PREFACE

Metal halide perovskites have attracted special attention in the field of photocatalysis because of their excellent photophysical properties, including high optical absorption coefficients, tunable band structures, and long carrier diffusion lengths. In recent years, the rapid development of halide perovskite has offered new opportunities for its photocatalytic applications, ranging from solar-to-chemical energy conversion to photocatalytic organic reactions. For example, recently, the photoredox properties of $CsPbBr_3$ have been explored for various organic transformations, including C–C, C–O, C–P, and C–N coupling reactions, as well as the selective oxidation of benzyl alcohols to benzaldehydes under visible light.

In this thesis, we have explored the application of halide perovskites in photocatalytic organic transformations, with a particular focus on the development of strategies to enhance their photogenerated charge carrier mobility, photoredox activity, and selectivity. Key strategies explored the introduction of cocatalyst, the construction of heterojunction with other photocatalysts, and the modulation of the perovskite's band structure. These approaches collectively improve the separation of photogenerated charge carriers (electrons and holes), thereby boosting both photocatalytic efficiency and selectivity. Improved charge carrier dynamics enable more effective redox reactions at the valence band (VB) and conduction band (CB), accelerating both oxidative and reductive processes. Collectively, these modifications significantly boost photocatalytic activity and offer better control over reaction pathways in organic synthesis.

The enhanced charge separation, transport, and suppression of charge recombination were confirmed through electrochemical impedance spectroscopy, photocurrent measurements, and photoluminescence studies. Femtosecond transient absorption spectroscopy further reveals an

accelerated relaxation rate when the halide perovskites' band structures were modified, combined with a cocatalyst, or a heterojunction was formed.

As a result, these metal halide perovskites produced excellent photoredox activity for different types of C−N bond formation reactions for the synthesis of substituted amines, amides, and isoquinolines, which offer pivotal role in the chemical and pharmaceutical industries (**Figure 1**).

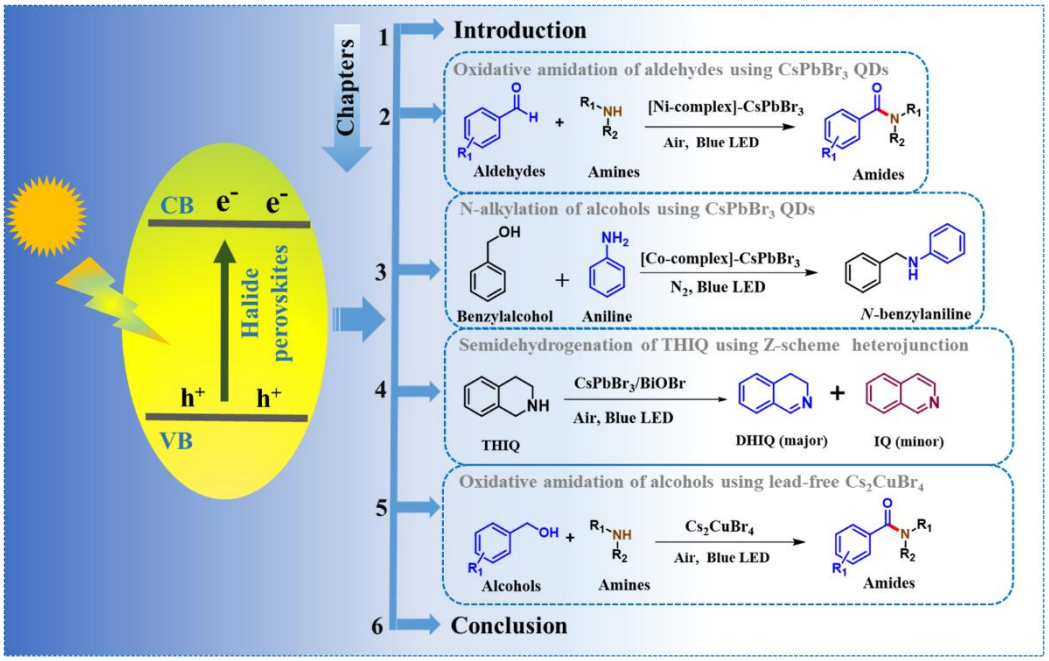

Figure 1. Schematic depiction of the specific objectives of the chapters of the thesis.

In chapter 1, a detailed study of the optical properties of metal halide perovskites is presented, along with their various applications in energy conversion processes such as solar cells, photocatalytic hydrogen evolution, photocatalytic CO_2 reduction, and photoredox organic transformation reactions, based on existing literature. The chapter also provides an in-depth analysis of the band structure characteristics of metal halide perovskites, highlighting their potential as efficient photocatalysts for organic transformations.

In Chapter 2, Ni(II) complexes-$CsPbBr_3$ quantum dots (QDs) have been explored for visible-light-driven photoredox C–N coupling. The cocatalyst $Ni(dmgH)_2$ (dmgH = dimethylglyoximato) significantly enhances the photocatalytic performance of QDs, enabling the synthesis of a wide range of amides. The synergistic interaction between the QDs and $Ni(dmgH)_2$ improves charge transfer while suppressing charge recombination. Notably, the photocatalytic activity is highly dependent on the cocatalyst loading, with 7 wt% $Ni(dmgH)_2$ yielding the highest amide conversion (92%). Femtosecond transient absorption spectroscopy indicates that the cocatalyst modulates the trap-state dynamics of the QDs. Additionally, $Ni(dmgH)_2$ facilitates the activation of molecular O_2 to generate superoxide radicals, which initiate the radical-mediated C–N coupling pathway. The catalyst was found to be recyclable five times with a minimum loss of its initial activity.

In Chapter 3, the importance of Co(II) complexes to tune the product selectivity in the N-alkylation of amines via photoredox catalysis using lead halide perovskites has been demonstrated. $CsPbBr_3$ QDs were employed for the selective N-alkylation of amines with alcohols by modulating the LUMO energy of cobaloxime cocatalysts. This was achieved by altering the electronic environment around the Co center, thereby tuning the LUMO energy barrier. The reaction follows a borrowing hydrogen (BH) strategy, where alcohols serve as both aldehyde precursors and hydrogen donors, offering a versatile pathway to synthesize pharmaceutically and agriculturally important compounds. The perovskite QDs offer several advantages, including low cost, ease of processing, high efficiency, air stability, and tunable band edges, making them promising tools in organic synthesis. Moreover, product selectivity can be easily controlled by adjusting the electronic environment of the Co catalyst.

In Chapter 4, the importance of singlet oxygen generation for the selective semidehydrogenation of tetrahydroisoquinoline has been explained using a Z-scheme $CsPbBr_3$/BiOBr heterojunction photocatalyst. This system combines BiOBr nanosheets with $CsPbBr_3$ QDs, enabling efficient conversion of THIQ to 3,4-dihydroisoquinoline (DHIQ). The internal electric field at the interface drives electron transfer from the conduction band of BiOBr to the valence band of $CsPbBr_3$, promoting effective charge separation. The highly negative CB of $CsPbBr_3$ activates triplet oxygen ($^3O_2$) to generate superoxide radicals, which then form singlet oxygen ($^1O_2$). Unlike $^3O_2$, $^1O_2$ is highly electrophilic and enables selective, region-controlled α-position oxidation of THIQ to DHIQ under mild, ambient conditions, minimizing over-oxidation to aromatic isoquinolines and avoiding harsh conditions.

The optimized heterojunction (Z-20, with 20 wt.% $CsPbBr_3$) achieved a 97% yield of DHIQ. Its favorable band alignment supports selective two-electron transfer, outperforming other heterojunctions. Transient absorption spectroscopy confirmed efficient exciton dynamics in Z-20, including rapid relaxation and trapping, contributing to its superior catalytic activity.

In Chapter 5, we introduce a lead-free metal halide perovskite (Cs_2CuBr_4) as a visible light-driven photocatalyst for oxidative amidation of alcohols via molecular oxygen activation. We modulated the band structure of Cs_2CuBr_4 by altering synthesis methods. Cs_2CuBr_4-1, prepared by hot injection, exhibits a more negative conduction band minimum than Cs_2CuBr_4-2, synthesized at room temperature. These features enabled Cs_2CuBr_4-1 to activate O_2 more effectively and promote radical-mediated dehydrogenation of alcohols and amine oxidation. Enhanced charge separation and reduced recombination in Cs_2CuBr_4-1 further improved its photocatalytic performance, achieving up to 98% yield in amide synthesis under visible light.

In conclusion (**Chapter 6**), this thesis establishes halide perovskites as efficient, sustainable photocatalysts for visible-light-driven C–N bond formation. A stabilization strategy using non-polar solvents and controlled atmospheres overcomes moisture sensitivity. Cocatalyst integration, heterojunctions, and band engineering enhance light absorption and charge dynamics, confirmed by spectroscopic analyses. Applications span amide synthesis, N-alkylation, and THIQ semidehydrogenation. Lead-free perovskites further demonstrate eco-friendly potential, advancing perovskite photocatalysis for pharmaceutical and fine chemical synthesis.