

NANOMATERIALS

One-dimensional van der Waals heterostructures

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We present the experimental synthesis of one-dimensional (1D) van der Waals heterostructures, a class of materials where different atomic layers are coaxially stacked. We demonstrate the growth of single-crystal layers of hexagonal boron nitride (BN) and molybdenum disulfide (MoS₂) crystals on single-walled carbon nanotubes (SWCNTs). For the latter, larger-diameter nanotubes that overcome strain effect were more readily synthesized. We also report a 5-nanometer-diameter heterostructure consisting of an inner SWCNT, a middle three-layer BN nanotube, and an outer MoS₂ nanotube. Electron diffraction verifies that all shells in the heterostructures are single crystals. This work suggests that all of the materials in the current 2D library could be rolled into their 1D counterparts and a plethora of function-designable 1D heterostructures could be realized.

The demonstration of two-dimensional (2D) van der Waals (vdW) heterostructures (1–3)—in which atomic layers are stacked on each other and different 2D crystals are combined beyond symmetry and lattice matching—represents a way of manipulating crystals to enable both the exploration of physics not observable in conventional materials and device applications (4–8). These 2D heterostructures have been fabricated by transferring preprepared layers (transfer approach) (5, 9) or by synthesizing layers onto a base layer (synthesis approach) (10). Whether such artificial materials and interfaces can be fabricated in other dimensions remains an open question. In 1D materials, for example, an ideal vdW heterostructure would be a coaxial structure with different types of nanotubes. Such ideal structures have been investigated in theoretical studies (11, 12) and would appear to require a synthesis approach. However, experimental attempts to fabricate coaxial nanotube structures have yielded only amorphous or very poorly crystallized coatings (13, 14).

We demonstrate the experimental discovery and controlled fabrication of true 1D vdW heteronanotubes. A typical structure was 4 to 5 nm in diameter but contained three different shells: an inner carbon nanotube (CNT), a middle hexagonal boron nitride nanotube (BNNT), and an outer molybdenum disulfide (MoS₂) nanotube. Electron diffraction (ED) and many other characterizations were used to confirm that each shell in this structure was a seamless,

perfect nanotube that realized the heteronanotubes studied in theoretical models. The heterostructures formed through an open-end growth mode that has rarely been observed in previous 1D nanostructure growth. We outline some basic geometric principles that governed the formation of these 1D vdW heterostructure nanotubes, including the absence of structural correlation between inner and outer shells and the requirement of a threshold diameter for MoS₂ nanotubes.

In this study, the base structure, a single-walled carbon nanotube (SWCNT) (15), was chosen as the starting material for several reasons. It is, so far, the best-studied 1D material and can be synthesized in many controlled geometries. Also, a SWCNT can be metallic or semiconducting, which means it could serve as the electrode or channel material for a heteronanotube device. The typical SWCNTs used in this study were 1 to 2 nm in diameter and a few micrometers in length and were self-suspended as a random network (16). Schematics comparing the 2D and 1D vdW heterostructures are presented in Fig. 1, A and B.

Structure analysis of SWCNT-BNNT heterostructure

We present the initial growth step: the formation of the SWCNT-BNNT 1D heterostructure. We used SWCNTs as a template and synthesized additional hexagonal boron nitride (BN) layers by chemical vapor deposition (CVD). Figure 1C shows a representative high-

resolution transmission electron microscope (HRTEM) image of this coaxial heterostructure (additional images are available in fig. S1A). In a conventional HRTEM image, this nanotube is not distinguishable from a triple-walled pure carbon nanotube. The aberration-corrected HRTEM image of a similar tube revealed a contrast of stacking of two perfect nanotubes (Fig. 1, D and E). However, given that the starting material is purely single-walled before we perform a post-BN coating, we expect that the outer wall or walls are BN. This is supported by electron energy-loss spectroscopic (EELS) mapping (Fig. 1F). Because the reaction occurs on the outer surface, unlike previous attempts inside a nanotube (17, 18), we achieve continuous coating and highly crystallized outer BNNTs. The number of outer BNNT walls can be adjusted from a minimum of one to a maximum of five to eight, depending on the duration of BN CVD (fig. S1, B and C). These different layers grow independently, but the first layer is always the longest. The walls of our SWCNT template are very clean, so the nucleation is usually observed at the end of a suspended region, where a SWCNT is connected with another SWCNT or a SWCNT bundle (fig. S2). Occasionally, nucleation also occurs simultaneously at both ends of a suspended SWCNT region. Nucleation from the middle of a SWCNT is rarely observed.

One critical feature of the current structure is that each layer is a single crystal, which distinguishes this study from all previously reported coaxial tubular structures. This perfect crystallization is shown by the ED patterns provided in Fig. 2, A to C, and fig. S1. The perfect SWCNT-BNNT coaxial single crystals could reach a few hundreds of nanometers to ~2 μm and were limited only by the length of individually isolated regions in our starting SWCNTs. The other important feature of the current structure is its small diameter. Many of our SWCNT-BNNT structures are thinner than 2 nm, and the ternary SWCNT-BNNT-MoS₂ are 3 to 5 nm (described in a later section). This small dimension is essential for accessing the distinctive properties of 1D materials, such as confinement of excitons in the 1D crystals.

We characterized these coaxial crystals with several other techniques. X-ray photoelectron spectroscopy (XPS) revealed B–N and C–C bonds in this sample but no apparent peaks of C–N and B–C, which confirmed that BN and carbon moieties were chemically isolated (fig. S3). Optical absorption spectra (fig. S4A) revealed a

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peak near 205 nm, and the peak intensity increased with growth time (number of outside BNNT layers). Cathode luminance spectra (fig. S4B) of the sample confirmed the existence of outer BN by emissions in the ultraviolet range. Also, the growth strategy was shown to apply to SWCNTs with different morphologies, including vertical arrays, horizontal arrays, random

networks, and suspended SWCNTs between silicon pillars (fig. S5).

The formation of this SWCNT-BNNT heterostructure follows an open-end growth mechanism (shown schematically in movie S1). In this scenario, the extension of the second layer happened only at the open edge of the BNNT. The third (and beyond) layer followed a sim-

ilar approach but nucleated in a later stage. This pattern is similar to the growth of additional layers in 2D material, but it has very rarely been observed in previous growth of carbon nanotubes (19). The open-edge growth mechanism is supported by the many atomic steps observed in heterostructures with incomplete growth of outer BNNT crystal layers

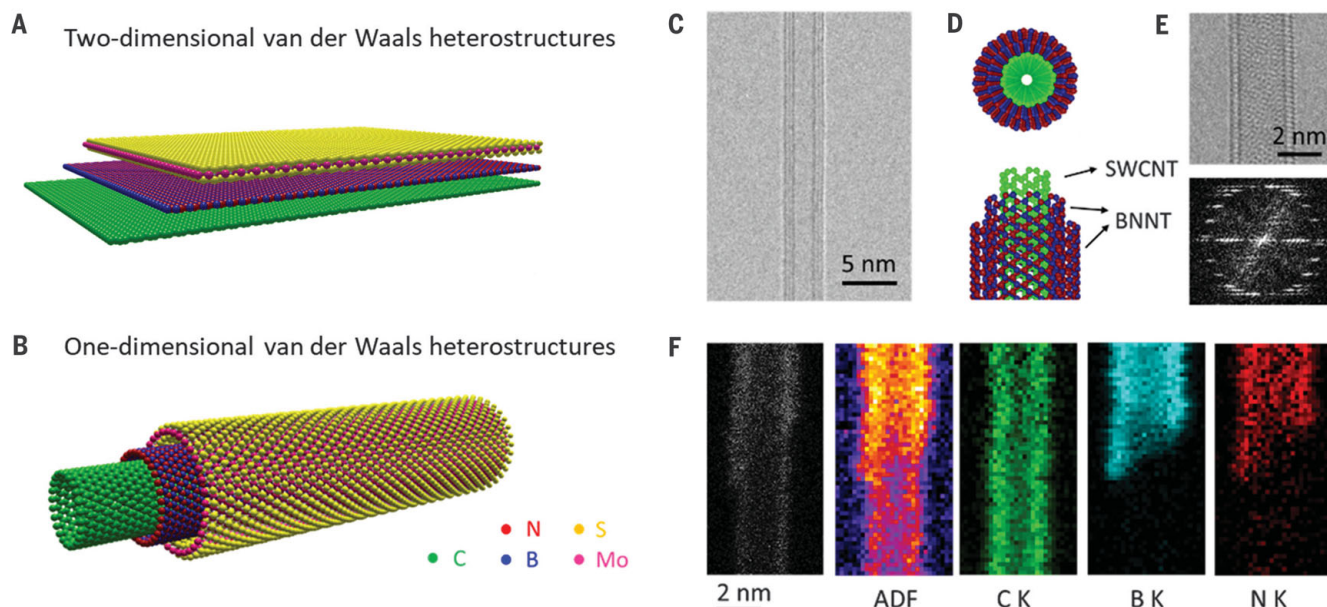


Fig. 1. Overview of 1D vdW heterostructures. (A and B) Atomic arrangement of two-dimensional planar vdW heterostructures (A) and one-dimensional coaxial vdW heterostructures (B). (C and D) TEM image (C) and structure models (D) of a SWCNT wrapped with two layers of BNNT. (E) Aberration-

corrected TEM image of a SWCNT-BNNT and its fast Fourier transform. (F) Annular dark-field (ADF) image and EELS mapping of a SWCNT partially wrapped with BNNT, showing that the inner layer is carbon and the outer layer is BN. C K, K₁ edge of C (green); B K, K₁ edge of B (cyan); N K, K₁ edge of N (red).

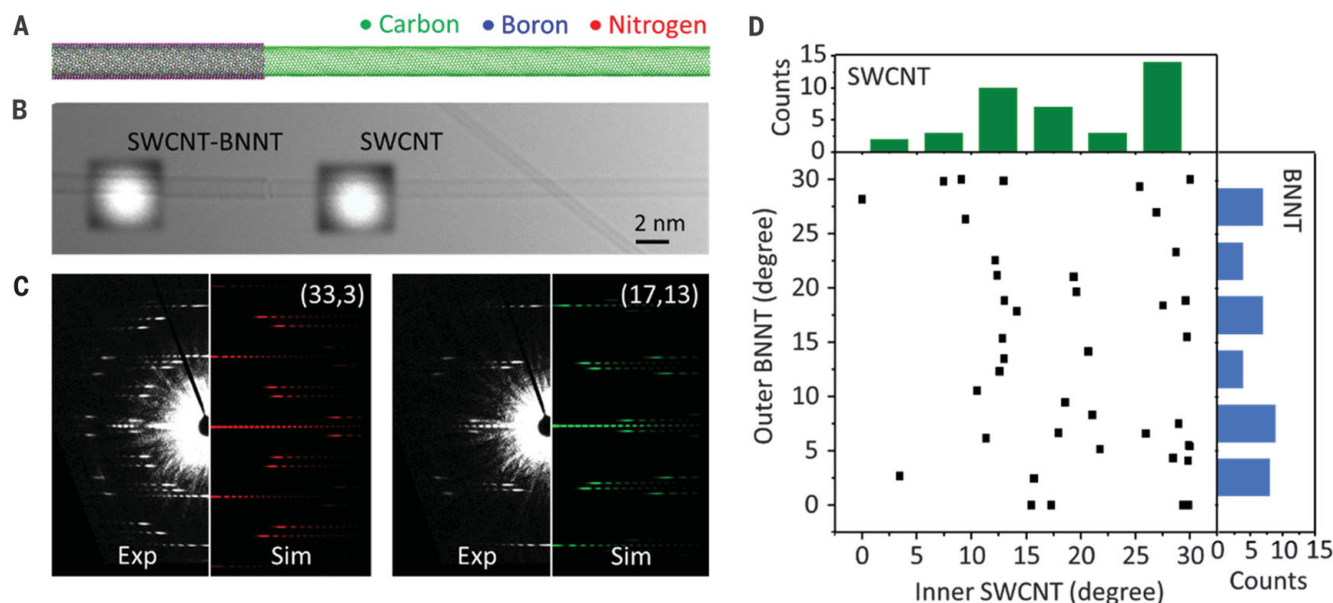


Fig. 2. Structural characterization of SWCNT-BNNT vdW heterostructures. (A and B) Atomic model (A) and TEM image (B) of SWCNT-BNNT atomic steps. (C) Experimental (Exp) and simulated (Sim) ED pattern of the inner (17, 13) SWCNT

and outer (33, 3) BNNT. (D) Plot of chiral angle of inner SWCNT versus the outer BNNT for double-walled SWCNT-BNNT, revealing that as-grown SWCNTs were enriched in the near-armchair form but that the outer BNNT was evenly distributed.

(Fig. 2, A and B). Our starting SWCNTs have an ultraclean surface and our CVD chamber is a clean, low-pressure system, which avoids any atomic impurities on the SWCNT surface or contamination from the chamber that could cause imperfection in the outer nanotube.

The atomic step in composition along the growing nanotube also allowed us to obtain nano-area ED patterns (20) of the pristine SWCNT and the same tube after BNNT growth, which allowed us to assign chirality of each layer. In Fig. 2C, the inside SWCNT is assigned as (17, 13) and the outside BNNT as (33, 3). In another case, a (34, 0) single-walled BNNT formed on the surface of a (16, 14) SWCNT

(fig. S6). Even without these atomic steps, the 2% difference between the lattice constants of SWCNT and BNNT (21) allows us to distinguish them in the ED patterns.

In a collection of 74 SWCNTs and 40 SWCNT-BNNT double-walled nanotubes (details shown in figs. S7 and S8 and table S1), a greater number of SWCNTs were in near-armchair form (Fig. 2D). This near-armchair enrichment was consistent with previous experimental and theoretical analyses (22, 23). However, the outer BNNTs were randomly distributed (with a slight preference for the zigzag conformation). No chiral angle dependence was observed in these SWCNT-BNNT heterostructures, so sym-

metry and lattice matching did not limit our ability to combine materials using our technique (24). This absence of correlation of inner and outer layers differed from what has been observed in CVD fabrication of 2D vdW heterostructures, where the growth layer is usually aligned with the base material. We attribute this difference to the symmetry breaking in 1D materials compared with that in their 2D counterparts.

Optical, thermal, and electronic characterization of SWCNT-BNNT heterostructure

Raman and photoluminescence (PL) spectra of the SWCNT-BNNT showed peaks typical

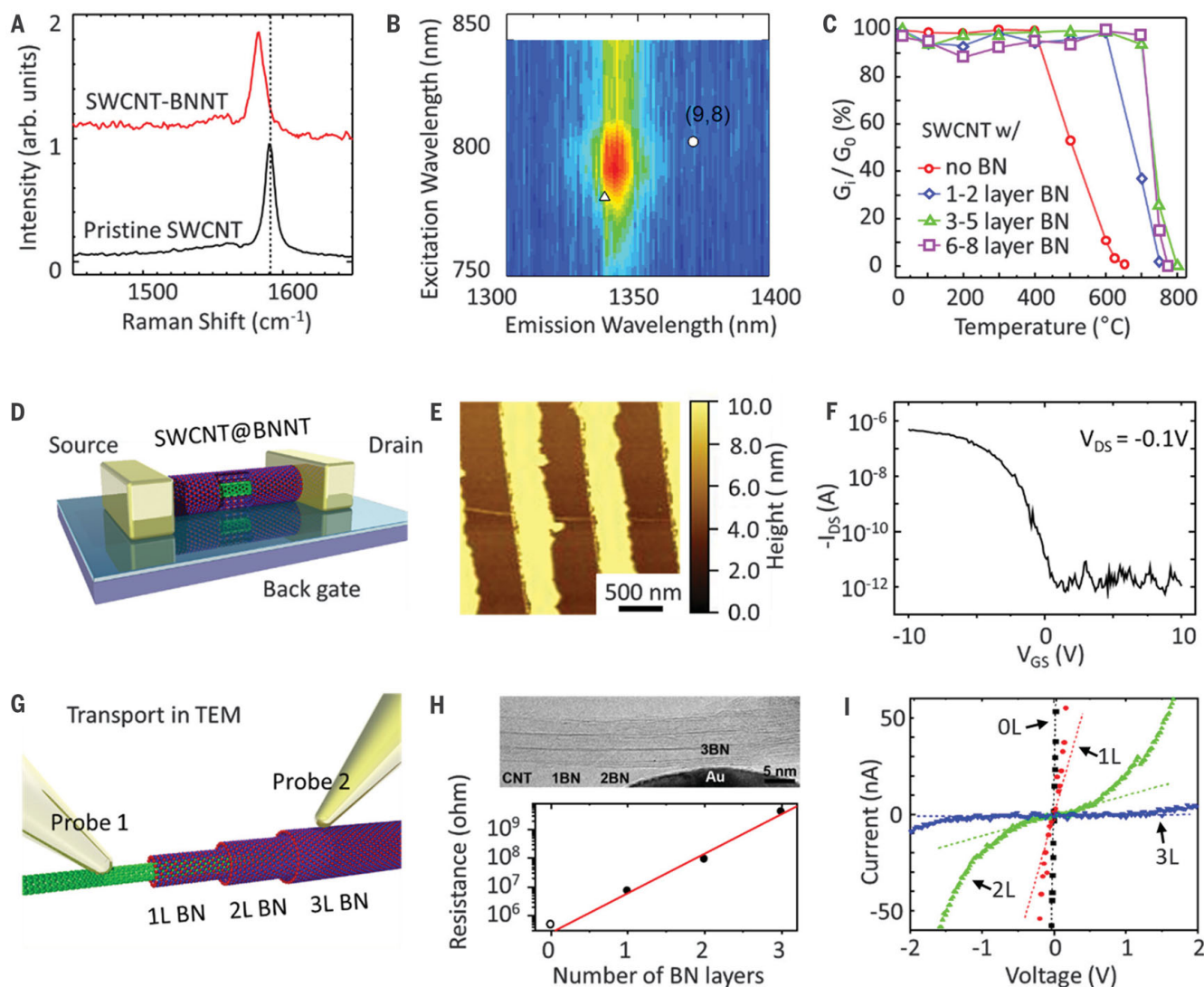


Fig. 3. Optical, thermal, and electronic characterization of SWCNT-BNNT heterostructures. (A) Typical G band of an individual SWCNT before and after BN coating. Arb. units, arbitrary units; dotted line indicates the original G band position at ~ 1590 cm⁻¹. (B) PL excitation-emission map of suspended (9, 8) SWCNT after BN CVD. Circle and triangle marks indicate the optical transition energy of suspended (9, 8) SWCNT in the ambient atmosphere (38, 39) and in vacuum (40). (C) Thermal stability of SWCNT and SWCNT-BNNT heterostructures obtained in an in situ

Raman reaction cell. The ratio of G-band intensity (G_i) after high-temperature burning to the original G-band intensity (G_0) before burning gives the relative loss of SWCNTs in these samples. (D to F) A schematic (D), AFM image (E), and characteristic transfer curve (F) of a back-gated FET built on a SWCNT-BNNT. I_{DS} , drain current; V_{GS} , gate voltage; V_{DS} , drain voltage. (G) Schematic of the transport measurement inside TEM. (H) Bright-field TEM image (upper) and resistance versus number of BN layers (lower). (I) Typical I-V curve obtained in electronic measurement inside TEM.

of pristine inner SWCNTs, which showed that their structural integrity was preserved (Fig. 3, A and B). However, a G band downshift of 5 to 10 cm^{-1} appeared in both isolated SWCNT-BNNT heterostructures and heterostructure networks. That downshift was a fingerprint for BNNT coating in our experiments. We tentatively attributed this downshift to the thermal strain between SWCNT and BNNT. The difference in thermal expansion during BN synthesis caused a slight distortion for SWCNTs along the tube axis. The outer BN layers acted as a protective coating and protected the inside of the SWCNTs against oxidation. Burning of the SWCNT inside BNNT started at 700°C in air, whereas naked SWCNTs burned at 400°C (Fig. 3C), as measured in a Raman cell. After annealing the heterostructure in oxygen, inside SWCNTs were removed, and clean and crystallized single-walled and few-walled BNNTs were obtained (fig. S9).

The BNNT coating did not change the intrinsic electronic transport of the inner SWCNT. We fabricated a back-gated field-effect transistor (FET) on an individual SWCNT-BNNT heterostructure (Fig. 3D). This SWCNT-BNNT was synthesized from a suspended SWCNT and then transferred onto a Si substrate. The SWCNT-BNNT FET showed performance similar to that of a SWCNT FET and had an on/off ratio of 10^5 (Fig. 3, E and F), which means that the high quality of the SWCNT was preserved. To further investigate the isolation and tunneling of outer BNNT layers, we measured the current through different BNNT layers in a TEM equipped with two probes (Fig. 3G). We distinguished the numbers of BNNT layers on SWCNTs directly from TEM and simultaneously mea-

sured the electron conduction at local positions separated by ~ 10 nm (Fig. 3, H and I). Current-voltage (I - V) curves—measured at the positions of the SWCNT-BNNT with zero, one, two, and three layers of BNNTs (Fig. 3I)—show the exponential increase of the zero-bias resistance with the layer number, indicative of direct tunneling through the insulating BN layers (Fig. 3H, bottom). This characteristic of tunnel current is similar to that of 2D BN layers exfoliated from bulk crystals (25, 26), and it was consistent with the layer quality being comparable to exfoliated crystals. The quality of these structures could allow for the experimental exploration of properties that have been theoretically predicted for 1D heterostructures, such as SWCNT-BNNT being a topological insulator if combined in a proper symmetry (12).

MoS₂-based binary and ternary heterostructures

MoS₂ 2D sheets have been studied intensively as the representative transition metal dichalcogenide material in recent years (27). Multiwalled MoS₂ nanotubes, with diameters usually >20 nm, and their hybrid materials are well known (28–30), but single-walled, single-crystal MoS₂ nanotubes have not been convincingly demonstrated in previous studies. Thus, we explored the growth of MoS₂ on SWCNTs. Figure 4, A to C, shows the atomic structure, TEM, and scanning TEM (STEM) images of SWCNT-MoS₂ coaxial nanotubes obtained after applying our growth strategy. The MoS₂ nanotube has much stronger image contrast than carbon in both TEM and STEM images (additional images and EELS mapping are shown in fig. S10). Single-walled MoS₂ nano-

tubes were predicted to have a direct band gap, in contrast to multiwalled nanotubes that have an indirect band gap (31), and to exhibit strong quantum confinement effects (32).

We observed a strong diameter dependence for the formation of single-walled MoS₂ nanotubes. Unlike BNNT wrapping, the yield of MoS₂ nanotubes was very low (less than 1%), and seamless wrapping was only observed on large-diameter (>3 nm) SWCNTs. We performed simulations of the strain energy of single-walled MoS₂ nanotubes with different diameters, D . A $1/D^2$ relation was obtained (Fig. 4D), which suggests that, in small diameter range, strain energy was much higher than for SWCNTs and BNNTs (31, 33, 34). This difference can be simply attributed to the thickness of a single layer of MoS₂, containing three atomic planes and becoming unstable when rolled into a tubular structure. This also explains why MoS₂ nanotubes were only seen previously as multiwalled or on multiwalled CNTs (14, 28). Thus, the minimum diameter of a single-walled MoS₂ nanotube should be much larger than that of SWCNTs. The MoS₂ nanotubes (fig. S10, C to F) have diameters ranging from 3.9 to 6.8 nm and formed only on SWCNTs with diameters of at least 3 nm. Because most of our starting SWCNTs were thinner than 3 nm, the yield of SWCNT-MoS₂ heterostructures was low.

Finally, we grew a ternary, SWCNT-BN-MoS₂ coaxial nanotube (Fig. 5, A to D). This 5-nm-diameter structure consisted of an inner SWCNT, a middle three layers of BNNT, and a single outer layer of MoS₂. The elemental information was visualized by EELS mapping (Fig. 5D). Typical ED patterns in Fig. 5E reveal diffractions from all three crystal layers, with MoS₂

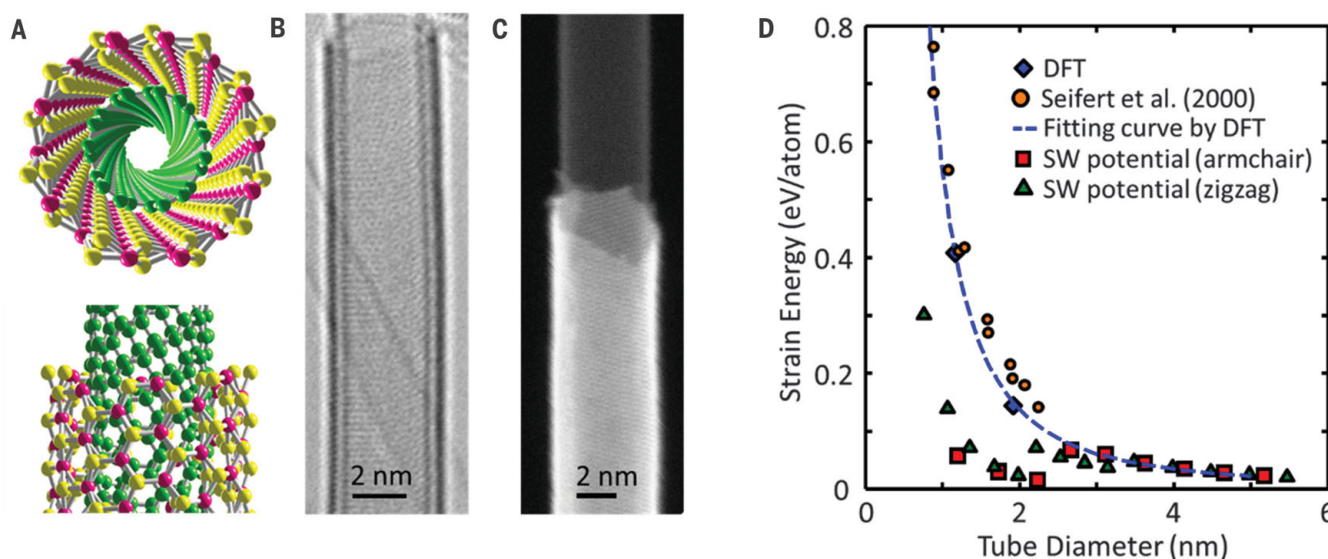


Fig. 4. SWCNT-MoS₂ 1D vdW heterostructure. (A to C) Atomic model (A), HRTEM image (B), and high-angle annular dark field (HAADF) STEM image (C) of a single-walled MoS₂ nanotube grown on a SWCNT. (D) Strain energy of a single-walled MoS₂ nanotube as a function of tube diameter, calculated by a modified Stillinger-Weber (SW) potential and density functional theory (DFT) simulation.

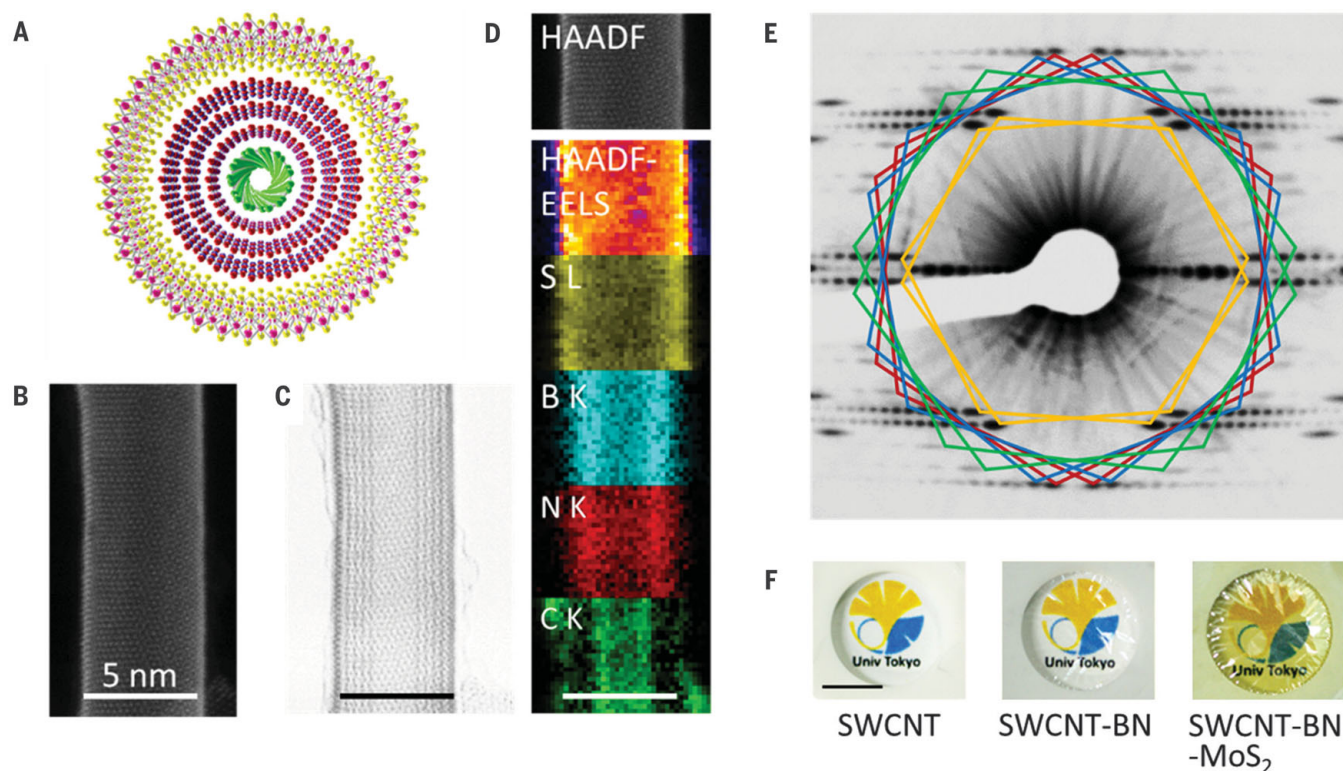


Fig. 5. SWCNT-BNNT-MoS₂ 1D vdW heterostructures. (A to D) Atomic model (A), HAADF-STEM image (B), annular bright field (ABF)-STEM image (C), and EELS mapping (D) of a 5-nm-diameter ternary 1D vdW heterostructure, consisting of one layer of carbon, three layers of BN, and one layer of MoS₂. Scale bars, 5 nm; S L, L_{2,3} edge of S (yellow). (E) An almost-ideal experimental

ED pattern of a SWCNT-BNNT-MoS₂ heterostructure, with different colors distinguishing the diffractions from different layers (L1 green, SWCNT; L2 blue, BNNT1; L3 red, BNNT2; and L4 yellow, MoS₂ nanotube). (F) Optical images of SWCNT, SWCNT-BNNT, and SWCNT-BNNT-MoS₂ films against a printed logo of the University of Tokyo. Scale bar, 10 mm.

having the strongest intensity and SWCNT and BNNT showing weaker but distinguishable contrast. The unidirectional distribution of the patterns also supports the coaxial feature. The four sets of hexagonal pairs with different colors indicate the orientation of atomic arrangement in the upper and lower surfaces to the electron beam.

Because the nanotube diameter increased from 2 to >3 nm after BNNT coating, the synthesis of an additional MoS₂ nanotube became much easier, and the yield of the SWCNT-BNNT-MoS₂ heterostructure reached ~10% after 20 min of MoS₂ CVD. A rough count of the yield of heterostructure versus CVD time is provided in fig. S11. The coating can be produced on the centimeter-length scale, and the difference can be observed between the original SWCNT, SWCNT-BNNT, and SWCNT-BNNT-MoS₂ films even with the naked eye (Fig. 5F). The optical absorption spectrum (fig. S12) of the sample revealed the photon absorption from three different layers.

We noticed that the innermost SWCNT and outermost MoS₂ in a SWCNT-BNNT-MoS₂ heterostructure are electronically coupled. This is supported by the different PL intensities of the SWCNT-BNNT-MoS₂ and BNNT-MoS₂ heterostructures. In the former case, PL of MoS₂ was

markedly quenched by the existence of SWCNT (fig. S13). In the latter case, however, PL of MoS₂ was 10 times as high. We calculated the band alignment of a graphene, BN, and MoS₂, and the Dirac point of graphene was found to be -4.26 eV, only 0.1 eV below the conduction band edge of MoS₂ (fig. S14). This calculation suggests that, if the starting SWCNT could be a small-diameter, semiconducting SWCNT, the SWCNT-BNNT-MoS₂ heterostructure is a type II junction. Interlayer excitons probably exist, even though electrons and holes are spatially separated by few layers of BNNT.

Discussion

We have extended the concept of vdW heterostructures to 1D materials. In these coaxial heteronanotubes, both cores and shells are single crystalline and form a seamless structure. We showed the controlled fabrication of SWCNT-BNNT and SWCNT-BNNT-MoS₂ coaxial structures with diameters <5 nm. We also developed some basic rules governing the fabrication of 1D heterostructures, including the absence of shell-shell epitaxial structure correlation and the requirement of a threshold diameter for MoS₂ nanotubes. This approach is likely extendable to other layered materials (35–37) and yields a large number of combinations, and

1D vdW heterostructures could host distinctive physics arising from curvature and diameter confinement.

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ACKNOWLEDGMENTS

We thank Y. Kato and K. Otsuka for the helpful discussion.

Funding: Part of this work is financially supported by JSPS KAKENHI grant nos. JP25107002, JP15H05760, JP15K17984, JP19K05223, JP16H06333, JP17K14601, JP18H05329, and

JP19H02543; IRENA Project by JST-EC DG RTD; Strategic International Collaborative Research Program, SICORP; JSPS-NSFC scientific cooperation program; and by the “Nanotechnology Platform” (project no. 12024046) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This research also received funding from projects 286546 (DEMEC), 292600 (SUPER), and 316572 (CNTstress), supported by the Academy of Finland, as well as projects 3303/31/2015 (CNT-PV) and 1882/31/2016 (FEDOC), supported by TEKES/Business Finland. Y.Q. is supported by JSPS DC fellowship (JP19J12932). D.T. acknowledges the support from the World Premier International (WPI) Center for Materials Nanoarchitectonics (MANA) and the TEM station of the National Institute for Materials Science (NIMS). **Author contributions:** R.X., T.I., and S.M. conceived and designed the experiments. E.I.K. and A.A. synthesized the SWCNT film. T.I., Y.Z., and M.L. performed the BN CVD. Y.Q. performed the CVD growth of MoS₂ nanotubes using powder precursors. Y.M. and Y.K. performed the MOCVD growth of MoS₂ nanotubes. R.X. took the HRTEM images of heterostructures. A.K. took the EELS mapping of SWCNT-BN. Y.S. took the aberration-corrected HRTEM image of SWCNT-BN, STEM image, and EELS mapping of SWCNT-MoS₂. A.K. and R.X. took the STEM image and EELS mapping of the SWCNT-BN-MoS₂ heterostructure. R.X. took the ED patterns of the SWCNT-BNNT. R.X. and D.G. assigned the chirality of SWCNT-BN. D.G. analyzed the chiral angle distribution. A.K. simulated the ED pattern. R.X. took and analyzed the ED patterns of the SWCNT-BNNT-MoS₂ nanotubes. Y.Z. and R.X. counted the yield

of SWCNT-BNNT and SWCNT-MoS₂. T.I. fabricated the FET device and measured the transfer curve. D.T. measured the electrical conduction of SWCNT-BNNT inside TEM. H.A. synthesized the suspended SWCNTs. S.Y. and T.O. measured the PL emission. J.G. studied the thermal stability of SWCNT-BNNT. T.I. measured and analyzed the XPS. M.L. burned SWCNT out of BNNT and measured the PL spectra of MoS₂-based heterostructures. Y.Z. and R.X. measured the cathodoluminescence. R.X. built the atomic structure of heterostructures. K.H. performed the molecular dynamics and DFT calculation of structure stability. M.M. and S.O. performed the DFT calculation of band alignment. R.X. wrote the manuscript. All authors joined the discussion and commented on the manuscript. **Competing interests:** None declared. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper or the supplementary materials.

SUPPLEMENTARY MATERIALS

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Materials and Methods

Figs. S1 to S15

Table S1

References (41–52)

Movie S1

26 August 2019; accepted 10 December 2019
10.1126/science.aaz2570