

**RESONANT NANOPHOTONICS IN PERIODIC
LATTICES FOR SOLAR ENERGY HARVESTING AND
ELECTROCHEMICAL APPLICATION**

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Resonant Nanophotonics in Periodic Lattices for Solar Energy Harvesting and Electrochemical Applications

by

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Submitted

in fulfillment of the requirement of the degree of Doctor of
Philosophy

to the



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Dedicated to my beloved Family

Certificate

This is to certify that the thesis entitled "**Resonant nanophotonics in periodic lattices for solar energy harvesting and electrochemical applications**" being submitted by **Saurabh Pandey**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics is a record of Bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the required standard. The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.



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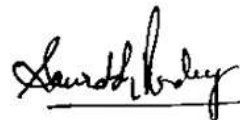
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Saurabh Pandey

Abstract

Beyond material composition and bandgap engineering, sustainable energy generation requires innovation. Solar energy applications like water splitting and photovoltaics require photoelectrodes' optical properties, especially their ability to catch and retain light interactions. Electrodes are typically passive electrical connections, but what if they could boost light-matter interactions and charge generation? The thesis explores nanophotonic improved charge harvesting for plasmon-driven water oxidation and photoelectrochemical applications and presents a broadband solar energy harvester using structural, nanophotonic, and electrochemical methods. The large-area periodic structures were fabricated using laser interference lithography (LIL) and electrochemical deposition, enabling precise control of optical and electrical properties.

Gold nanoparticles (GNPs) demonstrate localized surface plasmon resonance (LSPR), which enhances light absorption and catalytic activity; however, their photocatalytic efficiency is constrained by inadequate plasmonic charge separation and transport. To tackle this issue, a plasmonic particle grating (PPG) was established in Chapter 3 by arranging closely packed AuNPs within the grating grooves on a glass substrate coated with an ITO waveguide. The parameters for the grating were fine-tuned to ensure spectral overlap with various photonic modes, including guided-mode resonance, Rayleigh anomalies, and cavity modes, which in turn extend light-matter interactions and increase plasmonic hotspots, which is critical to plasmonic charge generation. The increase in porosity within the grating enhanced the metal-electrolyte interface, leading to improved plasmonic charge collection through the GNPs-adsorbed water molecules/ions interface. The PPG photoelectrode exhibited a 3.4-fold and 12.6-fold increase in incident photon- to-electron conversion efficiency (IPCE) when compared to gold bar gratings and randomly dispersed nanoparticles, respectively. The engineered gold photoelectrode exceeds the performance of earlier standalone plasmon photoelectrode, highlighting the critical role of nanoparticle size, refined grating design, and optical phenomena in facilitating effective plasmonic charge generation and its transfer.

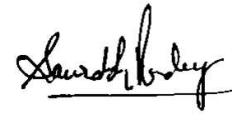
Next in Chapter 4, we added a TiO₂ semiconducting layer with the optimal nanoparticle grating arrangement. Plasmonic charge transfer from Au separated by TiO₂ bandgap is possible with the Au-TiO₂ Schottky junction photoelectrode. The TiO₂ layer integrating

with PPG-TiO₂ changes optical resonances and reveals SPP-coupled extraordinary transmittance phenomena and other photonic and plasmonic modes. In the visible spectrum, the suggested photoelectrode increased incoming photon to electron conversion efficiency (IPCE%) by seven and five times that of a bare TiO₂ waveguide layer for TM and TE incidence (light polarized perpendicular and parallel to the grating grooves). Ultrafast pump-probe spectroscopy shows that plasmon-GMR interaction extends plasmonic charge lifetimes. TM/TM and TE/TE pump/probe incidence assessed plasmonic-generated charge dynamics in grating-coupled SPP and LSPR. The observed PEC spectral response under polarized light supports these observations. In conclusion, our study might show a straightforward technique to integrate photonic and plasmonic materials for innovative broadband spectrum responses in photovoltaic and energy harvesting applications.

A simple and cost-effective method has been demonstrated to improve broadband bandgap absorption and optoelectronic performance for photovoltaic and energy harvesting applications by integrating abundant, environmentally friendly materials Cu and its oxides CuO and Cu₂O. Copper's composite broad absorption spectrum, charge carrier dynamics, and overall efficiency have been shown to enhance through its hexagonal nanoparticle lattice formation. The combination of photonics and plasmonic phenomena in structural engineering produces a nanoscale confined electromagnetic field that influences the inter- and intra-band excitation of Cu/Cu's oxide. Ultrafast transient absorption spectroscopy and photocatalytic dye degradation support the findings. Analyzing the charge dynamics with samples with different periods and randomly distributed nanoparticles with spectrally shifted optical resonance further unveils the effect of resonances for optoelectronic applications.

Tailored light-matter interaction with a tunable feature can extend its versatility in optical and its related applications. In essence, reconfigurable resonant phenomena in a 2D hexagonal periodic lattice of dielectric TiO₂ are brought out in Chapter 6 through the electrochemical deposition method. These resonant phenomena are guided mode resonance and quasi symmetry protected bound state in the continuum, which can be spectrally shifted, extinct, and interact with each other to realize tunable, switchable on-off state, and broadband absorption realization. Through cyclic voltammeter (CV) operation, more than 99.5% reversibility, >99% broadband absorption from UV-Vis-NIR region, and ~15 nm spectral shift in resonant positions were realized.

In the advancement of broadband absorber design for solar energy harvesting applications, the 3D square periodic racemic helix metamaterial has been investigated in Chapter 7, primarily concentrating on its potential fabrication using photolithography, as opposed to e-beam or mask aligner fabrication methods, which are time-consuming, complex, and challenging to implement over large areas. A 3D square periodic racemic helix was designed utilizing a 4+1 phase-controlled laser interference lithography technique through a double exposure method. Proof of concept has been demonstrated through the recording of cross-sectional images of the volumetric interference pattern on a CMOS camera, utilizing a spatial light modulator (SLM). Further, broadband absorption is illustrated through the analysis of its supporting optical modes and the constructive computation of chiral optical properties.



Saurabh Pandey

सार

सामग्री संरचना और बैंडगैप इंजीनियरिंग से परे, स्थायी ऊर्जा उत्पादन के लिए नवाचार की आवश्यकता होती है। जल विभाजन और फोटोवोल्टिक जैसे सौर ऊर्जा अनुप्रयोगों के लिए फोटोइलेक्ट्रोड के ऑप्टिकल गुणों की आवश्यकता होती है, विशेष रूप से प्रकाश की अंतःक्रिया को पकड़ने और बनाए रखने की उनकी क्षमता। इलेक्ट्रोड आम तौर पर निष्क्रिय विद्युत कनेक्शन होते हैं, लेकिन क्या होगा यदि वे प्रकाश-पदार्थ की अंतःक्रिया और आवेश उत्पादन को बढ़ावा दे सकें? थीसिस प्लाजमोन-संचालित जल ऑक्सीकरण और फोटोइलेक्ट्रोकेमिकल अनुप्रयोगों के लिए नैनोफोटोनिक बेहतर चार्ज हार्वेस्टिंग की खोज करता है और संरचनात्मक, नैनोफोटोनिक और इलेक्ट्रोकेमिकल विधियों का उपयोग करके एक ब्रॉडबैंड सौर ऊर्जा हार्वेस्टर प्रस्तुत करता है। बड़े क्षेत्र की आवधिक संरचनाओं को लेजर हस्तक्षेप लिथोग्राफी (एल. आई. एल.) और विद्युत रासायनिक निक्षेपण का उपयोग करके बनाया गया था, जो ऑप्टिकल और विद्युत गुणों के सटीक नियंत्रण को सक्षम करता है।

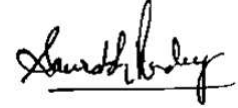
गोल्ड नैनोपार्टिकल्स (जी. एन. पी.) स्थानीय सतह प्लाजमोन अनुनाद (एल. एस. पी. आर.) प्रदर्शित करते हैं जो प्रकाश अवशोषण और उत्प्रेरक गतिविधि को बढ़ाता है; हालाँकि, उनकी प्रकाश उत्प्रेरक दक्षता अपर्याप्त प्लाजमोनिक चार्ज पृथक्करण और परिवहन द्वारा बाधित होती है। इस समस्या से निपटने के लिए, आईटीओ वेवगाइड के साथ लेपित कांच के सबस्ट्रेट पर ग्रेटिंग खांचे के भीतर बारीकी से पैक किए गए एयूएनपी को व्यवस्थित करके अध्याय 3 में एक प्लाजमोनिक पार्टिकल ग्रेटिंग (पीपीजी) की स्थापना की गई थी। ग्रेटिंग के लिए मापदंडों को विभिन्न फोटोनिक मोड के साथ वर्णक्रमीय ओवरलैप सुनिश्चित करने के लिए ठीक-ठाक किया गया था, जिसमें निर्देशित-मोड अनुनाद, रेले विसंगतियां और गुहा मोड शामिल हैं, जो बदले में प्रकाश-पदार्थ की बातचीत का विस्तार करते हैं और प्लाजमोनिक हॉटस्पॉट को बढ़ाते हैं, जो प्लाजमोनिक चार्ज उत्पादन के लिए महत्वपूर्ण है। ग्रेटिंग के भीतर सरंध्रता में वृद्धि ने धातु-इलेक्ट्रोलाइट इंटरफेस को बढ़ाया, जिससे जीएनपी-अवशोषित पानी के अणुओं/आयन इंटरफेस के माध्यम से प्लाजमोनिक चार्ज संग्रह में सुधार हुआ। पीपीजी फोटोइलेक्ट्रोड ने गोल्ड बार ग्रेटिंग्स और यादृच्छिक रूप से बिखरे हुए नैनोकणों की तुलना में क्रमशः घटना फोटॉन-टू-इलेक्ट्रॉन रूपांतरण दक्षता (आईपीसीई) में 3.4 गुना और 12.6 गुना वृद्धि का प्रदर्शन किया। इंजीनियर गोल्ड फोटोइलेक्ट्रोड पहले के स्टैंडअलोन प्लाजमोन फोटोइलेक्ट्रोड के प्रदर्शन से अधिक है, जो प्रभावी प्लाजमोनिक चार्ज उत्पादन और इसके हस्तांतरण को सुविधाजनक बनाने में नैनोकणों के आकार, परिष्कृत ग्रेटिंग डिजाइन और ऑप्टिकल घटनाओं की महत्वपूर्ण भूमिका को उजागर करता है।

इसके बाद अध्याय 4 में, हमने इष्टतम नैनोपार्टिकल ग्रेटिंग व्यवस्था के साथ एक TiO_2 अर्धचालक परत जोड़ी। TiO_2 बैंडगैप द्वारा अलग किए गए Au से प्लाज्मोनिक चार्ज स्थानांतरण Au- TiO_2 स्कॉटकी जंक्शन फोटोइलेक्ट्रोड के साथ संभव है। PPG- TiO_2 के साथ एकीकृत होने वाली टी. आई. ओ. 2 परत ऑप्टिकल अनुनाद को बदल देती है और एस. पी. पी.-युग्मित असाधारण संचरण घटनाओं और अन्य फोटोनिक और प्लाज्मोनिक मोड को प्रकट करती है। दृश्य स्पेक्ट्रम में, सुझाए गए फोटोइलेक्ट्रोड ने आने वाले फोटॉन को इलेक्ट्रॉन रूपांतरण दक्षता (आईपीसीई%) में सात गुना और टीएम और टीई घटना के लिए एक बेयर टीओओ₂ वेवगाइड परत की तुलना में पांच गुना वृद्धि की। (light polarized perpendicular and parallel to the grating grooves). अल्ट्राफास्ट पंप-प्रोब स्पेक्ट्रोस्कोपी से पता चलता है कि प्लाज्मोन-जी. एम. आर. अंतःक्रिया प्लाज्मोनिक चार्ज जीवनकाल को बढ़ाती है। टी. एम./टी. एम. और टी. ई./टी. ई. पंप/प्रोब घटना ने ग्रेटिंग-युग्मित एस. पी. पी. और एल. एस. पी. आर. में प्लाज्मोनिक-जनित आवेश गतिकी का मूल्यांकन किया। ध्रुवीकृत प्रकाश के तहत देखी गई पी. ई. सी. वर्णक्रमीय प्रतिक्रिया इन टिप्पणियों का समर्थन करती है। अंत में, हमारा अध्ययन फोटोवोल्टिक और ऊर्जा संचयन अनुप्रयोगों में अभिनव ब्रॉडबैंड स्पेक्ट्रम प्रतिक्रियाओं के लिए फोटोनिक और प्लाज्मोनिक सामग्री को एकीकृत करने के लिए एक सीधी तकनीक दिखा सकता है।

प्रचुर मात्रा में, पर्यावरण के अनुकूल सामग्री Cu और इसके ऑक्साइड CuO और Cu₂O को एकीकृत करके फोटोवोल्टिक और ऊर्जा संचयन अनुप्रयोगों के लिए ब्रॉडबैंड अवशोषण और ऑप्टोइलेक्ट्रॉनिक प्रदर्शन में सुधार करने के लिए एक सरल और लागत प्रभावी विधि का प्रदर्शन किया गया है। कॉपर के समग्र व्यापक अवशोषण स्पेक्ट्रम, चार्ज वाहक गतिशीलता और समग्र दक्षता को इसके षट्कोणीय नैनोकण जाली निर्माण के माध्यम से बढ़ाने के लिए दिखाया गया है। संरचनात्मक इंजीनियरिंग में फोटोनिक्स और प्लाज्मोनिक घटनाओं का संयोजन एक नैनोस्केल सीमित विद्युत चुम्बकीय क्षेत्र का उत्पादन करता है जो Cu/Cu के ऑक्साइड के अंतर और इंटर-बैंड उत्तेजना को प्रभावित करता है। अल्ट्राफास्ट ट्रांसिएंट अब्सोर्प्शन स्पेक्ट्रोस्कोपी और फोटोकैटालिटिक डाई डिग्रेडेशन निष्कर्षों का समर्थन करते हैं। स्पेक्ट्रली शिफ्टेड ऑप्टिकल रेज़ोनेन्स के साथ विभिन्न अवधियों और यादृच्छिक रूप से वितरित नैनोपार्टिकल्स के साथ नमूनों के साथ चार्ज डायनामिक्स का विश्लेषण करने से ऑप्टोइलेक्ट्रॉनिक अनुप्रयोगों के लिए रेज़ोनेन्स के प्रभाव का खुलासा होता है।

सौर ऊर्जा संचयन अनुप्रयोगों के लिए ब्रॉडबैंड अवशोषक डिजाइन की प्रगति में, अध्याय 7 में त्रिआयामी वर्ग आवधिक रेसमिक हेलिक्स मेटामेटेरियल की जांच की गई है, मुख्य रूप से ई-बीम या मास्क संरेखण निर्माण विधियों के विपरीत फोटोलिथोग्राफी का उपयोग करके इसके संभावित निर्माण पर ध्यान केंद्रित किया गया है, जो समय लेने वाले, जटिल और बड़े क्षेत्रों में लागू करने के लिए चुनौतीपूर्ण हैं। एक त्रिआयामी वर्ग आवधिक रेसमिक हेलिक्स को एक डबल एक्सपोजर विधि के माध्यम से 4+1 चरण-नियंत्रित लेजर हस्तक्षेप लिथोग्राफी

तकनीक का उपयोग करके डिजाइन किया गया था। एक स्थानिक प्रकाश मॉड्युलेटर का उपयोग करते हुए, एक सीएमओएस कैमरे पर वॉल्यूमेट्रिक हस्तक्षेप पैटर्न की क्रॉस-सेक्शनल छवियों की रिकॉर्डिंग के माध्यम से अवधारणा का एक प्रमाण प्रदर्शित किया गया है। (SLM). इसके अलावा, ब्रॉडबैंड अवशोषण को इसके सहायक ऑप्टिकल मोड के विश्लेषण और कायरल ऑप्टिकल गुणों की रचनात्मक गणना के माध्यम से चित्रित किया गया है।



Saurabh Pandey

Organization of the thesis

Chapter 1 presents the preface to the thesis, emphasizing the background of periodic nanostructures for tailored light-matter interaction by exploring the plasmonic and photonic phenomena facilitated by the diffraction of periodic grating structures. The contribution of such optical phenomena to energy production and the associated literature has been thoroughly reviewed in Chapter 1. Integrating top-down laser interference lithography with various bottom-up techniques, such as electrochemical deposition, has led to the realization and characterization of structures comprising metals, dielectrics, semiconductors, and composites. It has been systematically detailed through structural, elemental, steady, and transient absorption analyses-based methods in Chapter 2.

Chapters 3 and 4 detail the prospects of organizing plasmonic gold nanoparticles into a one-dimensional periodic grating to enhance solar energy production via photoelectrochemical current generation. It is achieved through a standalone plasmonic particle grating and an Au-TiO₂ Schottky junction-based photoelectrode. Chapter 3 emphasized the benefits of plasmonic particle grating compared to conventional metallic slabs or randomly distributed gratings. In contrast, chapter 4 established a direct correlation between photoelectrochemical spectra and charge dynamics findings through ultrafast transient absorption studies within the context of photonic modes that support plasmonic charge generation and collection. In this sequence, chapter 5 discusses the economical, non-toxic, and readily available plasmonic and semiconductor heterojunction composite as a hexagonal particle grating arrangement. The detailed investigation into the charge kinetics of plasmon relaxation and semiconductors, along with the synergistic interaction of plasmonic and photonic phenomena, is conducted and validated through photocatalysis measurements.

Reconfigurable resonant light-matter interaction has been introduced in Chapter 6 through electrochemical means to allow tunable, switchable On-Off state and broadband absorption realization with >99.5% reversibility. The 3D square periodic racemic helix metamaterial has been explored for solar energy harvesting applications in Chapter 7, with potential fabrication using phase-controlled laser interference lithography. The design was achieved using a 4+1 phase-controlled laser interference lithography technique, and its optical modes and chiral properties were analyzed for broadband absorption.

Chapter 9 concludes the thesis by examining the key highlights and concepts that have emerged throughout this journey, beginning with 1D periodic structures and culminating in 3D ones. The thesis examines most of these chapters from an application perspective, focusing on interference lithography to illustrate scalability and cost-effectiveness in realizing various nanophotonic architectures. As each chapter progresses, various mechanisms and concepts are introduced, increasing the structural complexity, ultimately addressed in this concluding chapter. A follow-up is also included beyond the scope of this thesis to inspire the community with potential future directions.

Table of Contents

Certificate	7
Acknowledgments	9
Abstract.....	12
Organization of the thesis.....	19
Table of Contents	1
List of Figures	1
List of Tables	1
Abbreviations.....	1
Symbols.....	1
1. Introduction: Resonant nanophotonics for tailored light-matter interaction	1
1.1 Research Motivation: Harnessing light-matter interactions for solar energy harvesting and beyond	2
1.2 Plasmon resonance and its optoelectronics properties	5
1.2.1 Surface plasmon polariton.....	6
1.2.2 Localized surface plasmon resonance	8
1.2.3 Plasmon resonance for optoelectronic applications	11
1.3 Diffraction-mediated resonances in periodic lattices	16
1.3.2 Plasmon surface lattice resonance:.....	23
1.3.3 Guided Mode Resonance.....	25
1.3.4 Bound States in the Continuum	29
1.4 Objective of the thesis	34
2. Methodological Framework: Design, Fabrication, and Characterization Methods	37
2.1 Introduction:.....	37

2.2 Laser Interference lithography: A cost-effective large-scale periodic structure's fabrication approach.....	38
2.3 Art of fabrication: deposition and pattern transfer.....	44
2.3.1 Thermal Evaporation method used for lift-off process.....	45
2.3.2 Electrochemical Deposition Methods	45
2.3.3 Reactive ion etching.....	48
2.4 Structural and elemental characterization methods	49
2.5 Computational (FDTD) and experimental details for optical mode study	54
2.6 Photoelectrochemical measurements.....	56
2.7 Ultrafast transient absorption spectroscopy.....	60
3. Hybrid photonic plasmonic photoelectrode for enhanced photoelectrochemical current generation: Direct plasmon–adsorbate charge transfer approach	64
3.1 Introduction	64
3.2. Theory	66
3.3 Design, Fabrication, and Characterization:.....	68
3.3.1 Design and Fabrication	68
3.3.2 The elemental and structural characterization	71
3.4 Spectral characteristics of resonating structure	72
3.4.1 Normal Incidence	72
3.4.2 Resonance modes at oblique incidence	77
3.5 Photoelectrochemical Photocurrent generation	79
3.5.1 White light PEC characterization:	80
3.5.3 Photoelectrochemical spectral response.....	82
3.5.3 Coupled resonant states for PEC current generation	86
3.6 Conclusion.....	91
4. Au-TiO ₂ plasmonic particle grating for engineered charge kinetics and broadband photoelectrochemical spectral response: charge collection through Schottky junction.....	92
4.1 Introduction	92
4.2 Theory and Principle	94
4.3 Fabrication of Au-TiO ₂ plasmonic particle grating.....	96

4.4 Optical transmittance and optical mode analysis	99
4.5 Photoelectrochemical photocurrent characterization	104
4.5.1 White Light PEC measurements	104
4.5.2 PEC spectral characterization.....	106
4.5.3 Optimizing photocurrent with TiO ₂ thickness.....	109
4.5.4 Stability of the Au-TiO ₂ photoelectrode.....	113
4.6 Ultrafast insights into charge dynamics	114
4.6.1: Ultrafast pump-probe transient absorption studies	115
4.6.2 Direct correlation of IPCE and TA measurements	120
4.7: Conclusion.....	120
5. Unveiling photonics-plasmonic resonating effects on advancing charge dynamics and photocatalytic activities in Cu/CuO/Cu ₂ O nano-hybrid hexagonal grating: Heterojunction charge transfer approach	122
5.1 Introduction:.....	122
5.2 Results and Discussion:	124
5.2.1 Fabrication, structural, and elemental studies	124
5.2.2 Optical Modes in Cu nano-hybrid PhC	127
5.2.3 Ultrafast transient absorption studies.....	134
5.2.4 Photocatalytic dye degradation	140
5.3 Conclusion.....	143
6. Electrochemically reconfigurable symmetry-protected quasi-BIC and guided mode resonance for spectral filtering and broadband absorption applications.....	144
6.1 Introduction	144
6.2 Theory.....	146
6.3 Optical resonances studies	148
6.4 Electrochemical reconfigurable nanophotonics.....	151
6.4.1 Normal Incidence: reconfigurable GMR.....	151
6.4.2 Oblique angle of incidence: Reconfigurable SP-BIC.....	153
6.4.3 Reconfigurable nanophotonics with CV cycles.....	157
6.5 Conclusion	160

7. Designing a square periodic racemic helix photonic metamaterial using phase-controlled interference lithography for broadband absorption and tailored chiral response	162
7.1 Introduction:	162
7.2 Design Methodology.....	164
7.3 Effect of phase in 2nd exposure	166
7.4 Experiment: Recording of 2D interference pattern.....	168
7.5. Designing of tapered racemic helix metamaterials	171
7.6 Optical properties and application insights: FDTD studies	172
7.6.1 Optical mode studies	173
7.6.2 Tailored circular dichroism response of racemic helix.....	177
7.6.3 Omnidirectional and polarization insensitive broadband absorber	182
7.7 Conclusion.....	184
8. Conclusion and Future Perspectives.....	186
8.1 Important conclusions of the thesis	186
8.2 Scope for Future Study	190
Bibliography	194
Appendices.....	207
List of Publications.....	222
Brief Academic Bio-Data	224

List of Figures

Figure 1.1(a) An illustration for overall solar energy harvesting scheme for PEC reaction for solar water splitting, (b) solar irradiance spectrum, (c) The photocatalytic and photoelectrochemical reaction mediated applications for clean and sustainable energy production. 3

Figure 1.2. (a) A schematic representation illustrating the transverse magnetic nature of a surface plasmon polariton (SPP) and the corresponding oscillations in charge density at the metal–dielectric interface. Adapted from ref ^[69]. The blue and green colors in the illustration symbolize the extent of penetration of the electromagnetic evanescent wave inside the metal and dielectric, respectively, (b) Dispersion curve for SPP excitation, and phase matching condition achieved via prism and grating coupling, (c) A schematic illustration for SPP excitation through prism (Kretschmann, and Otto configuration), and grating coupling. 6

Figure 1.3 (a) LSPR excitation in a single nanoparticle and corresponding absorbance spectra, (b) LSPR excitation in nanorod with longitudinal and transversal electron oscillation on excitation with incident light. Adapted from ref.^[406], (c) The longitudinal and transversal coupling of plasmonic response of individual nanoparticles in arrays, (d) upper plot features the dipolar transversal mode D (electric polarization vector E perpendicular to particle line, wave vector k perpendicular to particle line). The lower plot highlights the longitudinal sub-radiant and super-radiant modes. Black lines indicate the surface charge density integrated along the particle chain and perpendicular to it, respectively, (e) the longitudinal modes calculated with a constant inter-particle distance of 1.5 nm and varying chain lengths: extinction spectra of single particle and dimer lines are shown for chain lengths up to 60 repeat units. Adapted from ref.^[93]. .. 10

Figure 1.4 (a) plasmon excitation at time $t = 0$, followed by (b) the generation of thermal hot electron–hole pairs within the metal, which cannot be described using Fermi-Dirac statistics. This is succeeded by (c) thermalization through electron–electron and electron–phonon scattering, resulting in a Fermi-Dirac distribution of charge carriers’ indicative of elevated temperature. Finally, (d) thermal dissipation occurs through

phonon–phonon scattering. E_F represents the Fermi level, while the yellow and red regions denote the energy levels of holes and electrons, respectively. Adapted from reference^[100,407] 11

Figure 1.5 (a) A simplified band diagram of gold and an illustration depicting interband and intraband transitions. (b) Standard spectrum for the rate of electron generation in a localized plasmon wave within a metallic nanocrystal. There are two distinct categories of excited intraband carriers that can be identified, known as Drude carriers and hot carriers. The two blue regions represent the intervals during which interband holes and electrons are generated in gold. (c) Diagram illustrating the processes involved in plasmon decay. Adapted from reference^[97].....13

Figure 1.6 (a) The diffraction mechanism for the period (p) of the grating and wavelength(λ), where n is the grating medium effective index, (b) A pictorial representation of diffraction from 1D grating in transmission and reflection, (c) (i)Hexagonal grating and its direct and reciprocal lattice vector, (ii) a pictorial representation of diffracted orders from hexagonal grating, (d) schematic illustration of Fabry Perot and inter-slit cavity mode formation in 1D metallic grating, (e) a pictorial scheme for EOT excitation. Adapted from ref. (f) (i) Schematic of a gold grating with scanning electron microscope image in inset, on an n-type silicon substrate with a 2-nm Ti adhesion layer, oriented transverse to the laser polarization, (ii) surface plasmon polaritons (SPPs) around each gold pitch: a, SPPs oscillating at the top surface of gratings; b, SPPs oscillating through the slits and; c, SPPs oscillating at the bottom surface of gratings at the Ti–Si Schottky interface. (iii) Plasmonic heat absorption calculated by FDTD (shown with a logarithmic scale for clarity). Most of the hot electron generation occurs at the bottom surface of the gold layer, (iv) Photocurrent responsivities for three different gold layer thicknesses, $t=93$ nm (black), 170 nm (grey) and 200 nm (green), showing a strong intensity dependence on grating thickness. Adapted from ref.^[145]. 18

Figure 1.7 (a) Illustration of the one-dimensional chain and the interaction among dipoles oriented transversely that share a long-range photon. Adapted from ref.^[408] (b) Overview of LSPR and SLR within transmission spectra. Diagram of the structures examined: (i) individual particle, (ii) a periodic one-dimensional chain. The electric field of the incoming wave was oriented at a right angle to the direction of the chain, and for normal incidence. The gold particles had a radius of 80nm and surrounded with air

environment. The chain's period was 620nm, and it contained 1000 particles. Adapted from ref.^[149]..... 23

Figure 1.8 (a) GMR structure and the principle of operation, (b) Simulated reflectance and transmittance for TM incidence, inset shows electric field distribution corresponding to GMR, (c) Electromagnetic density ($|E|^2$) plot at grating-waveguide interface, inset shows $|E|^2$ corresponding to Rayleigh anomalies for grating period 500 nm, (d) temporal decay of electric field at grating-waveguide interface for on and off GMR resonance wavelength, (e) Photo response recorded with different LEDs launching light at an AOI $\approx 15^\circ$ corresponding to GMR-LSPR interaction (shown as dotted circle in angle of incidence vs wavelength plot). Adapted from ref.^[61]. 26

Figure 1.9 (a) Illustration of BIC. In an open system, the frequency spectrum has a continuum or many continua of spatially extended states (blue) and discrete levels of bound states (green) with no outward flux. Bound states are spatially localized by a confining structure or potential (black dashed line). Leaky resonances (orange) form when continuous spectrum states link to extended waves and radiate. Bound states in the continuum (BICs; red) are limited, radiation-free states inside the continuum. Adapted from reference^[191], (b) Dispersion plot representation explains the origin of BIC in the photonic system: photonic slab waveguide, and one dimensional grating waveguide, (c) (i) The leaky modes and bound states in the continuum (i) in a 1D-system, (ii) the SP-BIC condition (iii) leaky radiation in a 2D-system, (iv) FW-BIC through an avoided crossing, (d) (i) The dispersion band diagram of 2D-PhC shown in the inset, (ii) bio-detection scheme, (iii) sensitivity calculations. Adapted from ref.^[205]. 30

Figure 2.1 (a) 1D Lloyds two beam LIL setup, (i) A pictorial representation of two beam interference pattern using ray diagram, (ii) sinusoidal intensity modulation of resulting interference transverse to grating pattern, as illustrated in (iii), (iv) Lloyd's mirror mount used for recording the interference pattern placed on rotation stage, overlapping area i.e. interference region of direct and reflected beam made on sample plane through rotating the whole mount by θ , (b) Multi-exposure lithography methodology (i) rotation of the sample by angle α , (ii) MATLAB produced interference pattern corresponding to $\alpha = 0^\circ, 60^\circ, 120^\circ$, and their resultant intensity pattern, (c) (i) schematic of one-axis Lloyd's mirror interferometer with an additional mirror set, (ii) Two mirrors mount used for recording three beams interference pattern by rotating the mount normal to sample

plane by angle θ , (iii) FESEM image of recorded interference pattern on negative photoresist.....41

Figure 2.2 Overview of fabrication method involved after getting photoresist pattern, which includes (1) lift off process, electrochemical deposition (ECD), and reactive ion etching (RIE), and (2) removal of PR after (i) process..... 44

Figure 2.3 (a) The phenomenon of thermal evaporation in a schematic. Adapted from ref.^[409], (b) a pictorial representation of three electrode electrodeposition cell dipped in the electrolyte (in yellow), (c) In house electrochemical deposition setup with Pt wire as CE, Ag/AgCl as RE, and PR pattern over ITO coated glass or bare ITO/glass. 46

Figure 2.4 (a) A schematic representation of the RIE optimization process in terms of directionality and anisotropy resulting in etching profile for the (i) isotropic etching, (ii, iii) anisotropic etching, and completely anisotropic etching, i.e., etching in the horizontal and vertical direction are same, (b) RIE plasma chamber with detailed Mechanism of process involved..... 49

Figure 2. 5 A typical working principle and experimental arrangements in schematic for (a) SEM, (b)TEM. Adapted from ref.^[235],(c) Schematics of signals generated from SEM: secondary electrons (SE), backscattered electrons (BSE), and characteristic X-rays. Adapted from ref.^[237],(d) Electron – matter interactions: the different types of signals generated throughout volume of the sample. Adapted from ref.^[238]. 52

Figure 2.6 (a) (i) XRD simplest working principle and instrumentation, and (ii) Bragg's law in schematic. Adapted from ref.^[240] (b) (i) Basic components of XPS system. Adapted from ref.^[242] (ii) Principle of X-ray photoelectron spectroscopy (XPS). Adapted from ref.^[241]..... 53

Figure 2.7 (a) (i) FDTD layout for simulation of one dimensional gold nanoparticles grating, (ii) gold nanoparticles arrangements in form of grating grooves, (iii) cross sectional view (xy) of FDTD layout, where inset shows the magnified waveguide –grating configuration. (b) (i) FDTD top view layout of hexagonal Cu and its oxides based particle grating, where Cu particles are arranged in hexagonal cylindrical form, and surrounded by dielectric layer of refractive index 2.0 with high mesh refinement. (ii) index profile (xy view) at $z=50\text{nm}$ and 100nm respectively. (c) (i) Optical transmittance and reflectance

setup, (ii) Basic reflection spectroscopy setup for specular (θ°) direction, using two port fiber..... 55

Figure 2.8(a)PEC measurements with 1.5 G white light (i) an illustration, (ii) experiment setup used, (b) IPCE measurements setup (i) an illustration, (ii) experiment setup used. 59

Figure 2.9 (a) An illustration of sample illumination scheme with pump and probe beam with certain delay time, (b) Diagram illustrating the methodology of a transient absorption. At time $t < 0$, prior to the excitation of the sample by the pump laser and the incidence of the probe beam, the detector measures the intensity of the ground state (G) absorption, yielding the spectrum A_0 . At $t > 0$, the probe identifies absorption occurring from A to B, in addition to G to A. A new component emerges in the spectrum at A_t , characterized by photo-induced absorption (PIA) resulting from excited state absorption, alongside a decrease in ground state absorption. The reduction in $G \rightarrow A$ happens due to the depletion of the ground state by the pump pulse; this phenomenon is referred to as ground state bleach or photo bleaching (PB). The transient absorption spectrum ΔA_t quantifies the difference between A_t and A_0 , displaying the change in absorption induced by the pump laser pulse. As the sample returns to the G state, the ΔA spectrum evolves over time, ultimately approaching zero. 61

Figure 3.1 Plasmonic charge transfer mechanism in GNPs-PhC, (a) an illustration of Hybrid Photonic-Plasmonic structure supporting different optical modes (GMR, RA, and LSPR) under light illumination and charge transfer process. The red arrows show the diffracted wave from the grating, satisfying the waveguide mode condition, whereas the cut-off mode diffracted order RA along the interface. The plasmonic oscillation relaxed through the hot hole and electron transfer directly into the electrolyte and Pt electrodes respectively, (b). Illustration of plasmonic charge transfer into electrolyte through inter-band and intra-band excitation under applied potential and photon illumination.....66

Figure 3.2 Stepwise fabrication process: a) Schematic of fabrication of photoresist grating through i) exposure of two-beam interference pattern on photoresist coated ITO (green)/Glass(white), ii) PR (purple) grating after developing iii) corresponding SEM image, b). Schematic of fabrication of GB-PhC through i) Au sputtering over PR templates, followed by ii) lift-off metallic grating through acetone rinsing and sonication,

with corresponding SEM image iii), c). The process involved in the fabrication of GNPs-PhC: i) illustration of Electrochemical electrodeposition, ii) Sinusoidal applied potential strength in PR templates, iii) illustration of electrodeposited GNPs within the PR grating grooves, and iv) final GNPs grating corresponding v) final sample image and vi) SEM image, vii)-viii) elemental characterization using XRD and EDAX analysis methods, respectively. 69

Figure 3.3 (a) Schematic diagram of two beam laser interference lithography setup, b-i,ii) captured image of photoresist-coated ITO and PR grating on ITO, (c) Three electrode cells used for electrochemical deposition (ECD), (d). GNPs grating after ECD and removing the PR through acetone rinsing and sonication, (e) SAED pattern, f-g) Elemental characterization and elemental EDAX mapping of deposited GNPs. 72

Figure 3.4 (a). Spectral transmission response GNPs-PhC under normal incident illumination identified with all resonant modes, experimental results given the above panel and FDTD simulation represents the lower panel for unpolarized light, TE and TM polarized illumination b-f) intensity distribution of the resonant states in i) XZ plane and ii) XY plane at constant $z = 10$ nm above the ITO-water interface for GMR1, RA1, LSPR-TM, LSPR-TE and GMR2 respectively. 73

Figure 3.5 Oblique angular spectrum and field profiles, a) FDTD simulated angular optical transmission for GB-PhC, b) for GNPs-PhC, c) experimentally obtained transmission for GNPs-PhC, absolute square electric field profile corresponding to d) PSLR excited at 750 nm in normal incidence, e) at 10° angle of incidence (708 nm) showing enhanced electric field density in the coupled resonant state. 79

Figure 3.6 Photo-electrochemical water-splitting measurement with white light illumination. a) an illustration of experimental setup followed for white light PEC photocurrent measurement, b). linear scan voltammetry of the photonic-plasmonic hybrid structure and planer ITO waveguide deposited over SiO₂ substrate, c). Absorption UV-Vis-NIR spectrum of GNPs-PhC and ITO waveguide, d) Transient response measurements of bare ITO waveguide and GNPs-PhC, e). Electrochemical impedance spectroscopy (EIS) of GNPs-PhC under dark and light conditions, f) Stability test of GNPs-PhC WE for 1hour time duration. 80

Figure 3.7 PEC-WS response under TE/TM polarized illumination, a) absorption spectrum corresponding to GNPs-PhC, GB-PhC and RNPs for TM and TE polarized light, b) with their corresponding current density vs applied potential, c) IPCE vs polarization of incidence light where red stars and dotted line are corresponding absorption, d) spectral internal quantum efficiency response of TE and TM polarized light at 410 nm, 532nm and 632 nm respectively at 1.45 V vs RHE , e) average η calculated from TE and TM illumination vs photon energy for different applied potential, where inset shows $\eta^{(2/5)}$ vs. potential, verifying Brodsky and Pleskov's exponent law. 86

Figure 3.8 (a) Measured absorbance spectra of the GNPs-PhC at an incident angle of 10° as shown in red. The peaks are identified and fitted with the Lorentzian function. Both the hybrid state is shown by dotted fitted curve, (b) The dispersion curve shows the energy splitting of plasmonic SLR and GMR modes under coupled conditions. 88

Figure 3.9 Photonic-plasmonic resonant states response towards the current generation. (a) IPCE measurements corresponding to excitation wavelength 720 nm, 800 nm, and 880 nm under normal incidence and 700 nm under 10° angles of incidence, (b). FDTD simulated power absorption, demonstrating enhanced absorbed power corresponding to coupled state at 100° angle of incidence.. 90

Figure 4.1 Charge generation and transfer mechanism. An illustration of (a) Scattered light from GNPs, diffracted light and evanescent tails of GMR, are collected in TiO_2 , (b) plasmonic charge generation (blue dot- hole, red dot- electron) through plasmon resonance relaxation, (c) The overall photoelectrochemical current generation process resulting in bubble formation near the counter and working electrode surface as a signature of hydrogen and oxygen evolution reaction, where inset shows the direct plasmonic electron transfer to TiO_2 conduction band. 94

Figure 4.2 (a) An illustration for fabrication process involved in hybrid photonic plasmonic particles grating photoelectrode, (b) SEM image of photoresist grating and (c) FESEM image of gold nanoparticles plasmonic grating, where inset shows the image of magnified view of FESEM image, (d) X-ray diffraction analysis of PPG- TiO_2 photo electrode, (e) HRTEM images and its analysis, (i) HR-TEM images of Au particles surrounded by a TiO_2 layer with magnified portion of Au- TiO_2 interface as inset, (ii) zoomed image of Au- TiO_2 interface, corresponding to which SAED pattern was recorded

, displaying the different planes corresponding to TiO_2 and Au crystalline nature corresponding to Au- TiO_2 interface and where inset shows the interference pattern corresponding to lattice planes of Au and mixed phase of TiO_2 97

Figure 4.3 (a) HRTEM images of PPG- TiO_2 , (b) FESEM-EDX characterized elemental mapping for Au and Ti of TiO_2 , and its related EDAX spectra..... 98

Figure 4.4 Optical characterization of PPG- TiO_2 photoelectrode, (a) Transmission spectra at normal illumination in simulation (i)TM, (ii)TE illumination, in experiment (iii)TM, (iv)TE illumination case respectively.(b) Electric field distribution corresponding to optical modes such as (i) GMR1(G1), (ii) GMR2 (G2) in TE illumination, (iii) Fabry Perot (FP) mode, (iv) SPP, (v) SPP-EOT (vi) collective plasmon response due to GNPs, in TM illumination, (c) Experimentally obtained angular transmission plot (i), (ii) in simulation, (iii), (iv) in experiment for TM and TE case respectively, where dotted circle in violet, red, black and yellow corresponds to guided mode resonances, SPP-EOT, SPP and FP mode respectively. (d) Electric field distribution at 668 nm for 0° , 2° , 5° angle of incidence. 100

Figure 4.5 Photo-electrochemical characterization of the PPG- TiO_2 photoelectrode and bare TiO_2 over ITO waveguide with un-polarized white light source, (a) Absorption spectra, (b) Linear scan voltammetry(LSV) characterization under dark and light illumination conditions, (c) Source On-Off (transient) photocurrent density response at 1V vs Ag/AgCl, (d) Current density vs applied potential curve for PPG- TiO_2 and TiO_2 film in dark condition, (e) Steady state photoluminescence emission spectra of PPG- TiO_2 and bare TiO_2 film.....105

Figure 4.6 PEC spectral characterization (IPCE) at normal incidence. (a) IPCE (%) spectral response in UV region (320 nm-400 nm) for PPG- TiO_2 for TM and TE illumination, and TiO_2 film, (b) an illustration of TM and TE incidence scenario with respect to grating, IPCE (%) and absorption in (c) TM, (d)TE incidence, (e) IPCE (%) spectral response in visible region (400 nm-800 nm) for PPG- TiO_2 for TM and TE illumination, and TiO_2 film for comparative study, (d) maximum IPCE (%) obtained for different spectral region for photoelectrodes TiO_2 , PPG- TiO_2 for TM and TE incidence. 107

Figure 4.7 (a) Energy- angle of incidence dispersion curve for GMR and SPP resonant mode, (b) IPCE (%) and $|E|^2$ vs wavelength for 0° and 5° oblique illuminations in TM illumination condition. 108

Figure 4.8 Transmittance spectra with varying thickness of TiO_2 layer for (a) TM incidence, revealing SPP-EOT and SPP mode interaction for thickness 40nm of TiO_2 , (b) TE incidence with no active SPP mode. (c,d) IPCE plot TiO_2 thickness 40, 60, and 30nm under TM and TE incidence respectively, (e) $|E|^2$ plot for SPP-EOT interaction at thickness 30nm, 40nm 60nm respectively. 110

Figure 4. 9 (a) Stability test of PPG- TiO_2 photoelectrode at 1V vs Ag/AgCl for 3 hrs (180 minutes), IPCE spectra at $t = 0$ and $t = 180$ mins for (b) TM (c) TE incidence. 113

Figure 4.10 (a) An illustration of pump probe spectroscopy with broadband probe (400-800nm) and varying pump wavelength, (b) Transient absorption temporal response of TiO_2 bare film over ITO coated glass for different pump excitation at probe wavelength 500 nm..... 115

Figure 4.11 Broadband transient absorption response with pump wavelength 450 nm with (a)TM and (b) TE incidence, (c) and (d) absolute ΔA at probe wavelength 500 nm with pump excitation 360 nm, 450 nm and 720 nm following the TM/TM and TE/TE illumination respectively, (e) TA measurements at 500 nm probe wavelength with 450 nm, and 550 nm pump excitation under TM and TE incidence. 116

Figure 4.12(a) TA at probe wavelength 693 nm and 723 nm corresponding to SPP and SPP-EOT plasmonic mode under 450 nm pump excitation in TM illumination, (b) Probing at 500 nm with pump wavelength 675 nm for normal and 5° angle of incidence corresponding to coupled GMR-SPP conditions for TM/TM excitation, (c) TA obtained in normal illumination with pump excitation wavelength 650 nm and 675nm with probe 500 nm under TM and TE incidence, (d) the charge injection efficiency vs pump wavelength are plotted with respective IPCE values for TM and TE incidence. 118

Figure 5.1 (a) A schematic illustration of fabrication method involved, (i) PR coated ITO over glass substrate, (ii) An illustration for three beam laser interference lithography set up, inset a magnified view of two mirror mount and their interference scheme, (iii) hexagonal hole pattern formation after developing the recorded interference pattern ,

(iv) an illustration for electrochemical deposition with cell having three electrode assembly, insets show FESEM images before and after ECD process, with its illustration in (v) and (vi) represents the pictorial and its FESEM images after removing the PR material with acetone rinsing, (b) XPS spectra corresponding to Cu and its oxides.....125

Figure 5.2 (a) Experimentally and FDTD simulated optical transmittance spectra under normal incidence for (i) x polarized (line plot missing the tag), (ii) y polarized illumination, (b) Transmittance contour plot with varying period corresponding to nanoparticles arrangements in cylindrical geometry of (i) radius 65 nm, and radius 180 nm, (c) Electric field profile (XY view), and (d) phase for R= 65 and R=180 nm at 723 nm, (e) Line offset transmittance for varying angle of incidence (x polarized), (f) Electric field distribution corresponding to optical modes (i) GMR, (ii) RA, (iii) RA, and RA mediated cavity mode. 129

Figure 5.3 (a) Optical transmittance spectra (i) experimental, (ii) simulated for PhC390, PhC560, and PhC1020, (b) FDTD simulated spectral variation of local electromagnetic field density for three samples..... 131

Figure 5.4(a) Illustration of ultrafast transient absorption under pump-probe excitation, (b) excitation scheme of interband and intraband in Cu, (c) bandgap excitation illustration in CuO and Cu₂O under pump-probe excitation,.....135

Figure 5.5 Broadband transient absorption response of (a) randomly distributed Cu nanoparticles (RNPs), (b) PhC560, with pump wavelength 420 nm and broad probe wavelength span 450-780 nm, (c) Transient absorption temporal line spectra at probe wavelength (i) 480nm, (ii) 730nm, (c) near to interband edge excitation at probe wavelength (i) 560nm and (ii) 650nm under 420nm pump excitation for RNPs and PhC560. 136

Figure 5.6 (a) TA temporal spectra at probe wavelength 480nm on pump excitation 420 and 750 nm, (b) (i) TA line spectra for probe wavelength 450-750nm at time delay 2.4ps, (ii) corresponding to samples PhC390, PhC560, and PhC1020. 138

Figure 5.7 (a) Schematic illustration of proposed charge generation and transfer mechanism for photocatalytic activity using Cu/Cu₂O/CuO nanocomposites, (b) Time

dependent absorbance spectra of bare MB dye solution at $t=0$ and $t = 300$ minutes, and in presence of RNPs, PhC390, PhC560, PhC1020 on visible light irradiance for 300 minutes, (c), (d) single wavelength interrogated kinetic plot and first order rate constant values of MB dye degradation in presence of different samples, illuminating with 532nm and 660 nm respectively..... 141

Figure 6.1 Reconfigurable nanophotonics scheme by electrochemical means (a) an illustration for experimental setup used for recording the transmittance while electrochemical deposition of PANI occurs on the sample as working electrode in the electrochemical cell, (b) (i)cyclic voltammeter (CV) while electrochemical process occurs from oxidation to reduction states corresponding to ES and LS phase of PANI, (ii) a pictorial representation of deposition and its extinction coefficient as CV proceeds from -0.2V to 0.7V.....147

Figure 6.2 Optical characteristic of hexagonal periodic nanopillars, (a) FESEM image corresponding to unit cell of the grating (scale bar =500 nm), (b) Illumination scheme for normal incidence, (c) FDTD simulated and experimentally obtained transmittance curve for normal incidence, (d) Electric field distribution corresponding to GMR1 and GMR2.....149

Figure 6.3 Optical mode study at oblique incidence, (a) (i) experimental, (ii) FDTD simulated angle of incidence vs transmittance 2D contour plot, (b) (i) E_z field distribution corresponding to SP-BIC1 and SP-BIC2 respectively.....150

Figure 6.4 Variation in guided mode resonance spectral position in positive and negative half cycle for (a) GMR1, (b) GMR2 mode, (c) FDTD simulated spectral variation with different refractive index of PANI deposited at normal incidence corresponding to varying applied potential, (c) Resonant position shifting with ramp potential between - 0.2 to 0.3 V close to reduction dip and oxidation peak respectively, with transient interval of 20 seconds. 152

Figure 6.5 Electrochemically reconfigurable optical transmittance at oblique angle of incidence (a) 2° , (b) 4° , (c) 6° in (i) positive and (ii) negative CV operation of electrochemical deposition of PANI. 153

Figure 6.6 Transmittance drop defined as its attenuation from its initial value at -0.2V corresponding to resonance's dips (a) GMR1_(1, -1) (-1,1), (b) GMR2_(1,1), (c) SP-BIC1, and (d) SP-BIC2 with their corresponding to reversibility index (RI) in term of transmittance (%). 155

Figure 6.7 Variation of GMR1 and GMR2 spectral mode position and its quality factor for normal incidence (a) -0.2 V and (b) 0.7 V, (c) Quasi SP-BIC1 and Quasi SP-BIC2 spectral position and quality factor for 4° angle of incidence. 157

Figure 6.8 Transmittance for a 6° angle of incidence was measured at various CV cycles of polyaniline electrodeposition corresponding to applied potentials of (a) -0.2V and (b) 0.7V, respectively. (c) and (d) illustrate the transmittance for the 1st and 50th cycles at -0.2V and 0.7V, as well as the transmittance at these voltages after the removal of the deposited PANI layer by rinsing with a diluted 0.1M HNO₃ solution. 158

Figure 7.1 Designing methodology (a) Beams configuration in umbrella geometry with azimuthal angle ϕ_1 and ϕ_2 corresponding to 1st and 2nd exposure, (b) Three-dimensional perspective view of designed coupled helix square periodic lattice, below shows magnified view of single unit cell.....165

Figure 7.2 (a) Intensity distribution for (i) 1st exposure, (ii) 2nd exposure, and (iii) addition of intensity in 1st and 2nd exposure, resulting racemic helix structure, (b) resultant intensity distribution of 1st and 2nd exposure, with rotation of beams in 2nd exposure with respect to 1st exposure by (i) $\pi/4$, (ii) $\pi/2$, (iii) π , (iv) $\pi/4$, (v) $3\pi/2$, (vi) 2π 167

Figure 7.3 Experimental proof of concept of designing methodology, a) schematic illustration of experimental setup followed by 532 nm laser source, spatially light modulator(SLM), and CCD camera, b) phase profile addressed to SLM corresponding to (i) 1st and (ii) 2nd exposure, where inset shows the zoomed images, iii, iv) recorded 2D interference pattern at the camera corresponding to 1st and 2nd exposure respectively (scale bar = 10 μ m). After stacking 2D raw interference pattern, c) (i) top view of interference pattern (scale bar = 10 μ m) ii) cross-sectional (YZ) view of the stacked resultant 2D interference pattern recorded for total distance 6mm traversed in the z direction, revealing the coupled helical geometry (scale bar = 10 μ m). 169

Figure 7.4 Designing the tapered helical photonic structure, (a) bottom to top, (b) top to bottom decreasing helical radius corresponding to $\Delta\theta_{\text{int}} +1^\circ$ and -1° , respectively, (c) effect of $\Delta\theta_{\text{int}}$ on helical profile..... 171

Figure 7.5 (a) A schematic representation of coupled helix square unit lattice with its structural parameters, consist of right hand and left hand helix unit (RHH and LHH) adjacent to each other, (b), (c) and (d) represent the transmission spectra of LHH, RHH and CH lattices under RCP and LCP illumination respectively, black and green arrow denoted the symmetric and antisymmetric hybridized modes (e) current density vector plot for symmetric and antisymmetric hybridized mode formation in each individual helix at wavelength 972 nm and 545 nm in a single pitch coupled helix lattice, (f) (i),(ii)Electric field distribution, iii)(iv) Poynting vector at $z=115$ nm for x and y polarized incident light corresponding to coupled mode at wavelength 1580 nm, respectively, (g),(h) Transmission contour plot for angular dispersion and polarization independency of the coupled mode on illuminating with linearly polarized light. 174

Figure 7.6 (a) Electric field mapping at coupled mode at 1580nm and away of coupled mode(1800nm), (b) transmittance plot with different helix separation..... 176

Figure 7.7 Circular dichroism response of coupled helix metamaterial (a) Transmission spectra of coupled helix under RCP and LCP illumination with $HS = 200$ nm, $AP = 230$ nm, $FD = 50$ nm for $N = 1, 2$ and 3 , (b) a schematic representation of phase variation in helix, (c) CD enhancement through varying the phase of LHH unit in step of 90° at wavelength 630 nm and 1300 nm, (d) Local chiral field enhancement(CE) mapping at wavelength 1300 nm corresponding to (i), (ii) LHH, RHH with 0° phase and RCP and LCP illumination respectively, (iii) 180° phase in LHH with LCP illumination (e) differential absolute CE for 0° phase and 180° phase difference between the two adjacent opposite handed helix unit, (f) circular dichroism contour plot for varying angle of incidence for racemic helix metamaterial for 180° phase difference between two adjacent helix..... 179

Figure 7.8 (a) Comparative absorption studies for square periodic cylindrical nanorods, single handed units RHH and LHH and coupled helix, 3D absorption spectra, contour plot for varying (b) angle of incidence for y and x polarized light source (c), polarization angle respectively, showing omnidirectional perfect absorption characteristics, (d)

charge generation for cylindrical nanorods, RHH, LHH and coupled helix square periodic metamaterial.....183

Figure A0 (a) Captured image of real experimental setup, (b),(c) represents the pump and probe beam generation from a common source using OPA, and their respective ray diagram towards sample and detectors.....183

Figure A1 Optimization parameters of grating structure (a) and (b) FDTD simulated transmission spectra with variation in period and width of grating under TM polarized light incidence.....208

Figure A2 (a) FESEM images and corresponding particle distribution of 1D plasmonic particle grating, (b) Transmittance plot for different particle size GNPs-PhC, PEC linear scan voltammetry plot with white light illumination for (c) different nanoparticle sizes GNPs-PhC, and (d) optimized 22nm GNPs-PhC, GB-PhC, and RNPs. 209

Figure A3 (a) Schematic illustration of RNPs sample (b) FESEM image, (c) particle size distribution and (d) optical transmittance spectra. 210

Figure A4 Angular transmission spectra, (a) TM illumination, (b) TE illumination corresponding to GNPs-PhC with cover medium index 1.33, (c) transmission spectra under TM illumination with cover medium index 1.7 to provide homogenous medium supporting SLR., (d) A Mott-Schottky plot reveals flat-band potential 0.6V vs RHE. 210

Figure B 1 Optical transmittance contour plot with varying width of grating under for (a) TM incidence, (b) TE incidence for PPG-TiO₂ structural configuration, and similarly for PSG in (c,d).....211

Figure B2 (a) gold nanoparticle size distribution of PPG photoelectrode (b) Tauc plot of TiO₂ film deposited over ITO coated glass for band gap calculation of TiO₂, ellipsometry spectroscopy characterization of (c) ITO, and (d) TiO₂ coated thin film for refractive index measurements.....212

Figure B3 Optical transmittance of dielectric grating (Si₃N₄) over ITO waveguide covered with TiO₂(40nm), (a) FDTD simulated optical transmittance for TM and TE incidence. Inset shows the experimentally obtained transmittance for ITO and TiO₂

coated on ITO, revealing existence of Fabry Perot mode ≈ 450 nm. E field and H field profile of G1, G2 and FP mode (b), (c), (d) respectively 213

Figure B4 (a) SPP dispersion relation plot with diffracted order $m=1$, $m=2$ for ITO-Au interface, (b) Electric field distribution corresponding to cavity mode at wavelength 720nm, Electric field distribution (c)SPP-EOT, (d) SPP plasmon mode with respective charge distribution (e) and (f) respectively. 214

Figure C1 Tauc plot for band gap calculation of Cu's oxide.....215

Figure C2(a) Analytical interpretation of guided mode resonance (GMR) spectral position: Plot of the waveguide effective index as a function of wavelength corresponding to waveguide mode and 1st diffracted order, (b) Rayleigh Wavelength and its angular dispersion for (i,ii) PhC560, (iii,iv) PhC390 and (v,vi) PhC1020 sample corresponding to incident light medium i.e. $n=1$, and substrate medium i.e. ITO, $n=1.73$, (c) Transmittance plot for different height of the cylindrical pillar, revealing broadening in cavity mode formed between grating ridges as height decrease as result of low confinement of incident EM field, (d) Transmittance spectra for with dielectric nanoparticles hexagonal grating. 216

Figure C3 (a) Transmittance plot for ITO coated over glass substrate, bump corresponds to FP mode. (b) Transmittance spectra corresponding to the samples PhC1020, PhC560, PhC390, and RNPs, (c) TA dynamics contour map for Y polarization case, with pump excitation 420 nm. (d) Absorbance spectra for MB at $t=0$, and $t=300$ seconds under dark and broadband probe source. 217

Figure D1 (a) Refractive index of PANI deposited at (i) $-0.2V$ and (ii) $0.7V$, extracted from ellipsometry spectroscopy, (b) FSEM images (i) PANI deposited for (i) 10 CV cycle, (ii) 20 CV cycle on ITO coated glass, (ii) 30 CV cycle on hexagonal periodic structure on ITO coated glass substrate, (c) FDTD simulated transmittance with varying thickness of electrochemically deposited PANI layer as CV cycle increases at applied potential of (i) $-0.2 V$, and (ii) $0.7V$ 218

Figure E1 3D perspective and 2D top view of interference pattern recorded after (a)1st exposure (b) 2nd exposure only.....219

Figure E2 Transmittance of (a) SRR basis, (b) number of turns (N)=1 of CH, RHH, and LHH 219

Figure E3 Circular dichroism of coupled helix, right handed helix, left handed helix for N=3 (b) E field mapping for (i) CD=0 and (ii) CD≠0 at wavelength 900nm and 1300nm respectively in RCP and LCP illumination conditions, (c) Transmission spectrum with N=3 for varying phase of a particular handed helix unit for 00 to 2700 corresponding to RCP and LCP illuminations. Dotted line corresponds to wavelength 630 nm and 1300 nm. 220

Figure E4 Electric field distribution at plasmonic absorption peak wavelength 820nm (a) XZ (b) XY plane 220

List of Tables

3.1 Comparison of PEC-WS current generation based on plasmonic photoelectrode.....	89
4.1 Comparison of IPCE (%) of PPG-TiO ₂ with various Au-TiO ₂ photoelectrode configuration.....	111
7.1 Phase of four beams in 1 st and 2 nd exposure.....	166
E1. A comparison with perfect absorber proposed in literature to benchmark..... the proposed absorber	221

Abbreviations

PEC	Photoelectrochemical
WS	Water Splitting
OER	Oxygen Evolution Reaction
HER	Hydrogen Evolution Reaction
PhC	Photonic Crystal
TM	Transverse Magnetic
TE	Transverse Electric
SPP	Surface Plasmon Polariton
LSPR	Localized Surface Plasmon Resonance
SLR	Surface Lattice Resonance
GMR	Guided Mode Resonance
RA	Rayleigh Anomalies
FP	Fabry Perot
EOT	Extra-ordinary Transmittance
BIC	Bound State in the continuum
LIL	Laser Interference Lithography
RIE	Reactive Ion Etching
PCLIL	Phase Controlled Laser Interference Lithography
ECD	Electrochemical deposition
RE	Reference Electrode
WE	Working Electrode
CE	Counter Electrode
SEM	Scanning Electron Microscope

FESEM	Field Emission Scanning Electron Microscope
EDAX	Energy Dispersive X-ray Spectroscopy
TEM	Transmission Electron Microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
FDTD	Finite domain time difference
LSV	Linear Scan Voltammetry
IPCE	Incident photon to electron conversion efficiency
EIS	Electrochemical Impedance Spectroscopy
TAS	Transient Absorption Spectroscopy
PB	Photo Bleaching
PIA	Photo-Induced Absorption
GNPs	Gold Nanoparticles
GB	Gold Slab
MS	Metallic Slab
RNPs	Random Nanoparticles
RHE	Reversible Hydrogen Electrode
DCT	Direct Charge Transfer
PANI	Polyaniline
SLM	Spatial Light Modulator
LCP	Left Circular Polarization
RCP	Right Circular Polarization
CD	Circular Dichroism
LHH	Left Handed Helix
RHH	Right Handed Helix
CH	Coupled Helix

Symbols

k	Wave Propagation Vector/Boltzmann Constant
ω	Angular frequency
c	Speed of Light
h	Plank Constant
$\hbar$	Dirac Constant
ν	Frequency
λ	Wavelength
E	Electric Field/ Energy
H	Magnetic Field/ Hamiltonian
J	Current Density
ΔA	Transient Absorption
I	Current
V	Voltage/Potential
η	Internal Efficiency
Z	Impedance
t	Time
ε	Dielectric Permittivity
E_F	Fermi Energy Level
p	Period
θ	Angle of Incidence
n	Refractive index
G	Reciprocal lattice vector
Φ	Phase Offset
C	Capacitance/Optical Chiral Density
Q	Quality Factor