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

Biswajit Mishra

Department of Materials Science and Engineering

INDIAN INSTITUTE OF TECHNOLOGY DELHI

HAUZ KHAS, NEW DELHI-110016

October 2024

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

by

Biswajit Mishra

Department of Materials Science and Engineering

Submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

October 2024

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.

Prof. Bijay P. Tripathi

Associate Professor

Department of Materials Science & Engineering

Indian Institute of Technology Delhi

Hauz Khas, New Delhi - 110016

ACKNOWLEDGEMENTS

The realization of this extensive journey owes much to the collaborative efforts of many individuals. Without their support, guidance, and mentorship, this thesis and the preceding years would not have been achievable. First and foremost, I extend my heartfelt appreciation to my thesis advisor, Prof. Bijay P. Tripathi. I am deeply thankful to him for granting me the autonomy to pursue independent research and for nurturing the development of my scientific skills. His enthusiasm for interdisciplinary research fields has consistently motivated me. The advice from Prof. Tripathi, *"Don't limit yourself and always take challenging tasks*," remains a constant source of inspiration, driving me to maintain a steadfast work ethic. I am forever indebted to Prof. Tripathi for his trust and for providing me with the freedom and responsibilities that have significantly contributed to my professional development.

I would like to express my sincere gratitude to the SRC members, Prof. Bhabani. K. Satapathy, Prof. Leena Nebhani, and Prof. Bipin Kumar, for their invaluable suggestions, encouragement, and constructive criticisms throughout. Special thanks to Prof. Anup K. Ghosh, Prof. Josemon Jacob, and all the faculty members of DMSE for fostering a supportive and inspiring environment within the department. Expressing my sincerest gratitude to Prof. Haider and Prof. Dibyajyoti Ghosh for their assistance during our collaborative work.

I am grateful to all the staff members of the DMSE department, including Mr. Ashish Sharma, Mr. Gajraj Singh, Mr. E. Islam, Mr. Jitendra Kumar, Mr. Ashish Sharma, Mr. Gyanendra, Mr. Brijesh Kumar, Mr. Subhash Chand, Mr. Amit Kumar, Mr. Sudhir Pandey, Mr. Ramesh, Mr. Narendra, Mrs. Shalini, and Mrs. Jyoti, who have provided tremendous assistance in characterization, documentation, and purchasing activities. I am indebted to all the staff members of the CRF and NRF, particularly Mrs. Astha Sharma, Mr. Solanki, Mr. Mahesh, and Mr. Rajesh, for their unwavering support in characterization efforts.

I will forever be thankful to all the members of the Functional Materials & Membrane (FUNMEM) group, including Dr. Kanupriya Nayak, Dr. Anubhav Kumar, Dr. Supriya, Sandeep, Arun, Sushant, Sandip, Avoy, Divya, Sai, Swayam, Ankit, Sourya, Pooja, Naman, Vishal, Jayanta, Fizzah, Raghav, Mahesh, Nagesh, Lokesh, Surya, Nikita, and Mukul. I am particularly grateful to Dr. Anubhav Kumar for his invaluable support and assistance in setting up my initial organic reactions and engaging in collaborative discussions. Also, I am thankful to Supriya and Sandeep for their constant motivation and encouragement. I consider myself fortunate to have a lab member like Swayam. Our numerous inspiring scientific discussions, particularly on fundamental science (especially inorganic chemistry) and electrochemistry, along with our constructive debates, have been invaluable. As Prof. Einstein famously said, *"The important thing is not to stop questioning. Curiosity has its own reason for existence*." I will always be

grateful to Swayam for his inclination towards engaging in argumentative discussions rather than simply accepting what I say. This approach has greatly aided my understanding of the deeper mechanisms involved.

I will always be grateful to many individuals I have met on this journey. I particularly want to express my gratitude to Dr. Saroj Samantaray for his unwavering support and constant motivation. I vividly recall his words, "*Don't worry, Lord Jagannath has brought you this far; believe that He will always assist you*," which have served as a constant source of encouragement. I am profoundly grateful to Aiswarya and Lukkumanul for their unwavering support and motivation during my academic journey. Their belief in my abilities has been a constant source of inspiration, reminding me that every step forward is a step closer to success. As Oprah Winfrey once said, "Surround yourself with only people who are going to lift you higher." Lukkumanul and Aiswarya have uplifted me with their positivity and encouragement, making the challenging moments more manageable and the successful ones even sweeter. Additionally, I am grateful to my seniors and colleagues at DMSE, including Nidhi, Meenakshi, Vikram, Amit, Harshal, and Mayank. I am also thankful to Ussama for his support during our collaborative work. I may have inadvertently overlooked some individuals who have provided valuable assistance, but I am forever grateful to all those who have played a role in my journey.

I greatly acknowledge the generous financial support from the Ministry of Education, India, for my doctoral studies. I extend profound thanks to Prof. Bijay P. Tripathi for generous financial support after the completion of my institute fellowship.

Saving the best for last, I want to express my heartfelt gratitude to my parents (Mr. Prasanna Mishra and Mrs. Sukanti Mishra) and sisters (Sonu, Anshu, Kutty). Words fall short in capturing the depth of what you have done for me. Please accept my sincerest thanks and I am forever indebted for your unwavering support. This work stands as a testament to your dedication and sacrifice. Last but not least, I am forever thankful to God.

Biswajit

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 (TiO_{2-x}@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. TiO_{2-x}@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/cm^2, 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/cm^2. 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/cm^2.

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-N_4 configuration electrocatalyst (Ru_1/Ni-NPGC) displayed exceptional performance, needing only ~195 mV (for 10 mA/cm^2) and exhibiting a lower Tafel slope of ~52 mV/dec in alkaline conditions. Ru_1/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, Ru_1/CDGC showed impressive oxygen evolution reaction activity, needing only 173 and 211 mV for 10 and 50 mA/cm^2, surpassing commercial RuO_2. Moreover, Ru_1/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 पुन: प्रयोज्यता के कारण विषम उत्प्रेरण एक पसंदीदा प्रणाली के रूप में उभरा है। इसके बावजूद, उत्पाद चयनात्मकता और उच्च धातु सामग्री जैसी चुनौतियों ने नैनोकैटलिसिस और एकल परमाणु कटैलिसीस 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, नैनोक्लस्टर्स, 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 इलेक्ट्रोकैटलिटिक नाइट्रोजन कटौती प्रतिक्रिया के लिए ऑक्सीजन-रिक्त TiO_{2-x} NP (TiO_{2-x}@COF-Aq) को स्थिर करने के लिए व्यवस्थित रूप से एक एंथ्राक्विनोन-आधारित COF डिज़ाइन 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। TiO_{2-x}@COF-Aq ने उत्कृष्ट ENRR प्रदर्शन प्रदर्शित किया, जिसके परिणामस्वरूप पारंपरिक ENRR इलेक्ट्रोकैटलिस्ट 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 लिगैंड 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 नैनोक्लस्टर्स (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 इलेक्ट्रोकैटेलिस्ट (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-लिंक्ड 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 इलेक्ट्रोकैटेलिटिक 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 इलेक्ट्रोकैटेलिटिक कटैलिसीस 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 इलेक्ट्रोकैटेलिस्ट (Ru_1/Ni-NPGC) ने असाधारण प्रदर्शन प्रदर्शित किया, जिसे केवल ~195 mV (10 mA/cm^2 के लिए) की आवश्यकता थी और क्षारीय स्थितियों में ~52 mV/dec का निचला टैफेल ढलान प्रदर्शित किया। Ru_1/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-लिंक्ड इमाइन-आधारित COF को संश्लेषित किया गया था। ~1.9 wt% Ru लोडिंग के साथ, Ru_1/CDGC ने प्रभावशाली OER गतिविधि दिखाई, 10 और 50 mA/cm^2 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। थीसिस 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

LIST OF FIGURES

LIST OF TABLES

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-NH_2)

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
ν	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