Chapter

2D-Layered Nanomaterials for Energy Harvesting and Sensing Applications

Po-Kang Yang and Chuan-Pei Lee

Abstract

Nanoscale electromechanical and energy harvesting devices based on few-layer and monolayer two-dimensional (2D) materials with non-symmetric configuration have received enormous attention in recent years. Specifically, piezoelectric and triboelectric devices based on 2D materials for energy harvesting, physical/chemical sensing, healthcare, and optoelectronics applications have been a growing interest. In this chapter, the typical preparation methods of 2D-layered materials, such as exfoliation methods and chemical vapor phase deposition (CVD), will be discussed first. Then, various characterization techniques by atomic microscopic analysis for 2D materials will be provided briefly. Finally, future aspects of developing 2D piezoelectric and triboelectric devices and their potential applications will be introduced.

Keywords: electromechanical, energy harvesting, piezoelectricity, sensors, triboelectricity, two dimensional materials

1. Introduction

2D materials have been creating a renaissance in many scientific areas since the adventure of graphene in 2014 [1]. Recently, the family of 2D-layered materials has been profoundly growing up, including transition metal dichalcogenide (TMD) [2, 3], transition metal carbide (TMC) [4], and graphene-based materials [5, 6], as shown in **Figure 1** [7]. They cover the whole range of material properties from insulators, semiconductors, metals to superconductors, offering a broad portfolio of material's solutions with extraordinary chemical and physical properties for wide applications in promising energy and sensing application technologies [8–11].

For example, piezoelectricity, which is a unique material characteristic, allows effective conversion of ambient mechanical energy into electricity or vice versa. Previously, various TMDs have been applied to fabricate piezoelectric devices owing to their non-centrosymmetric, large piezoelectric coefficients, and layered crystal structure [12]. Prof. Alyörük and his co-workers theoretically predict the piezoelectric constants in various kinds of TMDs [13]. Moreover, Professor Wu's group first demonstrated that a monolayer molybdenum disulfide (MoS_2) is capable of generating piezoelectric response and piezotronics applications [14]. Meanwhile, Professor Kim's group also reported that bilayer tungsten diselenide (WSe_2) is a suitable candidate for next generation piezoelectric nanogenerators (PENG) [15]. More importantly, Prof. Li's group have measured the multi-directional piezoelectricity of

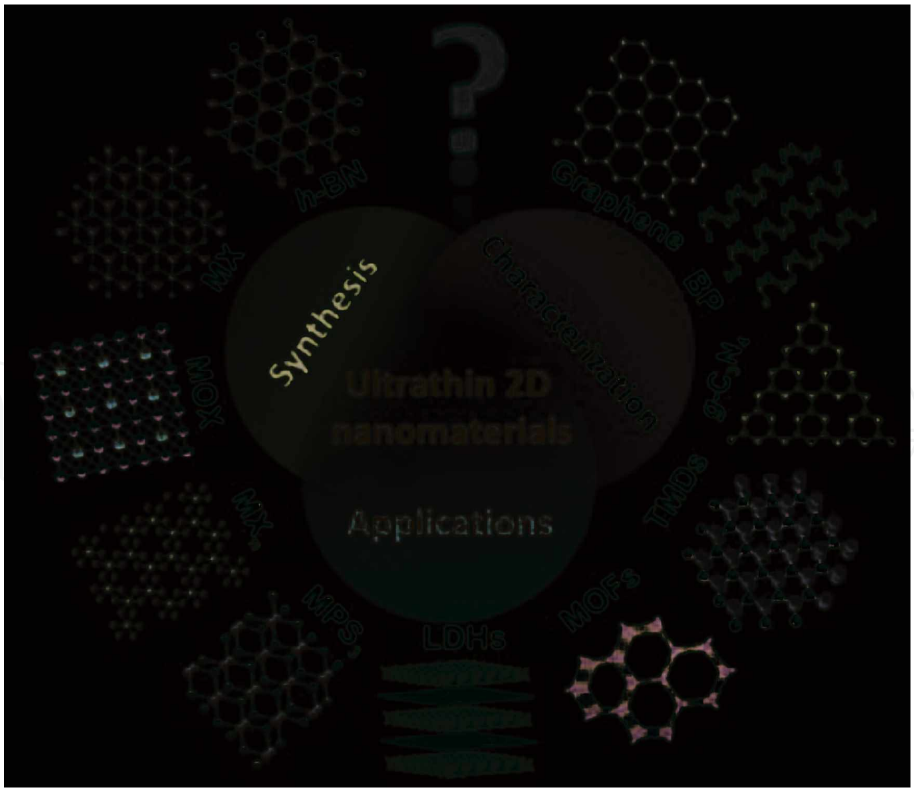

Figure 1.
The schematic assortments of synthetic methods, characterization techniques, and potential device applications of 2D materials [7].

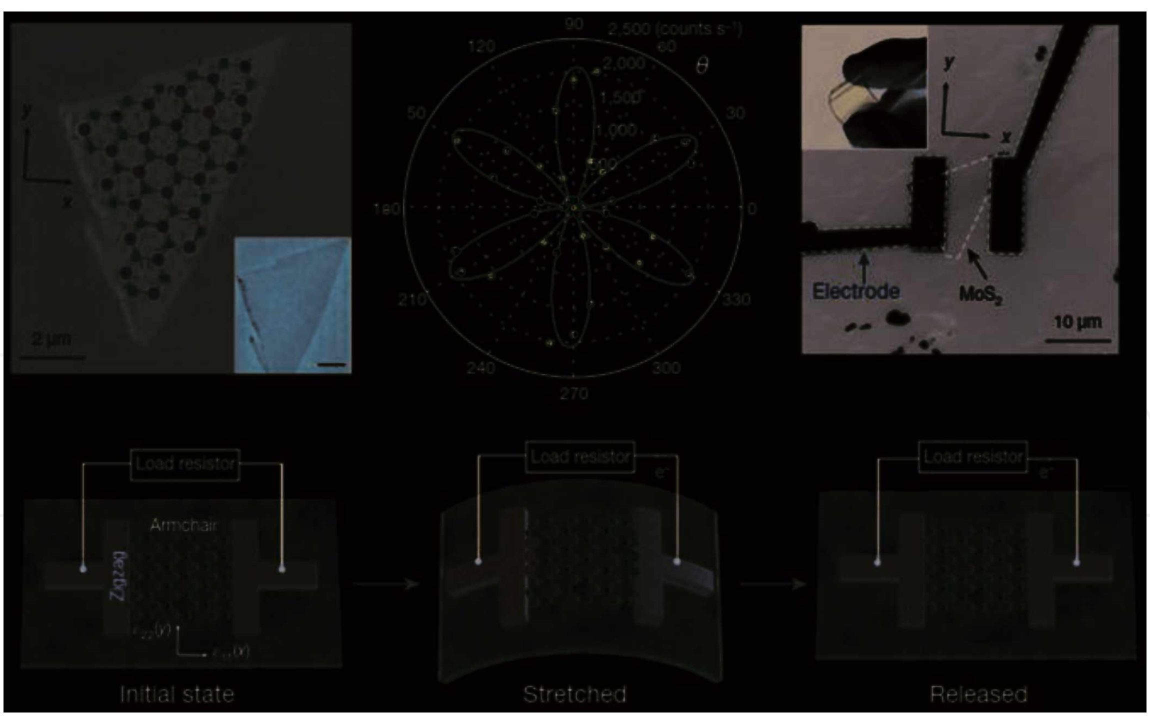

Figure 2.
Schematic of a monolayer MoS_2 piezoelectric device and operation scheme [14].

indium selenide (In_2Se_3) and demonstrated its potential as a biomechanical energy harvesting device for PENG applications [16]. As shown in **Figure 2**, a 2D material-based PENG is consisted of a monolayer MoS_2 with the multi-layer metal electrode Cr/Pd/Au.

Briefly, the basic sequence of the working principle of the as-fabricated PENG is shown in **Figure 2**. Three stages are involved in charge generation process by external mechanical stress, which are initial, stretched, and released states. First, the mechanical strain is applied to the few-layer MoS_2 on the PET substrate for different bending radius. Then, the as-fabricated piezoelectric device is coupled to an external load resistor, forming a total electric circuit loop to investigate piezoelectric response. In addition, several attempts of utilizing 2D materials in piezoelectric devices have been found in previous sensor network, including strain sensors [17], pressure sensors [18], and gas sensors [19]. Nevertheless, some challenges may still remain for 2D material-based piezoelectric devices, including material selection, device reliability, and low electric output power.

Recently, the rise of triboelectric nanogenerators (TENGs) starts a new route to generating electricity from ambient mechanical energy. The TENGs are operated at the basis of well-known contact electrification effect, which were first invented and explained in 2012 (**Figure 3**; [20]). Within the contact electrification effect, two different materials become mutually charged after it comes into contact with each other. Two electrically charged material causes an electrostatic potential difference, driving the induced electrons to flow via outer circuit loop to provide electricity.

Toward the development of TENGs, 2D materials also become one of the key features. For instance, Prof. Wang's group successfully introduced a monolayer MoS_2 as an electron acceptor layer to capture triboelectric charges that result in

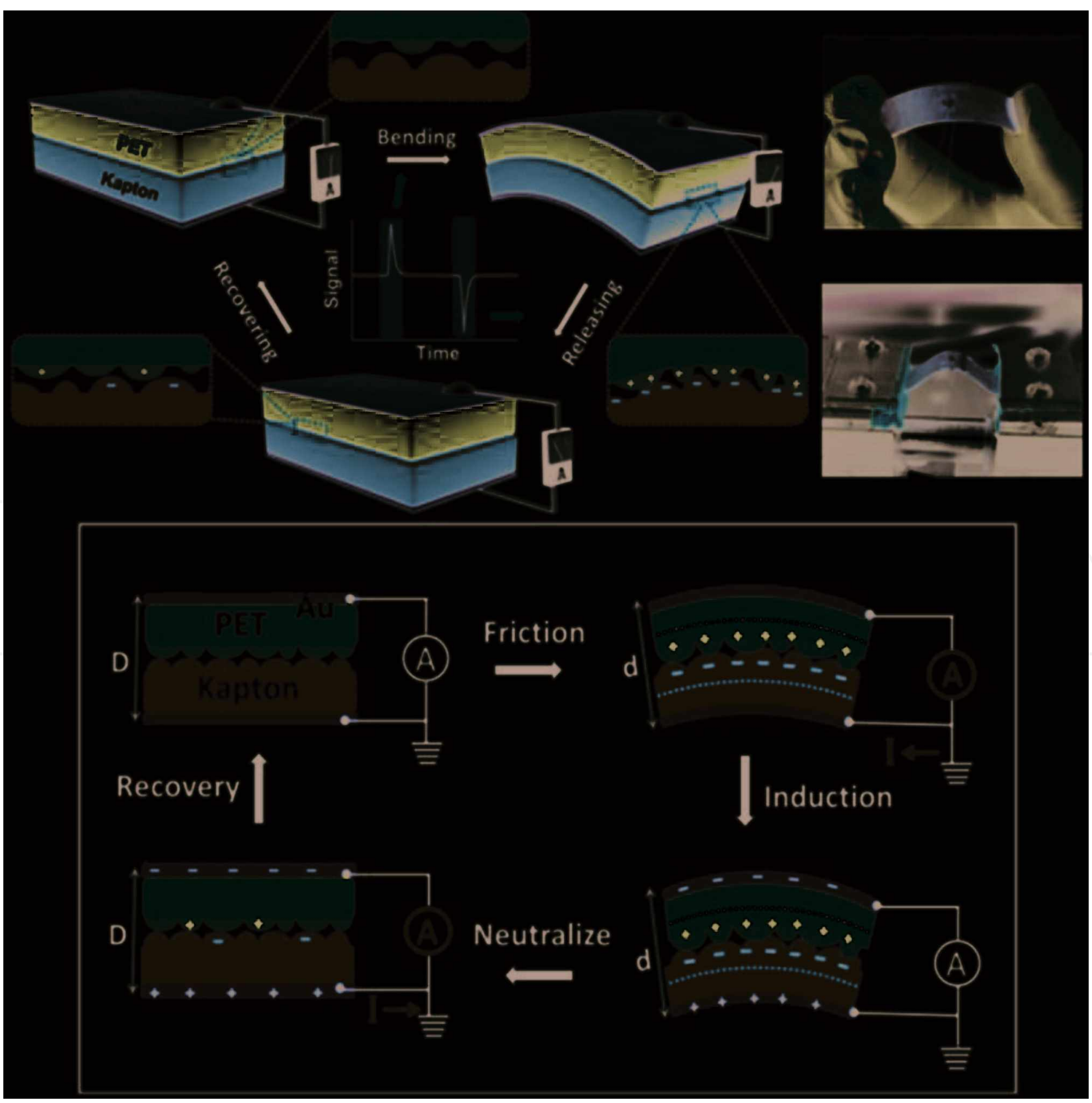

Figure 3.
First prototype triboelectric nanogenerator (TENG) [20].

Figure 4.
A contact-separation mode TENG with monolayer MoS_2 [21].

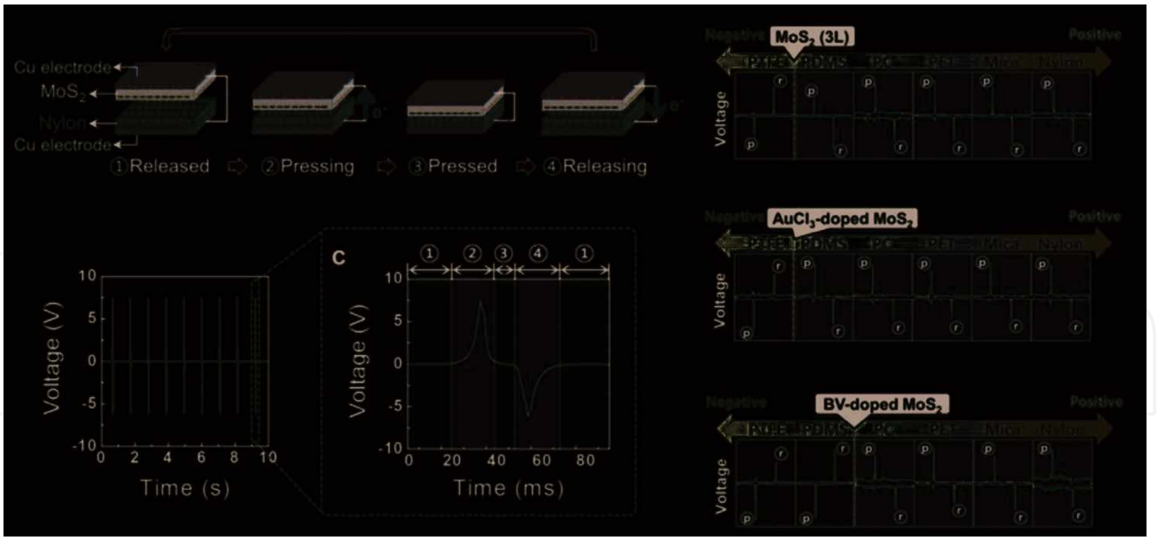

Figure 5.
Triboelectric properties of different 2D materials and their output characteristics [22].

significant output enhancement (**Figure 4**; [21]). In addition, Prof. Kim's group studied the triboelectric series with various promising 2D materials paving the way for future design rule of 2D material-based TENGs (**Figure 5**; [22]).

In this chapter, the electromechanical property of 2D materials and their subsequent applications in energy harvesting and sensing fields will be addressed adequately. To begin with, a variety of fabrication methods to prepare 2D materials are briefly described. Sequentially, the exciting progresses of these materials made in both energy harvesting and sensing applications, especially for piezoelectricity, triboelectricity, and multi-functional sensing designs, are explored and discussed. Furthermore, future prospects and further developments in above-mentioned research fields based on 2D materials are also commented.

2. Discussion

2.1 Preparation of 2D materials: exfoliation methods

Traditional approaches to extract single- and few-layer-thick 2D materials from their bulk solids are based on exfoliation methods, which can be categorized into mechanical exfoliation and chemical exfoliation [23]. For mechanical exfoliation (ME) process, it has been widely adopted in preparing diverse 2D materials, such as graphene [24], phosphorene [25] (**Figure 6**), and borophenes [26]. The ME process contains several advantages, making them promising for small-scale devices and fundamental researches. For instance, layed Materials prepared from ME process are commonly crystalline and the preparation process is usually rapid. However, the disadvantages of ME method are also obvious, limiting its large-scale production and future applications, such as low material yield, area uniformity, and layer-to-layer asymmetry. As one would like to obtain a certain 2D material with only a few layer or even monolayer, the ME process is relatively time-consuming and inefficient.

2.2 Preparation of 2D materials: chemical vapor deposition (CVD)

In contrast to the exfoliation methods, chemical vapor deposition method (CVD) has been profoundly investigated to produce 2D-layered thin film on desirable

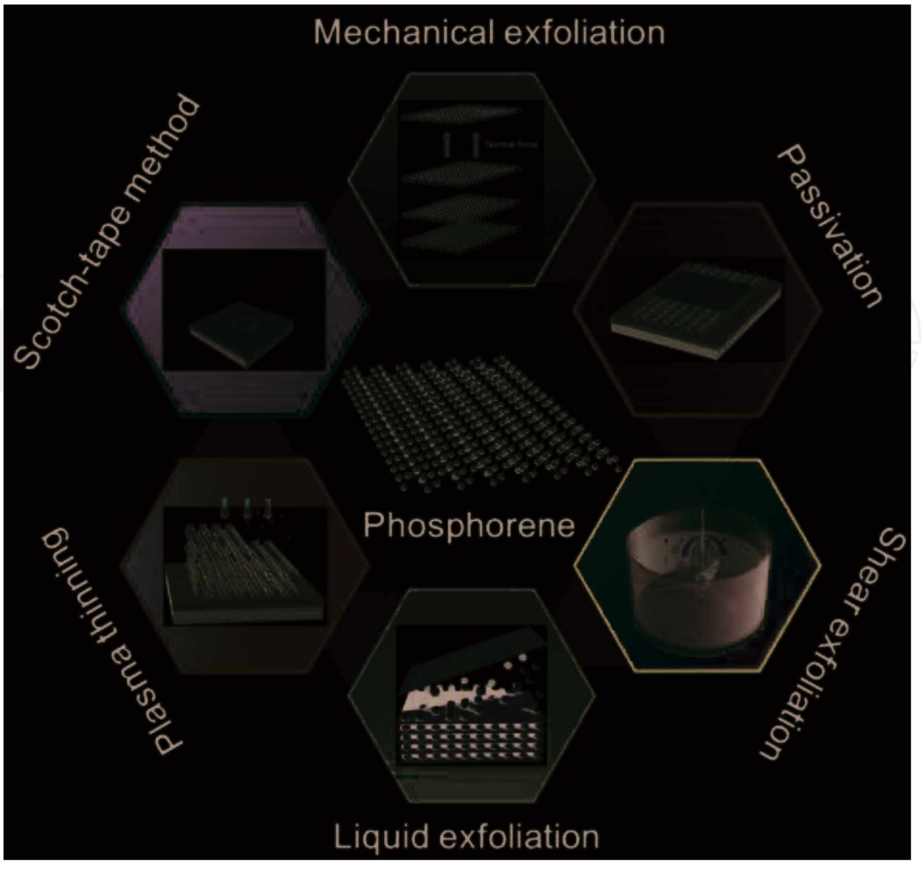

Figure 6.
Schematic representation for the evolution and overview on the Phosphorene fabrication process [25].

substrates via the chemical reaction of volatile precursors in recent years [27]. 2D materials grown by CVD methods have been demonstrated to obtain scalable size, controllable thickness, and high crystallinity. Take the tin disulfide (SnS_2) as an example, according to Yang et al. [28], SnS_2 nanosheets could be synthesized on SiO_2 substrates by CVD method using Sn and sulfur as the precursors. The as-synthesized SnS_2 flakes could be ranged from 50 to 70 μm in lateral dimensions. This synthesis method can produce ultrathin and highly crystalline SnS_2 flakes. Meanwhile, it is noted that the 2D materials with heterostructure can also be produced by multiple CVD process. Revannath et al. presented a p-MoS_2/n-MoS_2 vertical heterostructure by a multiple step CVD process, where the molybdenum oxide (MoO_3) and sulfur were served as precursors. The as-fabricated heterostructure can be further employed for future light-emitting diode (LED) applications [29]. As discussed above, one can found that 2D materials produced by CVD techniques possess several advantages, such as good quality, high yield, and uniform dimensions. Moreover, 2D material-based heterostructures can also be obtained by multiple CVD process, which is crucial to both research and industrial applications [30] (**Figure 7**).

2.3 Piezoelectricity in 2D materials

Piezoelectricity was first discovered in 1880, which is due to the accumulated electric charge polarization of materials in response to applied mechanical stress. Previously, bulk materials have been reported to possess the piezoelectric effect, including crystals and polymers. Accordingly, in 2D materials, piezoelectricity is usually attributed to the non-symmetric structure to generate polarization charges in response to the externally applied mechanical stimuli [31]. Recently, owing to the

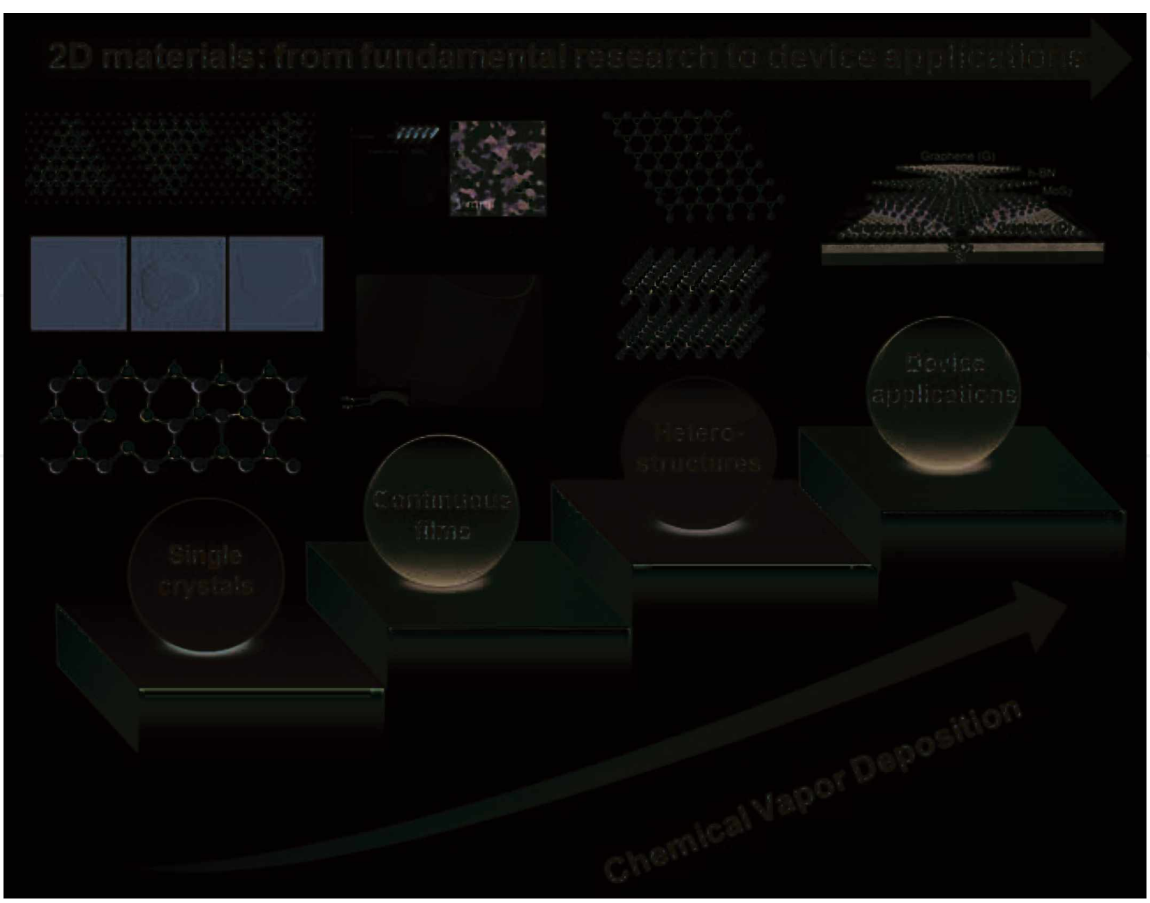

Figure 7.
Roadmap of 2D materials by CVD techniques, from single crystals to device applications [30].

continuous growth of wearable, flexible, healthcare, and artificial intelligent robots industry, the market demands for nanoscale and multi-functional sensing devices have become critical, especially for human-machine interface interaction and remote healthcare monitoring. Under these circumstances, 2D piezoelectric materials with their ultrathin geometry, excellent electromechanical response, and other unique physical properties are suitable candidates and of great importance. Moreover, to directly observe piezoelectricity inside 2D materials, piezoresponse force microscopy (PFM) method is widely implemented, which is based on the converse piezoelectric effect [32, 33] (**Figure 8**).

2.4 Piezoelectric devices based on 2D materials

As mentioned above, after successful inspection of piezoelectricity in 2D materials, a series of correlated applications, including field-effect transistors (FET), sensors, catalytic reactions, optoelectronics, and energy storage, are emerged [34–38]. Herein, we will briefly review the device application of 2D piezoelectric materials, especially for energy harvesting device development. For example, in 2017, Muralidharan et al. present a mechano-electrochemical device configuration based on sodiated black phosphorus (BP) nanosheets, where this device is capable of harvesting low frequency mechanical energy at 0.01 Hz [39] (**Figure 9**).

In addition, Lee et al. have also developed a monolayer WSe_2 piezoelectric nanogenerator (PENG), which can provide an output voltage of 45 mV (**Figure 9**). The output electrical signal will only appear during the moment of stretching and releasing from external strain. This proves the concept of using this device to generate electricity from mechanical stimuli. Moreover, one can also see that the output voltage and current increase with increasing tensile strain. Furthermore, the as-fabricated PENG can sustain stable electrical output even after 3 hours, demonstrating its excellent device reliability.

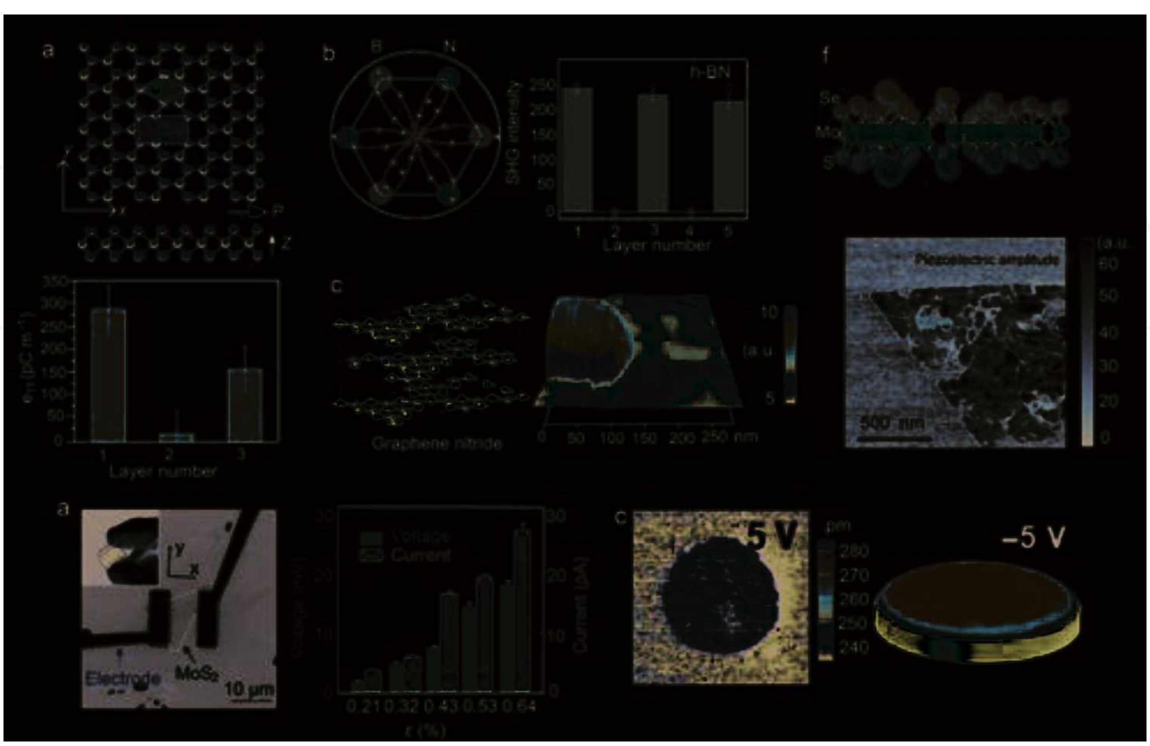

Figure 8.
Piezoelectricity observation in various 2D materials, including MoS_2, boron nitride, graphene nitride, and monolayer MoSSe [32, 33].

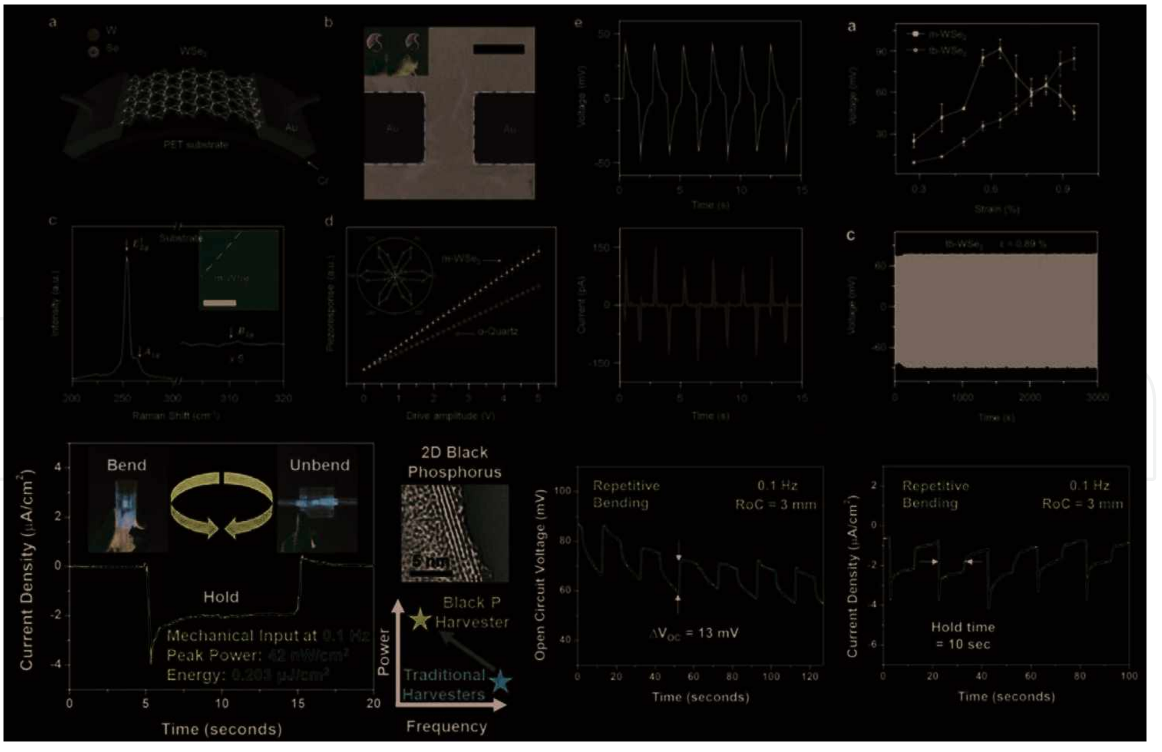

Figure 9.
Piezoelectric nanogenerator based on 2D materials, where WSe_2 and black phosphorus are shown as examples. [39].

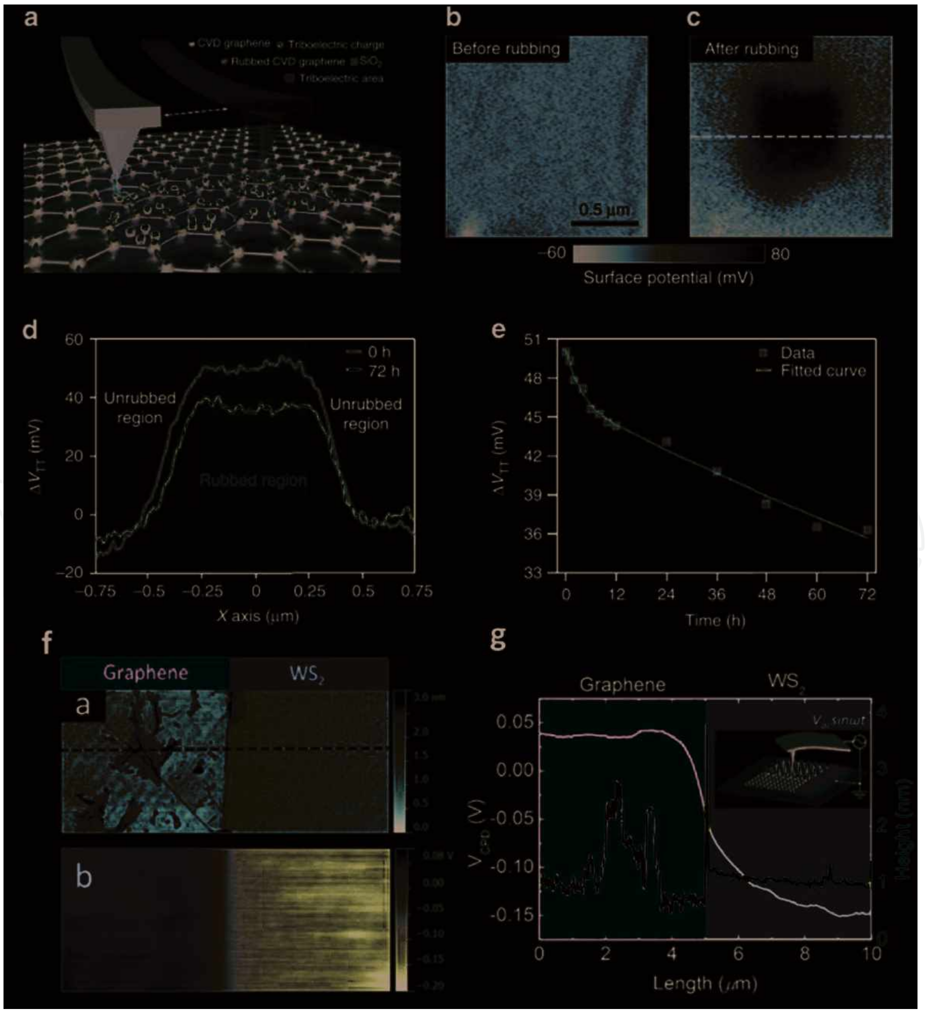

Figure 10.
Observing triboelectrification by friction of graphene with a Pt AFM tip (a–e). Schematic diagram for measuring the triboelectricity of the subpart labels of a and b in (f) show the topographic image of a graphene-WS2 heterojunction and corresponded surface potential measured by KPFM, respectively (f, g) [41–43].

2.5 Triboelectricity in 2D materials

Triboelectric charging is a well-known electrical charging phenomenon of materials, which has been studied for more than 2500 years [40]. The triboelectric charging phenomenon occurs at two different materials, which come into contact and separate with each other. Owing to the charge transfer during contact, charges of opposite signs accumulate on the surface of each material, thereby developing static electricity or so-called triboelectricity. In addition to conventional thin-film and bulk materials, recently, 2D materials, such as TMDs and graphene (GR), have also been found to exhibit considerable triboelectricity [41–43]. Generally, Kelvin probe force microscope (KPFM) and Scanning Kelvin Probe microscopy (SKPM) have been utilized into characterizing surface potential and surface work function. The KPFM method allows one to measure and compare the surface potentials of the dielectrics before and after friction, which is highly correlated to the triboelectricity (**Figure 10**).

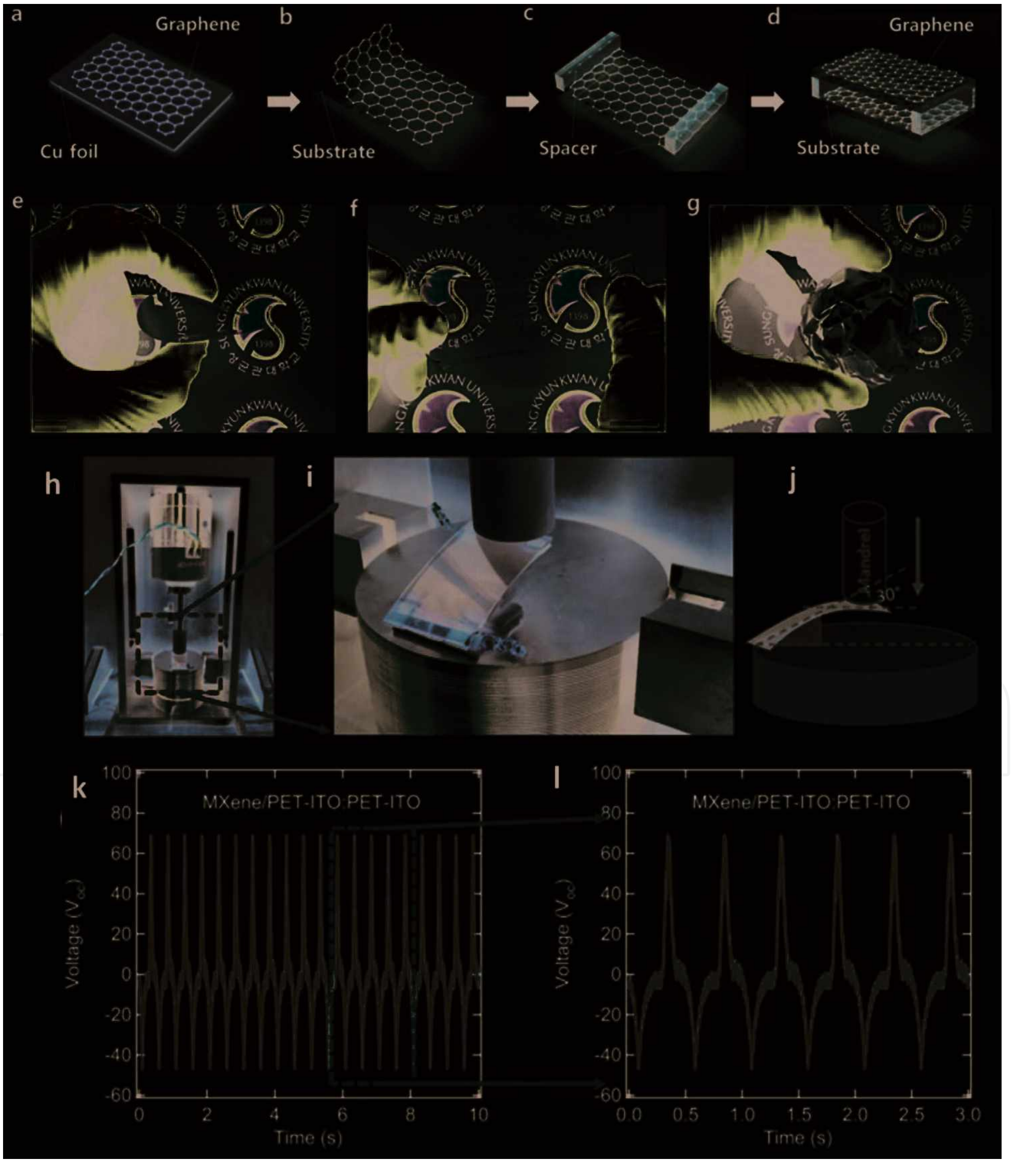

Figure 11.
Schematic diagrams of device fabrication and compatibility of graphene with an arbitrary substrate (a–g). The flexible MXene TENG was operated with a force of 1 N applied at 2 Hz by the mandrel (h–l) [44, 45].

2.6 Triboelectric devices based on 2D materials

To further understand and evaluate the triboelectricity inside 2D materials, several attempts have been made to fabricate triboelectric devices based on 2D materials. For instance, Kim et al. reported the first flexible, transparent TENG device using graphene [44]. The as-fabricated TENGs were able to power commercial LEDs by using the electrical power output generated from TENG without any other external energy source. Meanwhile, Dong et al. reported high-performance TENG device by new materials, such as fluorinated MXene, and successfully demonstrated to both rigid and flexible TENGs applications. Furthermore, these MXene-based TENGs can be further integrated into accessories, wrist bands, and textiles [45] (**Figure 11**).

3. Conclusion

For 2D materials, future challenges and aspects for fundamental research and industrial applications, especially for energy harvesting and sensing field, may be summarized as follows. Though various kinds of 2D materials have been explored to possess either piezoelectricity or triboelectricity, most of them are not well investigated owing to the difficult material preparation process via exfoliation or CVD method. To be more specific, several key factors still need to be further understood in both 2D piezoelectric and triboelectric materials. In 2D piezoelectric materials, first, it has been well known that the band structure could be affected by piezoelectric field created by strain; therefore, the influence of strain on band structure of 2D materials should be thoroughly investigated. Second, optimize synthetic methods of 2D piezoelectric materials are required, playing a key role for further improving output characteristics of piezoelectric devices. Meanwhile, as for 2D triboelectric materials, compared with traditional triboelectric materials, they have shown great advantages, such as ultrathin film feasibility, flexibility, and process compatibility with large array devices, advancing its applications as future wearable sensors and human-machine bridging interface. Nevertheless, further efforts still need to be made in the following aspects. First, an entirely qualitative and quantitative characterization of 2D triboelectricity should be implemented to understand the triboelectric charge transferring process. Moreover, 2D triboelectric materials in a large scale with low costs, high uniformity, and low-temperature synthesis process should be achieved, which will be beneficial for next-generation flexible device developments.

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Conflict of interest

The authors declare no competing financial interests.

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