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Flatlands in the Holy Land: The Evolution of Layered Materials Research in Israel

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The experimental identification of fullerenes in 1985, carbon nanotubes in 1991, inorganic nanotubes in 1992, and graphene in 2004 are cornerstone events that have marked the beginning of the layered nanostructures era of materials science. Nowadays, the synthesis of such low-dimensional systems is a routine practice allowing the controlled fabrication of 0-, 1-, and 2D layered structures of diverse chemical compositions. These systems possess unique physical properties that stem from their structural anisotropy characterized by strong intralayer covalent bonding and weaker interlayer dispersive interactions. This, in turn, results in promising functionality that attracts the attention of scientists from many disciplines including chemists, physicists, material scientists, engineers, as well as life scientists that are interested in both their basic and applied science aspects. Here, a short review of the contribution of the Israeli scientific community to this effort over the past 3 decades, is provided.

1. Introduction

Israel is the birthplace of inorganic fullerenes (IF) and nanotubes based on transition metal dichalcogenides,(TMDs) such as MoS_2 and WS_2.[1] More than 2 decades ago, Tenne and coworkers discovered that, like in graphitic systems,[2] inorganic fullerenes and nanotubes[1a,b] are spontaneously formed at high temperatures. Since then the research on the growth mechanism of such nanostructures and the characterization of their basic structural, chemical, mechanical, and electrical properties became a major research theme in Israel.[3] Following this pioneering work in inorganic 0D and 1D nanostructures, several important industrial applications were developed, the most recognized being solid-state lubrication additives[4] formulated by the Weizmann Institute spin-off company NanoMaterials Ltd. (ApNano).

Here, we present a brief overview of the scientific efforts that followed this original work by Tenne and co-workers in the field of low-dimensional layered materials over the last decades by the Israeli scientific community. We note that the aim of this article is to sketch a general picture of Israeli science in this field and it is not intended to provide a thorough review. Hence, due to lack of space, we were forced to omit many important contributions.

The structure of the review is as follows: In Section 2, the above-mentioned pioneering synthetic studies as well as more recent research on the growth of 2D layered materials are discussed. Section 3 describes characterization efforts aiming to study the structure–property relations in these systems using high-resolution transmission electron microscopy. Section 4 discusses theoretical and computational advances for modeling the structural, mechanical, and tribological properties as well as the sensing capabilities of layered materials. Furthermore, it demonstrates the synergic interplay between theory, computation, and experiment in this field. Section 5 turns to describe Israeli efforts toward the study and utilization of layered materials in electronic and optoelectronic applications. A brief summary and future outlook is presented in Section 6.

2. Synthesis

The recognition that in low-dimensional materials the size, aspect ratio, chemical composition, and phase have a tremendous impact on their physical and chemical properties, has driven the scientific community to study the growth of such entities with the purpose of controlling the above parameters and thus their properties. Starting from quasi-0D systems, early growth mechanism studies of closed-cage inorganic fullerenes via gas-phase reactions revealed that first metal

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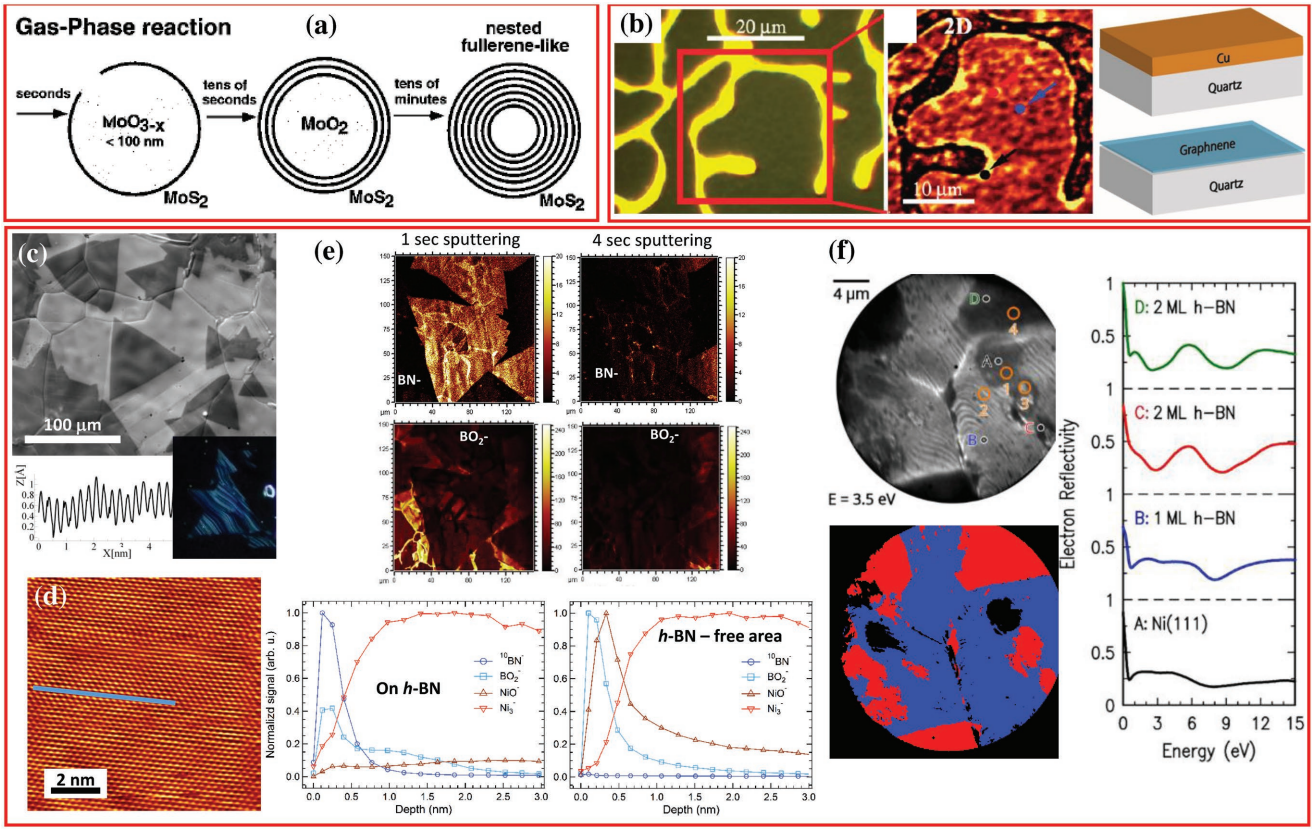

Figure 1. Synthesis and characterization of low-dimensional layered materials. a) Schematic representation of the growth mechanism of inorganic fullerenes and nanotubes. Reproduced with permission.[5b] Copyright 1996, American Chemical Society. b) Direct deposition of graphene on dielectrics by metal film dewetting. Reproduced with permission.[13] Copyright 2010, American Chemical Society. c) Scanning electron microscopy (SEM) image showing large monolayer and single-crystal *h*-BN triangular domains on Ni (the inset at the bottom right shows a dark-field optical microscopy image of a similar domain). d) Scanning tunneling microscopy of *h*-BN on Ni surfaces. e) Time of flight secondary ion mass spectroscopy imaging and profiling of *h*-BN on Ni. f) Large-scale thickness and number of layers characterization by low-energy electron microscopy. c–f) Reproduced with permission.[18] Copyright 2017, IOP Science.

oxide nanoparticles are formed, followed by their sulfurization into the metal disulfide 0D nanostructure (see **Figure 1**a).[1c,3b,5] For the corresponding quasi-1D inorganic nanotubes, two growth mechanisms were proposed by Tenne and co-workers. The first is in accordance with fullerenes, where an elongated metal oxide (or suboxide) is first formed and then sulfurized. However, an alternative route was also suggested, where during the breaking out of the volatile suboxide material and its sulfurization, an elongated 1D oxide metal disulfide nanotube is formed. This enables to achieve large-scale growth of such nanostructures with improved controllability,[1c,5a,6] as well as to expand the synthetic capabilities to other layered materials.[5b,6a,7]

For a successful implementation of the low-dimensional structures in applications such as nanoelectronics and optoelectronics, the ability to synthesize the nanostructures and organize them in a specific pattern is of high importance. To this end, Joselevich and co-workers developed an approach for the guided growth of single-wall carbon nanotubes (SWNTs) along atomic steps and nanofacets.[8] Such a methodology was employed for the assembly of SWNT-based electronic and optoelectronic devices.[9]

While the synthetic procedures to obtain the quasi-0D and 1D systems discussed above share many aspects, their extension to 2D planar systems is nontrivial. Nevertheless, the successful isolation of graphene in 2004,[10] and later on the isolation of transition metal dichalcogenides,[11] and their unique physical and chemical properties, as compared to their bulk counterparts,[10,11] encouraged the scientific community to develop alternative growth methodologies for the formation of single- and few-layer van der Waals solids on substrates. With this respect, in 2009 Ruoff and co-workers were able to grow single-layer graphene on copper substrates by understanding the importance of carbon solubility in the metal,[12] enabling by that the large-scale synthesis of high-quality graphene on cost-effective materials. The formation of graphene on copper forced its transfer to other substrates for further characterization and device fabrication. Such a transfer process induced defects and added impurities to the graphene layer. In an attempt to avoid such a damaging step, Ismach et al. developed a methodology to grow graphene directly on dielectric surfaces via a complex metal film dewetting process during and after the growth (see Figure 1b).[13] A similar approach involving the prepatterning of nickel into nanobars was used for the direct

synthesis of graphene nanoribbons on dielectrics.[14] Moving to other 2D materials, Ismach et al. studied the formation of hexagonal boron nitride (*h*-BN) films on metals with controlled thickness, from few-atomic layers to more than a hundred.[15] It was found that specific growth substrates tend to lead to different thicknesses. For example, the growth of graphene and *h*-BN on Ni and Co leads usually to multilayer films.[15,16] Copper, on the other hand, leads to the growth of monolayer graphene and ultrathin *h*-BN.[17] The understanding gained during such studies enabled to control the film thickness. In one example, Ismach et al. demonstrated that the growth of multilayer *h*-BN on Ni is inhibited by the formation of an intermediate thin B_2O_3 layer. This layer is then reduced in the presence of carbon and nitrogen species to form single- or bilayer *h*-BN[18] (see Figure 1c–f).[18,19]

Beside the gas phase synthesis described so far, Bar-Sadan and co-workers studied the formation of TMD nanoflakes and nanoflowers via wet chemical routes.[20] Moreover, they managed to control the chemical composition of $Mo_{1-x}W_xSe_2$ nanostructures within the range $x \in [0, 1]$, which, in turn, determined the electronic and optical properties of these nanostructures.[20] Furthermore, such nanoflowers were found to present improved chemical catalytic activity for the hydrogen evolution reaction.[21]

Albeit the great success in the synthesis of 0D, 1D, and 2D layered materials over the last years in Israel and around the world, there are many open questions yet to be addressed. The growth mechanism of single- and few-layer TMD materials is still unclear and much work with volatile precursors (such as metalorganics, -chlorides, etc.)[22] is needed in order to improve the quality and uniformity of the films as well as to implement new methodologies for the doping, alloying, and heterostructure formation over large areas. Furthermore, there are many interesting and promising materials, such as black phosphorous[23] that, to our knowledge, have not yet been synthesized at the single- or few-layer level. The rational synthesis of such materials is a limiting factor for their future integration into devices. Hence, these tasks are being currently addressed intensively by several groups in Israel,[24] and we believe will result in new exciting scientific outcomes in the coming years.

3. Characterization and Properties

Characterization is an integral part of the materials science paradigm, bridging between the synthesis, structure, and the obtained material properties. This is especially true in the field of nanomaterial science, where the properties of low-dimensional systems are strongly influenced not only by their chemical composition but also by their structure and morphology. This understanding spurred interest in deciphering the atomic-scale ordering of various layered nanostructures using transmission electron microscopy. To this end, Bar-Sadan et al. investigated the structure of 3D inorganic cages, based on MoS_2 and WS_2.[25,71,72] These studies demonstrated the importance of structural defects in these systems for inducing deviation from the prismatic coordination of the six S atoms around the metallic center. These, in turn, may lead to a change in the electronic structure of the defect and grant a metallic-like character to the system (see **Figure 2**).[25b–d] Such defects created at the grain boundaries, and especially at the seaming of facets within a 3D structure, are not easily annealed, leaving the structure with integral seams and patches that bear a metallic-like character.[25e] In addition, it was found that doping of the layered materials with electron donating atoms, such as Re, promotes the overall phase transformation to a metallic-like 1T phase.[26] For flat 2D layers, electron microscopy characterization studies showed that the domain boundaries within MoS_2 contain patches, where the layer direction is opposite to its surrounding, forming Mo–Mo bridges that induce a new electronic band at 2.5 eV below the Fermi level.[1e]

In addition to structural defects, the physical properties of 2D materials can be significantly affected by strain. For example, the mechanical response and electronic sensitivity of carbon and inorganic nanotubes toward torsional deformations have been extensively studied by Joselevich and co-workers.[27] It was found that the inorganic multiwalled nanotubes can exhibit considerably larger mechanical stiffness with respect to their carbon counterparts.[28] This can be attributed to the nature of the interlayer interactions in these materials and to the occurrence of circumferential faceting. Furthermore, it was shown that torsional strain may induce considerable modification of the electronic properties of carbon and boron–nitrogen–carbon (BNC) nanotubes, making them appealing building blocks for nano- and micro-electromechanical systems (NEMS and MEMS, respectively).[29] Another example of strain effects was found by optical measurements of the UV–vis spectrum of inorganic fullerenes of WS_2 and MoS_2, which showed a clear redshift in the exciton energy that increased with the number of closed layers in the IF nanoparticles.[30] The temperature dependence of the exciton energy was found to be similar to that of the exciton in the corresponding bulk, indicating that the redshift originates from the strain in the bent layers rather than from defects or dislocations.[30]

Israeli groups have also been involved in the study and characterization of the mutual effects of defects and strain on the properties of low-dimensional layered structures. In particular, it was found that defects in the strained surface of MoS_2 fullerenes may contribute to their surface plasmon resonances,[31] leading to free carrier concentrations of ≈1021 cm^{-3}.[31] Furthermore, studies of the optical properties of WS_2 nanotubes and MoS_2/WS_2 fullerenes using resonance Raman spectroscopy revealed interesting effects of defects and strain on their optical response.[32] For example, the intensity of the low-energy component of the A_{1g} vibrational mode was found to be enhanced in inorganic fullerenes and nanotubes, creating a new mode labeled DA_{1g}. It was found that the ratio of intensities between the DA_{1g} mode and the A_{1g} mode correlated with the amount of disorder in the nanostructure. The increase of this ratio with decreasing nanotube diameter indicated increased strain and a larger number of defects. Furthermore, this ratio was found to be larger in fullerenes than in nanotubes,[33] which further illustrated the larger number of defects occurring when a 2D layer is folded into a quasispherical structure than when it is folded into a cylinder.

Raman spectroscopy was also used by Livneh and Sterer for elucidating the role played by the resonantly tuned intermediate

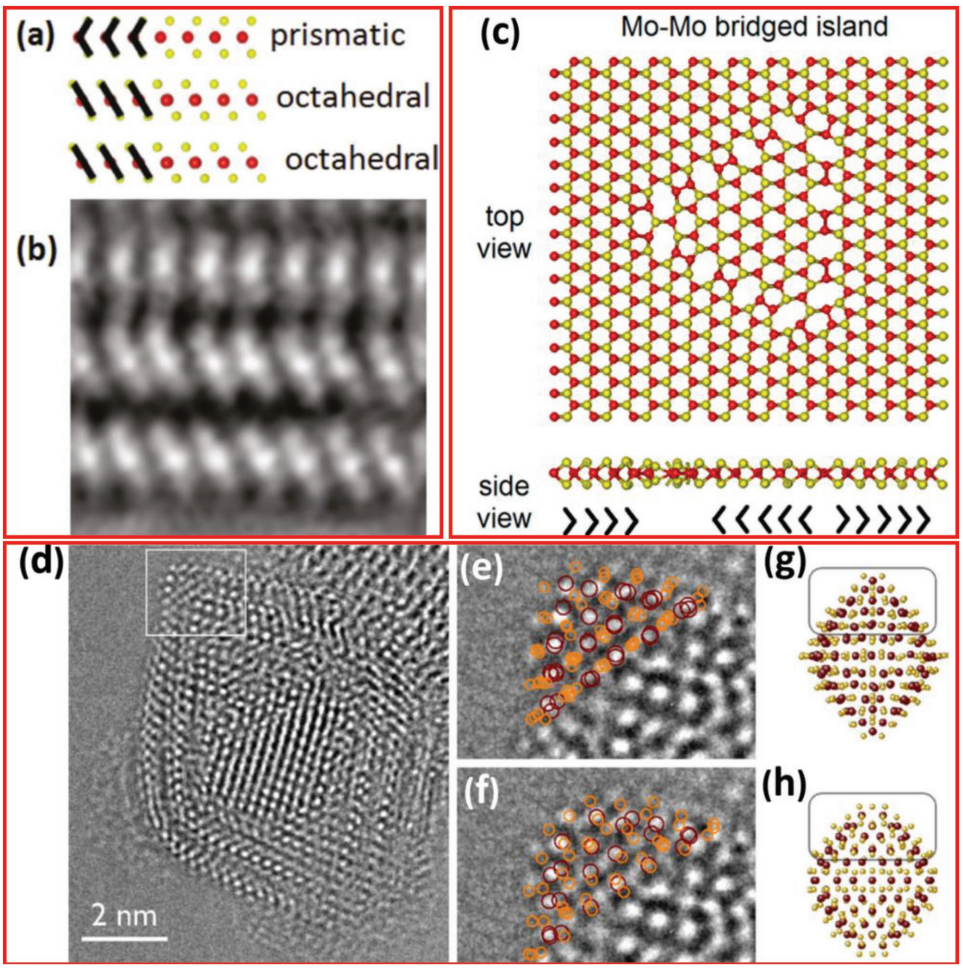

Figure 2. High-resolution characterization of low-dimensional layered material structures. a) Schematic representation of the prismatic and octahedral polytypes of MoS_2/WS_2. The prismatic (semiconducting) layer is imaged as a chevron pattern in TEM images, while the octahedral (metallic) one creates a diagonal pattern. Red and yellow spheres represent Mo/W and S atoms, respectively. b) Wave function reconstructed from a TEM focal series taken at 300 kV, showing the outermost walls of doped WS_2 nanotubes. As it is presented in (a), the two outermost layers are octahedral, and the inner one is prismatic. Reproduced with permission.[71] Copyright 2011, American Chemical Society. c) A density-functional-based tight binding (DFTB) model of grain boundaries in MoS_2 formed by inversion domains connected via Mo–Mo line defects, which were also found experimentally. Reproduced with permission.[72] Copyright 2011, American Chemical Society. d) Atomic resolution TEM image of a MoS_2 nanooctahedron taken in an image-side aberration-corrected FEI Titan 80–300 under negative spherical aberration imaging conditions. A magnified part of the tip of the octahedron revealing the sulfur atoms is shown in (e) and (f), with a superposition of the models presented in (g) and (h). The models in (g) and (h) correspond to two of the 15 hypothetical structures. In (e), one of the most stable structures coincides, showing metallic like apex and edges according to density functional theory (DFT) calculations, whereas the less stable structure fails to match (see panel (f)). Reproduced with permission.[25a] Copyright 2008, the National Academy of Sciences of the United States of America.

exciton states in bulk MoS_2[34a] under high-pressure and low-temperature conditions and to comprehensively explore symmetry assignment of multiphonon transitions.[34b] Going beyond binary TMD systems, low-wavenumber Raman spectroscopy[35] was also shown to enable the systematic determination of Mo/W compositions in mixed $Mo_xW_{(1-x)}S_2$ ternary alloys.

4. Theoretical and Computational-Layered Materials Science

Theoretical and computational research is an integral part of the broad field of layered materials science. Due to the characteristic low dimensions of the relevant systems, theory and computation provide a desired balance between accuracy and computational efficiency. This enables both the interpretation of experimental results and the prediction of novel materials with predetermined properties. Therefore, this field leads to a synergistic cooperation between the experimental efforts described above and theoretical and computational studies each providing complementary added values. Giving a full overview of the scientific activities in this subfield is impractical within the scope of such a short review. Hence, we focus on material science aspects of layered materials modeling in Israel in the past decade. Specifically, we address the study of the structural, mechanical,

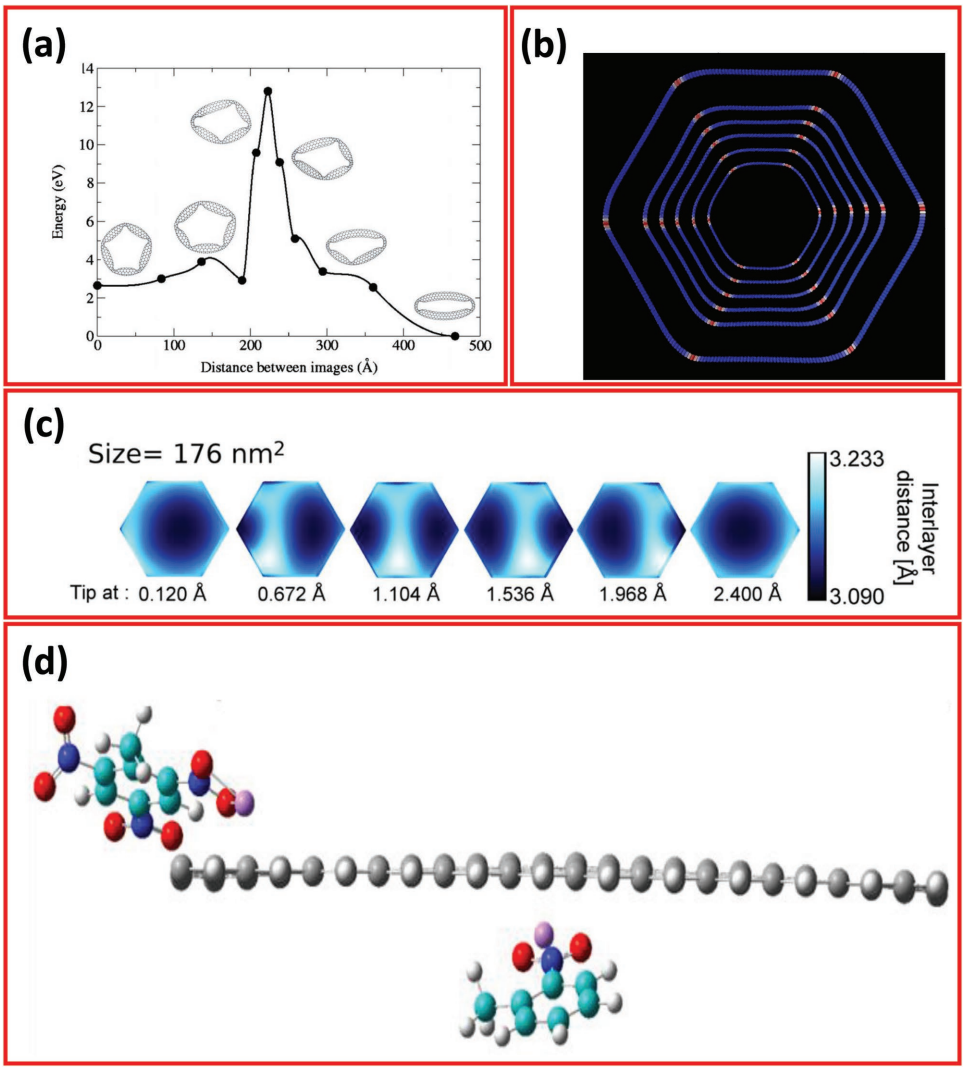

Figure 3. A few examples of Israeli computational studies involving low-dimensional layered material structures. a) Minimum-energy path for the internal conversion between two polygonal toroidal nanotube structures. Reproduced with permission.[36] Copyright 2003, American Physical Society. b) A set of facetted achiral double-walled boron nitride nanotubes exhibiting a hexagonal cross section. Reproduced with permission.[37] Copyright 2016, Nature Publishing Group. c) Soliton propagation during the lateral motion of a 176 nm^2 *h*-BN flake on a graphite substrate. Reproduced with permission.[46] Copyright 2017, Nature Publishing Group. d) Coadsorption of trinitrotoluene and orthomononitrotoluene atop lithium anchoring sites at the surface of a graphene nanoribbon. Reproduced with permission.[49a] Copyright 2017, American Chemical Society.

and tribological properties of these materials as well as their detection capabilities.

Following the enormous global impact that layered materials made over the past 2 decades, the attention of the theoretical and computational scientific community in Israel toward their modeling has picked up momentum over recent years. An early example can be found in the work of Rabani and co-workers, who studied the structural properties of pristine carbon nanotubes that are constrained to a fused toroidal geometry.[36] Surprisingly, the curved tubular structures were found to buckle forming polygonal structures, whose sides consist of nearly linear nanotube sections (see **Figure 3**a). The resulting tension was found to concentrate at the vertices that exhibit a buckled straw-like structure. A similar phenomenon was recently found to occur at the circumference of straight double-walled nanotubes.[37] Unlike the common understanding that nanotubes have a tubular structure, Hod et al. showed that when consecutive nanotube walls share similar chirality faceting occurs resulting in a polygonal cross section (see Figure 3b). This provided a rationalization for the abundance of faceting found in multiwalled boron nitride nanotubes that often present interwall chirality matching, over their carbon counterparts.[38] Furthermore, the factors that dictate the number of facets formed and the facet chirality were unravelled providing good qualitative agreement with experimental findings of faceting and nanotube wall corrugation.[28,39]

Going beyond pristine systems, Wagner and co-workers studied the effects of lattice defects on the structural, mechanical, and fracture properties of carbon nanotubes.[40] Using fully atomistic classical molecular mechanics calculations, it was demonstrated that stress tends to concentrate at defect

boundaries leading to brittle fracture at a relatively low strain. As a result, the ideal strength of single-walled carbon nanotubes was found to degrade by up to 60%. Notably, while all these phenomena were studied based on fully atomistic classical force-field simulations, continuum mechanics was found to provide a relatively reliable description down to the nanometer scale.

The unique structural and mechanical properties of quasi-1D layered materials mentioned above have strong impact on their tribological characteristics. A clear example for this structure/function relationship may be found in the interwall frictional properties of nanotubes. With this respect, Tosatti and co-workers have recently shown that upon interwall telescopic pull-out of the inner shell of facetted double-walled nanotubes substantial global facet reconfigurations occur.[41] These, in turn, open new energy dissipation channels that increase interwall friction, thus providing an explanation for recent experimental observation showing considerably enhanced interwall friction in multiwalled boron nitride nanotubes over their carbon counterparts.[42]

While for some practical applications, such as brake systems, enhanced friction is vital, reducing friction in mechanical system is considered an ultimate goal aiming to lower energy consumption and prevent wear. To this end, superlubric graphitic junctions have been suggested as a possible solution for achieving this goal.[43] Nevertheless, Urbakh and co-workers have shown that dynamical reorientation effects may eliminate superlubricity in nanoscale graphitic junctions.[44] To resolve this problem, Hod and co-workers suggested the use of heterogeneous junctions of layered materials that present robust superlubricity.[45] This prediction was recently verified computationally by Urbakh and co-workers, who have studied the tribological properties of planar heterojunctions of graphene and *h*-BN.[46] Here, it was found that soliton-like gliding of moiré pattern ridges (Figure 3c) during interlayer sliding eliminates the highly dissipative stick-slip motion observed in aligned homogeneous graphitic junctions. These findings gained further support by very recent experiments demonstrating robust superlubricity in micrometer scale heterojunctions of graphene and *h*-BN.[47] This experimental achievement, which followed theoretical predictions, is an important milestone toward the practical application of superlubricity for the reduction of friction and wear in realistic mechanical systems. Furthermore, it clearly demonstrates the interplay between theory and experiment in the contribution of Israeli science to this field.

Another theme that attracted the attention of Israeli theoretical and computational scientists with respect to 1D and 2D layered materials is their potential to serve as mass and chemical detectors. Specifically, zeptogram mass detection sensitivity was predicted by Adler and co-workers to be achievable via monitoring the phonon mode frequencies of single-walled carbon nanotubes.[48] Furthermore, in a series of studies by Krepel and Hod sensitive and selective chemical detectors were proposed based on narrow graphene nanoribbons. Here, lithium atoms were suggested to serve as anchoring sites for contaminant molecules atop the surface of graphene nanoribbon (see Figure 3d). The fingerprints of contaminant adsorption on the electronic transport characteristic of the system were then predicted to allow for highly sensitive detection.[49]

To summarize this section, the state of Israel is blessed with strong and active theoretical and computational physics, chemistry, and material science communities. The remarkable experimental breakthrough discoveries made in the past decades in the field of layered materials of various dimensions continue to catch the attention of these communities. Hence, their growing role in the study of the intriguing physical and chemical properties of these systems is expected to make a strong impact on the entire field.

5. Applications–Electronic and Optoelectronic Devices

In addition to the basic science aspects of the synthetic, characterization, and computational studies discussed above, the harnessing of their outcomes toward realistic technological applications is an important goal. With this respect, the two most notable layered-material semiconductors studied to date are MoS_2 and black phosphorus (BP) that, like most other 2D semiconductors, feature a thickness-dependent bandgap. The direct bandgap of BP varies from 2 eV in single layer to 0.3 eV in bulk.[50] Furthermore, BP features in-plane anisotropy that affects the mobility, current drivability, and their mechanical and optical properties.[23,51] This is an advantage for field-effect transistors having their channel along the high mobility (*x*) direction and contacts of higher effective mass (and thus current drivability) along the slow (*y*) axis of the crystal.[52] However, the sole disadvantage of BP is its sensitivity to humidity and oxygen that rapidly degrade its electronic properties, thus limiting its applicability. Several recent studies have addressed this problem with methods of BP passivation.[53] Specifically, Naveh and co-workers employed self-assembled molecular layers to provide a firm protective passivation to BP (see **Figure 4**c).[54]

In the case of MoS_2, the direct bandgap of 1.9 eV of the single layer is degenerate over two energy valleys that feature a valley–spin coupling on the spin–orbit split valence band.[55] This gives rise to efficient optical pumping of spin currents[56] and magnetization-dependent polarized electroluminescence.[57] Complementary to 2D semiconductors, *h*-BN ultrathin gate dielectrics that reduce the effects of charged impurities characteristic to oxide dielectrics[58] have been studied as essential building blocks of heterostructures[50a,58b,63c] spanning a vast combinatorial space of materials and devices.[59] Layered materials in their cylindrical form (i.e., nanotubes)[3c,27c,29a–d,60] are also a rich source for fascinating devices. This includes WS_2 transistors capable of carrying much higher currents as compared to their 2D counterparts[60] and building blocks for next-generation electronic systems, such as high-density, nonvolatile, random access memory based on arrays of crossed suspended carbon nanotubes.[61] Nanoelectromechanical devices based on 1D layered materials leverage the weak interlayer coupling for implementing torsional resonators based on sliding concentric cylinders in multiwall nanotubes.[27c,60] These unique nanobearing devices were implemented on various layered compounds demonstrating high efficiency and resonant frequencies.[62]

Another important property of such atomically thin semiconductors is their ultimate electrostatic constriction that leads to very efficient geometrical screening and to full depletion of

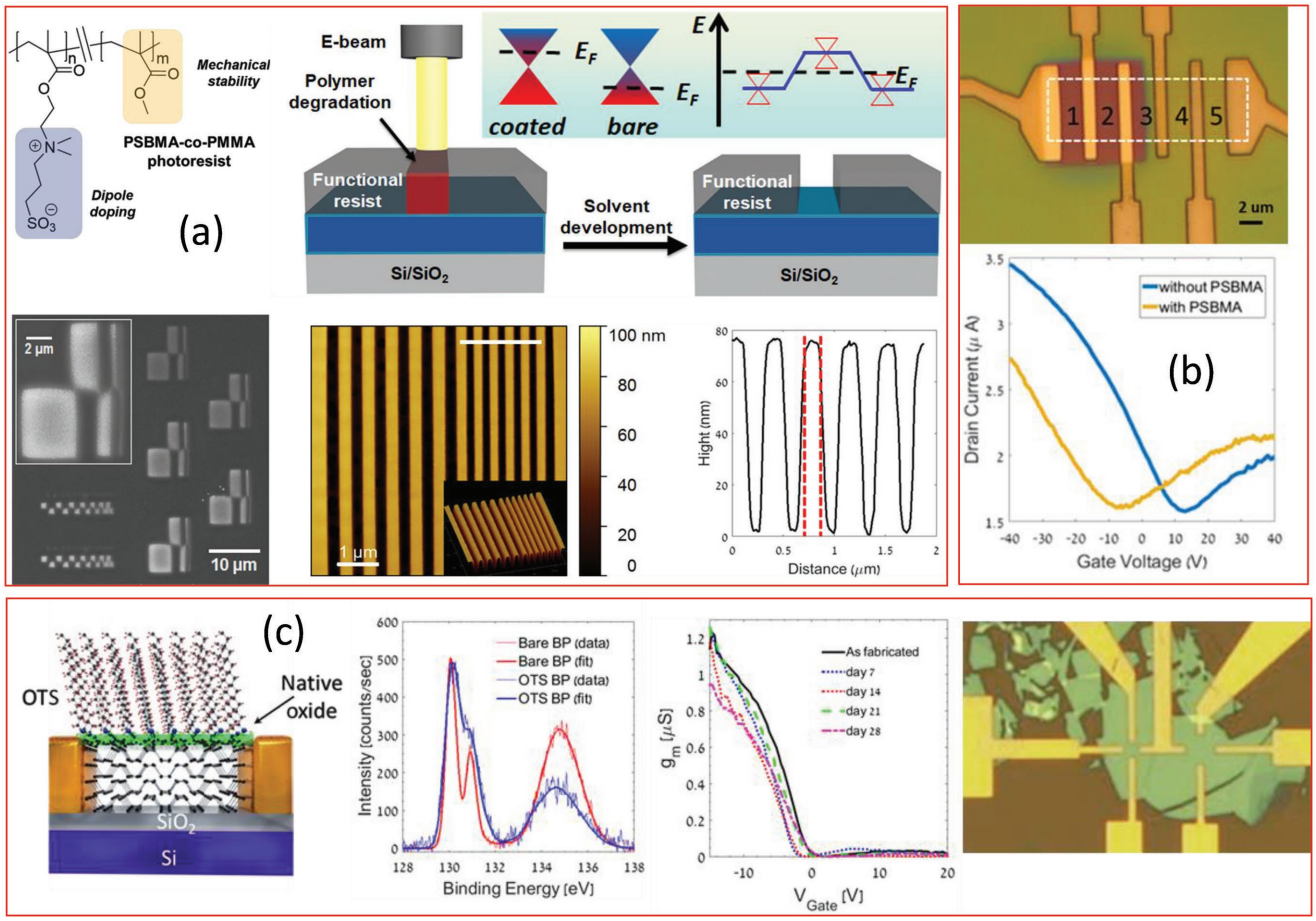

Figure 4. Toward electronic and optoelectronic device applications. a) Sulfobetaine methacrylate-*co*-polymethyl-methacrylate functional electron-beam resist for doping 2D materials, SEM images of resolution, and dose charts and atomic force microscopy topography maps demonstrating the high resolution and dose stability. b) Graphene devices patterned with a functional resist showing effective *n*-doping with 5×10^{11} cm^{-2}. Reproduced with permission.[70] Copyright 2018, American Chemical Society. c) Protective molecular layer of octadecyltrichlorosilane (OTS) on black phosphorus–device structure, X-ray photoemission spectroscopy measurement of OTS native oxide reduction, and transconduction measurements taken over 28 days from fabrication showing robust stability. Reproduced with permission.[54] Copyright 2017, Nature Publishing Group.

semiconductor transistor channels. This advantage translates to very low leakage currents and improved short channel effects in transition-metal dichalcogenide semiconductor field-effect transistors.[63] Leakage currents are also one of the main sources of noise in photodetectors, often referred to as dark currents. Photodiodes and phototransistors of 2D materials cover the spectrum from THz to UV electromagnetic radiation.[64] Despite their thickness-limited absorption, 2D photodetectors push the state-of-the-art technologies toward highly responsive, room temperature mid-infrared detection with graphene,[65] BP, and its arsenic alloys.[63c,66] Black phosphorus photodetectors recently also incorporated a mechanism of giant stark effect,[67] extending its spectral responsivity.[50a]

With all of the above-mentioned advances, the main frontier in device processing of 2D materials remains the control of charge carriers by doping. Since extrinsic impurities of, for example, ion implantation render 2D materials with defects,[68] an exquisite method of Fermi-level engineering is required for atomically thin materials. Soft doping,[69] a method that uses a soft/hard matter interface for doping 2D materials, recently proved to be effective and compatible with standard lithography processes. With this respect, Hadas Alon et al. used such a soft doping procedure to modify the Fermi-level of graphene by 0.2 eV at spatial resolution of 100 nm (Figure 4,a,b) thus opening opportunities for new fascinating technological applications.[70]

6. Conclusions and Outlook

The research of layered materials is intense and is expected to remain so for the foreseeable future. Albeit the great scientific and technological work done so far, there are still major scientific questions to be answered, ranging from their intrinsic physical and chemical properties to their rational synthesis and novel applications. As presented in this brief review, the number of research groups in Israel, studying the many aspects of low-dimensional layered materials in general and 2D materials in particular, has significantly grown in the past decade, targeting the core scientific and technological questions in this field. We believe that the synergic national and international cooperation within this growing community will continue to provide significant advances in this field.

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