Dedicated to……

My beloved parents

Declaration of Academic Integrity

"I declare that this written submission represents my ideas in my own words and where other's ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be cause for disciplinary action as per the rules and regulations of the Institute."

Suman Lahkar

Date: 21-11-2023 **(Suman Lahkar)**

Place: Tezpur University Regn No. TZ156024 of 2015

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CERTIFICATE FROM SUPERVISOR

This is to certify that the thesis entitled "***Development of Electrocatalysts for Hydrogen Evolution Reaction in Acidic Medium***" submitted to the School of Sciences, Tezpur University in partial fulfillment for the award of the degree of Doctor of Philosophy in Chemical Sciences is a record of research work carried out by **Ms. Suman Lahkar** under my supervision and guidance. She has been duly registered (Registration No. TZ156024 of 2015), and the thesis presented is worthy of being considered for Ph.D. Degree.

All help received by her from various sources have been duly acknowledged. No part of this thesis has been submitted elsewhere for award of any other degree.

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Place: Tezpur University

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Co-Supervisor

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Tezpur University ***Suman Lahkar***

ABBREVIATIONS AND SYMBOLS USED

Ag/AgCl	silver/silver chloride
As	arsenic
A	area
APS	ammonium persulfate
A g^{-1}	Ampere per gram
B	boron
BET	Brunauer-Emmett-Teller
BJH	Barrett−Joyner−Halenda
CO_2	Carbon dioxide
CO	carbon monoxide
CB	conduction band
CoS	cobalt sulphide
CoS_2	cobalt disulphide
Co	cobalt
Cu	copper
Cd	cadmium
CoP	cobalt phosphide
C	carbon
CV	cyclic voltammetry
C	capacitance
CA	chronoamperometry
C_1	resistance between two parallel circuits composed of resistors and constant phase elements
CPE	constant phase elements
C_{dl}	electrochemical double-layer capacitance (C_{dl})
C_{sc}	capacitance of the space charge layer
COOH	carboxylic acid
CH_3OH	methanol
$C_6H_5NH_2$	aniline
CH_3COOH	acetic acid
D	dimensional
DFT	density functional theory

eV	electron volt
e^-	electron
ECSA	electrochemical surface area
EDLC	electric double-layer capacitor
EG	expanded graphite
EDX	elemental dispersive X-ray spectrometry
EIS	electrochemical impedance spectroscopy
$\Delta E(H^*)$	energy change of hydrogen adsorption
E_{fb}	flat band potential
FeS	iron sulphide
F	Faraday constant
FTIR	Fourier transform infrared spectroscopy
FESEM	field emission scanning electron microscopy
$Fe(NO_3)_3.9H_2O$	iron (III) nitrate nonahydrate
GCE	glassy carbon electrode
ΔG_{Hads}	free energy of adsorbed hydrogen
GCD	galvanostatic charge-discharge
HER	hydrogen evolution reaction
H^+	proton
H_2O	water
H_2	hydrogen
h	hour
H_{ads}	adsorbed hydrogen
H_2SO_4	sulphuric acid
HDS	hydrodesulphurization
Hz	hertz
H_2PtCl_6	chloroplatinic acid
H_2O_2	hydrogen peroxide
HCHO	formaldehyde
IEA	International Energy Agency
IRENA	International Renewable Energy Agency
i_0	exchange current density
Ir	iridium
i	current

j	current density
J	current density
J_0	exchange current density
J-V plot	current-voltage plot
KOH	potassium hydroxide
kHz	kilohertz
KSCN	potassium thiocyanate
$KMnO_4$	potassium permanganate
kW kg^{-1}	kilowatt per kilogram
LSV	linear sweep voltammetry
Li	lithium
Mt	megatonne
M	active metal site
MoS_2	molybdenum disulphide
Mo	molybdenum
$MoSe_2$	molybdenum selenide
mA cm^{-2}	milliampere per centimeter square
mV	millivolt
Mo_2C	molybdenum carbide
MOF	metal−organic framework
MoB_2	molybdenum boride
MWCNT	multi-walled carbon nanotube
Mo_2N	molybdenum nitride
mV dec^{-1}	millivolt per decade
MnO_2	manganese dioxide
mHz	millihertz
mV sec^{-1}	millivolt per second
M-S	Mott-Schottky
mM	millimole
M	molar
NADPH	nicotinamide adenine dinucleotide phosphate hydrogen
nm	nanometer
NHE	normal hydrogen electrode
NiS_2	nickel disulphide

Ni	nickel
Ni_5P_4	penta nickel phosphide
Ni_3S_2	tri nickel disulphide
NiP	nickel phosphide
N	nitrogen
n	number of electrons transferred
Na_2SO_4	sodium sulphate
N_D	charge carrier density
NaDDBS	sodium dodecylbenzenesulfonate
$NaBH_4$	sodium borohydride
NaOH	sodium hydroxide
$NaNO_3$	sodium nitrate
Na_3PO_4	sodium hypophosphate
Na_2CO_3	sodium carbonate
$Na_3PO_4.12H_2O$	sodium phosphate dodecahydrate
$(NH_4)_2S_2O_8$	ammonium peroxodisulfate
OER	oxygen evolution reaction
O_2	oxygen
P	phosphorous
Pt	platinum
P	power density
PANI	polyaniline
PPY	polypyrrole
PDOS	Projected density of states
q	charge
Q	charge
RDS	rate-determining step
Ru	ruthenium
RGO	reduced graphene oxide
R	resistance
RHE	reversible hydrogen electrode
R_{ct}	charge-transfer resistance
R_2	charge transfer resistance
R_1	solution resistance arising from the electrolyte

R_f	roughness factor
rpm	rotation per minute
S	sulphur
SWCNT	single-walled carbon nanotube
SEM	scanning electron microscopy
ΔS	entropy change of adsorption H
SCE	standard calomel electrode
SCN^-	thiocyanate ion
Se	selenium
sec	second
TOF	turn over frequency
TMSes	transition metal selenides
TMSs	transition metal selenides
Ti	titanium
TiO_2	titanium dioxide
Ti_2O_3	titanium (III) dioxide
TMD	transition metal dichalcogenide
T	temperature in kelvin
TOF	Turn Over Frequency
TEM	transmission electron microscopy
TMPs	transition metal phosphides
TOP	trioctylphosphine
TiOOH	titanium (oxy)hydroxides
TTIP	titanium tetraisopropoxide
$TEABF_4$	tetraethyl ammonium tetrafluoroborate
UV	ultraviolet
V	volt
VB	valence band
V_{hexane}	volume of hexane
$V_{ethanol}$	volume of ethanol
W	tungsten
W h kg^{-1}	watt hour per kg
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

Zn	zinc
ΔZPE	zero-point energy change
γ	gamma
η	overpotential
α	symmetry factor
ε_0	permittivity of free space
ε_r	relative permittivity of the dielectric medium
λ	wavelength
θ	angle between the individual atomic planes
α_c	charge transfer coefficient for the cathodic potential
Ω	ohm
v	scanning rate
μF	microfarad
^{0}C	degree Celsius

LIST OF FIGURES

EXPERIMENTAL SCHEME

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