Extended Abstract

Novel Asymmetric Atomic Sites Semiconductor Catalysts for Enhanced Solar Water Splitting

Department of Energy & Human Sciences
Rajiv Gandhi Institute of Petroleum Technology
(An Institution of National Importance)
Jais, Amethi, Uttar Pradesh, India

Name of Student: Dileep Kumar **Roll Number: 21BS0015**

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Name of the Supervisor: Dr. Vipin Amoli

Abstract

The rapid increase in greenhouse gas emissions due to extensive fossil fuel consumption has created an urgent demand for sustainable and carbon-neutral energy technologies. Among the available alternatives, solar energy stands out as an abundant and renewable resource. In this context, solar-driven hydrogen production through photocatalytic and photoelectrochemical (PEC) water splitting has emerged as promising strategies. However, their large-scale implementation remains constrained by the lack of efficient catalysts, primarily due to poor visible light response, unfavourable band structures, rapid recombination of photogenerated charge carriers, and sluggish surface reaction kinetics.

Single-atom catalysts (SACs) involving metal single atoms are trapped on semiconductor supports, have demonstrated maximum atomic utilization efficiency and great potential in catalytic activity. The stabilization of single atoms requires specific anchoring sites that can be surface defects, unsaturated atoms, and any heteroatoms that stabilize single atoms through metal-support interactions. Defect-rich metal oxides have been identified as more suitable platforms in which oxygen or metal vacancies act as trap centers for single atoms. In particular, asymmetric atomic sites (AAS), generally expressed as M_{SA}-O_v-M_2 (where M_{SA} denotes the trapped metal single atom, O_v is an oxygen vacancy, and M_2 represents the semiconductor support), are identified as the most preferable active catalytic sites for catalytic activity. However, the generation of defect-rich supports involves undesired consumption of H_2 gas and/or H_2/Ar gas and energy-intensive processes rendering them impractical and uneconomic. Additionally, achieving precise control over AAS remains a significant challenge.

To address these challenges, this thesis explores faceted nanostructured semiconductors as alternative platforms to create AAS catalysts. Faceted nanostructures inherently possess under-coordinated surface atoms that can act as anchoring sites for metal single atoms, eliminating the need for external defect engineering. TiO_2, an extensively studied semiconductor, has been engineered to exhibit various exposed facets such as (101), (010), (001), and (111), each facet offering its own unique surface atomic arrangement. The presented work focuses on the rational design of asymmetric atomic sites catalysts (AASC) by doping metal single atom on faceted TiO_2 nanostructures, coupling the multiple advantages of crystal facet engineering with single atom catalysis in a single material for enhanced hydrogen production. The AASC are fabricated by a simple and scalable hydrothermal synthesis rout and characterized using state-of-art experimental techniques. The experimental findings are supported by theoretical calculations to establish structure–activity relationships. The presented work provides new insights into the role of AAS in solar hydrogen generation, contributing to the fundamental understanding and practical development of next-generation photocatalysts. The structure of the thesis is as follows:

Chapter 1: Introduction

This chapter introduces the fundamental principles of solar water splitting, including both photocatalytic and PEC approaches. It discusses the working mechanisms, commonly used catalysts, and their inherent limitations. The chapter further reviews recent advancements in SACs, asymmetric atomic sites, and facet engineering. Special emphasis is

placed on TiO_2-based systems, including facet-dependent properties and strategies for stabilizing single atoms.

Chapter 2: Materials, Synthesis Methods, Characterization Techniques, and Photocatalytic & Photoelectrochemical Testing Setup

This chapter presents a comprehensive description of the materials used, synthesis procedures, characterization techniques, and experimental setups employed for evaluating photocatalytic and PEC performance of the materials presented in the thesis. The chapter begins with details of the precursor chemicals and materials, synthesis methodology highlighting the conditions optimized for achieving controlled facet exposure and stable incorporation of single metal atoms. The chapter further outlines the various characterization techniques used to investigate the structural, morphological, optical, and electronic properties of the synthesized materials. Techniques such as X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM/TEM), nitrogen adsorption–desorption analysis, UV–Vis spectroscopy, and X-ray absorption spectroscopy (XAS) are described to provide insights into crystallinity, surface morphology, electronic structure, and defect states. In addition, charge carrier dynamics are analyzed using time-resolved photoluminescence (TRPL) and electrochemical measurements to understand charge separation and transport behaviour.

Finally, the chapter details the experimental setups used for evaluating the photocatalytic and PEC water splitting performance of the developed materials. This includes device designs, light sources, experimental conditions, gas analysis using gas chromatography (GC). The configuration of PEC systems including electrode fabrication using spray pyrolysis deposition, electrolyte selection, and measurement conditions are outlined.

Chapter 3: Cu_{SA}-O_v-Ti_{3c} Atomic Sites Catalyst for Enhanced Photocatalytic Water Splitting

This chapter presents the development of Cu_{SA}-O_v-Ti_{3c} AASC by doping Cu-single atoms on (111)-faceted TiO_2. Experimental results and density functional theory (DFT) calculations reveal that Cu_{SA} specifically substitutes for the five-coordinated Ti atoms (Ti_{5c}) next to three-coordinated Ti atoms (Ti_{3c}), with the creation of oxygen vacancy (O_v) resulting in the formation of Cu_{SA}–O_v–Ti_{3c} AAS. The optimized catalyst demonstrates excellent visible-light-driven photocatalytic performance, achieving hydrogen evolution rates of 8.3 mmol h^{-1} g^{-1}, approximately 250 times higher than pristine TiO_2-based catalysts. Experimental and theoretical investigations reveal that Cu_{SA}-O_v-Ti_{3c} sites play multiple roles in (i) enhancing light harvesting, charge transfer dynamics and redox capability of photoexcited electrons; (ii) enhanced adsorption and polarization of H_2O molecules due to intrinsic charge heterogeneity at HAAS; (iii) facilitating electron transfer from Cu_{SA}-O_v-Ti_{3c} to H_2O molecules; and (iv) elevating the *d*-band center towards the Fermi level, thus facilitating the better adsorption of intermediates. Furthermore, a comparative analysis with recent Cu/TiO_2-based photocatalysts is provided to highlight the superior performance of the developed system.

Chapter 4: Cu Single Atom (Cu_{SA}) Doped Faceted TiO_2 Thin Films Electrodes for Enhanced PEC Water Splitting

This chapter presents the fabrication of Cu single atom doped TiO_2 thin-film electrodes with (101) and (111) facets for PEC water splitting. The electrodes were prepared via single-step spray pyrolysis deposition technique and evaluated for PEC water splitting. The fabricated electrodes were tested using linear cyclic voltammetry (LCV) and chronoamperometry (CA) techniques to assess their performance in photoelectrochemical (PEC) water splitting. Despite their n-type semiconducting nature, $Cu_{SA}(0.85)T_{101}$ and $Cu_{SA}(0.85)T_{111}$ exhibit cathodic response. The optimized electrode $Cu_{SA}(0.85)T_{111}$ (with 0.85 at% Cu) (~50 µm thickness) delivers a photocurrent density of -2.22 mA cm^{-2} at −1.0 V vs reversible hydrogen electrode (RHE) under AM 1.5G illumination, approximately 2.92 times higher than its {101}-faceted analogue ($Cu_{SA}(0.85)T_{101}$). It further exhibits a low onset potential (−0.22 V vs RHE), a small overpotential (−0.28 V), and an incident photon-to-current efficiency (IPCE) of 27.1% at 420 nm. The enhanced PEC performance of $Cu_{SA}(0.85)T_{111}$ photoelectrode is due to the presence of Cu^{2+} single a and high concentration of O_v, which introduce shallow donor states, narrow the band gap, and improve visible-light absorption. The increased donor density reduces band bending and the depletion width, while defect-induced surface states partially pin the Fermi level. Together, these effects promote efficient charge separation and direct interfacial charge transfer (IFCT), leading to superior PEC performance. Furthermore, a comparative analysis with previously reported Cu/TiO_2-based photocathodes is provided to highlight the superior performance of the developed system for developing low-cost, solar-driven hydrogen production.

Chapter 5: Conclusion and Future Scope

This chapter summarizes the results and outlines the future scope of the work.

Research Publications:

1. Highly Asymmetric Cu_{SA}-O_v-Ti_{3c} Atomic Sites Catalyst for Unprecedented Solar Hydrogen Generation
   D. Kumar, A. Mishra, Shubham, Hemant, S. Bhattacharjee, R. R. Urkude, B. Ghosh, A. Bhaumik, A. K. Sinha*, A.S.K. Sinha and V. Amoli*
   Advanced Energy Materials, 2024, 14, 2401964
2. Defect-Induced Band Bending Mitigation Enables Bias and Photo-assisted Cathodic Response in Cu Single Atom Doped Faceted TiO_2 Thin Films Electrodes
   D. Kumar, Hemant, A. K. Verma, Siddhi Agrawal, Jaswant Singh Bhati, Shubham, Shikha Singh, Vipin Amoli*
   (Revision submitted)
3. Waste Ilmenite Sludge-derived Low-cost Mesoporous Fe-doped TiO_2: A Versatile Photocatalyst for Enhanced Visible Light Photocatalysis Without a Cocatalyst
   A. Mishra, V. Verma, A. Khan, ***D. Kumar***, T. S. Khan, V. Amoli*, A. K. Sinha*
   Journal of Environmental Chemical Engineering, 2023, 11, 110319.
4. A Novel Ternary Metal Oxide Cascade Z-scheme Heterojunction for Efficient CO_2 Photoconversion Without a Co-catalyst

P. K. Prajapati, D. Garg, A. Malik, ***D. Kumar***, V. Amoli, S. L Jain*
Journal of Environmental Chemical Engineering, 2023, 10, 108147.

5. Synthesis of Propylene Carbonate over Bimetallic Fe-Cu/SBA-15 Catalyst from CO_2 and Propylene Oxide
   Akash Mandal, Neelanjana Ghosh, Bhabani Malakar, ***Dileep Kumar***, Vipin Amoli*, Asim Bhaumik*, Biswajit Chowdhury*
   Asian Journal of Organic Chemistry 2025, 10, 202500432.
6. Highly Deformable and Durable PEDOT:PSS Printed Electrodes via Tailored Chemistry and Fabrication Synergy for Scalable Wearable Electronics
   Hemant, Shubham, ***Dileep Kumar***, Chaitanya Yadav, Pushkar Raj, Amandeep, Vipin Amoli*
   Advanced Materials Technologies, 2025, 0:e01625.
7. Dual Atom Doped Faceted TiO_2 for Enhanced Solar Hydrogen Generation.
   D. Kumar, Vipin Amoli ***(manuscript under preparation).***

Research publications 1 and 2 are included in the Thesis