Chapter

# Advances in Piezoelectric Two-Dimensional Materials for Energy Harvesting

*Rafael Vargas-Bernal*

## Abstract

The design of piezoelectric energy harvesting systems can be exploited for the development of self-powered sensors, human-powered devices, and regenerative actuators, as well as the development of self-sustained systems with renewable resources. With the introduction of two-dimensional materials, it is possible to implement piezoelectric nanostructures to exploit environmental energies, taking advantage of their flexible mechanical structures. This chapter aims to study the relevant contribution that piezoelectric two-dimensional materials have in energy harvesting. Among the two-dimensional piezoelectric materials analyzed are phosphorene, MXenes, Janus structures, heterostructured materials, and transition metal dichalcogenides (TMDs). These materials are studied through their performance from a piezoelectric point of view. The performance achieved by two-dimensional piezoelectric materials is comparable to or even better than that achieved by bulk piezoelectric materials. Despite the advances achieved so far, many more materials, as well as structures for the implementation of energy harvesting devices or systems, will be proposed in this century, so this research topic will continue to be interesting for research groups around the world.

**Keywords:** two-dimensional materials, piezoelectric materials, transition metal dichalcogenides (TMDs), heterostructures, energy harvesting, morphotropic phase boundary (MPB), Janus structures, MXenes, phosphorene

## 1. Introduction

The direct piezoelectric effect was discovered in 1880 by Pierre and Jacques Curie in quartz crystal (silicon dioxide, $SiO_2$) [1]. In the direct piezoelectric effect, it is possible to generate an electrical charge proportional to the applied mechanical effort. In the reverse piezoelectric effect, a proportional geometric deformation is achieved by an applied voltage [1]. It was not until 1947 that Shepard Roberts that the first polycrystalline piezoelectric ceramic based on barium titanate ($BaTiO_3$) was discovered to exhibit 100 times more piezoelectricity than quartz. In the 1950s, it was discovered that other oxides such as lead titanate ($PbTiO_3$) and lead zirconate ($PbZrO_3$) have twice the piezoelectric properties of barium titanate. Each material has a Curie

temperature above which piezoelectricity disappears. In addition, for each polycrystalline piezoelectric material, there is a cation ratio that must be optimized to reach the morphotropic phase boundary (MPB), which produces the presence of rhombohedral and tetragonal phases that allow adjusting the piezoelectric properties. In a piezoelectric material, through the applied mechanical stress, it is possible to achieve a total separation of positive and negative charges thanks to the non-centrosymmetric structure of the piezoelectric material. Due to the harmful influence of lead found in piezoelectric materials on the safety of workers who process these materials, as well as the damage to soil and water, researchers are investigating the possibility of developing lead-free piezoelectric materials. Piezoelectric materials are mainly applied to energy harvesting and sensing [2–36]. Without a doubt, one of the contributions that motivated energy harvesting was the use of zinc oxide (ZnO) nanowires as a piezoelectric nanogenerator using nanomaterials [26]. Through the use of two-dimensional materials, it is possible to exploit both semiconductor properties and piezoelectric properties for the tuning and transport of charge carriers [2–36].

The electromechanical interaction in these materials is related to a linear constant between the displacement or electric field and the stress or strain achieved mechanically called piezoelectric coefficient and expressed as C/N or m/V [1]. The piezoelectric coefficients of materials are not uniform along the crystalline directions, that is, are anisotropic, so it is necessary to consider the crystalline direction that will be used in the design of devices that take advantage of piezoelectric properties. Piezoelectric materials enable the development of applications such as energy harvesting in living environments by creating self-powered sources to power electronic devices at the nanoscale. To assess the piezoelectric performance of a material, four main piezoelectric coefficients can be distinguished: the piezoelectric charge coefficient or piezoelectric strain coefficient ($d$), the piezoelectric voltage coefficient or voltage output constant ($g$), the piezoelectric stress coefficient ($e$), and the piezoelectric stiffness coefficient ($h$). Of the 32 possible crystalline solid groups, there are 20 piezoelectric groups and 10 ferroelectric groups. All ferroelectric materials have pyroelectric behavior and all of them are piezoelectric; by contrast, piezoelectric materials are not necessarily pyroelectric or ferroelectric. The most frequently used piezoelectric coefficient is $d$ and it relates the open circuit charge density to the applied mechanical stress and regularly uses two subscripts. The first subscript states the direction in which the electrical polarization is induced, and the second subscript specifies the direction in which the stress is applied. This relates the electromechanical coupling coefficient $k$, to the relative dielectric constant $k^{\mathrm{T}}$ at a constant stress, and the elastic compliance at a constant electric field $s^{\mathrm{E}}$, as well as the electric permittivity of the vacuum $\varepsilon_0$, and this is expressed mathematically $asd = k\sqrt{\varepsilon_0 k^T s^E}$. The two most important $d$ constants in the case of nanomaterials are $d_{31}$ (induced strain in direction 1 per unit electric field applied in direction 3) and $d_{11}$ (induced strain in direction 1 per unit electric field applied in direction 1). The piezoelectric stress coefficient ($e$) can also be defined for the subscripts 11 and 31 of the material for the reverse piezoelectric behavior. For two-dimensional materials, subscripts 11 are considered the in-plane piezoelectric response, while subscripts 31 and 33 are used for the out-of-plane piezoelectric response.

The rest of this chapter has been organized as follows: In Section 2, a summary of the basic concepts associated with piezoelectricity and two-dimensional materials is presented. Next, novel piezoelectric materials are examined using comparative tables and graphs of their in-plane and out-of-plane performance in Section 3. In Section 4, applications of two-dimensional materials in energy harvesting and related topics

are described. Future research directions related to these materials are discussed in Section 5. Finally, the conclusions of this chapter are presented.

## 2. Basic concepts

A two-dimensional material is a crystalline solid with at least one of its dimensions on the nanoscale. In 2004, graphene was the first two-dimensional material to be discovered, and this is a carbon-based material with a thickness of one atom [2]. Two-dimensional layered materials can be classified as homoatomic when they only contain one chemical element in their structure, such as graphene, phosphorene, antimonene, and heteroatomic when they contain more than 1 chemical element in their structure as in the case of hexagonal boron nitride ($h$-BN), $\alpha$-phase indium sulfide ($\alpha$-$In_2S_3$), gallium arsenide (GaAs), etc. Two-dimensional layered materials with homostructure are naturally centrosymmetric because they do not show out-of-plane piezoelectricity and have in-plane piezoelectricity; however, this quality depends on the degree of ionization of their covalent bonds. The advantage of two-dimensional layered materials with heterostructure exhibits naturally in-plane and out-of-plane piezoelectricity. Two-dimensional materials are arranged in layers that are stacked and held together through weak van der Waals interactions. Since the discovery of graphene, a large set of two-dimensional materials based on the chemical elements of groups IVA, IIIA-VA, IIB-VIA, and other chalcogenide metals of group B have been discovered and proposed. These materials exhibit unique chemical and physical properties that sometimes differ from those of their bulky counterparts [3, 6–24]. Two-dimensional layered materials are interesting options for implementing energy conversion, harvesting, and storage applications due to their high surface area, processing, and assembly versatility, as well as multiple novel surface chemistries. In these materials, the $d_{33}$ and $g_{33}$ piezoelectric coefficients corresponding to out-of-plane piezoelectricity have zero or none, while the $d_{31}$ and $g_{31}$ piezoelectric coefficients corresponding to in-plane to out-of-plane piezoelectricity have a modest value. Two-dimensional materials to be exploited piezoelectrically must have a large surface-to-volume ratio, extraordinary electrical properties, and extremely low noise level, which also lead them to be used in sensing applications. When comparing sensors based on microelectromechanical systems (MEMS) with sensors based on two-dimensional materials, the latter are much lighter and smaller, have lower power consumption, have more flexibility, and show superior sensitivity. In addition to reducing the thickness of the two-dimensional material, other strategies that can be used to provide these same non-centrosymmetry properties are functionalization and doping of the crystal lattice to favor its anisotropy and thereby achieve better piezoelectric properties [11]. Other approaches that are being used to increase the piezoelectric properties are the generation of defects in the layers or the implementation of heterostructured materials based on two-dimensional materials. Because all the atoms in two-dimensional materials are exposed on their surface, it is possible to tune their physical properties. Within these properties, piezoelectric properties can be used to maximize energy harvest using micro- and nanoelectromechanical systems. Applications of nanoscale piezoelectric materials are transducers, actuators, and energy harvesters for fields such as piezotronics and nanorobotics.

For a material to present piezoelectric properties, the unit cell must not have a symmetrical center so that an anisotropic dipole moment occurs, which is called dielectric polarization [3]. This phenomenon is observed in crystalline and

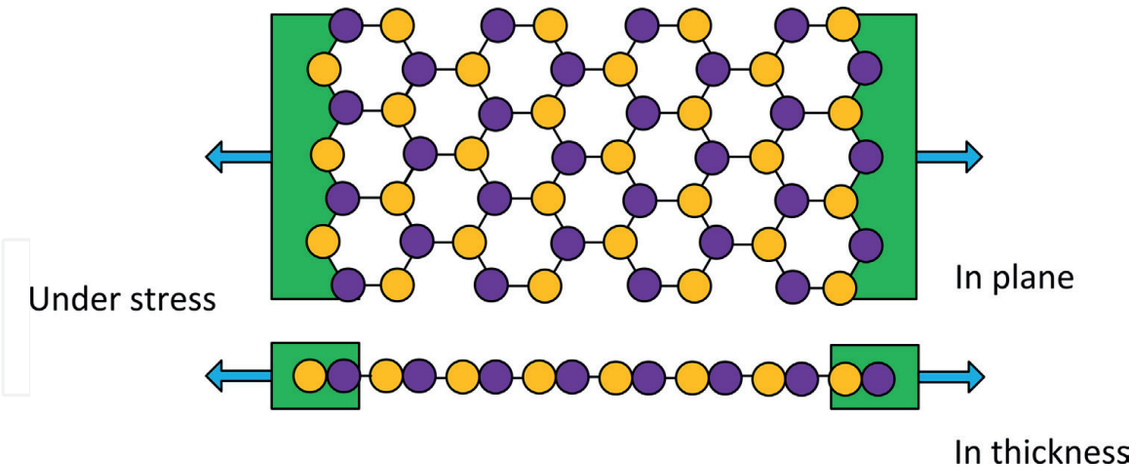


**Figure 1.**
*The basic principle of piezoelectricity in two-dimensional materials.*

semicrystalline dielectric materials when an electric field is applied. The polarization orients the cations and anions found in the material either partially or completely in the direction of the field, the higher the orientation the better the piezoelectric coefficient of the material, especially when this response is achieved under a continuously oscillating field. Traditional applications of piezoelectric materials are in microbalances, high-resolution mechanical actuators, and quartz oscillators [28].

Wearable nanogenerators to generate power can be implemented using mechanically flexible materials that present piezoelectric properties such as two-dimensional materials [2]. The piezoelectric properties of transition metal dichalcogenides (TMDs) appear only in monolayers and disappear in bilayers. So far, transition metal dichalcogenides (TMDs) with odd layer numbers have piezoelectric properties due to the absence of inversion symmetry. When the two-dimensional material is mechanically bent at both ends, the nanosheet is expanded, which causes the polarized charges to deliver a flow of electrons toward an external charge, as illustrated in **Figure 1**. When the two-dimensional material is mechanically released, the electron flow stops. The periodic stretching and releasing of the two-dimensional material can produce an alternating piezoelectric output. This output will be capable of generating a voltage that can be exploited to harvest energy from a source that can generate an oscillating mechanical stress on the two-dimensional material.

## 3. Novel piezoelectric materials

In Ref. [4] the authors using a data mining algorithm of more than 50,000 inorganic crystals identified that there are 1173 two-dimensional layered materials. Three hundred twenty-five of these materials have piezoelectric monolayers [4]. They also found that there are 98 loosely bound Van der Waals heterostructures. According to Refs. [3, 6], different types of two-dimensional materials with piezoelectric properties can be distinguished. The first type is made up of dichalcogenides based on conventional and Janus-type transition metals. The second type is based on compounds based on the elements of groups IIA and VIA. The third type is based on compounds based on the elements of groups IIIA and VA. The fourth type is made up of compounds based on conventional and Janus-type group IIIA-VIA elements. The fifth type is made up of compounds based on the elements of the IVA and VIA groups.

Finally, the sixth type is constituted by the compounds based on two elements of the VA group. To produce a non-centrosymmetric structure in materials, it is necessary to use methodologies to modify the interfacial interaction between the ions or layers of the two-dimensional material, produce atomic adsorption on the surface, and/or introduce different defects that can modify the piezoelectric properties [3].

Transition metal dichalcogenides have the $MX_2$ structure based on two different chemical elements, a transition metal *M* and a chalcogen *X* atom [3]. Transition metal dichalcogenides have an ultra-thin thickness, tunable bandgap, and unique mechanical, optical, and electronic properties [5]. Multiple derivatives of 2D materials can be obtained through alloying and van der Waals heterojunctions. The symmetry of two-dimensional materials can be modified through the application of stress or electric field, growth on substrates, or the formation of heterojunctions. Symmetry breaking can be achieved using the Janus structure by modifying chalcogenides based on chemical elements of groups VIA and/or IIIA. The Janus structure is obtained by changing the monolayer $MX_2$ by the *MXY* structure where *X*, *Y* = S, Se, and Te, and *X* is different from *Y*. This causes the electrical charge distributions between the *M-X* and *M-Y* layers to differ because the atomic radii and electronegativities are different for elements *X* and *Y*. Examples of these materials are the stable monolayers MoSSe, WSSe, WSeTe, and WSTe and the unstable monolayers MoSeTe and MoSTe.

Atomic layer substitution or Janus substitution can also be used on group IV monochalcogenides to break their symmetry to enrich optical and electrical properties [6]. Group IV two-dimensional monochalcogenides include the following materials: germanium sulfide ($GeS_2$), germanium selenide ($GeSe_2$), germanium telluride ($GeTe_2$), tin sulfide ($SnS_2$), tin selenide ($SnSe_2$), and tin telluride ($SnTe_2$). Due to the geometry of the parent materials, Janus substitution can be performed in three different ways: (1) A chalcogen (S, Se, or Te) is replaced to produce a ternary material, (2) a crystallogen (Ge) is replaced or Sn to produce a ternary material, and (3) both a chalcogen and a crystallogen are replaced to produce a quaternary material. With Janus substitution, 15 two-dimensional materials of group IV monochalcogenides can be produced: $Ge_2SSe$, $Ge_2STe$, $Ge_2SeTe$, $Sn_2SSe$, $Sn_2STe$, $Sn_2SeTe$, $GeSnS_2$, $GeSnSe_2$, $GeSnTe_2$, GeS/SnSe, GeS/SnTe, GeSe/SnS, GeSe/SnTe, GeTe/SnS, and GeTe/SnSe. These materials present mechanical stability, dynamic stability, and energetic stability. Only GeS/SnTe provides dynamic instability. These materials exhibit high piezoelectric coefficients, direct-to-indirect band transitions, as well as high figures of merit for thermoelectric effects. The symmetry breaking produced by Janus substitution leads to high vertical piezoelectric coefficients to increase the efficiency of energy harvesting and other applications that will be described in the chapter.

In the case of transition metal dichalcogenides, the $d_{11}$ piezoelectric coefficient ranges from 2.12 to 13.54 pm/V [3]. In the case of Janus-type transition metal dichalcogenides, the range of the in-plane $d_{11}$ piezoelectric coefficient is from 2.26 to 5.30 mp/V, and for the out-of-plane $d_{31}$ piezoelectric coefficient is from 0.007 to 0.30 pm/V. The $d_{11}$ piezoelectric coefficient for the IIA-VIA compounds ranges from −1.16 to 26.7 pm/V, and this value increases as the atomic number of the group IIA ion decreases and it decreases as the atomic number of the group VIA ion increases. In the case of IIIA-VA compounds with in-plane structure, the $d_{11}$ piezoelectric coefficient ranges from 0.09 to 5.5 pm/V. For these same materials with a non-planar structure, the $d_{11}$ piezoelectric coefficient ranges from 0.02 to 1.50 pm/V and the $d_{31}$ piezoelectric coefficient ranges from 0.02 to 0.57 pm/V. The values of both coefficients increase with decreasing the atomic number of group VA atoms or increasing the atomic number of the group IIIA atom except for aluminum, gallium, and indium nitrides.

For the IIIA-VIA compounds, the values of the $d_{11}$ piezoelectric coefficient are in the range of 1.12 to 1.98 pm/V. The values of the $d_{11}$ and $d_{31}$ piezoelectric coefficients for the IIIA-VIA Janus-type compounds range from 1.91 to 8.47 pm/V and from 0.07 to 0.46 pm/V, respectively. In the case of IVA-VIA compounds, the values of the $d_{11}$ piezoelectric coefficient range from 75.43 to 250.28 pm/V for a zigzag orientation. For these materials but with armchair orientation, the value of the $d_{11}$ piezoelectric coefficient is in the range of 20.7 to 921.56 pm/V. In the case of a hexagonal orientation, the $d_{11}$ piezoelectric coefficient ranges from −5.65 to −4.63 pm/V. Furthermore, the $e_{14}$ piezoelectric coefficient ranges from 345 to 381 pC/N. Finally, in the VA-VA compounds the alpha ($\alpha$) phase and the beta ($\beta$) phase occur, and the $d_{11}$ piezoelectric coefficients range from 6.94 to 243.45 pm/V and from 0.67 to 4.83 pm/V, respectively. The values of the piezoelectric coefficients for both phases increase as the atomic number of the VA ion increases.

Two-dimensional piezoelectric nanosheets that have been proposed for energy sensing and harvesting applications include hexagonal boron nitride (*h*-BN), molybdenum sulfide ($MoS_2$), and tungsten diselenide ($WSe_2$) by exploiting their excellent mechanical flexibility and excellent piezoelectric response [10]. The use of two-dimensional materials with an odd number of layers allows the inversion of symmetry to be broken, which leads to strong piezoelectricity. For very specific cases, it has been shown that an even number of layers can reach considerable piezoelectric coefficients [11]. Even the armchair or zigzag crystal orientation of the layers of the two-dimensional material used in the piezoelectric material influences the value of the achieved piezoelectric coefficient [12]. In addition to traditional two-dimensional materials, novel emerging materials based on post-transition metals such as tin disulfide ($SnS_2$) are being proposed as piezoelectric materials. These materials present an out-of-plane piezoelectric response of 2 ± 0.22 pm/V for a thickness of 4 nm, whose value is higher than that obtained for materials such as lithium niobate ($LiNbO_3$) whose average value is around 1 pm/V.

The authors in Ref. [7] have estimated through *ab initio* simulation using density-functional theory the piezoelectric coefficients of 37 two-dimensional materials among which are transition metal dichalcogenides, oxides, and III-V compounds. The values obtained in Ref. [7] have been plotted through **Figures 2–5**, to visualize the wide variety of possible piezoelectric two-dimensional materials. **Figure 2** shows the values reached for the coefficients $d_{11}$ and $e_{11}$ in the plane for two-dimensional transition metal dichalcogenides (TMDs) with a 2*H* phase. The $d_{11}$ coefficient for the dichalcogenides reaches values ranging from 2.12 pm/V for $WS_2$ to 13.45 pm/V for $CdTe_2$. In the case of the $e_{11}$ coefficient for the same materials, it ranges from 184

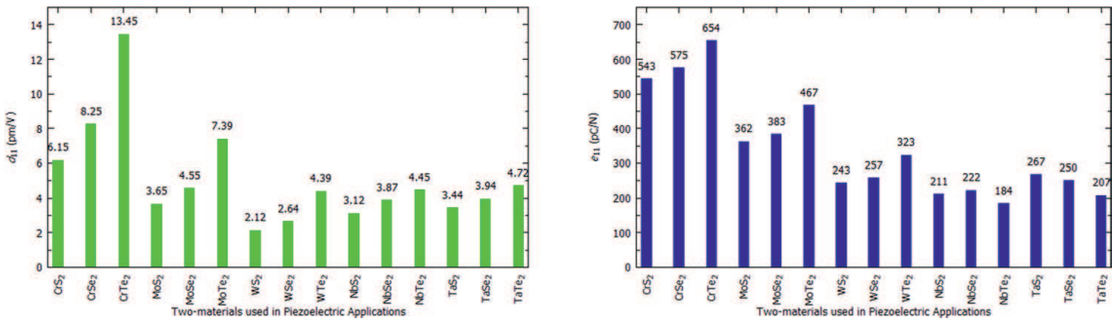


**Figure 2.**
*$d_{11}$ and $e_{11}$ piezoelectric coefficients for two-dimensional transition metal dichalcogenides with 2H phase.*

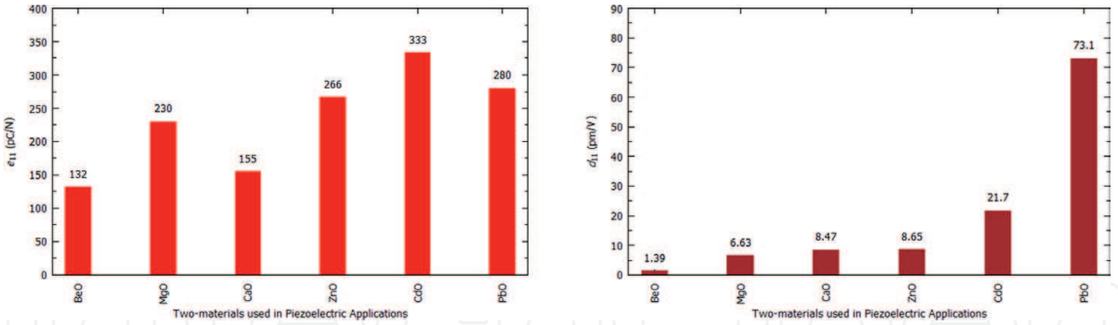


**Figure 3.**
*$d_{11}$ and $e_{11}$ piezoelectric coefficients for two-dimensional II-VI oxides.*

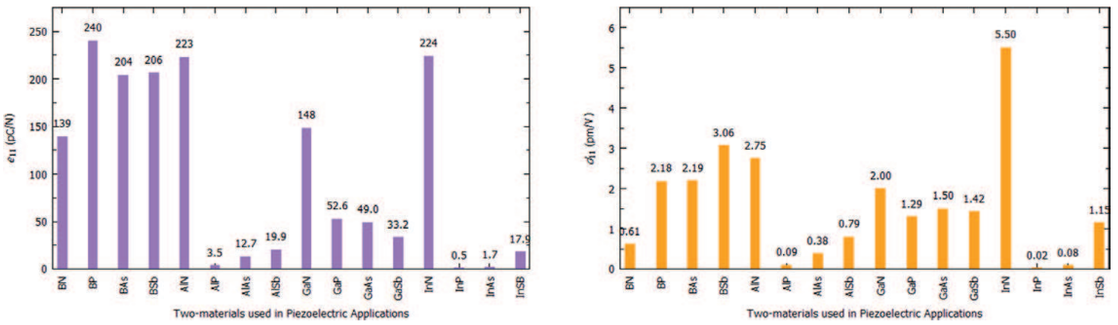


**Figure 4.**
*$d_{11}$ and $e_{11}$ piezoelectric coefficients for two-dimensional III-V compounds.*

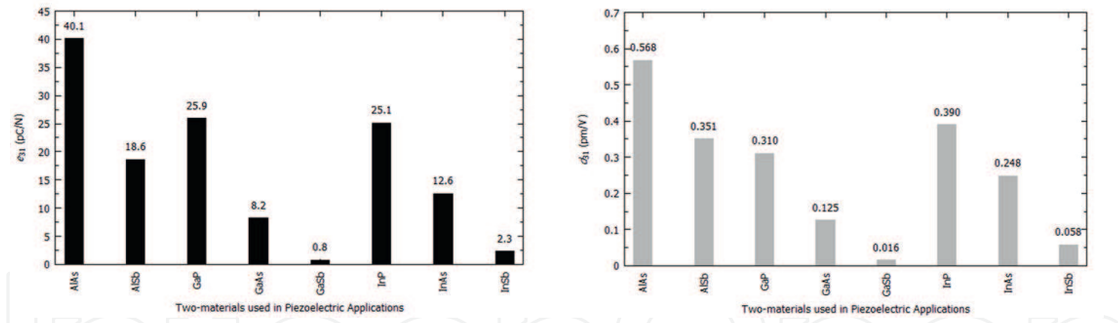


**Figure 5.**
*$d_{31}$ and $e_{31}$ piezoelectric coefficients for two-dimensional III-V compounds.*

pC/N for $NbTe_2$ to 654 pC/N for $CrTe_2$. The values of the piezoelectric coefficients $d_{11}$ are very similar to those achieved by bulk piezoelectric materials such as quartz-alpha ($\alpha$-$SiO_2$) (2.3 pm/V), gallium nitride (GaN) (3.1 pm/V), and aluminum nitride (AlN) (5.1 pm/V). Most volumetric lead zirconates (PZT) have piezoelectric coefficients $d_{11}$ on the order of 360 pm/V. Volumetric molybdenum disulfide ($MoS_2$) has a coefficient $e_{11}$ of 290 pC/N.

**Figure 3** depicts the values reached for in the plane coefficients $d_{11}$ and $e_{11}$ in the plane for different two-dimensional II-VI oxides with primitive ($p$) structures. The $d_{11}$ coefficient for the dichalcogenides reaches values ranging from 1.39 pm/V for BeO to 73.1 pm/V for PbO. In the case of the $e_{11}$ coefficient for the same materials, it ranges from 132 pC/N for BeO to 333 pC/N for CdO.

**Figure 4** illustrates the values reached for in the plane coefficients $d_{11}$ and $e_{11}$ in the plane for some two-dimensional III-V compounds with primitive ($p$) or blende

(b) structures. The $d_{11}$ coefficient for dichalcogenides reaches values ranging from 0.02 pm/V for InP to 5.50 pm/V for InN. In the case of the $e_{11}$ coefficient for the same materials, it ranges from 0.5 pC/N for InP to 240 pC/N for BP.

**Figure 5** shows the values reached for the out-of-plane coefficients $d_{31}$ and $e_{31}$ in the plane for different two-dimensional III-V compounds with hexagonal structures. The $d_{11}$ coefficient for dichalcogenides reaches values ranging from 0.016 pm/V for GaSb to 0.568 pm/V for AlAs. In the case of the $e_{11}$ coefficient for the same materials, it ranges from 0.8 pC/N for GaSb to 40.1 pC/N for AlAs.

The authors in Ref. [8] have predicted through first-principles calculations some piezoelectric coefficients of III-V compounds for gallium arsenide (GaAs), gallium phosphide (GaP), gallium antimonide (GaSb), indium arsenide (InAs), indium phosphide (InP), and indium antimonide (InSb). The simulations consider in their determination both clamped ions and relaxed ions [8]. In **Tables 1–4**, to study the behavior of piezoelectric two-dimensional III-V compounds, comparisons are made between the values obtained by Refs. [7, 8] for the piezoelectric coefficients $e_{11}$, $e_{31}$, $d_{11}$, and $d_{31}$, respectively. The simulated values illustrate trends related to the assumptions about the theoretical principle and the mechanical physical state in which the ions are simulated to operate, which do not necessarily illustrate the actual experimentally obtained piezoelectric coefficient but serve to confirm the relevance of using two-dimensional materials in energy harvesting compared to other conventional materials already used for years.

The authors of Ref. [9] used density functional perturbation theory (DFPT) and first-principles calculations to predict the piezoelectric coefficients of

| Nanomaterial | $e_{11}$ [7] | $e_{11}$ (clamped-ion) [8] | $e_{11}$ (relaxed-ion) [8] |
|---|---|---|---|
| GaP | 25.9 | 307 | 44 |
| GaAs | 49.0 | 289 | 33 |
| GaSb | 33.2 | 254 | 25 |
| InP | 0.5 | 290 | 40 |
| InAs | 1.7 | 281 | 32 |
| InSb | 17.9 | 252 | 24 |

**Table 1.**
*Compilation of $e_{11}$ piezoelectric coefficients for some two-dimensional III-V compounds predicted by different simulation techniques.*

| Nanomaterial | $e_{31}$ [7] | $e_{31}$ (clamped-ion) [8] | $e_{31}$ (relaxed-ion) [8] |
|---|---|---|---|
| GaP | 52.6 | 59 | 450 |
| GaAs | 8.20 | 90 | 280 |
| GaSb | 0.80 | 69 | 190 |
| InP | 25.1 | 100 | 480 |
| InAs | 12.6 | 130 | 310 |
| InSb | 2.3 | 84 | 170 |

**Table 2.**
*Compilation of $e_{31}$ piezoelectric coefficients for some two-dimensional III-V compounds predicted by different simulation techniques.*

| Nanomaterial | $d_{11}$ [7] | $d_{11}$ (clamped-ion) [8] | $d_{11}$ (relaxed-ion) [8] |
|---|---|---|---|
| GaP | 1.29 | 5.10 | 0.96 |
| GaAs | 1.50 | 6.06 | 0.93 |
| GaSb | 1.42 | 6.91 | 0.90 |
| InP | 0.02 | 6.33 | 1.45 |
| InAs | 0.08 | 7.48 | 1.20 |
| InSb | 1.15 | 8.36 | 1.16 |

**Table 3.**
*Compilation of $d_{11}$ piezoelectric coefficients for some two-dimensional III-V compounds predicted by different simulation techniques.*

| Nanomaterial | $d_{31}$ [7] | $d_{31}$ (clamped-ion) [8] | $d_{31}$ (relaxed-ion) [8] |
|---|---|---|---|
| GaP | 0.310 | 0.062 | 0.51 |
| GaAs | 0.125 | 0.12 | 0.40 |
| GaSb | 0.016 | 0.12 | 0.33 |
| InP | 0.390 | 0.13 | 0.74 |
| InAs | 0.248 | 0.20 | 0.51 |
| InSb | 0.058 | 0.17 | 0.35 |

**Table 4.**
*Compilation of $d_{31}$ piezoelectric coefficients for some two-dimensional III-V compounds predicted by different simulation techniques.*

| Nanomaterial | $d_{11}$ [7] | $d_{11}$ (clamped-ion) [9] | $d_{11}$ (relaxed-ion) [9] | $d_{11}$ (DFPT) [9] |
|---|---|---|---|---|
| BeO | 1.39 | 1.25 | 4.62 | 1.43 |
| MgO | 6.63 | 18.2 | 5.00 | 7.69 |
| CaO | 8.47 | 9.63 | 10.2 | 10.2 |
| SrO | — | 12.6 | 13.3 | 7.40 |
| BaO | — | 27.4 | 24.5 | 1.07 |
| ZnO | 8.65 | 5.90 | 9.29 | 8.57 |
| CdO | 21.7 | 8.57 | 8.21 | 23.4 |

**Table 5.**
*Compilation of $d_{11}$ piezoelectric coefficients for some two-dimensional IIA/IIB-VI oxides predicted by different simulation techniques.*

two-dimensional oxides of IIA/IIB groups. **Tables 5** and **6** present compilations of the values obtained for the $d_{11}$ and $e_{11}$ piezoelectric coefficients. The simulated values vary depending on the simulation conditions and these are very similar considering the second and last columns, but not for all materials. Through the tables and figures in this section, it can be broken down that the values obtained in the simulations must be verified because similar values, or with significant differences, were obtained.

The values are attractive from the point of view that these materials allow the implementation of applications where out-of-plane piezoelectric coefficients can be

| Nanomaterial | $e_{11}$ [7] | $e_{11}$ (clamped-ion) [9] | $e_{11}$ (relaxed-ion) [9] | $e_{11}$ (DFPT) [9] |
|---|---|---|---|---|
| BeO | 132 | 123 | 385 | 146 |
| MgO | 230 | 557 | 152 | 236 |
| CaO | 155 | 152 | 167 | 156 |
| SrO | — | 156 | 167 | 90.6 |
| BaO | — | 232 | 202 | 7.24 |
| ZnO | 266 | 174 | 261 | 253 |
| CdO | 333 | 112 | 109 | 319 |

**Table 6.**
*Compilation of $e_{11}$ piezoelectric coefficients for some two-dimensional IIA/IIB-VI oxides predicted by different simulation techniques.*

exploited, as opposed to where the materials only exhibit in-plane piezoelectric properties. The computational simulation with different approaches and the experimental corroboration of the piezoelectric performance of two-dimensional materials must be exhaustively studied to guarantee that the values of the piezoelectric coefficients are exploited more efficiently for all the applications that are proposed. In the previous discussion, it can be deduced that some materials do not present piezoelectric properties in bulk size; however, these are present when they are used with thicknesses of some atomic layers and thus are designated two-dimensional materials. Even the opposite of what was mentioned above is also feasible. These materials can be surface-modified appropriately under one or more crystal directions [28]. The addition of atoms and/or defects at the surface level is one of the possibilities to achieve materials with piezoelectric or ferroelectric properties. Even the free electrical charges in these materials must be controlled by either physical or virtual gates depending on the properties of the material to achieve piezoelectricity. The mechanical stability analysis of the piezoelectric behavior has allowed us to determine that the order of stability decreases in the following order: oxides, sulfides, selenides, and tellurides. Furthermore, the mechanical stability is reduced as the radius of the transition metal is decreased in the case of transition metal dichalcogenides (TMDs). To guarantee mechanical stability in a 2D piezoelectric material, it must have a low heat of formation.

A recent type of SnXY Janus monolayers (where X = Te, Se, S, O; Y = Te, Se, S, O; $X \neq Y$) is being investigated because it presents static, dynamic, electronic, and thermodynamic stabilities that can be exploited to produce two-dimensional piezoelectric materials [29]. Of this family of two-dimensional materials, those based on tin behave as direct band semiconductors (SnOS and SnOSe with band gaps of 1.74 and 0.33, respectively) or indirect band semiconductors (SnSSe, with band gap of 1.69 eV). The $d_{11}$ piezoelectric deformation coefficient of selenium tin oxide (SnOSe) reaches a value of 27.3 pm/V, which is an order higher than that reported for materials such as $MoS_2$ or quartz. Two-dimensional tin-based chalcogenides using Janus monolayers can be applied for piezoelectric applications such as energy harvesting and sensors.

## 4. Applications

The direct use of two-dimensional piezoelectric materials is in the implementation of compact sensors and actuators, flexible electronics, micro-electromechanical

systems (MEMS), as well as energy harvesting that takes advantage of both the direct and inverse piezoelectric effects [11, 12]. Piezoelectric materials can be applied in the implementation of nanogenerators, information storage, and piezo-catalysis, as well as in biomedicine [3]. With the introduction of sensor networks and the Internet of Things (IoT), batches of sensors that are capable of being self-powered and operating as energy harvesters that exploit piezoelectric properties need to be researched and developed [12]. The first piezoelectric microgenerator was proposed by Glynne-Jones et al. in 2001 [25]. The nanogenerator concept was first proposed by Zhong Ling Wang et al. in 2006 [26]. After this, researchers around the world launched extensive research to develop nanomaterials and nanosystems to convert mechanical energy into electrical energy. Energy harvesters can then be considered the miniaturized replacement for battery-based power supplies for fully portable and/or wearable applications. Piezoelectric nanogenerators provide green and sustainable energy to implement self-powered nanosensors and nanosystems that operate wirelessly and in real time [23]. Nanosystems that directly benefit from self-powered systems are resonators, optoelectronic devices, and biosensors [24]. Furthermore, these nanogenerators can be used in piezo-photonics to tune the performance of photovoltaic devices and/or solar cells. Self-powered systems avoid frequent charging and replacement that are required by battery-based power systems. Battery-based systems take up too much space and are very heavy, which limits their portability and ability to incorporate them into wearable systems. Human activities such as finger typing and breathing may be capable of generating electrical powers on the order of 6.9 mW and 0.83 W, respectively. Wearable electronics require powers of the order of 200 microwatts to 1 watt, which can be achieved by the natural biomechanics of the human being, and its reduction is feasible when designing all systems using nanomaterials. Among the biomechanical movements from which energy can be harvested are the movement of elbow joints, heel strikes, leg movements, and arm swings [26].

If a deformation by tension or compression is applied to a piezoelectric material, a piezo-potential is generated in the pair of metal electrodes found at the ends of the material [3]. Electrons and holes as electric carriers are attracted to the piezo-potential with opposite polarity and an electric current is generated on a charge. If the strain is produced continuously, then a continuous current and voltage are generated. In this way, the nanogenerator converts mechanical energy into electrical energy. Nanogenerators based on piezoelectric two-dimensional materials have been implemented using molybdenum diselenide ($MoSe_2$) [12], $\alpha$-phase indium selenide ($\alpha$-$In_2Se_3$) [13], black phosphorus or phosphorene (BP) [14], molybdenum disulfide ($MoS_2$) [15], $MoS_2/In_2Se_3$ Van der Waals heterostructure [16], hexagonal boron nitride ($h$-BN) [10], zinc oxide (ZnO) [17], tungsten diselenide ($WSe_2$) [18], and other materials.

A piezoelectric nanogenerator based on a molybdenum diselenide ($MoSe_2$) nanosheet has been used to power a molybdenum disulfide ($MoS_2$)-based pH sensor and a photodetector based on a molybdenum disulfide-tungsten diselenide ($MoS_2$/$WSe_2$) [12]. This molybdenum diselenide ($MoSe_2$)-based nanogenerator provides an output voltage of 60 mV with a strain of 0.6%, which is approximately 50% larger than for a molybdenum disulfide ($MoS_2$)-based nanogenerator. Thanks to its excellent performance, this nanogenerator is capable of non-invasively monitoring vital signs to determine the respiratory rate and heart rate.

A simple boron nitride (BN) nanosheet when mechanically deformed can produce an alternating piezoelectric output of 50 mV and 30 pA [10]. For this material, a piezoelectric voltage coefficient ($g_{11}$) was determined experimentally with a value of

$2.35 \times 10^{-3}$ Vm/N. When this material was deposited as active material on a polyimide substrate, an energy harvester was produced with an output voltage of 9 V, a current of 200 nA, and an output power of 0.3 μW.

Human skin is an organ capable of perceiving external environmental stimuli or changes against variables such as temperature, humidity, and pressure [19]. Applications such as prosthetics, medical equipment, wearable devices, robots, and others have benefited from the development of electronic skins. The concept of artificial or electronic skin was proposed in the early 1980s by George Lucas as a future application concept. The first versions implemented showed limited flexibility, low resolution, and poor sensitivity. Therefore, new versions must take advantage of artificial intelligence and wearable technology for the development of health monitoring and prosthetic devices. In addition, the active materials to design these electronic skins must be sensitive, flexible, and independent of their shape and size. The application of piezoelectric nanogenerators and piezotronics allows the implementation of electronic skins that can exceed even the performance of electronic skins for the development of sensors with high spatial resolution, fast response speed, ultra-sensitivity, low power consumption, excellent durability, and ability to electrical self-supply.

IIIA-VIA compounds exhibit the coexistence of in-plane and out-of-plane piezoelectricity caused by hexagonal stacking, which makes them interesting for energy harvesting and electronic skin [13]. An $\alpha$-phase indium selenide ($\alpha$-$In_2Se_3$)-based nanogenerator was implemented with 0.76% strain producing a peak voltage and current of 35.7 mV and 47.3 pA, respectively. The $d_{33}$ piezoelectric coefficient of $\alpha$-$In_2Se_3$ changes from 0.34 pm/V for a monolayer to 5.6 pm/V for the bulk version.

One of the great challenges of piezoelectric materials is to produce out-of-plane polarization in active materials by exerting stress along the direction perpendicular to the nanosheet [20]. Achieving this polarization could improve the efficiency of piezoelectric transfer and make medical devices such as sphygmomanometers (for indirect blood pressure measurement) and tactical sensors such as bionic robot skins a reality. Heterostructures based on two-dimensional materials such as tin nitride ($Sn_3N_4$)-indium oxide ($In_2O_3$), germanium nitride ($Ge_3N_4$)-gallium oxide ($Ga_2O_3$), and silicon nitride ($Si_3N_4$)-aluminum oxide ($Al_2O_3$) have been studied by first-principle calculations seeking to increase the out-of-plane piezoelectric coefficients. The piezoelectric coefficients $d_{33}$ and $e_{33}$ were determined for the two-dimensional materials and their values have been plotted in **Figure 6**. The maximum value of $d_{33}$ is 5290 pm/V corresponding to $Sn_3N_4$-$In_2O_3$ and the maximum value of $e_{33}$ is 3869 pC/N corresponding to $Si_3N_4$-$Al_2O_3$. These materials are made prospects for energy harvesting applications as well as for blood pressure meters or bionic skin of robots.

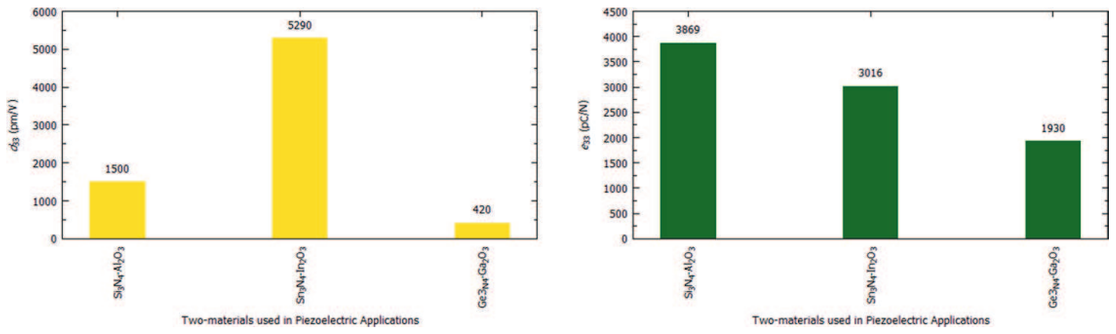


**Figure 6.**
*$d_{33}$ and $e_{33}$ piezoelectric coefficients for some heterostructures based on two-dimensional materials.*

Phosphorene or black phosphorus (BP) presents interesting properties such as thickness-dependent bandgap and high carrier mobility, due to its anisotropic optical, electronic, mechanical, thermal, and ionic transport characteristics [14]. Phosphorene has a $d_{11}$ piezoelectric strain coefficient of −9.48 pm/V in the armchair direction. Phosphorene nanosheets deliver an output current of 4 pA when a compression strain of −0.72% is applied to them. With all these qualities, phosphorene can be proposed for use in strain sensors, nanogenerators, and piezoelectrically tuned transistors.

Due to a low out-of-plane piezoelectric response of $\alpha$-$In_2Se_3$, research has been initiated on the possibility of modifying two-dimensional materials through heterostructures to increase their value. The use of the $\alpha$-$In_2Se_3$/$MoS_2$ heterostructure can increase the value of the $d_{33}$ piezoelectric coefficient [16]. The $d_{33}$ piezoelectric coefficient for the $\alpha$-$In_2Se_3$/$MoS_2$ heterostructure has a value of 17.5 pm/V. This value increases with the increase in the number of layers of the two-dimensional material but becomes saturated when it reaches 40 nm in thickness.

For a tungsten diselenide ($WSe_2$) bilayer nanosheet, the $d_{11}$ piezoelectric coefficient was 3.26 ± 0.3 pm/V, whose value is higher than the $d_{11}$ coefficient of 2.3 pm/V for volumetric $\alpha$-quartz [18]. The mechanical deformation for a bilayer is 0.95%, while for a monolayer it is 0.63%. $WSe_2$ bilayers feature high piezoelectric coefficients and good mechanical durability for a wide strain range that could be exploited to harvest the energy required by a small liquid crystal display without applying an external power supply.

Next, a diversity of two-dimensional materials is proposed for the development of sensors and energy harvesting, and the values of the piezoelectric coefficients reached are reported, seeking their application, especially for their application outside the plane. Materials such as graphene, thanks to surface modification techniques, can produce in-plane and out-of-plane piezoelectricity reaching 37,000 pC/N for the $d_{33}$ coefficient, 12,500,000 pm/V for the $e_{33}$ coefficient, and 0.3 pm/V for the $d_{31}$ coefficient [21]. For phosphorene, the values of the piezoelectric coefficients are 59 pC/N for the $e_{11}$ coefficient and 1.06 pC/N for the $e_{31}$ coefficient. The piezoelectric coefficient $e_{11}$ for $\alpha$-phase indium selenide ($\alpha$-InSe) is 57 pC/N, and for fluorinated hexagonal boron nitride (F-*h*-BN) it is 84 pC/N. For phosphorene oxide ($P_4O_2$)-two-dimensional monolayer, the piezoelectric coefficients reach values of 54 pm/V for $d_{11}$, −10 pm/V for $d_{31}$, and 21 pm/V for $d_{26}$. For lithium-doped black phosphor ($P_4Li_2$), the piezoelectric coefficient $d_{31}$ ranged from 2.5 to 6.28 pm/V depending on the approximation used. Two-dimensional materials such as antimonene and arsenene can reach strain limits of 58 and 24% in the armchair and zigzag directions, respectively, which are higher when compared to other two-dimensional materials such as graphene, molybdenum disulfide ($MoS_2$), or phosphorene. Other two-dimensional materials that offer out-of-plane piezoelectricity are oxygen-functionalized MXenes ($M_2CO_2$) where $M$ can be scandium (Sc), yttrium (Y), or lanthanum (La), which have a $d_{31}$ coefficient in the range of 0.4 to 0.78 pm/V, and a coefficient $e_{31}$ in the range of 88 to 196 pC/N, for the case of relaxed ions [22].

The use of vertically aligned two-dimensional flexible zinc oxide nanodiscs for the design of a piezoelectric nanogenerator was reported in Ref. [23]. This nanogenerator used thermally annealed discs and generated a direct current (DC) output voltage of 17 V and a current density of 150 nA/cm$^2$. These values increased by 7 times the voltage and 5 times the current density if the pristine version of the same material had been used. This performance improvement was achieved thanks to superficial passivation and the reduction of oxygen vacancies in the two-dimensional material.

A recent alternative that has been reported is the possibility of developing nanogenerators with piezoelectric and triboelectric properties to develop self-powered systems [24]. Achieving the maximum performance of this nanogenerator implies taking advantage of the synergistic coupling between both types of mechanisms leading to increased electrical outputs as well as raising the energy conversion efficiency. When two materials that are electrically charged are placed in friction with each other, electrification is produced which is induced by contact, giving rise to a triboelectric effect. Like the piezoelectric effect, a triboelectric couple is produced which is directly dependent on the relative electrical polarity induced by the induced electrical charge. Two-dimensional materials such as hexagonal boron nitride (*h*-BN), metal-organic scaffolds (MOFs), and transition metal dichalcogenides (TMDs) have been proposed to induce triboelectricity. Some of these materials exhibit both triboelectric properties and piezoelectric effects. Thanks to these qualities, it is possible to decrease the internal resistance, increase the generation of electrical charge, and produce additional electrical charge trapping sites. Involving both electrical mechanisms in the same design makes it feasible to increase the total power output since both effects work efficiently under mechanical deformation, be it compression, tension, and/or vibration. The triboelectric effect operates on the surface of the material, while the piezoelectric effect operates on the volume of the material below the surface. In this way, it is possible to increase polarization by changing the structure of the material, optimizing energy harvesting, and maximizing energy conversion.

According to the previous paragraphs, the main applications derived from energy harvesting with two-dimensional piezoelectric materials are summarized in **Figure 7**. In addition to the applications summarized in **Figure 7**, there is the possibility of developing humidity, magnetic field, and mechanical force sensing. These materials possess unique piezoelectric properties relative to their nanowire-based or volumetric counterparts. Laboratory tests as well as computer simulations have shown that two-dimensional piezoelectric materials can be easily modified to achieve different piezoelectric coefficients by including a different number of layers in the design [27].

An alternative strategic implementation for harvesting mechanical energy is the development of piezoelectric nanogenerators [30]. Materials such as molybdenum disulfide ($MoS_2$) can take advantage of their centrosymmetric structures to produce electricity through the distortion of the crystalline lattice due to the mechanical

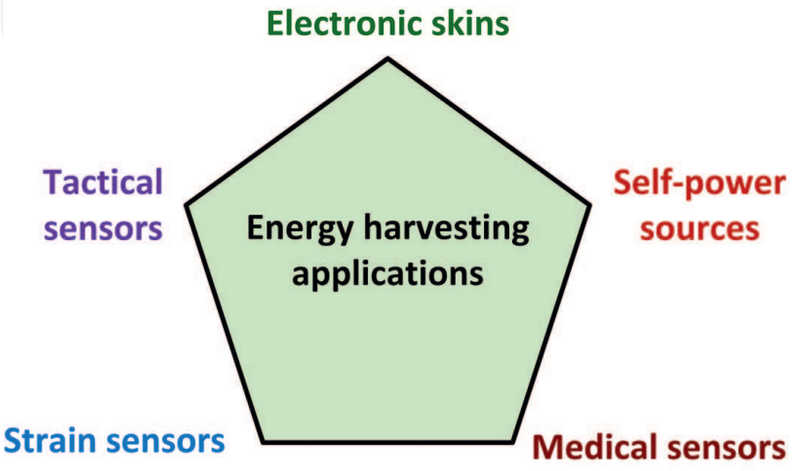


**Figure 7.**
*Main applications from energy harvesting with two-dimensional piezoelectric materials.*

deformation produced by the polarization of the charge of the constituent ions. However, an odd number of layers in the two-dimensional material structure must be used to achieve piezoelectric voltage and current outputs, which is not possible for structures with an even number of layers. Better results in piezoelectric performance are achieved when the number of layers tends to a smaller value.

Recently, a direct current generator using piezoelectric two-dimensional ZnO nanosheets has been implemented to produce an open-circuit voltage of 0.9 V, a current density for short-circuit current of 16.4 μA, and a power density of 600 nW/$cm^2$ for 4000 cycle operation using 4 kg of force [31]. Due to its mechanical reliability, flexibility, and high output power, this generator has the potential to be used as a power source for portable devices and as a mechanical sensor.

Due to the small thickness and light weight of two-dimensional materials, the suspended application of these materials produces significant mechanical fragility [32]. Therefore, the practical application of these materials involves the use of substrate materials to guarantee good quality of the layers as well as good stability in all the senses previously discussed. In this way, the deformation on the layers of the two-dimensional material can be homogeneous and precisely controlled throughout the substrate. Therefore, the use of polymer-based composite materials that include two-dimensional material is one of the common strategies to replace the use of a fixed and inflexible substrate, especially for wearable piezoelectric electricity generation applications.

Two-dimensional materials based on cobalt telluride ($CoTe_2$) can be used to generate electricity from waste heat using triboelectric and piezoelectric properties as energy harvesters [33]. The piezo-triboelectric nanogenerator can produce a voltage of 5 Volts when a force of 1 N is applied to it operating in a temperature range of 32 to 90 degrees Celsius.

Both mechanical flexibility and bandgap tunability are the strategic advantages of using two-dimensional materials in the implementation of data memories and electronic sensors [34]. To more appropriately exploit two-dimensional materials, it is necessary to increase the quality of their synthesis on a large scale and at a low cost, understand the relationship between the magnetic domain pattern and the applied external electric field, as well as determine the values of the piezoelectric coefficient, Curie temperature, and polarization value and in all crystalline directions of the material.

Piezoelectric materials take advantage of the mechanical deformation produced by ambient energies to develop applications such as nanogenerators as well as optical, mechanical, and magnetic sensors [35]. These make use of electrical polarization to perpendicularly deform a material by either stretching it when a positive voltage is applied or contracting it when a negative voltage is applied. Magnetic behavior is achieved when a two-dimensional material is doped or vacancies or defects are induced on the original structure.

Piezoelectric materials can replace batteries by exploiting energy from the environment for the design of self-powered devices with power consumption in the range of microwatts or milliwatts [36]. These materials offer an environmentally friendly alternative by avoiding the disposal of waste batteries that have not been manufactured and recycled with green technologies.

## 5. Future research directions

One of the great challenges of this century is to exploit the piezoelectric properties for the implementation of functional, sensitive, and innovative electronic devices

[21]. With the miniaturization of electronic devices, it is necessary to develop strategies for the selection of materials that can be exploited for this purpose. There are more than 7000 possible two-dimensional materials that can be modified to achieve optimization of piezoelectric properties. Among the strategies to modify the piezoelectric properties are deformation, atom or Janus substitution, functionalization, and introduction of defects in a premeditated way. Furthermore, it is possible to stack the two-dimensional nanosheets with similar or dissimilar materials to design heterostructured materials whose piezoelectric properties are completely different from those of their components. Since the piezoelectric properties thanks to these strategies can be tuned for the design of pressure sensors, piezotronics, piezo-catalysis, and energy harvesting, researchers around the world will continue to develop scientific research to take full advantage of piezoelectricity in two-dimensional materials. The suitability of the chosen material to exploit piezoelectricity comes from the following factors: difference in electronegativity between the atoms of the unit cell of the material, impact on health and the environment of the material, cost reduction and ease of the synthesis process of the material, as well as additional material properties. These factors must be considered to choose, design, and integrate the best two-dimensional materials to take the design from the laboratory phase to the practical phase for commercial production.

The study of piezoelectric two-dimensional materials is not complete [21]. Both computational modeling and experimental characterization should be further developed to predict in-plane and out-of-plane piezoelectric behaviors more accurately for various possible theoretical and technological possibilities. In addition, it is necessary to establish standards for test protocols, study the triboelectric effects involved, and complement the necessary terminology to be able to study the piezoelectric properties of two-dimensional materials. Despite the progress made in the research of two-dimensional piezoelectric materials, a lot of research must be carried out to understand their piezoelectric behavior because conventional models and theories are not able to explain the effects found in them. The use of density functional theory and molecular dynamics (MD) calculation will continue to be a vital reference source for calculating, optimizing, and predicting the piezoelectric properties of two-dimensional piezoelectric materials. A comprehensive study of the differential charge density, surface electronegativity, difference in atomic radii, anion-cation polarization ratio, effective Born charges, and elastic constants of two-dimensional piezoelectric materials must be developed to exploit the next generation of applications of high-added value.

## 6. Conclusions

Two-dimensional materials have undoubtedly attracted the interest of researchers around the world not only for their extraordinary properties but also for the innumerable possibilities of technological development and unprecedented scientific research. The wide range of possibilities to produce anisotropy in its piezoelectric properties extends its applications in energy harvesting, tactical sensors, medical devices, and electronic skins. Despite the advances achieved so far, computational modeling and experimental characterization of the piezoelectric properties of two-dimensional materials are still necessary to achieve a complete study of the most suitable materials to take advantage of the properties in conventional and emerging applications. The graphs of the piezoelectric coefficient values presented in this chapter illustrate, in

addition to the great diversity of possible materials, a wide possibility of both in-plane and out-of-plane coefficient values. Concerning the piezoelectric properties of commonly used zinc oxide (ZnO) and gallium nitride (GaN) nanowires, the piezoelectric coefficients of the two-dimensional materials are 2 orders of magnitude larger. 2D piezoelectric materials can withstand very large deformations for their dimensions. In this century, all two-dimensional materials must be synthesized and studied to exploit the piezoelectric properties, and these can be exploited with maximum efficiency by knowing the specific conditions suitable for each material.

## Acknowledgements

The author appreciates the support of the University of Guanajuato to develop this research. The author appreciates the support of the researchers who shared their publications to complement this study.

## Thanks

The author wants to thank his wife and son for their support and time to edit this book. The author appreciates the support of Tea Jurcic working for IntechOpen as an author service manager.

## Author details

Rafael Vargas-Bernal
University of Guanajuato, Salamanca, Guanajuato, Mexico

*Address all correspondence to: r.vargas@ugto.mx

## References

[1] Li J-F. Fundamentals of piezoelectricity. In: Lead-Free Piezoelectric Materials. Weinheim, Germany: Wiley-VCH; 2021. pp. 1-18. DOI: 10.1002/9783527817047.ch1

[2] Tahir MB, Fatima U. Recent trends and emerging challenges in two-dimensional materials for energy harvesting and storage applications. Energy Storage. 2022;**4**(1):e244. DOI: 10.1002/est2.244

[3] Zhang Q, Zuo S, Chen P, Pan C. Piezotronics in two-dimensional materials. InfoMat. 2021;**3**(9):987-1007. DOI: 10.1002/inf2.12220

[4] Cheon G, Duerloo K-AN, Sendek AD, Porter C, Chen Y, Reed EJ. Data mining for new two- and one-dimensional weakly bonded solids and lattice-commensurate heterostructures. Nano Letters. 2017;**17**(3):1915-1923. DOI: 10.1021/acs.nanolett.6b05229

[5] Li R, Cheng Y, Huang W. Recent progress of Janus 2D transition metal chalcogenides: From theory to experiments. Small. 2018;**14**(45):1802091. DOI: 10.1002/smll.201802091

[6] Seixas L. Janus two-dimensional materials based on group IV monochalcogenides. Journal of Applied Physics. 2020;**128**(4):045115. DOI: 10.1063/5.0012427

[7] Blonsky MN, Zhuang HL, Singh AK, Hennig RG. Ab initio prediction of piezoelectricity in two-dimensional materials. ACS Nano. 2015;**9**(10):9885-9891. DOI: 10.1021/acsnano.5b03394

[8] Gao R, Gao Y. Piezoelectricity in two-dimensional group III-V buckled honeycomb monolayers. Physica Status Solidi: Rapid Research Letters. 2017;**11**(3):1500412. DOI: 10.1002/psrr.201600412

[9] Alyörük MM. Piezoelectric properties of monolayer II-VI group oxides by first-principles calculations. Physica Status Solidi B. 2016;**253**(12):2534-2539. DOI: 10.1002/pssb.201600387

[10] Lee G-J, Lee M-K, Park J-J, Hyeon DY, Jeong CK, Park K-I. Piezoelectric energy harvesting from two-dimensional boron nitride nanoflakes. ACS Applied Materials & Interfaces. 2019;**11**(41):37920-37926. DOI: 10.1021/acsami.9b12187

[11] Wang Y, Vu L-M, Lu T, Xu C, Liu Y, Ou JZ, et al. Piezoelectric responses of mechanically exfoliated two-dimensional $SnS_2$ nanosheets. ACS Applied Materials & Interfaces. 2020;**12**(46):51662-51668. DOI: 10.1021/acsami.0c16039

[12] Li P, Zhang Z. Self-powered 2D material-based pH sensor and photodetector driven by monolayer $MoSe_2$ piezoelectric nanogenerator. ACS Applied Materials & Interfaces. 2020;**12**(52):58132-58139. DOI: 10.1021/acsami.0c18028

[13] Xue F, Zhang J, Hu W, Hsu W-T, Han A, Leung S-F, et al. Multidirection piezoelectricity in mono- and multilayered hexagonal α-$In_2Se_3$. ACS Nano. 2018;**12**(5):4976-4983. DOI: 10.1021/acsnano.8b02152

[14] Ma W, Lu J, Wan B, Peng D, Xu Q, Hu G, et al. Piezoelectricity in multilayer black phosphorus for piezotronics and nanogenerators. Advanced Materials. 2020;**32**(7):1905795. DOI: 10.1002/adma.201905795

[15] Han JK, Kim S, Jang S, Lim YR, Kim S-W, Chang H, et al. Tunable piezoelectric nanogenerators using flexoelectricity of well-ordered hollow 2D $MoS_2$ shells arrays for energy harvesting. Nano Energy. 2019;**61**:471-477. DOI: 10.1016/j.nanoen.2019.05.017

[16] Yuan S, Io WF, Mao J, Chen Y, Luo X, Hao J. Enhanced piezoelectric response of layered $In_2S_3/MoS_2$ nanosheet-based van der Waals heterostructures. ACS Applied Nano Materials. 2020;**3**(12):11979-11986. DOI: 10.1021/acsanm.0c02513

[17] Chen J, Qiu Y, Yang D, She J, Wang Z. Improved piezoelectric performance of two-dimensional ZnO nanodisks-based flexible nanogenerators via ZnO/Spiro-MeOTAD PN junction. Journal of Materials Science: Materials in Electronics. 2020;**31**:5584-5590. DOI: 10.1007/s10854-020-03124-0

[18] Lee J-H, Park JY, Cho EB, Kim TY, Han SA, Kim T.H, Liu Y, Kim SK, Roh CJ, Yoon H-J, Ryu H, Seung W, Lee JS, Lee J, Kim S-W. Reliable piezoelectricity in bilayer $WSe_2$ for piezoelectric nanogenerators. Advanced Materials 2017; 29(29): 1606667. DOI: 10.1002/adma.201606667

[19] Yuan H, Lei T, Qin Y, Yang R. Flexible electronic skins based on piezoelectric nanogenerators and piezotronics. Nano Energy. 2019;**59**:84-90. DOI: 10.1016/j.nanoen.2019.01.072

[20] Zhu D-R, Wu Y, Zhang H-N, Zhu L-H, Zhao S-N. New direction's piezoelectricity and new applications of two-dimensional group V-IV-II-VI films: A theoretical study. Physica E: Low-dimensional Systems and Nanostructures. 2020;**124**:114214. DOI: 10.1016/j.physe.2020.114214

[21] Sherrell PC, Fronzi M, Shepelin NA, Corletto A, Winkler D, Ford M, et al. A bright future for engineering piezoelectric 2D crystals. Chemical Society Reviews. 2022;**51**(2):650-671. DOI: 10.1039/d1cs00844g

[22] Tan J, Wang Y, Wang Z, He J, Liu Y, Wang B, et al. Large out-of-plane piezoelectricity of oxygen functionalized MXenes for ultrathin piezoelectric cantilevers and diaphragms. Nano Energy. 2019;**65**:104058. DOI: 10.1016/j.nanoen.2019.104058

[23] Verma K, Bharti DK, Badatya S, Srivastava AK, Gupta MK. A high performance flexible two dimensional vertically aligned ZnO Nanodisc based piezoelectric nanogenerator via surface passivation. Nanoscale Advances. 2020;**2**(5):2044-2051. DOI: 10.1039/c9na00789j

[24] Zhang J, He Y, Boyer C, Kalantar-Zadeh K, Peng S, Chu D, et al. Recent developments of hybrid piezo-triboelectric nanogenerators for flexible sensors and energy harvesters. Nanoscale Advances. 2021;**3**(19):5465-5486. DOI: 10.1039/d1na00501d

[25] Glynne-Jones P, Beeby SP, White NM. Towards a piezoelectric vibration-powered microgenerator. IEE Proceedings: Science, Measurement and Technology. 2001;**148**(2):68-72. DOI: 10.1049/ip-smt:20010323

[26] Wang ZL, Song J. Piezoelectric nanogenerators based on zinc oxide nanowire arrays. Science. 2006;**312**(5771):242-246. DOI: 10.1126/science.1124005

[27] Zhang J. On the piezopotential properties of two-dimensional materials. Nano Energy. 2019;**58**:568-578. DOI: 10.1016/j.nanoen.2019.01.086

[28] Hinchet R, Khan U, Falconi C, Kim S-W. Piezoelectric properties in

two-dimensional materials: Simulations and experiments. Materials Today. 2018;**21**(6):611-630. DOI: 10.1016/j.mattod.2018.01.031

[29] Zhang X, Cui Y, Sun L, Li M, Du J, Huang Y. Stabilities, and electronic and piezoelectric properties of two-dimensional tin dichalcogenide derived Janus monolayers. Journal of Materials Chemistry C. 2019;7(42):13203-13210. DOI: 10.1039/c9tc04461b

[30] Fan FR, Wu W. Emerging devices based on two-dimensional monolayer materials for energy harvesting. Research. 2019;**2019**:7367828. DOI: 10.34133/2019/7367828

[31] Lee Y, Kim S, Kim D, Lee C, Park H, Lee J-H. Direct-current flexible piezoelectric nanogenerators based on two-dimensional ZnO nanosheet. Applied Surface Science. 2020;**509**:145328. DOI: 10.1016/j.apsusc.2020.145328

[32] Nan Y, Tan D, Shao J, Willatzen M, Wang ZL. 2D materials as effective cantilever piezoelectric nano energy harvesters. ACS Energy Letters. 2021;**6**(6):2313-2319. DOI: 10.1021/acsenergylett.1c00901

[33] Negedu SD, Tromer R, Gowda CC, Woellner CF, Olu FE, Roy AK, et al. Two-dimensional cobalt telluride as a piezo-tribogenerator. Nanoscale. 2022;**14**(21):7788-7797. DOI: 10.1039/d2nr00132b

[34] Cui C, Xue F, Hu W-J, Li L-J. Two-dimensional materials with piezoelectric and ferroelectric functionalities. NPJ 2D Materials and Applications. 2018;**2**:18. DOI: 10.1038/s41699-018-0063-5

[35] Yang S, Chen Y, Jiang C. Strain engineering of two-dimensional materials: Methods, properties, and applications. InfoMat. 2021;**3**(4):397-420. DOI: 10.1002/inf2.12177

[36] Sachdeva PK, Bera C. Theoretical design and discovery of two-dimensional materials for next-generation flexible piezotronics and energy conversion. Applied Research. 2023:e202200116. DOI: 10.1002/appl.202200116