

The fast rise in carbon emissions from 9.4 million tons to 37 billion tons since the beginning of the industrial revolution highlights urgent requirement of sustainable energy sources as the world confronts climate change and endeavors to achieve sustainability. During daylight, the solar cells can offer constant power supply for low power residential to high power industrial usages, however the intermittent nature of solar radiation requires energy storage systems to store the solar energy into electrochemical energy for usage in nighttime or at later stage. This conventional combination of solar cell and battery reduces energy poverty, but is very bulky and expensive due to the use of complex and multiple electronic components, duplication of electrodes as well as require use of various materials for these two very different type of devices. In contrast, photo-batteries, also known as photo-rechargeable batteries (PRBs), offer a compact energy solution by integrating solar harvesting and energy storage functionalities in a single device. These PRBs are composed of either single or dual active materials which can perform solar energy harvesting like a PV device and concurrently stores it in the form of electrochemical energy like a battery. The overall performance of these PRBs highly depends upon the optoelectronic and electrochemical properties of the active materials. This thesis involves the investigation of advanced PRB systems by exploring the single active material systems based on metal halide perovskite (MHPs). Bulk (3D) MHPs of type AMX_3 (formula defined below) are solution processed semiconductors and offer an ideal material system for low-cost PVs, however these materials suffer from stability issues due to degradation of their structural and optical properties under atmospheric and illumination conditions. Therefore, due to improved structural and optical properties of two-dimensional (2D) MHPs, compared to 3D MHPs, this thesis work highlights the investigation of optoelectronic, electrochemical and photo-electrochemical properties of 2D MHPs for PRB applications. Briefly, the Ruddlesden Popper (RP) phase 2D MHPs $(R')_2(A)_{n-1}M_nX_{3n+1}$ ($n=1-4$) are studied by exploring their structural, optical, optoelectronic, electrochemical as well as photo-electrochemical properties. Here, R' is the monoammonium alkyl organic spacer cation, A is the smaller organic cation ($MA=CH_3NH_3$, $FA=HC(NH_2)_2$, Cs etc.), M is the divalent metal (Sn^{2+} , Pb^{2+} , Ge^{2+} etc.), X is the halide (Cl^- , Br^- , I^-) and n denotes the number of inorganic layers between the organic spacer cations. In order to study these properties, a wide range of samples and devices are fabricated ranging from photodetectors, Li-Ion batteries (LIBs) to PRBs. These 2D MHPs are found to be an interesting candidate for PRB applications due to their flexible structural properties, improved stability in electrolyte medium, tunable optical properties, compatibility with carbon additives and binders, matching energy levels to the charge transport materials such as rGO, PCBM, MoS_2 , MXene etc. as compared to their bulk counterpart.

A hybrid material using RP perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ ($n=1-4$) and a few layers of MoS_2 nanoflakes is developed to investigate the optoelectronic and photo electrochemical properties. This hybrid material has shown improved transient photocurrent response than pristine material. Such improvement in the photocurrent leads to responsivity of $\sim 97.7 \mu A W^{-1}$ and detectivity of $\sim 6.93 \times 10^8$ jones at 0.0 V bias under 1 sun illumination, which are ~ 16 and ~ 10 times higher respectively as compared to pristine device. In continuation of prior work, this RP perovskite- MoS_2 hybrid material based LIB exhibits an average discharge specific capacity of 129.17 mAhg^{-1} for 50 cycles at 294 mAg^{-1} current density. Whereas pristine RP perovskite LIB has shown a specific capacity of 25.60 mAhg^{-1} under similar conditions. Furthermore, the hybrid material-based Li-PRB has shown an average dark discharge specific capacity of 128.66 mAhg^{-1} at a current density of 64 mAg^{-1} which enhanced to 180.67 mAhg^{-1} (photo-enhancement: 40.42 %) under illumination. In addition, demonstrated hybrid Li-PRB has shown photo conversion and storage efficiency of 0.52 % under standard 1 Sun illumination, which outperforms other perovskite-based PRBs. An aromatic spacer cation-based RP perovskite of type $(CH)_2(MA)_3Pb_4Br_{13}$ and MXene nanoflakes based hybrid materials is fabricated and these RP perovskite-Mxene hybrid photodetector ($n=4 + 1.5 \text{ mM MXene}$) has shown responsivity of $\sim 1.51 \times 10^2 \text{ AW}^{-1}$ at 2.0 V bias under laser illumination ($\lambda_{ex} \sim 405 \text{ nm}$, $P_{in} \sim 0.62 \text{ mWcm}^{-2}$) which is ~ 8.39 times

higher than pristine RP Perovskite photodetector. Furthermore, the effect of smaller organic cation (A = MA and FA) on the optoelectronic properties of aromatic spacer cation-based RP perovskite of type $(\text{CH})_2(\text{A})\text{Pb}_2\text{I}_7$ is studied. Where perovskite with FA as a smaller cation has shown stable transient photocurrent response due to its high molecular weight which has resulted in responsivity of $\sim 2.6 \text{ AW}^{-1}$ and detectivity of $\sim 3.6 \times 10^{10}$ jones at 2.0 V bias under CW-laser illumination ($\lambda_{\text{ex}} \sim 405 \text{ nm}$, $P_{\text{in}} \sim 5.87 \text{ mW/cm}^2$). This thesis provides a novel approach to improve the optoelectronic, electrochemical as well as photo-electrochemical properties of 2D metal halide perovskites.

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Declaration

I hereby declare that the work presented in this Thesis titled *Investigation of Optoelectronic and Photo-electrochemical properties of Metal Halide Perovskites for Photo-Battery Applications* submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Shahab Ahmad. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.



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Certificate

This is to certify that the thesis titled *Investigation of Optoelectronic and Photo-electrochemical properties of Metal Halide Perovskites for Photo-Battery Applications*, submitted by *Rashid Malik Ansari (P19PH206)* to the Indian Institute of Technology Jodhpur for the award of the degree of *Doctor of Philosophy*, is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.



Dr. Shahab Ahmad

Ph.D. Thesis Supervisor

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List of Symbols

Symbol	Description
t	Tolerance Factor
E_g	Bandgap
a	Absorption Coefficient
$B.E$	Binding energy
μ	Mobility
τ	Charge carrier lifetime
L_D	Diffusion length
D	Diffusion coefficient
k_B	Boltzmann constant
q	Charge on electron/hole
I_{dark}	Dark Current
I_{light}	Photo Current
τ_{rise}/τ_{decay}	Photo response rise/decay
R	Responsivity
D	Detectivity
S	Effective area of the device
D_{min}	Smallest feature size
λ	Wavelength
K_1 and K_2	Process-related coefficient
D_f	Depth of focus
d	Interplanar spacing
2θ	Diffraction angle
L	Crystallite size
β	Full Width Half Maxima (FWHM)
ν	Frequency
Φ	Work function
ϵ	Molar extinction coefficient
C	Concentration of the material
c	Speed of light
l	Length of path travelled by light for the given solution
I_0	Intensity of light passed through reference/blank sample
I	Intensity of light transmitted through material
E	Energy of light
λ_{ex}	Excitation wavelength
λ_{em}	Emission wavelength
$E_{Discharge}$	Discharge Energy
P_{in}	Incident power density
t_{OCV}	OCV charging time
A_{illu}	Illuminated area
R_{ct}	Charge transport resistance
NEP	Noise equivalent power
LDR	Light-dependent resistor
V_{oc}	Open circuit voltage
$A+R+T=1$	Absorbance+Reflectance+Transmittance=1

List of Abbreviations

Abbreviation	Full form
MHP/MHPs	Metal halide perovskite/Metal halide perovskites
Li	Lithium
Li ⁺	Lithium-ion
LIB	Lithium-ion battery
PRB	Photo rechargeable battery
Li-PRB	Li-ion based photo rechargeable battery
3D	Three-dimensional
VBM	Valence band maximum
CBM	Conduction band minimum
n-i-p	Regular negative-intrinsic-positive
p-i-n	Inverted positive-intrinsic-negative
ETL	Electron transport layer
HTL	Hole transport layer
ETM	Electron transport materials
HTM	Hole transport material
PCE	Power conversion efficiency
FTO	Fluorine-doped tin oxide
ITO	Indium tin oxide
EQE	External quantum efficiency
FET	Field effect transistor
XRD	X-ray diffraction
CAI	Cyclopropylammonium iodide
RP	Ruddlesden-Popper
DJ	Dion-Jacobson
ACI	Alternating cation interlayer
GA	Guanidinium
ACA	Acetamidinium
QW	Quantum-well
BA	Butylammonium; CH ₃ (CH ₂) ₃ NH ₃ ⁺
HA	Hexylammonium; CH ₃ (CH ₂) ₅ NH ₃ ⁺
OA	Octylammonium; CH ₃ (CH ₂) ₇ NH ₃ ⁺
CH	2-(1-Cyclohexenyl)ethylammonium; C ₆ H ₉ C ₂ H ₄ NH ₃ ⁺
MA	Methylammonium; CH ₃ NH ₃ ⁺
FA	Formamidinium; CH(NH) ₂ ⁺
n=∞	3D
n	Number of inorganic octahedra layer
GCD	Galvanostatic charging-discharging
SEI	Solid electrolyte interface
OCV	Open circuit voltage
SoC	State of charge
LPET	Liquid phase exfoliation techniques
PR	Photoresist
e-beam	Electron-beam
SEM	Scanning electron microscope
FESEM	Field emission scanning electron microscopy
TEM	Transmission electron microscopy
HR-TEM	High resolution transmission electron microscopy
AFM	Atomic force microscope

SPM	Scanning probe microscopy
XPS	X-ray Photoelectron Spectroscopy
UPS	Ultraviolet Photoelectron Spectroscopy
UV-VIS	Ultraviolet-Visible
PL	Photoluminescence Spectroscopy
ISC	Intersystem crossing
TRPL	Time resolved Photoluminescence
TCSPC	Time-correlated single photon counting
EIS	Electrochemical impedance spectroscopy
CV	Cyclic voltammetry
redox	Reduction-oxidation
CCAMI	Current collector active material interface
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
rpm	Revolutions per minute
An.	Anhydrous
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
NMP	N-Methyl-2-pyrrolidone
DI	Deionized
IPA	Isopropyl Alcohol
PCBM	Phenyl-C61-butyric-acid methyl ester
PVDF	Polyvinylidene difluoride
PV	Photovoltaic
rGO	Reduced graphene oxide
BHJ	Bulk heterojunction
EDAX	Energy dispersive X-ray
MQWs	Multiple quantum wells
M-S-M	Metal-semiconductor-metal
PC-SE	Photo conversion and storage efficiency
e	Electron
h	Hole
°C	Degree centigrade
Å	Angstrom
µm	Micrometer
nm	Nanometer
eV	Electron volt
meV	Milli electron volt
µs	Microsecond
ps	Picosecond
wt%	Weight percentage
mM	Milli molar
mg	Milli gram
mm	Milli meter
Å/sec	Angstrom per second
Ohms/sq	Ohm per square
mA/W	Milliampere per watt
A/W	Ampere per watt
mA/g	Milli ampere per gram
mAh/g	Milli ampere hour per gram
V/m	Volt per meter
kV	Kilo volt
MHz	Mega hertz

nA/cm ²	Nanoampere per centimeter square
μA/cm ²	Microampere per centimeter square

