

SnS₂ Nanostructures, their Nanocomposites and Heterojunctions for Photoelectrochemical Water Splitting Applications

SARITA



**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2025**

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**SnS₂ Nanostructures, their Nanocomposites and
Heterojunctions for Photoelectrochemical Water
Splitting Applications**

by

SARITA

Submitted

**in fulfilment of the requirements for the degree of Doctor
of Philosophy to the**



**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2025**

Dedicated
to
my family

CERTIFICATE

This is to certify that the thesis entitled “**SnS₂ Nanostructures, their Nanocomposites and Heterojunctions for Photoelectrochemical Water Splitting Applications**” being submitted by Sarita to the Department of Physics, Indian Institute of Technology Delhi is worthy of consideration for the award of the degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by her under my guidance and supervision. She has fulfilled all the criteria for the submission of the thesis, which in my opinion has reached the necessary standard.

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

NChare

Prof. Neeraj Khare

Department of Physics

Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110016, India

ACKNOWLEDGMENTS

I am grateful to the Almighty God for his endless blessings, guidance, and strength, which have been a constant source of inspiration throughout my journey. His grace has instilled in me resilience and positivity. I extend my sincere appreciation to my supervisor, Prof. Neeraj Khare, for his invaluable guidance, encouragement, and expertise. His unwavering support and insightful mentorship have been instrumental in shaping this research. The knowledge and wisdom I have gained under his guidance will have a lasting impact on my academic and professional growth.

I am deeply grateful to my Student Research Committee (SRC) members, Prof. Sujeet Chaudhary, Prof. Brajesh Kumar Mani, and Prof. Bhaskar Mitra, for their continuous evaluation of my research progress at every stage and for providing invaluable suggestions that have greatly contributed to its improvement. Furthermore, I would like to express my gratitude to the DRC chairperson of the Physics Department at IIT Delhi for generously dedicating his time and offering support in overseeing the progress of my research work. I also wish to thank the Nanoscale Research Facility (NRF), Central Research Facility (CRF), and the Physics Department at IIT Delhi for providing access to various fabrication, characterization, and measurement facilities and all the technical staff of IIT Delhi for their assistance in completing my research work.

I also wish to express my sincere gratitude to Dr. Sangeeta Khare for her generous support and willingness to share her knowledge and experiences. Her valuable insights have broadened my perspective and significantly contributed to the progress of this research.

I extend my heartfelt gratitude to my colleagues at the Nano Functional Oxides and Superconductivity Laboratory (NFOSL), including Dr. Mohd. Faraz, Dr. Deepanshu Sharma, Dr. Rohit Kumar, Dr. Huidrom Hemojit Singh, Dr. Dheeraj Kumar, Dr. Mamta Dahiya, Dr. Amish Kumar Gautam, Dr. Mohit Khosya, Dr. Birendra Kumar, Dr. Gaurav Sharma, Mrs.

Abhilasha Chouksey, Mr. Aman Sharma, Mr. Gaurav Kumar, Dr. Manoj Singh, Dr. Arum Mondal, Mr. Sandeep Kumar, and Ms. Rajni. Their support and contributions have been invaluable in creating a conducive working environment in the lab. I offer special thanks to Dr. Mohit Khosya for generously sharing his experiences, knowledge, constant motivation, and all the discussions, which have been particularly beneficial to me. From each labmate, I have gained valuable insights and knowledge. I extend my best wishes to all of them for success in their future endeavours.

I deeply appreciate the unwavering support of my parents, Mrs. Kamla Devi and Mr. Roshan Lal Mittal; My brothers, Mr. Anjani Mittal, Mr. Ashwani Mittal, and Mr. Gaurav Gulati; My sister, Mrs. Ramta Aggarwal and her husband Mr. Jatin Jain. I dedicate this thesis to my family as a token of gratitude. I would also like to express my gratitude to my mentors, Prof. Sunita Srivastava and Prof. Tankeshwar Kumar, for their support and encouragement in guiding me toward the field of research. A special thanks to B.K. Sandeep Kumar and Mr. Vinay Partap Singh for their constant support throughout the journey. I owe my success to their continuous backing.

I sincerely thank my dear friends, Mr. Achyut Tiwari, Mr. Sandeep Kumar, Ms. Kiran Bedi, Ms. Palki Gakkhar, Ms. Savita Pannu, Mr. Sonu Kajla, Mr. Rahul Goyal, Mr. Naveen Beniwal, Mr. Rahul Singal, Mr. Rahul Joshi, Mr. Anuj Kumar, Ms. Sanchi Monga, Ms. Pooja Sachdeva, Mr. Ankur Kumar, Mr. Sahil Kumar, Mr. Himanshu Joshi, and Ms. Neetesh Dhakar for their unwavering support, companionship, and the countless cherished memories we have shared throughout my PhD journey. Their presence has made this experience truly special and unforgettable. I am also thankful for the opportunities, challenges, and experiences that have contributed to my learning and growth. The journey of research has been both enriching and fulfilling, and I cherish the knowledge and skills I have acquired along the way.

Finally, I sincerely acknowledge the Ministry of Electronics and Information Technology (MeitY) and the Department of Science and Technology (DST), India, for their generous financial support for this research. I am also deeply grateful to the University Grants Commission (UGC) for awarding me the Junior Research Fellowship (JRF) and Senior Research Fellowship (SRF), which greatly supported me throughout my PhD journey.



Sarita

Abstract

Energy harvesting from solar energy, using semiconducting materials, has attracted significant attention to surpass the growing demands for renewable energy production. The production of hydrogen (H_2) using solar energy is a viable approach to harness solar energy and tackle environmental issues that are raised due to the use of fossil fuels. Photoelectrochemical (PEC) water splitting has gained significant attention for generation of H_2 using solar energy and water. Recently, 2D materials have emerged as potential materials in energy storage and conversion applications due to their unique optoelectronic properties, large surface areas, and good charge mobilities. The present thesis focuses on designing photoanodes using different 2D semiconducting materials and strategies for developing efficient photoelectrodes to achieve high-performance PEC water splitting.

In this work, the visible light active 2D tin sulfide (SnS_2) has been synthesized using the hydrothermal method to study its potential in PEC water splitting application. Various characterization techniques are employed to analyze the morphological, structural, and optical properties of SnS_2 . The material exhibits suitable band positions that straddle the redox potentials of water, making it appropriate choice for PEC water splitting. However, the high recombination rate of photogenerated charge carriers limits its overall performance in this application. In order to enhance the PEC performance of SnS_2 photoanode, various strategies such as the formation of nanocomposites with conducting material, the formation of heterojunctions, and the doping of transition metals, are used.

The coupling of SnS_2 with carbon nanotubes (CNT) has been prepared with the help of an in-situ hydrothermal method, and its performance in PEC water splitting has been investigated. SnS_2 is coupled with 5, 10, and 20 wt. % of CNT to determine the optimal composition for enhanced PEC performance. The electron-accepting behavior of CNT is beneficial for the

SnS₂/CNT photoanode to improve PEC water splitting performance. The highest photocurrent density is achieved for 10 wt. % of CNT in SnS₂, $\sim 0.6 \text{ mA/cm}^2$, at 1.0 V with respect to Ag/AgCl which is ~ 3 times enhanced than pure SnS₂ photoanode. The enhancement in PEC performance is because of CNT providing the interfacial path for electron transport and reducing recombination rate of charge carriers.

Although the SnS₂/CNT nanocomposite shows some improvement, the enhancement in PEC performance is limited. To achieve further enhancement, a type-II heterojunction is formed between SnS₂ and g-C₃N₄. Visible light-active SnS₂/g-C₃N₄ type-II heterojunction is synthesized with 10, 20, and 30 weight % of g-C₃N₄ using the chemisorption method. The SnS₂/g-C₃N₄-20, a type-II heterojunction, which includes 20 wt. % of g-C₃N₄ with SnS₂, shows the maximum photocurrent density of $\sim 1.0 \text{ mA/cm}^2$, which is ~ 5 times higher compared of pure SnS₂. This observed enhancement is because of type-II heterojunction formation and self-induced internal electric field, which help to transfer charge carriers easily and effectively reducing the recombination rate.

Further, to tune the electrical and optical properties of SnS₂, the effect of Ni doping in SnS₂ is investigated. Ni-doping into SnS₂ improves the electrical conductivity and enhances optical absorption of the resultant photoanode. The Ni-doped SnS₂ photoanodes containing 3, 6, and 10 wt. % of Ni are synthesized using the hydrothermal technique. The 6 wt. % of Ni doping into SnS₂ (6-NSS) shows the highest photocurrent density of 2.5 mA/cm^2 , which is ~ 8 times higher compared to bare SnS₂. Ni doping in SnS₂ offers the maximum number of active sites for PEC water splitting reactions. The presence of defects acts as trapping sites for charge carriers, thereby reducing the recombination rate of charge carriers and hence enhancing PEC performance.

Finally, the combined effect of Ni doping and formation of type-II heterojunction on the PEC performance of SnS₂ is investigated. Next, a heterojunction is formed between Ni-doped SnS₂ and g-C₃N₄ using the chemisorption method, and its performance is compared with bare SnS₂. The Ni-SnS₂/g-C₃N₄ photoanode shows a photocurrent density of ~3.5 mA/cm² at 1.0 V with respect to the Ag/AgCl reference electrode, which is ~11.6 times higher than that of SnS₂. The enhanced PEC performance of Ni-doped SnS₂ is attributed to the broadening of its absorption spectrum, which facilitates the generation of more photogenerated charge carriers participating in redox reactions of water. Further, the enhanced PEC performance in Ni-SnS₂/g-C₃N₄ photoanode is also due to formation of a type-II heterojunction between Ni-SnS₂ and g-C₃N₄, which increases transfer and separation efficiency of photogenerated charge carriers.

सारांश

सौर ऊर्जा से ऊर्जा प्राप्ति (Energy harvesting) के लिए अर्धचालक (semiconducting) पदार्थों का उपयोग बढ़ती नवीकरणीय ऊर्जा की मांग को पूरा करने हेतु अत्यधिक ध्यान आकर्षित कर रहा है। सौर ऊर्जा की सहायता से हाइड्रोजन (H_2) का उत्पादन एक व्यावहारिक तरीका है, जिससे सौर ऊर्जा का उपयोग किया जा सकता है और जीवाश्म ईंधनों के उपयोग से उत्पन्न पर्यावरणीय समस्याओं का समाधान किया जा सकता है। फोटोइलेक्ट्रोकेमिकल (PEC) जल विभाजन, सौर ऊर्जा और जल की सहायता से हाइड्रोजन उत्पादन के लिए एक प्रभावी विधि के रूप में उभरा है। हाल ही में, द्वि-विमीय (2D) पदार्थों ने अपनी अद्वितीय ऑप्टोइलेक्ट्रॉनिक गुणों, बड़े सतही क्षेत्र, और अच्छे चार्ज गतिशीलता के कारण ऊर्जा भंडारण और रूपांतरण अनुप्रयोगों में अपार संभावनाएं दिखाई हैं। वर्तमान शोध कार्य में विभिन्न 2D अर्धचालक पदार्थों का उपयोग करके फोटोएनोड डिज़ाइन करने और उच्च दक्षता वाले PEC जल विभाजन के लिए प्रभावशाली फोटोइलेक्ट्रोड विकसित करने की रणनीतियों पर ध्यान केंद्रित किया गया है।

इस कार्य में द्रश्यमान प्रकाश सक्रिय 2D टिन सल्फाइड (SnS_2) को हाइड्रोथर्मल विधि द्वारा संश्लेषित किया गया है ताकि इसके PEC जल विभाजन अनुप्रयोग की संभावनाओं का अध्ययन किया जा सके। SnS_2 की संरचनात्मक, भौमितिक और प्रकाशीय गुणों का विश्लेषण विभिन्न वर्णनात्मक तकनीकों की सहायता से किया गया है। यह पदार्थ ऐसे उपयुक्त बैंड पोजीशनों को प्रदर्शित करता है जो जल के रेडॉक्स संभावनाओं के अनुरूप हैं, जिससे यह PEC जल विभाजन के लिए उपयुक्त बनता है। हालांकि, फोटोजनित चार्ज वाहकों के उच्च पुनर्संयोजन दर के कारण इसकी कुल प्रदर्शन सीमित रहती है। इस प्रदर्शन को बेहतर बनाने हेतु कई रणनीतियाँ अपनाई गईं जैसे कि सुचालक पदार्थों के साथ नैनोसंयोजन (nanocomposite) बनाना, हेटरोजंक्शन का निर्माण, तथा संक्रमण धातुओं से डोपिंग करना।

SnS₂ को कार्बन नैनोट्यूब्स (CNT) के साथ इन-सीटू हाइड्रोथर्मल विधि द्वारा जोड़ा गया और इसके PEC जल विभाजन प्रदर्शन का अध्ययन किया गया। SnS₂ को 5, 10 और 20 भार प्रतिशत CNT के साथ जोड़ा गया ताकि इष्टतम संरचना निर्धारित की जा सके। CNT की इलेक्ट्रॉन-स्वीकारने की क्षमता SnS₂/CNT फोटोएनोड के लिए लाभकारी साबित होती है, जिससे PEC प्रदर्शन में सुधार होता है। 10 wt. % CNT के साथ SnS₂ में लगभग 0.6 mA/cm² की अधिकतम फोटोक्रेन्ट घनता प्राप्त होती है (Ag/AgCl संदर्भ इलेक्ट्रोड के सापेक्ष 1.0 V पर), जो शुद्ध SnS₂ की तुलना में लगभग 3 गुना अधिक है। यह सुधार इस कारण है कि CNT इलेक्ट्रॉनों के परिवहन के लिए इंटरफेस प्रदान करता है और चार्ज वाहकों के पुनर्संयोजन दर को कम करता है।

हालांकि SnS₂/CNT नैनोसंयोजन कुछ सुधार दर्शाता है, परन्तु PEC प्रदर्शन में वृद्धि सीमित है। आगे बढ़ते हुए, SnS₂ और g-C₃N₄ के बीच एक टाइप-II हेटरोजंक्शन बनाकर और भी बेहतर परिणाम प्राप्त किए गए हैं। द्रश्यमान प्रकाश सक्रिय SnS₂/g-C₃N₄ टाइप-II हेटरोजंक्शन को 10, 20 और 30 wt. % g-C₃N₄ के साथ केमिसॉर्प्शन विधि द्वारा संश्लेषित किया गया। इनमें से SnS₂/g-C₃N₄ -20 (20 wt. % g-C₃N₄) सबसे अधिक ~1.0 mA/cm² की फोटोक्रेन्ट घनता देता है, जो कि शुद्ध SnS₂ की तुलना में लगभग 5 गुना अधिक है। यह वृद्धि टाइप-II हेटरोजंक्शन के निर्माण और स्वयं प्रेरित आंतरिक विद्युत क्षेत्र के कारण है, जो चार्ज वाहकों को स्थानांतरित करने में सहायता करता है और पुनर्संयोजन दर को प्रभावी रूप से कम करता है।

इसके अतिरिक्त, SnS₂ की विद्युत और प्रकाशीय गुणों को ट्यून करने हेतु उसमें निकल (Ni) डोपिंग का प्रभाव भी अध्ययन किया गया। Ni डोपिंग SnS₂ की विद्युत चालकता और प्रकाश अवशोषण को बढ़ाता है। Ni-डोपेड SnS₂ फोटोएनोड्स को 3, 6 और 10 wt. % डोपिंग स्तर के साथ हाइड्रोथर्मल तकनीक द्वारा तैयार किया गया। इनमें से 6 wt. % Ni डोपिंग (6-NSS) वाला फोटोएनोड लगभग 2.5 mA/cm² की फोटोक्रेन्ट घनता देता है, जो कि शुद्ध SnS₂ की तुलना में लगभग 8 गुना अधिक है। Ni

डोपिंग के कारण सक्रिय साइट्स की संख्या बढ़ती है, जिससे जल विभाजन अभिक्रियाओं के लिए अधिक प्रतिक्रिया क्षेत्र मिलता है। साथ ही, उत्पन्न दोष चार्ज वाहकों के ट्रैपिंग साइट्स के रूप में कार्य करते हैं, जिससे पुनर्संयोजन दर में कमी आती है और प्रदर्शन में वृद्धि होती है।

अंततः, Ni डोपिंग और टाइप-II हेटरोजंक्शन निर्माण के संयुक्त प्रभाव का PEC प्रदर्शन पर अध्ययन किया गया। इसके लिए Ni-डोपेड SnS_2 और $\text{g-C}_3\text{N}_4$ के बीच हेटरोजंक्शन बनाया गया और इसके प्रदर्शन की तुलना शुद्ध SnS_2 से की गई। Ni- $\text{SnS}_2/\text{g-C}_3\text{N}_4$ फोटोएनोड 1.0 V (Ag/AgCl संदर्भ इलेक्ट्रोड) पर लगभग 3.5 mA/cm^2 की फोटोक्रेन्ट घनता देता है, जो कि SnS_2 की तुलना में लगभग 11.6 गुना अधिक है। इस प्रदर्शन में वृद्धि का श्रेय Ni डोपिंग द्वारा प्रकाश अवशोषण स्पेक्ट्रम के विस्तार को जाता है, जिससे अधिक फोटोजनित चार्ज वाहक उत्पन्न होते हैं और रेडॉक्स अभिक्रियाओं में भाग लेते हैं। साथ ही, Ni- SnS_2 और $\text{g-C}_3\text{N}_4$ के बीच टाइप-II हेटरोजंक्शन का निर्माण चार्ज वाहकों के स्थानांतरण और पृथक्करण की दक्षता को बढ़ाता है, जिससे PEC प्रदर्शन और बेहतर होता है।

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Table 5.1: Comparison of PEC performance of different SnS₂-based nanostructures.

Nomenclature

Symbol	Description
α	Absorption coefficient
e	Electron Charge
ϵ_0	Permittivity of vacuum
ϵ_r	Dielectric constant
E_g	Band gap
N_d	Donor density
V	Applied potential
V_{fb}	Flat band potential
K_B	Boltzmann constant
ν	Frequency of photons
T	Absolute temperature
θ	Phase angle
Z'	Real part of the impedance
Z''	Imaginary part of the impedance
R_s	Electrolyte resistance
R_{ct}	Charge transfer resistance
C_{dl}	Double layer capacitance
J_{ph}	Photocurrent density
λ	Wavelength of monochromatic light
P	Incident power density
h	Planck's constant
η	Solar to hydrogen efficiency