OPTIMIZING HETEROGENEOUS PHOTOCATALYST DESIGN FOR CO_2 REDUCTION TO FUELS

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Optimizing Heterogeneous Photocatalyst Design for CO_2 Reduction to Fuels

by

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in fulfilment of the requirement for the award of the degree of

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To my inspiring parents
and loving husband, for
always nurturing my
curiosities…

Certificate

This is to certify that the thesis entitled **"Optimizing Heterogeneous Photocatalyst Design for CO_2 Reduction to Fuels"** submitted by **Mrs. Shreya Singh** to the Indian Institute of Technology Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Mrs. Shreya Singh worked under our guidance and supervision and has fulfilled the requirements, which to my knowledge has reached the requisite standard for the submission of this thesis. The results contained in this thesis are original and have not been submitted, partially or completely, to any other University or Institute for the award of any other degree or diploma.

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Singh

Shreya Singh

Research is to see what everybody else has seen, and to think what nobody else has thought

Albert Szent-Györgyi

Abstract

As global energy demands escalate, the resultant rise in greenhouse gas emissions, particularly carbon dioxide (CO_2), has galvanized the scientific community to seek sustainable alternatives to fossil fuels. A promising research direction is the photocatalytic reduction of CO_2 to produce solar fuels, offering a dual benefit: carbon sequestration and solar energy storage in high-energy-density fuels. Photocatalytic CO_2 reduction suffers from challenges such as low utilization of low-frequency spectrum of sunlight, high charge recombination rates and lack of understanding of reaction mechanisms. The effectiveness of this process relies heavily on the design of photocatalysts, which are crucial for efficiently harnessing solar energy for CO_2 reduction. This thesis presents a methodical approach to photocatalyst development, emphasizing the synthesis of materials with specific properties that enhance photon interaction, charge relaxation, and reaction activation potential, thereby boosting CO_2 conversion into solar fuels. Our research tackles two main challenges in photocatalysis: low light-utilization efficiency and charge recombination losses. We employ principles of rational design, such as heterojunctions (MoS_2-Cu_2O) to reduce charge recombination and improve redox potential, transition metal doping (M-TiO_2) to understand the effect of metal doping on governing the selectivity of products and investigating metastable states of Melon carbon nitride using computational and experimental approaches and role of conformations on the photocatalytic activity. In-situ IR measurements and density functional theory calculations were used to dissect the photocatalytic reaction mechanism, identifying crucial design factors that predominantly influence a system's activity. By analysing charge relaxation and reaction rates, we propose a reaction kinetics model that accounts for charge carriers concentration and elucidates the impact of various design elements at the elementary reaction level. This model guides the molecular-level strategic modifications of photocatalysts, paving the way for more efficient solar fuel production.

सार

वैश्विक ऊर्जा की मांगों में वृद्धि के साथ, ग्रीनहाउस गैसों के उत्सर्जन, विशेषकर कार्बन डाइऑक्साइड (CO_2) में बढ़ोतरी, ने वैज्ञानिक समुदाय को जीवाश्म ईंधन के स्थायी विकल्पों की तलाश करने के लिए प्रेरित किया है। एक आशाजनक शोध दिशा CO_2 का फोटोकैटालिटिक कमीकरण है जिससे सौर ईंधन का उत्पादन होता है, जिससे दोहरा लाभ होता है: कार्बन संग्रहण और सौर ऊर्जा का उच्च-ऊर्जा-घनत्व ईंधन में भंडारण। फोटोकैटालिटिक CO_2 कमीकरण में चुनौतियां जैसे कम-आवृत्ति स्पेक्ट्रम की सूर्य की रोशनी का निम्न उपयोग, उच्च चार्ज पुनःसंयोजन दरें और प्रतिक्रिया तंत्र की समझ की कमी शामिल हैं। इस प्रक्रिया की प्रभावशीलता मुख्य रूप से फोटोकैटालिस्ट के डिजाइन पर निर्भर करती है, जो CO_2 कमीकरण के लिए सौर ऊर्जा को कुशलतापूर्वक हासिल करने के लिए महत्वपूर्ण हैं। यह थीसिस फोटोकैटालिस्ट विकास के लिए एक विधिवत दृष्टिकोण प्रस्तुत करती है, जिसमें विशिष्ट गुणों वाले सामग्रियों के संश्लेषण पर जोर दिया गया है जो फोटॉन इंटरैक्शन, चार्ज रिलैक्सेशन, और प्रतिक्रिया सक्रियण क्षमता को बढ़ाते हैं, इस प्रकार CO_2 के सौर ईंधन में रूपांतरण को बढ़ावा देते हैं। हमारा शोध फोटोकैटालिसिस में दो मुख्य चुनौतियों से निपटता है: कम प्रकाश-उपयोग दक्षता और चार्ज पुनःसंयोजन हानियां। हमने तर्कसंगत डिजाइन के सिद्धांतों का उपयोग किया, जैसे कि हेटरोजंक्शन (MoS_2-Cu_2O) चार्ज पुनःसंयोजन को कम करने और रेडॉक्स क्षमता में सुधार करने के लिए, धातु डोपिंग (M-TiO_2) का उपयोग करके उत्पादों की चयनात्मकता पर धातु डोपिंग के प्रभाव को समझने के लिए, और मेलन कार्बन नाइट्राइड की मेटास्टेबल स्थितियों का पता लगाने के लिए कंप्यूटेशनल और प्रयोगात्मक दृष्टिकोण और फोटोकैटालिटिक गतिविधि पर संरचनाओं की भूमिका। इन-सिटू IR माप और घनत्व कार्यात्मक सिद्धांत गणनाओं का उपयोग करके फोटोकैटालिटिक प्रतिक्रिया तंत्र की विश्लेषण किया गया, जिससे प्रणाली की गतिविधि को प्रमुख रूप से प्रभावित करने वाले डिजाइन कारकों की पहचान की गई। चार्ज रिलैक्सेशन और प्रतिक्रिया दरों का विश्लेषण करके, हमने एक प्रतिक्रिया गतिविज्ञान मॉडल का प्रस्ताव किया जो चार्ज वाहकों की एकाग्रता के लिए खाता बनाता है और मौलिक प्रतिक्रिया स्तर पर विभिन्न डिजाइन तत्वों के प्रभाव को स्पष्ट करता है। यह मॉडल फोटोकैटालिस्ट्स के मोलेक्युलर-स्तर के सामरिक संशोधनों को निर्देशित करता है, जिससे सौर ईंधन उत्पादन के लिए अधिक कुशल मार्ग प्रशस्त होता है।

Table of Contents

Certificate iii

Acknowledgements iv

Abstract viii

Table of Contents x

List of Figures xii

List of Tables xvii

Chapter 1 - Introduction 1

1.1 Overview of the current issue and related solution 1

1.2 Photocatalytic CO_2 Embedding into Products 4

1.3 Choice of catalysts and need for modifications in the catalysts 6

1.4 Reaction Mechanism in CO_2 photo-reduction Process 10

1.5 Kinetic Considerations and Controlling Parameters 12

1.6 Limitations in scale up 20

1.7 Summary 20

1.8 Gaps and motivation for present work 21

1.9 Thesis objectives 22

1.10 Structure of thesis 24

Chapter 2 - Material and Methods 26

2.1 Abstract 26

2.2 Catalyst Synthesis 26

2.3 Characterization Methods 30

2.4 Reaction vessel and reaction conditions 45

2.5 Photo-deposition experiment 50

2.6 In-situ DRIFTS study 50

2.7 Computational Methods 51

Chapter 3 - Mechanistic Exploration in Controlling the Product Selectivity via Metals in TiO_2 for Photocatalytic Carbon Dioxide Reduction 60

3.1 Abstract 60

3.2 Introduction 60

3.3 Results and discussion 64

3.4 Discussion 92

3.5 Research significance 93

Chapter 4 - Effect of work-function and morphology of heterostructure components on CO_2 reduction photo-catalytic activity of MoS_2-Cu_2O heterostructure 95
4.1 Abstract 95
4.2 Introduction 95
4.3 Results and discussions 106
4.4 Research significance 134
Chapter 5 - Carbon-Nitride Polymorphs: Unveiling the Correlation between Synthesis-Induced Structural Variations, Electronic Properties, and CO_2 Photocatalytic Activity 136
5.1 Abstract 136
5.2 Introduction 136
5.3 Results and Discussions 147
5.4 Research significance 175
Chapter 6 - The cooperative role of nitrogen defects and cyano-group functionalization in carbon nitride towards enhancing its CO_2 photoreduction activity 176
6.1 Abstract 176
6.2 Introduction 176
6.3 Results & Discussion 179
6.4 Research significance 200
Chapter 7 - Conclusion and Future Recommendations 201
7.1 Conclusions 201
7.2 Future recommendations 205
References 207
Appendix i
Publications iv

Curriculum Vitae

List of Figures

Figure 1.1: (A) Country-wise emissions and fractions of the source contributing in emissions (Yang et. al 2022) (B) Emission scenarios of CO_2 up to 2100 (Quere et al. 2016) 2
Figure 1.2: (Left) Band gap energies of different Semiconductors with their respective band edges. (Right) Photo-excitation of electrons from valance to conduction bands for corresponding oxidation and reduction reactions (Singh et al. 2021) 6
Figure 1.3: Different classes of photocatalyst utilized for the CO_2 conversion process 7
Figure 1.4: Different proposed photocatalytic CO_2 reduction pathways: (a) Formaldehyde pathway 1 electron 1 proton (b) Carbene pathway (c) Glyoxal pathway (Singh et al. 2021) 10
Figure 1.5: Kinetic parameters dependence of photocatalytic reactions (Singh et al. 2021) 13
Figure 1.6: Schematic for the overall objective of the current thesis work with utilized techniques and domains 23
Figure 2.1: Different steps of formation of pristine and different M-TiO_2 27
Figure 2.2: Variation of colour in different steps in Cu_2O of different morphologies 28
Figure 2.3: Synthesized carbon nitride materials from melamine at different temperatures 29
Figure 2.4: Formation steps of cyano functionalization in carbon nitride structure 30
Figure 2.5: Schematic of different types of properties for photocatalyst characterization 30
Figure 2.6: Schematic of annular quartz reactor with inside light illumination 46
Figure 2.7: Picture of the experimental setup of the stainless steel and photoreactor setup with top illumination 47
Figure 2.8: (A) Controlled experiments for confirmation of the CO_2 photocatalytic reduction with carbon nitride catalyst (B) Mass spectrum of photocatalytic products generated during Isotopic $^{13}CO_2$ labelled photoreduction experiment over Carbon nitride photocatalyst 49
Figure 2.9: Schematic of in-situ FTIR, with DRIFTS cell of the HARRICK praying Mantis reaction chamber in Nicolet is50 (Manufacturer: Thermo Fisher scientific) 50
Figure 2.10: Wavefunction and Potential Analysis: Real versus Pseudopotential Beyond Crossover Radius 54
Figure 2.11: Calculation Model for heterojunctions of MoS_2 (002) facet and Cu_2O with (100) and (111) facets 57
Figure 2.12: DFT models for (A) Melon, (B) C≡N-Melon and (C) C≡N-N_v-Melon 58
Figure 3.1: XRD patterns for TiO_2 and P25 nanocrystals with marked diffraction peaks corresponding to the anatase and rutile phases of TiO_2 65
Figure 3.2: XRD patterns for different M-TiO_2 (M=Ag, Cu, Au) nanocrystals with varied metal loading amounts 65
Figure 3.3: Narrow range XRD pattern to observe the shifts in the diffraction peaks corresponding to the101 planes of M-TiO_2 (M=Ag, Cu, Au) 67
Figure 3.4: Raman spectra of TiO_2 doped with Cu, Au, and Ag (from left to right) at concentrations from 0.1 to 1 wt% of metal dopant 67
Figure 3.5: Narrow range Raman spectra of TiO_2 doped with Cu, Au, and Ag (from left to right) at concentrations from 0.1 to 1 wt% of metal dopant 68
Figure 3.6: Thermogravimetric analysis (A) and nitrogen adsorption isotherms (B) of TiO_2 doped with Au, Ag, and Cu, showing thermal stability and porosity characteristics, respectively 69
Figure 3.7: Particle size distribution profile for (A) Cu (B) Au and (C) Ag based TiO_2 samples 71

Figure 3.8: Transmission electron microscopy images of Au/TiO_2 nanoparticles: (A) low magnification, (B) high-resolution with inset showing selected area electron diffraction pattern, and (C) corresponding elemental mapping for O, Ti, and Au 72

Figure 3.9: Transmission electron microscopy images of Ag/TiO_2 nanoparticles: (A) low magnification, (B) high-resolution with inset showing selected area electron diffraction pattern, and (C) corresponding elemental mapping for O, Ti, and Ag 72

Figure 3.10: Transmission electron microscopy images of Cu/TiO_2 nanoparticles: (A) low magnification, (B) high-resolution with inset showing selected area electron diffraction pattern, and (C) corresponding elemental mapping for O, Ti, and Cu 73

Figure 3.11: Narrow Scan X-ray photoelectron spectroscopy (XPS) spectra showing the binding energy shifts for (A) Ti 2p, (B) O 1s, (C) Ag 3d, (D) Au 4f, and (E) Cu 2p in pure TiO_2 and metal-doped TiO_2 (Cu, Au, Ag) catalyst 75

Figure 3.12: Temperature-programmed reduction (TPR) profiles of pure TiO_2 and metal-doped TiO_2 catalysts: (A) TiO_2, (B) Cu-TiO_2, (C) Ag-TiO_2, and (D) Au-TiO_2 76

Figure 3.13: UV-Vis absorption spectra of TiO_2 and metal-doped TiO_2 catalysts with varying metal loadings: Ag-TiO_2 (left), Au-TiO_2 (centre), Cu-TiO_2 (right) 78

Figure 3.14: Photoluminescence spectra (A) and time-resolved decay curves (B) of pure TiO_2 and metal-doped TiO_2 (Ag, Au, Cu) catalysts 79

Figure 3.15: Electrochemical impedance spectroscopy (EIS) Nyquist plots (A) and linear sweep voltammograms (B) for pure TiO_2 and metal doped TiO_2 (Ag, Au, Cu) under dark ('d') and light ('l') conditions 81

Figure 3.16: Kelvin Probe Force Microscopy (KPFM) potential mapping of pure TiO_2 (A), and metal-doped TiO_2: Cu-TiO_2 (B), Au-TiO_2 (C), Ag-TiO_2 (D) 82

Figure 3.17: Ultraviolet photoelectron spectroscopy (UPS) spectra showing valence band maxima for TiO_2, and metal doped TiO_2 with copper (Cu), gold (Au), and silver (Ag) 83

Figure 3.18: Photocatalytic activity profiles for M-TiO_2 (M= Cu, Au, Ag) towards CH_4, CO CH_3OH and H_2 generation 84

Figure 3.19: Electron Selectivity comparison for HER or CO_2RR for different metal loadings in M-TiO_2 (M= Cu, Au, Ag) 86

Figure 3.20: CO_2 Temperature programmed desorption profiles at different ramp rates to evaluate the BE of different metals for M-TiO_2 (M= Cu, Au, Ag) 86

Figure 3.21: The time-resolved DRIFT spectra of (A) Cu (B) Au and (C) Ag incorporated TiO_2 on adsorbing CO_2/H_2O at 30 °C under dark 88

Figure 3.22: The time-resolved DRIFT spectra of (A) Au (B) Ag and (C) Cu incorporated TiO_2 after light-on with corresponding peak assignments 90

Figure 3.23: CO temperature programmed desorption profile for Ag and Cu-TiO_2 91

Figure 3.24: The scheme of plausible reaction pathway for CO, CH_4, CH_3OH production with boxed intermediates in green and pink demonstrating the stabilization over Cu and Ag surfaces 93

Figure 4.1: Alterations in the band edge potentials of wide gap semiconductor photocatalyst in the process of enhancing light absorption ability 96

Figure 4.2: Semiconductor coupling modes (A) type II heterojunction (B) direct z-scheme PC1 and PC2 stand for the conduction band, valence band, photocatalyst I and photocatalyst II, respectively 98

Figure 4.3: Field emission scanning electron microscopic images of (A) p-MoS_2 (B) n-MoS_2 (C) Cu_2O-cubic (D) Cu_2O-cubo-octahedrons (E) n-MoS_2−Cu_2O-c (F) p-MoS_2−Cu_2O-co (G) EDS mapping of p-MoS_2−Cu_2O-c composite with mapped individual elements G(b-e) 107

Figure 4.4: (A) HR-TEM image of Cu_2O-c over p-MoS_2 (B) SAED Patterns of Cu_2O-c over p-MoS_2 marked with the fringe spacings of MoS_2 in red, Cu_2O in yellow (C) HR-TEM image of Cu_2O-co over n-MoS_2 (D) SAED Patterns marked with the fringe spacings of MoS_2 in red, Cu_2O in yellow 108
Figure 4.5: (A) HR-TEM image and (B) SAED pattern of n-MoS_2 (C) HR-TEM image and (D) SAED pattern for p-MoS_2 109
Figure 4.6: XRD spectra of different individual (MoS_2 and Cu_2O) and their heterostructures 110
Figure 4.7: (A) Raman scattering spectra of p-MoS_2 and n-MoS_2 (B) High resolution X-ray photoelectron spectroscopy of S atom (left) and Mo atom (right) in p-MoS_2 (bottom) and n-MoS_2 (top) 112
Figure 4.8: Normalized room temperature EPR spectra of n-MoS_2 (red line) and the p-MoS_2 (black line) 114
Figure 4.9: CO_2 temperature programmed desorption (CO_2-TPD) spectra for Cu_2O cubic (blue, bottom) cubo-octahedrons (black, top) (B) CO_2 binding mode on {111} and {100} facets of Cu_2O 115
Figure 4.10: GCMS spectra of the liquid product sample obtained after photocatalytic reaction with p-MoS_2-Cu_2O-c catalysts with TEOA as the sacrificial agent 116
Figure 4.11: Photocatalytic activity of heterostructures. Methanol yield in batch mode in 4 h (A) With different catalyst loading of Cu_2O-co (B) for different photocatalysts and their heterostructures in absence of Sacrificial agent (TEOA) (C) for different photocatalysts and their heterostructures in presence of Sacrificial agent (TEOA) (D) Cyclic experiments for stability of the best performing heterostructure photocatalyst i.e. p-MoS_2-Cu_2O-c 118
Figure 4.12: XRD of the spent catalyst (black) in comparison to the fresh catalyst of p-MoS_2-Cu_2O-c catalyst 121
Figure 4.13: FE-SEM and EDS mapping of the used p-MoS_2-Cu_2O-c catalyst 121
Figure 4.14: (A and B) Mott–Schottky (MS) plot of n-MoS_2 and p-MoS_2(solid, black) along with the line fitted in the linear region of MS plot (dotted, red) (C) Linear sweep voltammetry (LSV) curves of individual photocatalysts (dotted lines) and heterostructures (solid lines) (D) Electrochemical impedance spectroscopy (EIS) Nyquist plots of all photocatalysts and equivalent circuit used to fit the shown data 123
Figure 4.15: Mott-Schottky Curve for (left) Cu_2O-c (right) Cu_2O-co 124
Figure 4.16: Band structures for MoS_2, Cu_2O and their heterostructure 126
Figure 4.17: Diffuse reflectance UV–Vis absorbance spectra of all photocatalysts in the wavelength range of 200–800 nm (Inset: Tauc's plots for Cu_2O-c (black) and Cu_2O-co (red)). 127
Figure 4.18: Partial density of states (PDOS) of MoS_2 without any change in d-spacing (B) with increased d-spacing (C) with increased d-spacing and oxygen incorporation 128
Figure 4.19: Partial Density of States for (A) Cu_2O-co (B) Cu_2O-c 129
Figure 4.20: Full-Survey XPS spectrum for different MoS_2 and Cu_2O Heterostructures 132
Figure 4.21: High resolution XPS spectra of Mo 3d and Cu 2p in (A) p-MoS_2-Cu_2O-c (B) n-MoS_2-Cu_2O-c (C) Direction of migration of electrons and holes upon heterostructure formation and band bending in p-MoS_2 and p-MoS_2-based heterostructures (D) Photo-deposition of Pt over Cu_2O in p-MoS_2-Cu_2O-c heterojunction catalyst (left) and zoomed image along with the SAED pattern (right) 134
Figure 5.1: Several structural forms of carbon nitride possible from basic building blocks 137
Figure 5.2: Synthetic routes for the formation of carbon and nitrogen-based molecules and advanced carbon nitride frameworks (reproduced with permission from Lau and Lotsch 2022) 138
Figure 5.3: Planar structure of melon as proposed by Lotsch et. al reproduced after permission from (Lotsch et al. 2007) 141
Figure 5.4: Clustering of different so obtained structural geometries based on RMSD <0.5Å 149
Figure 5.5: (A) Solid-state ^{13}C NMR of CN-500 with inset ^{1}H and (B) FTIR spectra of carbon nitride materials synthesized at temperatures ranging from 500 to 650°C 151

Figure 5.6: (A) XRD patterns and (B)Raman spectra of carbon nitride synthesized at different temperatures (500, 550, 600, and 650°C) with peak shift corresponding to 002 plane (inset of A) and crystallinity changes 153
Figure 5.7: (A) SEM images (B) elemental mapping (C) particle size distribution, and (D) HR-TEM images with SAED patterns of carbon nitride synthesized at different temperatures 155
Figure 5.8: Narrow range XPS Spectra for carbon nitride samples (A) N1s and (B) C1s elements 157
Figure 5.9: Photocatalytic activity test product yield for different carbon nitride samples 159
Figure 5.10: (A) UV-Vis absorption spectra, (B) photoluminescence spectra, (C) VB-XPS spectra, and (D) Band edge potential for different CN-T samples 160
Figure 5.11: (A) nitrogen adsorption-desorption isotherms with pore size distribution inset, (B) electrochemical impedance spectroscopy, (C) linear sweep voltammetry profiles of CN-T samples (D) surface potential distribution, and (E, F) Kelvin probe force microscopy (KPFM) under light-off and light-on conditions, respectively 163
Figure 5.12: (A) CO_2 Temperature programmed desorption profile for different CN-T samples, (B) Equation fit profile for CN-500, (C) Binding energy for different CN-T samples 165
Figure 5.13: EPR Profile (A) without and (B) with light irradiation and decay profile of time resolved luminescence spectra for different CN-T samples 166
Figure 5.14: Experimental and fitted photoreduction data for CO and CH_4 over carbon nitride synthesized at varying temperatures 171
Figure 5.15: Experimental and fitted photoreduction data for CO and CH_4 over CN-500 synthesized at varying sacrificial agent concentrations 174
Figure 6.1: Overview of synthesis process for cyano (C≡N) rich Nitrogen vacant (N_v) carbon nitride 179
Figure 6.2: (A and B) XRD spectra and IR spectra of CN, CN-300-N_2, CN-300-air, CN-400-N_2 CN-400-air, CN-500-N_2 and CN-500-air. (C) High-resolution N 1s XPS spectra of CN and CN-400-air. (D) High-resolution C 1s XPS spectra of CN and CN-400-air 182
Figure 6.3: (A) FTIR Spectra for different reheated and modified carbon nitride samples; (B) Narrow scan spectra for O1s in CN-400-air sample (C) Narrow scan spectra for C1s and N 1s in CN-500-air and CN-500-N_2 samples 184
Figure 6.4: (A) FESEM (top) and HRTEM (bottom) images with inset representing the corresponding selected area electron diffraction (SAED) pattern of pristine (CN) and modified carbon nitride (CN-400-air); (B) N_2 adsorption-desorption isotherms with Pore-size distribution (inset) 186
Figure 6.5: (A) Histogram for particle size distribution for CN-400-air sample (B) Elemental mapping and distribution for CN-400-air 187
Figure 6.6: Catalytic performance (yield) towards photocatalytic CO_2 reduction in presence of TEOA to (A) CH_4 (B) CO (C) Selectivity of synthesized photocatalysts. (D) Recyclability test result for CN-400-air 190
Figure 6.7: Catalytic performance (yield) in absence of sacrificial agent (TEOA) towards photocatalytic CO_2 reduction to (A) CO and CH_4 (B) Selectivity towards generated C products for different synthesized photocatalyst samples 190
Figure 6.8: (A) UV–visible diffusion reflectance absorption spectra for all the prepared catalysts (B) Surface potential distribution of CN and CN-400-air relative to the tip, obtained from kelvin probe force microscopy (KPFM) (C) Steady state photoluminescence (PL) spectra (D) Time-resolved PL decay spectra of pristine and CN-400-air 191
Figure 6.9: Calculated PDOS for different models of carbon nitride s (red), p (blue) and total (black) contribution of energy 192
Figure 6.10: Band structure profile for CN (left) and CN-C≡N-N_v (right) 194
Figure 6.11: (A) Linear sweep voltammetry (LSV) for transient cathodic photocurrent response under dark (dotted) and light for all materials (B) Electrochemical impedance spectroscopy (EIS) Nqyuist plots and

equivalent circuit (inset) (C) Mott–Schottky plots of CN and CN-T-env samples. (D) Electron paramagnetic resonance (EPR) spectrum under dark and light-irradiated conditions (E) VB-XPS spectra of CN and CN-400-air (F) Calculated band edge positions for CN and CN-400-air on the potential scale with respect to normal hydrogen electrode (NHE). Dashed lines show the standard reduction potentials of relevant reactions. 197

List of Tables

Table 1.1: Various catalytic approaches for CO_2 conversion 3
Table 1.2: Standard Redox Potentials for CO_2 Reduction Reactions (Equation 1.2-1.9) at P=1.0 atm and T=25°C (Singh et al. 2021) 7
Table 1.3: Different modification strategies of photocatalyst materials with their advantages and disadvantages 9
Table 3.1: Overview of Diverse Catalytic Systems Utilized in CO_2 Photoreduction Processes 62
Table 3.2: Pore characterization of TiO_2 and metal doped TiO_2 catalysts: total pore volume, micropore volume (V_m), BET surface area ($S_{a,BET}$), and mean pore diameter 70
Table 3.3: Relative population of different types of oxygens present in M-TiO_2 as obtained from XPS O1s spectra 75
Table 3.4: Triexponential decay parameters for pure TiO_2 and metal-doped TiO_2 (Cu, Ag, Au) catalysts: time constants (τ) and amplitudes (A) 80
Table 3.5: Comparison of binding energies (BE) of CO_2 and contact angles for metal-doped TiO_2 catalysts: copper (Cu), gold (Au), and silver (Ag) 87
Table 4.1: A comparative study among MoS_2-based materials for photocatalytic CO_2 reduction 104
Table 4.2: BET Surface Area Analysis for different individual component catalysts 106
Table 4.3: Atomic ratio of elements through CHNS Analysis 112
Table 4.4: Comparison of methanol productivity for p-MoS_2-Cu_2O-c and reported photocatalysts in the past few years 119
Table 4.5: Resistances obtained for different catalyst components and their hetero-structures in the equivalent circuit fit of the EIS Nyquist plots 124
Table 4.6: Calculated effective electron hole masses obtained through the parabolic fitting of conduction band minima and valance band maxima 127
Table 4.7: Fermi level determination through experimental and theoretical calculations with respect to vacuum 131
Table 5.1: Lattice parameters and ΔG values of the identified different carbon nitride polymorphs 149
Table 5.2: Variations in different kinetic parameters for different catalyst samples of carbon nitride synthesized at different temperatures 172
Table 5.3: Variations of different kinetic parameters with changing electron donor concentrations 173
Table 6.1: XPS surface ratio for C/N over prepared samples 183
Table 6.2: Element analysis for different modified carbon nitride materials 185
Table 6.3: Comparison of CO_2 reduction rates of CN-C≡N-N_v with reported modified carbon nitride 188
Table 6.4: DFT calculated energy gaps and fermi levels for different models 193
Table 6.5: Comparative table for the DFT calculated effective masses of electrons and holes, and fermi levels for CN (Model 1) and CN–N_v-C≡N (Model 4) 196
Table 6.6: Solution resistance (R_s), charge transfer resistance (R_{ct}), Constant phase element (CPE) and flat band potential (V_{fb}) of all synthesized materials 199