PREFACE

The energy demand worldwide continues to grow due to ongoing industrial development and population growth, while traditional fossil fuels such as oil, coal, and natural gas are being depleted rapidly. These fossil fuels are the primary source of energy that meets our current needs. However, the availability of fossil fuels in the future is a major cause for concern. The combustion of fossil fuels poses several environmental threats through the release of toxic gases and limits access to conventional energy sources. These adverse effects on the environment contribute to global warming. The search for alternative pathways has intensified due to the growing awareness of the energy crisis and greenhouse gas emissions. Research is currently divided into two main areas - one focused on renewable and environmentally friendly energy sources and the other on electrochemical devices capable of generating clean energy, such as photoelectrochemical cells, fuel cells, etc.

Harvesting solar energy sources through photoelectrochemical (PEC) water splitting to produce hydrogen is a promising approach to tackle energy and environmental concerns. Since 1972, when Honda and Fujishima introduced the application of titanium dioxide (TiO_2) in PEC water splitting, significant efforts have been directed toward enhancing photocathode stability and maximizing solar-to-hydrogen efficiency. While metal oxides such as TiO_2, Fe_2O_3, $BiVO_4$, and $SrTiO_2$ have been extensively explored, their wide band gap and slow charge transfer kinetics have typically constrained their solar-to-hydrogen conversion efficiency. CuO-based semiconductor materials have emerged as promising candidates for PEC water splitting because of their high efficiency, suitable band gap, and exceptional optical properties.

This thesis aims to develop a PEC device utilizing CuO-based semiconductor materials (e.g., CuO, CuO/Cu_2O, and $Cu_{1-x}Ni_xO$) as a photocathode for PEC hydrogen production. A viable strategy for designing a direct PEC water-splitting device involves identifying a band gap encompassing the entire solar spectrum, mainly the visible range, to achieve high photocurrent density, solar-to-hydrogen (STH) efficiency, and hydrogen production. The band edge alignment must straddle the redox potentials of hydrogen and oxygen and remain stable when exposed to electrolyte conditions and illumination. The primary obstacle currently involves creating reliable and effective systems for converting solar energy to chemical energy using CuO-based semiconductor materials for photoelectrochemical hydrogen production. Nanostructuring can overcome this obstacle by providing a larger surface area and active sites for the reaction. CuO is a low-cost and chemically stable transition metal oxide with excellent light absorption properties, making it an ideal material for harvesting solar energy in PEC. Additionally, the presence of plasmons significantly enhanced the PEC properties. Plasmon refers to collective oscillations of free electrons, where CuO's light absorption capabilities can be improved. The presence of plasmons can help reduce the overpotential required for the HER. The increased local fields and improved charge transfer dynamics lower the energy barrier for the reaction, making the PEC process more efficient.

The thesis is divided into seven chapters, and its brief explanation is given below:

Chapter 1 introduces a comprehensive review of the literature describing a detailed solution for renewable and sustainable energy sources, including a complete description of Photoelectrochemical cells, water splitting, and hydrogen production. In this chapter, the research work's motivation is described along with the background and fundamentals of Photoelectrochemical cells, the requirements for Photoelectrochemical cell components, the

photocathode's mechanism and reaction kinetics, the material selection for the photocathode, PEC hydrogen evolution reaction and an overview of several materials for PEC cell. This chapter also includes the main objective of the present work.

Chapter 2 discusses the various experimental techniques applied to the present investigation. It describes the experimental equipment, analysis techniques, and the various synthesis routes adopted to synthesize the samples. This chapter discusses pulsed laser deposition (PLD), which was used to synthesize the proposed system. This section discusses essential analysis techniques such as Finite Element Modeling (FEM) and Rietveld refinement analysis, as well as a detailed description of tools such as XRD, SEM, TEM, AFM, XPS, TGA, DSC, UV-visible, SERS, and cyclic voltammetry measurement, etc.

Chapter 3 aims to study anisotropic photoconduction CuO thin films, including extensive literature surveys. This chapter includes experimental and theoretical studies to check the photoconduction behavior of CuO ultrathin films. Moreover, two significant problems, anisotropy (directional dependence) in photoconduction behavior and non-reciprocity in the system have been described. The anisotropic photoconduction behavior of the thin films was observed by measuring and analyzing the I-V characteristics under AM1.5 G solar light.

Chapter 4 describes the study of plasmonic effects on hydrogen production using self-assembled CuO/Cu_2O as a photocathode in PEC cells. In this chapter, the formation of plasmons is evidenced through theoretical studies such as Finite Element Modelling (FEM) and Density Functional Theory (DFT) and experimental studies such as SERS, Ellipsometry, and XPS. The formation of plasmons significantly enhances hydrogen production. The photoelectrochemical investigations were done using cyclic voltammetry, linear sweep

voltammetry, and chronoamperometric measurements in dark and AM1.5 G solar light. This chapter also covers the main objectives of the present work.

Chapter 5 describes the facile synthesis of CuO nanoparticles using the hydrothermal method. The synthesized nanoparticles were used as photocathodes in a PEC cell to investigate the hydrogen evolution reaction (HER) activity. XRD, XPS, HR-SEM, and TEM measurements were analyzed to examine the structure and morphology. The light absorption property was investigated using UV-visible analysis. Semiconductor properties HER activity was investigated by Mott-Schottky plot, cyclic voltammetry, LSV, and chronoamperometric measurements, respectively.

Chapter 6 aims to study the effect of compositional variation of $Cu_{1-x}Ni_xO$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) on HER activity. The composition was varied by doping NiO in CuO with stoichiometric ratio. The compounds were synthesized using the solid-state reaction method at room temperature. In this chapter, the structural, thermal, morphology, and photoelectrochemical properties of all the pure and composite samples were analyzed. The primary aim of this chapter is to find the photocathode with high HER activity.

Chapter 7 concludes the thesis with results and future scope of the research work.