-carrying capacity up to 1.5×10^8 A·cm⁻², which is only slightly smaller than the value for semiconducting SWCNTs (Figure 4a,b). Besides, Raman

spectroscopic study suggests that the interchain interaction becomes stronger as the number of chains increases.³³

MWCNTs filled with concentric single layers of PbI₂ nanotubes show a higher conductivity than either bulk PbI₂ or empty MWCNTs.⁵⁷ Moreover, this structure holds optical activity, and the current flowing through the material considerably increases upon illumination, accounting for significant carrier photogeneration processes. The back-gated field-effect transistor based on a SWCNT-BNNT heterostructure had an on/off ratio of 10⁵, which compares favorably with a high-quality SWCNT device.⁵ In this device, an outer BNNT is believed to minimize substrate effects, reduce charge scattering, and protect the SWCNT from environmental influences. Current-voltage curves of the SWCNT-BNNT measured in a TEM equipped with two probes reveal an exponential increase of the zero-bias resistance with the layer number, suggesting a direct tunneling effect (Figure 4c). A strong rectifying effect is measured in a radial semiconductor-insulator-semiconductor heterojunction composed of a semiconducting SWCNT, an insulating BNNT, and a semiconducting MoS₂ nanotube. The performance of such a radial device surpasses a similar planar heterojunction diode, and the middle insulating BNNT layer, serving as a tunneling medium, improves the ON and OFF current of diode and its rectification ratio as shown in Figure 4d.⁵³

Similar to a 2D heterostructure, moiré patterns, caused by lattice parameter mismatch and orientation misalignment, can appear in coaxial nanotube or nanocrystalline structures, and have the potential ability to modulate periodic potentials. Moiré bands become flat at some discrete angles, resulting in

unique behaviors such as high-temperature superconductivity, superfluidity, and magnetism.⁵⁸ Interestingly, spiral topological heterostructures composed of a CNT inside a BNNT, where topological current flows spirally around the tube, function as nanoscale solenoids to induce remarkable magnetic fields due to the dense moiré nanopatterning (Figure 4f).⁵⁵ 1D vdW heterostructures may serve as an outstanding new component for photovoltaic devices. On one hand, electronic band alignment can be achieved by assembling diverse matched 1D counterparts. On the other hand, flexoelectric polarization from a strain gradient caused by tube curvature and a voltage shift inside the tube enable to change the offset of electron energy bands to a type II junction, which facilitates the charge separation under light and promotes electrical current generation.⁷

Thermal Property

Among different 1D materials, CNTs and BNNTs are outstanding candidates for a thermal interface material and exhibit superior thermal conductivity.^{8,9} In addition, BNNTs hold high thermal and chemical stability and can serve as protecting layers. The combination of 1D building blocks with an excellent thermal property also provides a chance to understand the underlying mechanisms for heat conduction across the heterogeneous curved interface and along the tube. Experimental and theoretical results show that the sheet thermal conductance of SWCNT films coaxially coating BNNTs is enhanced clearly over annealed SWCNT films, as BNNTs act as additional thermal transport channels as shown in Figure 4e.^{54,59} Besides, the film of SWCNT–BNNT heterostructures features higher thermal stability. The thermal oxidation of the SWCNTs inside BNNTs started at 700 °C in air, whereas that of bare SWCNTs started at about 400 °C.⁵ Ultralow thermal conductivity and high electric conductivity are predicted in monolayer black phosphorus for the reason that the prominent electric and thermal conducting directions are orthogonal to each other. Besides, its bandgap shows a strain dependence.⁶⁰ Therefore, we can expect that a black phosphorus nanotube or nanoribbon encapsulated and stabilized in a protective nanotube can show promising performance for thermoelectric devices with a high figure of merit *ZT* value.

Magnetic Properties

Early studies show an enhanced coercivity for CNTs filled with magnetic nanowires such as Fe, Co, Ni, and their alloy.⁶¹ Another significant property is their magnetic anisotropy, which is attributed to the high aspect ratio (shape anisotropy) of the filled nanowires. In addition, reversal switching of the magnetization direction can be achieved by applying a bias voltage between confined nanomagnets and the tip, which is likely useful in magnetic storage and spintronic devices.

Recently, a large number of 2D magnetic polarized materials emerge with inversion asymmetry factors and modulated degrees of freedom, including ferromagnetic, antiferromagnetic, and multiferroic materials. They have demonstrated fascinating quantum behaviors and were used to construct various devices involving spintronic devices, memories, and sensors.⁶² The representative family includes CrI₃, FeS₂, and MnBi₂Te₄. One may fold these monolayer sheets into nanotubes while preserving their magnetic orders, generating 1D vdW magnetic materials and heterostructures. These 1D magnetic materials may provide a fancy platform to study the interactions at the heterointerfaces such as the proximity effect.

Meanwhile, the external strain, intrinsic chirality, and diameter dependence endow new dimensions to flexibly vary the structural, energetic, and electronic properties.

In addition, modifying the interlayer spacing of 1D vdW heterostructures can boost electron and ion transport and reduce the reaction barrier, which optimizes the interfacial properties and leads to improved performance for electrochemical and energy storage devices.⁶³ Besides, structural superlubricity has been confirmed in double-walled CNTs where intershell friction is lower than 1 nN and independent of nanotube length.⁶⁴ For 2D heterostructures like graphene and hexagonal boron nitride, ultralow sliding friction and frictional anisotropy are observed between these two incommensurate heterojunctions,⁶⁵ which bring inspiration for research interest in 1D heterostructures.

CONCLUSION AND PROSPECTS

Nanotubes can serve as initial templates to integrate other 1D crystalline materials such as nanowires, nanoribbons, linear chains, and nanotubes to form 1D vdW heterostructures by either filling or coating processes. 1D vdW heterostructures offer a novel platform to research and modulate, in the confined 1D space, the formation, relaxation, and transfer of electrons, phonons, and excitons. It is predictable that 1D vdW heterostructures would represent the new frontier of materials research in the near future.^{6,52,66}

Currently, the highly efficient production of long-continuous crystal 1D vdW heterostructures with good uniformity and low cost is essential for property study but remains challenging. Based on the template-assisted growth method, the synthesis of high-quality 1D vdW heterostructures can be realized by following the basic strategy: (1) Choose a starting nanotube with a proper diameter, good isolation, and clean surface. (2) Search for a suitable growth window, optimize the key parameters for mass and thermal transport, and pay attention to phase, doping, and defect control. However, future improvement may be needed to (3) further increase the growth rate and yield as current experimental results hardly meet the requirement of application and (4) develop artificial-intelligence-assisted computations to discover and predict the properties of novel 1D heterostructures among the almost unlimited compositional and structural combinations. Furthermore, theoretical calculations for getting a deep insight into the formation mechanism of 1D heterostructures and techniques for visualizing the growth process are also urgently needed.

The dispersion and patterning of 1D vdW heterostructures may also be taken into consideration. In fact, nanotubes are always bundled because of the strong intertube vdW interactions. The coating or filling of foreign layers dramatically change the surface state and electric property of the nanotubes. However, the main concern is to find a suitable dispersion approach to increase the proportion of well-dispersed individual heterostructures. Another obstacle is that a normal dispersion process involves stirring, grinding, and ultrasonication, which unavoidably damage the structure and quality of the heterostructures. Moreover, to fabricate various electronic and photonic devices, patterning and alignment techniques need to be developed to enable 1D vdW heterostructures to be compatible with standard microfabrication technology. For highly aligned, densely packed CNTs, successful efforts include Langmuir–Blodgett assembly,⁶⁷ floating evaporative self-assembly,⁶⁸ vacuum filtration,⁶⁹

DNA-directed alignment,⁷⁰ and dimension-limited self-assembly.⁷¹ Although we can probably learn from these strategies developed for CNTs, a good dispersion is the first hurdle before we can achieve patterned 1D heterostructures as needed.

Overall, 1D vdW heterostructures, as a new frontier in low-dimensional material research, will likely attract more and greater attention in the near future. This is because not only that the high-quality 1D vdW heterostructures can modulate the properties of nanotubes and therefore enhance their performances in currently existing applications but also these 1D heterostructures may host new physics and facilitate the discovery of new applications. We strongly believe that novel 1D vdW heterostructures will bring us more exciting findings in fundamental research, and the research of 2D vdW heterostructures in the past decade may serve as a guide to open avenues for a plethora of next-generation applications of their 1D vdW analogues.

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Notes

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