Chapter – 7

Conclusion and Future Scopes

CHAPTER 7: Conclusions and Future Scopes

7.1 Conclusion of the Present Investigation

The primary objective of the current thesis work was to understand the photoelectrochemical behavior of CuO-based photocathodes for hydrogen evolution. Therefore, CuO/Cu_2O ultrathin films, CuO nanoparticles and $Cu_{1-x}Ni_xO$ was used as a primary system for investigation. The structural, thermal, optical, microstructural, and vibrational properties, along with the photoelectrochemical behavior of these systems, were investigated. Based on the work done, the results procured, and the conclusion presented in the previous chapters after discussion, the overall conclusion of the thesis work can be summarized as follows:

In the photoelectrochemical cell, light absorption plays a crucial role in hydrogen production. Therefore, it is essential to understand the material's light absorption properties. To investigate these features, three thin films were fabricated using the pulsed laser deposition technique, varying their thickness. The XRD result confirms the formation of CuO with Cu_2O as a defect. Prior to its use as a photocathode, the photoconduction properties of all the thin films were investigated and reported. An I-V study was performed to understand the photoconductive nature of the thin films. The investigations show that anisotropy (direction-dependent) is present in the thin film's photoconduction behavior irrespective of illumination conditions. However, it was observed that the defect concentration reduces with increased thickness. The nonreciprocity was explained through Bloch modes and the photonic Aharonov-Bohm (AB) effect. The AB effect depends upon the direction of propagation of the waveguide. Finite element modeling suggests that even for defect-free CuO, non-reciprocity can occur and lead to the observation of anisotropic photoconduction (AB effect). Despite their anisotropy

in the photoconduction behavior, the samples show significant enhancement in the photocurrent compared to the current in the dark.

In the extension of this, considering the photoconductive nature and favorable bandgap, the self-assembled CuO/Cu_2O thin films were used as a photocathode. In the theoretical study, finite element modeling (FEM) simulation shows that the configuration C-3 has the sharpest absorption maxima with reflection minima, which shows more photons are being absorbed and interact with free electrons to form plasmon resonance. DFT simulation was performed to understand in-depth, and the results show the existence of a metallic state at the CuO/Cu_2O interface, confirming the possibility of plasmons. The experimental results of ellipsometry, SERS, and XPS also confirm the formation of plasmons at the CuO/Cu_2O interface. The plasmons generated at the interface significantly increase the reaction rate of the photoelectrochemical (PEC) process and, hence, an increase in hydrogen production. The PEC behavior has been studied in an environment-friendly medium, i.e., a neutral medium (pH = 7) for the thin film and thin bulk samples in the dark and AM 1.5G (100 mW/cm^2) solar light. The parameters such as transient current kinetics, Tafel analysis, Mott-Schottky plot, and hydrogen evolution reactivity are measured. A specific capacitance of 36.62 F/g was obtained. The study shows that light-matter interaction was crucial in hydrogen production. A maximum of $\sim 0.59\ kmolh^{-1}g^{-1}$ H_2 production was achieved in the CuO/Cu_2O thin film of a thickness of 27 nm and the highest solar to hydrogen efficiency (η_{STH}) of ~ 12.2 % in T5 (13 nm thickness) was observed.

The CuO nanoparticles synthesized by the hydrothermal method are reported to possess good stability as analyzed by the chronoamperometric results. The corrosion study from the

Tafel plot also shows the sample's stability against corrosion. The TEM image confirms the formation of quasi-spherical nanoparticles of size ~ 34 nm. The synthesized CuO nanoparticles were pure, as confirmed by the XRD, XPS, and EDAX spectrum. However, slight Cu richness was observed from the EDAX spectrum. The Mott-Schottky plot analysis shows the p-type semiconductor nature of CuO. The chronoamperometric results indicate fast charge carrier dynamics under illumination conditions compared to the dark. A high HER photocurrent density of -41.57 mA/cm^2 was observed, which shows excellent photoelectrochemical HER activity in light conditions and the suitability of CuO nanoparticles as a photocathode.

The $Cu_{1-x}Ni_xO$ $(x = 0, 0.2, 0.4, 0.6, 0.8, 1)$ samples synthesized by solid-state reaction method. The samples were weighed and mixed in stoichiometric ratios. The XRD results confirm the composite formation in the samples N2, N4, N6, and N8. Further, no impurities were observed. A maximum mass loss of ~12.55% was observed in CuO, and after doping NiO and increasing the doping concentration, a gradual decrease in mass loss was observed. The HR-SEM images were analyzed to determine the sample's grain size. The reduction in the grain size of composite samples compared to the pure samples is due to the interaction between different materials (CuO and NiO) affecting nucleation and growth. In the photoelectrochemical study, the cyclic voltammograms show that the peak current density (J_p) increases by increasing the doping concentration in N0 and N2, while for the samples N4, N6, N8, and N10, the peak current density decreases by increasing the doping concentration. The Mott-Schottky plot analysis confirms that the samples N0, N2, N4, N6, N8, and N10 exhibit p-type behavior. In HER activity, the sample N2 showed a tremendous increase in the photocurrent density of -42.64 mA/cm^2 at 0 V vs. RHE, suggesting better HER activity in N2 compared to other samples.

Overall, it can be concluded that CuO exhibits a competent feature for its suitability as a photocathode material for efficient photoelectrochemical hydrogen production. In addition, nanostructuring (thin films and nanoparticles) gives more surface area and, hence, more active sites to increase the reaction rate, which leads to enhanced hydrogen production.

7.2 Outlook for Future Work

The potential for economic viability exists in the PEC pathway for hydrogen production. Still, the impracticality of using semiconductor photocathodes and the high cost of the fabrication process make it difficult. In this thesis, although the results for the CuO-based semiconductor photocathodes are promising, the following areas would need to be addressed in future work on the advancement of such photoelectrodes:

- Study the electrode-electrolyte interface to improve the charge transfer efficiency.
- Investigate the incorporation of co-catalysts such as Pt and MoS_2 on the CuO surface to enhance the catalytic activity for hydrogen production.
- Develop hybrid photoelectrochemical setups by integrating CuO photocathodes with additional photoactive materials or catalysts to enhance overall efficiency.
- Investigate different methods for altering the surface, including applying protective coatings (such as TiO_2 and NiO, etc.) or introducing other elements to improve the durability and effectiveness of CuO photocathodes.
- Investigate how CuO photocathodes can be combined with current solar cell technologies to develop tandem systems to improve solar to hydrogen efficiency.