

High-Performance Piezoelectric Nanogenerators Based on Hybrid Perovskite Nanomaterials for Energy- Harvesting

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

With the increasing drive to create self-powering nano/micro-electromechanical systems (NEMS/MEMS), maximizing the output performance of piezoelectric nanogenerators (PENGs) is essential. Organic-inorganic halide perovskites (OIHP) have unique advantages over century-old ceramic piezoelectrics, including mechanical flexibility, low-temperature processing, bio-friendliness, structural tunability and low cost, making them ideal candidates for electromechanical energy conversion devices and a wide range of applications. This research explores the piezoelectric properties of OIHPs and applies them to designing efficient piezoelectric nanogenerators. The novel perovskite materials which are studied here include cesium lead halide (CsPbX_3), (4-aminotetrahydropyran)₂ lead bromine chloride ((ATHP)₂PbBr₂Cl₂), (trimethylchloromethylammonium)₂ tin chloride ((TMCM)₂SnCl₆), N-ethyl-1,4-diazoniabicyclo [2.2.2] octonium copper chloride (EDABCO-CuCl₄), formamidinium (FA) lead bromine iodine (FAPbBr₂I), and polystyrene (PS) functionalized FAPbBr₂I. The perovskites are used to fabricate 0-3 type of piezoelectric composites (random distribution) and the PENG operation is assessed under 3-3 operational mode. The perovskite-polymer nanocomposites are employed to harvest mechanical energies from the vibration (< 50 Hz) to produce electricity and to use those nanogenerators as the power source to realize self-powered wireless sensing systems.

Firstly, the dissertation discusses the piezoelectric and dielectric properties of different OIHP nanomaterials and the fundamentals of PENGs (Chapter 1). It also provides insights on halogen regulation, the synergistic effect of molecular dipole rotation with octahedral displacement, and quasi-spherical cation with Jahn-Teller distortion, thus transforming blind material search into a guided design strategy for piezoelectrics. The influence of nanomaterial distribution, geometry, porosity, dielectric constants, force, frequency, and ferroelectric manipulation of the composite film is then systematically analyzed (Chapter 2). Through a series of PENGs that are fabricated, characterized, and evaluated from halogen-tuned (I/Br) piezoelectric CsPbX_3 ($\text{X}=\text{Br}/\text{Cl}$) (including piezo response force microscopy (PFM) and electric measurements), it is revealed that the highest piezoelectric charge constants ($d_{33} \sim 47$ pC/N) and output power density ($24 \mu\text{W}/\text{cm}^2 \cdot \text{N}$) come from the CsPbBr_2I PENG. This performance enhancement is attributed to the

anisotropic lattice strain and elastic softness. The findings of this research emphasize the potential of inorganic CsPbX_3 -based PENGs in self-powered NEMS/MEMS (Chapter 3).

The second part of the dissertation outlines the use of novel OIHP nanorods of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ to improve piezoelectric coefficients. These nanorods are synthesized through a ligand-assisted reprecipitation (LARP) method, which confers superior in-plane polarization, leading to d_{31} (transverse piezoelectric coefficient) of 3 times higher (~ 64 pC/N) than that of a commercial piezoelectric polymer of polyvinylidene fluoride (PVDF). Experiments also show that the nanorods can be dispersed in a flexible polydimethylsiloxane (PDMS) polymer, which leads to a large output voltage. The high output performance of the PENG is a result of the large surface area and bending of nanorods, which contribute to the d_{33} and d_{31} coefficients (Chapter 4).

The third part provides a design and synthesis route of a novel vacancy-ordered halide double perovskite of $(\text{TMCM})_2\text{SnCl}_6$ to improve the d_{33} and g_{33} of piezoelectric materials simultaneously. The molecular dipole moment and atomic displacement in the inorganic $[\text{SnCl}_6]^{2-}$ are influenced by the halogen bond between them, resulting in a large spontaneous polarization. Meanwhile, the presence of insulating molecules reduces the relative permittivity, leading to a high d_{33} of 137 pC/N, and g_{33} of 980×10^{-3} V•m/N. Experiments also demonstrate a high output voltage of 81 V at 40 Hz, 4.2 N in the PENG. This design showcases the potential of a heavy-metal free, highly piezoelectric materials in PENG design, which can potentially be integrated with batteries/capacitors to power an electrical circuit (Chapter 5).

The fourth part presents a green organic-inorganic metal halide EDABCO- CuCl_4 to fabricate PENGs. This study on symmetry breaking highlights the independent roles of quasi-spherical molecules and spherical molecules with Jahn-Teller active and inactive metal ion complexes. With its highly confined 0D architecture and large tetrahedral distortion, it possesses a high d_{33} of 165 pC/N, and a massive g_{33} of $2,110 \times 10^{-3}$ V•m/N, and its performance remains unchanged till ~ 180 °C. The high transduction coefficient produces an output power density of $43 \mu\text{W}/\text{cm}^2$ in a PENG at 50 kPa. The energy generation is also stably maintained up to ~ 160 °C. This study further demonstrates the design and fabrication of green PENGs capable of producing electrical energy in harsh environments (Chapter 6).

The fifth part presents a PENG design from the in-situ grown OIHP of FAPbBr₂I nanoparticles (NP) that create a highly porous structure inside a piezoelectric polymer composite. The mechanism of pore formation, its characterization, and its implications on the PENG performance are explored. The porous composite increases the output piezo potential by 5-fold, while the OIHP nanoparticles enhance the relative permittivity by interfacial polarization, reduce the film conductivity and thus increase the output current by ~ 15 -fold higher than the commercially available analog of PVDF. The PENG is used as a power source, successfully showcasing a self-powered wireless communication application between a PENG and smartphone, potentially realizing a proof-of-concept for future battery-independent IoT systems. The PENG is also capable of efficiently harvesting energy from the vibration of a car engine and storing it in capacitors-potentially applicable to other vibrating parts such as airframes, or the engine of an aircraft (Chapter 7).

The sixth part aims to enhance the output current by fabricating a cascade-type PENG structure. The research improves the OIHP's stability by functionalizing its surface with the polystyrene. As a result, the fundamental performance limiting factors of the perovskites, such as ion migration, crystallinity, and grain sizes are improved, all of which are conducive to PENG performance. The cascaded architecture by the newly designed piezoelectric composites results in a large current density of $\sim 100 \mu\text{A}/\text{cm}^2$, an enhancement of more than an order of magnitude for the OIHP-based PENGs (Chapter 8).

This dissertation is devoted to deepening our understanding of the piezoelectric behaviour of the new perovskite nanomaterials in a soft and flexible polymer. The findings of exciting piezoelectric and dielectric properties in novel perovskite material will also have a substantial impact on many areas, including the field of energy harvesters, sensors, actuators, flexible optoelectronics, and soft robotics. At the art at which this research is developing, it is anticipated that PENG-based power sources will soon be driving portable electronics.

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Table of Contents

Examining Committee Membership.....	ii
AUTHOR'S DECLARATION.....	iii
Abstract.....	iv
Acknowledgements.....	vii
List of Figures.....	xiii
List of Tables.....	xix
List of Abbreviations.....	xx
Chapter 1 Introduction to Piezoelectric Nanogenerator.....	1
1.1 Research motivation.....	1
1.2 Theoretical origin of the PENG.....	3
1.3 Piezoelectric perovskite materials.....	7
1.4 Status around the globe.....	11
1.5 Research objectives.....	15
1.6 Thesis overview.....	17
Chapter 2 Strategies to Control Piezoelectric Properties in Perovskite and Perovskite-polymer Composites.....	19
2.1 Motivation.....	19
2.2 Tuning the lattice strain via halogen regulation for improving the piezo potential.....	20
2.3 Dimension control of the perovskite material for enhancing the piezo potential.....	23
2.4 Halogen bond bridging in an organic-inorganic perovskite for simultaneous control of piezoelectric charge and voltage coefficients: A route towards achieving high power density PENGs.....	27
2.5 Improving the transduction coefficient in an organic-inorganic perovskite by a quasi-spherical molecule and a Jahn-Teller metal.....	32
2.6 Tuning the porosity in a perovskite-polymer composite film for generating high piezo potential.....	35
2.7 Conclusions.....	39

Chapter 3 Control of Halogen Atom in Inorganic Metal-halide Perovskites for Designing High-performance PENGs 40

3.1 Motivation.....	40
3.2 Experiments.....	41
3.2.1 Synthesis of halogen regulated perovskites.....	41
3.2.2 Fabrication of the PENG.....	41
3.2.3 Characterization of halogen regulated perovskites.....	42
3.2.4 Characterization of the PENG.....	43
3.3 Results and Discussion.....	44
3.3.1 Role of halogen control on the crystallographic viewpoint.....	44
3.3.2 Evaluation of the intrinsic piezoelectricity.....	47
3.3.3 Composition-related piezoelectric outputs.....	51
3.4 Conclusions.....	55

Chapter 4 Piezoelectric Nanogenerators Based on Organic-inorganic Hybrid Perovskite Nanorods.....56

4.1 Motivation.....	56
4.2 Experiments.....	57
4.2.1 Synthesis of the hybrid perovskite nanorods.....	57
4.2.2 Characterization of the hybrid perovskite nanorods.....	58
4.2.3 PENG fabrication.....	58
4.2.4 PENG characterization.....	59
4.3 Results and Discussion.....	59
4.4 Conclusions.....	68

Chapter 5 Ultrahigh Piezoelectricity in Hybrid Vacancy-ordered Halide Double Perovskite.....69

5.1 Motivation.....	69
5.2 Experiments.....	69
5.2.1 Materials.....	69
5.2.2 Synthesis of TMCM ₂ SnCl ₆ single crystals.....	70
5.2.3 Synthesis of TMCM ₂ SnCl ₆ @PDMS composite films.....	70

5.2.4 Fabrication of piezoelectric nanogenerators.....	70
5.2.5 Measurement and Characterization.....	70
5.3 Results and Discussion.....	71
5.4 Conclusions.....	77
Chapter 6 Enhanced Piezoelectric Response in a Jahn-Teller Distorted Molecular Metal Halide.....	78
6.1 Motivation.....	78
6.2 Experiments.....	78
6.2.1 Single crystal growth and structure characterization.....	78
6.2.2 SHG measurement.....	79
6.2.3 Dielectric permittivity measurement.....	79
6.2.4 Piezoelectric measurement.....	79
6.2.5 Preparation of EDABCO-CuCl ₄ @PVDF composite film-based PENG.....	80
6.2.6 Characterization of EDABCO-CuCl ₄ @PVDF composite film-based PENG.....	80
6.2.7 Synthesis of EDABCO-CuCl ₄ @PDMS based PENG.....	81
6.2.8 Characterization of EDABCO-CuCl ₄ @PDMS based PENG.....	82
6.3 Results and Discussion.....	82
6.4 Conclusions.....	88
Chapter 7 Piezoelectric Nanogenerator Based on Self-assembled Highly Porous Perovskite-polymer Composite.....	89
7.1 Motivation.....	89
7.2 Experiments.....	90
7.2.1 Synthesis of the pure PVDF films.....	90
7.2.2 Synthesis of the porous PVDF films.....	90
7.2.3 Synthesis of the FAPbBr ₂ I@PVDF composite films.....	91
7.2.4 Characterization and measurements.....	91
7.3 Results and Discussion.....	92
7.4 Applications of the PENGs as a sustainable power source in the IoT.....	99
7.5 Conclusions.....	103

Chapter 8 Cascade-type Perovskite-piezoelectric Nanogenerators for Enhancing Output Current Density.....	104
8.1 Motivation.....	104
8.2 Experiments.....	105
8.2.1 Synthesis of the pristine and PS-FAPbBr ₂ I precursor solution.....	105
8.2.2 Synthesis of the PS-FAPbBr ₂ I@PVDF composites.....	105
8.2.3 Multilayer assembly of the PS-FAPbBr ₂ I@PVDF composites.....	106
8.2.4 Structural, microscopic, and spectroscopic characterization.....	106
8.2.5 Electrical measurements.....	107
8.3 Results and Discussion.....	107
8.4 Conclusions.....	114
Chapter 9 Conclusions, Contributions and Recommendations.....	115
9.1 Conclusions.....	115
9.2 Contributions.....	117
9.3 Future work and Recommendations.....	121
9.4 List of Publications.....	123
References.....	128

List of Figures

FIGURE 1.1 Block diagram of a typical wireless sensing system.....	2
FIGURE 1.2 Schematic illustration of ‘direct’ and ‘inverse’ piezoelectricity.....	3
FIGURE 1.3 Schematic representation of the crystal structure of ABX_3 perovskite.....	8
FIGURE 1.4 (a) crystal structure of 2D Ruddlesden-popper (RP) perovskite of $(ATHP)_2PbBr_2Cl_2$. (b) Schematic of the relationship between the crystal structures of ABX_3 and A_2BX_6 (vacancy ordered double perovskite) perovskites [1].....	9
FIGURE 2.1 X-ray diffraction (XRD) patterns of the (020), (200), and (123) planes of $CsPbBr_3$ and $CsPbBr_2I$ after 3 months.....	21
FIGURE 2.2 Unit cell model of $CsPbBr_3$, and $CsPbBr_2I$. The increment of 0.05 Å in the lattice constants along c-axis of (a) $CsPbBr_3$ (b) $CsPbBr_2I$; corresponding electric potential distribution for (c) $CsPbBr_3$ unit cell and (d) $CsPbBr_2I$ unit cell. (e) Piezo potential as a function of unit cell displacement along + c-axis. The corresponding % tensile strain are also calculated and shown in the figure.....	22
FIGURE 2.3 TEM image of the $(ATHP)_2PbBr_2Cl_2$ NRs. Insets: close-in view of nanorods. (b) Stress and (c) electrical potential distribution in the nanorod under an applied pressure of 100 N/m ² . (d) Output voltages generated from the nanorod and a thin film model as a function of applied pressure.....	24
FIGURE 2.4 (a) Finite element simulation of the composite films by COMSOL Multiphysics, demonstrating (a) stress distribution (inset shows the close-in view of a single nanorods with higher bending stress) and (b) electric potential distribution.....	26
FIGURE 2.5 (a) Calculated and experimental XRD pattern of the $(TMCM)_2SnCl_6$. (b) Calculated band structure of $TMCM_2SnCl_6$. (c) Crystal structure of $TMCM_2SnCl_6$ double perovskites; (d) halogen bonding interaction. The arrow from Cl to N indicates the dipole direction of $TMCM^+$	28
FIGURE 2.6 The calculated total polarization of the $TMCM_2SnCl_6$ as a function of c_1 (crystallographic z-axis) by using the Berry phase method.....	30
FIGURE 2.7 (a) Side views of the unstrained structure for $c = 9.33864$ Å; and (b) the strained structure for $c = 9.29311$ Å. (c) The original and (d) the strained crystal structures of $(TMA)_2SnCl_6$. The original $(TMA)_2SnCl_6$ exhibit a high symmetry and the $[SnCl_6]^{2-}$ octahedrons is not distorted. The calculated polarization before and after the applied strain is 0 $\mu C/cm^2$, indicating the loss of piezoelectricity in $(TMA)_2SnCl_6$ (Cambridge Crystallographic Data Centre (CCDC) is 433240).....	31
FIGURE 2.8 The decomposed polarization of $[SnCl_6]^{2-}$ and $TMCM^+$ in $(TMCM)_2SnCl_6$. The polarization from $TMCM^+$ is approximated with $P_{TMCM} = \mu \cdot \cos(\beta) / V_u$, where μ is the dipole	

moment of the TMC^+ (4.65 Debye) and V_u represents the cell volume. The polarization from $[\text{SnCl}_6]^{2-}$ is estimated with $P_{\text{Sn}} = P_{\text{total}} - P_{\text{TMC}}$ 31

FIGURE 2.9 The modification of a spherical cation (DABCO) into a quasi-spherical cation (EDABCO) lowers molecular symmetry and creates dipole moment.....33

FIGURE 2.10 (a) Projected density of states (PDOS) of Cu^{2+} -3d orbitals in EDABCO- CuCl_4 . (b) Optical absorption spectrum of EDABCO- CuCl_4 exhibits two bands, a visible band associated with charge transfer and an infra band ascribed to d-d transition. (c) Energy level diagram for the Cu^{2+} -3d electronic configuration in a tetragonal (D_{2d}) crystal field showing the effect of Jahn-Teller distortion on the energy level splitting. (d) The averaged MSDs for Cu, Cl, N, and C atoms from AIMD simulations at 453 K for 20 ps.....34

FIGURE 2.11 (a) Cross-sectional SEM image of the $\text{FAPbBr}_2\text{I@PVDF}$ film. The pores are distributed across the cross section of the film having a length of 20-25 μm . (b) Surface topography of the $\text{FAPbBr}_2\text{I@PVDF}$ film by the AFM is depicting the pores diameter of approximately 3-5 μm 37

FIGURE 2.12 (a) Simulated stress distribution by the COMSOL for the pure PVDF, porous PVDF (20 wt. %) and $\text{FAPbBr}_2\text{I@PVDF}$ (20 wt. %) composite films. Stress distribution profiles for the pure, porous and perovskite PENG model (b) along horizontal axis (c) along the vertical axis. (d) Simulated piezo potential distribution by the COMSOL for the pure PVDF, porous PVDF (20 wt. %) and $\text{FAPbBr}_2\text{I@PVDF}$ (20 wt. %) composite films.....38

FIGURE 3.1 (a) Schematic illustration of the nanoparticle (CsPbBr_3) synthesis, and (b) PENG fabrication steps.....42

FIGURE 3.2 A photograph of the PENG characterization system, which consists of an electrodynamic shaker, oscilloscope, shaker-controller unit, a laptop with the software interface for the oscilloscope and the shaker, and a proof-mass.....43

FIGURE 3.3 The XRD pattern of (a) CsPbBr_3 (b) CsPbBr_2I 44

FIGURE 3.4 (a) DSC curves of CsPbBr_2I and CsPbBr_3 . (b) Peak emission intensity. High-resolution XPS spectra of (c) Br 3d, and (d) Pb 4f of CsPbBr_3 and CsPbBr_2I . The shifts in the binding energy (eV) indicates the change in strain-mediated chemical interaction between the Pb-X (halogen) chemical bonds.....46

FIGURE 3.5 Evaluating the out-of-plane piezo response. (a) Schematic of the V-PFM set-up. (b) Comparison of PFM resonance peaks. (c) Linear piezo response amplitude of the samples while increasing the ac bias to the cantilever. (d) Measured d_{33} values of the pure halide and mixed halide perovskite materials.....48

FIGURE 3.6 Investigation of the microscopic piezoelectricity in CsPbBr_2I by the V-PFM imaging. (a) Comparison of measured d_{33} of this work to the state-of-the-art piezoelectric cesium metal halide perovskites discovered to date. (b) Surface topography; (c) V-PFM phase of the CsPbBr_2I at +3 V dc bias and (d) -3 V dc bias. (e-f) Amplitude and phase hysteresis loops of the CsPbBr_2I with various ac bias levels (0.8 V_{ac} , 1.6 V_{ac} , and 4 V_{ac}) 49

FIGURE 3.7 Mechanical energy scavenging applications. (a) Photograph of the composite films made with CsPbI_3 , CsPbBr_2I , CsPbBr_3 , $\text{Cs}_2\text{PbBr}_2\text{I}_2$, CsPbCl_3 , CsPbCl_2I , and CsPbCl_2Br . (b)

Schematic of the piezoelectric energy harvesters. (c) Measured relative permittivity (ϵ_r) of CsPbX_3 ($\text{X}=\text{I}, \text{Br}, \text{Cl}, \text{Br/I}, (\text{Br/I})_2, \text{Cl/I}, \text{Cl/Br}$ perovskites with the PDMS matrix. (d) Measured d_{33} , and g_{33} of the composite films. (e) Peak output voltage and currents of the PENGs.....51

FIGURE 3.8 (a) Weight (g) dependent output voltage (p-p) and current (p-p) of the $\text{CsPbBr}_2\text{I@PDMS}$ PENG. Concentration dependent (5, 10, and 15 wt. % of CsPbBr_2I) output voltage (b) and current (c) of the PENGs. (d) Comparison of peak output power generation from the various halide substituted PENGs (5 wt. %). (e) Measurement of the highest output power from the 10 wt. % CsPbBr_2I PENG across various external resistances.....53

FIGURE 4.1 (i) Sketch of the synthesis process of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs; (ii-iii) the growth of composite films; and (iv) the fabrication of PENGs 59

FIGURE 4.2 (a) Surface topography of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs from the AFM. (b) Experimental (black) and simulated (red) XRD patterns of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs film. The $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs film gives sharp periodic (200) planar peaks in the XRD pattern denoting [100] orientation.....60

FIGURE 4.3 Origin of piezoelectricity from the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs: (a) a schematic representation of lateral (a) and vertical (b) PFM methods; (c) local lateral (transverse) piezoelectric response amplitude and phase hysteresis (inset) versus cyclic direct current (dc) voltage loops from -10 to 10 V; (d) comparison of the lateral PFM resonance amplitude of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NR and a commercial poled PVDF film; (e) surface topography; (f) lateral PFM amplitude and (g) phase images of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs (h) current density-voltage (J-V) curve and the integrated polarization-voltage (P-V) hysteresis loop of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ film at room temperature (25 °C) obtained by using the double-wave method.....61

FIGURE 4.4 Morphology of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs@PDMS composite films: (a) the cross-sectional SEM and (b) SEM-EDS mapping images of spin-coated 30 wt. % $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs @PDMS composite films on ITO/FTO substrate (inset shows (i-iv) elemental mapping of Si, Pb, Br, and Cl, respectively in the PDMS; and (v) a large area PENG device). (c) GIWAXS image for 30 wt. % $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs@PDMS composite films. (d) Schematic illustration of the orientation of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs in PDMS. (e) Surface potential distribution of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs measured by the Kelvin probe force microscopy (KPFM).....63

FIGURE 4.5 The output performance of the PENGs. (a) The measured d_{33}^* and g_{33}^* for the composite film with different $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ concentration; (b) the I_{sc} and (c) V_{oc} of the PENGs with different $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ concentration at an applied force of 4.2 N; (d) the polarity switching test of the I_{sc} of the PENG (20 wt. %, 4.2 N); (e) reliability testing for 1 min (30 wt. % PENGs, 30 Hz, 3.5 N); (f) measured output power-density of the PENGs across various loads from 0-75 M Ω . (g) Poling voltage dependent output performance of the PENGs. The generated output voltage of the PENGs measured at 30 Hz with different poling voltages with a same 1-hour of poling time for each film.....65

FIGURE 5.1 (a) Digital photograph of single crystal $(\text{TMCM})_2\text{SnCl}_6$; (b) XPS results of the $(\text{TMCM})_2\text{SnCl}_6$ powders: XPS spectra for Sn $3d_{3/2}$ and $3d_{5/2}$ orbits, where the peaks at binding energy of 495.8 eV and 487.3 eV are assigned to Sn^{4+} and the peak at 494.2 eV is assigned to Sn^{2+} ; (c) XPS spectra for $2p_{1/2}$ and $2p_{3/2}$ orbits of Cl^- , which is corresponding to binding energy of 200.6 eV and 198.8 eV, respectively. (e) FTIR spectra of pure TMCM-Cl molecules and $\text{TMCM}_2\text{SnCl}_6$ 72

FIGURE 5.2 Vertical PFM amplitude (a) and phase (b) images; (c) current density-voltage (J-V) curve and the integrated polarization-voltage (P-V) hysteresis loop of the $\text{TMCM}_2\text{SnCl}_6$ film at room temperature (25 °C) by using the double-wave method; (d) the temperature-dependent powder XRD measured at 298 K and 373 K, respectively; (e) temperature-dependent J-V curves. Voltage is swept from -70 to 70 V. The inset is the differential scanning calorimetry (DSC) curves of $\text{TMCM}_2\text{SnCl}_6$ crystals with the scanning rate of 10 K/min; (f) frequency-dependent permittivity tested from 0.01 to 1 MHz; (g) the d_{33} and g_{33} of $\text{TMCM}_2\text{SnCl}_6$ compared with the reported inorganic and molecular materials, including BTO, PZT, Triglycine sulfate (TGS), Imidazolium perchlorate (IP), PVDF, and $(\text{ATHP})_2\text{PbBr}_4$ 73

FIGURE 5.3 (a) The box chart of output voltages and currents collected from 5 PENGs. The applied mechanical excitation is 2.8 N and 40 Hz. The fraction of $\text{TMCM}_2\text{SnCl}_6$ NPs in the composite film is 18 wt. %. (b) V_{oc} and (c) I_{sc} of PENGs with the force from 2.8 to 4.9 N (40 Hz); (d) the device reliability tested for 10 mins. The output voltage (e) and current (f) of the PENGs with different mass fraction under an applied mechanical excitation of 2.8 N and 40 Hz. (g) Output voltage of PENGs based on 18 wt. % $(\text{TMCM})_2\text{SnCl}_6$ in composites after poling at various DC bias for 3 hours; (h) comparison of peak output voltage of PENGs measured under various applied DC bias. The applied mechanical excitation is 2.8 N and 40 Hz.....75

FIGURE 6.1 (a) Bulk single crystal of EDABCO- CuCl_4 grown by the slow-cooling method. (b) Experiment and simulated powder XRD patterns of EDABCO- CuCl_4 at room temperature. (c) SHG signal of EDABCO- CuCl_4 microcrystals at an excitation wavelength of 1510 nm. (d) The selected Cl-Cu-Cl and Cl-Zn-Cl bond angles of the $[\text{CuCl}_4]^{2-}$ and $[\text{ZnCl}_4]^{2-}$ tetrahedrons, representing those that deviate from the ideal 109.5° . The Jahn-Teller active Cu^{2+} enhances the deformation of the inorganic geometry. (e) Comparison of the crystal structures of DABCO- CuCl_4 , EDABCO- CuCl_4 , and EDABCO- ZnCl_4 . The combination of quasi-spherical cation and Jahn-Teller distortion results in the piezoelectric active structure. (f) Piezoelectric coefficient (d_{33}) of EDABCO- CuCl_4 single crystals as a function of temperature. (g) Young's modulus and hardness of EDABCO- CuCl_4 single crystals. (h) Dielectric constant as a function of frequency of EDABCO- CuCl_4 single crystals..... 83

FIGURE 6.2 (a) Comparison of solid-state phase transition temperature and $d_{33} \times g_{33}$ with previously reported molecular piezoelectrics. (b) The cross-sectional SEM image of the 10 wt. % EDABCO-CuCl₄@PVDF composite films. (c) Output voltage and (d) current with different EDABCO-CuCl₄ concentrations at an applied force of 15 N and a frequency of 5 Hz. (e) The output voltage and (f) the output current of the 10 wt. % EDABCO-CuCl₄@PVDF PENGs at 15 N with different frequencies (1 Hz, 3 Hz, and 5 Hz). (g) Polarity switching of the output current of the 10 wt. % EDABCO-CuCl₄@PVDF PENG. (h) The device reliability test for 35,000 cycles of the 10 wt. % EDABCO-CuCl₄@PVDF PENG at 30 Hz, and 136-gram weight on top of the device. (i) Comparison of the power density of a pure PVDF and 10 wt. % EDABCO-CuCl₄@PVDF PENG.....85

FIGURE 6.3 (a) The temperature-dependent output voltage of EDABCO-CuCl₄@PDMS composite PENG and reliability test for ~2,500 cycles at 433 K. (b) The cross-sectional SEM and (c) EDS mapping of EDABCO-CuCl₄@PDMS PENG after operating at 433 K for ~2,500 cycles. (d) Charging voltages of different capacitors by EDABCO-CuCl₄ PENG..... 86

FIGURE 7.1 Device structure of PENGs (a) fabrication process of PENGs; (b) XRD patterns of 20 wt. % FAPbBr₂I@PVDF composite film; (c) FTIR results of porous PVDF and FAPbBr₂I@PVDF composite films (25 wt. %); (d) digital photos of the large area composite film (15 cm × 15 cm) and the fabricated PENGs..... 93

FIGURE 7.2 (a) Cross-sectional SEM image of the self-assembled highly porous PVDF@FAPbBr₂I (20 wt. %) composite films (inset shows the close view of a pore); the corresponding element mapping of (b) fluorine (F) in PVDF and (c) lead (Pb) in FAPbBr₂I; (d) top-view SEM image of the porous PVDF film after the etching of the ZnO NPs (the inset is the enlarged view of pore); (e) schematic illustration of crystallization process of the PVDF and FAPbBr₂I perovskite nanoparticles. The y axis represents the total concentration of PVDF and FAPbBr₂I in the solution; (f) schematic diagram shows the interactions between FA⁺ and -CF₂- groups and the corresponding FTIR absorption peaks for the C-F bond in the range of 1350-1100 cm⁻¹.....95

FIGURE 7.3 Output performance of PENG: (a) output voltage and (b) current of the PENG with an applied load of 138 g, frequency 30 Hz and acceleration 2G. (c) Schematics of the PENG energy generation mechanism based on distributed stress on the film. (d) V_{oc} and (e) I_{sc} of PENGs made from pure PVDF, porous PVDF (with ZnO nanoparticles) and FAPbBr₂I@PVDF composite films. For the porous PVDF, and FAPbBr₂I@PVDF composite films, the original mass ratios of nanoparticles inside the final films are 20 wt. %. (f) Relative permittivity of the porous and 20 wt. % FAPbBr₂I@PVDF composite films; KPFM images of the (g) porous and (h) 20 wt. % FAPbBr₂I@PVDF composite films.....96

FIGURE 7.4 Framework of the self-powered integrated wireless electronics node (SIWEN) by simultaneously using the PENGs as a power source and a sensor.....99

FIGURE 7.5 Application of the PENGs for IoT: (a) the measured output power of the PENG with an applied acceleration of 2 G (30 Hz). The used load is a metal block of 138 g; (b) charging characteristics of the input (1 μF) and output capacitor (220 μF) of the SIWEN; (c) the digital photo of the sensor signal received by the cell-phone; (d) SIWEN used for car engine states

detection at a parking condition (inset shows the corresponding frequency domain distribution via Fast Fourier Transform); (e) charging of a commercial capacitor (1 μ F) by a single PENG while exciting by an automobile engine (Mercedes-Benz car); (f) the corresponding digital photo of engine vibration detection..... 101

FIGURE 8.1 (a) XRD pattern of pristine FAPbBr₂I@PVDF and PS-FAPbBr₂I@PVDF. (b) Raman spectroscopy of the FAPbBr₂I@PVDF and PS-FAPbBr₂I@PVDF film. (c) FE-SEM surface images of FAPbBr₂I and (d) 1 wt./vol% PS-FAPbBr₂I film.....108

FIGURE 8.2 (a) ToF-SIMS depth profiling of PS-FAPbBr₂I@PVDF and (b) FAPbBr₂I@PVDF films. (c) Dark current density of 0, 1, 10, and 20 wt./vol% PS-FAPbBr₂I@PVDF composites.....109

FIGURE 8.3 (a) PS concentration dependent output voltage and (b) output current density. (c) Polarity switching of output current of a 2-layers cascade PENG. (d) Output power density of 2-layer cascade PENG. The test force and frequency are 15 N, and 5 Hz.....111

FIGURE 8.4 (a) Schematic of a cascade type PENGs. (b) Output voltage and (c) current density of 1-, 4-, 8-, and 14-layers cascade PENGs at 30 Hz, 4.2 N.....113

List of Tables

TABLE 1.1 A list of piezoelectric constants.....	6
TABLE 1.2 Piezoelectric properties of some typical perovskites' materials.....	10
TABLE 1.3 Output performance comparison of perovskite-polymer composite based PENGs.....	14
TABLE 2.1 Lattice parameters of CsPbBr ₃ and CsPbBr ₂ I.....	21
TABLE 3.1 Lattice parameters of CsPbCl ₃ , CsPbCl ₂ Br, and CsPbCl ₂ I.....	45
TABLE 3.2 Lattice parameters of Cs ₂ PbBr ₂ I ₂	45

List of Abbreviations

AI	artificial intelligence
ADC	analog to digital converter
ac	alternating current
AFM	atomic force microscopy
ATHP	4-aminotetrahydropyran
BTO	barium titanate
CNT	carbon nanotube
CBM	conduction band minimum
DFT	density functional theory
dc	direct current
DMF	dimethylformamide
DSC	differential scanning calorimeter
DABCO	1,4-diazabicyclo [2.2.2] octane
EDS	energy dispersive spectroscopy
EDABCO	N-ethyl-1,4-diazoniabicyclo [2.2.2] octonium
FA	formamidinium
FDTS	perfluorodecyltriethoxysilane
FEM	finite element method
FTIR	Fourier transform infrared spectroscopy
GIWAXS	grazing-incidence wide-angle X-ray scattering
HHP	hybrid halide perovskite
IoT	internet of things
ITO	indium tin oxide
J-V	current density-voltage
KPFM	kelvin probe force microscopy
L-PFM	lateral piezo response force microscopy
MNS	micro-/nano system
MA	methylammonium
MSDs	mean-squared displacements
NW	nanowire
NCP	nanocrystal powder
NR	nanorod
NP	nanoparticle
NEMS/MEMS	nano/micro-electromechanical systems
OIHP	organic-inorganic halide perovskites
OTA	octylamine
PZT	lead zirconate titanate
P-V	polarization-voltage
PF	polycrystalline film
PPLN	periodically poled lithium-niobate
PDOS	projected density of states

PBE	Perdew-Burke-Ernzerhof
PS	polystyrene
PDMS	polydimethylsiloxane
PVDF	polyvinylidene fluoride
PFM	piezo response force microscopy
PENG	piezoelectric nanogenerator
RP	ruddlesden-popper
SHM	structural health monitoring
SEM	scanning electron microscope
SHG	second-harmonic generation
SIWEN	self-powered integrated wireless electronic node
SoC	system on chip
SIMS	second ion mass spectroscopy
TENG	triboelectric nanogenerator
TMCM	trimethylchloromethylammonium
TrFE	trifluoro ethylene
TEM	transmission electron microscope
V-PFM	vertical piezo response force microscopy
VBM	valence band maximum
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

Chapter 1

Introduction to Piezoelectric Nanogenerator

1.1 Research motivation

As the world is advancing toward the era of artificial intelligence (AI) and the internet of things (IoT), the development of multifunctional sensor systems will form the true foundation for an intelligent world. In the world of IoT-the network of trillions of interconnected sensors, there is an urgent necessity for distributed power sources that can be supplied by wind, solar, thermal, and mechanical vibrations. Piezoelectric nanogenerator (PENG) is one of the best choices for micropower sources in small electronics and as self-powered sensors due to its compact structure and capability of converting mechanical vibration to electricity.

Since the first demonstration of the “direct piezoelectric effect” by Pierre and Jacques Curie in 1880, and the “inverse piezoelectric effect” by Gabriel Lippmann in 1881- it has revolutionized the field of electromechanical sensing, actuation, and energy-harvesting. Acoustic sensors, pressure sensors, strain sensors, and other sensing devices that use the piezoelectric effect have dominated the sensing industry for decades. The accelerated growth of sensors and their integration with state-of-the-art electronics has enabled various micro-/nano systems (MNSs) which have dramatically improved our healthcare experience, communication, and structural health monitoring [2]. Typical MNSs for structural health monitoring consist of four subsystems-sensing, power supply, data processing and communication. The sensor provides real-time continuous information, which is processed by a microcontroller, and then transferred to a receiver by a radio frequency (RF) transmitter or by a wired connection (**FIGURE 1.1**) [3]. In this way, the structural integrity of an object such as a vehicle or aircraft is assessed for its safe operation. An external power supply is required for the continuous operation of sensors and for powering up the microprocessors for data processing and wireless transmission. Although wired sensing modules provide design freedom and immunity to electromagnetic interference when compared to wireless systems, they are error-prone, require more maintenance, and pose a risk when deployed in harsh conditions. Fault occurrence in some spots in the aircraft will often require dismantling

of its external structure. In contrast, a wireless sensing system can effectively eliminate wiring problems, and is easy to deploy for remote monitoring of structural health. Therefore, the development of the wireless SHM of the aircraft will provide unprecedented advantages of reducing the weight, fuel cost, and maintenance complexities [4],[5]. Moreover, the wireless communication capability of a sensor would make the IoT dream possible, where many MNSs will be interconnected themselves. Given the mobility of this large group of sensors in the MNSs, the crucial limitation of the electrical power has been traditionally met by a battery. The battery has a limited lifespan and requires frequent replacement. In a large network of sensors, error identification and periodic replacement of batteries will impose tremendous costs and instability on the system.

Energy harvesting technology has strong potential to not only meet the burgeoning energy demand but also support a wide range of MNSs. The PENG can efficiently harness tiny vibration from the environment and generates electricity that can be stored to providing with power in a small or large network of sensors. The scalability, small size and compact structure of the PENG will widen the scope of its application as a power source for realizing self-powered MNSs and for wearable/flexible electronics. Highly stable piezoelectric technology can also provide dependable sensing and power generation in harsh environments where solar or thermoelectric energy harvesting technology is ineffective.

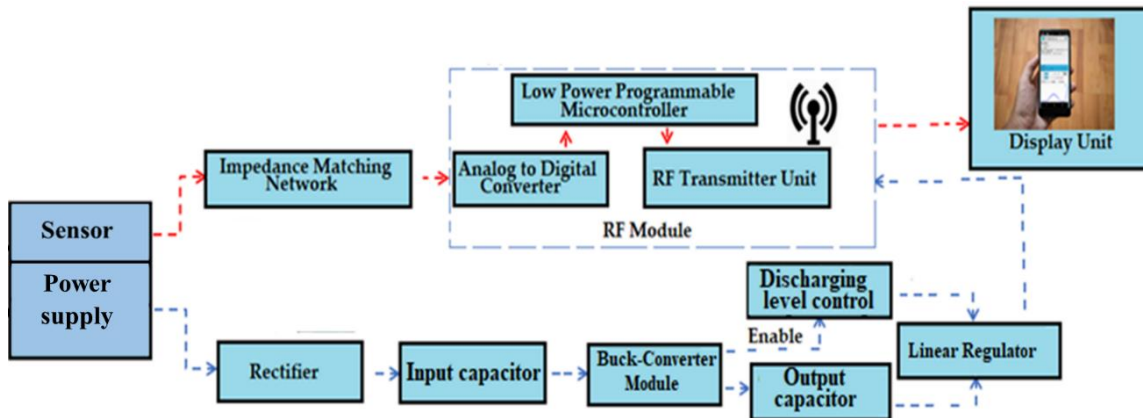


FIGURE 1.1 Block diagram of a typical wireless sensing system

1.2 Theoretical origin of the PENG

A piezoelectric nanogenerator is a mechanical energy-scavenging device which can convert tiny kinetic energy to electrical energy via the piezoelectric effect. When stress is applied to a material, the geometry of the crystal structure changes due to the net movement of positive and negative ions, inducing polarization (**FIGURE 1.2**). Conversely, an application of an electric field creates dipoles, and the movement of these dipoles causes the deformation of a material (inverse piezoelectricity). The direct piezoelectric effect is the basis of mechanical energy harvesting, whereas the inverse effect is harnessed for transducer design [6]. Although piezoelectricity is a century-old concept, the piezoelectric nanogenerator was first proposed in 2006, by the Z. L. Wang group [7],[8].

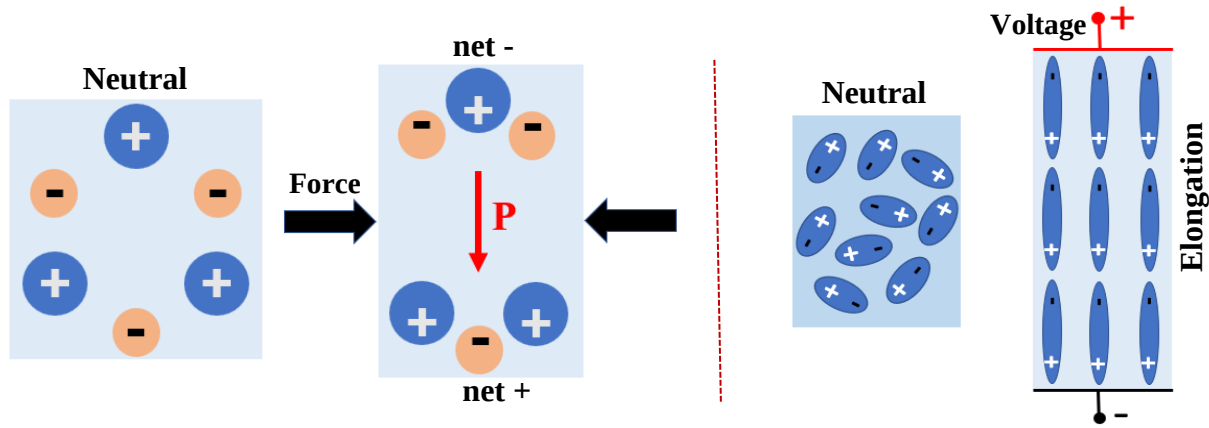


FIGURE 1.2 Schematic illustration of ‘direct’ and ‘inverse’ piezoelectricity.

If a force is applied on the piezoelectric material, induced polarization charges (which are immobile) create an electrostatic potential across the two electrodes attached on the opposite sides, which is balanced by the following of electrons to the external circuit. The physics behind the origin of the nanogenerator is derived from Maxwell’s equation [9],[10]. Maxwell’s displacement current (J) and the output of the nanogenerator nanogenerators can be directly correlated from the ampere circuital law with maxwell’s addition:

$$\nabla \times H = J + \frac{\partial D}{\partial t} \quad (1.1)$$

$$D = \epsilon_0 E + P \quad (1.2)$$

Here, H is magnetic field, D is displacement field, E is the electric field, and P is the polarization field. So, the Maxwell's displacement current can be expressed as:

$$J_D = \frac{\partial D}{\partial t} = \epsilon_0 \frac{\partial E}{\partial t} + \frac{\partial P}{\partial t} \quad (1.3)$$

The first part of this equation is the origin of electromagnetic wave, and the second part correlates the output of nanogenerators, and sensors. If the polarization charge density on the surface of the PENG is σ_p , and there is no external electric field exists, then the displacement field will be the polarization vector. So, the displacement current will be:

$$J_D = \frac{\partial D}{\partial t} = \frac{\partial P}{\partial t} = \frac{\partial \sigma_p}{\partial t} \quad (1.4)$$

Equation (1.4) is the observed current for the PENG. The displacement current is crucial in converting mechanical energy into electricity, analogous to the Lorentz force-driven electron flow in an electromagnetic generator's conduction wire.

For a linear piezoelectric material, the constitutive equation relating between stress (T), strain (S), and electric field (E), electric displacement (D) can be written as tensor notation [11]:

$$S_{ij} = S_{ijkl}^E T_{kl} + d_{kij} E_k \quad (1.5)$$

$$D_i = d_{ikl} T_{kl} + \epsilon_{ik}^T E_k \quad (1.6)$$

Here S_{ij} is the strain, D_i is electric displacement, T_{kl} is the stress, E_k the electric field, S_{ijkl}^E is the mechanical compliance (inverse of elastic modulus), d_{kij} the piezoelectric strain coefficients, ϵ_{ik}^T is the relative permittivity measured at zero stress. The piezoelectric strain constants are commonly expressed as the reduced Voigt matrix notation (d_{km}) where the k denotes the components of the electric displacement or field along the Cartesian reference frame (x_1, x_2, x_3), and the index $m=1, \dots, 6$ is used to define the mechanical stress or strain. Here, the index $m=1,2,3$ denotes the corresponding normal stress or strain along normal to the x_1, x_2, x_3 axes, whereas $m=4,5,6$ stands for the shear stresses or strains, respectively.

According to the symmetry of the tensors, equation (1.5) and (1.6) can be written in terms of the matrix form:

$$\begin{Bmatrix} S \\ D \end{Bmatrix} = \begin{bmatrix} S^E & d' \\ d & \varepsilon^T \end{bmatrix} \begin{Bmatrix} T \\ E \end{Bmatrix} \quad (1.7)$$

Where the superscript depicts the transpose.

Based on the Voigt notation- $\{(S_1= S_{11}, T_1=T_{11}), (S_2=S_{22}, T_2=T_{22}), (S_3=S_{33}, T_3=T_{33}), (S_4= S_{23}+S_{32}, T_4=T_{23}+T_{32}), (S_5= S_{13}+S_{31}, T_5=T_{13}+T_{31}), (S_6=S_{12}+S_{21}, T_6=T_{12}+T_{21})\}$

So, the constitutive matrices for an orthogonal material can be further written as follows:

$$\begin{Bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{Bmatrix} = \begin{bmatrix} \frac{1}{Y_1^E} & -\frac{\nu_{12}}{Y_1^E} & -\frac{\nu_{13}}{Y_1^E} & 0 & 0 & 0 \\ -\frac{\nu_{12}}{Y_1^E} & \frac{1}{Y_2^E} & -\frac{\nu_{23}}{Y_1^E} & 0 & 0 & 0 \\ -\frac{\nu_{31}}{Y_3^E} & -\frac{\nu_{32}}{Y_3^E} & \frac{1}{Y_3^E} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G_{23}^E} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G_{13}^E} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G_{12}^E} \end{bmatrix} \begin{Bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{Bmatrix} + \begin{bmatrix} 0 & 0 & d_{13} \\ 0 & 0 & d_{23} \\ 0 & 0 & d_{33} \\ 0 & d_{24} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} E_1 \\ E_2 \\ E_3 \end{Bmatrix} \quad (1.8)$$

$$\begin{Bmatrix} D_1 \\ D_2 \\ D_3 \end{Bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{13} & d_{23} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{Bmatrix} + \begin{bmatrix} \varepsilon_{11}^T & 0 & 0 \\ 0 & \varepsilon_{22}^T & 0 \\ 0 & 0 & \varepsilon_{33}^T \end{bmatrix} \begin{Bmatrix} E_1 \\ E_2 \\ E_3 \end{Bmatrix} \quad (1.9)$$

Here the elastic compliance matrix in the equation (1.8) has been expressed in terms of -Y the elastic modulus, ν the Poisson's ratio, and G the shear modulus.

In the design consideration of a piezoelectric material, there are four piezoelectric constants can be written as the partial derivatives evaluated as constant stress (subscript T), constant electric field (subscript E), constant electric displacement (subscript D), and constant strain (subscript S).

TABLE 1.1 A list of piezoelectric constants

Symbol	Name	Definition
d	Piezoelectric charge or strain constant	$d_{ij} = \left(\frac{\partial D_i}{\partial T_j} \right)_E = \left(\frac{\partial S_j}{\partial E_i} \right)_T$
g	Piezoelectric voltage constant	$g_{ij} = - \left(\frac{\partial E_i}{\partial T_j} \right)_D = \left(\frac{\partial S_j}{\partial D_i} \right)_T$
e	Piezoelectric stress constant	$e_{ij} = - \left(\frac{\partial T_j}{\partial E_i} \right)_S = \left(\frac{\partial D_i}{\partial S_j} \right)_E$
h	Piezoelectric stiffness constant	$h_{ij} = - \left(\frac{\partial E_i}{\partial S_j} \right)_D = - \left(\frac{\partial T_j}{\partial D_i} \right)_S$

A PENG has two operating modes of the most practical significance, 33-mode and 31-mode. In the 33-mode the applied stress is in the direction of polarization (polar axis), and in the 31-mode they are perpendicular to each other [12],[13]. The shear mode or 14 mode is not used generally as most of the vibration in nature necessitates the operation of the PENG in vertical compression and releasing basis.

The piezoelectric charge (d) and voltage constants (g) are two fundamental properties of a piezoelectric material, and they are directly proportional to the output current and output voltage of the PENGs [14]. The output voltage and current can be theorized as [15]:

$$V = \frac{d_{33}}{\epsilon_{33}^T} \times t_h \times \Delta\sigma = g_{33} \times t_h \times \Delta\sigma \quad (1.10)$$

$$I = d_{33} \times A \times \frac{\Delta\sigma}{\Delta t} \quad (1.11)$$

Where t_h is the thickness, $\frac{\Delta\sigma}{\Delta t}$ is the rate of change of pressure applied to the PENG.

At low frequency, the PENG can be considered as a parallel-plate capacitor, and the available electrical energy that can be extracted is [16] :

$$U_e = \frac{1}{2} CV^2 = \frac{1}{2} (d \times g) \left(\frac{F}{A} \right)^2 \quad (1.12)$$

Where F is the applied force and A is the electrode area.

The transduction coefficient ($d \times g$) of a piezoelectric material determines the output power density from the PENG [17],[18]. The design of the PENG with high output power density requires material with high g , and d values.

1.3 Piezoelectric perovskite materials

When a non-centrosymmetric crystal is subjected to external stress, the resulting asymmetric ionic displacements generate electrical polarization inside a piezoelectric material [19]. In a centrosymmetric crystal, induced displacements of ions almost cancel each other out therefore no net polarization is developed [20]. As a result, crystal symmetry is an important consideration for a material to be a piezoelectric type. Twenty of the 32 crystallographic point groups are non-centrosymmetric, and all the crystals in these classes are piezoelectric. Ten of these 20 groups are polar, and crystals that belong to them have spontaneous polarisation along a polar axis even in the absence of an electric field or mechanical stress are known to be ferroelectric.

Since the first discovery of perovskite by Lev perovski in 1792, perovskites with ABX_3 chemical formula (A, B = cations of dissimilar materials; X = oxygen or halides (Cl, F, I, Br)) have been a key material of choice for sensors and actuators [21]. In the family of oxide perovskites with titanium as the B-site cation (such as calcium titanate ($CaTiO_3$), strontium titanate ($SrTiO_3$), barium titanate ($BaTiO_3$) and lead titanate ($PbTiO_3$)), a slight cationic displacement can effectively induce structural distortion, thus breaking the crystal symmetry. These ABO_3 oxide perovskites are energetically favourable and have huge flexibility in structurally accommodating a wide range of elements to achieve the desired properties. Perovskite ceramics especially lead zirconate titanate ($PbZr_xTi_{1-x}O_3$) or known as PZT has a large d_{33} of 300-400 pC/N and is the most widely commercialized piezoelectric materials since the course of World War II [22]. They have high dielectric constants, curie temperature (T_c) of $\sim 365^\circ\text{C}$, and polarization that can be retained till $\sim 150^\circ\text{C}$ and thus conveying their applicability in high temperature ambient [23]. But the ceramics material especially the trademark PZT possesses a high processing temperature ($\sim 1000^\circ\text{C}$) and pressure and is inherently brittle.

In contrast to the oxide ceramics, halide perovskites are very promising for their low-temperature synthesis process, biocompatibility, and the piezoelectric coefficients are comparable to the ceramic perovskites. Halide perovskites have the same structure as the oxide perovskites except that the monovalent halide ions occupy the sites populated by the divalent oxygen ions [24]. So,

the halide perovskites can only host inorganic metal cations in the B-site with a 2^+ valence state (such as Sn^{2+} , Pb^{2+} , Ge^{2+}) for charge neutrality. But the halide perovskites can allow the accommodation of a monovalent organic cation in the A-site, creating a new organic-inorganic halide perovskite class (**FIGURE 1.3**). The formation and stability of halide perovskites are measured by their tolerance factor (t) and an octahedral factor (μ), $t = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)}$, where R_A , R_B , and R_X are the effective ionic radius of A, B, and X ions. The ratio of R_B/R_X is defined as the octahedral factor, μ [25]. The allowable tolerance factor and octahedral factor for the OIHP ranges in $0.83 < t < 1.107$ and $0.44 < \mu < 0.9$. Interestingly, the OIHP forms a cubic structure when $0.8 < t < 1$, orthorhombic if $t < 0.8$, and hexagonal if $t > 1$ [26]. In a methylammonium lead iodide (MAPbI_3) perovskite the reorientation of the MA^+ (CH_3NH_3^+) cations lead to a distortion of the PbI_6 octahedra by reducing the symmetry and thus causing spontaneous polarization [27]. Moreover, depending on the size of organic cations allow an easy transformation from a 3D perovskite to a 2D structure with improved dielectric and piezoelectric properties. For example, higher piezoelectric properties were observed in 2D ferroelectric $(\text{ATHP})_2\text{PbBr}_4$ compared to the oxide ceramics BaTiO_3 (known as BTO) or PZT [28]. The polar organic cations also have a permanent dipole moment, and their orientation order contributes to the net piezoelectricity. Given the concerns related to the stability of 3D perovskites and inferior piezoelectricity, two dimensional Ruddlesden-popper (RP) perovskite (**FIGURE 1.4a**) and ordered double perovskites (**FIGURE 1.4b**) are intensively studied for their incorporation in the PENG applications.

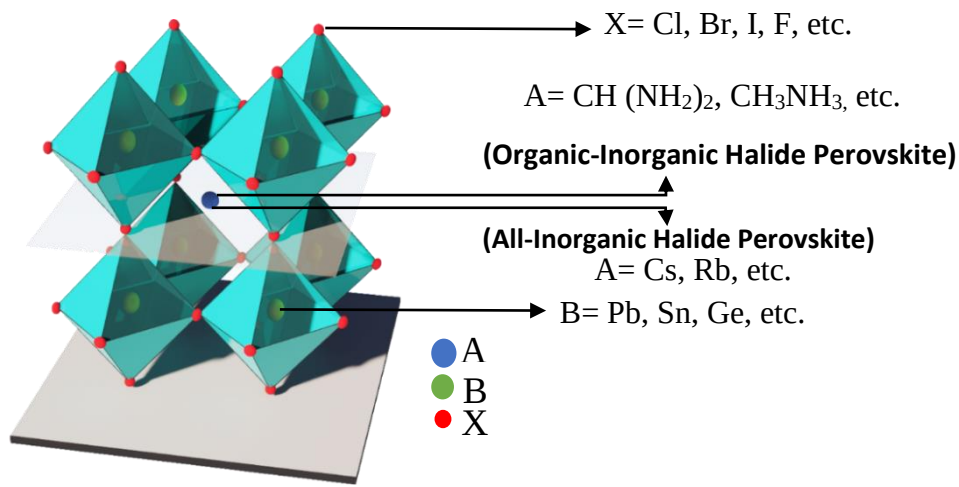


FIGURE 1.3 Schematic representation of the crystal structure of ABX_3 perovskite.

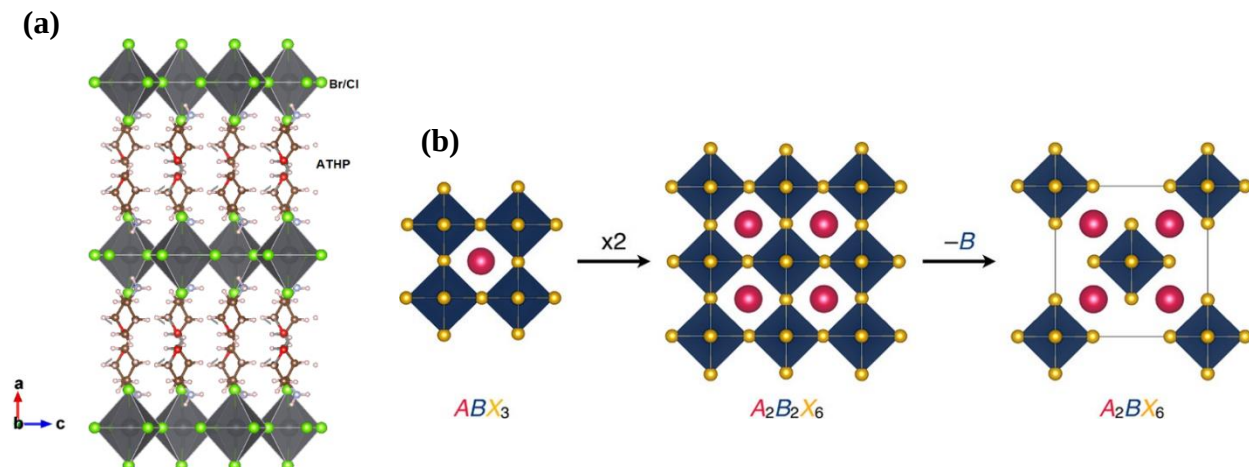


FIGURE 1.4 (a) crystal structure of a 2D Ruddlesden-Popper perovskite of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$. (b) Schematic of the relationship between the crystal structures of ABX_3 and A_2BX_6 (vacancy ordered double perovskite) perovskites [1].

In the RP perovskite structure, the corner-sharing octahedral is separated by the insulating cation bilayers and forms a natural quantum well [29]. The vacancy-ordered double perovskites are derived by doubling the ABX_3 unit cell along its three crystallographic axes and then discarding its every-other B-site cation (**FIGURE 1.4b**). Recently, Xiong et al. developed some promising energy harvesting systems based on molecular perovskites of TMCm-MnCl_3 , $(\text{TMCm})\text{FeBr}_4$, etc. [30]. Such molecular perovskites can rival or even exceed in performance of the inorganic oxide perovskites, organic polymer ((PVDF, polyvinylidene fluoride)) or its copolymer with trifluoroethylene (PVDF-TrFE). Their lightweight, mechanical flexibility, large spontaneous polarization, high curie temperature (T_c) and stability are showing the enormous potentialities of environment-friendly energy harvesting (**TABLE 1.2**).

The OIHP perovskites are available in single-crystals, nanocrystals [31], or even thin-film forms [32]. Thin-film perovskites are long been used in piezoelectric sensing, especially the ceramic-type materials. Hybrid or inorganic perovskites such as MAPbI_3 , CsPbBr_3 , or CsSnI_3 can be deposited directly onto a flexible substrate by spin-coating, and screen-printing methods. By exciting with a mass at the end of such harvesters can periodically bend and release the substrate to produce electricity [33]. These types of structures are best suited for the bending mode, as they cannot withstand force directly impinging on them. The PENG should be able to respond consistently to a wide range of mechanical stimuli, such as high compression, stretching, or twisting, to generate electricity.

TABLE 1.2 Piezoelectric properties of some typical perovskites' materials

Materials	Perovskites type	d₃₃ (pC/N)	T_c (° C)	References
BaTiO ₃	Inorganic	190	120	[34]
PZT-4	Inorganic	289	328	[35]
SM-PT	Inorganic	127	364	[36]
(ATHP) ₂ PbBr ₄	Hybrid (RP)	75	230	[28]
TMCM-CdBr ₃	Hybrid	139	72	[37]
MAPbI ₃	Hybrid	5	54	[38]
FASnI ₃	Hybrid	73	NA	[39]
CsPbBr ₃	Inorganic	40.3	NA	[40]
CsSnI ₃	Inorganic	28.4	NA	[41]
MDABCO-NH ₄ I ₃	Hybrid	14	166	[42]
FAPbBr ₃	Hybrid	25	NA	[43]

The nanocrystals of the OIHP can be embedded into a soft polymer such as PDMS, PVDF, etc. to enhance the durability under mechanical deformation, an approach which is considered a giant shift towards the real-world energy harvesting applications of perovskites materials [31],[44]. Perovskite-polymer composite systems have received a great deal of attention as they can combine the excellent piezoelectric properties of the organic/inorganic nanomaterials, the flexibility of the polymers, scalability, and low-temperature synthesis process.

1.4 Status around the globe

To form the perovskite-polymer nanocomposites, there are sixteen connectivity patterns from 0-0 (where neither phase is connected) to 3-3 (where phases are connected three-dimensionally between them [45]). The incorporation of the perovskite nanoparticles in a polymer can be realized by simple blending, nanoparticle growth in a polymer, or in-situ polymerization in the presence of nanoparticles. In recent years, a lot of PENGs are reported based on various types of perovskite piezoelectric materials including PZT, BTO, CsPbX_3 ($\text{X}=\text{I}, \text{Br}, \text{Cl}$), MAPbX_3 , FAPbX_3 , TMCM-MnCl_3 , and piezoelectric polymers of PVDF, PVDF-TrFE, etc. Perovskites-polymer composites possess advantageous properties of high mechanical strength, desirable flexibility, ease of synthesis, chemical stability, and cost-effectiveness [46],[47]. As a result, they have created a widespread belief that they can be used as a power source for a variety of applications in flexible, wearable, and biocompatible electronic devices.

In 2015, Ding et al. demonstrated a perovskite-polymer composite by dispersing 35 wt. % FAPbBr_3 nanoparticles in the PDMS, which produced a maximum output voltage of 8.5 V and a current density of $3.8 \mu\text{A}/\text{cm}^2$ (at a pressure of 0.5 MPa) [43]. To achieve homogeneous nanoparticle dispersion, Park et al. used carbon nanotubes (CNTs) as the dispersion promoter with the PZT nanoparticles in the PDMS to fabricate a large-area PENG [48]. The CNTs also created a conductive path throughout the composite film to enhance the PENG performance.

Due to the viscosity of the PDMS, the PVDF polymers are better suited to be used in designing the host matrix for the perovskites. The same FAPbBr_3 nanoparticles used in the reference [43] could generate an output voltage and current of 30 V and $6.2 \mu\text{A}/\text{cm}^2$ at 0.5 MPa due to their excellent dispersion in the PVDF [31]. Moreover, the electrostatic interaction between the OIHP cations (FA^+/MA^+) and $-\text{CH}_2$ dipoles of the PVDF could facilitate preferable nucleation of electroactive β -phase composites. This β -phase PVDF was the piezoelectric phase of this polymer producing high spontaneous polarization of $185 \text{ mC}/\text{m}^2$ [49],[50].

Rui et al. demonstrated a novel liquid-solid polymer composite by embedding 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (FDTS) droplets as liquid fillers in the PVDF [51]. The FDTS NPs formed strong intramolecular hydrogen bonds with the PVDF chain and significantly promoted the β -phase from 45.2 % to 83.6 %. The liquid NPs in the PENG could produce an output voltage

of 62 V and a current of 3 μA by acting as the active deformation constituent in the composite with the enhanced stress transfer abilities. Stress-transfer efficiency to the nanoparticles can be improved by chemically functionalizing their surfaces. Functionalizing PZT nanoparticles with the amine groups ($-\text{NH}_2$), chemically reinforced composites were fabricated inside a host matrix of a thermoplastic triblock copolymer grafted with maleic anhydride [52]. The strong chemical linkage between the nanoparticles and polymer increased the stress on the PZT NPs, and a high piezoelectric potential of 65 V is generated with a current of 1.6 μA .

Compared to the randomly distributed nanoparticles, the stress transfer ability can also be boosted if the nanoparticles are interconnected. By using the freeze-drying method, a skeleton of samarium/titanium doped BiFeO_3 (BFO) was fabricated and then silicone rubber was used to fill the micro voids of the BFO skeleton to make an interconnected nanofiller composite [53]. Stem from a similar concept, Wang et al. fabricated three-dimensionally interconnected PZT macro foams which provided a continuous pathway for load transfer and produced an output voltage of 85 V [54]. In another study, a gradient porous structure in the PZT was fabricated and the PDMS acted as a filler which could generate a voltage and current of 152 V, and 17.5 μA [55]. An alternating electric field induces opposite charges on nanoparticles and aids them to rearrange in a column via the head-to-tail configuration (dielectrophoresis). This can potentially align the nanoparticles or nanofibers in a composite film and reduces the inter-particle distance, which improves the transduction coefficient [45]. By using dielectrophoresis, the transduction coefficient in a potassium sodium lithium niobate (KLN) and PDMS composite was raised to a large value close to the PZT composites ($18 \text{ pm}^3 \text{ J}^{-1}$).

While a dc electric field (poling) uniaxially aligns the electric dipoles in a ferroelectric material (e.g., PVDF) resulting in a high polarization charge density, composite films that contain two materials of opposite polar axes require a more sophisticated poling method. To address this, Sun et al. employed a two-step poling method to improve the piezoelectric performance of PVDF-BTO composites [56]. While the BTO and the PVDF possessed positive and negative piezoelectric coefficients, respectively, electrical poling in two separate steps in the opposite polarity aided an equidirectional d_{33} of 38.8 pC/N and a power density of 7.8 $\mu\text{W}/\text{cm}^2$.

Stacking up composite films has been another approach to enhance output performance. The stacking of piezoelectric composite fibres by heat lamination promotes overall polarization, bound

surface charge density, and inter-lamellar electric field. Yang et. al increased the output voltage and power of a multilayer PENG by the factors of 3.4 and 6.5 than the single-layer device [57]. An intercalated electrode in the interface between two composite films with opposite polar axes boosts the output current of the PENG in a multilayer configuration. Traditional ceramic piezoelectric of samarium (Sm) doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (known as Sm-PMN-PT) and PVDF composites were assembled in a multilayer structure via 3D intercalated electrodes which could generate a record current density of $290 \mu\text{A}/\text{cm}^2$ [58]. The PENG could cumulatively add the polarization charges of 12 different units of composite film and charged a $1 \mu\text{F}$ capacitor from 0 to 8 V in only 21 working cycles.

The PENG devices and materials have been both scientifically and commercially significant with a market size of approximately US \$25 billion as of 2014 and are expected to grow rapidly by 60 % in 3 years with a market value of US \$40 billion in 2017 [22]. These devices have been able to successfully harvest energy from foot-stepping, wrist-twisting, speaking, air-blowing, kinetic heartbeat, machine vibration, wheel rotation, etc. [59]. Impressive progress made on the PENG had enabled them to fabricate battery-less cardiac pacemakers, wireless sonomicrometry sensors, pressure sensors, strain sensors, etc. [60],[61]. With the arrival of the IoT, the PENG has been potentially a vital enabler technology for self-powered active sensing, and self-powered micro/nano system design. As individual electronic device power consumption decreases, self-powered wireless intelligent systems aimed at standalone, mobile, and ubiquitous sensory networks have become a critical research focus. Deng et al. proposed a flexible piezoelectric sensor for gesture recognition and remote control in a human-machine interactive (HMI) system [62]. Piezoelectric acoustic sensors can be coupled with the AI engine to detect and distinguish sounds precisely. The applications of piezoelectric materials and devices also include mechanically programmed non-volatile memory, wearable health monitoring, environment monitoring, ultrasonic transducers, ultrasonic imaging, SONAR, soft robotics, and drug delivery [63],[64],[65]. Thanks to its fast response and self-powering characteristics, flexibility, scalability, long-term reliability, and a well-established theoretical framework for its further development.

TABLE 1.3 Output performance comparison of perovskite-polymer composite based PENGs

Piezoelectric composites	Output voltage (V)	Output current (μA)	Output power density ($\mu\text{W}/\text{cm}^2\cdot\text{N}$)	Applications	References
CsPbBr ₃ @PVDF fiber	103 V	170 $\mu\text{A}/\text{cm}^2$	14 $\mu\text{W}/\text{cm}^2$	Motion sensing	[66]
CsPbBr ₃ @PVDF fiber	12	0.3	0.035	Self-powered sensing	[67]
PMN-PT@PDMS	7.8	4.58 $\mu\text{A}/\text{cm}^2$	NA	Strain sensor	[68]
MAPbI ₃ -PVDF	45.6	4.7 $\mu\text{A}/\text{cm}^2$	NA	LED driving	[69]
CsPbBr ₃ @PVDF	33	300 nA/cm^2	1.24	Driving 120 LEDs, electronic watch.	[70]
CsPbI ₃ @PVDF	20	6	3.86	Piezo-phototronics	[71]
Cs ₃ Bi ₂ I ₉ @PVDF	3.9	2	0.072	Voice recognition	[72]
CsPbBr ₃ @NOA63	5.1	0.6 $\mu\text{A}/\text{cm}^2$	0.08	NA	[73]
Cs ₂ SnI ₆ @PVDF	9	5	1.6	Pressure sensing	[74]
FAPbBr ₃ @PVDF	30	6.2 $\mu\text{A}/\text{cm}^2$	0.33	Self-powered electronics	[31]
FAPbBr ₃ @PDMS	8.5	3.2 $\mu\text{A}/\text{cm}^2$	0.08	LED driving	[43]
MASnBr ₃ @PDMS	18.8	13.76 $\mu\text{A}/\text{cm}^2$	0.17	Wearable sensor	[75]
FASnI ₃ @PVDF	23	6.15	0.86	LED driving	[39]
BaTiO ₃ @PVDF	10	2.5	0.36	Pressure sensor	[76]
CsPbCl ₃ @PVDF	168	2	7 μW	Walk-in charger	[77]
PZT@PVDF	55	NA	36 $\mu\text{W}/\text{cm}^2$	Biomechanical energy harvesting	[78]
PZT@PDMS	4.7	NA	NA	Tactile sensing	[79]

1.5 Research objectives

This dissertation aims to study the perovskite-polymer composite-based piezoelectric nanogenerator to deploy them as a standalone power source in a self-powered wireless sensing system crucial for SHM applications, self-powered electronics, and IoT. Despite active research and rapid development around the globe, the PENG technology is still in its premature stage, which calls for more fundamental and technical headway for large-scale practical applications.

The output power density one of the most critical parameters for the PENG is limited by its low output current density, while material challenges including but not limited to low piezoelectric coefficients, stability, process compatibility, and flexibility need to be addressed in a wide range of circumstances. High output current density from the PENG is required for charging the capacitors faster, and so being able to powering-up wireless electronics nodes for reliable data communication. The PENG should be easily integrated into structures, have a small physical and operational footprint, and be light in weight. It should be free of detrimental heavy metals and capable of operating in a wide temperature and external pressure range. The PENG should be flexible to easily respond to vibration, however, needs to be mechanically strong enough to sustain million of vibration cycles. Moreover, the PENG should possess low electrical impedance for high energy transfer efficiency between the PENG and electrical energy storage circuitry.

Such requirements possess great challenges for the existing piezoelectric materials and the PENGs. Firstly, the conventional ceramic piezoelectric materials have high d_{33} , but they are brittle and require a high processing temperature (~ 1000 °C). As a result, ceramic-based piezoelectrics have limited freedom of applications, and mechanical reliability is a concern due to the unpredictable pattern of natural vibration with various magnitudes of forces present. Secondly, ceramic piezoelectrics can be mixed with a polymer to achieve flexibility, but non-homogeneous dispersion or the need for external dispersion promoters makes the composite system very difficult to control. Thirdly, while organic-inorganic hybrid perovskites have a low-synthesis temperature but their intrinsic d_{33} coefficient is low, which further causes low output current in the PENG. Fourthly, the chemical degradation of hybrid perovskites in an ambient environment is concerning long-term reliability and device performance. Fifthly, most of the piezoelectric materials with high piezoelectric coefficients are lead (Pb) based which poses a significant risk to the environment and

human health. Replacement of Pb with other metals alters the tolerance factor, resulting in defects in the perovskites at ambient temperatures, which reduces device performance. Sixthly, enhancement of d_{33} in a piezoelectric material is associated with the increase in the relative permittivity, which in turn decreases the g_{33} . Therefore, the maximum energy density for energy harvesting gets lower while increasing the d_{33} of ceramic perovskite. This imposes a severe challenge for the material scientists to explore ideal piezoelectric material which will simultaneously have large d_{33} and g_{33} values to design PENG with high current and voltage.

In my doctoral thesis, I am devoted to developing high-performance PENG to yield a susceptible and economical solution for fundamental challenges of energy sustainability. At the initial phase of this research, it was vital to complete the literature review to gather a solid understanding of the piezoelectric materials and their historical evolution, piezoelectric energy harvesting techniques, and identify the gaps in the existing knowledge towards achieving a fully self-powered micro/nano system. Then the following research objectives were challenged: **(1)** to explore fundamental performance limiting factors of perovskite-based piezoelectric materials for achieving high d_{33} , g_{33} , stability, flexibility, and environment-friendly properties; **(2)** to provide a route towards synthesis and nanoscale characterization of novel high-performance piezoelectric materials, especially the development of low temperature, low cost, and reproducible synthesis processes; **(3)** to deploy novel perovskite materials in fabricating high-performance PENGs with focuses on improving the performance metric such as output voltage, current and power by various nanocomposite thin film design, fabrication, manipulation, integration, and packaging; **(4)** to apply the fabricated PENG devices in self-powered wireless sensing systems.

1.6 Thesis overview

The chapter of this thesis is organized as follows:

Chapter 1 is a short introduction to the research field with some basic concepts and terminologies of the OIHP perovskite and the PENG devices. **Chapter 2** gives a brief overview of the strategy for designing piezoelectric materials, and perovskite-polymer composites for the high-performance PENG. The chapter discusses the role of halogen control, halogen-bond mediated molecular rotation and atomic displacement, quasi-spherical cations, and Jahn-teller distortion in optimizing the piezoelectric properties or developing novel perovskite piezoelectric materials. This accounts for the density functional theory (DFT) for the calculation of spontaneous polarization, elastic modulus, and atomic displacement, all of which affect the d_{33} , g_{33} , flexibility, and stability. The chapter discusses COMSOL Multiphysics and the finite element method (FEM) for the simulation of the composite film. It addresses the influence of the following factors on the piezo potential: force, strain, nanoparticles concentration, nanomaterials' dimension, and porosity. The aim here is to change the design parameters of a composite polymer material to enhance the piezoelectric potential.

Chapter 3 is the study to find an easy and low-temperature synthesis method that consistently can grow inorganic CsPbX_3 perovskite nanoparticles. In this study, the role of the halogen atom in improving the d_{33} coefficients is discussed to achieve the best-performing piezoelectric material. It uses state-of-the-art PFM to quantify the piezoelectric properties and fabricates efficient PENGs for mechanical energy harvesting applications. **Chapter 4** demonstrates the synthesis and characterization of new OIHP nanorods of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$. The purpose is to enhance the piezoelectric coefficients and flexibility of previous materials. This study provides insights into how the change in the dimension from nanoparticles to nanorods affects the piezoelectric performance of OIHP material and PENG devices.

Chapter 5 discusses an approach to simultaneously achieve high d_{33} and g_{33} in a piezoelectric material at room temperature. This study designs a novel lead-free vacancy-ordered halide double perovskite of $(\text{TMCN})_2\text{SnCl}_6$ for efficient PENGs. It demonstrates the synthesis of material, piezoelectric characterization, and PENG fabrication steps. It also includes measurements of the output voltage, current and power from the PENGs. **Chapter 6** shows a route to further enhance

the transduction coefficient, stability, power density and operating temperature of previous piezoelectric materials and the PENGs. This study synthesizes a green organic-inorganic molecular metal halide of EDABCO-CuCl₄ and measures the d_{33} , g_{33} , and phase transition temperature ($> 180\text{ }^{\circ}\text{C}$). It shows the successful deployment of this heavy-metal-free material to realize PENGs with excellent power generation capability, and high-temperature ($> 150\text{ }^{\circ}\text{C}$) stability.

Chapter 7 demonstrates a composite film design to increase the output current of the PENGs. It synthesizes a highly porous composite film structure via the in-situ growth of PVDF and FAPbBr₂I nanoparticles. It illustrates the homogenous distribution of nanoparticles by the SEM-EDS and the physiochemical mechanism of pore formation. This study shows the measurements of output current, voltage, and charges from the PENG, which can drive a commercial Bluetooth module within a few minutes. It demonstrates different practical applications of the PENG in harvesting tiny vibrations from automobile engines, electrodynamic shakers, and self-powering wireless data communication systems for structural health monitoring.

Chapter 8 is the study of a cascade-type PENG to improve the output current density of the previous devices. It studies the functionalization of polystyrene with the FAPbBr₂I nanoparticles for reducing ion migration and enhancing grain sizes, crystallinity, and homogeneity. It includes the detailed characterization of the PS-FAPbBr₂I interaction, grain-surface topography, crystal structure, I-V characteristics, and the electrical output measurements from the PENGs. The study shows that the cascade-type perovskite-polymer PENG raises the output current density by at least an order of magnitudes higher than the previous OIHP-based piezoelectric nanogenerators.

Chapter 9 concludes a summary of the research presented in this thesis and provides future research direction.

Chapter 2

Strategies to Control Piezoelectric Properties in Perovskite and Perovskite-polymer Composites

2.1 Motivation

The fundamental understanding of the origin of piezoelectricity in the perovskite material and the strategy to control it is vital for high-performance PENG fabrication. The structural tunability of perovskites fuels the ongoing drive to develop new materials with diverse properties and applications. Therefore, developing the structure-property relationship of perovskite materials encompassing piezoelectric applications is required. In this chapter, the design hypothesis of highly piezoelectric perovskites and perovskite polymer composite film is theoretically investigated. The role of halogen atom regulation on the piezoelectric potential of an inorganic metal halide perovskite is investigated at the beginning of this chapter (section 2.2). In section 2.3, the effect of perovskite dimension (from nanoparticle to nanorod) on the piezoelectric potential is calculated. In section 2.4, the strategy to simultaneously achieve high d_{33} and g_{33} coefficients in a perovskite material is evaluated via halogen bond bridging between an organic molecule and an inorganic octahedron. In section 2.5, a design method is demonstrated by a quasi-spherical molecule and Jahn-Teller metal to fabricate piezoelectric material with high d_{33} and g_{33} . This will be critical to realizing PENGs with high power density. In section 2.6, a perovskite-polymer composite film design is investigated. It discusses the contribution of porosity in piezoelectric polymer, and the relative permittivity of perovskites to obtain high output voltage and current in a PENG.

2.2 Tuning the lattice strain via halogen regulation for improving the piezo potential

Over the past decades, inorganic metal halide perovskites (ABX_3 ; A= Cs; B=Pb, Sn, Ge; X=I, Br, Cl) containing cesium in the A-site have been of extensive interest in solar energy harvesting due to enhanced stability compared to its organic counterpart (A= FA, MA) [70]. Record-breaking solar power conversion efficiency ($> 25\%$) has been recently achieved, and excellent ferroelectric properties are being unveiled making it one of the most promising material systems for electromechanical and piezo-phototronic applications [80],[81]. Residual strain in a perovskite alters the electronic band structure which enables demanding ferroelectric and optoelectronic properties [82]. Moreover, strain (compressive or tensile) in a non-centrosymmetric piezoelectric perovskite generates electrical charges via the piezoelectric effect, a phenomenon which has revolutionized energy harvesting and sensing fields [83]. Kim et al. [32] demonstrated that $\pm 0.75\%$ anisotropic strain could be induced in the epitaxially grown $CsPbBr_3$ film by changing the substrate orientation in a concave or convex plane which increases its d_{33} to 23.2 pC/N. In another study, Chan et al. [84] observed interfacial stress while growing a thin film PZT on a structured silicon substrate modified by Ni nanodots arrays. The mismatch in thermal expansion coefficients induces a large local compressive stress around the nanodots resulting in a $\sim 33\%$ increase in its d_{33} . These strategies are applicable for manipulating strain in an epitaxial thin film, demonstrated that it can be achieved by changing geometry, thermal and mechanical properties of the substrate, or further design of a new buffer layer is needed.

Recently, Zhang et al. chemically modified a wurtzite ZnO lattice by substituting its O^- atom with a halogen Br^- (ionic radius greater than oxygen), producing 0.45% tensile strain and, in turn doubling the piezoelectric performance [85]. In a ABX_3 perovskite, tuning the halide ions varies the dielectric properties, surface potential, and binding energy [86]. Moreover, for the ABX_3 type perovskites the stereochemical activity of lone pair electrons in the metallic B-site (Pb, Ge, Sn) and its interactions with the halide anions creates a large anharmonic energy landscape favourable for polar distortion. Yang et al. showed that the mechanism of ferroelectric domain formation in $CsGeX_3$ (X = Cl, Br, or I) was highly dependent on halogen composition in its octahedra [87], whereas spontaneous polarization increased with gradual off-centering of the Ge going from Cl^- to I^- . These studies potentially create a foundation for future halogen-regulated piezoelectric material discoveries. I control the halogen atoms (I, Br) in the $CsPbX_3$ (X=Br, Cl) lattice and

unleash a series of materials highlighting their intriguing piezoelectric properties (CsPbBr₃, CsPbBr₂I, Cs₂PbBr₂I₂, CsPbI₃, CsPbCl₃, CsPbCl₂Br, and CsPbCl₂I). It is discovered that the CsPbBr₂I is the best piezoelectric material among the cesium metal halide perovskites reported to date. This high piezoelectricity originates from I⁻ incorporation in the CsPbBr₃ lattice which produces 0.51 % tensile strain due to the difference in the ionic radius between I⁻ (220 pm) and Br⁻ (196 pm) and increases the dipole moments.

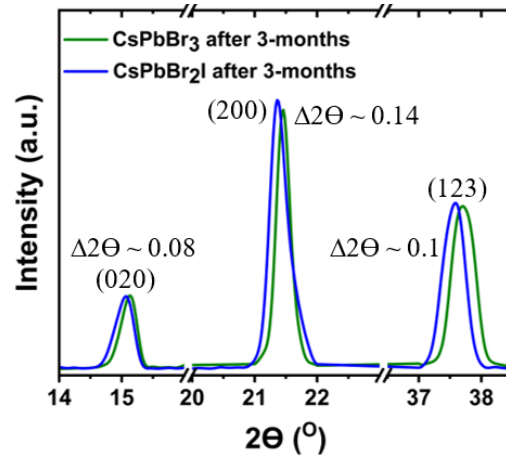


FIGURE 2.1 X-ray diffraction (XRD) patterns of the (020), (200), and (123) planes of CsPbBr₃ and CsPbBr₂I after 3-months.

TABLE 2.1 Lattice parameters of CsPbBr₃ and CsPbBr₂I

CsPbBr ₃	CsPbBr ₂ I	Crystal planes
2 Θ = 30.325 (d_{hkl} = 2.94495)	30.18 (d_{hkl} =2.95885)	(004)
2 Θ = 37.49 (d_{hkl} =2.39683)	37.49 (d_{hkl} = 2.39726)	(024)
2 Θ = 30.64 (d_{hkl} =2.91546)	30.50718 (d_{hkl} =2.92786)	(220)
a=8.318, b=8.1758, c=11.779 Orthorhombic	a= 8.386, b=8.18, c= 11.835 Orthorhombic	0.51% of tensile strain along c-axis

FIGURE 2.1 represents the XRD patterns of the CsPbBr₃ and CsPbBr₂I, which are used to characterize the structural transformation with mixing the halogen atoms. The XRD peaks of (020), (200), and (123) planes of CsPbBr₂I shifts to lower angles than the peaks of CsPbBr₃. The lower angular shifts represent the signature of lattice strain which gradually stretches the lattice according

to Bragg's law, $n\lambda = 2d_{hkl} \sin\theta$. If the XRD peak position is converted to lattice constant according to $((d_{hkl})^{-2} = h^2/a^2 + k^2/b^2 + l^2/c^2)$, where, a, b, and c are the lattice constants, d is the lattice spacing, and h, k, and l are the Miller indices, it is possible to estimate the strain in the unit cell (TABLE 2.1).

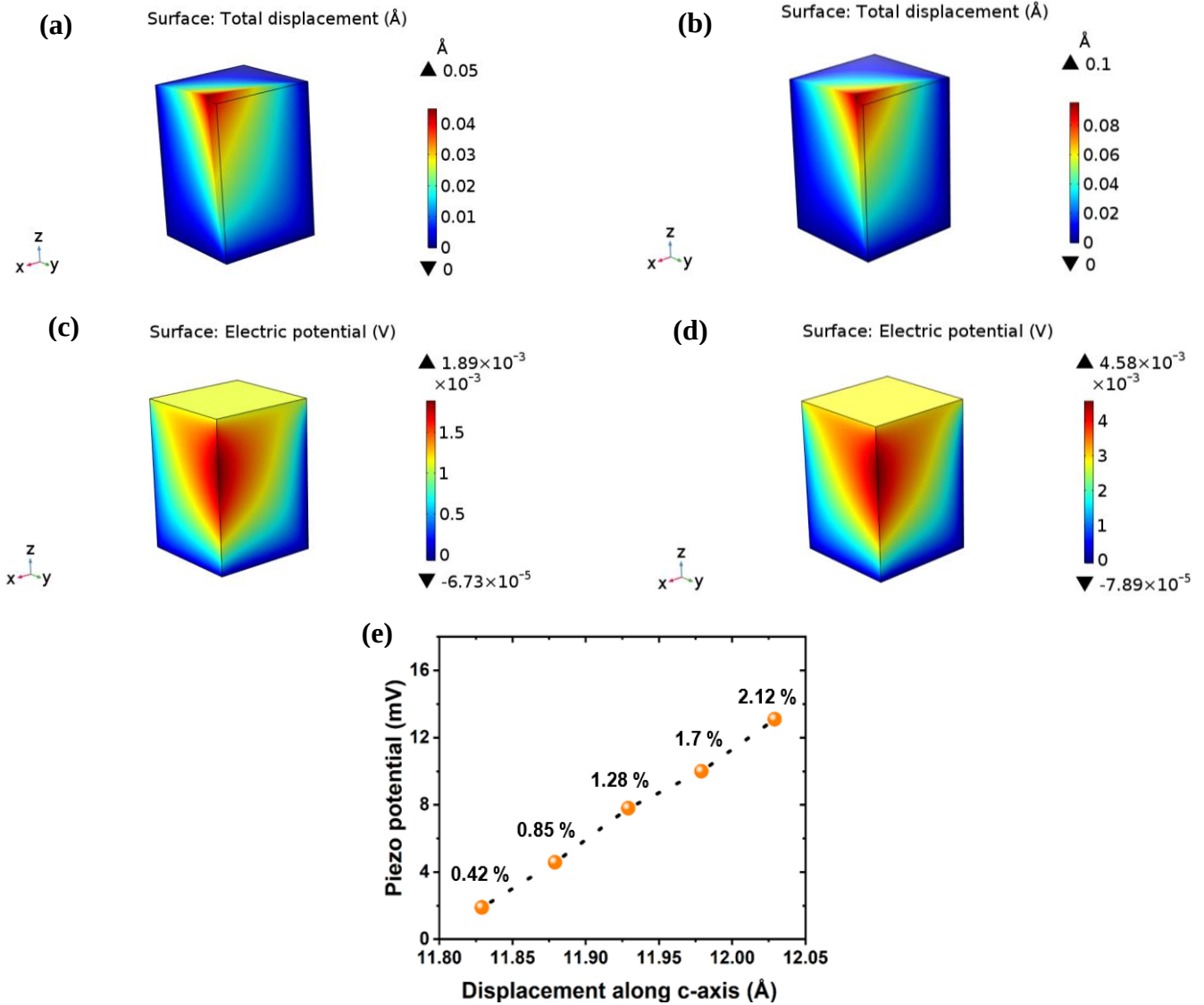


FIGURE 2.2 Unit cell model of CsPbBr₃, and CsPbBr₂I. The increment of 0.05 Å in the lattice constants along c-axis of (a) CsPbBr₃ (b) CsPbBr₂I; corresponding electric potential distribution for (c) CsPbBr₃ unit cell and (d) CsPbBr₂I unit cell. (e) Piezo potential as a function of unit cell displacement along + c-axis. The corresponding % tensile strain are also calculated and shown in the figure.

For example, the calculated lattice constant along the c-axis which increases from 11.78 Å to 11.84 Å in the CsPbBr₂I, corresponding to a tensile strain of 0.51%. The extended octahedra along the

c-axis is likely to result in larger dipole moment and cause the change of polarization in that direction. Total polarization change along the c-axis can be written as $\Delta P_3 = e_{33}\eta_3 + e_{31}(\eta_1 + \eta_2)$, where e_{33} , and e_{31} are piezoelectric stress constants, and η_{1-3} are the strains along the a, b, and c-axes. It can be realized that strain along the a, and c-axis will change the polarization charges.

A unit-cell model of CsPbBr_3 and CsPbBr_2I is implemented in the COMSOL Multiphysics to understand the changes in piezo potential with the tensile strain (**FIGURE 2.2**). I elongate the unit cell of CsPbBr_3 along the c-axis from 11.78 Å to 11.84 Å (corresponding to the length of CsPbBr_2I unit cell) and find an increase in piezo potential of ~ 2.5 times. The calculated strain and corresponding piezo potential distribution are illustrated in **FIGURE 2.2a-d**. The piezo potential is also calculated and plotted as a function of unit-cell displacement with an increment of 0.05 Å (**FIGURE 2.2e**). With the increase of displacement, the potential increases linearly and only 2.12 % tensile strain in the unit cell can amplify the induced voltage to ~ 7 times.

2.3 Dimension control of the perovskite material for enhancing the piezo potential

As a promising alternative to inorganic ceramics, organic-inorganic hybrid perovskites conjoin the benefits of an organic molecule and inorganic crystal at the molecular level. Besides their distinct optical and electronic properties, the OIHs are highly desirable for their structural tunability, mechanical flexibility, and low-temperature solution-based process [88],[89].

In the piezoelectric crystals, the variation in the electric dipole moment is originated from the applied compressive or torsional mechanical stress. Under uniaxial compression, the induced dipole moment can be parallel or perpendicular to the compressive stress, which is called longitudinal or transverse piezoelectric effects, respectively. In other words, from the analogy of inverse piezoelectric effects-the piezoelectric coefficients d_{33} and d_{31} fundamentally quantifying the efficacy of piezoelectric material are the measure of the deformation of a material in a parallel and perpendicular direction, respectively, regarding an applied electric field. The transmission electron microscope (TEM) image in **FIGURE 2.3a** demonstrates a novel piezoelectric nanorods (NRs) of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ for a composite film based PENGs integration, where the piezoelectric performance from the NRs is mainly attributed to their transverse piezoelectric coefficient d_{31}

rather than d_{33} . The length and width distribution of the NRs, the average length of the nanorods is 771.3 nm with a minimum of 351.8 nm, and a maximum of 1480 nm. The average width is 175.65 nm with a minimum of 151.2 nm and a maximum of 227.8 nm. Two-dimensional finite element simulation is performed to examine the piezoelectric response of the nanorod of with a width and the height of 100 nm and 450 nm, respectively. By applying a pressure of up to 100 N/m^2 , the piezoelectric response from the nanorod and

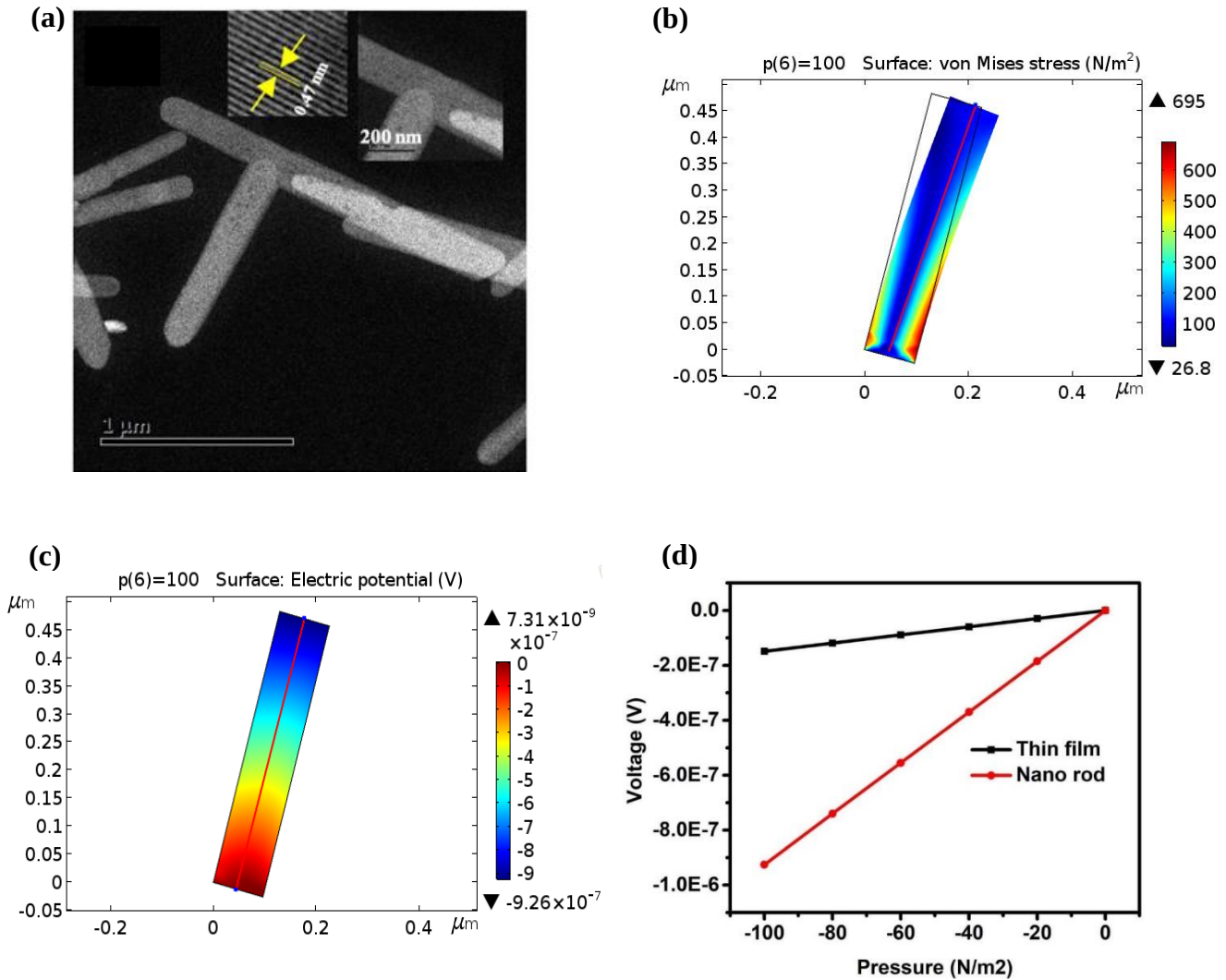


FIGURE 2.3 TEM image of the (ATHP)₂PbBr₂Cl₂ NRs. Insets: close-in view of nanorods. (b) Stress and (c) electrical potential distribution in the nanorod under an applied pressure of 100 N/m^2 . (d) Output voltages generated from the nanorod and a thin film model as a function of applied pressure.

a thin film (width of 450 nm, height of 100 nm) is compared **FIGURE 2.3d**. The distribution of applied stress and the induced electric potential is demonstrated in **FIGURE 2.3b-c**. By the applied

pressure of 100 N/m^2 , the maximum potential developed in the nanorod model is $(-9.26 \times 10^{-7} \text{ V}) \sim 4$ times higher than the thin film $(-1.49 \times 10^{-7} \text{ V})$ of similar area (45000 nm^2). The mechanical stress is maximum at the perpendicular direction of the applied stress (from 0 to 100 N/m^2) due to the bending of the nanorods. Consequently, the induced electric potential is maximized at the planes, perpendicular to the applied stress direction. From the finite element calculation, the nanorod with a high aspect ratio structure generating potential in the transverse direction due to its induced tensile and compressive stress in its two sides; the stress is, however, asymmetric and depends on the orientation of the nanorods. The maximum generated output voltage from the nanorod and the thin film structure is calculated and plotted with a pressure ranging from (0 to 100 N/m^2) in **FIGURE 2.3d**, where the slope will depict the effective piezoelectric voltage coefficient (g_{33}^*). The higher g_{33}^* from the nanorod-type structure is inducing higher piezoelectric potential, which is well-aligned with my experimental observation.

The nanorods are dispersed in the PDMS polymer for the PENG fabrication. The finite element simulation is performed further to explore the origin of high piezoelectric potential for this composite film structure. The simulation results are shown in **FIGURE 2.4a-b**. The random orientation of the NRs in the composite film is found to generate an effective static potential along the vertical strain direction. As the NRs are supported by the polymer scaffold, the compressive stress will eventually induce an effective bending moment on them (stress distribution in **FIGURE 2.4a**). Besides the vertical strain, due to its flexible rod-like feature much higher lateral bending in the NRs can synergistically enhance device piezoelectric performance. Therefore, the resulting piezoelectric potential in the composite film in **FIGURE 2.4b** can be attributed to the combined contribution from their d_{33} and d_{31} coefficients (or the effective d_{33}), in which the d_{31} plays a dominant role.

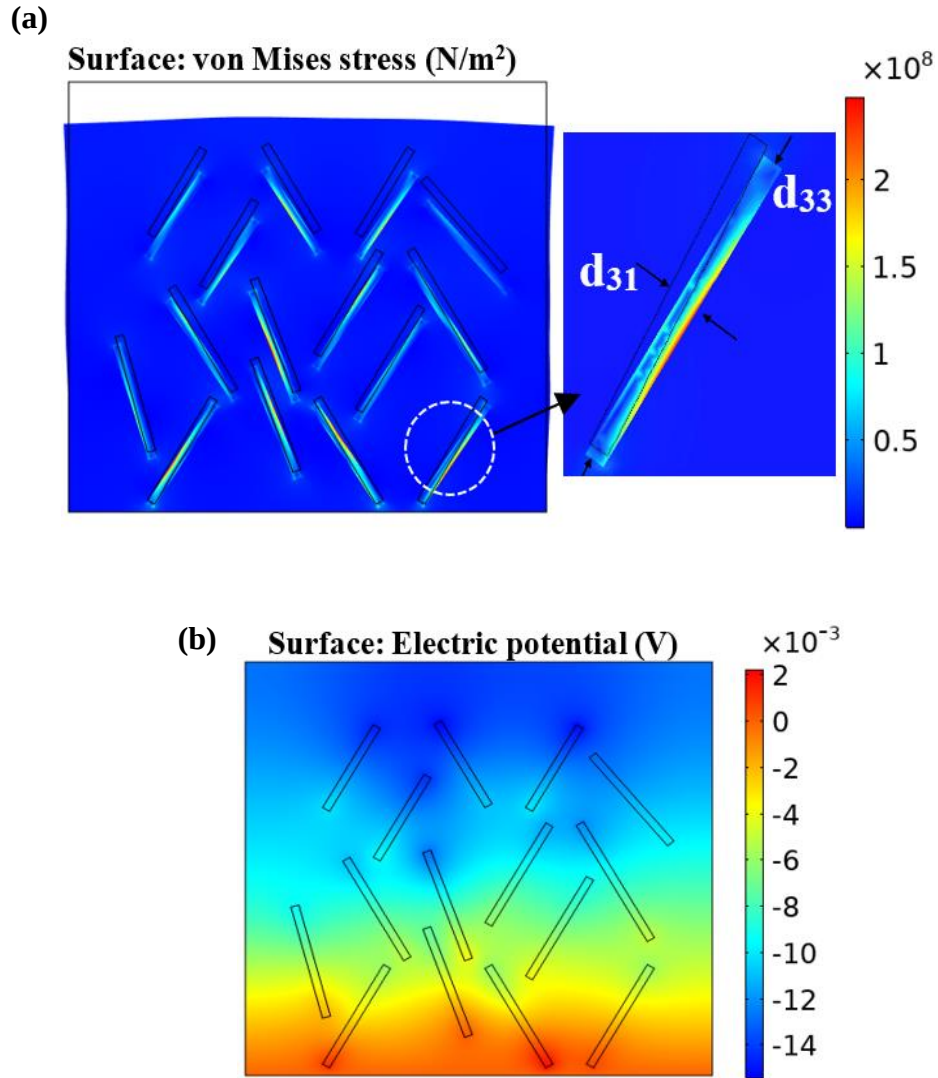


FIGURE 2.4 (a) Finite element simulation of the composite films by COMSOL Multiphysics, demonstrating (a) stress distribution (inset shows the close-in view of a single nanorods with higher bending stress) and (b) electric potential distribution.

2.4 Halogen bond bridging in an organic-inorganic perovskite for simultaneous control of piezoelectric charge and voltage coefficients: A route towards achieving high power density PENGs

To maximize the output power of PENGs, both the d_{33} and g_{33} of the piezoelectric host are important, which determines the output current ($I_{sc} = (d_{33} \times \Delta F) / \Delta t$, where ΔF is the applied force and Δt is the time) and voltage ($V_{oc} = g_{33} \times \Delta P \times L$, where ΔP is the applied pressure and L is the original film thickness), respectively [90],[91]. In the past decade, a wide range of piezoelectric materials, targeting high g_{33} or d_{33} , have been synthesized for efficient PENGs. For example, the organic polyvinylidene fluoride possesses a high g_{33} ($\sim 286 \times 10^{-3} \text{ V}\cdot\text{m/N}$), leading to a high output piezoelectric voltage. Unfortunately, the resultant current is limited because of its relatively low d_{33} ($\sim 30 \text{ pC/N}$). Conversely, inorganic perovskite oxide ceramics, including PZT and BTO exhibit a high d_{33} ($>100 \text{ pC/N}$) but their g_{33} is rather low ($\sim 20 \times 10^{-3} \text{ V}\cdot\text{m/N}$) [92],[93],[94]. Considering the relation between d_{33} and g_{33} ($g_{33} = d_{33} / (\epsilon_0 \times \epsilon_r)$), where ϵ_r is relative permittivity, it is challenging to improve d_{33} while maintaining a high g_{33} because the increase of d_{33} is usually associated with an even larger increase of ϵ_r [36]. Therefore, extensive efforts have been devoted to searching for highly piezoelectric OIHPs. Remarkably, one dimensional ABX_3 -type OIHPs with high d_{33} , including the TMCM- MnCl_3 and A-site mixed $(\text{TMFM})_x(\text{TMCM})_{1-x}\text{CdCl}_3$, were synthesized in 2017 and 2019, respectively [95],[96]. In 2020, the OIHPs were further developed and successfully employed in energy harvesting applications, including $(\text{FMTMA})\text{PbCl}_2\text{I}$, HETMACdCl_3 , $(\text{TMFM})\text{FeBr}_4$, and $[\text{Ph}_3\text{MeP}]_4[\text{Ni}(\text{NCS})_6]$ [97],[98],[99],[100]. Despite their high piezoelectric coefficients, the newly developed OIHPs may face significant challenges in mass production and implementation. For example, the TMCM- MnCl_3 has intrinsic chemical instability as the bivalent Mn is prone to be oxidized to tetravalent, while the Cd (or Pb) in $(\text{TMFM})_x(\text{TMCM})_{1-x}\text{CdCl}_3$ or $(\text{ATHP})_2\text{PbBr}_4$ is not environmental-friendly. Unlike the ABX_3 -type OIHPs, the A_2BX_6 OIHPs (such as K_2PtCl_6) are potentially more chemically stable because their B-site is already in the tetravalent state [101]. Herein, I propose an alternative crystal model, which is vacancy-ordered double OIHPs, for novel piezoelectric material design. The large d_{33} of 137 pC/N and a giant g_{33} of $980 \times 10^{-3} \text{ V}\cdot\text{m/N}$ is experimentally measured for the $\text{TMCM}_2\text{SnCl}_6$ crystal, which is further confirmed by the density functional theory study.

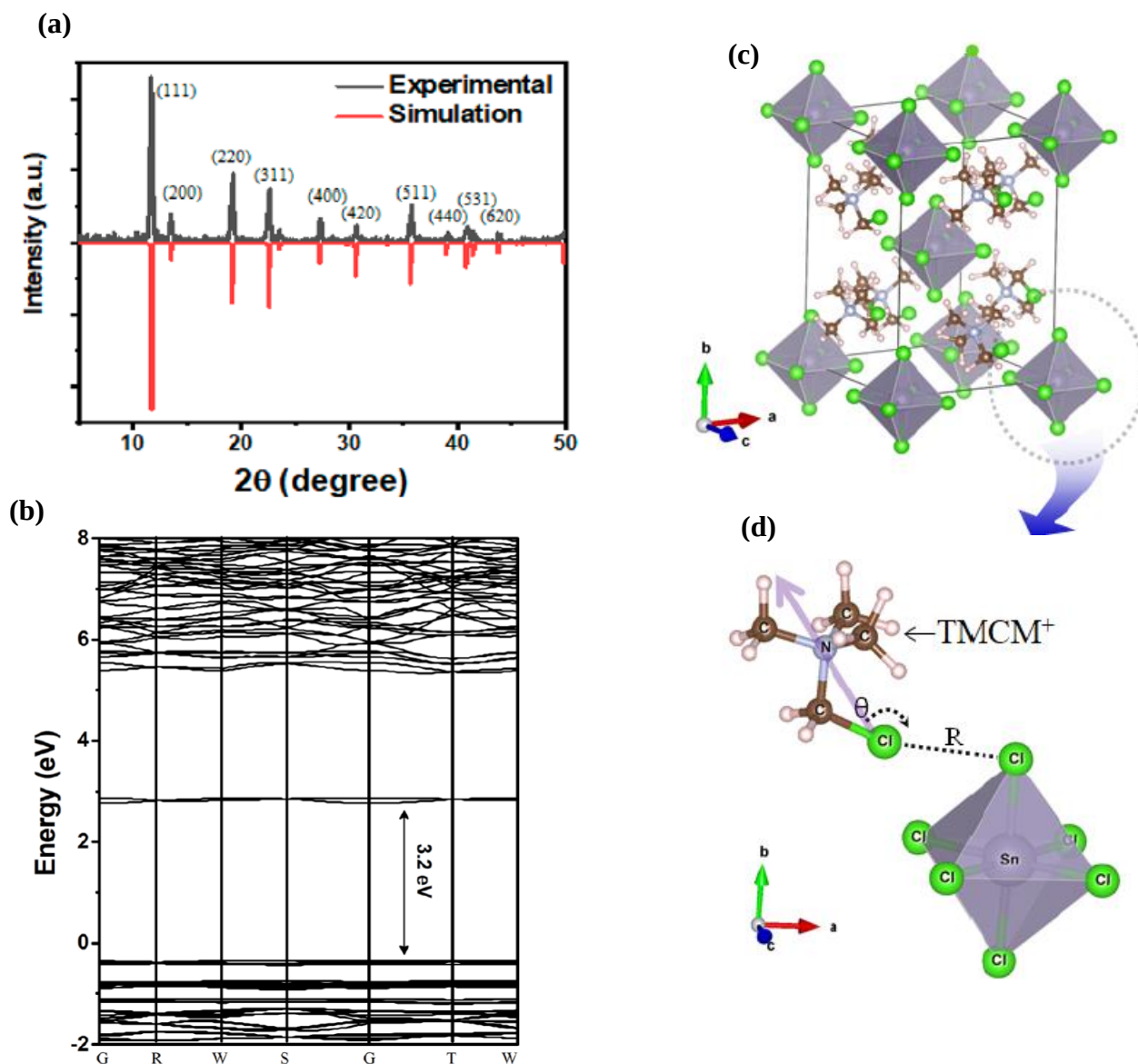


FIGURE 2.5 (a) Calculated and experimental XRD pattern of the $(\text{TMCM})_2\text{SnCl}_6$; (b) calculated band structure of $\text{TMCM}_2\text{SnCl}_6$. (c) Crystal structure of $\text{TMCM}_2\text{SnCl}_6$ double perovskites; (d) halogen bonding interaction. The arrow from Cl to N indicates the dipole direction of TMCM^+ .

$\text{TMCM}_2\text{SnCl}_6$ is a vacancy-ordered double perovskite because its 50% $[\text{SnCl}_6]^{2-}$ octahedrons are replaced by periodic vacancies, in which the asymmetric TMCM^+ takes the A sites (chemical formula confirmed by the XRD in **FIGURE 2.5a**). The $\text{TMCM}_2\text{SnCl}_6$ crystal has an insulating property where the calculated bandgap is of above 3.2 eV (**FIGURE 2.5b**). Unlike to the structural rigidity in inorganic perovskites, molecular perovskites facilitate introducing intermolecular

interactions for achieving desirable packing structure and physicochemical properties. On this note, a halogen bonding interaction between an electrophilic region of a halogen atom in a molecular entity and a nucleophilic region in another or the same molecular entity allows to drive self-assembly of molecules with predictable magnetic, optical, and electronic properties [37]. A halogen bond has been considered as an efficient driving force to achieve the well-defined crystal structures with excellent piezoelectric properties of the $\text{TMCM}_2\text{SnCl}_6$. In the $\text{TMCM}_2\text{SnCl}_6$, there is a net attractive interaction between an electrophilic region associated with the Cl atom in TMCM^+ and the nucleophilic Cl^- in the $[\text{SnCl}_6]^{2-}$ octahedron (**FIGURE 2.5c-d**). The attractive nature of the halogen bond is determined by the bond distance (R , in the range of 2-6 Å) and the bond angle (θ , in the range of 150-180°), especially when R is shorter than the sum of Van der Waals radii (~ 3.5 Å).

To investigate the piezoelectric origin of $\text{TMCM}_2\text{SnCl}_6$ double perovskites, the polarization (P_{total}) is calculated by the Berry phase method as a function of c_1 , where c_1 is the lattice constant during the applied strain along the c axis (**FIGURE 2.6**). DFT calculations, including geometry optimization, electrical structure, and deformation charge density, are performed with a plane-wave implementation of the Perdew-Burke-Ernzerhof (PBE) density functional in the QUANTUM-ESPRESSO software package. The following valence-electron configurations are considered in all the calculations: Sn: 5s, 5p; Cl: 3s, 3p; C: 2s, 2p; N: 2s, 2p; and H: 1s. Plane wave cut-offs of 50 R_y and 500 R_y are adopted for the expansion of the wave function and the electron density, respectively.

The slope of the linear P_{total} vs. c_1 curve yields the piezoelectric stress coefficient (e_{33}) [102]. By fitting the P_{total} vs. c_1/c_0 curve, e_{33} is evaluated as 1.7 C/m². According to the calculated elastic modulus tensor ($c_{33} = 187.7$ kBar) the d_{33} is calculated as 90 pC/N by using the expression of $d_{33} = e_{33}/c_{33}$. The calculated d_{33} is lower than the experimental value of 137 pC/N as the P_{total} contribution resulted from lateral strain was neglected. **FIGURE 2.7 a and b** show the geometry resolved crystal structure (side view) of unstrained $\text{TMCM}_2\text{SnCl}_6$ with a lattice constant c_1 of 9.33846 Å and that of strained $\text{TMCM}_2\text{SnCl}_6$ with c_1 of 9.29311 Å (corresponding to a strain of -0.4%), respectively. Under the applied strain, the angle (α) in the dipole direction of TMCM^+ with respect to c axis decreases from 12.31° to 9.907°. According to the equation of $P_{\text{TMCM}} = \mu \times \cos(\alpha) / V_u$, where μ is the dipole moment of TMCM^+ (4.65 Debye) and V_u is the cell volume, the polarization from the TMCM^+ increases when α decreases. The Cl atom in TMCM^+

is involved in the formation of the covalent bond. In addition, there is a region of lower electron density (σ -hole) where the potential is positive, which generates a cap of depleted electron density on the elongation of the covalent bond. Thus, a halogen-bonding interaction will be formed between the Cl of TMCM^+ and the electron-rich Cl atoms in $[\text{SnCl}_6]^{2-}$. Therefore, the rotation of TMCM^+ can trigger the atomic displacement in $[\text{SnCl}_6]^{2-}$ octahedrons simultaneously, indicated by the increased angle (β) of Cl-Sn-Cl in $[\text{SnCl}_6]^{2-}$ octahedrons from 175.6° to 176.5° . For the $(\text{TMCM})_2\text{SnCl}_6$ under the applied strain, the displacement of Sn along the c axis with respect to the center of its $[\text{SnCl}_6]^{2-}$ octahedrons decreased, indicated by the increased angle of Cl-Sn-Cl from 175.6° to 176.5° . The separation of positive and negative charge centers in $[\text{SnCl}_6]^{2-}$ will generate an efficient polarization (P_{Sn}). After replacing the asymmetric TMCM^+ by spherical symmetric TMA^+ , the $[\text{SnCl}_6]^{2-}$ in $\text{TMA}_2\text{SnCl}_6$ is not distorted (**FIGURE 2.7c, d**). The polarization from $\text{TMA}_2\text{SnCl}_6$ is 0 and not changed under an applied strain, indicated the loss of piezoelectricity. The polarization from $[\text{SnCl}_6]^{2-}$ is calculated by the equation of $P_{\text{Sn}} = P_{\text{total}} - P_{\text{TMCM}}$. Via fitting the decomposed polarization P_{TMCM} and P_{Sn} in **FIGURE 2.8**, the e_{33} of $[\text{SnCl}_6]^{2-}$ and TMCM^+ is 1.5 C/m^2 and 0.2 C/m^2 , respectively. The $[\text{SnCl}_6]^{2-}$ contributes nearly all the piezoelectricity. Unlike the traditional perovskite ceramics where the piezoelectricity is primarily arising from the atomic displacement (i) the organic TMCM^+ in $\text{TMCM}_2\text{SnCl}_6$ can break its crystal symmetry and (ii) the piezoelectricity in $\text{TMCM}_2\text{SnCl}_6$ is from the halogen bond-mediated synergistic movement of atomic displacement in inorganic $[\text{SnCl}_6]^{2-}$ octahedrons and the molecular rotation of TMCM^+ .

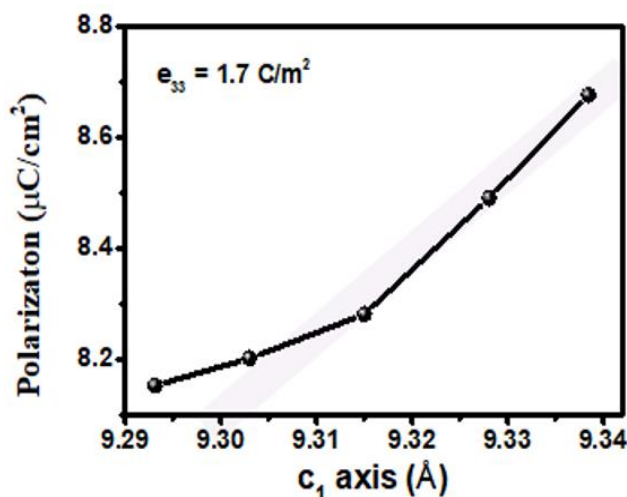


FIGURE 2.6 The calculated total polarization of the $\text{TMCM}_2\text{SnCl}_6$ as a function of c_1 (crystallographic z-axis) by using the Berry phase method.

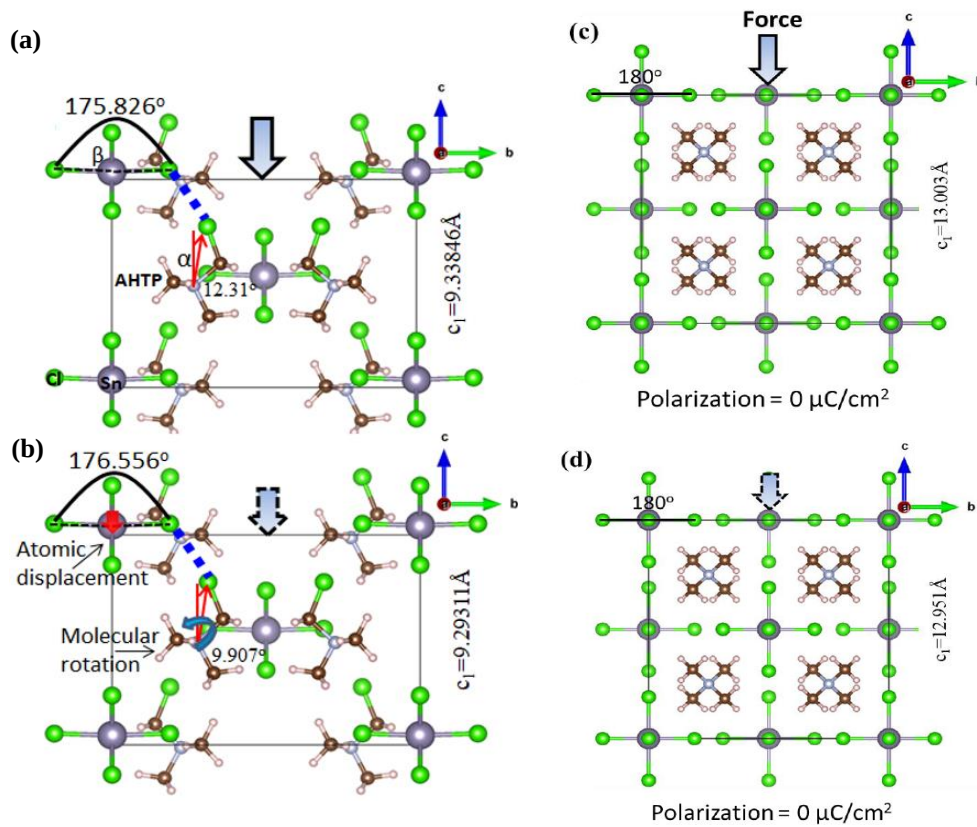


FIGURE 2.7 (a) Side views of the unstrained structure for $c = 9.33864 \text{ \AA}$; and (b) the strained structure for $c = 9.29311 \text{ \AA}$. (c) The original and (d) the strained crystal structures of $(\text{TMA})_2\text{SnCl}_6$. The original $(\text{TMA})_2\text{SnCl}_6$ exhibit a high symmetry and the $[\text{SnCl}_6]^{2-}$ octahedrons is not distorted. The calculated polarization before and after the applied strain is $0 \text{ \mu C/cm}^2$, indicating the loss of piezoelectricity in $(\text{TMA})_2\text{SnCl}_6$ (Cambridge Crystallographic Data Centre (CCDC) is 433240).

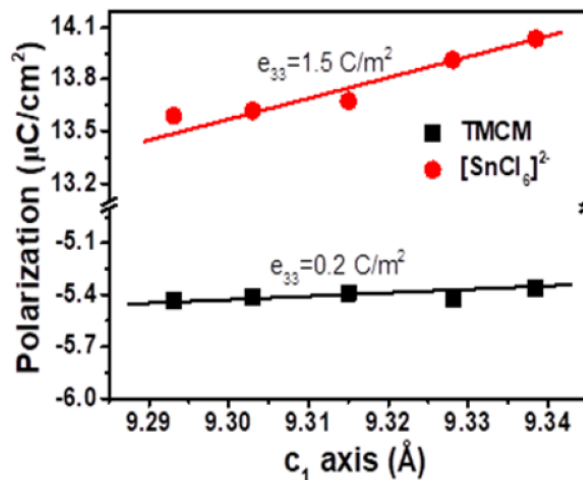


FIGURE 2.8 The decomposed polarization of $[\text{SnCl}_6]^{2-}$ and TMCM^+ in $(\text{TMCM})_2\text{SnCl}_6$. The polarization from TMCM^+ is approximated with $P_{\text{TMCM}} = \mu \cdot \cos(\beta) / V_u$, where μ is the dipole moment of the TMCM^+ (4.65 Debye) and V_u represents the cell volume. The polarization from $[\text{SnCl}_6]^{2-}$ is estimated with $P_{\text{Sn}} = P_{\text{total}} - P_{\text{TMCM}}$.

2.5 Improving the transduction coefficient in an organic-inorganic perovskite by a quasi-spherical molecule and a Jahn-Teller metal

Molecular metal halide piezoelectrics, which include metal halide perovskites are attractive materials for enhancing the transduction current of piezoelectric energy harvesters because they combine the benefits of organic and inorganic moieties at the molecular level [103]. Piezoelectricity arises in crystalline materials without inversion symmetry and is caused by polarization changes due to lattice distortion under stress. Ideally, a material will exhibit either strong polarization or large crystallographic distortion under stress. Reports have shown that plastic ferroelectric crystals with spherical molecular structures exhibit prominent piezoelectricity due to the mechanical softness of their lattices [104]. However, plastic crystals tend to crystallize in highly symmetric cubic crystal systems due to the disordered orientation of spherical molecules, making it challenging to obtain non-centrosymmetric structures [105].

Quasi-spherical theory- which explains how subtle modifications to spherical molecules, can impart symmetry breaking into this material system and cause significant polarization changes under external stress, giving rise to large d_{33} [106]. By changing 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 [103]. The Jahn-Teller distortion arising due to transition metal ions has been noted to induce low-symmetric geometric distortions by promoting degenerate electronic states, which in turn leads to intriguing properties that include lattice distortion and high mechanical softness [107],[108]. Combining Jahn-Teller distortion within a framework of quasi-spherical cations could provide a non-centrosymmetric crystal structure that is more easily deformed under mechanical stress; thus, strong piezoelectric properties could be expected. A novel design of a quasi-spherical cation N-ethyl-1,4-diazoniabicyclo [2.2.2] octonium (EDABCO) as the A-site organic molecule is achieved by adding an ethyl group to break the mirror plane of the 1,4-diazabicyclo [2.2.2] octane (DABCO) molecule; splitting the σ_h mirror plane results in a lower C_{3v} symmetry, giving rise to molecular dipole moment (**FIGURE 2.9**). With considering the goal of achieving a significant Jahn-Teller effect, it is noted that the $3d^9$ Cu^{2+} could induce pronounced Jahn-Teller distortion because of the unequal occupancy of degenerate orbitals. As a result, the quasi-spherical cation with Jahn-Teller

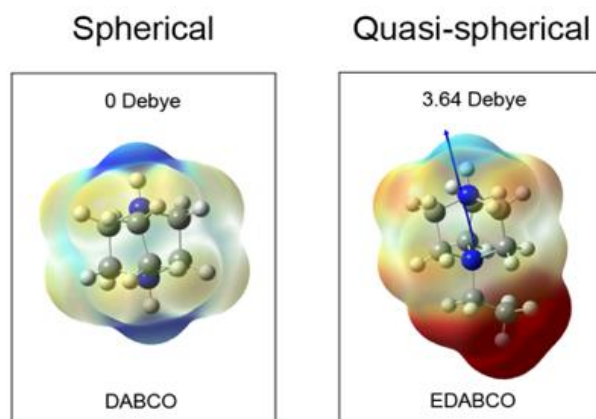


FIGURE 2.9 The modification of a spherical cation (DABCO) into a quasi-spherical cation (EDABCO) lowers molecular symmetry and creates dipole moment.

active Cu^{2+} ions should improve the piezoelectric response of the resulting molecular metal halide and increase the energy yield of a piezoelectric energy harvester. Density functional theory calculations and steady-state optical absorption is performed to elucidate the Jahn-Teller effect in EDABCO- CuCl_4 . From the projected density of states (PDOS) of the Cu^{2+} -3d orbitals (**FIGURE 2.10a**) it is found that the triple-degenerate t_2 d-levels split into two double-degenerate states d_{xz} , d_{yz} and a single state d_{xy} ; the double-degenerate e d-levels split into a single state d_z^2 and $d_{x^2-y^2}$, which is attributed to the Jahn-Teller distortion. The optical absorption spectrum of the EDABCO- CuCl_4 consists of two intense bands (**FIGURE 2.10b**). The visible band at 2.6 eV is associated with a ligand-to-metal charge transfer consistent with the bandgap from DFT. The secondary, near-infrared peak corresponds to d–d electronic transitions within the tetrahedral crystal-field of $[\text{CuCl}_4]^{2-}$, where the local symmetry of Cu^{2+} is reduced from T_d to D_{2d} by Jahn-Teller distortion. The Cu^{2+} -3d orbitals energy level splitting is illustrated in (**FIGURE 2.10c**). Ab-initio molecular dynamics (AIMD) simulation is performed to evaluate the structural stability of EDABCO- CuCl_4 at 453 K (well above the automotive norm for piezoelectric stability, ~ 423 K) [109]. The averaged mean-squared displacements (MSDs) of AIMD simulations for 20 ps at 453 K show that Cu, Cl, N, and C atoms have constant small values with respect to their original equilibrium positions (**FIGURE 2.10d**), which indicates that the structure of EDABCO- CuCl_4 in $P2_12_12_1$ symmetry is stable and no solid-state structural transformation is observed.

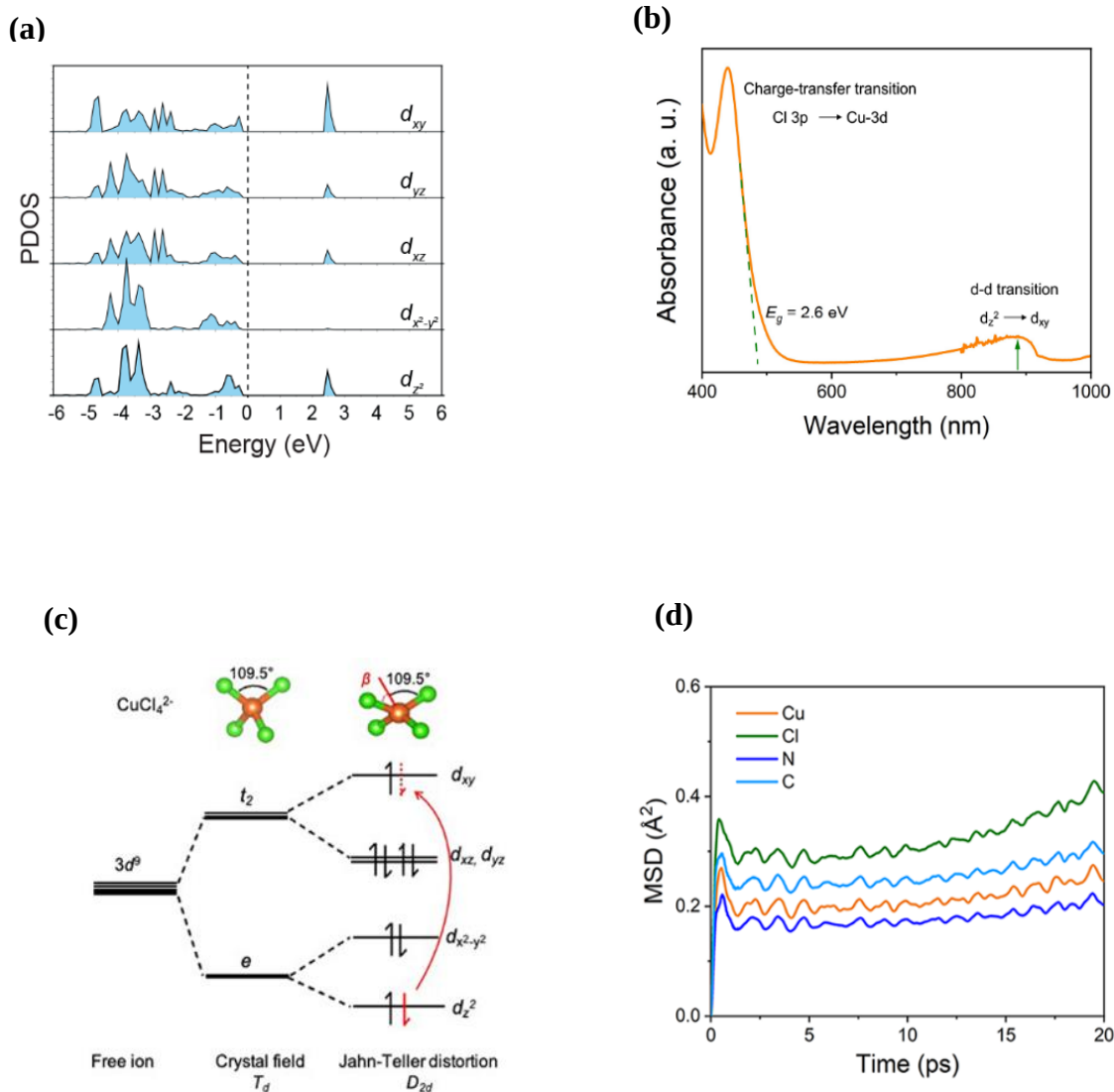


FIGURE 2.10 (a) Projected density of states (PDOS) of Cu²⁺-3d orbitals in EDABCO-CuCl₄. (b) Optical absorption spectrum of EDABCO-CuCl₄ exhibits two bands, a visible band associated with charge transfer and an infra band ascribed to d–d transition. (c) Energy level diagram for the Cu²⁺-3d electronic configuration in a tetragonal (D_{2d}) crystal field showing the effect of Jahn-Teller distortion on the energy level splitting. (d) The averaged MSDs for Cu, Cl, N, and C atoms from AIMD simulations at 453 K for 20 ps.

2.6 Tuning the porosity in a perovskite-polymer composite film for generating high piezo potential

Altering the microstructures of piezoelectric films to enhance the strain-dependent piezoelectric polarization has proven to be an effective energy-harnessing mechanism. For instance, adopting nanowires, aspect ratio tuning, film porosity modulation through a multi-stage etching process, and reducing charge screening effects are remarkable structure-driven techniques, further pushing the piezoelectricity limit [110],[111]. By creating pores in ZnO nanowires, Su et al. [112] demonstrated 23-fold boosted output current in the PENGs (27.7 nA), with an elevated porosity percentage of 5.4%. By using random and highly porous (50%) polyvinylidene fluoride structures (through etching process), Mao et al. enhanced the output voltage and current of the PENG to 11.1 V and 9.7 μ A, respectively, which was higher than those of a lithography assisted porous PVDF nanowire array [92]. Although piezoelectricity can be enhanced by these strategies, optimally unifying appropriate mechanical and electrical properties in a single piezoelectric film remains to be a challenge.

Composite films can be developed by dispersing highly piezoelectric NPs in a flexible polymer, which has proven to be an appealing, yet simpler approach in terms of fabrication scalability, device flexibility, improved mechanical strength, and increased electrical output. Nevertheless, nanoparticle dispersion promoters need to be employed to improve the homogeneous dispersion of the NPs in a polymer scaffold which adversely impacts device performance. As a trade-off, this issue was addressed by functionalizing the surface of piezoelectric NPs before mixing with polymer [52] or replacing NPs with organic-inorganic metal halide perovskites [113]. By mechanically reinforcing a polymer scaffold (PVDF) with the homogeneously dispersed formamidinium lead halide (FAPbBr₃), Ding et al. recorded (the highest output of this type) a piezo potential of 30 V and current density of 6.2 μ A/cm², by an applied pressure of 0.5 MPa [31]. By optimally quantifying the content of uniformly distributed methylammonium lead iodine (MAPbI₃) in the PVDF matrix, a cost-effective solution approach for the MAPbI₃-PVDF piezoelectric composites was also introduced as a result [69].

Here, a design of a novel self-assembled highly porous perovskite/polymer composite film is introduced via the simultaneous control of film structure and material design, which can be used for the efficient PENG fabrication. The composition of a polymer (PVDF) with a novel hybrid

halide perovskite–FAPbBr₂I, can significantly enlarge the bulk film strain by forming self-assembled high-density and ordered pores, and can reduce the film impedance due to the high relative permittivity of FAPbBr₂I.

The porosity in ferroelectric polymers will remarkably boost the piezoelectric potential by forming stress concentration centres around each pore. **FIGURE 2.11a-b** illustrates the pore morphology by the cross-sectional SEM image and the AFM image, respectively. A PENG model for the perovskite/polymer composite is constructed to reveal the effects of self-assembled highly porous characteristics on the output piezo-potential and is simulated by using COMSOL Multiphysics 5.3. **FIGURE 2.12a** clearly shows that, under uniaxial compressive stress of 800 kPa, the induced displacement of the three different PENG models (the same film thickness of 30 μm) is drastically different. The pure PVDF film is the least deformed, whereas the hybrid halide perovskite induced porous PVDF is the most deformed. It is evident that the pore position and size, influences the mechanical stress distribution, which is attributed to the increase in the average stress distribution profiles inside the films. From the finite element calculation along the cut lines of AB, CD, and EF of the **FIGURE 2.12a**, the stress inside the pure PVDF film is quite uniform under uniaxial vertical stress (**FIGURE 2.12b-c**). In contrast, in the circular porous PVDF structure, the stress distribution is asymmetric in nature. The presence of pores significantly disrupts the stress distribution in the circular porous PVDF model when compared to pure PVDF. In such circular porous structures (the middle model of **FIGURE 2.12a**), the stress is mainly confined around each pore but is particularly higher along the direction of the applied force, namely, at the top and bottom pore sides. Therefore, the localized compressive strain of each pores results in a bulk film strain mainly in the vertical direction (x-direction strain $S_1 \sim 0\%$, y-direction strain $S_2 \sim 3.4\%$) and modifies the internal coupling. Excitingly, unlike the uniform and circular porous PVDF (the deformation mainly occurred in the vertical direction), the highly ordered porous structure (the right most model of **FIGURE 2.12a**) of the FAPbBr₂I@PVDF film is not only deformed along the vertical direction ($S_2 \sim 17\%$) but also significantly elongated along the horizontal direction ($S_1 \sim 57\%$). The stress concentration spots at the top exert a pushing force on the pores of the perovskite/polymer composite, inducing a relaxing strain on the two sides. **FIGURE 2.12c** shows the linear stress-enhancing characteristics of this larger pore to the sidewall of the structure. This phenomenon is like the flex-tensional mechanism [114], which underlines the structural

modification of the mechanical body that could further amplify the applied vertical stress into the horizontal direction.

Since the strain-induced piezo potential is a collective outcome from the strains around each of the pores, the piezoelectric potential in the circular porous PVDF structure is therefore higher (**FIGURE 2.12d**) than that in the non-porous PVDF piezoelectric films. The vibration-induced electric displacement D_3 (charge per unit area) is calculated by-

$$D_3 = e_{333}S_{33} + |e_{331}| S_{31} \quad (2.1)$$

where e_{331} and e_{333} are the piezoelectric constants and S_{31} and S_{33} are induced strains along the horizontal and vertical directions, respectively. The D_3 of the FAPbBr₂I@PVDF composite film is synergistically influenced by the bidirectional (horizontal and vertical) strains S_1 (~ 57%) and S_2 (~ 17%). Therefore, the proposed novel PENG structure greatly increases the strain-induced piezo-potential or voltage output (according to the parallel plate capacitor model, $V = Q/C$, where Q is the total induced charge and C is the device capacitance), which was confirmed by the finite element simulation in **FIGURE 2.12d**. It demonstrates the maximum piezoelectric potential of ~ 40 V for FAPbBr₂I@PVDF composite films, which is ~ 11 V and ~ 15 V for pure and 20% porous PVDF films, respectively (with the same applied stress of 800 kPa).

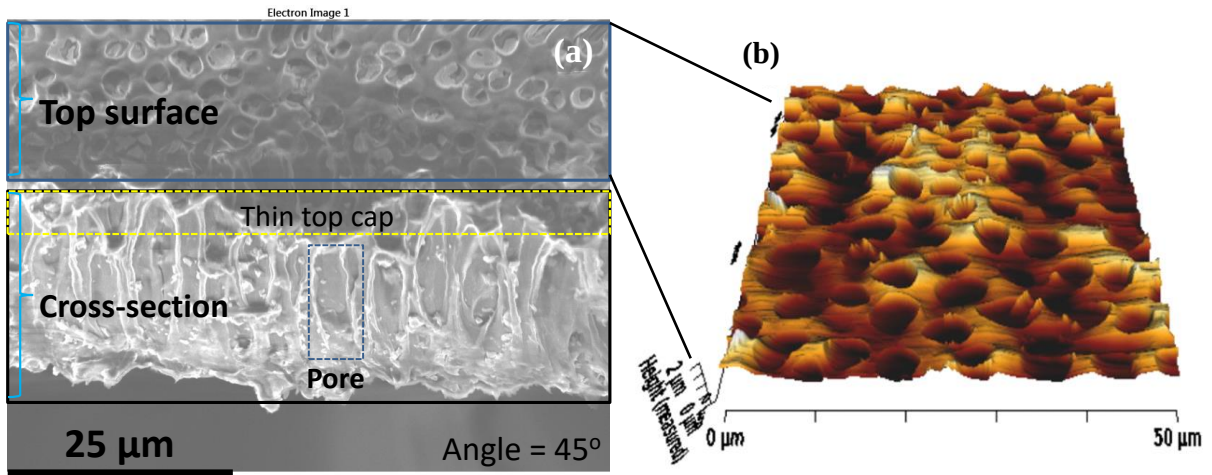


FIGURE 2.11 (a) Cross-sectional SEM image of the FAPbBr₂I@PVDF film. The pores are distributed across the cross section of the film having a length of 20-25 μm. (b) Surface topography of the FAPbBr₂I@PVDF film by the AFM is depicting the pores diameter of approximately 3-5 μm.

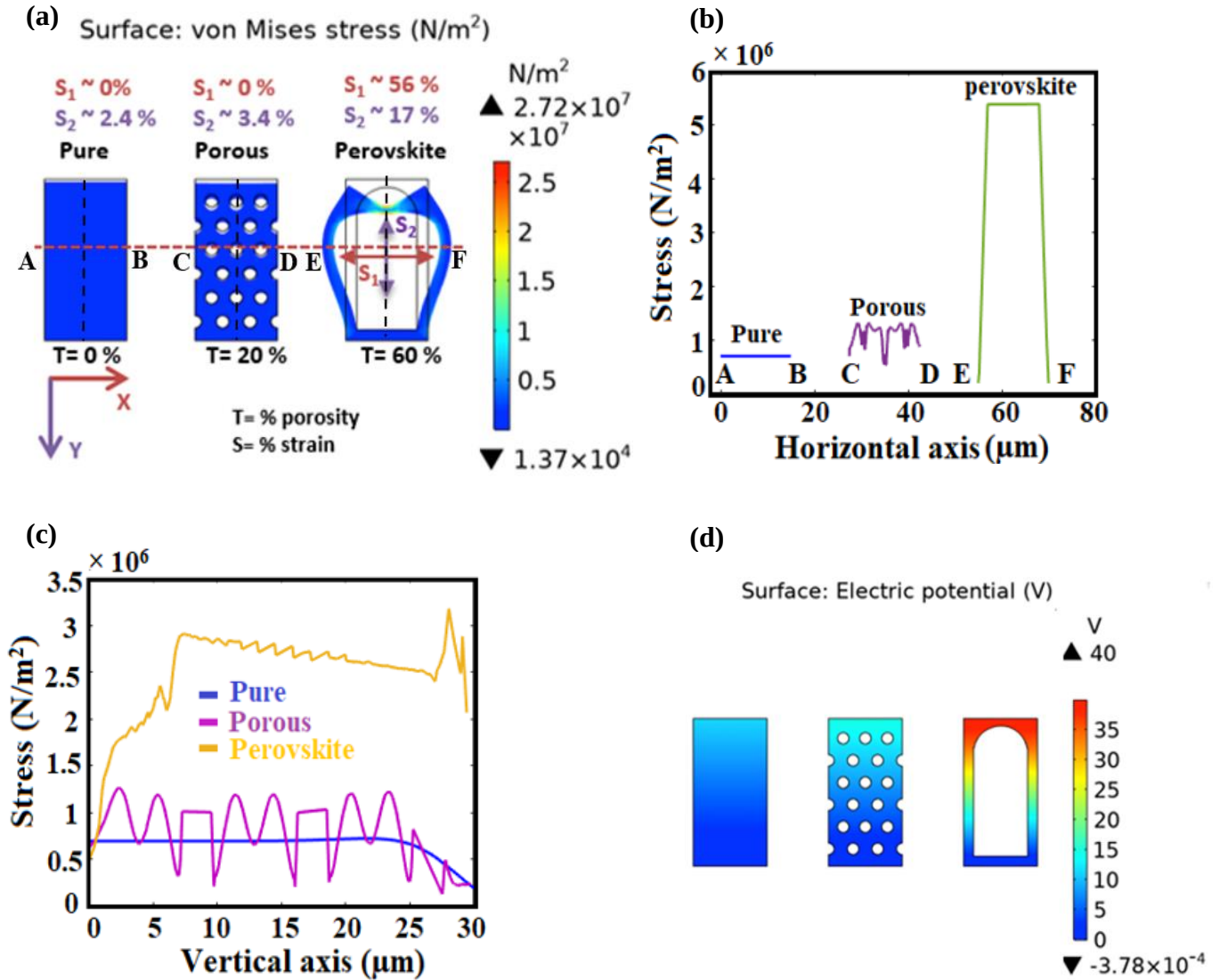


FIGURE 2.12 (a) Simulated stress distribution by the COMSOL for the pure PVDF, porous PVDF (20 wt. %) and FAPbBr₂I@PVDF (20 wt. %) composite films. Stress distribution profiles for the pure, porous and perovskite PENG model (b) along horizontal axis (c) along the vertical axis. (d) Simulated piezo potential distribution by the COMSOL for the pure PVDF, porous PVDF (20 wt. %) and FAPbBr₂I@PVDF (20 wt. %) composite films.

2.7 Conclusions

Compared to the wurtzite class of piezoelectrics (e.g., ZnO), perovskite materials are promising for energy harvesting applications due to their higher intrinsic piezoelectric coefficients. Incorporating perovskites in a polymer to fabricate composite-film based PENGs will provide higher flexibility, stability, and piezo potential. In this chapter, the design, and calculation of the piezoelectric properties are described for the perovskites such as CsPbX_3 , $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$, $(\text{TMCM})_2\text{SnCl}_6$, EDABCO-CuCl_4 , and FAPbBr_2I . By using these organic-inorganic perovskites with flexible polymers such as PVDF, and PDMS, an efficient PENG composite film model is developed. The role of halogen atoms and strains in the CsPbX_3 unit cell for creating high d_{33} piezoelectrics is discussed. The contribution of quasi-spherical cations, atomic displacement, halogen-bond interaction between organic and inorganic components, and Jahn-Teller distortion are theoretically analyzed as a highly effective route to design OIHP material for PENG applications. The Berry phase method is used to calculate the spontaneous polarization and the d_{33} coefficient as a function of the lattice parameter. The effect of piezoelectric OIHP in a real PENG device is realized from the composite film model as calculated by the finite element method. Moreover, in a composite film, the effect of nanorods, porosity, and nanoparticle distribution on piezoelectric potential is discussed. The above-mentioned parameters and effects contribute to high piezoelectricity and serve as the foundation for designing advanced PENG devices in this thesis. It should be noted that the experimental PENGs don't completely coincide with the theoretical model, as the stationary model is considered in these studies. The theoretical model is not able to fully reflect the exact film morphology, and non-uniform piezoelectricity arising from the devices due to different growth conditions, electrical poling, etc. Also, the DFT calculation is simplified for unidirectional force and strain, rather than considering their multi-dimensionality.

Chapter 3

Control of Halogen Atom in Inorganic Metal-halide Perovskites for Designing High-performance PENGs

3.1 Motivation

Regulating the strain of inorganic perovskites has emerged as a critical approach to control their electronic and optical properties. Since the first discovery of strain in a perovskite material in 2015 [115], manipulating it inside the thin film or at the interface of a substrate was proceeded with incorporating a buffer layer, bending the substrate, controlling the thermal gradient during annealing [116],[17], using chemical dopants [117], and light exposure. Light can induce photogenerated electron-hole pairs in a halide perovskite. This process weakens the covalent bonds, and the elongation of lead-halide bonds causes isotropic lattice expansion [118]. Benefitting from this lattice expansion, 20.5% solar cell efficiency has been achieved where the strain relaxation plays a key role in lowering the energy barrier between perovskite-contact interfaces. However, for generating piezoelectricity, the engineered strain should be anisotropic, rather than light-induced isotropic in nature. Here, in this chapter I demonstrate an alternative strategy to further control the piezoelectric properties by substituting the halogen atom (I/Br) in the CsPbX_3 perovskite ($\text{X} = \text{Cl}, \text{Br}$) structure. I unveil a series of piezoelectric materials with excellent piezoelectric coefficients (d_{33}). Iodine incorporated CsPbBr_2I demonstrates the record intrinsic piezoelectric response ($d_{33} \sim 47 \text{ pC/N}$) among all inorganic metal halide perovskites. This leads to an excellent electrical output power of $\sim 0.375 \text{ mW}$ ($24.8 \mu\text{W}/\text{cm}^2 \cdot \text{N}$) in the PENG which is higher than those of the pristine/mixed perovskite references with CsPbX_3 ($\text{X} = \text{I}, \text{Br}, \text{Cl}$). With its structural phase remaining unchanged, the strained CsPbBr_2I retains its superior piezoelectricity in both thin film and nanocrystal powder forms, further demonstrating its repeatability and versatility of applications. The origin of high piezoelectricity is found to be due to halogen-induced anisotropic lattice strain in the unit-cell along the c-axis, and octahedral distortion. This study reveals an avenue to create new piezoelectric materials by modifying their halide constituents and paves the way to design efficient PENGs for improved electromechanical energy conversion.

3.2 Experiments

3.2.1 Synthesis of halogen regulated perovskites

To prepare the precursor solution of CsPbBr₃, 0.2 mmol of CsBr and 0.2 mmol of PbBr₂ is dissolved in 2.8 mL of DMF (**FIGURE 3.1a**). In a similar way, 0.2 mmol of CsI and 0.2 mmol of PbBr₂ are used to synthesize CsPbBr₂I, and 0.4 mmol of CsI and 0.2 mmol of PbBr₂ are used for Cs₂PbBr₂I₂. The CsPbI₃ is synthesized using 0.2 mmol of CsI, and 0.2 mmol of PbI₂, and CsPbCl₃ by 0.2 mmol of CsCl and 0.2 mmol of PbCl₂. The CsPbCl₂Br precursor is synthesized by 0.2 mmol of CsBr, and 0.2 mmol of PbBr₂, and CsPbCl₂I by 0.2 mmol of CsI and 0.2 mmol of PbCl₂. The corresponding reactions are provided below to illustrate the synthesis process. To prepare the thin film samples, the precursors are spin-coated at ~ 500 rpm on a clean aluminum coated (~ 100 nm) silicon wafer for ~ 1 minutes. After that, the films are dried in a hot plate at ~ 60 ° C for 30 minutes and stored in a nitrogen rich ambient.



To prepare the nanocrystal powders (NCP), the precursors are slowly dropped onto toluene under vigorous stirring at room temperature. After that, the solutions are kept for 5-6 hours for the precipitation of the nanocrystals. The nanocrystals are then cleaned with acetone, and dried. Finally, the particles are ground by a mortar and pestle to reduce the size for PENGs fabrication.

3.2.2 Fabrication of the PENG

The PENGs are fabricated by dispersing the NCP CsPbX₃ in a PDMS base with a mass ratio of 5 wt. % (**FIGURE 3.1b**). Stirring overnight a curing agent is added into the mixture with a mass ratio of 1:10 with the PDMS base. Then, the as-prepared solutions are drop-casted on a glass

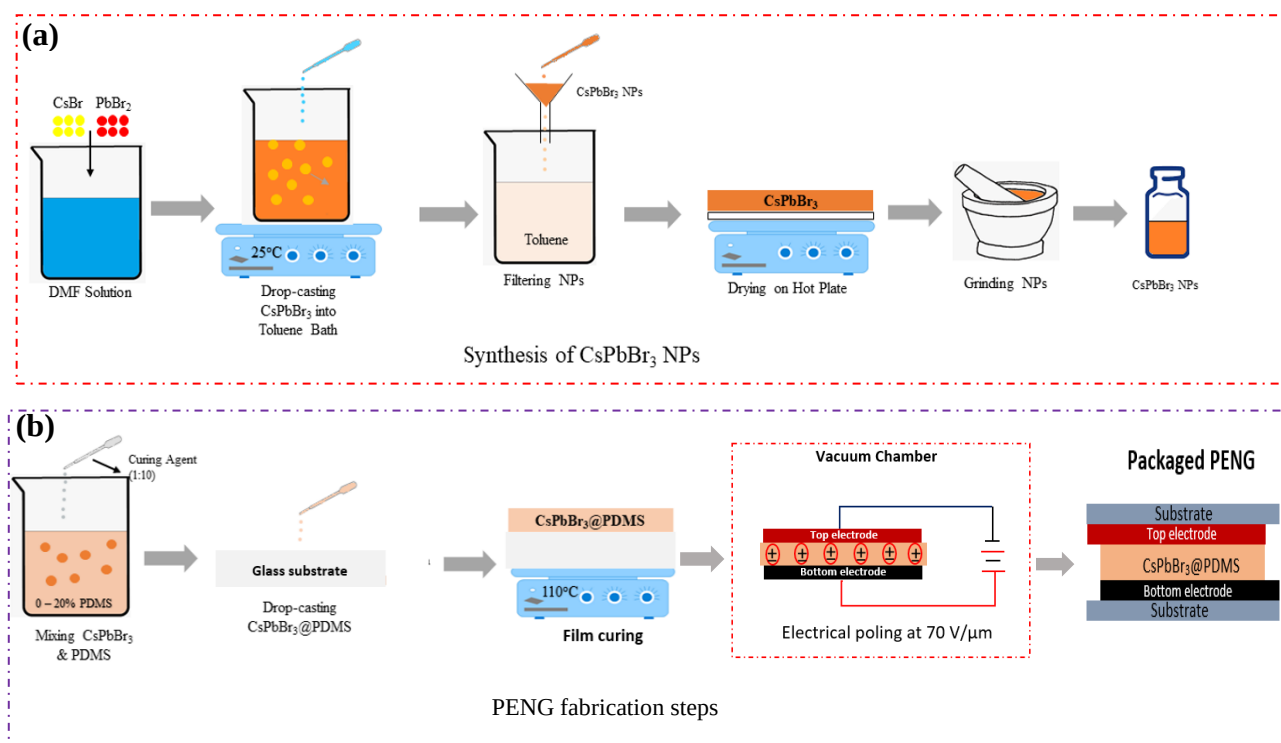


FIGURE 3.1 (a) Schematic illustration of the nanoparticle (CsPbBr₃) synthesis, and (b) PENG fabrication steps.

substrate and degassed for ~ 3 hours. After that, the films dried at a temperature of ~ 80 – 110 °C. Then, the as-prepared films are peeled off, and an electric field of ~ 70 V/ μ m is applied for 3 hours to align the dipoles and enhance the ferroelectricity. Finally, the films are sandwiched between the copper electrodes and laminated in a thermal laminator.

3.2.3 Characterization of halogen regulated perovskites

The vertical piezo response force microscopy (V-PFM) is recorded via Bruker AFM (Dimension Icon). The probe used for the V-PFM is an n-doped (Antimony) silicon probe coated with reflective Pt/Ir on the back and a conductive coating on the tip, having nominal stiffness of 3 N/m. This enables proper measurement of piezo response amplitude and phase during operation. To minimize the substrate induced roughness artifacts, all the samples are prepared on a smooth silicon substrate (roughness < 5 nm) coated with a thin aluminum electrode (~ 100 nm) by RF magnetron sputtering. The piezoelectric coefficients (d_{33}) are measured by applying an ac bias (range of 0 to 10 V) to the samples and grounding the aluminum electrodes. From the measured amplitude vs bias curves, the

slope is calculated to be the d_{33} of the sample. Ferroelectric hysteresis loops are measured by applying a sequence of direct current (dc) voltage range from -10 to 10 V with a superimposed ac voltage of ~ 0.5 V. X-ray powder diffraction investigations are carried out by using the Bruker D8-Discover diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). The scanning electron microscope (SEM) and element mapping test are performed by using JSM-7200F electron microscope. A few milligrams (mg) of CsPbX_3 are weighed, sealed in an aluminum pan, and placed in a differential scanning calorimeter (DSC, Q2000, TA Instruments, USA). The sample undergoes consecutive heating-cooling cycles at 10 °C/min. The dielectric properties of the samples (C–V characteristics) are measured using a Keithley-4200 semiconductor parameter analyzer.

3.2.4 Characterization of the PENG

In this study, the electrical output performance of the PENGs is measured by an electrodynamic shaker (Lab Works Inc.) controlled by a power amplifier and a controller (**FIGURE 3.2**). The PENGs are mounted on the shaker, and a metal weight of (136 g) was attached on top of the device. With the vibrating shaker a fixed weight on top of the device impinging mechanical stress, the PENGs generate electricity by the excellent piezoelectric properties of the CsPbX_3 perovskites. A digital oscilloscope and a low-noise current preamplifier (SR 570, Stanford Research Systems Inc.) are used to measure the electrical signal output from the PENGs.

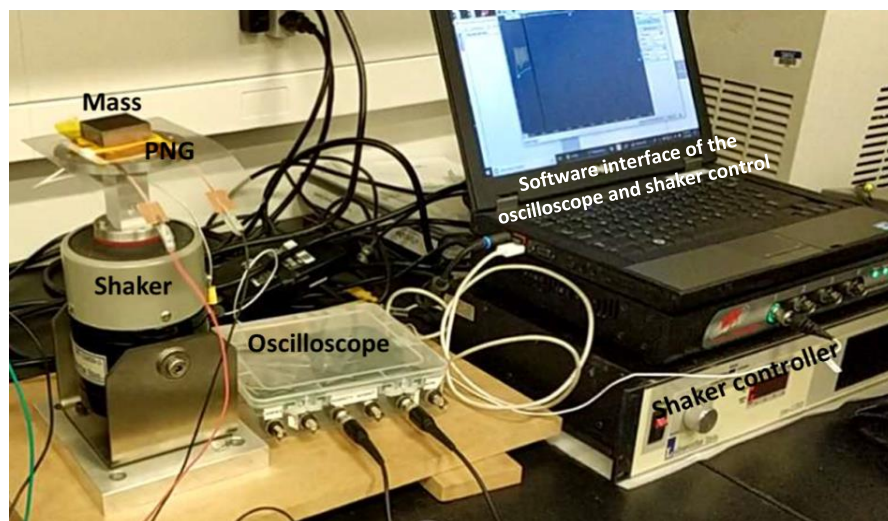


FIGURE 3.2 A photograph of the PENG characterization system, which consists of an electrodynamic shaker, oscilloscope, shaker-controller unit, a laptop with the software interface for the oscilloscope and the shaker, and a proof-mass.

3.3 Results and Discussion

3.3.1 Role of halogen control on the crystallographic viewpoint

In a binary halide composition, two halogen atoms with different sizes (e.g., I, Br) can occupy the equatorial (in-plane) and vertical (out-of-plane) lattice sites in the Pb-centered octahedron. The larger halide in the vertical position can yield a distorted octahedra with a possible elongation, whereas its equatorial positioning can produce a compression. So, the XRD patterns are used to characterize the structural transformation with mixing the halogen atoms. At room-temperature CsPbBr_3 possess an orthorhombic phase and it undergoes two successive increases in the crystal phase symmetry with the rise in temperature, which are orthorhombic to tetragonal ($\sim 88^\circ\text{C}$) and tetragonal to cubic ($\sim 130^\circ\text{C}$). The emergence of piezoelectricity in CsPbBr_3 is due to the phase change from cubic to the orthorhombic structure. The XRD pattern of the CsPbBr_3 in my experiment (**FIGURE 3.3a**) suggests a distorted orthorhombic structure as the calculated lattice parameters for the CsPbBr_3 ($a=8.318$, $b=8.1758$, $c=11.779$) is different from than the standard orthorhombic unit cell ($a=8.207$, $b=8.255$, $c=11.759$) [119]. The b/a ratio of the CsPbBr_3 changes from the ideal orthorhombic value of 1.005 to 0.982, consequently the octahedral distortion of the $[\text{PbBr}_6]^{4-}$ and the off-centering of the Cs^+ will results in the symmetry breaking to creating a slightly separated positive and negative charge centers. The XRD of CsPbBr_2I

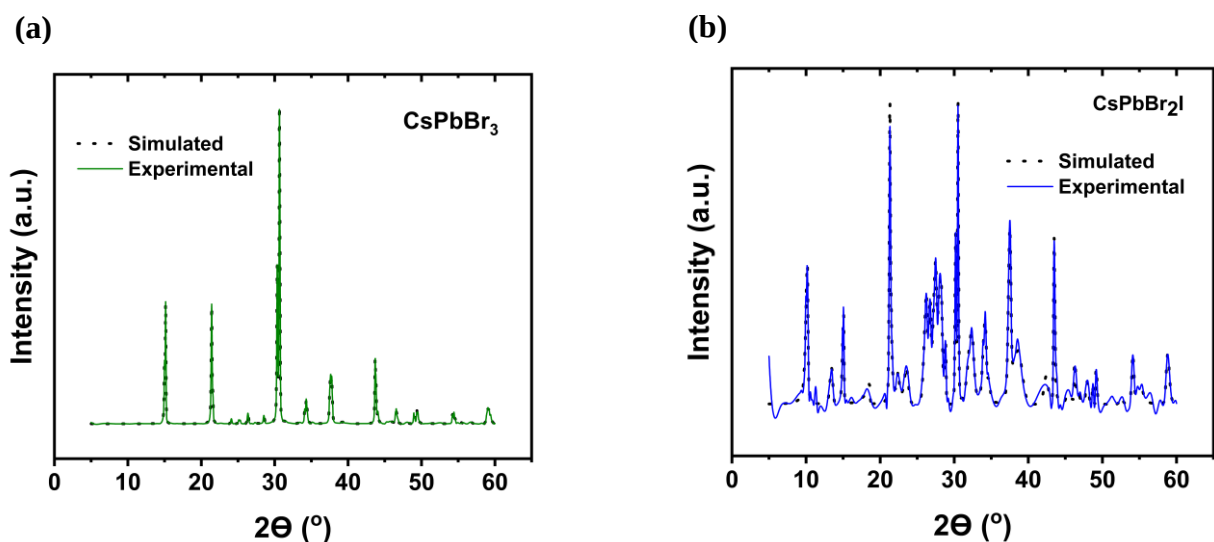


FIGURE 3.3 The XRD pattern of (a) CsPbBr_3 (b) CsPbBr_2I

(FIGURE 3.3b) shows even larger lattice distortion ($b/a = 0.975$) which will also result in the symmetry breaking as confirmed by the induced piezoelectricity. In another study I choose Br/I atom to incorporate in the CsPbCl_3 perovskite for inducing lattice elongation, as Cl has smaller ionic radius of ~ 175 pm. Interestingly, I find a reduction in the unit cell volume from $183.78 \text{ \AA}^3$ in the CsPbCl_3 to $183.6 \text{ \AA}^3$ in the CsPbCl_2Br and $176.1 \text{ \AA}^3$ in the CsPbCl_2I (TABLE 3.1). This can be associate to the counterbalancing of spontaneous strain by the formation of vacancy defects in the CsPbCl_3 [120]. I calculate a compressive strain percentage of -2.7 %, and -4%

TABLE 3.1 Lattice parameters of CsPbCl_3 , CsPbCl_2Br , and CsPbCl_2I .

CsPbCl_3	CsPbCl_2Br	CsPbCl_2I	Crystal planes
22.35 ($d_{\text{hkl}} = 3.975 \text{ \AA}$)	22.04 ($d_{\text{hkl}} = 4.029 \text{ \AA}$)	22.360 ($d_{\text{hkl}} = 3.9727 \text{ \AA}$)	(110)
32.13 ($d_{\text{hkl}} = 2.783 \text{ \AA}$)	31.46 ($d_{\text{hkl}} = 2.841 \text{ \AA}$)	31.940 ($d_{\text{hkl}} = 2.799 \text{ \AA}$)	(200)
39.196 ($d_{\text{hkl}} = 2.296 \text{ \AA}$)	38.77 ($d_{\text{hkl}} = 2.32 \text{ \AA}$)	39.359 ($d_{\text{hkl}} = 2.287 \text{ \AA}$)	(211)
$a = 5.566 \text{ \AA}$, $b = 5.678 \text{ \AA}$, $c = 5.815 \text{ \AA}$	$a = 5.682 \text{ \AA}$, $b = 5.713 \text{ \AA}$, $c = 5.656 \text{ \AA}$	$a = 5.598 \text{ \AA}$, $b = 5.638 \text{ \AA}$, $c = 5.582 \text{ \AA}$	Orthorhombic

along the c-axis of the CsPbCl_2Br , and the CsPbCl_2I , respectively. However, both mixed halide compounds remain in their distorted orthorhombic phase, like the $\text{CsPbBr}_3/\text{CsPbBr}_2\text{I}$. Unlike to the previous single/mixed halide examples, in this study $\text{Cs}_2\text{PbBr}_2\text{I}_2$ belongs to the layered mixed halide perovskite with the Ruddlesden–Popper phase and have a tetragonal structure (TABLE 3.2) [121]. The nanocrystal of the $\text{Cs}_2\text{PbBr}_2\text{I}_2$ ($2\text{CsI} + \text{PbBr}_2$) forms by the stacked layers of corner sharing $[\text{PbI}_2\text{Br}_4]^{4-}$ octahedra, charge balanced by the Cs^+ counterions, and individual layers are separated by the size differences of halogens (I, Br).

TABLE 3.2 Lattice parameters of $\text{Cs}_2\text{PbBr}_2\text{I}_2$

$\text{Cs}_2\text{PbBr}_2\text{I}_2$	Crystal planes
21.14 ($d_{\text{hkl}} = 4.199 \text{ \AA}$)	(103)
31.67 ($d_{\text{hkl}} = 2.823 \text{ \AA}$)	(200)
29.32 ($d_{\text{hkl}} = 3.043 \text{ \AA}$)	(114)
$a = 5.646 \text{ \AA}$, $b = 5.635 \text{ \AA}$, $c = 18.843 \text{ \AA}$	Tetragonal

Controlling the halogen composition (x) in $\text{CsPbI}_{3-x}\text{Br}_x$ can alter the phase transition temperature and the bandgap changes with the x value in accordance with Vegard’s law [122]. As the temperature increases, CsPbBr_3 perovskites change their phase to a higher temperature phase via

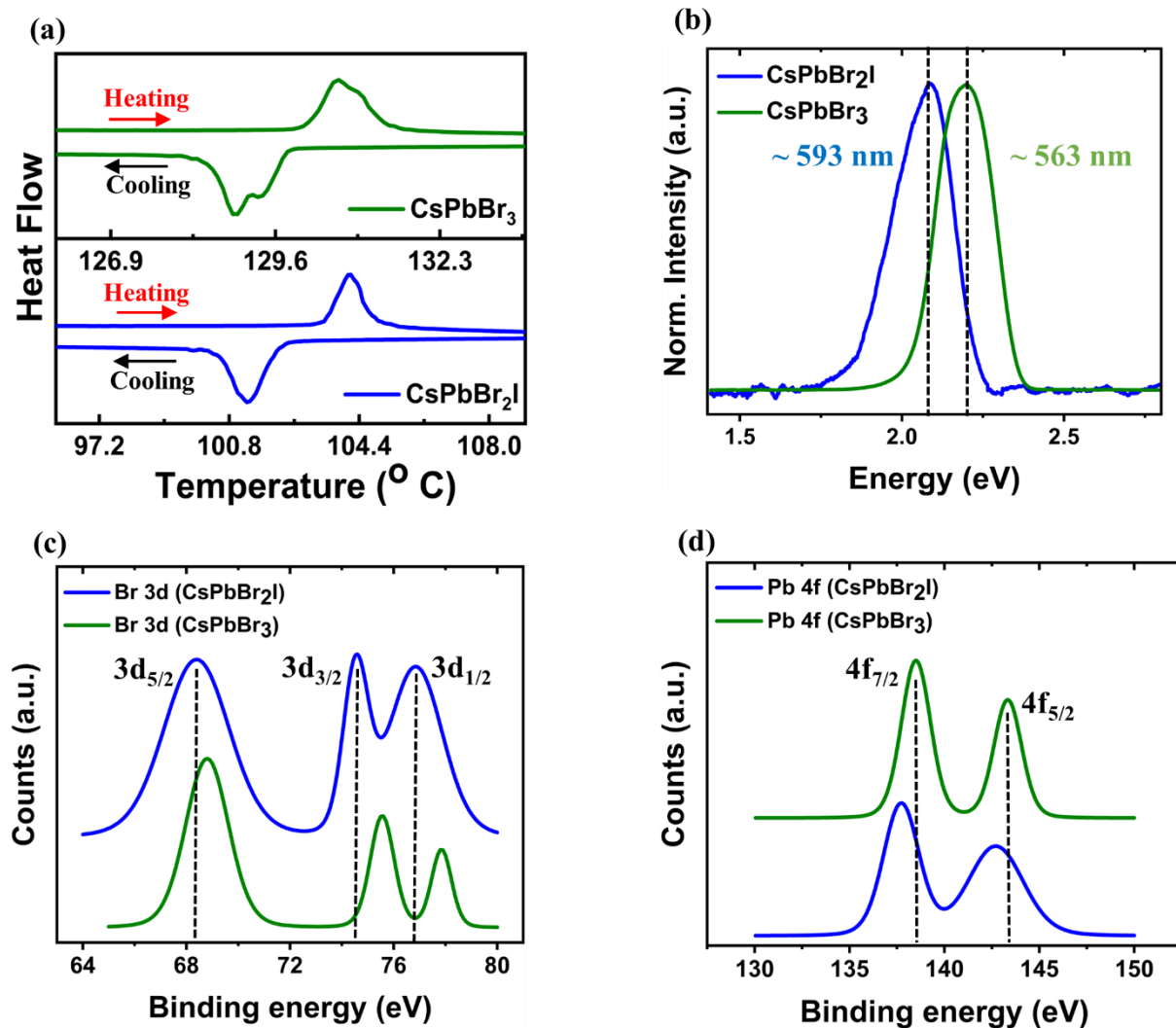


FIGURE 3.4 (a) DSC curves of CsPbBr₂I and CsPbBr₃; (b) peak emission intensity. High-resolution XPS spectra of (c) Br 3d, and (d) Pb 4f of CsPbBr₃ and CsPbBr₂I. The shifts in the binding energy (eV) indicates the change in strain-mediated chemical interaction between the Pb-X (halogen) chemical bonds.

changing the octahedral tilting and symmetry. While increasing the iodine composition in the CsPbI_{3-x}Br_x, enthalpy-change for its transition to higher temperature phase increases from essentially zero in CsPbBr₃ (transiting from orthorhombic to tetragonal structure) to 14.1 kJ/mol for CsPbI₃ (orthorhombic to cubic) [123]. The phase transition temperature varies in parallel to the phase transition enthalpies. During the heating and cooling cycle of the DSC (**FIGURE 3.4a**) I observe a reversible tetragonal to cubic phase transition of the CsPbBr₃ at ~ 129° C and an orthorhombic to tetragonal phase transition for the CsPbBr₂I at ~ 104° C. On the other hand, the orthorhombic to tetragonal transition for the CsPbBr₃ occurs at ~ 91° C. This increase in the phase

transition temperature reflects the higher enthalpy change in the CsPbBr₂I. I also measure a shift in the optical bandgap (E_g) from ~ 2.20 eV in CsPbBr₃ to ~ 2.09 eV for the CsPbBr₂I (**FIGURE 3.4b**). This accompanies a gradual redshift in the emission wavelength from ~ 563 nm to ~ 593 nm typically assigned to band-edge recombination [124]. The valence band maximum (VBM) of the CsPbI_{3-x}Br_x is consist of the antibonding hybridization of Pb 6s and X np orbitals, where the dominant contribution came from the X np. As I control the halogen from Br (4p) to I (5p), the energies of the halide p orbital increases, lifting the VBM toward higher energy. Previous studies suggested that the Pb 6p orbital mainly contributes to the conduction band minimum (CBM) with a minor effect from the X nP character [125]. The extent of hybridization for the CsPbBr₂I is anticipated to decrease due to the longer bond lengths of Pb-I, hence it can move the CBM to lower energies. Although the spin-orbit coupling may influence the CBM energy, the coupling constant for all the halide compositions are (I/Br/Cl) found nearly constant at ~ 1.1 eV [126]. Therefore, my experimental findings match the previously explored trends of decrease in the optical gap moving forward from smaller to larger halide compounds. The XPS (X-ray photoelectron spectroscopy) results show that peaks of CsPbBr₂I shift to lower binding energy in both Br 3d and Pb 4f spectrums (**FIGURE 3.4c-d**). The shift in the core level spectrum of Pb 4f to lower energy indicates reduced interaction with the halides due to lattice elongation.

3.3.2 Evaluation of the intrinsic piezoelectricity

The correlation of lattice strain with piezoelectricity is understood by measuring the out-of-plane piezo response by the vertical piezo response force microscopy (scheme in **FIGURE 3.5a**). Each of the samples is prepared by spin-coating at ~ 600 rpm on a flat aluminum coated (~ 100 nm) silicon substrate. While the substrate is kept electrically grounded, ac voltage is applied to the probe, and the out-of-plane deflection of the cantilever is recorded. Each of the films of CsPbX₃ (X= I, Br, Cl), CsPbBr₂I, CsPbCl₂Br, CsPbCl₂I, Cs₂PbBr₂I₂, and PPLN (periodically poled lithium-niobate) is driven to resonance response for four different ac biases. Based on the contact-resonance frequency of different samples, the ac drive frequency varies between ~ 290 -360 kHz as shown in **FIGURE 3.5b**. The highest peak amplitude response is found for the CsPbBr₂I thin film among the measured samples. This is significant as it denotes the large electromechanical response of the CsPbBr₂I, the characteristic critical for sensing and actuating applications.

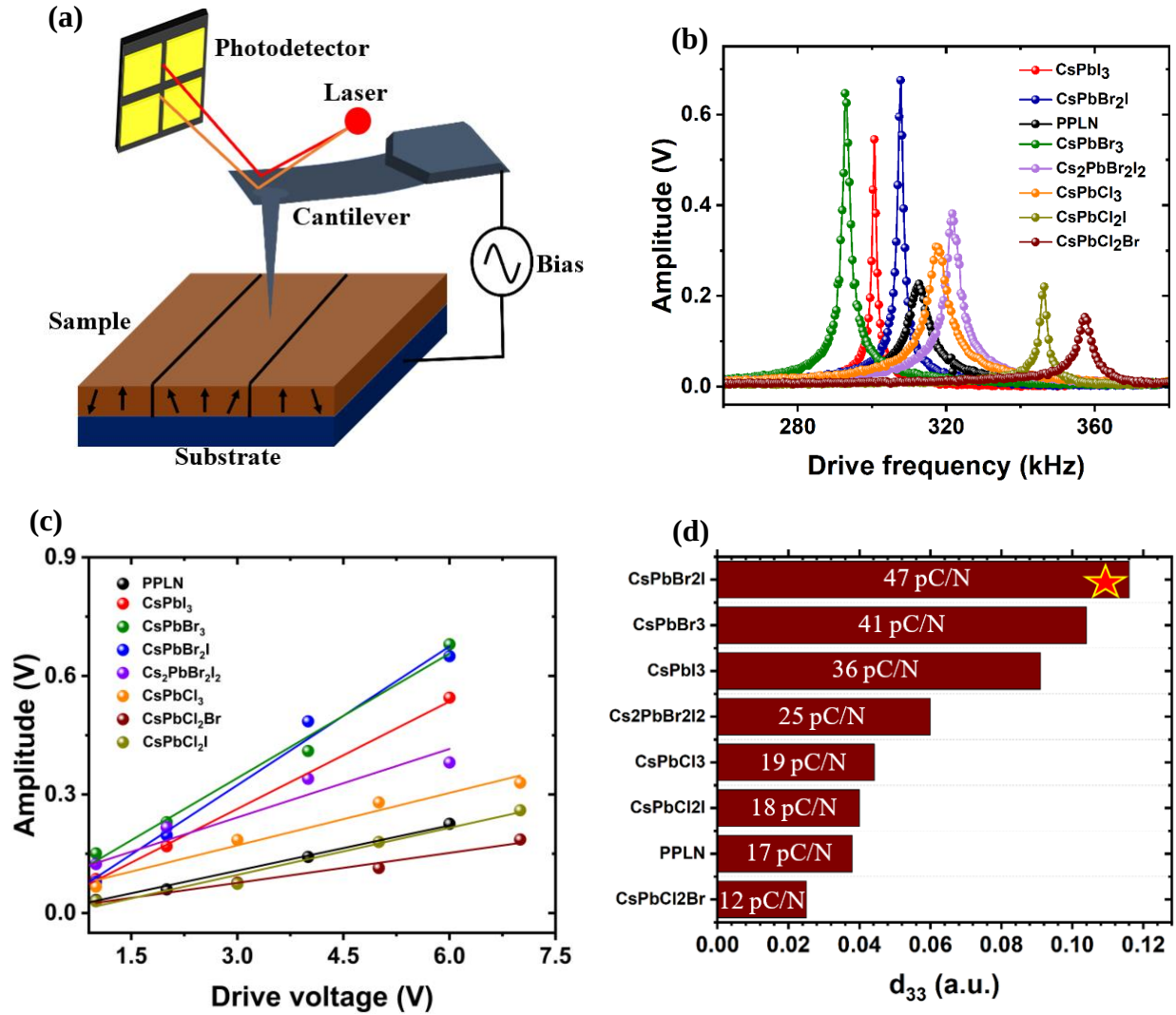


FIGURE 3.5 Evaluating the out-of-plane piezo response. (a) Schematic of the V-PFM set-up. (b) Comparison of PFM resonance peaks. (c) Linear piezo response amplitude of the samples while increasing the ac bias to the cantilever. (d) Measured d_{33} values of the pure halide and mixed halide perovskite materials.

I emphasize that the spontaneous lattice strain in the CsPbBr₂I is the key factor dominating this large electromechanical response. To measure the d_{33} of CsPbBr₂I, point-wise amplitude-voltage measurements are carried out with an ac voltage range from 1.5 to 7.5 V (**FIGURE 3.5c**). For a piezoelectric material, the amplitude response with changing the ac bias should follow a linear trend, whereas the slope will be d_{33} coefficient ($S=d_{33}E$, S strain, E the applied ac bias field) [127]. I observe a linear curve for the samples which indicates the piezoelectric origin of the V-PFM response. I use the reference of periodically poled lithium-niobate ($d_{33} \sim 14 \pm 3$ pC/N) to

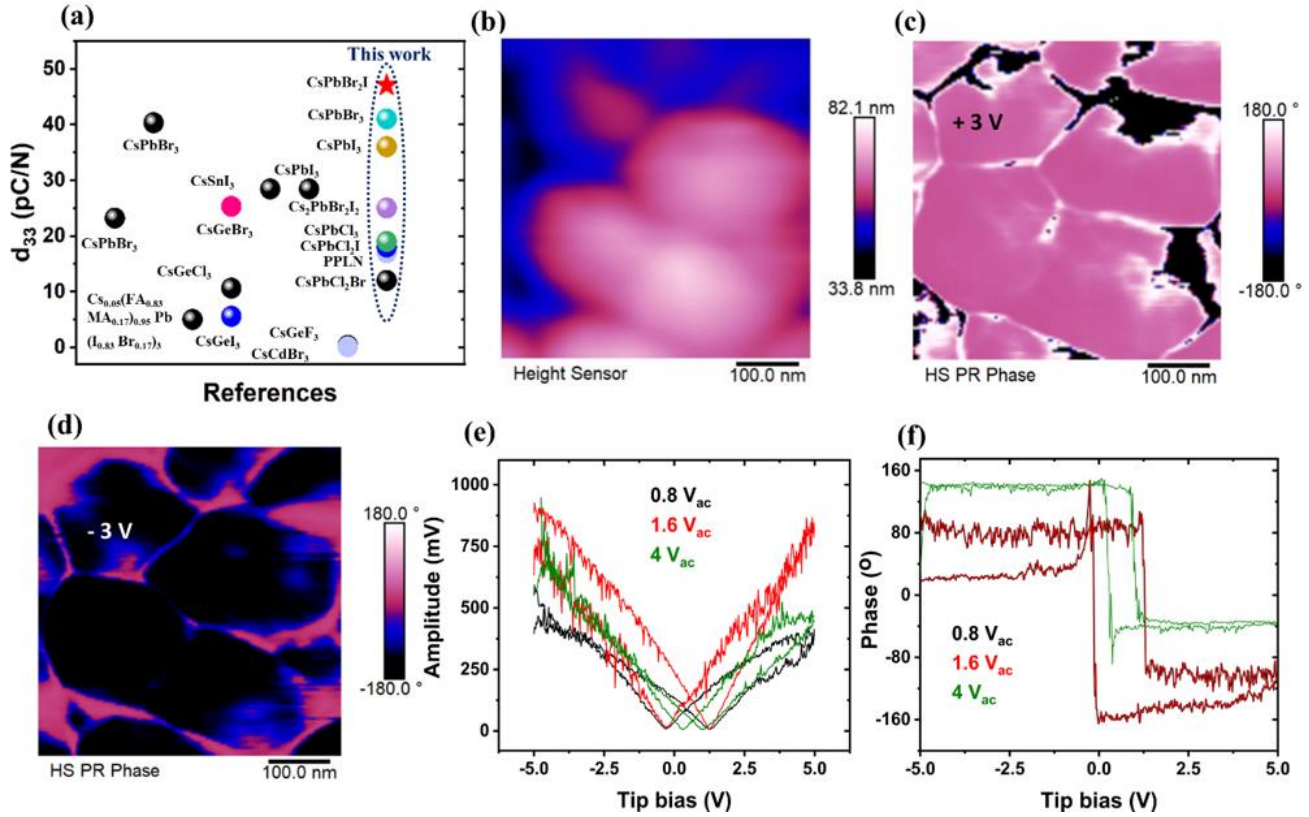


FIGURE 3.6 Investigation of the microscopic piezoelectricity in CsPbBr₂I by the V-PFM imaging. (a) Comparison of measured d_{33} of this work to the state-of-the-art piezoelectric cesium metal halide perovskites discovered to date. (b) Surface topography; (c) V-PFM phase of the CsPbBr₂I at +3 V dc bias and (d) -3 V dc bias. (e-f) Amplitude and phase hysteresis loops of the CsPbBr₂I with various ac bias levels (0.8 V_{ac}, 1.6 V_{ac}, and 4 V_{ac}).

quantify the d_{33} (pC/N) of the samples in my measurements [128],[129]. The calculated d_{33} values are plotted in **FIGURE 3.5d**. The CsPbBr₂I exhibits an excellent d_{33} of ~ 47 pC/N which is $\sim 300\%$ higher than the commercially available PPLN sample. Notably, in the measurements CsPbBr₂I shows 116%, 133%, and 275% higher d_{33} than the CsPbBr₃, CsPbI₃, and CsPbCl₃, respectively. This measured d_{33} of the CsPbBr₂I is the highest among the scarcely reported family of piezoelectric cesium metal halide perovskites (**FIGURE 3.6a**) and the first of its kind of piezoelectric mixed-halide type perovskites [40],[130],[131],[132],[133],[134],[135]. Among pristine cesium metal halides, the CsPbCl₃ shows the lowest piezoelectric response with a value of 19 pC/N. With a strong Pb-Cl bond strength, [PbCl₆]⁴⁻ octahedral framework is expected to result in a less deformation than the other pure cesium metal halides under the same applied bias. The measured d_{33} of the CsPbCl₂I (18 pC/N) shows almost the same value of CsPbCl₃ (18 pC/N), and it decreases to 12 pC/N for the CsPbCl₂Br. It is anticipated that the decrease in the d_{33}

coefficient is due to the reduction in the relative permittivity, according to the equation of $d_{33} = 2Q\epsilon P_s$, where Q denotes electrostriction coefficient, ϵ is relative permittivity, and P_s is spontaneous polarization [136],[137]. To further probe the microscopic piezoelectricity on the surface of thin film, V-PFM imaging was performed. The surface topography image of the CsPbBr₂I in **FIGURE 3.6b** shows the largest grain size with an average of ~ 200 nm, higher than the other halide compounds. Large grain sizes are critical to enhancing the d_{33} , as it makes it easier to achieve displacement of domain walls.

In a ferroelectric material under the influence of an opposite-polarity dc electric field (poling voltage), the spontaneous polarization should be switchable. Driven by this curiosity, a dc poling field is applied to the V-PFM mode for discovering the ferroelectric-type characteristics of CsPbBr₂I. When we do the poling at +3 V dc bias on the grains, I observe a phase contrast in different regions of the grains in the subsequent phase image, which varies from -180° to 180° and can be identified as the small domains with the opposite spontaneous polarization directions (**FIGURE 3.6c**). While poling at a dc bias of -3 V the corresponding phase image (**FIGURE 3.6d**) shows reverse color contrast than the +3 V image in **FIGURE 3.6c**. The opposite color contrast in the two-phase images is the evidence of polarization switching behaviour of the CsPbBr₂I. Now, if the dc field changes in a periodic order the V-PFM amplitude response follows a butterfly shaped loop and phase shows the hysteresis nature which are regarded as a fundamental fingerprint of a ferroelectric material (**FIGURE 3.6e** and **FIGURE 3.6f**) [138],[139]. The butterfly loops are measured with simultaneously applying ac biases of $0.8 V_{ac}$, $1.6 V_{ac}$ and $4 V_{ac}$ to the PFM tip. I notice that when the magnitude of the ac bias varies below the coercive voltage (~ 1.5 V) the hysteresis behaviour is not influenced by the ac bias. If the ac bias reaches higher than the coercive voltage ($4 V_{ac}$), the butterfly loop starts to collapse, and coercive voltage becomes smaller. In a non-ferroelectric material, though such hysteresis loops can be found due to the electrostatic charges, however, such loop remains independent of the ac bias [140]. These phenomena discard the notable influence of electrostatic effects during the experiments. Despite stark debates on the ferroelectric- proof of inorganic metal-halide perovskites, it is envisioned that the combined effect of stereochemical lone-pair electrons of Pb ($6s^2$) and halogen substitution, will create and stabilize the polar distortion in metal-halide octahedra and resulting the spontaneous polarization. Anisotropic strain in the lattice will further enhance this spontaneous polarization with an increase in the d_{33} .

3.3.3 Composition-related piezoelectric outputs

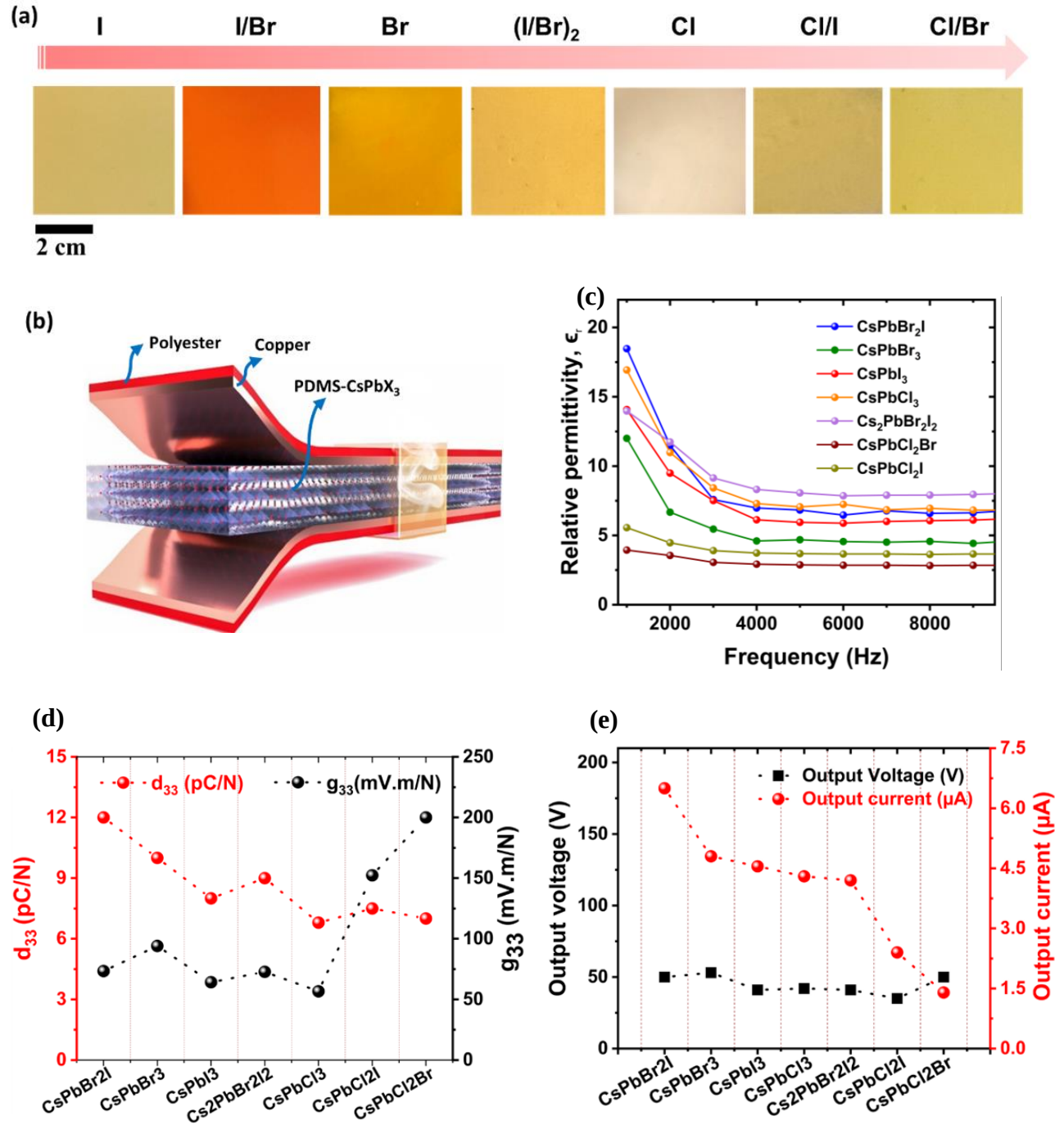


FIGURE 3.7 Mechanical energy scavenging applications. (a) Photograph of the composite films made with CsPbI₃, CsPbBr₂I, CsPbBr₃, Cs₂PbBr₂I₂, CsPbCl₃, CsPbCl₂I, and CsPbCl₂Br. (b) Schematic of the piezoelectric energy harvesters. (c) Measured relative permittivity (ϵ_r) of CsPbX₃ (X=I, Br, Cl, Br/I, (Br/I)₂, Cl/I, Cl/Br) perovskites with the PDMS matrix. (d) Measured d_{33} , and g_{33} of the composite films. (e) Peak output voltage and currents of the PENGs.

Followed by the investigation of piezoelectricity on the nanoscale, I employ them in real-world mechanical energy harvesting. The PENGs are fabricated by distributing the NCP CsPbI₃, CsPbBr₂I, CsPbBr₃, CsPbCl₃, CsPbCl₂Br, CsPbCl₂I and Cs₂PbBr₂I₂ in a polydimethylsiloxane (PDMS) polymer scaffold. The PDMS is mechanically flexible but has no piezoelectric property and possesses an inert chemical environment for hosting the inorganic perovskites. Briefly, 5 wt. % of NCPs are mixed in a PDMS solution and drop cast on a glass substrate. The 5 wt. % concentration is chosen deliberately to avoid the aggregation of the nanoparticles, and to make a fair comparison between the PENGs. Films are peeled off after annealing at 80° C and photographs are shown in **FIGURE 3.7a**. The different colors of the films are expected due to their different optical bandgap, which is tunable by halide regulation as described earlier. Then two copper electrodes are attached to polyester substrates and pressed into a sandwiched structure by a thermal laminator (schematic in **FIGURE 3.7b**). After the electric poling at 70-100 V/μm for several hours' devices are investigated for piezoelectric energy generation. The output current of the PENGs is directly correlated with the d_{33} coefficient, whereas the voltage coefficient (g_{33}) relates to piezoelectric voltage output [141],[142]. Considering the relation between d_{33} and g_{33} ($g_{33}=d_{33}/\epsilon_r$), the relative permittivity (ϵ_r) of the composites is also measured in **FIGURE 3.7c** to calculate the g_{33} coefficients. The calculated ϵ_r of CsPbBr₂I-PDMS is found to be ~ 18.47 at a frequency of 100 Hz. The measured d_{33} of the CsPbBr₂I composite is ~ 12 pC/N, which is 120%, 133%, 150%, 185%, 180%, and 170% of the CsPbBr₃, CsPbI₃, Cs₂PbBr₂I₂, CsPbCl₃, CsPbCl₂Br and CsPbCl₂I, respectively. This result convincingly showcases that the superior d_{33} of the CsPbBr₂I prevails in the composite films. This leads to a g_{33} of $75 \times 10^{-3} \text{ V}\cdot\text{m/N}$ in **FIGURE 3.7d**, which is ~ 200% of commercial PZT-based ceramics ($< 40 \times 10^{-3} \text{ V}\cdot\text{m/N}$) [143]. In contrast, the g_{33} of the CsPbBr₃ composite is ~ $95 \times 10^{-3} \text{ V}\cdot\text{m/N}$, due to its relatively lower permittivity (~ 12). This is in line with the Landau–Devonshire theory of free-energy, which depicts the proportional changes of permittivity with d_{33} , hence fundamentally capping the piezoelectric voltage coefficient [144]; a problem persists in designing piezoelectric materials. The permittivity values for the CsPbCl₂I and CsPbCl₂Br are found to be the lowest in the series (5.56, 4.69) which lead to a large g_{33} of $142 \times 10^{-3} \text{ V}\cdot\text{m/N}$ and $163 \times 10^{-3} \text{ V}\cdot\text{m/N}$, respectively. I measure the output voltage and current of the PENGs by impinging a periodic weight (136 g) on the devices at 30 Hz are shown in **FIGURE 3.7e**. The peak output voltage of the CsPbBr₂I device is ~ 49 V, and the current is ~

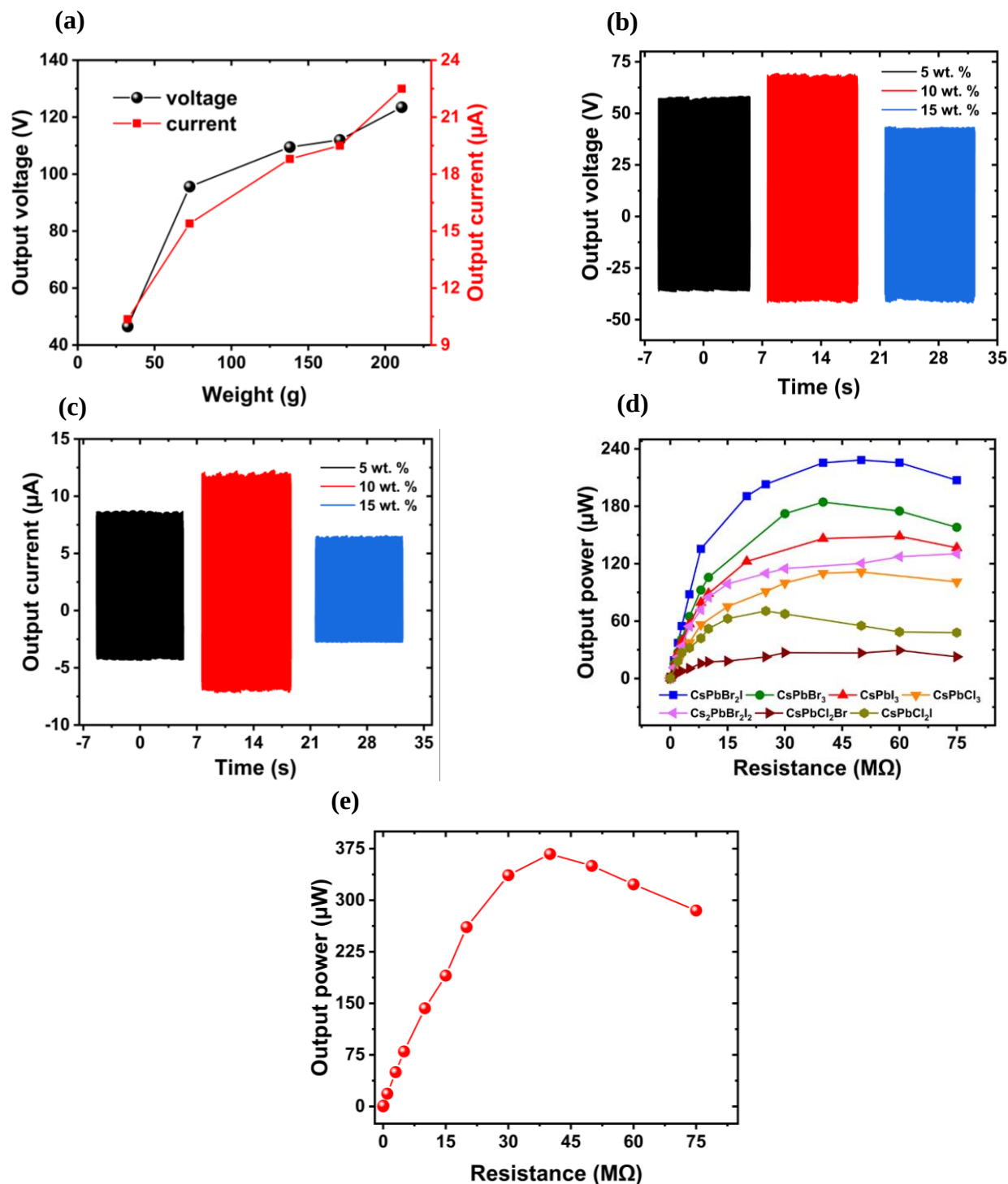


FIGURE 3.8 (a) Weight (g) dependent output voltage (p-p) and current (p-p) of the CsPbBr₂I@PDMS PENG. Concentration dependent (5, 10, and 15 wt. % of CsPbBr₂I) output voltage (b) and current (c) of the PENGs. (d) Comparison of peak output power generation from the various halide substituted PENGs (5 wt.%). (e) Measurement of the highest output power from the 10 wt. % CsPbBr₂I PENG across various external resistances.

6.5 μA , compared to the $\sim 53\text{ V}$ and $\sim 4.7\text{ }\mu\text{A}$ for the CsPbBr_3 PENGs. I vary the force on the CsPbBr_2I device by changing the weights from 30 g to 210 g, which increases the voltage and current to $\sim 60\text{ V}$ and $\sim 11\text{ }\mu\text{A}$ (**FIGURE 3.8a**). Then I fabricate the PENGs device by changing the loading amount of the dispersed nanoparticles of the CsPbBr_2I to 10 wt. %, and 15 wt. %. At 10 wt. % and 210 g of applied weight the peak output voltage and current is the maximum of $\sim 65\text{ V}$ and $\sim 12\text{ }\mu\text{A}$ (**FIGURE 3.8b-c**). When the concentration increases to 15 wt. %, the device output start to decrease due to the agglomeration of nanoparticles.

To evaluate its maximum transferred power to the electrical load, the generated output power from the halide substituted PENG devices are compared across a wide range of external resistances from zero to $75\text{ M}\Omega$ (**FIGURE 3.8d**). The output power from the 5 wt. % CsPbBr_2I PENG reaches to 0.22 mW (milliwatt) at a resistance of $\sim 40\text{ M}\Omega$. Similar measurements are conducted for other samples of CsPbBr_3 , CsPbI_3 , CsPbCl_3 , $\text{Cs}_2\text{PbBr}_2\text{I}_2$, CsPbCl_2Br , and CsPbCl_2I based PEGs, yielding maximum power of $\sim 0.18\text{ mW}$, $\sim 0.14\text{ mW}$, $\sim 0.09\text{ mW}$, $\sim 0.11\text{ mW}$, $\sim 0.067\text{ mW}$, and $\sim 0.027\text{ mW}$, respectively. The maximum output power from the 10 wt. % CsPbBr_2I device is measured to be 0.375 mW at a tiny weight of 210 g (**FIGURE 3.8e**).

3.4 Conclusions

In summary, the halogen substitution strategy is demonstrated as an effective method to control the piezoelectricity and energy harvesting capability of inorganic metal halide perovskites. The nanoparticles of CsPbI₃, CsPbBr₂I, CsPbBr₃, CsPbCl₃, CsPbCl₂Br, CsPbCl₂I and Cs₂PbBr₂I₂ are synthesized by a low temperature (60 °C), low cost and one-step LARP method. The state-of-the-art PFM is used to probe their piezoelectric properties on the nanoscopic resolution. By measuring their piezoelectric coefficients (d_{33}), this comprehensive study reveals a series of piezoelectric materials for mechanical energy harvesting applications. This study also reports the record d_{33} in CsPbBr₂I among all the cesium metal halide perovskites. To coin the origin of high d_{33} , changes in the unit-cell parameters are investigated by the XRD and XPS. Regulation of the iodine atom causes lattice elongation, which softens the perovskite structure to generate more polarization, hence tensile strain is reasoned for the improved piezoelectricity. The correlation between tensile strain and piezoelectricity is also established by structural simulation. The influence of force, frequency, and nanoparticle concentration are investigated for the device performance optimization. Excellent electromechanical energy conversion capability is found from the 10 wt. % CsPbBr₂I@PDMS PENG, with an output electrical power of 0.375 mW (24.8 μ W/cm².N) which is higher than the test PENG devices made from pure/mixed halide perovskites (CsPbX₃; X=I, Br, Cl, (Cl/Br), (Cl/I), (I/Br)₂), and among the very few reported PENGs made from organic/inorganic metal halide perovskites. It is anticipated the experimental findings in this work will inspire future piezoelectric material exploration with high d_{33} by modifying the existing one.

Chapter 4

Piezoelectric Nanogenerators Based on Organic-inorganic Hybrid Perovskite Nanorods

4.1 Motivation

Developing highly piezoelectric nanoparticles with inherent mechanical-electrical coupling effect is critically important for energy harvesters, self-powered sensors, and actuators. Over the past decades, the NPs with a high longitudinal piezoelectric coefficient (d_{33}) were developed for piezoelectric nanogenerators that operate under periodic vertical compression mode. Due to their high d_{33} value, perovskite-type ceramics such as BTO, PbTiO_3 , and PZT, are the most widely explored piezoelectric materials for the PENG applications. Unfortunately, these highly piezoelectric inorganic ceramics are inherently brittle, and their synthesis is often associated with very high temperatures. Atomically thin layered two-dimensional Ruddlesden-Popper piezoelectric OIHPs, such as (benzylammonium)₂ lead halide $[(\text{PMA})_2\text{PbX}_4]$, (cyclohexylammonium)₂ lead halide $[(\text{CHA})_2\text{PbX}_4]$ and (4-aminotetrahydropyran)₂ lead halide $[(\text{ATHP})_2\text{PbX}_4]$, have emerged from the shadows of the above ABX_3 type perovskites and are expected to have numerous applications in the next generation smart electronics and sensors [145],[28]. Previous studies have revealed the 2D piezoelectric OIHPs films can rival or exceed inorganic ferroelectrics in performance, such as high piezoelectric voltage coefficient, large piezoelectric response (d_{33}), and high spontaneous polarization. Even though the excellent piezoelectric performance was reported, however, during the fabrication of an efficient nanogenerator, the pristine 2D OIHP thin films still possess similar brittleness and inflexibility issues as the inorganic piezoelectric materials; hence inhibiting its practical applications where it endures a repeated cycle of mechanical vibration. Moreover, its complex synthesis approach makes it incompatible to be incorporated with the polymer materials for fabricating a high-quality piezoelectric composite film. In this work, I successfully synthesize an OIHP nanorods of (4-aminotetrahydropyran)₂ lead bromine chlorine $[(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2]$ that exhibits a large d_{31} of 64.2 pC/N, which is 3 times higher than the PVDF, which is the most widely used piezoelectric polymer in the market. A saturated polarization of $5.4 \mu\text{C}/\text{cm}^2$ and a piezoelectric voltage coefficient of $900 \times 10^{-3} \text{ V}\cdot\text{m}/\text{N}$ are also reported. The $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs can be dispersed homogeneously in a

polymer matrix to make piezoelectric composite films. Due to their excellent flexibility, uniform dispersion, and large surface area the concurrent vertical strain and lateral bending yield a high piezoelectric performance. I fabricate a unique piezoelectric composite film for PENGs, which can produce an output voltage (V_{oc}) of 90 V and a short-circuit current (I_{sc}) of 6.5 μ A under an applied force of only 4.2 N, outperforming many state-of-the-art PENGs. This is the first work, that not only reveals the large transverse piezoelectricity in the (ATHP)₂PbBr₂Cl₂ NRs, but also coins a route to employ it in practical energy harvesting devices.

4.2 Experiments

4.2.1 Synthesis of the hybrid perovskite nanorods

2 mmol ATHP-HCl and 1 mmol PbBr₂ are dissolved in 20 mL of DMF. When the ATHP-HCl is mixed with the metal halide of PbBr₂ with a molar ratio of 2:1, long organic cation of ATHP doesn't fit into the inorganic octahedral framework of Pb (Br/Cl)₆; rather anchor on the octahedron through hydrogen bonding interaction between the protonated N-H⁺ of the ATHP and the halogen of the octahedron. Then 60 μ L octylamine (OTA) is added into the solution followed by constant stirring at 60 °C for 30 minutes. The role of the octylamine is to control the preferential growth of the perovskite nanostructures. More specifically, controlling the amount of the OTA will be resulting in the growth of different perovskite microstructures, whereas a lower concentration of OTA will favor the growth of nanorods type structures. For example-by introducing more OTA in the reaction can electrostatically bind it with the preformed monolayer perovskite nuclei, suppress its vertical oligomerization, and leads to the growth of nanosheets/nanoplates [146],[147]. However, a lower concentration of OTA will partially cover the surface of the perovskite nuclei and will favor the growth of nanorods type structures. The as-prepared precursor solution is slowly dropped into 350 mL of toluene under vigorous stirring at room temperature (25 °C). Along with the mixing, the color of the solution turns from clear to slight white, indicating the formation of NRs. The NRs are purified via centrifuging at 6500 rpm for 2-3 minutes and then re-dissolved in 2 mL toluene for the composite film growth.

4.2.2 Characterization of the hybrid perovskite nanorods

X-ray powder diffraction investigations are carried out by using the Bruker D8-Discover diffractometer with Cu K α radiation ($\lambda=1.5418$ Å). The transmission electron microscopy is recorded by using FEI Tian 80-300 HB electron microscope with an acceleration voltage of about 200 kV. The scanning electron microscope and element mapping test are performed by using JSM-7200F electron microscope. The vertical and lateral piezo response force microscopy (PFM) is recorded via Bruker AFM (Dimension Icon). The probe used for the PFM is an n-doped (Antimony) silicon probe coated with reflective Pt/Ir on the back and a conductive tip coating, having nominal stiffness of 3 N/m. The sample for the PFM is prepared by drop-casting the diluted NRs solution on the n-doped silicon wafer. The piezoelectric response curves are collected via applying a sequence of direct current (dc) voltages from -10 to 10 V with a superimposed alternating current (ac) voltage of 2 V to probe tip. For the Kelvin probe force microscopy, the sample is probed by using a JPK NanoWizard II AFM instrument with Kelvin Probe Module enabled. The KPFM images are collected simultaneously in the intermittent contact mode with the KPFM hovering height at 50 nm. The resonance frequency of the probe is around 305 kHz, and the drive frequency are set at 304.45 $\pm$ 0.03 kHz for all the images taken. Electrical characterizations including I-V curves and P-V loops are carried out by Keithley 4200 semiconductor characterization system by tuning the applied voltages from -200 V to 200 V. The relative permittivity (ϵ_r) of the composite film, is also measured by using the Keithley 4200 semiconductor characterization system with the frequency from 1 kHz to 1 MHz. The efficient piezoelectric coefficient of the composite film is measured via the quasi-static method (Polyk d_{33} meter).

4.2.3 PENG fabrication

The fabrication processes of the PENGs based on (ATHP) $_2$ PbBr $_2$ Cl $_2$ NRs are consecutively illustrated in **FIGURE 4.1**: (i) (ATHP) $_2$ PbBr $_2$ Cl $_2$ NRs are synthesized via the LARP technique (more details are provided in the section 4.2 above). (ii) Piezoelectric composite precursor is prepared via dispersing the (ATHP) $_2$ PbBr $_2$ Cl $_2$ NRs into PDMS; (iii) a piezoelectric composite film is formed by drop-casting the step-ii precursor onto a polyethylene terephthalate (PET) substrate coated with a conductive indium tin oxide (ITO) and then curing the solution at 150 °C for 40 minutes; (iv) then a copper (Cu) tape is attached to the top surface of the OIHP piezoelectric composite film as a top electrode and then a high electrical poling voltage of 6.0 kV is applied

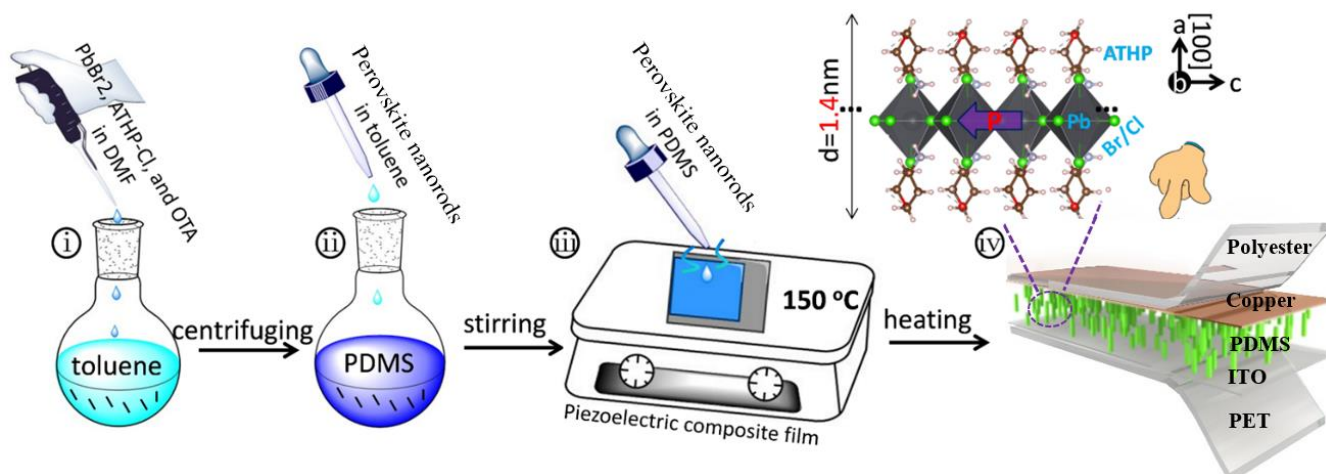


FIGURE 4.1 (i) Sketch of the synthesis process of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs; (ii-iii) the growth of composite films; and (iv) the fabrication of PENGs.

between the electrodes for 2-3 hours to align the piezoelectric dipoles of the film. Finally, the device is thermally laminated with a top polyester substrate.

4.2.4 PENG characterization

To measure the electrical output from the PENGs, an electrodynamic shaker system (ET-140, Lab works Inc.) is used to create periodic mechanical excitation. The generated output voltage from the device is recorded by a digital oscilloscope (Tektronix 2004C) with a $100\text{ M}\Omega$ probe, and the short-circuit current is measured by a low-noise current preamplifier (SR570, Stanford Research Systems, Inc.). Fixed resistances are used in a range from $100\text{ K}\Omega$ to $75.4\text{ M}\Omega$ to optimizing the output power density.

4.3 Results and Discussion

The average width of the NRs is 175.65 nm with a minimum of 151.2 nm and a maximum of 227.8 nm . The thickness of as-synthesized NRs is confirmed by the AFM in **FIGURE 4.2a**. From the AFM, the thicknesses of the NRs ranges are measured from 100 to 200 nm . Compared with the simulated XRD in **FIGURE 4.2b**, the measured XRD of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs film on silicon only exhibits sharp (100) planar peaks ($l = 2, 4, 6, 8, 10, 12$), suggesting that the NRs are mostly oriented in the [100] direction.

The piezoelectric polarization in the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs is examined via the lateral (transverse) (**FIGURE 4.3a**) and vertical (longitudinal) PFM methods (**FIGURE 4.3b**). In the lateral PFM measurements (L-PFM), in-plane displacement (laser deflection in the x-axis) arises from the shear

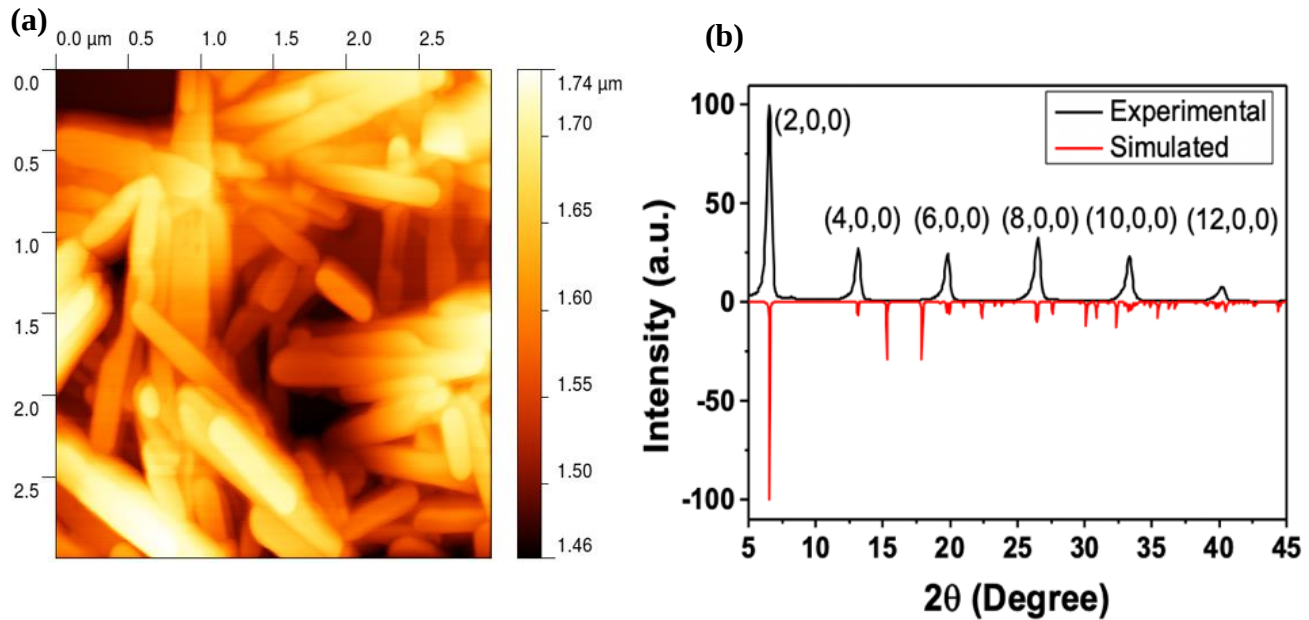


FIGURE 4.2 (a) Surface topography of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs from the AFM. (b) Experimental (black) and simulated (red) XRD patterns of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs film. The $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs film gives sharp periodic (200) planar peaks in the XRD pattern denoting [100] orientation.

strain between the PFM cantilever tip and the sample (**FIGURE 4.3a**). To probe the PFM cantilever tip a sequence of direct current (dc) voltages from -10 to 10 V with a superimposed alternating current (ac) voltage of 2 V was applied. In principle, the electric domain forms in the ferroelectric material can be switched by an external electric field. Due to the inherent polarization switching characteristics, and remnant polarization phenomena at zero bias, the sequential application of an electric field to the ferroelectric material generate a phase loop and a butterfly-shaped amplitude loop in the PFM measurement. During the transverse piezo response measurements by lateral piezo response force microscopy (L-PFM) the phase-hysteresis loop exhibits a 180° change (inset in Figure 2c) and the amplitude curve in **FIGURE 4.3c** shows a characteristic butterfly feature. The L-PFM is a strong indicator of the in-plane transverse piezo response produced by the in-plane polarization in the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs. During the L-PFM measurements, the deformation of the sample is perpendicular to the cantilever motion and deformation-amplitude varies proportionally with the applied voltage. To determine the d_{31} in the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs, we use a standard poled PVDF film (Polyk Technologies, USA) as a

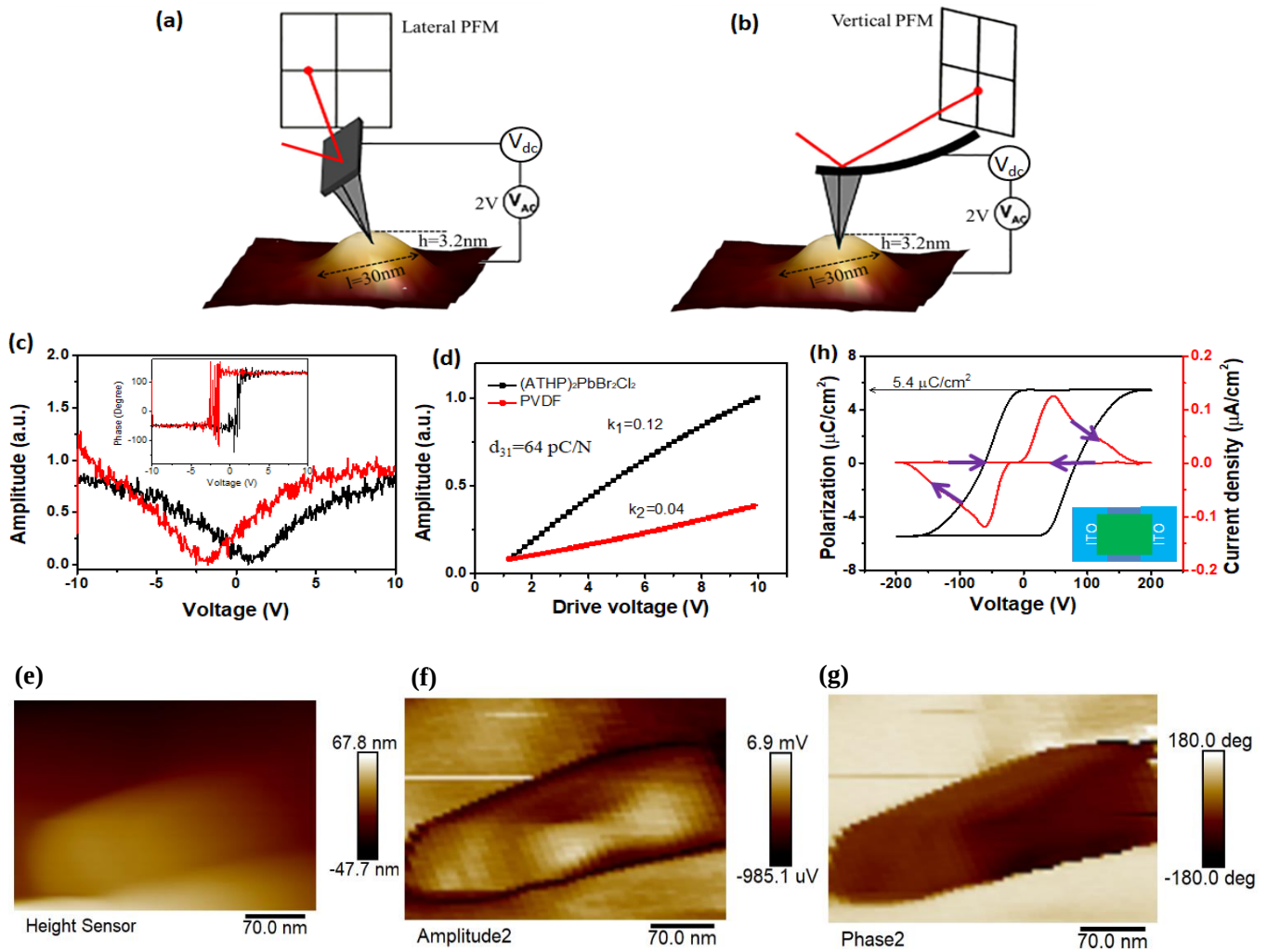


FIGURE 4.3 Origin of piezoelectricity from the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs: (a) a schematic representation of lateral (a) and vertical (b) PFM methods; (c) local lateral (transverse) piezo response amplitude and phase hysteresis (inset) versus cyclic direct current (dc) voltage loops from -10 to 10 V; (d) comparison of the lateral PFM resonance amplitude of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NR and a commercial poled PVDF film; (e) surface topography; (f) lateral PFM amplitude and (g) phase images of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs. (h) The current density-voltage (J-V) curve and the integrated polarization-voltage (P-V) hysteresis loop of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ film at room temperature (25 °C) obtained by using the double-wave method.

benchmark in the L-PFM measurements, whereas the tip-cantilever is aligned perpendicular to the a-axis of the PVDF. As shown in **FIGURE 4.3d**, the slope of the measured L-PFM amplitude vs. drive voltage curve of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ ($K_1=0.12$) is almost 3 times that of the reference PVDF sample ($K_2=0.04$). Therefore, the d_{31} of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ should be ~ 64 pC/N, which is rather

competitive in comparison to traditional perovskites and other molecular materials. Then the ferroelectric domain pattern of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ in the lateral mode is investigated in **FIGURE 4.3e-g**. There is a clear contrast in the lateral amplitude and phase (-180° to 180°) images in **FIGURE 4.3f-g** (small noises are present due to the lower bias voltage of 3.6 V). The minimum signal values in the amplitude image (**FIGURE 4.3f**) are the domain walls separating the adjacent domains. This evidence of domains is the indication of in-plane ferroelectricity in the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs. In contrast, out-of- plane deformation (laser deflection in the y-axis) from the sample is estimated from the vertical bending motion of the tip during the vertical PFM (longitudinal) measurements. The V-PFM measurements does not exhibit a measurable phase change and the piezo response amplitude contrast was weaker than the L-PFM measurements. This superior polarization in the transverse direction is yielding higher piezoelectric coefficient (d_{31}). It should be noted that the piezoelectric response from the PFM techniques may contain long-range electrostatic interactions and non-local interactions between the tip and sample surface. Therefore, I perform kelvin probe force microscopy KPFM on the surface of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ (**FIGURE 4.4e**) NRs. Since the surface topography in the KPFM does not exhibit any patterns as found in the PFM images; we exclude any significant influence of the topography on the domain patterns. The homogeneous surface-potential distribution on the surface of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ (**FIGURE 4.4e**) rules out any contributions from the domains. The polarization switching behavior at room temperature can also be observed by measuring the current density-voltage (J-V) curve and polarization-voltage (P-V) hysteresis loop. For this measurement, a sample is prepared by drop-casting and curing the NRs film between two ITO electrodes (the inset in **FIGURE 4.3h**). As shown in **FIGURE 4.3h**, two peaks with opposite signs in the J-V curve are observed at $\pm 50\text{V}$, revealing two stable states with opposite polarization. The saturated polarization (P_s) is estimated from the P-V hysteresis loop to be $5.4 \mu\text{C}/\text{cm}^2$.

FIGURE 4.4a shows the cross-sectional scanning electron microscopy (SEM) image of a fabricated PENG. The piezoelectric composite film loaded with 30 wt. % $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ has a thickness of about $\sim 300 \mu\text{m}$ and is sandwiched uniformly between a top copper electrode and a bottom ITO-coated PET substrate. **FIGURE 4.4b** is a zoomed-in SEM energy dispersive spectroscopy (EDS) mapping over the cross-section of the fabricated PENGs device (elemental mappings of Si, Pb, Br, and Cl in the insets (i-iv), and a fabricated device photo is shown in the inset (v) of **FIGURE 4.4b**).

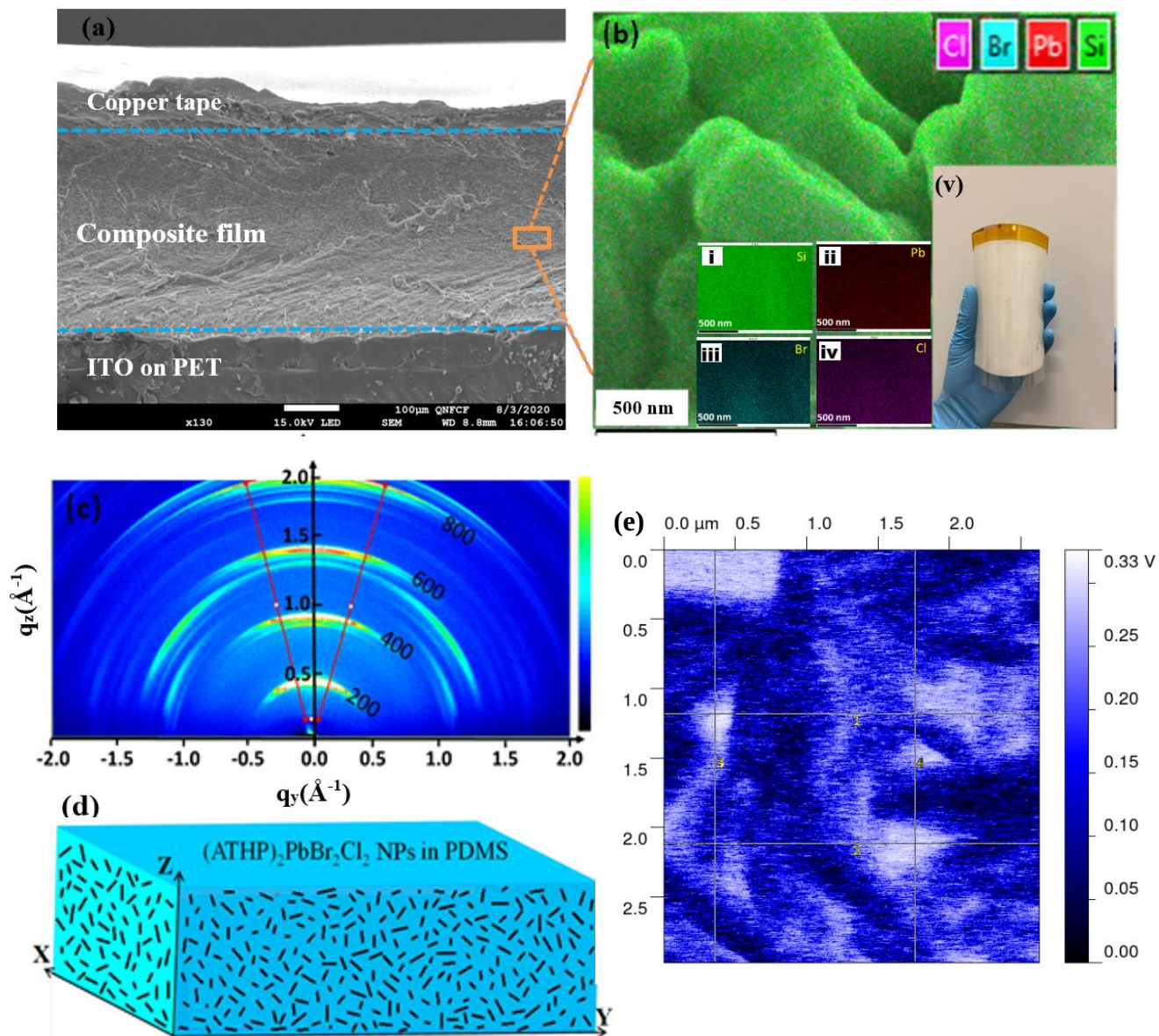


FIGURE 4.4 Morphology of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs@PDMS composite films: (a) the cross-sectional SEM and (b) SEM-EDS mapping images of spin-coated 30 wt. % $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs@PDMS composite films on ITO/FTO substrate; (inset shows (i-iv) elemental mapping of Si, Pb, Br, and Cl, respectively in the PDMS and (v) a large area PENG device). (c) GIWAXS image for 30 wt.% $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs@PDMS composite films; (d) schematic illustration of the orientation of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs in PDMS. (e) Surface potential distribution of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs measured by the Kelvin probe force microscopy (KPFM).

From the SEM-EDS images in **FIGURE 4.4b**, the (ATHP)₂PbBr₂Cl₂ NPs (corresponding to the elemental mapping of Br, Cl, and Pb) are dispersed homogeneously in the PDMS (corresponding mapping of Si) matrix. The uniform dispersion of the NPs in the composite film is critical to obtain optimum piezoelectric performance, as the NPs will act as the mechanical load- carrying center and homogeneous NPs distribution will increase the high voltage poling breakdown-strength of the film. The orientation of polarization in the NRs is important for the piezoelectric performance as elucidated in the earlier studies of 2D MoS₂-based PENGs. From the grazing-incidence wide-angle X-ray scattering (GIWAXS) of the (ATHP)₂PbBr₂Cl₂@PDMS composite film in **FIGURE 4.4c**, quasi-Debye-Scherrer rings are observed, which is expected due to the random orientation of the NRs (**FIGURE 4.4d**). This is different from the reported 2D perovskite quantum wells orientation- where the polarization is perpendicular to the vertical compression [148]. This phenomenal discrepancy should be attributed to supporting the flexible NRs by the PDMS scaffold.

The piezoelectric output of the PENGs is measured by mounting the test device on an electrodynamic shaker, which goes through a periodical vertical compressing and releasing process. According to the equation of short-circuit current density $J_{sc} = (d_{33}^* \times \Delta P) / \Delta t$, (where d_{33}^* is the effective piezoelectric coefficient of the composite film, ΔP is applied pressure, and Δt is time) the output J_{sc} is proportional to the d_{33}^* . **FIGURE 4.5a** shows that the measured d_{33}^* of a pure PDMS film is close to zero, which implies that the measured d_{33}^* value of the composite films is mainly attributed to the addition of the (ATHP)₂PbBr₂Cl₂ NRs. When the mass ratio of embedded NRs in the PDMS matrix increases from 10 to 40 wt. %, the d_{33}^* value of the composite film linearly increases from 19 to 56 pC/N, which is measured by a quasi-static d_{33} meter. It is experimentally found that the mass ratio of the NRs in the PDMS beyond 40 wt. % is rather difficult for thermal curing hence to fabricate a practical device. Note that the highest d_{33}^* of the composite film is two times higher than the commercial poled PVDF (28 pC/N) film. In contrast, the output voltage (V_{oc}) is determined by the piezoelectric voltage coefficient (g_{33}^*) which is defined as $(d_{33}^* / (\epsilon_0 \times \epsilon_r))$ and expressed in the unit of V•m/N.

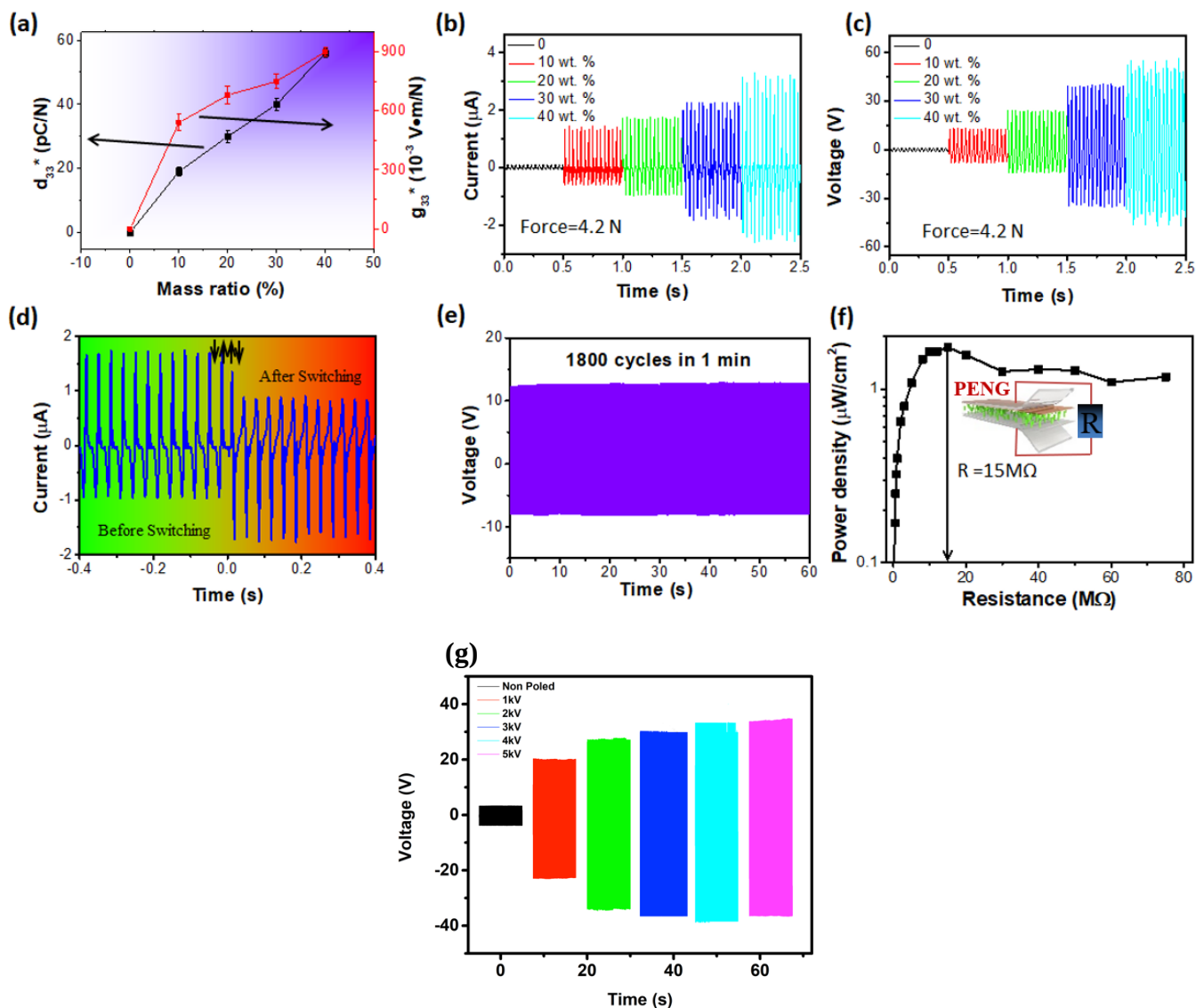


FIGURE 4.5 The output performance of the PENGs: (a) the measured d_{33}^* and g_{33}^* for the composite film with different $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ concentration; (b) the I_{sc} and (c) V_{oc} of the PENGs with different $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ concentration at an applied force of 4.2 N; (d) the polarity switching test of the I_{sc} of the PENG (20 wt. %, 4.2 N); (e) reliability testing for 1 min (30 wt. % PENGs, 30 Hz, 3.5 N); (f) measured output power-density of the PENGs across various loads from 0-75 MΩ. (g) Poling voltage dependent output performance of the PENGs. The generated output voltage of the PENGs measured at 30 Hz with different poling voltages with a same 1-hour of poling time for each film.

From the equation of $V_{oc} = g_{33}^* \times \Delta P \times L$, (where L is the original thickness of the composite film) a high output voltage is associated with a high g_{33}^* value which is inversely proportional to the relative permittivity (ϵ_r). The ϵ_r of the (ATHP)₂PbBr₂Cl₂ film is measured to be ~ 28 -18 at frequencies ranging from 1 kHz to 1 MHz which is relatively much smaller than most of the reported highly piezoelectric perovskite ceramics, such as BTO or PZT (having high ϵ_r value of above hundreds). Along with the measured quasi-static (110 Hz, 0.25 N) d_{33}^* values of the film, the g_{33}^* of the composite films are calculated and plotted in **FIGURE 4.5a**. Comparing **FIGURE 4.5a** with **FIGURE 4.5c** the rising trend of g_{33}^* from 560 to a high value of $900 \times 10^{-3} \text{ V}\cdot\text{m/N}$ is consistent with that of the measured high V_{oc} (peak to peak) from 30 to a maximum of 90 V. More specifically, the higher d_{33}^* value yields a maximum I_{sc} (peak to peak) of 6.5 μA (**FIGURE 4.5b**). Notably, the highest g_{33}^* of $900 \times 10^{-3} \text{ V}\cdot\text{m/N}$ from the 40 wt. % (ATHP)₂PbBr₂Cl₂@PDMS composite film is ~ 4 times that of standard piezoelectric PVDF film. The I_{sc} of the PENGs switches its polarity from positive to negative direction during the electrical connection reversal in **FIGURE 4.5d**, arguably anticipated due to the surface piezoelectric polarization charges. Moreover, a non-symmetrical feature of the I_{sc} value across the x-axis (time) is observed during the experiments, which can be explained by the difference in the strain rate while applying and removing the stress on the PENGs. The reliability of the PENGs is explored by continuously testing the device for 1 min (1800 cycles). Throughout the complete time span, no observable degradation (**FIGURE 4.5e**) in the amplitude of the output voltage is found. To optimize the maximum power delivered to the loads, the electrical output power of the PENGs is measured as a function of load resistance ranging from 0.09 to 75.4 M Ω (**FIGURE 4.5f**). The maximum output power density of 1.7 $\mu\text{W}/\text{cm}^2$ is obtained with an external load resistor of 15 M Ω , and an applied force of 4.2 N. This power density value is well anticipated because the I_{sc} of the PENGs varies proportionally with the applied pressure where the power density increases proportionally with the squared of the I_{sc} value. To optimize the PENG performance, the effect of the poling voltages on the PENG's output is also studied in **FIGURE 4.5g**. The generated output voltages are recorded at 30 Hz for a range of poling voltages from 0 V (non-poled) to 5 kV. The low output voltage (~ 7 V) from the non-poled PENG device is increased to ~ 75 V when the device is poled at 5 kV for 1-hour. As the poling voltage increases the electric field strength across the piezoelectric film, it is needed to align the electric dipoles of the piezoelectric film in the direction of the applied electric field. Hence, the dipole moment will increase, higher polarization charge density will yield higher

output voltage from the PENGs. The piezoelectric properties enhances at a higher rate at the beginning of the poling due to the easily switchable 180° domains than non- 180° domains. However, poling for a longer time may generate more free carriers , which may change the conductivity of the film. As a result the temperature of local region may rises due to high electric current flow to cause the degradation of poling dependent piezoelectric properties. This optimized PENG performance, including the $V_{oc (p-p)}$ of 90 V, $I_{sc (p-p)}$ of 6.5 μ A, and power density of 1.7 μ W/cm² under an applied force of only 4.2 N, are rather competitive in terms of output power to input mechanical energy comparison to that of previously reported PENGs using the same PDMS matrix.

4.4 Conclusions

In summary, a novel OIHP piezoelectric NRs of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ is synthesized by the LARP method, and its structure is characterized by using TEM, AFM and XRD. The superior transverse piezoelectricity of 64.2 pC/N (3 times higher than the PVDF) is discovered by using state-of-the-art piezoelectric material characterization tools. The $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ is classified as ferroelectric having switchable polarization and a high saturated polarization charge density of $5.4 \mu\text{C}/\text{cm}^2$ is measured. From the PFM measurement, the polarization in the pristine $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NR is found along the [001] direction in the (100) plane. Due to its excellent solubility in the organic solvent, the piezoelectric composite film is prepared by dispersing the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ NRs in the PDMS. The energy-dispersive X-ray elemental mapping and GIWAXS characterizations unfold the uniform and spontaneous distribution of the NRs in the PDMS matrix. Benefiting from the improved flexibility and a rod-like nanostructure with a large surface area, the transverse piezoelectricity contributes greatly to the effective longitudinal piezoelectricity of the composite film. The effective d_{33} and g_{33} of the 40 wt. % $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ @PDMS composite is measured as $\sim 55 \text{ pC}/\text{N}$, and $\sim 900 \times 10^{-3} \text{ V}\cdot\text{m}/\text{N}$, respectively. The fabricated devices show the highest peak outputs in the V_{oc} of 45 V, I_{sc} of 3.2 μA , and a power density of $1.7 \mu\text{W}/\text{cm}^2$ with an applied force of only 4.2 N, signifying successful manufacturing of an efficient PENG. The polarity switching of the PENG device is verified to discard the artifacts from electrostatic charges. The effect of electrical poling is found to be highly effective in the performance improvement of the ferroelectric OIHP-based PENG. Compared to a non-poled PENG of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ @PDMS, the output piezo potential is enhanced by a factor of ~ 10 with the electrical poling at 5 KV for one-hour. It is predicted that the piezoelectric performance of these organic-inorganic perovskite NRs can be significantly improved further to realize a highly efficient piezoelectric nanogenerator for the next generation of sensing and actuating applications.

Chapter 5

Ultrahigh Piezoelectricity in Hybrid Vacancy-ordered Halide Double Perovskite

5.1 Motivation

Despite significant advancement in the development of the OIHPs, their impressive piezoelectric performance is traded with the presence of heavy metal (Pb, Cd) in their crystal structure. Replacing those heavy metals with the lighter elements (Mn) causes their chemical instability at the ambient. To improve both piezoelectric coefficients d_{33} and g_{33} simultaneously, a heavy-metal free vacancy-ordered double perovskite of $\text{TMCM}_2\text{SnCl}_6$ (where TMCM is trimethylchloromethyl ammonium) with a large d_{33} of 137 pC/N and g_{33} of $980 \times 10^{-3} \text{ V}\cdot\text{m/N}$ has been proposed. The piezoelectric coefficients are considered from the halogen-bonding mediated synergistic movements of atomic displacement in inorganic $[\text{SnCl}_6]^{2-}$ octahedrons, as well as the molecular rotation of organic TMCM^+ . The $\text{TMCM}_2\text{SnCl}_6$ possesses a high saturated polarization (P_s) of $8.7 \mu\text{C}/\text{cm}^2$, a high Curie temperature of 365 K, and a low coercive field (E_c) of 0.6 kV/cm. The open circuit voltage (V_{oc}) and short circuit current (I_{sc}) of the PENGs are 81 V and 2 μA at an applied mechanical excitation of (4.9 N, 40 Hz). This work will provide guidance in energy harvesting by innovatively designing highly piezoelectric perovskites for the PENGs.

5.2 Experiments

5.2.1 Materials

Tin (II) chloride (98%), acetonitrile (99%), trimethylamine solution (45 wt. % in H_2O) and dichloromethane (99%) are purchased from Sigma-Aldrich; The PDMS (Sylgard 184) is purchased from Dow Corning. TMCM is synthesized by the reaction of equimolar of trimethylamine and dichloromethane in acetonitrile at room temperature for one week. The white power is obtained by removing the solvent under continuous nitrogen (N_2) flow and should be stored in vacuum desiccator.

5.2.2 Synthesis of $\text{TMCM}_2\text{SnCl}_6$ single crystals

SnCl_2 (18.9g, 0.1 mol) and TMCM-Cl (14.4g, 0.1 mol) are dissolved in 250 mL of 37 % HCl solution under constant stirring, to form a colorless solution. For that reason, the solution is stirred at 60 °C for one night. Finally, the colorless single crystals of $\text{TMCM}_2\text{SnCl}_6$ have been grown by slow evaporation of the above solution at room temperature in an ambient atmosphere for 1 month.

5.2.3 Synthesis of $\text{TMCM}_2\text{SnCl}_6$ @PDMS composite films

The PDMS precursor is prepared by adding a curing agent to the PDMS elastomer base in a 100 mL beaker (where the weight ratio of PDMS elastomer base and curing agent is 10:1). To improve the fluidity of PDMS precursor, the PDMS is further dissolved in the toluene by the PDMS/toluene mass ratio of 1:1. Then, 1g of ground $\text{TMCM}_2\text{SnCl}_6$ nanoparticles is mixed uniformly with 18 g PDMS precursor and stirred for 2 hours at the room temperature. The final solution is dropped onto a flat glass substrate and is degassed overnight to remove all the bubbles. Then the films are cured at 100 °C for 80 minutes and then it is peeled off.

5.2.4 Fabrication of piezoelectric nanogenerators

The dipoles of the $\text{TMCM}_2\text{SnCl}_6$ @PDMS composites are firstly aligned by using electrical poling. Specifically, (i) the composite film is sandwiched between two Au-coated Cu electrodes and pressed tightly by a clip. The edge of the electrodes is polished smoothly to avoid point discharge; (ii) the desiccator is pumped to a low vacuum (~ 10 Torr). The vacuum can protect the poling voltage breakdown from the pinhole in the composite film; (iii) the poling voltage is increased gradually to 4.5 kV and kept for 3 hours. Then, the films are inserted between two patterned copper electrodes taped on the laminating pouches. Finally, the sandwich structure of copper/ $\text{TMCM}_2\text{SnCl}_6$ @PDMS/copper is pressed tightly by a commercial thermal laminator to eliminate air gaps. The purpose of this step is to improve the contact between the copper electrodes and the piezoelectric films.

5.2.5 Measurement and Characterization

To examine the electrical output of PENGs, an electrodynamic shaker (Lab works Inc.) is utilized, which is controlled by a power amplifier and a controller. A digital oscilloscope (Tektronix 2004C) and a low-noise current preamplifier (Model-SR 570, Stanford Research System Inc.) are used to measure the voltage and current, respectively. The applied mass (m) is 0.138 kg and the acceleration (a) of electrodynamic shaker is tuned from 2 to 3.5 G. The bottom area of the load mass is 2 cm². The calculated force (F) is 2.8 to 4.9 N according to the equation of $F = ma$. XRD investigation is carried out using the D8-Discover (Bruker) diffractometer with Cu K α radiation ($\lambda=1.5418$ Å). The piezoelectric domain is evaluated using PFM (Dimension Icon, Bruker) under AC bias of 2 V. The d_{33} is measured via quasi-static method (Polyk d_{33} meter). FTIR spectra are collected using a Nicolet iS50 from the Thermofisher Company. The SEM and EDS are performed by a field-emission SEM (JSM-7200F). The relative permittivity is measured by using the Keithley-4200 semiconductor parameter analyzer. XPS measurements are performed with an Mg K α ($h\nu=1254.6$ eV) X-ray source using a VSW HA100 photoelectron spectrometer with a hemispherical photoelectron analyzer, working at an energy pass of 20 eV for the surveying and to resolving the spectra. The experimental resolution is 1.0 eV. Electrical characterizations including I-V curves and P-V loops are carried out by using Keithley 4200 semiconductor characterization system with a scan step of 0.1 V and scan speed of 0.8V/s. Differential scanning calorimetry (DSC) measurements are performed on DSC Q2000 under nitrogen atmosphere in aluminum crucibles with a heating rate of 10 K/min. The TMCM₂SnCl₆ single crystal are polished with a size of (length = 5 mm; width = 4 mm; thickness = 2 mm) for d_{33} and relative permittivity measurements. The top and bottom electrodes are copper tapes, which are attached to the sample tightly.

5.3 Results and Discussion

The single crystal of TMCM₂SnCl₆ with a length of 1.8 cm is shown in **FIGURE 5.1a**. The chemical states of (TMCM)₂SnCl₆ are measured via XPS in **FIGURE 5.1b-c**. The peaks at binding energy of 495.8 eV and 487.3 eV are assigned to Sn⁴⁺ and corresponding to its 3d_{3/2} and 3d_{5/2} orbitals, respectively. The peaks at 200.6 eV and 198.8 eV are assigned to 3p_{1/2} and 3p_{3/2} orbitals of Cl⁻. This is well consistent to the chemical states in [SnCl₆]²⁻ octahedrons, where Sn is in tetravalent state and Cl in minus state. A halogen bond has been considered as an efficient driving

force to achieve the well-defined structures. The halogen bond in the $\text{TMCM}_2\text{SnCl}_6$ is reflected by Fourier transform infrared spectroscopy (FTIR) in **FIGURE 5.1d**. The absorption peak at 793 cm^{-1} (black line) is attributed to the stretching vibration of Cl-C bond of TMCM^+ .

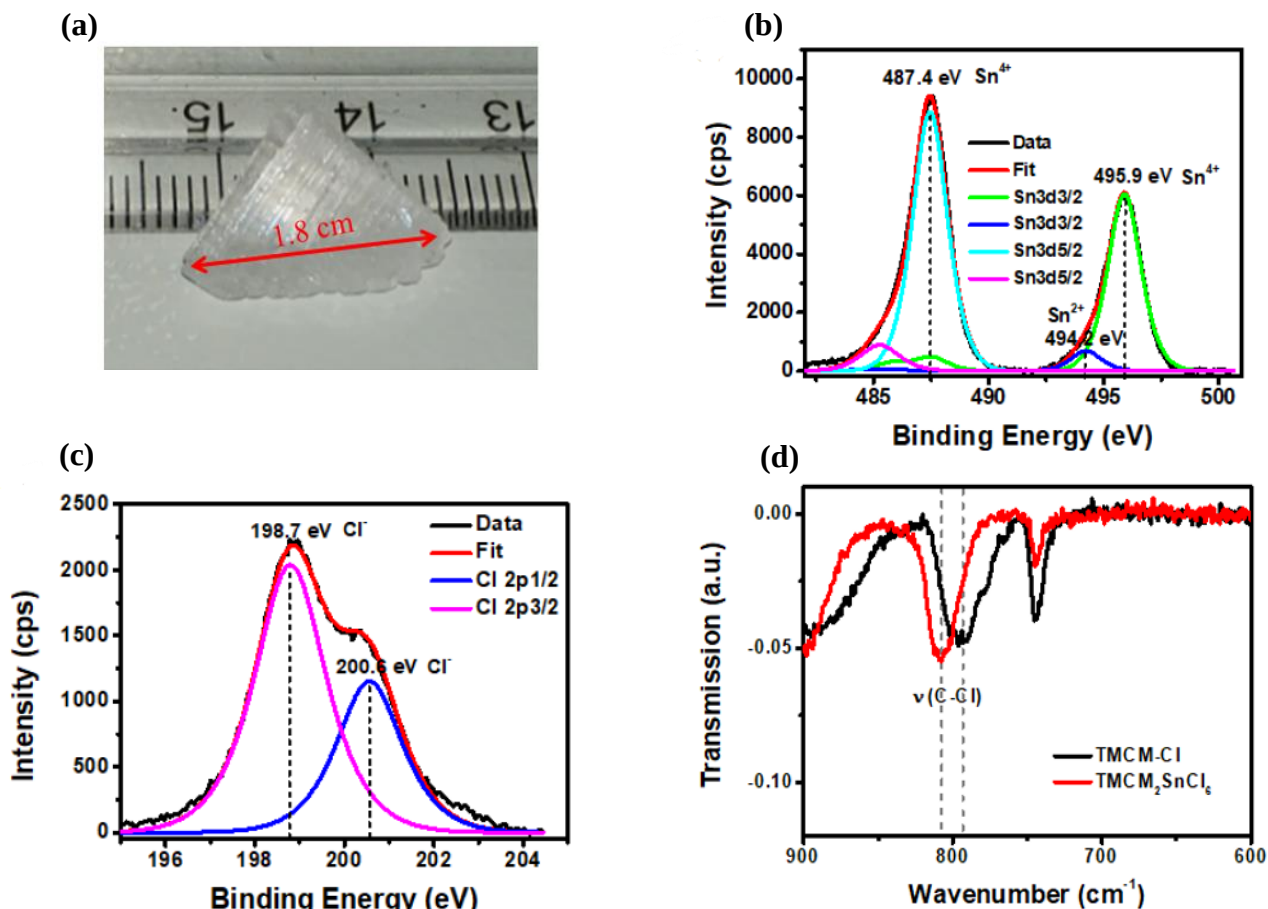


FIGURE 5.1 (a) Digital photograph of single crystal $(\text{TMCM})_2\text{SnCl}_6$. (b) XPS results of the $(\text{TMCM})_2\text{SnCl}_6$ powders: XPS spectra for Sn $3d_{3/2}$ and $3d_{5/2}$ orbits, where the peaks at binding energy of 495.8 eV and 487.3 eV are assigned to Sn^{4+} and the peak at 494.2 eV is assigned to Sn^{2+} ; (c) XPS spectra for $2p_{1/2}$ and $2p_{3/2}$ orbits of Cl^- , which is corresponding to binding energy of 200.6 eV and 198.8 eV, respectively. (e) FTIR spectra of pure TMCM-Cl molecules and $\text{TMCM}_2\text{SnCl}_6$.

For the $\text{TMCM}_2\text{SnCl}_6$, the absorption peak has a red-shift of 14 cm^{-1} to 807 cm^{-1} (red line). The red shift should be attributed to the increased force constant when the electrophilic Cl in TMCM^+ is attracted by the nucleophilic Cl in $[\text{SnCl}_6]^{2-}$ octahedron according to harmonic motion for diatomic model. The d_{33} of $\text{TMCM}_2\text{SnCl}_6$ perovskites is measured to be 137 pC/N by using a quasi-static method. The ferroelectric domains are confirmed by a clear contrast in amplitude and

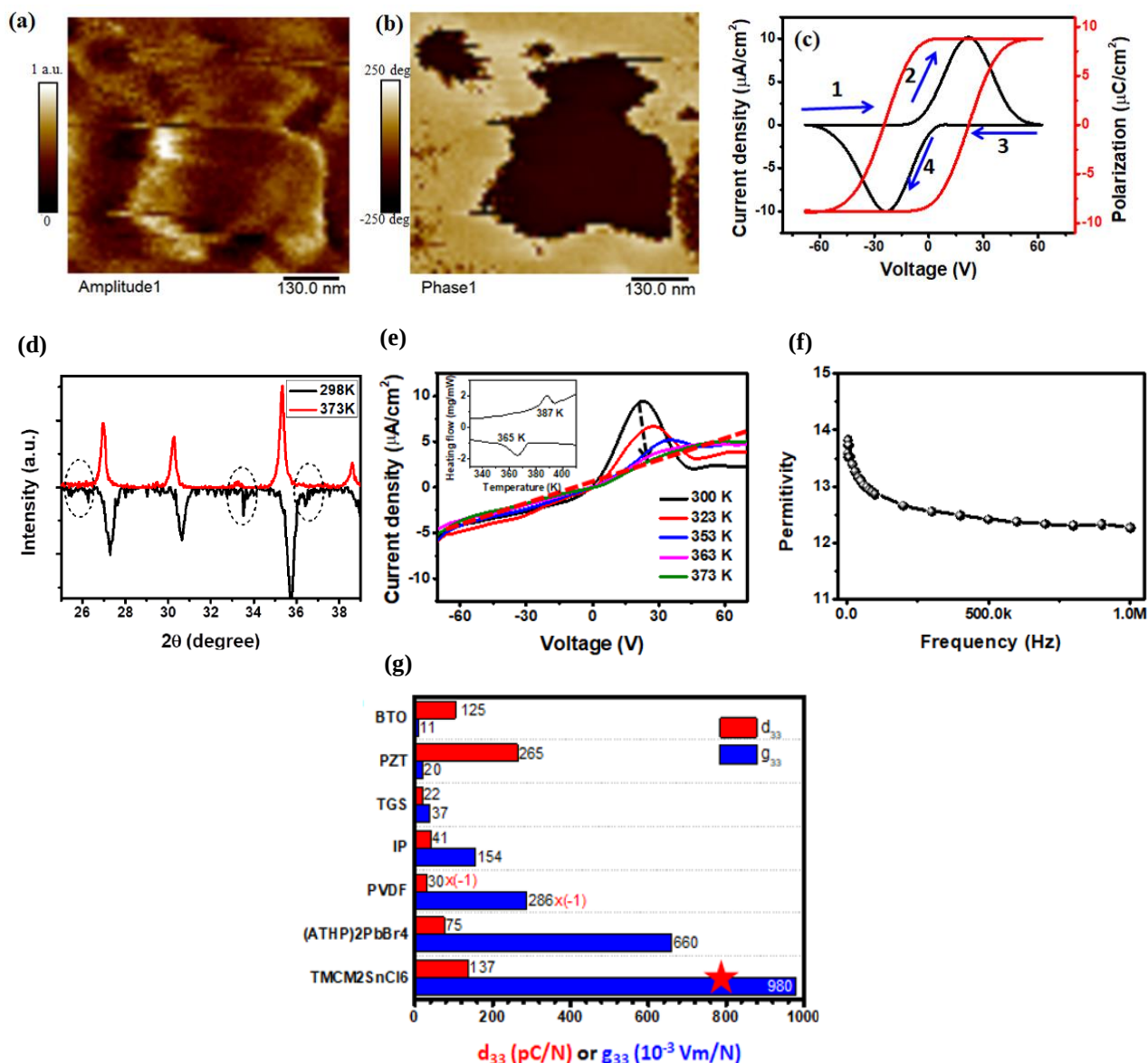


FIGURE 5.2 Vertical PFM amplitude (a) and phase (b) images; (c) current density-voltage (J-V) curve and the integrated polarization-voltage (P-V) hysteresis loop of the TMCM₂SnCl₆ film at room temperature (25 °C) by using the double-wave method. (d) The temperature-dependent powder XRD measured at 298 K and 373 K, respectively; (e) temperature-dependent J-V curves (voltage is swept from -70 to 70 V). The inset is the differential scanning calorimetry curves of TMCM₂SnCl₆ crystals with the scanning rate of 10 K/min; (f) frequency-dependent permittivity tested from 0.01 to 1 MHz; (g) the d_{33} and g_{33} of TMCM₂SnCl₆ compared with the reported inorganic and molecular materials, including BTO, PZT, triglycine sulfate (TGS), imidazolium perchlorate (IP), PVDF, and (ATHP)₂PbBr₄.

phase images of vertical piezo response force microscopy in **FIGURE 5.2a-b**. The P-V hysteresis loop is measured for TMCM₂SnCl₆ films with the thickness of 400 μm by using the double-wave method (DWM) in **FIGURE 5.2c** [149]. The arrows in the J-V curve indicate the voltage sweep directions (-60 V → 0 V → 60 V → 0 V → -60 V). The J-V curve exhibits two apparent current peaks at the ferroelectric switching voltage of ± 23 V. The E_c of TMCM₂SnCl₆ is expressed by the ratio of switching voltage to the film thickness, is 0.6 kV/cm. This value is comparable to that of conventional piezo ceramics such as bulk BTO single crystals (1 kV/cm) [150]. The P_s from the P-V hysteresis loop is up to 8.7 μC/cm², close to the calculated value of 8.4±0.3 μC/cm². When the temperature is higher than T_c, the ferroelectric material will undergo a phase transition and lose its spontaneous polarization. The phase transition of TMCM₂SnCl₆ is considered from orthorhombic to cubic as indicated by some disappearing diffraction peaks at around 26.3°, 33.5° and 36.5° in temperature dependent XRD (**FIGURE 5.2d**). The T_c of TMCM₂SnCl₆ is studied via monitoring the change of peak intensity at 23 V in the temperature-dependent J-V curves. As indicated in **FIGURE 5.2e**, the current peaks disappear when the temperature rises to 353-363 K. This is consistent to a pair of thermal anomalies at 365/387 K in the DSC curves (the inset of **FIGURE 5.2e**). The TMCM₂SnCl₆ possesses a T_c above room temperature, making it suitable for PENG applications. The ε_r of perovskite oxide ceramics, such as PZT, is observed as thousands, which stems from the hopping polaron within semiconducting grains and interfacial polarization at the insulating grain boundary. The TMCM₂SnCl₆ exhibits a relatively low ε_r of 14-12 with the frequency from 0.01 to 1 MHz in **FIGURE 5.2f**. This should be attributed to the insulating properties of TMCM₂SnCl₆: where the calculated bandgap of above 3.2 eV. According to $g_{33}=d_{33}/(\epsilon_0 \times \epsilon_r)$, where ε₀ is the permittivity of free space and ε_r = 16, the calculated g₃₃ is 980 × 10⁻³ V•m/N. Notably, a higher ε_r is chosen to match the following PENG working frequency at 40 Hz. In comparison to traditional metal oxides and other molecular materials listed in **FIGURE 5.2g**, the TMCM₂SnCl₆ perovskites are more favorable for the PENG applications due to both large d₃₃ and giant g₃₃. The piezoelectricity in the TMCM₂SnCl₆ is further demonstrated by the outputs of fabricated PENGs. The outputs of the TMCM₂SnCl₆@PDMS based PENGs is measured by mounting the device on a shaker in a vertical compressing and releasing process. For the PENGs with 29 wt. % TMCM₂SnCl₆ in the composite film, the output V_{oc} and I_{sc} of 40 V and 0.9 μA is achieved under the force of 2.8 N at a frequency of 40 Hz. The device output is reproducible as indicated by the statistical analysis of V_{oc} in **FIGURE 5.3a**. With the applied force increases from

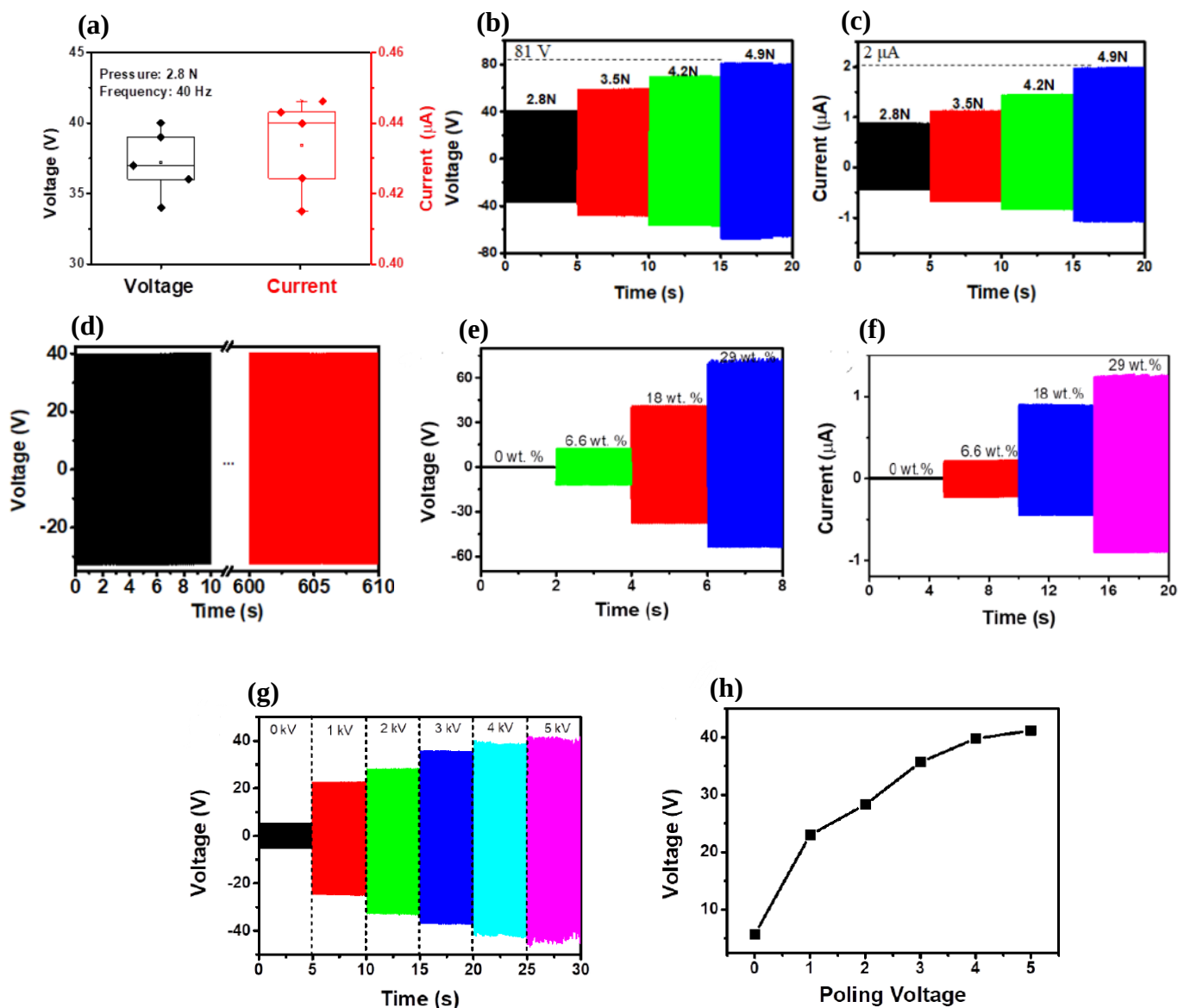


FIGURE 5.3 (a) The box chart of output voltages and currents collected from 5 PENGs. The applied mechanical excitation is 2.8 N and 40 Hz. The fraction of $(\text{TMCM})_2\text{SnCl}_6$ NPs in the composite film is 18 wt. %. (b) V_{oc} and (c) I_{sc} of the PENGs with the force from 2.8 to 4.9 N (40 Hz); (d) the device reliability tested for 10 mins. The output voltage (e) and current (f) of the PENGs with different mass fraction under an applied mechanical excitation of 2.8 N and 40 Hz; (g) output voltage of PENGs based on 18 wt. % $(\text{TMCM})_2\text{SnCl}_6$ in composites after poling at various dc bias for 3 hours; (h) comparison of peak output voltage of PENGs measured under various applied dc bias. The applied mechanical excitation is 2.8 N and 40 Hz.

2.8 to 4.9 N, the piezoelectric outputs (V_{oc} and I_{sc}) of the PENGs increase linearly in **FIGURE 5.3b-c**. The V_{oc} and I_{sc} reach 81 V and 2 μ A, respectively, at an applied force of 4.9 N. In comparison with traditional inorganic perovskite ceramics the $TMCM_2SnCl_6$ are prepared at room temperature and the PENGs exhibit the competitive piezoelectric outputs. The reliability of the PENGs is explored by continually testing the device for 10 minutes and the amplitude of the output voltage shows a negligible degradation (**FIGURE 5.3d**) confirming its excellent mechanical durability. The V_{oc} is enhanced with the loading $TMCM_2SnCl_6$ NPs in the composite film as shown in **FIGURE 5.3e-f**. These verify the claim that - the high performance of PENGs is determined by the incorporation of $TMCM_2SnCl_6$; (iii) the effect of electrical poling on the PENG outputs is investigated. A detailed comparison of output voltage of PENGs is measured under various applied poling fields is shown in **FIGURE 5.3g-h**. Compared with the outputs of unpoled ones, the PENGs after poling at 4.5 kV exhibits drastic increase in V_{oc} and I_{sc} under the same measurement conditions (2.8 N, 40 Hz).

5.4 Conclusions

In summary, to achieve high d_{33} and g_{33} simultaneously in a piezoelectric material, a novel vacancy-ordered double perovskite of $\text{TMCM}_2\text{SnCl}_6$ is synthesized for energy harvesting applications. The piezoelectric coefficients from the $\text{TMCM}_2\text{SnCl}_6$ are firstly experimentally measured, then verified by the DFT study, and finally confirmed by the piezoelectric output of the PENGs. The quasi-static piezoelectric measurement exhibits a large d_{33} of 137 pC/N and a giant g_{33} of $980 \times 10^{-3} \text{ V}\cdot\text{m/N}$. The $\text{TMCM}_2\text{SnCl}_6$ perovskite possesses ferroelectric characteristics with a high P_s of $8.7 \mu\text{C}/\text{cm}^2$, a low E_c of 0.6 kV/cm and a high T_c of 365 K. The curie temperature is identified from the DSC, temperature-dependent J-V, and XRD experiments. The ultrahigh piezoelectricity is attributed to the halogen bonding-mediated synergistic movements of atomic displacement in the inorganic $[\text{SnCl}_6]^{2-}$ octahedron and the dipole alignment of organic TMCM^+ . The halogen-bond interaction is evident from the red-shifts in the FTIR transmission spectrum of TMCM-Cl and $\text{TMCM}_2\text{SnCl}_6$.

The piezoelectric composite films are prepared by dispersing $\text{TMCM}_2\text{SnCl}_6$ NPs into the PDMS matrix. The peak values of V_{oc} and I_{sc} of the 29 wt. % PENGs reaches up to 81 V and 2 μA at an applied mechanical excitation of 4.9 N, 40 Hz. It is found that the PENG output voltage and current increase with the applied force, and poling voltage. The reproducibility of the PENG outputs with an accuracy of $\pm 6 \text{ V}$, $\pm 0.04 \mu\text{A}$ is also verified by fabricating a total of 5 PENGs. The piezoelectric coefficients in the $\text{TMCM}_2\text{SnCl}_6$ surpass the previously demonstrated OIHP of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$, and many other well-established piezoelectrics such as PVDF, PZT, BTO, etc. This study also shows the high piezoelectricity in a lead-free perovskite and its deployment in PENG-based energy harvesting.

Chapter 6

Enhanced Piezoelectric Response in a Jahn-Teller Distorted Molecular Metal Halide

6.1 Motivation

In prior piezoelectrics, an increase in polarization usually accompanies a dramatic rise in the dielectric constant, resulting in a trade between d_{33} and g_{33} . This recognition led me to this design concept: increase polarization through Jahn-Teller lattice distortion; and reduce dielectric constant using a highly confined 0D molecular architecture. I seek to insert a quasi-spherical cation into a Jahn-Teller distorted lattice, increasing mechanical response for a large piezoelectric coefficient. I implement this concept by developing EDABCO-CuCl₄ (EDABCO = N-ethyl-1,4-diazabicyclo [2.2.2] octonium) a molecular piezoelectric with a d_{33} of 165 pm/V and g_{33} of $\sim 2110 \times 10^{-3} \text{ V}\cdot\text{m/N}$, one that achieved thusly a combined transduction coefficient of $348 \times 10^{-12} \text{ m}^3 \text{ J}^{-1}$. This enables piezoelectric energy harvesting with a peak power density of $43 \text{ }\mu\text{W}/\text{cm}^2$ (at 50 kPa), the highest value reported for mechanical energy harvesters based on heavy-metal free molecular piezoelectric.

6.2 Experiments

6.2.1 Single crystal growth and structure characterization

1-Ethyl-1,4-diazabicyclo [2.2.2] octanium iodide (EDABCOI) is synthesized by the Menshutkin reaction. N, N'-diazabicyclo [2.2.2] octonium (DABCO) and ethyl iodide are reacted in acetone with a 1:1.2 mole ratio at room temperature for 24 h. The resulting precipitate is washed with a large amount of diethyl ether and collected by filtration. Single crystals of EDABCO-CuCl₄ are grown by the slow-cooling method. 0.5 mmol of CuCl₂ and 0.5 mmol of EDABCOI are dissolved in 2.5 ml hydrochloric acid (38 %). The mixture is placed on a hot plate and stirred at 80 °C for 30 minutes so that the saturated solution is totally dissolved. Then, the clear solution is put into an oven, the initial temperature is set to 80 °C, and the cooling rate is 1 °C/h. I obtain the orange bulk crystals by slowly cooling the solution to room temperature.

Single crystal X-ray diffraction data are collected at 290 K on a Bruker APEX-DUO diffractometers with graphite-monochromatic Mo-K α radiation (Burker Triumph, $\lambda = 0.71073 \text{ \AA}$). The APEX3 software is used for data reduction. The crystal structure is solved by direct method and then it is refined anisotropically by full-matrix least-squares on F^2 using the SHELXLTL software package. Hydrogen atoms of the EDABCO cations are generated in the geometrical mode. Deposited CCDC number: 2180969.

The powder XRD measurements are conducted on a Rigaku MiniFlex 600 diffractometer (Bragg-Brentano geometry) equipped with a monochromatized Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$, 40 kV and 15 mA). For temperature-dependent measurements, samples are heated using the TS 500 high-temperature attachment and data are collected at intervals of 20 °C.

6.2.2 SHG measurement

For second-harmonic generation (SHG) measurement, a ytterbium-doped gadolinium potassium tungstate regenerative amplifier is used to generate the 1030 nm fundamental wave (5 kHz). The beam is then sent through an optical parametric amplifier (Orpheus, Light Conversion) to generate a wavelength of 1510 nm. The scattered light from the sample is then collected by two lenses into a 400 μm multimode fiber (Thorlabs), which is sent to a USB2000+ spectrometer (Ocean Optics).

6.2.3 Dielectric permittivity measurement

Bulk single crystals are used for dielectric permittivity measurement, which are sandwiched between two ITO substrates that served as top and bottom electrodes. The dielectric permittivity (ϵ_r) is measured on a potentiostat electrochemical workstation (AUT50690, PGSTAT204, The Netherlands) with a frequency ranging from 1 kHz to 1 MHz with an ac voltage of 0.5 V.

6.2.4 Piezoelectric measurement

The macroscopic piezoelectric coefficient (d_{33}) is measured by a commercial piezometer (Polyk, PKD3-2000-F10N) using "Berlincourt" method (also called "quasi-static" method). The crystal is placed in between two flat metal plates which clamp the sample and I apply a small oscillating force (0.25 N, 110 Hz) along the normal direction, while the piezoelectric charge is measured. For temperature-dependent measurements, the crystals are heated using a miniature temperature chamber, and the temperature is controlled by an omega temperature controller.

6.2.5 Preparation of EDABCO-CuCl₄@PVDF composite film-based PENG

PVDF powders (polyvinylidene fluoride $\geq 99.9\%$, Sigma-Aldrich) are dissolved in the DMF (N, N-dimethylformamide $\geq 99\%$, Sigma-Aldrich) solvent, followed by stirring at room temperature (25 °C) for 24 hours. The final concentration of the PVDF solution is kept at 10 wt. %. Fine ground nanoparticles of the EDABCO-CuCl₄ single crystal are used to prepare the EDABCO-CuCl₄@PVDF composite solution. To optimize the concentration, 10 wt. %, 20 wt. % and 30 wt. % composite solutions are prepared by rigorously stirring the solution for 24 hours, followed by ultrasonic stirring for 30 minutes. The as-prepared solutions are spin-coated on a clean glass substrate (cleaned with O₂ plasma treatment) for 20 s at 160 rpm. The spin-coated solution is stored for 30 minutes for degassing purposes. Then the solution is cured by a slow curing process at 75 °C on a flat hot plate. Finally, the film is annealed at 110 °C for 10 minutes and it is peeled off from the glass substrate.

To fabricate a PENG, four units of composite film are used. Two PVDF thin films are prepared by spin-coating 10 wt. % PVDF solution at 400 rpm for 20 s. The composite films are sandwiched between the PVDF thin films by pressing them with a heat press machine at 160 °C for 2 minutes. Two copper electrodes are attached to the thermal laminating pouches (4 mills thick), and then the device is encapsulated between the electrodes by pressing them in a thermal laminator. A piece of copper tape is attached to one of the surfaces of the thermal laminating pouches to minimize the static charge build up during the periodic application of force by a metallic hammer.

6.2.6 Characterization of EDABCO-CuCl₄@PVDF composite film-based PENG

The mechanical energy harvesting capability is tested by mounting the PENG on an L-shaped steel stopper and applying a periodic compressing force of ~ 15 N at 5 Hz from a custom-made linear motor. The output voltage is measured by a digital oscilloscope (Tektronix 2004 C) and a 100 X cable. To measure the short-circuit output current, a low-noise current preamplifier (SR 570, Stanford Research Systems Inc.) is used in this experiment. The output of the PENG is rectified by a full-wave bridge rectifier circuit (Digi-Key Electronics, B80C800G-E4/51). The rectified output is directly fed to different commercial capacitors to store the charges. The output voltage of the capacitors is measured by the 100 X cable and is recorded by the oscilloscope. The reliability testing of the PENG is performed with an electrodynamic shaker (ET-126-1). A controller unit (VR 9500) generates different control signals which are amplified by a power amplifier (Lab works

Inc. pa 138) to regulate the vibration of the shaker. The controller unit is operated by a workstation interface (Vibration View 9). The device is attached on top of the hammer unit of the shaker with double sided Kapton tape, and a metal block (steel) is placed on top of the device. The outer side of the metal block is bound to a Kapton top which only allows it to move vertically. The dielectric properties of the film are measured by using a Keithley-4200 semiconductor parameter analyzer. The morphology of the composite film is analyzed by using a field emission scanning electron microscope (Hitachi SU5000 SEM) capable of performing energy-dispersive X-ray spectroscopy (EDS).

6.2.7 Synthesis of EDABCO-CuCl₄@PDMS based PENG

To fabricate the high-temperature stable EDABCO-CuCl₄-based PENG, the host polymer matrix is redesigned with PDMS (Polydimethylsiloxane, Sylgard 184 Silicone Elastomer, Dow Corning), as it can operate from a temperature ranging from - 45 °C to 200 °C (in contrast to a low melting point of ~ 170 °C of PVDF). The piezoelectric composite solution is prepared by mixing the fine-ground EDABCO-CuCl₄ NPs in the PDMS base for 24 hours with a mass ratio of 5 wt. %. The mass ratio is kept to a lower level (5 wt. %) for this case to prevent the clustering of the nanoparticles, and to preserve the flexibility of the PDMS.

Two 128 µm thick flexible Kapton films are chosen as the substrate due to their excellent thermal stability (-75 °C to 260 °C). The Kapton films are coated with Ag (silver) ink as the electrodes by the screen-printing method and are cured at 100 °C.

Before drop-casting the composite solution on the Ag electrodes, a curing agent is added to the mixture with a weight ratio of 1:10 with the PDMS base. Followed by further stirring and ultrasonication for one hour, the solution is drop casted on the Ag-coated Kapton substrates and is degassed for one hour. The solution is partially cured at 100 °C for ~ 30 minutes on a hot plate. Then the partially cured composite films are gently pressed together by the adhesion of PDMS. Finally, the device is completely cured in a vacuum oven at 90 °C for overnight.

6.2.8 Characterization of EDABCO-CuCl₄@PDMS based PENG

Two electrical connections are brought out for the measurements by single-core insulated Al (Aluminum) cables. The electrical poling is performed at an electric field of 50–120 V/µm for 2–

3 hours. To investigate the thermal stability of the PENG, it is directly mounted on an electric heater which is used as the stopper. A linear motor is used to generate a pushing force of ~ 15 N at 5 Hz on the PENG. To eliminate the error between the set temperature and the actual temperature on the device, an infrared thermometer temperature gun is used to measure the PENG temperature simultaneously. The generated output voltage from the PENG is continuously monitored by a digital oscilloscope (Tektronix 2004 C).

6.3 Results and Discussion

Single crystals of EDABCO-CuCl₄ are prepared using a slow cooling method (**FIGURE 6.1a**) and the crystal structure is determined by using single-crystal X-ray diffraction. The phase purity of as-grown crystals is confirmed by the powder XRD, which fits well with the simulated pattern (**FIGURE 6.1b**). Structural analysis reveals that EDABCO-CuCl₄ crystallizes in a non-centrosymmetric space group P2₁2₁2₁, among the 20 piezoelectric active point groups. The nonlinear optical properties are verified by measuring second harmonic generation (SHG) (**FIGURE 6.1c**). This contrasts with its spherical analogue, DABCO-CuCl₄, which crystallizes in the centrosymmetric crystal structure of P2₁/c. These results indicate that the EDABCO cation plays an important role in the generation of symmetry breaking. To gain insight into the role of Jahn-Teller distortion on symmetry breaking, EDABCO-ZnCl₄ is also synthesized, where the 3d¹⁰ Zn²⁺ is Jahn-Teller inactive (**FIGURE 6.1d**). Single-crystal structure analysis indicates that EDABCO-ZnCl₄ adopts a 0D structure composed of [ZnCl₄]²⁻ tetrahedrons and EDABCO cations, like that of the EDABCO-CuCl₄ (**FIGURE 6.1e**). However, EDABCO-ZnCl₄ belongs to the centrosymmetric space group P2₁/c [151]. Structural distortion is evaluated by using the geometry index $\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$, where α and β are the two largest Cl-Cu-Cl (or Cl-Zn-Cl) angles of the four-coordinate species. Cl-Cu-Cl angles exhibit significant variation away from the ideal 109.5° (95.87° to 132.36°) for a τ_4 of 0.88 (where $\tau_4 = 1$ for a perfectly symmetric structure) while the Cl-Zn-Cl angles show only slight distortion (108.11° to 115.31°) for a τ_4 of 0.94. This demonstrates that the lattice distortion originates, in part, from the Jahn-Teller effect of the

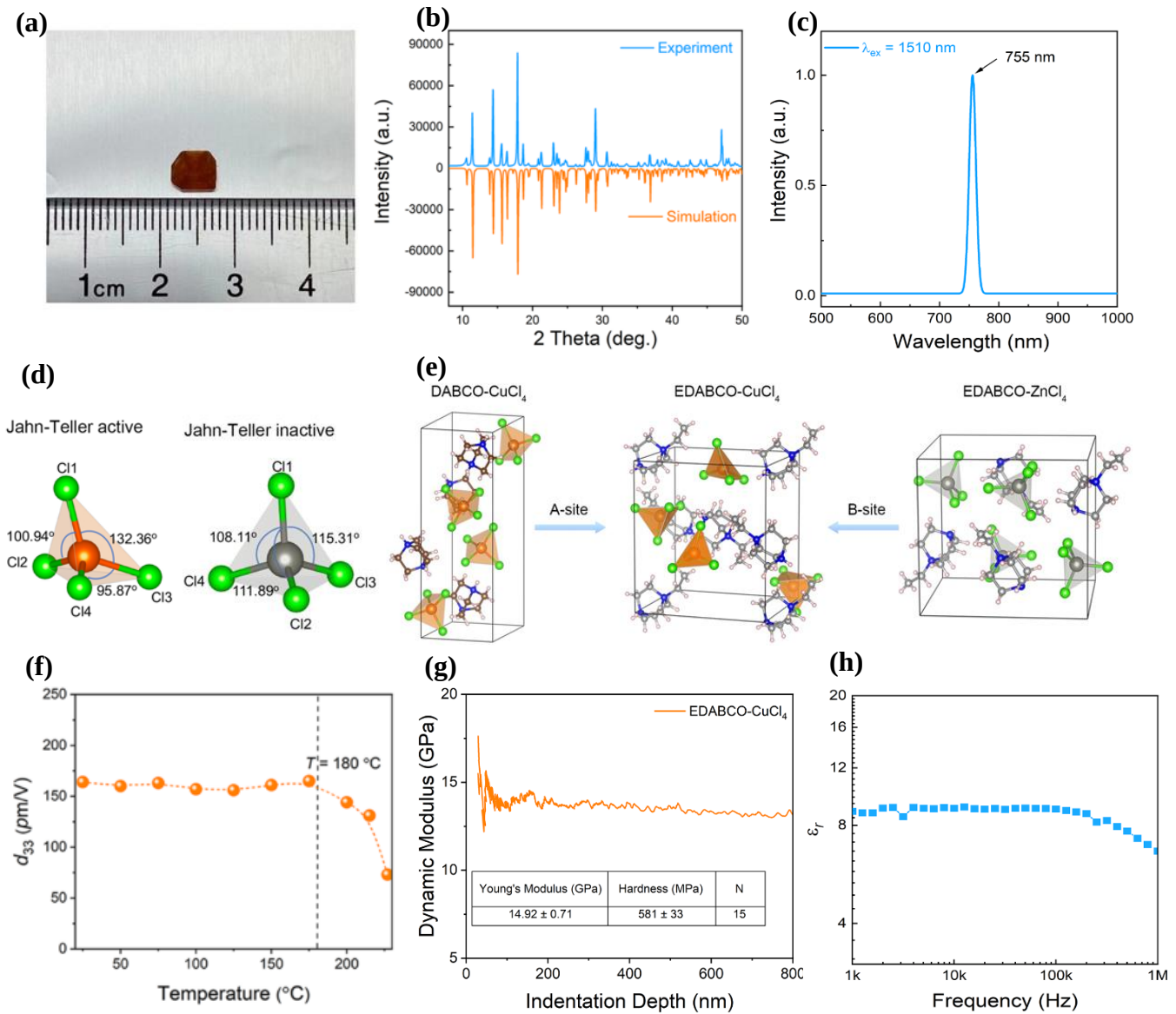


FIGURE 6.1 (a) Bulk single crystal of EDABCO-CuCl₄ grown by the slow-cooling method. (b) Experiment and simulated powder XRD patterns of EDABCO-CuCl₄ at room temperature. (c) SHG signal of EDABCO-CuCl₄ microcrystals at an excitation wavelength of 1510 nm. (d) The selected Cl-Cu-Cl and Cl-Zn-Cl bond angles of the $[\text{CuCl}_4]^{2-}$ and $[\text{ZnCl}_4]^{2-}$ tetrahedrons, representing those that deviate from the ideal 109.5° . The Jahn-Teller active Cu^{2+} enhances the deformation of the inorganic geometry. (e) Comparison of the crystal structures of DABCO-CuCl₄, EDABCO-CuCl₄, and EDABCO-ZnCl₄. The combination of quasi-spherical cation and Jahn-Teller distortion results in the piezoelectric active structure. (f) Piezoelectric coefficient (d_{33}) of EDABCO-CuCl₄ single crystals as a function of temperature. (g) Young's modulus and hardness of EDABCO-CuCl₄ single crystals. (h) Dielectric constant as a function of frequency of EDABCO-CuCl₄ single crystals.

incompletely filled 3d electronic configuration of the Cu^{2+} ($3d^9$) ion. The piezoelectric coefficient (d_{33}) is measured by using the quasi-static method on the single crystal of EDABCO- CuCl_4 . For the $\text{P2}_1\text{2}_1\text{2}_1$ phase (point group 222), the piezoelectric coefficient matrix is as follows [152]:

$$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}$$

A longitudinal d_{33} in the $[111]$ -direction is possible, which is equal to $d_{14} + d_{25} + d_{36}$. A maximum d_{33} of ~ 165 pC/N is recorded along the $[111]$ direction at room temperature, which shows no significant decrease until the temperature was increased to above 180°C (**FIGURE 6.1f**). This is significant as molecular metal halides tend to suffer from a low Curie temperature (typically $< 150^\circ\text{C}$), so they cannot meet the operational requirements specified for automotive applications. The high piezoelectric coefficient of EDABCO- CuCl_4 is attributed to the increased mechanical flexibility, as it is reflected by Young's modulus measurement (**FIGURE 6.1g**). The Young's modulus of EDABCO- CuCl_4 is significantly smaller than those of the piezoelectric ceramics, indicating favorable mechanical flexibility.

EDABCO- CuCl_4 shows a relatively low ϵ_r of 7 – 9 within the frequency range from 1 kHz to 1 MHz (**FIGURE 6.1h**), which I attribute to the high dielectric confinement in the 0D structure. Its g_{33} is therefore calculated to be $2110 \times 10^{-3} \text{ V}\cdot\text{m}/\text{N}$ at 1 kHz, $\sim 60\times$ higher than PZT-based piezoelectric ceramics. Given its impressive g_{33} and d_{33} values, the energy density per unit volume ($d_{33}*g_{33}$) of EDABCO- CuCl_4 is evaluated to be $348 \times 10^{-12} \text{ m}^3 \text{ J}^{-1}$, among the highest value for non-toxic piezoelectric materials (**FIGURE 6.2a**).

The excellent piezoelectric response of EDABCO- CuCl_4 motivates me to explore its energy-harvesting capability. Homogeneous polymer composites with 10 wt. %, 20 wt. %, and 30 wt. % of EDABCO- CuCl_4 are prepared by dispersing the corresponding quantities in PVDF (polyvinylidene fluoride) under vigorous mechanical stirring. PVDF is a stiff polymer with excellent mechanical strength (elastic modulus 0.03-17.1 GPa) and low viscosity for proper nanoparticle dispersion. Devices are fabricated by sandwiching the active composite films between two copper electrodes (**FIGURE 6.2b**). The 10 wt. % EDABCO- CuCl_4 @PVDF devices generate the largest output, with a maximum output voltage (V_{OC}) of 63 V and a current

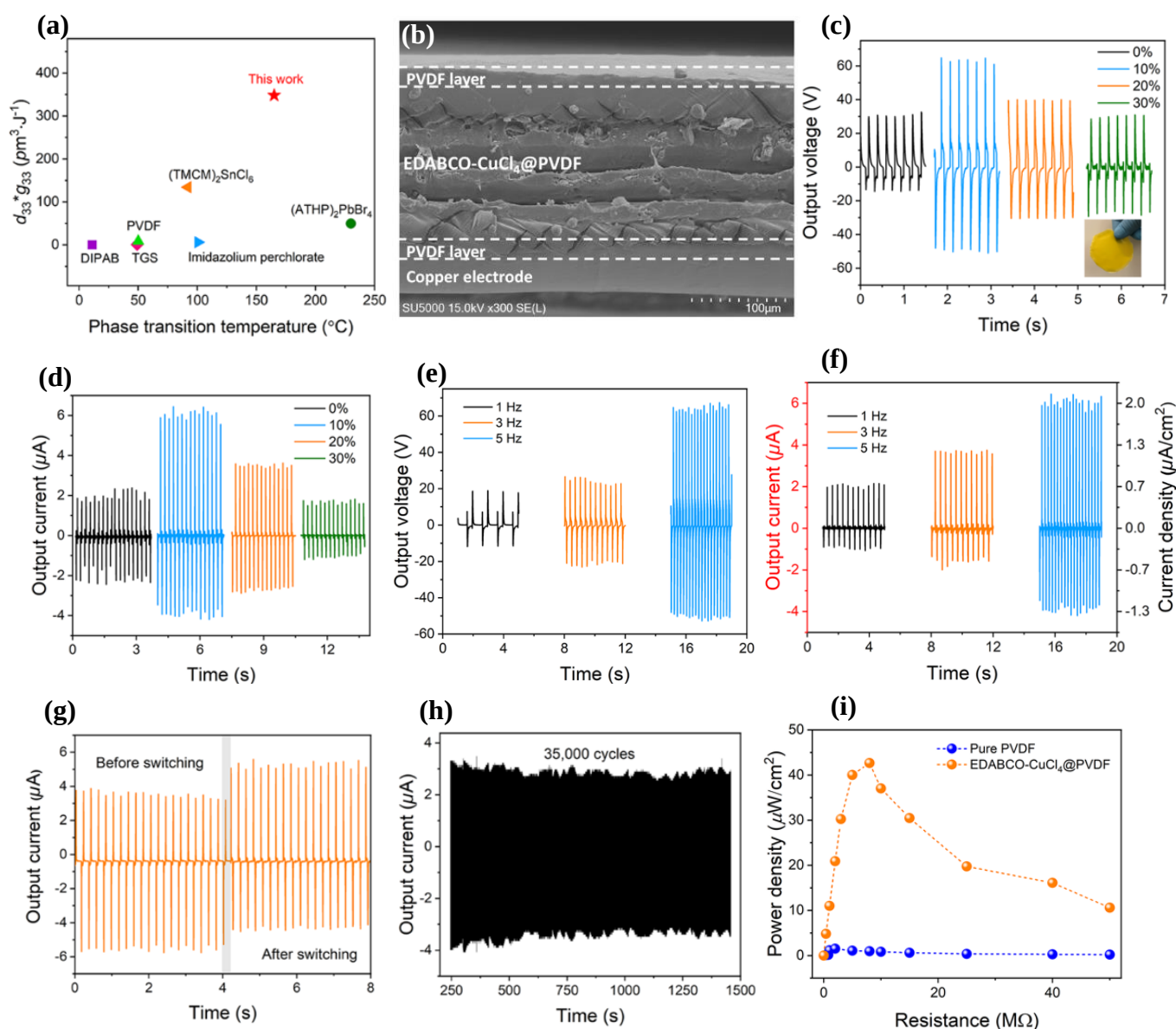


FIGURE 6.2 (a) Comparison of solid-state phase transition temperature and $d_{33} \cdot g_{33}$ with previously reported molecular piezoelectrics. (b) The cross-sectional SEM image of the 10 wt.% EDABCO-CuCl₄@PVDF composite films. (c) Output voltage and (d) current with different EDABCO-CuCl₄ concentrations at an applied force of 15 N and a frequency of 5 Hz. (e) The output voltage and (f) the output current of the 10 wt.% EDABCO-CuCl₄@PVDF PENGs at 15 N with different frequencies (1 Hz, 3 Hz, and 5 Hz). (g) Polarity switching of the output current of the 10 wt.% EDABCO-CuCl₄@PVDF PENG. (h) The device reliability test for 35,000 cycles of the 10 wt.% EDABCO-CuCl₄@PVDF PENG at 30 Hz, and 136-gram weight on top of the device. (i) Comparison of the power density of a pure PVDF and 10 wt. % EDABCO-CuCl₄@PVDF PENG.

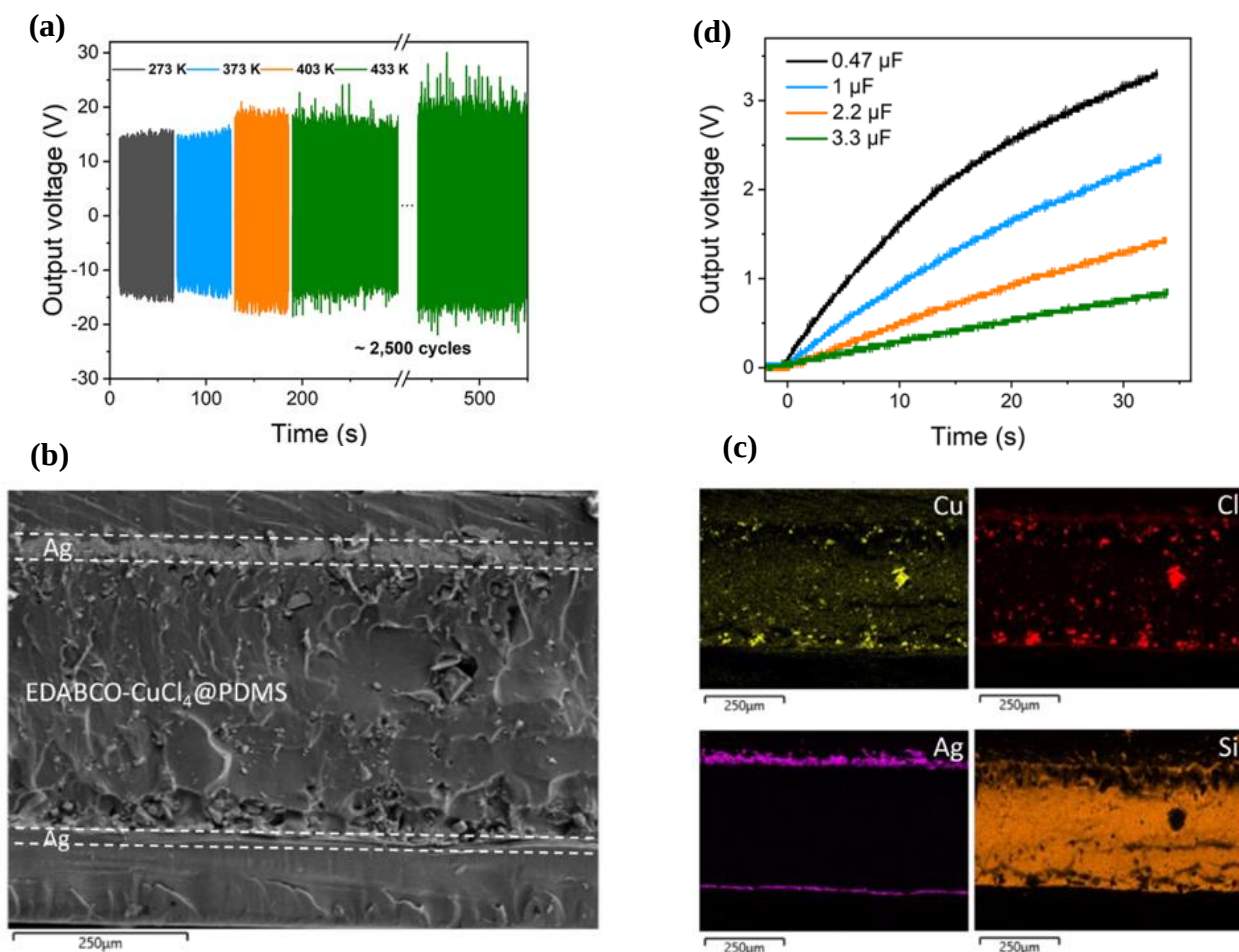


FIGURE 6.3 (a) The temperature-dependent output voltage of EDABCO-CuCl₄@PDMS composite PENG and reliability test for ~ 2,500 cycles at 433 K. (b) The cross-sectional SEM and (c) EDS mapping of EDABCO-CuCl₄@PDMS PENG after operating at 433 K for ~ 2,500 cycles. (d) Charging voltages of different capacitors by EDABCO-CuCl₄ PENG.

density (J_{sc}) of $2.1 \mu\text{A}/\text{cm}^2$ (15 N applied force, 5 Hz frequency) (**FIGURE 6.2c-f**). Compared with a pure PVDF device, the incorporation of the EDABCO-CuCl₄ nanoparticles increase the output voltage and current density by a factor of 2 and 3, respectively. The decrease in the output performance at higher EDABCO-CuCl₄ concentrations attributes to particle aggregation, which leads to the randomization of dipoles [153]. I perform switching-polarity tests to verify that the generated output signals originate from intrinsic piezoelectric properties (**FIGURE 6.2g**) rather than any electrostatic interactions. Fatigue experiments show no noticeable reduction in output current even after 35,000 mechanical pressing and releasing cycles, indicating high durability and potential for long-term operation (**FIGURE 6.2h**).

The peak instantaneous output power density is measured as a function of external load resistance from 0 to 50 M Ω (**FIGURE 6.2i**). The maximum power density of the pure PVDF PENG is measured to be 1.5 $\mu\text{W}/\text{cm}^2$ at a threshold load resistance of 2 M Ω . The 10 wt. % piezoelectric nanogenerators (which contain only 5 mg of EDABCO-CuCl₄) produce a maximum power density of 43 $\mu\text{W}/\text{cm}^2$ at a threshold load resistance of 8 M Ω ; the best reported for a heavy-metal free molecular energy harvester (**Table 1.2**).

I seek to challenge the applicability of EDABCO-CuCl₄ for use in sensing and actuating in harsh environments. Polymer composites with 5 wt. % EDABCO-CuCl₄ are prepared by dispersing the nanoparticles in the polydimethylsiloxane. PDMS is a heat-resistant flexible polymer where thermal degradation occurs at > 400 °C, in contrast to the low melting point of PVDF (~ 160 °C). With increasing temperature (273 K to 433 K) the average V_{oc} of the piezoelectric generators remains stable (~ 20 V) after ~ 2,500 working cycles, indicating its operability over a large temperature range (**FIGURE 6.3a**). The device and material exhibit no noticeable degradation following high-temperature operation (cross-sectional SEM and EDS mapping in **FIGURE 6.3b-c**). The noise-like spikes in the output signal can be due to the declining adhesive strength that is used to mount the device on the electric heater.

To demonstrate active energy harvesting, the electrical energy from EDABCO-CuCl₄ is stored in a series of capacitors (**FIGURE 6.3d**). At a low frequency (5 Hz) the stored charges across the 0.47 μF capacitor reach an electronic node voltage level of ~ 3 V in less than half a minute, illustrating the potential for use as a power source for low consumption micropower electronics.

6.4 Conclusions

The enhanced piezoelectric response of molecular metal halide EDABCO-CuCl₄ is reported by the combination of quasi-spherical theory and Jahn-Teller distortion. The non-centrosymmetric geometry of the EDABCO-CuCl₄ is confirmed by the observed second harmonic generation from the single-crystal. The Jahn-Teller effect is observed from the steady-state optical absorption measurement. The near-infrared absorption peak corresponds to the d-d electronic transition within the tetrahedral crystal-field of [CuCl₄]²⁻, where the local symmetry of Cu²⁺ is reduced from T_d to D_{2d} by Jahn-Teller distortion. Improved flexibility via Jahn-Teller distortion led to a high d₃₃ ~ of 165 pC/N, while the lower permittivity (~ 8) due to the highly confined 0D molecular architecture yields a g₃₃ of 2,110 × 10⁻³ V•m/N. Thus, the EDABCO-CuCl₄ demonstrates the largest energy density potential of any recorded heavy metal-free material, and its piezoelectric properties remain stable till 180 °C.

The 10 wt. % EDABCO-CuCl₄ nanoparticles are dispersed in a PVDF matrix to fabricate PENGs. A peak output voltage of ~ 63 V, current of 6 μA and a high-power density of 43 μW/cm² (at 50 kPa) are found superior to the best-reported molecular hybrid energy harvesters free of regulated metal. The inclusion of EDABCO-CuCl₄ in the PVDF boosts the output power density to ~ 28 times compared to a pure PVDF-based PENG (1.5 μW/cm²). Moreover, with the aid of this material, the energy harvesting performance of the PENGs is also recorded at ~ 160 °C which is above the automotive temperature norm (> 150 °C). It marks an advancement deemed necessary for designing micropower sources capable of operating in harsh environments (spaceships, automobile engines, etc.). This work contributes to continuing progress in the quest for heavy-metal-free molecular metal halides with a high transduction coefficient for efficient piezoelectric energy harvesting.

Chapter 7

Piezoelectric Nanogenerator based on Self-assembled Highly Porous Perovskite-polymer Composite

7.1 Motivation

There is an urgent demand in the industry for the development of compact, flexible, and sustainable power sources for self-powered Internet of Things micro/nano device. To fully satisfy the operational requirements of practical electronics, the quest for novel composite materials and device structures is critical. Previously, highly piezoelectric perovskites have been used as a piezoelectric center with either a piezoelectric or non-piezoelectric flexible polymer to fabricate the PENGs. This has dramatically enhanced the output voltage, current, power density of the PENGs. However, considering the practical needs of commercial electronics, such as a wireless electronics node for establishing remote communication requires high output current. Due to the insulating nature of the polymer materials, the output current/power from the PENG to the low-impedance practical electric load is severely limited. Therefore, optimally unifying appropriate mechanical and electrical properties in a single piezoelectric film remains to be a challenge. Herein, a novel, self-assembled, highly porous perovskite/polymer (PVDF in this case) composite film is developed for fabricating high-performance piezoelectric nanogenerators. The macroscopic porous structure can significantly enlarge the bulk strain of the piezoelectric composite film, which leads to a ~ 5 -fold enhancement in the strain-induced piezo potential. In addition, the novel OIHP-formamidinium (FA, CH_5N_2^+) lead bromine iodine (FAPbBr_2I) material can improve the conductivity of the final composite film due to its enhanced permittivity, providing a ~ 15 -fold amplification of the output current. The highly efficient perovskite /polymer PENG is used to run a self-powered integrated wireless electronic node (SIWEN). The PENG application is then extended to real-life scenarios including wireless data communication between the nanogenerators and personal electronics, efficient energy harvesting from automobile vibrations and from biomechanical motion. This perovskite-PENG based on a low-temperature full-solution synthesis approach, may initiate a paradigm shift by opening the realms of flexible PENGs as sustainable power sources.

7.2 Experiments

7.2.1 Synthesis of the pure PVDF films

To prepare the PVDF solution, PVDF is purchased as a powder form (Sigma Aldrich) and is dissolved in the N, N-DMF (N, N-dimethylformamide $\geq 99\%$, Sigma Aldrich) solvent (10 wt. %) by stirring for 12 hours at 40 ° C. The temperature is maintained at 40 ° C and is used to prevent agglomeration and achieving better dissolution. To prepare the PVDF film, the solution is drop casted on a standard glass wafer that is placed on a very flat hotplate. The sides of the glass substrates are covered with polyamide tape, to prevent the solution from flowing outwards. Before starting the annealing process, the solution is kept under ambient conditions for 30 minutes for degassing. To form the spontaneous electroactive β - phase in the PVDF, the curing temperature is adjusted carefully and is kept at 80 ° C for 1 hour. Then as grown thin film (~ 40 -50 μm) is peeled off from the glass substrate. Finally, a high voltage electrical poling (50-120 V/ μm) is performed for 2-4 hours to align the electric dipoles. For the high-voltage poling purpose- two gold coated electrodes are prepared via the electroplating method. To minimize the negative influence of the ambient moistures or the dust particles, the electrical poling is performed in a vacuum box. After that, to make the PENG, the films are placed between two copper tapes, and are thermally laminated between two polyester substrates.

7.2.2 Synthesis of the porous PVDF films

PVDF powder is dissolved in the N, N-DMF by stirring the solution for 12 hours at 40 °C. To create different porosities (named as the circular porous model), zinc oxide (ZnO) nanoparticles (NPs) (35–45 nm, US Research Nanomaterials, Inc.) are dispersed into the PVDF solution and again is stirred at 40 °C for 24 hours. The mass ratios between the PVDF and ZnO NPs (20 wt. % for this experiment) are adjusted to create different pores inside the PVDF. To achieve a uniformly mixed ZnO@PVDF composite solution, it is further treated in an ultrasonic bath for 1 hour. Then the uniform solution is drop casted onto a glass substrate and is degassed for 30 minutes. The solution is cured at 75 °C inside a vacuum oven for 30 minutes. Afterward, the ZnO@PVDF composite film is peeled off from the glass substrate. To obtain the porosity inside the PVDF, one-step etching of the ZnO NPs is performed in an ultrasonic bath by immersing the ZnO@PVDF composite film in a 37 wt. % HCl solution for 4 hours. Then the porous film is cleaned with DI

water and is dried in a nitrogen filled oven at 60 °C for 3 hours. Finally, high-voltage electrical poling (50-120 V/ μm) is performed for 2–4 hours to align the dipole. Then the films are placed between two copper tapes and is thermally laminated to encapsulate them between the polyester substrates.

7.2.3 Synthesis of the FAPbBr₂I@PVDF composite films

The FAPbBr₂I precursor solution is prepared by dissolving FAI (formamidinium (FA) iodide (CH_5IN_2) $\geq 99\%$, Sigma-Aldrich) and PbBr₂ (lead (II) bromide $\geq 98\%$, Sigma-Aldrich) at an equal molar ratio (0.5:0.5) in the N, N- DMF solvent, followed by stirring at 60 °C for 12 hours. The PVDF solution is dissolved in the N, N DMF with constant stirring at 50 °C for 24 hours. The final concentrations of FAPbBr₂I and PVDF in DMF are kept at 20 wt. % and 10 wt. %, respectively. Then, the FAPbBr₂I@PVDF composite precursor solutions are prepared by homogeneously mixing 20 wt. % FAPbBr₂I and 10 wt. % PVDF. To optimize the concentration, the 10 wt. %, 20 wt. %, and 30 wt. % composite solutions are synthesized. Then the mixed solution is drop-cast onto a glass substrate and is stored for approximately 1 hour for the degassing process, immediately followed by annealing at 120 °C. Highly crystalline composite films are obtained after 2-3 hours. To align the dipoles in the FAPbBr₂I@PVDF film, high-voltage electrical poling is completed with an electric field of 50-120 V/ μm for 2-3 hours. After poling, the films are sandwiched between two copper electrodes. Finally, the sandwiched structure of the polyester/copper/FAPbBr₂I-PVDF/copper/polyester film is pressed through thermal lamination, which eliminates air gaps and provides uniform adhesion between the copper electrodes and the piezoelectric film.

7.2.4 Characterization and measurements

To investigate the crystallinity of the hybrid halide into the ferroelectric PVDF scaffold the XRD is performed. A Bruker D8 DISCOVER is used with a Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$) to scan the optimized thin film samples (20 wt. % FAPbBr₂I-PVDF) from an angular range of zero to seventy degrees. Fourier transform infrared spectroscopy (Nicolet iS50) is employed to confirm the ferroelectric β -phase formation inside the porous PVDF and hybrid halide-embedded PVDF film by measuring the characteristic absorbance peak in a wavenumber range from 400 to 1000 cm^{-1} . The dielectric properties of the samples (C-V characteristics) are measured using a Keithley-4200 semiconductor parameter analyzer. JSM-7200F field-emission scanning electron microscopy tools are used to obtain surface morphologies and nanoparticles distributions inside PVDF are

mapped by analysing energy dispersive X-rays in a cleanroom environment (Class-100). The AFM and KPFM images are captured using a JPK Nanowizard II, is configured in intermittent-contact mode (a scan rate of 0.3 Hz). For the KPFM imaging, a cantilever probe (spring constant 42 N/m) with a platinum-coated tip (radius < 20 nm) is used to probe a grounded sample. A constant tip-sample interaction is maintained with a phase-locked loop and the internal reference of the lock-in amplifier is an applied ac voltage (3 kHz) to the sample surface. To study the electrical output performance of the PENGs an electrodynamic shaker (Lab Works Inc.) is used, which is controlled by a power amplifier and a controller. A digital oscilloscope (Tektronix 2004 C) and a low-noise current preamplifier (SR 570, Stanford Research Systems Inc.) are used to measure the electrical signal output from the nanogenerators.

7.3 Results and Discussion

FIGURE 7.1a depicts a schematic illustration of the final perovskite PENG (or known as P-PNG) device fabrication step, where the composite film is sandwiched between two copper electrodes and is encapsulated between polyester substrates, through a thermal lamination process. To elucidate the perovskite crystal formation inside PVDF, XRD scans over a wide range (diffraction angle 2θ ranging from 10 to 50 degrees) were conducted. The major diffraction peaks in **FIGURE 7.1b** at diffraction angles (2θ) of 14.64, 29.43, 42.12 and 44.39 can be assigned to the (100), (220), (222), (224) and (300) crystal planes of the cubic perovskite, respectively. It is noteworthy to mention that replacement of MA (CH_3N^+) with FA cation (CH_3N_2^+) in the FAPbBr_2I crystal, greatly enhance the structural stability, which is more suitable for the PENG device fabrication. Since it is well known that semi-crystalline PVDF polymer has four distinct phases (α , β , γ , and δ) where β -phase is the only one that possess spontaneous polarization, the existence of β -phase can be confirmed by the Fourier transformed infrared spectrum. The FTIR spectrum in **FIGURE 7.1c** demonstrates that, compared with the conventional pure porous PVDF [154], the coherently grown films of FAPbBr_2I crystals with polymer PVDF, have a higher intensity at a wavenumber of $\sim 475\text{ cm}^{-1}$, and a similar intensity at 840 cm^{-1} . This result is attributed to the improved β -phase crystallinity of the PVDF, due to the existence of dipolar interactions between the FA^+ cations of FAPbBr_2I and the anionic

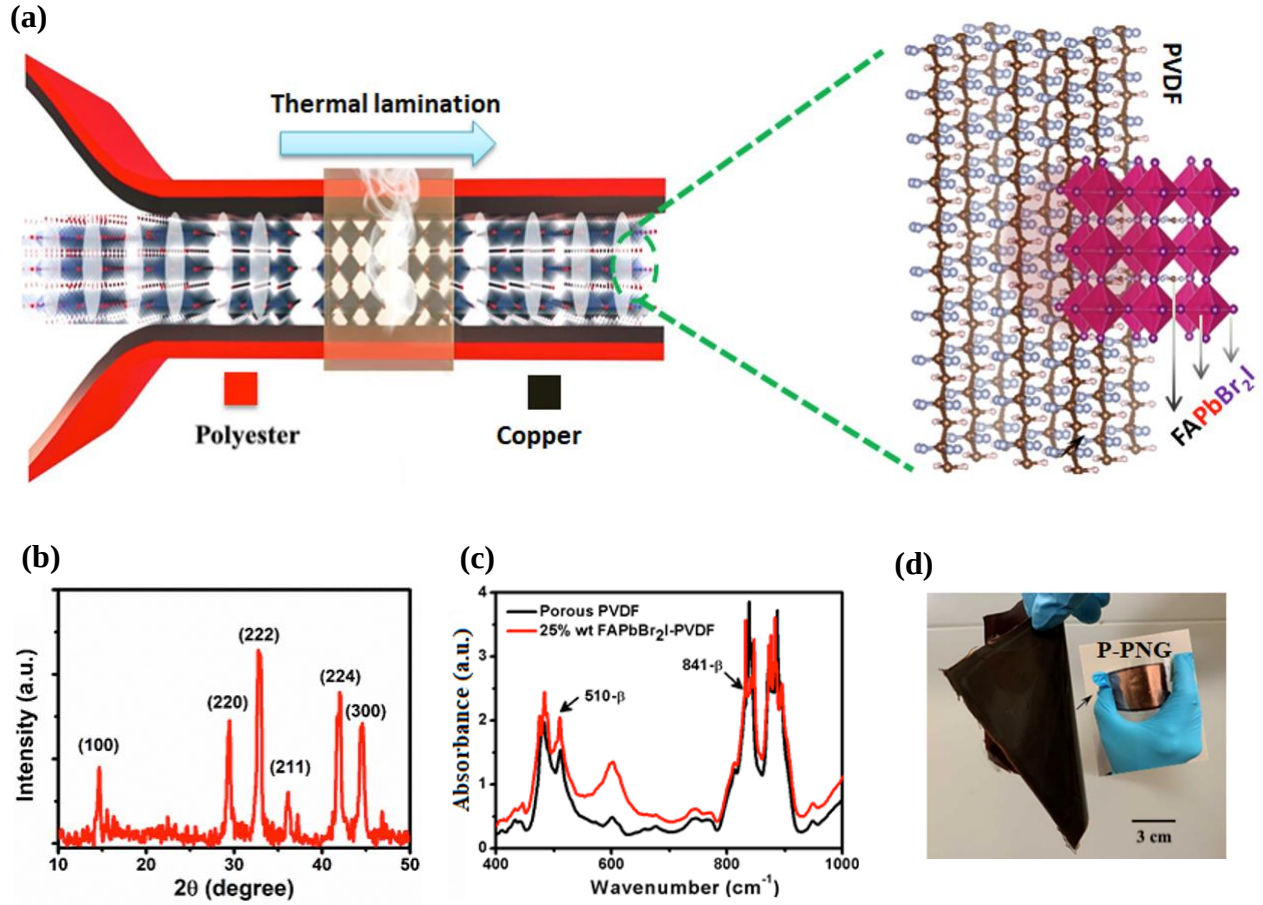


FIGURE 7.1 Device structure of PENGs (a) fabrication process of PENGs; (b) XRD patterns of 20 wt. % FAPbBr₂I@PVDF composite film; (c) FTIR results of porous PVDF and FAPbBr₂I@PVDF composite films (25 wt. %); (d) digital photos of the large area composite film (15 cm × 15 cm) and the fabricated PENGs.

fluorine (-CF₂-) groups of the PVDF. The piezoelectric coefficient (D_3) of the composite films can be written as

$$D_3 = \alpha_1 L_E \phi d_1 + \alpha_2 (1 - \phi) d_2 \quad (7.1)$$

where α_1 and α_2 are the poling rate, d_1 and d_2 are the piezoelectric coefficients of different materials in the composite film, respectively, L_E is the local field coefficient and ϕ is the mass fraction. Assuming organic and inorganic phases are fully poled, i.e., $\alpha_1 = \alpha_2 = 1$, and $\phi = 0.2$, the piezoelectric coefficient D_3 can be estimated. The local electric field ($L_E = 3\epsilon / (2\epsilon + \epsilon_c)$) is related to the relative permittivity of the FAPbBr₂I (ϵ_c) nanoparticles as well as the composite film (ϵ). A previous report suggested that the ϵ_c can reach to 1000, which is much larger than ϵ . Therefore, L_E

is estimated to be approximately 0.1-0.3 [155]. It has been identified that the piezoelectric coefficients of the PVDF and FAPbBr₂I phases are opposite. The approximated D_3 is calculated to be -23 pC/N when taking $d_1 \sim 25$ pC/N and $d_2 \sim -29$ pC/N. Moreover, other predominant factors such as the nanoparticles distribution and film geometry also significantly influence the piezoelectricity of this complex hybrid composite material system. The scalable FAPbBr₂I@PVDF composite film (15 cm × 15 cm) and a fabricated flexible PENG device are shown in **FIGURE 7.1d**. Across the cross-section of the film, an array of almost periodic vertical pores is observed, from the scanning electron microscopy image in (SEM and EDS mapping **FIGURE 7.2a-c**). In contrast to a conventional porous PVDF film (circular porous model) with pore sizes of hundreds of nanometers (nm) (**FIGURE 7.2d**) [92],[156], a uniquely self-assembled and highly porous structures are found in the FAPbBr₂I@PVDF composite film. The pores are ~ 20 -25 μm in length and approximately ~ 3 -5 μm in diameter. During the crystallization process, phase separation usually plays an important role in the formation of porous structure in the composite film. As a result, the crystallization process of PVDF@FAPbBr₂I can be divided into the following two stages [157]. During the first stage (i) while heating up the solution at 60° C, the N, N-DMF solvent starts to evaporate and the PVDF crystallizes firstly due to its relatively lower solubility. Then it transforms to a colourless film and remains in an intermediate state (schematic illustration in **FIGURE 7.2e**). (ii) After that, the FAPbBr₂I solution begins to approach to its supersaturated concentration (C_0) and then forms into nanoparticles, which is indicated by the change in colour from colourless to red. The keys to the self-assembly process of FAPbBr₂I nanoparticles embedded into the PVDF scaffold are two different crystallization processes of the PVDF and the FAPbBr₂I. During the second stage, the strong interactions between NH_3^+ in the formamidinium cations of the FAPbBr₂I and $-\text{CF}_2-$ groups of the PVDF, the perovskites nanoparticles tend to anchor on the PVDF scaffold. This interaction is reflected by the blue-shift of the infra-red absorption peaks of C-F bond in the wave number range of 1350-1100 cm^{-1} due to the decreased force constant according to the expression of $(\nu=1304\sqrt{(k/u)} (\text{cm}^{-1}))$, where ν is the frequency, k the force constant (N/m) and u the effective mass (**FIGURE 7.2f**). In addition, this interaction can also be observed from the mapping of the fluorine (F) atoms and lead (Pb) atoms which corresponds to the PVDF polymer chain (**FIGURE 7.2b**) and the FAPbBr₂I crystal (**FIGURE 7.2c**). The perovskite clusters (in **FIGURE 7.2c**) are attached with the PVDF polymer because of their common solubility in the DMF solvent (two materials can grow in one step) and the dipolar interactions between NH_3^+ in

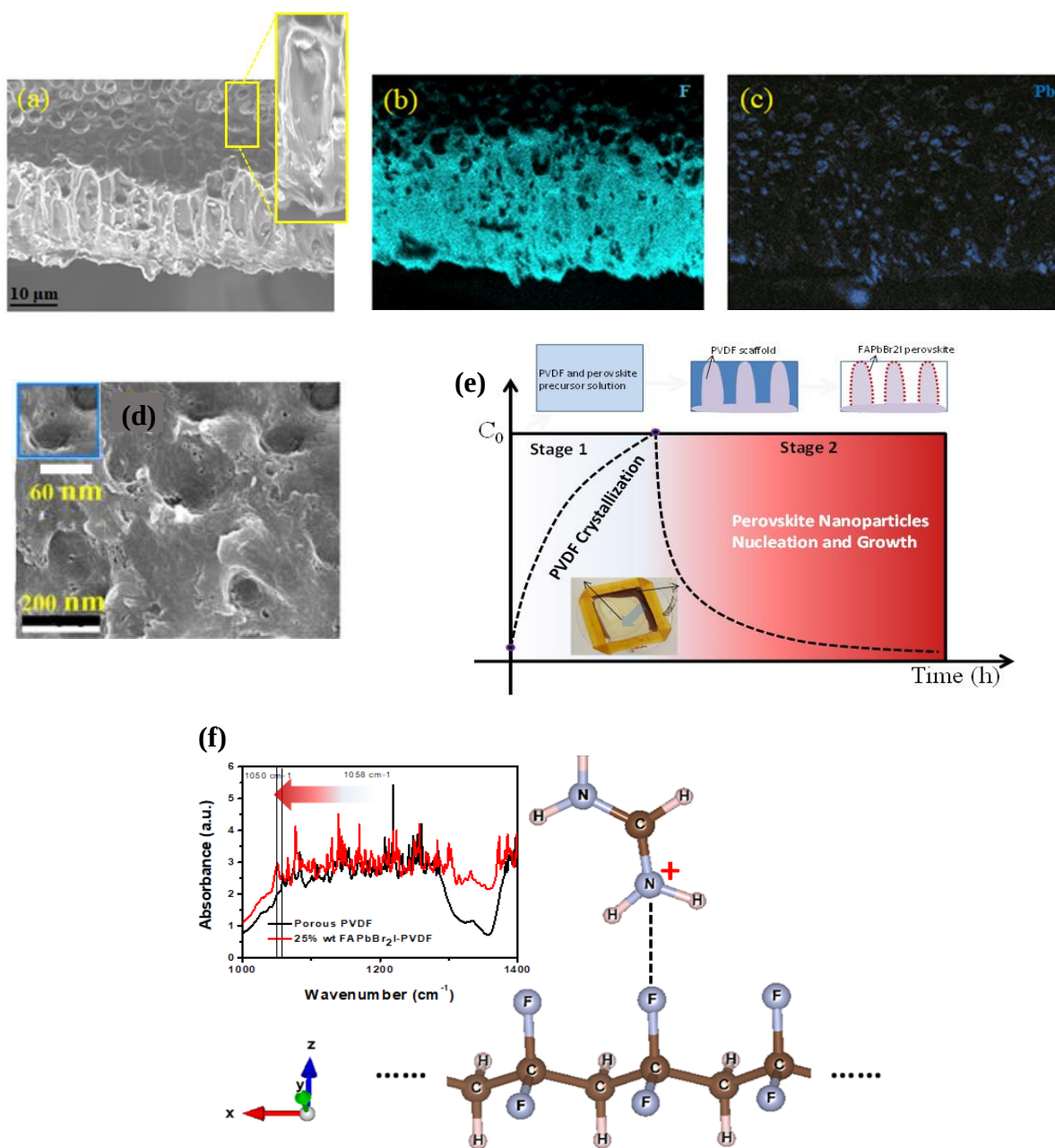


FIGURE 7.2 (a) Cross-sectional SEM image of the self-assembled highly porous FAPbBr₂I@PVDF (20 wt.%) composite films (inset shows the close view of a pore); the corresponding element mapping of (b) fluorine (F) in PVDF and (c) lead (Pb) in FAPbBr₂I; (d) top-view SEM image of the 20 % porous PVDF film after the etching of the ZnO NPs (the inset is the enlarged view of pore); (e) schematic illustration of crystallization process of the PVDF and FAPbBr₂I perovskite nanoparticles. The y axis represents the total concentration of PVDF and FA perovskites. The porosity and size of the pores can be well controlled via tuning the mass ratios of the hybrid halide FAPbBr₂I in the solution; (f) schematic diagram shows the interactions between FA⁺ and -CF₂- groups and the corresponding FTIR absorption peaks for the C-F bond in the range of 1350-1100 cm⁻¹.

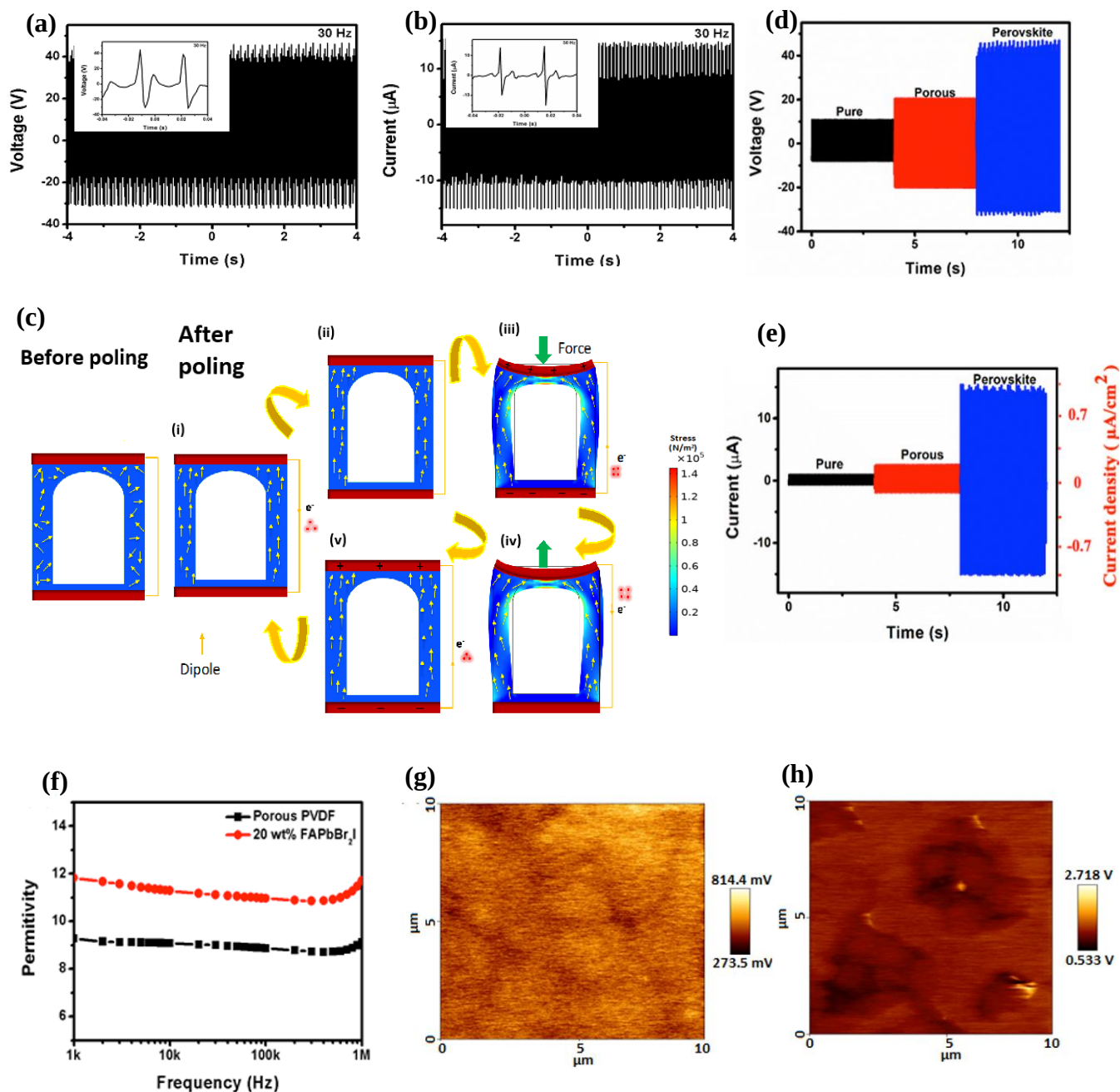


FIGURE 7.3 Output performance of the PENG: (a) output voltage and (b) current of the PENG with an applied load of 138 g, frequency 30 Hz and acceleration 2G. (c) Schematics of the PENG energy generation mechanism based on distributed stress on the film. (d) V_{oc} and (e) I_{sc} of PENGs are made from pure PVDF, porous PVDF (with ZnO nanoparticles) and FAPbBr₂I@PVDF composite films. For the porous PVDF, and FAPbBr₂I@PVDF composite films, the original mass ratios of nanoparticles inside the final films are 20 wt. %. (f) Relative permittivity of the porous and 20 wt. % FAPbBr₂I@PVDF composite films; KPFM images of the (g) porous and (h) 20 wt. % FAPbBr₂I@PVDF composite films.

(perovskite) and $-\text{CF}_2-$ groups of the PVDF. During the crystallization process, the increase in volume fraction (wt.%) should lead to the agglomeration of FAPbBr_2I NPs. The reason should be the strong dipolar interactions between the FA^+ cations and the anionic fluorine ($-\text{CF}_2-$) groups of the PVDF.

The highly porous $\text{FAPbBr}_2\text{I}@\text{PVDF}$ film provides an excellent platform for developing scalable PENGs, which only need two thin metal electrodes (copper) on both sides. Exploiting the unique microstructure features along with the formation of beneficial FAPbBr_2I nanocrystals, I investigate the effect on practical PENG performance. The generated output voltage and current are measured at various frequencies (10-50 Hz) and an acceleration of 2G, from the periodic mechanical vibration produced by an electrodynamic shaker. The device is placed on the shaker hammer and sandwiched by a 138 g metal block (stainless steel) on top. I measure an output voltage of ~ 85 V (peak to peak) and short-circuit current of $30\ \mu\text{A}$, respectively, from an active device area of $3.8\ \text{cm} \times 3.8\ \text{cm}$ at 30 Hz (**FIGURE 7.3a-b**). In **FIGURE 7.3c**, the electricity generation mechanisms of the device are schematically illustrated from the stress mapping by employing finite element simulation (COMSOL Multiphysics 5.3). When there is no applied electric field, the net dipole moment inside the film is almost zero (**FIGURE 7.3c(i)**). By applying a high electric field (50-120 $\text{V}/\mu\text{m}$) for 2-3 hours, dipoles are aligned to the direction of the electric field (**FIGURE 7.3c(ii)**). Now, if a compressive force is applied to the device, that due to rapid change in the net dipole moment by the flex-tensional mechanism will promote a polarization change in the poled PENG, yielding an even higher potential (**FIGURE 7.3c (iii)**)[158],[159]. If the two electrodes are connected to each other, then an electric current will flow to balance this piezo potential. While releasing the force, the piezo potential returns to zero because of the diminished film strain, and then the accumulated electrons will flow back (**FIGURE 7.3c (iv)**). Due to the formation of larger porous structures, the piezoelectric film could undergo an additional damping cycle, leading to the observation of a second output current pulse (**FIGURE 7.3c (v)**).

It is found that the voltage and current increases as the composition of FAPbBr_2I increases from 0 to 20 wt. % and decreases afterwards. The possible reasons are firstly, PVDF per unit volume is decreased due to the very high porosity. Secondly, the film impedance is reduced by higher wt. % of FAPbBr_2I , as a result, causing the earlier dielectric breakdown before maximum polarization charges are achieved by electrical poling. Thirdly, the defects generated by the agglomeration of

FAPbBr₂I NPs. Therefore, the device with 20 wt. % of FAPbBr₂I demonstrates highest output performance, and after the certain threshold margin, the device performance starts to degrade with further addition of excess FAPbBr₂I NPs. Then the highest measured output voltage and current of the PENG with 20 wt. % FAPbBr₂I is compared with the pure and 20 % circular porous PVDF based PENG devices (in **FIGURE 7.3d** and **FIGURE 7.3e**). Notably, the output voltage and current of the 20 wt. % PENGs are boosted by ~ 5 times and ~ 15 times, respectively, compared to those of the pure PVDF based PENG model (~ 17 V, and ~ 2 μA). They are also substantially higher than those of the 20 % circular porous PVDF PENG (~ 40 V, ~ 6 μA). I seek further evidence by investigating the intrinsic material properties to explain the sharp enhancement in the output current of the PENG device. The relative permittivity of the porous PVDF and 20 wt. % FAPbBr₂I@PVDF films are measured in a frequency range of 1 kHz to 1 MHz (**FIGURE 7.3f**). For both films, at the lower frequency regime, permittivity is high at the beginning due to the interfacial polarization effect [160] between the nanoparticles and polymer interface, which arises from the free carriers in the polymer material. However, with an increase in the applied electric field frequency, the interfacial polarization cannot cope up with the frequency change, which results in the decreased permittivity. Lastly the increasing pattern of the relative permittivity can be correlated with the arising of a high frequency stray capacitance during the measurements. The higher permittivity of the composite FAPbBr₂I@PVDF film (~ 12 at 1 KHz) enhances the piezoelectric performance, as it increases the piezoelectric coefficient (D₃). In addition, the enhanced permittivity of FAPbBr₂I perovskites give rise to the output current by reducing the internal impedance (Z) of the film-

$$Z = R - j \frac{d}{2\pi A \epsilon_0 \epsilon_r} \quad (7.2)$$

where, R is the film resistance, d the thickness, A the area, ϵ_0 vacuum permittivity and ϵ_r the relative permittivity. The charges due to the internal polarization are also affected by the relative permittivity of FAPbBr₂I. I measure the surface potential of the FAPbBr₂I @PVDF film by employing Kelvin probe force microscopy. The relationship between the permittivity and polarization can be expressed as [161]

$$\vec{P} = \epsilon_0(\epsilon_r - 1)\vec{E} \quad (7.3)$$

where, $\vec{P}$ is the electric polarization within the material, ϵ_0 the permittivity of free space ($8.854 \times 10^{-12} \text{ F m}^{-1}$), ϵ_r the relative permittivity and $\vec{E}$ the electric field. From equation (7.3), the higher permittivity of the composite film due to the presence of perovskite will certainly change the strain induced electric field inside the composite film, and as a result the magnitude of the surface potential will be different. In general, for perovskite PENGs, the surface potential is of particular interest because it affects band bending and carrier transport at the interfaces [162], [163]. By measuring the contact potential difference using a platinum (Pt) KPFM tip ($\sim 20 \text{ nm}$ radius) in intermittent contact mode, the average surface potential of FAPbBr₂I @PVDF is found to be 1.1 V, which is more than twice that of porous PVDF (**FIGURE 7.3g-h**). The observed variation in the average surface potential in FAPbBr₂I@PVDF film is very small ($<100 \text{ mV}$), which eliminates possible surface contamination by the remnant precursors-formamidinium iodide or lead bromide.

7.4 Applications of the PENGs as a sustainable power source in the IoT

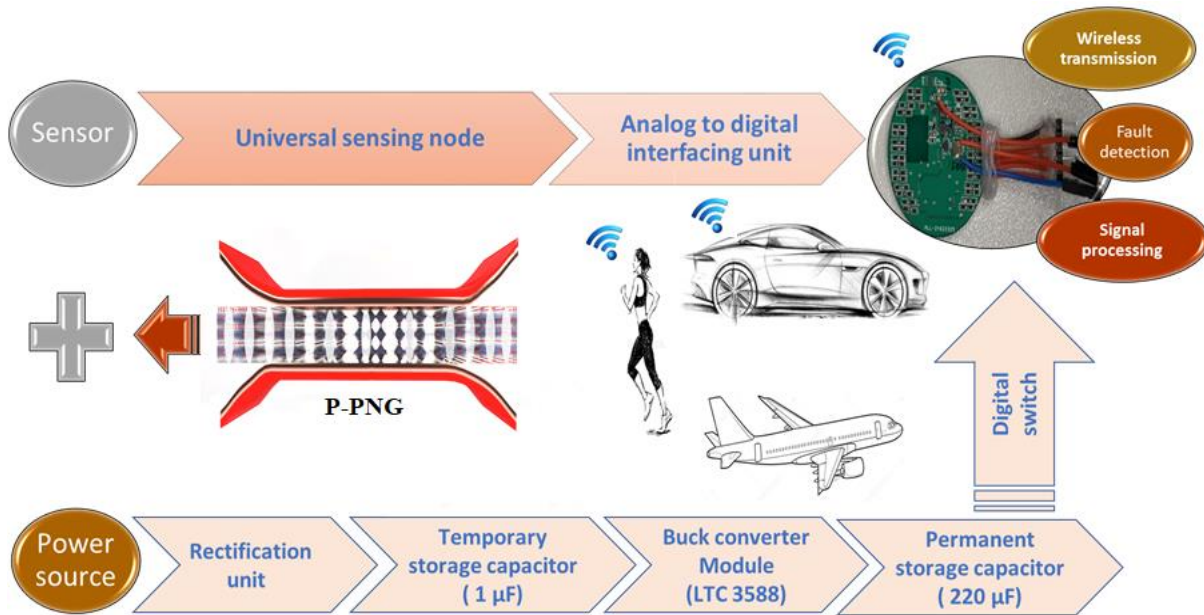


FIGURE 7.4 Framework of the self-powered integrated wireless electronics node by simultaneously using the PENGs as a power source and a sensor.

Despite vast efforts in the past decade, the implementation of composite PENGs, especially in real-time applications, is still limited. To address these limitations, we employ our novel flexible PENGs as a power source to implement a true SIWEN for the distributed IoT network. This SIWEN can remotely communicate with any Bluetooth-compatible personal electronics to transfer data from many distributed sensors. The functional block diagram of the SIWEN is shown in **FIGURE 7.4**. The SIWEN incorporates a rectification unit, two-stage energy transfer system, regulated switches, and a low-power system on chip (SoC) for conditioning the sensor signal and transmitting it to a remote end receiver. Before integrating the PENG with SIWEN, a practical load-driving capability is confirmed. The maximum instantaneous power delivered to the load is measured from the output currents of the P-PNG with a wide range of external load resistances (100 K Ω to 80 M Ω). A peak output power of $\sim 105 \mu\text{W}$ and a power density of $10 \mu\text{W}/\text{cm}^2$ are obtained at a load resistance of 7 M Ω (**FIGURE 7.5a**). In **FIGURE 7.4**, a PENG is exemplified as an electrical power source, which is capable of harnessing mechanical energy from wide range of vibration sources (human motion, vibration of aircrafts and automobiles). However, during the experiment, an electrodynamic shaker is used to generate mimic vibrations at a frequency of 30 Hz and an acceleration of 2G.

The energy harnessed by the PENG is being stored to powering up the SIWEN to initiate data transfer. The measured charging characteristics of the two-stage energy transfer system is enabled by two capacitors (C_p) are shown in **FIGURE 7.5b**. When the voltage of an input capacitor (1 μF) reaches $\sim 5 \text{ V}$, which is regulated by a Zener diode, it discharges energy through a buck converter module to an output capacitor (220 μF). The buck converter module consists of two metal oxide semiconductor field-effect transistor (MOSFET) switches. After the output voltage of the 1 μF input capacitor is dropped down to a regulated voltage of $\sim 2\text{-}3 \text{ V}$, the 220 μF output capacitor is disconnected from it by the MOSFET switches and the input capacitor stops discharging and starts to be charged. In this manner the output capacitor is charged until $\sim 3.1 \text{ V}$ with high energy transfer efficiency, and can power up any electronics node. The electrical energy stored in the 220 μF output capacitor is used to drive the Bluetooth-compatible system on chip (SoC). Another PENG is incorporated in the system as a sensing unit which is connected with an analogue to digital converter (ADC) of the SoC via an impedance matching bridge.

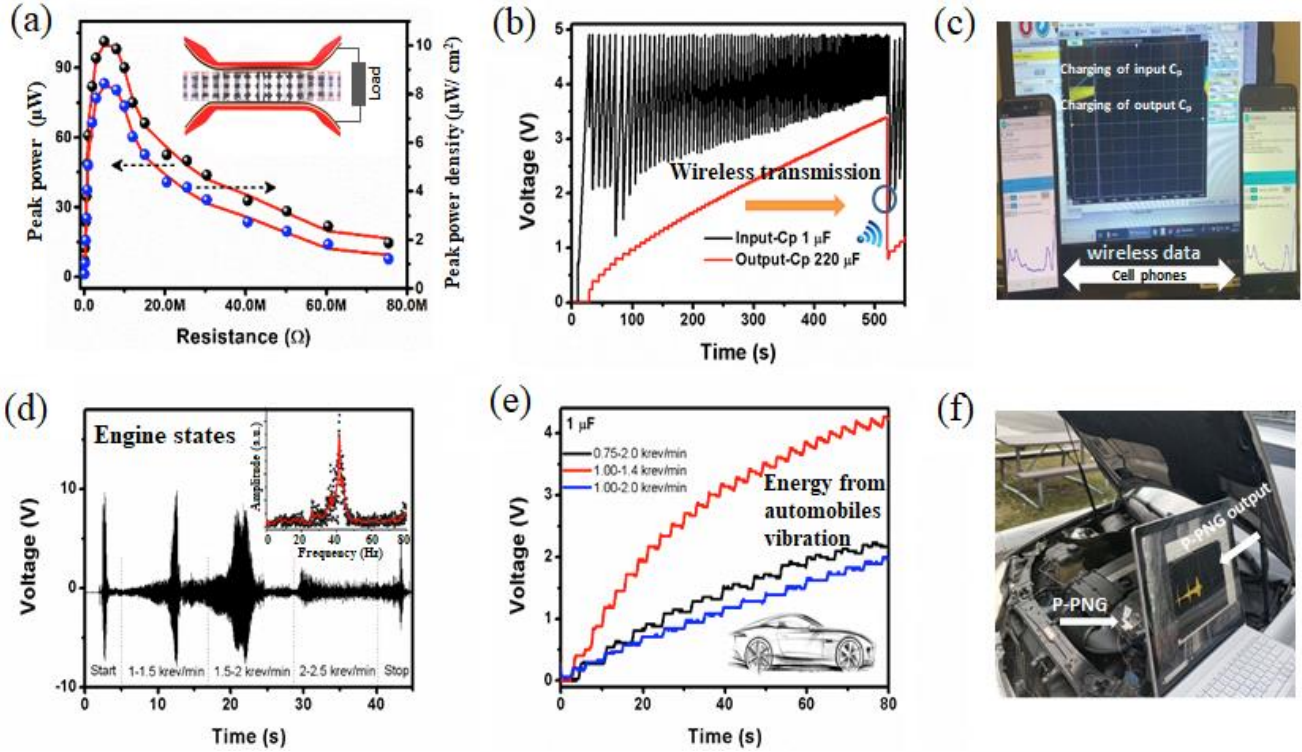


FIGURE 7.5 Application of the PENGs for IoT: (a) the measured output power of the PENG with an applied acceleration of 2 G (30 Hz). The load here is a metal block of 138 g. (b) Charging characteristics of the input (1μF) and output capacitor (220 μF) of the SIWEN; (c) the digital photo of the sensor signal received by the cell-phone; (d) SIWEN used for car engine states detection at a parking condition (inset shows the corresponding frequency domain distribution via Fast Fourier Transform); (e) charging of a commercial capacitor (1 μF) by a single PENG while exciting by an automobile engine (Mercedes-Benz car); (f) the corresponding digital photo of engine vibration detection.

Immediately after reaching the output voltage of the 220 μF capacitor to 3.1 V, a trigger signal turns on a switch through which the output capacitor discharges energy to power-up the SoC and transmits the digital sensor data from the sensor to a remote receiver (**FIGURE 7.5c**).

To assess more versatile applicability, the PENGs are used in harnessing vibration from an automobile vehicle (the car in is park mode while the engine is turned on). **FIGURE 7.5d** depicts the measured output voltage from the PENG when it is mounted on the car (while the engine is running), where device output reflects the acceleration and rotational speed- dependent vibration pattern of the engine. After the engine is turned on, the rpm (revolutions per minute) is varied from

a range of 1-1.5, 1.5-2, 2-2.5 kilo revolutions per minute (Krev/min) while maintaining a constant acceleration between each rpm regimes. Initially, a peak-to-peak voltage of ~ 13 V is measured, which is attributed to the abrupt engine vibration when getting started. Later, the PENG output is dropped, due to a gradual decrease in the vibration magnitude in the higher rpm regimes. We also perform a fast Fourier transform (inset of **FIGURE 7.5d**) revealing the major contribution of the device output produced from the vibration components of approximately 40 Hz, which is close to the resonance frequency of the PENG. By harnessing energy from such minute engine vibrations, a commercial capacitor of 1 μ F is charged up to 4 V in ~ 1 minute (**FIGURE 7.5e-f**). The capacitor is continuously charged up by switching the car rpm back and forth between 1-1.4 krev/min (red curve), 1-2 krev/min (blue curve) and 0.75-2 krev/min (black curve). The best charging performance at 1-1.4 krev/min is attributed to the highest acceleration and more frequent excitation to the capacitor (lower rpm switching time). For the other two wider rpm regimes, acceleration is lower and their longer switching time allows the capacitor to further discharge its energy. Hence, scalable PENGs are critical for industrially viable nanogenerator applications.

7.5 Conclusions

To summarize, a novel self-assembled highly porous phenomenon in a composite piezoelectric polymer film is discovered by employing a hybrid halide perovskites (FAPbBr₂I) precursor, which is significant for designing high-performance nanogenerators for next-generation self-powered devices. An efficient, flexible, and all-solution processed perovskite-piezoelectric nanogenerator is successfully fabricated. The mechanism of pore formation, the strategy of tuning the porosity and its correlation with the PENG performance are established. The film morphologies including the perovskite structure, pores, nanoparticle distribution, β -phase formation, and surface potential are revealed by the XRD, SEM, AFM, FTIR and KPFM tools. The enhanced permittivity is observed from the frequency-dependent dielectric measurement and higher surface potential in the KPFM image. Because of the enlarged film strain of the self-assembled highly ordered porous scaffold (PVDF) and the enhanced relative permittivity of the novel perovskite FAPbBr₂I, the 20 wt. % composite film's piezoelectricity is dramatically boosted, yielding a strain-induced piezo potential of 85 V (~ 5 times greater than PVDF PENGs) and a current of $\sim 30 \mu\text{A}$ (~ 15 times more than PVDF PENGs), with an applied load of 138 g. It is found that the concentration of the NPs more than 20 wt. % decreases the device performance, is anticipated due to the formation of large pores and NPs agglomeration. The experimental results are supported by the numerical simulation of three different PENG device models (pure PVDF, porous PVDF and the perovskite-polymer composite film).

In this study, the advancements made in the device performance led to deploying it in many practical applications. A self-powered universal wireless electronics node capable of communicating remotely with personal electronics is demonstrated by using the PENG as an alternative means of a battery. At 30 Hz, the PENG can trigger the SIWEN to transmit raw sensor data to the remotely located mobile phones every ~ 2 minutes. Therefore, the PENG shows a proof-of-concept to be used as a solo power source in the micro/nano systems for the IoT. The PENG is also used in generating electricity by harnessing energy from automobile vibrations and detecting engine states and biomechanical motion which can be extended easily to many other applications as well. This study in return paves a way to achieve the practical implementation of PENG-based self-powered technologies which are compact, flexible, and industrially viable.

Chapter 8

Cascade-type Perovskite-piezoelectric Nanogenerators for Enhancing Output Current Density

8.1 Motivation

Since the invention of the PENGs in 2006, great efforts have been devoted to enhancing their output performance to use them as a power source for portable electronic devices. The OIHP and their composites have been a promising material system for flexible, cost-effective, and room-temperature processing technique which yields high-performance PENGs. The output voltage of the individual OIHP-based PENGs has been raised to ~ 100 V, and the current density reached $6.2 \mu\text{A}/\text{cm}^2$ in 2017 [31]. The output voltage from the PENG is sufficiently large enough for the power requirements of modern electronic devices, however, the output current density is the most important bottleneck for its future development.

Many efforts had been done to improve the current density; however, those were mainly encompassed by ceramic piezoelectrics. By stacking PZT NW arrays Gu et al. fabricated PENG with a current density of $23 \mu\text{A}/\text{cm}^2$ in 2013 [164]. In the following year 2014, Park et al. developed PZT thin film-based PENG with interdigitated electrodes and reported a record current density of $150 \mu\text{A}/\text{cm}^2$ [165]. In 2020, Gu et al. marked another record of output current density to $290 \mu\text{A}/\text{cm}^2$ by stacking 72-layers of ceramic Sm-PMN-PT nanowires and PVDF composites [58]. However, despite the decade-old development of OIHP-based PENGs, its output current density has not greatly improved. The stability in the ambient is a great concern, which severely limits its applications. Under the electrical poling field, migration of the ionic species of the OIHP causes faster dielectric breakdown and reduces the applied bias.

In this study, I have functionalized polystyrene (PS) with the FAPbBr_2I perovskites and have improved its stability. I evidence that, with the PS functionalization the crystallinity of the FAPbBr_2I perovskites improves, and grain sizes are enhanced by a factor of 2. Ion migration of the perovskites' species is significantly reduced whereas an order of magnitude suppressed leakage current density is observed from the dark-current measurement. The enhanced homogeneous dispersion of the PS- FAPbBr_2I yield piezoelectric composite films with excellent quality, whereas

output current density from the individual device is increased by a factor of 1.5 ($\sim 7 \mu\text{A}/\text{cm}^2$) than the composites with pristine FAPbBr₂I. Improved material stability aids to fabricate a cascade-type PENG. The cascade-type PENG with intercalated copper electrodes generates a high output current density of $\sim 100 \mu\text{A}/\text{cm}^2$ (peak to peak) at 30 Hz, and 4.2 N. The order of magnitude enhancement in the output current density of the OIHP-based PENGs will further push the limit towards achieving a renewable power source for flexible electronics in IoT.

8.2 Experiments

8.2.1 Synthesis of the pristine and PS-FAPbBr₂I precursor solution

The FAPbBr₂I precursor solution is prepared by dissolving an equimolar ratio (0.5:0.5) of FAI (formamidinium iodide $\geq 99\%$, Sigma-Aldrich) and PbBr₂ (lead (ii) bromide $\geq 98\%$, Sigma-Aldrich) in an N, N-DMF (N, N-dimethylformamide $\geq 99\%$, Sigma-Aldrich) solvent, followed by stirring at 60 °C for 12 hours. To prepare PS-FAPbBr₂I precursor solutions of varying concentration (1, 10, and 20 wt./vol%), a corresponding number of PS (average Mw 35 kDa, Sigma-Aldrich) is added to the perovskite precursor solution and stirred for 30 min.

8.2.2 Synthesis of the PS-FAPbBr₂I@PVDF composites

The PVDF solution is dissolved in N, N DMF with constant stirring at 50 °C for 24 hours. The final concentrations of the PVDF in DMF are kept at 10 wt. %. Then, the PS-FAPbBr₂I@PVDF composite precursor solutions are prepared by homogeneously mixing 1 wt./vol % PS-FAPbBr₂I and 10 wt. % PVDF. To optimize the concentration, the 1, 10, and 20 wt./vol% composite solutions are synthesized. Then the mixed solution is drop-cast onto a glass substrate and is stored for approximately 1 hour for the degassing process, followed by annealing at 120 °C. Highly crystalline composite films are obtained after 2 hrs. To align the dipoles in the PS-FAPbBr₂I@PVDF film, high-voltage electrical poling is completed with an electric field of 50-120 V/ μm for 2-3 hours. After poling, the films are sandwiched between two copper electrodes. Finally, the sandwiched structure of the polyester/copper/PS-FAPbBr₂I@PVDF/copper/polyester film is pressed through thermal lamination, which eliminates air gaps and provides uniform adhesion between the copper electrodes and the piezoelectric film.

8.2.3 Multilayer assembly of the PS-FAPbBr₂I@PVDF composites

Each of the poled composite films is cut into 1.3 cm × 0.6 cm dimensions. Copper tapes with a size of 1 cm × 0.45 cm are used as an electrode. Polyurethane solution is used as an adhesive between the electrode and the composite film. First, a few drops of the polyurethane solution are poured on the copper electrode and is spread with a glass rod to achieve uniformity. Second, the composite film is pressed tightly on the copper for adhesion. Third, another copper electrode is attached to the top of the composite film by using step one. Fourth, a few drops of polyurethane solution are poured on another composite film and spread uniformly with a glass rod. Fifth, the composite film is pressed tightly on the copper electrode of step 3. Sixth, step 1 is repeated to grow the top copper electrode. In this way, two units of the composite films are cascaded. Then, steps 4, 5 and 6 are repeated to assemble 14 different layers. The polarity (polarization direction) of the composite film is determined by the electrical poling direction. Between two consecutive films, opposite polarities are maintained. Electrodes at the positive interfaces are shorted to make a single positive terminal, and similarly, electrodes of the negative interfaces are shorted to make a single negative terminal for the electrical measurements. Finally, the device is packaged in between thermal laminating pouches.

8.2.4 Structural, microscopic, and spectroscopic characterization

The X-ray diffraction characterization is carried out on the PANalytical Empyrean diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). A Zeiss Ultraplus field emission scanning electron microscopy (FE-SEM) is utilized for visualizing the surface topology and grain size distribution of the pristine and polymer-integrated perovskite films. The Raman spectroscopy for all films is performed using a Horiba HR800 spectrometer at an excitation wavelength of 532 nm and 6 mW power in the backscattering configuration. The time-of-flight second ion mass spectroscopy (ToF-SIMS) is performed to analyze depth profiling of freshly prepared perovskite and polymer-perovskite films using Cs⁺ ion source (500 eV) for sputtering and Bi³⁺ (30 keV) for analysis over ToF-SIMS 5, ION-ToF GmbH.

8.2.5 Electrical measurements

The dark current measurement on the planar vertical device configuration is conducted using a probing station in two probe mode. A Keysight 6614C 50-Watt system power supply is used for applying an external bias and the current is measured using a Keysight 3458A Digital multimeter. The perovskite film is connected in series with the multimeter and power supply to complete the circuit. To study the electrical output performance of the PENGs an electrodynamic shaker (Lab Works Inc.) is used, which is controlled by a power amplifier and a controller. A digital oscilloscope (Tektronix 2004 C) and a low-noise current preamplifier (SR 570, Stanford Research Systems Inc.) are used to measure the electrical signal output from the nanogenerators. A 10X signal cable is used to collect the voltage signals from the PENGs.

8.3 Results and Discussion

The X-ray diffraction pattern (**FIGURE 8.1a**) shows the presence of the dominant peaks corresponding to (1 1 0) (2 2 0) and (3 1 2) lattice planes and signifies the formation of the mixed halide perovskite phase in both pristine FAPbBr₂I@PVDF and PS-FAPbBr₂I@PVDF films [166], [167]. The narrowing of the peak (reduction in the full width and half maximum value) and increase in the peak intensity in the PS-FAPbBr₂I@PVDF XRD pattern indicates improved crystallinity and an increase in the crystallite size. An additional shoulder peak of residual PbX₂ (X=I, Br) is observed at 2 θ of 12.4 ° exclusively in the pristine FAPbBr₂I. The absence of the PbX₂ (X=I, Br) peak in the PS-perovskite composite film can be ascribed to the ability of PS chains to interact with PbI₂, a weak Lewis acid formed intermittently during solvation of perovskite precursors, eventually leading to enhanced perovskite phase conversion [168]. There also exists a shift in the reflection positions to lower 2 θ value in PS-FAPbBr₂I@PVDF films, signifying relaxation in the perovskite lattice [169]. This can be attributed to the higher ionic radii of the 6-coordinated I⁻ ($r_{I^-} = 2.06$ Å) with respect to Br⁻ ($r_{Br^-} = 1.82$ Å) ion as the cation- π interaction between FAI and PS facilitates relatively higher inclusion of the I⁻ leading to subtle variation in the halide composition (FAPbBr_{2-x}I_{1+x}) of the perovskite [170].

The specific molecular-level interaction between perovskite precursor and PS is characterized by Raman spectroscopy (**FIGURE 8.1b**). The pristine FAPbBr₂I@PVDF and PS-FAPbBr₂I@PVDF films exhibit sharp characteristic peaks of Pb–X (X=I, Br) lattice mode centered at 80 cm⁻¹ and a

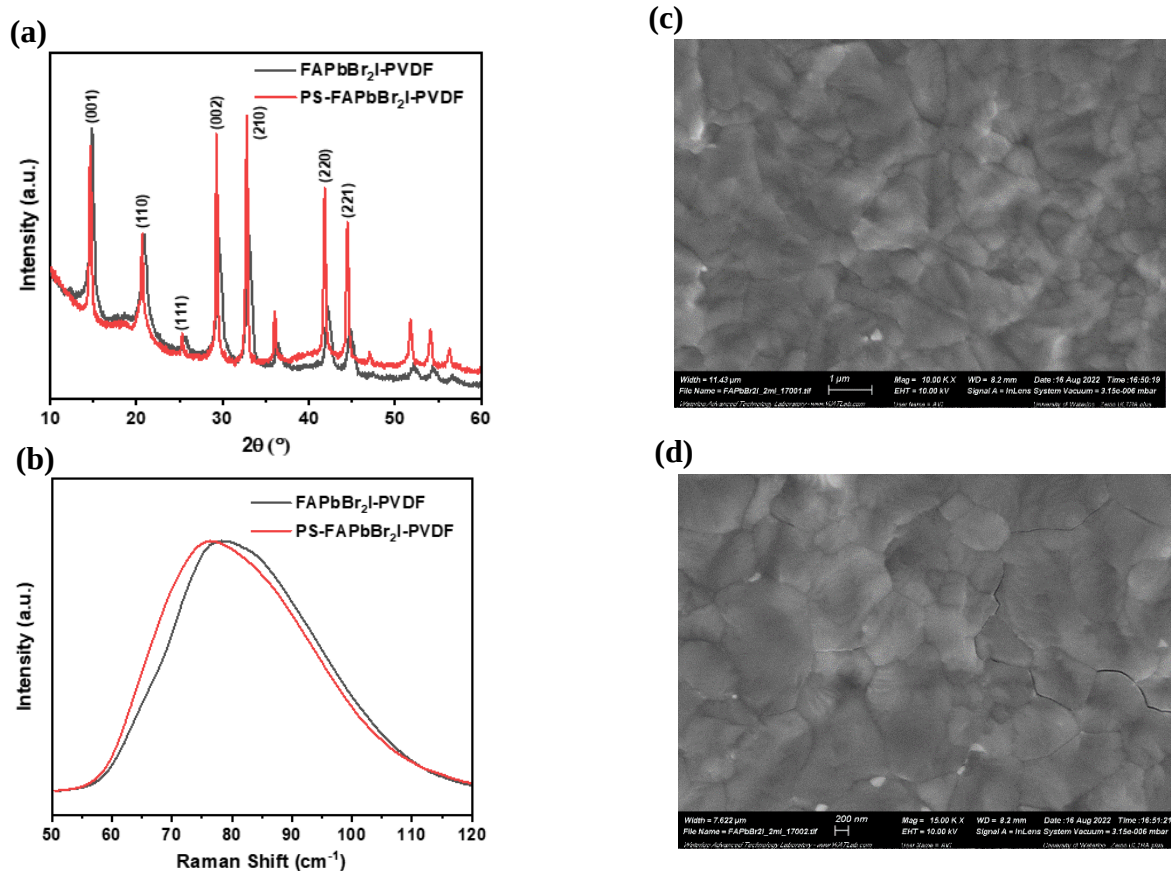


FIGURE 8.1 (a) XRD pattern of pristine FAPbBr₂I@PVDF and PS-FAPbBr₂I@PVDF. (b) Raman spectroscopy of the FAPbBr₂I@PVDF and PS-FAPbBr₂I@PVDF film. (c) FE-SEM surface images of FAPbBr₂I and (d) 1 wt./vol% PS-FAPbBr₂I film.

broad peak (160-250 cm⁻¹) corresponding to the organic moiety [171]. As it is observed in **FIGURE 8.1b**, the peak corresponding to the Pb–X (X=I, Br) lattice mode shifts to a lower wavenumber with the inclusion of the PS. Typical cation– π interaction between FA⁺ and PS chains also leads to variation in the corresponding Raman peak intensity in the PS-FAPbBr₂I@PVDF film. Such variation in the Raman active modes of the perovskite signifies an enhanced molecular-level interaction between PS and perovskite precursors which forms the basis of the inclusion of PS in the FAPbBr₂I@PVDF film [172]. Similar interaction between PS and the organolead halide perovskite precursors has been previously confirmed by gel permeation chromatography and the growth of single perovskite crystals [173].

The direct interaction of PS chains with the perovskite precursors leads to relatively larger grain size in the PS-FAPbBr₂I films (**FIGURE 8.1d**) in comparison to that of pristine FAPbBr₂I (**FIGURE 8.1c**) as evident in the lateral field emission scanning electron microscopy images. This matches well with previous studies demonstrating that the incorporation of PS in the perovskite matrix leads to modulation of the nucleation and the growth rate of crystal grains, along with reduced defect density [174].

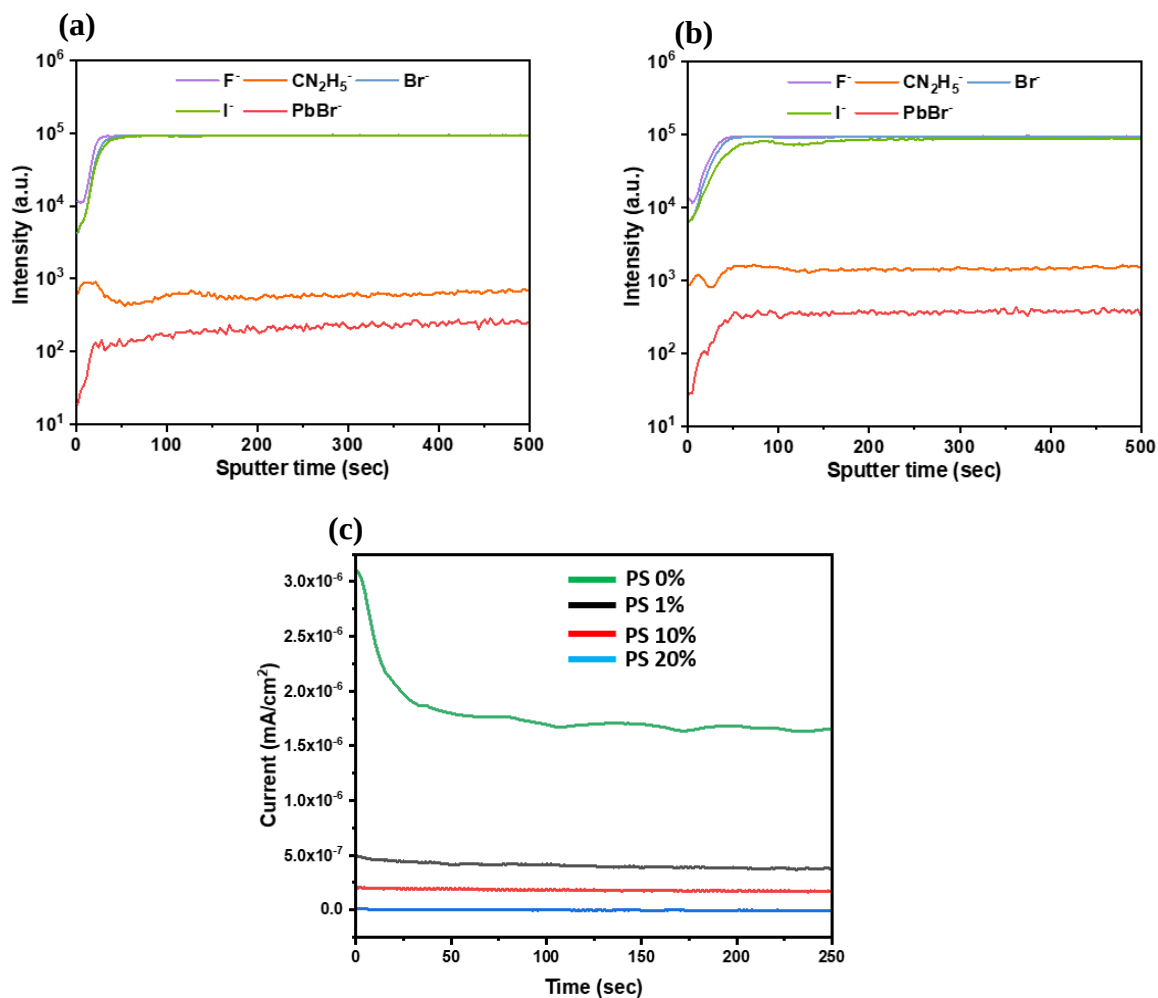


FIGURE 8.2 (a) ToF-SIMS depth profiling of PS-FAPbBr₂I@PVDF and (b) FAPbBr₂I@PVDF films. (c) Dark current density of 0, 1, 10, and 20 wt./vol% PS-FAPbBr₂I@PVDF composites.

The Time-of-Flight Secondary Ion Mass Spectroscopy depth profiling results further ascertain that owing to its interaction with the PS, a relatively higher concentration of I^- is included in the PS-FAPbBr₂I@PVDF composite film. The depth profiling data (**FIGURE 8.2a**) reveals that the signal intensity of the I^- ion is maintained at the same level as that of the F^- ion (representative of PVDF) across the entire depth of the sputtering time. This is representative of the uniform presence of the iodide anion across the entire depth of the perovskite film. On the other hand, a relatively lower I^- signal intensity is evident in the pristine FAPbBr₂I@PVDF film especially during the initial 0-200 sec of sputtering time signifying the non-uniform distribution of the iodide moiety in the pristine FAPbBr₂I@PVDF films (**FIGURE 8.2b**).

The extent of decay in the dark currents is typically associated with the ion migration effects persisting in the perovskite film [175],[176]. Briefly, under applying an external bias in dark, an electronic current is instantly observed owing to the fast movement of the electronic charge carriers. At the same time, the mobile ions with low activation energy drift towards metal electrodes. As the oppositely charged ions begin accumulating at the metal electrodes, the ion-induced electric field partially cancels the external bias and reduces the overall current. Such transient decay in current is observed until the ion accumulation reaches an equilibrium condition. The pristine FAPbBr₂I film owing to the higher density of mobile ionic defects and halide ion segregation exhibits faster decay [177]. As seen in the **FIGURE 8.2c**, the dark current in the pristine FAPbBr₂I film decays rapidly from its initial value of 3.10×10^{-6} mA/cm² and reaches 1.86×10^{-6} mA/cm² (~ 40% decay) within 35 sec. In contrast, the ability of PS to interact with both perovskite precursors significantly reduce the extent of ion migration effects.

The total current in the PS-containing perovskite films decreases with an increase in PS wt./vol% as the overall film resistance increases. Further, the dark currents show negligible decay and exhibit relatively stable values across the entire measurement duration. Such reduced ion migration effects contribute to enhanced stability of the composite films as the structural integrity of the perovskite is maintained. Improved crystallinity and reduced ion migration provide enhanced stability of the composite film during the electrical poling of the PENG. The output voltage and current density of the PENGs are measured for different PS concentrations.

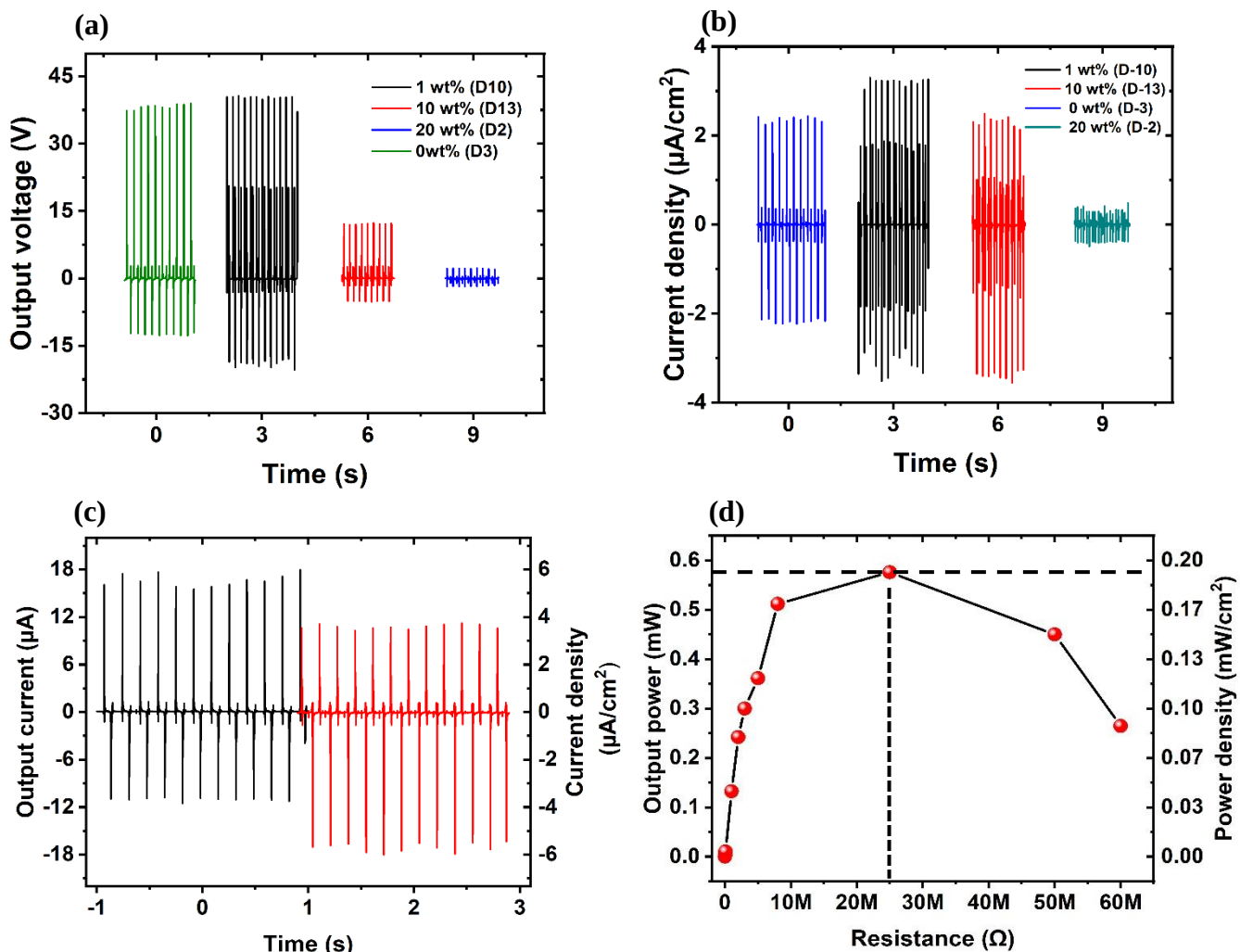


FIGURE 8.3 (a) PS concentration dependent output voltage and (b) output current density. (c) Polarity switching of output current of a 2-layers cascade PENG. (d) Output power density of 2-layer cascade PENG. The test force and frequency are 15 N, and 5 Hz.

The 1 wt./vol% PENG device demonstrates the highest output performance (**FIGURE 8.3a-b**), with an output voltage, that reaches ~ 60 V (p-p) and current density of ~ 7 $\mu\text{A}/\text{cm}^2$ at 5 Hz, 15 N. Compared to the pristine FAPbBr₂I@PVDF PENG the 1 wt. /vol% PS-FAPbBr₂I@PVDF PENG enhances the current density to 1.5 times. Further increasing the PS concentration reduces the output current density due to the agglomeration of the polymer which I notice from gel formation in the precursor solution. The higher current density and stability arising from the PS-

functionalization with perovskites motivates me to use it as a building block for the multilayer assembly.

In a PENG, the piezoelectric polarization charges are utilized to produce output current to the external circuit. Under mechanical stress, the opposite polarization charges are formed at the two interfaces of the top electrodes and bottom electrodes. If it is possible to create many such interfaces by two-dimensional electrodes inside a piezoelectric film, output current density can be significantly enhanced [58]. I use the bottom-up approach to assemble the composite films to fabricate the cascade type PENG. Initially, two films are cascaded to make a single PENG unit. The output current becomes double, with a peak-to-peak current reaches to $\sim 30 \mu\text{A}$ and a current density of $\sim 10 \mu\text{A}/\text{cm}^2$ (**FIGURE 8.3c**) at 15 N, and 5 Hz. I perform a polarity switching test of the output current which shows the exact reversal of the waveshape, without any reduction of its magnitude. Then I measure the output power of the PENG across different electrical resistances from 0 to 60 M Ω values. The peak output power reaches 0.58 mW, with a power density of $\sim 0.19 \text{ mW}/\text{cm}^2$ ($\sim 190 \mu\text{W}/\text{cm}^2$). Such high output power density is among the very few best-reported PENGs, to date [55].

When a force is applied to the PENG, the dipole moments become smaller along the thickness direction of each composite film. However, the small current generates each unit added up via the interfacial electrodes to produce larger current output. When the force is released, the dipoles are returned to their initial state, and a reverse current peak is obtained. In this manner, surface polarization charges get multiplied across the interfaces, for increasing the overall current.

I fabricate a few cascade-type PENGs with 4, 8, and 14 layers of the PS-FAPbBr₂I@PVDF composites to increase the current output. The schematic of the cascade device is shown in **FIGURE 8.4a**. The output voltage and current of the devices are shown in **FIGURE 8.4b-c**, which are measured at 30 Hz, and 4.2 N. As the layer number increases from one to four, the output voltage decreases from 20 V to 7 V, and for the 14 layers PENG it reaches to 2.7 V (**FIGURE 8.4b**). It can be explained from the simple capacitor model, that the parallel connection of capacitors will increase the overall capacitance, and the voltage should decrease ($V=Q/C$; V = voltage, Q = charge, C = capacitance). In addition, the force which is applied on the top of the device will be depleted to the bottom layers, which could reduce the output. In contrast, with the help of increased polarization charges from the collective contribution from each layer, overall

current density increases almost in a linear fashion. The peak-to-peak output current density increases from $\sim 10 \mu\text{A}/\text{cm}^2$ for a single layer PENG to $\sim 100 \mu\text{A}/\text{cm}^2$ for the 14-layer cascade type PENGs (FIGURE 8.4c).

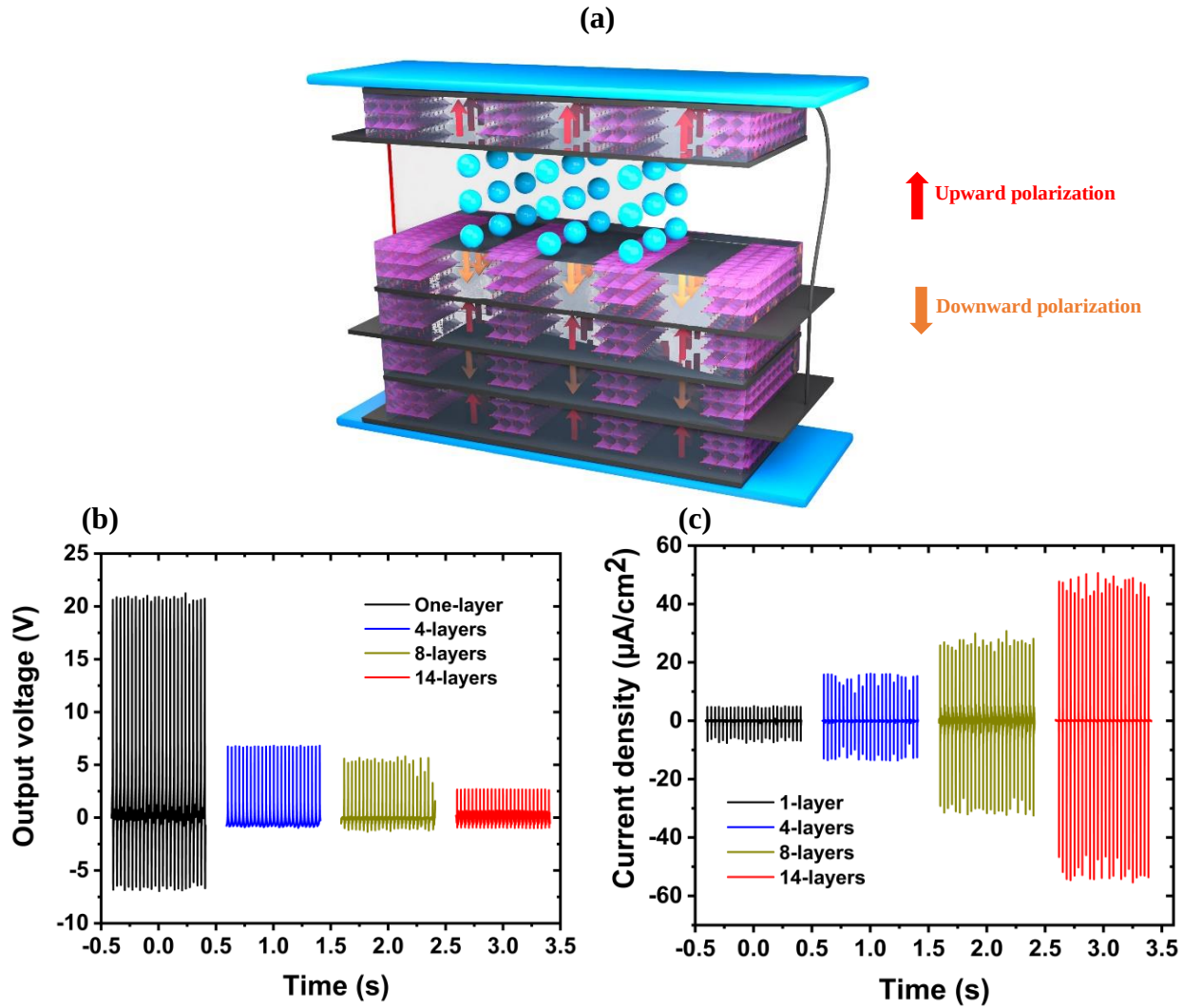


FIGURE 8.4 (a) Schematic of a cascade-type PENG. (b) Output voltage and (c) current density of 1-, 4-, 8-, and 14-layers cascaded PENGs at 30 Hz, 4.2 N.

8.4 Conclusions

Polystyrene functionalization with perovskite (FAPbBr₂I) is adopted as an innovative route to enhance the output current density of the PENG. Optimized PS concentration in FAPbBr₂I precursors reduce the defects density and ion migration under an electric field. It is found that the 1 wt./vol% PS reduces the leakage current to one order of magnitude by significantly suppressing ion migration. Moreover, the controlled nucleation of perovskites by the PS enlarges the grain sizes twice than the pristine perovskites. The improved material stability and uniform nanoparticle dispersion concurrently improve the output current density of the PENG to ~ 1.5 times that of the pristine FAPbBr₂I@PVDF based PENG. With the aid of layer-by-layer assembly of as-developed high-performance composite films, the output current density from the cascade type PENG is recorded to be $\sim 100 \mu\text{A}/\text{cm}^2$, which is an order of magnitude higher than the available PENGs made from organic-inorganic hybrid perovskites. An excellent output power density of $0.19 \text{ mW}/\text{cm}^2$, with a total power of 0.58 mW is also recorded. The high-performance PENG with an ultrahigh current density developed in this study will enable a giant shift toward achieving a sustainable power source for portable and flexible electronics.

Chapter 9

Conclusions, Contributions and Recommendations

9.1 Conclusions

This research has carried out a comprehensive study on perovskite-based piezoelectric nanogenerators, focusing on their modeling, fabrication, and characterization. The role of halogen atom substitution on the piezo potential of the CsPbX_3 perovskite structure is calculated. Tensile strain in the unit cell is found as the dominant effect contributing to the piezoelectricity. The difference in the ionic radius between the halogen atoms (I, Br) induces a tensile strain of 2.12% in the unit cell which can enhance the piezo potential by a factor of ~ 7 . By substituting the halogens, a series of inorganic perovskite materials are developed, whereas, for the first time, CsPbBr_2I is reported as the highest piezoelectric material in the CsPbX_3 family with a d_{33} of 47 pC/N. The output power density from the CsPbBr_2I reaches to the highest value of $24 \mu\text{W}/\text{cm}^2$. N in the cesium lead halide perovskites based PENGs. In addition, nanorods of organic-inorganic perovskites $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$ are developed, which demonstrates high transverse piezoelectricity of 64 pC/N, which is 3-times higher than the PVDF, the most popular polymer piezoelectric. The geometry influence of the perovskite on piezo potential is analyzed. It is found that the nanorod can increase piezo potential by a factor of 4, compared to their thin film counterpart of the same dimension. With the same applied pressure, the stress distribution in the nanorod is higher due to the bending. The combined contribution of longitudinal and transverse piezoelectric coefficients of nanorods produce a high output voltage of $\sim 90 \text{ V}$ (p-p) and a current of $6.5 \mu\text{A}$ from the PENG. The effect of electrical poling on the PENG performance is also experimentally analyzed, which can enhance the output voltage from 7 V to 75 V due to the ferroelectric nature of the $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$.

To simultaneously increase the d_{33} and g_{33} of a perovskite material (transduction coefficient), a vacancy-ordered halide double perovskite of $(\text{TMCm})_2\text{SnCl}_6$ is designed. The d_{33} and g_{33} are measured to be 137 pC/N and $980 \times 10^{-3} \text{ V}\cdot\text{m}/\text{N}$, respectively. Synergistic dynamics between molecular dipole rotation (TMCm^+) and atomic displacement in the inorganic $[\text{SnCl}_6]^{2-}$ octahedron via halogen-bonding are proposed to be the root cause of yielding such high-piezoelectricity, is also validated with the density functional theory. The polarization contribution from the organic

and inorganic parts are distinguished, whereas the atomic displacement in the inorganic octahedron contributes mostly. Subsequently, the application of the newly developed material in the PENG is realized with a peak output voltage of ~ 81 V, and a current of $2 \mu\text{A}$, at 40 Hz and 4.9 N. The rotation of the organic molecules and the distortion of the inorganic cage via halogen bonding interaction plays a key role in obtaining highly piezoelectric OIHP materials.

To enhance the transduction coefficient further, an organic-inorganic molecular metal halide of EDABCO- CuCl_4 is synthesized with a d_{33} of 165 pC/N and a giant g_{33} of $\sim 2110 \times 10^{-3} \text{ V}\cdot\text{m}/\text{N}$, thusly a combined transduction coefficient of $348 \times 10^{-12} \text{ m}^3 \text{ J}^{-1}$. The role of a quasi-spherical molecular cation and the effect of a Jahn-teller active metal Cu^{2+} ($3d^9$) on the distortion of the inorganic cage are investigated. Thereafter, a combination of the quasi-spherical cation with the Jahn-teller active metal is hypothesized as an excellent material design strategy to achieve a non-centrosymmetric crystal structure that can produce a large transduction coefficient. By using the EDABCO- CuCl_4 an efficient PENG is fabricated which can generate a maximum output power density of $43 \mu\text{W}/\text{cm}^2$ (at 50 kPa). Furthermore, the effect of temperature on the crystal structure is studied, whereas the highly confined 0D molecular architecture of EDABCO- CuCl_4 is found to remain stable till 180°C and enables the PENG operation at 160°C .

Instead of using highly piezoelectric perovskites, a composite film model is developed with the FAPbBr_2I and PVDF, which increases the piezo potential of the PENG by forming an array of self-assembled porous structures and increases the output current by the high relative permittivity of the in-situ grown FAPbBr_2I NPs. The macroscopic porous structure inside PVDF enhances the piezo potential by a factor of 5, and the high relative permittivity of the FAPbBr_2I perovskite reduces the conductivity of the PVDF which boosts the output current by a factor of ~ 15 . The effect of percentage (%) porosity inside the PVDF is also simulated and experimentally analyzed from the fabricated devices. With the increase of % porosity, the piezoelectric film can deform more easily, and yield an improved electromechanical coupling. The ordered pores in the simulation model also indicate the proof of a high mechanical stress inside the film that potentially produces more polarization charges and increases the voltage from 11 V in the non-porous structure to 40 V in the 60% porous film. The device generates an output voltage of ~ 85 V (p-p) and a current of $\sim 30 \mu\text{A}$, which is used to demonstrate a self-powered wireless sensing system.

Considering the high current requirements of electronic circuits, a cascade-type PENG is fabricated by the OIHP composites. Stability, which is the fundamental limitation of the OIHP is improved by functionalizing its surface with an organic PS molecule. It is experimentally discovered that a particular concentration (1 wt. /vol%) of PS reduces ion migration, enhances crystallinity, and grain sizes of the FAPbBr₂I all of which are conducive to increasing the piezoelectric performance. The homogeneity of the OIHP NPs distribution inside the polymer matrix is also improved compared to the perovskite without surface functionalization. The PENG delivers a high output power density of $\sim 190 \mu\text{W}/\text{cm}^2$. The cascade type PENG with 14 layers of PS-FAPbBr₂I@PVDF composites produces an output current density of $\sim 100 \mu\text{A}/\text{cm}^2$ at 4.2 N, which is the largest among the OIHP-based PENGs fabricated to date.

9.2 Contributions

In this section, I have provided a qualitative summary of each of the chapters highlighting their contribution and scopes in the nanogenerator fields, and beyond.

(1) Halogen-regulated piezoelectrics for high-power PENGs

Inorganic (cesium) metal halide perovskites have been of extensive interest, due to their higher stability, low-temperature synthesis, and breakthrough performance in solar energy conversion. To control piezoelectric potential, the development of novel piezoelectric materials takes a complex path, rather engineering the existing ones can be more sustainable. In this innovative study, I provide a very fundamental insight to create new piezoelectrics by simply regulating the halide ions in a CsPbX₃ lattice. I reveal a series of piezoelectric materials and further quantified their piezoelectric coefficients (d_{33}) which were previously unexplored. Excitingly, by controlling the halogen atom, I achieve a record d_{33} coefficient among the family of cesium metal halide perovskites and further enrich its library. As of proof-of-concept, I also fabricate piezoelectric nanogenerators with high electromechanical energy generation capabilities. This will be highly beneficial as a ready-to-use material to be incorporated in practical electromechanical sensors, actuators, and harvesters.

(2) Piezoelectric nanogenerators based on organic-inorganic hybrid perovskite nanorods

The exciting prospect of nanometer-scale active devices (e.g., switches, sensors, and stretchable electronics) largely depends on the availability of ultrathin piezoelectric materials having strong piezoelectric properties even in the fundamental limit of the thickness (one or few-atom thick sheet materials). Longitudinal and transverse piezoelectric coefficients are the two fundamental parameters quantifying the efficacy of a piezoelectric material. However, till now, the intriguing transverse piezoelectricity of the material is not under the limelight and the research in this field is mostly directed at improving the d_{33} coefficient. Herein I report a novel organic-inorganic hybrid perovskite nanorods of $(\text{ATHP})_2\text{PbBr}_2\text{Cl}_2$, which exhibits a large transverse piezoelectric coefficient of 64.2 pC/N, almost three times higher than the most-widely used polymeric piezoelectric PVDF film (21 pC/N). The rod-like morphology with excellent flexibility, superior d_{31} coefficient, and larger surface area than conventional nanoparticles, can be a promising candidate for designing efficient PENGs. Through careful material synthesis, PENG device fabrication schemes, and finite-element simulation, I have revealed the excellent mechanical energy harvesting performance, which is a synergistic effect of both d_{31} and d_{33} , where d_{31} plays a dominating role. Finally, the PENG's successful integration with energy storing and regulation unit unfolds its capabilities for real-life self-powered electronics applications.

(3) Ultrahigh piezoelectricity in a hybrid vacancy-ordered halide double perovskite

To achieve a large piezoelectric charge coefficient, d_{33} and piezoelectric voltage coefficient, g_{33} simultaneously in one host material is critical to maximizing the short-circuit current and open-circuit voltage of piezoelectric nanogenerators. Due to the interplay of d_{33} and g_{33} ($g_{33}=d_{33}/(\epsilon_0*\epsilon_r)$, where ϵ_r is relative permittivity), it is challenging to improve d_{33} while maintaining a high g_{33} because the increase of d_{33} is usually associated with an even larger increase of ϵ_r . The organic-inorganic hybrid halide perovskites combine the merits of the organic molecules and inorganic crystals at an atomic level, implying great opportunities for designing and creating materials with novel properties. I report such an example as well as its energy harvesting applications. I developed and demonstrated a green vacancy-ordered double perovskite of $\text{TMCM}_2\text{SnCl}_6$ with a large d_{33} of 137 pC/N and a giant g_{33} of $980 \times 10^{-3} \text{ V}\cdot\text{m}/\text{N}$. The microscopic origin of the ultrahigh piezoelectricity in the $\text{TMCM}_2\text{SnCl}_6$ perovskites is considered from the halogen-bonding mediated

synergistic movements of atomic displacement in inorganic $[\text{SnCl}_6]^{2-}$ octahedrons, as well as the rotation of organic molecular TMCM. The $\text{TMCM}_2\text{SnCl}_6$ perovskite possesses a high saturated polarization of $8.7 \mu\text{C}/\text{cm}^2$, a high Curie temperature of 365 K, and a low coercive field of 0.6 kV/cm. This study not only shows a pathway to develop novel lead-free perovskite piezoelectric materials with outstanding properties but to deploy them successfully for electrical energy generation in real life.

(4) Enhanced piezoelectric response in a Jahn-Teller distorted molecular metal halide

In this study, I begin by seeking to understand, mechanistically, why it is that the extensive prior library of piezoelectrics explored to date has failed to produce simultaneously large d_{33} and g_{33} . Prior molecular perovskites have impressive g_{33} values, but their d_{33} fails to reach that of oxide perovskites because of their low polarization. In seeking to achieve high $d_{33} \cdot g_{33}$, I reason that large lattice distortion and softness in molecular perovskite leads to enhanced polarization, which can produce high d_{33} . Meanwhile, the desirably low dielectric constant promises high g_{33} . I hypothesize that to achieve these properties, combining the Jahn-Teller distorted polyhedron with quasi-spherical cations can provide a good pathway to enhance the lattice distortion and softness of molecular perovskites. To implement this new concept, I develop molecular metal halide EDABCO- CuCl_4 , using a quasi-spherical cation EDABCO and a Jahn-Teller distorted $[\text{CuCl}_4]^{2-}$ tetrahedron, which exhibits a large d_{33} (165 pC/N) and g_{33} ($\sim 2110 \times 10^{-3} \text{ V} \cdot \text{m}/\text{N}$) simultaneously. The impressive piezoelectric response allows me to fabricate high-performance piezoelectric nanogenerators with a peak power density of $43 \mu\text{W}/\text{cm}^2$, the best-reported composite mechanical energy harvester based on molecular perovskite. This work demonstrates the ability of molecular piezoelectrics to exceed ceramic perovskites in performance and allows the PENG operation in harsh environments ($> 150^\circ\text{C}$).

(5) Piezoelectric nanogenerator based on self-assembled highly porous perovskite-polymer composite

To fully satisfy the operational requirements of practical electronics, I introduce a novel perovskite/polymer composite film for high-performance piezoelectric nanogenerator applications. This study provides a new route toward PENG design and creates an unprecedented perspective on perovskite-polymer composite piezoelectric films. The novel hybrid halide perovskite- formamidinium lead bromine iodine is used to create an ordered porous film. By the virtue of enlarged film strain and higher relative permittivity, piezoelectricity generation is dramatically boosted. Notably, strain-induced piezoelectric potential and output current are enhanced by ~ 5 times and ~ 15 times ($85 \text{ V}_{\text{p-p}}$, and $30 \text{ } \mu\text{A}_{\text{p-p}}$, respectively) compared to traditional PVDF-based PENGs. The PENG is capable to drive a custom-designed self-powered integrated electronics node – which is a demonstration of a self-powered wireless communication system. This is an important milestone for enabling the dream of IoT where trillions of devices will be interconnected, and dependency on batteries will become risky, and infeasible. The demonstrated applications also include harnessing tiny mechanical vibrations from a running automobile car engine to efficiently charge up energy-storing capacitors and monitoring the engine states by the PENG, as well as harvesting energy from biomechanical energy sources.

(6) Cascade-type piezoelectric nanogenerators for large output current density

Most modern electronics require a high current (mA range), compared to a standard voltage level of only $\sim 3 \text{ V}$. In contrast, the PENG produces high voltage output ($> 3 \text{ V}$), but the output current is typically low (μA -level). To address this fundamental concern, cascade-type PENG is studied to enhance the output current density from the PENGs. The stability of the OIHP perovskites is the most serious constraint for its repeatability, scalability, and manipulation of its piezoelectric properties. The stability of the perovskite material under the electric field is considered and ion migration of the FAPbBr_2I is suppressed. By the functionalization of the perovskite surface with polystyrene, crystallinity and grain sizes are enhanced, and more homogeneous dispersion capability in the polymer is achieved. The improved piezoelectricity enables a cascade-type PENG with a record high output current density of $\sim 100 \text{ } \mu\text{A}/\text{cm}^2$ among the OIHP-based composites.

This study will further push the boundary of PENG-powered micro/nano systems and fill the gaps for fabricating industrially viable OIHP-based efficient piezoelectric devices.

9.3 Future work and Recommendations

To guide the future endeavours in the field of PENG, a key priorities, challenges, and directions are summarized as follows:

- (1) Stability is a great concern for the organic-inorganic perovskites. Protecting the perovskites in a flexible polymer is somehow helpful for many applications, their lack of stability still blurs the impressive material benefits and imposes serious challenges for commercialization. After identifying the complex degradation mechanism some strategies can be adopted such as doping, mixed cation or halogen engineering, and the use of additives. Some additives such as butyl phosphonic acid 4-ammonium chloride (4-ABPACl) can cross-link between adjacent perovskite grains to reduce moisture vulnerability, can provide a nucleation site, and produce uniform films. Moreover, 2-D perovskite can be synthesized where large spacer cations (polymers) act as a protective shield for the inorganic cage. However, the trade between performance and stability in the 2-D perovskites should be addressed properly.
- (2) Although polymer composite-based PENGs have many advantages, random nanoparticle distribution, and particle agglomeration reduces the device yields. A strategy needs to develop for precisely controlling the nanoparticle dynamics inside the polymer matrix. The concept of dielectrophoresis can be used to further control the nanoparticle distribution in the OIHP-based piezoelectric composites.
- (3) Piezoelectric nanocomposites can help realize the benefits of highly piezoelectric nanomaterials up to a certain extent. Especially, more than 20-30 wt. % of the NPs inside a polymer can create agglomeration, disrupts electric field distribution, and cause dielectric breakdown earlier than reaching the saturated polarization. Crucially, the insulating nature of most of the polymers increases the internal impedance of the PENG, thus lowering the

output current generation. To exploit the full benefits of highly piezoelectric materials, the robust thin film can be grown by optimizing the vapour deposition processes or sputtering techniques.

- (4) There is a clear lack of a unified performance metric of the PENGs, which does not allow for precisely comprehending the property enhancement. The comparison of different properties has not achieved true uniformity between different types of parameters such as thickness, area, mass, density, and operation methods. Moreover, a fundamental understanding of mechanical quality factors and electromechanical energy conversion is necessary for the output optimization of the PENGs.
- (5) Layer-wise parallel assembly of the PENGs enhances the output current density but decreases the output voltage. Maximum power delivery to the electrical load and impedance at the maximum power point will also be considered while optimizing the number of layers.
- (6) Direct charging of the energy-storing capacitors or batteries by the PENGs are not efficient especially due to their internal impedance mismatch. It is emphasized to develop advanced electrical circuitry to maximize the energy storing efficiency. Multi-stage charging by using different capacitors was developed, but the leakage current accumulation with the increased number of regulation stages is still an issue. Self-charging a power pack by using a common piezoelectric material both in the PENG and the solid electrolyte of an integrated battery would be a worthwhile direction to investigate.
- (7) Ferroelectric materials are a subclass of pyroelectric and piezoelectric materials. It is investigated that the OIHP of MAPbI_3 possesses pyroelectricity [178]. By exploiting the pyroelectric property of other OIHP materials, multimodal energy harnessing would be possible from a single PENG device. This will increase the energy conversion efficiency of the PENGs.

- (8) One of the fundamental prerequisites for a piezoelectric material is that its structure should be non-centrosymmetric. Very recently, evidence of piezoelectricity in the centrosymmetric material is experimentally observed under the applied electric field [179]. In a centrosymmetric ionic crystal, controlling the distribution of mobile ions can be a route to explore piezoelectricity. However, the study is currently infancy and can revolutionize the field of sensors and actuators if it is possible to expand the study, particularly the effect of the electric field, and photo-induced piezoelectric properties for a range of commonly used materials.

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