1 | Suitable Semiconductor Photocatalyst: An Introduction

This chapter presents the introduction to the field of photocatalysis and the steps involved in designing an efficient photocatalyst. An elaborate discussion highlighting the development of novel photocatalysts and their current status with the perspective of research and technological advancement provided thereafter. The scope and objectives mentioned in this chapter will govern the flow of forthcoming working chapters. With the functionalized semiconductor as a highlight, existing shortcomings in the literature have been marked.

1.1 Photocatalysis

The interaction of photons with the photo-responsive material and acceleration of reaction rate defines photocatalysis. When the photon of energy equivalent or greater than the band gap value of the semiconductor is incident on the catalyst, excitation of electrons from the valence band (VB) to the conduction band (CB) takes place. This results in the formation of a photo-generated electron-hole ($e^- - h^+$) pair as illustrated in Fig. 1.1. These electrons and holes migrate to the surface of the catalyst participating in the reduction and oxidation, respectively as presented in Steps-1 and 2. Reduction reaction where an electron plays a pivotal role in the formation of hydrogen molecules/superoxide anions by reducing water/oxygen, $HCOO^-/CH_4$ through carbon dioxide reduction, and ammonia via nitrogen reduction. On the other hand, holes oxidize adsorbed water molecules to generate hydroxyl radicals followed by oxygen evolution reaction (OER) and dye degradation. Photocatalysis is accompanied by two more significant physical phenomena as shown by Step-3 and 4 in Fig. 1.1 represented as bulk and surface recombination of photogenerated charge carriers. The recombination within the band structure is termed bulk recombination whereas on the other hand over the surface it is known as surface recombination. These recombinations reduce the lifetime of the charge carrier thus delaying the surface reaction rates.

1.2 Designing Photocatalyst

To design a novel effective photocatalyst for efficient water splitting, a material should possess the following characteristics: (a) Band gap value larger than 1.23 eV, 1.23 V is the potential difference at which water decomposition is possible, (b) Optical absorbance within the visible region of the spectrum, (c) Band edge straddling the reduction/oxidation potentials, reduction/oxidation potential of water decomposition is -4.44/-5.67 eV (for vacuum level), and (d) Overpotential value

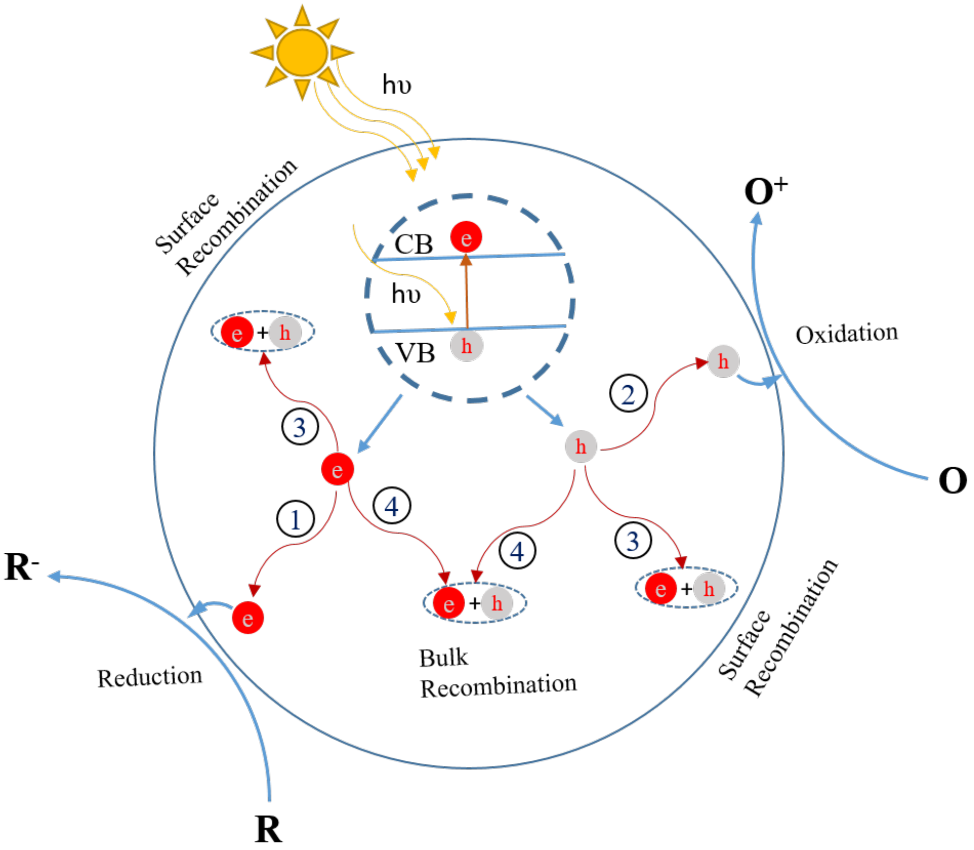

Figure 1.1: The steps involved in the photocatalysis mechanism with possible ways of charge carrier recombination.

smaller than the band edges value, this requirement assures water splitting within the energy provided by incident photon.

In the present scenario, the computational design and investigation of an effective photocatalyst is one of the most promising, cost-effective, and well-known techniques in the scientific community. Computational tools such as density functional theory (DFT) have directed us toward prominent approximation methods that result in accuracy for the investigation. The density of states (DOS), band structure, optical properties and charge distribution analysis using Löwdin charges used to investigate the band gap, band edges, effective mass, absorption spectra, and active sites on the surface of photocatalysts. However, the investigation of overpotential requires intermediate adsorption over the surface of the photocatalyst, thereafter the computed energy barrier determines the feasibility of the reaction. Overpotential is the additional energy required by the catalyst to undertake the surface reaction, Fig. 1.2 illustrates the feasibility of band edge configuration along with

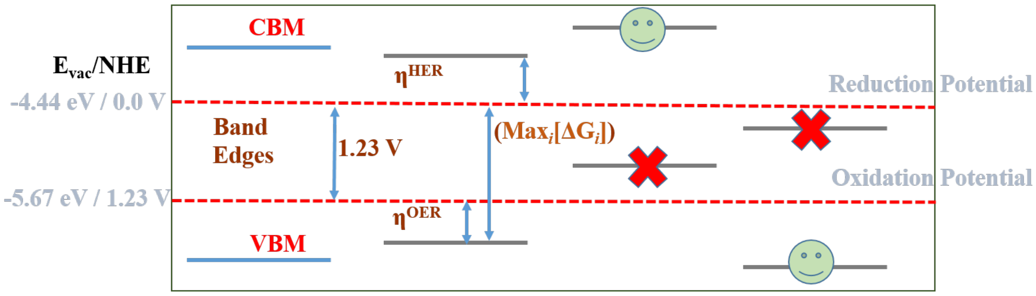

FIGURE 1.2: Various band edge positions across the reduction-oxidation potential for feasible/prohibitive reaction, potential scale is shown against E_{vac}/NHE.

the concept of overpotential for water splitting reaction. Along with the mandatory prerequisites of photocatalysts, a few intrinsic properties play a pivotal role in determining the life and efficiency of the photocatalytic material. The presence of a direct band gap within the VB/CB of the material increases the probability of photocatalysis, as the direct band gap provides the shortest, photon-based transition path, rather than the phonon-assisted optical transition. Effective mass (m*), calculated from the curvature of the VB/CB maxima/minima, via the parabolic fitting method, determines the charge carrier migration and recombination rate. High charge carrier migration and low recombination rate assures the high reaction activity at the surface of the photocatalyst.

1.3 Functionalization Methods

The requirement to achieve high photocatalytic activity, photocatalyst in the current scenario for pollution remediation, H_2 production, and CO_2 reduction have invited several modification techniques in the existing pristine photocatalyst such as structure/surface modification through strain/vacancy induction, non-metal and/or metal-atom/s, cluster doping, loading, decoration, and heterostructures formation. However, the lack of high quantum yield and efficiency caused due to limited charge separation and migration pertains to a bottleneck for its large-scale applications. Limited reports with extensive theoretical studies are available on photocatalyst-based themes, thus to enhance the performance for the efficient photocatalytic applications band gap engineering of functionalized semiconductors is the primary technique.

To date, a variety of photocatalysts in their, bulk, two-dimension (2D), one-dimension (1D), and cluster (0D) configurations have been studied and reported. Among these photocatalysts, metal oxide/sulfide semiconductors in their lower dimension have directed us toward their effectiveness as photocatalysts for the remediation and decomposition of polluted water. Beginning with, TiO_2 [10, 11], WO_3 [12], ZnS [13], ZnO [14], and CdS [15], recently designed and synthesized 2D materials like MXenes [16] have proved their significance in the photocatalytic applications [17] owing to their stable low dimension structure, high quantum yield, band edges suitable for redox reactions, and large surface area providing large reactive centers. Multi-functional applications of TiO_2 due to the presence of multiple phases in multiple facets have attracted tremendous attention, its viability for promising photocatalyst owes to its band gap value. This wide band gap provides shelter to cationic and anionic impurity resulting in the creation of metastable states within the forbidden region for effective charge separation [18]. Meanwhile, polymorphic ZnO is known for its high thermal stability, and promising efficient surface functionalization leading to high performance in the organic pollutants degradation. However, the presence of heavy metals in high content and band gap in the ultraviolet region limits its usefulness in the visible region of light. Despite promising properties displayed by these metal oxide/sulfide in photocatalytic applications, failure to utilize the maximum region of the visible spectrum even by various approaches has not been able to overcome the heavy-metal ion issue [19]. Therefore, an efficient low-dimensional semiconductor with low/no-metal content, physical flexibility for heavy ion decoration, and rapid charge carrier migration needs to be thoroughly investigated.

Berzelius and Liebig [20] (1834) reported the synthesis of carbon nitride (C_3N_4), marking it as one of the oldest synthetic polymers. Construction of the beta phase by replacing Si from the $\beta - Si_3N_4$ by Liu and Cohen [21], was observed as a birth of polymorphism in C_3N_4. A further addition to the sequence of eight *polymorphs* includes α-C_3N_4, cubic-C_3N_4, pseudocubic-C_3N_4 and graphitic carbon nitride $g - C_3N_4$ (denoted as CN throughout the thesis) containing s-triazine-based orthorhombic structure, s-triazine based hexagonal structure, and tri-s-triazine based structure also known as heptazine, which have been synthesized and studied as a multifunctional compound between 1989 and 1996, each having a separate role [22]. CN is the modified form of graphene framework with substituted nitrogen heteroatom imparting π-conjugation over the N-C bond. Numerous photo-reactive/photo-induced sites/charge carriers owing to the sp^2 hybridization of N- and C-atoms in the graphitic planes establish it as a potential candidate for photo-responsive applications. Thus, CN is a popular photocatalyst availing high visible light absorption, thermal-chemical stability, non-toxicity, and a multi-layered porous structure, however rapid charge carrier ($e^- - h^+$ pair) recombination capability significantly reduces the overall photocatalytic efficiency. Therefore, utilization of CN for large-scale photocatalytic applications considering its environment-friendly character, modifications are required to increase its visible light response of spectrum along with a reduction in the rate of recombination of photo-induced charge carriers [23].

1.3.1 Doping and Loading of Atoms

Among the known structural modification methods *doping*, substituting an existing element or adding an atom in the interstitial region, and *loading*, anchoring adatom over the surface of the material is primarily performed. The doping method is utilized for photocatalysts to enhance the optical performance of 2D semiconductors by band gap narrowing resulting in the high visible light absorbance. The pristine CN monolayer has been investigated for H, B, C, O, F, Si, P, S, Cl, As, Se, Br, Te, and I non-metal doping [24]. The importance of the formation of impurity states within the forbidden energy region in the non-metal doped CN has been studied. However, on one hand, the integrated ultraviolet region reduces by 7% for H-, B-, C-, Si-, and Se-atom while on the other the

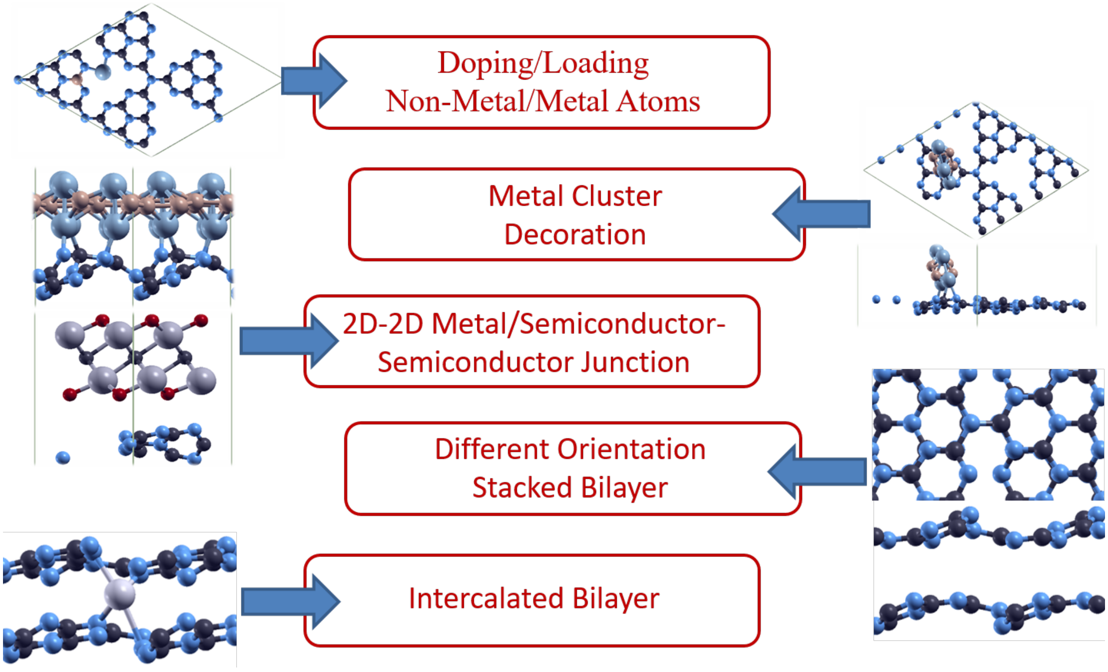

Figure 1.3: Different functionalization techniques shown in the sequential form.

integrated ultraviolet region and for all dopants increases by about 14%-71% [1]. A study on P and S doped systems emphasized enhanced photo-response and charge carriers imparted prolonged lifetimes for the π-conjugation activation and reduction in Gibbs free energy by 0.28 eV for CO_2 reduction, respectively. Similar work showed effective charge carriers for O-, P-, B-, and S-doped CN [1] resulting in 1.9, 1.4, 1.7, and 2.4-folds high CH_4 generation. An investigation of O-, F-, S-atom doping, and C(N)-impurity over CN showed an improvement in the visible absorption modifying the reduction-oxidation potential due to production of impurity states and facilitation of charge carriers. Among all the anions, thermal instability was seen for Br and I, while lower energy shifting of Fermi energy (E_F) of all the specimens except that of the I-doped monolayer is reported. Thus owing to high charge separation, π-localization, high photo-activity, and conduction band edges (E_{CB}) crossing reduction potential, anion-doped CN is suitable for reduction capability, but lacks oxidation as seen from Fig. 1.4.

Cation doping over the CN facilitates charge carrier migration, and the Metal-Nitrogen interaction governs the photocatalytic properties. As reported, Co-doped CN and Fe/Ni/Cu/Zn-penetration into CN forms a metal-N bond and reduces recombination of photogenerated charge carriers, respectively [25]. A first-principles study on the functionalization of $g - C_6N_8$ nano-sheets with 3d-transition metal (TM) has shown the high capability of CO_2 adsorption with suitable adsorption energies (-0.15 to -1.0 eV) [26]. Adsorbed alkali metals Li, Na, K, Rb, and Cs, demonstrate metallic nature with band gap within visible light spectrum for photocatalytic application, meanwhile, the workfunction (Φ) dependence over alkali atom size shows its potential in sensor detection application [27]. Another report on the Na, K, Rb, and Cs intercalated CN detailed theoretically and experimentally shows the generation of an interfacial electric field governed by the formation of the interlayer bridge. Except for the Na-doping, K, Rb, and Cs decoration shows an increase in the oxidation potential as a result of positive shifted VB position and the decrease in electronic localization [28, 29] however, with 18.7 $\mu mol/h$, Na-doped CN photocatalyst displays 3.7 times hydrogen generation [28].

A large number of reports show cation stabilized over the surface of CN on the void or over the triazine moieties as a decoration rather than the dopant, this phenomenon is ruled by the ionic radius of cation. High Z-atoms and noble metals prefer a void site compared to the surface due to energetic stability. Machine learning using the d-band center and the electronegativity of TM atom facilitated to screen of single-atom catalysts (SAC) based on the adsorption strength of formic acid [30]. Thereafter computation of the energy barrier for the formic acid dehydrogenation was performed over Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Pd, Ag, W, Os, Ir, Pt, Zr, Mo, Ru, Rh, and Au@CN, where Rh-, Pd- and Pt@CN exhibit kinetic feasibility and thermodynamical stability which makes it an efficient photocatalyst beneficial for hydrogen storage and transport. Li et al. [31] have investigated overall water splitting over the single metal (Pt, Cu, Ni, Pd, Ag, and Au) atom decorated in CN. A dependence of overpotential values on the conductive bonding nature based on ionic/covalent bond relaxations and charge redistribution was established. Recombination rate suppression for Ni, Cu, Pd, and Pt due to the separation of valence band maxima (VBM), and conduction band minima (VBM) was seen whereas on the other hand overpotential for Pt/Pd with intermediates adsorption over the void (TM) decreased by 4 (3) fold for OER and Hydrogen evolution reaction (HER) [31]. Experimental synthesis of a single Pt metal atom dispersed over CN monolayer is endergonic due to Pt clustering, although computationally it exhibits an anisotropic nature. Effective redistribution of Highest occupied molecular orbital (HOMO)- Lowest unoccupied molecular orbital (LUMO) is an essential property that can alter the reaction barrier therefore the overall water-splitting capability of a photocatalyst should not be predicted based on the band edge straddling only but the overpotential should be considered.

On one hand where anion doping facilitates the charge migration and its separation, while on the other cation doping/decoration enhances the optical absorption through the generation of impurity states in the forbidden region. This cation doping/loading governs the effective mass of photogenerated charge carriers leading to a reduction in the recombination rate. Effective charge compensation and alignment of CBM and VBM caused by the synergistic effect of metal/non-metal loading/doping are known to be highly useful for simultaneous reduction and oxidation reactions. An increase in the activity of Rhodamine B degradation by 4.2 times, as a result of suppression of recombination rate is seen in the plasmonic Ag nanoparticle along with B in CN. Increased electron mobility along with narrowing of the band gap resulted in higher visible region absorption [7]. An improved charge migration due to electron-affinity of alkali metal in the porous structure of (Na, P)-CN indicates the birth of non-radiative charge transfer pathways leading to higher efficiency of photocatalyst. P, Ba co-doped in CN showed high hydrogen generation of 12 $\mu molh^{-1}$ under spectrum region greater than 420 nm attributed to larger surface area and delocalized DOS distribution [32]. O was primarily added to the CN lattice to modify the band structure, which led to increased absorption and redshift at the same time. Furthermore, Na doping improved the migration and separation of photogenerated carriers under visible light [33]. In the band gap of the P/Ni co-Doped CN nanotubes, Ni and P co-doping can form a new intermediate state close to the CB, and the porous nanotube structure increases its BET surface area along with the light

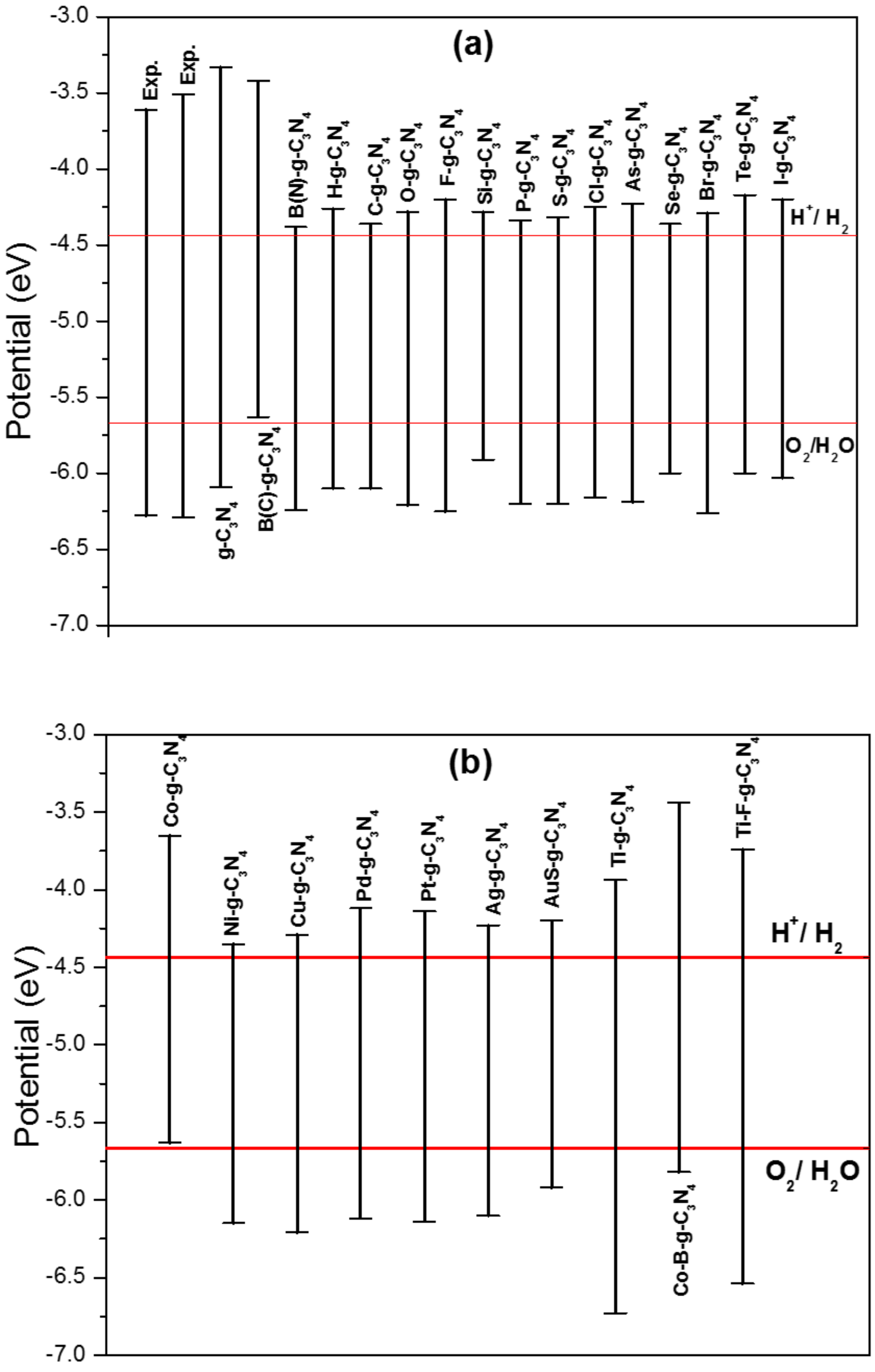

FIGURE 1.4: (a) Band Edges for experimental and theoretical pristine and non-metal doped g-C_3N_4 [1], (b) Band Edges for metal and anion-cation doped g-C_3N_4 (Potential vs E_{vac})

reflection path. These properties demonstrate a synergistic ability to broaden the absorption of visible light, facilitate the separation of photogenerated charges and the light-electron excitation rate of CN, and provide additional reaction sites for the photocatalytic HER. The enhanced photocatalytic disinfection efficacy was likely ascribed to the complementary impact of Ti and O co-doping over CN, resulting in prolonged visible light response and heightened charge transport efficiency [34]. (F, Ti) codoped heptazine/triazine based CN heterostructure inhibits carrier recombination [35]. As-synthesized CN co-doped with K and Fe shows p-type semiconductor properties with enhanced current density. In the end, enhanced photocatalytic performance is shown because of the larger specific surface area, stronger light absorption capacity, lower recombination rate, and more photo-generated carriers [36]. The band edges of the pristine semiconductor are impacted by anion and cation doping as well as co-doping. These band edges are shown in Fig. 1.2, where it is evident that the VB and CB edges are greatly moved in the direction of the redox potentials.

1.3.2 Cluster Decoration and Stacked Heterostructure

After reviewing the literature, we concluded that the conversion of earth-abundant molecules (such as $H_2O, CO_2, or N_2$) into fuels and high-value products (like H_2, hydrocarbons, oxygenates, or NH_3) may be achieved by photocatalytic energy conversion. The fundamental component of photocatalysis is the driving force derived from $e^- - h^+$ pairs produced in semiconducting materials upon light irradiation meanwhile, the performance of the photogenerated charge carriers can also be improved by either the addition of co-catalysts or by the formation of a junction by alignment of same/different materials. Hence, forming a 0D/2D metal-semiconductor, 2D/2D semiconductor-semiconductor, cluster decorated heterostructure, bilayer/heterostructure shown in Fig. 1.5, directed towards improving visible light absorption and enhancing photogenerated $e^- - h^+$ pairs produced in semiconducting materials upon light irradiation meanwhile, the performance of the photogenerated charge carriers can also be improved by either the addition of a co-catalyst separation. It is most feasible to form a heterostructure with narrow band gaps and appropriate band edge positions to maximize the benefits of each component. As shown in Fig. 1.5, each type of heterojunction whether it is a type II heterojunction, Schottky Junction/Ohmic contact, or Z-scheme heterojunction possesses a unique character of light absorbance and charge transfer. On one hand where Schottky Junction/Ohmic contact thrives on the band bending governed by the charge transfer process, while on the other inhibition of recombination along with a quick path for charge transfer is seen. While Type II heterostructures and Z-schemes have similar band structures, a semiconductor with a high CB position is ideal for a reduction process, while a semiconductor with a low VB position is good for an oxidation reaction. Electrons from the VBs of both materials are excited to the corresponding CBs when light irradiates the interface. This causes a delay in charge carrier recombination by increasing the lifetime that occurs across the interface, following a unique "Z"-shaped transport pathway that preserves the pair by strong redox capability and also allows for a wide light response range. Amorphous metal borides do not meet the criteria for becoming a photo-responsive material because they lack a forbidden zone, even though a photocatalyst needs a broad band gap to absorb visible light and a low rate of recombination of photo-generated charge carriers over a long relaxation period. There are published scientific papers on the decoration of semiconductor graphitic carbon nitride (CN) with metal borides for hydrogen generation, oxygen evolution [37, 38], and oxygen reduction species for inactivation of Staphylococcus aureus [39]. The HER, which is carried out over transition metal phosphide/phosphate (TMP/Pi) and CN hybrid systems, including $NiFeP/CN$ [40], and $NiCo - Pi/CN$ [41], is attributed to its high efficiency due to many active sites, a shortened lifetime at the heterostructure interface, and directional electron delivery. Two studies on amorphous CoB and CN have shown charge transfer efficiency for photocatalytic antibacterial elimination procedure [38] and charge transfer resistance for OER [37], as well as the development of Schottky

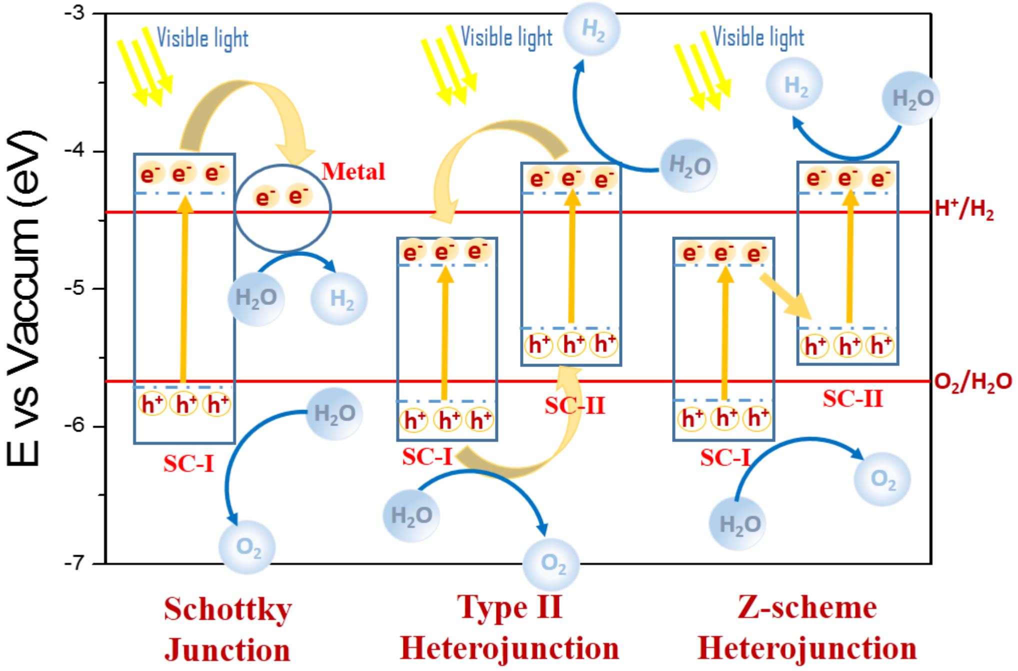

FIGURE 1.5: Different types of heterostructure, Schottky junction within metal-semiconductor interface, type-II and z-scheme categorized for semiconductor-semiconductor heterojunction.

junction regulating the synthesis of peroxide molecule.

For the current work, a recently developed, synthesized, and widely used family of 2D layered compounds known as MXenes—which, depending on the component transition metal and surface functional group, contain both conductors and semiconductors are taken into consideration. In addition to suppressing carrier recombination and exhibiting rapid charge separation, MXenes-based photocatalysts [17] have Fermi levels that are identical to those of widely used wide-band gap photocatalysts like ZnO and TiO_2. If a heterojunction forms, Fermi alignment promotes electron migration to MXene surfaces, resulting in the creation of a Schottky barrier at the interface to stop electron backflow. MXenes, therefore, ought to be the first choice for 2D-2D semiconductor heterojunctions and co-catalysts in their metallic form due to their ability to align their band edges, form a Z-scheme for interlayer charge transfer from CB to VB, and lengthen their lifetimes for longer reactivity over the surface. MXenes are found to be suitable for Z-scheme semiconductors for the formation of heterostructure with CN. Like,

$Sc_2C(OH)_2$ shows high HER photocatalytic activity, attributable to an indirect band gap of around 2.0 eV and CBM above HER theoretical potential [42].
The photocatalytic characteristics of 2D CN/Ti_2CO_2 van der Waals (vdW) heterostructure have been investigated from the first-principles method using hybrid functional. The heterostructure in discussion belongs to the type-II category, exhibiting staggering band alignment and the generation of an interfacial electric field integrated due to accelerated charge transfer from CN to Ti_2CO_2. Reduced overpotential values attributed to the spatially distinct VB and CB edges provided evidence of the high light-harvesting capability, suppression of charge carrier recombination, and increased catalytic activity of CN/Ti_2CO_2 towards both HER and OER, suggesting the possibility of a direct Z-scheme photocatalytic mechanism. Lamellar CN on Ti_3C_2 surface synthesized by Li et al. [43] was studied in an additional study, where it was reported that the formation of a Schottky barrier facilitated electron immigration, contributing to the excellent conductivity of MXene at the interface. This composite material was found to be highly efficient for photo-conversion and produced six times more hydrogen than pure pristine material. In comparison to CN, the study of Liu et al. [44] using CN/Ti_3C_2 composite produced 2.75 times larger photocurrent and improved photocatalytic capacity of ciprofloxacin degradation. A thorough examination of the HER performance for a completely O-terminated MXene, including seven bi-metal carbides and ten mono-metal carbides, was conducted by Ling et al. [45]. TiO_2/C_3N_4 (2D/2D) core–shell vdW heterojunction was synthesized by He et al. [46], and 0D MXene was deposited to provide an S-scheme charge transfer channel between the 2D structure and the trapping of electrons from C_3N_4. Multi-junction interface tuning for regulated increased Carbon dioxide reduction reaction (CO_2RR) and controlled charge migration is provided in this work. Work on the alkalinized Ti_3C_2 with CN decoration is attributed to larger Fermi level difference and superior electrical conductivity for photo-induced carrier separation for 5.9 fold photocatalytic CO_2RR compared to pristine CN. It also suggests that MXene is a low-cost, noble metal-free co-catalyst for photocatalysis [17].

1.4 Role of charge transfer in enhancing photocatalytic activity

Understanding charge transfer is crucial to comprehending photocatalytic reactions. The process of charge transfer is essential for the creation of the active site in a redox reaction, the distribution of charge, and the separation of $e^- - h^+$ pairs produced in semiconducting materials upon light irradiation meanwhile, the performance of the photogenerated charge carriers can also be improved by either the addition of co-catalysts pairs or the transfer of electrons from VB to CB. The creation of the charge transfer channel in CN following modifications by doping, loading, and heterostructure formation has been explained in several ways. It is shown that the bonding between intermediates (OH, O, OOH, H_3O, and H) and the reaction site determines the overpotential of HER and OER. In comparison to the electropositive atoms on the photocatalyst surface, more electronegative atoms engage more actively in the redox process and provide a lower value of overpotential. To improve the photocatalytic activity in the case of P and S doped CN, a charge transfer channel via the N–S–N–C–N–P route is proposed [1]. Transition metal atoms are thought of as regulators in the study of TM doping in CN, helping to modify the active site's electronegativity and, therefore, the overpotential reduction.

1.5 Reaction Mechanism

1.5.1 Hydrogen/Oxygen Evolution Reaction

Overall water splitting by photocatalysis is a thermodynamically uphill process ($\Delta H_{\Phi} = 285.5\ KJmol^{-1}$). It is made up of two half-reactions, which are the HER and the OER. It can be achieved by shining solar light on photocatalysts and this has emerged as one of the most promising methods for producing clean energy because of its many benefits, including its high physicochemical stability, low cost, and cleanness. HER occurs as a cathode reaction within the water electrolyzer system, where water is reduced to generate H_2 ($2H^+ + 2e^- \implies H_2$). It is a two-electron transfer system with one catalytic step in general. Therefore, to achieve high kinetic effectiveness for electrochemical water splitting, an active electrocatalyst must be used to reduce the overpotential that drives the HER process. OER is the four electron transfer step, where the water molecule is converted into the hydroxyl ion, followed by further deprotonation forming O, the addition of another water molecule leads to the formation of another O, and the presence of two O-atoms combine to form dioxygen molecule.

1.5.2 CO_2/N_2 Reduction Reaction

For every CO_2 reduction reaction, H^+ is needed as an extra reactant throughout the steps that take place on the photocatalyst or photoelectrocatalyst. Hydrogen is produced by photocatalysts or photoelectrocatalysts from a variety of sources, including water alcohol, and even oxidizable trash. Hydrocarbon synthesis requires the production of H. On the other hand, the formal potentials of the reactions associated with the photo-reduction of CO_2 and H_2O are given as follows:
$2CO_2$+ $e^- \implies CO_2^-$ - 1.8 V (vs. NHE)
CO_2 (g)+ H_2O (l)+ $2e^- \implies HCOO^-$ (aq) + $2OH^-$ (aq) - 0.61 V (vs. NHE)
CO_2 (g)+ H_2O (l)+ $2e^- \implies CO$ (g) + $2OH^-$ (aq) - 0.53 V (vs. NHE)
CO_2 (g)+ $3H_2O$ (l)+ $4e^- \implies HCHO^-$ (l) + $4OH^-$ (aq) - 0.48 V (vs. NHE)
CO_2 (g)+ $5H_2O$ (l)+ $6e^- \implies CH_3OH$ (g) + $6OH^-$ (aq) - 0.38 V (vs. NHE)
CO_2 (g)+ $6H_2O$ (l)+ $8e^- \implies CH_4$ (g) + $8OH^-$ (aq) - 0.24 V (vs. NHE)

Six protons and six electrons are transferred during photocatalytic Nitrogen reduction reaction (N_2RR) into NH_3, a strong endothermic process that produces stoichiometric O_2 by water oxidation ($N_2 + 3H_2O \implies 2NH_3 + 3/2O_2$, $\Delta G = +7.03$ eV). To produce photoexcited $e^- - h^+$ pairs produced in semiconducting materials upon light irradiation energy larger than the band gap is required meanwhile, the performance of the photogenerated charge carriers can also be improved by either the addition of a co-catalysts pairs and the energy > 1.17 eV required for the total NH_3 production, photons with an energy higher than the energy band gap of a semiconductor photocatalyst must be absorbed. This starts the photochemical N_2RR, which requires a potential of at least 1.17 eV per electron. When photo-irradiation is applied with enough energy, electrons jump into the CB, and holes are generated at the VB at the same time. This causes the reduction of N_2 to NH_3 with photo-excited electrons and water oxidation with the holes that are formed.

1.6 Motivation of the Thesis

Numerous methods utilized to tailor the efficiency of catalysts along with enhancement of absorbance in visible light have been proposed and reported to realize efficient photocatalysts for reduction-oxidation reactions. Apart from the bulk phase of photocatalysts, lower dimensional materials have also been studied in their pristine and modified geometry to achieve high efficiency for photocatalytic reactions. Among the reported photocatalysts, graphitic carbon nitride in its heptazine/tri-s-triazine morphology shows exceptional capability due to its intrinsic properties. Large reactive sites on the surface due to easy exfoliation of its stacked layers, high charge carrier migration, and formation of a large number of photo-induced $e^- - h^+$ pairs produced in semiconducting materials upon light irradiation meanwhile, the performance of the photogenerated charge carriers can also be improved by either the addition of a co-catalysts pairs, and band edge straddling of the reduction-oxidation potential are among those properties. The presence of a wide band gap for impurity accommodation, the formation of deep/shallow trap/recombination sites, π-conjugation over the CN mesh, and polymeric nature providing high elastic limit has attracted the attention of the scientific community around the world to investigate its capability as efficient photocatalyst.

Various functionalization methods are identified to improve the π-conjugation offering large reactive sites for surface adsorption, narrowing of band gap towards the visible region, and reducing of overall reaction barrier modulating the reaction dynamics over the surface, therefore these methods have gained a keen interest for further exploration. However, the rapid recombination of charge carriers, and ineffective separation of $e^- - h^+$ pairs produced in semiconducting materials upon light irradiation meanwhile, the performance of the photogenerated charge carriers can also be improved by either the addition of a co-catalysts pair for simultaneous reduction-oxidation reaction and lack of in-depth understanding of the charge transfer dynamics over and within the surface for the functionalized CN leaves room for the design of an efficient photocatalyst.

Our motivation was drawn from the insufficiency seen in the existing reports to understand the step-wise design procedure of an efficient photocatalyst, rather than random modification. Our work demonstrates an extensive investigation of the various functionalization techniques, charge dynamics within the tailored semiconductor, and the role of this modification on the overall water dissociation into hydrogen and oxygen molecules. We designed and explored the photocatalytic properties of Metal/non-metal loaded/doped CN monolayers which are characterized by electronic and optical properties. Investigation of the interface charge dynamics on the dimensionality variation of the co-catalyst over CN based heterostructures includes 0D/2D metal-semiconductor. Whereas, first-principles calculation on 2D-2D semiconductor-semiconductor junction demonstrates the importance of the formation of the interfacial electric field in the photocatalytic properties. A study of the modified bilayer of CN with different stacking configurations and Li-atom intercalation within the bilayer shows the effect of interlayer orbital interaction on the reaction barrier of the water-splitting process. Finally, to understand the CO_2 conversion to CH_4, and N_2 to NH_3, various pathways for CO_2RR and N_2RR have been explored on the Co-loaded CN.

1.7 Objectives Achieved and Thesis Layout

Motivated by the requirement of design techniques, and understanding of modified photocatalysts in terms of charge transfer mechanism, we list the major objectives directing the computational work done for this thesis.

1. Influence of TM loading, non-metal element doping, and loading-doping together on the electronic and optical properties have been checked.
2. Analysed different types of heterostructures, mechanisms of Z-scheme, interfacial and Schottky barrier potential in terms of charge transfer, cohesive energy, and Φ for a detailed understanding of the photocatalytic process.
3. Investigated the possible structure modification and changes in electronic properties of heterostructure by determination of ground state structure. Electronic band structure and DOS at different conditions with vdW interaction have also been studied.
4. Along with the detailed photocatalytic reaction mechanism, the photocatalytic behavior of the designed materials has been studied by calculating the band gap, valence band edge (E_{VB}), and E_{CB} for HER and OER, and analysis of band structure curves for the effective mass calculations to compute the rate of recombination of electrons and holes.

This thesis is comprised of seven chapters, with four chapters consisting of work done based on the objective proposed.

CHAPTER 1 introduces photocatalysis, various methods to design an efficient photocatalyst, a literature review, and the reaction mechanism to be studied based on the motivation and objective determined for the thesis. Computational tools employed in the investigation performed in this thesis are discussed in the **CHAPTER 2**. Here, we explore the history of the origin of DFT, and formalism existing before its birth. We discussed the approximation methods based on the eigenfunction and an electron density to solve the many-body problem with the Schr$\ddot{o}$dinger equation for periodic systems. Thereafter we present different exchange correlations functional along with pseudopotential approximation, and energy correction by inclusion of the vdW dispersive parameter to achieve computational accuracy of the investigated systems. Formalism to determine the structural stability of the designed photocatalyst, its absorbance, dielectric function, and charge carrier mobility has been presented. We have discussed the conventional, and self-modified mechanism for HER, and OER, whereas CO_2RR, and N_2RR have been mentioned. Methodologies developed for the determination of reaction barriers during reactions are elaborately discussed. Methods such as maximally localized wannier function have been presented owing to its significance in computing band structure with hybrid functional.

CHAPTER 3 begin with our present investigation on the design of Metal(Co/Ag/Fe), Non-metal(B/P/O), loading, doping, and loading with doping (Co-B, Ag-P, Fe-O) configuration over CN-monolayer. With first-principles calculations computation of electronic property helped us to screen a material suitable for redox potential straddling. Thereafter, Co-loaded, B-doped, and $(Co-B)$-CN were studied from the perspective of optical and photocatalytic properties. The role of, intermediate band (IB) formation, p/n type extrinsic semiconductor, the effective mass ratio of charge carriers, and charge transfer dynamics over photocatalytic properties were investigated. A suitable reaction site determined using Löwdin charge analysis was thereafter considered for HER, and four electron-based OER to understand the overall water splitting potential.

In **CHAPTER 4** CN based heterostructures consisting of 0D/2D-2D metal-semiconductor junction along with 2D-2D semiconductor-semiconductor junction have been investigated of structural, electronic, optical, and photocatalytic properties. Cobalt boride owing to its metallic nature has been decorated, and vertically stacked in 0D, and 2D configurations, respectively. Whereas, Hf_2CO_2/CN (Hf_2CO_2/CN) heterostructure including Hf-based MXene, has been studied to understand the electron transfer scheme across the heterojunction. The role of dimensionality of the co-catalyst and its interfacial interactions with CN over the overpotential of the reaction have been discussed in detail. While, for later cases, possible band alignment, formation of the built-in electric field at the interface, and electron migration between two semiconductors are discussed. Followed by the adsorption of the reaction intermediate to study the variation of the reaction barrier with interface functionalization.

CHAPTER 5 encompass modification in the pristine CN through the design of CN-bilayer with different stacking arrangements. Screening of suitable bilayer configuration based on electronic properties, followed by a comparative study between the monolayer, planar- and corrugated-bilayer has been demonstrated. The role of interlayer orbital coupling in the modification of optical, and catalytic properties has been discussed in detail. Owing to the promising results, predicted by the bilayer bridging led us to intercalate Li into CN-bilayer. This Li-CN has been subjected to systematic screening, while Nudged elastic band (NEB) calculation of reaction barrier for HER, OER, and simultaneous HER with OER. Volmer-Heyrovsky and Volmer-Tafel reaction mechanisms were explored to understand the interaction of adsorbate over adsorbent, over the most suitable site recognized from the conventional method of HER/OER. The role of orbital coupling is summed with the influence of intercalant bridging of the bilayer was elaborately discussed to evaluate its potential for photocatalytic HER/OER.

CHAPTER 6 comprises of the computation of possible reaction intermediates for CO_2RR, and N_2RR over Co decorated CN using dispersion corrected DFT calculations. A suitable adsorption site was computed, and thereafter the probable reaction pathways including all the reaction intermediates, were discussed. Adsorption energy was considered to be a crucial parameter in understanding the behavior of the reaction barrier over the complete reduction reaction. The application of this chapter proliferates into the realm of energy conversion and fuel production.

At the end, **CHAPTER 7** demonstrates the summary of all the studies performed in the four working chapters. This chapter elaborates on the prospects in the field of photocatalysis, and its scope to rational design strategies for the efficient photocatalyst for the given reaction mechanisms.