Contents

		page
Abstract		I
Declaration		ii
Certificate		v
Acknowledgements		vii
Contents		ix
List of Figures		xiii
List of Tables		xix
List of Symbols		xxi
List of Abbreviations		xxiii
Chapter 1: INTRODUCTION		**1**
1.1	Perovskite Crystal Structure	2
1.2	Three-dimensional (3D) MHPs	3
1.3	Electronic and optical properties of MHPs	3
	1.3.1 Absorption Coefficient (α)	5
	1.3.2 Binding Energy (B.E)	5
	1.3.3 Mobility (μ)	5
	1.3.4 Charge Carrier Lifetime (τ)	5
	1.3.5 Diffusion Length (L_D)	6
1.4	Challenges in 3D MHPs	6
1.5	Two dimensional (2D) MHPs: Ruddlesden-Popper (RP) perovskite, Dion–Jacobson (DJ) perovskite, Alternating cation interlayer (ACI) perovskite and Aurivillius perovskite	8
	1.5.1 Dielectric and Quantum Confinement Effects in 2D MHPs	10
	1.5.2 Role of different spacer cations on the structural, optical, optoelectronic properties of RP perovskite	11
	1.5.3 Effect of different n-values on the optical and optoelectronic properties of RP perovskite of type $(R)_2(A)_{n-1}M_nX_{3n+1}$	12
1.6	3D and 2D MHPs based photodetector: Photodiode, Photoconductor and Phototransistor	13
	1.6.1 Photodiode	13
	1.6.2 Photoconductor	13
	1.6.3 Phototransistor	13
1.7	3D and 2D MHPs based Li-ion batteries	14
	1.7.1 Intercalation, Conversion and alloying mechanisms in MHP based LIBs	15
	1.7.2 Specific capacity variation in RP perovskite-based LIBs	16
1.8	MHP for Photo Rechargeable Batteries (PRBs) applications	17
	1.8.1 Three-electrode and two-electrode configuration based PRBs, their challenges and working mechanisms	18
1.9	Motivation	20
1.10	Salient features of the Thesis	20
Chapter 2: Fabrication and Characterization Techniques		**23**
2.1	Synthesis process of 2D and Quasi-2D RP perovskites	24
	2.1.1 Material Used	24
	2.1.2 Synthesis of RP perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$, n=1-4	24
	2.1.3 Synthesis of RP perovskite $(CH)_2(MA)_3Pb_4Br_{13}$, n=4	25
	2.1.4 Synthesis of RP perovskite $(CH)_2(MA)Pb_2I_7$, n=2 and $(CH)_2(FA)Pb_2I_7$, n=2	25
2.2	Synthesis of MoS_2 Nanoflakes	26
2.3	Synthesis process of etched MAX phase, MXene nanosheets and MXene nanoflakes	27
	2.3.1 Synthesis of etched MAX phase	27
	2.3.2 Synthesis of MXene nanosheets	27
	2.3.3 Synthesis of MXene nanoflakes	27
2.4	Additive Engineering and their importance	27
	2.4.1 Preparation of RP Perovskite-MoS_2 hybrids	28
	2.4.2 Preparation of RP Perovksite-MXene nanoflakes hybrids	28

2.5 Preparation for thin/ drop-casted film 28
2.5.1 Drop-casing technique 28
2.5.2 Spin coating technique 28
2.6 Physical Vapor Deposition (PVD) technique 29
2.7 Preparation of photodetector 29
2.7.1 Vertical Photodetector 29
2.7.1.1 Photolithography 30
2.7.1.2 Photoresist (PR) 30
2.7.1.3 Preparation of pattern to fabricate photodetector 31
2.8 Structural Characterization 32
2.8.1 X-ray powder diffraction (XRD) 32
2.9 Morphological Characterizations 33
2.9.1 SEM/FESEM 33
2.9.2 Transmission electron microscopy (TEM) 34
2.9.3 Atomic Force Microscope (AFM) 35
2.10 Electronic characterization 36
2.10.1 X-ray Photoelectron Spectroscopy (XPS) 36
2.10.2 Ultraviolet Photoelectron Spectroscopy (UPS) 36
2.11 Optical Characterizations 37
2.11.1 Ultraviolet-Visible (UV-VIS) Spectroscopy 37
2.11.2 Photoluminescence Spectroscopy 39
2.11.3 Time Resolved PL Spectrometer 40
2.12 Optoelectronic Characterizations 41
2.12.1 Current-Voltage (I-V) Characteristics 42
2.12.2 Transient Photocurrent (I-T) response 43
2.12.3 Different optoelectronic performance parameter for photodetector 43
2.13 Electrochemical Techniques 44
2.13.1 Cyclic Voltammetry (CV) 44
2.13.2 Galvanostatic Charging-Discharging (GCD) 44
2.13.3 Electrochemical Impedance Spectroscopy (EIS) 44
2.13.4 Fabrication of electrodes for pristine/hybrid LIBs 45
2.13.5 LIB Fabrication 46
2.14 Photoelectrochemical Techniques 46
2.14.1 Fabrication of electrodes for hybrid Li-PRBs 46
2.14.2 Li-PRB Fabrication 47
2.14.3 Photoconversion and Storage Efficiency (PC-SE) calculations 47

Chapter 3: Strong Photocurrent from Solution Processed Ruddlesden Popper 2D Perovskite-MoS_2 Hybrid Heterojunctions 49
3.1 General characteristics of 2D MoS_2 for their potential application in MHP based Optoelectronic devices 50
3.2 Brief discussions on the synthesis procedure of RP perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n=1-4) and few layer of MoS_2 nanoflakes 50
3.3 Brief discussions on the fabrication of RP perovskite-MoS_2 hybrids 51
3.4 Structural properties 52
3.4.1 Crystal structure for RP perovskite and RP perovskite-MoS_2 hybrids 52
3.4.2 Crystal structure for MoS_2 and exfoliated MoS_2 nanoflakes 53
3.5 Morphological properties 53
3.5.1 Surface morphology for dropcated exfoliated MoS_2 nanoflake 53
3.5.2 Surface morphology for spin coated RP perovskite and RP perovskite-MoS_2 hybrid films 54
3.5.3 Surface morphology for the dropcasted RP perovskite and RP perovskite-MoS_2 hybrid film 55
3.5.4 Elemental Composition for perovskite-MoS_2 hybrids 55
3.6 Optical properties 56
3.6.1 Absorbance spectra for RP perovskite and RP Perovskite-MoS_2 hybrids 56
3.6.2 PL and lifetime spectra for RP perovskite and RP perovskite-MoS_2 hybrids 57
3.7 Optoelectronic properties 58
3.7.1 Energy band diagram for RP perovskite and MoS_2 58
3.7.2 J-V characteristics for RP perovskite and RP perovskite-MoS_2 hybrids 59
3.7.3 Transient photocurrent for pristine RP perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n=2) and its hybrid with MoS_2 with different concentrations 60

3.7.4 Transient photocurrent for pristine RP perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n=4) and its hybrid with MoS_2 with different concentrations 61
3.7.4.1 J-V characteristics and Transient photocurrent for MoS_2 nanoflakes 62
3.7.5. Stability analysis for RP perovskite and RP perovskite-MoS_2 hybrid 63

Chapter 4: Ruddlesden-Popper 2D Perovskite-MoS_2 Hybrid Heterojunctions based Anodes for Efficient Li-Ion Batteries 65
4.1 Different MHP based energy storage devices 66
4.2 Structural properties using gaussian fitting 66
4.3 Morphological properties 67
4.3.1 Top view surface morphology for n=4 and n=4+MoS_2 dropcasted films 67
4.3.2 Cross-sectional view surface morphology for n=4 and n=4+MoS_2 dropcasted films 68
4.3.3 Top view surface morphology for hybrid electrode 68
4.4 Composition of pristine and hybrid electrodes for LIB 69
4.5 Electrochemical Properties 69
4.5.1 CV for pristine and hybrid LIBs 69
4.5.2 GCD for pristine and hybrid LIBs 70
4.5.3 Rate cycling performance for pristine and hybrid LIBs 71
4.5.4 EIS for pristine and hybrid LIBs 72

Chapter 5: Ruddlesden-Popper 2D Perovskite-MoS_2 Hybrid Heterojunction Photoelectrodes for Efficient and Scalable Photo-Rechargeable Li-Ion Batteries 75
5.1 MHP based PRBs 76
5.2 Composition of hybrid electrodes for Li-PRB 77
5.3 Device configuration of hybrid Li-PRBs 77
5.4 UPS spectra for RP perovskite material $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (for n=4) and MoS_2 77
5.5 Energy band diagram for hybrid Li-PRBs 78
5.6 Photo-electrochemical properties of hybrid Li-PRBs 79
5.6.1 CV for LIB and hybrid Li-PRBs under dark and illumination 79
5.6.2 GCD profiles for hybrid Li-PRBs under dark and illumination 80
5.6.3 Rate cycling performance for hybrid Li-PRBs under dark and illumination 81
5.7 Temperature dependent study for hybrid Li-PRBs 82
5.8 In-Situ and OCV measurements for hybrid Li-PRBs 82
5.9 Spectral intensity distribution comparison between Xe-Lamp (Standard 1 Sun) and white LED 83
5.10 Ex-Situ measurements for hybrid Li-PRBs 84
5.11 Photo-battery module 85

Chapter 6: Additive Engineering of Ruddlesden-Popper Perovskites with MXene Nanoflakes: Towards Enhanced Photoresponsivity, Detectivity and Stability 87
6.1 General characteristics of 2D MXene for their potential application in MHP based Optoelectronic devices 88
6.2 Morphological Properties of MXene and RP Perovskite-MXene hybrids 88
6.2.1 Surface morphology for bulk MAX phase, Etched MAX phase, MXene nanosheets and MXene nanoflakes 88
6.2.2 Elemental composition for bulk MAX phase and etched MAX phase powder 89
6.2.3 TEM analysis for MXene nanoflakes 90
6.2.4 Effect of MXene concentration on the Surface Morphology of RP perovskite-MXene hybrid Thin film 90
6.2.5 Elemental composition for pristine RP perovskite and RP perovskite-MXene hybrid thin films 91
6.3 Structural properties 92
6.3.1 Crystal structure for bulk MAX phase and etched MAX phase powders 92
6.3.2 Crystal structure for pristine RP perovskite and perovskite-MXene hybrid thin films 92
6.4 Electronic properties 94
6.4.1 XPS spectra for pristine RP perovskite and perovskite-MXene hybrid thin film 94
6.4.2 UPS spectra for pristine RP perovskite and perovskite-MXene hybrid thin film 95
6.5 Optical properties 95
6.5.1 UV-vis spectra for pristine RP perovskite and perovskite-MXene hybrid thin film 95
6.5.2 PL and TRPL spectra for pristine RP perovskite and perovskite-MXene hybrid thin film 95
6.6 Electrochemical impedance spectroscopy for pristine RP perovskite and perovskite-MXene hybrid thin film 96

6.7 Optoelectronic properties 97
6.7.1 Photodetector fabrication and energy band diagram 97
6.7.2 I-V characteristics and transient photocurrent measurements for pristine RP perovskite and perovskite-MXene hybrid thin film-based photodetector under fixed incident illumination power 98
6.7.2.1 Responsivity (R), external quantum efficiency (EQE), detectivity (D) and noise equivalent power (NEP) and ON-OFF ratio for pristine and hybrid photodetector under fixed incident illumination power 99
6.7.3 Stability analysis for pristine RP perovskite and perovskite-MXene hybrid thin film based photodetector 99
6.7.4 I-V characteristics and transient photocurrent measurements for pristine RP perovskite and perovskite-MXene hybrid thin film-based photodetector under variable incident illumination power 100
6.7.4.1 Responsivity (R), external quantum efficiency (EQE), detectivity (D) and noise equivalent power (NEP) and ON-OFF ratio for pristine and hybrid photodetector under variable incident illumination power 101

Chapter 7: Role of Smaller Organic Cation in the Optoelectronic Properties of Ruddlesden-Popper Perovskites 103
7.1 Effect of different smaller organic cations 104
7.2 Structural properties 104
7.2.1 Schematic diagram for CH-MA and CH-FA RP perovskite 104
7.2.2 Crystal structure for CH-MA and CH-FA RP perovskite thin films 105
7.3 Morphological properties for CH-MA and CH-FA RP perovskite thin films 106
7.4 Optical properties for CH-MA and CH-FA RP perovskite thin films 106
7.5 Optoelectronic properties for CH-MA and CH-FA RP perovskite 107
7.5.1 Device schematic and energetics 107
7.5.2 Long cycling transient photocurrent measurements for CH-MA and CH-FA RP perovskite 108
7.5.2.1 Day wise transient photocurrent measurements for CH-MA and CH-FA RP perovskite 108
7.5.3 Power dependent I-V characteristics and transient photocurrent measurements for CH-MA and CH-FA RP perovskite 109
7.5.3.1 Variation in the optoelectronic parameters vs. incident power for CH-MA and CH-FA RP perovskite 109

Chapter 8: Conclusions and Future Scope 111
8.1 Conclusions 111
8.2 Future Scope 113

References 115
Appendix 129