Investigation of Optoelectronic and Photo-electrochemical properties of Metal Halide Perovskites for Photo-Battery Applications

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Conclusions and Future Scope

8.1 Conclusions

This thesis begins with the introduction of 3D MHPs of type AMX_3, and their general characteristics such as how tolerance factors affect their crystal structures, how structural flexibility (i.e., replacement of A, M and X) affects the electronic properties of MX_6 octahedra, role of the inorganic metal halide network in controlling their energy band gap as well as other appealing optical properties such as absorption coefficient, binding energy, mobility, charge carrier lifetime, diffusion length are explained in detail. Further the thesis provides a detailed description about the low-dimensional MHPs and their different structural phase including RP perovskite, DJ perovskite, ACI perovskite, and Aurivillius perovskites to overcome the challenges associated with their bulk counterpart. Dielectric and quantum confinement effects associated with the low-dimensional MHPs are discussed. Further, the dependency of structural and optical properties, for fixed number of inorganic layers (n-value is constant) in RP perovskite, is discussed for various spacer cations of different lengths. Moreover, the effect of different n-values on optical properties, optoelectronic and electrochemical performance of RP perovskite are also discussed in order to select suitable material as per the applications. In addition to that, basic principles of various optoelectronic devices such as photodiodes, photoconductors and phototransistors of different configurations are covered. Moreover, their different optoelectronic parameters such as dark current, photo current, responsivity, detectivity, NEP, EQE and ON-OFF ratio are defined. The thesis provides a detailed overview about emerging MHPs based energy storage devices such as LIBs and PRBs, where the Li-ion intercalation, conversion and alloying mechanisms are explained, as well as brief overview about the degradation of these devices are also discussed. The concept PRBs are introduced and their working mechanism, various configurations, as well as technical challenges are covered. The Chapter 2 provides a detailed insight about the synthesis of different types of RP perovskite materials using solution processing routes and fabrication of their hybrids using one step additive engineering methods. Finally, in order to investigate the optoelectronic, electrochemical and photo-electrochemical performance of these RP Perovskites, various devices such as photodetectors, LIBs and PRBs are fabricated and investigated using wide range of characterization techniques.

Chapter 3 of the thesis proposed self-biased vertical photodetectors for the hybrid material which are composed of $(BA)_2(MA)_3Pb_4I_{13}$ (n=4) + 12.8 mM MoS_2. This hybrid material has successfully shown ~16 times higher responsivity (97.7 μA/cm^2) and ~10 times higher detectivity (6.93 x 10^8 jones) under 1 Sun illumination as compared to its pristine device which is attributed to the robust interface formation between RP perovskite and MoS2 nanoflakes. Moreover, under CW-laser illumination (λ_{ex} ~ 405 nm, P_{in} ~ 630 mW/cm^2), the peak photocurrent response of freshly prepared self-biased hybrid device has degraded only 9.6% after 200 cycles in ambient air without encapsulation, whereas the peak photocurrent of pristine device has shown 39% degradation just after 50 cycles under similar conditions. This work is highly useful in the development of LIBs, Li-PRBs, solar cells, and other renewable energy applications.

In chapter 4, the RP perovskite-MoS_2 based active materials are demonstrated as anode for LIBs to investigate their electrochemical. Here, hybrid electrodes have been successfully fabricated with the composition of $(BA)_2(MA)_3Pb_4I_{13}$ (n=4; 84.6 wt %), MoS_2 (0.4 wt %), rGO, (3 wt %), super-P (5 wt %) and PVDF (7 wt %). The hybrid LIB has shown discharge specific capacity of 156 mAhg^{-1} (capacity retention of 72.6 %), which is around 3 times higher than the specific capacity shown by pristine LIB

(49.70 $mAhg^{-1}$, capacity retention of 36.0 %) at current density of 117 mAg^{-1}, after 50th cycle. Further, at higher current densities of 176 and 294 mAg^{-1}, hybrid LIB has shown average discharge specific capacities of 144.46 $mAhg^{-1}$ and 129.17 $mAhg^{-1}$ respectively for 50-cycles each. Moreover, the hybrid LIB has demonstrated highly stable performance with a discharging specific capacity of 122 $mAhg^{-1}$ after 1250th cycle with coulombic efficiencies of 99.71%, when operated at a current density of 294 mAg^{-1} after rate cycling. Whereas, pristine LIB has shown very low specific capacity of 20.19 $mAhg^{-1}$ under similar conditions with a coulombic efficiency of 99.80%. EIS measurements, performed for pristine and hybrid LIBs on the same LIBs (after rate cyclability test) have shown series resistances (R_s) of 15.8 Ω and 4.5 Ω respectively, whereas charge transfer resistances (R_{ct}) are found to be 10 Ω and 3.75 Ω respectively. The overall improved electrochemical performance of hybrid LIB is attributed to the formation of type-II heterojunction between RP perovskite and MoS_2 nanoflakes which has resulted in the formation of an interconnected network of perovskite crystallites in the dropcasted sample. The use of demonstrated MoS_2 nanoflakes and RP perovskites based heterostructures can offer new avenues for the development of efficient and scalable PRBs.

In continuation of the previous chapter, in chapter 5 the RP perovskite-MoS_2 based photoelectrodes are demonstrated for Li-PRBs applications and their photo-electrochemical properties are investigated. CV curves of conventional LIB and Li-PRB of hybrid active material have shown similar redox peaks confirming the similar operation of both the devices. The hybrid Li-PRBs demonstrated large increase in photo-enhanced specific capacities from 202.61 $mAhg^{-1}$ to 251.75 $mAhg^{-1}$ (photo enhancement: 24.25 %) at a current density of 58 mAg^{-1}, from 128.66 $mAhg^{-1}$ to 180.67 $mAhg^{-1}$ (photo enhancement: 40.42 %) at a current density of 64 mAg^{-1} and so on for higher current densities. For the demonstrated Li-PRB, the in-situ monitoring of cell voltage under light has shown gradual drop, from 0.47 to 0.30 V in 8.56 hours, whereas under dark the cell voltage dropped sharply, from 0.30 V to 0.02 V in 4.12 hours, which provides evidence of simultaneous OCV charging and discharging processes occurring in photo-battery. These heterojunction-based Li-PRBs have shown good cyclability with a promising PC-SE of ~0.52 % under standard 1 Sun illumination, which is ~16 times higher than previously reported 2D perovskite-based Li-PRB. Further, the ex-situ optical reflection measurements of hybrid photocathode shown the recovery of exciton reflectance peaks after complete charging and discharging cycle, which confirmed that hereditary of RP perovskite material remains unchanged during lithiation and delithiation. The scalability of these low-temperature solution processed hybrid photoelectrodes is demonstrated by fabricating a photo-battery module, comprising of three Li-PRB cells, which is operated between 5.00 V to 0.02 V at 68 mAg^{-1} and shown photo-enhanced discharge time of ~74 %. The improved performance of these RP perovskite-MoS2 based Li-PRB is attributed to improved crystallinity, stability in electrochemical environment and extraction of photoelectrons from RP perovskite to MoS_2, which is also confirmed from the UPS measurements. These energy storage devices are essential to meet the power requirements at the off-grid locations to power standalone sensors and other autonomous devices.

In chapter 6, the heterointerface between the RP perovskite ($(CH)_2(MA)_{n-1}Pb_nBr_{3n+1}$) crystallites and layered MXene ($Ti_3C_2T_x$) nanoflakes are discussed. The additive engineering of RP perovskite is done using synthesized MXene nanoflakes which has retarded the crystallization rate in the hybrid (n=4 + 1.5 mM MXene) thin films. Such retardation has caused to improve the crystallinity and surface morphology as confirmed by XRD and FESEM studies respectively, as well as the transport of photocharge carriers (electron) from RP perovskite to MXene as observed by UPS measurements. The surface terminal groups of MXene nano flakes has shown ionic bond formation with halide and metal of the RP perovskite, which has resulted in the modified chemical environment of the [$PbBr_6$] inorganic octahedra. The lateral configuration photodetector, fabricated using photolithography technique, for the hybrid material has shown responsivity of ~1.51 x 10^2 A/W and detectivity of ~14.21 x 10^{12} cm $Hz^{1/2}$/W at 2.0 V bias under laser illumination (λ_{ex} ~ 405 nm, P_{in} ~ 0.62 mW/cm^2) which are ~8.39 and ~7.55 times higher respectively as compared to pristine device. Moreover, under long cycle hybrid photodetector shows stable peak photocurrent response after 50 cycles in ambient air without encapsulation under similar bias and incident illumination power, whereas peak photocurrent response of pristine device has degraded by 34.74 %. This chapter offers a unique platform to explore the additive engineering of RP perovskite with wide range of MXenes to

overcome the stability issues associated with perovskites and develop their high performance optoelectronic devices.

Chapter 7 is focused on the investigation and comparison of smaller cations, caged between octahedra layers, based RP perovskite on the structural, optical, morphological and finally optoelectronic properties of these materials. RP perovskite materials $(CH)_2(MA)Pb_2I_7$ (or, CH-MA) and $(CH)_2(FA)Pb_2I_7$ (or, CH-FA) have been synthesized, where CH-FA RP perovskite has shown relatively narrow bandgap of ~2.37 eV as compared to CH-MA RP perovskite (~2.38 eV). The day wise transient photocurrent measurement has shown that CH-FA RP perovskite has ~60% retention of peak photocurrent response when device is exposed to ambient air for 48 hours continuously. Whereas CH-MA RP perovskite has only ~18% retention under similar conditions, confirming that the CH-FA RP perovskite is more stable in air than CH-MA RP perovskite. This is due to the lower acidic nature with high molecular weight of FA cation than MA cation. Finally, CH-FA perovskite has shown responsivity of ~2.6 A/W, detectivity of ~3.6×10^{10} jones and NEP of ~4.4×10^{-13} $W/Hz^{1/2}$ at 2.0 V bias under CW-laser illumination (λ_{ex} ~ 405 nm, P_{in} ~ 5.87 mW/cm^2).

Challenges or Limitations Faced:
Initially, the preparation of a homogeneous suspension of RP perovskite and additives (MoS_2) was attempted using only magnetic stirring only. However, this method resulted in rapid segregation of the additives; where additives settle down within 5 minutes after discontinuing the magnetic stirrer. Such non-uniform suspension is not ideal for any device fabrication. Therefore, in order to overcome this challenge, the protocol was optimized by introducing a sonication step before magnetic stirring. In this protocol the hybrid suspension was first sonicated for 15 minutes, followed by magnetic stirring for an additional 15-20 minutes. This combined approach significantly improved the dispersion stability, preventing the additive from settling for an extended period in the perovskite precursor solution.

The use of optimum volume of liquid electrolytes in the development of LIBs was also a challenge faced in the development of LIBs. Initially 100 µl volume of $LiPF_6$ electrolyte was used, which caused the degradation of the electrode material due to dissolution of RP perovskite in the liquid electrolytic medium. This has also resulted in degradation in charging-discharging specific capacity of LIBs. Therefore, in order to overcome this challenge, the volume of electrolyte is reduced stepwise and found that 25-30 µl of $LiPF_6$ is the optimum volume of electrolyte to get stable performance of LIBs and then Li-PRBs during charging and discharging process.

Overall, this thesis gives thorough information on how to leverage the optoelectronic features of RP perovskite to enhance the photo-electrochemical performance of PRBs.

8.2 Future Scope

Broadly this thesis provided a successful demonstration and photo-physical investigations of 2D RP phase MHPs in stabilizing their structural, optical, optoelectronic, electrochemical properties which can directly improve the performance of wide range of optoelectronic and ionic devices such as photodetectors, batteries and photo-batteries. Below are a few potential future research directions in which the results of thesis work can be effectively employed:

i. **Scalability:** The fabrication of large area optoelectronic devices such as photodetector, solar cells etc. is still a big challenge because large area perovskite film possess higher number of defects which results in reduced performance. On the counterpart, my demonstrated hybrid thin films have shown improved surface morphologies and enhancement in crystallinity with improved optoelectronic parameters, making these materials scalable for device applications.

ii. **Use of ETL/HTLs or both:** These hybrid materials based photodetectors can be further explored in diode configuration, where these materials can be layered between appropriate

ETL and HTL such as TiO_2, PCBM, SnO_2 Spiro-OMeTAD, P3Ht, NiO_x, PEDOT:PSS etc. Such approach will further enhance their performance.

iii. **Photodetector Channel Length:** Channel length of the lateral photodetector can be further reduced using advanced photolithography or electron beam lithography techniques so that electrons and holes can efficiently transport to their corresponding electrodes at low bias voltage. This methodology will result in low power lateral photodetectors with least dark currents, which can in turn improve the performance of the devices.

iv. **Specific capacity for LIBs and Li-PRBs:** Since the specific capacity of LIBs is proportional to the number of inorganic octahedra layers given by n-value, therefore the RP perovskite with higher number of n-values (n>4) and their different heterojunctions can be further explored to improve the performance of LIBs and Li-PRBs.

v. **Exploration of MXene:** This thesis includes the use of hybrid material of type $(BA)_2(MA)_3Pb_4I_{13}$ (n=4) + MoS_2 for optoelectronic, electrochemical and photo-electrochemical applications. Moreover, only optoelectronic performance is investigated for hybrid material of type $(CH)_2(MA)_3Pb_4Br_{13}$ (n=4) + MXene. So, in this regards, investigation of electrochemical and photo-electrochemical performance can also be explored in future which will provide useful insights in the development of LIBs and Li-PRBs based on RP perovskite-MXene based hybrids.

vi. **Temperature dependent analysis of PRBs:** The OCV of Li-PRBs based on RP perovskite-MoS2 hybrid is measured from room-temperature to 55 °C, by keeping the photobattery on the thermal stage. In order to get further insight about the role of external temperature, experiments can be done by mounting the temperature sensors inside the PRB and varying the external temperature of the PRB.

vii. **Temperature dependent analysis of CH-FA and CH-MA based RP Perovskites:** The incorporation of smaller cation FA has shown much improved photocurrent stability, rise time and fall time parameters, however further experiments can be planned to observe the thermal stability of these materials and how their optical and structural phase undergo change with temperature.

viii. **Powering IoT Sensors and Drones:** IoT sensors are electronic devices that detect and measure environmental changes (such as temperature, pressure, motion, light, or sound) and transform them into digital data. These sensors serve as the necessary bridge between the physical and digital worlds, allowing the collection of real-time information that can be transferred over networks for analysis, automation, and decision-making. These PRBs can be utilized to provide continuous power to the remotely located IoT sensors which are away from the grid. Similarly considering the light weight of the PRBs, when compared with the conventionally combined solar cells and batteries, these PRBs can also be used to give continuous power to drones or unmanned air vehicles (UAVs) which require continuous power and low-weight power supply.

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