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Opportunities and challenges in integrating 2D materials with *inorganic* 1D and 0D layered nanostructures

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The birth of nanoscience more than 50 years ago fueled the renaissance in layered materials research leading to many materials discoveries with unprecedented scientific and technological impacts. Following the early reports on carbon fullerenes and nanotubes, the discovery of *inorganic* one-dimensional (1D) nanotubes and zero-dimensional (0D) fullerenes created a major playground for new physicochemical observations. The meteoric rise of two-dimensional (2D) materials in concert set off outstanding advances in the synthesis and manipulation of layered materials with atomic precision. This review identifies new directions in materials science that emerge through integrating the two layered systems—2D with *inorganic* 1D and 0D. Summarizing the key developments in the two distinct nanomaterials families, we highlight preliminary instances of integrating them into functional nanostructures. A few gedankenexperiments regarding prospective applications of the integrated system are then introduced to stimulate further experimental and theoretical investigations that can potentially result in unforeseen scientific observations.

Introduction

The birth of nanoscience more than half a century ago [1] spurred a deluge of research activities in the preparation of nanoscale materials with new dimensionality, morphology, and phase paving the way to designer nanostructures with predetermined functionalities. Engineering such nanostructures through advanced processing and subsequently integrating them into practical devices have significantly contributed to developing next-generation energy harvesting, computing, and medical diagnostic tools. Further, the intricate structure–function relations in low-dimensional materials have propelled fundamental discoveries in quantum condensed matter physics [2], and even, space science [3]. An example of such a platform is a layered heterostructure, where two or more layered materials are combined systematically to create a compound solid offering many unique functionalities that the component materials do not individually offer. A naive analogy of such a system is a *mille-feuille* where the ingredient layers are analogous to the individual materials in the system. Especially, adding geometries (or textures) to the layered system (e.g., *mille-feuille*) in the form of “curved rather than flat” surfaces (e.g., icing and cherries) results in an even more compound nanostructure with exotic interfaces and unusual properties. This mini review will explore the exciting structure–function relationships and properties that emerge when low-dimensional systems such as nanomaterials with curved surfaces are integrated with flat nanostructures.

Low-dimensional materials are those in which at least one of their three dimensions is on the order of a few nanometers ($\sim 10^{-9}$ m). Based on this definition, low-dimensional materials are classified into three broad categories—zero-dimensional (0D) materials (e.g., nanoparticles, quantum dots), one-dimensional (1D) materials (e.g., nanotubes, nanowires), and two-dimensional (2D) materials (e.g., graphene and other layered materials). Integrating two or more of such materials gives rise to complex nanostructures with miscellaneous dimensionality, morphology, and interfaces. Such complex artificial nanostructures are not new, and they have been reported previously by several researchers and will be referenced as the review evolves. This review will focus on a system that, to the best of our knowledge, is almost unexplored yet an appealing platform. The system is generated through the combination of 2D materials [4, 5] with *inorganic* 1D nanotubes and 0D fullerene-like nanoparticles

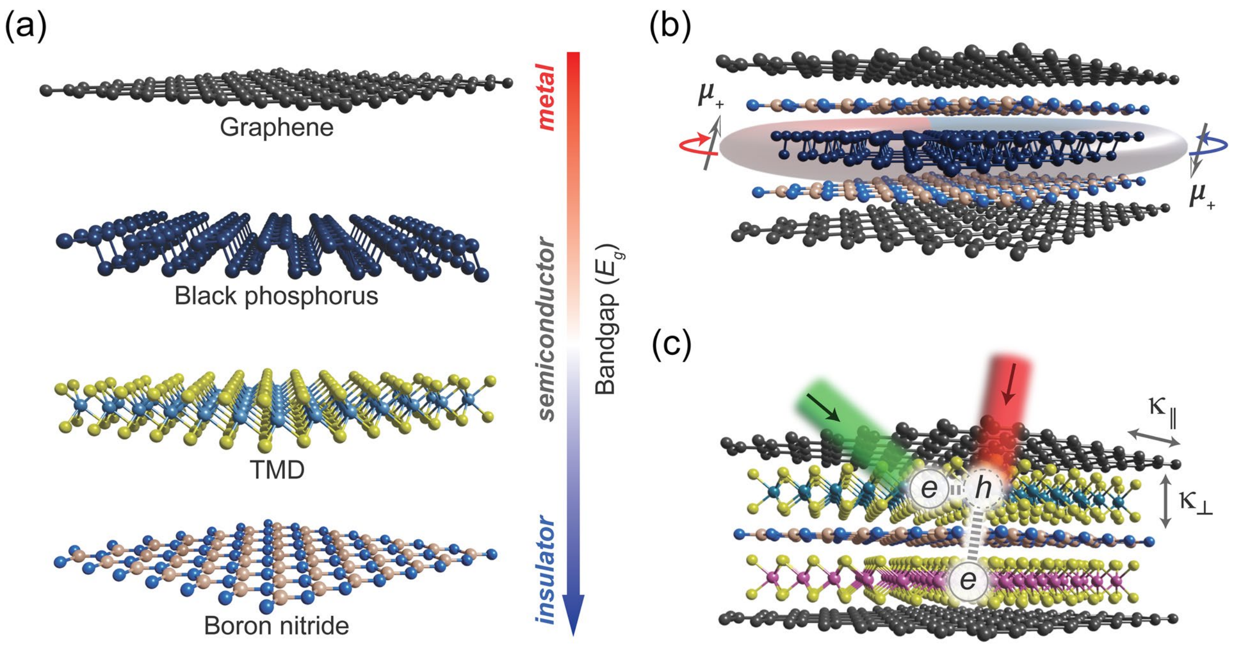

Figure 1: Schematic illustrations of (a) 2DMs with diverse atomic thicknesses, chemical compositions, and bandgaps (E_g), and (b, c) vdW heterostructures formed by stacking 2DMs as *"deck of cards"* in various sequences manifesting edge-mediated magnetism (b), intralayer and interlayer electron (*e*)–hole (*h*) bound states (or excitons) (c), in-plane ($\kappa_\parallel$) and out-of-plane ($\kappa_\perp$) thermal conductivities (c).

[6–8]. Here, we emphasize on the inorganic nature of the 1D and 0D ingredients to distinguish them from the widely researched carbon nanotubes (CNT) and fullerenes [9–11]. For brevity, we will occasionally refer to the 2D materials, inorganic 1D nanotubes and 0D fullerenes as 2DM, INT, and IF, respectively. We will begin by briefly reviewing 2DM, INT, and IF for context. The following section will describe the coupling of INTs with other inorganic nanostructures. Next, early examples of integrating 2DMs with various inorganic nanostructures will be discussed, and how the ensuing interface introduces unique structural features distinct from the conventional all-2D heterostructures will be analyzed. The subsequent section will focus on the possible approaches to engineer hierarchical nanostructures for functional device fabrication. Finally, we will conclude by providing an outlook to conceive future experiments with the newly proposed nanostructure, thereby expanding the status of layered materials research to new researchers in the field.

Two-dimensional materials (2DMs)

2DMs are generally classified as materials with one of their three dimensions close to or less than one nanometer. At this atomic thickness (~ 5–10 Å) [Fig. 1(a)], these materials start behaving as "all-surface" materials dramatically different from their bulk counterpart primarily due to the drastic change in their electronic density of states (DOS). 2DMs by design create a platform where sub-atomic particles (e.g., electrons, photons, phonons) can freely move in two dimensions, but are tightly confined in the third, thus forming a two-dimensional electron gas (2DEG) critical to comprehend most solid-state electronic and logic circuit operations.

2DMs are derived, in most cases, from layered compounds, which can be described as a *"deck of cards"* [Fig. 1(b), (c)], i.e., molecular slabs where the atoms are held tightly to each other via covalent bonds within the layer and the layers are stacked together into a 3D lattice by weak van der Waals (vdW) force. Layered materials, like WS_2 are highly anisotropic exhibiting large differences in their physio-chemical behavior along the different axes. For instance, the electrical conductivity within the layer (*a*–*b* plane) can be one to two orders of magnitude larger than that in perpendicular to the layers (along the *c*-axis) [12]. Similarly, since the surface of the *a*–*b* plane (basal surface) is atomically smooth and fully bonded, its chemical reactivity is relatively low toward many chemical reactions. Contrarily, the prismatic surfaces along the *c*-axis (*a*–*c* plane) suffer from abundance of dangling bonds and consequently, are chemically reactive. In practice, however, no surface is perfect and the defects on the basal surfaces serve as "hot-spots" inducing highly anisotropic chemical reactivity, which is conducive for reactions such as laser-induced layer-by-layer removal in MoS_2 [13].

Layered (vdW) compounds can be "peeled off" from their bulk crystals into monolayers of materials. It is the same vdW force that drives the layer-by-layer assembly of different 2DMs resulting in vdW heterostructures [Fig. 2(c)] [4, 5, 14, 15], so long as the 2DM surfaces are free from coordinatively unsaturated (or dangling) bonds and charge traps. Assembling

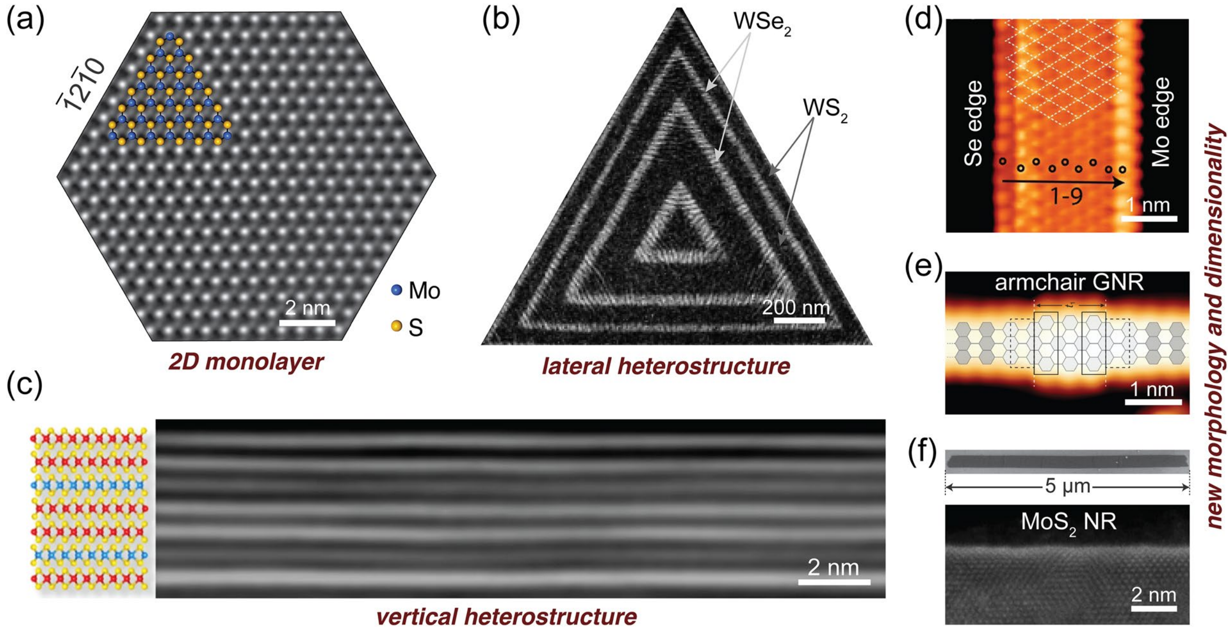

Figure 2: (a) Atomic resolution HAADF-STEM (FFT-filtered) image of a monolayer MoS$_2$ crystal (redrawn from Ref. [38]). (b) SEM image of monolayer coherent *lateral* TMD heterojunction. Reprinted with permission from Ref. [23], copyright 2018 American Association for the Advancement of Science. (c) Cross-sectional STEM image of vertical TMD heterostructure consisting of multiple TMD monolayers. Reprinted with permission from Ref. [37] copyright 2021 Nature Publishing Group. High resolution STM images of ultranarrow (d) 1D-MoSe$_2$ nanoribbon crystal (reprinted with permission from Ref. [42], copyright 2017 American Chemical Society), and (e) graphene nanoribbons (GNRs) (reprinted with permission from Ref. [43], copyright 2021 American Chemical Society) with spatially modulated edges. (f) SEM (top) and HAADF-STEM (bottom) images of an MoS$_2$ nanoribbon (redrawn from Ref. [38]).

several 2DMs into vdW heterostructure is a powerful tool to exploit the synergetic effects creating a panoply of opportunities to manipulate the complex motions of electrons, excitons, and phonons within the heterostructure [Fig. 1(b), (c)]. For instance, vdW heterojunctions comprising of *p*- and *n*-type semiconductors manifest gate-tunable diode like current rectification at the *p*–*n* junction, vastly different from bulk heterojunction [16–18]. The interactions between constituent 2DM layers in a vdW heterostructure give rise to interlayer (type II) excitons and other interesting spin-valley properties [19–21], which essentially dictates the new charge-transfer dynamics in the system. Studies on phonon dynamics in 2DMs have significantly refined our understanding of heat transport in solids. It has been demonstrated recently that stacking large area semiconducting 2DMs with random interlayer rotations produces a highly anisotropic solid offering a pathway to heat-management in digital electronics [22]. Importantly, lattice-commensurate 2DMs can be "stitched" synthetically forming atomically sharp and defect-free coherent lateral heterojunctions with major implications in their strain properties and band structures [Fig. 2(b)] [23, 24]. Another emerging direction in the 2D field is stacking and twisting of 2DMs to create moiré superlattices with unconventional electronic and magnetic correlations, which has spawned "twistronics" as a major sub-field in 2DM research [25, 26].

Layer-by-layer synthesis of materials has been practiced for decades via molecular beam epitaxy (MBE) [27], metal organic vapor phase epitaxy (MOVPE) [28], atomic layer deposition (ALD) [29], and even vdW epitaxy (vdWE) [30]. Although these techniques laid the foundation of synthetic layered materials, the high operational cost and low throughput of such ultrahigh vacuum (UHV)-based methods prevented them from achieving scalability and versatility required for large-scale applications, such as energy harvesting device fabrication. Recent advances in the synthesis of 2DMs via chemical vapor deposition (CVD) and metal organic chemical vapor deposition (MOCVD) have greatly expanded the scope of new discoveries in the 2D field. From the large-scale production of graphene [31], transition metal dichalcogenides (TMDs) [32, 33], and other materials [34] with exceptional properties to the monolithic integration of the 2DMs into functional devices [15, 35], these new methods have led to versatile 2DM platforms as potential candidates for ultra-fine device technologies. Notably, a recent study has demonstrated a contact resistance of 123 Ω-µm, an on-state current density of 1135 µA µm^{-1} and an on-off ratio larger than 10^7 in a CVD-grown monolayer MoS$_2$ transistor defining benchmark figures of merit for large-scale 2D semiconductor technologies [36]. Advances in materials synthesis have not only been limited to achieving high-quality and pristine monolayer 2DMs but also resulted in vdW heterostructures [37] and morphologically

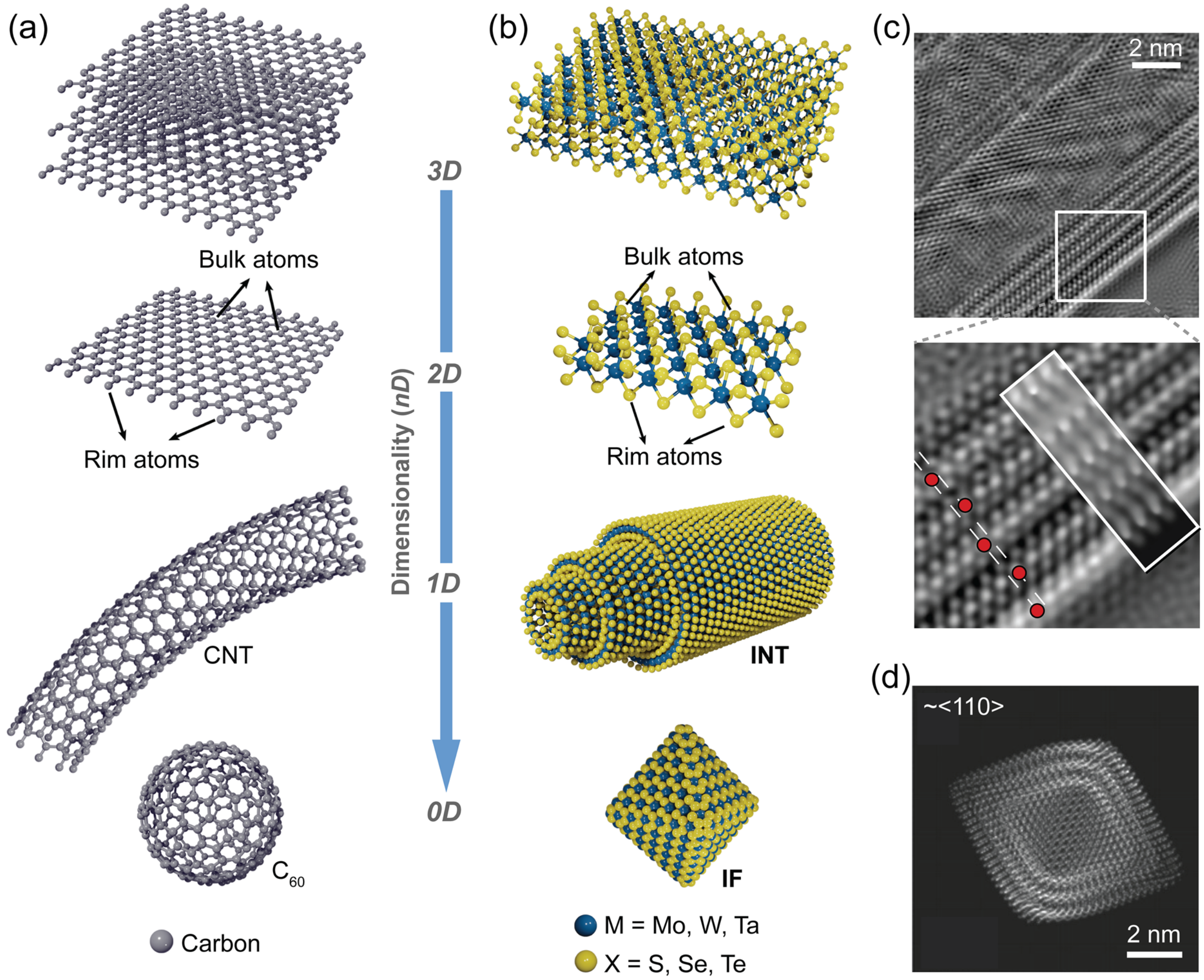

Figure 3: Atomic models illustrating dimensional transformation of (a) graphite (3D) via graphene (2D) and carbon nanotube (1D) to fullerenes (0D). (b) Schematic illustrating the graphitic analogue of MX_2 (M = Mo, W, Ta; X = S, Se, Te) from 3 to 0D. (c) Focal series reconstruction of a WS_2 nanotube taken in HRTEM (top). Zoomed-in HRTEM image of the five-shell nanotube (bottom). The dotted line shows the chirality of the shells. A simulated best fit is enclosed by the white box. (d) Calculated electrostatic potential image of a WS_2 nanooctahedra (the smallest IF available) (redrawn from Ref. [50]).

diverse layered materials [38–43] [Fig. 2(d)–(f)] with proven significance in developing functional low-dimensional architectures beyond 2D [44]. Considering the current state-of-the-art in synthetic 2DMs and the possibility of integrating them into practical electronic devices, it will be critical to establish robust and scalable synthetic routes for 2DMs encompassing all manner of topologies, phases, and electronic states.

Summarizing the enormous research output in the 2DM field is a daunting task, and there are major review articles on this topic published elsewhere [4, 5, 14, 45–49]. This article aims to deliver the key message that 2DMs are a powerful class of materials exhibiting properties that no other materials system can emulate. Most importantly, we wish to underscore 2DMs' importance as a potent materials platform for generating nanoscale architectures well-beyond the traditional all-2D vdW heterostructures.

1D inorganic nanotubes (INTs) and 0D inorganic fullerenes (IFs)

Another important virtue of inorganic layered compounds is that they can form hollow closed nanostructures in 1D (INT) or 0D (IF) (Fig. 3) [6–8, 50]. From physicochemical principles, the notion of hollow closed nanostructures is not trivial at all. First, hollow core of mesoscopic dimensions (> 1 nm) is not favorable from the thermodynamic standpoint. No chemical bond (electron density) is stable at these interatomic distances, and atoms in materials generally prefer to maximize their bonding to their neighboring atoms. Nonetheless, the propensity of layered compounds, like WS_2 and MoS_2 to fold and form such hollow structures stems also from the anisotropy of layered materials. When brought to small dimensions (~ 100 nm), the ratio between surface atoms having dangling bonds (n) to the number of fully bonded "volume" atoms (m) in the layer increases as

$1/(n+m)$. Owing to the large anisotropy of 2DM, the surface atoms accumulate a large chemical energy in the dangling bonds on the prismatic faces. This stored energy is released upon folding the layer and seaming, which heals the dangling bonds. In general, the 1D and 0D nanostructures are metastable, i.e., they are more stable than the material having flat surface with the same number of atoms, but are overall, less stable than the infinite (flat) layer. [51] The energetic budget of folding the layers requires initial investment of energy, which is why these 1D/0D nanostructures are usually formed at elevated temperatures. The initial invested energy is more than compensated upon healing of the dangling bonds and forming the hollow cage structures. In rare cases, like imogolite, the nanotube structure is more stable than the infinite flat layer [52], which is probably the reason they are mined, i.e., they are stable over geological timescales. However, further discussion of this phenomenon is beyond the scope of this review.

The synthesis of fullerene-like nanoparticles and nanotubes of WS_2 by sulfurizing WO_3 nanoparticles was studied first [53]. The sulfurization reaction, was shown to start on the metal-oxide nanoparticle surface, proceeding layer-by layer inwards until all the oxide core is consumed and is converted into the respective metal dichalcogenide hollow 0D and 1D nanostructures. In fact, the metal oxide nanoparticle serves also as a consumable template facilitating thereby the folding and seeming of the closed MS_2 layers. This reaction was gradually scaled-up to produce commercial quantities of "industrial grade" IF-WS_2 nanoparticles. MoS_2 and WS_2 nanotubes were synthesized by variety of methods, including CVD [54] and careful sulfurization of MO_3 ($M = Mo, W$) nanowhiskers [55]. This synthetic methodology was confirmed by other studies [56–58].

Once MS_2 nanotubes and fullerene-like nanoparticles became available in adequate quantities, their properties were elucidated in a systematic fashion and several potential applications were identified. In fact, the most eminent application of the IF-WS_2 nanoparticles, which was later commercialized on a large scale, was for heavy duty lubrication [59, 60] and machining of metal surfaces with aqueous emulsions containing the nanoparticles. More recently, the favorable effect of adding small amounts of IF-WS_2 nanoparticles and their nanotubes on the mechanical, thermal and tribological properties of various polymers were investigated [61, 62]. Most captivating, however, are the electrical [63–65], optical [66, 67], mechano-electrooptical [68, 69] and electromechanical [70] phenomena, which provide intriguing prospective for device applications of MS_2 nanotubes.

Nanotubes and IF nanoparticles from variety of binary and ternary compounds with lamellar structure were prepared in the past and studied by *in silico* methods [71, 72]. In particular, numerous nanotubes from the non-stoichiometric so-called misfit layered compounds (MLC) were synthesized in recent years [73, 74]. These compounds can be generally described as a superstructure consisting of periodically alternating layers of a compound with rocksalt structure- MX and a layer of a compound with hexagonal structure, i.e., $(MX)_{1+y}(TX_2)_m$ (with M = Sn, Pb, Sb, Bi, rare earth atoms (Ln); T = Sn, Ti, V, Cr, Nb, Ta; X = S, Se, Te; $0.08 < y < 0.32$; $m = 1, 2, 3$). However, no further reference to the structure and properties of MLC nanotubes will be given in this minireview.

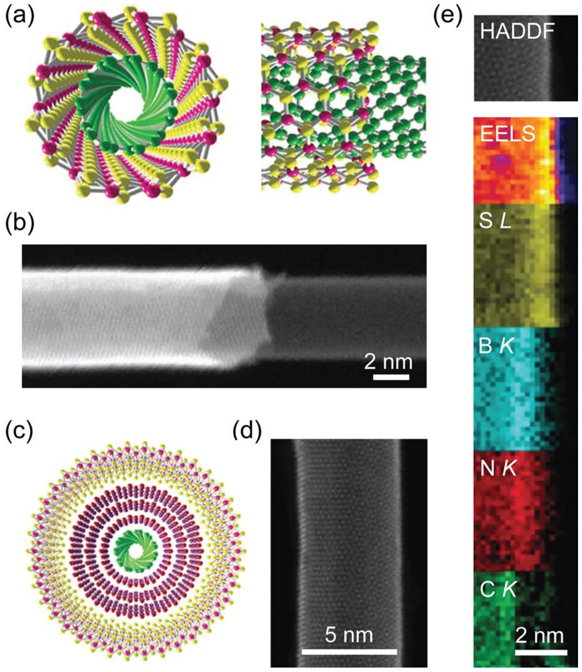

Figure 4: (a) Atomic models of SWCNT-MoS_2 1D vdW heterostructure. (b) HAADF-STEM image of a single-walled MoS_2 nanotube grown on a SWCNT. (c) Atomic model of an SWCNT–BNNT–MoS_2 1D ternary vdW heterostructure. HAADF-STEM image (d) and EELS mapping (e) of a 5-nm-diameter 1D ternary vdW heterostructure. Reprinted with permission from Ref. [75], copyright 2020 American Association for the Advancement of Science.

Integrating INTs with other nanoparticles and nanotubes

The synthesis of hybrid nanoparticles with inorganic nanotubes backbone shows some promise for different applications. For example, light absorption followed by energy or vectorial charge transfer from the nanotube can be beneficial for energy harvesting and storage and catalytic processes among others. An outstanding example is presented by the core–shell C–BN–MoS_2 nanotubes, developed originally by Maruyama and co-workers (Fig. 4) [75]. Fast pump (in the IR range) probe (in the visible) excitation of such nanotubes, revealed two distinct processes [76]. Reduced absorption of the A and B excitons of MoS_2 in the ultra-fast ($\sim 10^{-15}$ s) time domain, which was attributed to Columbic interaction between the straddled biexciton of the carbon nanotube (in the IR range) and the A and B excitons of

MoS_2. Subsequently, in the picosecond (~ 10^{-12} s) time domain a slower process attributed to a charge transfer from the carbon nanotube to the MoS_2 surface was observed. This process was enabled by electron tunneling through the insulating BN nanotube layer. In another work [77], single layer MoS_2 (shell) nanotubes conformably coating multiwall (core) carbon nanotubes were obtained via hydrothermal synthesis. X-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy measurements strongly indicated an electron transfer from the carbon nanotube in the core to the MoS_2 shell.

Another interesting example is provided by films made of WS_2 nanotubes decorated with gold nanoparticles [78]. First, the surface modified nanotubes were assembled into films. Next, Platinum contacts were established on the film surface, which was exposed to dry air flow with different NO_2 concentrations. Illuminating the film, periodically with 530 nm light and measuring the resistivity of the film, the authors found that they can detect NO_2 gas with a remarkable sensitivity (250 ppb–2 ppm).

In another work, a binary hybrid of the polymer poly(3 hexylthiophene) (P3HT) and CdSe quantum dots was prepared to which WS_2 nanotubes were added [79]. Energy transfer from the quantum dots to the nanotubes led to substantial fluorescence quenching, which was documented via transient fluorescence measurements. In a related study, single layer PbI_2 (ZnI_2) nanotubes were grown by pulsed laser melting in the hollow core of multiwall carbon nanotubes (MWCNT), which served as a template [80]. Irradiation of the material with 465 nm light source led to excitation of the PbI_2 sheath and a photocurrent was recorded, due to an effective charge transfer to the conductive MWCNT. In another recent study [81], Cs_4PbBr_6/$CsPbBr_3$ nanoparticles with perovskite structure were precipitated onto WS_2 nanotubes and their structural and electrooptical characteristics were elucidated. It was shown that the coupling between the perovskite nanocrystals and the nanotubes led to 96% quenching of the perovskite photoluminescence, which was attributed to a fast electron transfer from the former to the latter. Figure 5(a) is a schematic illustration of this process. Moreover, this fast charge transfer led to effective photodegradation (96–98% in 90 min) of methylene blue dye in aqueous solutions as illustrated in Fig. 5(b).

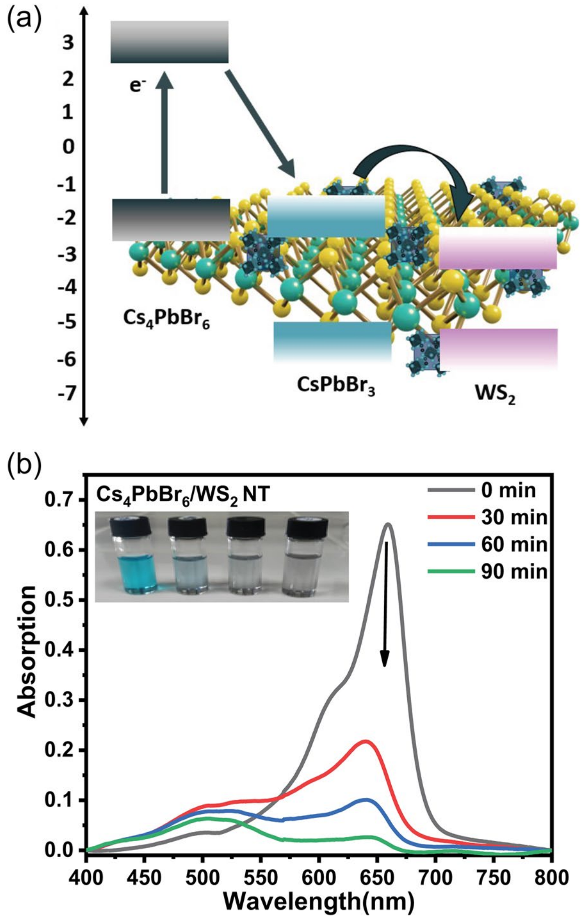

Figure 5: (a) Schematic illustration of the charge transfer route from Cs_4PbBr_6 nanoparticle to WS_2 nanostructures. (b) Time-dependent absorption spectra of methylene blue (MB) decolorization process by Cs_4PbBr_6–WS_2 nanotube composite. *Inset:* Photographs of degraded MB after sequential irradiation every 30 min. Redrawn from Ref. [81].

The combination of WS_2 nanotubes with carbon nanoparticles/nanotubes bears some technological promise for energy storage technology. The large storage volume of the WS_2 nanotubes, e.g., for intercalation of alkali ions in the van der Waals gap and their electrocatalytic reactivity together with the high electrical conductivity of the carbon nanostructures makes these hybrid nanostructures highly warranted for electrical energy storage and electronic applications. One example to this effect is a study in which hydrothermal treatment of multiwall carbon nanotubes led to a conformal sheathing of closed MoS_2 layer onto MWCNT, i.e., MWCNT@MoS_2 nanotubes [77]. Electron transfer from the MWCNT to the conformal MoS_2 sheath was confirmed, which led also to higher density of field emission currents from this nanostructure compared to the pristine MWCNT. In another study, fullerene-like WS_2 nanoparticles anchored to graphene sheets were prepared via ball milling of WO_3 nanoparticles together with graphene sheets and their subsequent high-temperature sulfidation [82]. This composite material served as anode for rechargeable Li-ion batteries exhibiting very good capacities (587.1 mAh g^{-1}) for a charging/discharging current of 200 mA g^{-1}). To improve the charge–discharge recyclability of the material, the IF-WS_2 nanoparticles were coated by a conformal thin film of amorphous carbon, producing a highly reversible charge–discharge capacity (371.9 mAh g^{-1}) under high current density (1000 mA g^{-1}). In a related recent work [83], multiwall WS_2 nanotubes were conformably coated with thin amorphous carbon sheath, lending itself for a highly stable recyclable lithium-ion and sodium-ion batteries with reasonable charge density capacities.

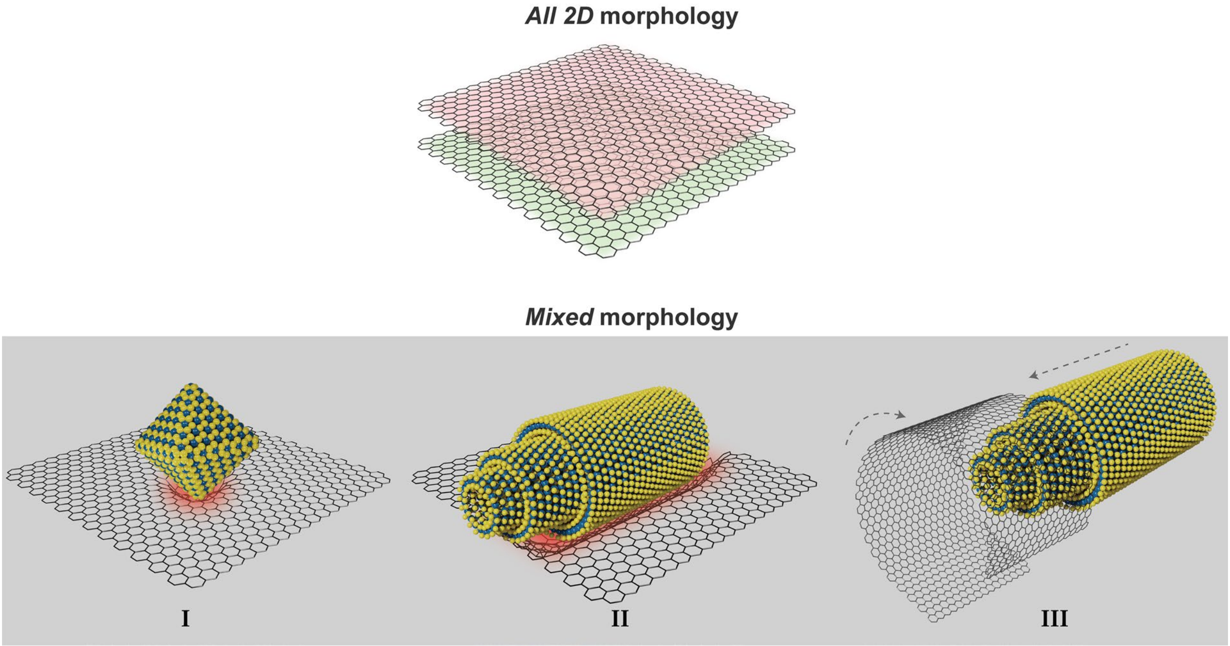

Figure 6: Schematics illustrating the integration of 0D IF (**I**) and 1D INT (**II**, **III**) with 2DMs generating mixed morphology, dimensionality, and interfaces distinct from those of an all-2D vdW heterostructure.

Integrating 2DMs with 1D INTs and 0D IFs

As briefly discussed in the previous section, it is evident that vdW interactions are not confined within the purview of 2DMs. So long as the surfaces in direct contact in the heterostructure are free of dangling bonds, they can form vdW heterostructures. Interacting surfaces satisfying these two criteria, irrespective of their morphology and dimensionality, will lead to vdW heterostructures with "mixed" dimensionality [14, 84, 85]. In such system, the participating candidates are not constrained by lattice matching criteria rendering them ideal to realize nearly infinite number of vdW materials. As articulated by Jariwala et al. [85] the drastic transition of the DOS at the "mixed" interface has many implications in the electronic properties of the system. For instance, atomic defects, charge impurities, disorder in covalently bonded systems (e.g., all-2D in-plane vdW heterostructures) result in trap states that often give rise to non-radiative carrier recombination [86]. Another critical factor is the orbital hybridization at the covalently bonded interfaces that dictates the interfacial charge transfer, thereby leading to band-tailing and built-in potential. In the case of vdW interfaces, the hybridization factor is essentially absent due to the coordinatively saturated surface/edge states of the constituents, which, in turn, minimizes carrier delocalization and diffusive charge transport across the interface [87, 88]. In essence, the key message here is that the standard carrier transport physics for solid state electronic devices ought to be revisited in the light of the new vdW interfaces.

As mentioned in the above, 2DM surfaces are free from dangling bonds and so are (mostly) those of the closed shell 0D/1D inorganic nanostructures. Therefore, as illustrated in Fig. 6, 2D crystals (e.g., graphene, TMDs) can be coupled with 0D and 1D structures in multiple ways all leading to diverse interfaces distinct from the all-2D vdW interface. As discussed previously in this review, the semiconducting nature of IFs (**I** in Fig. 6) and nanotubes (**II**, **III** in Fig. 6) elicits efficient photo-absorption and carrier diffusion under electrical or optical stimuli. Semiconducting nanotubes offer enhanced optical absorption cross-section in the visible to near-infrared range due to the formation of ultranarrow optical cavities and 1D joint DOS (jDOS) [89]. Moreover, the curvatures of the nanotubes induce chiral properties to the nanostructures that can be characterized by the two-integer (n, m) indices and the chiral angle (θ) (Fig. 7). Multiwall chiral WS_2 nanotubes lack time reversal symmetry and exhibit Berry curvature, which is commensurate with 1D superconductivity [63], and the bulk photovoltaic effect observed in devices based on such nanotubes [68]. On the other hand WS_2 nanotubes of large diameter (> 80 nm) were shown to confine optical cavity modes, which is conductive for strong coupling effect (e.g., exciton-polaritons) and strong light scattering [66]. Similarly, 2DMs have a wide range of potential applications in optoelectronics and spintronics owing to their diverse band dispersion, spin-valley degrees of freedom, and chiral properties. Therefore, combining 2DMs with the inorganic low-dimensional structures—0D IFs and 1D INTs—will allow the creation of exotic interfaces with diverse morphologies and properties.

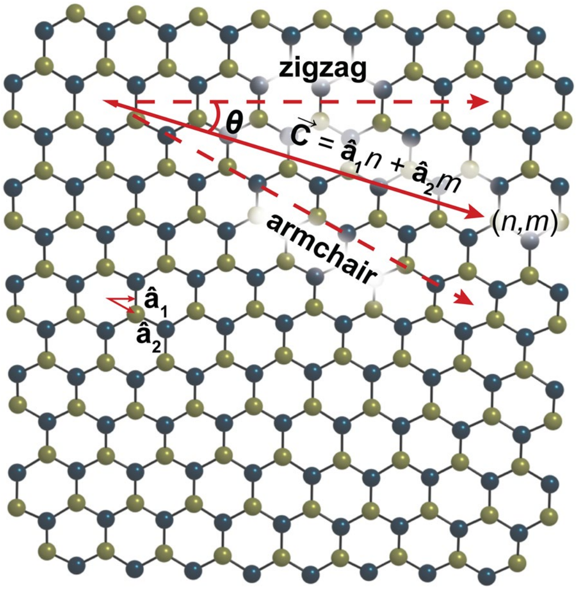

Figure 7: Schematic illustrating the two-integer (n, m) indices, chiral angle (θ), and the chiral vector (**C**) on a WS_2 sheet (top view) before it folds into a nanotube. Folding along the dotted and the solid lines generates achiral and chiral nanotubes, respectively.

By design, such novel interfaces will drive the curiosity both in applied and fundamental sciences. For instance, one might ask what happens to the jDOS of a 1D nanotube when it is in the vdW proximity (~3–5Å) to a direct gap 2DM (or a high κ dielectric)? A recent study has shown graphene contacts to a WS_2 nanotube manifesting photocarrier collection at zero bias with an external quantum efficiency (EQE) of ~ 1% [90]. Although defects in the WS_2 nanotubes could be responsible for such performance, it is critical to consider the nanoscopic structure of the interface between the nanotubes and 2DM due to the non-planar contact geometry. One might also inquire how does the diffusive carrier transport in nanotubes vary with different 2DMs in contact? Gaining insights from Shen et al.'s seminal work on achieving ultralow contact resistance [36, one can inspect how do the carrier mobility and doping levels vary with different contact geometries such as *end-to-end* (1D–1D) and *end-to-face* (1D–2D) nanotube junctions? The demonstrations of various co-axial and mixed-junction geometries are not rare in the nanowire and the 2D fields [91–94], but studies on INT-based hybrid configurations—both co-axial and mixed-junction—addressing Ohmic, Schottky, and *p*–*n* junctions are rare. Xiang et al.'s demonstration of electrical transport measurements inside a TEM is notable since it could lead to exciting research directions in electrically significant co-axial, hybrid nanotubes (Fig. 8). [75]. One effective route to create mixed-dimensional interfaces is through utilizing intercalation-driven "roll up" processes leading to higher order vdW superlattices with diverse compositions, topology, and chirality. The key conclusions from the early reports on CNT-based flexible devices Ref. [95], Ref. [95] and more recent TMD-based nano scrolls Ref. [97] have laid a strong foundation to develop material platforms bottom-up for technological applications, such as nanoscale capillarity in nanofluidic devices. Another important question is—how the localized strain emanating from the mixed-dimensional interface modifies the optical and optoelectronic properties of the 2DM ingredient. While there are reports concerning the strain-induced optical property modulation in 2DM within mixed-dimensional nanostructures such as 1D silicon nanowire–2D TMD, 0D nanoparticles–2D TMD or just strained nanobubbles (0D) in 2D TMD [95–97], not much is known about the strained 2DMs integrated with INTs or IFs despite them being an equally appealing materials platform. From a fundamental science perspective too, the new interface between 2D and 1D/0D introduces significant tunneling barrier between the components thereby creating great demands for new theories and model systems, yet to be explored.

One major issue with the study of inorganic nanotubes/fullerene-like (1D/0D) materials is their poly dispersible nature.

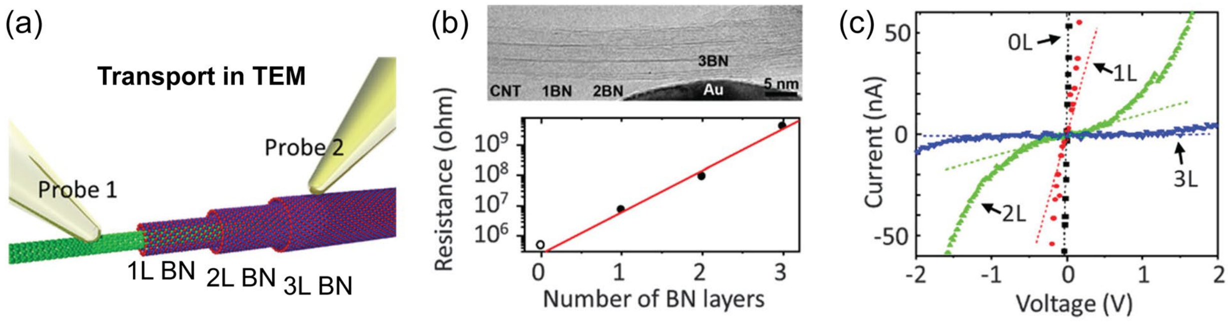

Figure 8: (a) Schematic of the transport studies of coaxial, multiwall nanotubes in a TEM. (b) Bright-field TEM image of the device (top) and resistance vs number of BN layers (bottom). (c) *I–V* curves obtained in transport measurement inside TEM. Reprinted with permission from Ref. [75], copyright 2020 American Association for the Advancement of Science. Adapted from Ref. [75].

Not only each nanoparticle is made of 5–20 WS_2 (MoS_2) layers of different diameters (i.e., different number of atoms, chirality, and defect density), but the synthesized nanotubes also have different lengths, which calls for a tedious separation process [66]. Further exacerbating their research is their diminished photoluminescence intensity, which is a direct consequence of the indirect bandgap occurring in multiwall WS_2 (or MoS_2). Establishing reliable electrical contacts to curved surfaces is not straightforward and requires extensive troubleshooting.

Also, curved surfaces are more difficult to probe with atomic resolution than flat 2DM via any of the high-resolution techniques, like transmission electron microscopy or scanning probe microscopy. These factors are among the reasons why the study of such nanotubes has not spawned large number of researchers.

Generating the new integrated system

Now that we have established an understanding of the various prospects and challenges in obtaining the coupled mixed-dimensional nanostructures, it is critical to provide possible directions on how one can proceed to generate such structures. It is evident from the foregoing discussion that an assembly of two or more dimensionally and morphologically dissimilar nanostructures relies on innovative fabrication techniques addressing two crucial factors—spatial controllability (or resolution) and atomically sharp interfaces. While existing literature on manually stacked vdW materials provide some insights on achieving high-quality 2D interfaces, it is important to recognize that similar techniques cannot be implemented to produce atomically smooth mixed-dimensional interfaces mainly due to the non-planar interfacial geometry between the constituents. To this end, leveraging robotic technologies to “pick-up” and “put-down” nanostructures under vacuum environment would ensure sub-micron (or below) spatial resolution and ultrasharp interfaces with unprecedented structural uniformity, scalability and reproducibility [98]. For example, a recent study by Mannix et al. demonstrated that large area TMD-based vdW stacks can be manufactured by robotic assembly with unprecedented speed and spatial and angle control [Fig. 9(a)] [99]. This study underscored the importance of polymer adhesive (e.g., composition, glass transition temperature, materials compatibility of polymers) to precisely and non-invasively carry out the “pick-up” and “put-down” processes. For generating the mixed-dimensional structure in a similar robotic system, the polymer will be the critical component in a sense that its viscoelastic property will dictate the integrability of the 0D, 1D, and 2D components ultimately determining the quality of the ensuing non-planar interfaces. Another study by Kim and co-workers presented large-scale programmed assembly of graphene and BN, expanding further the purview of vdW assembly amenable to direct device integration [Fig. 9(b)]. [100]

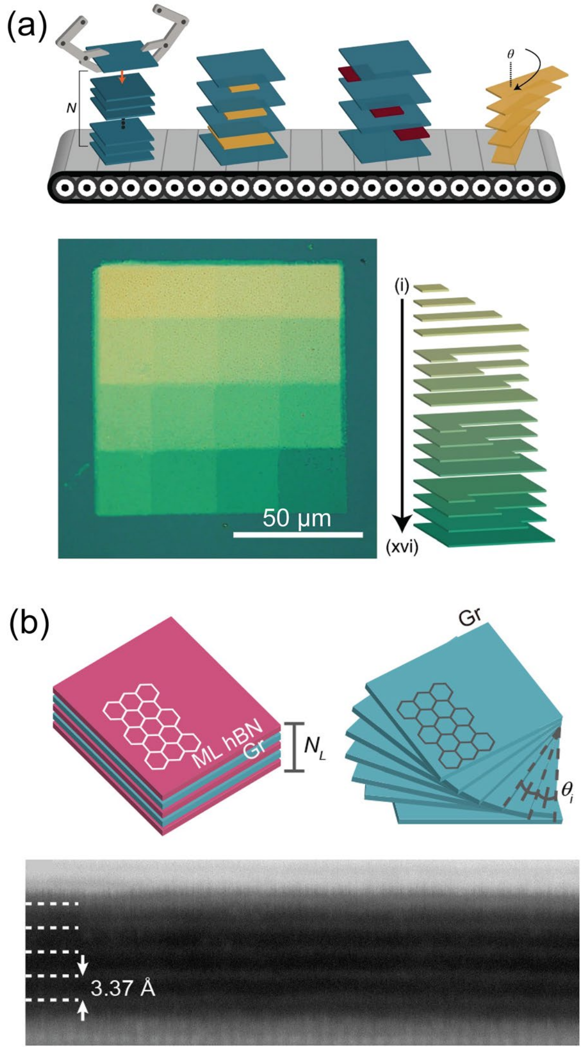

Figure 9: (a) Schematic of the robotic assembly set up (top). Optical micrograph of robotically assembled 1–16-layer MoS_2 grid structure (bottom). Reprinted with permission from Ref. [99], copyright 2022 Nature Publishing Group. (b) Schematic of graphene (Gr) and BN heterostructures (top). Cross-sectional STEM of a Gr-BN vertical superlattice with atomically smooth interfaces (bottom). Adapted with permission from Ref. [100], copyright 2022 American Chemical Society.

Notwithstanding the large body of studies published on heterobilayers of metal dichalcogenides, the number of works dealing with the coupling of TMD nanotubes with single or few layers of another TMD compound is practically close to a neal. A possible direction will be to explore the heteroexcitons (e.g., type II) between WS_2 nanotube and monolayer $MoSe_2$. While such excitons can propagate anywhere in the a–b plane of a WS_2/$MoSe_2$ double layer junction, the bound hole in the $MoSe_2$ monolayer would drift along the axial direction of the electron in a 1D nanotube. Combined with the lack of inversion symmetry and built-in piezoelectric character, an array of WS_2 nanotubes placed on $MoSe_2$ or even graphene monolayer

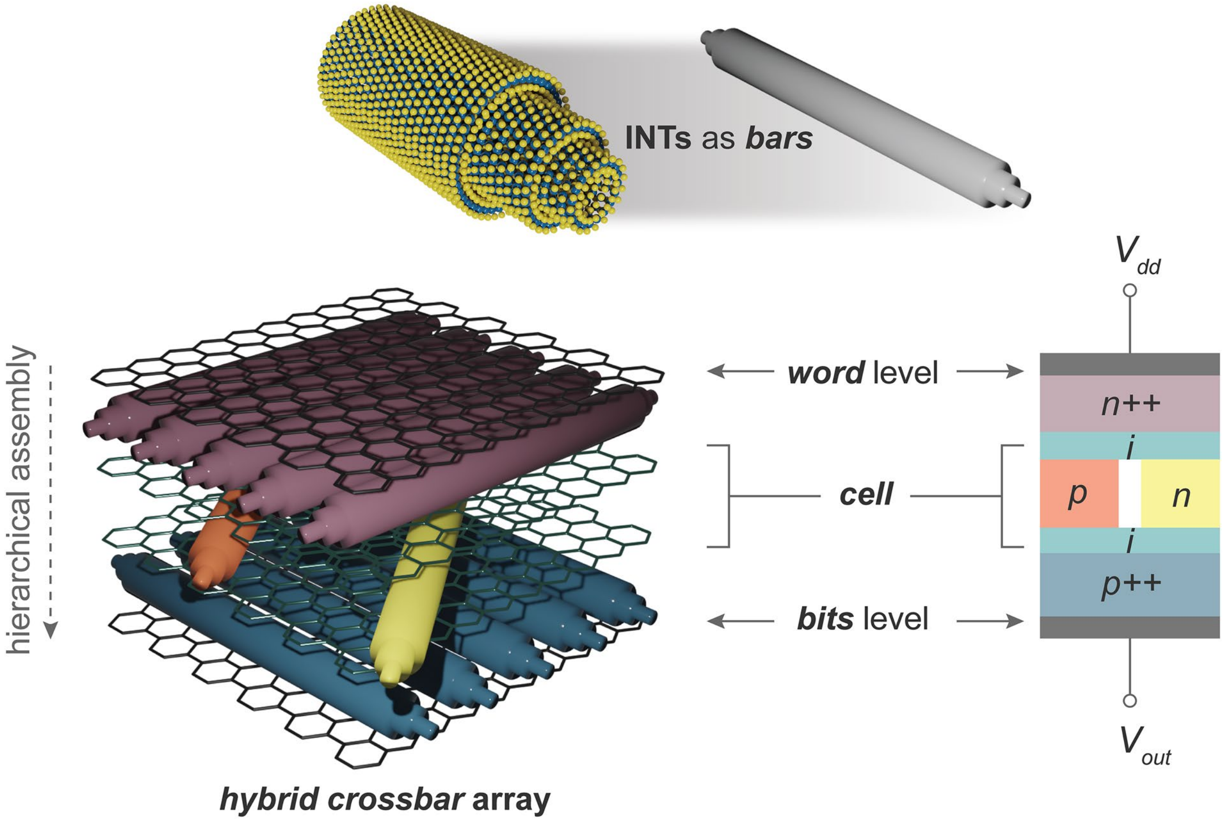

Figure 10: Schematic of the hierarchically assembled hybrid crossbar array as memory/storage device.

could be the basis of ultrahigh density memory/storage devices as illustrated in Fig. 10. In the same vein, in analogy with the work of Guo and co-workers [69], placing an array of WS_2 nanotubes on graphene sheet, perhaps with a BN monolayer as separator and irradiating, could lead to establishing new energy harvesting and storage concept, not exploited so-far. Utilizing automated assembly one can think of creating a hybrid crossbar array where differently doped nanotubes can serve as “bars” in a typical metal-insulator-metal (MIM) geometry [101]. Here heavily doped nanotubes at the top and the bottom layers can be thought of as word lines and bit lines, respectively. Another layer of moderately doped nanotubes (separated from the top and bottom layers by insulating 2DMs such BN) can be sandwiched between the outermost nanotubes forming a “cell” to readout the conductance [Fig. 10]. A carefully engineered crossbar device can minimize the unwanted current flow through the cell by ensuring the high-quality, defect-free interface between the 1D and 2D components. Such hierarchical devices with high-quality interface could address issues such as leakage current in the resistive random-access memory (RRAM) and phase change memory (PCM), among other memristive phenomena. Given the tremendous progress of lithography and robotics, we believe that the scalable production of such high-performance hybrid devices is no longer an illusion.

Conclusions

Compounds with layered structure are investigated extensively for over a century. In this short review, we have briefly described two new paradigms which emerged over the last two–three decades in the research of layered nanostructures, i.e., the *inorganic* fullerenes (IF) and nanotubes (INT), and 2D materials (2DM). Little has been done so-far to advance the merging of these two disciplines with the goal of demonstrating new physics and potential applications in energy harvesting and storage, memory, and catalysis. The very few, but insightful, examples in the literature indicate that the systematic materials integration approach can lead to the observation of unique phenomena, which cannot be revealed by either of them, separately. Hence, we believe that this article will spark interest and kindle curiosity among materials researchers to examine the integrated hybrid platform for many exciting discoveries and impacts.

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Data availability

The data that support the findings of this review article are available from the corresponding authors (T.C. and R.T.) upon reasonable request.

Declarations

Conflict of interest The authors declare no conflict of interest.

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