Prospects of Metal-Free Perovskites for Piezoelectric Applications

Han-Song Wu, Bayu Tri Murti, Jitendra Singh, Po-Kang Yang,* and Meng-Lin Tsai*

Metal-halide perovskites have emerged as versatile materials for various electronic and optoelectronic devices such as diodes, solar cells, photodetectors, and sensors due to their interesting properties of high absorption coefficient in the visible regime, tunable bandgap, and high power conversion efficiency. Recently, metal-free organic perovskites have also emerged as a particular class of perovskites materials for piezoelectric applications. This broadens the chemical variety of perovskite structures with good mechanical adaptability, light-weight, and low-cost processability. Despite these achievements, the fundamental understanding of the underlying phenomenon of piezoelectricity in metal-free perovskites is still lacking. Therefore, this perspective emphasizes the overview of piezoelectric properties of metal-halide, metal-free perovskites, and their recent progress which may encourage material designs to enhance their applicability towards practical applications. Finally, challenges and outlooks of piezoelectric metal-free perovskites are highlighted for their future developments.

1. Introduction

Since first discovered in 1839, thousands of compounds in the perovskite (ABX$_3$, where A and B are cations and X is an anion, respectively) structure shown in Figure 1 have been reported.[1] Various applications such as capacitors, piezoelectric devices, and ferroelectric devices have been designed by using traditional inorganic perovskite materials, such as barium titanate (BTO, BaTiO$_3$) and lead zirconate titanate (PZT, PbZr$_x$Ti$_{1-x}$O$_3$).[2,3] Recently, metal halide perovskites have attracted wide attention due to their remarkable properties, such as high absorption coefficient, tunable bandgap, high power conversion efficiency, mechanical flexibility, and low-cost processing.[4] These intriguing properties make them potential candidates for various electronic and optoelectronic applications such as diodes, photodiodes, high-efficiency solar cells, light-emitting diodes, and sensors.[4–6] In addition, they have also been studied to exhibit ferroelectric and piezoelectric properties which are comparable to conventional perovskites.[3,7–10] However, the toxicity of the lead component in both conventional PZT and most of metal halide perovskites hinders the development of such materials for practical applications, especially for eco-friendly electronics. Therefore, the development of lead-free perovskites has become an urgent matter. Fortunately, a new class of metal-free halide perovskite materials has been reported to exhibit significant piezoelectricity very recently, making them ideal candidates for future piezoelectric applications.

The piezoelectricity is usually observed in materials with noncentrosymmetric crystal structures which can produce electrical energy upon the external mechanical stimuli or displacement due to the change in the dipole moment within materials. This conversion of energy was first reported in 1880.[11] Since then, the remarkable discovery of piezoelectricity has facilitated the fast progress of applications including inkjet printing, injectors, actuators, transducers, sensors, ultrasonic wave detectors, speakers, and nanogenerators.[12–15] Over the past several decades, various piezoelectric materials have also been discovered, such as BTO, PZT, zinc oxide (ZnO), polyvinylidene fluoride (PVDF), peptides, amino acids, and proteins.[12,16–22] Among them, PZT has shown great success in practical applications due to its superior piezoelectric coefficient. However, the lead element within PZT is toxic and can be harmful in the future demands of eco-friendly and sustainable products. Therefore, lead-free piezoelectric materials with high piezoelectric coefficient, mechanical softness, and eco-friendly processing were further investigated.[21–31] Among them, metal-free organic halides...
have gained significant attention due to their promising properties such as low-temperature processability, biocompatibility, and high piezoelectric coefficient as compared to traditional ceramics.\[28–31\] The first development of metal-free piezoelectric perovskite materials can be traced back to 2002, when full organic perovskites, which include C_8N_2H_12·NH_4Cl_3·H_2O with 3D corner-sharing structure and C_6N_2H_14·NH_4Cl_3 with 2D face-sharing structure have been reported.\[31\] Recently, quasi-spherical and momentum matching theories have been applied to precisely design a series of metal-free perovskites with polar structures.\[32\] In these studies, materials including MDABCO-NH_4I_3 (MDABCO = N-methyl-N‘-diazabicyclo[2.2.2]octonium) and hmtaH_2-NH_4Br_3 (hmta = hexamethylenetetramine) have been reported to exhibit non-centrosymmetric structures that can induce high ferroelectric and piezoelectric constants.\[33–35\] The schematic representation of these organic perovskites is shown in Figure 2. Thus, these works show a wide diversity of material combinations in metal-free perovskites that can be designed to make a polar structure, enabling the control of ferroelectric, piezoelectric, and optical properties for various applications.

To explore the above-mentioned promising properties of metal-free perovskites, many strategies have been developed for achieving functional electronic, optoelectronic, and ferroelectric devices. However, the fundamental understanding of piezoelectricity and their piezoelectric device applications is still scarce and challenging. Therefore, in this perspective, we explore the molecular design by understanding the symmetry breaking of metal-free perovskites. Later, piezoelectric devices and applications due to the control of structure and composition will be discussed. Finally, the potential and challenges of metal-free perovskites will be highlighted since these novel designs can provide new possibilities to further extend the applications of metal-free perovskites.

2. Design Theories

2.1. Symmetry Breaking

It has been investigated that the origins of both ferroelectricity and piezoelectricity arise from non-centrosymmetric crystal structures. A slight displacement of cations can effectively induce structure distortion.\[36,37\] This kind of phenomenon can be observed in the family of oxide perovskites having titanium as the B-site cation, such as CaTiO_3, SrTiO_3, BaTiO_3, and PbTiO_3.\[38\] For organic–inorganic hybrid perovskites, it was not until recently that the effect of organic cation has been reported to play a role in the symmetry-breaking mechanism.\[39\] As shown in Figure 3, the quasi-spherical theory is a phenomenological theory based on the Curie’s symmetry principle.\[32,35,40\] By modifying the spherical cation to a low-symmetric quasi-spherical geometry and combining it with the momentum matching of cation and anion, a molecular rotation can be formed at a suitable rate (Figure 3a–c).\[32,35\] In addition, the self-polarization of the material is dominated by the number of polarization directions.\[41\] Therefore, the symmetry change induced by the quasi-spherical modification results in the production of multi-axial materials. The highly ordered dipole directions and dipole switching behaviors in the polycrystalline state become ideal properties for ferroelectric/piezoelectric applications.

2.2. External Stimulus

It is very crucial to induce the phase suitable for piezoelectric applications.\[42\] Piezoelectric materials, such as PVDF exhibiting piezoelectricity in β-phase.\[43\] It was reported that electric field or heat can be used to facilitate the formation of β-phase in PVDF-based piezoelectric generators.\[44\] In addition, by adopting electric field-induced phase transition or structure distortion, inorganic metal-halide perovskites such as CsPbBr_3 can show higher piezoelectric constants. The piezoelectric coefficient (d_33) increases from 7.7 to 40.3 pm V\(^{-1}\).\[45\] In addition, the PbBr_6 octahedra in the orthorhombic lead bromide can be well-aligned by applying an electric field.\[46\] Similar strategy can also be applied to 3D metal-free perovskites to improve piezoelectricity. As for the heat-induced piezoelectricity, a new type of metal-free perovskite H_2DABCO(NH_4)(BF_4)_3 has been synthesized serving as a temperature-stimulus responsive material (TSRM) due to a low phase transition temperature at ≈332–333 K.\[47\] This type of TSRM can be adopted in specific devices that switches piezoelectric response into different temperatures.
2.3. Morphotropic Phase Boundary

To design materials with high piezoelectric response, a morphotropic phase boundary (MPB) is a versatile feature to enhance electromechanical properties of lead-based and organic lead-free perovskites.[48] MPB materials display transition regions in composition phase diagrams where materials change their lattice structure abruptly with a lower energy barrier of polarization rotation, indicating a high coupling of strain and polarization.[49,50] Indeed, MPB is a phase coexistence area in the phase diagram correlated to the competition of the two phases with different orientations of polarization.[51] It has been discovered that higher electro-mechanical coupling efficiency occurs within the MPB to exhibit a large piezoelectric constant ($d_{33}$) due to polarization rotation between two competition phases in perovskites.[50] Meanwhile, it should also be noted that some critical factors are required to form a solid solution MPB. The requirements are shown as below:

1) Goldschmidt tolerance factor: a stable perovskite structure should obey the tolerance factor between the range of 0.825–1.059.[52] When it comes to determining a composition of solid solution, the tolerance factor can be a tool to evaluate whether the structure will be stable.

2) Solubility: the solubility acts as a key role in forming a solid solution MPB since low solubility will cause phase separation and limit the final composition.[53,54]

3) Slope of the phase boundary in the phase diagram: the slope of the phase boundary is critical to the phase stability under transition.[55] By adjusting the composition, the MPB phase can be stable in a wider temperature range.[55,56]

Previously, many researchers have focused on tuning the MPB of PZT in which the largest piezoelectric constant can be obtained with a Zr/Ti ratio of 52:48.[25] Recently, a halide perovskite molecular solid solution (TMFM), (TMMCM)$_{1-x}$CdCl$_x$ has been demonstrated to show a piezoelectricity stronger than PZT.[32] However, this type of solid solution faces toxicity issues due to the presence of cadmium ions. Therefore, non-toxic metal-free perovskites such as MDABCO-NH$_4$Br, exhibiting a high $d_{15}$ piezoelectric response ($d_{15} = 248$ pm V$^{-1}$) and A-site cation variability, have become ideal candidates for developing a non-toxic halide perovskite molecular solid solution MPB.[36,57]

2.4. Design Route

In general, the toxicity and stability of the perovskite’s devices are the two foremost issues to be considered prior to designing eco-friendly and highly efficient metal-free perovskites.[58–60] The fundamental chemical design offers an efficient route by considering the ionic radius and formal charge neutrality, and replacing toxic elements with low/non-toxic elements.[60–64] For instance, Pb$^{2+}$ in lead-halide perovskite was first replaced by divalent Sn$^{2+}$ and Ge$^{2+}$ cations due to their adequate charge balance and coordination.[65,66] Interestingly, first-principle studies and machine-learning methods (ML) have been recently employed to predict and provide the accurate prerequisite and rational design of the materials for structurally stable and low-toxic metal-free perovskites.[60,67,68] The systematic high-throughput simulation with first-principle studies (or density-functional theory [DFT] calculations) offers a plausible tool to design and explore the material’s structure and electronic properties particularly to screen the most probable candidates from a large material database.[67,69] ML in conjunction with DFT calculations have been employed to efficiently discover inorganic double perovskites structures as well as hybrid (organic–inorganic) halide perovskites (e.g., C$_2$H$_5$0InBr$_3$, C$_2$H$_5$OSnBr$_3$, and C$_3$H$_7$NSnBr$_3$) for stable, non-toxic, and highly efficient solar cells development.[70–74] ML technology has also been applied to design Pb-free BTO-based piezoelectrics with large electrostrains.[75] ML and DFT could also be useful to evaluate the structure–property relationship of the material candidates such as to map the bandgaps, band structures, and density-of-states of the novel materials for highly stable and environmentally friendly metal-free perovskites.[67,76,77] In piezoelectric-induced metal-free perovskites, the use of DFT and ML in combination with experimental observation may accelerate the discovery of highly efficient, stable, and low/non-toxic perovskites materials.
3. Properties and Applications

Inorganic materials exhibit piezoelectricity from the displacement of ions inside crystals. As the inorganic piezoelectric materials undergo an external electric field, the atomic structure of the crystal changes in such a way that the balance of ions shifts and a dipole moment is produced. To develop net polarization in the crystal, the generated dipole should not be canceled out with other dipole moments present in the unit cell of the crystal. Therefore, the piezoelectric atomic structure should be non-centrosymmetric. On the other hand, in the case of organic materials, the piezoelectricity arises due to the reorientation of molecular dipoles within the materials and can be obtained under the application of high electric field and stretching. Recently, various organic materials such as PVDF, glycine, collagen, and silk have been widely investigated. Unlike inorganic piezoelectric materials, PVDF exhibits a negative piezoelectric constant ($d_{ij}$) attributed to the self-consistent quantum redistribution of electron molecular orbitals, the shifting of charged atomic nuclei, and the dipole reorientation upon the application of electric field. Most recently, metal-free perovskites including C4N2H12-NH4Cl3-H2O, C6N2H14-NH4Br3-H2O, and hmta-NH4Br3, (H2DABCO)-NH2NH3+-(ClO4)3 have been successfully synthesized to show their potential in ferroelectric and piezoelectric applications.[31,34,78–81] A breakthrough on metal-free organic perovskite ferroelectrics has been reported to include 23 new compounds with a general formula of A(NH4)X3 (A = divalent organic cation and X = Cl, Br, or I). Of these, MDABCO-NH4I3 has been reported to show a spontaneous polarization of 22 mC cm$^{-2}$ (close to that of BTO), a high phase transition temperature of 448 K (higher than BTO), and 8 obvious polarization directions.[33]

Further, the piezoelectric constant ($d_{ij}$) of organic MDABCO-NH4I3 has been reported as 14 pC N$^{-1}$, which is lower than many competing materials (Table 1). However, simulation results show that MDABCO-NH4X$_3$ type metal-free perovskites exhibit large piezoelectric strain components in the $d_{ij}$ direction (Figure 4a), which can be originated from the large elastic compliance (Figure 4b).[57] It reveals that MDABCO-NH4X$_3$ type metal-free organic perovskites are good candidates for various piezoelectric applications as pressure sensors, actuators, generators, and piezotronic devices.

Moreover, as shown in Table 1, the huge differences in piezoelectric constants of metal-halide perovskites and metal-free perovskites can be attributed to several structural factors, such as phase transition, dependence on polar direction, and elemental composition. Typically, the piezoelectric constant can be expressed by Equation (1) below:

$$d_{33} = 2Q_{33} \varepsilon_{33} P_r$$

where $d_{33}$ is the piezoelectric coefficient, $2Q_{33}$ is the electrostrictive constant, $\varepsilon_{33}$ is the permittivity, and $P_r$ is the remanent polarization.[82] The above formula could be further written in tensor form where piezoelectric constants of different directions are involved. As shown in Equation (2) below:

$$d_{ij} = \frac{\partial S_{ij}}{\partial E_m} = \frac{Q_{ijk}P_i}{E_m} \frac{\partial P_j}{\partial E_m} + \frac{Q_{ijk}P_i}{E_m} \frac{\partial P_j}{\partial E_m}$$

$$= Q_{ijk}P_i \varepsilon_{jm} + Q_{ijk}P_i \varepsilon_{jm}$$

| Material | Piezoelectric constant [pC N$^{-1}$] | Reference |
|----------|----------------------------------|-----------|
| MDABCO-NH4I$_3$ | $d_{33} = 14$ | [36] |
| CH$_3$NH$_3$PbI$_3$ | $d_{33} = 5.12$ | [83] |
| PVDF | $d_{33} = 34$ | [84] |
| Poly-L-lactic acid (PLLA) | $d_{33} = 11$ | [28] |
| Cellulose nanocrystal | $d_{33} = 2.61$ | [85] |
| ZnO | $d_{33} = 3$ | [86] |
| GaN | $d_{33} = 3.1$ | [90] |
| PZT | $d_{33} = 290$ | [13] |
| BaTiO$_3$ | $d_{33} = 190$ | [91] |
| NaNbO$_3$ | $d_{33} = 52.5$ | [92] |
| Disopropylammonium bromide (DIPAB) | $d_{33} = 11$ | [93] |
| LiNbO$_3$ | $d_{33} = 11$ | [28] |
| ImClO$_4$ | $d_{33} = 41$ | [94] |
| Croconic acid | $d_{33} = 5$ | [95] |
| Triglycine sulfate | $d_{33} = 22$ | [28] |
| Nylon | $d_{33} = 2$ | [28] |
| [Me$_2$NCH$_2$ClMnCl$_3$, (TMCM-MnCl$_3$)] | $d_{33} = 185$ | [28] |
| TMCM-ClO$_3$ | $d_{33} = 220–240$ | [28] |
| N$_4$+Bi$_4$(Pb$_{0.003}$Fe$_{0.003}$)$_{1-x}$O$_{3}$ (BNBT-100:Fe, x = 0.01) | $d_{33} = 168$ | [28] |
| Ba$_2$(Ti$_x$Zr$_{1-x}$)$_2$O$_7$ (Ti$_{2.00}$Ca$_{0.00}$)$_2$O$_7$ | $d_{33} ≈ 620$ | [98] |
| (Ba$_{2.00}$Ca$_{0.00}$)$_2$O$_7$ (Ti$_{2.00}$Zr$_{0.00}$)$_2$O$_7$ | $d_{33} ≈ 755$ | [99] |
| CuO-doped (Ba$_2$(Ca$_{0.00}$)$_2$(Ti$_{0.00}$)Sn$_{0.00}$)$_2$O$_7$ | $d_{33} = 683$ | [100] |
| Bi$_2$O$_3$(Nd$_{0.5}$Ti$_{1.10}$, Mn$_{0.10}$O$_{3-δ}$ (BNMT100000x, x = 0.25%) | $d_{33} = 105$ | [101] |
| Zr-modified Bi$_{2}$O$_3$(Na$_{0.78}$K$_{0.22}$)$_2$Ti$_3$O$_9$ ceramics (BNKNTZ-100, x = 0) | $d_{33} = 168$ | [102] |
| Bi$_2$O$_3$(Na$_{0.78}$K$_{0.22}$)$_2$Ti$_3$O$_9$-xCuO (x = 0) | $d_{33} = 146$ | [103] |
| 0.93Bi$_2$O$_3$(Nb$_{1.10}$Ti$_{0.90}$)(Bi$_{0.50}$Ti$_{0.50}$)O$_3$-xPr$_{0.25}$ (BNBT-xPr, x = 0.003) | $d_{33} = 194$ | [26] |
| [(Bi$_{1.25}$Na$_{1.75}$)$_2$Bi$_{0.05}$(Bi$_{0.05}$)$_{0.05}$] ,La$_2$Ti$_{0.05}$O$_{3-δ}$ (x = 0.02) | $d_{33} = 151$ | [104] |
| (1–x)0.67Bi$_{1.05}$Fe$_{0.05}$O$_3$-0.33BaTiO$_3$ | $d_{33} = 324$ | [104] |
| XBi$_{1.05}$(Zn$_{0.5}$Ti$_{0.5}$)O$_3$ (x = 0.03) | $d_{33} = 402$ | [105] |
| 0.67Bi$_{1.05}$(Fe$_{0.75}$Ga$_{0.25}$)O$_3$-0.33BaTiO$_3$ (x = 0.03) | $d_{33} = 270$ | [106] |
| MnO$_x$-doped (K$_{0.5}$Na$_{0.5}$)$_2$Nb$_2$O$_7$ | $d_{33} = 110$ | [107] |
| K$_{0.4}$Na$_{0.6}$NbO$_3$ | $d_{33} = 220$ | [107] |
| Rhombohedral 0.72 Pb(Mg$_{0.53}$Nb$_{0.47}$)$_2$O$_{3-δ}$-0.28 PbTiO$_3$ (PMN-28PT) | $d_{33} > 1200$ | [109] |

Table 1. Piezoelectric constants of various materials.
GaN, and ZnSnO₃ have become popular candidates owing to piezoelectric pressuresensors (Figure 5). In vitro applications, in vivo applications of using organic films to fabricate using a compressive bandage can be useful and their biodegradability is desired for hygienic purposes. [115] In addition, the biodegradability of metal-free perovskites has yet to be studied, the synergic properties of metal-free and organic molecular plants (Figure 5c–f) have also been developed. [87,116] Although the biodegradability of metal-free perovskites has yet to be studied, the synergic properties of metal-free and organic molecular films were explored as sensor applications due to a low-electric potential induced by polarization will affect the sensitivity of piezoelectric sensors. On the other hand, metal-free perovskites, such as MDABCO-NH₄I₃ which exhibit higher resistivity (i.e., lower mobility and larger bandgap) and strong spontaneous polarization can also be a potential candidate for piezoelectric sensor applications. For example, the fabrication of a ZnO and ZnSnO₃ nanowire-based piezoelectric strain sensors have been designed to exhibit high flexibility and gauge factors (the ratio of relative change in electrical resistance to the mechanical strain). For example, MDABCO-NH₄I₃ has been reported to exhibit the highest piezoelectric constant of d₁₅ = 179 pm V⁻¹ due to its preferred orientation along <111>. [112,114] Additionally, the electromechanical coupling induced by MPB is another reason that certain piezoelectric materials possess remarkable values in d₁₃ (Table 1). However, this mostly occurs in materials with solid solution instead of pure elements.

3.1. Piezoelectric Sensors

Piezoelectric sensors for monitoring physiological signals have become a popular research field due to advancements in wearable electronics technology and the development of Internet of Things (IoT). [110] Notably, lead-free materials like BaTiO₃, ZnO, GaN, and ZnSnO₃ have become popular candidates owing to their excellent environmental friendliness, sustainability, and biocompatibility. [111–114] For example, the fabrication of a ZnO and ZnSnO₃ nanowire-based piezoelectric strain sensors have been designed to exhibit high flexibility and gauge factors (the ratio of relative change in electrical resistance to the mechanical strain) of 1250 and 3740, respectively. [112,114] This can be attributed to the higher polarization of ZnSnO₃ (59 μC cm⁻²) as compared to ZnO (≈5 μC cm⁻²), indicating that the piezoelectric potential induced by polarization will affect the sensitivity of piezoelectric sensors. On the other hand, metal-free perovskites, such as MDABCO-NH₄I₃ which exhibit higher resistivity (i.e., lower mobility and larger bandgap) and strong spontaneous polarization can also be a potential candidate for piezoelectric sensor applications. It has been shown that organic piezoelectric films were explored as sensor applications due to a low-cost and low-temperature processing requirement. The sensors fabricated using a compressive bandage can be useful and their biodegradability is desired for hygiene purposes. [115] In addition to in vitro applications, in vivo applications of using organic films for piezoelectric pressure sensors (Figure 5a,b) and cochlear implants (Figure 5c–f) have also been developed. [87,116] Although the biodegradability of metal-free perovskites has yet to be studied, the synergic properties of metal-free and organic molecular structure are highly desired for achieving the above-mentioned demands.

3.2. Piezoelectric Actuators

The working principle of the actuator is based on the inverse piezoelectric behavior and electrostrictive response induced by Maxwell stress or intrinsic electrostrictive effect. [83] The inverse piezoelectric effect is a first-order electro-mechanical coupling in which strain and electric field show linear relation. As an electric field is applied to a piezoelectric material, localized dipole moments are generated due to the stretching of the material along the direction of the electric field. [83] These mechanisms have been widely applied in ultrasonics, sonars, position controllers, and microelectromechanical systems (MEMs). [117,118] The electrostrictive response is a second-order electro-mechanical coupling in which the strain is proportional to the square of the electric field. The intrinsic electrostrictive response is generated by a harmonic displacement of positive ions and negative ions under applied bias. Maxwell stress originates from the imperfect screening on electrodes where the uncompensated charges form Coulombic interactions and induce the strain. [83,119]

To the best of our knowledge, only few literatures have addressed the electrostriction constant (Q) of metal-free perovskites and their corresponding actuator performance. Nevertheless, it may be inferred from the piezoelectric formula in the tensor form (Equation (2)). The relationship between the piezoelectric coefficient and the electrostrictive coefficient expressed by tensor calculation indicates that electrostrictive coefficient is proportional to piezoelectric coefficient. [83] For example, if a specific perovskite possesses high d₁₅, it also possesses high Q₁₅. Further, the correlation between electric field and polarization is given by Equation (3) below:

$$S_{ij} = Q_{ijkl} P_i P_j = M_{ijkl} E_i E_j$$

where $S_{ij}$ is the strain, $Q_{ijkl}$ and $M_{ijkl}$ are electrostriction coefficients, $P_i$ and $P_j$ are polarizations, and $E_i$ and $E_j$ are electric fields. Herein, the electric field-induced strain is proportional to the square of polarization. Therefore, the metal-free perovskites with high polarization might exhibit good performance in actuator applications.

Previously, a large electrostrictive coefficient ($Q_{15}$) was observed in only relaxor-based ferroelectric materials.
like Pb(Zn_{1/3}Nb_{2/3})O_3–PbTiO_3, Pb(Mg_{1/3}Nb_{2/3})O_3–PbTiO_3, Ba(Zr_{0.2}Ti_{0.8})O_3–(Ba_{0.7}Ca_{0.3})TiO_3, and PVDF composites. The organic PVDF composites-based actuator and tissue stimulator shown in Figure 5g consists of a thin film of PVDF printed with silver ink on both sides as electrodes. Recently, MAPbI_3, an organic-inorganic metal halide perovskite has been reported to exhibit a large electrostrictive response (Q_{33} = -730 \text{ nm}^2 V^{-2}) originated from lattice deformation caused by iodine Frenkel defects. The results suggest that halide-based perovskites might hold a great potential in electrostriction applications due to their low defect formation energy and high defect tolerance. In addition, it has been demonstrated that chirality can induce relaxor properties and bring out striking electrostriction behaviors. The combination of defect-induced deformation and chirality induced electrostriction in metal-free perovskites can provide diverse potential applications in non-toxic biomedical MEMS actuators.

3.3. Piezoelectric Generators

The power shortage problem has been treated as a critical issue for current wearable electronics. Therefore, auxiliary power technologies have been proposed to solve these issues, and...
Figure 6. a) Device schematic of a CsPbBr$_3$ nanogenerator and self-powered physiological signal characterizations from b) coughing/yawning. Reproduced with permission.$^{[129]}$ Copyright 2020, Royal Society of Chemistry. Output of the real-time sensor in terms of waveforms measured from c) wrist, d) neck, e) arm, and f) drinking movements. Reproduced with permission.$^{[130]}$ Copyright 2020, American Chemical Society. Schematics of g) aligned M13 bacteriophage nanopillars and h) the piezoelectric dipole on vertical direction. Reproduced with permission.$^{[21]}$ Copyright 2015, Royal Society of Chemistry.
piezoelectric generator (PENG) is one of the typical examples. Perovskite-based PENGs have been widely investigated in various technological aspects owing to their outstanding piezoelectric properties.\cite{129} The origin of the ultra-high piezoelectric output of inorganic halide perovskite has been discovered as shown in Figure 6a,b.\cite{129} Due to the high piezoelectric constant ($d_{33}$) of $\beta$-phase PVDF, it has also been widely used as the thin film PENG or the matrix of piezoelectric nanocomposites.\cite{86} For example, a self-powered human health monitoring e-skin sensor using highly aligned PVDF nanofibers arrays has also been developed and shown in Figure 6c–f.\cite{130} Other organic piezoelectric materials such as PLA (polylactic acid), chitin, chitosan, cellulose, and even M13 bacteriophage have shown potential as piezoelectric nanogenerators.\cite{21,105,131–133} The characteristics of bacteriophage piezoelectric nanogenerators are indicated in Figure 6g,h.\cite{130} Recently, SnO$_2$ sheet/PVDF nanocomposites with a self-cleaning ability for smart wearable energy harvesters or sensors have also been fabricated and shown in Figure 7a,\cite{134}

Due to the unique properties of lead-based halide perovskites, several attempts have been made in exploring related applications, such as pyroelectric, flexoelectric, triboelectric, and piezoelectric.\cite{85,133–137} For instance, MAPbI$_3$ has been demonstrated to be applicable for PENG design.\cite{85} Additionally, FAPbBr$_2$I/PVDF nanocomposites designed as self-powered integrated wireless electronic node (SIWEN) devices are shown in Figure 7b–e.\cite{138} On the other hand, metal-free perovskites can also possibly be explored due to non-toxicity. According to the simulation results, MDABCO-NH$_4$X$_3$ series have large piezoelectric responses in the $d_{15}$ direction, showing great potential in high power density PENGs to be integrated in Internet of Things (IoT) devices or physiological monitoring systems.\cite{51}

3.4. From Piezoelectronics to Piezotronics

The word “piezotronics” is the combination of “piezoelectrics” and “electronics” that first proposed in 2007 by coupling piezoelectric and semiconducting properties of materials.\cite{139} Piezotronic can be applied to design and fabricate electronic devices, such as piezoelectric-gated diodes, piezoelectric-gated transistors, and piezotronic effect-enhanced photodetectors, solar cells, and light-emitting diodes shown in Figure 8a–
g.139–144 Besides, it can also be widely used in sensors, energy harvesters, human-robotic interfaces, and self-powered devices. For halide perovskite piezotronics, examples including piezotronic-enhanced solar cells and photodetectors have been reported.143,145 It is expected that metal-free perovskites may also contribute to piezotronics devices such as piezotronic enhanced X-ray photodetector or strain gated transistors.145 However, piezotronics devices based on metal-free perovskites are still scarce due to their low mobilities and large bandgaps. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of metal-free perovskites are defined by the A-site organics.64 Therefore, by properly designed A-site cations, it is possible to overcome the barrier of low mobility (DABCO-NH4Br3: 2.08 cm²V⁻¹s⁻¹) and large bandgap (MDABCO-NH4I3: 3.9 eV).133,145 This can largely enhance the potential of metal-free perovskites in either piezotronics or semiconductor applications.

4. Challenges and Outlooks

Although metal-free perovskites have been reported to have outstanding performance in various applications, the stability, durability, and toxicity are still critical issues that remain to be solved. In terms of stability, despite their superior advantages in eco-friendliness and sustainability (compared to lead-halide perovskites or inorganic semiconductors), the recent developments on metal-free perovskites emerge as a crucial challenge on the material and device instability and thereby limit large-scale production as well as commercial feasibility. Substituting a stable metal cation with organic cation apparently diminishes the crystal’s bonding network. Such metal-free perovskites mainly rely on the hydrogen bonding during the formation of ABO₃ crystal, the thermodynamic and environmental stability (i.e., oxygen, moisture, UV light, heat, and chemicals exposure) need to be thoroughly considered and further tested upon the development of highly stable metal-free perovskites.60,64 The most efficient way to enhance the stability and durability of halide perovskites is to encapsulate them with hydrophobic polymer or to develop halide perovskite/polymer composites. Therefore, halide perovskite composites based on biodegradable matrix-like cellulose and PVA have been recently investigated to exhibit strong improvement on stability. Moreover, tuning metal-free perovskites by A-site or X-site substitution has been demonstrated as an effective approach to show distinct properties. For example,
MPB can be utilized to enhance the electro-mechanical properties by inducing the polarization rotation. Furthermore, due to the widely developed techniques for synthesizing halide perovskite nanostructures, engineering metal-free perovskite nanostructures based on nanocrystals, nanoplatelets, nanorods, and nanowires can be considered the next step. For instance, halide perovskite nanoarrays for piezoelectric energy harvesting and miniature photovoltaic devices have been successfully demonstrated. Therefore, it is expected to utilize metal-free perovskites for various applications via effective structure engineering approaches.

5. Conclusion
In this perspective, we have summarized the fundamental mechanisms and recently designed metal halide perovskite-based piezoelectric devices that can possibly be implemented for various metal-free perovskites. The design theories of ABX₃ perovskite structures in terms of symmetry breaking have also been discussed. The factors which induce or enhance the electromechanical property of the organic perovskite such as external stimuli and MPB have also been discussed. Various possible applications of metal-free material-based piezoelectric devices such as piezoelectric sensors, actuators, nanogenerators, piezotronic devices were explained. In the last, challenges and outlooks of piezoelectric metal-free organic perovskites for various aspects were highlighted for future applications.

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Conflict of Interest
The authors declare no conflict of interest.

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Han-Song Wu received his B.S. (2019) and M.S. (2021) degrees in Materials Science and Engineering from National Taiwan University of Science and Technology, Taipei, Taiwan. His current research activities include the synthesis of metal-free perovskites and the fabrication of piezoelectric and wearable devices.
Bayu Tri Murti received his Bachelor’s in Pharmacy from Faculty of Pharmacy, University of Jember, Indonesia. He then pursued his Master’s degree in Department of Chemistry, Durban University of Technology, South Africa. He is currently a PhD student in the Graduate Institute of Biomedical Materials and Tissue Engineering (GIBMTE), College of Biomedical Engineering, Taipei Medical University, Taiwan. His current research concentrates on the development of low dimensional nanomaterials-based biosensors for the detection of neurological biomarkers.

Jitendra Singh received his Ph.D. degree from the Inter-University Accelerator Centre, New Delhi, India, affiliated with Jawaharlal Nehru University, New Delhi. After that, he joined the National Taiwan University of Science and Technology, Taipei, Taiwan as a Postdoctoral Researcher. Now, he is a Postdoctoral Researcher with the National Central University, Taoyuan, Taiwan. His current research interests include the growth mechanism of low dimensional new materials for electronic and opto-electronic devices.

Po-Kang Yang received his MS and PhD degree from the Department of Materials Science and Optoelectronics Engineering in National Taiwan University (NTU), respectively. He is currently an Assistant Professor at Department of Biomedical Sciences and Engineering, National Central University (NCU). After starting his research career at NCU, he puts all his efforts into novel nanomaterials fabrication, multi-functional nano electronic devices design, and system integration for biomedical applications, which include point-of-care diagnosis, an Internet of things (IoT) sensor network, and telemedicine.

Meng-Lin Tsai received his PhD degree from the Department of Materials Science and Engineering in National Tsing Hua University (NTHU) in July 2016. He joined National Taiwan University of Science and Technology (NTUST) as an Assistant Professor in August, 2018. His main research interests are low-temperature and large-scale growth of 2D materials and synthesis of air-stable inorganic perovskite quantum dots for display applications.