Extended Abstract

(For Pre-PhD Open Seminar)

Fabricating Heterostructured Transition Metal Electrocatalysts for Energy-Saving H_2 Production Coupled with Organic Molecule Oxidation

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The rise in worldwide energy consumption, depletion of fossil fuel sources and an immediate need for mitigation of greenhouse gas emissions has accelerated the move towards clean and sustainable energy technologies. Within this context, hydrogen has become an attractive energy carrier due to its high gravimetric energy density (120 MJ/Kg) as well as net zero carbon emissions. Of the several routes for hydrogen synthesis, the electrochemical water splitting driven by renewable energy sources is regarded as one of the most sustainable and environmentally friendly approaches. However, the slow kinetics of the oxygen evolution process (OER), which proceeds at high overpotentials and consumes a large share of the energy during electrolysis, limits the broad application of conventional water electrolysis. To overcome these limitations, the replacement of OER by thermodynamically favourable alternative anodic oxidation reactions, such as sulfur oxidation reaction (SOR), ethanol oxidation reaction (EOR), and hydrazine oxidation reaction (HzOR), has emerged as an effective strategy to reduce cell voltage and enhance efficiency of the hydrogen production. The successful implementation of these alternative oxidation reactions depends on the development of highly active, durable, and cost-effective electrocatalysts. In this context, transition metal-based catalysts, especially nitrides, sulfides, phosphides, oxides and their heterostructures, are attracting significant attention due to their earth abundance, adjustable electronic structures and superior electrocatalytic activity. This thesis covers the global energy situation, basic principles of electrochemical hydrogen generation, limitations of traditional water electrolysis, and recent advancements in catalyst design strategies for replacing the anodic oxidation of water with other reactions, which provides a basis for the design of next-generation electrocatalysts for sustainable and energy-saving hydrogen production.

Chapter 1: Introduction

This chapter starts with an introduction of the increase in global energy demand for green and sustainable environment, leading to the growth in the research of electrochemical technologies. The use of water electrolysis is a sustainable method for hydrogen production; however, the efficiency is restricted by sluggish kinetics of OER. To overcome these limitations, this chapter discusses the need of alternate anodic oxidation reactions like SOR, EOR, HzOR etc. that have been proved to be a successful technology for reducing the energy consumption and to improve the efficiency of electrochemical H_2 production.

Chapter 2: Materials & Methodology

This chapter describes the materials and experimental methods used in the experiments of the research work. It further highlights all the characterizations opted to analyse the crystal structure, morphology, composition, oxidation state. Additionally, the description of all the electrochemical techniques employed to study the electrocatalytic performance of the catalysts are reported.

Chapter 3: Porous Mo Modified Ni_3N/Ni_3S_2 Hetero Interfacing for Facile Sulfur Oxidation Mediated Green H_2 Production

Development of nano catalyst systems with extended durability toward sulfion oxidation reaction (SOR) offers an energy efficient route to green H_2 production and process harmful industrial waste to value added chemical. However, most of the reported nanocatalysts for the above operation suffer from sulfur poisoning leading to compromised durability. In this work, a Mo doped Ni_3N/Ni_3S_2 heterointerface is designed that exhibits superior SOR activity and adequate durability together by combining the advantages of transition metal nitrides and sulphides. The study further revealed that a certain amount of Mo doping is desirable for the resulting Mo@Ni_3N/Ni_3S_2 to exhibit optimized catalytic activity well supported by the density functional theory (DFT) analysis. A current density (j_{SOR}) value of 100 mA cm^{-2} is realized at low potential (V_{RHE}) of 0.36 V in 1.0 M Na_2S + 1.0 M NaOH solution. The heterostructure with a porous cactus like morphology possibly resisted S_8 deposition and the SOR durability beyond 100 h is witnessed without compromising the efficiency. The efficacy is reflected in the two-electrode mode and j_{SOR} value of 100 mA cm^{-2} is observed at a cell voltage value of 0.45 V in 1.0 M Na_2S + 1.0 M NaOH supporting the viability of the system.

Chapter 4: Tuning the Crystal Facets of MoP_2 in a Phosphide–Nitride Heterostructure via Interface Engineering for Energy-Efficient Ethanol Oxidation-Coupled H_2 Production

Efforts to enhance the electrocatalytic activities of transition-metal-based nanocatalyst systems are important to improve their viability and commercial exploitation. In this work, the crystal facets of MoP_2 in an MoP_2/MoN heterojunction are tailored using a controlled hydrothermal procedure. The active facets of MoP_2 (131) and MoN (200) phases in this heterostructure possess similar lattice spacing and display effective EOR-promoted H_2 production ability under alkaline conditions. The j_{EOR} and j_{HER} values of 100 mA cm^{-2} are realized at 1.34 and −0.18

V_{RHE}, respectively, in a 1.0 M KOH + 1.0 M EtOH solution, supporting the activity. The *j* value of 100 mA cm^{-2} is realized at a reasonable potential value of 1.62 V in a 1.0 M alkaline solution in the two-electrode mode. Importantly, the EtOH to acetate conversion is realized at a relatively high yield of 75.78 % at 1.60 V, supporting the viability of the process. The post-electrolysis characterization revealed retention of major structural features, supporting the durability of the heterostructure and the viability of further practical implications. The study revealed that tuning of the crystal facets offers an effective means to fine-tune the electrocatalytic behaviour and improve the energy efficiency of the overall electrocatalytic operation.

Chapter 5: Dual-Heterointerfacing for Facet Oriented Shape Modulation in VP for Hydrazine Oxidation Coupled Energy Efficient H_2 Production

Facet engineering remains one of the key avenues to develop nano-electrocatalyst with tailored activity and durability. In this report, a dual-heterointerfacing strategy is utilized to develop phosphide heterostructure with high energy facet of the active component exposed for effective catalytic activity. As a proof of concept, sequential heterointerfacing between VP and Ni_2P followed by MoO_3 is carried out to gradually expose the (101) facet of the active VP component in the dual heterostructure. The gradual change in intensity of the key facets with each heterointerfacing have supported the viability of the strategy. The resulting $Ni_2P/VP/MoO_3$-NF displayed superior HzOR activity with j_{HzOR} value of 100 mA/cm^2 realized at an ultralow potential of 0.033 V_{RHE} with extended durability. This performance of the system was observed to be notably superior compared to that of the other controls (0.076-0.170 V_{RHE}) supporting the viability of the strategy. The electrode displayed bifunctionality and a symmetrical electrolyzer employing the same as both the electrodes operated at 50 mA/cm^2 at 0.02 V for 120 h without loss in activity supporting the viability for practical energy efficient H_2 production. The strategy is general and employable in other heterostructures to optimize the activity and sustainability for various electrocatalytic applications.

Chapter 6: Conclusion

The chapter provides a brief overview of the thesis findings and highlights the possible directions of future research for enhancing the efficiency, feasibility and scalability of alternate oxidation-assisted hydrogen production systems. In the third chapter, the synergistic interaction between the nitride and sulfide phases, along with optimized Mo incorporation, was exploited to enhance HER and SOR electrocatalytic performance. In the fourth chapter, crystal facet engineering of phosphide-nitride heterostructures was utilized to improve MOR coupled HER. In the fifth chapter, dual heterointerfacing was adopted to simultaneously regulate crystal facet exposure, morphology, and interfacial electronic interactions, thereby enhancing hydrazine-assisted HER performance.

List of Publications

1. **Setia, Y.**; Paltasingh, S. N.; Nayak, S. K.; Sinha, A. S. K.; Ojha, U.; Sahoo, M. K. Porous Mo modified Ni_3N/Ni_3S_2 Hetero interfacing for facile sulfur oxidation mediated Green H_2 production. *Adv. Sustainable Syst.* **2025**, *9* (9), e00407.
2. **Setia, Y.**; Paltasingh, S. N.; Nayak, S. K.; Ojha, U.; Sahoo, M. K. Tuning the crystal facets of MoP_2 in a phosphide–nitride heterostructure via interface engineering for energy-efficient ethanol oxidation-coupled H_2 production. *J. Mater. Chem. A* **2026**, *14* (20), 12207–12222.
3. **Setia, Y.**; Samal, A.; Nayak, S. K.; Ojha, U.; Sahoo, M. K. Dual-Heterointerfacing for Facet Oriented Shape Modulation in VP for Hydrazine Oxidation Coupled Energy Oxidation H_2 Production. (Communicated)

Book Chapters

1. **Setia, Y.**; Bhatt, N.; Bellamkonda, S.; Sahoo, M.K. Electrokinetics of High-Entropy Materials for Energy Storage Devices. Wiley **2026**.
2. **Setia, Y.**; Bhatt, N.; Kumar, M.; Sahoo, M.K. Noble-Metal-Free High-Entropy Alloys for Energy Storage Applications. Wiley **2026**.

List of Conferences

1. *"Twenty Fourth National Convention of Electrochemists"* **NCE-24**, Amrita Vishwa Vidyapeetham-**Coimbatore**, 27^{th}-28^{th} April **2026**.
2. *"Second International Conference on Next Generation Sustainable Materials for Water and Energy Solutions"* **SuWatE$^+$**, VIT-AP, **Andhra Pradesh**, 26^{th}-28^{th} March **2026**. **(Awarded with Best Poster Presentation)**
3. *"Nanomaterials and Sustainable Applications"* **NANO-SA**, Chhatrapati Sambhajinagar, Aurangabad-**Maharashtra**, 11^{th}-12^{th} **2026**.

4. *"International Conference on Advanced Materials for Energy, Environment and Sustainability"* **AMEES**, IIT-Bhubaneswar, **Odisha**, 16th-18th May **2025**.
   (Awarded with Best Poster Presentation)
5. *"International Conference on Shaping the Energy Future: Challenges and Opportunities"* **SEFCO**, CSIR-IIP, Dehradun, **Uttarakhand**, 23rd-25th April **2025**.
6. *"International Symposium on Advances in Electrochemical Science and Technology"* **iSAEST**, Thiruvananthapuram, **Kerala**, 08th-10th January **2025**.
7. *"International Union of Materials Research Societies-International Conference in Asia"* **IUMRS-ICA**, UGC-DAE, Indore, **Madhya Pradesh**, 03rd-06th December **2024**.
8. *"National Conference on Students Chemical Engineering Congress"* **SCHEMCON**, Rajiv Gandhi Institute of Petroleum Technology, RGIPT, **Uttar Pradesh**, 20th-21st September **2024**.

- **Exhibition:**

  India Energy Week-2025 (New Delhi)

  Showcased the prototype on Electrochemical Generation of Hydrogen from Sour Water in Collaboration with **NRL** (**Numaligarh Refinery Limited**)