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# Advanced Materials for Energy Harvesting and Soft Robotics: Emerging Frontiers to Enhance Piezoelectric Performance and Functionality

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Piezoelectric energy harvesting captures mechanical energy from a number of sources, such as vibrations, the movement of objects and bodies, impact events, and fluid flow to generate electric power. Such power can be employed to support wireless communication, electronic components, ocean monitoring, tissue engineering, and biomedical devices. A variety of self-powered piezoelectric sensors, transducers, and actuators have been produced for these applications, however approaches to enhance the piezoelectric properties of materials to increase device performance remain a challenging frontier of materials research. In this regard, the intrinsic polarization and properties of materials can be designed or deliberately engineered to enhance the piezo-generated power. This review provides insights into the mechanisms of piezoelectricity in advanced materials, including perovskites, active polymers, and natural biomaterials, with a focus on the chemical and physical strategies employed to enhance the piezo-response and facilitate their integration into complex electronic systems. Applications in energy harvesting and soft robotics are overviewed by highlighting the primary performance figures of merits, the actuation mechanisms, and relevant applications. Key breakthroughs and valuable strategies to further improve both materials and device performance are discussed, together with a critical assessment of the requirements of next-generation piezoelectric systems, and future scientific and technological solutions.

### 1. Introduction

Piezoelectricity is a phenomenon by which a class of materials with a noncentrosymmetric crystal structure can inter-convert mechanical and electrical energy. The piezoelectric effect refers to the mechanism of electromechanical coupling through which materials can induce charges on their surfaces in response to an applied stress (the "direct" piezoelectric effect), and vice versa, where an electric field applied across the material leads to a mechanical strain (the 'converse' piezoelectric effect). Furthermore, ferroelectricity is the property of certain piezoelectric materials that are able to change, or reverse, their direction of spontaneous polarization following the application of an electric field. The discovery of new piezoelectric materials, and the continuous technological advances in the improvement of their properties, play an important role in a variety of applications ranging from energy harvesting to biomedical engineering, environmental/healthcare monitoring, and robotics. This leads to a

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variety of devices and platforms, which include sensors, transducers, and actuators with a self-powered functionality. For example, up to tens of mW per  $m^2$  can be produced by using lightweight and free-standing energy harvesting architectures based on the piezoelectric effect.<sup>[1,2,3]</sup>

Piezoelectric energy harvesting allows a system to capture ambient forms of mechanical energy that are ubiquitous and readily available; this ranges from mechanical vibrations, the movement of objects and bodies, impact events, and air/fluid flows. The underlying mechanism is based on the intrinsic polarization of a material that can be engineered to maximize the electrical power that is generated.<sup>[4]</sup> The harvested energy can be used to support wireless communication, electronic components, sensors, and even provide specific functions in tissue engineering and biomedical devices.<sup>[5,6,7,8,9]</sup> In addition, piezoelectric materials and devices are highly appealing for the next-generation of soft robots. Such robotic systems, which are based on soft and highly compliant materials, have the potential to withstand large levels of deformation and adapt to arbitrary geometries,<sup>[10]</sup> making them highly suitable for wearables, epidermal electronics, and components where delicate interactions with fragile objects or humans are needed. These systems can be also equipped with sensors and end-effectors such as suction cups, grippers, and manipulators, which allow pre-defined and multiple tasks to be performed.<sup>[11]</sup> In this regard, piezoelectric sensors and actuators, which can provide a rapid and reversible response, high actuation frequency, large operational bandwidth, lightweight nature, and mechanical flexibility are highly desirable for integration with soft robotic systems.<sup>[10,12,13]</sup>

This review offers insight into the mechanisms for enhancing piezoelectricity in advanced materials, which have been used for energy harvesting applications and soft robotics. We focus on the chemical and physical strategies employed to enhance the piezoelectric response and address the challenges of scaling for creating large-area systems and integration into complex electronics and systems. The classes of materials to be overviewed include perovskites, polymers, and biomaterials. The working mechanisms and operation modes are highlighted for each material class, along with their application potential for device architectures. The range of applications of energy harvesting for soft robotics is examined, along with their primary performance figures of merit. An outlook is provided on how the range of synthesis and processing methods can be adopted to produce a range of materials platforms with enhanced piezoelectric performance; the strategies used to improve important aspects such as material life cycle and sustainability are also examined. Finally, a critical assessment of the requirements of next-generation piezoelectric systems is provided, highlighting promising strategies and the potential future scientific and technological solutions.

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### 2. Piezoelectric Materials

### 2.1. Background

Piezoelectric effect was first discovered in 1880. Pierre and Jacques Curie provided experimental evidence for "direct" piezoelectricity due to the generation of surface charges by certain crystals, such as quartz, during the application of mechanical stress. The concept of 'converse' piezoelectricity, where an applied electric field produces a strain, was predicted based on fundamental thermodynamic principles by Gabriel Lippmann. The first practical application of the piezoelectric effect dates back to 1917, when Paul Langevin developed the first ultrasonic submarine detector based on quartz crystals.<sup>[14]</sup> Ferroelectricity was found in Rochelle salts in 1921, and a high piezoelectric coefficient (2700 pC N<sup>-1</sup>) was measured.<sup>[15]</sup> However, due to their relatively low stability, crystals based on Rochelle salts were not largely used for practical applications. A larger, worldwide interest in ferroelectric materials, and their applications, was raised on discovering ferroelectricity in polycrystalline barium titanate (BaTiO<sub>3</sub>, hereinafter abbreviated as BTO) in 1946<sup>[16]</sup> and in PbTiO<sub>3</sub> (PT) and PbZrO<sub>2</sub>, by Bernard Jaffe, in 1954.<sup>[17]</sup> Today these materials are widely used to build surface acoustic wave devices, actuators, sensors, hydrophones and microphones, and generators in a variety of commercial sectors.

A significant amount of research has been subsequently performed to develop new materials with improved piezoelectric performance. The application of an intense electric field to achieve 'poling', and other methods to produce a preferred orientation such as mechanical drawing, can be used to achieve a piezoelectric response from potential materials. Other synthetic crystalline materials such as LiNbO<sub>3</sub>, LiTaO<sub>3</sub>, and ZnO, as well as semiconductors such as AlN, GaN, and CdS were found to exhibit piezoelectricity; although non-ferroelectric materials such as ZnO, AlN, GaN, and CdS usually exhibit lower piezoelectric coefficients, compared to ferroelectric perovskites.[18] Piezoelectricity has also been found in a range of other material classes, including polymers, natural polymers, and biomolecules. These materials, despite exhibiting a generally lower piezoelectric performance, offer numerous advantages in terms of mechanical flexibility, a low cost, and availability of processing technologies, thereby enabling large-scale applications, and construction at the micro- and nano-scale. In addition, a range of two-dimensional (2D) layered materials have been recently predicted to exhibit piezoelectric properties, opening a route to potential applications in nonvolatile memories, programmable junctions, and photocatalysis.[19,20]

A number of piezoelectric materials have a well-defined polar axis, and the direction of the applied stress relative to such an axis is critically important in determining the resulting response. In this respect, the relevant axis can be defined by orientational features in the crystalline structure of the material, or may depend on the poling direction, in particular for ferroelectric materials.<sup>[21]</sup> The Cartesian components,  $P_i$ , of the polarization vector, **P**, upon applying a mechanical stress (*X*), are defined as:  $P_i = \sum_{j=1}^{6} d_{ij} X_j$ .<sup>[22]</sup> Here the electro-mechanical behavior is described in terms of piezoelectric modulus or coefficient,  $d_{ij}$ , for i= 1–3 and j = 1–6, where the 3-direction is identified with the direction of the polar axis, as specified above. The i subscript



**Figure 1.** Potential energy harvesting modes (for instance, in a soft robot) using a piezoelectric material a)  $d_{33}$ -mode (longitudinal load), b)  $d_{31}$ -mode (transverse load or bending), c)  $d_{15}$ -mode (shear loads).

indicates the direction (i.e., x, y, or z) of the electric displacement in the piezoelectric material, namely, the direction along which a voltage bias is generated, whereas the *j* subscript indicates the direction of applied stress (for i = 1-3), and if a shear-stress is involved then j = 4-6. The parameters  $d_{31}$ ,  $d_{32}$ , and  $d_{33}$  are therefore coefficients that are taken into consideration to describe the material behavior for transverse and longitudinal modes, while  $d_{14}$ ,  $d_{15}$ , and  $d_{16}$ , describe a voltage bias generated perpendicularly to the original polar axis for applications where a shear-stress is involved. A widely used index for the efficiency of energy conversion by piezoelectric materials is the electromechanical coupling coefficient,  $k_{ii}^2$ , defined as the stored mechanical (electrical) energy divided by input electrical (mechanical) one, given by  $k_{ij}^2 = \frac{d_{ij}^2}{\epsilon_{ii}^K s_{ij}^E}$ , where  $\epsilon_{ii}^X$  is the permittivity at constant stress and  $s_{ii}^E$  is the mechanical compliance of the material under a constant electric field (E).<sup>[23]</sup> The potential of these materials to harvest mechanical energy is now outlined.

### 2.2. Energy Harvesting

Piezoelectric energy harvesting is a mechanism whereby an active material is used to convert mechanical strains, motion, fluid flows, impact events or vibrations into electrical power. Priya et al.<sup>[24]</sup> developed the first criteria and "figures of merit" for the selection of piezoelectric materials for energy harvesting and Roscow et al.<sup>[23]</sup> later reported on modified energy harvesting figures of merit for both stress- and strain-driven piezoelectric systems. To understand the materials properties of interest for energy harvesting and sensing, we consider a piezoelectric element with a cross-sectional area *A*, and thickness *t* where the material is polarized along the device thickness and is operating off-resonance. If we consider the case shown in **Figure 1a**, where a load, *F* is applied along the polarization direction of the energy harvester, the harvester is operating in  $d_{33}$ -mode and the charge generated, *Q* by the "direct" piezoelectric effect is given by;

$$Q = d_{33} F \tag{1}$$

where  $d_{33}$  is the longitudinal piezoelectric charge constant (C N<sup>-1</sup>) of the material. The capacitance (*C*) of the piezoelectric element can be determined from,

$$C = \frac{A\varepsilon_{33}^{\chi}\varepsilon_0}{t} \tag{2}$$

where  $\varepsilon_{33}^X$  is the relative permittivity at a constant stress of the piezoelectric, and  $\varepsilon_0$  is the permittivity of free space.

Since ferroelectric ceramics, single crystals, polymers, and their composites are typically dielectric and electrically insulating, we consider the energy-harvesting element as a simple capacitor. The open-circuit voltage generated from the applied mechanical load in Figure 1a can be calculated from the simple relationship  $Q = CV_{oc}$ . The open-circuit voltage from an applied force is,

$$V_{oc} = \frac{d_{33}}{\varepsilon_{33}^X \varepsilon_0} \cdot \frac{F}{A} \cdot t = \frac{d_{33}}{\varepsilon_{33}^X \varepsilon_0} \cdot X \cdot t \tag{3}$$

where *X* is the applied stress. As a result, the open-circuit voltage for a given applied stress and device geometry (*t*) can be maximized by having a large thickness, large stress, or selecting materials with a high piezoelectric voltage constant,

$$g_{33} = \frac{d_{33}}{\varepsilon_{33}^X \varepsilon_0} \tag{4}$$

**Table 1.** Properties of piezoelectric materials used in harvesting. Data from <sup>[18]</sup> unless indicated. PMN-33%PT is a 0.67(Pb<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.33PbTiO<sub>3</sub> multidomain engineered single crystal poled in [001]. PYN-PMN-PT is a highly textured ceramic based on Pb(Yb<sub>1/2</sub>Nb<sub>1/2</sub>)O<sub>3</sub>-Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>. k<sub>33</sub> is the electromechanical coupling factor; *p* is the pyroelectric coefficient,  $s^{E}_{33}$  is the compliance at constant electric field in the polarization direction.

Material	PZT-5H 'soft PZT'	PMN-33%PT	PYN-PMN-PT <sup>[25]</sup>	BaTiO <sub>3</sub>	PVDF	ZnO
Form	Ceramic	Single crystal	Grain orientated	Ceramic	Polymer	Whiskers
Piezoelectric	$\checkmark$	1	1	1	1	1
Pyroelectric	$\checkmark$	1	1	1	1	1
Ferroelectric	$\checkmark$	1	1	1	1	X
$\epsilon_{33}^{X}$	3400	8200 <sup>[26]</sup>	≈2200 <sup>a)</sup>	1200	7.6	11.0
d <sub>33</sub> [pC N <sup>-1</sup> ]	593	2820 <sup>[26]</sup>	1087	149	-33	12.4
<i>d</i> <sub>31</sub> [pC N <sup>-1</sup> ]	-274	-1330 <sup>[26]</sup>	-	-58	21	-5.0
d <sub>15</sub> [pC N <sup>-1</sup> ]	741	146 <sup>[26]</sup>	-	242	-27	-8.3
k <sub>33</sub>	0.75	0.94 <sup>[26]</sup>	0.9	0.49	0.19	0.48
- <i>p</i> [μC m <sup>-2</sup> K <sup>-1</sup> ]	260–533	568 <sup>[27]</sup>	-	200	33	9.4
s <sup>E</sup> 33 [pPa <sup>-1</sup> ]	20.8	119.6 <sup>[26]</sup>	-	9.1	472	6.94
$g_{33} = \frac{d_{33}}{\epsilon_{33}^{X}\epsilon_{0}}$ [10 <sup>-3</sup> V m <sup>-1</sup> Pa <sup>-1</sup> ]	19.7	38.9	56.4	14.0	491	127
$FoM_{33} = \frac{d_{33}^2}{\frac{e_{33}^2}{e_{33}e_0}}$ [10 <sup>-12</sup> m <sup>2</sup> N <sup>-1</sup> ]	11.7	109.5	61.3	2.9	6.2	1.6

<sup>a)</sup> Estimated for harvesting figure of merit,  $d_{33}$ , and  $g_{33}$ .

The  $g_{33}$  parameter is therefore a good figure of merit to select materials for piezoelectric sensing since it measures the electric field generated per unit stress.

The short circuit current from the applied mechanical load can be determined from Equation 1 since  $I_{sc} = dQ/dt$ , so that,

$$I_{sc} = d_{33} \quad \frac{dF}{dt} = d_{33} A \frac{dX}{dt}$$
(5)

Therefore, to maximize the short circuit current in response to an applied load there is a need for a high  $d_{33}$ , large area, and rapid changes in stress. For energy harvesting applications, the energy generated by an applied stress is more appropriate than either the open circuit voltage or short circuit current; where the energy stored in a capacitor is given by ( $E = \frac{1}{2} CV_{oc}^2$ ); hence,

$$E_{harvester} = \frac{1}{2} \frac{d_{33}^2}{\epsilon_{33}^{X} \epsilon_0} \frac{F^2}{A} t = \frac{1}{2} \frac{d_{33}^2}{\epsilon_{33}^{X} \epsilon_0} X^2 A t$$
(6)

where  $E_{harvester}$  represents the energy generated for single stress cycle. When the harvesting element is subject to periodic stress, the power ( $P_w$ ) can be estimated from  $P_w = E_{harvester} \cdot f$ , where *f* is the frequency. As a result, Equation (6) highlights that to maximize the harvested energy during a single stress cycle, there is a need to maximize the material volume (*At*) and applied stress (*X*), or one can select materials that present a high off-resonance harvesting figure of merit (*FoM*<sub>33</sub>):

Fo 
$$M_{33} = \frac{d_{33}^2}{\varepsilon_{33}^X \varepsilon_0} = d_{33} \cdot g_{33}$$
 (7)

There is potential to harvest in other modes, such as using the transverse  $d_{31}$ -mode (for example, during bending, as in Figure 1b) and the  $d_{15}$ -mode to harvest shear loading, as seen in

Figure 1c. For actuation applications, the  $d_{33}$ ,  $d_{31}$ , and  $d_{15}$  modes, and their associated  $d_{ij}$  coefficients, are also of interest since they are also a measure of the piezoelectric strain per unit electric field, as a result of the converse piezoelectric effect.

Table 1 outlines a range of prototypical piezoelectric materials<sup>[18,25-27]</sup> used for energy harvesting; this includes inorganic perovskite-based ferroelectric materials, such as PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> (PZT), single crystal materials (Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub>, PMN-PT), textured materials, and a ferroelectric polymer (poly(vinylidene fluoride), PVDF). We will see later that many composites of such materials are also used, such as macro fiber composites (MFCs) or particles embedded within a polymer matrix, which aim to tailor the mechanical and electrical properties. It can be seen in Table 1 that the PZT ceramics and single crystals exhibit relatively high harvesting figures of merit, which originates from the high  $d_{33}$  coefficients of the materials, and  $FoM_{33} = d_{33} \cdot g_{33} \propto d_{33}^2$  in Equation (7). Since single crystal materials are costly to manufacture and are only available in limited geometries, significant effort has been made to produce highly textured grain-orientated ceramics materials which can exhibit single-crystal like piezoelectric properties; these include  $Pb(Yb_{1/2}Nb_{1/2})O_3-Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$  (PYN-PMN-PT) in Table 1 which was specifically developed for energy harvesting applications.<sup>[25]</sup> ZnO is also included in Table 1 as an example of a non-perovskite-based piezoelectric material, which exhibits a relatively low harvesting figure of merit due to its low piezoelectric  $d_{33}$  coefficient. Since the ZnO material is not ferroelectric, its polarization direction cannot be switched by an applied electric field. Therefore, such materials must be used in aligned or highly textured form; this includes single crystal, thin films, or nano-wire configurations.

The low relative permittivity of PVDF leads to a high energy harvesting figure of merit, despite its small piezoelectric  $d_{33}$  coefficient. This polymer material tends to be used as a thin film of

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low thickness or in other micro- or nanostructured forms which can reduce the harvested energy (see Equation 6); it is also often used in  $d_{31}$ -mode during stretching, thereby using the lower  $d_{31}$ piezoelectric coefficient. The low permittivity of PVDF in Table 1 also leads to a high  $g_{33}$ , making them well-suited for piezoelectric sensing. The inverse relationship of both the harvesting figure of merit and g<sub>33</sub> with permittivity has led to an interest in the use of low-permittivity porous materials for applications in soft robotics, which we will see in some of the examples below. Overall, there is continued effort in the development of materials and composites with high harvesting figures of merits to improve performance and build upon the materials in Table 1. The range of potential materials is subdivided into three main groups, namely perovskites, polymers, and natural biomaterials that are outlined in detail in the following sections.

### 2.3. Perovskites

Perovskites, named after Lev Perovski, are a family of materials that can exhibit piezoelectricity. They exhibit the general stoichiometry, ABX<sub>3</sub>, where A and B are cations and X is an anion, with a network of corner-sharing  $BX_6$  octahedra surrounding the B-site cation (Figure 2a).<sup>[28-30]</sup> As an example, the classic perovskite systems adopt a cubic crystal structure with space group  $Pm\bar{3}m$  that have A and B cations with a total charge of +6, and have oxides as their X anions.<sup>[28]</sup> The BX<sub>6</sub> octahedra create a three-dimensional network throughout the crystal lattice. The structure is highly versatile since it can accommodate A and B cations with varied sizes and oxidation states to enable numerous compounds with fascinating properties to be formed<sup>[29]</sup> that can support various degrees of symmetry and structural stability, as indicated by the empirical Goldschmidt tolerance factor,  $t^*:[^{28a}] t^* = \frac{r_a + r_x}{\sqrt{2} (r_b + r_x)}$ . Here,  $r_A$ ,  $r_B$ , and  $r_X$  are the ionic radius of the A, B, and X ions, respectively, and a  $t^*$  value of 1 represents an ideal perovskite structure that does not exhibit piezoelectricity, due to its centrosymmetry. In addition, to enhance the precision of the tolerance factor in predicting the stability of perovskite structures, modified versions of the Goldschmidt tolerance factor have been formulated and applied.<sup>[31b,32]</sup> Values of  $t^*$  between 0.75 and 1.0 indicate the existence of distorted structures with tetragonal, rhombohedral, or orthorhombic symmetry.<sup>[31]</sup> For example, in oxide perovskites the variation in the A and B sites results in crystal distortion that correlates to the change in the B-O interaction, B-O-B angle, BB transfer integral, and deviations from the ideal cubic structure to maintain stability.<sup>[29,31,33]</sup> The changes in interactions ( $\sigma$  or  $\pi$ bonds) that affect the B-O bonding, the B-O-B bond angle, tolerance factor, and disorder, resulting from the change in the A and B site cations, can result in properties that range from high-temperature superconductivity, to giant magnetoresistance, and multiferroic features.<sup>[31a,34]</sup> The delicate balance between long-range forces due to dipole-dipole interaction, that favor low-symmetry structures that promote ferroelectricity, and shortrange Coulombic-type repulsion, that favor high symmetry cubic phases, can lead to the emergence of ferroelectric materials.<sup>[34-36]</sup> This subtle balance can be disrupted by octahedral distortions, off-centering of A- and B- site atoms, or even rotations of specific ions.<sup>[37-39]</sup> Deviations from the ideal cubic structure

break the symmetry, thereby enabling local electric dipoles to be formed that produce a spontaneous polarization  $(P_s)$  within the Three possible orientations of  $P_s$  in monoclinic perovskites ("A", "B", or "C") are shown in Figure 2b ( $M_A$ ,  $M_B$ ,  $M_C$ ,

respectively).<sup>[40,41]</sup> The piezoelectric response is the result of intrinsic (extension or rotation of polarization under an external stimulus) and extrinsic mechanisms (such as domain motion).<sup>[14]</sup> Polarization extension is caused by the application of an electric field that enhances the polarization magnitude compared to the spontaneous one (Figure 2c(i)), while polarization rotation is caused by an electric field that rotates the polarization from its zero-field orientation to improve the alignment with the applied field (Figure 2c(ii)). The corresponding changes in the unit cells are associated with lattice-polarization coupling. The extrinsic piezoelectric response is due to the motion of mobile interfaces (domain walls, or phase boundaries), namely boundaries between regions with different P<sub>s</sub> orientations (Figure 2c(iii)).<sup>[42]</sup> In oxide perovskites, the slight displacement of cations from their ideal positions in the crystal lattice can effectively break the condition of centrosymmetry, thus ultimately leading to piezoelectricity.<sup>[33,43]</sup> Examples of oxide perovskites that exhibit piezoelectric properties are PT,<sup>[44]</sup> BTO,<sup>[45]</sup> and BiFeO<sub>3</sub><sup>[46]</sup> ceramics.

material.

The number of polarization directions in a material, namely its either uniaxial or multiaxial characteristics, is also important in determining its piezoelectric properties.<sup>[47]</sup> Materials with a large number of polarization directions can exhibit specific dipole configurations and dipole switching behavior in the polycrystalline state, making them appealing for many applications.<sup>[43,48–50]</sup>

Furthermore, studies on the composition-temperature phase diagrams indicate that the piezoelectric response can increase in a specific region (i.e., in the composition-related phase transition) where the crystal structure changes from tetragonal to rhombohedral, known as the morphotropic phase boundary (MPB).<sup>[14,51]</sup> The monoclinic intermediate phase has been proposed to cross over the tetragonal to rhombohedral transitions through the MPB region, and suggests the existence of larger intrinsic and extrinsic piezoelectric effects at the MPB.<sup>[52]</sup> Such a transition was also reported for pure PT at a higher pressure, where the transition occurs through monoclinic intermediates.<sup>[53]</sup> The high electromechanical response in this region can be related to the existence of a larger number of switchable polarization directions, additional interphase transformations, symmetry-allowed polarization rotations (a main factor contributing to the large shear piezoelectric response), flatting of the free-energy profile near the MPB, the presence of nanodomains, and an adaptive ferroelectric phase state.[53,54]

By varying the material composition, a variety of oxide perovskite materials, such as PZT, Pb(Zr<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PZN-PT) and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PMN-PT), which exhibit large piezoelectric coefficients, are obtained. A very high value of  $d_{33}$  > 2500 pC N<sup>-1</sup> and strains of up to 1.7% have been shown for PZN-PT single crystals.<sup>[55]</sup> Additional relevant examples of materials with excellent piezoelectric properties are polycrystalline ceramics based on doped PZT.<sup>[56]</sup> They are usually categorized as soft (donor-doped) PZT, such as PZT-5A, -5H, -5J, or hard (acceptor-doped) PZT, such as PZT-4 and -8. The soft PZT ceramics usually exhibit higher piezoelectric constants and are www.advancedsciencenews.com

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**Figure 2.** a) Structure of oxide perovskite (ABO<sub>3</sub>). Reproduced with permission<sup>[30]</sup> Copyright 2001 Elsevier Ltd. b) Schematic of the polarization directions ( $M_A$ ,  $M_B$ , and  $M_C$ ) in monoclinic perovskites. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[40]</sup> Copyright 2015, The author, licensee MDPI. c) Contributions to the piezoelectric effect in an ABO<sub>3</sub> perovskite unit cell. Reproduced with permission.<sup>[14]</sup> Copyright 2021, Wiley-VCH GmbH. d) Halide perovskite structure with a large monovalent metal (inorganic) or small organic cation (hybrid) at the center of the unit cell. Reproduced with permission.<sup>[72]</sup> Copyright 2019, American Chemical Society. e) Structure and constituents of metal-free 3D perovskites of the family ABX<sub>3</sub>. Reproduced with permission under the terms of the Creative Commons CC-BY-NC license.<sup>[79]</sup> Copyright 2019, The Royal Society of Chemistry.

easier to polarize, compared with the hard PZT systems.<sup>[57]</sup> For example,  $(Pb_{1-y}La_y)(Zr_xTi_{1-x})O_3$  (PLZT) ceramics, obtained by substituting  $La^{3+}$  at the A-site of PZT, show both improved piezo-electricity and optical transparency, and exhibit good potential for optoelectronic devices.<sup>[58]</sup> Another example of a piezoelectric material with piezoelectric properties enhanced by compositional engineering is the samarium-doped Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (Sm-PMN-PT), which, after poling at 10 kV cm<sup>-1</sup> and 20–60 °C for 10 min in silicone oil, exhibits a high  $d_{33} = 1500$  pC N<sup>-1</sup> and a relative permittivity of >13 000.<sup>[59]</sup> Table 2 summarizes the synthesis methods, piezoelectric oxide perovskites.<sup>[45,55,59–69]</sup>

Hooper et al.<sup>[56]</sup> have provided an excellent overview of the design and manufacture of perovskite-based materials and composites and the resulting piezoelectric  $g_{ij}$  voltage coefficients, which correlate to voltage output and sensitivity; see Equations (3) and (4). The supplemental section of this detailed review provides an excellent database that is rich in relevant data for the selection of polycrystalline materials, single crystals, and composites with high  $d_{ii}$  and  $g_{ij}$  coefficients.

Despite the advantages associated with the availability of numerous suitable metal ions and with versatile compositional engineering, their applicability is often limited by the harmful character of metals such as Pb,<sup>[70]</sup> as well as by the high processing

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Material	Material type, synthesis method	Piezoelectric coefficient $d_{33}$ [pC N <sup>-1</sup> ]	Relative permittivity	$T_{c}$ [°C]	Poling	Refs.
PZT-5H	Single crystal, SSCG <sup>a)</sup>	≈1800	_	-		[60]
PZT-5H	Ceramic, -	593	3400	-	-	[ <mark>6</mark> 1]
PZN-PT	Single crystal, HT solution method	2500	5000	-		[55]
PMN-PT	Single crystal, BM <sup>b)</sup>	>2100	>7500	-	-	[ <mark>62</mark> ]
PMN-PT	Ceramic, Hot-press sintering	650	4500	-		[ <mark>63</mark> ]
Sm-PMN-PT	Single crystal, BM <sup>b)</sup>	3400-4100	≈12000	-	-	[ <mark>64</mark> ]
Sm-PMN-PT	Ceramic, HT <sup>c)</sup> solid-state processing	1500	13000	89	$\checkmark$	[ <b>59</b> ]
Sm-PMN-PT	Film, Sol-gel method	380	-	-	-	[ <mark>65</mark> ]
BiScO <sub>3</sub> -PT	Single crystal, HT solution method	1150	3000	402		[ <mark>66</mark> ]
$Pb(Fe_{1/2}Nb_{1/2})O_3 - Pb(Yb_{1/2}Nb_{1/2})O_3 - PT$	Single crystal, HT solution method	1100	1620	325		[ <mark>67</mark> ]
BTO	Ceramic, solid state reaction	424 <sup>d</sup> )	_	-		[ <mark>45</mark> ]
Mn-KNN	Single crystal, HT solution method	350	850	416		[ <mark>68</mark> ]
LiNbO <sub>3</sub>	Thin film, RF magnetron sputtering	0.25-5.3 <sup>e)</sup>	-	-	-	[ <mark>69</mark> ]

 Table 2. Representative oxide perovskites: synthesis method, piezoelectric properties, and permittivity.

<sup>a)</sup> Solid-state crystal growth (SSCG); <sup>b)</sup> Modified Bridgman method (BM); <sup>c)</sup> High Temperature (HT); <sup>d)</sup>  $d_{33}$  measured at a sintering temperature of 1450 °C; <sup>e)</sup> Measured by varying the film thickness in the interval 1.84–24.3  $\mu$ m.

temperature that reduces the potential for device integration and makes high-quality crystal growth complicated due to the lattice thermal mismatch.<sup>[47]</sup>

Recently, metal halide perovskites (HP) have gained significant attention due to their low-temperature processability, that make them suitable for soft and organic electronics, and provide excellent optoelectronic properties. In the ABX<sub>3</sub> composition of HP, the X ions consist of halides such as chloride, iodide, bromide.<sup>[28b]</sup> Since these ions are monovalent, divalent metal cations such as  $Pb^{2+}$ ,  $Ge^{2+}$ , or  $Sn^{2+}$  are common at the B-sites, while the A-site accommodates monovalent cations such as Cs<sup>+</sup>.<sup>[28b,71]</sup> In addition, small organic molecules such as ethyl-ammonium (MA) or formamidinium (FA), can be accommodated as A-site cations, leading to the class of hybrid materials called organic-inorganic halide perovskites (Figure 2d).<sup>[28b,33,71]</sup> Systems ranging from zero-dimensional (0D) to three-dimensional (3D) structures are obtained depending on the type of ions and their ionic radii (Figure 2d).<sup>[28b,72]</sup> The tolerance factor values for HP materials fall within the range of 0.8 to 1.11, with octahedral factor values ranging from 0.44 to 0.90. The calculated  $t^*$  values for cubic, orthorhombic, and hexagonal structured HPs were shown to be within the ranges of 0.8 to 1.0, less than 0.8, and greater than 1, respectively.<sup>[73 and references therein]</sup> In addition to optoelectronic performance, HPs exhibit high power conversion efficiency and unique features such as outstanding piezoelectric and triboelectric properties.<sup>[74b,75]</sup> For this reason they hold promise in mechanical energy harvesting for piezoelectric nanogenerators (PENGs) and triboelectric nanogenerators (TENGs), as well as for other portable power sources and flexible electronics due to their low relative permittivity.<sup>[76]</sup> A more detailed discussion on various types of HPs and their applications can be found in other recent viewpoint articles and reviews.<sup>[28b,29a,74]</sup>

Metal-free (purely organic) perovskites have potential to address toxicity issues, thereby enabling better integration of perovskites-based PENGs/TENGs into wearables and implantable medical devices. They can also reduce processing costs compared to metal-based systems and their high processing temperatures.<sup>[77,78]</sup> The molecular perovskites share the same general formula ABX<sub>3</sub> and in recent systems,<sup>[78b]</sup> A is a divalent organic cation, while B is ammonium ion  $(NH_4^+)$  and X is chloride, bromide, or iodide. The corner shared  $(NH_4)X_6$  forms a 3D network with divalent cations inside the octahedral cavities, and are held together by ionic and/or hydrogen-bonding interactions (Figure 2e).<sup>[78b,79]</sup> Apart from the ionic size mismatch, molecular interactions such as Van der Waals forces and hydrogen bonding are important to form a stable 3D molecular perovskite.<sup>[78b]</sup> The organic-based composition provides these materials with a lightweight nature, low cost, mechanical flexibility, structural tunability, and ease of processing, making them of interest to applications such as soft robotics.

Although the general properties of metal-free perovskites have been reported much earlier, the observation of piezoelectricity and ferroelectricity in such systems dates back to 2018 in Nmethyl-N'-diazabicyclo[2.2.2]octonium (MDABCO) perovskite. Ye et al. employed a molecular design strategy to realize a family of metal-free ABX<sub>2</sub>-type perovskite ferroelectrics.<sup>[78b]</sup> Compared to N-N'-diazabicyclo[2.2.2]octonium (DABCO), the slight deviation of the shape of MDABCO from a spherical geometry is key in providing ferroelectricity, while also maintaining the ease of molecular reorientation to facilitate polarization reversal. In fact, the methyl group attached to DABCO led to a dipole moment, whose alignment resulted in symmetry breaking. MDABCO-NH<sub>4</sub>I<sub>3</sub>, and several other crystals of the metalfree ABX<sub>3</sub> systems have been obtained through slow evaporation of ammines, inorganic ammoniums, and dilute hydrohalogen acid. Studies of the piezoelectric  $d_{33}$  coefficient measured using the Berlincourt or quasi-static method,<sup>[80]</sup> domain switching using piezo-response force microscopy (PFM) and polarizationelectric field (P-E) hysteresis loop measurements of single crystal MDABCO-NH4I3 have provided evidence for ferroelectric and piezoelectric properties, with a  $P_s$  value of 19  $\mu$ C cm<sup>-2</sup> and a measured  $d_{33}$  of  $\approx 14$  pC N<sup>-1</sup> along the [111] direction of the crystal.<sup>[78b]</sup>

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**Figure 3.** Piezoelectric properties and PENG device performance of MDABCO–NH<sub>4</sub>I<sub>3</sub>; a) PENG scheme, b) Leakage currents for MDABCO-NH<sub>4</sub>I<sub>3</sub> thin films obtained with various precursor concentrations. c) Exemplary piezo-response loop. d,e)  $V_{OC}$  and  $I_{SC}$  of poled and unpoled devices and their corresponding waveforms (insets). f) Stability performance of PENG device upon cycling. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[81]</sup> Copyright 2022, The Authors, published by Wiley-VCH GmbH. g–i) PFM characterization of NDABCO-NH<sub>4</sub>Br<sub>3</sub>. g,h) PFM phase and amplitude images, respectively. i) Piezoelectric phase loops and amplitude loops, showing local PFM hysteresis behavior. Reproduced with permission.<sup>[83]</sup> Copyright 2023, American Chemical Society.

The use of MDABCO-NH<sub>4</sub>I<sub>3</sub> for wearables and biomedical applications were evaluated by Tsai and Yang et al.<sup>[81]</sup> A film of MDBACO-NH<sub>4</sub>I<sub>3</sub> was coated on a polyimide (PI) substrate within an architecture that included poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as a conductive layer. The film, prepared using a variety of precursor concentrations (*c* in the range 0.25–1.0 M), exhibited an X-ray diffraction (XRD) intensity peak of the (200) plane that increased with concentration, *c*, which was due to a preferred orientation that was induced by a high precursor concentration during material growth. The film showed an optimal performance at *c* = 0.75 M, where a large crystal grain size and a low leakage current were observed. The average  $d_{33}$  coefficient was 12.81 pC N<sup>-1</sup>. A PENG device was fabricated, and the application of a 0.55% strain re-

sulted in an open-circuit voltage and short-circuit current of 9.6 V and 38.3 nA for an unpoled PENG, and 15.9 V and 54.5 nA for a poled PENG, respectively. The poled PENG exhibited excellent stability when subject to a 0.55% strain, without deterioration over 5000 bending cycles (**Figure 3a**–f). The MDABOC-NH<sub>4</sub>I<sub>3</sub> material, which exhibits a spontaneous polarization at room temperature, had a relatively small coercive field (6–30 kV cm<sup>-1</sup>).<sup>[78b,81]</sup> To make these compounds more suitable for switching applications, Loh et al. replaced the I<sup>-</sup> with PF<sub>6</sub><sup>-</sup> which led to a higher coercive field of 110 kV cm<sup>-1</sup>.<sup>[82]</sup> The modified perovskite structure has a tolerance factor of 0.914 and the material adopted a polar trigonal *R3* space group at room temperature. The increased coercive field was associated with stronger intermolecular H-bonding, where the interaction played

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Table 3.	Metal-free perovskites	: synthesis method	, piezoelectric and	ferroelectric performance,	biocompatibility.
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Material	Synthesis method	Goldschmidt tolerance factor	Piezoelectric coefficients - d <sub>33</sub> [pC N <sup>-1</sup> ]	Spontaneous polarization – P <sub>s</sub> [µC cm <sup>-2</sup> ]	Т <sub>с</sub> [К]	Bio-compatible	Refs.
MDABCO-NH <sub>4</sub> I <sub>3</sub>	Slow evaporation <sup>a)</sup>	0.93	≈14	22	448	Yes	[78b,81]
NDABCO-NH <sub>4</sub> Br <sub>3</sub>	Slow evaporation <sup>a)</sup>	0.94	63	10.4	420/430	-	[83]
(hmtaH <sub>2</sub> )- NH <sub>4</sub> Br <sub>3</sub>	Slow evaporation <sup>a)</sup>	-	-	0.09	> 400 <sup>b)</sup>	-	[85]
MDABCO- H <sub>4</sub> (PF <sub>6</sub> ) <sub>3</sub>	Slow evaporation <sup>a)</sup>	0.91	_	5.7	311	_	[82]
$(H_2 dabco)-NH_4 (BF_4)_3$	Hydrothermal reaction	0.99	-	_	333	_	[88]

<sup>a)</sup> Slow evaporation. Stoichiometric amounts of starting materials were dissolved in a suitable solvent and allowed to slowly evaporate at room temperature; <sup>b)</sup> No phase transition was observed up to 400 K.

an important role in ferroelectric switching and phase transitions.

Recently, Zhang et al. reported on the piezoelectric response of a new metal-free 3D perovskite ferroelectric, NDABCO-NH4Br3 (NDABCO = N-amino-N'-diazabicyclo[2.2.2]-octonium), whichwas obtained by replacing the methyl group of MDABCO with an amino group.<sup>[83]</sup> Single crystal XRD measurements supported the characteristic perovskite structure of this compound, showing the location of NDABCO at the cavities surrounded by a 3D network of corner-sharing  $(NH_4)Br_6$ , held together by ionic and hydrogen bonding. The tolerance factor was 0.94. NDABCO-NH<sub>4</sub>Br<sub>3</sub> crystallizes at room temperature in a polar R3 space group, with the NDABCO and NH<sub>4</sub><sup>+</sup> cations positioned on threefold rotational symmetry axes. The symmetry site induces molecular C<sub>3</sub> pseudo-symmetry in NDABCO, resulting in a three-fold symmetrical distribution of hydrogen atoms on the amino group. This stacking arrangement generates a spontaneous polarization along the [111] direction. Using the Berlincourt method, the measured piezoelectric  $d_{33}$  coefficient at room temperature along the [111] axis, for a testing frequency of 110 Hz, was found to be 63 pC  $N^{-1}$ ; this is substantially higher than other organic systems, such as MDABOC-NH4I3 and imidazolium perchlorate (Figure 3g-i).<sup>[78b,84]</sup>

Tsunashima et al. reported on doubly protonated hexamethylenetetramine (hmtaH<sub>2</sub>)(NH<sub>4</sub>)Br<sub>3</sub> in a metal-free perovskite-type structure, in which the A and B sites are occupied by hmtaH<sub>2</sub><sup>2+</sup> and ammonium cations, respectively,<sup>[85]</sup> and the hmta is non-centrosymmetric. The spontaneous polarization has been attributed to BX<sub>6</sub> octahedral distortion that is associated with H-bonding and orientational ordering of the positive charge on hmtaH<sub>2</sub>. This material exhibited a Curie point, *T<sub>c</sub>*, above 400 K which is similar to values reported for other organic ferroelectrics such as croconic<sup>[86]</sup> and (—)-camphanic acid,<sup>[87]</sup> The reported polarization and coercive field were 90 nC cm<sup>-2</sup> and 3.7 kV cm<sup>-1</sup>, respectively.

A summary of metal-free perovskites, including their piezoelectric and ferroelectric figures of merit, along with the synthesis method, is presented in **Table 3**.<sup>[78b,81–83,85,88]</sup>

### 2.4. Polymers

Piezoelectric polymers typically exhibit lower piezoelectric coefficients and lower electromechanical coupling factors compared to piezoelectric perovskites.<sup>[23,89,90]</sup> However, they exhibit specific

advantages that make them suitable for a number of applications, including soft robotics. For example, polymers are more mechanically flexible and have a higher toughness than ceramics, making them less prone to mechanical failure. This property makes them attractive for long-term energy harvesting applications since they are less likely to suffer from the effects of fatigue. Piezoelectric polymers are also generally lower cost and easier to fabricate than their ceramic counterpart, which often require high-temperature sintering and/or other energy-intensive fabrication processes. In addition, piezoelectric polymers may be more suitable for applications where biocompatibility is a requirement, for example in biomedical and wearable devices.

One of the most well-studied piezoelectric polymers is PVDF,<sup>[91]</sup> which is both ferroelectric and pyroelectric. Other exhibiting polymer families piezoelectricity include polyamides,<sup>[92]</sup> polyureas<sup>[93]</sup> and polyesters.<sup>[94]</sup> There has been significant interest in piezoelectric polymers, in particular for energy harvesting, sensing, and actuation, as will be extensively discussed in Section 4. The lower piezoelectric coefficients and electromechanical coupling factors exhibited by piezoelectric polymers are not necessarily a major disadvantage for mechanical-to-electrical energy conversion where the material is being mechanically deformed under a constant stress. Indeed, piezoelectric polymers, since they are highly compliant, are able to store a large amount of mechanical strain energy which is then available for conversion into a substantial amount of electrical energy, in spite of its low  $k_{ii}^{2}$ .<sup>[95]</sup> On the other hand, the relatively low elastic moduli and  $k_{ii}^2$  limit the usefulness of piezoelectric polymers for actuation compared to ceramics. As a result of their high compliance, piezoelectric polymers exert lower levels of mechanical force compared to ceramics, even though they may produce a greater amount of strain.<sup>[96]</sup> In the case of piezoelectric ceramics, applications in actuation mainly involve ultrasonic transducers, or applications requiring nanoscale/microscale deformations, particularly in cases where precision actuation is required, for example in the control of tip or sample displacement in scanning probe microscopy (SPM).<sup>[97]</sup> In addition, piezoelectric polymers have a lower acoustic impedance compared to piezoelectric ceramics, which are better matched with water or body tissue for certain medical or water-borne applications.<sup>[98]</sup> However, high electric fields are often required to actuate these materials. In order to overcome some of the inherent shortcomings of piezoelectric polymers for actuators, relaxor ferroelectric polymers with a high  $k_{33}$  have



been recently reported, which exhibit large electromechanical coupling at low electric fields, thus paving the way for possible applications in practical devices.<sup>[99,100]</sup> However, these materials continue to be limited in terms of mechanical energy density due to their low elastic moduli compared to piezoceramics. More recently, there have been reports on the properties of nanocomposites based on ferroelectric polymers, and their co-polymers, which have been shown to exhibit high levels of strain via electrostriction when driven by electric fields,<sup>[96]</sup> and whose performance is comparable to relaxor single-crystal ferroelectrics and can outperform conventional piezoelectric polymer nanocomposite actuators.

As discussed in Section 2.3, piezoelectricity in crystalline materials with a regular crystal structure is generally described as an effect that results from the displacement of ions within non-centrosymmetric unit cells. Piezoelectric polymers are generally semi-crystalline in nature, comprising crystalline regions where polymer chains form small crystallites, surrounded by an amorphous matrix, hence the description of the origin of piezoelectricity in polymers is more complex than in crystalline materials. Nevertheless, the requirement for noncentrosymmetry in the material still holds in the case of piezoelectric polymers.<sup>[101]</sup> While individual polymer chains may possess non-centrosymmetry, this may be lost in an amorphous network, which is isotropic. Therefore, in order for the polymer material to exhibit piezoelectricity (i.e., with no overall center of symmetry) one could achieve crystallization via controlled heat treatment or annealing. However, in reality, crystalline regions are found to grow within an amorphous matrix resulting in semicrystalline polymers, and these crystalline regions may be randomly oriented with respect to one another thus resulting in an isotropic structure, with no overall observable piezoelectricity. In order to introduce anisotropy within the polymer material, which is a prerequisite for piezoelectricity, a variety of processing methods can be employed, such as mechanical drawing and/or electrical poling <sup>[101]</sup> Mechanical drawing works in the case of piezoelectric polymers which possess a helical conformation of the polymer chain, for example, poly-1-lactic acid (PLLA).<sup>[102,103]</sup> In the case of ferroelectric polymers, such as PVDF and polyamides in the form of odd-numbered Nylons, an electric field can be used to pole the material. Such a poled piezoelectric polymer will exhibit both shear and normal modes of piezoelectricity,<sup>[104,105]</sup> with nonzero  $d_{31}$  and  $d_{33}$  coefficients (where the '3' direction corresponds to that along which the electric field is applied). In some mechanistic models, the piezoelectric effect in polymers is attributed solely to the crystalline regions of the polymer, whereby the effect arises due to the changes in the lattice constant of the unit cell.<sup>[104]</sup> In other models, the molecular dipoles present in the chains of piezoelectric polymers, such as PVDF, are considered to be fixed and unchanged by an externally applied stress, rather it is the movement of the external electrodes with respect to the field created by the fixed molecular dipoles which gives rise to a change in polarization across the material.<sup>[106,107]</sup> There are also reports that indicate the amorphous regions of a piezoelectric polymer can have a partial contribution to piezoelectricity, in particular in the presence of some degree of molecular alignment.<sup>[108,109]</sup> Examples of how fabrication and processing methods lead to piezoelectric behavior in specific piezoelectric polymers are discussed below.

PVDF is a semi-crystalline polymer, with interspersed crystalline and amorphous regions, the relative amounts of which affect the piezoelectric properties of the material. The PVDF molecule has fluorine and hydrogen atoms arranged symmetrically along the carbon backbone, and dipole moments along the C-F and C-H bonds, due to differences in electronegativity. In the all-*trans* chain conformation ( $\beta$ -phase), a net polarization occurs across the backbone, and PVDF exhibits piezoelectric behavior (Figure 4a).  $\beta$ -phase PVDF films can be obtained by biaxial stretching or electrical poling under high electric fields of  $\alpha$ -PVDF films, where the  $\alpha$ -phase is the thermodynamically stable non-polar phase.<sup>[110]</sup> The  $\beta$ -phase of PVDF remains piezoelectric up to its melting temperature,  $T_{m}$ , since the ferroelectric Curie temperature,  $T_c$  ( $\approx$ 195 °C) is higher than  $T_m$  ( $\approx$ 166 °C). In order to facilitate the formation of the  $\beta$ phase, poly(trifluoroethylene) (PTrFE) is often introduced to create P(VDF-TrFE), Figure 4a, which usually assumes an all-trans conformation because of steric effects, thereby eliminating the need for mechanical stretching. P(VDF-TrFE) is well soluble in common organic solvents and can easily be processed into piezoelectric thin films by thermal annealing close to the crystallisation temperature.<sup>[111]</sup> However, due to the F atoms interspersed in between the H atoms, the magnitude of the net polarization across the chain is smaller than that of PVDF. Furthermore, the reduced dipole interaction due to interspersed F atoms in the middle of the H atoms gives rise to a lower  $T_c$  (110 °C), leading to less robust thermal stability compared to PVDF.

Polyamides, or Nylons, are semi-crystalline polymers with repeating units linked by amide bonds. These bonds generate hydrogen bonding between the oxygen atom in one amide group and a hydrogen atom, which is bound to an adjacent nitrogen atom. The crystalline regions are made up of stacked chains with multiple hydrogen bonds. In one repeating unit, Nylon-*n* has a methylene group  $(CH_2)_{n-1}$  and an amide group. The Nylon is "even-numbered" or "odd-numbered" depending on the number of carbon atoms (*n*) in a repeating unit. Even-numbered Nylons have no net polarization because of the alternating amide groups, while all of the dipoles in odd-numbered Nylons point in the same direction, generating a net polarization (Figure 4b). Hence, odd-numbered Nylon exhibits piezoelectricity. However, ferroelectric hysteresis loops have been reported even for evennumbered Nylons with a metastable melt-quenched phase.<sup>[112]</sup> In fact, mesophases with enlarged interchain spacing and disordered hydrogen bonds can also potentially give rise to piezoelectric behavior in Nylons. Of the various crystalline phases of Nylon-11, only the pseudo-hexagonal  $\delta'$ -phase has been investigated extensively, where a field-induced dipole reversal could be achieved in randomly oriented crystal structures.[112,113] Mechanical drawing has been shown to improve crystallinity and molecular orientation,<sup>[114]</sup> while thermal annealing,<sup>[115]</sup> quenching,<sup>[112]</sup> and electrical poling<sup>[116]</sup> have been employed to achieve the desired piezoelectric phase in Nylons.

Poly(lactic acid) (PLA) is a synthetic chiral polymer derived from biological materials<sup>[103]</sup> with two optical isomers: PLLA, and poly(D-lactic acid) (PDLA). The main chain of both PLLA and PDLA have a helical structure, where the PDLA helical structure is left-handed, while the PLLA helical structure is right-handed. PLLA is the stereoisomer more commonly used and its helical conformation is shown in Figure 4c. By aligning the polymer





Figure 4. Schematic molecular structures of a) PVDF (left) and its co-polymer P(VDF-TrFE) (right); b) even-numbered (top) and odd-numbered polyamide (bottom); c) PLLA (the red dotted line indicates the helical axis).

chains it is possible to give rise to a shear-mode piezoelectric response. PLLA is found to crystallize with a volume crystalline fraction of  $\approx 30-50\%$  when annealed at temperatures between 80 and 140 °C,<sup>[117–119]</sup> and a positive, albeit weak, correlation was observed between the crystalline fraction and the measured piezoelectric coefficient.<sup>[120]</sup> As with PVDF and Nylons, PLLA is also polymorphic ( $\alpha$  and  $\alpha$ ' phases are the most common). Mechanical drawing can lead to molecule orientation in the crystals and the quasi-crystalline regions can generate a shear-mode piezoelectric response. <sup>[121]</sup> In addition, mechanically stretched PDLA is piezoelectric and the calculated effective piezoelectric coefficient  $d_{14}$  in films of PLLA and PDLA were 10.2 and 9.4 pC N<sup>-1</sup>, respectively.<sup>[122]</sup>

The properties of some representative piezoelectric polymers are reported in **Table 4**.<sup>[123–131]</sup>

### 2.5. Natural Biomaterials

The piezoelectric effect also widely exits in many natural biomaterials, namely materials that have originated from a biological system itself. Natural piezoelectric biomaterials are small molecules or polymers that contain pairs of oppositelycharged groups such as positive amino group (-NH<sub>2</sub>) and negative carboxyl (-COOH) or hydroxyl (-OH) groups. Typical examples include amino acids,<sup>[132]</sup> peptides,<sup>[133]</sup> proteins,<sup>[134,135]</sup>

Material	Synthesis method	Piezozoelectric coeff. [pC N <sup>-1</sup> ]	$\epsilon_{\rm r}$	Elastic modulus	Bio-degradable	Bio-compatible	Refs.
PVDF	Drop casting/uniaxial drawing	d <sub>33</sub> ,34	I	1	I	I	[123]
PVDF-HFP	Extrusion	d <sub>33</sub> ,24	I	I	I	I	[124]
PLA with embedded Diphenylalanine microrod-	Self-assembly	d <sub>33</sub> ,12.4	I	I	Yes	Yes	[125]
Polyamide 11,11	Hot press-quenching	d <sub>33</sub> ,-3.9	I	I	I	I	[126]
Polyurea	Evaporation	$d_{31}, 10$	4	2.2 GPa	I	I	[127]
P (VDCN/VAc)	Casting/rolling	d <sub>31</sub> ,5	9	1	I	I	[128]
PDLA	Solid state extrusion	d <sub>14</sub> , 11-18.9	I	2.9-5.3 GPa (longitudinal modulus)	I	I	[129]
D-PLA/L-PLA multilayer	Coextrusion	<sup>a)</sup> d <sub>ap</sub> , 114–170	I	1.98-2.08 GPa (Young's modulus)	Yes	Yes	[130]
L-PLA/ РМ МА-РВА-РМ МА	Melt-quenching	<sup>b),c)</sup> e, 11.1-22.9 (mC/m <sup>2</sup> )	I		I	I	[131]

applied mechanical strain; <sup>cj</sup> The measured values of e, depend on the polymer blend molar and weight ratio, and on the drawing temperature and drawing ratio used during fabrication. P(VDCN/VAc): Poly (Vinylidene evaluated from Piezoelectric stress coefficient e, layerl; one of a single HFP: hexafluoropropylene with the 2 Diezoelectric d coefficient of a multilaver PMMA: poly(methyl methacrylate). PBA: poly(butyl acrylate). coemcient [as defined in ret. [130] to compare the and Vinyl Acetate). PHB: poly- $\beta$ -hydroxybutyrate. Apparent piezoelectric Cyanide the

and polysaccharides.<sup>[136,137]</sup> They are also fundamental building blocks of biological components, such as bone, tendon, and skin, which have also been discovered to be piezoelectric.<sup>[138-141]</sup> Compared to the inorganic and synthetic polymer piezoelectric compounds, this group of materials offers excellent biocompatibility and biosafety. The majority of materials in this class are mechanically flexible and some are even biodegradable. Therefore, piezoelectric biomaterials are considered to be the optimal choice to interface electromechanically with biological and soft systems for sensing, tissue engineering, stimulation, and energy harvesting applications.<sup>[8,133,142,143]</sup> As will other piezoelectric materials, piezoelectric biomaterials need to form a well-organized and long-range aligned dipole arrangement in order to exhibit bulkscale piezoelectricity. The development of methods to achieve a long-range ordered structure with an aligned polarization direction continues to remain the main challenge toward the practical application of piezoelectric biomaterials. In this Section, we therefore overview the molecular structure-related piezoelectricity of four classes of piezoelectric biomaterials, comprising amino acids, peptides, proteins, and polysaccharides. Representative approaches for assembling desired piezoelectric phases, aligning the polarization direction, and improving the piezoelectric properties are also discussed.

### 2.5.1. Amino Acids

Amino acids are the simplest biomolecule that can assemble into a piezoelectric crystal. They have a general molecular structure that consists of an amino group and a carboxyl group, where different amino acids are differentiated by their side groups (R) (Figure 5a).<sup>[144]</sup> An electric dipole moment exists in amino acid molecules pointing from the negatively-charged carboxyl group to the positively-charged amino group. The arrangement of the carboxyl and amino groups along the same direction in a periodic structure allows for the accumulation of dipole moments, which thereby induce a bulk piezoelectric response in a noncentrosymmetric amino acid crystal. Due to the general structural features of amino acids, piezoelectricity has been experimentally confirmed in 17 of the 20 natural amino acids and their compounds.<sup>[145,146]</sup> Computational predictions suggested that amino acid crystals have the potential to exhibit high shear piezoelectric coefficients. For example, a shear piezoelectric coefficient ( $d_{16}$ ) of 195 pC N<sup>-1</sup> is calculated for  $\beta$ -phase glycine.<sup>[132]</sup> The high shear piezoelectric coefficients in amino acid crystals could be a result of supramolecular packing, which enables high shear elasticity and compliance to the molecular assembly, and thus large dipole displacements.<sup>[147,148]</sup> Nevertheless, for some practical applications, shear piezoelectricity is less suitable and the longitudinal, out-of-plane piezoelectric effect, namely  $d_{33}$ , is often considered the most useful coupling mode for energy conversion and sensing (see Figure 1).

The highest  $d_{33}$  in amino acid crystals was predicted from  $\gamma$ -glycine crystals,<sup>[132]</sup> where the  $\gamma$ -phase glycine has a non-centrosymmetric structure belonging to the P32 space groups.<sup>[149,150]</sup> This structure allows for longitudinal non-zero piezoelectric coefficients along three crystal axes, with the highest predicted  $d_{33}$  to be 10.4 pC N<sup>-1</sup> along the chain direction; this is comparable to those of piezoelectric polymers and wurtzite www.advancedsciencenews.com

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**Figure 5.** a) General molecular structure of amino acids. Reproduced with permission.<sup>[144]</sup> Copyright 2022, American Chemical Society. b) Calculated piezoelectric coefficients for  $\gamma$ -glycine with experimentally measured  $d_{11}$ ,  $d_{22}$ , and  $d_{33}$  values marked. Reproduced with permission.<sup>[132]</sup> Copyright 2017, Springer Nature Limited. c) Schematic of interface-directed crystallization process of PVA-glycine-PVA sandwich structure formation. Reproduced with permission.<sup>[153]</sup> Copyright 2021, The American Association for the Advancement of Science. d) Piezoelectric  $d_{33}$  coefficients and voltage outputs of glycine–PVA films grown on different substrates with different crystal orientations. Reproduced with permission.<sup>[154]</sup> Copyright 2022, Royal Society of Chemistry. e) Angle dependence of in-plane piezoresponse for peptide nanotubes and Y-cut LiNbO<sub>3</sub>. Reproduced with permission.<sup>[157]</sup> Copyright 2010, American Chemical Society. f) Comparison of the piezoelectric coefficient of Boc-Dip-Dip and other common piezoelectric materials. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[158]</sup> Copyright 2020, American Chemical Society.

crystals, such as zinc oxide.<sup>[151]</sup> This magnitude of the piezoelectric coefficient was confirmed by piezometer measurements on  $\gamma$ -glycine single crystals, which led to a  $d_{33}$  of 9.93 pC N<sup>-1</sup> (Figure 5b). PFM measurements were performed on  $\gamma$ -glycine microcrystals grown from solution on a Pt/SiO<sub>2</sub>/Si substrate with a  $d_{33}$  of 10 pC N<sup>-1</sup>.<sup>[132,152]</sup> It should be noted that those measurements were performed on the micrometer scale, which usually yields larger values compared with those measured on bulk sample films due to the much better alignment of piezoelectric dipoles within small crystals. For practical applications, the formation of a large-scale assembled piezoelectric phase remains challenging, as the piezoelectric  $\gamma$ -phase is the high-energy state, and most self-assembly processes naturally lead to the formation of low-energy non-piezoelectric  $\alpha$ -phase.<sup>[8]</sup> Additional additives, or modifiers, are usually needed to modulate the crystallization pathway to form piezoelectric  $\gamma$ -glycine, such as by adjusting the solution pH value,<sup>[143,145]</sup> adding inhibitor additives,<sup>[143,146]</sup> intro-

ducing external interference from laser illumination<sup>[147]</sup> or using an applied electric field.<sup>[148]</sup>

A recent breakthrough in large-scale oriented piezoelectric amino acid self-assembly was achieved through an interfacedirected crystallization process (Figure 5c).<sup>[153]</sup> In the precipitation process of a mixed aqueous solution of polyvinyl alcohol (PVA) and glycine, the rich hydroxyl groups on the PVA films selectively bond with the carboxyl groups on glycine molecules and direct the formation of  $\gamma$ -glycine crystals with the same orientation. The continuous and wafer-scale manufacture of a PVA film therefore enabled the formation of piezoelectric  $\gamma$ -glycine thin films with a bulk  $d_{33}$  of 5.3 pC N<sup>-1</sup>. The piezoelectric activity was further improved to 6.13 pC N<sup>-1</sup> by aligning the nucleation orientation so that its (001) facets were more parallel to the film surface (Figure 5d).<sup>[154]</sup> An interface-guided self-assembly process may be used for controlled synthesis of piezoelectric thin films from other amino acid crystals.

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### 2.5.2. Peptides

Peptides are short chains of amino acids were the electric dipoles in amino acids can make the same contribution to piezoelectricity as with organized peptide molecules. Many peptide-based periodic structures exhibit piezoelectric properties,<sup>[155,156]</sup> in which diphenylalanine (FF) is the most studied system due to its predicted strong piezoelectric effect and relatively simple molecular structure.[157,158] One FF molecule contains two head-to-tail joined phenylalanine (Phe) amino acids, and these molecules can assemble into a non-central symmetric structure with a *P*6<sub>1</sub> space group to enable piezoelectricity.<sup>[157]</sup> Due to the chainlike molecule, the FF dipeptides often self-assemble into onedimensional (1D) nanostructures, such as nanowires or nanotubes, through the intermolecular interactions between the side functional groups and benzyl rings.<sup>[159,160]</sup> In these structures, the strong piezoelectric polarization is along the axial direction, i.e., the "1" direction. Similar to amino acid assemblies, the peptide crystals are also highly responsive to the shear strains. Therefore, the shear piezoelectric coefficients,  $d_{15}$ , are often quantified to represent the piezoelectric properties. For example, 100 nmthick FF nanotubes exhibited an effective  $d_{15}$  of  $\approx$ 35 pC N<sup>-1</sup> from PFM measurements (Figure 5e).<sup>[157]</sup> A strong  $d_{15}$  of 80 ± 15 pC N<sup>-1</sup> was measured from micrometer-sized FF tubes by PFM.<sup>[161]</sup>

These nanostructures were often used as building blocks for assembling large-scale films for practical applications. An external force field is usually needed to align the structure orientation and electrical polarization. For example, an electric field was applied to align the polarization of self-assembled FF microrods and enhance the out-of-plane  $d_{33}$  coefficient up to 17.9 pC N<sup>-1</sup>.<sup>[133]</sup> The use of a capillary force is another strategy to align the nanoscale building blocks in solvent-based assemblies.<sup>[162]</sup> When a substrate was slowly pulled out from the FF solution, the meniscus at the air-liquid-solid interface was able to drive the FF nanostructures to the interface, and align them parallel to the pulling direction. The thin film formed by the laterally aligned FF nanotubes exhibited a high  $d_{15}$  of 46.6 pC N<sup>-1</sup>. This interface-driven strategy is versatile and can be adapted to different fabrication processes, such as microfluidics, capillary methods, and inkjet-based 3D printing.<sup>[160,163-166]</sup> Generally, the printing head creates a solvent meniscus pattern, where the peptides can be quickly crystalized and constructed as 2D or 3D architectures with designed mechanical and piezoelectric properties. The introduction of additional peptides to co-assemble crystals may further improve the piezoelectric response through enhanced intermolecular interactions. Specifically, modification with bulky molecular groups, such as phenyl rings, could improve the piezoelectric response of the assembled FF structures.<sup>[167]</sup> The direct substitution of one phenylalanine in FF by aromatic-rich peptides, such as  $\beta$ , $\beta$ -diphenyl-Ala-OH (Dip) residue, was found effective in increasing the piezoelectric response. A substantially enhanced piezoelectric coefficient of 73.1  $\pm$  13.1 pC N<sup>-1</sup> was discovered for tert-butyloxycarbonyl (Boc)-Dip-Dip molecular assemblies (Figure 5f).<sup>[158]</sup>

In addition to FF, other more complex peptides, such as fluorenylmethyloxycarbonyl diphenylalanine (Fmoc–FF),<sup>[168]</sup> cyclo-glycine-tryptophan (*cyclo*-GW),<sup>[169]</sup> cyclo-phenylalanine-tryptophan,<sup>[170]</sup> and bis-cyclic- $\beta$ -peptide<sup>[171]</sup> have all exhibited a certain level of piezoelectricity. Their reported shear piezoelec-

tric coefficients were up to 33.7 pC  $N^{-1}$ . However, their larger molecules complicate the intermolecular interactions, which bring additional challenges in long-range assembly and polarity alignment, and thereby lower their macroscopic piezoelectric effect.

### 2.5.3. Proteins

Proteins are macromolecules consisting of a large number of different amino acids. The sequential arrangement of amino acids in protein molecules can also provide a piezoelectric response. Considering the wide variety of protein types and their high structural complexity, we will discuss three of the most common piezoelectric proteins, namely collagen, silk and elastin, as representative examples to illustrate their structure – piezoelectric property relationships.

Collagen is the most abundant structural protein in animals. It typically exhibits a fibril morphology with three helix polypeptide chains (Figure 6a).<sup>[9,172]</sup> The alignment of electric dipoles in the peptide chains was believed to be the origin of piezoelectricity in collagen fibrils.<sup>[147,173,174]</sup> Since the first discovery in 1957,<sup>[134,175-177]</sup> the piezoelectric properties of collagen materials have been widely investigated. PFM on a single type I collagen fibril revealed a shear piezoelectric coefficient of  $\approx 2$  pC N<sup>-1</sup>.<sup>[174]</sup> To date, the most active piezoelectric collagen was found to originate from rat tail tendons with a shear coefficient of -12pC N<sup>-1</sup>.<sup>[147,178]</sup> It is noted that most measurements were conducted on collagen at the nano- or micro-scale and, in contrast to amino acid or peptides, large-scale piezoelectricity from assembled structures is rarely observed from collagen; this is possibly due to the difficulty in assembling such large molecules to provide long-range ordered polarity.

Silk exhibits a certain level of piezoelectricity, although it has been historically considered as a structural material. Silk fibroin displays crystalline polymorphism (Figure 6b),<sup>[179]</sup> including  $\alpha$ -helix silk I, antiparallel  $\beta$ -sheet silk II, and unstable silk III.<sup>[135,180–182]</sup> However, since it is limited by its low crystallinity and mixed-phase structure, silk typically shows a rather low piezoelectric activity with an observed coefficient of approximately 1 pC N<sup>-1</sup>.<sup>[183]</sup> As a result of its widespread availability as a natural biomaterial, silk-based materials have recently experienced growing research attention to explore and improve their piezoelectric properties. For example, a controlled process to align silk structures achieved a  $d_{14}$  coefficient of 1.5 pC N<sup>-1</sup> and a  $d_{33}$  of 38 pC N<sup>-1</sup>.<sup>[135,180]</sup>

Elastin, an extracellular matrix protein, is abundantly available in mechanically stressed tissues such as the lung, skin, and blood vessel walls.<sup>[184,185]</sup> It also exhibits weak piezoelectricity from its amino acid building blocks. PFM measurements indicate a piezoelectric coefficient of aortic elastin of  $\approx 1 \text{ pC N}^{-1}$ .<sup>[185,186]</sup> Compared to the protein molecules mentioned above, elastin is relatively hard to obtain in large quantities with a uniform structure and polarity. Therefore, piezoelectric studies on this protein are less common.

It can be seen from above discussion that the piezoelectric response from proteins is generally weak and is mainly shearbased. This is mostly due to their large and complex structures, which hinders long-range ordering. Consequently, only limited characterization data of the structure and piezoresponse have www.advancedsciencenews.com

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**Figure 6.** a) Schematic of collagen triple-helix structure formed by three twisted polypeptide chains. Reproduced with permission.<sup>[172]</sup> Copyright 2018, American Chemical Society. b) Schematics of components and structures in spider silk. Reproduced with permission.<sup>[179]</sup> Copyright 2018, Elsevier Ltd. c) Schematics of the vertical alignment mechanism of CNCs. d) Cross-sectional scanning electron microscopy image and surface PFM image of vertically aligned CNC film. Reproduced with permission.<sup>[193]</sup> Copyright 2020, American Chemical Society. e) Molecular structures of chitin and chitosan. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[198]</sup> Copyright 2023, The Authors. Published by Wiley-VCH GmbH. f) Piezoelectric response measured from PENGs made by gelatin, chitin, and collagen nanofibers. Reproduced with permission.<sup>[197]</sup> Copyright 2018, Elsevier Ltd.

been reported; as a result, practical application of these materials remain elusive.<sup>[187]</sup>

### 2.5.4. Polysaccharides

Polysaccharides, widely found in organisms, are the most abundant natural carbohydrates with a general formula of  $C_x(H_2O)_y$ . Research interest in piezoelectric polysaccharides can be dated back to 1950s' when piezoelectricity was discovered from wood.<sup>[188,189]</sup> The piezoelectric response from woods originates from cellulose, which represents the most common and abundant linear polysaccharide in nature and can be found in the cell walls of most plants.<sup>[190]</sup> Plants have a hierarchical and multi-level organization that enables the extraction of different types of nanocellulose and, in particular, cellulose nanocrystals (CNCs) can be produced in large quantities from natural lignocelluloses.<sup>[191]</sup> The piezoelectric properties of CNCs primarily arises from their monoclinic structure that is composed of polarized glucose units. In order for CNCs to exhibit a practical bulk-scale piezoelectric response, CNC crystallites need to be further organized into a long-range ordered structure. The effective piezoelectric coefficient  $d_{25}$ , measured on an aligned 38 nm CNC film manufactured through a combination of shear loading and applied electric fields, reached a value of 210 pC N<sup>-1</sup>.<sup>[192]</sup> As a result of it fibrous structure, CNC assemblies typically manifest themselves as sheet-like structures with their polarization direction aligned in-plane, where this configuration usually yields a small out-of-plane piezoelectric activity. Recent research used a confinement cell in an attempt to align CNC fibrils vertically into a large-scale film (Figure 6c,d). This process effectively improved the out-of-plane piezoelectric coefficient  $d_{33}$  to  $19.3 \pm 2.9$  pC N<sup>-1</sup>, close to the one obtained for a PVDF polymer film.<sup>[193]</sup>

Chitin is the second abundant polysaccharide, and is mostly found in marine crustacean shells.<sup>[194]</sup> It is a large molecule composed of N-acetyl-D-glucosamine and can be converted to chitosan through deacetylation.<sup>[195]</sup> Figure 6e illustrates the monomer structures of chitin and chitosan. Both chitin and chitosan exhibit piezoelectricity due to their non-centrosymmetric crystal structure. Density functional theory calculations have indicated that the overall polarization of  $\beta$ -conformation-rich chitin crystal is along the  $[00\overline{1}]$  direction.<sup>[196]</sup> Experimentally, the  $d_{33}$ of  $\beta$ -rich chitin film was measured to be 3.99 pC N<sup>-1</sup> by PFM. Similar to CNCs, it is necessary to align the electrical dipoles in the film to enable a bulk-scale piezoelectric response. An aligned chitin film manufactured by an air gap electrospinning method exhibited a much stronger piezoelectric response compared to randomly oriented chitin nanofibers (Figure 6f).<sup>[197]</sup> The enhancement of piezoelectricity in chitosan was achieved through a post-casting neutralization process, resulting in an effective piezoelectric coefficient,  $d_{33}^{eff}$ , of 15.56 pC N<sup>-1</sup>, which was estimated from the electric field-induced displacement under PFM.<sup>[198]</sup> The  $d_{33}$  coefficients also varied in chitosan films prepared with different organic acids and under different mechanical pressures.<sup>[199]</sup> The response was stable up to 330 K and reached a maximum of 18.4 pC N<sup>-1</sup> under an applied load of 5 tons.

Compared to other piezoelectric biomaterials, the fabrication strategies of polysaccharides films are well-developed, allowing for the production of large-scale films. Despite these progresses, their piezoelectric output has not been improved significantly, possibly constrained by the nature of their large molecules. However, as the most abundant natural piezoelectric biomaterials, this limitation has not hindered the increasing research interest for their applications in piezoelectric energy harvesting and conversion.

Overall, natural piezoelectric biomaterials are a unique group of piezoelectric materials that have potential for interfacing with biological and other soft systems. The four major types of natural piezoelectric biomaterials reviewed in this section provide representative examples of how they exhibit a piezoelectric response and how they may be assembled for practical applications. To provide a direct comparison, the piezoelectric coefficients of typical examples in these four groups of biomolecules are summarized in **Table 5**.<sup>[132,133,135,153,154,157,158,162,168,169,178,180,185,192,193,196,198,200-203]</sup> As discussed above, they can exhibit high levels of piezoelectric activity, which mainly result from a shear response. The more practical transverse piezoelectric responses, such as  $d_{33}$  response, are typically lower than their ceramic or synthetic polymer counterparts. Their large molecules and complex functional groups introduce additional challenges to align their polarization over a long range, which could further reduce their bulk piezoelectricity from the values measured at the nano- or micro-scale. Nevertheless, their unique advantages that stem from being derived from nature are still inspiring growing research interests to improve their potential for practical applications, including soft robotics.

Summarizing, the different classes of materials outlined here exhibit a range of advantages in terms of ease of compositional engineering, mechanical flexibility, a lightweight nature, or widespread availability, and biocompatibility as a natural biomaterial. The corresponding piezoelectric properties are also widespread and diverse; for example, the measured  $d_{33}$  coefficient spans over three orders of magnitude, and it typically lower in biomaterials which often exhibit higher shear mode coefficients. The choice of the most appropriate material for device construction is therefore often driven by the targeted application and by the achievement of a more favorable performance outcome, or a desired combination of properties. For a more complete overview of this section, Figure 7 summarizes the historical evolution of the  $d_{33}$  coefficient for perovskites, polymers, and natural materials according to data reported in Tables 2-5. Engineering material functions through different strategies has enabled a further increase in the piezoelectric coefficients, and will be outlined in the following section.

### 3. Strategies to Enhance Material Functions

In this section chemical strategies (e.g., chemical modification, control over interfaces, and synthesis of nanocomposite materials) and physical strategies (e.g., micro- and nano-structuring, material processing, and cooperativity in networks of fibers), that have been employed to enhance the piezo-response and facilitate the integration of piezoelectric materials into complex electronic systems, are reviewed.

### 3.1. Chemical Modification Strategies

Engineering the chemical composition of piezoelectric materials is a widely explored strategy to enhance their piezoelectric functionality. In particular, the search for lead-free materials that can show properties comparable to Pb-based PZT has stimulated research effort in this respect.<sup>[14,204-206]</sup> For a number of years, the compositional optimization of crystalline materials has been driven by the observation of significantly enhanced piezoelectric properties at the MPB.<sup>[14,204]</sup> Recently, Liu et al.<sup>[207]</sup> reported on a MPB-like behavior in piezoelectric polymers. Ferroelectric P(VDF-TrFE) copolymers were considered with variable contents of the VDF monomer ( $C_{VDF}$ , varying in the interval 45-80 mol%). XRD analysis of the crystallographic phases (Figure 8a) indicated the presence of an intermediated region where 3/1 helical and trans-planar phases coexist, suggesting the formation of MPB in samples with  $C_{\text{VDF}} \leq 55$ mol%. The presence of the two phases was also supported by infrared spectroscopy (Figure 8b,c) and additional analyses which included differential scanning calorimetry, dynamic mechanical analysis, and the characterization of the tacticity.<sup>[207]</sup>

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Table 5. Comparison of the piezoelectric coefficients of natural biomaterials.

Туре	Materials	Piezoelectric coefficient [pC N <sup>-1</sup> ]	Refs.
Amino Acids	$\beta$ -glycine microcrystal	d <sub>16</sub> : 178	[132]
	Glycine- polycaprolactone (PCL) nanofiber	<i>d<sup>eff</sup></i> <sub>33</sub> : 19	[200]
	$\gamma$ -glycine single crystal	d <sub>11</sub> : 1.7	[132]
		<i>d</i> <sub>22</sub> : -1.1	
		d <sub>33</sub> : 9.93	
	PVA-(γ-glycine)-PVA sandwich	d <sub>33</sub> : 5.3	[153,154
	Film	d <sub>33</sub> : 6.13	
	DL-alanine microfiber	$d_{33}^{e\!f\!f}:5.5$	[201]
	Valine sheet	<i>d<sub>eff</sub></i> : 11.4	[202]
	L-leucine film	<i>d</i> <sub>33</sub> : ≈1.5	[203]
Peptides	Diphenylalanine (FF) nanotube	d <sub>15</sub> : 35	[157]
	Vertically aligned FF microrods	d <sub>33</sub> : 17.9	[133]
	Horizontally aligned FF nanotubes	<i>d</i> <sub>15</sub> : 46.6	[162]
	Boc-Dip-Dip crystal	<i>d</i> <sub>33</sub> : 73.1	[158]
	Fmoc-FF nanotube	d <sub>15</sub> : 33.7	[168]
	Cyclo-GW crystal	d <sub>14</sub> : 4.6	[169]
		d <sub>16</sub> : 13.8	
Proteins	Rat tail tendon	d <sub>14</sub> : -12	[178]
		d <sub>33</sub> : 0.89	
	Oriented silk film	d <sub>14</sub> : 1.5	[135]
	Electrospun silk fibroin	d <sub>33</sub> : 38	[180]
	Aortic elastin	$d_{eff} \approx 1$	[185]
Polysaccharides	Aligned CNC film	d <sub>25</sub> : 2.1 Å/V	[192]
	Vertically aligned CNC film	d <sub>33</sub> : 19.3	[193]
	$\beta$ -rich chitin film	d <sub>33</sub> : 3.986	[196]
	Neutralized chitosan film	d <sup>eff</sup> <sub>33</sub> : 15.56	[198]

Interestingly, the piezoelectric properties of the copolymers showed a marked increase upon increasing  $C_{VDF}$ , with a maximum longitudinal  $d_{33}$  coefficient of -63.5 pC N<sup>-1</sup> at  $C_{\rm VDF}$ = 50 mol%, as shown in Figure 8d. Additional studies<sup>[208]</sup> have shown that the competition between the two conformations occurred mainly at the intramolecular scale, rather than at the intermolecular one. Han et al.<sup>[209]</sup> reported an MPBlike behavior in poly(vinylidene difluoride-co-trifluoroethyleneco-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] terpolymers, by varying the CTFE contents ( $C_{\text{CTFE}}$ ). XRD spectra and crystallographic data (Figure 8e,f) of terpolymers with different CTFE contents showed the coexistence of ferroelectric and relaxor ferroelectric phases for  $C_{CTEE}$  in the interval 1.7–5 mol%. Their assessment of the piezoelectric properties highlights a significant increase of the  $d_{33}$  coefficient, up to -55.4 pC N<sup>-1</sup>, in the mixed phase region (Figure 8g); this resulted in an increase of almost 85% compared to the  $d_{33}$  coefficient of the P(VDF-TrFE) copolymer (65/35 mol %).

In another study, Chen et al.<sup>[99]</sup> demonstrated that the addition of <2 mol% of fluorinated alkyne monomers to a relaxor ferroelectric P(VDF-TrFE-CTFE) further enhanced the copolymer properties, with a resulting  $d_{33}$  coefficient of -1050 pC N<sup>-1</sup>. Recently, an MPB was found in a polarized piezoelectric polymer alloy based on poly(vinylidene fluoride-trifluoroethylenechlorofluoroethylene) [P(VDF-TrFE-CFE)] and P(VDF-TrFE), by varying the content of the latter copolymer (Figure 8h–k).<sup>[210]</sup> Crystallographic and infrared spectroscopy data showed the coexistence of the 3/1-helical and all-trans  $\beta$  phases in P(VDF-TrFE) (26.7 wt%), with a maximum value of the  $d_{33}$  coefficient of 32 pC N<sup>-1</sup>.

The presence of a MPB was also reported in a molecular perovskite, namely  $(TMFM)_x(TMCM)_{1-x}CdCl_3$  (TMFM is the trimethylfluoromethyl ammonium, TMCM the trimethylchloromethyl ammonium, and  $0 \le x \le 1$ ).<sup>[211]</sup> Specifically,



**Figure 7.** Historical evolution of the piezoelectric  $d_{33}$  coefficient for different classes of piezoelectric materials. Data from Tables 2–5.





**Figure 8.** a) XRD spectra of P(VDF-TrFE) copolymers with different content of VDF ( $C_{VDF}$ ). b,c) Infrared absorption spectra of P(VDF-TrFE) copolymers with  $C_{VDF}$  = 45, 50, 65 mol%. The vertical dashed arrows highlight the peaks characteristic of all-trans (b) and 3/1 helix (c) conformations, respectively. d) Dependence of the modulus of  $d_{33}$  on  $C_{VDF}$ . The MPB interval is highlighted by the colored shaded area. Reproduced with permission.<sup>[207]</sup> Copyright 2018, Springer Nature Limited. e) XRD spectra of P(VDF-TrFE-CTFE) copolymers with different contents of CTFE ( $C_{CTFE}$ ). f) Dependence of the lattice parameters (*d* spacing) on  $C_{CTFE}$  for the ferroelectric phase (blue squares) and the relaxor phase (red circles). g)  $d_{33}$  as a function of  $C_{CTFE}$ . Reproduced with permission.<sup>[209]</sup> Copyright 2022, American Chemical Society. h) XRD spectra of a polarized piezoelectric polymer alloy with different content of P(VDF-TrFE), expressed as wt%. i,j) Corresponding infrared absorption spectra measured around 505 and 1280 cm<sup>-1</sup>, respectively. Characteristic peaks of the 3/1 helical and all-trans  $\beta$  phases are marked by dashed arrows. k) Measured and simulated  $d_{33}$  vs. content of P(VDF-TrFE). Inset shows the result of the measurement by a quasi-static piezoelectric tester. Reproduced with permission.<sup>[210]</sup> Copyright 2023, American Physical Society.

the MPB occurred for  $0.25 \le x \le 0.3$ , which was identified by the coexistence of two ferroelectric phases, namely the monoclinic *m* and the hexagonal 6*mm* phases. In such a regime, a remarkably high  $d_{33}$  coefficient was estimated that was in the region of 1100–1540 pC N<sup>-1</sup>. Overall, these results have opened up exciting opportunities to enhance the piezoelectric properties of polymers and have offered new chemical design rules for the creation of piezoelectric polymers.

Alternative approaches examined for enhancing the piezoelectric properties consist of chemically designing molecular ferroelectrics, with an aim to optimize performance,<sup>[212]</sup> and forming organic-inorganic hybrid piezoelectric materials, such as the  $C_6H_5N(CH_3)_3CdBr_2Cl_{1-x}I_x$  in which iodide substitution is effective in improving the piezoelectric properties (a  $d_{33}$  coefficient of 367 pC N<sup>-1</sup> was reported when x = 0.25), while the weakening of the metal-halide bonds decreases the Young modulus (800 MPa at x = 0.25).<sup>[213]</sup> Heavy halogen substitution has also enhanced the piezoelectric properties of a hybrid perovskite ferroelectric, [Me<sub>3</sub>NCH<sub>2</sub>Cl]-CdBrCl<sub>2</sub>, for which a  $d_{33}$  coefficient of 440 pC N<sup>-1</sup> was obtained.<sup>[214]</sup>

Furthermore, compositionally graded piezoelectrics<sup>[215–218]</sup> are emerging as a novel class of materials, in which the spatiallyvarying composition can be engineered to enhance the piezoelectric response. For example, large and temperature-insensitive









**Figure 9.** a,b) Schematics of the cross section of a sample before (a) and after (b) deposition of penetrated electrodes. c,d) SEM micrographs of the metal electrodes penetrating into a fibers mat, without plasma treatment (c) and with plasma treatment (d). The insets show magnified images of the electrode interface shown in (c) and (d), respectively. Reproduced with permission.<sup>[222]</sup> Copyright 2019, American Chemical Society. e) Schematic illustration of the formation of the complex interconnection interface between P(VDF-TrFE) and PEDOT:PSS. f) SEM cross-sectional micrographs of the P(VDF-TrFE)/PEDOT:PSS composite interface. Right image of (g) shows the energy dispersive map of fluorine. h) Map and intensity profile of the SO<sub>3</sub> as obtained by TOF-SIMS. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[223]</sup> Copyright 2023, The Authors, published by Springer Nature. i) High-angle annular dark-field scanning transmission electron image and energy dispersive X-ray spectroscopy maps of a single GaIn droplet. j) Illustration of the interaction between PVDF-TrFE molecules and GaIn droplets. k) Dependence of  $d_{33}$  on the GaIn mass. Inset: Schematics of a GaIn anodroplets/P(VDF-TrFE) composite device. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[241]</sup> Copyright 2023, The Authors. Published by Wiley-VCH GmbH.

electric field-induced strains,<sup>[219]</sup> and improved temperature stability of the  $d_{33}$  coefficient<sup>[220]</sup> were obtained for compositionally graded lead-free KNN ceramics. An increase in the output voltage was reported for PZT films with a graded composition, compared to uniform films.<sup>[221]</sup> Recently, nanocomposites with a 3D graded composition were realized by co-deposition of polymer nanofibers with a different composition and successive hot pressing.<sup>[218]</sup> In these materials, an enhanced tensile strength and output voltage were achieved compared to a nanocomposite with a uniform distribution of nanofillers.<sup>[218]</sup>

### 3.2. Material Interface and Nanocomposite Strategies

In piezoelectric devices, the piezo-active layers are usually in contact with electrodes or other dielectric materials. Interfacial properties therefore play a fundamental role in determining the final device performance, especially when nanostructured and flexible piezoelectric layers are used. The control of the composition and the structure of any interfaces constitutes an effective strategy to improve the overall piezoelectric properties. Examples include the use of electrodes that penetrate into the piezoelectric layer,<sup>[222,223]</sup> thereby increasing the contact area and the conductive pathways, and ultimately improving an electromechanical output as a consequence of the charges accumulated nearby the electrodes. Moreover, with the use of penetrating electrodes, the degree of adhesion between the metal contact and the piezoelectric layer is improved, thus contributing to increase the long-term stability of the devices under multiple bending or compressing cycles.<sup>[222-224]</sup> One approach is outlined in Figure 9a,b, where a metal contact is deposited on a layer of a nanostructured piezoelectric material, namely an array of nanofibers of P(VDF-TrFE) incorporating barium titanate (BTO) nanoparticles, after treating the nanostructured layer with O<sub>2</sub> plasma to improve its hydrophilicity.<sup>[222]</sup> This method substantially increased the depth of the metalized active

piezoelectric layer (up to 20 µm, Figure 9c,d) compared to the untreated samples. Recently, a complex interconnected interface was realized between a conductive polymer (PEDOT:PSS) that was used as an electrode and a piezoelectric P(VDF-TrFE) film.<sup>[223]</sup> Here, a dimethyl sulfoxide (DMSO) solvent was used to create an interdiffusion layer between PEDOT:PSS and P(VDF-TrFE), as shown in Figure 9e. The presence of a PEDOT:PSS/P(VDF-TrFE) mixed layer was evidenced by cross-sectional scanning electron microscopy (SEM) (Figure 9f), energy dispersive spectroscopy (Figure 9g) and time-of-flight secondary ion mass spectrometry (TOF-SIMS, Figure 9h). A significantly improved  $d_{33}$  coefficient of -86 pC N<sup>-1</sup> was achieved compared to P(VDF-TrFE) films with standard electrode contacts, and a high sensitivity of 2.2 V kPa<sup>-1</sup> in the pressure range of 0.025–100 kPa.<sup>[223]</sup>

Another widely explored method used to enhance the material function consists in the realization of piezoelectric composites, usually based on the incorporation of inorganic fillers into a polymer matrix. By adjusting the relative ratio of the two components, or aligning the filler within the polymer, it is possible to form new composite materials with excellent mechanical and piezoelectric properties. Enhancement of the piezoelectric properties of nanocomposites can also be achieved through a careful evaluation of their interfacial properties. Indeed, the interfacial properties between the nanofiller surface and the polymer chains can be suitably designed to drive the formation of the ordered and crystalline phases of interest for piezoelectric applications, while the nanofillers can constitute nucleating centers for the development of the polymer crystalline phases. In addition, nanofillers can also be exploited to improve stress transfer by acting as stress-reinforcing components, or they can add a piezoelectric contribution to the polymer matrix. Here, important and recent achievements will be presented, while a comprehensive overview of material design strategies used to improve piezoelectricity in nanocomposites can be found elsewhere.<sup>[225-227]</sup> Tian et al.<sup>[228]</sup> used hydroxyl groups at the surface of layered double hydroxides (LDHs) dispersed in a PVDF matrix to induce the spontaneous polarization in the composite films, where hydrogen bonds were formed between the -CF<sub>2</sub> groups of the PVDF macromolecules and the hydroxyl groups. PFM measurements led to the observation of enhanced piezoelectric coefficients of the composite compared to the pristine PVDF film, without the need of additional electrical poling. The fraction of  $\beta$ -phase in PVDF was also improved by the addition of glycine-modified-MoS<sub>2</sub> nanosheets,<sup>[229]</sup> and of MoS<sub>2</sub> quantum sheets.<sup>[230]</sup> An enhancement in the fraction of  $\beta$ -phase and the piezoelectric response in P(VDF-TrFE) was also achieved by the embodiment of GeSe<sup>[231]</sup> and SnSe<sup>[232]</sup> nanosheets.

In a recent study,<sup>[233]</sup> the microscopic properties of the interfacial layer of PVDF and embedded TiO<sub>2</sub> nanoparticles were studied by SPM and spectroscopies.<sup>[233]</sup> A double polymer layer structure was observed around the nanoparticles: a polar inner layer (about 10 nm thick) with oriented dipoles and a polar outer layer (thickness > 100 nm) where dipoles were randomly oriented. Based on these observations, the optimal content of dispersed TiO<sub>2</sub> nanoparticles was determined to enhance the piezoelectric properties. A maximum  $d_{33}$  of -30 pC N<sup>-1</sup> at 0.35 vol.% of TiO<sub>2</sub> was obtained, which is a twofold enhancement compared to pristine PVDF.<sup>[233]</sup> Other recent examples of nanocomposite

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piezoelectric materials are  $H_2(Zr_{0.1}Ti_{0.9})_3O_7$  (HZTO) nanowires in PLA biopolymer,<sup>[230]</sup> and organic–inorganic hybrid perovskite nanoparticles in polydimethylsiloxane (PDMS).<sup>[234]</sup> The assembly of the nanofillers in polymer matrices can be also controlled to create ordered structures by dielectrophoresis,<sup>[235–239]</sup> a technique that typically creates aligned chains of particles. The resulting composite features improved piezoelectric properties.<sup>[237,238]</sup>

To enhance stress transfer, a network of interconnected particles of samarium/titanium-doped BiFeO<sub>3</sub> was created by freezedrying and mixing with silicone rubber.<sup>[240]</sup> The so-formed 3D porous ceramic structures significantly enhanced the stress transfer compared to uniformly distributed particles, leading to a five-fold improvement of both the open circuit voltage and the short-circuit current.<sup>[240]</sup>

The use of soft materials as fillers of piezoelectric polymeric matrices is emerging as a valuable composite design approach, especially since soft fillers have mechanical properties that are more similar to the polymer matrices when compared to rigid nanofillers. The improved matching of the mechanical properties of the host and guest materials can limit deterioration of device performance when subject to long-term cyclic stimulation, as well as providing more efficient stress transfer.<sup>[241,242]</sup> Liu et al.<sup>[241]</sup> realized a composite piezoelectric material made of a P(VDF-TrFE) matrix with embedded liquid metal nanodroplets (GaIn eutectic alloy), which were obtained by ultrasonication (Figure 9i). The liquid metal nanodroplets have a native oxide surface layer (Figure 9i), which is beneficial for inducing an all trans conformation of the  $\beta$ -phase by electrostatic interactions at the surface of the liquid metal droplets and an alignment of the polymer chain, as schematized in Figure 9j. By varying the mass loading of the liquid metal droplets, both the percentage of  $\beta$  phase and the  $d_{33}$  coefficient were optimized, the latter being enhanced by almost a factor of four compared to pure P(VDF-TrFE) (Figure 9k). Interestingly, the output of the piezoelectric energy harvesting devices realized using the GaIn nanodroplets / P(VDF-TrFE) composite (inset of Figure 9k) were highly stable, with almost null degradation after  $3.6 \times 10^4$  cycles. A synergistic exploitation of the enhanced piezoelectric properties of inorganic nanoparticle dopants and of the mechanical properties of soft liquid metal fillers can further enhance the performance of piezoelectric composites, as recently demonstrated for a ternary composite made of a PVDF polymer matrix doped with polydopamine (PDA)-modified BTO nanoparticles and 1H,1H,2H,2H-perfluorodecyltriethoxysilane liquid nanodroplets.<sup>[242]</sup>

### 3.3. Micro- and Nano-Structuring Strategies

In the following section, the mechanical and structural methods of modifying the morphology of the material by template-based methodologies are introduced and discussed. Bhavanasi et al.<sup>[243]</sup> fabricated PVDF-TrFE nanotubes using anodic aluminum oxide (AAO) porous templates with a 200 nm pore diameter and 60  $\mu$ m pore length. The piezoelectric performance of the nanotubes was measured using piezo-force spectroscopy and within nanogenerator devices; results were compared with films measured in the same experimental conditions. The poled nanotubes exhibit a  $d_{33}$  coefficient of 44 pm V<sup>-1</sup>, approximately a factor of two larger than



the films, and the performance of nanogenerators in terms of generated voltage and power density was significantly enhanced (by a factor 6 and 36, respectively). Such enhancements were attributed to improved strain confinement in the 1D geometry, resulting in a strain increase along the nanotube length and/or increased surface area of the nanotubes with respect to conventional films. Using a similar nanofabrication process based on AAO templates and in situ poling, nanowires of PVDF-TrFE with a diameter of approximately 400 nm and a length of 10 µm, when compared to bulk film, exhibited a nine times improved voltage output when subject to applied bending stress. The enhancement was primarily attributed to the increase of the piezoelectric  $\beta$ -phase content, as measured by Fourier transformed infrared spectroscopy and XRD.<sup>[244]</sup> Further details on the enhancement of the piezoelectric properties of PVDF and its copolymer by AAO templating and on the corresponding structure-property relationship can be found in a recent review by Surmenev et al.<sup>[245]</sup>

Alternative technologies to pattern the surface of piezoelectric materials are known as top-down methods, also termed as soft and nanoimprint lithographies.<sup>[246]</sup> In this approach, master templates that exhibit micro- and nano-reliefs are produced by conventional optical or electron-beam lithography, followed by reactive ion etching. Such a pattern can be transferred to the surface of the target material directly (by applying an external pressure and /or by heating the system above the glass transition temperature of the target material) such as in nanoimprinting lithography, or they can be copied onto the surface of soft elastomeric molds, which are then used to transfer the pattern onto the final target material. A hot embossing process, where both pressure and high temperature were used to transfer the pattern from a PDMS mold to the piezoelectric material, was realized at 160 °C for 1 h, to pattern micropillars of a composite system based on PVDF-TrFE/BTO nanoparticles. The resulting device, when subject to a compressive stress, exhibited an enhancement of the voltage output by a factor 7.3 compared to a pure PVDF-TrFE film. Here, the incorporation of the nanoparticles and the flexible micropillar structure are responsible for such an enhancement.<sup>[247]</sup> Using the same processing method, PVDF-TrFE micropillars without fillers were realized and used as a tactile sensor under a vertical compressive force, showing an enhancement in sensitivity by a factor of four compared to conventional films.<sup>[248]</sup> The geometrical microstructure due to the formation of pillars enables strain confinement and consequently an enhancement of the piezoelectric potential, which is strongly influenced by the pillar size, height, and density per unit of area. A similar hot-embossing process at 180°C for 1 hr was applied to a nanocomposite film of PVDF-TrFE/boron nitride nanotubes to realize an array of micropillars with 80 µm diameter and 120 µm height (Figure 10a(i)).<sup>[249]</sup> Upon contacting the array in a sandwich structure and by using PDMS as insulating layer to both prevent dielectric breakdown during electrical poling and increase the mechanical stability of the composite array [Figure 10a(ii)], the measured output voltage under cyclic compression at 0.4 MPa was 22 V with a sensitivity of 55 V/MPa; this corresponded to a 11-fold enhancement with respect to a pristine P(VDF-TrFE) film. Moreover, the device exhibited excellent radiation shielding capabilities (Figure 10a(iii)), making it promising for space exploration applications.

Micropillar structures with a reduced aspect ratio (8 µm diameter and 4 µm height, named microdomes) were realized by spin coating a porcine skin gelatine solution on top of a PDMS mold; this material was treated with oxygen plasma to increase its hydrophilicity. The gelatine pillars were dried at 40 °C in different humidity conditions, peeled away from the PDMS mold, and crosslinked with glutaraldehyde. The microdomes that were formed exhibited an enhancement of the  $d_{33}$  coefficient by six times compared to conventional planar films (≈24 pC N<sup>-1</sup> vs 6 pC N<sup>-1</sup>), which was attributed to an enhanced molecular packaging of polypeptide chains in the microdomes that induces polarization confinement and gives rise to ferroelectric properties.<sup>[250]</sup> In particular, the formation of an anisotropic molecular structure through cross-linking by glutaraldehyde can decrease the symmetry compared to the quasi-hexagonal symmetry ( $C_6$ ), thereby providing the gelatine microdomes with a high degree of ferroelectricity (Figure 10b-d). Finally, a lightweight  $(2.75 \text{ mg cm}^{-2})$  and thin  $(42.2 \text{ }\mu\text{m})$  device was realized by embedding the microdome films between Mg and a Cu-Ni plated adhesive conducting fabric to achieve a high pressure sensitivity of approximately 41 mV Pa<sup>-1</sup> in the range 0.005–1.7 Pa.

As an alternative to surface microstructuring, the formation of bulk porous architectures in polymer films can enhance the piezoelectric response for energy harvesting, which is mainly due to the increased i) local stress at morphologies discontinuities and ii) materialcompressibility under the same applied pressure. A comprehensive overview of porous film fabrication and their use in nanogenerator configurations can be found in Lu et al.<sup>[251]</sup> Representative examples of the use of porous materials in energy harvesting and soft robotics are reported in Section 4.

The use of physical confinement in 3D nanostructures has been also exploited to change the crystallization conditions of PVDF-based copolymers, for example by promoting the formation of the  $\beta$ -phase. It was found that the crystallization of PVDF, confined inside spherical nanodomains of 180 nm made by emulsion polymerization, induces the formation of the  $\beta$ -phase which is promoted by a homogeneous nucleation mechanism, while an heterogeneous nucleation is observed during zero, one, and two dimensional confinement.<sup>[252]</sup> Semicrystalline polymers can also be confined in the form of nanodomains using a bottom-up approach based on the self-assembly of triblock copolymers, and changing the ratio between the blocks.<sup>[253]</sup> In this case, the ferroelectric  $\beta$ -phase is formed in 3D domains while the 1D confinement within lamellar domains preferentially induces the formation of the non-ferroelectric  $\alpha$ -phase, unless polar interactions between the blocks during melt recrystallization occur.<sup>[253]</sup> A further reduction in size, for example through the formation of flakes of 7 nm thick PVDF by hot pressing,<sup>[254]</sup> influences the  $\alpha$ - to  $\beta$ -phase transformation, with a  $d_{33}$  of -36 pm V<sup>-1</sup>, resulting in a sixfold enhancement compared to that of nanoparticles with a 250 nm diameter. This transformation was attributed to the combined effect of the processing technology employed (heat treatment and compressive forces) and the resultant nanoconfinement effect. A scheme of the process used is reproduced in Figure 10e. Regarding the use of inorganic materials, wavy PZT ribbons showed an enhancement of the piezoelectric effect by up to 70% ( $d_{33} = 130 \text{ pm V}^{-1}$ ) when compared with flat surfaces due to the formation of a strain gradient that depends on the specific localized probing and the absence of physical www.advancedsciencenews.com

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constrains (clamping) by the substrate.<sup>[255]</sup> The dependence of the piezoelectric performance in nanostructured PZT materials with different morphologies (nanoparticles, nanowires, and needle-tipped nanowires) was investigated by Hazra et al.[256] Needle-tipped nanowires are shown to exhibit the maximum power density due to a combination of an enhanced surface-tovolume ratio (which provides a stable mechanical contact with the electrode and a reduced internal resistance) and an enhanced piezoelectric coefficient related to the highest tetragonality exhibited by the needle-like morphology. An in-depth analysis of the dependence of piezoelectricity on different growth factors such as aspect ratio and orientation in 1D inorganic nanostructures is reported in ref. [257] Han et al. reported on the transformation of lithographically-defined 2D patterns (which include electrodes and a PVDF thin film) in complex 3D microsystems, where the 3D geometries yield unique mechanical properties that can lead to multifunctional modes of operation.[258]

### 3.4. Material Processing Strategies

# 3.4.1. Enhancement Through Application of External Stimuli and Radiation

Physical methods to enhance the piezoelectric properties of materials have been investigated extensively. Traditional approaches include the use of mechanical stretching, electrical poling, thermal annealing, high pressures, and their combinations. In such approaches, the processing variables need to be finely tuned to effectively enhance the formation of the electroactive crystalline phases and the resulting piezoelectric coefficients.<sup>[206,259–262]</sup> Examples of recent advances include enhancing the electromechanical properties of ceramics by high-temperature poling<sup>[263,264]</sup> and mechanical annealing using a pressing machine improved the piezoelectric coefficient of amino acid crystals by more than one order of magnitude.<sup>[265]</sup>

Among the less conventional strategies based on physical stimuli, the use of controlled irradiation with light beams is emerging as an advanced strategy for enhancing the piezoelectric properties of materials. Light can be used for inducing thermal annealing in a highly controlled way, due to the ability to precisely modulate the intensity of light and the irradiation time interval (potentially down to femtoseconds using high-energy ultrafast pulsed lasers). These processing parameters allow for a high degree of control of the heating process, with a minor impact on the underlying substrates, thus enabling the use of substrate materials with a lower  $T_m$ , as recently demonstrated for PZT films.<sup>[266]</sup> In addition, light can be precisely localized in space to submicron scales, a property that opens the possibility of controlling the piezoelectric properties of materials at microscale and potentially

with a resonant 405 nm laser, capable to excite free carriers.<sup>[268]</sup>

### 3.4.2. Electrospinning

The processing conditions employed during nanofabrication processes are critically important for enhancing the piezoelectric properties of materials. This is particularly relevant for the electrospinning of piezoelectric polymers, which is a highly versatile technology that enables the realization of continuous fibers from a highly concentrated polymer solution, where the ratio of the polymer weight to the solvent weight is typically in the 5-30% range.<sup>[269]</sup> The high solution concentration favors the formation of molecular entanglements and improves the viscoelastic properties of the fluid. The solution is then loaded in a syringe and pumped at a constant rate, while a high electric field  $(10^5-10^6 \text{ V m}^{-1})$  is applied between the syringe needle and a metallic collector. A charged polymer jet is produced from the needle when the forces generated by the electric field overcome the solution surface tension and the viscoelastic forces. The solvent evaporates rapidly, while the polymer jet experiences high strain rates in the order of  $10^3 \text{ s}^{-1}$ .<sup>[270,271]</sup> In such conditions a substantial alignment of the polymer chains can be induced along the jet axis, which can be retained in the solid state fibers deposited on the collector.<sup>[272]</sup> Moreover, these processing conditions can induce a complex internal structure in the nanofiber core for some polymers and nanocomposites.<sup>[273,274]</sup> These properties of the electrospinning process, and of its variants, such as near-field electrospinning,<sup>[275]</sup> melt-spinning,<sup>[276]</sup> melt electrospinning,<sup>[277]</sup> and needleless electrospinning,<sup>[278]</sup> make these methods interesting for the enhancement of the electroactive phases of piezoelectric materials. The high electric field applied between the spinneret and the collector can provide localized poling, without the need of additional postprocessing. These capabilities were reported for nanofibers made of PVDF and copolymers.<sup>[275,277,279-282]</sup> The degree of enhancement of the piezoelectric properties can be tailored with process variables (e.g., solution concentration and flow rate, applied voltage intensity and polarity, spinneret-collector distance, ambient humidity, substrate speed, and heating temperature), as summarized in other reviews.<sup>[260,269,283]</sup> Moreover, electrospun nanofibers can be decorated with a variety of nanostructures, such as the ZnO nanorods shown in Figure 11a,b, which enables

**Figure 10.** a) SEM micrograph of P(VDF-TrFE)/boron nitride micropillar array before (i) and after (ii) coating with PDMS. iii) Macroscopic thermal neutron cross sections and neutron shielding rates of films of P(VDF-TrFE) (pristine) and of P(VDF-TrFE)/boron nitride (nanocomposite). Reproduced with permission.<sup>[249]</sup> Copyright 2019, Elsevier. b) Scheme of a biodegradable device based on gelatin highlighting the transient character of the realized electronics from biosynthesis to decomposition. c) Ferroelectric properties of the gelatin film both planar and with interlocked microstructure: polarization vs electric field (left panel) and strain vs electric field (right panel) hysteresis loops. d) Mechanism of enhanced ferroelectricity in microdome films: formation of an anisotropic molecular structure through cross-linking by glutaraldehyde. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[250]</sup> Copyright 2021 The Authors, published by Wiley-VCH GmbH. e) Scheme of hot-pressing to fabricate ultrathin PVDF nanoflakes. While PVDF nanoparticles (left side) show intermixed lamellar structure with both  $\alpha$  and  $\beta$ -phases, the nanoflakes (right side) show highly aligned lamellar crystals, mainly exhibiting  $\beta$ -phase. Reproduced with permission.<sup>[254]</sup> Copyright 2019, American Chemical Society.



![](_page_23_Figure_1.jpeg)

**Figure 11.** a) SEM micrograph of an array of hierarchically microstructured PVDF/ZnO fibers. Scale bar: 5  $\mu$ m b) SEM cross-sectional micrograph of the PVDF/ZnO fiber. Scale bar: 1  $\mu$ m. Adapted with permission.<sup>[284]</sup> Copyright 2020, Elsevier Ltd. c) SEM micrograph of PVDF nanofibers with in situ grown CsPbBr<sub>3</sub> nanocrystals. Inset: optical image of the PVDF/CsPbBr<sub>3</sub> nanocomposite sample upon illumination with UV light (365 nm). d) TEM micrograph of a PVDF nanofiber with embedded CsPbBr<sub>3</sub> nanocrystals. Reproduced with permission.<sup>[290]</sup> Copyright 2021, Wiley-VCH GmbH. e, f) Scheme of PVDF nanofibers doped with barium titanate (BTO) without (e) and with PDA coating (f). Insets: images of the nanofibers. Scale bars: 1  $\mu$ m. Reproduced with permission.<sup>[291]</sup> Copyright 2021, Wiley-VCH GmbH. g) Schematics of the electrospinning of the composite nanofibers. The top right inset shows an illustration of the intermolecular interactions between PVDF and MXene. The 2×2 crystallographic supercell of the *Sm*-PMN-PT is schematized in the bottom right inset. h) High-resolution TEM micrograph of the inorganic–organic interface. Scale bar: 5 nm. i) Dependence of the *d*<sub>33</sub> coefficient on the MXene mass fraction. Data are obtained by PFM. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[294]</sup> Copyright 2022, The Authors. Published by Springer Nature. j) Schematics of the PVDF chain arrangement induced by intermolecular interactions during electrospinning. k) TEM micrograph of PVDF and dopamine (DA) interface. Top inset: high-resolution TEM image of the aligned PVDF chains. Bottom inset: FFT image. I, m) Dependence of the PVDF chains. Bottom inset: FFT image. 2020, Wiley-VCH GmbH.

the formation of complex hierarchical, nanostructured piezoelectric materials.<sup>[284]</sup> The growth of ZnO nanorods led to the creation of a 3D hierarchical structure of interlocked PVDF electrospun nanofibers, which enhanced the piezoelectric response of the overall system, thereby increasing the sensitivity and output signals during both pressing and bending modes.<sup>[284]</sup> Interconnected arrays of nanofibers made by piezoelectric BTO and by conductive antimony-doped tin oxide (ATO) were recently realized by co-electrospinning polymer nanofibers that contain the necessary precursors for the synthesis of both the piezoelectric material and conductive inorganic fibers.<sup>[285]</sup> In particular, the ATO nanofibers provided a conductive path for charge transfer, which increased the output voltage of piezoelectric nanogenerators made from the hybrid nanofibers mats by a factor of six compared to a device based on only BTO nanofibers.<sup>[285]</sup> Nanocomposite fibers can be realized by adding the nanofillers into the electrospun solution, thus synergistically exploiting the enhancement of the electroactive properties of the polymers provided by the electrospinning process and the additional piezoelectric functions of the nanofillers. Recent examples of nanocomposite piezoelectric electrospun nanofibers used PVDF doped with Au nanocages,<sup>[286]</sup> BTO nanoparticles and graphene nanosheets,<sup>[287]</sup> polyaniline-coated halloysite nanotubes,<sup>[288]</sup> and MXene nanosheets.<sup>[289]</sup>

Preventing the aggregation of nanoparticles in the solution is critically important to avoid clogging of the spinneret and obtaining a uniform distribution of the fillers in the nanofibers. This issue can be prevented by the *in-situ* growth of nanofillers,

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as reported for CsPbBr<sub>3</sub> perovskite nanocrystals in PVDF.<sup>[290]</sup> Here, a PVDF solution with PbBr<sub>2</sub> and CsBr precursors was electrospun, while CsPbBr<sub>3</sub> nanocrystals with a uniform size and distribution were formed in the nanofibers upon deposition (Figure 11c,d).<sup>[290]</sup>

The surface of the nanofillers can be also functionalized to tailor the interfacial properties and improve their dispersion,<sup>[291,292]</sup> as shown in Figure 11e,f where BTO nanoparticles are surfacemodified with PDA. This surface modification improves significantly the output signals of devices based on the nanocomposite fibers compared to those with untreated BTO nanoparticles, since the use of PDA improves the interfacial contact between the continuous phase and the dispersed phase and enhances the stress transfer between the two components.<sup>[291]</sup>

Similar to bulk nanocomposites, the interfacial properties between nanofillers and polymer macromolecules can be engineered in electrospun nanofibers to create additional nucleating agents to enhance the fraction of crystalline electroactive phases. Moreover, the induced crystalline phases can be concomitantly ordered by the electrospinning electric field. Recently, this has been investigated for MXene nanofillers, whose extended available free surface can be modified with functional groups (e.g. hydroxyl groups) to promote the nucleation of the  $\beta$ -phase of PVDF and its copolymers<sup>[293,294]</sup> (Figure 11g). A ternary composite nanofiber was realized, which was composed of a PVDF matrix and Sm-PMN-PT and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets.<sup>[294]</sup> Molecular dynamics simulations showed that the presence of hydroxyl groups on the MXene nanosheets leads to the creation of hydrogen bonds in the polymer chains (Figure 11h). The combination of the electrospinning process conditions, the MXene nanofillers/PVDF interfacial properties, and the piezoelectric features of the Sm-PMN-PT, led to an enhancement of the  $d_{33}$ coefficient (Figure 11i).

An interesting approach was recently proposed to realize the formation of self-formed core-sheath electrospun nanofibers with a high  $\beta$ -phase content and oriented nanocrystals by doping of the PVDF solution with either hydroxylamine hydrochloride<sup>[295]</sup> or DA.<sup>[296]</sup> As shown in Figure 11j in the case of DA,<sup>[296]</sup> the  $-NH_2$  groups of the dopant molecules were able to drive the formation of  $\beta$ -phase by an interaction with the  $-CF_2$  groups of PVDF. Moreover, the  $-NH_2$  groups are positively charged in the presence of the electrostatic field of the electrospinning process, leading to a migration of dopant molecules toward the polymer jet surface due to electrostatic repulsion, and the formation of a core-shell structure with the inner part being rich in  $\beta$ -phase domains (Figure 11k). Using this approach, an increase in the degree of crystallinity and the  $d_{33}$  coefficient was achieved compared to pristine PVDF fibers (Figure 111,m).<sup>[296]</sup>

The substrate shape can also modify the material function. A new topological design was introduced to enhance the electromechanical response of electrospun membranes of PVDF for acoustic sensing.<sup>[297]</sup> Here, nanofibers were directly electrospun on different pattern arrays (squares, triangles, and cylinders with both lateral size and height of a few millimeters), and a mathematical model was introduced to achieve a topologically optimized design that was capable of modulating the fiber orientation and mechanical vibrations. Upon exposure to sound waves, the topologically optimized membranes exhibited a 300% increase in the electric output with respect to traditional electrospun membranes.

### 3.4.3. 3D Printing

Research performed on nanofibers has demonstrated the crucial role of 3D and hierarchical structures for enhancing the electromechanical properties of piezoelectric materials. Additive manufacturing (AM) and 3D printing technologies constitute a strategy to further improve the functions of piezoelectric materials by structural design.<sup>[298,299]</sup> AM and 3D printing methods build the object layer-by-layer, by using its sliced digital version. These technologies comprise various approaches to shape materials (e.g. polymers, nanocomposites, metals, ceramics, and soft matter), which include exposure to light of a liquid photosensitive pre-polymer, the deposition of molten polymers, inks, or solutions with suitable viscoelastic properties, and the sintering of powders by focused laser beams.<sup>[300,301]</sup> Among the relevant features of AM and 3D printing technologies it is worth mentioning i) the design flexibility, which allows complex, nonplanar architectures to be realized,<sup>[302]</sup> ii) more efficient use of resources, including a decrease of the material waste compared to top-down manufacturing technologies,<sup>[303]</sup> and iii) the capability of multi-material processing, by which devices with spatially varying composition can be realized in a single step.<sup>[302,304]</sup> To date, piezoelectric materials have been shaped into complex 3D architectures by different AM technologies, including projection micro-stereolithography (Figure 12a),[305-307] direct ink writing,<sup>[304,308,309]</sup> selective laser sintering,<sup>[310,311]</sup> and fused deposition modeling.<sup>[312–315]</sup> To enhance the piezoelectric properties of the printed materials, standard 3D printing equipment can be modified either to perform in situ poling,<sup>[312,313]</sup> or to introduce additional shear strains to the deposited polymer filaments using a rotating extrusion nozzle.<sup>[315]</sup> An example of 3D piezoelectric components made by projection micro-stereolithography is shown in Figure 12b. The 3D component was obtained by dispersing boron nitride nanotubes (BNNTs) in a photocurable polyethylene glycol diacrylate-based resin.<sup>[307]</sup> The surface of the BNNTs was functionalized with 3-trimethoxysilylpropyl methacrylate (TMSPM), which allowed for improved dispersion of the nanofillers in the resin, and improved incorporation of the BNNTs into the polymer network formed upon photopolymerization. This process exploits the crosslinking of the acrylate groups of the TMSPM molecules with the polymer backbone, leading to improved stress transfer from the polymer matrix to the piezoelectric fillers.<sup>[307,306]</sup> Characterization of the piezoelectric properties of the 3D printed structures made from TMSPMfunctionalized BNNTs highlighted a 2.4-fold improvement of the open circuit voltage upon applying a periodic stress by an electromechanical vibrator, compared to non-functionalized BNNTs, while the  $d_{33}$  coefficient was increased by approximately a factor two for the printed components with functionalized BNNTs.<sup>[307]</sup>

Moreover, the shape of the 3D printed materials can be designed to spatially control the stress-strain properties.<sup>[307,306]</sup> Figure 12c-h shows six different printed structures created by 3D printing, ranging from a flat uniform structure ("Film" in Figure 12c), to structures with increasing porosity ("Struct A, B, C" in Figure 12d,e and g, respectively) and complex architectures obtained through a topology optimization for increasing vertical strain ("Struct B-P" and "Struct C-P" in Figure 12f,h, respectively). The latter were designed by maintaining the mass fraction compared to the "Struct B" and "Struct C", respectively. SCIENCE NEWS \_\_\_\_\_\_

![](_page_25_Picture_1.jpeg)

![](_page_25_Figure_2.jpeg)

**Figure 12.** a) Schematics of the projection micro-stereolithography. b) Photographs of a 3D printed piezoelectric component on the tip of a hand model, (i) and (ii), and corresponding SEM images at different magnification, (iii) and (iv). c-h) SEM micrographs of various 3D structured made of BNNT-based composites (cross-sectional views shown in the insets). i) Output voltage obtained with the 3D structures shown in (c)–(h), respectively. j) Measured (left vertical scale, blue symbols) and simulated (right vertical scale, red symbols) output voltage as a function of the mass fraction of the printed 3D structures. Star symbols refer to the topology-optimized structures shown in (f) and (h), respectively. The bulk sample shown in (c) is considered as 100% of weight percentage, while the structures shown in (d), (e), and (g) have 80%, 60, and 40% of weight percentage, respectively. Reproduced with permission.<sup>[307]</sup> Copyright 2020, Elsevier Ltd.

Interestingly, the topologically-optimized structures exhibited the highest output voltage (Figure 12i,j). In another example, 3D architectures made of PVDF by solvent-assisted precipitation and 3D printing were designed to achieve improved performance by exploiting the sample morphology, such as different crosssectional shape of the filaments (cylindrical or elliptical) and different internal microstructures (porous and nonporous).<sup>[316]</sup> Compared to films made by solvent casting, constructs formed by solvent-assisted precipitation showed an increase of 1.5 times of the  $\beta$ -phase content, while cylindrical filaments exhibited an increased deformation and strain compared to elliptical filaments, hence the piezoelectric performance in terms of output voltage, sensitivity, power density and stability was enhanced. He et al.<sup>[314]</sup> fabricated a PVDF-based energy harvester by integrating the electrohydrodynamic (EHD) pulling technology with fused deposition modeling. The piezoelectric construct exhibited a high

 $\beta$ -phase content (92%) which leads to a piezo-potential that was approximately eight times higher than in conventional films. These results were ascribed to the high temperature and voltage applied during the EHD process, which facilitates isothermal crystallization and in situ polarization.

Yuan et al.[317] introduced a highly interesting system realized by 3D printing. They fabricated a multilayered P(VDF-TrFE) energy harvester with a rugby ball-structure that exhibited enhanced piezoelectric properties without extra-processing or annealing. The rugby ball geometry, which consisted of a multilayer of PVDF-TrFE (six thin layers with positive and negative polarization directions along the radial direction that alternated and were electrically connected in parallel) and surrounded by PDMS, employed a flextensional mechanism that converted the applied normal force into an amplified horizontal force. The force amplification factor affected the peak output power, which is also enhanced by increasing the number of layers, where the multilayer structure features a  $d_{33}$  of 130 pC N<sup>-1</sup>, and decreasing the width of the PVDF-TrFE belt led to a higher compressive stress for the same normal load applied. A high power density of 16.4 mW cm<sup>-2</sup> was achieved, corresponding to a 22-fold enhancement compared to a flat architecture. The possibility of enhancing the electromechanical properties of piezoelectric material through structural design was also evidenced in micro-architected lattice structures.[306]

# 3.5. Cooperative Effects and Electromechanical Interaction in Networks

In networks of nanofibers or nanowires, a cooperative effect among adjacent building blocks, that is relevant in enhancing the piezoelectric response of the material, was reported using numerical modeling studies.<sup>[318]</sup> Simulations through a finite element multi-physics environment were able to describe the electromechanical interaction taking place at the microscale between fibers, and demonstrate that the polarization measured along the fiber length depends on the shape of the fiber cross section and on the number of fibers that are in mutual contact. The inter-fiber interaction was analyzed depending on the stacking directions of individual nanostructures, exhibiting a piezoelectric response which is boosted upon an increasing number of contiguous cylindrical fibers by building arrays both in the planar (Figure 13a) and in the vertical direction (Figure 13b). The underlying mechanism, termed a "cooperative effect", was primarily attributed to a restraint of the transverse deformation and a corresponding increase of the transverse stress. Upon building the array along the vertical direction, in addition to the cooperative effect, the reduction of the mechanical stiffness on increasing the thickness of the array leads to a piezoelectric response which is enhanced by almost two orders of magnitude compared to the bulk film. The model was experimentally confirmed by studies of nanoindentation performed on isolated fibers along with arrays of PVDF-TrFE,[318] by bending studies on arrays of PVDF fibers,<sup>[319]</sup> and by piezoforce microscopy on PVDF-TrFE fibers with a variety of architectures based on random, aligned (both individual and superimposed fibers) and multiple fibers arrays<sup>[320]</sup> (Figure 13c). An overall enhancement of the scaffold piezo-response ( $d_{33} = -36.5 \pm 3.8$ pm V<sup>-1</sup> and piezoelectric voltage constant,  $g_{33} = -0.41$  V m

N<sup>-1</sup>) was measured in the multiple fibers array due to the electromechanical interaction among adjacent fibers and the thickness gradient. In order to account for the response of arrays and networks under tensile loading, where a simple stacking model is limited due to the possible separation of fibers, a stochastic piezoelectric network model was introduced by Wang et al.<sup>[321]</sup> where fibers exhibit both a uniform or normal distributed orientation and where the fibers interaction was sim-

ness gradient. In order to account for the response of arrays and networks under tensile loading, where a simple stacking model is limited due to the possible separation of fibers, a stochastic piezoelectric network model was introduced by Wang et al.<sup>[321]</sup> where fibers exhibit both a uniform or normal distributed orientation and where the fibers interaction was simulated using cross-linkers (Figure 13d,e). The electromechanical studies of the response of the network highlighted that the effective elastic constants and piezoelectric stress constants depend linearly on the relative density of fibers, which was consistent with a deformation mechanism of the networks dominated by stretching. This analysis can be applied to other classes of filaments and manufacturing processes, regardless of their constituent material, thus stimulating further research. For example, Liu et al.<sup>[322]</sup> developed piezoelectric  $\beta$ -PVDF architectures where the piezoelectric output voltage, sensitivity, and response time were tailored by the design of 3D latticed cells with customized inter-filament spacing. Figure 13f(i) shows a standard cell composed of filaments homogeneously distributed in each layer, with the same interlayer distance along the z-axis direction, while Figure 13f(ii) shows a sandwiched structure where two types of layers alternate along the *z*-axis direction: one layer with a denser margin and a sparser central area, and the other layer with a complementary distribution. By changing the 3D interconnected architectures, the inhomogeneous density distribution led to a different internal stress distribution (upon applying the same external pressure), thus affecting the piezoelectric performance. The maximum piezoelectric output measured for the sandwiched structure (8.6 V on applying a periodic compression using an external force of 100 N), was over two times greater than the voltage measured by the standard cell. A summary of the strategies adopted to enhance the piezoelectric coefficient of materials and which have been discussed in this Section is presented in Table 6. In addition, Figure 14 highlights the enhancement factor for the different classes of materials discussed. [99,207,209-211,213,214,223,231-233,241-243,250,255,265,294,296,307,320,323-326]

Overall, the enhancement strategies discussed above have led to piezoelectric materials with improved properties, with specific examples of polymers and perovskites featuring a  $d_{33}$  coefficient similar to materials currently used in commercial devices. Despite such advancements in the piezoelectric response, some limitations are still present. For example, blending materials to form a nanocomposite architecture is a valuable strategy for improving the piezoelectric properties. Using this approach the properties of the matrix and the nanofillers are synergistically exploited, as well forming specific electroactive phases in the matrix enhanced through interactions occurring at the nanofiller/matrix interface. The primary limitations are related to the maximum amount of nanofiller that can be uniformly dispersed in a matrix and the potential aggregation of the nanofillers. In general, a tradeoff has to be determined, which is typically examined empirically, in order to determine the maximum concentration of the nanofillers to achieve the maximum enhancement. Similar considerations also apply to material processing, such as electrospinning and 3D printing. For example, while the electrospinning process can effectively enhance the piezoelectric properties, there are stringent requirements in terms of molecular weight,

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![](_page_27_Figure_1.jpeg)

**Figure 13.** Dependence of output voltage distribution on the number of aligned fibers for horizontally (a) and vertically (b) stacked fibers. Nanofibers have either circular (red circles) or rectangular (black squares) cross-section. Reproduced with permission under the terms of the Creative Commons CC-BY-NC license.<sup>[318]</sup> Copyright 2014, The Authors, published by WILEY-VCH GmbH. c) PFM amplitude and phase images of random, aligned individual fibers, aligned superimposed fibers, and dense array of fibers (multiple fibers) which shows the highest piezoelectric coefficient. Reproduced under the terms of the Creative Commons CC-BY license.<sup>[320]</sup> Copyright 2021, The Authors, published by Wiley-VCH GmbH. d) Representative volume element adopted in a stochastic model to describe the complex fiber network composed of fibers (long blue lines) with uniformly distributed fiber orientations in the  $x_1$ - $x_3$  plane. e) High magnification view of (d) which highlights cross-linkers (short red line) used in the model to connect adjacent long fibers. Reproduced with permission.<sup>[321]</sup> Copyright 2021, Elsevier Ltd. f) 3D view of two examples of 3D piezoelectric cell design: i) standard and ii) sandwiched structure. Reproduced with permission.<sup>[322]</sup> Copyright 2022, Wiley-VCH GmbH.

concentration, and viscoelastic properties of the starting solution, which can limit the number of polymers, nanofillers, and solvents that can be used for manufacturing nanofibers. The chemical modification strategies have demonstrated a significant potential for improving the piezoelectric properties, despite the existence of constraints such as the anion and cation size, as defined by the Goldschmidt tolerance factor for perovskites. A synergic combination of the various enhancement strategies and an integration of the different processing/patterning technologies can be pursued for overcoming the limitations of the single methods and further enhancing the piezoelectric properties.

Materials	Enhancement method	d <sub>33</sub> of pristine materials [pC N <sup>-1</sup> ]	$d_{33}$ of optimized materials [pC N <sup>-1</sup> ]	Enhancement factor, $\xi^{\rm a}$	Refs.
P(VDF-TrFE) copolymers	MPB	-30 <sup>b)</sup>	-63.5	III	[207]
P(VDF-TrFE-CTFE) copolymers	MPB	≈-28.5	-55.4	94	[209]
P(VDF-TrFE-CFE) and P(VDF-TrFE) alloy	MPB	12 <sup>c)</sup>	32 <sup>c</sup> )	167	[210]
(TMFM) <sub>x</sub> (TMCM) <sub>1-x</sub> CdCl <sub>3</sub>	MPB	≈220 <sup>d)</sup>	$\sim$ 1540	600	[11]
P(VDF-TrFE-CFE) with <2mol% of fluorinated alkyne monomers	Chemical substitution	I	- 1050	I	[66]
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>3</sub> CdBr <sub>2</sub> Cl <sub>1x</sub> I <sub>x</sub>	Chemical substitution	≈68	324	376	[213]
[Me <sub>3</sub> NCH <sub>2</sub> Cl]-CdBrCl <sub>2</sub>	Chemical substitution	≈220 <sup>e)</sup>	440	100	[214]
P(VDF-TrFE) with PEDOT:PSS electrodes	Penetrating electrodes	≈20 <sup>c)</sup>	86 <sup>c)</sup>	330	[223]
P(VDF-TrFE) with GeSe nanosheets	Nanocomposites	15.94	27.92	75	[231]
P(VDF-TrFE) with SnSe nanosheets	Nanocomposites	≈15	25.06	67	[232]
PVDF and TiO <sub>2</sub> nanoparticles	Nanocomposites	-15	-30	100	[233]
P(VDF-TrFE) and Galn nanodroplets	Nanocomposites	≈14	51.1	265	[241]
PVDF with functionalized BTO nanoparticles and liquid nanodroplets	Nanocomposites	14. I	60.2	327	[242]
P(VDF-TrFE) nanotubes	Nanostructuring	20	44	120	[243]
Porcine skin gelatine	Nanopatterning	4	24	500	[250]
PZT	Nanopatterning	75	130	73	[255]
Amino acid crystals	Mechanical annealing	0.1 <sup>f)</sup>	1.2 <sup>f)</sup>	1100	[265]
PVDF with DA	Electrospinning	≈22 <sup>c)</sup>	59.4 <sup>c)</sup>	170	[396]
PVDF-TrFE and polycarbonate	Electrospinning of core-shell fibers	23.49	49. 1 <sup>c)</sup>	011	[323]
PVDF with Sm-PMN-PT particles and $\text{Ti}_3\text{C}_2\text{T}_{x}$ nanosheets	Electrospinning of nanocomposite	≈26	66	154	[294]
Polyethylene glycol diacrylate-based resin with TMSPM-functionalized BNNT	3D printing and nanocomposite	6 ≈	≈13.5	50	[307]
PVDF-HFP/Li-KNN	3D Printing of lamellar metamaterial	16.1 <sup>g)</sup>	150 <sup>(h)</sup>	832	[324]
P(VDF-TrFE) with TMSPM-functionalized BTO particles	3D printing and nanocomposite	17	35	106	[325]
P (VDF-TrFE)	Fiber alignment and cooperativity effects in dense arrays	16.92	36.5	911	[320]
MDABCO-NH $_41_3$ and polyvinyl chloride	Nanocomposite and electrospinning	14	175	1150	[326]
<sup>a)</sup> The enhancement factor, $\xi$ , is calculated as: $\xi = \frac{d_{o}^{\text{polimized}} - d_{o}^{\text{pristine}}}{d_{o}^{\text{sistine}}} > away from the MPB region is considered, i.e., C_{\text{UPF}} = 65 \text{ moles}, 0/v_{e}$	× 100, where $a_{33}^{\text{optimized}}$ is the piezoelectric alues of the modulus of the $d_{33}$ coefficients.	coefficient of the material upon it ([d <sub>33</sub> ]). The copolymer P(VDF B), (1, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2,	optimization, and $a_{33}^{\text{pristine}}$ is one o -TrFE-CFE) is considered a pristin	f the pristine materials; <sup>b)</sup> d <sub>33</sub> of t <del>/</del> e material; <sup>d)</sup> d <sub>33</sub> of (TMCM)CdCl	ne copolymer 3; Equivalent

Table 6. Examples of methods for the enhancement of the piezoelectric properties of materials.

![](_page_28_Picture_6.jpeg)

![](_page_28_Picture_7.jpeg)

![](_page_29_Figure_2.jpeg)

Figure 14. Graphical illustration of the enhancement factor of the modulus of the  $d_{33}$  coefficient for perovskites, composite materials, polymers, and natural materials. Data from Table 6.

# 4. Applications in Energy Harvesting and Soft Robotics

The sections above have overviewed the key performance criteria for piezoelectric harvesting, the range of piezoelectric material classes that are available, and the strategies that can be employed to enhance functionality. Specific examples of the use of piezoelectric materials in energy harvesting and their application for soft robotics are now examined.

### 4.1. Recent Applications and Directions in Energy Harvesting

Recent developments in terms of energy harvesting performance, characterization methods, and their potential for soft robotic applications are outlined here. In terms of recent developments, to improve the properties of ferroelectric polymers, Abdolmaleki et al.<sup>[327]</sup> employed interfacial engineering, with aminefunctionalized graphene oxide (GO) to tailor the intermolecular interactions with PVDF-TrFE to facilitate the formation of the ferroelectric  $\beta$ -phase. This led to an improved harvesting figure of merit of  $d_{33}$ ,  $g_{33} = 14 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ , which is higher than PVDF in Table 1. Composites of ferroelectric ceramic particles in the ferroelectric polymer matrix have been formed to combine the mechanical compliance of a polymer with the high piezoelectric activity of a ferroelectric ceramic. To achieve this goal and to overcome the need for a poling process, Huang et al.<sup>[328]</sup> applied a dynamic pressure during the manufacture of a PVDF/BTO composite with a high  $g_{33} \approx 1610 \times 10^{-3}$  Vm N<sup>-1</sup>. Interestingly they also provided a density-specific voltage coefficient  $g_{33}^{ds} = g_{33}/\rho$ , where  $\rho$  is the density. The  $g_{33}^{ds}$  figure of merit was thought to be suited to the selection of materials for applications that required low weight, such as soft robots. Composites were also formed by Mahanty et al.,<sup>[329]</sup> who produced a polyaniline-coated P(VDF-TrFE)/BTO nanocomposite nanofiber mat by electrospinning, which exhibited a high harvesting  $FOM_{33} = d_{33} \cdot g_{33} \sim 144$ 

×10<sup>-12</sup> m<sup>2</sup> N<sup>-1</sup>. The high performance was thought to be due to the presence of barium titanate nanoparticles which led to interfacial interactions between the nanoparticles and the P(VDF-TrFE) chains to improve the amount of the ferroelectric  $\beta$ -phase in the nanocomposite. In addition, the electrically conductive properties of the polyaniline coating were thought to facilitate charge transport.

A novel approach to producing polymer composites was the use of a thermophilic BKH2 bacterial strain to produce a porous biocompatible bio-organic piezoelectric PVDF film for harvesting.<sup>[330]</sup> The bacterial protein was thought to interact with the PVDF chain to induce the formation of a polarised ferroelectric  $\beta$ -phase, increase the level crystallinity, and engineer the microstructure to form a porous, soft, and flexible piezoelectric film. The resulting porous material exhibited a harvesting  $FOM_{33} = d_{33}.g_{33} \approx 18.8 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ . Modeling demonstrated that the presence of porosity leads to stress concentrations and higher deformation strains, leading to an enhanced output.

Porosity was also exploited by Yan et al.<sup>[227]</sup> to produce highperformance energy-harvesting ferroelectric ceramics, which exhibited potential for both sensing and energy-harvesting applications. The presence of porosity reduced the relative permittivity to improve the piezoelectric voltage coefficients (see Equation 4) and the harvesting figures of merit (Equation 7) since both are inversely proportional to permittivity. Their approach combined a highly aligned porous structure, to facilitate the polarization of the ferroelectric, with a multi-layer architecture, to increase the thickness/volume of material for harvesting (Equation 6). The intelligent use of aligned porosity in the ferroelectric ceramic led to the formation of a composite material that exhibited a high  $d_{33}$  $\approx$ 354 pC N<sup>-1</sup> and a low relative permittivity at constant stress of  $\varepsilon_{33}^X \approx 556$ . As a result, the materials exhibited a high  $g_{33} \approx 72 \times$  $10^{-3}$  Vm N<sup>-1</sup> for sensing and a high  $d_{33}g_{33} \approx 25.5 \times 10^{-12}$  m<sup>2</sup> N<sup>-1</sup> for energy harvesting;<sup>[331]</sup> these values are higher than that of dense PZT ceramics in Table 1. In addition, the pores can also

![](_page_30_Picture_0.jpeg)

![](_page_30_Figure_2.jpeg)

**Figure 15.** Historical evolution of the harvesting figure of merit ( $FoM_{33}$ ) for different classes of piezoelectric materials.

be filled with a polymer to provide a degree of toughness and flexibility, making them more compatible with soft robots. It is worth highlighting that recent advances in the synthesis of perovskites materials have led to the achievement of high levels of piezoelectric activity ( $d_{33} \sim 440 \text{ pm V}^{-1}$  and  $g_{33} \sim 6215 \times 10^{-3} \text{ V m N}^{-1}$ ) in a hybrid perovskite crystal, through the softening of the metal-halide bonds that increase the lattice deformation and charge formation under the application of an external electric field or stress.<sup>[214]</sup> The availability of methods to embed these materials into soft elastomeric matrix could enable further progress in the field of robotics.

An exciting approach, which is relevant to the area of soft robotics, was recently reported by Hu et al.<sup>[213]</sup> who developed molecular ferroelectric materials with a unique combination of soft mechanical properties, coupled with high piezoelectric charge  $(d_{ij})$  and voltage coefficients  $(g_{ij})$ . By bond engineering a molecular ferroelectric, a solid solution based on  $C_6H_5N(CH_3)_3CdBr_2Cl_{0.75}$   $I_{0.25}$  exhibited a high piezoelectric charge constant of  $d_{33} = 367$  pc N<sup>-1</sup> and a very high voltage constant of  $g_{33} = 3595 \times 10^{-3}$  Vm N<sup>-1</sup>; this led to a giant harvesting figure of merit  $(d_{33}\cdot g_{33} > 1200 \times 10^{-12} \text{ m}^2 \text{ N}^{-1})$  which greatly exceeds that of piezoelectric materials shown in Table 1, such as PZT and PVDF. These impressive piezoelectric properties were combined with a low stiffness (0.8 GPa), making them well-suited to harvesting and sensing applications for soft robots.

The historical trend of the energy harvesting figure of merit,  $FoM_{33} = d_{33} \cdot g_{33}$ , for the different classes of materials here reported is highlighted in **Figure 15**.<sup>[44,180,207,213,214,233,237,327,328,329–369]</sup> This shows that efforts towards the synthesis of new perovskites and composite materials with high  $FoM_{33}$  values have largely increased in the last five years.

When considering the properties of piezoelectric materials, it is important to make some additional considerations regarding the measurement systems that are used to determine parameters such as the open-circuit voltage and short-circuit current. Su et al. pointed out the contradiction between the measured output voltage and the theory-predicted open-circuit voltage of the piezoelectric devices,<sup>[370,371]</sup> as shown in **Figure 16**a. They experimentally found that the output voltage significantly relies on the resistance of the voltmeter used. The measured voltage has a peak value of  $\approx$ 0.2 V and  $\approx$ 2 V when using the voltmeter with a resistance of 10 M $\Omega$  (Figure 16b) and 55 G $\Omega$  (Figure 16c), respectively.<sup>[371]</sup> This discrepancy was explained by the leakage of charges through the resistance of the voltmeter. Further experiments showed that the output voltage was related to the strain rate when a voltmeter with relatively low resistance is used, whose value was not reported in many works. An easy-to-use standard was proposed to ensure the open-circuit condition, requiring the resistance of the voltmeter to be greater than a critical value in terms of the effective capacitor, loading frequency, and accuracy requirement of the measured voltage. The influence of the inner resistance of the voltmeter on the output voltage was also found in an electrospun PVDF nanofiber mat,<sup>[372]</sup> which converts the mechanical energy into electrical energy via the piezoelectric, triboelectric, and electret effect simultaneously. The measurement circuit and results with the 1 M $\Omega$ -resistance and 1 G $\Omega$ -resistance probe are shown in Figure 16d-f, respectively. This suggests the above findings exist in many other mechanical-to-electrical energy converters such as the triboelectric and electret devices. The frequency-response behavior of piezoelectric voltage, which is important for the piezoelectric sensor, can also be influenced by the inner resistance of the voltmeter. Qiu et al. found that the output voltage enhances with the increase of the stimuli frequency and is stable beyond a critical frequency which decreases with the increases of the inner resistance of the voltmeter.<sup>[373]</sup> This feature can be used to adjust the frequency range of the piezoelectric sensor or ensure less critical frequency dependence. Nadaud et al. found the asymmetric phenomenon when measuring the output voltage with a commercial large-resistance voltmeter or a simple buffer circuit.[374] The peak voltages that were measured were quite different when connecting the voltmeter to the piezoelectric device in a forward and reverse way (Figure 16g). A double buffer circuit was then developed to not only ensure the high impedance of the measurement circuit, but to also avoid the generation of asymmetric voltage signals. The output performance when the piezoelectric device is connected to an AC-DC converter, also termed a rectifier, is important, in particular for piezoelectric energy harvesters. Nadaud et al. showed that using different types of rectifiers and diodes with different reverse leakage currents and threshold voltages induces different average voltages (Figure 16h).<sup>[375]</sup> Electrical current measurements were systematically studied by Zhang et al.<sup>[376]</sup> who analyzed the influence of the device capacitance and the load resistance on the current output characteristics both experimentally and theoretically. A maximum peak current (MPC) that is unaffected by strain rate (Figure 16i), but has a linear relationship with the magnitude of the applied force, was proposed. It is therefore considered a suitable standard to evaluate and compare piezoelectric performance.

A procedure was then rationally designed to measure the MPC with high accuracy and stability. Specific examples of the use of piezoelectric materials for soft robotics are now outlined.

### 4.2. Soft Robotics

Robots based on soft materials (known as *soft robots*) have several advantages compared to rigid robots: they are able to undergo large deformations, adapt to arbitrary geometries, execute complex actions, and withstand impacts without self-damage.<sup>[10]</sup>

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![](_page_31_Figure_1.jpeg)

**Figure 16.** Measured output voltages and currents of piezoelectric devices depend on the properties of the measurement circuit. a) Contradiction between the theoretical and experimental voltage of the piezoelectric device. Output voltage of the piezoelectric device was measured with b) 10 MΩ-resistance and c) 55 GΩ-resistance voltmeters. a–c) Reproduced with permission.<sup>[371]</sup> Copyright 2017, Elsevier Ltd. d) Schematics of the circuit for measuring the open-circuit voltage of mechano-electrical energy conversion. Measured voltage curve with the e) 1 MΩ-resistance and f) 1 GΩ-resistance probe. d–f) Reproduced with permission.<sup>[372]</sup> Copyright 2022, Elsevier Ltd. g) Voltage measured by the Keithley electrometer and double buffer circuit when connecting forward and reverse. Reproduced with permission.<sup>[374]</sup> Copyright 2018, AIP Publishing. h) Average voltage measured when different circuit topologies and diodes are used as a function of the resistive load ( $R_L$ ). FW stands for fullwave rectifier and LVD stands for Latour voltage doubler. Reproduced with permission.<sup>[375]</sup> Copyright 2021, Elsevier Ltd. i) Strain rate independent output current measured by the rationally designed procedure. A constant force was applied by a 0.5 kg weight and the strain rate was varied by changing the impact velocity in the range: 2.5–50 mm s<sup>-1</sup>. Reproduced with permission.<sup>[376]</sup> Copyright 2016, Elsevier Ltd.

Therefore, they are appropriate for many applications, including those requiring a safe interaction with fragile objects, people, animals, and the surrounding environment.<sup>[377]</sup>

The design of soft robots usually requires integrating different components for their movement, sensing capability, and control. Given their stimuli-responsive behavior, piezoelectric materials may make a valuable contribution to the design of soft robots. They can be used for different purposes, including actuation, powering, and sensing, as discussed in the following.

### 4.2.1. Actuators for Soft Robotics

Soft actuators are key actors responsible for the motion of soft robots and are generally classified based on the method employed for their actuation. Accordingly, different types of soft materials can be used to realize soft actuators. A review of these materials is beyond the present scope, and the interested reader is referred to comprehensive reviews and books for details.<sup>[10,378,379]</sup> The present section will focus on the state-of-the-art piezoelectric

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systems employed for soft actuation and robotics, and it will also discuss current challenges and future perspectives in the field.

Today, piezoelectric-based actuators are attracting significant attention in the creation of soft robots as a result of their fast and reversible response, good electro-mechanical coupling (Table 1), low weight, possible wireless actuation, high actuation frequency, large operation bandwidth, high precision, simple control, easy modulation of electronic signals, and suitability for high-force applications.<sup>[10,12,13]</sup> Moreover, they can be easily integrated into robotic systems since they require only a power supply without complex additional systems (e.g., magnetic/optical devices, air pumps). In contrast, they generally require large voltages that may be non-trivial to supply, in particular for untethered robots.<sup>[10,13]</sup> In this respect, developing low-voltage piezoelectric materials is an important research focus for future advances in soft actuators.

Soft actuators have been engineered from both rigid piezoelectric materials as ceramics (e.g., PZT, <sup>[380,381]</sup> PMN-PT, and PZN– PT),<sup>[382]</sup> and soft polymer-based piezoelectric materials [e.g., PVDF and P(VDF-TrFE)].<sup>[13,383–388]</sup> Using metal-free perovskites as soft actuators is still rare. Only a few papers exist which suggest that halide-based perovskites might be relevant in electrostriction applications <sup>[389,390]</sup> and in non-toxic biomedical microelectromechanical systems actuators (see ref. [43] and references therein).

Piezoelectric materials usually generate relatively high forces (in particular, piezoelectric ceramics with high stiffness) but limited actuation strains; for example, Evenchik et al.[391] reported strain values lower than 0.5% and 7% for PZT and PVDF-TrFE or poly(vinylidene difluoride-trifluoroethylene) copolymers, respectively. Therefore, the strain must be amplified mechanically for many practical robot-based applications. Nevertheless, soft organic piezoelectric materials are a good actuator choice due to their high mechanical flexibility and ease of preparation. In particular, PVDF has good mechanical strength and chemical resistance, is thermally durable and stable, and can blend with organic/inorganic compounds.<sup>[392]</sup> The addition of conductive fillers, such as carbon nanofibers (CNF), carbon black (CB), graphene, carbon nanotubes (CNTs), and ionic liquid (IL), is also widely used to enhance PVDF electromechanical properties, as discussed previously. Furthermore, changes in actuator properties, including stiffness/thickness reduction and drivability improvement, can help in achieving high-performing actuators, as in examples made for haptic device applications via a printing process using a composite material made of P(VDF-TrFE), singlewalled carbon nanotubes (SWCNTs), conductive polymers, and GO.<sup>[393]</sup> The actuators were driven at high frequencies, resulting in displacements almost double than that of the pure actuator, and in an increased mechanical life.

Based on these discussed features, piezoelectric actuators are particularly suited for soft microrobots that necessitate precise, lightweight, and easy-to-miniaturize components.<sup>[12]</sup> In this regard, a variety of solutions have been proposed, and they can be classified according to the mechanism by which the microrobots achieve mobility. For a detailed discussion and classification that distinguishes between ambulatory, friction-based, flapping-wing, amphibious, and swimming locomotion, the reader is referred to ref. [12].

As an example of ambulatory locomotion, a tethered, legged robot based on a flexible piezoelectric bimorph PVDF actuator

was proposed<sup>[394]</sup> (**Figure 17**a), with a flat main body (50 mm x 10 mm) and two pre-curved legs, each of 20 mm length. Its deformation in the elongation direction was generated after applying a voltage across the actuator in the poling direction: one film of the bimorph actuator elongates while the other shrinks since the PVDF films were connected in series. It is worth highlighting that the main aspect to consider when focusing on ambulatory locomotion-based microrobots is their robustness to failure and damage tolerance. Individual legs may be sensitive to failure,<sup>[395]</sup> and therefore their cyclic behavior has to be carefully analyzed both from the experimental and design point of view.

As an example of friction-based locomotion, Wu et al.<sup>[396]</sup> reported on insect-scale (3 cm  $\times$  1.5 cm) soft robots that were based on a tethered curved unimorph structure made of an 18-umthick layer of PVDF, two 50-nm-thick Pd/Au electrodes, a 25µm-thick adhesive silicone layer, and a 25-µm-thick polyethylene terephthalate substrate. The ferroelectric PVDF layer was shown to produce a periodic extension and contraction by the converse piezoelectric effect when subject to an alternating voltage. The robots were able to climb slopes and carry loads that were six times their own weight at about one-sixth of their original speed. Using electrostatic footpads, an untethered version with greater mobility and agility was also proposed.<sup>[397]</sup> The robot was loaded with 1660 mg due to the control circuit, a battery, and photoresistors and was able to follow a 27.9 cm-long "S"-shaped path in 36.9 s. Liu et al.<sup>[381]</sup> proposed a tethered millirobot (length of 58 mm and weight of 42.55 g) that was composed of three piezoelectric segments, each made of a leg segment (2A12 duralumin) and eight PZT elements made from PZT-4. The millirobot demonstrated a variety of features such as a high resolution (0.44 µm), fast response (dozens of milliseconds), high agility and adaptability, and broad speed range (516.3-0.26 mms) depending on the excitation scheme and ground type (Figure 17b). It could also carry loads (up to 4.7 times of its own weight), climb slopes, and cross obstacles (Figure 17b). In general, friction-based locomotion robots are stable and can move on different types of grounds, however their performance may be affected by surface properties.<sup>[12]</sup>

Among the flapping-wing locomotion-based robots, the first tethered 60 mg robotic insect was developed in 2008.<sup>[398]</sup> More recently, low-power PZT actuators and onboard solar cells have enabled short-term untethered flight, with durations in the order of seconds (Figure 17c).<sup>[380]</sup> Ma et al.<sup>[399]</sup> used voltage-driven piezoelectric PVDF bimorphs to achieve a flapping-wing robot with a 3 cm wingspan and an 80 mg weight. The robot used high-power density piezoelectric flight muscles that could generate a lift force higher than 1.3 mN. It is noted that the main challenges for achieving high-performance flapping-wing robots include the development of efficient actuators with a high lift-to-weight ratio and the capability to handle air disturbances to stabilize the flight. Despite these challenges, this type of locomotion is not hindered by obstacles on the ground.<sup>[12]</sup>

Both amphibious and swimming microrobots provide versatility and have advantages in a variety of applications, such as biomedical drug delivery and underground system monitoring. However, they are generally restrained to aquatic environments.<sup>[12]</sup> To increase their versatility, Chen et al.<sup>[400]</sup> developed a 1.6 g quadrupedal microrobot that can walk on land,

![](_page_33_Picture_0.jpeg)

![](_page_33_Figure_1.jpeg)

**Figure 17.** Examples of piezoelectric-based microrobots capable of different types of locomotion: a) ambulatory, b) friction-based, c) flapping wing, and d) both amphibious and swimming. a) Schematics of the robot consisting of a main body with two legs, and of its fabrication procedure. Reproduced under terms of the Creative Commons CC-BY license.<sup>[394]</sup> Copyright 2019, The Authors, published by Springer Nature. b): i) Robot exhibiting different velocities on different substrates (glass, acrylic, iron, wood, paper, and marble); ii, iii) it can run through a transparent tube with point contact or climb the tube with a dip angle of 9.8°; iv) it can cross different obstacles such as: gully, pothole, and bump. Reproduced under terms of the Creative Commons CC-BY license.<sup>[381]</sup> Copyright 2021, The Authors, published by Wiley-VCH GmbH. c, i) Photograph of robot with four wings and a wingspan of 3.5 cm, solar cells, and drive electronics. ii) Frame of a time-lapse video of an untethered flight. Reproduced with permission.<sup>[380]</sup> Copyright 2019, The Author(s), under exclusive license to Springer Nature Limited. d) Photograph of robot illustrating hybrid locomotion possibilities: walking on ground, swimming on a water surface, diving into the water, walking underwater, and emerging from the water-air interface. Scale bar: 5 cm. Reproduced under terms of the Creative Commons CC-BY license.<sup>[400]</sup> Copyright 2018, The Authors, published by Springer Nature.

swim on water, and transition between the two (Figure 17d). The authors started from the so-called Harvard ambulatory microrobot (i.e., a 1.43 g and 4 cm  $\times$  2 cm  $\times$  2 cm quadrupedal robot with eight independently actuated degrees of freedom) to enable locomotion on the water surface, governable sinking, as well as the transition from underwater to land. Two piezoelectric actuators were used to control the swing and lift motion of each leg. About 10  $\mu$ m of Parylene C were added as a coating to avoid electrical shorts circuit underwater.

These examples highlight that the control of microrobots is essential to achieve stability and movement precision, follow specific trajectories, and avoid environmental interference. This issue was addressed by adding dampers, or using neural network strategies.<sup>[12]</sup> In general, piezoelectric materials are appealing in terms of achieving high levels of control due to their nano-positioning capability, especially when combined with closed-loop control.<sup>[401]</sup> Accordingly, Chen et al.<sup>[401]</sup> developed nanoscale self-bending soft actuators based on PZT/shape memory polyurethane (SMPU) composites. The choice of using PZT particles and an SMPU matrix was motivated by the high biological compatibility of the SMPU matrix and the extensive use of PZT actuators in a variety of nanotechnological tools. Without controlling environmental parameters, these actuators could self-bend with the largest displacement error of  $\pm 8$  nm.

To employ piezoelectric actuators at a larger scale, researchers have exploited the advantages of other actuation approaches in combination with piezoelectric material features. As an example, Gariya et al.<sup>[392]</sup> recently proposed the combination of a tethered soft pneumatic actuator with a piezoelectric membrane consisting of a dielectric PVDF matrix and IL. On the one hand, the membrane provided high deformation, a rapid stimuli response, low density, tunable morphology, low cost, flexibility, resilience, as well as ease of fabrication. On the other hand, the pneumatic actuator, which also had a low fabrication cost, showed large deflection, fast reaction speed, and significant output force. The resulting combined actuator (120 mm long, 20 mm wide, and 19 mm high), fabricated using multi-step casting and molding techniques, was tested for finger rehabilitation (**Figure 18**a).

Overall, piezoelectric-based robots require functionalization strategies to be significantly extended beyond the simple motion of the robot.<sup>[13]</sup> Future perspectives include integrating sensing capabilities to promote autonomous interaction with the surrounding environment, or adding new functions for feedback and closed-loop control.<sup>[12]</sup> Sensing capabilities may include tactile sensing, crack detection, and sensing for health monitoring. Furthermore, the combination of piezoelectric materials with other smart materials provides a route to create new systems with multiple functionalities, improved performance (i.e., reduced brittleness or increased deformability), and programmable behavior to adapt to specific application needs or to dynamic environmental conditions.<sup>[402]</sup> This combination has been proposed by Guan et al.<sup>[403]</sup> who prepared multi-functional

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![](_page_34_Figure_1.jpeg)

**Figure 18.** Example applications of piezoelectric actuators in the biomedical and tissue engineering field. a) Rehabilitation exercise of index finger using a tethered soft pneumatic actuator with a piezoelectric membrane. Reproduced with permission under Creative Commons CC-BY-NC-ND license.<sup>[392]</sup> Copyright 2023, The Authors, published by Elsevier Ltd. b) Photographs showing grasping (1-4) and removal (5-9) of a thrombosis sample using PLLA fibers controlled by an applied voltage. Reproduced with permission.<sup>[409]</sup> Copyright 2005, Taylor & Francis. c) In vivo regeneration of rat cranial defects using AESO-10ATP scaffolds. Microcomputed tomography images of the cranial defect site at four and eight weeks in sagittal view and top view (left side). Hematoxylin and eosin staining (top right side) and Masson's trichrome staining images of scaffolds embedded in tissues after implantation for eight weeks (bottom right side). High-magnification images of scaffolds in the edge and central area of defects (abbreviations: S, scaffold; NB, new bone; HB, host bone). Reproduced with permission.<sup>[410]</sup> Copyright 2023, Wiley-VCH GmbH.

nanofibers from PZT particles and SMPU by electrospinning. Due to the combination of a shape memory and piezoelectric effect, the PZT/SMPU nanofibers could be deformed easily by varying the temperature, could adapt to complex structures, and could be employed to harvest energy from external sinusoidal vibrations. An advanced 3D printing approach for creating multi-functional piezoelectric components was employed for manufacturing lightweight, untethered metamaterial-based microrobots.<sup>[404]</sup> Cui et al. used a multi-material additive manufacturing technique to combine piezoceramic, metallic, and

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structural materials.<sup>[404]</sup> Walking robots with distributed sensorimotor capabilities were produced by printing piezoelectrically active lattices with spatially programmed actuators and electrode features.

This latter example highlights the importance of new processing and manufacturing techniques for further developing piezoelectric actuators to improve their design freedom, provide control over the orientation and polarization directions. Selfassembly methods, inkjet printing, 3D printing, and electric fieldinduced alignment methods have addressed these issues.<sup>[155]</sup>

As a further topic of discussion, it is important to highlight that piezoelectric materials have significant potential in the field of bio-actuators and biomedical devices.[405-408] A limited number of inorganic piezoelectric materials are biocompatible (such as BTO, ZnO, and quartz), although many materials can become biocompatible after being encapsulated. Organic materials, such as PVDF, PLLA (Figure 18b),<sup>[409]</sup> and PDLA, are also biocompatible. In this framework, it is worth highlighting the recent use of piezoelectric actuators in the tissue engineering field, particularly for tissue regeneration. The piezoelectric effect might play a crucial role in the regeneration process of tissues, which can be found in some mammalian tissues, e.g., those containing collagen, such as bone, cartilage, ligaments, and tendons. Accordingly, many studies have focused on the use of piezoelectric materials (e.g., ceramic materials such as BTO, lithium sodium potassium niobate, LiNbO<sub>3</sub>, and KNN) in bone defect positions to control the physiological electrical microenvironment and to promote bone regeneration. Recently, Li et al.[410] proposed to combine the advantages of shape memory polymers (including biocompatibility, processability, and shape memory effect) and BTO (including high piezoelectric coefficient and biocompatibility) to manufacture scaffolds for bone regeneration (Figure 18c). Specifically, novel piezoelectric acrylate epoxidized soybean oil (AESO) scaffolds doped with piezoelectric TMSPM grafted on the surface of the PDA-coated BTO nanoparticles (pBT) and then loaded with Ag nanoparticles (Ag-TMSPM-pBT, ATP) were prepared via digital light processing. The AESO scaffolds doped with 10 wt% Ag-TMSPM-pBT nanoparticles (labeled as AESO-10ATP) exhibited promising piezoelectric properties, similar to the piezoelectric constants of bone tissue (i.e., a piezoelectric coefficient of 0.9 pC N<sup>-1</sup> and an output current of 146.4 nA). In addition, these scaffolds exhibited good shape memory function by quickly recovering their original shape under near-infrared light irradiation. Despite these recent successes, several challenges still need to be overcome for a better use of piezoelectric materials in biotechnologies and in bio-medicine, and the use of natural biopolymers is a relevant research direction to explore, as discussed in Section 2.5.

Finally, it should be highlighted that, due to the wide range of actuation materials and stimuli, no standard protocols or parameters are available to characterize and define the performance of piezoelectric soft actuators and robots. At present, important parameters that need to be considered and reported include the generated force, strain and stress field, response time, size, reliability (in terms of cycling tests), electric stimulus parameters (frequency, amplitude, distance from the actuator), and shelf life. Work in this direction still needs to be undertaken in the near future, towards improved standardization and commercialization of piezoelectric-based soft actuators and robots.

### 4.2.2. Energy Harvesting of Soft Robots

Power and energy sources have a crucial role in the actuation and operation of soft microrobots.<sup>[12]</sup> Despite this importance, power and energy source delivery still represents one of the most challenging topics.<sup>[11-13,411-415]</sup> In this context, among the advantages of piezoelectric-based actuators, as mentioned previously, there is the possibility of wireless actuation via, e.g., batteries, radio-frequency and photovoltaic power supply, or energy harvesting technology. These solutions are advantageous compared to heavy and bulky tethered devices, as demonstrated by the previously discussed untethered examples. However, commercial technologies, such as lithium-ion and lead-acid batteries, may have limited capacity and need fluid circuits and high-voltage converters. Moreover, the volume and mass of batteries are still more rigid and bulky than the soft robot, which may limit the robot's dexterity. Piezoelectric energy harvesters, solar cells, and nanogenerators represent potential solutions to be adopted in the near future to overcome these challenges, as largely discussed in ref. [12]. Lu et al.<sup>[416]</sup> examined a soft millirobot system that couples magnetic and piezoelectric effects for applications in a variety of in vivo and in vitro biomedical settings (see Figure 19). While a magnetic particle/PDMS composite limb was used to impart locomotion to the robot under an externally applied magnetic field, a flexible piezoelectric ceramic composite film was used to recover energy. Under the application of the external magnetic field, the millirobot was able to achieve remote locomotion, environmental monitoring, and wireless communication without the need for an onboard battery or external wired power supply. The soft and flexible construction of the robot, including the piezoelectric harvester, enabled stretching, compressing, bending, and twisting of the robot. The multilayer piezoelectric harvesting element consisted of a ceramic piezoelectric foam composite based on the 3D interconnected ceramic structure, two electrode layers to collect charge, and structural substrates (PI and PDMS film). The piezoelectric ceramic element served as both an energy harvester and an interface to provide a sensing capability.

Since charge is generated by an applied force, as in Equation (1), piezoelectric materials are often described as 'selfpowered sensors'; this contrasts with other forms of sensor, such as piezo-resistive sensors that require the application of current to measure the resistance. The porous nature of the piezoelectric ceramic foam facilitated infiltration by a PDMS polymer during the fabrication process to provide mechanical flexibility for soft robot applications. The piezoelectric foam exhibited a highpressure sensitivity (10–30 mV kPa<sup>-1</sup>) in a large pressure range (kPa–MPa) with good stability. The use of foamed ceramics also provides the potential to reduce the permittivity and increase both the sensitivity  $(g_{33})$  and harvesting figure of merit  $(d_{33} \cdot g_{33})$ , see Equations 4 and 7). When subjected to a compressive load of 10 N, as in Figure 1a, the output voltage and current were 20 V and 50 nA, and during bending at a range of curvatures, as in Figure 1b, the outputs were up to 3.5 V and 20 nA. Long-term testing of up to 10,000 cycles was also undertaken, and it would be interesting to characterize and use the harvesting energy in more detail.

A number of harvesting soft-robots have been inspired by fish or sea-life. Salazar et al.<sup>[417]</sup> investigated the integration of a

![](_page_36_Picture_0.jpeg)

![](_page_36_Picture_1.jpeg)

![](_page_36_Figure_2.jpeg)

**Figure 19.** a) Schematic of the milli-scale device, showing wireless communication module, piezoelectric energy generator, and multilegged soft robot. b) Illustration of fundamental robot functions: achieved combining locomotion and tapping mode; locomotion, interface sensing, and wireless communication are executed concurrently. c) voltage response on being stretched, pressed, bent, and twisted. Reproduced under Creative Commons CC-BY license.<sup>[416]</sup> Copyright 2020, The Authors, Published by WILEY-VCH GmbH.

piezoelectric energy harvester in a bioinspired fish-like aquatic unmanned vehicle. Their modeling-based research examined the development of a non-linear fish-like robotic energy harvesting model to identify the complexities related to the undulatory motion of the robot. The impact of non-linear properties on the activation of super-harmonic resonances and parametric resonance was explored. For potential mass manufacture applications, Matharu et al.<sup>[418]</sup> examined the 3D printing of biologically inspired soft robots for safe robot-animal interactions (**Figure 20**a). This work examined the design, development, and swimming performance of flexible thermoplastic polyurethane printed biomimetic jellyfish soft robots, whose natural frequency of actuation, which was achieved using shape memory alloys, was similar to that of natural jellyfish. Energy harvesting of water oscillation and free vibrations was demonstrated using a twistron harvester and a piezoelectric composite that was integrated into the robot (Figure 20b). The harvested energy was used to supply low-power electronics, including an LED display and communications. For the harvesting elements, two MFCs were located diametrically opposite to

![](_page_37_Figure_1.jpeg)

Figure 20. a) Schematic sectional views of the robot, with an indication of dimensions and subcomponents. b) Illustration of the energy harvesting setup using MFCs integrated with jellyfish bell, c) setup of MFCs and 3D printed strain sensors on silicone skirt, d) voltage vs resistance plot at different actuation frequencies for MFC (8528-P2 type), e) power vs resistance plot for different actuation frequencies. Reproduced with permission.<sup>[418]</sup> Copyright 2023, Elsevier Ltd.

each other in the silicone skirt of the robot. MFCs are PZTceramic fiber-based piezoelectric composites with interdigitated electrodes and have the advantage of being relatively mechanically flexible and also commercially available (Figure 20c). The robot-harvester combination was subject to a range of flow frequencies (1.35, 0.65, and 0.4 Hz) to demonstrate the feasibility of the concept. The output voltage for different flow frequencies and load resistances varied from 40 mV to 400 mV, while the output power varied from 0.1 to 15  $\mu$ W (see Figure 20d,e).

Using a similar fish-inspired approach, Tan et al.<sup>[419]</sup> undertook detailed experimental studies on a trout-inspired multifunctional robotic fish as an underwater swimming robot and an energy harvester. The piezoelectric elements consisted of MFCs where, for actuation, a pair of MFCs were led out of phase to expand and contract each side of a fin structure to create bending and propulsion. Energy harvesting was also performed using the same materials to convert flow-induced vibrations in the wake of a range of cylindrical bluff bodies in a water tunnel into electrical energy. This again demonstrates the multi-functional nature of piezoelectric materials, where both the direct and converse piezoelectric effects can be used for harvesting/sensing or actuation. For energy harvesting, the flexible tail of the fish was positioned in the wake of a cylindrical bluff body. When the shed vortex frequency was at the first vibration mode of the fish tail, it yielded an average electrical power of 120 µW at resonance due to large displacements for a water flow speed of 0.3 m s<sup>-1</sup> and a bluff body

of diameter 28.6 mm. A potential application of this approach is that the swimming robot can rest behind a bluff body to harvest energy from any shedding vortices. It was highlighted that the harvested power is lower than the one needed for locomotion, and the harvested energy might power small sensors, such as in ecological monitoring. Likewise, if the swimming robot can rest in a vortex field for a sufficiently long period, it may be able to harvest and store sufficient energy for a short-term swimming mission for relocation.

Kativer et al.<sup>[420]</sup> took an original approach to understand the coupling between the adaptive morphology of a robot, its control, and consequent behavior to harvest energy and increase energy efficiency. Energy harvesting may need to adapt to the morphology of a robot, since the morphology may change the energy usage of a robot and its subsequent behavior and efficiency. This was examined by developing a shape-changing robot based on an elastic structure that achieved locomotion using vibration controlled by a single motor; the dynamics of the robot could be characterized by its resonance behavior. The robot was based on an inverted U-shape curved beam robot (IUCBR), where locomotion was achieved using a DC motor attached to the rear leg, and any resulting vibrations were collected by a PZT-based piezoelectric ceramic element (Mide 509-PPA-1021) that was placed on the other leg of the robot. The shape of the robot could be changed on command to investigate the effects of robot morphology on behavior and energy needs. Using motor control, the control of the shape of the robot, and the harvester operating conditions were

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![](_page_38_Figure_1.jpeg)

**Figure 21.** a) Magnetic-controlled energy harvesting from 3D piezoelectric structures; strain distribution of 3D ribbon with magnetic field, b) image of piezoelectric ribbon at initial and magnetic-controlled states (top) and corresponding time-domain output voltage (bottom). Scale bar: 5 mm (c) images/finite element analysis of strain distribution of 3D piezoelectric serpentine. Scale bar: 5 mm. a–c) Reproduced with permission.<sup>[421]</sup> Copyright 2021, Wiley-VCH GmbH. d) Schematic of (i) synclastic and (ii) anticlastic effect, (iii) structure of the auxetic-piezoelectric harvester. Reproduced with permission under terms of the Creative Commons CC-BY-NC license.<sup>[325]</sup> Copyright 2023 The Authors, published by Wiley-VCH GmbH. e) SEM image of nanowires on silicon. f) Schematics after parylene C and metal deposition on the nanowires. Reproduced with permission.<sup>[424]</sup> Copyright 2017, WILEY-VCH GmbH.

centrally determined, to understand how the coupling between the "brain" and the morphology of the motor could increase energy efficiency via harvesting. It was shown that implementing energy harvesting at the correct time was more important than maximizing the harvesting capacity to increase energy efficiency. It was also shown that the shape of the robot affects the level of energy usage during locomotion and that energy harvesting can feedback additional energy to affect robot behavior during motion. The work highlighted how a harvesting robot could deform when moving in confined spaces, minimizing the power needed to vary its shape, as well as maximizing overall energy efficiency.

Buckling and deformation of thin-film harvesters have been considered for soft robotic applications. Han et al.<sup>[258]</sup> exploited a controlled and nonlinear buckling process to convert twodimensional patterned piezoelectric polymer thin films and electrodes, formed by lithography, into sophisticated 3D piezoelectric microsystems. Potential applications were related to robotic interfaces and compliant systems, including multi-functional sensors for robotic prosthetic interfaces with improved responsivity. The 3D piezoelectric microsystems were based on a PVDF middlelayer and outer electrode layers of Cr/Au on the upper and lower surfaces. The low stiffness of the 3D meso-structures provided a route to create complex modes of motion induced by the application of external vibrations, creating opportunities for energy harvesting for small-scale systems. There was also potential for broadband vibrational energy harvesting due to the nonlinear deformation mechanism due to the low stiffness, particularly the serpentine microstructures that were formed or the activation of compressive buckling in the compliant architectures. In addition, the 3D serpentine configurations enable motion operation in multiple directions.

Using a similar approach, Miao et al.<sup>[421]</sup> employed magnetic materials with temporary magnetization as mechanical guidance and assembly processes to convert laser-patterned 2D-magnetic materials into engineered 3D-structures. The 3D soft structures exhibited tailorable mechanical properties and geometries and achieved a range of locomotion mechanisms during the application of a magnetic field (**Figure 21**a). In this regard, energyharvesting systems were demonstrated by coupling the magnetically actuated soft robots with a piezoelectric material to convert mechanical to electrical energy and/or active motion sensing. The novel approach to creating magnetic-controlled 3D soft structures was thought to provide promise for enhanced energy harvesting applications and multimodal sensing, robotic interfaces, and biomedical devices.

The fabrication process began with laser-patterning of a commercial film of a piezoelectric PVDF polymer. A PDMSneodymium iron boron composite (PNC) magnetic actuator film, which formed the basis for the actuation of the soft robot body, was subsequently spin-coated on the patterned piezoelectric PVDF film. The resulting multilayer structure was transferred onto a pre-stretched elastomer substrate; the 3D piezoelectric structure was formed on the release of a pre-strain. A range of shapes was assessed, and the geometrical parameters of the PNC film were shown to determine the level of the piezoelectric output (Figure 21b). To achieve compressive-buckling and magneticcontrolled deformation, serpentine patterns were created with ultralow bending stiffness (14 mN mm<sup>-1</sup>), typically more than one order of magnitude smaller than that of a simple 3D ribbon structure (476 mN mm<sup>-1</sup>; Figure 21c). The combination of the magnetic layer and piezoelectric structure generated a continuous piezoelectric output during magnetic movement, where the peak current reached  $\approx 2 \mu A$  and the maximum power was 0.16  $\mu$ W at a load resistance of 25 M $\Omega$ .

Zhou et al.<sup>[325]</sup> employed a piezoelectric polymer film, due to its mechanical flexibility, as a piezoelectric generator to act as both a sensor and harvester of mechanical energy from the environment. The inherent synclastic effect of an auxetic structure, which exhibits a negative Poisson's ratio, was used to produce an energy harvesting device having a dome-shape with a double-curved geometry, where bending of the energy harvesting element increased the output voltage by over eight times (Figure 21d). The potential applications were to harvest motion and the vibration of machines. In addition to increasing the strain on the piezoelectric materials, the flexible nature of the auxetic structure was able to reduce the operating frequency range. The maximum power density for a 5 mm bending displacement, for a 17 mm curvature, at a frequency of 1.5 Hz was 36 nW cm<sup>-2</sup> when used with a load resistance of 100 M $\Omega$ . As a hybrid approach, Lui et al.<sup>[422]</sup> developed a flexible and stretchable nanogenerator for human motion sensing and information interaction, where the approach was based on integrating piezoelectric and triboelectric principles. The device was based on a piezoelectric PVDF polymer layer and a silicone polymer to provide mechanical flexibility and a high degree of stretchability, up to 33%. Using Morse code and logic gates, both text and logic information could be encoded using an electrical waveform that was created by touching the surface of the nanogenerator. When the device was stretched by a linear motor at frequencies ranging from 1 Hz to 2.5 Hz,  $V_{oc}$  and short circuit charge ( $Q_{sc}$ ) were  $\approx 16$  V and 8.8 nC, respectively. The current density of the device was approximately 166.7 nA cm<sup>-2</sup> at 2 Hz. When attached to an electrical load, the power was  $\approx$ 490 nW, whereas the typical internal resistance was 200 M $\Omega$ . The low power (<1 mW) indicates that such materials are likely more appropriate for sensing applications.

There has also been a wide variety of research related to energy harvesting for wearable applications, where there is also a need for flexible and soft energy harvesting materials and systems<sup>[423]</sup> Dahiya et al.<sup>[424]</sup> reported on an easily fabricated, cost-effective, and industrially scalable process to fabricate a high-performance and mechanically robust nanocompositebased stretchable nanogenerator using a PDMS substrate. The active piezo-layer of the energy harvester was based on piezoelectric ZnO nanowires encapsulated in a Parylene C polymer matrix (Figure 21e,f). An open-circuit voltage of approximately 10 V, a short-circuit current density of 0.11  $\mu$ A cm<sup>-2</sup>, and a peak power of  $\approx$ 3  $\mu$ W was achieved when the harvester was subjected to a vertical compressive force of 13N at 5Hz. When pressed by a human palm, a higher power of 35  $\mu$ W was achieved.

Khanbareh et al.<sup>[425]</sup> produced a porous piezoelectric composite based on adding PZT particles, as a piezoelectric filler, into a flexible polyurethane polymeric matrix to maximize the piezoelectric sensitivity. Porosity was added to improve the piezoelectric voltage coefficient ( $g_{33}$ ) for enhanced sensing performance, where a reduction of the relative permittivity increased the  $g_{33}$ (see Equation 4) and mechanical flexibility. The potential of the sensors for touch-sensing devices was highlighted; the increased  $g_{33}$  also provides a potential for a high energy harvesting figure of merit ( $FoM_{33}$ ). It is also worth highlighting recent novel examples from the current literature, such as microswimmers powered by microalga,<sup>[426]</sup> that can inspire future advances in the field.

# 4.2.3. Energy Harvesting Using External Devices and Power Requirements

One approach to providing additional power to a soft robot of finite dimensions is to employ an external energy harvestin device, which is then tethered to a soft robot. In this regard, Lu et al.<sup>[411]</sup> developed a triboelectric-driven piezoelectric soft robot, which used a rotary freestanding TENG to drive a soft robot that was based on a piezoelectric unimorph with electrostatic footpads. The motivation for energy harvesting was based on the limited capacity of lithium-ion or lead-acid batteries and the need for control circuits and/or high-voltage converters, which can lead to additional overall mass. The soft robot system consisted of a triboelectric nanogenerator for harvesting, a piezo-actuated robot, and a control module. The piezoelectric soft robot was based on a PVDF/PI unimorph actuator that was combined with a support structure and electrostatic footpads. The robot was actuated at its resonance frequency (f = 300 Hz), where the energy for a single actuation cycle was approximately 350 mJ, which led to a  $P_w$  requirement of approximately 100 mW. The soft robot achieved a maximum speed of 10 cm s<sup>-1</sup> and a turning rate of 89.7° per second. A micro-camera was equipped with the soft robot to provide real-time video streaming of the soft robot, enhancing its detection capability.

Ultrasound has been used as an external power source. Zhang et al.<sup>[427]</sup> used an implantable piezoelectric ultrasound energy harvesting device that used highly active Sm-PMN-PT single-crystal elements combined with polydimethylsiloxane layer to provide flexibility and stretchability. A record power density of 1.1 W cm<sup>-2</sup> was achieved in vitro, and a 1-MHz ultrasound signal with an intensity of 212 mW cm<sup>-2</sup> was able to produce an effective output total power of 280 mW. Schematics of the working principle of the device and architecture are shown in **Figure 22a**,b, respectively. Additional photographs show evidence of the stretchable electrical connections with a serpentine configuration (Figure 22c) and of the overall construction flexibility (Figure 22d,e). A low weight (0.78 g) and small size (20.5 mm diameter, Figure 22f) are additional attractive features of this implantable harvester. Although the approach was used in

![](_page_40_Picture_0.jpeg)

![](_page_40_Picture_1.jpeg)

![](_page_40_Figure_2.jpeg)

**Figure 22.** Schematics of the implantable piezoelectric ultrasound energy harvesting device working principle (a) and architecture (b). Photographs highlighting the stretchable electrical connections (c), the device flexibility (d,e), and device size (f). Red lines in (e) indicate the bending angle,  $\theta$ , which is larger than 30°. Reproduced with permission under the terms of the Creative Commons CC-BY-NC license.<sup>[427]</sup> Copyright 2022. The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science.

a biomedical device, the flexible nature of the energy harvester provides scope for deployment in soft robotic applications by employing an externally applied ultrasound or vibrations to produce power.

While piezoelectric materials exhibit a change in polarization with stress to produce charge, a change in polarization with temperature can also lead to the generation of charge; this is termed the *pyroelectric* effect and pyroelectric coefficients, *p*, are shown in Table 1, which are a measure of the charge produced per unit area for a 1 °C change in temperature. This provides scope for using heat as an externally applied, non-contact, and non-mechanical form of energy harvesting. An interesting approach was developed by Zhao et al.,<sup>[428]</sup> who reported on a flexible infrared-driven non-contact pyroelectric generator to harvest a fluctuating heat source that used PVDF and CNTs as electrodes. This approach avoids direct contact between the pyroelectric generator and the

heat source to achieve remote energy transfer using the photothermal and penetrative nature of the infrared light. The output voltage and short-circuit current of a pyroelectric generator based on a CNT/PVDF/CNT multi-layer were reported to be 1.2 V and 9 nA, respectively, when illuminated by a 1.45 W cm<sup>-2</sup> near-infrared laser. When illuminated in a vacuum chamber externally, the pyroelectric generator operated a liquid crystal display. This approach can potentially generate non-contact thermal energy when local mechanical energy sources are unavailable.

Given the range of energy harvesting approaches and the range of power levels reported to date, it is interesting to examine the range of power requirements for soft robots. Johnson et al.<sup>[429]</sup> provided an excellent summary of the power requirements of a range of small-scale robots whose minimum power during motion ranged from 50 mW to 40 mW and posed the important question, 'is it possible to design an autonomous, battery-free robot?' This was combined with a simple but effective linear scaling analysis, which indicated that energy harvesting for robots favors a small-scale approach since the kinetic energy required to reach a target velocity, v, is  $1/2mv^2$ , and the mass, m scales with the robot (characteristic length)<sup>3</sup>. Clearly, many of the power levels reported to date are smaller than 50 mW to 40 mW, necessitating increased power generation and the use of more efficient robots; this has led to the interest in larger external generators.

In addition to the energy requirements, there is a need to consider the overall energy efficiency of the soft robot system, including any input from energy harvesting. To examine this concept, Shui et al.<sup>[430]</sup> developed a framework to evaluate the energy efficiency by considering the efficiency of the energy source and the process of actuation and locomotion to gain insight on how to improve the efficiency of soft robotic systems. The potential for exploiting energy harvesting to provide additional energy to supplement the whole system was also explored. The energy balance includes the energy efficiency of the major components such as the power source, the actuation method, computational units, sensors, feedback systems, and any contribution from energy harvesting. The robot energy harvesting efficiency can be defined as:

$$\eta = \frac{E_{\text{harvesting}}}{E_o} \cdot 100\%$$
(8)

where  $E_{harvesting}$  is the harvested energy, and  $E_o$  is the total energy requirement; in many cases, this is not assessed in the literature. It was noted that the energy efficiency of soft robots reported in the literature, both from an experimental and theoretical viewpoint, is low and often below 0.1%. This was thought to contrast with hard machines, which usually have a higher efficiency. Despite the low power levels reported to date for soft robotic harvesting, this low efficiency may provide a space for energy harvesting to contribute to the overall energy balance.

### 5. Outlook and Future Perspective

The understanding of the properties of piezoelectric materials and the development of effective strategies to enhance their properties have made constant progress in the last decade, with a number of key breakthroughs. Despite such achievements, the increasing demand for portable, flexible and self-powering devices for the Internet of Things and for artificial intelligence applications<sup>[431]</sup> requires additional research effort aimed at creating and discovering new materials and processing methods capable of enhancing a few key aspects: i) the performance and durability of piezoelectric devices for harvesting mechanical energy with improved efficiency and from a broader set of energy sources, ii) the sensitivity of self-powered piezoelectric sensors and iii) actuation strains. Optimizing the material composition by extensive experiments is highly resourceconsuming, but it can be significantly improved using a synergy with simulation and modeling of the electromechanical and piezoelectric properties of materials, aided by machine-learning approaches.<sup>[432,433]</sup> Modelling and advanced calculations of material properties would be critically important for discovering new materials and biomaterials with piezoelectric features. They can effectively drive the experimental efforts, as already demonstrated for various high-temperature ferroelectric perovskites, nanocomposites and biomolecules.<sup>[132,432,433]</sup>

The advent of all-organic perovskites has opened up new possibilities for creating materials with excellent piezoelectric properties. This has been evidenced by the achievement of a piezoelectric coefficient as high as 63 pC  $N^{-1}$  with NDABCO-NH<sub>4</sub>-Br<sub>3</sub>,<sup>[83]</sup> while a device fabricated with MDABCO-NH4I3 exhibited outstanding harvesting capability with remarkable stability over 5,000 bending cycles.<sup>[81]</sup> However, the rapid advancement of this field is limited by the size constrain of organic cations and anions that conform to the Goldschmidt tolerance factor.<sup>[83]</sup> Achieving ferroelectricity in all-organic perovskites is also challenging, as polar molecules preferentially adopt an antiparallel arrangement to minimize electrostatic energy. Moreover, film thickness and charge leakage can significantly influence the piezoelectric performance. Processing of piezoelectric films at higher temperatures can lead to a larger grain size and fewer pinhole defects, but caution must be exercised as excessive processing temperature may induce decomposition. Performance enhancement can generally be achieved by employing a MPB, a technique commonly used in oxide perovskites and recently applied to polymers.<sup>[207,210]</sup> In general, structural engineering and composites can be explored as promising future directions.

However, since the variety and applications of piezoelectric energy harvesting, sensing and actuating devices are expected to increase, the search for new electroactive materials cannot disregard the need for an in-depth assessment of the material life cycle and sustainability. These latter issues are critical to prevent potential raw material shortages and reduce environmental impact. A significant amount of research effort is focused on the synthesis of lead-free compounds, a reduction in processing temperatures and an enhancement of their piezoelectric properties.<sup>[14]</sup> Such studies are crucial for decreasing the environmental impact of disposed piezoelectric devices, as well as for developing piezoelectric sensors and actuators with non-toxic elements, suitable for biological and biomedical applications. Among the various lead-free materials studied to date, KNN has emerged as a potential alternative to PZT, although a thorough life-cycle analysis for KNN has not evidenced significant improvement in terms of the overall environmental impact.<sup>[434]</sup> Regarding the environmental impact issue, the development of sustainable manufacturing technologies for piezoelectric materials is very important. In fact, most of the materials used in large-scale applications entails either high temperature processing, with associated high energy consumption, or the use of hazards chemicals during the synthesis and fabrication. The availability of alternative and lessenergy consuming technologies for processing and fabrication, such as cold sintering and room temperature densification,<sup>[435]</sup> would improve the sustainability of the piezoelectric devices. AM technologies constitute a valuable platform for sustainable manufacturing, since they typically combine a reduction in raw materials waste, with an improvement of the properties of the manufactured materials through the 3D architecture. Methods for recycling and reuse of piezoelectric materials from disposed devices are also urgently needed in view of enhancing the sustainability of piezoelectric components, given that only a few examples of recycling methods have been proposed so far.<sup>[436,437]</sup>

Furthermore, to decrease the environmental impact of piezoelectric materials, naturally "greener" piezoelectric biomaterials

![](_page_42_Picture_1.jpeg)

would be preferable, despite the several challenges that remain open for their implementation in practical applications, where the exploitation of the  $d_{33}$  coefficient would be more convenient than shear effects, such as via the  $d_{15}$  coefficient<sup>[438-440]</sup> (see Section 2.5). At the molecular level, biomaterials exhibit rich functional groups that offer attractive opportunities to modulate their internal electric dipoles by incorporating other ions or polarized molecules. While initial success has been achieved, a fully rational design would benefit from a greater quantitative understanding of the dipole-structure relationship from the molecular level. Macroscopically, controlling the long-range ordering is essential to align their dipoles and maximize their bulk-scale piezoelectricity. Additional driving forces associated with electric fields, interfacial tension, and capillary force are often applied to assist self-assembly. Guided by better knowledge of intermolecular interactions, these strategies can potentially be integrated with other large-scale manufacturing techniques and eventually enable scalable production of piezoelectric biomaterials.

Improving the durability of piezoelectric devices is also important for efficiently managing raw materials. The use of interpenetrating and polymeric electrodes and soft material nanofillers was already demonstrated to enhance the lifetime of piezoelectric devices.<sup>[224,241]</sup> Additional strategies to enhance the device lifetime could exploit materials with self-healing capabilities. Recent reports showed the self-healing capability of piezoelectric sensing devices made by sandwiching elastomeric layers doped with PZT nanoparticles and Ag nanowires, which were used as the piezoelectric and electrode layers, respectively.<sup>[441]</sup> These devices also demonstrated a stable output voltage after cutting and healing cycles.<sup>[441]</sup> Self-healing properties were also obtained in devices with a lactate-based piezoelectric elastomer.<sup>[442]</sup>

The optimization of the energy extraction circuits should also be considered, especially for increasing the output power density of piezoelectric energy harvesting devices. Khan et al. reported on an optimized harvesting circuit, which enhanced the energy extraction by  $\approx$ 500% compared to a conventional harvesting circuit based on a standard full bridge rectifier.<sup>[443]</sup>

The storage of the harvested energy represents another critical challenge for energy harvesting applications. Piezoelectric supercapacitors can offer an integrated solution combining energy harvesting and storage functions.<sup>[444–446]</sup> In these devices, a piezoelectric material, either PVDF or a nanocomposite, might be used as the separator of the supercapacitor.<sup>[444–446]</sup> Recent advances concerning piezoelectric supercapacitors demonstrated the capability of these devices to power optoelectronic components such as LEDs, displays, and portable electronics.<sup>[444,446,447]</sup>

Regarding energy harvesting in soft robotics, most approaches have used kinematic energy harvesting, which aims to couple the energy harvester to the relative movement of different robot parts, and does not rely on inertia or resonance. The concept of inertial energy harvesting has been used for soft robots to a lesser extent. This approach typically depends on the resistance to acceleration of a mass when connected to a base at a single point. In this case, the vibration amplitude is not simply related to the base amplitude when the system is at resonance and can be significantly larger than the amplitude of the base movement; this could be potentially examined to increase power generation for soft robotic applications.

The use of larger external energy harvesting devices or external sources of energy such as ultrasound (for piezoelectric energy) or infra-red (for pyroelectric energy) also provides scope to increase the power level; indeed, there is also potential to combine a range of harvesting approaches, such as photovoltaics. The range of materials examined to date, as outlined in Table 1, are relatively small and often based on well-known materials; in this regard, the recent developments in piezoelectric gels, as outlined by Vijayakanth et al.,[415] can provide new avenues for integrating piezoelectric materials with soft robots. The multifunctional nature of piezoelectric materials for actuation, sensing (vibrations and temperature changes), and harvesting provides potential when used as low-power piezoelectric or pyroelectric sensors. There is a need for more work on energy harvesting and soft robotic systems that consider and employ the holistic framework of Shui et al.<sup>[430]</sup> This is particularly important since work to date indicates that piezoelectric power from harvesting is significantly smaller than the total power requirements, necessitating an increase in energy harvesting output, a reduction in soft robot power requirements, or applying such materials primarily as sensors or actuators.

From a future perspective, blue energy, consisting of scavenging kinetic energy from seawater (sea currents and sea waves), is one of the most promising and attractive renewable energy sources that could be harvested using piezoelectric devices. According to recent estimations,<sup>[448]</sup> the average wave energy along the world's coasts is approximately 40 MW per km, and sea currents have several advantages, including high predictability and wide distribution. It follows that such kinetic energy is highly promising as input of next-generation energy harvesting devices (specifically named blue energy harvesters), which, in turn, could be used to provide a stable power supply to a distributed network of marine sensors for monitoring turbidity, temperature, pH, pressure and chemical substances as chlorophyll, nitrate and oxygen, to name a few examples. The current technological solutions for ocean exploration and offshore applications based on soft robotics were reviewed by Aracri et al.<sup>[449]</sup> highlights energy consumption and efficiency with a brief overview of energy recovery approaches.

While electromagnetic and triboelectric harvesters appear to be the most promising in terms of high power density and output voltage,<sup>[448]</sup> the development of efficient and high-power piezoelectric devices can represent a further direction of growth. In this respect, piezoelectric systems can offer mechanical advantages such as reduced size (lateral size and thickness), mechanical flexibility, and low-cost manufacturing processes. An et al. propose an interesting example of an ultrathin and flexible piezoelectric harvester based on nanofibers.<sup>[450]</sup> A simple device architecture consisting of a mat of electrospun fibres of P(VDF-TrFE) with embedded ferroelectric barium strontium titanate nanoparticles and Al foils as electrodes was successfully used to harvest gravitational water waves in a house-made wave motion device. A similar device architecture was reported by Ghosh et al., where a gadolinium-doped hematite-based PVDF membrane was exploited under a water flow, generating approximately 8 V.<sup>[451]</sup>

The design of hybrid devices that combine various harvesting mechanisms represents a valuable strategy for enhancing the performance of piezoelectric nanogenerators. Different

![](_page_43_Picture_1.jpeg)

nanostructured materials that are suitable for combining triboelectric, piezoelectric, photovoltaic and thermoelectric harvesting mechanisms in hybrid devices have been studied.[452-454] Overall, the use of hybrid harvesters combining energy conversion capabilities from different sources such as triboelectric and electromagnetic<sup>[455]</sup> and triboelectric-electromagnetic and piezoelectric<sup>[456]</sup> effect is an intriguing direction. Hybrid technologies allow for joint advantages and enable efficient energy harvesting under different conditions and in a wide range of operating frequencies, thus increasing the overall system performance and robustness. Such devices can also efficiently be used underwater to harvest the kinetic energy of near-surface water waves, currents, and tides. A successful prototype example was reported by Ahmed et al.,<sup>[7]</sup> who describes a blue harvester designed to convert into electricity the hydrokinetic energy generated by ocean currents in shallow water within the neritic zone of the ocean. The nanogenerators can generate a voltage of  $\approx 400$ V, with a power of 200 mW, and are used to power two wireless sensors (pH and turbidity) for application in the environmental monitoring of oceanic water. A microcontroller was connected to the device circuitry (which includes a battery and a rectifier) and to the sensors through a Bluetooth circuit for data collection and parameter monitoring.

Although several challenges need to be addressed, the emerging frontiers in materials science presented here offer exceptional opportunities for improving energy harvesting technologies and for the more widespread use of piezoelectric and ferroelectric systems in modern applications, including soft robotics.

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### **Conflict of Interest**

The authors declare no conflict of interest.

### **Keywords**

energy harvesting, energy materials, ferroelectrics, piezoelectricity, soft robotics  $% \left( {{{\left[ {{{c_{\rm{m}}}} \right]}_{\rm{max}}}} \right)$ 

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Adv. Mater. 2024, 36, 2405363

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![](_page_51_Picture_4.jpeg)

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![](_page_51_Picture_6.jpeg)

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![](_page_52_Picture_4.jpeg)

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![](_page_52_Picture_6.jpeg)

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