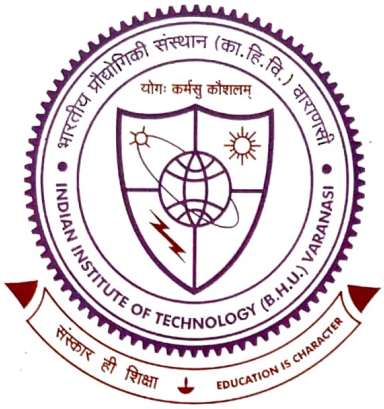
Heterostructure Photocatalysts for H_2O_2 Production



Thesis submitted in partial fulfillment for the
Award of Degree

Doctor of Philosophy

By

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I, ***"Uttam Kumar"***, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of ***"Prof. Indrajit Sinha"*** from ***"January 2021"*** to ***"May 2025"***, at the ***"Department of Chemistry"***, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credit to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports, dissertations, theses, *etc.*, or available at websites, and have not included them in this thesis and have not cited as my own work.

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It is certified that the above statement made by the student is correct to the best of my knowledge.

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DEDICATED TO MY LOVING PARENTS…

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Uttam Kumar

Abbreviations

Abbreviation	Full Form
DDW	Double-distilled water
DI	Deionized water
TC	Tetracycline
MAPS	Materials and Process Simulation
MD	Molecular dynamics
MNDO	Modified neglect of diatomic overlap
RDF	Radial distribution function
LAMMPS	Large-scale Atomic/Molecular Massively Parallel System
XRD	X-ray diffractometer
FCC	Face-centered cubic
WCA	Water Contact Angle
VSM	Vibrating sample magnetometry
SEM	Scanning electron microscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
UV-DRS	Ultraviolet diffuse reflectance spectroscopy
PL	Photoluminescence
FT-IR	Fourier transform infrared spectroscopy
TEM	Transmission electron microscopy
TOF	Turnover frequency
$^{\bullet}OH$	Hydroxyl radical

$^{\bullet}OOH$	Hydroperoxyl radical
OH^-	Hydroxide ion
NaOH	Sodium hydroxide
$O_2^{\bullet-}$	Superoxide radical
H_2O_2	Hydrogen peroxide
VB	Valence band
CB	Conduction band
NBT	Nitro blue tetrazolium
EIS	Electrochemical Impedance Spectroscopy
MS	Mott-Schottky
IPA	Isopropyl alcohol
NHE	Normal hydrogen electrode
PBQ	para-Benzoquinone
EDTA	Ethylene diamine tetra-acetic acid

Table of Contents

List of Figures

Chapter 8

List of Tables

Preface

Hydrogen peroxide (H_2O_2) is a widely utilized green oxidizing agent in various applications, including chemical synthesis, pulp bleaching, cleaning, and disinfection. The photocatalytic synthesis of H_2O_2 represents a safer, more sustainable, and cost-effective approach, relying solely on sunlight, water, and an appropriate photocatalyst. Homogeneous photocatalysis involves a molecular catalyst in the same phase as the reactants. In other words, if the reactants are liquids, then the catalyst is also a liquid and is soluble in the reaction mixture. In contrast, heterogeneous photocatalysis employs solid catalyst particles suspended in a liquid medium, enabling straightforward separation and reuse. Nevertheless, single-component photocatalysts commonly face limitations such as insufficient visible light absorption, rapid charge carrier recombination, and restricted redox capabilities.

To overcome the limitations of single-component photocatalysts, this thesis focuses on developing advanced heterogeneous systems for efficient H_2O_2 production. One approach involves designing composite or heterostructure photocatalysts combining two components with distinct roles, one acting as an electron donor (reducing) and the other as an acceptor (oxidizing). Another strategy incorporates plasmonic metal-semiconductor systems to enhance visible light activity. However, the role of reactant adsorption affinity in heterojunction design is often overlooked, despite its critical influence on photocatalytic efficiency. Large-scale molecular dynamics (MD) simulations were used to investigate the interaction of oxygen and water molecules with the different parts of the heterojunction photocatalyst surface. Additionally, challenges in photocatalyst recovery, especially with non-magnetic nanoparticles, hinder practical

applications due to separation difficulty, increased cost, and potential secondary pollution. To address this, the thesis also explores magnetically recoverable heterostructure photocatalysts for effective in situ H_2O_2 generation and improved Fenton degradation performance.

In this context, the present thesis focuses on designing various heterostructure photocatalysts for H_2O_2 production. Thus, the thesis deals with the synthesis 2D $MoS_2/MnIn_2S_4$, $Ag/NiFe_2O_4/CuWO_4$, $Ag/s\text{-}(Co_3O_4/NiFe_2O_4)$, Ag loaded starch functionalized-Fe_3O_4, and Ag loaded starch functionalized-Fe_3O_4/AgI, heterostructure photocatalyst samples. These samples were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Vibrating sample magnetometer (VSM), and X-ray photoelectron spectroscopy (XPS). Bandgaps were determined using solid-state UV-visible diffuse reflectance spectroscopy (UV-DRS). Mott-Schottky (MS) and Nyquist plots were generated through electrochemical studies on an electrochemical workstation. The adsorption property of photocatalysts was observed by measuring the water contact angle.

The thesis then evaluates the photocatalytic activities of the prepared samples with respect to H_2O_2 production. The photocatalysts were used to degrade TC using in-situ produced H_2O_2. The H_2O_2 production studies in the present thesis have been compared with the data in the recently reported literature. Simultaneously, MD simulations have been made to investigate the mechanisms involved in the adsorption of O_2 and H_2O over the photocatalyst's surface. The specific objectives of this thesis are outlined below.

Chapter 1 of this thesis provides a concise introduction to the importance of H_2O_2, outlining various methods of its production with a particular emphasis on photocatalytic

approaches. The chapter delves into the fundamental mechanisms of H_2O_2 generation via photocatalysis, specifically through the oxygen reduction reaction (ORR) and water oxidation reaction (WOR). It further introduces the concept of heterostructure photocatalysis, explaining the principles behind their design and the critical role they play in enhancing photocatalytic performance. Key factors such as light absorption, charge separation, charge migration, and charge utilization in oxidation and reduction reactions are discussed as essential elements influencing photocatalytic efficiency.

In this context, the construction of efficient photocatalysts becomes vital, and the design of staggered heterostructures is highlighted as a promising strategy to overcome existing limitations. Particular attention is given to the photocatalytic production of H_2O_2 and its in situ application for antibiotic degradation. The chapter also includes a comprehensive review of previously reported photocatalysts employed for H_2O_2 generation, which provides valuable insights for identifying current challenges and research gaps. This literature survey forms the basis for defining the scope and objectives of the present study, which are clearly outlined at the end of the chapter.

Chapter 2 outlines the experimental procedures in detail, including the materials used, the photocatalytic methodologies applied, and the instrumentation employed for characterizing the synthesized photocatalysts and analyzing their reaction kinetics. It also includes the basics of MD simulation.

Chapter 3 presents the design of a novel 2D $MoS_2/MnIn_2S_4$ heterostructure photocatalyst synthesized via a two-step hydrothermal method with different weight % of $MnIn_2S_4$. A variety of characterization techniques such as including XRD, SEM, TEM, UV-DRS, PL,

contact angle measurements, and electrochemical analyses, were employed to explore the intrinsic relationship between the 2D heterointerface structure and the significantly enhanced photocatalytic performance of the heterostructure. The photocatalytic H_2O_2 production activity of the synthesized heterostructure photocatalysts was evaluated under different conditions. Furthermore, the underlying mechanism of H_2O_2 generation was systematically investigated. Scavenger tests were conducted to identify the reactive species involved in the photocatalytic H_2O_2 production process.

Chapter 4 focuses on the design and development of a magnetically recyclable, visible-light-responsive composite photocatalyst $Ag/NiFe_2O_4/CuWO_4$ engineered for efficient H_2O_2 production from pure water under oxygen purging. Later, the produced H_2O_2 was in situ utilized for tetracycline degradation. Various characterization techniques, such as XRD, TEM, VSM, BET, PL, EIS, and XPS, were employed to investigate the structural, morphological, magnetic, optical, and electronic properties of the photocatalyst. The selection of the composite components was guided by two key considerations: firstly, the suitable positions of the valence band (VB) and conduction band (CB) positions of the individual photocatalysts; and secondly, the requirement for effective oxygen adsorption on the reduction component, which is essential for H_2O_2 generation via photocatalysis. To evaluate the latter, classical molecular dynamics (MD) simulations were used, as they can reasonably predict oxygen affinity. The experimental results were quantitatively compared with relevant experimental results reported in the literature, providing insights into the material's photocatalytic behavior.

Chapter 5 focuses on the preparation of a silver-loaded, starch-functionalized $Co_3O_4/NiFe_2O_4$ ($Ag/s\text{-}Co_3O_4/NiFe_2O_4$) heterojunction photocatalyst for H_2O_2 production,

which was subsequently used in situ for the TC degradation. To better understand the system, large-scale classical MD simulations were employed, revealing that Co_3O_4 exhibits a relatively higher affinity for oxygen in water compared to $NiFe_2O_4$. The synthesized photocatalysts were thoroughly characterized using XRD, TEM, XPS, UV-DRS, and Mott-Schottky analysis, and PL studies were conducted to evaluate the band gaps, band alignments, and charge recombination behavior of the composites. A comprehensive understanding of the photocatalytic mechanism was achieved through the integration of experimental observations and computational insights.

Chapter 6 describes the photocatalytic H_2O_2 production activity on Ag-loaded starch functionalized magnetite (abbreviated as ASM) composite nanoparticles. The optical properties and band edges of the composite nanoparticles are thoroughly investigated. Their H_2O_2 production photocatalytic activity is compared to pristine Fe_3O_4 nanoparticles and Ag-loaded Fe_3O_4 nanoparticles (without starch functionalization). Photogenerated charge transfer and separation are examined using PL and electrochemical analysis. XPS analyzed the chemical species and their oxidation states on the composite surface. Large-scale classical MD simulations investigated the adsorption affinity of O_2 and H_2O molecules on the Fe_3O_4, SM, and ASM systems. Several control experiments and MD simulations were conducted to obtain insight into the photocatalytic H_2O_2 production mechanism.

Chapter 7 of this thesis investigates a Z-scheme heterojunction photocatalyst composed of Ag-loaded, starch-functionalized Fe_3O_4 nanoparticles integrated with AgI. The system was synthesized via a stepwise precipitation method. AgI was incorporated into the Ag-loaded starch-functionalized Fe_3O_4 due to its well-matched band alignment and strong

reduction capability, which are favorable for Z-scheme charge transfer. To optimize photocatalytic performance, AgI was loaded at varying concentrations of 5, 10, 20, and 30 wt% onto the Ag-loaded Fe_3O_4 composite. The composition, structure, morphology, optical properties, and band structure were investigated. Their photocatalytic performance was evaluated for the H_2O_2 production, as well as the in-situ utilization of the generated H_2O_2 for both neutral pH dark Fenton and photo-Fenton reactions. Moreover, the photocatalytic mechanism of this cascade reaction is examined and proposed based on a series of control experiments.

Chapter 8 presents a comprehensive summary of the photocatalytic performance of all the heterostructured photocatalysts developed in this thesis for H_2O_2 production. The photocatalytic activities are systematically compared under different reaction conditions, including pure water and water with continuous O_2 purging, to evaluate their efficiency and practical applicability. The results are also benchmarked against recently reported photocatalysts from the literature, highlighting the advantages and improvements achieved through the designed heterostructures. In conclusion, the chapter outlines the future directions and potential applications of the research, suggesting ways to further enhance photocatalyst design and expand their use in environmental and energy-related applications.