BAND GAP ENGINEERING OF FUNCTIONALIZED SEMICONDUCTORS FOR PHOTOCATALYTIC APPLICATIONS

Synopsis

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DOCTOR OF PHILOSOPHY

IN

PHYSICS

By

Brajesh Rajesh Bhagat

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Under the Supervision of

Dr. Alpa Dashora

Physics Department, Faculty of Science

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

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Abstract

In this thesis, we have studied the electronic and optical properties of functionalized $g-C_3N_4$ along with possible photocatalytic reaction mechanisms mainly for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) using Density Functional Theory. Starting from the study of monolayer $g-C_3N_4$ and its quantum confinement from bulk-phase, functionalization of $g-C_3N_4$ by doping of non-metals (B, O, P)/loading of metals (Co, Fe, Ag) along with suitable doping-loading (B-Co, O-Fe, P-Ag) have been studied. A system with suitable band edges was screened to perform overall water splitting. Next, functionalization of $g-C_3N_4$ by the formation of metal-semiconductor heterojunction using Cobalt-boride (Co_2B_2) in 0D and 2D form has been considered in order to understand the role of dimensionality in charge transfer across the interface. Further, the semiconductor-semiconductor heterostructure comprising of MXene (Hf_2CO_2) over $g-C_3N_4$ provides insights into band bending in OER/HER. Structural modification in the pristine $g-C_3N_4$ by different stacking of bilayer and Li intercalation in the most favorable bilayer have also been investigated. An elaborative study of charge transfer over conventional and simultaneous water-splitting reactions using climbing image nudge elastic band (CI-NEB) shows it as a potential photocatalyst. This thesis also unravels the other photocatalytic reaction mechanisms like carbon dioxide reduction reaction and nitrogen reduction reaction over the single atom catalyst ($Co-g-C_3N_4$) with possible reaction intermediates and reaction pathways to determine the most feasible reaction. Overall, this thesis describes the role of different functionalization over photocatalytic activities and defines strategies to engineer band gap of $g-C_3N_4$, in order to tailor the photocatalytic performance from the variation at the atomistic level.

Contents

Objectives

The main aim was to investigate the monolayer, functionalized monolayer, modified bilayer of $g - C_3N_4$, heterostructure of $g - C_3N_4$ with other 2D materials like MXene and MBene (2D/0D) on $g - C_3N_4$ as co-catalyst with the vdW energy correction using *ab initio* calculations and to search for new more efficient photocatalytic materials.

1. Influence of transition metal decoration, non-metal element doping, and loading on the electronic and optical properties have been checked.

2. Different types of heterostructures, mechanisms of Z-scheme, interfacial and Schottky barrier potential by charge transfer, cohesive energy, and work function in heterostructures have also been studied for a detailed understanding of the photocatalytic process.

3. Investigated the possible structure modification and changes in electronic properties of functionalized heterostructure by determination of ground state structure. Electronic band structure of states at different conditions with van der Waals interaction.

4. Photocatalytic behavior of the designed materials have been studied by calculating band gap, valence band, and conduction band edges 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.

Thesis Outline

This thesis has been divided into seven chapters, starting with the introduction consisting of the basic functionality of photocatalysts and photocatalysis. Work done on the proposed objectives of various functionalization methods and different reaction mechanisms has been reported in Chapter 1. Chapter 2 consists of the computational methodology utilized and the reaction mechanism performed to study the photocatalytic activity of the proposed functionalized semiconductors. Electronic properties, optical properties and photocatalytic activity for metal/non-Metal loaded/doped $g - C_3N_4$ monolayer has been discussed in Chapter 3. $g-C_3N_4$ based heterostructures consists of (0D/2D)-2D metal-semiconductor junction along with 2D-2D semiconductor-semiconductor junction have been investigated and reported in Chapter 4 based on the charge transfer scheme. Chapter 5 shows a study of modified bilayer of $g - C_3N_4$ with different stacking configurations and Li-atom intercalation within the bilayer. Various pathways for carbon dioxide reduction reaction and nitrogen reduction reaction have been explored on the Co-loaded $g - C_3N_4$, a Single atom catalyst, in Chapter 6. Conclusions and future aspects of the work done over the photocatalytic applications on the functionalized $g - C_3N_4$ are discussed in the last Chapter.

1 Suitable Semiconductor Photocatalyst: An Introduction

Energy is the basic requirement of every being that ever existed on this land. From energy harnessing to its conversion, there exist various methods in the natural cycle, Photosynthesis being one of them. [1] And, humans since the discovery of fire have been looking for ways to do the same, although energy storage has emerged as the new way of conserving energy since the industrial revolution for tackling any futuristic energy crisis. Today, due to a shortage of non-renewable energy sources, time demands innovative technological advancement for enhanced solar energy conversion along with efficient materials for sustainable utilization of natural sunlight for conversion of greenhouse gases into fuels. [2] Photocatalyst, a material

utilized for the rapid conversion of naturally abundant molecules into fuels is the solution to the grave energy crisis. [3]

Polymeric and polymorphic semiconductor, graphitic Carbon Nitride ($g - C_3N_4$) has been a priority of investigation in scientific communities owing to its large surface area for reactant adsorption, rapid photogenerated charge carrier mobility, high optical absorbance in the visible spectrum, non-toxic, eco-friendly, lamellar structure with ease in chemical exfoliation, the feasibility of reactions over the surface due to presence of π-conjugation and double π-conjugation between C-N atom in the web, and two layers separated by weak van der Waals interaction, respectively. [4] Wide band gap capable of culminating intermediate states formed on the doping/loading/decoration of non-metal, metal, metallic cluster-based impurities, stable structural corrugation on reducing dimensionality or on introducing heavy atom in $g - C_3N_4$ mesh, the affinity of sustaining its electronic property on high lattice mismatch, suitable workfunction for interface charge transfer on the formation of the heterostructure, and band edges value corresponding to reduction-oxidation potential promotes capability of $g - C_3N_4$ as promising photocatalyst. [5–7]

Although, the fast recombination rate of charge carriers, localization of electrons over the C-N bond over the surface, high prohibitive overpotential for oxygen evolution reaction (OER), and band gap tending towards ultraviolet region on reducing dimensionality due to quantum confinement challenge its suitability as an efficient photocatalyst. Whereas transition metal (TM) oxides since their synthesis have shown promising applications in electrochemical photolysis, the presence of heavy metals, and transition metal sulfides despite their high optical absorbance contain the toxic sulfur which, if utilized for contaminant degradation or water splitting could affect human health. Substantial reduction in the concentration of heavy metals on the other hand will fulfill the importance of the metal oxide/sulfide-based photocatalyst while reducing the health hazard created. [8] TM and noble metals (Ag, Au, Pd, Pt) due to $p_\pi - d_\pi$ interaction between N atom of $g - C_3N_4$ and metal atom have shown the formation of charge transfer channel for adsorption site activation along with red shifting of optical absorbance for higher photogeneration of electron-hole pair. Surface plasmon resonance on light-matter interaction has been shown to increase the efficiency of photocatalysts on noble metal loading over $g - C_3N_4$. Non-metal doping in place of C/N or self-doping

due to its stability increase either the concentration of electrons or holes, leading to the formation of either n-type or p-type semiconductor enhancing the mobility of electron/hole due to variation in the band structure curvature of impurity states. The synergistic effect of non-metal doping/metal loading affects the electronic, and optical properties of the pristine material while the activation of sites reduces the energy barrier between the intermediate of the reactions due to the formation of photoanodic/photocathodic sites. [9–11]

Metal-Semiconductor/Semiconductor-semiconductor heterojunction [12–14] owing to their difference in work function and band edges position governs the charge transfer directionality and specific mechanism for enhancement of charge separation capability. Charge transfer across the Schottky junction leads to balanced Fermi generating the interfacial electric field for unidirectional electron transfer as seen for various metal-semiconductor interfaces. The band edge governing the straddling, staggering, or breaking of band alignment in semiconductor-semiconductor junction leads to band bending for feasible migration of electron-hole pair enhancing the reduction-oxidation capability of either of two semiconductors, this synergistic effect controls whether the junction will show reduced band gap due to band mismatch or individual integrity of the material for optical absorbance will be maintained. For the former, 0D/2D structure of metallic nature decorated over the semiconductor shows a huge difference in the work function, the variation in dimensionality provides variation in the charge transfer channel and availability of reaction sites. While, in the latter case, two semiconductors capable of either reduction or oxidation on vertical stacking lead to a simultaneous redox reaction enhancing the overall capability of the photo-redox mechanism. [15, 16]

Stacking of bilayer in different configurations controls the interlayer orbital interaction governing the surface activation sites and optical absorbance originating from the activation of forbidden transitions promotes the interlayer and intralayer charges for enhanced photocatalytic activity. The intercalation of alkali and alkaline earth metals within the layers of $g - C_3N_4$ strengthen the Coulomb's interaction with the layer forming the interlayer charge transfer channel due to localization of charges over the intercalated atom [17], promoting charge migration and separation hence reducing the rate of recombination of the photogenerated charge carriers. [18–21] The single-atom catalyst with its unique structural features,

improved absorbance in the visible spectrum, formation of intermediate states within the forbidden region, and electronegativity difference between the N atom of $g - C_3N_4$ and Metal atom establish the reactive sites for the carbon dioxide reduction reaction (CO_2RR) and nitrogen reduction reaction (N_2RR). The enhanced charge transfer channel further enhances the feasibility of complex reaction mechanism. Exciting results on the functionalized of $g-C_3N_4$ have been seen in this thesis. A detailed literature review is available for various functionalization over $g-C_3N_4$ towards the improvement of photocatalytic efficiency. [22–25]

2 Computational Methodology

Advancements in computational facilities have empowered condensed matter physicists in solving the many body problem through formulated Schrödinger equation by Hohenberg-Kohn in 1964. [26,27] The solution of the Kohn-Sham equation was based on the electron density rather than the traditional coordinate-based electron wavefunction. The self-consistent field cycle proposed by the Sham-Kohn in 1965 based on the variational principle changed the course of history for electronic property calculations. In this thesis, we have performed all the calculations within the density functional theory (DFT) based on a plane wave-based method and full potential linearized augmented plane waves-based solutions through Quantum Espresso (QE) [28] and Wein2K code, [29] respectively. The accurate band gap for the semiconductor material was performed using hybrid functional within QE and Trans Blaha-modified Becke Johanson (TB-mBJ) potential within Wein2k software. Computation of optical properties have been performed using the epsilon.x subroutine of QE code. Maximally localized wannier functions (MLWF) is also considered for correct band structure calculation using the hybrid functional. conventional method of Nørskov et al., for OER/HER along with simultaneous water splitting using CI-NEB [30–35] have been considered for HER, OER and CO_2RR/N_2RR. HER has been investigated with H-atom and H_3O molecule adsorbed over the surface. OER was investigated with H_2O, *OH, *O, and *OOH as reaction intermediates to understand the rate-determining step, hence the overpotential. CO_2RR and N_2RR were performed with all the thermodynamically possible reaction intermediates and various reaction pathways were undertaken including the possible intermediates formed as the reaction proceeds. CO_2RR and N_2RR were investigated on the basis of the adsorption energies of the adsorbed intermediate on the single atom catalyst. [30–32, 36, 37]

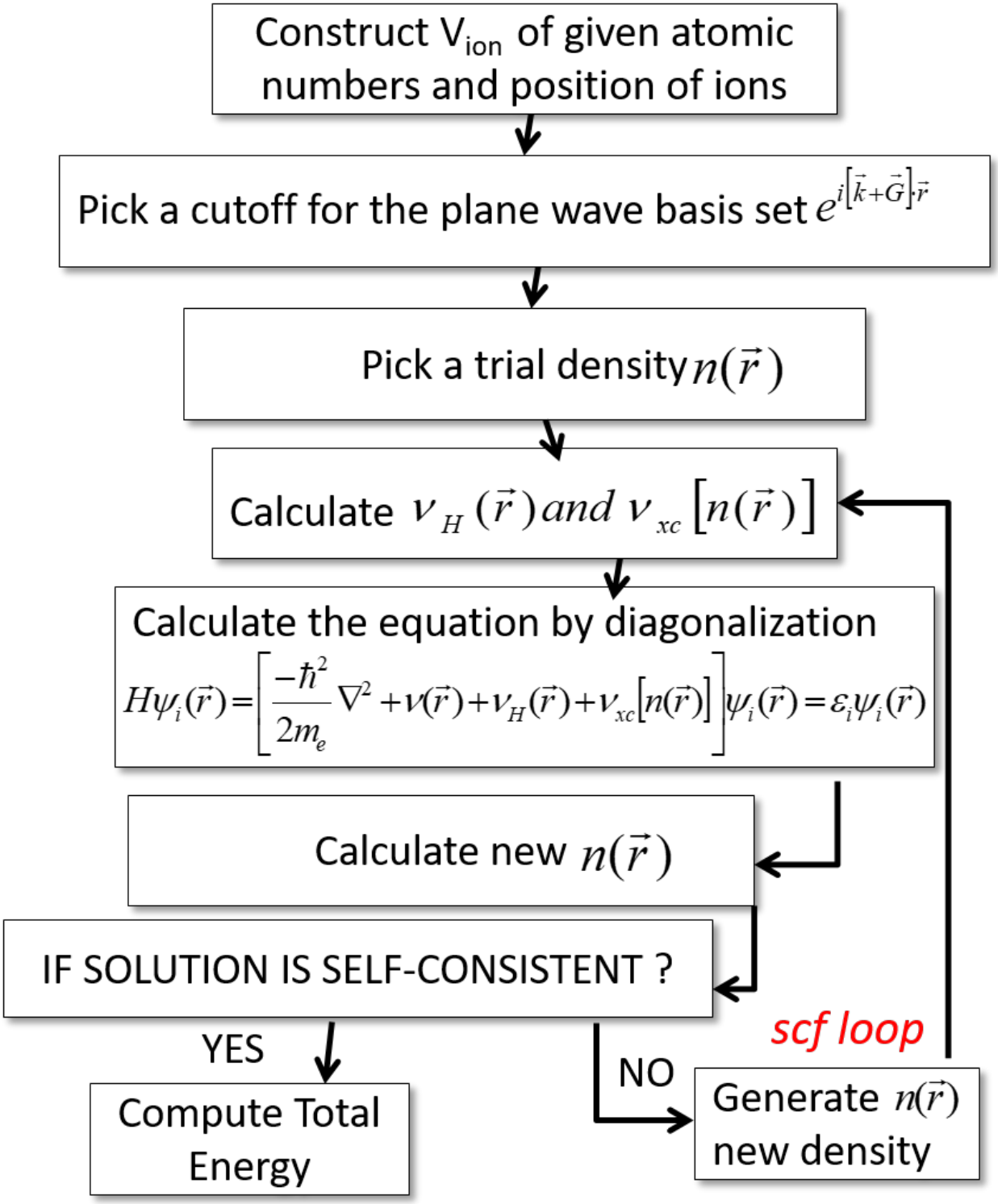

Figure 1: Self-consistent field cycle for the solution of Kohn-Sham equation.

3 Metal/Non-Metal Loaded/Doped $g - C_3N_4$ Monolayer

With the variation in the electronic properties on doping/loading of non-metal/metal atoms in the $g - C_3N_4$, the suitability of band edges for the photocatalytic reduction/oxidation could be tuned. On the backdrop of the synergistic effect seen on doping with loading, a combination of (B/Co, O/Fe, P/Ag) in $g - C_3N_4$ was investigated based on the electronic properties to screen the suitable combination for simulating the study of overall water splitting. $(Co, B) - g - C_3N_4$ was further studied to understand the role of the intermediate band on the optical absorbance and effective mass of the material to form an efficient photocatalytic material. The free energy change value confirmed the enhanced efficiency compared to the pristine monolayer overcoming the prohibitive overpotential reported for OER. [38–40]

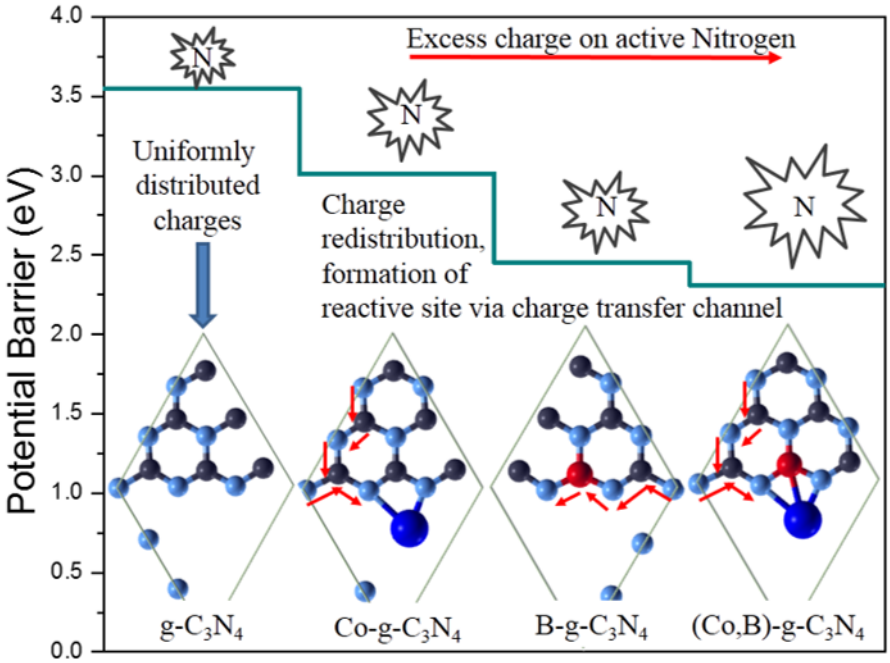

Figure 2: Relationship between overpotential and charge enhancement over the active site on B-doping, Co-loading, B-doping with Co-loading.

4 $g - C_3N_4$ based Heterostructure

Two materials with different electronic properties in close contact form a Heterostructure, based on the type of material and their interation giving rise to the culmination of interfacial properties from both materials. This interface engineering promises multifunctional characteristics of the hybrid materials. Interface charge transfer across the junction is governed by the type of contact, the work function of materials, and their dimensionality. Based on the dimensionality and based on the type of material following sub-sections are provided with a brief description:

4.1 Metal-Semiconductor Heterostructure

Cobalt boride (Co_2B_2) based metallic materials have been considered as decoration over $g - C_3N_4$ with two different dimensionalities. The study of dimension-based metallic decoration over semiconductors and its role in the directional charge transfer for tailoring photocatalytic activity has been studied. Metallic cluster of Co_2B_2 (0D) and 2D Co_2B_2 MBene over $g-C_3N_4$ forms a Schottky barrier providing directionality to electron transfer and enhancing the reduction/oxidation potential on either substrate or decoration.

4.2 Semiconductor-Semiconductor Heterostructure

Band edge position is an essential requirement of the semiconductor materials for a redox reaction, lateral contact of two semiconductors with different band edges is prone to three varieties of alignment. Charge transfer across the interface is determined by the band bending caused due to balance between the Fermi levels of both semiconductors. Here, $Hf_2CO_2/g - C_3N_4$ is investigated to study the role of band bending in the functionality of photocatalysts. [13, 14]

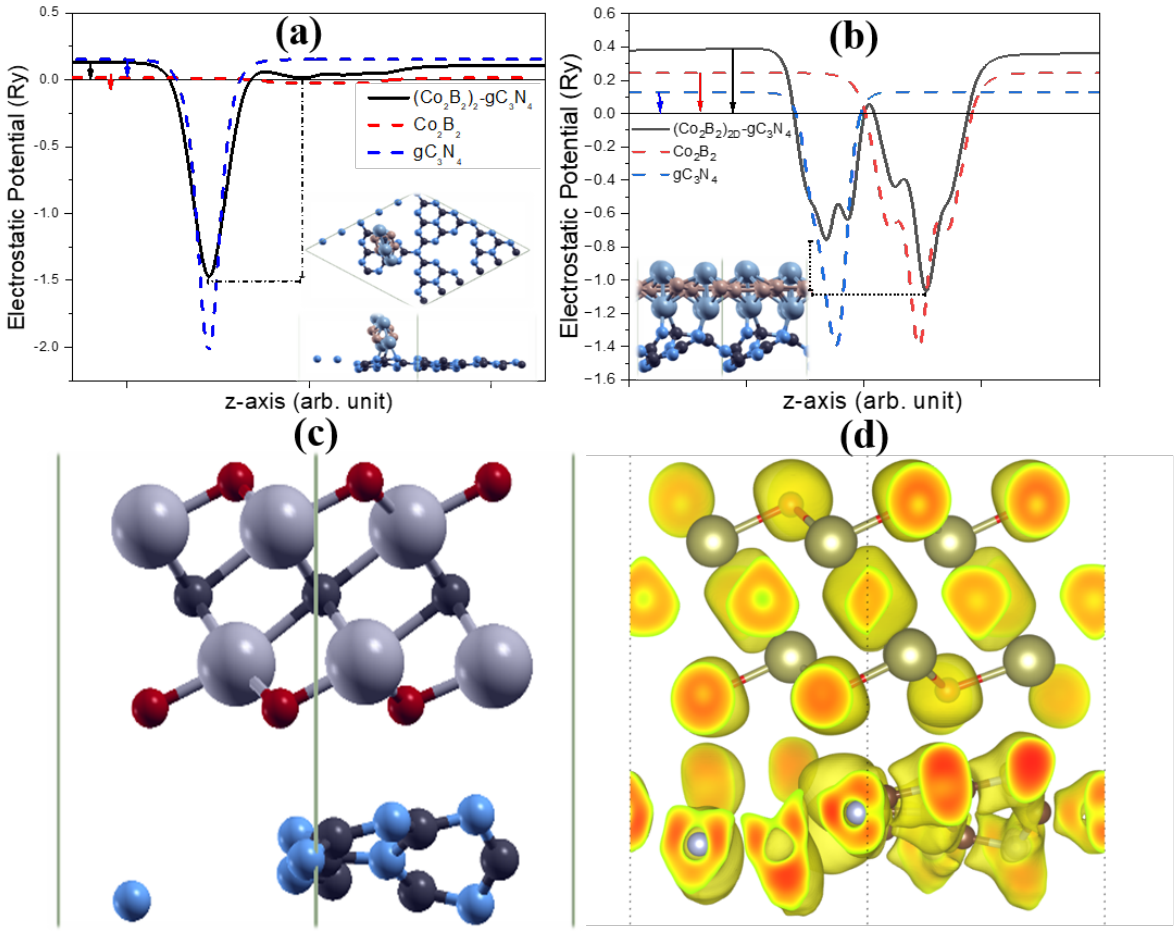

Figure 3: (a, b) Electrostatic potential profile for 0D/2D-2D Metal-Semiconductor heterojunction, (c, d) Structure and electron localization function of $Hf_2CO_2/g-C_3N_4$.

5 Modified Bilayer of $g - C_3N_4$

Stacking/twisting of the bilayer modifies the interface property affecting the photocatalytic activity of a material. In this chapter, the 9 different stacked bilayers with AA and AB configuration are studied. The structural variation along with the electronic and optical properties modification emphasizes the role of interlayer orbital interaction over the overpotential of redox reaction. Intralayer charge redistribution separated the photoanodic and photocathodic sites. Further to eliminate the shortcoming of the bilayer structure and to build an interlayer bridge for easy charge migration between the layers, Li intercalated $g - C_3N_4$ was investigated. Conventional and simultaneous OER/HER were performed and verified the results of free energy change and CI-NEB. Optical properties emphasize the activation of forbidden transitions within bands for enhanced light absorption capabilities along with a reduced rate of recombination. [17]

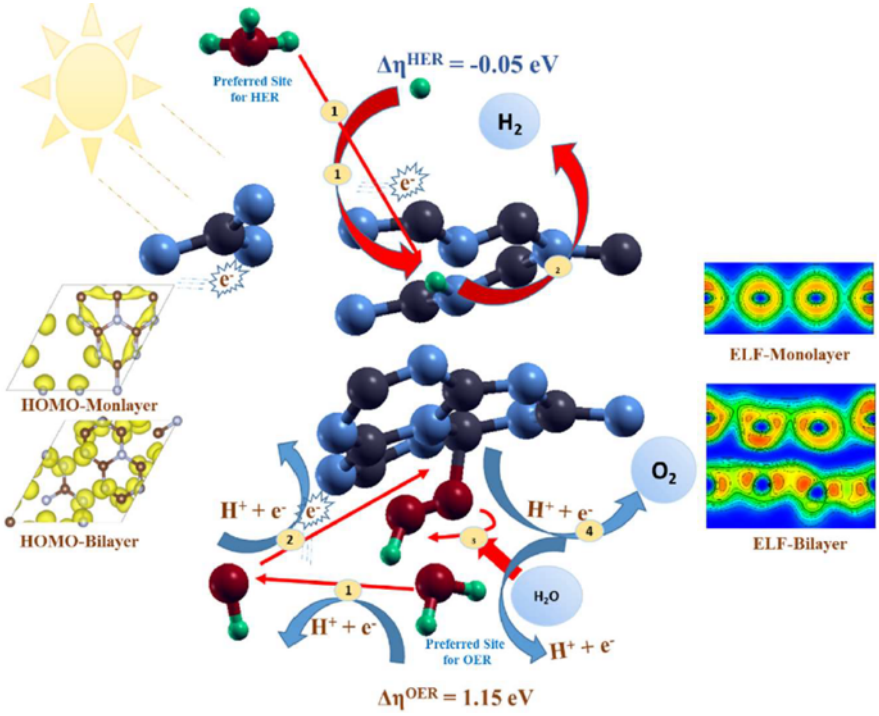

Figure 4: Interlayer and intralayer charge dynamics over suitable bilayer and activation of sites for HER/OER.

6 CO_2RR & N_2RR over Co Decorated $g - C_3N_4$

The increase of greenhouse gases, abundant nitrogen in the atmosphere, and the suitability of single-atom catalysts for adsorption for a wide range of molecules directed the path for this chapter. Among the single metal atom loaded $g-C_3N_4$ studied in Chapter 3, and receptivity of Co atom seen from its role in electrocatalyst, $Co - g - C_3N_4$ was screened for CO_2RR and N_2RR. Possible reaction intermediates formed over the surface with different adsorption sites were simulated and the reaction pathway was devised/anticipated. The most feasible reaction mechanism on the basis of adsorption energy over the suitable site confirmed the complete reduction of CO_2 and N_2 into fuel.

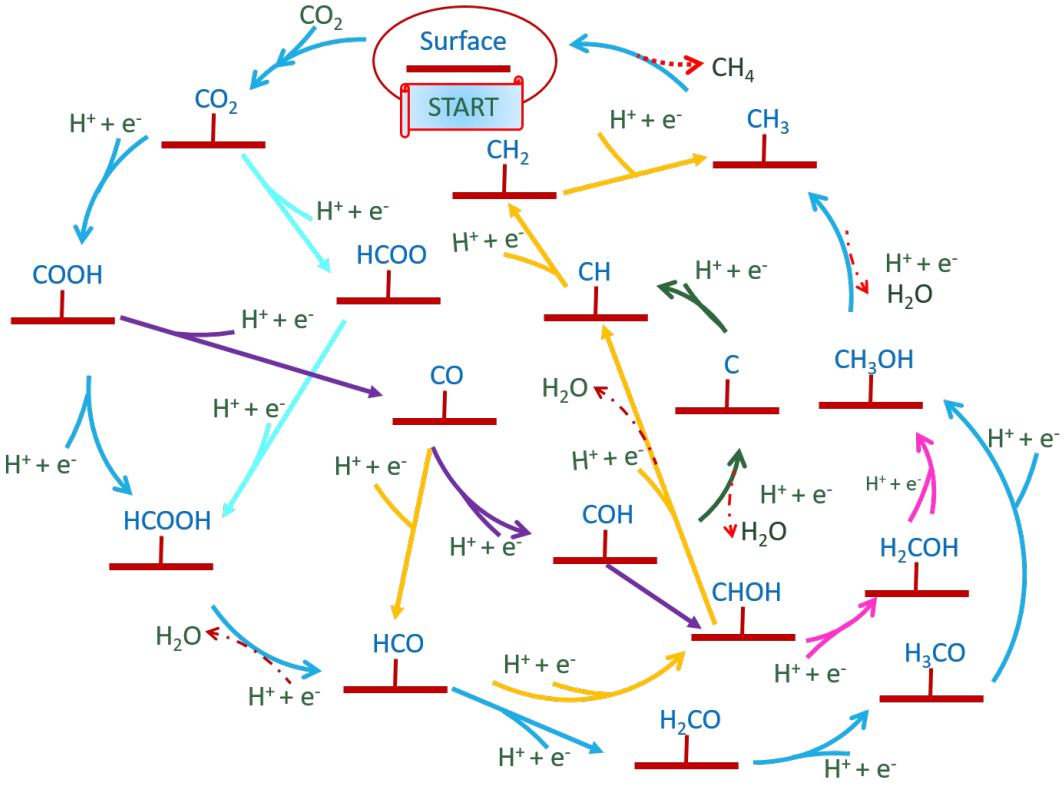

Figure 5: Possible reaction intermediates and pathways for carbon dioxide reduction to methane/methanol.

7 Conclusions and Future Prospects

This chapter comprises of a compilation of results and discussions contained in the preceding chapters on the canvas of the objectives proposed at the beginning of this thesis. The key features of the thesis will be mentioned in brief with the spotlight on the different functionalization techniques and the results obtained from the *ab-initio* calculations. With modification in the basic structure of $g - C_3N_4$, the variation in the electronic and optical properties has been explored leading to the discovery of new materials as efficient photocatalysts. In the successive parts of the chapter discussed different ways to explore the reaction mechanism over modified $g - C_3N_4$ and the future prospects. The scope of exploration from the perspective of excitonic effects will provide the conclusions of this thesis with a new perspective for understanding the inherent nature responsible for the improvement of the efficiency of photocatalysts.

Accolades and Achievements

- University, Faculty, and Department coursework have been completed successfully and passed with flying colors.
- Participated and presented poster in **VII - Rajasthan Science Congress**, Mohanlal Sukhadia University, 2019. on "Enhancing photocatalytic behavior of ZnS: A Computational Perspective", won **Prof. R.S.Paroda Best Presentation Award**
- Participated and gave an oral presentation in **National Research Scholars' Meet on Condensed Matter Physics and Materials Science (CMPMS-23)**, Gujarat University, 2023. on "Possible CO_2 reduction pathways on single atom catalyst ($Co - g - C_3N_4$)", won **Best Oral Presentation Award**

Publications related to thesis

- **B.R. Bhagat**, Alpa Dashora "Investigating dimensionality dependence of overpotential for HER/OER over $g-C_3N_4$ based metal-semiconductor heterojunction", Under Drafting (2023).

- **B.R. Bhagat**, Alpa Dashora "$Hf_2CO_2/g-C_3N_4$ semiconductor-semiconductor heterostructure for enhanced overall water splitting: An *ab-initio* study", Under Drafting (2023)

- **B.R. Bhagat**, Alpa Dashora "Study of systematic charge dynamics for simultaneous oxygen and hydrogen evolution reaction over Li intercalated $g-C_3N_4$", Under Communication (2023).

- **B.R. Bhagat**, Kishan H. Mali, Alpa Dashora "Surface activation of the $g-C_3N_4$ by π-conjugation and interlayer orbital interaction to promote OER and HER", The Journal of Physical Chemistry C, 126 2573–2586 (2022).

- **B.R. Bhagat**, Alpa Dashora Photocatalyst: Potential Materials for Energy Production and Conversion", Energy Conversion and Green Energy Storage, CRC Press 3-28, ISBN: 9781003258209 (2022)

- **B.R. Bhagat**, Alpa Dashora "Understanding the synergistic effect of Co-loading and B-doping in $g-C_3N_4$ for enhanced photocatalytic activity for overall solar water splitting", Carbon, 178 666-677 (2021).

- **B.R. Bhagat**, Alpa Dashora "Charge transfer mediated hydrogen evolution reaction of Co loaded $g-C_3N_4$", Proceedings of the 65th DAE Solid State Physics Symposium (2021).

- Kishan H. Mali, **B.R. Bhagat**, Alpa Dashora "Tailoring electronic property of bilayer tri-s-triazine using spatial modification: An *ab initio* Study", Journal of Physics: Conference Series, 1849(1) 012028 (2021).

Publications not-related to thesis

- Suraj Gupta, Chayathorn Prapaitrakool, **Brajesh Bhagat**, Alpa Dashora, Nainesh Patel, Matjaz Spreitzer, Jeffrey C.S. Wu, and Marjeta Macek Krzmanc"Promoting photocatalytic hydrogen evolution rates in layered graphitic carbon nitride through integrated non-noble Co-B co-catalysts", Drafting (2023).

- Avani Chunduri, Aniruddha Bhide, Suraj Gupta, Kishan H. Mali, **Brajesh Rajesh Bhagat**, Alpa Dashora, Matjaž Spreitzer, Rohan Fernandes, Rupali Patel, and Nainesh Patel "Exploring the Role of Multi-Catalytic Sites in an Amorphous Co–W–B Electrocatalyst for Hydrogen and Oxygen Evolution Reactions", ACS Applied Energy Materials (2023) In Press.

- H.S. Mund, Kishan H. Mali, Kishor Kumar, Shailja Tiwari, **B.R. Bhagat**, Y. Sakurai, H. Sakurai, Alpa Dashora, B.L. Ahuja "Understanding the effect of Ni and Co doping in magnetic properties of $La_{0.7}Ca_{0.3}MnO_3$: Magnetic Compton spectroscopy and DFT strategies", Journal of Magnetism and Magnetic Materials, 565, 170255 (2023).

- Soumalya Kundu, Rahul Majumder, **B.R. Bhagat**, Subhadip Roy, Rabindranath Gayen, Alpa Dashora, Manish Pal Chowdhury "An in situ synthesis of polyaniline/reduced graphene oxide nanocomposite flexible thin film on PET for the room temperature detection of trace level ammonia at ppb level", Journal of Materials Science, 58, 3147 (2023).

- Aditi Gaur, **B.R. Bhagat**, Jagrati Sahariya, Amit Soni, Alpa Dashora "Design and study of $SrSnX_2$ (X=N, P, Sb, As, Bi) semiconductors using density functional theory", Optik, 270, 170088 (2022).

- Rahul K. Chodhury, **B.R. Bhagat**, Kishan H. Mali, Rushikesh Pokar, Alpa Dashora "Effect of the surface functional group over tungsten carbide MXene for efficient NH_3 gas sensing using density functional theory", Applied Surface Science, 603, 154426 (2022).

- A. Yadav, S. Gupta, **B.R. Bhagat**, M. Yadav, Alpa Dashora, R.S. Varma, N. Thorat, R. Patel, N. Patel "Unraveling the synergy between oxygen doping and embedding Fe nanoparticles in gC_3N_4 towards enhanced photocatalytic rates", Applied Surface Science, 603, 154404 (2022).

- Aditi Gaur, Karina Khan, **B.R. Bhagat**, J. Sahariya, A. Soni, Alpa Dashora "Role of intermediate band and carrier mobility in Sn and Fe-doped $CuAlS_2$ thin film for solar cell: A computational modelling", Solar Energy, 215 144-150 (2021).

- M. Saleem, **B.R. Bhagat**, A. Mishra "Influence of Lead Free $Bi_{0.5}Na_{0.5}TiO_3$ Substitution on the Structural and Electrical Properties of Ferromagnetic Metallic Phase $La_{0.8}Sr_{0.2}MnO_3$", Journal of Inorganic and Organometallic Polymers and Materials, Springer 29(6) 2103-15 (2019).

- **B.R. Bhagat**, Rushikesh Pokar, Alpa Dashora First Principles Study of Novel $BaSn_{1-x}In_xN_2$ (X=0, 0.25) for Thermoelectric Applications", Intelligent Computing Techniques for Smart Energy Systems. Lecture Notes in Electrical Engineering, 862 463–472 (2022)

- Kishan H. Mali **B.R. Bhagat**, Alpa Dashora Ab-Initio Investigation of Electronic and Magnetic Properties of 2D Mn Doped Mo_2NT_2 (T: O/F)", Intelligent Computing Techniques for Smart Energy Systems. Lecture Notes in Electrical Engineering, 862 553–563 (2022).

- Athira K.M., **B.R. Bhagat**, Alpa Dashora "Tuning of Electronic and Magnetic Properties in 2D van der Waals Hybrid Ferromagnet (Fe_3GeTe_2/Co_3GeTe_2)", AIP Conference Proceedings, 2369, 020079 (2021).

- M. Saleem, N. Bajpai, **B. Bhaghat**, M. Soni, M. Varshney, A. Mishra and D. Varshney "Studies on composites of homo-structured $La_{0.8}Sr_{0.2}MnO_3$ and $Bi_{0.5}Na_{0.5}TiO_3$: Synthesis, structure and dielectric properties", AIP Conference Proceedings 2142(1) 040001 (2019)

References

[1] S. Ye, C. Ding, R. Chen, F. Fan, P. Fu, H. Yin, X. Wang, Z. Wang, P. Du, C. Li, Mimicking the key functions of photosystem ii in artificial photosynthesis for photoelectrocatalytic water splitting, J. Am. Chem. Soc. 140 (9) (2018) 3250–3256.

[2] S. Lian, C. Rong, D. Yin, S. Liu, Enhancing solar energy conversion efficiency: A tunable dual-excitation dual-emission phosphors and time-dependent density functional theory study, J. Phys. Chem. C 113 (15) (2009) 6298–6302.

[3] D. Adekoya, M. Tahir, N. A. S. Amin, Recent trends in photocatalytic materials for reduction of carbon dioxide to methanol, Renewable Sustainable Energy Rev. 116 (2019) 109389.

[4] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J. M. Carlsson, Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts, J. Mater. Chem. 18 (2008) 4893–4908.

[5] J. Jia, Q. Zhang, K. Li, Y. Zhang, E. Liu, X. Li, Recent advances on g–c3n4–based z-scheme photocatalysts: Structural design and photocatalytic applications, Int. J. Hydrog. Energy 48 (1) (2023) 196–231.

[6] A. Hayat, A. G. Al-Sehemi, K. S. El-Nasser, T. Taha, A. A. Al-Ghamdi, Jawad Ali Shah Syed, M. A. Amin, T. Ali, T. Bashir, A. Palamanit, J. Khan, W. Nawawi, Graphitic carbon nitride (g–c3n4)–based semiconductor as a beneficial candidate in photocatalysis diversity, Int. J. Hydrog. Energy 47 (8) (2022) 5142–5191.

[7] Y. Yu, H. Huang, Coupled adsorption and photocatalysis of g-c3n4 based composites: Material synthesis, mechanism, and environmental applications, J. Chem. Eng. 453 (2023) 139755.

[8] P. Dharmalingam, G. Palani, R. Apsari, K. Kannan, S. K. Lakkaboyana, K. Venkateswarlu, V. Kumar, Y. Ali, Synthesis of metal oxides/sulfides-based nanocom-

posites and their environmental applications: a review, Mater. Today Sustain. 20 (2022) 100232.

[9] J. Sirijaraensre, Effects of doping a boron atom in g-c3n4 on the catalytic activity of deposited pd atom for the dehydrogenation of formic acid: A dft study, Appl. Surf. Sci. 599 (2022) 153950.

[10] H. Li, Y. Wu, L. Li, Y. Gong, L. Niu, X. Liu, T. Wang, C. Sun, C. Li, Adjustable photocatalytic ability of monolayer g-c3n4 utilizing single–metal atom: Density functional theory, Appl. Surf. Sci. 457 (2018) 735–744.

[11] S. Lu, C. Li, H. Li, Y. Zhao, Y. Gong, L. Niu, X. Liu, T. Wang, The effects of nonmetal dopants on the electronic, optical and chemical performances of monolayer g–c3n4 by first-principles study, Appl. Surf. Sci. 392 (2017) 966–974.

[12] H. Guo, C.-G. Niu, Y.-Y. Yang, C. Liang, H.-Y. Niu, H.-Y. Liu, L. Li, N. Tang, Interfacial co-n bond bridged cob/g-c3n4 schottky junction with modulated charge transfer dynamics for highly efficient photocatalytic staphylococcus aureus inactivation, J. Chem. Eng. 422 (2021) 130029.

[13] J. Li, L. Zhao, S. Wang, J. Li, G. Wang, J. Wang, In situ fabrication of 2d/3d g-c3n4/ti3c2 (mxene) heterojunction for efficient visible-light photocatalytic hydrogen evolution, Appl. Surf. Sci. 515 (2020) 145922.

[14] L. Biswal, S. Nayak, K. Parida, Recent progress on strategies for the preparation of 2d/2d mxene/g-c3n4 nanocomposites for photocatalytic energy and environmental applications, Catal. Sci. Technol. 11 (2021) 1222–1248.

[15] Y. Qu, X. Duan, Progress, challenge and perspective of heterogeneous photocatalysts, Chem. Soc. Rev. 42 (2013) 2568–2580.

[16] D. Li, R. Li, F. Zeng, W. Yan, M. Deng, S. Cai, The photoexcited electron transfer and photocatalytic mechanism of g-c3n4/tio2 heterojunctions: Time-domain ab initio analysis, Appl. Surf. Sci. 614 (2023) 156104.

[17] B. R. Bhagat, K. H. Mali, A. Dashora, Surface activation of the g-c3n4 bilayer by -conjugation and interlayer orbital interaction to promote oer and her, J. Phys. Chem. C 126 (5) (2022) 2573–2586.

[18] X. Dong, J. Li, Q. Xing, Y. Zhou, H. Huang, F. Dong, The activation of reactants and intermediates promotes the selective photocatalytic no conversion on electron-localized sr-intercalated g-c3n4, Appl. Catal. B 232 (2018) 69–76.

[19] J. Li, W. Cui, Y. Sun, Y. Chu, W. Cen, F. Dong, Directional electron delivery via a vertical channel between g-c3n4 layers promotes photocatalytic efficiency, J. Mater. Chem. A 5 (2017) 9358–9364.

[20] J. Li, Z. Zhang, W. Cui, H. Wang, W. Cen, G. Johnson, G. Jiang, S. Zhang, F. Dong, The spatially oriented charge flow and photocatalysis mechanism on internal van der waals heterostructures enhanced g-c3n4, ACS Catal. 8 (9) (2018) 8376–8385.

[21] T. Xiong, W. Cen, Y. Zhang, F. Dong, Bridging the g-c3n4 interlayers for enhanced photocatalysis, ACS Catal. 6 (4) (2016) 2462–2472.

[22] B. Bhagat, A. Dashora, Photocatalyst: Potential materials for energy production and conversion (2022) 3–28.

[23] D. Zhou, X. Li, H. Shang, F. Qin, W. Chen, Atomic regulation of metal–organic framework derived carbon-based single-atom catalysts for the electrochemical co2 reduction reaction, J. Mater. Chem. A 9 (2021) 23382–23418.

[24] M. Li, H. Wang, W. Luo, P. C. Sherrell, J. Chen, J. Yang, Heterogeneous single-atom catalysts for electrochemical co2 reduction reaction, Adv. Mater. 32 (34) (2020) 2001848.

[25] P. Li, Z. Fang, Z. Jin, G. Yu, Ammonia electrosynthesis on single-atom catalysts: Mechanistic understanding and recent progress, Chem. Phys. Rev. 2 (4) (2021) 041305.

[26] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, Phys. Rev. 136 (1964) B864–B871.

[27] W. Kohn, L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133–A1138.

[28] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. D. et al, Quantum espresso: a modular and open-source software project for quantum simulations of materials, J. Condens. Matter Phys. 21 (39) (2009) 395502.

[29] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. H. Madsen, L. D. Marks, Wien2k: An apw+lo program for calculating the properties of solids, J. Chem. Phys. 152 (7) (2020) 074101.

[30] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, Origin of the overpotential for oxygen reduction at a fuel-cell cathode, J. Phys. Chem. B 108 (46) (2004) 17886–17892.

[31] J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov, U. Stimming, Trends in the exchange current for hydrogen evolution, J. Electrochem. Soc. 152 (3) (2005) J23.

[32] J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J. Nørskov, Electrolysis of water on oxide surfaces, J. Electroanal. Chem. 607 (1) (2007) 83–89.

[33] D. R. Hamann, Optimized norm-conserving vanderbilt pseudopotentials, Phys. Rev. B 88 (2013) 085117.

[34] G. Henkelman, B. P. Uberuaga, H. Jónsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, Chem. Phys. 113 (22) (2000) 9901–9904.

[35] G. Henkelman, H. Jónsson, A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives, Chem. Phys. 111 (15) (1999) 7010–7022.

[36] S.-h. Kim, H. C. Song, S. J. Yoo, J. Han, K.-Y. Lee, H. C. Ham, Impact of the dopant-induced ensemble structure of hetero-double atom catalysts in electrochemical nh3 production, J. Mater. Chem. A 10 (2022) 6216–6230.

[37] Z. Li, N. H. Attanayake, J. L. Blackburn, E. M. Miller, Carbon dioxide and nitrogen reduction reactions using 2d transition metal dichalcogenide (tmdc) and carbide/nitride (mxene) catalysts, Energy Environ. Sci. 14 (2021) 6242–6286.

[38] B. Bhagat, A. Dashora, Understanding the synergistic effect of co-loading and b-doping in g-c3n4 for enhanced photocatalytic activity for overall solar water splitting, Carbon 178 (2021) 666–677.

[39] A. Yadav, S. Gupta, B. Bhagat, M. Yadav, A. Dashora, R. Varma, N. Thorat, R. Patel, N. Patel, Unraveling the synergy between oxygen doping and embedding fe nanoparticles in gc3n4 towards enhanced photocatalytic rates, Appl. Surf. Sci. 603 (2022) 154404.

[40] Y. Chen, X. Ren, X. Wang, Z. Tian, X. Yang, J. Lu, H. Bai, T. Jiao, H. Huang, J. Hu, Construction of ag decorated p-doped g-c3n4 nanosheets schottky junction via silver mirror reaction for enhanced photocatalytic activities, Int. J. Hydrog. Energy 47 (1) (2022) 250–263.