
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 H₂O₂ generation and improved Fenton degradation performance.

In this context, the present thesis focuses on designing various heterostructure photocatalysts for H₂O₂ production. Thus, the thesis deals with the synthesis 2D MoS₂/MnIn₂S₄, Ag/NiFe₂O₄/CuWO₄, Ag/s-(Co₃O₄/NiFe₂O₄), Ag loaded starch functionalized-Fe₃O₄, and Ag loaded starch functionalized-Fe₃O₄/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 H₂O₂ production. The photocatalysts were used to degrade TC using in-situ produced H₂O₂. The H₂O₂ 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 O₂ and H₂O 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 H₂O₂, outlining various methods of its production with a particular emphasis on photocatalytic

approaches. The chapter delves into the fundamental mechanisms of H₂O₂ 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 H₂O₂ and its in situ application for antibiotic degradation. The chapter also includes a comprehensive review of previously reported photocatalysts employed for H₂O₂ 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 MoS₂/MnIn₂S₄ heterostructure photocatalyst synthesized via a two-step hydrothermal method with different weight % of MnIn₂S₄. 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 H₂O₂ production activity of the synthesized heterostructure photocatalysts was evaluated under different conditions. Furthermore, the underlying mechanism of H₂O₂ generation was systematically investigated. Scavenger tests were conducted to identify the reactive species involved in the photocatalytic H₂O₂ production process.

Chapter 4 focuses on the design and development of a magnetically recyclable, visible-light-responsive composite photocatalyst Ag/NiFe₂O₄/CuWO₄ engineered for efficient H₂O₂ production from pure water under oxygen purging. Later, the produced H₂O₂ 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 H₂O₂ 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 Co₃O₄/NiFe₂O₄ (Ag/s-Co₃O₄/NiFe₂O₄) heterojunction photocatalyst for H₂O₂ 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 Fe₃O₄ composite. The composition, structure, morphology, optical properties, and band structure were investigated. Their photocatalytic performance was evaluated for the H₂O₂ production, as well as the in-situ utilization of the generated H₂O₂ 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 H₂O₂ production. The photocatalytic activities are systematically compared under different reaction conditions, including pure water and water with continuous O₂ 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.