Abstract

This thesis work aims to address the energy-environmental issue currently faced by the world, with a particular focus on mitigating water pollution. The work underscores that, although numerous water treatment technologies are currently employed for wastewater decontamination and reuse, there remains significant scope for their optimization and advancement. The tertiary stage of water treatment is critical in determining the final water quality, thereby defining its suitability and permissible reuse for specific applications**.** Among the various methods that are categorised under tertiary treatment techniques, advanced oxidation processes pose as one of the superior pollutant removal techniques. Heterogeneous photocatalysis, one of the advanced oxidation processes, harnesses light (solar energy) as an energy source to perform useful chemical reactions on the solid catalyst's surface by generating reactive species in aqueous medium. Metal oxide semiconductor photocatalysts, including TiO_2, ZnO, and $BiVO_4$, have demonstrated excellent performance in dye pollutant degradation, exhibiting high reusability with negligible loss of photocatalytic efficiency over multiple cycles. Benchmark photocatalysts such as TiO_2 exhibit excellent photocorrosion resistance but are intrinsically inactive under visible light, restricting their solar energy utilization. To overcome this limitation, extensive research has focused on enhancing visible-light responsiveness through strategies such as doping, defect and surface engineering, and heterojunction formation with other semiconductors. This drive stems from the higher intensity and larger proportion of visible light in the solar spectrum compared to UV radiation. Therefore, in the pursuit of visible light active photocatalysts with efficient performance, researchers have explored another genre of photocatalysts called plasmonic photocatalysts. Plasmonic photocatalysts employ noble metal nanoparticles as antennas or co-catalysts to significantly enhance photocatalytic activity. When tailored into nanostructures of specific size and morphology, these particles exhibit localized surface plasmon resonance, enabling efficient absorption of visible or desired spectral regions. Coupling such plasmonic nanostructures with wide-bandgap semiconductors transforms them into highly efficient, visible-light-responsive photocatalysts. Only a limited number of noble metals, primarily Ag, Au, and Pt, are known to exhibit strong surface plasmon resonance properties. The phenomenon does

not strictly restrict the type of host semiconductor or semiconductors that can be used for plasmonic photocatalysis. However, the overall activity builds upon the semiconductor's original redox power and depends on the careful integration of the plasmonic metal and semiconductor. To advance the development of plasmon-assisted semiconductor photocatalysts, this thesis presents original research organized into seven chapters as outlined below:

Chapter 1

A thorough investigation starting from the present day water availability status to the suitable photocatalytic materials is presented in this chapter. A gradual exploration is carried out throughout the chapter connecting the water pollution issue to the plasmonic photocatalysis as a potential solution. This chapter establishes the essential role of water for all life forms and identifies industrial wastewater discharge as a major contributor to water pollution. It reviews conventional water treatment techniques and highlights the role of photocatalysis, emphasizing solar energy as a sustainable energy source. The chapter traces the evolution of photocatalyst development over recent decades, critically examining strategies to enhance photocatalytic performance along with their respective advantages and limitations. It then narrows its focus to plasmonic photocatalysts, which offer solutions to key challenges in traditional photocatalysis. Finally, potential materials and design approaches are discussed, leading to the formulation of the study's research objectives.

Chapter 2

This chapter elaborates on the different synthesis methodologies and procedures adopted for performing the research experiments. Also, the chapter presents the various characterization techniques used to evaluate the properties of synthesized photocatalysts, along with the essential mathematical formulations and equations for calculating key observables.

Chapter 3

This chapter presents the experimental study done on developing a multi-junction band gap engineered photocatalyst. The underlying wisdom for this study was that heterojunction photocatalysts show enhanced charge separation efficiency compared to single semiconductor based photocatalysts and that doping reduces the band gap of the high band gap semiconductor making it visible-light responsive. The photocatalyst was therefore accordingly prepared to achieve the targeted outcomes. The study presented in this chapter revealed the reduction of band gap due to Co ion doping on titania and the emergence of anatase-rutile homojunction and a heterojunction in the composite photocatalyst Co-TiO_2/$CoTiO_3$. The photocatalytic evaluation experiment was done against the degradation of methylene blue and the results showed a highly enhanced photocatalytic activity under visible light. Notably, this visible light active Co-TiO_2/$CoTiO_3$ photocatalyst has the potential for the application of large-scale solar-induced dye removal.

Chapter 4

The work presented in this chapter builds upon the findings of the previous chapter to develop a multi-junction photocatalytic system and additionally assisted with plasmonic Ag metal to further benefit the system with plasmonic phenomena. The successful synthesis of a plasmonic-heterojunction hybrid photocatalyst was accordingly reported in this chapter. The hybrid photocatalyst possesses a ternary junction between metal oxide semiconductors observed between the host TiO_2 and the co-catalysts CuO and Cu_2O. Additionally, the material features bulbous, branched Ag nanostructures, deliberately tailored to exhibit broad visible light absorption extending into the near-infrared region. These arrangements in the material collectively endow the material to show excellent photocatalytic degradation, far surpassing the performance of its pristine counterparts under visible light illumination. The kinetic studies were performed using two different pollutants: methylene blue dye and phenol. The improved photocatalytic degradation is attributed to the synergistic impact of reduced electron-hole pair recombination owing to Cu_2O-CuO/TiO_2 ternary junction, broad visible light absorption and near-field enhancement through the surface plasmon resonance effect.

Chapter 5

This chapter presents another novel plasmon assisted heterojunction photocatalyst showing enhanced performance through multiple possible plasmonic energy transfer phenomena. This study reports the synthesis of a Ni-Cr layered double hydroxide material integrated with metallic Ag in-situ via the co-precipitation method. Upon calcination, this precursor transforms into a metal oxide semiconductor heterojunction photocatalyst integrated with plasmonic Ag, designated as Ag@NiO/Ag_2CrO_4. The detailed study and evaluation of the band edge positions of the constituent semiconductors and composite photocatalyst reveals the formation of a Z-scheme heterojunction photocatalyst. The photocatalytic evaluation, transient photochemical measurements, and active radical quenching experiments verify the charge transfer mechanism, that includes not only direct electron transfer but also plasmon-induced resonant energy transfer.

Chapter 6

This chapter reports a comparative study on the photocatalytic performance of titania based photocatalysts each incorporated with different shape of Ag nanoparticles. Three different shapes of Ag: spherical, cubic and bulbous branched structures were successfully prepared and characterized. The distinct shapes of Ag nanoparticles show distinct plasmonic resonance behaviour as evidenced by spectroscopic studies. This chapter experiments on the influence of these different shapes on the photocatalytic performance. Furthermore, optimization of calcination temperature and Ag loading amount were performed to achieve the highest activity and to arrive at a conclusion for the size and shape effects.

Chapter 7

This chapter marks the accomplishment of all the objectives framed in the thesis by mentioning the specific objectives fulfilled in each experimental chapter. The significant results and findings of all the previous chapters are summarized and finally the future scope of the present study are discussed emphasizing on its potential implications in the energy-environmental sector.

Appendix I: Journal publications and book chapter details

Appendix II: Workshops and conferences