

**PERFORMANCE OF HEMATITE AND BISMUTH
VANADATE BASED PHOTOCATALYSTS IN
PHOTOELECTROCHEMICAL REACTOR FOR
HYDROGEN PRODUCTION**

ADITYA SINGH



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

NEW DELHI – 110016

JULY 2022

©Indian Institute of Technology Delhi (IITD), New Delhi, 2022

**Performance of Hematite and Bismuth Vanadate based
Photocatalysts in Photoelectrochemical Reactor for
Hydrogen Production**

by

**ADITYA SINGH
(2016CHZ8288)**

Submitted

In fulfilment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

UNDER THE SUPERVISION
OF
PROF. SUDDHASATWA BASU
&
MR. SUJAY KARMAKAR



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
NEW DELHI – 110016**

JULY 2022

Certificate

This is to certify that the thesis entitled “**Performance of Hematite and Bismuth Vanadate based Photocatalysts in Photoelectrochemical Reactor for Hydrogen Production**” submitted by **Mr. Aditya Singh** to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.



Prof. Suddhasatwa Basu
Supervisor
Director, CSIR-Institute of Minerals & Materials
Technology (IMMT), Bhubaneswar, Odisha
Department of Chemical Engineering (on lien)
Indian Institute of Technology Delhi



Mr. Sujay Karmakar
Co-supervisor
GM Green Chemicals
NTPC Vindhyachal, Madhya Pradesh

Acknowledgments

It was a once-in-a-lifetime opportunity that will be an important chapter of my life. There are number of people without whom this thesis might not have been written and to whom I am greatly indebted for their part in my success. It is a pleasant aspect that I now have the opportunity to express my gratitude for all of them.

First of all, I would like to express my special thanks of gratitude to my supervisor **Prof. Siddhasatwa Basu**, and **Mr. Sujay Karmakar**. This work would not have been possible without their guidance, support, and encouragement. They have given me full liberty to pursue my research work. Under their guidance, I successfully overcame many difficulties and learned a lot.

I am also thankful to the Head of the Department of Chemical Engineering Indian Institute of Technology, Delhi. I would also like to thank my thesis committee members and all the faculty members of the Department of Chemical Engineering. I am thankful to all the administrative and technical staff members Department of Chemical Engineering, Indian Institute of Technology, Delhi, for their help and cooperation. I am also thankful to all the members of the Nanoscale Research Facility (NRF) and Central Research Facility (CRF) for providing me with the facilities to carry out my research work.

I also gratefully acknowledge National Thermal Power Corporation (NTPC) Limited and the Ministry of Electronics and Information Technology (MeitY) India for the financial support which made my Ph.D. work possible without having to worry about earning a living.

I express my special thanks to my respected seniors and juniors Dr. Ravi, Dr. Madhav, Dr. Manoj, Dr. Pankaj, Dr. Hari, Dr. Debabrata, Dr. Ayan, Dr. Baijnath, Dr. Shahid, Mr. Biswajit, Mr. Ram ji, Mr. Vicky, Mr. Prateek Yadav, Mr. Abhas, Ms. Priyanka, and Mr. Venkanna for their time-to-time outstanding scientific guidance and for making research work more cordial.

Acknowledgments

I also thank Mr. Sundar for making the Fuel cell Lab more easily accessible and helping me a lot whenever I required. I would like to specially acknowledge my friends Mohit, Bipin, Prashant, Reena, Rishiraj, Satirtha, Puneet, Pushpraj, Rit Prateek, and Prateek for their help, moral support, and motivation.

But most of all, I would like to thank those whom I deeply love, respect, and admire and to whom I dedicate this thesis– my family. I express my heartfelt gratitude to my parents, my brothers Mr. Deepak, Mr. Ashish, Mr. Adarsh, and sisters Ms. Anupama and Ms. Anjana for their unconditional love, encouragement, and blessings. They have always sacrificed their own wishes and happiness just for the upliftment of my career. I also want to express my sincere thanks to all those who directly and indirectly helped me at various stages of the work, but I could not mention their name due to the shortage of space.

At last, thanks to the almighty God who has given me the spiritual support and courage to carry out this work.



Aditya Singh

Abstract

The development in renewable energy sources is growing rapidly to compensate for the ever-increasing energy consumption demands. Storing solar energy in the form of green fuel like hydrogen (H_2) has been given much importance. The photoelectrochemical (PEC) water splitting is an efficient way of producing H_2 and oxygen (O_2) simultaneously in a single cell using sunlight. The hematite and bismuth vanadate ($BiVO_4$) based-photoanodes stand out due to their narrow optical bandgap, long-term stability, nontoxicity, and earth abundance. The present work focuses on the fabrication of nanostructured materials by different methods such as electrodeposition, chemical route, and sputtering for application in PEC water splitting. The hematite nanorods decorated with $NiMnO_3$ co-catalyst photoanode was prepared by a simple two-step hydrothermal method. $NiMnO_3$ suppressed the charge-carrier recombination on the hematite and significantly decreased the photoanode-electrolyte interface charge-transfer resistance.

The performance of $BiVO_4$ was limited by the surface states electron-hole recombination. This was addressed by devising an integrated photocatalytic (PC) and PEC system to achieve enhanced water oxidation performance of a $BiVO_4$ photoanode. The reduced gC_3N_4 (R- gC_3N_4) photocatalyst was suspended in the anode compartment electrolyte of the PEC reactor to integrate the PC-PEC systems. The R- gC_3N_4 produced hydroxyl radicals and hydrogen peroxide in the electrolyte, which reduced the onset potential for oxygen evolution reaction (OER) at the $BiVO_4$ photoanode.

The performance of $BiVO_4$ was further enhanced by preparing a heterojunction with WO_3 . The $WO_3/BiVO_4$ heterojunction was synthesized by sputtering WO_3 , followed by spin-coating of $BiVO_4$. The sputtered WO_3 enhanced electron-hole separation in the heterojunction. The incorporation of Cr into NiFe-layered double hydroxide (LDH) co-catalyst increased the

electrical conductivity of LDH. This resulted in an enhanced charge-carrier transfer with significant promotion of the OER kinetics. The heterojunction with sputtered WO_3 underlayer and NiFeCr-LDH co-catalyst provided photocurrent density of 4.9 mA cm^{-2} at 1.23 V vs. RHE with an incident photon to current conversion efficiency (IPCE) greater than 56% in the 350-470 nm range, with H_2 and O_2 evolution of 98 and $47 \text{ } \mu\text{mol cm}^{-2} \text{ h}^{-1}$, respectively.

Furthermore, the patterned metal grid was sputtered under the $\text{WO}_3/\text{BiVO}_4$ heterojunction to reduce resistive losses and improve the homogeneity of distributed potential in large-area substrates ($5 \text{ cm} \times 5 \text{ cm}$), and thus increased the PEC performance of the heterojunction. A PEC reactor was designed to enable electrolyte flow which exhibited prolonged stability of 80 h owing to fast bubble detachment from the photoanode surface and reduced the crossover of gas products. The electrolyte flow replenished the H^+/OH^- species near the electrode surface, which resulted to suppression of pH gradient across the electrode. Overall, the study was focused on the development of electrochemical engineering strategies to achieve enhanced PEC performance of large area photoanode.

सार

बढ़ती ऊर्जा खपत की मांगों की भरपाई करने के लिए नवीकरणीय ऊर्जा स्रोतों के विकास में तेजी से वृद्धि हो रही है। सौर ऊर्जा के भंडारण के लिए हाइड्रोजन (H₂) जैसे रासायनिक बंधों के रूप को बहुत महत्व दिया गया है। प्रकाशिक विद्युत् रसायनिकी (प्र.वि.र.) द्वारा सूर्य के प्रकाश की मदद से एक ही सेल में पानी का विभाजन करके एक साथ हाइड्रोजन और ऑक्सीजन (O₂) का उत्पादन करना एक प्रभावी तरीका है। हेमेटाइट और बिस्मथ वैनाडेट (BiVO₄) आधारित प्रकाशिक धनाग्र अपने छोटे प्रकाशीय उर्जा अंतराल, दीर्घकालिक स्थिरता, निराविराशुता और पृथ्वी में प्रचुरता के कारण सबसे श्रेष्ठ हैं। वर्तमान कार्य प्र.वि.र. जल विभाजन में उपयोग के लिए नैनोसंरचित पदार्थ के निर्माण के विभिन्न तरीकों जैसे इलेक्ट्रोडीपोजिशन, रासायनिक मार्ग, और स्पटरिंग पर केंद्रित है। NiMnO₃ सह-उत्प्रेरक से लेपित हेमेटाइट नैनोरोड्स प्रकाशिक धनाग्र को एक सरल और दो-चरणीय जलतापीय विधि द्वारा तैयार किया गया है। NiMnO₃ ने हेमेटाइट पर आवेश-वाहक पुनर्संयोजन को दबा दिया और प्रकाशिक धनाग्र-विद्युतअपघट्य अंतराप्रस्थ में आवेश-स्थानांतरण के प्रतिरोध को काफी कम कर दिया।

BiVO₄ का प्रदर्शन सतही अवास्थाओं में इलेक्ट्रॉन-होल के पुनर्संयोजन द्वारा सीमित था। इसका संबोधन प्रकाशिक उत्प्रेरकीय (प्र.उ.) और प्र.वि.र. प्रणाली को एकीकृत करके किया गया, जिसके परिणामस्वरूप BiVO₄ प्रकाशिक धनाग्र पर पानी ऑक्सीकरण के प्रदर्शन में वृद्धि हुई। प्र.उ. और प्र.वि.र. प्रणाली को एकीकृत करने के लिए अपचयित gC₃N₄ (R-gC₃N₄) प्रकाशिक उत्प्रेरक को प्र.वि.र. रिएक्टर के धनाग्र विभाग वाले विद्युतअपघट्य में परिक्षेपित कर दिया गया। R-gC₃N₄ ने विद्युतअपघट्य में हाइड्रॉक्सिल रेडिकल्स और हाइड्रोजन पराक्साइड का उत्पादन किया, जिसने BiVO₄ प्रकाशिक धनाग्र में ऑक्सीजन उद्भव अभिक्रिया (ऑ. उ. अ.) के शुरुआत के लिए आवश्यक वोल्टेज को कम कर दिया।

BiVO₄ के प्रदर्शन को और अधिक बढ़ाने के लिए, BiVO₄ का WO₃ के साथ एक विषमसंधि बनाया गया। WO₃/BiVO₄ विषमसंधि को तैयार करने के लिए पहले WO₃ को स्पटरिंग द्वारा बनाया गया, इसके बाद BiVO₄ की स्पिन-कोटिंग की गयी। स्पटर्ड WO₃ ने विषमसंधि में इलेक्ट्रॉन-होल के प्रथक्करण को बढ़ाया। NiFe-लेयर्ड डबल हाइड्रॉक्साइड (LDH) सह-उत्प्रेरक में Cr को संयुक्त करने से LDH की विद्युत चालकता में वृद्धि हुई। इसके परिणामस्वरूप आवेश-वाहक के स्थानांतरण में वृद्धि के साथ-साथ ऑ. उ. अ. गतिकी में सार्थक बढ़ावा हुआ। स्पटर्ड WO₃ निचलीसतह और NiFeCr-LDH सह-उत्प्रेरक के साथ तैयार किये गए विषमसंधि ने 4.9 mA cm⁻² (1.23 V बनाम RHE) का प्रकाशिक धारा घनत्व, 350-470 nm सीमा में 56% से अधिक IPCE तथा H₂, और O₂ का क्रमशः 98 और 47 μmol cm⁻² h⁻¹ उत्पादन दिया।

इसके अतिरिक्त, सांचा धातु ग्रिड को $WO_3/BiVO_4$ के नीचे स्पटर्ड किया गया, ताकि प्रतिरोधी नुकसान को कम किया जा सके और बड़े क्षेत्रफल ($5\text{ cm} \times 5\text{ cm}$) के अधःस्तर में वोल्टेज के वितरण की समरूपता में सुधार किया जा सके, और इसके परिणामस्वरूप विषमसंधि के प्र.वि.र. प्रदर्शन में वृद्धि हुई। विद्युतअपघट्य के प्रवाह के लिए एक प्र.वि.र. रिपेक्टर की रचना की गयी, जिसके फलस्वरूप 12 घंटे की लम्बी स्थिरता मिली, तथा गैस के बुलबुलों को बड़े क्षेत्रफल वाले प्रकाशिक धनाग्र की सतह से तेजी से प्रथक करने का प्रावधान किया और गैस उत्पादों के आर-पार को कम कर दिया। विद्युतअपघट्य के प्रवाह ने इलेक्ट्रोड सतह के पास H^+/OH^- आयन को पुनः भर दिया, जिसके परिणामस्वरूप इलेक्ट्रोड में पीएच प्रवणता की कमी हुयी। कुल मिलाकर, यह अध्ययन बड़े क्षेत्रफल वाले प्रकाशिक धनाग्र में अधिकतम प्र.वि.र. प्रदर्शन को प्राप्त करने के लिए विद्युत् रसायनिक अभियांत्रिकीय उपायों के विकास पर केंद्रित था।

Table of Contents

Title	Page No.
<i>Certificate</i>	<i>i</i>
<i>Acknowledgement</i>	<i>iii</i>
<i>Abstract</i>	<i>v</i>
संसार	<i>vii</i>
<i>Table of contents</i>	<i>ix</i>
<i>List of figures</i>	<i>xiv</i>
<i>List of tables</i>	<i>xix</i>
<i>Abbreviation</i>	<i>xx</i>
Chapter 1: Introduction	1-12
1.1 Global Energy Problem	1
1.2 Sustainable Energy Sources	1
1.3 Global Energy Scenario: Role of Hydrogen	3
1.4 Role of Hydrogen produced by Photoelectrochemical water splitting	5
1.5 Concept of PEC cell	6
1.6 Scale-up of PEC water splitting: Opportunities and Challenges	8
Chapter 2: Literature Review	13-31
2.1. Energetic possibilities of water splitting for hydrogen production	13
2.2 Role of Semiconductor Materials: Working Electrode (WE)	13
2.3 Semiconductor Modifications	15
2.4 Counter electrode (CE)	17
2.5 Electrolyte	17
2.6 Photon absorption and exciton generation	18
2.7 Photogenerated charge carrier separation and transport mechanism	19

Table of Contents

2.8 Semiconductor/electrolyte interface and product formation	20
2.9 Photoanode for PEC water oxidation application	21
2.9.1 Hematite (α -Fe ₂ O ₃)	23
2.9.2 Graphitic carbon nitride (gC ₃ N ₄)	23
2.9.3 Tungsten oxide (WO ₃)	25
2.9.4 Bismuth Vanadate (BiVO ₄)	25
2.9.5 WO ₃ /BiVO ₄ heterojunction	26
2.10 Surface modification by OER co-catalyst	27
2.11 Large area photoanode and scaled-up PEC water splitting	29
Chapter 3: Experimental & Simulation Studies	32-50
3.1 Material and Methods	32
3.2 Preparation of NiMnO ₃ -HNRs photoanode	32
3.2.1 Hematite (HNRs) photoanode synthesis	32
3.2.2 NiMnO ₃ -HNRs photoanode synthesis	33
3.3 Preparation of BiVO ₄ photoanode and anode compartment electrolyte	33
3.3.1 Synthesis of BiVO ₄ photoanode	33
3.3.2 Preparation of R-gC ₃ N ₄ and anode compartment electrolyte	34
3.4 Fabrication of WO ₃ /BiVO ₄ -NiFeCr LDH photoanode	35
3.4.1 Fabrication of spin coated WO ₃ layers	35
3.4.2 Fabrication of sputtered WO ₃ film	35
3.4.3 Fabrication of WO ₃ -BiVO ₄ heterojunctions	36
3.4.4 Decoration of NiFeCr-LDH onto WO ₃ -BiVO ₄ heterojunction surface	36
3.5 Fabrication of large area (5 cm × 5 cm) WO ₃ /BiVO ₄ -CoPi photoanode	37
3.5.1 Preparation of patterned Ni metal grid onto large area FTO substrates	37
3.5.2 Preparation of WO ₃ /BiVO ₄ -CoPi onto patterned large area substrate	37

Table of Contents

3.6 Material characterization	38
3.7 Photoelectrochemical study	39
3.7.1 Electrode preparation	39
3.7.2 Photoelectrochemical characterizations	40
3.7.3 Electrochemical cell design for integrating the PEC with PC system	43
3.7.4 ·OH free radical detection and H ₂ O ₂ concentration measurement	44
3.8 Simulation of the potential drop across large area FTO substrate	46
3.9 Simulation of the species concentration near the photoelectrode surface: Effect of electrolyte flow	47
Chapter 4: α-Fe₂O₃ Nanorods Decorated with NiMnO₃ Co-catalyst as Photoanode for Enhanced Oxygen Evolution Reaction in Photoelectrochemical Water Splitting	51-66
4.1. Results and Discussion	
4.1.1 Morphology of Synthesized Nanostructures	51
4.1.2 Phase analysis	51
4.1.3 Surface composition analysis	53
4.1.4 Optical characterization	55
4.1.5 Photoelectrochemical analysis	56
4.2. Summary	65
Chapter 5: Photocatalytic H₂O₂ generation assisted photoelectrochemical water oxidation for enhanced BiVO₄ photoanode performance	67-83
5.1 Results and Discussion	
5.1.1 Crystallinity and Phase Study of BiVO ₄ Photoanode	67
5.1.2 Morphology, composition, and UV-visible analysis of BiVO ₄	68
5.1.3 FTIR and Surface chemical composition of gC ₃ N ₄ and R-gC ₃ N ₄	69
5.1.4 UV-visible absorption of different concentration of R-gC ₃ N ₄	74

5.1.5 Photoelectrochemical analysis of BiVO ₄ photoanode	73
5.1.6 ·OH free radical detection and H ₂ O ₂ concentration measurement	79
5.2 Summary	83
Chapter 6: Role of sputtered WO₃ underlayer and NiFeCr-LDH co-catalyst in WO₃-BiVO₄ heterojunction for enhanced photoelectrochemical water oxidation	84-102
6.1 Results and Discussion	
6.1.1 Morphology and textural analysis	84
6.1.2 Structural and phase analysis	86
6.1.3 Surface composition analysis	88
6.1.4 Optical response analysis	89
6.1.5 Photoelectrochemical analysis	91
6.2 Summary	101
Chapter 7: Large area WO₃/BiVO₄-CoPi heterojunction photoanode for efficient photoelectrochemical water splitting: Role of patterned metal grid and flow of electrolyte	103-122
7.1 Results and Discussion	
7.1.1 Substrate conductivity and mass transfer limitation analysis	103
7.1.2 Surface morphology analysis	108
7.1.3 Crystallinity and optical response analysis	108
7.1.4 Photoelectrochemical analysis	110
7.1.5 Mitigation of pH gradient and gas crossover by electrolyte flow	119
7.2 Summary	122
Chapter 8: Summary and Future Scope	123-127
8.1 Summary	123
8.2 Future Scope	126

Table of Contents

Appendices	128-131
Appendix A	128
Appendix B	131
References	133-163
Brief Resume of Author	164-166

List of Figures

Figure No.	Title	Page No.
Figure 1.1	Global hydrogen demand by sector in the Net-zero Emissions scenarios, 2020-2050	4
Figure 1.2	Projection of Hydrogen demand in India with Low-Carbon scenario, 2020-2050	5
Figure 1.3	Basic configuration of PEC cell	6
Figure 1.4	Schematic of photoelectrochemical water splitting reactor	9
Figure 2.1	Positions of band edge in semiconductors used for PEC water splitting	14
Figure 2.2	Band edge position of ideal semiconductor	15
Figure 2.3	Types of semiconductors with different band edge alignments	16
Figure 2.4	AM 1.5 solar spectrum and the integral power density of the solar spectrum, projected to the thermodynamic energy requirements of water splitting and water decomposition	22
Figure 2.5	Schematic diagram of the PEC water splitting on the WO ₃ -BiVO ₄ working electrode and counter electrode (Pt)	27
Figure 3.1	Schematic of (a) BiVO ₄ photoanode (b) anode compartment electrolyte preparation	35
Figure 3.2	Schematic of fabrication of metal grid patterned large area WO ₃ /BiVO ₄ -CoPi photoanode	37
Figure 3.3	(a) Schematic of large area photoanode (5 cm × 5 cm) and photoelectrochemical water splitting reactor, (b) Real image of photoelectrochemical water splitting reactor	38
Figure 3.4	Image of Photoanode and cell used in PEC characterizations	40
Figure 3.5	(a) Schematic of cell design for integrating the PEC water splitting with PC system, (b) real image of cell, and (c) magnified view of Figure 3.5 (b)	45

Figure 3.6	Schematic of the 2D electrochemical cell with electrolyte flow configuration and consisting solid anode and cathode	47
Figure 4.1	SEM images of (a) HNRs, (b) HNRs (magnified), (c) MnO ₂ -HNRs (d) NiMnO ₃ -HNRs, inset in Figure 4.1 (c, d) shows the corresponding magnified image	52
Figure 4.2	(a) TEM image of NiMnO ₃ -HNRs sample, HR-TEM image of (b) α -Fe ₂ O ₃ and (c) NiMnO ₃	53
Figure 4.3	(a) XRD pattern, (b) Raman pattern of HNRs, MnO ₂ -HNRs, and NiMnO ₃ -HNRs samples	54
Figure 4.4	(a) Fe 2p XPS spectra in (i) HNRs, (ii) MnO ₂ -HNRs, and (iii) NiMnO ₃ -HNRs, (b) Mn 2p XPS spectra in (i) MnO ₂ -HNRs and (ii) NiMnO ₃ -HNRs, (c) O 1s XPS spectra in (i) HNRs, (ii) MnO ₂ -HNRs, and (iii) NiMnO ₃ -HNRs, (d) Ni 2p XPS spectra in NiMnO ₃ -HNRs	57
Figure 4.5	(a) Optical absorption, (b) PL spectra of HNRs, MnO ₂ -HNRs, and NiMnO ₃ -HNRs	58
Figure 4.6	(a) Schematic of the photogenerated e ⁻ -h ⁺ transfer pathways for PEC water splitting with the NiMnO ₃ -HNRs photoanode and Pt counter-electrode (b) LSV plots for HNRs, MnO ₂ -HNRs, and NiMnO ₃ -HNRs photoanodes, (c) EIS Nyquist plots for HNRs, MnO ₂ -HNRs, and NiMnO ₃ -HNRs under illumination condition	61
Figure 4.7	(a) Mott-Schottky plots for HNRs, MnO ₂ -HNRs, and NiMnO ₃ -HNRs photoanodes at 1 kHz under the dark condition in 1 M NaOH (b) Transient photocurrent plots for HNRs, MnO ₂ -HNRs, and NiMnO ₃ -HNRs at 1.23 V vs. RHE applied bias	62
Figure 4.8	(a) ABPE (b) IPCE plots for HNRs, MnO ₂ -HNRs, and NiMnO ₃ -HNRs photoanodes	64
Figure 4.9	(a) Hole-injection efficiency (η_{inj}), (b) CV measurements of HNRs and NiMnO ₃ -HNRs in 1 M NaOH under dark condition, (c) CA plot for NiMnO ₃ -HNRs at 1.23 V vs. RHE, (d) Faradaic efficiency plot for NiMnO ₃ -HNRs photoanode	65
Figure 5.1	(a) XRD, (b) Raman spectra, (c) SEM images, and (d) TEM and HR-TEM image of BiVO ₄	69

Figure 5.2	XPS elemental spectra of BiVO ₄ (a) Bi 4f, (b) V 2p, (c) O 1s, and (d) UV-visible absorption spectra of BiVO ₄ photoanode	70
Figure 5.3	(a, b) XPS spectra of gC ₃ N ₄ , and (c, d) XPS spectra of R-gC ₃ N ₄	72
Figure 5.4	(a) FTIR of gC ₃ N ₄ and R-gC ₃ N ₄ photocatalysts, (b) UV-visible absorption spectra of R-gC ₃ N ₄ photocatalyst and different concentrations of R-gC ₃ N ₄ suspended in 0.1 M PBS	73
Figure 5.5	(a) LSV plots under light and dark conditions of BiVO ₄ photoanode in 0.1 M PBS, 2-propanol + 0.1 M PBS and R-gC ₃ N ₄ + 2-propanol + 0.1 M PBS electrolyte	76
Figure 5.6	(a) Transient photocurrent of BiVO ₄ photoanode in 0.1 M PBS electrolyte, 2-propanol + 0.1 M PBS and R-gC ₃ N ₄ + 2-propanol + 0.1 M PBS (b) Stability analysis of BiVO ₄ in R-gC ₃ N ₄ + 2-propanol + 0.1 M PBS (c) ·OH detection by fluorescence spectroscopy (d) ·OH detection by HPLC	78
Figure 5.7	(a) XRD spectra, XPS elemental spectra (b) Bi 4f, (c) V 2p, (d) O 1s of BiVO ₄ photoanode after 3 h PEC stability	79
Figure 5.8	(a) H ₂ O ₂ production after photoreaction over the gC ₃ N ₄ and R-gC ₃ N ₄ photocatalyst, (b) stability test of R-gC ₃ N ₄ (1 mg/mL) for 3 h PEC water splitting, (c) ABPE (d) IPCE pattern of BiVO ₄ photoanode	81
Figure 5.9	Schematic of integrated PC and PEC water splitting process	82
Figure 6.1	FE-SEM images of (a) WO-60s, (b) WO-3L, (c) WO-3L/BVO, (d) WO-60s/BVO, (e) WO-60s/BVO-NiFeCr (f) EDX elemental spectrum of WO-60s/BVO-NiFeCr, AFM images of (g) WO-60s, (h) WO-3L, roughness plots of (i) WO-60s, (j) WO-3L	86
Figure 6.2	(a) TEM image of WO-60s/BVO-NiFeCr, HR-TEM image of (b) BiVO ₄ , (c) NiFeCr-LDH (d) XRD spectra of WO-60s, WO-3L, WO-3L/BVO, WO-60s/BVO and WO-60s/BVO-NiFeCr	87
Figure 6.3	XPS spectra of WO-60s/BVO-NiFeCr: (a) W 4f, (b) Bi 4f, (c) V 2p, (d) Ni 2p, (e) Fe 2p, (f) Cr 2p and (g) O 1s. (h) Optical absorption spectra WO-60s, WO-3L, BVO, WO-3L/BVO, WO-60s/BVO, WO-60s/BVO-NiFe, and WO-60s/BVO-NiFeCr	90

Figure 6.4	XPS spectra of spin coated WO-3L layer (a) W 4f, (b) O 1s	90
Figure 6.5	(a) LSV (b) EIS (c) transient response of WO-60s, WO-3L, WO-3L/BVO, WO-60s/BVO, WO-60s/BVO-NiFe and WO-60s/BVO-NiFeCr (d) Mott-Schottky patterns of WO-60s, BVO, WO-60s/BVO, WO-60s/BVO-NiFe and WO-60s/BVO-NiFeCr	95
Figure 6.6	(a) Schematic of the PEC water splitting on the WO-60s/BVO-NiFeCr WE and CE (Pt), (b) charge transfer (c) charge separation efficiency of WO-3L/BVO, WO-60s/BVO, WO-60s/BVO-NiFe, and WO-60s/BVO-NiFeCr	98
Figure 6.7	(a) OCV decay plots of WO-3L/BVO, WO-60s/BVO, WO-60s/BVO-NiFe and WO-60s/BVO-NiFeCr while illumination was off, (b) IMPS spectra	100
Figure 6.8	(a) CA patterns of WO-60s/BVO and WO-60s/BVO-NiFeCr (b) H ₂ and O ₂ production rate and Faradaic efficiency of WO-60s/BVO-NiFeCr photoanode under incident light	100
Figure 7.1	Colour gradient plot of the simulated voltage distribution over the FTO substrate (a) 1 cm × 1 cm (NP), (b) 5 cm × 5 cm (NP), (c) 5 cm × 5 cm (P) for a current density of 3 mA cm ⁻² , (d) CV curve for photoelectrochemical deposition of CoPi with Ni metal grid and electrolyte flow	105
Figure 7.2	FE-SEM image of (a) WO ₃ /BVO heterojunction, (b) WO ₃ /BVO-CoPi (NP/NF), (c) WO ₃ /BVO-CoPi (NP/F), and (d) WO ₃ /BVO-CoPi (P/F) photoanode	109
Figure 7.3	(a) XRD pattern and (b) UV-visible absorption spectra of WO ₃ /BVO, WO ₃ /BVO-CoPi (NP/NF), WO ₃ /BVO-CoPi (NP/F), and WO ₃ /BVO-CoPi (P/F) photoanode	110
Figure 7.4	(a) LSV, (b) OCV, (c) EIS, and (d) transient response of WO ₃ /BVO-CoPi (NP/NF), WO ₃ /BVO-CoPi (NP/F), and WO ₃ /BVO-CoPi (P/F) photoanode.	112
Figure 7.5	(a) ABPE, (b) IPCE plots of WO ₃ /BVO-CoPi (NP/NF), WO ₃ /BVO-CoPi (NP/F), and WO ₃ /BVO-CoPi (P/F) photoanode, (c) LSV plots for the WO ₃ /BVO-CoPi (NP/NF) and WO ₃ /BVO-CoPi (P/F) photoanode, measured on centre and	115

	corner, (d) Transmittance spectra of WO ₃ /BVO-CoPi (NP/NF), WO ₃ /BVO-CoPi (NP/F), and WO ₃ /BVO-CoPi (P/F)	
Figure 7.6	(a) LSV, (b) CA curve for WO ₃ /BVO-CoPi (P/F) under different flow rate of electrolytes, (c) Image of large area photoanode after 30 min water splitting, (d) LSV curve on initial inserting, after 30 min, and reinserting after 30 min of water splitting	119
Figure 7.7	Concentration of H ⁺ (cH ⁺) at anode and cathode surface under different flow rates of electrolyte	120
Figure 7.8	Concentration of H ₂ (cH ₂) and O ₂ (cO ₂) under different flow rates of electrolyte	121
Figure 8.1	Comparison of NiMnO ₃ -HNRS and WO-60s/BVO-NiFeCr photoanode for oxidation	125
Figure 8.2	Schematic of tandem PEC water splitting using WO ₃ /BiVO ₄ -NiFeCr photoanode and Sb ₂ Se ₃ /TiO ₂ -MoS ₂ photocathode with TEMPO mediated HMF oxidation	127
Figure A.1	SEM images of the as synthesized BiVO ₄ and corresponding EDX elemental mapping of Bi, V and O	128
Figure A.2	Structure of gC ₃ N ₄ photocatalyst	128
Figure A.3	LSV plots of BiVO ₄ photoanode in 0.1 M PBS and R-g-C ₃ N ₄ + 0.1 M PBS electrolyte (absence of electron donor)	129
Figure A.4	XRD pattern of NiFeCr-LDH electrodeposited for 90 s over WO-60s/BVO photoanode	130
Figure A.5	(a) Raman spectra of sputtered WO-60s film, (b) spin-coated WO-3L, (c) spin-coated BiVO ₄ layer, and (d) WO-60s/BVO and WO-60s/BVO-NiFeCr photoanode	130
Figure A.6	(a) Transmittance spectra of WO-60s, WO-3L/BVO, WO-60s/BVO, WO-60s/BVO-NiFeCr	130
Figure B.1	(a) Mesh of optimized geometry, (b) Reynolds number at different velocity of electrolyte.	132

List of Tables

Table No.	Title	Page No.
Table 1.1	Summary of global power producing capacity of sustainable energy sources	2
Table 2.1	Background of photoanodes for PEC water splitting with geometric	30
Table 4.1	Atomic compositions for the decorated Co-catalyst determined by XPS	59
Table 4.2	Values of the parameters fitted in the equivalent circuit model	61
Table 5.1	XPS elemental analysis of N 1s	72
Table 5.2	XPS elemental analysis of C 1s	72
Table 6.1	Comparison of photocurrent density and onset potential shift in this work with OER co-catalyst modified WO ₃ -BiVO ₄ heterojunction in literature	93
Table 7.1	Values of the fitted parameters fitted in the equivalent circuit model	114
Table 7.2	The quantity of W, Bi, V, and Co in the electrolyte after stability testing	117
Table 7.3	Overview of photoanodes for PEC water splitting with geometric area >6 cm ²	118
Table B.1	Table of baseline parameters used in the simulations	131

List of Abbreviations

ABPE	Applied Bias to Photon conversion Efficiency
AFM	Atomic Force Microscopy
CA	Chronoamperometry
CB	Conduction Band
CE	Counter Electrode
DC	Direct Current
EDX	Energy Dispersive X-ray (spectroscopy)
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transformed Infra-red (spectroscopy)
GC	Gas Chromatography
FTO	Fluorine Doped Tin Oxide
gC ₃ N ₄	Graphitic Carbon Nitride
HER	Hydrogen Evolution Reaction
HPLC	High Performance Liquid Chromatography
HRTEM	High-Resolution Transmission Electron Microscopy
IMPS	Intensity-Modulated Photocurrent Spectroscopy
IPCE	Incident Photon-to-Current Conversion Efficiency
LSV	Linear Sweep Voltammetry

MUMPS	Multifrontal Massively Parallel Sparse Direct Solver
NF	Non-Flow
NHE	Normal Hydrogen Electrode
NP	Non-Patterned
OCV	Open Circuit Voltage
OER	Oxygen Evolution Reaction
PBS	Phosphate Buffer Solution
PC	Photocatalytic
PEC	Photoelectrochemical
PL	Photo Luminescence
PVD	Physical Vapor Deposition
RE	Reference Electrode
RF	Radio Frequency
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
VB	Valence Band
WE	Working Electrode
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction