DEVELOPMENT OF PLASMON ASSISTED NANOCOMPOSITE SEMICONDUCTOR MATERIALS FOR PHOTOCATALYTIC APPLICATIONS

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Conclusion and future scope

This thesis work was initiated with the motivation to address the urgent and ongoing detrimental environmental issues, particularly the water pollution problem, using a sustainable approach. In this context, the thesis was appropriately titled 'Development of plasmon assisted nanocomposite semiconductor materials for photocatalytic applications' to underscore the strategic focus on leveraging plasmonic phenomena to enhance the efficiency and functionality of semiconductor-based photocatalytic systems for environmental remediation and energy applications. This work explores semiconductor photocatalysts to harness visible light, the region that constitutes ~43% of the solar energy spectrum, and to channel this energy to produce oxidizing and reducing agents, allowing them to react with dye molecules in water to degrade the dye molecules. Furthermore, this work utilized the knowledge of hierarchical development of semiconductor photocatalysts over the decades of research in the world to fabricate a better and promising version of photocatalysts, primarily plasmonic photocatalysts, by using Ag metallic nanoparticles as a sensitizer or co-catalyst to improve the photocatalytic performance of heterojunction semiconductor photocatalyst under visible light. Accordingly, each chapter has been designed to efficiently execute the research plan and fulfil the objectives of the thesis as follows:

The introductory chapter establishes water pollution as a critical and pervasive environmental issue, predominantly driven by industrial effluent discharge and other anthropogenic activities, emphasizing the urgent need for effective preventive strategies to mitigate its impact and ensure a sustainable future. The chapter duly highlights solar energy as an abundant and renewable energy source that, when effectively harnessed by advanced photocatalytic systems, holds significant potential to drive sustainable solutions for freshwater generation and environmental remediation. The chapter systematically outlined the evolution of photocatalysts, progressing from conventional semiconductor based systems to the advanced concept of plasmonic photocatalysts. The different mechanisms involved in plasmonic photocatalysts were described, and the various factors that affect the properties of the plasmonic behaviour of the metal counterpart were studied. The chapter concludes by examining suitable materials for the development of plasmonic photocatalysts, alongside a discussion of potential synergistic strategies to enhance their photocatalytic performance.

In the second chapter, a comprehensive overview of the methodologies and techniques employed throughout the research study is presented. The chapter highlighted the distinct methods that were used for the synthesis of photocatalysts, including the procedures in the preparative stages. In the subsequent sections, the characterization techniques and analysis protocols used for obtaining the data results were specified in a concrete form.

The third chapter "Bandgap engineered multi-junction photocatalyst for enhanced visible-light-driven degradation of organic pollutants" delved into the experimental study of a photocatalyst prepared using modified sol-gel method. The study resulted into the successful development of a multi-junction photocatalyst between anatase, rutile TiO_2, and $CoTiO_3$. The two junctions: homo and heterojunction in the Co-TiO_2/$CoTiO_3$ enabled swift separation of charge carrier across them. The bandgap of the material was found to be lower than the pristine TiO_2 resulting in a high absorption across the visible light range. The photocatalytic study revealed that this material is 42-times faster than that of pristine TiO_2 in degrading dye pollutant MB. The work presented in this chapter thus fulfils the two objectives of the thesis, by fabricating multi-junction photocatalytic system, and developing a bandgap engineered photocatalyst to observe enhanced performance.

The development of efficient solar light active heterojunction photocatalyst by plasmonic nanoparticle sensitization was extensively experimented and presented in Chapter 4, titled "Strategically developed plasmonic-activated heterojunction system for high-efficiency visible-light-driven photocatalysis". The study led to the successful fabrication of Ag@Cu_2O-CuO/TiO_2 photocatalyst in which the Ag nanostructure exhibits a peculiar plasmonic behaviour of broad absorption spectrum over visible light. This material possess two heterojunction observed between Cu_2O and TiO_2, and between CuO and TiO_2. Consequently, a novel plasmonic-heterojunction photocatalyst was developed here showing broad visible light absorption. The photocatalytic evaluation experiment showed that this material has 26.5 times higher activity than the pristine TiO_2 counterpart towards methylene blue degradation without sacrificial reagents. Therefore, the objective to prepare efficient solar light active heterojunction photocatalyst by plasmonic nanoparticle sensitization is thereby accomplished in the fourth chapter. Moreover, the work demonstrated another fabrication of multi-junction photocatalytic system with enhanced performance.

The fifth chapter titled "Surface plasmon resonance enhanced Z-scheme photocatalysis using Ag integrated heterojunction of an emerging semiconductor" further explored the beneficial outcomes of plasmonic resonance phenomena occurring on heterojunction photocatalytic system. An enhanced photocatalytic performance was achieved here by utilizing the suitable plasmonic energy transfer mechanisms feasible in the synthesized photocatalyst Ag@NiO/Ag_2CrO_4. This material was formed intriguingly after the calcination of Ag incorporated Ni-Cr LDH, which was prepared using co-precipitation method. The characterization studies established the formation of heterojunction between NiO and Ag_2CrO_4, and the presence of metallic Ag in the system. Further calculations and analysis associated with the band edge alignments suggests the formation of an efficient Z-scheme charge transfer between Ag_2CrO_4 and NiO, due to the intermediary role of Ag nanoparticles. The Ag nanoparticles owing to its strong LSPR effect boosts the electron dynamics and enhance catalytic performance. Additionally, the spectral overlap between the Ag LSPR absorption and the NiO band-edge absorption at around 400 nm (~3.1 eV) facilitates resonant energy transfer, wherein Ag LSPR dipoles can relax nonradiatively, thereby generating electron–hole pairs within NiO. This finding agrees with the results obtained in charged species quenching experiments and TRPL analysis to definitely imply the occurrence of efficient Z-scheme charge transfer between Ag_2CrO_4 and NiO, with PIRET from Ag. The rate constant of Ag@NiO/Ag_2CrO_4 was found to be 1.3 and 34 times higher than Ag_2CrO_4 and Ni-Cr LDH derived NiO counterpart, respectively, for the degradation of MB without the aid of sacrificial reagents. Therefore, the objective to prepare efficient solar light active heterojunction photocatalyst by plasmonic nanoparticle sensitization is thereby accomplished in the fifth chapter. This study also aligns with the objective of developing a viable photocatalyst through bandgap engineering and surface modification, taking into account of the lower bandgap observed in Ag@NiO/Ag_2CrO_4 in comparison to NiO counterpart.

In the sixth chapter, "Influence of plasmonic nanostructure geometry on a host semiconductor and optimization of key parameters for enhanced photocatalytic efficiency", three different shapes of Ag were separately synthesized and verified to observe spherical, cubic, and bulbous branched structures. The plasmonic resonance of each shaped Ag was observed to be distinct from each other, with the cubical shape showing two discernible peaks. These Ag shapes were separately used to synthesize three different Ag@TiO_2 photocatalysts to compare their photocatalytic performances. The kinetic studies revealed that the Ag@TiO_2 photocatalyst prepared with cubical Ag and calcined at 600 ^{0}C shows the highest photocatalytic performance towards the degradation of MB. This observation suggests that the cubical morphology of Ag nanoparticles offers better plasmonic resonance effects, thereby promoting more efficient charge separation and transfer in the TiO_2 matrix, leading to superior photocatalytic activity. It was demonstrated that the suitable size of cubical Ag in the range 20-70 nm along with its shape having facets and edges supports stronger plasmonic resonance and induces stronger local electric field enhancement. Among the three prepared shapes, only the cubical shape shows two plasmonic peaks, in contrast to the sphere showing a single peak, and different from bulbous branched nanostructures having only a broad absorption pattern. Moreover, one resonance peak of cubic Ag lie in a short wavelength region, which implies that the resonance at this wavelength generate higher energetic plasmonic electrons to transfer to the conduction band of TiO_2. When these energetic electrons relax radiatively, stronger photoluminescence can be observed, consistent with PL analysis results. In comparison to this, the size of the spherical Ag nanoparticles was found to be smaller and distributed over a limited range, so that in this case, the plasmonic resonance pattern only exhibits one single peak broadened over a finite range of visible light wavelengths. On the other hand, the sizes of bulbous branched nanostructures were measured to be significantly larger than cubic Ag, ranging from 100-400 nm, and consequently, due to the size effect, its plasmonic resonance spectrum was observed as a broad absorbance in the visible light range, with no single intense peak.

Thus, in this chapter, the objective to study the effect of the size and shape of plasmonic nanostructures on the photocatalytic activity of a host material was accomplished. Additionally, the photocatalytic activities of different photocatalysts were evaluated at different temperatures and different loading amount of cubical Ag to realize the optimized loading amount and temperature. Therefore, this study also aligns with the objective to optimize the various parameters of the host semiconductor and co-catalysts to obtain maximum efficiency.

All the objectives of this thesis have been successfully accomplished in the manner stated above. The findings in these studies naturally generate curiosity and pathways for further research. The work presented in the sixth chapter features the size and shape based dependence of plasmonic photocatalysis, and it demands the existence of a particular shape of plasmonic metal nanoparticle with suitable dimensions, which can improve the photocatalytic performance of the host semiconductor to the maximum efficiency. In this regard, a hybrid plasmonic-heterojunction photocatalyst can be prepared using the plasmonic counterpart having only the optimized shape and size. This photocatalyst is expected to show high performance. Also, the results in the fifth chapter clearly revealed that a highly active photocatalyst may not exhibit consistent activity across different dye pollutants. Therefore, a specific pollutant targeting photocatalyst is what can be prepared by suitable synthesis of a composite plasmonic photocatalyst that is equipped with the most favourable band edge positions for that pollutant, such as for degrading microplastics. Furthermore, a suitable design of plasmonic photocatalysts that are active in the near-infrared region and are effective for pollutant removal would be highly regarded, as the solar light spectrum has ~52% energy designated to infrared. The successful synthesis of such a material would also pave the way to developing infrared sensors. It is also understood that an intense plasmonic resonance peak could provide more enhancing effects than the broad ones because of the absence of competition that can occur in particles showing multiple wavelength resonances. Therefore, a plasmonic photocatalyst can be prepared with different plasmonic metallic nanostructures, each supporting resonance over a unique wavelength, which can then be studied to observe their collective effect on the activity of the photocatalyst. The arrangement of these plasmonic particles in this system would play a crucial role, and therefore, careful study and arrangement mechanisms would be required.

Ensuring the reusability of a photocatalyst is another essential factor, and this can be realized by carefully selecting and optimizing active materials and incorporating them into a device design that maintains high efficiency. Thin film growth of plasmonic photocatalysts holds significant potential, especially if high efficiency can be attained by controlling film thickness and employing well-designed reactors to maximize light absorption. Theoretical approaches and AI models also need to be explored for the development of efficient photocatalysts, where mathematical tools, machine learning algorithms, and computational simulations can play a crucial role. These are a few studies that can be sought for, in the future, concerning the plasmonic photocatalyst and pollutant removal. Additionally, plasmonic and or hybrid photocatalysts hold immediate potential for diverse applications, including hydrogen generation, dye-sensitized solar cells, biomedical uses, and CO_2 reduction.