CHAPTER-6

Summary, Future Scope and Perspective

6.1. Conclusions

In this thesis, we have demonstrated the application of metal halide perovskite-based photocatalysts for the efficient synthesis of functionalized amines, amides, and dihydroisoquinolines either through C−N cross-coupling or by semidehydrogenation reactions. The C−N bond-formation reactions play a pivotal role in the synthesis of pharmaceuticals and fine chemicals. Conventionally, such transformations have relied on noble metal catalysts, which, despite their efficiency, are often cost-prohibitive and less sustainable for large-scale applications. Our findings underscore the potential of perovskite-based, earth-abundant semiconductor photocatalysts as a viable alternative for scalable, cost-effective, and environmentally friendly C−N bond formation. The target compounds, substituted amines, amides, quinolines, and DHIQ, are of significant importance in pharmaceutical development, peptide synthesis, agrochemicals, and various therapeutic agents, including antibacterial, anticancer, and antimicrobial drugs.

Although the optoelectronic properties of halide perovskite are suitable for the visible-light photoredox reactions, the major limitation originates from their inherent instability in the presence of moisture and protic solvents. Hence, the reaction protocol was designed such a way that it avoids the use of protic solvents or water. However, the conditions become more critical when H_2O is produced during the reaction as a part of O_2 activation process. This drawback severely restricts the wide applications of halide perovskite in organic transformations. To alleviate this issue, previously, the reactions were carried out in an inert atmosphere. This approach reduces the efficiency of the photocatalyst compared to the molecular O_2 activation mechanism. In this thesis, we have designed an alternative protocol of molecular O_2 activation to produce H_2O_2, avoiding the formation of H_2O in the reaction. This strategy helps to retain the structural integrity of the halide perovskites throughout the catalytic process. As a result, the catalysts showed improved stability and they were recycled for at least five times with a minimum loss in the photoactivity. Even the structural characterization of the used catalyst (after recycling) revealed its structural integrity.

Further, to enhance the photocatalytic performance, we have developed efficient photocatalyst systems employing strategies like (i) integration of metal complex as cocatalyst, (ii) heterojunction formation, and (iii) electronic band structure modulation. These modifications significantly improved charge carrier separation and hence photocatalytic activity. Interestingly, the metal complex also has a significant impact on the product selectivity through the HAT process.

Comprehensive photoelectrochemical and spectroscopic characterizations, including EIS, photocurrent measurements, and PL spectroscopy, confirmed enhanced charge separation and suppressed charge recombination. Additionally, femtosecond transient absorption spectroscopy revealed accelerated exciton relaxation dynamics, further validating the improved charge carrier kinetics in the optimized photocatalysts.

In **Chapter 2**, $CsPbBr_3$ QDs coupled with $Ni(dmgH)_2$ as a cocatalyst enabled efficient photoredox C–N coupling, delivering high amide yields (7% [Ni]-$CsPbBr_3$) due to optimal band alignment, rapid charge transfer, and suppressed trap-state recombination. To maintain perovskite stability, we implemented a robust strategy using non-polar solvents, controlled atmospheres, and avoiding water formation by employing molecular oxygen as an oxidant. The reaction proceeds via superoxide radical formation, yielding H_2O_2 instead of H_2O. The process proceeds under additive-free and mild conditions, with the catalyst demonstrating excellent recyclability, retaining its activity over five consecutive cycles without any loss of performance.

Similarly, in **chapter 3**, we have utilised $CsPbBr_3$ QDs catalyzed visible-light N-alkylation of amines with alcohols via a borrowing hydrogen mechanism. Here, the cobalt complex avoids the production of water in the reaction mixture, instead producing H_2 gas through the hydrogen borrowing process, and maintains $CsPbBr_3$ stability during the photoredox reaction. Cobaloxime cocatalysts enhanced charge separation and aldehyde formation, with [Co-4] achieving 97% selectivity due to favorable LUMO, tuned by the ligand backbone.

In **chapter 4**, we developed a heterojunction photocatalyst for selective DHIQ synthesis via semidehydrogenation of THIQs under visible light. The $CsPbBr_3$ activates $^3O_2$, while BiOBr tunes the valence band to facilitate the oxidation of THIQ to generate the radical cation and also facilitate the $^1O_2$ generation through the electron transfer process at the VB of BiOBr. The high electrophilic character of singlet oxygen enables selective THIQ dehydrogenation to DHIQ under mild conditions, minimizing over-oxidation and avoiding harsh reagents. To maintain perovskite stability, water formation was avoided by redirecting the reaction pathway toward H_2O_2 production via $^\bullet OOH$ radical intermediates.

Finally, in **chapter 5**, we successfully implemented lead-free perovskites (Cs_2CuBr_4), underscoring their potential as environmentally benign alternatives. Overall, this work paves the way for the development of stable, efficient, and sustainable perovskite-based photocatalysts for the photocatalytic amidation of alcohols through the activation of molecular O_2. In this chapter, we have explored how the electronic structures and particle size of the perovskite are tuned to the photoredox activity, with a more negative conduction band minimum and more positive valence band maximum, enabling efficient O_2 reduction to superoxide radicals, thereby enhancing C–N coupling activity.

6.2. Future scope and perspective

In this work, we have demonstrated the application of $CsPbBr_3$ as a photocatalyst, in conjunction with Ni and Co metal complexes (dmgH = dimethyl glyoximato), for the synthesis of functionalized amines and amides via C−N cross-coupling reactions. Additionally, we developed a Z-scheme heterojunction photocatalyst by combining $CsPbBr_3$ with BiOBr to enable the semidehydrogenation of THIQ to DHIQ. Moreover, we explored the use of a lead-free metal halide perovskite, Cs_2CuBr_4, for oxidative amidation of alcohols through C−N coupling. This thesis lays the foundation for future research, which could be extended to address the following directions:

(i) This work provides a foundation for future advancements in photocatalytic research. One promising direction involves the electronic modulation of $CsPbBr_3$ QDs through the incorporation of various transition metals and lanthanide ions (e.g., Mn^{2+}, Ni^{2+}, Zn^{2+}, Ce^{3+}) into the perovskite lattice. Such dopant engineering allows for precise tuning of the band structure and photoluminescence behaviour, which are critical parameters for enhancing charge separation dynamics, suppressing charge recombination, and improving electron mobility. These enhancements are pivotal for boosting photocatalytic performance in organic transformations and solar-to-chemical energy conversion applications.

(ii) Further research is necessary to explore Cs_2CuBr_4 and other transition metal-based lead-free halide perovskites as photocatalysts, with a focus on understanding their photoredox potentials and photophysical properties. A comprehensive investigation of these materials will facilitate their application in diverse areas such as solar energy conversion, photocatalytic organic transformations, water purification, and environmental remediation, including plastic degradation.

(iii) In addition, the Cu(I) center in Cs_2CuBr_4 exhibits a higher ability to activate molecular oxygen compared to the Pb(II) site in traditional lead-based perovskites. This inherent redox activity of Cu(I) offers a promising opportunity to exploit Cs_2CuBr_4 as a lead-free photocatalyst for the efficient generation of H_2O_2 under visible-light irradiation. Given the environmental and safety advantages of H_2O_2 as a green oxidant, future research can focus on optimizing the photocatalytic performance of Cs_2CuBr_4 for scalable H_2O_2 production.

(iv) Furthermore, the construction of heterojunction systems based on Cs_2CuBr_4 with suitable semiconductors presents a promising strategy to enhance photocatalytic efficiency by improving charge separation and suppressing recombination. By carefully selecting semiconductors with complementary band structures, type-II or Z-scheme heterojunctions can be engineered to facilitate directional charge transfer, thereby boosting redox potentials and overall activity. Future studies should focus on exploring the photophysical behavior, interfacial charge carrier dynamics, and lifetime of photoexcited species within these heterostructures. Such insights will be crucial for designing efficient photocatalytic systems tailored for selective organic transformations, under visible-light-driven C–N coupling, oxidative functionalization, and environmentally benign synthesis pathways.