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Title:	Development of Hybrid Ferroelectric–Halide Perovskite Systems for Piezo- and Pyro-phototronic Functionalities.
Authors:	Mallick., Zinnia.
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Abstract:	<p>The properties exhibited by non-centrosymmetric materials includes piezo-, pyro- and ferro- electricity, contributing to a wide range of emerging applications. It ranges from transducers, sensors, actuators, non-volatile memories to thermal detectors. In particular, ferroelectricity coupled with semiconducting property give rise to piezo- and pyro-phototronic effect. Though many materials have been researched in this direction, including BaTiO₃, ZnO, PZT, and BiFeO₃, the bottlenecks of toxicity, expensive production methods, poor mechanical strength and lack of flexibility limits several applications. In this endeavor, an alternative approach of hybrid system of ferroelectric polymers and halide perovskite materials have been adopted. In particular, polyvinylidene fluoride (PVDF) and its copolymers, e.g., poly(vinylidene fluoride- trifluoroethylene) (P(VDF-TrFE)) and poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP)) are well known ferroelectric due to their mechano-sensitivity, mechanical strength, flexibility, biocompatibility as well as they follow cost effective fabrication techniques. On the other hand, halide perovskites are emerging materials in the field of optoelectronics due to tunable bandgap, broad light absorption capability and long charge carrier lifetime. In the first attempt, in order to understand the piezo- and ferroelectricity in polymers, different nanostructures (0D, 1D and 2D like architectures) was investigated. For this purpose, the copolymer of PVDF, i.e., P(VDF-TrFE) was utilized due to its inherent polar β-phase, which serves as a model system for ferroelectric polymers. This study reveals that the C-F molecular dipole orientation, can be tuned by modulating the morphology of the polymer, which serves as the key to polar phase in polymers. The dipolar orientation significantly alters the local piezo- and ferro-electric characteristics in the nanostructures. In addition, the dipole orientation also modulates the surface potential, as well as the work function of the nanostructures. The tunable work function opens up the possibility to utilize these nanostructures in practical device applications ranging from energy harvesting to optoelectronic devices. The next work is focused on the effect of halide perovskite (CsPbI₃) inclusion on the piezo-and ferro-electric properties of P(VDF-HFP) copolymer. It was found that, CsPbI₃ induces the preferentially oriented electroactive polar β-phase in P(VDF-HFP). It has been found that the enhancement of degree of dipolar orientation directly benefits the piezo- and ferro-electric properties of the CsPbI₃-P(VDF-HFP) hybrid system. For instances, the magnitude of local effective piezoelectric coefficient (d_{33}) of the hybrid systems leads to ~ 30 pm/V and the lower decay constant for polarized domains ($\tau_{\text{composite}} \approx 17$) indicates higher ferroelectric polarization retention behaviour. Hence, this study establishes the fact that the ferroelectric properties along with the piezoelectric properties of P(VDF-HFP) can be improved by inclusion of CsPbI₃ perovskite. In the following study, along with concentrating on the impact of perovskite on ferroelectric polymers, the influence of piezo- and ferro-electric properties due to semiconducting perovskite were investigated in a hybrid system of Cs₂Snl₆-PVDF. The double perovskite structure of Cs₂Snl₆ successfully nucleates electroactive β- and γ- phases in PVDF. The strain induced piezo-phototronic effect was investigated in this hybrid system. It was found that 1% of applied tensile strain can increase the photocurrent by ~ 6.5 times. Whereas, the compressive strain would cause decrement in photocurrent by modulation of Schottky barrier height (SBH) at the interface of electrode and the hybrid material. Hence, the realization of piezo-phototronic behavior in this hybrid system indicates its promising use in the strain induced optical sensor, along with other conventional use such as mechanical energy harvester and pressure sensor. The next study is focused on the influence of pyroelectric effect onto the optical and semiconducting properties of Cs₂Snl₆. For this purpose, we have utilized the P(VDF-TrFE) copolymer, which possess electroactive β-phase inherently. The hybrid system of Cs₂Snl₆-P(VDF-TrFE) has been utilized to investigate primarily visible light induced pyro-phototronic effect. The visible light was found to increase the temperature of the hybrid system by ~ 2.5K with an exposure time of 10 sec and it can significantly enhance the photocurrent due to the pyroelectric effect. Hence, the pyro-phototronic effect can significantly enhance the photodetection capability of the hybrid system and has potential use in sensing and visible light communication. Finally, a ferroelectric organic-inorganic layered halide perovskite of (3-FBA)₂CuCl₄ has been synthesized by slow evaporation crystallization technique. The single crystal X-ray diffraction pattern proves that the hybrid perovskite system crystallized into a polar space group of Pca2₁. The presence of ferroelectric domains is confirmed by scanning probe microscopy-based nanoscale technique. The ferroelectric to paraelectric phase transition (Curie transition) of (3-FBA)₂CuCl₄ occurs at temperature, $T_c \sim 412$ K. The pyro-phototronic characteristics was also confirmed in 2D layered perovskite of (3-FBA)₂CuCl₄, which can be utilized as a self-powered photodetector. Hence, this thesis concludes the hybrid system of ferroelectric-polymer-perovskite can be a worthwhile approach to achieve the flexible piezo-phototronic and pyro-phototronic based sensors.</p>
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