

# Contents

<b>CERTIFICATE</b> .....	<b>i</b>
<b>DECLARATION BY THE CANDIDATE</b> .....	<b>iii</b>
<b>COPYRIGHT TRANSFER CERTIFICATE</b> .....	<b>v</b>
<b>Acknowledgments</b> .....	<b>xi</b>
<b>Contents</b> .....	<b>xiii</b>
<b>LIST OF FIGURES</b> .....	<b>xix</b>
<b>LIST OF TABLES</b> .....	<b>xxix</b>
<b>LIST OF SYMBOLS AND ABBREVIATIONS</b> .....	<b>xxxii</b>
<b>PREFACE</b> .....	<b>xxxii</b>
<b>CHAPTER 1: Introduction</b> .....	<b>1</b>
1.1 Introduction .....	1
1.2 Renewable Energy: The Future Solution.....	2
1.2.1 Benefits of renewable energy .....	3
1.3 Solar energy.....	4
1.3.1 Solar spectrum .....	5
1.3.2 Photoelectrochemical cell.....	6
1.3.3 Components of PEC cells .....	7
1.4 Hydrogen as a fuel.....	8
1.5 Water splitting .....	11
1.5.1 Solar water splitting.....	12

1.6	Fundamentals of water splitting.....	13
1.7	Photoelectrochemical hydrogen evolution reaction.....	17
1.7.1	The overall reaction in HER.....	17
1.7.2	Mechanism involved in HER.....	18
1.7.3	Tafel slope in HER.....	18
1.8	Evaluation parameters for PEC hydrogen production.....	19
1.9	Issues in PEC cells.....	21
1.10	Materials for PEC cells.....	23
1.11	The objective of current research.....	28
	<b>CHAPTER 2: Materials and Methods.....</b>	<b>31</b>
2.1	Overview.....	31
2.2	Specification of the Materials.....	31
	<b>Table 2.1: Details of the raw materials.....</b>	<b>32</b>
2.3	Synthesis of Materials.....	32
2.3.1	Solid State Reaction (SSR) Method.....	32
2.3.2	Pulsed Laser Deposition (PLD) Technique.....	34
2.3.3	Hydrothermal Method.....	35
2.4	Characterization Techniques.....	36
2.4.1	X-ray diffraction (XRD).....	36

2.4.2	Thermogravimetric Analysis (TGA) .....	38
2.4.3	Differential Scanning Calorimetry (DSC) .....	40
2.4.4	Scanning Electron Microscopy (SEM) .....	41
2.4.5	Transmission Electron Microscopy (TEM) .....	43
2.4.6	X-ray Photoelectron/Ultraviolet Photoelectron Spectroscopy (XPS/UPS) .....	44
2.4.7	Atomic Force Microscopy .....	46
2.4.8	Ultraviolet-visible (UV - Vis) Spectroscopy .....	47
2.4.9	Surface Enhanced Raman Spectroscopy (SERS) .....	49
2.4.10	Cyclic Voltammetry (CV) .....	50
2.5	Analysis techniques .....	52
2.5.1	Rietveld Refinement Technique .....	52
2.5.2	Software to Analyze the Obtained Data .....	54
<b>CHAPTER 3: Anisotropic photoconduction in ultrathin CuO .....</b>		<b>55</b>
3.1	Introduction .....	55
3.2	Experimental .....	58
3.2.1	Thin film fabrication.....	58
3.2.2	Characterization techniques.....	58
3.2.3	Numerical simulations.....	59
3.3	Result and discussion .....	60

3.3.1	Structural and bandgap study .....	60
3.3.2	Anisotropic photoconduction .....	62
3.3.3	Possibility of photonic non-reciprocity .....	69
3.4	Conclusion .....	73

**CHAPTER 4: Catalyzing hydrogen production: Exploring plasmonic effects in self-assembled CuO/Cu<sub>2</sub>O thin films via pulsed laser deposition..... 75**

4.1	Introduction.....	75
4.2	Methods and Materials.....	81
4.2.1	Synthesis techniques .....	81
4.2.2	Characterization .....	82
4.2.3	Theoretical simulations .....	84
4.3	Results.....	86
4.3.1	Plasmonics at the CuO/Cu <sub>2</sub> O .....	86
4.3.2	Photo-electrochemical behaviour.....	96
4.3.3	Kinetics of HER.....	104
4.3.4	Discussions .....	110
4.3.5	Benchmarking .....	114
4.4	Conclusion .....	118

**CHAPTER 5: CuO nanoparticles for enhanced photoelectrochemical HER activity . 119**

5.1	Introduction.....	119
-----	-------------------	-----

5.2	Experimental Section.....	122
5.2.1	Synthesis.....	122
5.2.2	Material Characterization .....	122
5.3	Results and Discussion.....	123
5.3.1	Structural Study.....	123
5.3.2	Thermogravimetric Analysis (TGA) .....	125
5.3.3	HR-SEM and HR-TEM Analysis.....	126
5.3.4	Optical Studies of CuO NPs .....	127
5.3.5	XPS Analysis.....	130
5.3.6	Photoelectrochemical Studies of CuO NPs .....	131
5.3.7	Mott – Schottky Plot Analysis.....	138
5.3.8	HER Activity in CuO Photocathode.....	139
5.3.9	Transient Current Kinetics via Chronoamperometry .....	142
5.4	Conclusion.....	143
	<b>CHAPTER 6: Compositional effect on Solar-Driven Hydrogen Evolution Reaction in</b> <b>Cu<sub>1-x</sub>Ni<sub>x</sub>O. ....</b>	<b>145</b>
6.1	Introduction .....	145
6.2	Experimental Procedure .....	145
6.3	Characterization Techniques .....	146

6.4	Results and Discussion .....	147
6.4.1	Structural Studies .....	147
6.4.2	Thermal study .....	148
6.4.3	Microstructural study .....	149
6.5	Photoelectrochemical study .....	151
6.5.1	Mott – Schottky plot analysis.....	153
6.5.2	HER Activity .....	154
6.6	Conclusion .....	156
	<b>CHAPTER 7: Conclusions and Future Scopes .....</b>	<b>157</b>
7.1	Conclusion of the Present Investigation.....	157
7.2	Outlook for Future Work .....	160
	<b>References .....</b>	<b>161</b>
	<b>List of Publications .....</b>	<b>185</b>