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A photocatalyst absorbs light (UV or visible) energy to drive a reaction. The absorption of energy higher than the material's bandgap causes the formation of photo-excited electrons and holes. These excited species may then reduce and oxidize adsorbed molecules. Photocatalysis plays a significant role in resolving environmental issues because of the lower costs and environment-friendly protocols.

Photocatalytic processes over single semiconductors suffer from poor photocatalytic efficiency due to low photostability and high recombination of photogenerated excitons. Thus, improving the photostability and photocatalytic efficiency of these semiconductor-based materials is quite a fascinating research area. Development of p-n heterojunction by coupling two or more semiconductors with suitable band edge position can reduce recombination phenomena by transfer of charge carriers. Iron oxides and oxyhydroxide phases are likely candidates for the construction of efficient p-n heterojunction photocatalysts. These phases are economical and have visible range bandgaps.

The present thesis uses iron oxide phases to fabricate p-n heterojunctions with  $\text{Ag}_2\text{O}$  and  $\text{Cu}_2\text{O}$  phases. Thus, the thesis deals with the synthesis of starch functionalized  $\text{Fe}_3\text{O}_4/\text{Ag}/\text{Ag}_2\text{O}$ ,  $\text{Fe}_3\text{O}_4/\text{Cu}_2\text{O}$ ,  $\alpha\text{-FeOOH}/\beta\text{-FeOOH}$ , and  $\alpha\text{-FeOOH}/\beta\text{-FeOOH}/\text{Cu}_2\text{O}$  p-n heterojunction photocatalysts. These heterostructures were characterized by X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), magnetic property measurement system (MPMS), and X-ray photoelectron spectroscopy (XPS). Bandgaps were determined using solid-state UV-visible diffuse reflectance spectroscopy (UV-DRS). Mott-

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Schottky (MS) and Nyquist plots were generated through electrochemical studies on an electrochemical workstation.

The thesis then evaluates the visible light photocatalytic activities of the prepared heterostructures. The starch functionalized  $\text{Fe}_3\text{O}_4/\text{Ag}/\text{Ag}_2\text{O}$  nanoparticles were found to be effective for the photoproduction of  $\text{H}_2\text{O}_2$ . The other photocatalysts were used to degrade PNP and MO through photo-Fenton reaction. For a better comparison of photocatalytic activities obtained in the present thesis with studies in literature, turnover frequencies (TOF) are reported in this thesis. Efforts have been made to investigate the mechanisms involved in photocatalytic  $\text{H}_2\text{O}_2$  production and photo-Fenton degradation of PNP and MO. The pointwise objectives of this thesis are enumerated below.

**Chapter 1** gives a brief introduction to photocatalysis. Special attention has been given to list and explain the mechanisms possible in p-n heterojunction photocatalysts. This chapter also contains a detailed literature survey on iron oxide-based p-n heterojunction photocatalysts. The in-depth knowledge gained from this literature survey enables the framing of the scope and the objectives of the present investigation. These have been highlighted at the end of this chapter.

**Chapter 2** describes the experimental specifications, including materials used, photocatalytic methodologies, and instrumentation used to characterize the photocatalysts prepared and studying the reaction kinetics.

**Chapter 3** is on the preparation, characterization and photocatalytic properties of superparamagnetic starch functionalized  $\text{Fe}_3\text{O}_4/\text{Ag}/\text{Ag}_2\text{O}$  nanostructures. The nanostructures were prepared by a step-wise co-precipitation protocol. Synthesized nanostructures were characterized

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by XRD, TEM, MPMS, and XPS techniques. UV-DRS and MS plots were employed to determine the bandgaps and the band positions of the different components of the composite nanoparticles. Starch functionalized magnetite (SM) and Ag<sub>2</sub>O components were found to have staggered band alignment with a p-n heterojunction. The p-n heterojunction lowers the valence band (VB) position of magnetite. These nanostructures are efficient visible-light catalyst for H<sub>2</sub>O<sub>2</sub> production from water and air. Appropriate control experiments confirm that H<sub>2</sub>O<sub>2</sub> production proceeded by water oxidation. Water oxidizes into oxygen on lower VB of the SM component, and oxygen reduction to produce H<sub>2</sub>O<sub>2</sub> occurred at the Ag co-catalyst. The results suggest that the photocatalyst works by a p-n heterojunction mechanism. An increase in H<sub>2</sub>O<sub>2</sub> production with the Ag percentage indicates that the 2-electron oxygen reduction occurred on this component. Moreover, these nanostructures showed excellent recyclability. Superparamagnetic properties of these photocatalysts facilitate easy recyclability for H<sub>2</sub>O<sub>2</sub> production.

**Chapter 4** deals with the synthesis of starch functionalized Fe<sub>3</sub>O<sub>4</sub>/Cu<sub>2</sub>O nanocomposites for the photo-Fenton degradation of PNP and MO under visible light irradiation. XRD, TEM, MPMS, and XPS techniques were used to investigate different aspects of nanostructures. The bandgap and band edge positions of the nanostructures were found from respective UV-DRS and MS plots. The joining of p-type Cu<sub>2</sub>O with n-type magnetite results in a p-n junction that improves the charge separation. The nanocomposite exhibits effective photocatalytic activity towards photo-Fenton degradation of PNP and MO. Moreover, the superparamagnetic properties of the photocatalysts facilitate easy recyclability.

**Chapter 5** investigates the green synthesis of  $\alpha$ -FeOOH/ $\beta$ -FeOOH and starch functionalized  $\alpha$ -FeOOH/ $\beta$ -FeOOH nanocomposites. XRD, FTIR, and TEM were used to

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characterize these nanocomposites. Starch functionalization resulted in rice-shaped nanocomposite particles with the same phase composition but increased hydrophilicity. These heterostructures were used to degrade PNP and MO through the Fenton and photo-Fenton process. An increase in (dark) Fenton reaction activity of starch functionalized  $\alpha$ -FeOOH/ $\beta$ -FeOOH nanocomposites suggested that starch surface modification alters the active sites. Photo-Fenton efficiencies for PNP and MO oxidation increased on starch functionalization. Starch functionalization alters the photocatalyst's band structure, making it more efficient. The formation of p-n heterojunction led to efficient charge separation in both the nanostructures. Functionalization by starch significantly enhanced the photocatalytic activity with good reusability.

**Chapter 6** includes the co-precipitation protocol to synthesize  $\alpha$ -FeOOH/ $\beta$ -FeOOH/ $\text{Cu}_2\text{O}$  p-n-p heterostructure. The nanocomposites were characterized by XRD, TEM, and XPS. MS plot confirms the formation of p-n-p heterojunction. The Fenton and visible light photo-Fenton activities of this unique p-n-p type  $\beta$ -FeOOH/ $\alpha$ -FeOOH/ $\text{Cu}_2\text{O}$  nanocomposite were evaluated for the degradation of PNP and MO. The nanocomposite shows enhanced activity towards photo-Fenton degradation of PNP and MO. The formation of p-n-p heterojunction enhances the charge separation, thus results in increased photocatalytic activity. Moreover, the nanocomposites show excellent recyclability.

**Chapter 7** summarizes the photocatalytic activities of iron oxide-based p-n heterojunction prepared as a part of this thesis. The thesis ends with a short discussion on the future scope of this work.