

MODULATION FROM NANOPARTICLES TO SINGLE ATOM OVER CRYSTALLINE POROUS FRAMEWORKS FOR HETEROGENEOUS CATALYSIS

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by

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Submitted

*in fulfilment of the requirements of the degree of
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Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled "Modulation from Nanoparticles to Single Atom Over Crystalline Porous Frameworks for Heterogeneous Catalysis" being submitted by Mr. Biswajit Mishra to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Mr. Mishra has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

Catalysis plays a vital role in energy sector transformation, offering cost-effective and environmentally sustainable alternatives. Heterogeneous catalysis has emerged as a preferred system due to its high efficiency and reusability. Despite this, challenges such as product selectivity and high metal content have prompted exploration into nanocatalysis and single atom catalysis. In recent years, considerable efforts have been directed towards reducing metal particles to atomic levels in heterogeneous catalysts, recognizing the significant impact of metal size on reactivity and selectivity. These advanced systems, characterized by their high surface area and structural stability, deliver efficient catalytic performance while minimizing metal usage. Thus, selecting the appropriate support and metal center becomes crucial in designing efficient catalyst systems. Therefore, the primary objective of this thesis is to rationally design crystalline porous frameworks (MOFs and COFs) to stabilize nanoparticles, nanoclusters, and SAC for heterogeneous catalysis, specifically for energy-related applications. Through a combination of experimental and theoretical analyses, a comprehensive understanding was achieved regarding the significance of stabilization and its influence on catalytic activity enhancement. In chapter 2, we systematically designed an anthraquinone-based COF to stabilize oxygen-vacant TiO_{2-x} NP ($\text{TiO}_{2-x}@\text{COF-Aq}$) for the electrocatalytic nitrogen reduction reaction with the aim of overcoming the challenges associated with the Haber-Bosch process. Through meticulous investigations, we confirmed the uniform distribution of oxygen-vacant TiO_{2-x} nanoparticles (average size ~ 7 nm) across the COF-Aq support through a strong metal-support interaction. $\text{TiO}_{2-x}@\text{COF-Aq}$ exhibited outstanding ENRR performance, resulting in significantly higher ammonia yield and Faradaic efficiency compared to conventional nitrogen reduction electrocatalysts. Addressing the inherent functionality limitations of the parent MOF, in Chapter 3, we extensively explored the effects of a PSM strategy involving a polydopamine layer on stabilizing ultrafine AgPd nanoalloys. The application of a thin PDA layer onto the MOF (MIL-125-NH_2) effectively stabilized ultrasmall AgPd nanoalloys (size 2.2 ± 0.3 nm). Synthesized catalyst exhibited exceptional heterogeneous catalytic activity across multiple reactions, including FA dehydrogenation, Suzuki-Miyaura coupling, aldehyde hydrogenation, and continuous nitrophenol reduction. In Chapter 4, a ligand engineering strategy was employed to create a thiol-functionalized MOF (Ni-MOF-SH) aimed at stabilizing ultrasmall Ru nanoclusters (Ru NC) to enhance the alkaline oxygen evolution reaction. The homogeneous distribution of thiol functionalities enabled uniform dispersion of ultrasmall Ru NCs (1.5 nm in size). With a Ru content of 3.58 wt%, the resulting electrocatalyst (RuNC/Ni-MOF-SH) exhibited remarkable activity in alkaline oxygen

evolution reaction, requiring only 248 mV of overpotential to achieve a current density of 10 mA/cm², along with excellent long-term stability. To further reduce the size of Ru NCs, we synthesized three different β -ketoenamine-linked COFs using linear aliphatic diamines as linkers. Pore size control was achieved by varying the chain lengths of diamines (ethylene diamine, diethylenetriamine, and triethylenetetramine). Among the COFs synthesized, TFG-TETA was selected to stabilize Ru NCs due to the abundance of amine sites in triethylenetetramine and the COF's iminic sites. The size of the Ru NC over the TFG-TETA support was found to be 1.25 nm. The integration of Ru NCs with the TFG-TETA support demonstrated excellent performance in both alkaline oxygen evolution reaction and hydrogen evolution reaction, requiring only 222 mV for OER and 71 mV for hydrogen evolution reaction to reach a current density of 10 mA/cm². Moreover, RuNC/TFG-TETA exhibited remarkable water-splitting efficiency when used as both the cathode and anode, requiring only 1.53 V to achieve a current density of 10 mA/cm².

To further minimize the noble metal atom concentration and maximize the electrocatalytic water splitting activity, single atoms of active metal sites was stabilized over the MOF and COF and how the supports affect the electrocatalytic catalysis was studied in chapter 6. In chapter 6a examines MOFs' role in stabilizing single-atom Ru through controlled pyrolysis process in presence of semicarbazide as N-dopant. The resulting Ru-N₄ configuration electrocatalyst (Ru₁/Ni-NPGC) displayed exceptional performance, needing only ~195 mV (for 10 mA/cm²) and exhibiting a lower Tafel slope of ~52 mV/dec in alkaline conditions. Ru₁/Ni-NPGC also exhibits superior oxygen evolution reaction activity across various pH levels and maintains a long-term electrocatalytic activity. To prepare a metal-free support with abundant metal complexation sites, a hydrazone-linked imine-based COF was synthesized to stabilize single-atom Ru in chapter 6b. With ~1.9 wt% Ru loading, Ru₁/CDGC showed impressive oxygen evolution reaction activity, needing only 173 and 211 mV for 10 and 50 mA/cm², surpassing commercial RuO₂. Moreover, Ru₁/CDGC exhibits superior oxygen evolution reaction performance across all pH levels and maintains structural integrity during prolonged oxygen evolution reaction activities. The thesis concludes by analyzing the structural stability after long-term catalytic activity, paving the way for designing the next generation functional crystalline porous framework supports to stabilize catalysts for various energy-related catalytic applications.

सार

कैटालिसिस ऊर्जा क्षेत्र के परिवर्तन में महत्वपूर्ण भूमिका निभाता है, जो लागत प्रभावी और पर्यावरणीय रूप से टिकाऊ विकल्प प्रदान करता है। अपनी उच्च दक्षता और पुनः प्रयोज्यता के कारण विषम उत्प्रेरण एक पसंदीदा प्रणाली के रूप में उभरा है। इसके बावजूद, उत्पाद चयनात्मकता और उच्च धातु सामग्री जैसी चुनौतियों ने नैनोकैटालिसिस और एकल परमाणु कैटालिसिस में अन्वेषण को प्रेरित किया है। हाल के वर्षों में, प्रतिक्रियाशीलता और चयनात्मकता पर धातु के आकार के महत्वपूर्ण प्रभाव को पहचानते हुए, विषम उत्प्रेरक में धातु के कणों को परमाणु स्तर तक कम करने की दिशा में काफी प्रयास किए गए हैं। अपने उच्च सतह क्षेत्र और संरचनात्मक स्थिरता की विशेषता वाली ये उन्नत प्रणालियाँ धातु के उपयोग को कम करते हुए कुशल उत्प्रेरक प्रदर्शन प्रदान करती हैं। इस प्रकार, कुशल उत्प्रेरक प्रणालियों को डिजाइन करने में उचित समर्थन और धातु केंद्र का चयन महत्वपूर्ण हो जाता है। इसलिए, इस थीसिस का प्राथमिक उद्देश्य विशेष रूप से ऊर्जा-संबंधित अनुप्रयोगों के लिए विषम उत्प्रेरण के लिए नैनोकणों, नैनोक्लस्टर, और एसएसी को स्थिर करने के लिए कई क्रिस्टलीय छिद्रपूर्ण ढांचे (MOF and COF) को तर्कसंगत रूप से डिजाइन करना है। प्रायोगिक और सैद्धांतिक विश्लेषणों के संयोजन के माध्यम से, स्थिरीकरण के महत्व और उत्प्रेरक गतिविधि वृद्धि पर इसके प्रभाव के बारे में एक व्यापक समझ हासिल की गई। अध्याय 2 में, हमने इलेक्ट्रोकेटलिटिक नाइट्रोजन कटौती प्रतिक्रिया के लिए ऑक्सीजन-रिक्त TiO_{2-x} NP ($\text{TiO}_{2-x}@\text{COF-Aq}$) को स्थिर करने के लिए व्यवस्थित रूप से एक एंथ्राक्विनोन-आधारित COF डिजाइन किया है, जिसका उद्देश्य इससे जुड़ी चुनौतियों पर काबू पाना है। हैबर-बॉश प्रक्रिया. सावधानीपूर्वक जांच के माध्यम से, हमने एक मजबूत धातु-समर्थन इंटरैक्शन के माध्यम से COF-Aq समर्थन में ऑक्सीजन-रिक्त TiO_{2-x} नैनोकणों (औसत आकार ~ 7 एनएम) के समान वितरण की पुष्टि की। $\text{TiO}_{2-x}@\text{COF-Aq}$ ने उत्कृष्ट ENRR प्रदर्शन प्रदर्शित किया, जिसके परिणामस्वरूप पारंपरिक ENRR इलेक्ट्रोकेटलिस्ट की तुलना में काफी अधिक अमोनिया उपज और फैराडिक दक्षता प्राप्त हुई। मूल एमओएफ की अंतर्निहित कार्यक्षमता सीमाओं को संबोधित करते हुए, अध्याय 3 में, हमने अल्ट्राफाइन एजीपीडी नैनोएलॉय को स्थिर करने पर पॉलीडोपामाइन परत से जुड़े पोस्ट-सिंथेटिक संशोधन रणनीति के प्रभावों का व्यापक रूप से पता लगाया। एमओएफ (MIL-125- NH_2) पर एक पतली पीडीए परत का अनुप्रयोग प्रभावी ढंग से अल्ट्रास्मॉल एजीपीडी नैनोएलॉय (आकार 2.2 ± 0.3 एनएम) को स्थिर करता है। संश्लेषित उत्प्रेरक ने कई प्रतिक्रियाओं में असाधारण विषम उत्प्रेरक गतिविधि प्रदर्शित की, जिसमें फॉर्मिक एसिड डीहाइड्रोजनेशन, सुजुकी-मियाउरा युग्मन, एल्डिहाइड हाइड्रोजनीकरण और निरंतर नाइट्रोफेनॉल कमी शामिल है। अध्याय 4 में, एक लिगेंड इंजीनियरिंग रणनीति

का उपयोग करके एक थिओल-फंक्शनलाइज्ड MOF (Ni-MOF-SH) बनाया गया था, जिसका उद्देश्य क्षारीय ऑक्सीजन विकास प्रतिक्रिया (OER) को बढ़ाने के लिए अल्ट्रास्मॉल Ru नैनोकलस्टर्स (Ru NC) को स्थिर करना था। थिओल कार्यात्मकताओं के समरूप वितरण ने अल्ट्रास्मॉल Ru NCs (आकार में 1.5 nm) के समान फैलाव को सक्षम किया। 3.58 wt% की Ru सामग्री के साथ, परिणामी इलेक्ट्रोकेटलिस्ट (RuNC/Ni-MOF-SH) ने क्षारीय OER में उल्लेखनीय गतिविधि प्रदर्शित की, जिसमें 10 mA/cm² की वर्तमान घनत्व प्राप्त करने के लिए केवल 248 mV ओवरपोटेंशियल की आवश्यकता थी, साथ ही उत्कृष्ट दीर्घकालिक स्थिरता भी। Ru NCs के आकार को और कम करने के लिए, हमने लिंकर के रूप में रैखिक एलिफैटिक डायमाइन का उपयोग करके तीन अलग-अलग β -कीटोएनामाइन-लिंकड COFs को संश्लेषित किया। डायमाइन (एथिलीन डायमाइन, डाइएथिलीनट्रायमाइन और ट्राइएथिलीनटेट्रामाइन) की श्रृंखला लंबाई को बदलकर छिद्र आकार नियंत्रण प्राप्त किया गया। संश्लेषित COFs में, TFG-TETA को ट्राइएथिलीनटेट्रामाइन में अमीन साइटों और COF के इमिनिक साइटों की प्रचुरता के कारण Ru NCs को स्थिर करने के लिए चुना गया था। TFG-TETA समर्थन पर Ru NC का आकार 1.25 nm पाया गया। TFG-TETA समर्थन के साथ Ru NCs के एकीकरण ने क्षारीय OER और HER दोनों में उत्कृष्ट प्रदर्शन का प्रदर्शन किया, जिसमें 10 mA/cm² की वर्तमान घनत्व तक पहुँचने के लिए OER के लिए केवल 222 mV और HER के लिए 71 mV की आवश्यकता थी। इसके अलावा, RuNC/TFG-TETA ने कैथोड और एनोड दोनों के रूप में उपयोग किए जाने पर उल्लेखनीय जल-विभाजन दक्षता का प्रदर्शन किया, जिसमें 10 mA/cm² की वर्तमान घनत्व प्राप्त करने के लिए केवल 1.53 V की आवश्यकता थी। उत्कृष्ट धातु परमाणु सांद्रता को और कम करने और इलेक्ट्रोकेटलिटिक जल विभाजन गतिविधि को अधिकतम करने के लिए, सक्रिय धातु साइटों के एकल परमाणुओं को MOF और COF पर स्थिर किया गया था और समर्थन कैसे इलेक्ट्रोकेटलिटिक कटैलिसिस को प्रभावित करते हैं, इसका अध्ययन अध्याय 6 में किया गया था। अध्याय 6a में N-डोपेंट के रूप में सेमीकार्बेज़ाइड की उपस्थिति में नियंत्रित पायरोलिसिस प्रक्रिया के माध्यम से एकल-परमाणु Ru को स्थिर करने में MOF की भूमिका की जांच की गई है। परिणामी Ru-N4 विन्यास इलेक्ट्रोकेटलिस्ट (Ru₁/Ni-NPGC) ने असाधारण प्रदर्शन प्रदर्शित किया, जिसे केवल ~195 mV (10 mA/cm² के लिए) की आवश्यकता थी और क्षारीय स्थितियों में ~52 mV/dec का निचला टैफल ढलान प्रदर्शित किया। Ru₁/Ni-NPGC विभिन्न pH स्तरों में बेहतर OER गतिविधि भी प्रदर्शित करता है प्रचुर मात्रा में धातु संकुलन स्थलों के साथ एक धातु-मुक्त समर्थन तैयार करने के लिए, अध्याय 6बी में एकल-परमाणु Ru को स्थिर करने के लिए एक हाइड्राज़ोन-लिंकड इमाइन-आधारित COF को संश्लेषित किया गया था। ~1.9 wt% Ru लोडिंग के साथ, Ru₁/CDGC ने प्रभावशाली OER गतिविधि दिखाई, 10 और 50 mA/cm² के लिए केवल 173 और 211 mV

की आवश्यकता थी, जो वाणिज्यिक RuO_2 से आगे निकल गया। इसके अलावा, Ru1/CDGC सभी pH स्तरों पर बेहतर OER प्रदर्शन प्रदर्शित करता है और लंबे समय तक OER गतिविधियों के दौरान संरचनात्मक अखंडता बनाए रखता है। तीसरी लंबी अवधि की उत्प्रेरक गतिविधि के बाद संरचनात्मक स्थिरता का विश्लेषण करके समाप्त होती है, जो विभिन्न ऊर्जा-संबंधित उत्प्रेरक अनुप्रयोगों के लिए उत्प्रेरकों को स्थिर करने के लिए अगली पीढ़ी के कार्यात्मक क्रिस्टलीय छिद्रपूर्ण ढांचे के समर्थन को डिजाइन करने का मार्ग प्रशस्त करती है।

TABLE OF CONTENTS

CERTIFICATE	i
ACKNOWLEDGEMENTS.....	ii
ABSTRACT	iv
LIST OF FIGURES	xiii
LIST OF TABLES	xxvii
LIST OF ABBREVIATIONS.....	xxix
LIST OF SYMBOLS	xxxii
CHAPTER 1: INTRODUCTION, LITERATURE REVIEW, MOTIVATION, AND OBJECTIVES	1
1.1. Catalysis	2
1.2. Heterogenous catalysis.....	2
1.2.1. Metal NPs in heterogeneous catalysis.....	3
1.2.2. SAC.....	6
1.3. Role of support materials in metal particle stabilization	7
1.3.1. Metal-support interactions.....	7
1.4. CPFs as support	12
1.5. MOFs	13
1.5.1. Historical perspective	14
1.5.2. Synthesis of MOFs.....	15
1.5.3. Support effects of MOFs in heterogeneous catalysis	17
1.5.4. Methods of synthesis NPs, NCs and SAC in MOFs.....	21
1.6. COFs.....	27
1.6.1. Brief overview of COFs	27
1.6.2. COF building blocks	29
1.6.3. Synthesis procedure of COFs.....	31
1.6.4. Role of COFs in catalysis	33
1.7. Key questions	36
1.8. Objectives of the thesis	36
1.9. Format of the thesis	36
CHAPTER 2: RATIONALLY DESIGNED OXYGEN VACANT TiO ₂ DECORATED WITH COVALENT ORGANIC FRAMEWORK FOR ENHANCED ELECTROCATALYTIC NITROGEN REDUCTION TO AMMONIA	40
2.1. Introduction.....	41
2.2. Experimental sections.....	45

2.2.1. Materials	45
2.2.2. Synthesis of TFP.....	45
2.2.3. Synthesis of COF-Aq.....	46
2.2.4. Synthesis of self-doped TiO _{2-x} @COF-Aq	46
2.2.5. Material characterizations.....	47
2.2.6. ENRR performance.....	48
2.2.7. Computational methods and models	51
2.3. Results and discussion	52
2.3.1. Synthesis of COF-Aq and TiO _{2-x} @COF-Aq.....	52
2.3.2. Characterization of materials	53
2.3.3. Electrochemical Nitrogen fixation	61
2.3.4. Mechanistic insights.....	73
2.4. Conclusions.....	77
CHAPTER 3: FINELY DISPERSED AgPd BIMETALLIC NANOPARTICLES ON A POLYDOPAMINE MODIFIED METAL ORGANIC FRAMEWORK FOR DIVERSE CATALYTIC APPLICATIONS.....	79
3.1. Introduction.....	80
3.2. Materials and methods	82
3.2.1. Materials	82
3.2.2. Synthesis of MIL-125-NH ₂	83
3.2.3. Synthesis of PDA modified MIL-125-NH ₂	83
3.2.4. Silver and palladium NP synthesis on MIL-125-NH ₂ -PDA.....	83
3.2.5. Characterizations.....	84
3.2.6. Catalytic activity analysis	85
3.2.7. Computational Method	86
3.3. Results and discussion	87
3.3.1. Synthesis and morphology of the synthesized catalyst	87
3.3.2. Chemical structure and thermal properties	92
3.3.3. Catalytic activity evaluation	99
3.4. Conclusions.....	117
CHAPTER 4: BOOSTING OXYGEN EVOLUTION REACTION BY STABILIZATION OF ULTRASMALL RUTHENIUM NANOCLUSTERS ON THIOL-FUNCTIONALIZED METAL-ORGANIC FRAMEWORK.....	119
4.1. Introduction.....	120
4.2. Materials and Methods.....	124
4.2.1. Materials	124

4.2.2. Synthesis methods.....	124
4.2.3. Instrumentation.....	127
4.2.4. ICP-MS data calculation.....	128
4.2.5. EXAFS measurement and fitting parameters	129
4.2.6. Electrocatalytic OER	130
4.3. Results and discussion.....	134
4.3.1. Synthesis and characterization of RuNC/Ni-M-SH	134
4.3.2. Electrocatalytic OER activity of catalysts	141
4.3.3. Stability of electrocatalyst	147
4.3.4. In-situ studies for OER mechanisms	149
4.4. Conclusion	152
CHAPTER 5: LINEAR ALIPHATIC DIAMINE-BASED COVALENT ORGANIC FRAMEWORK SYNTHESIS AND STABILIZATION OF ULTRASMALL RUTHENIUM NANOCLUSTERS FOR OVERALL WATER SPLITTING	153
5. 1. Introduction.....	154
5.2. Materials and Methods	157
5. 2.1. Materials	157
5. 2.2. Synthesis of TFG	157
5.2.3. Synthesis of COF thin film over porous support via interfacial polymerization ..	158
5.2.4. Instrumentation.....	158
5. 3. Results and discussion	159
5.3.1. Synthesis of aliphatic diamine-based COF thin film	159
5. 3.2. Characterization of COFs thin films	164
5.4. Stabilization of Ru Nanocluster for electrocatalytic applications.....	170
5. 4.1. Synthesis of RuNC/TFG-TETA	171
5.4.2. Characterization	171
5. 5. Results and Discussion	172
5. 5.1. Synthesis and characterization of RuNC/TFG-TETA.....	172
5. 5.2. Electrocatalytic OER activity.....	176
5. 5.3. Electrocatalytic alkaline HER activity.....	180
5. 5. 4. Overall water splitting and stability of RuNC/TFG-TETA.....	182
5. 6. Conclusion	183
CHAPTER 6a: ATOMICALLY DISPERSED HIGHER VALENT OF RUTHENIUM OVER N-DOPED NICKEL BASED METAL-ORGANIC FRAMEWORK pH- UNIVERSAL OVERALL WATER SPLITTING	185

6(a).1. Introduction	186
6(a).2. Materials and Methodologies	188
6(a).2.1. Chemicals.....	188
6(a).2.2. Synthesis of Ni-MOF	189
6(a).2.3. Synthesis of Ru ₁ /Ni-NPGC	189
6(a).2.4. Instrumentation.....	189
6(a).2.5. Electrochemical measurements	190
6(a).3. Results and Discussion	191
6(a).3.1. Chemical state and atomic structure analysis of Ru ₁ /Ni-NPGC	193
6(a).3.2. Electrocatalytic performance for alkaline OER	197
6(a).3.3. Electrocatalytic performance for alkaline HER	200
6(a).3.4. pH-universal overall water splitting performance	203
6(a).3.5. In situ spectroscopic studies.....	205
6(a).4. Conclusions	207
CHAPTER 6b: RUTHENIUM SINGLE ATOM STABILIZED OVER IMINE-BASED COVALENT ORGANIC FRAMEWORK-DERIVED CARBON AS A BIFUNCTIONAL ELECTROCATALYST FOR OVERALL WATER SPLITTING	208
6(b).1. Introduction.....	209
6(b).2. Materials and Methods.....	212
6(b).2.1. Materials	212
6(b).2.3. Synthesis of Ru ₁ /CDGC.....	212
6(b).3. Results and discussion	213
6(b).3.1. Synthesis and characterization of electrocatalysts	213
6(b).3.2. Electrochemical OER activity.....	218
6(b).3.3. Electrochemical HER activity.....	221
6(b).4. Conclusion	226
CHAPTER 7: CONCLUSIONS AND FUTURE OUTLOOK	228
7.1. Conclusions.....	229
7.2. Future outlook	233
BIBILOGRAPHY	235
APPENDIX: I.....	270
APPENDIX: II	282
CURRICULUM VITAE: Biswajit Mishra.....	285

LIST OF FIGURES

Figure 1.1. (A) Potential energy diagram demonstrating the role of catalyst in a typical chemical reaction between A+B to form product B (blue line indicated catalyzed pathway, green line indicated non-catalyzed pathway), (B) the schematic illustrates each step of the catalytic process. initially, reactant molecules are adsorbed onto the catalyst surface (adsorption step), followed by the occurrence of the reaction, In the final step, the product desorbs from the catalyst surface, returning the catalyst to its original state for the next cycle-----	3
Figure 1.2. Effect of Iron carbide particle size on turnover frequencies for CO conversion.-----	4
Figure 1.3. Changes in the geometric and electronic structures occur when the size of the metal sites changes from NPs to NCs to single atoms-----	6
Figure 1.4. (A) Schematic representation for the catalytic acetylene hydrogenation by Pd and PdIn alloys supported over Al ₂ O ₃ , and (B) TOF and selectivity for the catalytic acetylene hydrogenation by Pd/Al ₂ O ₃ and Pd-In/Al ₂ O ₃ -----	9
Figure 1.5. Self-assembly of metal clusters and organic linkers to form MOF-----	13
Figure 1.6. Basic structural unit combination to form 1D, 2D and 3D MOFs-----	14
Figure 1.7. Schematic representation for the synthesis of COF-5-----	28
Figure 1.8. Topology diagrams serve as a fundamental framework for the design and synthesis of (A) 2D COFs and (B) 3D COFs-----	30
Figure 2.1. (A) ¹ H NMR and (B) ¹³ C NMR (CDCl ₃) spectra of TFP-----	46
Figure 2.2. Stepwise schematic illustration for the synthesis of TFP, formation of COF-Aq, and TiO _{2-x} @COF-Aq in presence of dilute HNO ₃ -----	52
Figure 2.3. (A, B) FE-SEM image of COF-Aq and TiO _{2-x} @COF-Aq and (C-D) low-magnification TEM image and High-resolution TEM of COF-Aq and TiO _{2-x} @COF-Aq, respectively showing a sheet-like structure and distribution of TiO ₂ NPs. (E) SEM-EDS Spectrum and elemental quantification of TiO _{2-x} @COF-Aq-----	53

Figure 2.4. (A) Low magnification bright-field HRTEM image of $\text{TiO}_{2-x}\text{@COF-Aq}$ showing the fine distribution of the TiO_{2-x} particles (inset figure shows the particle size distribution of TiO_{2-x}), (B) High magnification HRTEM images, (C) HRTEM lattice fringe image, (D) SAED pattern (scale bar 5 $\text{\AA}/\text{nm}$), (E) Dark-field HRTEM image of $\text{TiO}_{2-x}\text{@COF-Aq}$ (F) FESEM-EDS mapping images-----54

Figure 2.5. TEM images of bulk TiO_{2-x} synthesized in the absence of COF-Aq-----55

Figure 2.6. (A) ^{13}C -NMR spectra of COF-Aq. (B) FT-IR spectra as-prepared catalyst --
-----55

Figure 2.7. (A) PXRD spectra of COF-Aq and $\text{TiO}_{2-x}\text{@COF-Aq}$. (B) N_2 adsorption/desorption isotherm, (C) pore size distribution of COF-Aq and $\text{TiO}_{2-x}\text{@COF-Aq}$, (D) BET isotherm of $\text{TiO}_{2-x}\text{@COF-Aq}$ and TiO_{2-x} -----57

Figure 2.8. (A) XPS survey spectra (B) deconvoluted spectra of N 1s spectra of $\text{TiO}_{2-x}\text{@COF-Aq}$, (C) comparative N 1s XPS spectra between COF-Aq and $\text{TiO}_{2-x}\text{@COF-Aq}$, (D) Area ratio of Ti 2p, (E) deconvoluted O 1s spectra, (F) Deconvoluted C 1s spectra, (G) Deconvoluted Ti 2p spectra, (H) deconvoluted high resolution O 1s spectra of TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$, (I) TGA graph of COF-Aq and $\text{TiO}_{2-x}\text{@COF-Aq}$ -----59

Figure 2.9. (A) ESR spectra of $\text{TiO}_{2-x}\text{@COF-Aq}$ and TiO_2 , (B) EPR spectra of TiO_{2-x} , $\text{TiO}_{2-x}\text{@COF-Aq}$, (C) Raman spectra of TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$, (D) Tauc analysis for band gap calculations-----60

Figure 2.10. (A) DFT calculations for oxygen vacancy formation energy on the pure TiO_{2-x} surface, and (B) $\text{TiO}_{2-x}\text{@COF-Aq}$. (The schematics represent the oxygen vacant sites at anatase TiO_{2-x} and TiO_{2-x} NC mounted on the COF-Aq) -----61

Figure 2.11. (A) LSV curves of $\text{TiO}_{2-x}\text{@COF-Aq}$ measured under different atmosphere (N_2 and Ar). in 0.1 M HCl with a scan rate of 5 mV/sec, (B) LSV curves of Carbon black and $\text{TiO}_{2-x}\text{@COF-Aq}$ in 0.1 M HCl measured under N_2 -saturated atmosphere with a scan rate of 5 mV/sec-----62

Figure 2.12. ENRR performance for COF-Aq, TiO_{2-x} , and $\text{TiO}_{2-x}\text{@COF-Aq}$ in N_2 saturated electrolytes (0.1 M HCl, pH 1). (A) LSV curves of COF-Aq, TiO_{2-x} , and $\text{TiO}_{2-x}\text{@COF-Aq}$ measured under N_2 atmosphere, (B) chronoamperometry data at various

potential for 1 h, (C) corresponding UV-visible spectra of electrolytes recorded after stained with indophenol indicator. NH_3 yield and FE of (D) $\text{TiO}_{2-x}\text{@COF-Aq}$ at a different potential, (E) TiO_{2-x} at different potentials, (F) Hydrazine hydrate detection after electrolysis (Watt and Crisp Method) (Measured in 0.1 M HCl under N_2 -saturated atmosphere).-----63

Figure 2.13: ENRR control experiments of $\text{TiO}_{2-x}\text{@COF-Aq}$ (A) UV-vis adsorption spectra of electrolyte before and after bubbling into N_2 (Indophenol method), (B) UV-vis absorption spectra of the electrolytes stained with indicator before and after 2 h electrolysis under open circuit conditions. (Indophenol method), (C) UV-vis absorption spectra of the electrolyte stained with indicator before and after 2 h electrolysis at the potential of -0.5 V under Ar-saturated solution. (Indophenol method), (D) UV-vis absorption spectra of N_2H_4 before and after 2 h electrolysis in N_2 atmosphere at different potential. (Watt and Crisp Method), (E) The UV-Vis absorption spectra of the 0.1 M HCl electrolyte and N_2 gas cylinder using N-(1-naphthyl)-ethylenediamine dihydrochloride spectrophotometric method for NO_x detection, (F) NH_3 yields and FEs for $\text{TiO}_{2-x}\text{@COF-Aq}$ with alternating 2 h cycles between N_2 -saturated and Ar-saturated electrolytes-----65

Figure 2.14. (A) NH_3 yield and FE of $\text{TiO}_{2-x}\text{@COF-Aq}$ at different temperatures at -0.55 V vs. RHE, (B) comparison of ENRR activity with the state-of-the-art NRR electrocatalyst in 0.1 M HCl at room temperature, (C) TOF values of TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$ for ENRR (D) cycling test of $\text{TiO}_{2-x}\text{@COF-Aq}$ at -0.5 V vs. RHE, (E) long-term chronoamperometry curves at -0.5 V vs. RHE (inset figure shows the initial and post- NH_3 yield and FE)-----67

Figure 2.15. Stability test of $\text{TiO}_{2-x}\text{@COF-Aq}$ after 60 h of continuous ENRR operation (A) PXRD pattern, (B) Ti 2p XPS spectra, (C) TEM image with the inset image showing the particle size distribution of TiO_2 NPs, (D) EPR spectra, (E) Dissolved Ti during long-term electrolysis, (F) elemental mappings of $\text{TiO}_{2-x}\text{@COF-Aq}$ -----69

Figure 2.16. Effect of oxygen vacancy on ENRR performance (A) EPR spectra, (B, C) HRTEM images, (D) N_2 -TPD analysis, (E) Ammonia yield and FE (ENRR activity was performed in 0.1M HCl N_2 -saturated electrolyte)-----70

Figure 2.17. (A) Nyquist plots, (B) CV at different scan rates in the non-faradaic region of TiO_2 and $\text{TiO}_{2-x}\text{@COF-Aq}$, (C) Mott-Schottky experiment with TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$ in 0.1 M HCl. UPS spectra in the (D) secondary electron cutoff energy (E_{cutoff}) regions and (E) onset energy (E_{onset}) regions of TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$, (F) calculated donor density (N_d) and work function calculated from the Mott-Schottky and UPS analysis, respectively, (G) N_2 TPD profiles of TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$, (H) schematic representation of the electrochemical NRR process on $\text{TiO}_{2-x}\text{@COF-Aq}$ --72

Figure 2.18. In-situ operando electrochemical ATR-FTIR spectra over TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$ at -0.5 V vs. RHE in 0.1M HCl electrolyte under N_2 -saturated atmosphere (spectra was taken after chronoamperometry for 15 min)-----73

Figure 2.19. (A, D) N_2 and H adsorption on top Ti atom adjacent to the oxygen vacancy, (B, E) N_2 and H adsorption on bridging between the two Ti atoms (Ti_b), (C, F) N_2 and H adsorption on top of the oxygen atom (O_t)-----74

Figure 2.20. DFT calculation to assess the effect of oxygen vacancy (A,C) N_2 adsorption energy on oxygen vacant TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$, (B,D) N_2 adsorption energy on TiO_{2-x} and $\text{TiO}_2\text{@COF-Aq}$ without oxygen vacancy-----75

Figure 2.21. (A) Competing adsorption of adsorption of N_2 and H for the NRR and HER (B) N_2 adsorbed on the oxygen vacant (O_v) TiO_{2-x} (101) sites and on (C) TiO_{2-x} cluster mounted on the COF ($\text{TiO}_{2-x}\text{@COF-Aq}$), (D) Adsorption energies of H and N_2 molecule on TiO_{2-x} and $\text{TiO}_{2-x}\text{@COF-Aq}$, (E) shows the RESP charge analysis of N_2 and H after adsorption, where red, blue, cyan, white, and orange colors represent the oxygen, nitrogen, carbon, hydrogen, and titanium. Bond distances are shown in Å--77

Figure 3.1. Schematic representation for the steps involved in the synthesis of $\text{AgPd@MIL-125-NH}_2\text{-PDA}$ -----88

Figure 3.2. The effect of polymerization time on coating thickness while maintaining a constant dopamine concentration of 2 mg/ml -----89

Figure 3.3. FE-SEM image of MIL-125- NH_2 , MIL-125- $\text{NH}_2\text{-PDA}$, and $\text{Ag-Pd@NH}_2\text{-MIL-125-PDA}$ -----90

Figure 3.4. Energy dispersive-X-ray spectroscopy for elemental analysis and mapping of AgPd@MIL-125-NH ₂ -PDA -----	90
Figure 3.5. TEM image of (A) MIL-125-NH ₂ , (B) AgPd@MIL-125-NH ₂ (C) MIL-125-NH ₂ -PDA, and (D) AgPd@MIL-125-NH ₂ -PDA NPs -----	91
Figure 3.6. Isotherm of N ₂ adsorption/desorption at various PDA polymerization times-----	92
Figure 3.7. Morphology and particle distributions: (A-B) HR-TEM images of AgPd@MIL-125-NH ₂ -PDA, inset image in figure (A) is the low-resolution TEM image of AgPd@MIL-125-NH ₂ , (C) Particle size distribution of AgPd@MIL-125-NH ₂ , (D-E, F) lattice spacing and SAED pattern of AgPd@MIL-125-NH ₂ -PDA, respectively.-----	93
Figure 3.8. Structural and stability results: (A) PXRD pattern, (B) TGA thermogram of MIL-125-NH ₂ , MIL-125-NH ₂ -PDA, and AgPd@MIL-125-NH ₂ -PDA-----	94
Figure 3.9. FTIR (A) and Raman (B) spectra of synthesized MOF and catalysts-----	95
Figure 3.10. High resolution XPS survey spectra and Composition data of AgPd@MIL-125-NH ₂ -PDA-----	96
Figure 3.11. High-resolution XPS spectra of (A) C 1s, (B) N 1s, (C) O 1s, (D) Ti 2p, (E) Ag 3d, and (F) Pd 3d for AgPd@MIL-125-NH ₂ -PDA -----	97
Figure 3.12. Solid-state UV-Vis spectra of synthesized catalyst-----	98
Figure 3.13. N ₂ adsorption/desorption isotherm of MIL-125-NH ₂ , MIL-125-NH ₂ -PDA, and AgPd@MIL-125-NH ₂ -PDA (inset images depict the pore-size distribution of the corresponding catalyst)-----	99
Figure 3.14. Stability of MIL-125-NH ₂ and AgPd@MIL-125-NH ₂ -PDA in 1M FA, (A,B,C) XRD pattern, TEM, SEM images of MIL-125-NH ₂ and (D,E,F) XRD pattern. TEM and SEM images of AgPd@MIL-125-NH ₂ -PDA. (The catalyst was kept in known concentration of FA[1M] for 48 h. After that the catalyst was thoroughly washed with deionized water prior to analysis)-----	101
Figure 3.15. (A) Effect of FA: SF ratio on FA dehydrogenation (10 mg of catalyst dosage at 35 °C, (B) Volume of gas released using FA (without SF)-----	102

Figure 3.16. (A) The volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time (B) TOF values for the dehydrogenation of FA over ($[\text{FA}] = 0.3 \text{ M}$ and $[\text{SF}] = 1.0 \text{ M}$ in 10.0 mL aqueous dispersion, catalyst amount 10 mg) at 35°C -----**103**

Figure 3.17. (A) volume of gas generated ($\text{CO}_2 + \text{H}_2$) Vs. time, (B) TOF values [inset plot of the gas generation rate Vs. catalyst dosage (both in log scale, $y = 1.8745x + 1.55$ and $R^2 = 0.92$] for the dehydrogenation of FA over $\text{AgPd@MIL-125-NH}_2\text{-PDA}$ ($[\text{FA}] = 0.3 \text{ M}$ and $[\text{SF}] = 1 \text{ M}$ in 10.0 mL aqueous dispersion) starting with different catalyst dosage at 35°C , (C) temperature dependence of gas ($\text{CO}_2 + \text{H}_2$) evolution from FA over $\text{AgPd@MIL-125-NH}_2\text{-PDA}$, and (D) TOF values [inset, Arrhenius plot $\ln \text{TOF}$] vs $1/T$ ($y = -4764.4x + 22.503$ and $R^2 = 0.9153$) for the dehydrogenation of FA over $\text{AgPd@MIL-125-NH}_2\text{-PDA}$ ($[\text{FA}] = 0.3 \text{ M}$ and $[\text{SF}] = 1 \text{ M}$ in 10.0 mL aqueous dispersion, 10 mg Catalyst) at different temperature-----**104**

Figure 3.18.(a) The energy profiles for reactants, intermediates, and products of dehydrogenation reaction of FA on Pd (111) and AgPd (111) surface. The optimized structure of reaction intermediates on (b-d) Pd (111) and on (e-g) AgPd (111). Keys: Pd (grey), Ag (orange), C (cyan), O (red), and H (white)-----**106**

Figure 3.19. Recyclability test (5 cycles) for the dehydrogenation of FA/SF over $\text{AgPd@MIL-125-NH}_2\text{-PDA}$ ($[\text{FA}] = 0.3 \text{ M}$ and $[\text{SF}] = 1 \text{ M}$ in 10.0 mL aqueous dispersion, 10 mg catalyst at 55°C). After each cycle, the catalyst was recovered by filtration and thoroughly washed with deionized water and dried prior to next cycle-----**108**

Figure 3.20. Stability test of $\text{AgPd@MIL-125-NH}_2\text{-PDA}$ after five consecutive cycle for FA dehydrogenation: (A) PXRD pattern, (B) FT-IR spectra, (C) N_2 adsorption/desorption isotherm, and (D) HR-TEM image-----**109**

Figure 3.21. Schematic representation of plausible mechanism for Suzuki-Miyura Coupling reaction using $\text{AgPd@MIL-125-NH}_2\text{-PDA}$ -----**114**

Figure 3.22. Catalyst recycling and stability test for Suzuki-Miyura coupling using $\text{AgPd@MIL-125-NH}_2\text{-PDA}$ -----**115**

Figure 4.1. Synthesis steps for TPA-SH-----**126**

Figure 4.2. (A) ^1H -NMR, (B) ^{13}C -NMR spectra of TPA-SH (DMSO- d_6 , *indicates the solvent peaks)-----	126
Figure 4.3. Synthesis of thiol-linked MOF (Ni-M-SH)-----	127
Figure 4.4. (A) Stepwise schematic representation for the synthesis of Thiol grafted MOF (Ni-M-SH) and supported Ru NC (RuNC/Ni-M-SH), Characterization of synthesized electrocatalysts (B) PXRD, (C) N_2 adsorption/desorption isotherm, and (D) Pore-size estimation from BET using NLDFT method-----	135
Figure 4.5. (A) FTIR spectra, (B) TGA plots of Ni-M-SH and RuNC/Ni-M-SH, Stability test of Ni-M-SH in both acidic (1M HCl) and basic (1M KOH) at 50 °C for 48 hr (C, D) FESEM images, (E) FTIR spectra, (F) PXRD spectra-----	137
Figure 4.6. (A) FESEM image of Ni-M-SH, (B) TEM image of Ni-M-SH, (C) FESEM image of RuNC/Ni-M-SH, (D) TEM image of RuNC/Ni-M-SH, (E) FESEM-EDS mapping images of RuNC/Ni-M-SH -----	138
Figure 4.7. Characterization of RuNC/Ni-M-SH (A) low-magnification HRTEM image, the inset image demonstrates the particle size distribution with an average diameter of 1.5 nm, (B) higher magnification TEM image, (C) high-resolution TEM image showing the lattice spacing of Ru nanoclusters, (D) STEM image, (E) SAED pattern, (F) STEM imaging and corresponding elemental mapping of RuNC/Ni-M-SH. -----	139
Figure 4.8. (A) High-resolution XPS survey spectra (B) Deconvoluted C_{1s} XPS spectra of RuNC/Ni-M-SH -----	140
Figure 4.9. Characterization of synthesized electrocatalysts. High-resolution XPS (A) Ni 2p spectra, (B) Ru 3p spectra, (C) S 2p spectra. XAS analysis (D) XANES spectra and (E) FT-EXAFS spectra of RuNC/Ni-M-SH along with standard RuO_2 , Ru foil samples, (F) Fitting of RuNC/Ni-M-SH EXAFS spectra, Wavelet transform (WT) EXAFS spectra of (G) Ru Foil, (H) RuO_2 and, (I) RuNC/Ni-M-SH-----	141
Figure 4.10. (A) OER performance for the RuNC/Ni-M-SH_X (X is the wt% Ru) catalysts at various Ru loadings, (B) LSV curve of RuNC/Ni-M-SH before and after iR correction -----	143

Figure 4.11. Electrocatalytic OER performance of Ni-M-SH, RuNC/Ni-M-SH and RuO₂ in O₂-saturated 1 M KOH. (A) iR-corrected LSV curves at a scan rate of 0.001 V/ sec, (B) Tafel slope, (C) OER performances of the catalysts expressed as overpotentials required for 10 mA/cm², 30 mA/cm² and 100 mA/cm², (D) Comparison of mass activity for Ru atoms in RuNC/Ni-M-SH and RuO₂ as a function of overpotential, (E) TOF for RuNC/Ni-M-SH and RuO₂ electrocatalysts, (F) Generated O₂ amount (in mmol) and corresponding FE over a range of time-intervals on RuNC/Ni-M-SH, (G) ESCA normalized current density, (H) Activation energy of electrocatalysts using Arrhenius equation, (I) Comparative plot with state-of-art OER electrocatalyst in 1 M KOH---144

Figure 4.12. (A) TEM images of Ru (unsupported), (B) LSV curve of RuNC/Ni-M-SH at a scan rate of 0.001 V/sec, (C) Corresponding Tafel slope -----147

Figure 4.13. (A-C) CVs were conducted in a non-Faradaic region of voltammogram at different scan rates (10,20,30,40,50 mV/sec), (D) estimation of double-layer capacitance (C_{dl}) from the slope of current density at an underpotential plotted against scan rate, (E) Nyquist plots of electrocatalysts recorded in 1 M KOH solution-----147

Figure 4.14. Electrocatalytic OER performance of RuNC/Ni-M-SH and RuO₂ in O₂-saturated 1 M KOH. (A) Chronopotentiometry of RuNC/Ni-M-SH (at 1.5 V) and RuO₂ (at 1.6 V) in 1 M KOH (inset digital photographs for alkaline electrolytes after long-term stability test of electrocatalysts), (B) Dissolved Ru and Ni ion concentration in electrolyte for RuNC/Ni-M-SH and RuO₂ determined using ICP-MS, (C) UV-vis spectrum of the electrolyte (1M KOH) after long-term stability test, (D) XPS analysis of catalysts before and after OER-----149

Figure 4.15. Stability of RuNC/Ni-M-SH after long-term OER activity in 1M KOH, (A, B) FESEM images, (C, D) HRTEM images, (E) PXRD analysis, (F) High-resolution Ni2p XPS spectra, (G) C1s spectra, (H) S 2p spectra, (I) O1s spectra-----150

Figure 4.16. In-situ Electrocatalytic OER study of RuNC/Ni-M-SH and RuO₂ in O₂-saturated 1 M KOH. (A) In-situ FTIR spectra (650- 900 cm⁻¹) of RuNC/Ni-M-SH obtained at different applied potential and OCP, (B) In-situ FTIR spectra (650- 900 cm⁻¹) comparison for RuNC/Ni-M-SH and RuO₂, (C) In-situ FTIR spectra (1050- 1400

cm⁻¹) of RuNC/Ni-M-SH obtained at different applied potential and OCP, (D) In-situ FTIR spectra (1050- 1400 cm⁻¹) comparison for RuNC/Ni-M-SH and RuO₂, (E) In-situ Raman spectra of RuNC/Ni-M-SH obtained at different applied potential and OCP, (F) In-situ Raman spectra comparison for RuNC/Ni-M-SH and RuO₂-----152

Figure 5. 1. ¹³C CP-MAS spectra of (A) TFG-EDA, (B) TFG-DETA, and (C) TFG-TETA COFs -----162

Figure 5. 2. Synthesis procedure, growth mechanism, and morphology of COF films. (A) Schematic fabrication process for COF-based thin film and the thin film transfer process to a porous membrane support, (B) Optical microscopy image of TFG-EDA on silicon wafer, (C-E) Cross-sectional FE-SEM images demonstrating the thickness of TFG-EDA thin film at different IP times, (F) Growth of film thickness with time measured using ellipsometry, and (G-I) AFM images showing the growth of film thickness at different polymerization times, (J-L) High-resolution TEM images of TFG-EDA, TFG-DETA, and TFG-TETA films (the interfacial films was removed, dispersed, and drop-cast on a TEM grid)-----163

Figure 5. 3. Characterization of COF thin films. (A) Low magnification FESEM image of large area TFG-EDA thin film, (B-D) FESEM-Cross-sectional images showing COF layer thickness after 120 min, Schematic structure of synthesized COF structures (E) TFG-EDA, (F) TFG-DETA, (G) TFG-TETA, (i) FESEM, (ii) TEM, and (iii) AFM images of the corresponding COF thin films-----164

Figure 5. 4. FTIR spectra of interfacially crystallized COFs (A) TFG-EDA, (B) TFG-DETA, and (C) TFG-TETA -----165

Figure 5.5. High-resolution XPS spectra of COF thin films, (A) survey spectra (inset pie chart shows the elemental composition), (B-D) deconvoluted C1s spectra, (E-G) deconvoluted O1s spectra of TFG-EDA, TFG-DETA, and TFG-TETA. (H-J) deconvoluted N1s spectra for TFG-EDA, TFG-DETA, and TFG-TETA-----166

Figure 5.6. XPS and BET characterization of TFG-EDA, TFG-DETA, and TFG-TETA thin films. (A-C) show the deconvoluted N1s spectra for TFG-EDA, TFG-DETA, and

TFG-TETA. (D-F) N₂ adsorption/desorption isotherm for TFG-EDA, TFG-DETA, and TFG-TETA, respectively-----167

Figure 5. 7. Crystal structure determination of synthesized COF using theoretical modelling and PXRD analysis, (A, C, E) AA-stacking of TFG-EDA, TFG-DETA and TFG-TETA, (B, D, F) PXRD pattern with experimental PXRD pattern (circles), Pawley refinement plot (line), and difference between experimental and simulated profiles of TFG-EDA, TFG-DETA and TFG-TETA, respectively-----169

Figure 5.8. Characterization of TFG-EDA, TFG-DETA, and TFG-TETA thin films. (A-C) SAXS scattering data of TFG-EDA, TFG-DETA, and TFG-TETA, respectively. The inset figures in A-C show the 2D scattering image of corresponding COFs. (D) corresponding Log-Log plot of SAXS profile, (E) Guinier plot. (F) Porod plot with point-collimation, which shows a linear plateau without any deviation-----171

Figure 5.9. Synthesis and characterization of RuNC/TFG-TETA. (A) Schematic representation for the synthesis of RuNC/TFG-TETA, (B) PXRD pattern of TFG-TETA and RuNC/TFG-TETA, (C) N₂ adsorption/desorption isotherm, (D) Pore-size distribution (obtained using NLDFT method)-----174

Figure 5. 10. Morphological analysis of TFG-TETA and RuNC/TFG-TETA. (A) FESEM image of TFG-TETA, (B) FESEM image of RuNC/TFG-TETA, (C) TEM image of RuNC/TFG-TETA, (D) low-magnification TEM of RuNC/TFG-TETA, (E) high-magnification of RuNC/TFG-TETA, (F) HRTEM image of RuNC/TFG-TETA, (G) Dark-field HRTEM image of RuNC/TFG-TETA, (H) SAED pattern of RuNC/TFG-TETA, (I) FESEM-EDS mapping images of RuNC/TFG-TETA-----175

Figure 5.11. XPS analysis of RuNC/TFG-TETA, (A) Survey spectra, (B) C 1s spectra of TFG-TETA and RuNC/TFG-TETA, (C) Comparative Ru 3p spectra of RuNC/TFG-TETA and precursor RuCl₃, (D) Ru 3d spectra of RuNC/TFG-TETA, (E) N 1s spectra of TFG-TETA and RuNC/TFG-TETA-----177

Figure 5.12. Electrocatalytic alkaline OER performance of RuNC/TFG-TETA, (A) iR-corrected LSV curves compared with RuO₂, (B) Overpotential for different current density (10, 50 and 100 and 200 mA/cm²), (C) Mass activities of RuNC/TFG-TETA and

RuO₂, (D) Corresponding Tafel slopes, (E) EIS analysis, (F) TOF values of different catalysts, (G) E_a of electrocatalysts, (H) Evolved O₂ in mmol and FE throughout 48 hr operation, (I) Chronoamperometry measurements (inset RuO₂ chronoamperometry and LSV plot of RuNC/TFG-TETA for before and after long-term OER operation), (J) Dissolved Ru ion in electrolyte during long-term OER operation-----179

Figure 5.13. Electrocatalytic alkaline HER performance of RuNC/TFG-TETA, (A) LSV curves of RuNC/TFG-TETA, (B) Corresponding Tafel plot, (C) TOF (s⁻¹) of RuNC/TFG-TETA, (D) Mass activity of RuNC/TFG-TETA, (E) Long-term chronoamperometry plot of RuNC/TFG-TETA at ~31 mA/cm² current density-----182

Figure 5.14. Overall water splitting and stability test of RuNC/TFG-TETA in 1 M KOH (A) LSV curve, (B) Long-term HER and OER operation at different current densities, (C) XPS Ru 3p spectra after long-term OER, (D) HRTEM image after long-term OER, (E) FESEM-EDS mapping after long-term OER-----184

Figure 6(a).1. (A) Schematic representation of the synthesis procedure, (B) PXRD spectra (C) N₂ adsorption/desorption isotherm, (D) Pore size estimated using NLDFT, (E) Raman spectra -----193

Figure 6(a).2. XPS analysis (A) XPS survey spectra, (B) deconvoluted N1s spectra, (C) Comparative N1s spectra, (D) Ni 2p XPS spectra, (E) Ru 3p XPS spectra of Ru₁/Ni-NPGC (F) Ru 3p spectra comparison with standard materials (RuO₂ and RuCl₃)---195

Figure 6(a).3. (A) AC-HAADF-STEM image of Ru₁/Ni-NPGC, (B) STEM mapping image of Ru₁/Ni-NPGC -----196

Figure 6(a).4. Structural Characterizations of electrocatalysts (A) Ru K-edge XANES spectra (B) k²-weight Fourier-transformed (FT) Ru K-edge EXAFS spectra of Ru₁/Ni-NPGC, RuO₂, Ru precursor salt (RuCl₃), and Ru foil, (C) First shell (Ru-N) fitting of FT-EXAFS spectra for Ru₁/Ni-NPGC, (H-I) Wavelet transform EXAFS spectra of Ru foil, RuCl₃, RuO₂ and Ru₁/Ni-NPGC, respectively-----197

Figure 6(a).5. Electrocatalytic OER activity in 1M KOH, (A) LSV polarization curves at different Ru loadings, (B) Corresponding overpotential at 10 mA/cm², (C) corresponding Mass activity at 1.53 V vs RHE, (D) iR-corrected OER polarization

curves (scan rate 1 mV/s), (E) corresponding Tafel slopes of various electrocatalyst, (F) TOF of Ru₁/Ni-NPGC and RuO₂, (G) Mass activity comparison for Ru atoms in Ru₁/Ni-NPGC and RuO₂ as a function of overpotential, (H) activation energy (E_a) of electrocatalysts estimated using Arrhenius equation, (I) O₂ amount (in mmol) generation and corresponding FE over a range of time-intervals on Ru₁/Ni-NPGC, (J) stability test of Ru₁/Ni-NPGC and RuO₂ during long-term OER operation, (K) comparison of the OER performances with previously reported electrocatalysts in alkaline medium. -----199

Figure 6(a).6. Electrocatalytic HER activity in 1M KOH, (A) *iR*-corrected HER polarization curves (scan rate 1 mV/s), (B) HER performances of the catalysts expressed as overpotentials required for cathodic 10, 30 and 100 mA/cm², (C) corresponding Tafel slopes of various electrocatalyst, (D) Mass activity comparison for Ru atoms in Ru₁/Ni-NPGC and Pt/C as a function of overpotential, (E) stability test of Ru₁/Ni-NPGC and Pt/C during long-term HER operation, (F) comparison of the HER performances with previously reported electrocatalysts in alkaline medium-----202

Figure 6(a).7. pH universal OER and overall water splitting by Ru₁/Ni-NPGC, (A) Schematic diagram of water splitting in a two-electrode configuration, *iR*-corrected HER polarization curves (at a sweep rate 1 mV s⁻¹) in (B) 0.1 M HClO₄ (pH 1), (C) neutral pH (pH 7.4), (D) 1M KOH (pH 14), and (E) chronoamperometric test of Ru₁/Ni-NPGC at overpotential of 195 mV and 280 mV.-----205

Figure 6(a).8. Post-catalytic study of electrocatalysts (A) PXRD spectra, (B) FESEM-EDS mapping image of Ru₁/Ni-NPGC, (C) Dissolved ion in electrolyte during long-term OER operation, (D) Ni 2p XPS, (E) Ru 3p XPS spectra-----206

Figure 6(a).9. In situ electrocatalytic OER study of Ru₁/Ni-NPGC and RuO₂ in O₂-saturated 1 M KOH. (A) In situ FTIR spectra (650–900 cm⁻¹) of Ru₁/Ni-NPGC obtained at different applied potentials and OCP, (B) in situ FTIR spectra (650–900 cm⁻¹) comparison for Ru₁/Ni-NPGC and RuO₂, (C) in situ FTIR spectra (1160–1350 cm⁻¹) of Ru₁/Ni-NPGC obtained at different applied potentials and OCP, (D) in situ FTIR spectra (1160–1350 cm⁻¹) comparison for Ru₁/Ni-NPGC and RuO₂, (E) in situ Raman

spectra of Ru₁/Ni-NPGC obtained at different applied potential and OCP, and (F) in situ Raman spectra comparison for Ru₁/Ni-NPGC and RuO₂-----207

Figure 6(b).1. (A) Schematic illustration of the synthetic procedure of Ru₁/CDGC, (B) PXRD pattern of CDGC and Ru₁/CDGC, (C) Raman spectra of as-synthesized compounds, (D) N₂ adsorption/desorption isotherm of Ru₁/CDGC (inset Figure illustrates the pore size distribution), (E) Low-magnification and (F) High magnification HRTEM images of Ru₁/CDGC, (G) STEM EDS-mapping images of Ru₁/CDGC-----215

Figure 6(b).2. Atomic and electronic structure of Ru₁/CDGC. (A) XPS survey spectra of COF-Hy and Ru₁/CDGC, (B) comparative deconvoluted N 1s spectra, (C) Ru 3p XPS spectra, (D) Ru K-edge XANES spectra of Ru₁/CDGC, Ru foil, RuCl₃ and RuO₂, (D) FT-EXAFS (k₂-weighted) spectra of Ru₁/CDGC and other standards, demonstrating the indication of Ru-N₄ and excluding the possibility of a Ru-O-Ru linkage interaction. (F) Model based fitting of Ru-K-edge EXAFS spectra of Ru₁/CDGC, (G-I) WT for the k₂-weighted EXAFS (WT-EXAFS) signal of Ru foil, RuCl₃, RuO₂ and Ru₁/CDGC sample-----217

Figure 6(b).3. OER activity of synthesized electrocatalyst in 1M KOH. (A) iR compensated LSV polarization curve, (B) overpotential required by different electrocatalyst to achieve current density of 10, 50 and 100 mA/cm², (C) Corresponding Tafel slope different electrocatalysts, (D) Mass activity of Ru₁/CDGC and RuO₂, (E) TOF values, (F) Activation energy of different electrocatalyst, (G) O₂ evolution (in mmol) and FE of Ru₁/CDGC, (H) Long-term electrocatalytic performance by chronoamperometry measurement-----220

Figure 6(b).4. Electrocatalytic HER performance of Ru₁/CDGC and other electrocatalysts. (A) LSV polarization curves at different Ru loadings on COF, (B) Corresponding overpotential at 10 mA/cm², (C) corresponding Mass activity at 1.55 V vs RHE. (D) iR compensated LSV polarization curve, (E) overpotential required by different electrocatalyst to achieve current density of 10, 50 and 100 mA/cm², (F) Corresponding Tafel slope different electrocatalysts, (G) Mass activity of Ru₁/CDGC and RuO₂, (H) TOF values, (I) Activation energy of different electrocatalyst, (J) O₂

evolution (in mmol) and FE of Ru₁/CDGC, (K) Long-term electrocatalytic performance by chronoamperometry measurement. -----223

Figure 6(b).5. pH universal overall water splitting (A) Chronoamperometry curves of Ru₁/CDGC in acidic pH (0.1 M HClO₄⁻), (B) Chronoamperometry curves of Ru₁/CDGC in simulated seawater pH (pH 7), (C) overall electrocatalytic performance by fabricated cell (Ru₁/CDGC|| Ru₁/CDGC) at different current density (inset is the LSV curve)-----225

Figure 6(b).6. Post-catalytic stability and Electrochemical performance of electrocatalysts (A) Ru 3p XPS spectra, (B) Ru dissolution at different time intervals estimated using ICP-MS analysis, (C) FESEM-EDS mapping analysis of Ru₁/CDGC after electrolysis, (D) EIS spectra, (E) non-faradaic scan for Ru₁/CDGC at different scan rate, (G) double layer capacitance measurement-----226

Figure 7.1. Schematic representation of the future work plan based on linker design, dual atom stabilization, and the development of a standalone electrolyzer by designing a bipolar membrane electrode assembly for electrolyzers-----235

LIST OF TABLES

Table 2.1: Comparison table of the ENRR activity with state-of-art ENRR electrocatalyst	67
Table 3.1: TGA analysis data of the synthesized MOF and catalyst system	93
Table 3.2: Specific surface areas and pore volumes of synthesized materials.	99
Table 3.3: Comparison of FA dehydrogenation data in presence of SF using various catalytic materials reported in literature with the current study	104
Table 3.4: ICP-MS data	110
Table 3.5: Optimization of temperature and base for the Suzuki–Miyaura cross-coupling reaction conditions.	111
Table 3.6: Catalytic efficiency for the Suzuki-Miyura coupling reaction between bromobenzene and phenylboronic acid using different catalysts.	112
Table 3.7: The Suzuki-Miyura coupling reaction of different aryl halides with phenyl boronic acids using AgPd@MIL-125-NH ₂ -PDA.	113
Table 3.8: Reaction condition optimization for the hydrogenation reaction	116
Table 3.9: Catalytic hydrogenation reaction with conversion (%) of aryl/alkyl aldehyde using AgPd@MIL-125-NH ₂ -PDA.	117
Table 4.1: Comparison of electrocatalytic OER performances of RuNC/Ni-M-SH with previously reported OER electrocatalysts in alkaline media.	145
Table 4.2: Solution and charge-transfer resistance from EIS analysis	147
Table 5.1: OER performance of RuNC/TFG-TETA and other reported OER electrocatalysts	179
Table 5.2: HER performance of RuNC/TFG-TETA and other reported HER electrocatalysts	181
Table 6(a).1: OER Comparison table of Ru ₁ /Ni-NPGC with Pt/C and other reported catalysts in 1.0 M KOH	199
Table 6(a). 2: HER Comparison table of Ru ₁ /Ni-NPGC with Pt/C and other reported catalysts in 1.0 M KOH	202
Table 6(b). 1: Comparison of OER activity of Ru ₁ /CDGC with other reported Ru-based OER electrocatalysts in alkaline media	220
Table 6(b). 2: Comparison of HER activities of Ru ₁ /CDGC with the previous reported literature in alkaline KOH	223
Table A.1: Fractional atomic coordinates for the unit cell of COF Aq calculated based on crystal structure analysis wizard of MAUD.	270
Table A.2: Optimized coordinated while N ₂ adsorb at Ti _b site	271
Table A.3: Optimized coordinated while N ₂ adsorb at oxygen vacant TiO ₂ -vac site	271
Table A.4: Optimized coordinated while N ₂ adsorb at Ot site of TiO ₂ -x site	272

Table A.5: Solvation effect on N₂ adsorption-----272

Table A.6: N₂ adsorption at (TiO₂)₁₂@COF-Aq-----273

Table A.7: TiO_{2-x} cluster adsorption at N site of COF-Aq-----273

Table A.8: (TiO₂)₄ cluster adsorption at O site of COF-Aq-----274

Table A.9: (TiO₂)₄ cluster adsorption at ring site of COF-Aq-----274

Table A.10: N₂ adsorption at the (TiO₂)₄ cluster without oxygen vacant on COF-Aq -----275

Table A.11: Fractional atomic coordinates for the unit cell of TFG-EDA -----276

Table A.12: Fractional atomic coordinates for the unit cell of TFG-DETA-----277

Table A.13: Fractional atomic coordinates for the unit cell of TFG-EDA -----279

LIST OF ABBREVIATIONS

1

1,3,5-benzene tricarboxylic acid (BTC)

1,3,5-triformylphloroglucinol (TFP)

2

2-(1-Naphthylamino) ethylamine
dihydrochloride (NEDH)

2,6-diaminoanthraquinone (DAAQ)

2-amino terephthalic acid (TPA-NH₂)

2,4,6-triformylphloroglucinol (TFG)

A

Aberration correction high-angle annular
dark-field scanning transmission electron
microscopy (AC-HAADF-STEM)

Atomic force microscopy (AFM)

Attenuated total reflectance (ATR)

B

Barrett-Joyner-Halenda (BJH)

Brunauer-Emmett-Teller (BET)

C

Chemical vapor deposition (CVD)

Covalent organic framework (COF)

Cross-polarization/magic-angle spinning
(CP-MAS)

Crystalline porous framework (CPF)

Cyclic voltammetry (CV)

D

Density functional theory (DFT)

Diethylenetriamine (DETA)

dimethylformamide (DMF),

Double-solvent approach (DSA)

E

Ethylene diamine (EDA)

Electrochemical active surface area (ECSA)

Electrochemical impedance spectroscopy
(EIS)

Electrochemical nitrogen reduction reaction
(ENRR)

Electron paramagnetic resonance (EPR)

Extended X-ray absorption fine structure
(EXAFS)

F

Faradaic efficiency (FE)

Field emission scanning electron microscope
(FE-SEM)

Formic acid (FA)

Fourier transform (FT)

H

Highest occupied molecular orbital
(HOMO)

High-resolution transmission electron
microscopy (HRTEM)

Hydrogen evolution reaction (HER)

I

Inductively coupled plasma mass
spectrometry (ICP-MS)

Interfacial polymerization (IP)

J

Johnson-Kendall-Roberts (JKR)

L

Linear sweep voltammogram (LSV)

Lowest unoccupied molecular orbital
(LUMO)

M

Metal organic framework (MOF)

Metal-organic polyhedra (MOP)

N

Nanocluster (NC)

Nanofiltration (NF)

Nanoparticle (NP)

Nitrogen temperature-programmed desorption (N_2 -TPD)

Non-local density functional theory (NLDFT)

Nuclear magnetic resonance (NMR)

O

Oxygen evolution reaction (OER)

Oxygen vacant Titanium dioxide (TiO_{2-x})

P

Perdew-Burke-Ernzerh (PBE)

Polydopamine (PDA)

Polyethylene terephthalate (PET)

Post-synthetic modification (PSM)

Powder X-ray diffraction (PXRD)

Projector augmented wave (PAW)

Proton coupled electron transfer (PCET)

R

Restrained electrostatic potential (RESP)

Reversible hydrogen electrode (RHE)

S

Scanning transmission electron microscopy (STEM)

Selected area electron diffraction (SAED)

Single atom catalyst (SAC)

Small-angle X-ray scattering (SAXS)

Sodium formate (SF)

Sodium hypochlorite (NaClO)

Strong metal-support interaction (SMSI)

T

Tetraisopropyl orthotitanate (TTIP)

Thermogravimetric analysis (TGA)

Titanium dioxide (TiO_2)

Transmission electron microscopy (TEM)

Triethylenetetramine (TETA)

Tris(hydroxymethyl)aminomethane (tris-HCl)

Turnover frequency (TOF)

U

Ultraviolet photoelectron spectroscopy (UPS)

Ultraviolet-visible (UV-Vis)

V

Vienna ab-Initio Simulation Package (VASP)

X

X-ray absorption near-edge structure (XANES)

X-ray absorption spectroscopy (XAS)

X-ray photoelectron spectroscopy (XPS)

LIST OF SYMBOLS

P_o	atmospheric pressure
R	universal gas constant
T	temperature
n	mole number
t	time
E_a	activation energy
A	Arrhenius constant
v	scan rate
V_{fb}	flat band potential
N_d	donor density
e	electron charge
ϵ	dielectric constant
ϵ_o	vacuum permittivity
V	applied potential
Q	total charge
F	Faraday constant
j	current density
C_{dl}	electrochemical double layer capacitance
η	overpotential