

Materials Science

Building blocks for one-dimensional van der Waals heterostructures

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Abstract: We recently demonstrated experimentally the synthesis of one-dimensional (1D) van der Waals (vdW) heterostructure, where single-crystal hexagonal boron nitride or molybdenum disulfide nanotubes seamlessly wrapped a single-walled carbon nanotube and formed a coaxial hetero-nanotube with the diameter typically being 1–5 nm. 1D vdW heterostructures have created large room for fundamental research from synthesis to application, but most directions are still at their initial stages. The materials that can be employed to construct 1D vdW heterostructures are limited to only a few types. In this review, we provide an outlook to the question: what are the building blocks available now and could be available in the future for the fabrication of 1D vdW heterostructures?

Keywords: one-dimensional van der Waals heterostructure, carbon nanotube, molybdenum disulfide

Introduction

The past few decades have witnessed a rapid growth of the research field of nanomaterials. This field started when researchers realized that reducing the size of a material at least in one dimension can give rise to new physics and possibly lead to novel applications. Carbon nanomaterials composed of sp^2 carbon bonded atomic layer(s) soon emerged as a typical material family in the field. Depending on the arrangement, carbon sp^2 system can form a zero-dimensional (0D) fullerene, one-dimensional (1D) carbon nanotube (CNT) or two-dimensional (2D) graphene [1–3]. Later, several other materials fabricated into atomic thickness have been recognized. For example, hexagonal boron nitride (hBN) and tungsten disulfide (WS_2) nanotubes were experimentally demonstrated [4,5], although only CNTs have attracted broad attention in the early time.

The situation began to change earlier this century. There has been a bloom of research on 2D atomic layers

initiated from the isolation of monolayer grapheme [3,6]. Many materials other than pure carbon started to join the game and significantly expanded the library of atomic-thin crystals. The representative materials include transition metal mono- or di-chalcogenide (TMMC or TMDC), black phosphorus (BP), MXene (transition metal carbide), oxide, silicene, borophene, etc. [7–9]. The number increases in the material library allowed to build a variety of hetero-material stacks, called van der Waals (vdW) heterostructures because the layers are usually bounded with vdW forces [10].

Previously, vdW heterostructures were possible only for 2D materials. In 2020, we demonstrated the experimental synthesis of 1D vdW heterostructure, in which crystalized BN and MoS₂ nanotubes were grown on a single-walled CNT (SWCNT) template by chemical vapor deposition (CVD) [11]. A typical 1D vdW heterostructure is a coaxial hetero-nanotube with the diameter of 1–5 nm, consisting of two or more different crystal nanotubes (Figure 1). 1D vdW heterostructure is a new group of materials that may stimulate broad research interest but is still at a very early stage. In this review, we deliver a prospect mainly from the standpoint of materials science, on the possibility of synthesizing nanotubes with diameters of a few nanometers beyond TMDC nanotubes such as MoS₂. This review is to answer the question: what are the building blocks available now and could be available in the future for the fabrication of 1D vdW heterostructures?

Possible building blocks beyond molybdenum disulfide

Figure 2 shows several representative atomic layer crystals in their 2D forms, together with the atomic geometries rolled into 1D nanotubes. Their 2D sheets have already been experimentally demonstrated for most materials presented here, but only several 1D nanotubes have been synthesized so far. As the first example shown in the figure, hBN shares the same honeycomb-like hexagonal atomic arrangement with grapheme. It is the least surprising material that can form a heterostructure on the surface of SWCNT because hBN is only one-atom thick and has a lattice constant nearly identical to grapheme [12]. However, forming a TMDC (e.g., MoS₂) nanotube on an SWCNT template, as shown in Figure 2B, is less straightforward. Unlike grapheme or hBN, a MoS₂ monolayer is three-atom thick, and therefore one will expect that it is more difficult for MoS₂ to roll up into a nanotube. With SWCNT as the structural template, the smallest MoS₂ nanotube we synthesized is about 3.5 nm in diameter. Other TMDC nanotubes may be synthesized following a similar approach. These small diameter TMDC nanotubes and their 1D heterostructures are emerging quantum

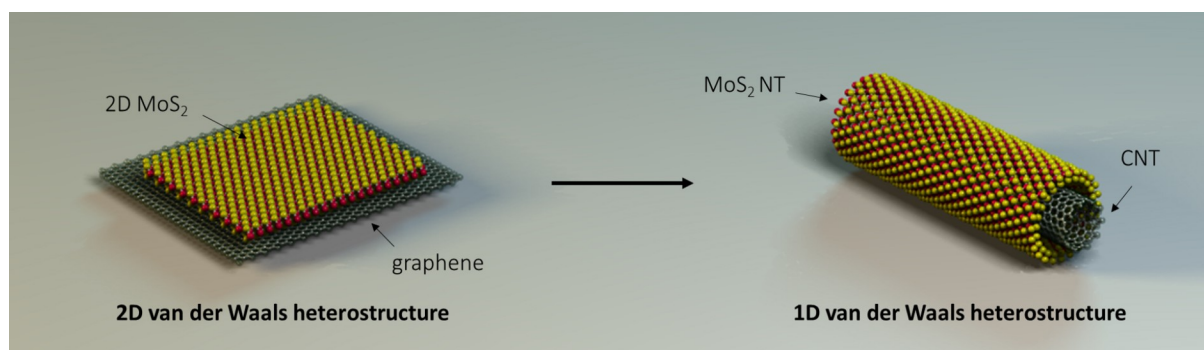


Figure 1 A schematic image showing the geometry of two-dimensional and one-dimensional vdW heterostructures.

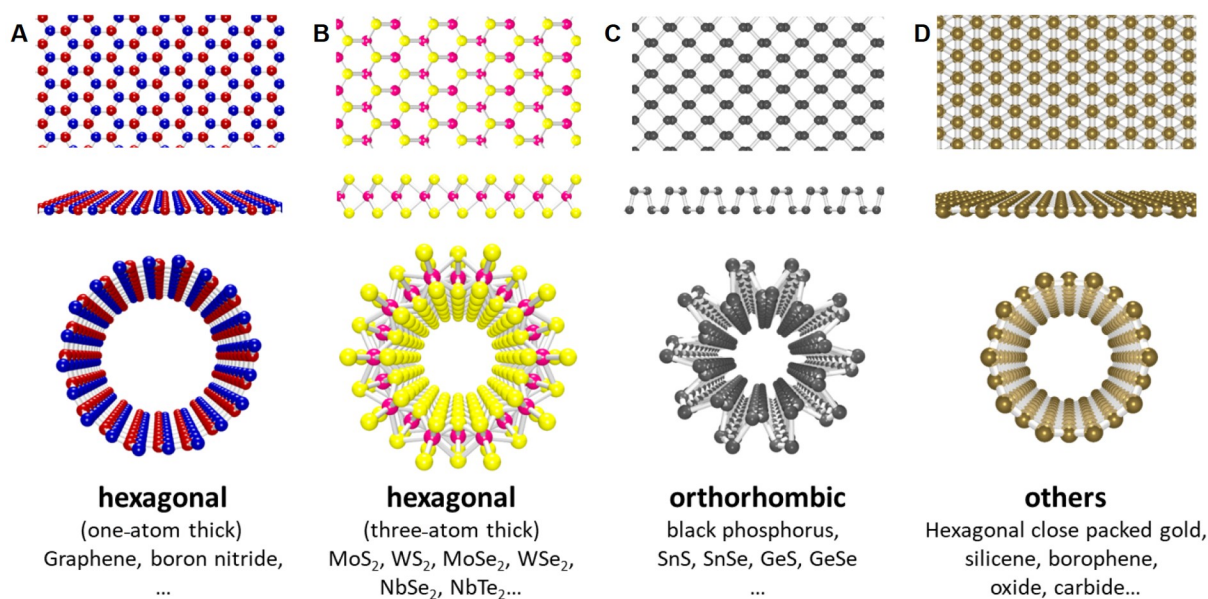


Figure 2 Different types of atomic-thin crystals in their 2D and 1D forms. (A) Hexagonal boron nitride; (B) MoS₂-like hexagonal transition metal dichalcogenide; (C) SnS-like orthorhombic transition metal monochalcogenide; (D) hexagonal-close-packed metal monolayer.

materials that could bring great attention.

Figure 2C illustrates a different group of atomic layers with orthorhombic unit cells. The representative materials are black phosphorus and many transition metal monochalcogenides (TMMCs), e.g., SnS. When rolling these atomic sheets into nanotubes, the strain energy caused by curvature could be smaller than the case of TMDC, as a monolayer of TMMC is usually two-atom thick (vs. three-atom thick for TMDC). However, orthorhombic TMMCs are less symmetric in structure than hexagonal C, BN, and TMDC. Rolling TMMC into a nanotube at different angles may lead to a significant variation in terms of structural stability. The geometry described in Figure 2C is probably one of the most stable tubular structures upon different rolling angles. More discussions have been presented in previous theoretical work [13]. Overall, these orthorhombic nanotubes could be more difficult to form due to the lower degree of structural symmetry. However, if synthesized, orthorhombic nanotubes could exhibit many interesting properties. For example, BP nanotubes are expected to be a narrow gap semiconductor, while SnS is predicted to have giant piezoelectricity and ferroelectricity when the stacking symmetry is broken in a small-diameter nanotube [14].

In addition to TMDC-like hexagonal and TMMC-like orthorhombic crystals, recently there also has emerged other 2D atomic-thin crystals, such as silicene, borophene, MXene, oxides, and 2D metals. At this stage, the synthesis techniques of these materials, even for 2D forms, are not well established, so their 1D counterparts will probably be even more challenging to produce. However, it is not impossible that such emerging 2D crystals may also be rolled into 1D nanotubes if proper strategies are found and then become available in the future for the construction of 1D vdW heterostructures. Compared with 2D layers, one general difference and thus potential advantage for tubular 1D material/heterostructure is the absence of edges and dangling bonds. This means at the same scale, particularly when the width of the material is several nanometers, there will be no geometry defects that will cause scattering and degradation for the transport of

electrons or other particles. Furthermore, crystals are highly curved in 1D nanotubes, which can result in interesting phenomena such as giant bulk photovoltaic effect and enhanced flexoelectricity [15,16]. All these effects can be interesting research topics once the material is ready.

More sophisticated 1D heterostructures

As discussed in the previous section, TMDC nanotubes would likely be the first group of material candidates for fabricating more sophisticated 1D heterostructures. One exciting feature for TMDC materials is that they hold a large diversity for their electronic properties. There are different types of semiconductors as well as metals and insulators. Therefore, TMDC materials alone can lead to quite large freedom to modulate the property of 1D vdW heterostructures and build different geometry of junctions.

The most straightforward cases are two types of junctions, a radial one and an axial one, as shown in Figures 3A and 3B. The former corresponds to the vertical junction analogous to 2D heterostructures, and the latter corresponds to the in-plane junction. In both cases, many fundamental research interests could arise from these 1D junctions. Previously, many exciting studies have been done at the material interfaces, and many proof-of-concept devices, particularly optoelectronic devices, have been demonstrated in 2D hetero-junctions. 1D version of these junctions could be employed to manifest more exciting and unique geometry-specific phenomena such as solid polarization dependence and enhanced charge separation.

Besides junctions, alloy nanotubes may also be fabricated as shown in Figure 3C. Many TMDC materials, such as MoS_2 and WSe_2 , have very similar lattice constants and are expected or demonstrated to fully alloy with each other in a wide range of compositions. The small difference in lattice constant can also ensure a minor strain and, therefore, a high degree of crystal quality. Alloying in the full range will allow to continuously tune the properties, e.g., the bandgap of a semiconducting TMDC nanotube.

Another interesting structure, which is not even fully developed in 2D, is a nanotube version of the Janus structure. A Janus 2D TMDC is an atomic sheet where top and bottom chalcogen atoms are different [17]. In a 1D nanotube, an analogous structure is that atoms at the inner surface and outer surface will be different,

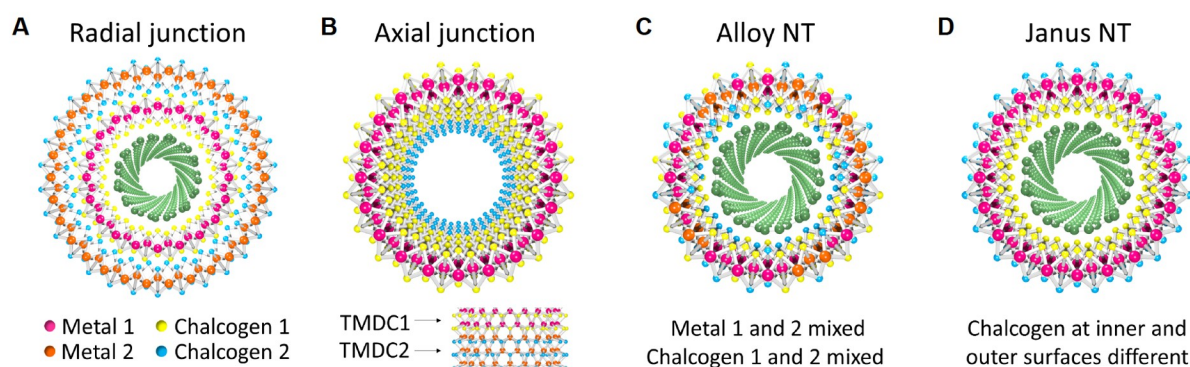


Figure 3 Various sophisticated 1D vdW heterostructures that could be built using more than one TMDC material. (A) Radial junctions where two TMDC nanotubes are at different shells; (B) axial junctions where two TMDCs are at the same shell connecting each other (in this case inner CNT is hidden to reveal the junction interface); (C) alloy nanotubes where different metal atoms and/or different chalcogen atoms are fully mixed; (D) Janus nanotubes where inner and outer surfaces have different chalcogen atoms.

e.g., MoSSe nanotube shown in Figure 3D, where Se atoms are located only at the outer surface. Janus structures will be challenging to synthesize by a single-step CVD. One possible approach is atomic exchange. This method should be more feasible in the case of 1D vdW heterostructures than 2D ones, as the inner surface is in contact with other nanotubes and the only outer surface is exposed to the atmosphere of foreign atoms. In addition, the seamless and tubular structure makes expanding the shell-shell spacing more complicated than the case of 2D, so the intercalation of foreign atoms, e.g., Se to replace S, would also be more difficult (maybe nearly impossible) at the inner surface. Janus structure in 2D has a large Rashba spin-orbit coupling and piezoelectric polarization [17,18]. 1D Janus TMDC nanotubes have curvature, an additional degree of freedom to break the structural symmetry. This could further enhance these effects and possibly also lead to other unconventional properties, such as negative quantum capacitance, as recently predicted [19]. Beyond Janus, there is a recent report on the 1D vdW superlattice formed by rolling existing 2D heterostructures [20]. It is also appealing if these 1D vdW rolls can be directly synthesized by CVD.

Researching these more sophisticated 1D vdW heterostructures requires significant efforts on both synthesis and characterization. Their structural characterization with atomic precision, mainly using advanced transmission electron microscopy (TEM), would also be inevitable. High-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) is one of the best tools to image the atomic structure of these 1D structures. Electron energy loss spectroscopy (EELS) is a powerful way to obtain the elemental distribution and/or electronic structure of these junctions. It is particularly efficient for light elements. In addition, various spectroscopic methods including Raman, photoluminescence, and ultraviolet-visible near-infrared (UV-vis-NIR) absorption may be employed to characterize these materials. Despite many scientific and technical challenges, once successfully fabricated, these more sophisticated structures can certainly unlock new possibilities for many interesting studies.

Macrostructures and their applications

In addition to the synthesis and characterization of 1D vdW heterostructures at a small scale and at a single-tube level, e.g., in electron microscopy, it is also essential to obtain these materials in a macroscopic form and demonstrate their functions. Fortunately, the 30 years' development of CNT allows us to synthesize CNT assemblies in many different geometries and alignments. For example, both vertical arrays and random networks of high-quality SWCNTs are available nowadays (Figure 4A) [21–23]. They may serve as convenient starting templates for fabricating macrostructures of 1D hetero-nanotubes.

Figure 4B illustrates the expected geometry of these heteronanotube macrostructures, and two optical images of experimentally obtained centimeter-scale films are shown in Figure 4C. The left image is an SWCNT-BNNT film sitting on a silicon frame, and the right is an SWCNT-BNNT-MoS₂ film on a ceramic washer. In both cases, the sizes of films are on the centimeter scale and only limited by the availability of the starting materials. Also, these macrostructures can be manipulated and transferred onto various substrates for further processes. These macrostructures can possess different functions depending on the building blocks used in the individual hetero-nanotubes and their combination sequences [24,25]. Let us take the application in photovoltaic devices as an example to extend the discussion.

One exciting scenario is that a properly designed heterostructure film may be used as the active layer in

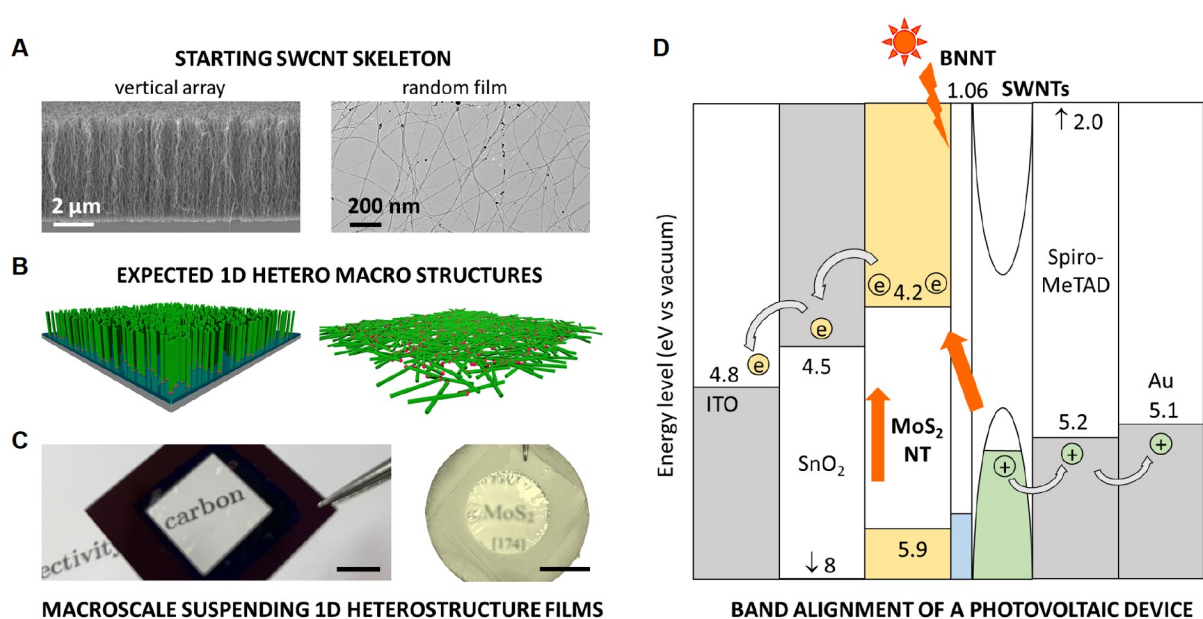


Figure 4 Macroscopic 1D vdW heterostructures and their potential applications. (A) Various types of starting SWCNTs that may serve as the skeleton for the fabrication of macroscopic 1D vdW heterostructures; (B) schematic showing the expected geometry of macrostructures; (C) optical images of a macroscopic SWCNT-BNNT film self-suspending on a silicon frame and a SWCNT-BNNT-MoS₂ heterostructure film on a ceramic washer (scale bar 5 mm); (D) possible band alignments of a hetero-nanotube-based photovoltaic device.

solar cells [23]. Figure 4D shows a chart of band-alignments in a solar cell using 1D hetero-nanotubes as the active layer. In such a case, the axial junction between SWCNT and outer material, e.g., MoS₂, will be essential for the device's performance. Therefore, carefully choosing the materials is critical to ensure a large absorption, a high quantum yield, and a good stability. The confirmation of the direct band gap feature for small-diameter MoS₂ nanotubes, strong quenching of photoluminescence of MoS₂ nanotubes by inner SWCNT, and the observation of inter-tube excitons in MoS₂-based 1D heterostructures could facilitate the application of such hetero-nanotubes in the photovoltaic devices as the active materials [26,27]. The inter-tube excitons due to strong coupling of MoS₂ nanotubes and inner SWCNTs are responsible to the strong and broad-band absorption of the heterostructures. We can expect that the dissociation of inter-tube excitons will result in the free electrons on MoS₂ nanotubes and free holes on SWCNTs, the ideal separation of carriers. Meanwhile, other layers may also need to be optimized to comply with the structure of the hetero-nanotube active layer. This new conceptual solar cell may hold advantages in simultaneously achieving flexibility, durability, non-toxicity, and sustainability, which would exceptionally be important for future applications such as wearable devices. The unique geometry of hetero-nanotubes may result in other interesting physical and chemical properties and enable other possibilities from many aspects beyond photoelectronic and photovoltaic devices, which are being discussed in recent publications from various research groups [16,26–41]. For example, Zhang *et al.* [42] studied the property of a SWCNT-BNNT 1D heterostructure film as the saturable absorber and demonstrated a high optical damage threshold; Suzuki *et al.* [38] observed a memristive behavior in CNT-BNNT heterostructure bulk assemblies and proposed these fibers could be useful for future neuromorphic computing and conventional nonvolatile memory devices. Also, the performance of 1D heterostructures in an electrochemical reaction is also interesting and could be quickly investigated. Some

preliminary demonstrations and brief discussion are already available [33,34,43].

Conclusions

The research of 1D vdW heterostructure is still at its early stage. Great efforts would be needed for material synthesis, structural characterization, and property investigation. While breakthroughs in the synthesis technique discussed here have to be achieved first to trigger the follow-up research, the investigation on the unique properties of these 1D heterostructures, from both theoretical and experimental approaches, will be most critical for developing this field. We foresee an increasing impact for 1D vdW heterostructures not only because this new material group has created vast room for fundamental research but also because their macrostructures may be easily fabricated in the near future and directly employed into a variety of applications.

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Conflict of interest

The authors declare no conflict of interest.

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