Ferroelectric Properties and Applications of Hybrid Organic-Inorganic Perovskites

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Abstract—Hybrid organic-inorganic perovskites (e.g., CH$_3$NH$_3$PbI$_3$) have attracted tremendous attention due to their promise for achieving next-generation cost-effective and high performance optoelectronic devices. These hybrid organic-inorganic perovskites possess excellent optical and electronic properties, including strong light absorption, high carrier abilities, optimized charge diffusion lengths, and reduced charge recombination etc., leading to their widespread applications in advanced solar energy technologies (e.g., high efficiency perovskite solar cells). However, there is still a lack of investigations regarding fundamental properties such as ferroelectricity in these perovskites. As conventional ferroelectric ceramics are prepared at high temperature and have no mechanically flexibility, low-temperature proceed and flexible perovskite ferroelectrics have become promising candidates and should be exploited for future flexible ferroelectric applications. Here, ferroelectric properties in hybrid organic-inorganic perovskites and several state-of-the-art perovskite ferroelectrics are reviewed. Novel ferroelectric applications of hybrid organic-inorganic perovskites are discussed as well, providing guideline for realizing future high performance and flexible ferroelectric devices.

Index Terms—Ferroelectricity, ferroelectric materials, flexible devices, organic-inorganic perovskites.

1. Introduction

Hybrid organic-inorganic perovskites are crystalline materials adopting chemical formula of ABX$_3$, where A and B are cations with different sizes and X are anions. The unit cubic crystal structure of perovskites consists of five atoms, in which cation B has six nearest-neighbor anions X (corner-sharing BX$_6$ octahedral network) and cation A in the interstices. Such unit cell can be converted into orthorhombic or tetragonal phases by distorting the BX$_6$ octahedral network. By using various combinations of different components to satisfy the formula ABX$_3$, the perovskites are able to form all kinds of organic-inorganic structures. The widely studied organic-inorganic perovskites generally possess cations A of methylammonium (MA$^+$ or CH$_3$NH$_3^+$) and/or formamidinium (FA or HC(NH$_2$)$_2^+$) together with halide anions (X$^-$) [10].

Holding advantages of solution-proceed synthetic method and intrinsic organic-inorganic structures, these hybrid perovskite materials have emerged as a new class of materials promising for applications in optoelectronic and electronic devices including field-effect transistors (FETs), photodetectors, light-emitting diodes (LEDs), lasers, and solar cells [14]-[16]. In particular, organic-inorganic MAPbI$_3$ has been widely investigated and demonstrated to be very promising in photovoltaic (PV) devices, for instance, boosting the efficiency of perovskite solar cells to be as high as ~20% [17]. Although there is a rapid development regarding optoelectronic devices based on hybrid organic-inorganic perovskites, more fundamental issues such as ferroelectric properties that are promising in ferroelectric devices including FETs, non-volatile memories, and nanogenerators [16]-[18], have not been well studied and understood. More importantly, these perovskites can be synthesized at low temperature and are mechanically flexible as compared with conventional ferroelectric ceramics processed at high temperature with no flexibility [19]. Hence, it is significant to conduct theoretical and experimental investigations in terms of ferroelectricity in these organic-inorganic perovskite materials. And developments of more types of hybrid organic-inorganic perovskite ferroelectrics are essential for next-generation flexible ferroelectric devices [10].

In this review, notable progresses of theoretical and experimental studies regarding ferroelectricity in hybrid organic-inorganic perovskites are reviewed. Some novel ferroelectric perovskites with good ferroelectric properties and their applications (such as nanogenerators) are discussed in detail. In addition, future improvements of ferroelectric perovskites are proposed, paving the way towards prospective high-performance flexible and wearable ferroelectric devices.
2. Theoretical Investigations

Theoretical investigations have proved the existence of ferroelectricity in hybrid organic-inorganic perovskite materials\cite{20,21}. For example, Frost et al. calculated the electronic structure of MAPbI$_3$ perovskites and proposed the presence of ferroelectric domains in these perovskites, which leads to the efficient charge separation and reduced recombination in perovskite solar cells\cite{20}. A similar investigation by Sherkar et al. used a three-dimensional (3D) drift-diffusion model to study the impact of ferroelectricity on MAPbX$_3$ (X=Cl, Br, I) perovskite solar cells. They found both the polarization orientation in ferroelectric domains and their sizes can influence the device performance, resulting in reduced charge recombination and optimized PV parameters (e.g. short-circuit current, fill factor) in these MAPbX$_3$ perovskite solar cells\cite{21}.

Based on 3D periodic boundary conditions, Fan et al. have used the density functional theory (DFT) calculation to explore the ferroelectricity in MAPbI$_3$, demonstrating a ferroelectric structure with calculated polarization value of ~8 μC/cm$^2$ in the most stable tetragonal structure of MAPbI$_3$ perovskites, as shown in Fig. 1. Figs. 1 (a) and (b) exhibit the most stable tetragonal structure of MAPbI$_3$ perovskites along the c axis and random axis, respectively. A pseudocubic cell of tetragonal structured MAPbI$_3$ perovskites is denoted by red dotted line in Fig. 1 (b). Fig. 1 (c) shows the relative position of MA$^+$ cation in PbI$^-$ structure. The direction of calculated polarization is denoted by the red arrow in Fig. 1 (d)\cite{21}.

![Fig. 1. Most stable tetragonal structure of MAPbI$_3$ perovskites along the (a) c and (b) random axes; (c) relative position of MA$^+$ in PbI$^-$ structure; (d) direction of calculated polarization. Reproduced with Permission [21]. Copyright 2015, American Chemical Society.](image)

Liu et al. studied the electronic and structural properties of ferroelectric domain walls in MAPbI$_3$ perovskites by using discrete Fourier transformation (DFT) calculation. This theoretical calculation demonstrated that both charged and uncharged ferroelectric domain walls could be formed in MAPbI$_3$ by engineering the orientational order of the MA cations. These charged ferroelectric domain walls lead to the tunable bandgap of MAPbI$_3$, offering the possibility to optimize the devices by engineering the domain walls\cite{22}. They further used DFT calculation to study the ferroelectric properties (i.e. piezoelectric coefficient) of MAPbI$_3$ perovskites, which are demonstrated to be strongly dependent on the molecular ordering in these perovskites\cite{23}.

Bi et al. also theoretically studied the influences of ferroelectric domain walls on the optical and electronic properties of MAPbI$_3$ perovskites by using nonequilibrium Green’s function (NEGF) theory. They clarified that the presence of ferroelectric domain resulted in a reduced charge recombination and improved charge transport in MAPbI$_3$, advancing understanding of high performance MAPbI$_3$-based PV devices\cite{24}.

Theoretical calculation has demonstrated the existence of ferroelectricity in hybrid organic-inorganic perovskite materials. The ferroelectric properties are strongly dependent on the structure of perovskites, such as molecular ordering, polarization orientation, and sizes of ferroelectric domain. The unique ferroelectricity can result in the tunable bandgap, reduced charge recombination, and optimized PV parameters in MAPbI$_3$ perovskite based PV devices, meanwhile providing guidelines for future organic-inorganic perovskites-based ferroelectric devices.

3. Experimental Investigations

Although theoretical studies have paved the way to explore ferroelectricity in hybrid organic-inorganic perovskite materials, experimental investigations are essential to demonstrate its authenticity. In this regard, Kutes et al. utilized piezoresponse force microscopy (PFM) to study the ferroelectric properties in high-quality MAPbI$_3$ perovskite thin films and directly observe the ferroelectric domain with the grain size of ~100 nm. Through direct current poling, the reversible ferroelectric domain switching was proved, providing new insights of ferroelectricity in MAPbI$_3$ perovskites\cite{25}.

Bisquert’s group studied the ferroelectric properties of MAPbI$_3$ perovskites via employing both PFM and macroscopic polarization approaches. Phase and amplitude hysteresis loops exhibited the distinct polarization in MAPbI$_3$, which decreased with lower frequency, demonstrating that there is no permanent polarization at room temperature, as proved via standard macroscopic polarization measurement. A largely increase of piezoelectric response was achieved under light illumination, which is related to the largely photoactivated dielectric constant at low frequencies. Possible derivation of such effect is the intrinsic charge transfer photoactivated dipole in the MAPbI$_3$ perovskite\cite{26}. The origin of abnormal current-voltage (I-V) hysteresis phenomenon that hinders the PV performance in MAPbI$_3$ perovskites has been studied by
Seol et al. Although the ferroelectricity in MAPbI$_3$ observed in the PFM measurement was proposed to be responsible for this drawback, the scan-rate-dependent $I$-$V$ measurements of MAPbI$_3$ perovskite thin films in nanoscale and macroscale demonstrated that the ion motions were the dominating contribution to macroscopic $I$-$V$ hysteresis. Nevertheless, ferroelectricity in MAPbI$_3$ perovskites was clearly exhibited in [28].

In an investigation of Wang et al., the linear piezoelectricity in MAPbI$_3$ was proved by using both macroscopic and microscopic measurements, which is derived from spontaneous polarization in ferroelectric MAPbI$_3$ perovskites. It was demonstrated that such spontaneous polarization could be switched without external electric fields, which is attributed to the ionic motions and PV field in MAPbI$_3$ perovskites. This study provides an instance to correlate spontaneous polarization, ionic motion, and photoinduced charges, offering more information of ferroelectricity with respect to PV properties in MAPbI$_3$ perovskites\(^{[29]}\).

To further confirm the existence of ferroelectricity in MAPbI$_3$, Ratika et al. offered several experimental evidence that demonstrates the ferroelectricity in MAPbI$_3$ with tetragonal phase. Ferroelectric properties measurement (polarization inversion as a function of external bias) indicated that MAPbI$_3$ was a ferroelectric bulk material. The lack of inversion symmetry was verified by the presence of second harmonic generation (SHG) response. The existence of polar domain and spontaneous polarization were also revealed by the pyroelectric response measurement and chemical etching\(^{[30]}\), respectively.

Recently, Rohm et al. investigated and observed the polarized ferroelectric domains of alternating polarization in MAPbI$_3$ perovskites by using both horizontal and vertical PFM measurements, as presented in Fig. 2. Fig. 2 (a) shows the patterns of polarized domains in a grain of MAPbI$_3$, exhibiting parallel stripes shaped-polarization with a width of ~90 nm, and the spontaneous polarization leads to the formation of these ferroelectric domains with various orientations. Identical patterns were clearly shown in photo-conductive atomic force microscopy (pc-AFM) imaging (Fig. 2 (b)) even with the parameters close to resolution limits, which is possibly attributed to a polarization component of the MAPbI$_3$ along vertical direction. Fig. 3 (c) displays the morphology of sample’s surface, showing no parallel pattern as observed in Figs. 2 (a) and (b), excluding any effect of the grain’s morphology on these ferroelectric domain patterns. Fig. 2 (d) exhibits the Kelvin probe force microscopy (KPFM) imaging of the MAPbI$_3$ grain, showing no effect of its ferroelectric polarization on the surface potential. Over all, the PFM helped confirm the direction of domain polarization that is related to the pc-AFM, KPFM, and the morphology of the sample, demonstrating that MAPbI$_3$ perovskites are certainly ferroelectric\(^{[31]}\).

Other than commonly used MAPbI$_3$ perovskites, various kinds of hybrid organic-inorganic perovskite ferroelectrics were developed in recent years\(^{[32,33]}\). Ye et al. synthesized a new type of (3-pyrollinium) (CdCl$_3$)-perovskite ferroelectric by tuning the organic cation. Such perovskite ferroelectric shows a Curie temperature of 316 K that is above room temperature, as well as a spontaneous polarization value of 5.1 microcoulomb per...
centimeter squared (μC/cm²). PV effect was also demonstrated in this semiconducting perovskite ferroelectric, holding the promise for possible optoelectronic devices[34]. Another ferroelectric perovskite of (benzylammonium) PbCl₃ was studied by Liao et al. This perovskite ferroelectric shows a high Curie temperature of 438 K, a bandgap of ~3.65 eV, and a high spontaneous polarization value of 13 μC/cm², indicating potential optoelectronic and ferroelectric applications in this unique perovskite ferroelectric[35].

Ye et al. then synthesized a novel semiconducting ferroelectric of (CHA)ₓPbBr₃₋ₓIₓ (x=0 to 1) (CHA=cylohexylammonium) with the tunable bandgap ranging from 2.74 eV to 3.65 eV, showing outstanding ferroelectric properties and optoelectronic properties. Due to the feasible deposition of its thin film and the tunable energy bandgap, this type of perovskite ferroelectric holds pronounced promise for possible applications in the field of optoelectronics and semiconducting ferroelectrics[36].

As a breakthrough in hybrid organic-inorganic perovskite ferroelectrics, Xiong’s group synthesized an innovative perovskite ferroelectric of trimethylchloromethyl ammonium trichloromanganese(II) [Me₃NCH₂ClMnCl₃, (TMCM-MnCl₃)] at room temperature by using a solution method. Such low-temperature processing indicates that the as-synthesized TMCM-MnCl₃ can be grown on various low-melting point, large-area, and flexible substrates. Several temperature-dependent measurements demonstrate a phase-transition (ferroelectric to paraelectric) temperature of 406 K in TMCM-MnCl₃, which is even higher than conventional high performance inorganic piezoelectric ceramic of BaTiO₃ (BTO). More importantly, perovskite ferroelectric TMCM-MnCl₃ shows a very high piezoelectric coefficient of 185 picocoulombs per newton (pC/N) that is also comparable to conventional inorganic ferroelectric of BTO.

In this type of organic-inorganic perovskite ferroelectric, ferroelectric domains were clearly observed in PFM phase and amplitude imaging, as shown in Figs. 3 (a) and (b). The sample surface exhibited an ordered lamellar multidomain structure. Fig. 3 (c) displays the local piezoresponse of LiNbO₃, BTO, triglycine sulfate (TGS), and as-prepared TMCM-MnCl₃ as a function of the macroscopic piezoelectric coefficient (d₃₃), which shows a good linear relationship and confirms the reliability of high piezoelectric coefficient. The local piezoresponse was derived from the “butterfly” curve (piezoresponse amplitude spectrum as a function of applied voltage), as shown in the inset image in Fig. 3 (c). Based on the analysis of PFM and crystal structure of TMCM-MnCl₃, it is concluded that there are six polar axes that lead to 12 different polarization directions in this perovskite ferroelectric as shown in Fig. 3 (d). The multipolar-axes feature therefore induces the large variation of polarization, giving rise to extremely large piezoelectric response.

Unlike the most widely used inorganic piezoelectric ceramics, which are toxic, inflexible, and usually demand high-temperature processing and high-voltage poling[37], the organic-inorganic perovskite ferroelectric of TMCM-MnCl₃ is intrinsically compatible with mechanically flexible substrates thanks to its low-temperature processing and organic-inorganic molecular nature. It could ultimately be useful for future applications in next-generation large-area flexible and wearable devices[38].

Ferroelectricity in hybrid organic-inorganic perovskite MAPbI₃ has been confirmed by various experimental investigations. The ferroelectric domains in these perovskite materials are clearly observed by PFM. The relationship between ferroelectricity and fundamental PV mechanisms including PV conversion, charge carrier separation, and transport, and macroscopic hysteresis are studied in hybrid organic-inorganic perovskite MAPbI₃. More types of hybrid organic-inorganic perovskite ferroelectrics are proposed, showing great promise in future optoelectronic and piezoelectric applications, especially for flexible and wearable devices.

4. Applications

The appropriate utilization of ferroelectric properties in hybrid organic-inorganic perovskites leads to various emerging applications. For example, Chen et al. fabricated a new type of ferroelectric solar cell based on a hybrid inorganic-organic perovskite ferroelectric of MAPbI₃·Cl, with the dielectric-structure of TiO₂/MAPbI₃·Cl/Au. The as-fabricated ferroelectric solar cell shows an unprecedented power conversion efficiency as high as 6.7% with respect to inorganic ferroelectric oxide-based ferroelectric solar cells. Tunable PV parameters (tuning the polarization) such as the open circuit voltage and photocurrent are found in these ferroelectric devices, paving the way for the high efficiency ferroelectric solar cell based on hybrid inorganic-organic perovskite ferroelectrics[39].

Studied by Kim et al., MAPbI₃ thin films with excellent ferroelectric properties and switchable polarization were used to fabricate piezoelectric nanogenerators with the architecture of fluorine-doped SnO₂ (FTO) glass and Au/Ti/polyethylene terephthalate (PET). Different performances of the poled generator compared with the non-poled one demonstrated that the ferroelectric domain orientation of the MAPbI₃ thin film could effectively improve the performance of as-fabricated piezoelectric nanogenerators[40].

A high-performance and flexible nanogenerator based on ferroelectric perovskite of FAPbBr₃ nanoparticles and polydimethylsiloxane (PDMS) polymer was fabricated by Ding et al. The schematic diagram of as-fabricated nanogenerator was illustrated in Fig. 4 (b). To fabricate the nanogenerator, FAPbBr₃ perovskites were first incorporated in PDMS, the mixed FAPbBr₃-PDMS composites (Fig. 4 (a)) were then deposited on the substrate of ITO-capped PET by using the spin-coating approach. The device fabrication was completed by incorporating the composites film with a top aluminum (Al) foil electrode. Fig. 4 (c) shows the cross-sectional scanning electron microscopy (SEM) imaging of the as-fabricated...
nanogenerator, exhibiting that the thickness of the composites film was ~150 μm.

Fig. 4. High-performance and flexible nanogenerator based on ferroelectric perovskite of FAPbBr₃ nanoparticles and polydimethylsiloxane (PDMS) polymer: (a) optical image of FAPbBr₃-PDMS composites, (b) schematic diagram of as-fabricated flexible nanogenerator, and (c) cross-sectional SEM image of the nanogenerator. Reproduced with Permission [41]. Copyright 2016, John Wiley & Sons, Inc.

The PFM measurements show very good ferroelectric properties (high piezoelectric coefficient \(d_{33}\) of 25 pm/V⁻¹) of such type of FAPbBr₃ perovskites. As-fabricated high performance flexible nanogenerator shows a good piezoelectric output voltage (8.5 V) and current density (3.8 μA/cm²) when subjected to a 0.5 MPa vertical compression. The alternating energy produced by this nanogenerator is able to light up a red LED. It is hence suggested that ferroelectric FAPbBr₃ perovskites are promising in high performance energy harvesting applications[41].

Recently, Ding et al. optimized the ferroelectric FAPbBr₃ perovskites-based nanogenerator by using piezoelectric polymer of poly (vinylidene fluoride) (PVDF). The architecture of nanogenerator is Au/Cr-capped PET/ FAPbBr₃+PVDF/Au/ Cr-capped PET, showing the maximum piezoelectric output voltage of 30 V and current density of 6.2 μA/cm², which are unprecedented values regarding hybrid organic-inorganic ferroelectric perovskites-based nanogenerators[42].

Ferroelectric properties of hybrid organic-inorganic perovskites have been utilized in applications such as high performance ferroelectric solar cells and nanogenerators, showing that hybrid organic-inorganic perovskites are good candidates for future energy technologies, especially flexible and wearable devices due to their intrinsic light weight feature and mechanical flexibility.

5. Conclusions and Perspectives

In summary, theoretical calculation, experimental investigations, and applications of ferroelectric properties in hybrid organic-inorganic perovskite materials are reviewed. Theoretical investigations of ferroelectric properties in commonly used MAPbI₃ perovskites are discussed in detail. The structure of perovskites (such as cations ordering), polarization orientation, and sizes of ferroelectric domain etc. have been theoretically demonstrated to influence the ferroelectricity in MAPbI₃ perovskites, resulting in the tunable bandgap, suppressed charge recombination, and improved PV parameters in their PV devices. Various types of experimental studies have confirmed the existence of ferroelectricity in hybrid organic-inorganic perovskite MAPbI₃. The ferroelectric domains in these perovskite materials have been clearly seen by PFM. The relationship between ferroelectricity and fundamental PV mechanisms including PV conversion, charge carrier separation and transport, and macroscopic hysteresis are investigated. More hybrid organic-inorganic perovskite ferroelectrics are discovered, which hold great promise in future optoelectronic and piezoelectric applications. Hybrid organic-inorganic ferroelectric perovskites have been utilized in various applications, such as high performance ferroelectric solar cells and nanogenerators, suggesting that these perovskites are good candidates for future flexible and wearable devices as they are light weight and mechanically flexible.

Based on these investigations of ferroelectric perovskites, it will be better to focus future work on the theoretical studies of other emerging types of ferroelectric perovskites rather than commonly studied MAPbI₃. For experimental studies, composition and structure engineering of hybrid materials coupling with other physical properties (such as magnetism, photoluminescence etc.) are promising towards multifunctional applications of current ferroelectric perovskites. Component replacement (such as the substitution of metal cations) can be considered for more high-temperature molecular ferroelectrics and the fine-tuning of metal-halide hybrid structure may lead to its bandgap engineering. There is still space to improve the performance of ferroelectric properties in perovskites, such as optimization of saturate polarization. Open questions also remain about the mechanical durability of ferroelectric perovskites, which is an important factor in practical ferroelectric energy harvesting devices. All kinds of applications of emerging ferroelectric perovskites highlight their future promising utilizations in electrical-mechanical sensing, microelectromechanical systems (MEMS), and large-area flexible and wearable devices.

References


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