

**Engineering of Metal-Oxide Semiconductors to Amend a Robust
Photoanode for Photoelectrochemical Water Splitting**

SONIYA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
APRIL 2021**

**Engineering of Metal-Oxide Semiconductors to Amend a Robust
Photoanode for Photoelectrochemical Water Splitting**

by

SONIYA

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy
to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

May 2021

Dedicated to My Parents

CERTIFICATE

This is to certify that the thesis entitled, “**Engineering of Metal-Oxide Semiconductors to Amend a Robust Photoanode for Photoelectrochemical Water Splitting**” being submitted by **Miss SONIYA** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. She has worked under our supervision and has fulfilled the requirements, which to our knowledge, has reached the requisite standard for the submission of the thesis.

The results contained in this thesis have not been submitted to any other university or institute either in part or full for the awards of any other degree or diploma.



Prof. Pravin P. Ingole
Associate Professor,

Department of Chemistry

Indian Institute of Technology

Hauz Khas, New Delhi, 110016.



Dr. Fatwa Firdaus Abdi

Deputy Head of Institute for Solar Fuels

Helmholtz Zentrum Berlin, Germany

Hahn-Meitner-Platz 1, Berlin, 14109.

ACKNOWLEDGEMENTS

This thesis owes a debt of gratitude to many people; probably, the words will fall short.

First, I would like to acknowledge my supervisor ***Prof. Pravin. P. Ingole*** for his constant guidance, patience, and support during this journey. His confidence in my research work stimulated me to achieve this goal finally. In earlier days, his insightful lectures on “electrochemical methods and analysis” are appreciable for improving my understanding of this subject.

I would like to express my sincere gratitude to ***Dr. Fatwa Firdaus Abdi*** for availing me the opportunity to work with him in HZB, Berlin. His constant support, motivation, guidance, and discussions owe my deepest appreciation. His immense knowledge in this field has reshaped my concepts and fundamentals. It was a great pleasure to work with him and it is difficult for me to express my gratitude in words for him.

I wish to extend my special thanks to ***Dr. Ibbi. Y. Ahmet***, a person who is always excited about science. I am very thankful for his support and guidance. I have learned a lot from him.

I thank my SRC members profusely: Prof. S. Basu, Prof. A. Ramanan, and Prof. Sameer Sapra, for their comments and suggestions to improve my work. I am thankful to CSIR (work done in IITD) and DAAD (work done in HZB, Germany) for the financial support. Also, I thanks CRF, NRF, and the Chemistry department, IIT Delhi, for the facilities. I would like to acknowledge the chemistry department head in this period: Prof. Ravi Shankar, Prof. Ashok K. Ganguly, and ***Prof. Anil J. Elias***.

I thank ***Prof. Roel Van de Krol*** for the wonderful scientific environment and facilities in HZB, Berlin. I have learned a lot from his lectures (along with Dr. Fatwa) on PEC water splitting.

Besides, I would like to express my gratitude to all my friends, collaborators, and lab mates in IITD and HZB. I am grateful to Dr. Kajal Dey, Dr. Pavitra, Dr. Priyanka Pandey, Dr. Nimai Bhandary, and Dr. Arvind Kumar for creating a joyful environment and scientific discussions in the lab. I am very much indebted to Dr. Priyanka Pandey for her love and care. Also, I am thankful to Dr. Nusrat Rashid for the wonderful time during coffee breaks.

I owe a great debt of gratitude to Patrick Schnell and Dr. Rowshanak Irani for the discussions, friendly environment, and motivation. I appreciate the support of my friends outside the workplace. Thanks to Patrick Schnell, Yogita Chabra, Sapna Gahlot, Avi Tomar, Swati Khurana, Rajat Joshi, Jyoti Rohilla, Dr. Samim, Dr. Iqra, Krupen khaki, Dr. Nikunj, Tamo, and Abishek Singh for always adding joy and fun to my life.

My most profound appreciation to my parents and brothers for their continuous and unparalleled love and support.

Soniya Gahlawat

Abstract

Having insights into the existing trends in the worldwide energy scenario, both in terms of demand and resources, is really thought-provoking. Currently, fossil fuels are satisfying ~ 85% of the worldwide energy requirements. However, the depleting fossil fuels cannot keep up with the ever-increasing energy demands in the coming years, and their impact on the environment is harmful, to say the least. Therefore, we need to switch to sustainable energy sources. Nature has blessed us with sunlight, surplus stock of energy. However, we need to be able to store it, owing to its intermittent nature. Among the most promising and sustainable approaches is the conversion of solar energy into hydrogen (H_2) via the photoelectrochemical (PEC) water splitting process. The key component of PEC water splitting is photoelectrode, which should be of low fabrication cost, built of material having appropriate band gap, suitable band edge positions, high absorption coefficient & charge separation efficiency, and electrical conductivity. In order to make the photoelectrode affordable, we have emphasized the usage of transition metal-oxides. Water splitting is a redox reaction, and the oxidation half reaction (OER) is the kinetically more demanding process. This thesis is devoted to facilitating this process. Herein, we have explored three different photoanodes: Fe_2O_3 , $BiVO_4$, and $BaSnO_3$. This thesis's main emphasis is on engineering the band structure of these photoanodes to stimulate the electrical properties & higher absorption in the visible region and, consequently, enhance the PEC performance.

In the first part of **Chapter 1**, different energy sources and their scope and impact on the environment are presented, which help us understand the need for hydrogen production and opted route. In the second part, the basic principle of the PEC cell and the fundamentals of the process are discussed. Moreover, an extensive literature survey covering the choice of photoanodes, their physical & chemical properties, and their current status are presented. Also,

the challenges that need to be overcome to transform them into a robust photoanode are highlighted.

In **Chapter 2**, we have presented the synthesis approaches used in the thesis, the preparation of electrode & cell, various characterization techniques used to explore the properties of semiconductor photoelectrode material, and the methodology to carry out the PEC water splitting.

In **Chapter 3**, we have studied nickel incorporated hematite ($\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$). To improve the bulk properties of Fe_2O_3 , Ni was incorporated, and we found some unexpected though interesting optical absorption phenomena, explained by Burstein-Moss (B-M) effect. This study shines light on the exploration of the electronic structure using the combination of B-M shift determined from optical study and band edge positions determined from cyclic voltammogram, further confirmed by the hard x-ray photoelectron spectroscopy (HAXPES). It has been observed that the conduction band minimum shifts towards water reduction potential due to the B-M effect. Ni incorporation results in the delocalization of charge carriers along with the reduction of the bulk recombination of charge carriers. Overall, Ni incorporation is observed to improve the photovoltage and the photocurrent density of hematite photoanodes. Despite this, the photocurrent onset is at a much higher potential than the flat band potential. Therefore, we aimed to improve the surface catalytic properties of Fe_2O_3 . The state-of-art employed for this work (Chapter 4) was developing a Z-scheme heterojunction.

In **Chapter 4**, we have studied electrodeposited $\text{Cu}_2\text{O}/\text{Fe}_2\text{O}_3$ heterojunction. Films were deposited via the electrodeposition method as it consumes less energy and time. $\text{Cu}_2\text{O}/\text{Fe}_2\text{O}_3$ heterojunction followed well known Z-scheme. As a result, the bulk and surface charge separation efficiency was improved along with the catalytic efficiency. The heterojunction with 25 cycles of electrodeposited Cu_2O layer shows the best PEC water splitting performance

compared to other heterojunction films indicating optimum tuning of cuprous oxide thickness. Nevertheless, the obtained results are far away from the expected photocurrent density as per the theoretical calculations.

In **Chapter 5**, we have contributed to the most successful photoanode in terms of demonstrated efficiency, i.e., BiVO₄, to take it one more step ahead. The PEC performance of BiVO₄ is limited mainly due to its large band gap of ~2.4 eV. In order to extend the absorption range, sulfur incorporated BiVO₄ (S-BiVO₄) was synthesized. S-BiVO₄ has shown a band gap reduction of ~ 300 meV compared to pristine BiVO₄, which corresponds to a 30% increase in the theoretical efficiency. However, the primary concern associated with S-BiVO₄ is its instability in the electrolyte. We have successfully addressed this issue by the addition of ~20 nm NiO_x protection layer.

Chapter 6 accounts for an emerging material in this field: highly stable BaSnO₃ perovskite oxide. For the first time, we have developed a scalable spray pyrolysis synthesis recipe for the deposition of BaSnO₃ thin film. Furthermore, we have successfully tuned the band structure to shift the absorption in the visible region via H₂S treatment. In depth study of charge carrier dynamics and their impact on PEC activity is presented.

In **Chapter 7**, we have attempted to modify the properties of BaSnO₃ films by employing a reduction strategy. BaSnO₃ films were reduced under the flow of H₂ gas, resulting in the band gap shift to 1.5 eV. Furthermore, H₂-treated BaSnO₃ film demonstrates a photocurrent density of 0.45 mA/cm² at 1.23 V vs. RHE, which is > 2 times higher than that for the H₂S-treated BaSnO₃ and represents a record for spray-deposited BaSnO₃ photoanodes. Moreover, the photocurrent onset of H₂-treated BaSnO₃ film is found to be at ~0 V vs. RHE. BaSnO₃ treatment studies depict a perfect example of defect engineering.

Overall, this thesis is devoted to tune the metal-oxide semiconductors' properties using various strategies to boost their PEC efficiency. Our findings show that ternary metal-oxide semiconductors are more accommodating for defects/ dopants and, therefore, offer more potential for improving the PEC performance.

Abstract (संक्षेप)

मांग और संसाधनों दोनों के संदर्भ में, विश्वव्यापी ऊर्जा परिदृश्य में मौजूदा रुझानों में अंतर्दृष्टि होना वास्तव में विचारोत्तेजक है। वर्तमान में, जीवाश्म ईंधन दुनिया भर की ऊर्जा आवश्यकताओं का ~ 85% भाग पूरा कर रहे हैं। हालांकि, घटते जीवाश्म ईंधन, आने वाले वर्षों में लगातार बढ़ने वाली ऊर्जा मांगों को पूरा नहीं कर सकते हैं और पर्यावरण पर उनका प्रभाव अतिहानिकारक है। इसलिए, हमें स्थायी ऊर्जा स्रोतों का उपयोग करने की आवश्यकता है। प्रकृति ने हमें सूर्य, ऊर्जा का अतिरिक्त भंडार प्रदान किया है। हालांकि, हमें इसकी आंतरायिक प्रकृति के कारण इसे संग्रह करने की आवश्यकता है। फोटोइलेक्ट्रोकेमिकल (PEC) जल विभाजन प्रक्रिया के माध्यम से सौर ऊर्जा का हाइड्रोजन (H_2) में रूपांतरण सबसे आशाजनक और टिकाऊ दृष्टिकोणों में से एक है। PEC जल विभाजन का प्रमुख घटक फोटोइलेक्ट्रोड है, जो कम निर्माण लागत का होना चाहिए, उपयुक्त बैंड अंतराल, उपयुक्त बैंड किनारे की स्थिति, उच्च अवशोषण गुणांक और आवेश पृथक्करण दक्षता और विद्युत चालकता वाली सामग्री से निर्मित होना चाहिए। इसे वहनीय बनाने के लिए हमने संक्रमण धातु-ऑक्साइड के उपयोग पर जोर दिया है। जल विभाजन एक रेडॉक्स प्रतिक्रिया है और ऑक्सीकरण आधा प्रतिक्रिया (OER) गतिज रूप से अधिक मांग वाली प्रक्रिया है। यह शोध प्रबंध इस प्रक्रिया को सुविधाजनक बनाने के लिए समर्पित है। यहाँ, हमने तीन अलग-अलग फोटोएनोड्स का चयन किया है: Fe_2O_3 , $BiVO_4$ और $BaSnO_3$ । इस शोध प्रबंध का मुख्य जोर दृश्य क्षेत्र में विद्युत गुणों और उच्च अवशोषण को प्रोत्साहित करने के लिए इन फोटोएनोड्स की बैंड इंजीनियरिंग पर है और परिणामस्वरूप, पीईसी प्रदर्शन को बढ़ाता है।

अध्याय 1 के पहले भाग में विभिन्न ऊर्जा स्रोत और उनके दायरे और पर्यावरण पर प्रभाव प्रस्तुत किए गए हैं, जो हमें हाइड्रोजन उत्पादन और चुने हुए मार्ग की आवश्यकता को समझने में मदद करते हैं। दूसरे भाग में, पीईसी सेल के मूल सिद्धांत और प्रक्रिया के मूल सिद्धांतों पर चर्चा की गई है। इसके अलावा फोटोएनोड्स के विकल्प, उनके भौतिक और रासायनिक गुणों और उनकी वर्तमान स्थिति को

प्रकट करने वाला एक व्यापक साहित्य सर्वेक्षण प्रस्तुत किया गया है। इसके साथ, उन्हें एक मजबूत फोटोनोड में बदलने के लिए जिन चुनौतियों को दूर करने की आवश्यकता है, उन पर भी प्रकाश डाला गया है।

अध्याय 2 में, हमने शोध प्रबंध में प्रयुक्त संश्लेषण दृष्टिकोण, इलेक्ट्रोड और सेल की तैयारी, सेमीकंडक्टर फोटोइलेक्ट्रोड सामग्री के गुणों का पता लगाने के लिए उपयोग की जाने वाली विभिन्न विशेषता तकनीकों और पीईसी जल विभाजन को पूरा करने की पद्धति प्रस्तुत की है।

अध्याय 3 में, हमने Ni निगमित हेमेटाइट ($\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$) का अध्ययन किया है। Fe_2O_3 के थोक गुणों में सुधार करने के लिए, Ni का प्रयोग किया गया था और हमें कुछ अप्रत्याशित हालांकि दिलचस्प ऑप्टिकल अवशोषण घटना मिली, जिसे बर्स्टीन-मॉस (B-M) प्रभाव द्वारा समझाया गया। यह अध्ययन ऑप्टिकल अध्ययन से निर्धारित B-M शिफ्ट के संयोजन का उपयोग करके इलेक्ट्रॉनिक संरचना की खोज पर प्रकाश डालता है और चक्रीय वोल्टमोग्राम से निर्धारित बैंड किनारे की स्थिति पता की जाती है तथा हार्ड एक्स-रे फोटोइलेक्ट्रॉन (HAXPES) स्पेक्ट्रोस्कोपी द्वारा पुष्टि की जाती है। यह देखा गया है कि B-M प्रभाव के कारण कंडक्शन बैंड न्यूनतम वोल्टेज की ओर शिफ्ट हो जाता है। Ni निगमन के परिणामस्वरूप आवेश वाहकों के निरूपण के साथ-साथ आवेश वाहकों के थोक पुनर्संयोजन में कमी आती है। कुल मिलाकर, Ni निगमन को फोटोवोल्टेज और हेमेटिट फोटोनोड्स के फोटोकंट घनत्व में सुधार करने के लिए मनाया जाता है। इसके बावजूद, फ्लैट बैंड क्षमता की तुलना में फोटोकंट की शुरुआत बहुत अधिक क्षमता पर है। इसलिए, हमने Fe_2O_3 की सतह उत्प्रेरक गुणों में सुधार करने का लक्ष्य तय किया है। इस काम के लिए नियोजित अत्याधुनिक (अध्याय 4) एक Z-स्कीम हेटेरोजंक्शन विकसित कर रहा था।

अध्याय 4 में, हमने इलेक्ट्रोडेपोजिटेड $\text{Cu}_2\text{O}/\text{Fe}_2\text{O}_3$ हेटेरोजंक्शन का अध्ययन किया है। फिल्मों को इलेक्ट्रोडपोजिशन विधि के माध्यम से जमा किया गया क्योंकि इसमें कम ऊर्जा और समय लगता है। $\text{Cu}_2\text{O}/\text{Fe}_2\text{O}_3$ विषमयुग्मन ने प्रसिद्ध Z-योजना का अनुसरण किया। परिणामस्वरूप, उत्प्रेरक दक्षता के साथ-साथ थोक और सतह चार्ज पृथक्करण दक्षता में सुधार हुआ। इलेक्ट्रोडेपोजिटेड Cu_2O परत के 25 चक्रों वाली हेटेरोजंक्शन फिल्म, अन्य हेटेरोजंक्शन फिल्मों की तुलना में सबसे अच्छा पीईसी जल विभाजन प्रदर्शन दिखाता है। फिर भी, प्राप्त परिणाम सैद्धांतिक गणना के अनुसार अपेक्षित फोटोकॉरंट घनत्व से बहुत दूर हैं।

अध्याय 5 में हमने BiVO_4 जो की सबसे सफल फोटोएनोड है, उसे एक और कदम आगे ले जाने के लिए प्रयास किया है। BiVO_4 का PEC प्रदर्शन मुख्य रूप से ज्यादा ($\sim 2.4 \text{ eV}$) बैंड गैप के कारण सीमित है। अवशोषण सीमा का विस्तार करने के लिए, सल्फर निगमित BiVO_4 (S- BiVO_4) को संश्लेषित किया गया। S- BiVO_4 ने BiVO_4 की तुलना में $\sim 300 \text{ meV}$ बैंड गैप में कमी दिखाई है, जो सैद्धांतिक दक्षता में 30% की वृद्धि के अनुरूप है। हालांकि, S- BiVO_4 से जुड़ी प्रमुख चिंता, इलेक्ट्रोलाइट में इसकी अस्थिरता है। हमने $\sim 20 \text{ nm}$ NiO_x सुरक्षा परत को जोड़कर इस मुद्दे को सफलतापूर्वक संबोधित किया है।

अध्याय 6 ने इस क्षेत्र में एक उभरते हुई फोटोइलेक्ट्रोड पदार्थ के लिए जिम्मेदार है: अत्यधिक स्थिर BaSnO_3 पेरोसाइट ऑक्साइड। पहली बार, हमने BaSnO_3 की पतली फिल्म के जमाव के लिए एक स्केलेबल स्प्रे पायरोलिसिस संश्लेषण नुस्खा विकसित किया है। इसके अलावा, हमने H_2S उपचार के माध्यम से दृश्य क्षेत्र में अवशोषण को स्थानांतरित करने के लिए बैंड संरचना को सफलतापूर्वक ट्यून किया है। चार्ज कैरियर डायनामिक्स और पीईसी गतिविधि पर उनके प्रभाव का गहन अध्ययन प्रस्तुत किया गया है।

अध्याय 7 में, हमने रिडक्शन प्रक्रिया को नियोजित करके BaSnO_3 फिल्मों के गुणों को संशोधित करने का प्रयास किया है। BaSnO_3 फिल्में, H_2 गैस के प्रवाह के तहत रेड्यूस् हो गईं, जिसके

परिणामस्वरूप बैंड गैप 1.5 eV हो गया। इसके अलावा, H_2 उपचारित BaSnO_3 फिल्म, 1.23 V vs. RHE पर 0.45 mA/cm^2 फोटोकंट घनत्व को प्रदर्शित करती है, जो कि H_2S -उपचारित BaSnO_3 की तुलना में 2 गुना अधिक है और स्प्रे- डेपोसिटेड BaSnO_3 फोटोऐनोड्स के लिए एक रिकॉर्ड का प्रतिनिधित्व करता है। इसके अलावा, H_2 उपचारित BaSnO_3 फिल्म की फोटोकंट शुरुआत at ~ 0 V vs. RHE पर पाई जाती है। अंत में, BaSnO_3 उपचार अध्ययन डिफेक्ट इंजीनियरिंग का एक आदर्श उदाहरण दर्शाते हैं।

कुल मिलाकर, यह शोध प्रबंध पीईसी दक्षता को बढ़ावा देने के लिए विभिन्न रणनीतियों का उपयोग करके धातु-ऑक्साइड अर्धचालकों के गुणों को ट्यून करने के लिए समर्पित है। हमारे निष्कर्ष बताते हैं कि टर्नरी मेटल-ऑक्साइड सेमीकंडक्टर्स डिफेक्ट / डोपेंट के लिए अधिक अनुकूल हैं और इसलिए, पीईसी प्रदर्शन में सुधार के लिए अधिक क्षमता प्रदान करते हैं।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

PEC	Photoelectrochemical water splitting
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
VBM	Valence band maxima
CBM	Conduction band minima
STH	Solar-to-hydrogen efficiency
DFT	Density functional theory
LSV	Linear sweep voltammetry
CV	Cyclic Voltammetry
EIS	Electron impedance spectra
MS	Mott-Schottky
TRMC	Time-resolved microwave conductivity
PCAS	Photoconductivity action spectroscopy
IPCE	Incident photon-to-current conversion efficiency
DOS	density of state
Fe ₂ O ₃	Hematite
BiVO ₄	Bismuth vanadate
BaSnO ₃	Barium stannate
HDN	Hematite dendrite nanostructures
h	Hour
min	Minute
s	Second
eV	Electron volt
°C	degree centigrade
M	molar
mmol	millimole
E _g	band gap
mL	milliliter
λ	wavelength
Ar	argon
H ₂ S	Hydrogen sulfide
PLD	pulse laser deposition

XRD	X-Ray diffraction
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray spectroscopy
XPS	X-ray photoelectron spectroscopy