BAND GAP ENGINEERING OF FUNCTIONALIZED SEMICONDUCTORS FOR PHOTOCATALYTIC APPLICATIONS

Executive Summary
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1. INTRODUCTION

Substantial requirement of the energy to fulfil the basic need of human being require either large amount of fuels or the technology for energy conversion. Existing fuel sources are on the verge of extinction due to its current rate of mining. As an alternate to such fuel crisis scientific world is aiming towards sustainable energy conversion methods which utilize the renewable sources of energy for large-scale applications. Amongst such techniques, photocatalysis is known to human kind since the understanding of plant anatomy. Photocatalysis comprises of four steps, (i) formation of photo-generated charge carriers on light illumination, (ii) migration of charge carriers to the surface of the photocatalyst, (iii) participation of respective photo-induced charges in the respective reaction, and (iv) annihilation of electron-hole pair (e^--h^+). Here, with the help of photo-generated charge carriers, the rate of reaction over the surface is enhanced with an aid of solar energy. So far, this technology have gained its fame for pollutant degradation, such as dye disintegration, toxic micro-organism removal, and self-cleaning glasses. But, its utilization in hydrogen production, oxygen evolution, conversion of carbon dioxide/carbon mono-oxide into methane or methanol, and nitrogen reduction to ammonia has presented photocatalysts as potential energy conversion materials in last half century.

Owing to fascinating properties such as, high absorbance in visible spectrum of light, large surface area for reactions, multiple sites acting as reduction/oxidation centres, rapid charge migration for feasible reaction mechanism, photocatalysts have shown its usefulness among energy materials. Various semiconducting materials with band gap (E_g) larger than 1.23 eV such as TiO_2, CdS, ZnS, ZnO, $SrTiO_3$, g-C_3N_4, MoS/Se_2, have been studied as an efficient photocatalysts. Based on the feasibility of charge migration to the surface, band edges straddling across the reduction/oxidation potential, suppressed recombination of photo-induced carriers, and large surface activity, two-dimensional (2D) photocatalysts were preferred. These 2D-materials were then screened on the basis of their capability to accommodate the impurity within their forbidden region, low toxicity, and environmental friendliness. Graphitic carbon nitride (g-C_3N_4), one among eight polymorphs and formed by bridging three triazine ring with a single N. g-C_3N_4 (CN) is found in hexagonal geometry synthesized from melamine/urea using thermal poly-condensation method. Its feasible exfoliation is result of its weak binding via van der Waals (vdW) forces, and its π-conjugated structure provides high surface reactivity.

The rapid recombination of e^--h^+ in CN provide us room to design and utilize the strategy to enhance the photocatalytic activity by functionalization. This thesis comprises of design mechanism of efficient photocatalyst along with various functionalization techniques to reduce the rate of recombination either by spatial separation or formation of charge transfer channel across the interface. Structural modification, loading/doping of cation/anion, co-catalyst decoration, and vertical metal/semiconductor, semiconductor/semiconductor stacking over CN have been studied in this work for overall water splitting detailing oxygen/hydrogen evolution mechanism. While potential photocatalyst for reduction reaction is selected to investigate the CO_2/N_2 reduction to useful fuels. Work done in this thesis focuses on different modification strategies, charge dynamics dependence, and their role on the overpotential of simulated reactions.

2. COMPUTATIONAL METHODOLOGY

The proposed work have been undertaken computationally where structural, electronic and optical properties were computed using Density Functional Theory (DFT) based Quantum Espresso and Wein2k codess. DFT allows us to by-pass the computational difficulty in solving the many-body wave function by considering the electron density instead of the electron wave function. In DFT, Kohn and Sham have changed the problem of solving the ground state energy and particle density of an N-electron system to that of solving a set of independent-particle equations therefore total energy of the system is a unique functional of density. These Kohn–Sham equations consist of N single-particles (three-dimensional) Schrödinger-like equations with a modified effective potential and are much easier to solve than the original (3N-dimensional) many-body problem. The modified potential is itself a functional of the total particle density $\rho(\vec{r}\,)$ and contains a contribution from the quantum-mechanical exchange and correlation $\upsilon_{xc}(\vec{r}\,)$ of the particles. In DFT scheme, the one particle Kohn-Sham Hamiltonian operator is defined as

$$H = -\frac{\hbar}{2me}\nabla^2 + \upsilon_{eff}(\vec{r})$$

Where,

$$\upsilon_{eff}(\vec{r}) = \upsilon(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_{xc}(\vec{r})$$

which includes the external potential, Coulomb potential and exchange-correlation potential, respectively. In order to calculate the accurate E_g hybrid DFT (h-DFT) with HSE06 functional has been utilized accompanied by Maximally Localized Wannier Functions for band structure computation. Layered system were relaxed with the Grimme-D2 dispersion correction within a vacuum region for truncation of periodic image interaction. Initial computation for structural relaxation was performed with converged lattice parameters, kinetic energy cutoff for wave-function as well as for charge density.

Effective mass computation using parabolic approximation, real/imaginary part of dielectric function using Kramer-Kronig relationship, reaction barrier using Nudge elastic band calculation, and Gibbs free energy change using Computational Hydrogen Electrode model has been performed in studied cases. Band edges were computed using Normal Hydrogen Electrode model, while for simulation of water splitting over the surface of photocatalyst was performed following Rossmeisl and Nørskov's formulation. CO_2 reduction reaction was performed with all the possible reaction intermediates and the possible reaction pathways consisting of existing intermediates adsorbed over the surface meanwhile N_2 reduction was simulated using alternating, enzymatic and distal reaction mechanism.

3. METAL/NON-METAL LOADED/DOPED g-C_3N_4 MONOLAYER

Formation of charge transfer channel aids to the rapid charge migration at the surface of the photocatalyst. Cation (Co/Fe/Ag) loading over the surface, anion (B/O/P) doping within pristine framework of CN, an atomic monolayer has affected the π-conjugation and enhanced the optical absorption. These cation-anion pairs Co-B/Fe-O/Ag-P, have been screened on the basis of their band edges as a potential photocatalyst. Band edges straddling across the reduction-oxidation potential has been seen for Co-B, loaded-doped CN, hence it is studied further. The pristine CN, B_{int}-CN (B substituted at bay C site), $B_{non-int}$-CN (B substituted at corner C site), Co-CN, $(Co-B)_{int}$-CN, and $(Co-B)_{non-int}$-CN were analysed based on the structural, electronic, and optical properties for the application of photocatalytic activity utilizing the h-DFT.

B-doping and Co-loading resolved the limited photo-generation of charge carriers and rapid rate of e^--h^+ pair recombination in CN. In B doped CN, the partially filled B-2p orbitals aids in spatial charge migration and their redistribution across the surface. $(Co-B)_{int}$-CN [$(Co-B)_{non-int}$-CN] shows the formation of intermediate band on Co-loading while narrowing [widening] impurity band when B directly interact with Co [B indirectly interact with Co]. Curvature of band structure (conduction band minima and valence band maxima) determines the effective mass of the electrons and holes hence their mobility. The large variance in the effective mass ratio of e^--h^+ in $(Co-B)_{int}$-CN show reduced rate of e^--h^+ recombination, increasing the efficiency of photocatalytic reduction-oxidation reaction. An excess negative charge is accumulated on the N_{edge} atom due to the influence of Co-B short- and long-range interaction and charge redistribution. This alters the adsorption energy of intermediates in hydrogen evolution reaction (HER) and oxygen evolution reaction (HER). The simulation of HER/OER result in an overpotential (η^{OER}) values of 2.32, 1.22, 1.27, 1.78, 1.28, and 1.08 V for pristine CN, B_{int}-CN, $B_{non-int}$-CN, Co-CN, $(Co-B)_{int}$-CN, and $(Co-B)_{non-int}$-CN, respectively. Whereas, η^{HER} value for pristine CN, B_{int}-CN, $B_{non-int}$-CN, Co-CN, $(Co-B)_{int}$-CN, and $(Co-B)_{non-int}$-CN is calculated as -0.69, -2.11, -2.37, 0.06, 0.27, and 0.37 V, imparting Co-CN as the best reducing capability. Considering the band edge straddling and reported prohibitive overpotential, (Co-B)-CN in long and short range interaction shows reduction in η^{OER}. Therefore, on the basis of E_g reduction, high optical absorbance in visible range, high variance of effective mass ration and low $\eta^{OER/HER}$ value (Co-B)int-CN is the most potential photocatalyst for overall water splitting.

4. g-C_3N_4 BASED HETEROSTRUCTURE

The role of Co and B over the photocatalytic activity of CN has been performed by decorating/stacking cobalt boride (CoB) cluster/slab over CN monolayer. As a metal-semiconductor heterostructure, the work function (Φ) of metal/semiconductor govern the charge transfer dynamics at the interface. In the case of CoB-CN based 0D/2D-2D metal-semiconductor heterostructure $\Phi_M < \Phi_S$ before the contact leading to electron transfer from metal to semiconductor leading to the downward band bending. The type of contact based on the extrinsic semiconductor, for n-type (corrugated-CN) shows low-resistance junction while for p-type (planar-CN) rectifying contact is generated. This two systems along with a smaller cluster is systematically studied to comprehend the optical behavior, charge dynamics, and impact of dimensionality variation on the $\eta^{OER/HER}$. Heterostructures investigated in this report have attained several necessary conditions required for an effective photocatalyst, these conditions includes large number of reactive sites, low reaction barrier for HER and OER, wide charge carrier separation due to formation of interface and interfacial electric field (E_{if}). Relative variance in the band structure across the Fermi energy promotes low recombination rate of photo-induced charge carriers, while high optical absorbance in the visible range enhances the numbers of photo-generated carriers within photocatalyst. The electron transfer on the heterojunction formation inhibit formation of E_{if} due to charge accumulation at the semiconductor, this E_{if} promotes feasible electron transfer across the interface for Ohmic contact. On the other hand prohibited migration of holes from metal to semiconductor in the Schottky barrier promotes either side with OER/HER. E_{if} and surface dipole generation has been attributed for the enhanced photocatalytic activity seen from the $\eta^{OER/HER}$, and cluster decorated CN with ordered-disordered geometry is seen to show efficient capability for overall water splitting owing to Schottky barrier formation at the interface.

In order to get a deeper understanding of the interplay between semiconductor-semiconductor heterostructures, we have examined the Hf_2CO_2/CN system, in which the CN-photocatalyst supports Hf-based MXene. Hafnium based MXene are widely known semiconductor utilized for the vertical stacking owing to its suitable band edge alignment, and high charge carrier mobility across the surface. The ΔΦ of the semiconductors causes electron transfer, this result in the equilibrium of Φ and band bending across the interface along with E_{if}. The unidirectionality of charge transfer and band alignment leading to straddling of reduction-oxidation potential imparts either side with simultaneous OER/HER capability. The electron localization function (ELF) plot showed the interlayer orbital interaction, this character governs the narrowing of E_g resulting in a large number of photogenerated charge carriers. Based on effective mass ratio/band curvature, effective charge carrier migration, decreased recombination, and spatial separation indicates the potential applications of Hf_2CO_2/CN heterostructure as an excellent water-splitting photocatalyst.

5. MODIFIED BILAYER OF g-C_3N_4

Structural modification is known as effective method among the photocatalysts fraternity as an efficient way to modulate the charge mobility over and within the surface. In this work h-DFT based computation has been utilized to analyze structural, electronic, optical, and photocatalytic properties of monolayer (ML) and spatially tailored bilayer (BL) of CN. The screened BL showing efficient photocatalytic properties has been investigated for the reaction kinematics of HER and OER. The ineffective π-localization in ML-CN has been tuned by structural changes in BLs, this changes affect the E_g depending on the corrugation/planar geometry of BL. This geometry variation increased spatial charge distribution, and higher electron mobility in the corrugated BL. Such BL displays interlayer π-lone pair hybridization reducing the photogenerated e^--h^+ pair recombination and also increases the absorption in the visible region for BLs by allowing forbidden transitions within the band structure. The water dissociation reaction is the limiting step for all OER sites, according to charge transfer studies. The formation of an E_{if} on water adsorption is seen owing to the double layer model, whereas the influence of additional H_2O is seen in substantially reducing the free energy change value for highly efficient HER. Charge accumulation and dispersion at the edges strengthen the ability of reaction sites due to in-plane π-conjugation driven by interlayer orbital interaction. This is evident from the decrease in the adsorption energy of intermediates, which results in a modification of the overpotential with values of -1.15 eV for OER and -0.20 eV (-0.05 eV with additional H_2O molecule) for HER enhanced photoactivity compared to ML and navigates-up possibilities for its application in flexible nano-devices for complete water splitting.

Absence of intercalant, which prevents effective charge transfer across the BL before illumination and intermediate adsorption is a major issue hindering in the efficient photocatalytic activity of BLs. Li is intercalated in the BL-CN to resolve this issue attributing to its ionic radius, and feasible diffusion within layers on synthesis. Li intercalation has an crucial impact on the system's charge transfer mechanism due to the development of a charge transfer channel within the CN BL. An interlayer electric field (E_{il}) within the layers of CN is formed on the intercalation of Li due to partial charge transfer and formation of potential difference. The simultaneous oxygen/hydrogen production with couple of water molecules have been formulated to study the overall water splitting using the climbing image nudge elastic band approach. As the reaction progresses, reactant contact with the photocatalyst surface, E_{if} is produced. The E_{if} and E_{il} pair to promote effective reactant adsorption. Li-mediated BL-CN bridging modifies the optical and electrical characteristics. Because of this, Li-CN is a more effective photocatalyst than BL-CN because of its high absorbance in the visible region, band edge straddling of the reduction-oxidation potential, and variation in E_{il}, E_{if}, and adsorption energy of the reactants as the reaction proceeds. The significance of two H_2O molecules highlighted in this study to comprehend the charge transfer channel and simultaneous HER and OER reaction mechanism justify the intercalation techniques as effective functionalization method.

6. CO_2RR & N_2RR OVER Co DECORATED g-C_3N_4

Co-based CN show brilliant charge transfer dynamics owing to the p_π-d_π interaction of N and Co atom facilitating the charge migration axially and spatially. Wide forbidden gap prepares existing material to absorb a large number of photons resulting in equally large photo-generated charge carriers hence efficient for photo-conversion of solar energy. The presence of π-conjugation and IB provide Co-CN large adsorption sites for CO_2 and N_2 reduction, high adsorption in the visible region of the spectrum, and reduced rate of recombination of photogenerated charge carriers. Potential adsorption energy value in physisorption and low difference of the adsorption energy for reaction steps display Co-CN as a potential photocatalyst for efficient CO_2RR/N_2RR.

CONCLUSIONS

As a conclusion of all the chapters, various functionalization techniques have been considered and discussed to understand its dependence on the reaction overpotential. With the initialization by cation-loading, anion-doping over CN, a narrowing of the band gap along with a reduction in the $\eta^{HER/OER}$ verifying its role on the increase of absorbance, and feasibility of reaction has been observed. Moving to the metal-semiconductor heterojunction formation, CoB decorated CN in two configurations, $(CoB)_{0D}$-CN, and $(CoB)_{2D}$-CN have been studied to utilize the synergistic effect of Co and B atoms in cluster and slab form, respectively. High performance in photocatalytic activity has been evidenced from $\eta^{HER/OER}$, along with red shifting of absorbance curve, and formation of a unidirectional charge transfer channel. This study has been further explored over the semiconductor-semiconductor heterojunction, where Hf-based MXene has been supported over CN. Hf_2CO_2/CN shows an alternating charge transfer pathway for spatial separation of photogenerated charge carriers for the reduction in the recombination rate, followed by reduced $\eta^{HER/OER}$ value in comparison to CN. The modification method used to corrugate the bilayer through orbital interaction and intercalation of alkali metal for interlayer charge transfer channel creation has shown extraordinary results with increment in the band gap value for bilayer accommodating the $\eta^{HER/OER}$ within band edges. Whereas, Li-CN has further improved the overall water splitting efficiency by the lowest value of η^{OER} among the studied photocatalyst, $\eta^{HER/OER}$ smaller than band edges and optical absorption in the visible region of the spectrum making it perfect photocatalyst for complete water dissociation. The study then explores more about the reaction mechanism over the best-reducing photocatalyst among the studied for CO_2RR, and N_2RR.

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