

**Design and Development of Nanostructured Robust Support
Efficient Electrochemical Energy Conversion**

BY

Munzir H. M. Suliman

A Dissertation Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMISTRY

April 2020

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

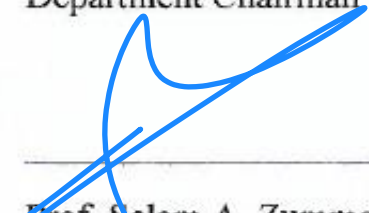
DEANSHIP OF GRADUATE STUDIES

This thesis, written by Munzir H. M. Suliman under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMISTRY**.



Dr. Jameel Al-thagfi

Department Chairman


Prof. Salam A. Zummo
Dean of Graduate Studies

23-4-2020

Date



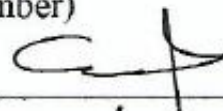
Prof. Mohammad Nahid Siddiqui
(Advisor)



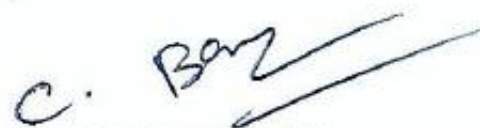
Dr. Mohammed Qamar
(Co-Advisor)



Prof. Abdulrahman Al-Arfaj
(Member)



Dr. Abdulaziz Al-Saadi
(Member)



Dr. Basheer Chanbasha
(Member)

© Munzir H. M. Suliman

2020

Dedication

This thesis is dedicated to my parents, brother and sister for their continuous prayer and support...

ACKNOWLEDGMENTS

I would like to thank my great creator almighty Allah for giving me life, health, strength, patience, power and science to finish my study. Also, I would like to express my deepest appreciations to my thesis Advisor Prof. Mohammad Nahid Siddiqui for guiding me throughout the doctorate program, encouragement, significant comments, and continuous help and support during the study. I want to show my deep gratitude to my Co-adviser Dr. Mohammad Qamar, who supported me throughout the PhD project with patience. His insightful comments and expertise assisted me in cultivating my scientific research ability. I wish to extend my gratitude to thesis committee members Dr. Abdulaziz A. Al-Saadi, Prof. Abdulrahman A. Al-Arfaj and Dr. Basheer Chanbasha for their valuable advice, encouragement and significant comments which supported me to complete this research.

It's my pleasure to acknowledge the Ministry of Education, Saudi Arabia, through the King Fahd University of Petroleum and Minerals for giving me this opportunity to pursue my Ph.D. degree. My deep thank is extended to the chemistry department chairman Dr. Khalid Alhooshani and Dr. Jameel Althagafi, Dr. Bassam El-Ali (Graduate coordinator) and all faculty members and staff. I take this opportunity to express my sincere gratitude to the center of excellence in nanotechnology (CENT) for their help and support.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	IX
LIST OF FIGURES	X
LIST OF ABBREVIATIONS	XIII
ABSTRACT	XV
ملخص الرسالة	XVI
CHAPTER 1	1
INTRODUCTION.....	1
CHAPTER 2	4
LITERATURE REVIEW	4
2.2 Statement of the problem.....	9
2.3. Research Objectives	10
2.4. Research Methodology	11
CHAPTER 3	16
FACILE SYNTHESIS OF ULTRATHIN INTERCONNECTED CARBON NANOSHEETS AS A ROBUST SUPPORT FOR SMALL AND UNIFORMLY DISPERSED IRON PHOSPHIDE FOR THE HYDROGEN EVOLUTION REACTION	16

3.1. Introduction	16
3.2 Experimental	18
3.2.1. Preparation of interconnected ultrathin carbon nanosheets (CN)	18
3.2.2. Preparation of iron phosphide/carbon nanosheets (FeP/CN)	19
3.2.3. Characterization	19
3.2.4. Electrochemical characterization	20
3.2.5. Calculation of turnover frequency (TOF)	21
3.3. Results and discussion	21
3.3.1. Structural characterization of FeP/CN	21
3.3.2. Microstructural characterization of FeP/CN	23
3.3.3. Evaluation of electrocatalytic performance towards hydrogen evolution reactions (HER)	25
 CHAPTER 4	 38
 THE IMPACT OF MICROSTRUCTURAL FEATURES OF CARBON SUPPORT ON THE ELECTROCATALYTIC HYDROGEN EVOLUTION REACTION 38	
4.1. Introduction	38
4.2. Experimental	40
4.2.1. Chemicals.	40
4.2.2. Preparation of Interconnected Ultrathin Carbon Nanosheets (CN).	40
4.2.3. Preparation of Iron Phosphide/Carbon.	41
4.2.4. Characterization.	41
4.2.5. Electrochemical Characterization.	41
4.3. RESULTS AND DISCUSSION	42
4.3.1. Structural Characterization.	42
4.3.2. Electrocatalytic Hydrogen Evolution Reaction.	46
4.3.3. Specific Surface Area and Electrochemically Active Surface area.	47
4.3.4. Electrical Conductivity and Charge Transport.....	49
4.3.5. Turnover Frequency.....	52
4.3.6. Tafel Slopes and Reaction Kinetics.	53
4.4. Conclusions	54
 CHAPTER 5	 56
 THE INFLUENCE OF MESOPOROUS STRUCTURE OF THE CARBON SUPPORT IN THE DISPERSION AND THE GROWTH OF ELECTROCATALYTIC ACTIVE SITES FOR THE HYDROGEN EVOLUTION REACTION 56	
5.1. Introduction	56

5.2. Experimental	58
5.2.1. Preparation of Highly mesoporous carbons (HMC)	58
5.2.2. Preparation of Iron Phosphide/ Highly mesoporous carbon	58
5.2.3. Characterization	59
5.2.4. Electrochemical characterization	59
5.3. Results and discussion	60
5.3.1. Structural characterization of FeP/HMCs	61
5.4. Conclusion.....	72
 CHAPTER 6	 74
 FeP/MoS₂ ENRICHED WITH DENSE CATALYTIC SITES AND HIGH ELECTRICAL CONDUCTIVITY FOR THE HYDROGEN EVOLUTION REACTION	 74
6.1. Introduction.....	74
6.2. Experimental	77
6.2.1. Preparation of two-dimensional ultrathin nanosheets of molybdenum disulfide (2D MoS ₂)	77
6.2.2. Preparation of iron monophosphide and 2D MoS ₂ (FeP/MoS ₂).....	77
6.2.3. Characterization	78
6.2.4. Electrochemical characterization	78
6.3. Results and discussion	79
6.4. CONCLUSIONS	94
 REFERENCES.....	 95
 VITAE.....	 107

LIST OF TABLES

Table 1 The HER activity comparison between FeP/CN and carbon-based electrocatalysts and porous electrocatalysts.....	27
Table 2 Textural characteristics HMCs obtained via nitrogen adsorption at 77 K.....	61

LIST OF FIGURES

Figure 1: Figure 1. Preparation, characterization and activity results of the CoMoP@C catalyst 26	6
Figure 2: Activity comparison of different phases of CoP and effect of nitrogen doping.....	9
Figure 3: XRD patterns and XPS signatures of FeP/CN.	22
Figure 4: FESEM (a and b), TEM of pure carbon nanosheets (c), TEM/HR-TEM (d-f) of FeP/CN.....	24
Figure 5: Comparative polarization curves in acidic (a) and basic media (b). Current-time curve (c) and polarization curves (d) obtained before and after potentiostatic experiment.	26
Figure 6: Cyclic voltammograms recorded at different scan rates between 5 and 100 mVs ⁻¹ corresponding plots of the current density at 0.248 VRHE vs. scan rate; Fig. a and b – FeP nanoparticles, c and d – FeP/CN. Nyquist plots of FeP nanoparticles (e) and FeP/CN (f) confirming the ECSA values estimated by CVs. All these measurements were performed in 0.5 M H ₂ SO ₄ aqueous electrolyte.	30
Figure 7: Potential-dependent Nyquist plot of FeP (a) and FeP/CN (b), Nyquist (c) and Bode (d) plots of FeP/CN at 150 mV showing the presence of two time constant in 0.5 M H ₂ SO ₄ . Nyquist plots of FeP/CN in the presence and absence of 2×10 ⁻² M KCN in 1.0 M KOH solution (e), and Nyquist plot of FeP/CN at 150 mV fitted with 1CPE model (f). All the measurements were performed at cathodic (negative) overpotentials.	32
Figure 8: Tafel slopes of FeP (a) and FeP/CN (b) estimated from EIS, Tafel slopes of Pt/C (c), FeP (d) and FeP/CN (e) estimated from polarization curves and galvanostatic measurement.	35
Figure 9: . Cyclic voltammograms recorded between -0.2 and 0.6 VRHE (a) and their corresponding TOF profiles vs. overpotential (b). Experiments were performed in a phosphate buffer solution with pH 7.....	36
Figure 10: Powder XRD of (a) pristine carbon supports and (b) FeP-modified carbon supports.	43
Figure 11: XPS signatures of FeP/CNT.	44
Figure 12: TEM and HR-TEM of FeP/XC (a-c), FeP/CNT (d-f) and FeP/CN (g-i).	46
Figure 13: Comparative polarization curves of FeP/XC, FeP/CNT and FeP/CN.....	46
Figure 14: LSV of FeP/XC, FeP/CNT and FeP/CN in 0.5M H ₂ SO ₄	47
Figure 15: Pristine carbon electrodes: CVs (a-c) and their respective plots of the current density (d-f) at 0.248 V _{RHE} vs scan rate. The linear slopes are equivalent to twice of the electrochemical double layer capacitance (C _{dl}).	48
Figure 16: FeP-modified carbon electrodes: CVs (a-c) and their respective plots of the current density (d-f) at 0.248 V _{RHE} vs scan rate. The linear slopes are equivalent to twice of the electrochemical double layer capacitance (C _{dl}).	49

Figure 17: Potential-dependent evolution in Nyquist plots of pristine and FeP-modified carbon electrodes.....	50
Figure 18: Cyclic voltammograms (a) and corresponding TOF profiles vs overpotential (b).	53
Figure 19: N ₂ adsorption desorption isotherms (a) and the BJH pore size distribution. ..	61
Figure 20: XRD and XPS of FeP/C4-11.....	62
Figure 21: TEM image of pristine carbon: C4-11 (a), C20-11(b) and C20-21 (c).	63
Figure 22: TEM and HR-TEM of FeP/C4-11 (a-c), FeP/C20-11 (d-f) & FeP/C20-21 (g-i)	64
Figure 23: Comparative polarization curve of the electrocatalysts FeP/C4-11, FeP/C20-11, FeP/C20-21 & FeP/XC (a) and Tafel plots for the electrocatalysts (b).	66
Figure 24: Pristine HMCs CVs (a-c), and their respective slopes at scan rates range between 5 to 100 mV s ⁻¹ (d-f).	66
Figure 25: FeP modified HMCs CVs (a-c), and their respective slopes at potential range between 5 to 100 mV s ⁻¹ (d-f).....	68
Figure 26: Comparative Nyquist plots of pristine HMCs at 0 mV (a) and 450 mV (b) in 0.5M H ₂ SO ₄	69
Figure 27: Comparative Nyquist plots of FeP modified HMCs at 0 mV (a) and 90 mV (b) in 0.5 M H ₂ SO ₄	69
Figure 28: CVs recorded between -0.2 and 0.6 VRHE (a) and their corresponding TOF vs. η (b). Measurements were carried out in a phosphate buffer solution (pH 7).	70
Figure 29: XRD of FeP, MoS ₂ and FeP/MoS ₂ , and XPS signatures of FeP/MoS ₂	80
Figure 30: FESEM, TEM and HR-TEM of MoS ₂ nanosheets (a, b and c) and FeP/MoS ₂ nanosheets (d, e and f).	82
Figure 31: Comparative polarization curves of MoS ₂ , FeP, FeP/MoS ₂ and Pt/C (a) and the current-time profile in the presence of FeP/MoS ₂ for 45 h. All the measurements were performed in 0.5 M H ₂ SO ₄	83
Figure 32: Cyclic voltammograms, recorded at different scan rates between 5 and 100 mV s ⁻¹ , and their corresponding plots of the current density at 0.248 VRHE vs. scan rate.....	85
Figure 33: Bode plot of FeP/MoS ₂ obtained at η = 150 mV, comparative Nyquist plots recorded at η = 0 mV (b) and η = 130 mV (c), Tafel slopes of FeP (d), MoS ₂ (e) and FeP/MoS ₂ (f) determined by EIS. All the measurements were performed in 0.5 M H ₂ SO ₄ at cathodic (n.....	87
Figure 34: a) CVs MoS ₂ , FeP and FeP/MoS ₂ in pH 7.0 b) the TOF MoS ₂ , FeP and FeP/MoS ₂	90
Figure 35: Comparative polarization curves (a), CVs with their corresponding plots of the current density vs. scan rate (b and c), Nyquist plot (d), CVs (e) and corresponding TOF vs. η (f) of FeP/XC and FeP/MoS ₂	92

Figure 36: Top view of (a) FeP (011) facet and (b) FeP/MoS₂ composite model. The possible reactive sites are encircled and labeled in red. (c) Free energy profiles of MoS₂, FeP (011), and FeP/MoS₂ on various reaction sites..... 94

LIST OF ABBREVIATIONS

FESEM	: Field emission scanning electron microscope
HRTEM	: High resolution transmission electron microscope
LSV	: Linear Sweep Voltammetry
HER	: Hydrogen Evolution Reaction
OER	: Oxygen Evolution Reaction
RHE	: Reversible Hydrogen Electrode
CN	: Carbon nanosheets
XRD	: X – ray Diffractometer
PEC	: Photoelectrochemical
Min	: Minute
s	: Second
mA	: Milliampere
nm	: Nanometer
mL	Milliliter
eV	: Electron Volt
°C	: Degree Celsius
V	: Volt
θ	: Theta
R_s	: Solution resistance
C_{dl}	: Electrical double layer capacitance
J	: Geometric current density
Deg.	: Degree

GR & RGO	: Graphene and reduced graphene oxide
η	: Overpotential
NPCNT:	: nitrogen & phosphorous-doped carbon nanotubes
NC	: Nitrogen doped Carbon
NP	: Nanoparticles
NA	: Nanoarray
NW	: Nanowire
NPs	: Nanoparticles
CC	: Carbon cloth
CF	: Carbon fiber
ND/FG	: Nanodot/ fluffy graphene sheet
NTs	: Nanotubes

ABSTRACT

Full Name : [Munzir H. M. Suliman]

Thesis Title : [Design and Development of Nanostructured Robust Support Efficient Electrochemical Energy Conversion]

Major Field : [Chemistry]

Date of Degree : [April, 2020]

In supported catalytic systems, solid supports play crucial role in determining the catalytic activity, selectivity and overall performance of the catalysts. We, therefore, aim to develop two types of solid supports – active and passive solid supports, for electrochemical energy conversion. While active solid supports would participate in catalytic process, passive solid supports would be spectator. Nanosheets of transition metal sulfide was prepared and explored as potential active supports, while carbon-based materials endowed with unique microstructural attributes, such as high surface area, high conductivity, two-dimensional orientation was synthesized and used as passive supports. Metal chalcogenides, such as phosphides, was used as active sites. As-synthesized catalytic compositions was characterized using standard techniques, such as Powder X-ray diffraction (XRD), Transmission and High-Resolution Transmission Electron Microscopy (TEM/HRTEM), Field Emission Scanning electron microscope (SEM), BET surface analyzer, X-ray photoelectron spectroscopy (XPS), and so forth. The efficacy of electrodes comprising as-prepared catalytic compositions was demonstrated in electrochemical energy conversion application by studying hydrogen evolution reaction (HER) from water splitting. The HER reactions was investigated both in acidic and basic electrolytes. The HER performance of all electrocatalysts was compared with that of benchmark commercial Pt/C. A detailed study elucidating electrode kinetics was performed, and the performance of electrodes was correlated to specific surface area, electrochemically active surface area (EASA), electrical conductivity, interfacial charge transfer resistance and turn over frequency (TOF).

ملخص الرسالة

الاسم الكامل: منذر حمد النيل محمد سليمان

عنوان الرسالة: تصميم وتطوير مادة داعمة نانوية قوية فعالة لتحويل الطاقة الكهروكيميائية بكفاءة عالية

التخصص: الكيمياء

تاريخ الدرجة العلمية: أبريل 2020

في الأنظمة الحفزية المدعومة تقوم المادة الداعمة الصلبة بدور مهم جدا لتحديد النشاط الحفزي، الانتقائية والنشاط الكلي للحفاز. لذلك تم استهداف تطوير نوعين من المواد الداعمة الصلبة، نشطة وغير نشطة لتحويل الطاقة الكهروكيميائية. في حين المادة الداعمة النشطة تشارك في العملية الحفزية، المادة الداعمة غير النشطة تكون ايضا مميزة. كبريتيد معدن انتقالي على الهيئة النانو ورقية تم تحضيرها واختبارها كمادة داعمة نشطة، بينما تم تحضير مادة كربونية تمتلك خواص تركيبية دقيقة فريدة ، كمساحة سطح عالية، توصيلية عالية و بنية ثنائية الابعاد و اختبارها كمادة داعمة غير نشطة. تم استخدام جلايكونيدات المعدن كالفوسفيدات كمواقع حفزية نشطة. تم تشخيص التركيب الذي تم تحضيره باستخدام الطرق التشخيصية القياسية مثل حيود الاشعة السينية للبدة، مجهر العبور و مجهر العبور الالكتروني ذو الجودة الفائقة ، المجهر الماسح الالكتروني، المطيافية السينية للالكترون الضوئي، وتقنيات اخرى. تم توضيح كفاءة القطب الذي تم تحضيره لتحويل الطاقة الكهروكيميائية عن طريق تفاعل تحرر الهيدروجين عن طريق انقسام الماء. تم اختبار التفاعل في الوسطيين الحمضي و القاعدي. تمت مقارنة فعالية الحفازات المحضرة مع الحفاز التجاري المرجعي Pt/C. تم عمل دراسة تفصيلية لحركية القطب، وتم ربط فعالية مع مساحة السطح، مساحة السطح النشطة كهريا، التوصيلية الكهربائية، مقاومة انتقال الشحنة السطحية و تردد الدوران

CHAPTER 1

INTRODUCTION

In recent decades, there has been a renewed interest in harnessing solar energy to produce chemical energy, which is perceived as a viable strategy to combat the energy as well as environmental problems. Due to the weather-driven reliance of sunlight, developing processes to store the produced energy in the form of electrical and/or chemical energy is of great significance. Storage of solar energy in the form of chemical energy, particularly H_2 , has received significant attention. Molecular hydrogen (H_2) is perceived as a sustainable and environmentally friendly energy carrier, which has potential to address the increasing global energy demand.

Among various technologies, photoelectrochemical technology utilizing abundant & ultimate source of renewable energy (sunlight) for conversion of solar to chemical energy has received significant attention. Coupling of light absorber, as a photoanode, and electrocatalysts, as a cathode, for oxygen and hydrogen evolution mimics the photosynthesis process. Large-scale production of H_2 via photoelectrochemical or electrochemical processes has great prospect due to its low energy consumption, high purity of H_2 and environmentally benign features. Currently, Pt is used as the electrocatalyst. In addition to the cost, Pt-based electrocatalysts suffer from performance loss during the course of operation as a result of catalyst degradation and corrosion of

carbon support. Development of electrocatalysts alternative to Pt remains at the fore front of the technology development. Developed cathodes could be employed in photoelectrochemical and/or electrochemical water electrolysis process. Consequently, considerable amount of research is underway to develop cathodes consisting of transition metal-based electrocatalysts for hydrogen evolution reaction. A variety of materials consisting of non-precious metals, such as metal carbides, metal sulfides and selenides, metal nitrides, metal oxides, metal borides, metal phosphides and so forth, have been explored hoping to reduce the overpotential of hydrogen evolution reaction (HER). Although noticeable reduction in overpotential has been achieved, there exists tremendous opportunity to further push this to lower threshold (closer to Pt).⁴ fundamentally, the overpotential can be substantially lowered, in first hand, by choosing appropriate composition of electrocatalysts. Recently, transition metal phosphides are reported to show high and stable HER with lower overpotential, and endeavored as potential alternative to noble metal-based electrocatalysts. In spite of the fact that alloying could modify distribution of electronic potential and thus revamp the electrocatalytic performance, studies focusing on this facet are few.

We, therefore, aim to develop cost-effective, active and stable cathode materials for large scale H₂ generation from water. Transition metal phosphides will be explored as an alternative to Pt for hydrogen evolution reaction (HER) from water. Specifically, owing to the abundance and HER-active attributes, tungsten phosphide (WP) is chosen as a model transition metal phosphide for the proposed study. A methodical compositional tuning of WP will be carried out by incorporating other transition metals into the lattice. Effect of different molar ratio of nickel (Ni) and cobalt (Co) would be investigated – a composition-

performance relationship will be established. This will be achieved by preparing nickel tungsten phosphide (Ni_xW_yP) and cobalt tungsten phosphide (Co_xW_yP) supported on carbon-based materials. Pristine or nitrogen-doped CNTs (N-doped CNTs) will be used as a carbon support. Samples will be characterized and evaluated for their propensity for HER. Performance and stability of the electrodes will be scanned in acidic, neutral, basic and brine water. A detailed evaluation of the electrode kinetics will be undertaken – electrochemical active surface area, Tafel slope, and charge transfer kinetics will be determined. In addition, Faradic efficiency of representative electrocatalysts will be estimated by quantifying the produced amount of H₂. Since electrochemical polarization may induce reduction, amorphization, and modification in hydrogen adsorption during HER reaction, attempt will be made to investigate any surface reconstruction of electrodes.

The breadth of the proposed study extends not only to photoelectrochemical or electrochemical technologies, but also to several processes of industrial relevance as these materials find applications in metallurgy, hydrodesulfurization, hydroprocessing, hydrodenitrogenation, pesticides, lithium ion batteries, and so forth.

[CHAPTER 2

LITERATURE REVIEW

Recently, development of cost-effective transition metal-based electrocatalysts has drawn considerable attention due to their excellent activity towards hydrogen evolution from water. 1-2 As a result, a wide variety of electrocatalysts, nickel, cobalt, molybdenum, tungsten, copper and iron are explored as a potential alternative to noble metal-based electrocatalysts. Metal phosphides are particularly marked owing to its high activity and stability. Phosphides are found to be active in acidic, alkaline and neutral aqueous media.3-6 Different methods were pursued for the synthesis of transition metal phosphides, mostly operated at rather low temperature ranging from 250-325 °C. Low temperature synthesis is carried out using trioctylphosphine ($\text{P}(\text{C}_8\text{H}_{17})_3$) or sodium hypophosphite (NaPO_2H_2) as a source of phosphorous.

The electrochemical performance of metal phosphides depends on various factors, such as size & surface area, morphology, surface texture (porosity), crystal phase, catalysts support, and so forth. For instance, different phases of nickel phosphide, a well-known catalyst for the hydrodesulphurization and hydrogen evolution 7, 8, such as Ni_2P , Ni_5P_4 , NiP_2 , and Ni_{12}P_5 , were prepared and Ni_2P was identified as the most active phase toward the hydrogen evolution reaction in acidic solution.9 This catalyst was synthesized by mixing nickel precursor with trioctylphosphine at 320°C 10, similarly, cobalt phosphide deposited on Ti foil was prepared using trioctylphosphine and showed excellent activity in

acidic media – required only 85 mV for producing 20 mAcm⁻².¹¹ Cobalt phosphide was also prepared on carbon cloth by phosphidizing the hydrothermal product (Co(OH)F/CC) at 300 °C. The catalyst gave very low onset potential (38 mV) ¹, and generated 10 mAcm⁻² at 67 mV. Following similar preparation technique, CoP/CNT composite was also synthesized and the catalyst showed a good performance - the overpotential required to obtain 10 mA/cm² was 110 mV ¹².

Joshua et al. showed that amorphous molybdenum phosphide (with diameter of 4.5 nm) deposited on titanium foil produced 10 mAcm⁻² at overpotential of 90 mV in acidic media.¹³ Zhu and co-authors reported the synthesis of MoP₂ nanosheet supported on the carbon cloth. The electrocatalyst was prepared by phosphidizing the MoS₂NS/CC using sodiumhypophosphite at 300 °C, it required only 58 mV to generate current of 10 mAcm⁻².¹⁴ Tian et al, reported the synthesis of self-supported copper phosphide nanowires at low temperature using sodiumhypophosphide, 10 mAcm⁻² current was obtained at overpotential 143 mV.¹⁵ Xiaoping and coworkers synthesized copper phosphide nanocubes (198 nm) at low temperature using sodiumhypophosphite, this electrocatalyst showed overpotential of 148 mV required to obtain 16 mAcm⁻².¹⁶ FeP spherical nanoparticles were prepared at low temperature using trioctylphosphine at 340 °C, this electrocatalyst on titanium electrode showed excellent HER activity with overpotential of 50 mV to generate 10 mAcm⁻².¹⁷ Zhang et al, prepared FeP nanoparticles supported on the graphene sheet prepared at 350 °C using sodiumhypophosphide, the current of 10 mAcm⁻² was afforded at overpotential of 240 mV.¹⁸ High temperature (650-850 °C) approach was also used to synthesize some phosphides such as Mo₃P, MoP, MoP₂ and WP.¹⁹⁻²²

Another effective strategy to boost the HER performance of transition metal phosphide (TMP) is electronic structure modulation through alloying with other elements. Recently, several bimetallic phosphides were prepared and showed very promising activity towards HER.²³⁻²⁸ A nickel-cobalt phosphide nanosheet supported on the carbon cloth was prepared by depositing the metals hydroxides electrochemically followed by phosphidization in the presence of sodium hypophosphite. The bimetallic electrocatalyst required overpotential of 85 mV to obtain 10 mA cm⁻² current.²⁴ Another investigation indicated that the amount of Ni and Co are crucial to high performance.²⁵ For instance, nickel cobalt phosphide was supported on the carbon nanotubes consisting of different ratios Co_{0.5}Ni_{1.5}P/CNT, Co_{1.1}Ni_{0.9}P/CNT, and Co_{1.6}Ni_{0.4}P/CNT.

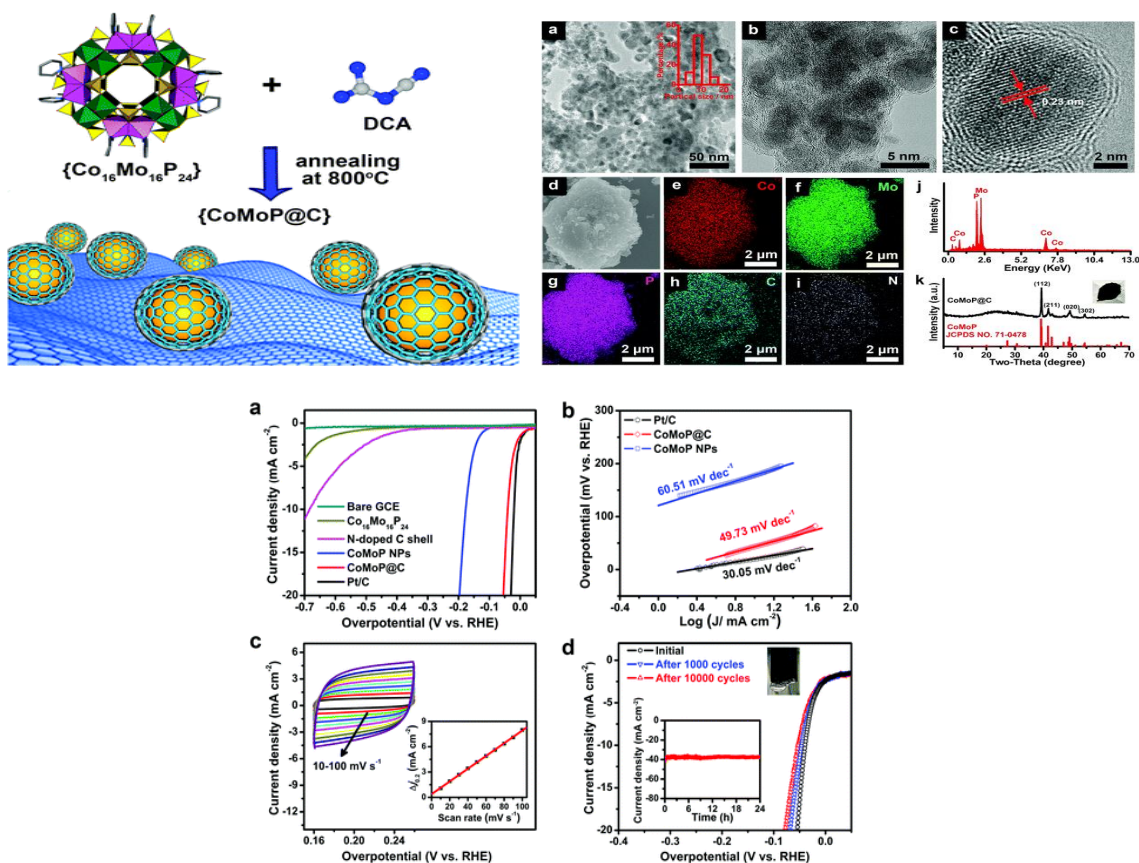


Figure 1: Preparation, characterization and activity results of the CoMoP@C catalyst

The activity was found to be dependent on elemental composition – the overpotentials for 20 mA cm⁻² were recorded to be 169.8, 135.4, and 118.8 mV for Co_{0.5}Ni_{1.5}P/CNT, Co_{1.1}Ni_{0.9}P/CNT, and Co_{1.6}Ni_{0.4}P/CNT, respectively.²⁵ Similarly, carbon-supported cobalt-molybdenum phosphide was prepared, and demonstrated to be highly active towards HER reaction; needed only 41 mV to obtain current of 10 mA cm⁻² under acidic medium. Furthermore, this electrocatalyst was found to be highly efficient to evolve H₂ from sea water.²⁶ Few other bi-metallic molybdenum-based catalysts, such as Co–Mo–N and Ni–Mo–S, were also prepared and activity was evaluated for HER reaction. These hybrid catalysts showed higher activity than that their counterparts consisting of monometallic system.^{27, 28}

To this end, due to unique d-band electronic structure, tungsten phosphide is another potential candidate for hydrogen evolution reaction. Yet, it remains less investigated. Recently, few studies are reported on the preparation and electrocatalytic HER performance.^{29 - 33} For instance, tungsten phosphide was supported on carbon cloth using hydrothermal method, then phosphidized using red phosphorus at 800 °C. the catalysts needed low overpotential of 130 mV to generate 10 mA cm⁻².³⁴ Joshua M. and co-workers synthesized nanoparticles of tungsten phosphide in the presence of trioctylphosphine at 320 °C.³⁵ The electrocatalyst showed excellent performance – required 120 and 140 mV to deliver 10 and 20 mA cm⁻², respectively. Like other electrocatalysts, the HER performance of tungsten phosphide also depends on the phase and composition. For instance, Zhicai Xing and co-workers prepared WP₂ by heating tungsten precursor with di-ammonium hydrogen phosphate at 500 °C under H₂/Ar 20% gas. The electrode generated 10 mA cm⁻² at overpotential of 161 mV.³⁶

As discussed above, the performance of WP could be further improved by alloying with other elements.³⁸ However, bimetallic phosphides consisting W and other elements are less studied, and only few reports are available. For instance, a porous bi-metallic tungsten molybdenum phosphide supported on the carbon cloth was synthesized in the presence of sodium hypophosphite. This electrocatalyst revealed a promising activity for the hydrogen evolution – required only 138 mV for 100 mAcm⁻², significantly higher compared to molybdenum and tungsten phosphides.³⁸

Besides the active sites, catalysts supports are imperative for the less usage of metals and high electrocatalytic performance. Accordingly, a variety of carbon-based supports, such as commercial carbon black, ^{39, 40} reduced graphene oxide, ^{41, 42} graphene, ^{43, 44} and carbon nanotubes ^{39, 45} are used. After the introduction of carbon nanotubes and graphene, carbon based composites have started playing a very important role in wide applications such as heterogeneous catalysis ^{46, 47}, so in order to enhance the efficiency of these carbon materials a surface functionalization is required, such as oxidation of the surface and introduce some oxygen functionality such hydroxyl, carbonyl and carboxyl, however presence of oxygen groups tumble some properties such as electrical, thermal and some mechanical properties. ⁴⁸ So different heteroatoms doping was investigated. Nitrogen doping is one of the process which can enhance the structural properties without tumbling the electrical properties ⁴⁹, and the difference in the electronegativity between carbon and nitrogen provides excess pi-electrons on the surface which can increase the surface energy and reactivity ⁵⁰. There are some examples for metals phosphide catalysts on nitrogen doped carbon base support, cobalt phosphide was prepared on N-doped carbon support using low temperature method, and the catalyst had an excellent hydrogen evolution

activity about 90 mV overpotential corresponding to 10 mA current ⁵¹, another example cobalt phosphides (Co₂P and CoP), cobalt phosphides supported on carbon nanotubes and supported on nitrogen doped carbon nanotubes using trioctylphosphine for cobalt phosphide and triphenylphosphine for dicobalt phosphide at 330 °C, the catalytic activity was investigated and compared at acidic media at current of 20 mA cm⁻², and they figured out that the CoP/NCNT (overpotential of 99 mV) showed two times better hydrogen evolution activity than CoP/CNT (overpotential of 198 m) and Co₂P/NCNT 2.21 time better than Co₂P/CNT. ⁵²

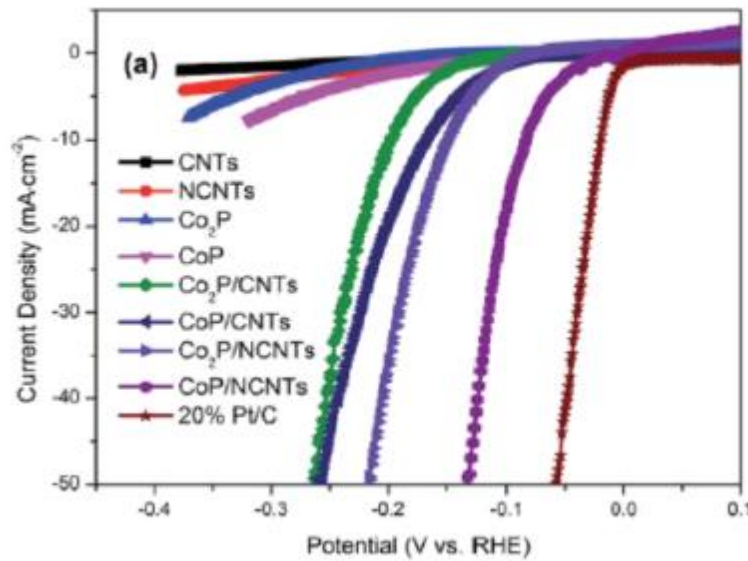


Figure 2: Activity comparison of different phases of CoP and effect of nitrogen doping.⁵²

2.2 Statement of the problem

Hydrogen gas is as an alternative, sustainable and renewable source of energy. Platinum and noble metals are well known as the best electrocatalyst for hydrogen production, however the occurrence of these noble metals in nature are very rare. The development of

abundant and efficient non-noble transition metal-based electrocatalysts for hydrogen evolution is in utmost need. Iron is very cheap and highly abundant in nature. Developing 2based catalysts is very attractive approach. FeP has shown promising activity for H-Irongeneration from water. However, its activity is limited by its poor dispersion on supports. Attempt will be made to design and develop robust solid supports that could render the formation of smaller and uniformly-dispersed FeP and/or CoP, endowing the electrodes with benign attributes, such as high specific surface area, high electrochemically active surface area, low electrical impedance and charge transfer resistance and high turnover frequency. .

2.3. Research Objectives

- 1- Designing and synthesis of ultrathin and interconnected carbon nanosheets as potential passive solid support. .
- 2- Development of hierarchical mesoporous carbon as potential passive solid support. .
- 3- Development of molybdenum sulfide nanosheets as potential active solid support.
- 4- To design electrodes comprising as-developed supports and metal chalcogenides.
- 5- To characterize as-prepared nanostructured electrode materials by standard techniques.
- 6- To study the efficacy of as-derived electrodes in electrochemical energy conversion, by studying hydrogen evolution reaction.
- 7- To elucidate detailed electrode kinetics, and establish important hypothesis about how the critical microstructural attributes, such as specific surface area, electrochemically

active surface area, electrical impedance, charge transfer resistance, turnover frequency, of supports/electrodes correlate to the HER performance.

2.4. Research Methodology

Preparation of Carbon Nanosheets (CN)

Around 5g of sodium citrate will be heated under inert environment of Argon at 800°C/min, after that the sample will be washed with 10% o for 2h, the heating rate is 3hydrochloric acid and with plenty amount of deionized water, then the sample will be dried with oven and the black powder will be collected.

Preparation of Hierarchical Mesoporous Carbons (HMPCs)

Two types of colloidal silica (based on particles size) were obtained 4 and 20 nm respectively. The HMCs were prepared by mixing a specific amounts of sucrose with the silica, the prepared carbon was donated CY-AB, were Y is the average size of the silica (4 or 20 nm), were AB is the silica to sucrose ratio respectively, for example to prepare 4-11, a ratio of 1:1 between sucrose and colloidal silica (4 nm), Next the mixture was placed in the freeze drying system, After a dry powder was collected, the as-prepared mixture was subjected to temperature 1000oC (3oC/min) under N2 atmosphere for 3h. The collected black powder was placed in 3M NaOH at 80oC for overnight. Then the powder was washed with DI water several time until the PH restore to 7. Finally the sample was dried at 70oC under vacuum. To prepare HMCs (2011 and 2021), the same above method was applied by varying the ratio between silica and sucrose and the use of silica (20 nm size).

Iron Phosphide supported on carbon support

A measured amount (40 mg) of iron chloride (FeCl_2) was dissolved in ethanol, followed by addition of as-prepared carbon nanosheets (25 mg) in a capped vial. The solution was kept under stirring for 5 h at room temperature. Subsequently, the suspension was poured on a petri dish and the solvent was allowed to evaporate under a vigorous stirring at ambient conditions. Upon solvent evaporation, a black powder was obtained which was dried at 90°C for overnight. Finally, the desired amount of as-prepared precursor and sodium hypophosphite (NaPO_2H_2) was placed in two separate alumina crucibles and transferred in a tube furnace under the flow of nitrogen. The weight ratio of precursor and NaPO_2H_2 was 1:20. The NaPO_2H_2 was placed at the upstream side of the furnace. The temperature of furnace was raised to 400°C with heating rate of $3^\circ\text{C}/\text{min}$, and maintained for 2 h. After the reaction, the product was collected and used as electrocatalyst for HER reaction. For comparison, FeP nanoparticles were also prepared following the same method, but without carbon nanosheets.

Preparation of Two-Dimensional Ultrathin Nanosheets of Molybdenum Disulfide (2D MoS_2).

The 2D MoS_2 was prepared as follows. Briefly, ammonium heptamolybdate tetrahydrate (1.25 g, 99.98%) and thiourea (2.30 g, 99.0%) were dissolved in deionized water (20 mL). After complete dissolution, the solution was poured into a 45 mL Teflon container (acid digestion vessel) and heated at 220°C for 20 h. After 20 h of reaction, the oven was allowed to cool down. The precipitate was collected from the bottom of the Teflon vessel, rinsed with water and ethanol several times, and dried under vacuum at 60°C overnight.

Preparation of Iron Monophosphide and 2D MoS_2 (FeP/ MoS_2).

The FeP/MoS₂ was prepared as follows. The as-prepared 2D MoS₂ (25 mg) was dispersed in 20 mL ethanol solution, which was prepared by dissolving iron dichloride (40 mg, 98.0%) in a closed glass vial. The suspension was stirred at room temperature for 5 h, and then poured on a glass Petri dish to remove the solvent through evaporation. The evaporation was carried out under ambient conditions while stirring. Black powder was obtained upon complete solvent evaporation, which was crushed and dried under vacuum at 60°C. The phosphidation of Fe precursor was carried out in the presence of phosphine gas (PH₃), which was generated through decomposition of sodium hypophosphite (NaPO₂H₂). In this phosphidation process, calculated amounts of dried Fe/MoS₂ precursor and phosphine source were transferred into two ceramic boats. The ratio, by weight, of Fe/MoS₂ and NaPO₂H₂ was adjusted to 1:20. The crucibles were placed in a uniform temperature zone of a tube furnace, and nitrogen was flown for 45 min at room temperature. The crucible loaded with NaPO₂H₂ was kept at the upstream side. The thermal treatment was carried out at 400 °C for 2 h. Upon reaction, the electrocatalyst was used as it is for the preparation of electrode to test the HER performance. Also, FeP nanoparticles were synthesized for performance comparison. A similar procedure was pursued to prepare FeP, but in the absence of MoS₂.

Characterization of iron phosphide

All the prepared electrocatalysts will be characterized using different characterization techniques such as X-ray diffraction, Transmission and High-Resolution Transmission Electron Microscopy (TEM/HRTEM), Scanning electron microscope (SEM), BET surface analyzer and X-ray photoelectron spectroscopy (XPS) Electrochemical characterization Activity will be studied in a three-electrode cell, connected to a potentiostat (EG&G 273A),

at ambient conditions. Working electrode will be prepared by sonicating slurry of electrocatalyst (5 mg), water and ethanol (50% V/V) and 40 μ l of 1.66 % wt. Nafion® for approximately 30 min. The sonicated solution will be dropped on a pre-cleaned glassy carbon (GC) disc electrode (5.0 mm diameter, 0.196 cm², Pine Instruments), and dried at ambient conditions. The deposition steps will be repeated to achieve 1 mgcm⁻² catalyst loading. Saturated calomel electrode (Hg/HgCl₂, SCE) and coiled platinum wire will be used as reference and the counter electrode, respectively. The SCE potential will be converted and presented against normal hydrogen electrode (NHE). Linear sweep voltammetry will be performed in a 1.0 M KOH or 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mV s⁻¹. All current density will be normalized to the geometric area of the glassy carbon electrode and presented after iR compensation. Electrochemical impedance spectroscopy (EIS) measurements will be carried out in 0.5 M H₂SO₄ between the frequency range of 105 Hz and 0.01 Hz with ac amplitude of 10 mV. All the EIS data will be normalized to the geometric area of the working electrode. Calculation of turnover frequency (TOF)

To elucidate the active sites, TOF will be estimated using the following eqn (1). 54

$$\text{TOF} = JA/2FN \quad (1)$$

Where, J (A/cm²) is the geometric current density recorded during the LSV measurement in 0.5MH₂SO₄, A is the geometric area of the glassy carbon electrode GC (0.196 cm²), 1/2 denotes that two electrons are required to form one hydrogen molecule from water, F is the Faradic constant (96485 Cmol⁻¹), N is the number of active sites (mol). N was determined by carrying out CV measurements between -0.2 V and +0.6 V RHE in 1.0M

phosphate buffer solution with a scan rate of 20 mV/s. While it is difficult to assign the observed peaks to a given redox couple, N should be proportional to the integrated charge over the whole potential range.

$$N = Q/2F$$

Where Q is voltammetric charge.

CHAPTER 3

FACILE SYNTHESIS OF ULTRATHIN INTERCONNECTED CARBON NANOSHEETS AS A ROBUST SUPPORT FOR SMALL AND UNIFORMLY DISPERSED IRON PHOSPHIDE FOR THE HYDROGEN EVOLUTION REACTION

3.1. Introduction

Prospects of global energy demand and adverse climate change are driving scientists to explore sustainable and eco-friendly sources of energy. Among energy carriers, molecular hydrogen (H_2) show great promise, owing to (1) highest gravimetric energy density [55] and (2) environmentally benign characteristic – produces only water as the by-product. Currently, large scale production of H_2 is achieved through steam–methane reforming ($CH_4 + H_2O \rightleftharpoons CO + H_2$). This is an energy intensive process and consumes fossil fuel and, more importantly, adds to CO_2 emission through water – gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$). Quest for a H_2 -based economy derived from non-fossil resources remains at the forefront of future fuels.

To this end, large scale and sustainable H_2 production through water electrolysis holds great potential, particularly due to carbon-free attributes [55-58]. However, the requirement of high potential to split water is an overriding limitation. Currently, tremendous efforts are underway to address this technological challenge by designing and developing low-cost, stable electrocatalysts that require low potential. As a

result, a wide variety of materials comprising non-precious compositions, such as carbides [40, 59 - 61], sulfides [62 - 65], nitrides [27, 66], phosphides [6, 67-69], and borides [70, 71], of transition metals, have been explored. The activation potential is determined by catalytic composition, and could significantly be reduced at first hand by targeting the right elements of electrocatalyst. In this context, phosphides of transition metals are viewed as potential alternatives to Pt-based electrocatalyst owing to their low-cost, high activity and excellent stability under harsh electrochemical conditions [67]. In particular, owing to low cost and high activity, iron phosphides have been investigated as potential electrocatalyst for hydrogen evolution reaction (HER) [72-79]. In supported catalytic systems, besides the active sites, the performance of electrode is predominantly dictated by the support. Coupling between active surfaces and support may induce unique metal-support-interaction, and thus may have significant impact on critical electrode processes such as the interfacial equilibrium, adsorption and/or desorption of reactive species and their interaction with electrocatalysts surface, electrical conductivity, and so forth. As a result, FeP has been dispersed on different carbon-based supports and its electrocatalytic performance was investigated towards HER. For instance, Sun and coworkers supported iron phosphide on nitrogen-doped carbon nanotube, and investigated the HER performance [76]. Similarly, phosphorous doped single wall carbon nanotubes are used as support for iron phosphide nanoparticles for HER in acidic and basic solutions [77]. In another study, FeP nanoparticles were grown on graphene sheets and evaluated as non-precious-metal electrocatalysts for HER [18]. Tang and coworkers employed candle soot as support for FeP nanoparticles, and demonstrated efficient HER in acidic electrolyte [78].

Recently, scalable synthesis of carbon-shell-coated FeP nanoparticles is demonstrated for robust HER [79].

The synergistic chemistry between active sites and support could favorably be amplified by achieving higher and uniform surface coverage of support by functional sites. In this study, we demonstrate the direct synthesis of ultrathin and interconnected nanosheets of carbon by pyrolysis of sodium citrate for the first time, and its use as a robust solid support for dispersion of iron phosphide (FeP) nanoparticles to fabricate electrode material for HER. Ultrathin nanosheets are obtained by thermal decomposition of sodium citrate in the presence of nitrogen. The intended composition (FeP/CN) is prepared through phosphidation of carbon nanosheets impregnated with molecular source of iron. The catalytic composition is characterized by standard techniques, and the propensity of FeP/CN electrode is investigated towards HER in 0.5 M H₂SO₄ or 1.0 M KOH aqueous electrolytes. The electrocatalytic performance of FeP/CN is compared with commercial Pt/C and FeP nanoparticles. Operational stability of electrode is assessed by performing potentiostatic measurement. Key electrode attributes, such as specific surface area, electrochemically active surface area (ECSA), interfacial charge transfer resistance (R_{ct}) and turnover frequency (TOF) were estimated and correlated to the performance. Underlying mechanism is deduced by estimating Tafel slope employing electrochemical impedance spectroscopy (EIS).

3.2 Experimental

3.2.1. Preparation of interconnected ultrathin carbon nanosheets (CN)

Approximately 5 gm of sodium citrate was taken in alumina crucible and transferred in a tube furnace under the flow of nitrogen. The temperature was raised to 800 °C with

heating rate of 3 °C min⁻¹, and maintained for 2 h. After the reaction, the product was collected and washed with 10% hydrochloric acid and with plenty of deionized water. Finally, the product was dried at 90 °C in an oven.

3.2.2. Preparation of iron phosphide/carbon nanosheets (FeP/CN)

A measured amount (40 mg) of iron chloride (FeCl₂) was dissolved in ethanol, followed by addition of as-prepared carbon nanosheets (25 mg) in a capped vial. The solution was kept under stirring for 5 h at room temperature. Subsequently, the suspension was poured on a petri dish and the solvent was allowed to evaporate under a vigorous stirring at ambient conditions. Upon solvent evaporation, a black powder was obtained which was dried at 90 °C for overnight. Finally, the desired amount of as-prepared precursor and sodium hypophosphite (NaPO₂H₂) was placed in two separate alumina crucibles and transferred in a tube furnace under the flow of nitrogen. The weight ratio of precursor and NaPO₂H₂ was 1:20. The NaPO₂H₂ was placed at the upstream side of the furnace. The temperature of furnace was raised to 400 °C with heating rate of 3 °C min⁻¹, and maintained for 2 h. After the reaction, the product was collected and used as electrocatalyst for HER reaction. For comparison, FeP nanoparticles were also prepared following the same method, but without carbon nanosheets.

3.2.3. Characterization

Morphological and detailed microstructural attributes of the materials were discerned with the aid of field emission scanning electron microscope (FESEM, Tescan Lyra-3), transmission and high-resolution transmission electron microscope (TEM/HR-TEM,

FEI Tecnai TF20). Other techniques employed for characterization of the samples were: X-ray diffractometry (XRD, Rigaku MiniFlex), BET surface area analyzer (Micromeritics ChemiSorb 2750) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi).

3.2.4. Electrochemical characterization

Activity was studied in a three-electrode cell, connected to a potentiostat (EG&G 273A), at ambient conditions. Working electrode was prepared by sonicating slurry of electrocatalyst (5 mg), water and ethanol (50% V/V) and 40 μ l of 1.66 % wt. Nafion® for approximately 30 min. The sonicated solution was dropped on a pre-cleaned glassy carbon (GC) disc electrode (5.0 mm diameter, 0.196 cm², Pine Instruments), and dried at ambient conditions. The deposition steps were repeated to achieve 1 mgcm⁻² catalyst loading. Saturated calomel electrode (Hg/HgCl₂, SCE) and graphite rod were used as reference and the counter electrode, respectively. The SCE potential was converted and presented against reversible hydrogen electrode (RHE). Linear sweep voltammetry was performed in a 1.0 M KOH or 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mVs⁻¹. The galvanostatic measurement was performed in a 0.5 M H₂SO₄ aqueous solution in the current range of 20 mA to 0.01 μ A at a scan rate of 0.1 mAs⁻¹ [80]. All current density was normalized to the geometric area of the glassy carbon electrode and presented after iR compensation. Electrochemical impedance spectroscopy (EIS) measurements were carried out in 0.5 M H₂SO₄ between the frequency range of 105 Hz and 0.01 Hz with ac amplitude of 10 mV. All the EIS data was normalized to the geometric area of the working electrode. All the electrochemical measurements were carried out in electrolyte solution saturated with H₂ gas.

3.2.5. Calculation of turnover frequency (TOF)

To elucidate the active sites, TOF was estimated using the Equation (1) [54];

$$\text{TOF} = JA/2FN \quad (1)$$

Where, J (A/cm^2) is the geometric current density recorded during the LSV measurement in $0.5 \text{ M H}_2\text{SO}_4$, A is the geometric area of the glassy carbon electrode GC (0.196 cm^2), $1/2$ denotes that two electrons are required to form one hydrogen molecule from water, F is the Faradic constant (96485 Cmol^{-1}), N is the number of active sites (mol). N was determined by carrying out CV measurements between -0.2 V and $+0.6 \text{ VRHE}$ in 1.0 M phosphate buffer solution with a scan rate of 20 mV s^{-1} . While it is difficult to assign the observed peaks to a given redox couple, N should be proportional to the integrated charge over the whole potential range. Assuming a one electron redox reaction, the upper limit of active sites was calculated as given in the following equation:

$$N = Q/2F$$

Where Q is voltammetric charge.

3.3. Results and discussion

3.3.1. Structural characterization of FeP/CN

Powder X-ray diffraction of FeP/CN is shown in Fig. 3. Broad and low-intensity diffractions centered at 26.5° and 43.2° correspond to (002) and (100) planes of carbon [81], and suggest that carbon nanosheets are of amorphous characteristics. The diffraction peaks located at 32.8° (011), 37.2° (111), 48.3° (211), and 56.1° (013) are attributed to FeP with a orthorhombic structure (JCPDS 65-2595) [82]. Figure 3

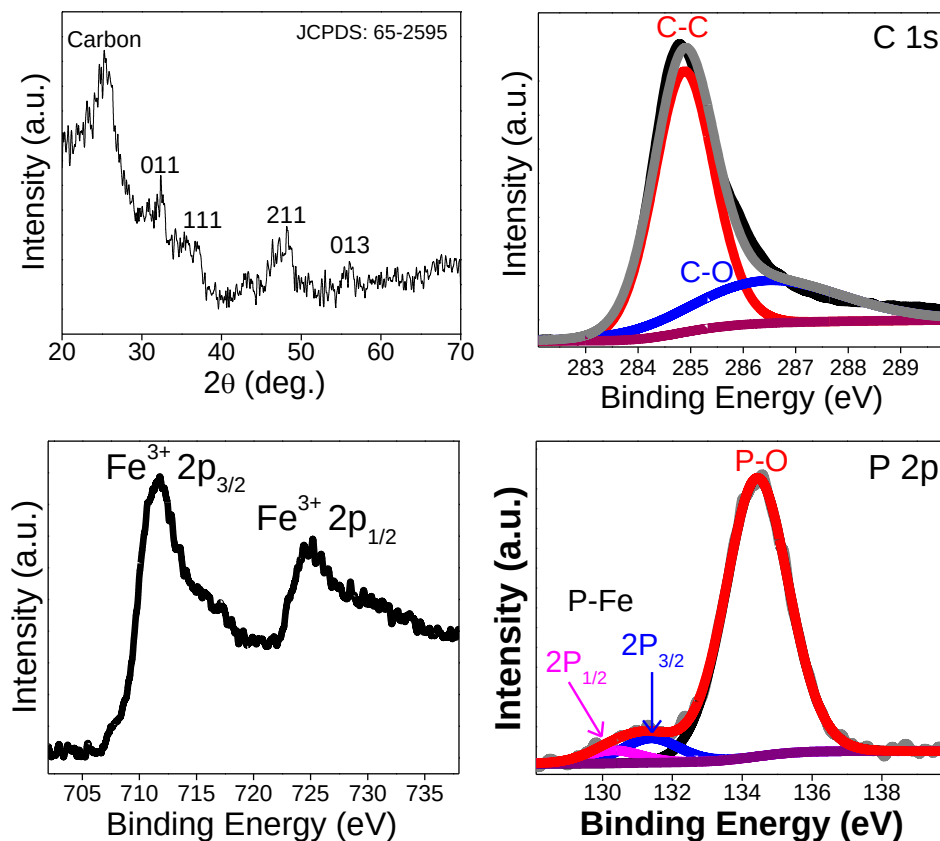


Figure 3: XRD patterns and XPS signatures of FeP/CN

includes the details of chemical compositions and oxidation states analyzed by X-ray photoelectron spectroscopy (XPS). Survey spectrum, not shown here, corroborated the elemental compositions, which included iron (Fe), phosphorous (P), and carbon (C). In the spectrum of C 1s, presence of C–O (at 286.5 eV) [83] groups in the layers of as-prepared FeP/CN was registered, besides characteristic peak of graphitic carbon at 284.9 eV. In the Fe 2p spectrum, the peaks centered at 711.6 and 724.8 eV account for Fe³⁺ 2p_{3/2} and Fe³⁺ 2p_{1/2} respectively, which agrees well with those reported in the literature for Fe coordinated to P [76, 77, 84]. The peaks at 130.3 and 131.4 eV in

the P 2p spectrum are ascribed to 2p_{3/2} and 2p_{1/2} of P bonded to Fe [85]. In addition, the intense and broad peak observed at 134.4 eV is assigned to PO₄-3 [84].

3.3.2. Microstructural characterization of FeP/CN

Microstructural and morphological features of carbon nanosheets and FeP/CN were collected with the aid of scanning and transmission electron microscopes (Fig. 4). FESEM image of carbon directly derived from carbonization of sodium citrate (Fig. 4a) clearly indicates the presence of homogeneous and interconnected nanosheets of carbon. It is further corroborated by low-magnification TEM analysis (Fig. 4c). Both FESEM and TEM confirm that the carbon is in FeP/CN and elemental mapping of carbon, iron and phosphorous.

the form of interconnected nanosheets. Furthermore, the edges of these sheets are slightly rolled up, resembling to the characteristics of graphene layers. Each sheet consists of several layers, and the thickness of nanosheets was determined by TEM, which is estimated to be <5 nm. The FESEM image of FeP/CN, Fig. 4b, indicates homogeneous distribution of fine-grained FeP nanoparticles on carbon nanosheets. This was corroborated by TEM analysis. The TEM images shown in Fig. 4d and e highlight the size, morphology and homogeneity of FeP dispersed on nanosheets. The FeP nanoparticles were highly homogeneous and spherical in shape with size in the range of 3 to 15 nm, uniformly distributed across the surface of carbon nanosheets. This finding reinforces our assumption that use of carbon in the form of ultrathin nanosheets modifies the self-assembling behavior of molecular iron and renders discrete nucleation and growth of fine and uniformly dispersed FeP after phosphidation. The HR-TEM microscopy image of FeP, Fig. 4f, shows high degree of crystallinity.

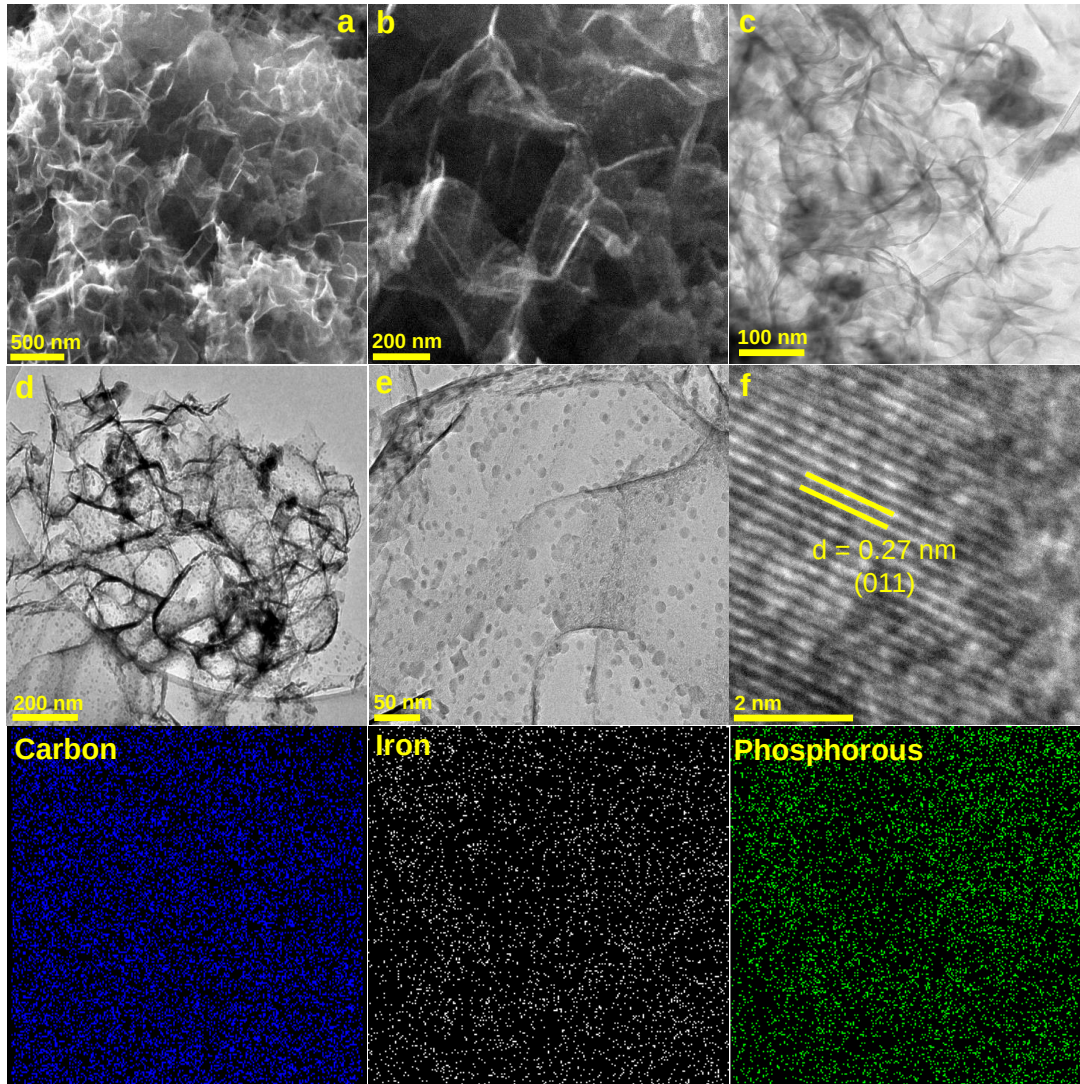


Figure 4:FESEM (a and b), TEM of pure carbon nanosheets (c), TEM/HR-TEM (d-f) of FeP/CN

The interplanar distance is estimated to be 0.27 nm, in good agreement with 0.27 nm based on XRD data for the (011) plane. Elemental mapping of FeP/CN was performed, and results of C, Fe and P are included in Fig. 4. All the elements seemed to be evenly distributed throughout the surface of nanosheets.

3.3.3. Evaluation of electrocatalytic performance towards hydrogen evolution reactions (HER)

The activity of as-synthesized electrocatalysts was evaluated towards hydrogen evolution reaction (HER) both in acidic (0.5 M H₂SO₄) and basic (1.0 M KOH) aqueous electrolytes. The current density was normalized to geometric area of the glassy carbon electrode. Before recording the linear sweep voltammograms (LSV), working electrodes were swept for 10 cycles between +0.1 and -0.3 VRHE to allow interface to attain equilibrium, if any.

3.3.1. Comparative electrocatalytic performance

The performance of FeP/CN electrode is compared with that of FeP nanoparticles and commercial Pt/C. Comparative electrocatalytic performance was carried out under identical experimental conditions with same mass of catalyst loaded on GC electrode. Cathodic polarization (current density vs. potential) profiles under acidic and basic media are shown in Fig. 5a and b, respectively. Under acidic conditions, the overpotentials estimated to produce current density of 10 mA cm⁻² were ~41, ~104 and ~254 in the presence of Pt/C, FeP/CN and FeP nanoparticles, respectively. Table 1 compares the activity of as-synthesized FeP/CN electrode with FeP-based electrocatalysts reported in the literature. The performance is compared in terms of potential required to produce a current density of 10 mA cm⁻² per geometric area; a standard or benchmark current density [57]. The performance is also compared with other porous electrodes (Table 1) for higher current densities. As could be seen, the requirement of HER overpotential for as-prepared FeP/CN electrode compares favorably to most of the carbon-supported FeP electrodes reported as ye

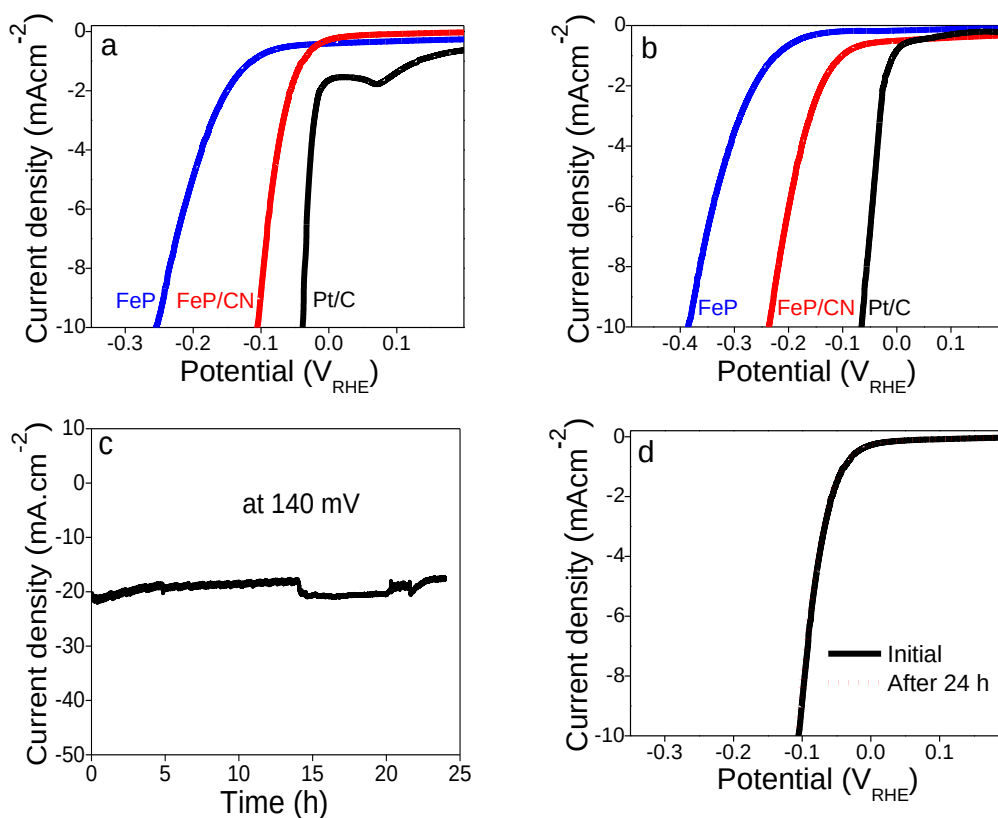


Figure 5: Comparative polarization curves in acidic (a) and basic media (b). Current-time curve (c) and polarization curves (d) obtained before and after potentiostatic experiment.

For instance, FeP dispersed on graphene sheets required overpotential 123 mV [18]. In another study, the electrode comprising candle soot supported-FeP required 112 mV [78]. Phosphorus doped single wall carbon nanotubes is also utilized as support for nanoparticles of iron phosphide; the required overpotential for the electrode was ~145 mV [77]. The electrode comprising iron phosphide/nitrogen-doped carbon nanotubes required 113 mV [76]. It is noteworthy, however, that high efficiency electrodes are usually obtained with the electrocatalysts supported on carbon cloth and metallic substrate such as titanium foil. A similar activity trend, though requiring higher potential as compared to acidic electrolyte, was discerned in basic electrolyte. For the

identical current density, respective potentials were calculated to be ~65, ~235 and ~385 mV. As expected, commercial Pt/C exhibited the best HER performance. The electrode comprising FeP/CN required substantially lower potential as compared to that of FeP nanoparticles. Superior performance of FeP/CN electrode could presumably be ascribed to improved dispersion of FeP on carbon nanosheets, as discerned through microscopy.

Table 1: The HER activity comparison between FeP/CN and carbon-based electrocatalysts and porous electrocatalysts.

Electrocatalyst	Electrolyte	Overpotential			Ref.
		$\eta_{10 \text{ mAcm}^{-2}}$	$\eta_{100 \text{ mAcm}^{-2}}$	$\eta_{250 \text{ mAcm}^{-2}}$	
FeP-NPs	H ₂ SO ₄	151	-	-	[74]
FeP/N-CNT	H ₂ SO ₄	130	-	-	[76]
FeP-FeC @P-doped SWNT	H ₂ SO ₄	150	-	-	[77]
Candle soot- FeP	H ₂ SO ₄	121	-	-	[78]
FeP NWs/rGO	H ₂ SO ₄	107	-	-	[83]
FeP/CNT	KOH	110	-	-	[94]

FexP@NPC	H ₂ SO ₄	227	-	-	[95]
FeP-NA/CC	H ₂ SO ₄	58	-	-	[4]
FeP-NW/CF	H ₂ SO ₄	45	-	-	[96]
Fe ₂ P-ND/FG	H ₂ SO ₄	91	-	-	[97]
FePNTs	H ₂ SO ₄	88	-	-	[98]
FeP-NW	H ₂ SO ₄	96	-	-	[99]
FeP ₂ -NW	H ₂ SO ₄	61	-	-	[99]
Porous Ni ₃ Al	KOH	-	>1340	-	[100]
Porous Ni/Zn	NaOH	-	301	-	[101]
Porous NiP	KOH	-	248	-	[102]
Porous Ni-Mo-P	KOH	-	-	359	[103]
Porous NiAl _{5.95} Mo _{0.66}	KOH	-	-	67	[93]
FeP/CN	H ₂ SO ₄	104	262	475	This work

NA: nanoarray, NW: nanowire, NPs: nanoparticles, CC: carbon cloth, CF: carbon fiber,

ND/FG: nanodot/ fluffy graphene sheet, and NTs: nanotubes

3.3.2. Evaluation of electrode stability

Figures 6c and d show the stability of FeP/CN electrode measured under identical experimental conditions; catalyst loading 1 mg cm^{-2} and $0.5 \text{ M H}_2\text{SO}_4$. Potentiostatic measurement was performed at constant potential of 140 mV for 24 h . The time-dependent profile of current density at constant applied potential of 140 mV is shown in Fig. 5c. A steady current flow was recorded for $>24 \text{ h}$ without any noticeable drop in the current density indicating the stability of the electrode. In addition, after 24 h of potentiostatic experiment, the used-electrode was re-polarized and current density was quantified as a function of potential. Polarization curves recorded before and after potential hold test are compared in Fig. 6d. As evident, the required overpotential to drive 20 mA cm^{-2} remained almost intact, indicating excellent endurance of the electrode.

3.3.3. Estimation of electrochemically active surface area (ECSA)

The better performance of FeP/CN than FeP electrode is correlated to electrochemically active surface area (ECSA), charge transfer resistance (R_{ct}) and turnover frequency (TOF). The BET surface areas of pure FeP and FeP/CN were measured to be 43.9 and $167 \text{ m}^2 \text{ g}^{-1}$, respectively. The ECSA of the electrodes was quantified by measuring double layer capacitance (C_{dl}) of cyclic voltammograms (CVs) recorded at different scan rates. Usually, higher C_{dl} translates into higher electrochemically accessible area. The CVs with corresponding plots for FeP and FeP/CN electrodes are shown in Fig. 6. As evident, the FeP/CN electrode exhibits substantially higher C_{dl} as compared to FeP electrode – C_{dl} for FeP and FeP/CN electrodes were calculated to be $\sim 1.25 \text{ } \mu\text{F cm}^{-2}$ and $\sim 41.8 \text{ mF cm}^{-2}$, respectively.

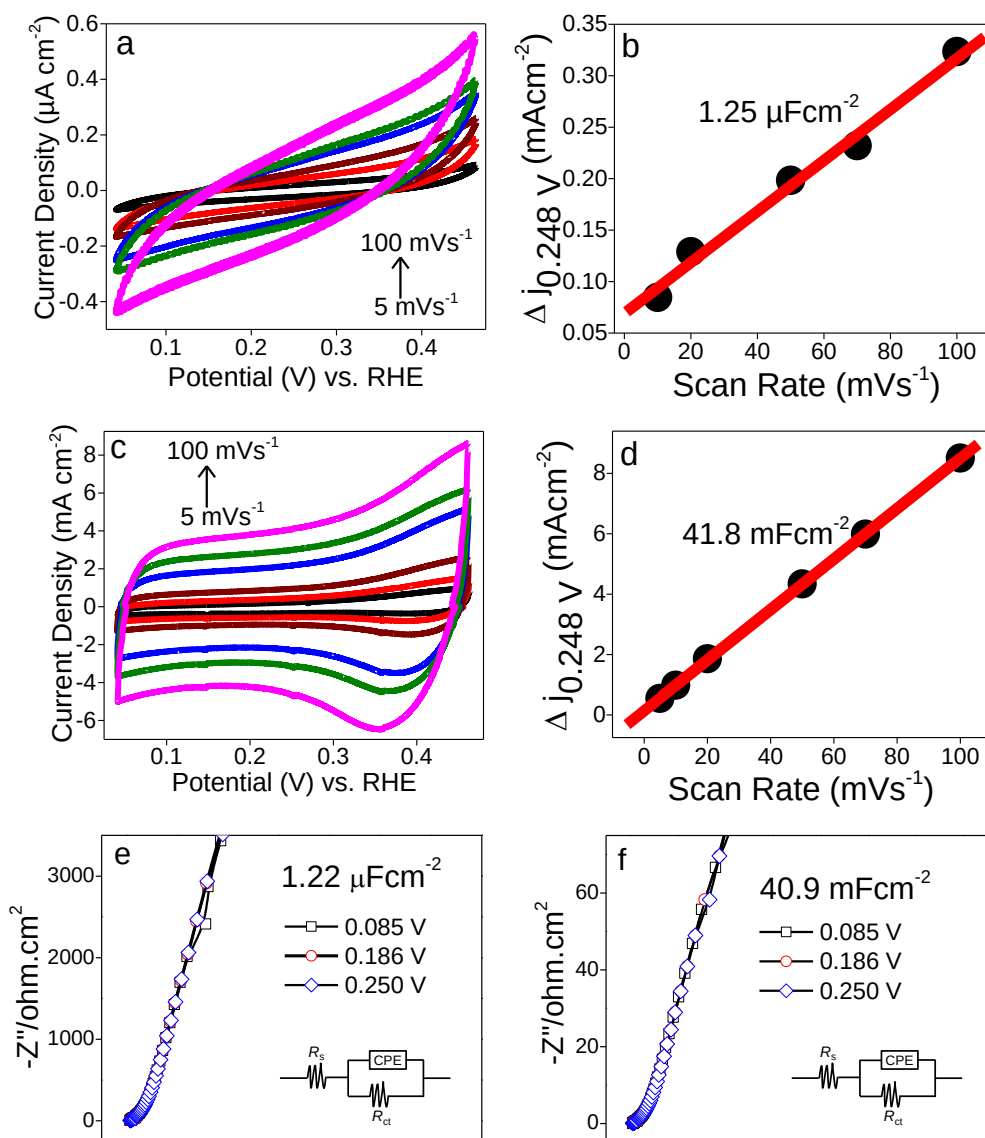


Figure 6: Cyclic voltammograms recorded at different scan rates between 5 and 100 mVs⁻¹ corresponding plots of the current density at 0.248 VRHE vs. scan rate; Fig. a and b – FeP nanoparticles, c and d – FeP/CN. Nyquist plots of FeP nanoparticles (e) and FeP/CN (f) confirming the ECSA values estimated by CVs. All these measurements were performed in 0.5 M H₂SO₄ aqueous electrolyte.]

These estimated ECSA values are verified by EIS; Cdl was calculated by recording Nyquist plots in the non-faradic potential range between 0.085 and 0.25 V [90, 91].

The data was fitted employing one-time constant model, R(QR), shown in Fig. 6e and f inset. The plots of FeP and FeP/CN are included in Fig. 6. The values calculated from EIS measurements, $1.22 \mu\text{Fcm}^{-2}$ and 40.9mFcm^{-2} for FeP and FeP/CN, are in good agreement to those obtained by cyclic voltammetry experiments.

3.3.4. Estimation of electrochemical impedance

Electrochemical impedance spectroscopy (EIS) is employed to obtain further kinetic insights about electrical conductivity and surface charge transfer resistance. All the measurements are performed from 105 Hz to 0.01 Hz with ac amplitude of 10 mV at different cathodic or negative overpotentials ($\eta = 0$ to 150 mV vs. RHE) in acidic medium. Potential-dependent Nyquist plots of FeP and FeP/CN electrodes are shown in Fig. 7a and b, respectively. Findings indicate a significant dependency of Surface charge transfer on the applied potential; charge transfer resistance (R_{ct}) decreased with increasing overpotential, implying a faster charge transfer kinetics at high overpotential. For instance, R_{ct} values of FeP/CN electrode decreased noticeably from $\sim 11 \Omega \text{cm}^2$ at 60 mV to approximately $2.5 \Omega \text{cm}^2$ at 150 mV overpotential. When R_{ct} of both FeP/CN and FeP electrodes were compared, the former exhibits much faster charge transfer kinetics at all applied potential. For instance, at 90 mV, R_{ct} for FeP and FeP/CN electrodes are estimated to be $\sim 480 \Omega \text{cm}^2$ and $\sim 5.2 \Omega \text{cm}^2$, respectively.

This could presumably be attributed to smaller particle size and uniform dispersion of FeP nanoparticles on carbon nanosheets. The EIS findings for hydrogen evolution reaction have been predominantly construed by three types of electrical equivalent circuit models; one-time constant model [38], two-time constant parallel model [39] and two-time constant serial model [40]. In this study, based on Nyquist and Bode

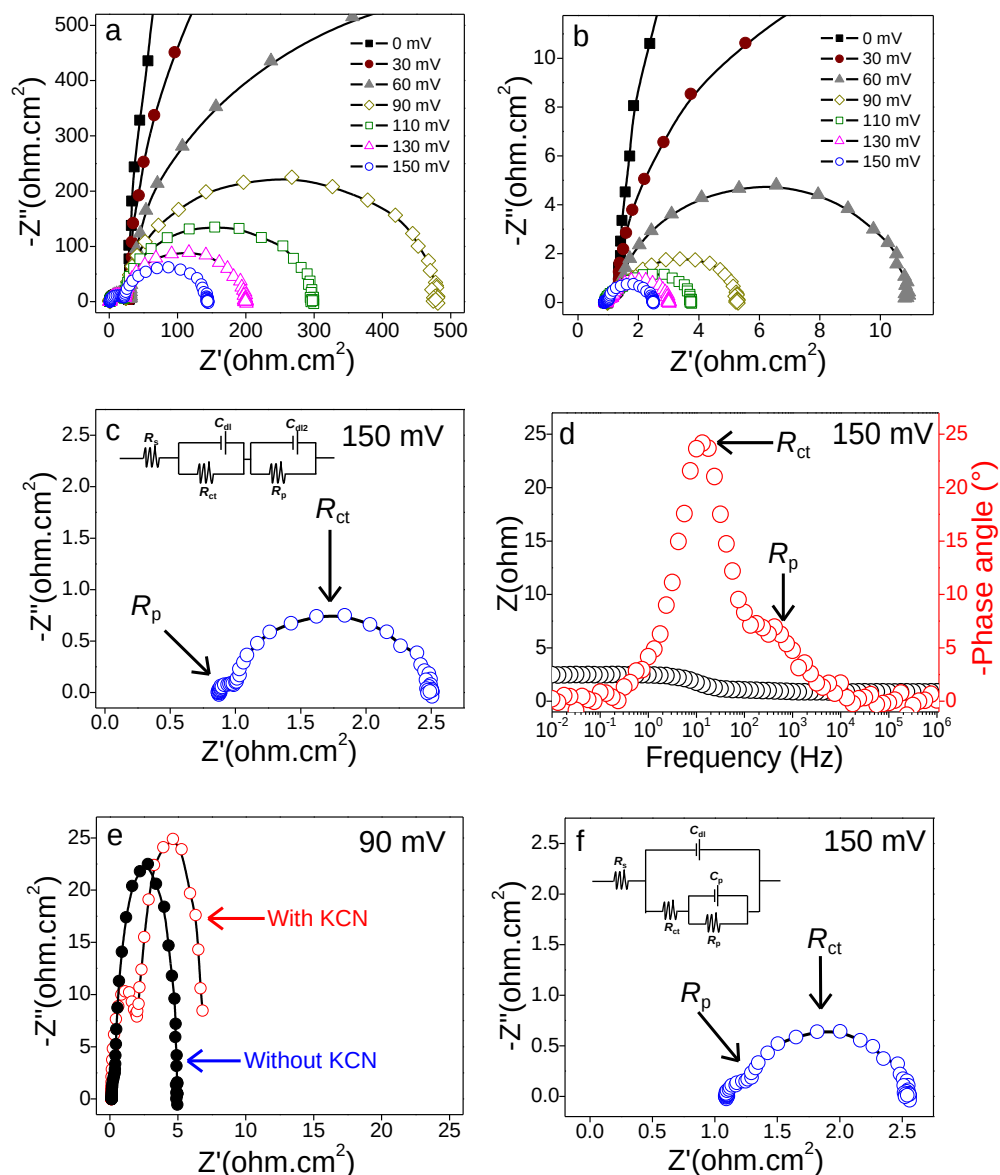


Figure 7: Potential-dependent Nyquist plot of FeP (a) and FeP/CN (b), Nyquist (c) and Bode (d) plots of FeP/CN at 150 mV showing the presence of two time constant in 0.5 M H₂SO₄. Nyquist plots of FeP/CN in the presence and absence of 2×10^{-2} M KCN in 1.0 M KOH solution (e), and Nyquist plot of FeP/CN at 150 mV fitted with 1CPE model (f). All the measurements were performed at cathodic (negative) overpotentials.]

results, the two-time constant parallel model (inset in Fig. 7c) was exercised to fit the experimental data. This model consists of solution resistance (R_s) in series with two parallel constant phase element-resistance, where R_s constitutes a collective resistance which includes the resistance coming from wiring (R_{wiring}), carbon support (R_{carbon}),

resistance of FeP (R_{FeP}), and the solution resistance (R_{soln}) [41]. For both the electrodes, the Nyquist plot indicated the presence of two semicircles. For instance, the Nyquist plots of electrode comprising FeP/CN recorded at 150 mV is shown in Fig. 7c. Corresponding Bode plot, shown in Fig. 7d, corroborates the presence of two-time constants in FeP/CN. The semicircle observed at higher frequency could be attributed to the surface porosity, while the other semicircle at lower frequency corresponds to the charge transfer process of hydrogen evolution reaction. The resistance ($R_p = 0.16 \Omega cm^2$) caused by high frequency semicircle was found to be independent of applied potential, suggesting a porous nature of the surface. This was further substantiated by performing the measurement in the presence of 5×10^{-2} M potassium cyanide (KCN) in the electrolytic solution. This experiment was carried out in alkaline medium to avoid the reaction between KCN and H_2SO_4 , which releases lethal hydrogen cyanide (HCN) gas. The Nyquist plots were recorded before and after the addition of KCN, and the results are shown in Fig. 7e. As evident, the diameter of both the semicircles increased in the presence of KCN, suggesting that these resistances are related to electrode kinetics [45]. For electrode kinetics related to the porous surface, another equivalent circuit models, 1CPE ($R_s(Cdl(R_{ct}(R_p \parallel C_p)))$), can also be used to approximate the experimental complex plane plots [45]. The result obtained with 1CPE circuit model is shown in Fig. 7f. A comparative analysis of the test F suggests that both equivalent circuit models are valid to approximate the complex plots.

3.3.5. Estimation of Tafel slope

In acidic electrolyte, HER proceeds following two different mechanisms, which includes three probable reactions – (1) Volmer reaction (adsorption), (2) Tafel reaction

(chemical desorption) and (3) Heyrovsky reaction (electrochemical desorption), as shown below [6].

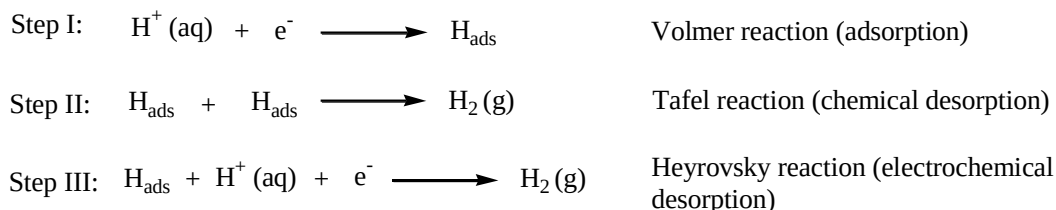


Figure 8 shows the Tafel slopes of the electrodes determined from EIS, polarization curve (for Fig. 5a) and galvanostatic measurements. Tafel slopes estimated from EIS results represent entirely charge transport kinetics. Calculation of the semi-logarithmic values of the inverse of R_{ct} against η results in a linear relationship with a gradient, which corresponds to the Tafel slope. Respective slopes of FeP and FeP/CN electrodes are shown in Fig. 8a and b. The Tafel values are calculated to be 76.5 and 63.5 mVdec⁻¹. Tafel slopes of Pt/C, FeP and FeP/CN calculated from LSV and galvanostatic experiment are shown in Fig. 8c-e. As evident, the values estimated by EIS, polarization curve and galvanostatic measurement are comparable.

In all the cases, calculated Tafel values imply that HER reaction occurs via Volmer-Heyrovsky mechanism, in which the electrochemical desorption of hydrogen ion and atom (Heyrovsky step) is more likely the rate-determining step [83, 89].

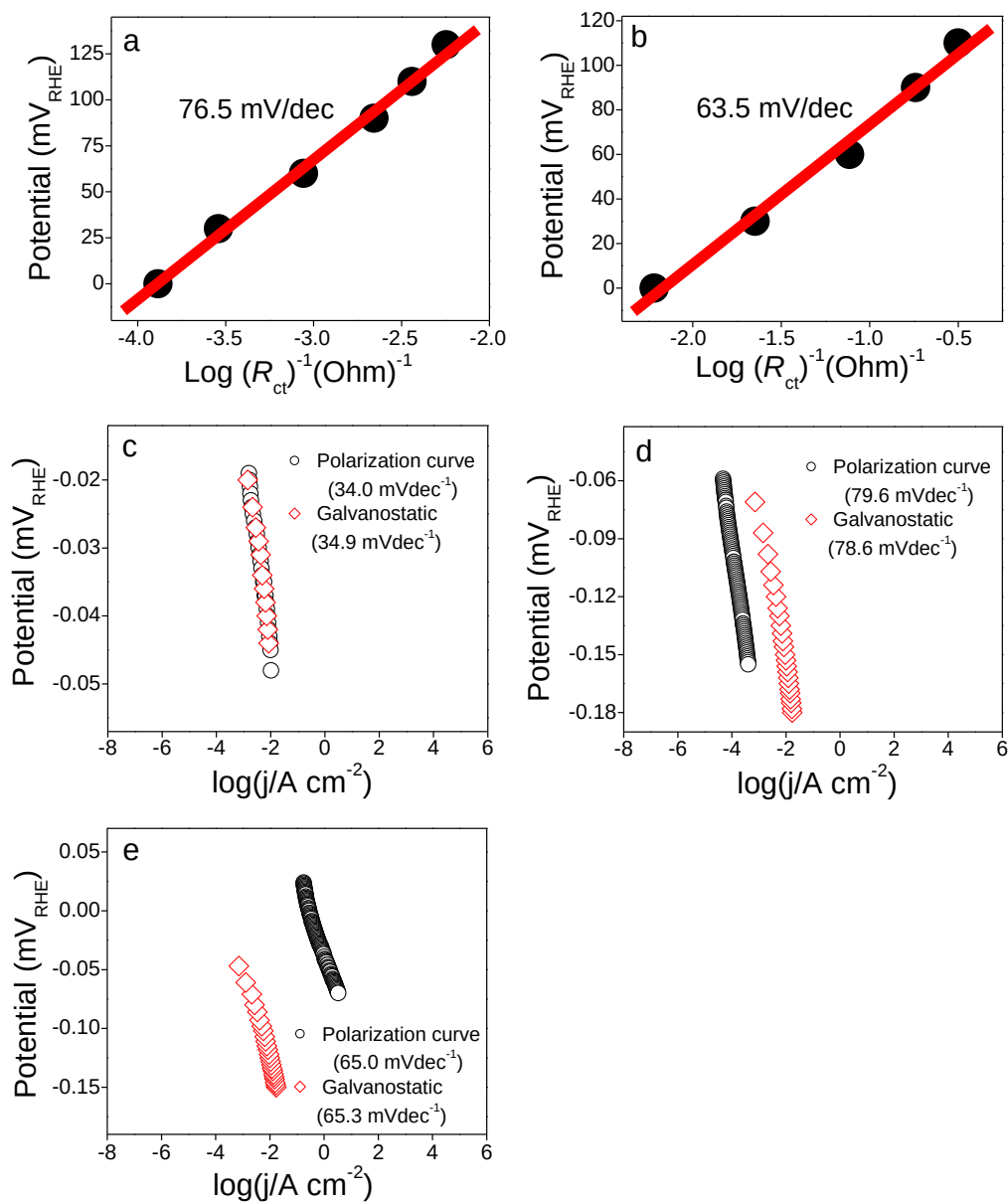


Figure 8: Tafel slopes of FeP (a) and FeP/CN (b) estimated from EIS, Tafel slopes of Pt/C (c), FeP (d) and FeP/CN (e) estimated from polarization curves and galvanostatic measurement

3.3.6. Estimation of turnover frequency (TOF)

Further, the intrinsic catalytic ability of electrodes comprising FeP/CN and FeP towards HER is evaluated by estimating the turnover frequency (TOF). The TOF

relates to the number of reactant molecules reacted per active site in unit time. Higher TOF values are translated into higher catalytic ability. In addition, as the electrocatalytic performance depends on catalysts mass deposited on working electrode (catalyst loading) and usually measurements are performed with different mass loadings, estimation of TOF would allow the comparison of catalytic performance of electrocatalysts reported in the literature [2]. Firstly, the number of active sites was quantified by electrochemical method. Figure 9a compares the cyclic voltammograms of FeP/CN and FeP electrodes recorded between -0.2 V and +0.6 VRHE. Measurements were conducted in neutral phosphate buffer solution (pH = 7) with a scan rate of 20 mVs⁻¹. The number of active sites for FeP/CN and FeP was calculated to be 1.83×10^{-8} and 0.62×10^{-8} mole, respectively. The number of active sites was used to determine TOF using eqn. (1). The TOF are plotted against potential, as shown in Fig. 9b. At $\eta = 104$ mV (the required potential to drive a geometric current density

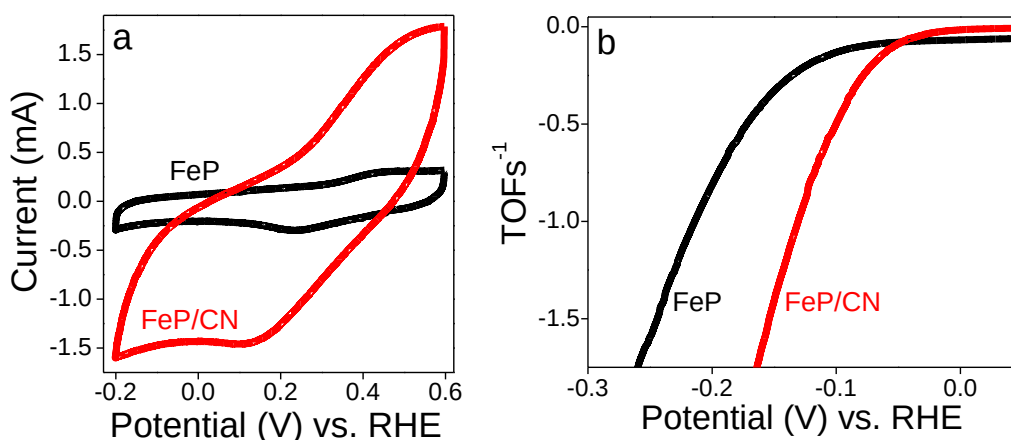


Figure 9: . Cyclic voltammograms recorded between -0.2 and 0.6 VRHE (a) and their corresponding TOF profiles vs. overpotential (b). Experiments were performed in a phosphate buffer solution with pH 7.

of 10 mA), FeP/CN electrode exhibits significantly higher TOF (0.55 s^{-1}) as compared to FeP (0.14 s^{-1}). This could presumably be attributed to uniform dispersion of FeP on carbon nanosheets, which renders more functional sites accessible for H^+ .

3.4. Conclusions

In summary, ultrathin and interconnected nanosheets of carbon were obtained in a single step by pyrolysis of low cost sodium citrate. Owing to high surface area and unique morphological features, carbon nanosheets guided the growth of fine-grained FeP nanocrystals with high dispersion qualities. Small particle size with improved dispersion imparted benign attributes, such as small surface-charge-resistance, high specific and electrochemically active surface area and high turnover frequency, to the electrode comprising FeP/CN. As a result, the electrode exhibited remarkable hydrogen evolution reaction, requiring only 104 mV to drive 10 mA cm^{-2} in acidic electrolyte. Estimated value of Tafel slope confirmed that electrochemical desorption (Heyrovsky reaction) was the rate-determining step. The findings of this study reveal a simple, cost-effective and scalable synthesis of ultrathin and interconnected carbon nanosheets, and its use as a robust support for the discrete nucleation and growth of active sites.

CHAPTER 4

The impact of microstructural features of carbon support on the electrocatalytic hydrogen evolution reaction

4.1. Introduction

Owing to carbon-free footprints, water electrolysis for large scale and sustainable H_2 production remains at the forefront of technology development. One of the essential elements of water electrolysis is the catalytic component. Currently, platinum (Pt) or Pt-based composition (Pt/C) are used as electrocatalyst. Owing to high cost and scarcity, development of Pt-less or Pt-free electrocatalysts for large scale deployment of electrolysis is inevitable. As a result, tremendous efforts are exerted to design and develop electrocatalysts with desired properties, such as high activity, low-cost and high operational stability. A wide variety of Pt-less electrocatalysts, such as transition metal-based carbides [39, 40, 59, 61, 104, 105], sulfides [106 - 108], nitrides [27], phosphides [6, 9, 67 - 69, 109], and borides [70, 110], are explored. In catalytic systems, use of conductive solid carbon as support for active sites is desired and remains essential, both from cost and performance viewpoints. It increases the utilization of the active sites by preventing their agglomeration, and reduces the metals usage. Furthermore, electrical synergy between catalytic centers and carbon surfaces may induce unique metal-support-interaction, resulting in substantial impact on critical electrode processes such as the interfacial equilibrium, adsorption and/or desorption of reactive species and their interaction with electrocatalysts surface, electrical conductivity, and so forth [111 - 113]. To this end,

besides the active sites, the role of solid supports is crucial in determining the catalytic activity, selectivity and overall performance of electrodes. Most of the HER-based investigations used carbon materials as solid support. These carbon-based supports significantly vary in their microstructural properties, such as surface area & porosity (microporous, mesoporous and macroporous), shape and morphology (spherical, nanotubes, nanofibers, nanosheets), electrical conductivity, and so forth. This variation is likely to have substantial impact on the properties and the performance of as-derived electrodes. For instance, Šljukić and coworkers dispersed Mo₂C on carbon nanotubes and carbon xerogel, and variation in HER performance was noticed [114]. In another investigation, Mo₂C dispersed on carbon nanotubes and XC exhibited significantly different performance towards HER [39]. However, no detailed interpretation was presented. Recently, we demonstrated superior HER performance of Mo₂C embedded within metal-organic framework-derived mesoporous carbon than that of commercial carbon [40]. Numerous examples could be presented here highlighting the significance of carbon support in determining electrocatalytic activity [115 - 118].

In spite of the fact that the contribution of carbon supports is significant in designing and developing high performance HER electrocatalysts, a systematic study highlighting the impact of key microstructural attributes of carbon, such as specific surface area, morphology and electrical conductivity, on the properties and performance of the electrode towards HER reaction is lacking. Herein, an attempt is made to investigate the effect of carbon features on the properties and performance of electrocatalyst towards HER. To accomplish this, three types of carbon supports, namely carbon black – Vulcan XC-72 (denoted as XC), carbon nanotubes (denoted as CNTs) and carbon nanosheets (denoted as

CN), endowed with different surface area, morphology and electrical conductivity are selected. The surface of these carbon materials are modified with iron monophosphide (FeP), a low cost and high performance electrocatalyst for HER. The propensity of the electrodes is investigated in 0.5 M H₂SO₄ aqueous electrolytes. As expected, the performance of the electrodes was driven by microstructural features of carbon supports. The modifications, before and after FeP loading, in predominant features of the electrodes, such as specific surface area, electrochemically active surface area (ECSA), intrinsic electrochemical impedance, charge transfer resistance (R_{ct}), turnover frequency (TOF), and Tafel slopes, are quantified and correlated to the performance.

4.2. Experimental

4.2.1. Chemicals.

Sodium citrate ($\geq 99\%$), iron dichloride (99.9%), ethanol anhydrous, hydrochloric acid (37%), sodium hypophosphite ($\geq 99\%$), and multiwalled carbon nanotubes (CNTs) were purchased from Sigma-Aldrich. Carbon black Vulcan XC and Pt/C (20% on carbon) were obtained from Johnson Matthey Fuel Cells.

4.2.2. Preparation of Interconnected Ultrathin Carbon Nanosheets (CN).

Approximately 5 g of sodium citrate was taken in alumina crucible and transferred in a tube furnace under the flow of nitrogen. The temperature was raised to 800 °C (3 °C min⁻¹) and kept constant for 2 h. After the heat treatment, the product was collected and washed with 10% hydrochloric acid and with plenty of deionized water. Finally, the product was dried at 90 °C in an oven.

4.2.3. Preparation of Iron Phosphide/Carbon.

A measured amount (40 mg) of iron chloride (FeCl_2) was dissolved in ethanol, followed by addition of 25 mg carbon supports (carbon black Vulcan XC, carbon nanotubes, or carbon nanosheets) in a glass vial. After 5 h of stirring, the suspension was transferred to a watch glass to evaporate the ethanol at ambient conditions. Upon solvent evaporation, the sample was kept in an oven at 90 °C for 24 h. A calculated amount of as-prepared iron containing carbon precursor and sodium hypophosphite (NaPO_2H_2) were taken in two crucibles and transferred in a tube furnace under the flow of nitrogen. The crucible containing NaPO_2H_2 was placed at the upstream. The weight ratio of precursor and NaPO_2H_2 was 1:20. The temperature of furnace was raised to 400 °C ($3\text{ }^\circ\text{C min}^{-1}$) and the heat treatment was performed for 2 h. Upon phosphidation, carbon-supported FeP was obtained and used for the preparation of working electrode for HER.

4.2.4. Characterization.

The as-prepared electrocatalysts were characterized by transmission and high-resolution transmission electron microscope (TEM/HR-TEM, FEI Tecnai TF20), X-ray diffractometry (XRD, Rigaku MiniFlex), X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi), and BET surface area analyzer (Micromeritics ChemiSorb 2750).

4.2.5. Electrochemical Characterization.

A suspension comprising electrocatalyst (5 mg), water and ethanol (50% v/v) and 40 μl of 1.66 % wt. Nafion® was prepared and sonicated for approximately 30 min. The suspension was drop-cast on a glassy carbon (GC) disc (5.0 mm diameter) and

allowed to dry. The drop-cast process was repeated to obtain a catalyst loading of 1 mgcm⁻². A three-electrode cell assembly with saturated calomel electrode (mercury/mercury chloride, SCE), graphite rod, and working electrodes was used to evaluate the electrocatalysts performance. The reference electrode is calibrated and reported against reversible hydrogen electrode (RHE). An aqueous solution of 0.5 M H₂SO₄ is used as electrolyte. The dissolved oxygen was removed from the working electrolyte using hydrogen gas. Linear sweep voltammetry was recorded at a scan rate of 5 mVs⁻¹. The current density was estimated using the geometric area of the GC electrode, and reported after *iR* correction. Electrochemical impedance spectroscopy (EIS) was performed in 0.5 M H₂SO₄ between the frequency range of 10⁵ Hz and 0.01 Hz with ac amplitude of 10 mV. The results are normalized to the geometric surface area of the GC electrode.

4.3. RESULTS AND DISCUSSION

4.3.1. Structural Characterization.

Powder X-ray diffraction of pristine and FeP-modified carbon supports are shown in Figure 10a and b, respectively. Broad and low-intensity diffractions centered at 26.5° and 43.2° correspond to (002) and (100) planes of carbon [82]. As compared to XC and CNT, the intensity of diffraction peaks in the case of carbon nanosheets was somewhat

Lower, indicating amorphous characteristics. The XRD of all the three carbon supported-FeP samples were similar; the diffraction peaks located at 32.8° (011), 37.2° (111), 48.3° (211), and 56.1° (013) are attributed to iron monophosphide (FeP) with a orthorhombic structure (JCPDS 65-2595) [83].

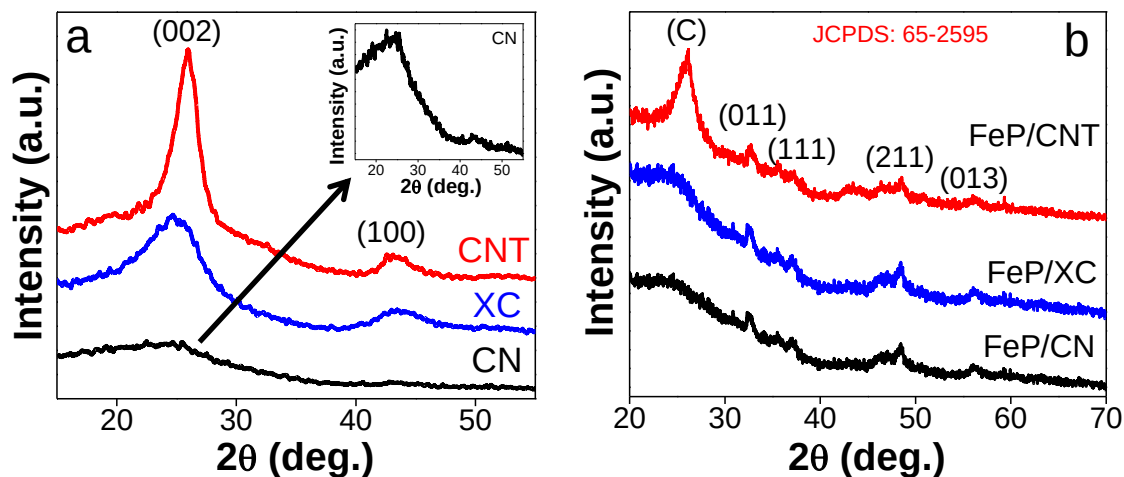


Figure 10: Powder XRD of (a) pristine carbon supports and (b) FeP-modified carbon supports.]

X-ray photoelectron spectroscopy (XPS) is employed to verify the chemical compositions and the oxidation states of the electrocatalysts. The XPS analyses of the three specimens were comparable – FeP/CN spectra are shown in Figure 11, while those for FeP/CNT and FeP/XC are presented in Figures S10, 11. Survey spectrum substantiated the formation of intended elemental composition, which includes iron (Fe), phosphorous (P), and carbon (C). In the spectrum of C 1s, besides characteristic peak of graphitic carbon at 284.9 eV, presence of C–O (at 286.5 eV) [84] was registered. The peaks at 711.6 and 724.8 eV in the Fe 2p spectrum are attributed to Fe 2p_{3/2} and Fe 2p_{1/2} respectively, which agrees well with those reported in the literature for Fe coordinated to P [85, 119]. The peaks at 130.3 and 131.4 eV in the P 2p spectrum account for 2p_{3/2} and 2p_{1/2} of P bonded to Fe [85]. In addition, the intense and broad peak observed at 134.4 eV is assigned to PO₄³⁻[85]. Importantly, the analyses confirmed the presence of identical FeP amount (40 wt%) on each carbon support.

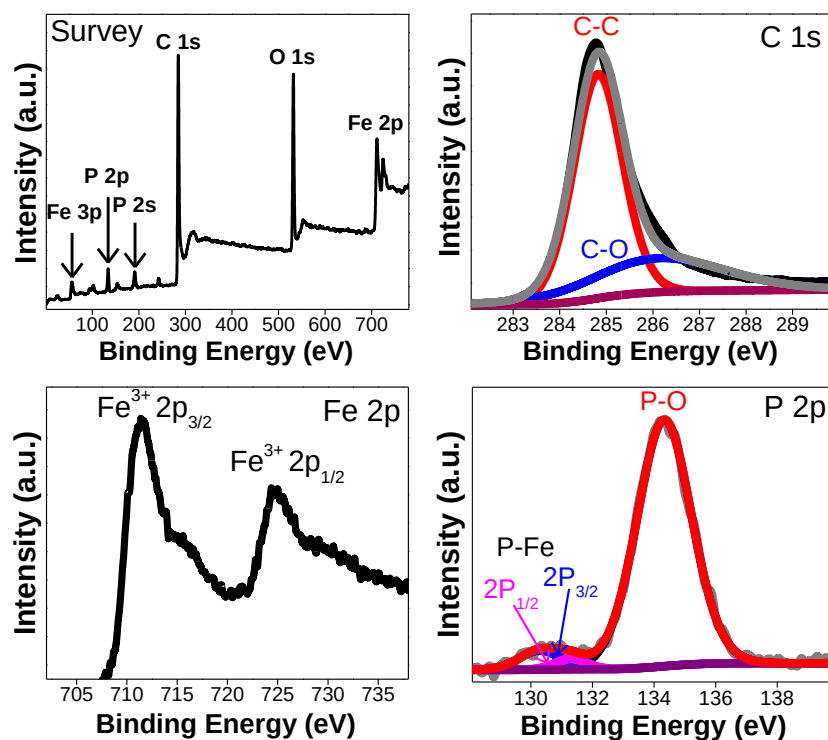


Figure 11: XPS signatures of FeP/CNT

Microstructural and morphological features of electrocatalysts were collected with the aid of transmission electron microscopes (Figure 12). Figure 12a,b show the morphological features of FeP/XC. The FeP/XC possessed irregular and ill-defined morphology, closely resembling to the shape and morphology of pristine XC. The FeP particles were agglomerated, with size in the range of 20 to 50 nm. The FeP particles were agglomerated, with size in the range of 20 to 50 nm. The particle size and dispersion of FeP on CNT surface are highlighted in Figure 12d,e. Unlike FeP on XC, the size of FeP spherical nanoparticles dispersed on CNT was smaller (between 10 and 30 nm) with better dispersion qualities. The TEM images shown in Figure 12g,h highlight the size, morphology and homogeneity of FeP dispersed on carbon nanosheets. The TEM of carbon derived from

pyrolysis of sodium citrate indicates the formation of homogeneous and interconnected nanosheets of carbon. Furthermore, the edges of these sheets are slightly rolled up, resembling to the characteristics of graphene layers. Each sheet consists of several layers, and the thickness of nanosheets, determined by TEM, was estimated to be <5 nm. Interestingly, in the case of FeP/CN, the FeP nanoparticles were highly homogeneous, spherical in shape with size in the range of 3 to 15 nm, and uniformly distributed across the surface of carbon nanosheets. High surface area and unique 2D morphology of nanosheets seem to improve the surface interaction between carbon functionalities and iron chloride, resulting in fine and uniformly dispersed FeP after phosphidation. The HR-TEM images of FeP, Figure 12c,f,i, show high degree of crystallinity. In all the cases, the interplanar distance is computed to be 0.27 nm, in good agreement with 0.27 nm estimated using XRD data for the (011) plane.

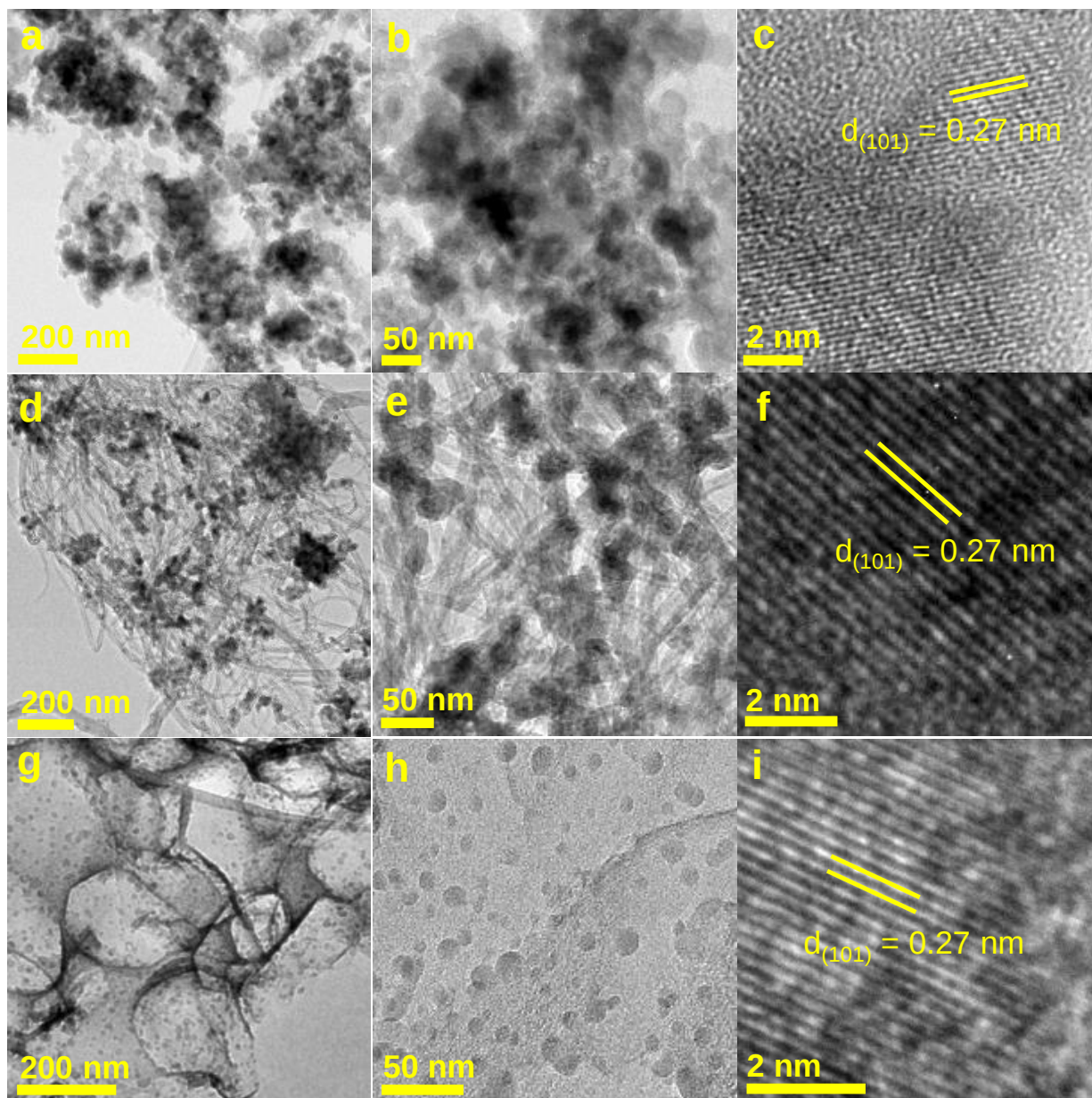


Figure 12: TEM and HR-TEM of FeP/XC (a-c), FeP/CNT (d-f) and FeP/CN (g-i)

4.3.2. Electrocatalytic Hydrogen Evolution Reaction.

The performance of as-prepared electrodes was evaluated towards hydrogen evolution reaction (HER) in acidic electrolyte (0.5 M H_2SO_4). The current density was obtained after normalization of absolute current with the geometric area of the glassy carbon electrode. The performance is evaluated in terms of overpotential (η), required to drive benchmark current density 10 mAcm^{-2} . Figure 13 compares the performance of FeP/XC, FeP/CNT and

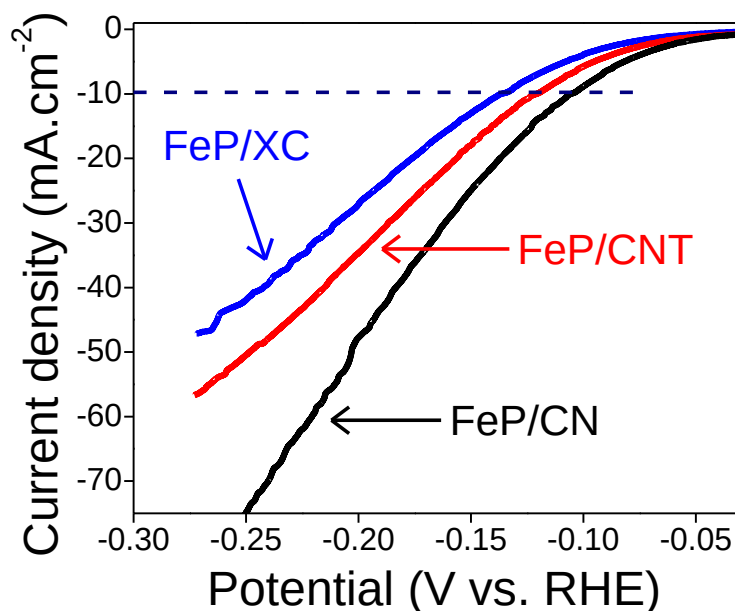


Figure 14: LSV of FeP/XC, FeP/CNT and FeP/CN in 0.5M H₂SO₄

FeP/CN electrodes. The respective η are measured to be 138, 123 and 104 mV, though potential difference increases with increasing current density. For instance, FeP/XC required 263 mV, while FeP/CNT and FeP/CN needed 231 mV and 193 mV to generate 45 mAcm⁻². As expected, distinct difference in the performance is noticed. Attempt is made to correlate the variation in performance to specific and electrochemically active surface area (ECSA), intrinsic electrical conductivity, surface charge transfer resistance (R_{ct}), and turnover frequency (TOF).

4.3.3. Specific Surface Area and Electrochemically Active Surface area.

The BET surface area, of pristine XC, CNTs and CN are determined to be 222.1, 150.9 and 364.8 m²g⁻¹, respectively. In all the cases, the surface area was substantially reduced upon FeP loading, presumably due to reduction in carbon content. The respective surface areas for FeP/XC, FeP/CNT and FeP/CN are measured to be 82.1, 78.4 and 167.1 m²g⁻¹. Contrary

to specific surface area, the ECSA increased after FeP loading. The double layer capacitance (C_{dl}) of cyclic voltammograms (CVs), obtained at different scan rates between 5 and 100 mVs^{-1} , is measured and used to estimate the ECSA of the electrodes. The CVs and the respective slopes of electrodes comprising pristine carbon materials are shown in Figure 14. Usually, higher C_{dl} corresponds to higher ECSA [5]. The ECSA of XC, CNTs and CN are quantified to be 4.01, 13.1 and 26.9 mFcm^{-2} , respectively. Although the specific surface area of XC was higher than that of CNT, later showed > 3 folds higher ECSA presumably due to unique morphological and electrical characteristics.

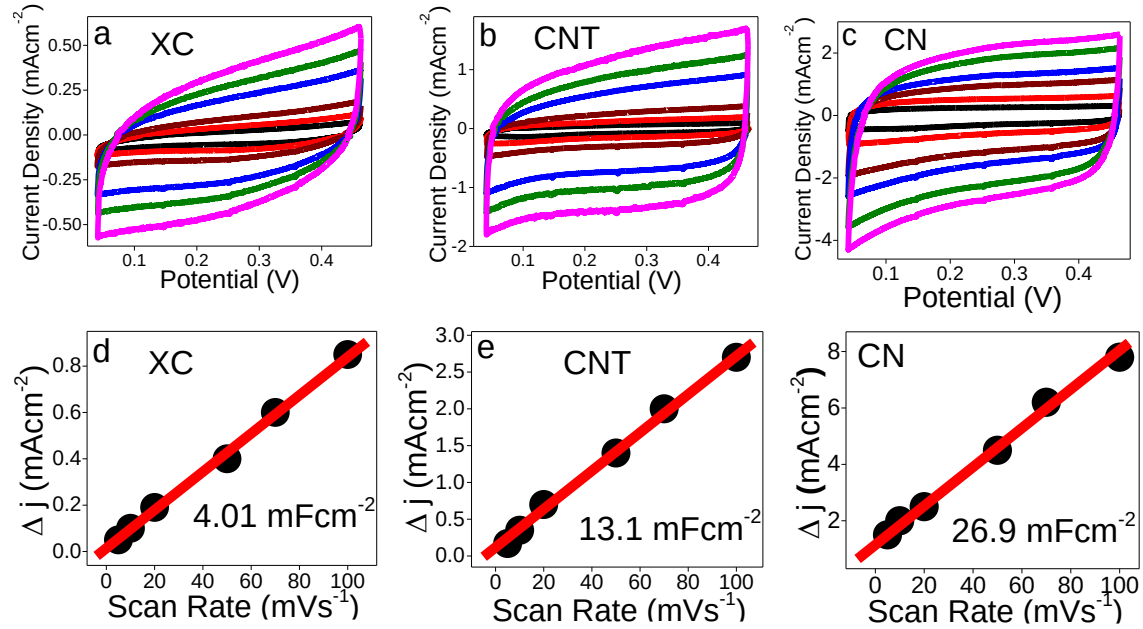


Figure 15: Pristine carbon electrodes: CVs (a-c) and their respective plots of the current density (d-f) at 0.248 V_{RHE} vs scan rate. The linear slopes are equivalent to twice of the electrochemical double layer capacitance (C_{dl})

This suggests that the microstructural attributes of carbon materials have substantial impact on the ECSA. The CVs and corresponding slopes of FeP-modified carbon electrodes are shown in Figure 15. As evident, an increase in ECSA was discerned after FeP loading – the respective ECSA of FeP/XC, FeP/CNT and FeP/CN are determined to be 7.30, 25.8

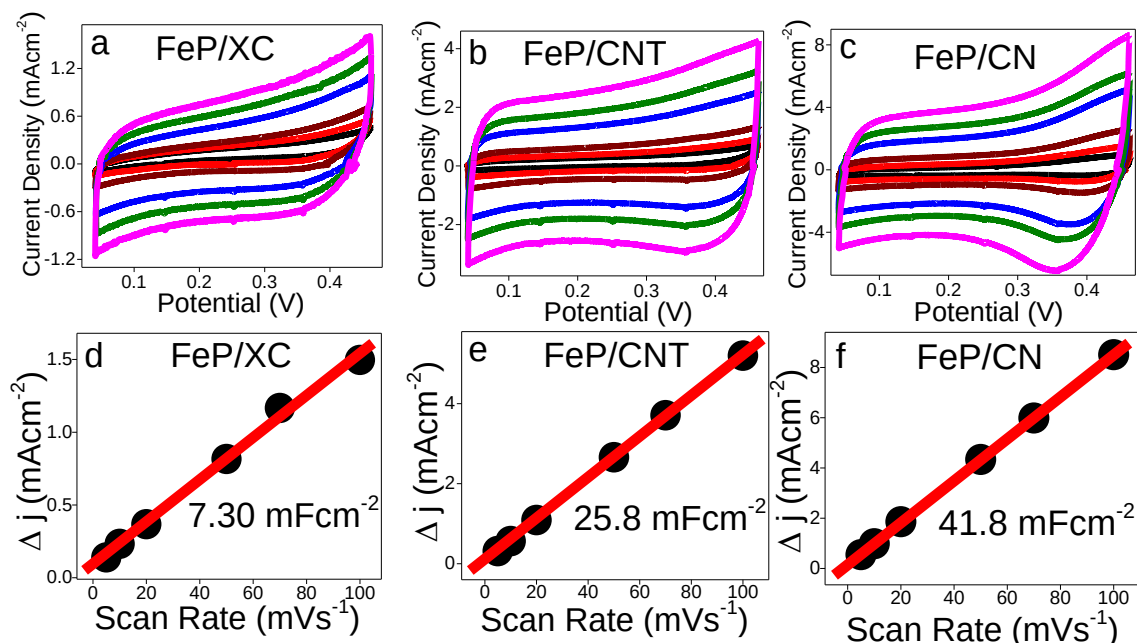


Figure 16: FeP-modified carbon electrodes: CVs (a-c) and their respective plots of the current density (d-f) at 0.248 VRHE vs scan rate. The linear slopes are equivalent to twice of the electrochemical double layer capacitance (C_{dl})]

and 41.8 mFcm^{-2} . This clearly implies that FeP has strong affinity towards H^+ , which renders considerable accumulation of charges.

4.3.4. Electrical Conductivity and Charge Transport.

In addition to specific surface area and ECSA, other critical features that determine the electrode's performance are bulk conductivity and charge transport. Electrochemical impedance spectroscopy (EIS) was employed to estimate the intrinsic electrical conductivity and surface charge transfer resistance (R_{ct}) before and after FeP loading. The variation in electrodes properties is correlated to the performance. The frequency range was specified between 10^5 Hz and 0.01 Hz keeping ac amplitude 10 mV . The geometric surface area of the working electrode was used to normalize the impedance plots. On the basis of EIS findings, the two-time constant parallel model was selected to fit the data. This equivalent circuit model (Figure S13) consists of R_s in series

with two parallel constant phase element-resistance. The R_s accounts for concerted resistances, including the resistances arising from wiring (R_{wiring}), carbon support (R_{carbon}), FeP ($R_{\text{phosphide}}$) and solution (R_{soln}) [120]. In addition, R_{ct} , R_p and C_{dl} correspond to charge transfer resistance, resistance arising from porous surface texture, and capacitance, respectively.

The potential-dependent evolution in Nyquist plots (real vs. imaginary impedance) of pristine XC, CNTs and CN are shown in Figure 16a-c (corresponding Bode plots are presented in Figure S14-16). Plots were constructed as a function of overpotential ($\eta = 110, 150, 200, 250, 300, 350$, and 400 mV). The kinetics of the charge transfer at the interface of electrode surface/electrolyte is manifested by the semicircular dispersion of impedance – shorter semicircular dispersion is translated into faster charge transfer and vice versa. In all cases, faster electron transfer kinetics is registered with increasing η . Among pristine carbons, the electrode comprising CNTs exhibits the highest electrical conductivity

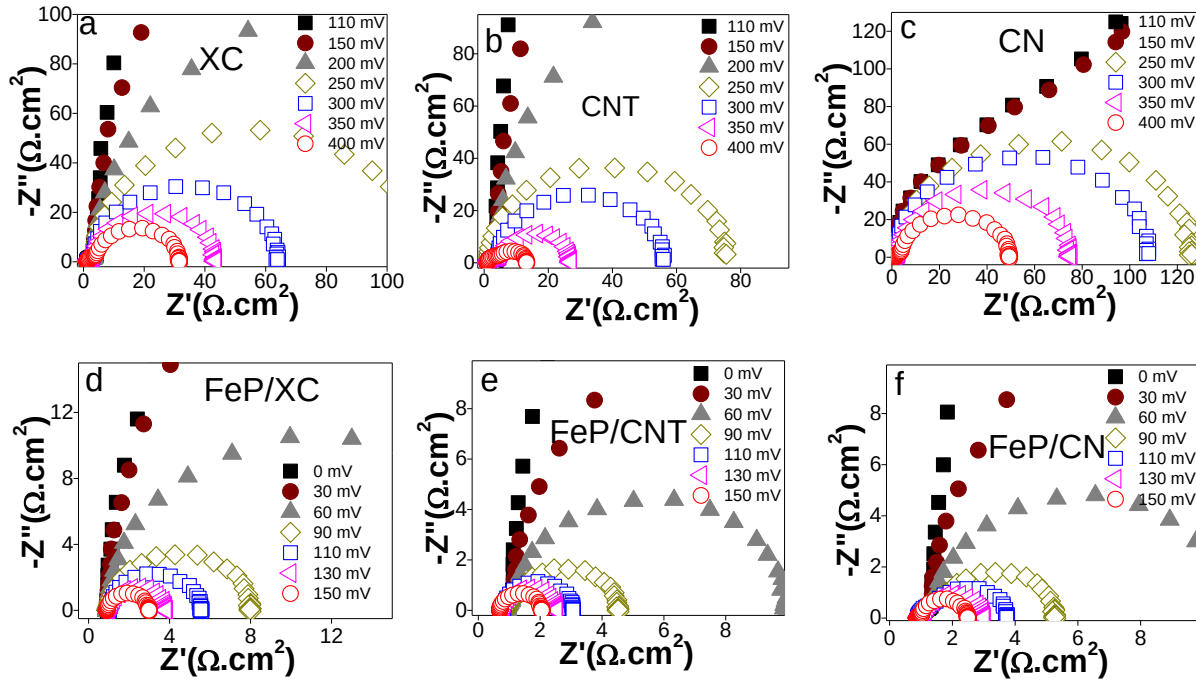


Figure 17: Potential-dependent evolution in Nyquist plots of pristine and FeP-modified carbon electrodes^[5]

followed by XC and CN at all applied overpotential. This finding is consistent with (1) the degree of crystallinity or graphitic nature of carbon, as shown by XRD (Figure 10), and (11) one-dimensional morphology which favors directional flow of electrons. The potential-dependent evolution in Nyquist plots of FeP/XC, FeP/CNT and FeP/CN

is shown in Figure 16d-f. The measurements were conducted at $\eta = 0, 30, 60, 90, 110, 130$, and 150 mV. Evidently, R_{ct} decreases significantly with increasing η . Resistance values, R_s , R_p , and R_{ct} , obtained by fitting of electrochemical data are listed Table S1 and S2. In all the cases, FeP-modified carbon electrodes exhibited substantially lower impedance as compared to their pristine carbon counterparts, suggesting highly electrically conductive characteristics of FeP. The notion that FeP is intrinsically more conductive than pristine carbon is reinforced by Nyquist plots (Figure S17) at 0 mV. As evident, the FeP electrode possess the lowest impedance. The electrode comprising FeP/CNT is found to be the most electrically conductive among FeP-modified carbon electrodes at all applied overpotentials (Figure 16d-f). For instance, at $\eta = 0$ mV, the size of semicircle was determined to be $\text{FeP/XC} > \text{FeP/CN} > \text{FeP/CNT}$, implying lower and higher intrinsic conductivity of FeP/XC and FeP/CNT, respectively. Furthermore, at $\eta = 90$ mV, the R_{ct} for FeP/XC, FeP/CNT and FeP/CN are computed to be ~ 8 , ~ 4.5 , and $\sim 5.3 \text{ } \Omega \cdot \text{cm}^2$, respectively. Although the pristine XC was electrically more conductive than CN, FeP/CN exhibits lower impedance than that of FeP/XC. This could presumably be ascribed to the virtue of particle size and dispersion of FeP. In the case of FeP/CN, smaller and well-dispersed FeP nanoparticles are likely to produce effective metal-support-interaction, which can improve not only the intrinsic conductivity and R_{ct} but also the catalytic ability. In addition to smaller ECSA, lower conductivity and higher R_{ct} explains the inferior performance of the

FeP/XC electrode. Interestingly, FeP/CNT electrode exhibits slightly better conductivity and lower R_{ct} as compared to FeP/CN. This is attributed to better electrical conductivity of pristine CNTs. Despite the fact that the FeP/CNT electrode is intrinsically more conductive than that of FeP/CN, it exhibited lower HER performance. This is attributed to notably high specific and ECSA of FeP/CN, which seem to offset poor conductivity by rendering greater number of active sites. This was corroborated by estimating the turnover frequency (TOF).

4.3.5. Turnover Frequency.

The TOF relates to the number of molecular reaction occurring at per catalytic center per unit time. Estimation of TOF gives fair idea about specific activity of active sites – larger TOF values translate into better catalytic ability. The TOF can be quantified by eqn (1);

$$TOF = JA / 2FN \quad (1)$$

Where, J ($A\text{cm}^{-2}$) accounts for the geometric current density, which is determined through LSV measurements, A is the working electrode's geometric area, $1/2$ includes two electrons that are consumed in the formation of one H_2 gas from water, F is the Faradic constant (96485 Cmol^{-1}), N is the number of catalytic centers or active sites (mol).

The N was determined by performing LSV measurements in phosphate buffer solution (1.0 M). The potential was scanned in the range of $-0.2 - +0.6\text{ V}_{RHE}$ applying a scan rate of 20 mV s^{-1} . Owing to the difficulty in ascribing the LSV peaks to any redox couple, N should be proportional to the integrated charge over the potential between -0.2 V_{RHE} and $+0.6\text{ V}_{RHE}$. The upper limit of catalytic sites can be calculated using eqn (2), if a one electron redox reaction is assumed.

$$N = Q/2F \quad (2)$$

Q is the voltammetric charge.

The cyclic voltammograms of all the three electrodes are compared in Figure 17a. The respective number of active sites for FeP/XC, FeP/CNT and FeP/CN is determined to be 1.32×10^{-8} , 1.56×10^{-8} and 1.83×10^{-8} mole, respectively. Figure 17b shows the profile of TOF vs potential. At $\eta = 105$ mV, the electrode comprising FeP/CN exhibits the highest TOF (1980 h^{-1}) followed FeP/CNT (1548 h^{-1}) and FeP/XC (1332 h^{-1}). The findings corroborate that the FeP/CN electrode is endowed with comparatively higher catalytic sites and thus TOF. Higher surface area and 2D morphology of the nanosheets seem to collectively assist in the formation of small and uniformly-dispersed FeP nanoparticles.

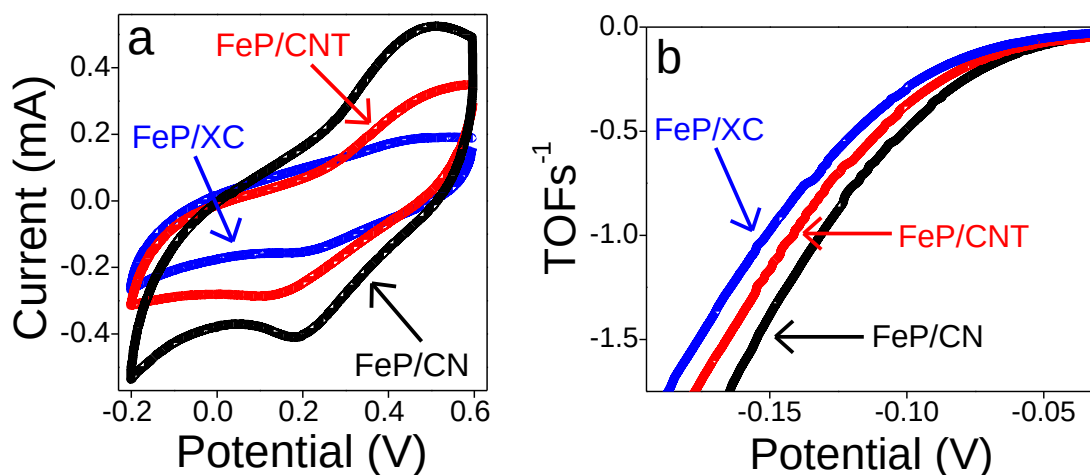
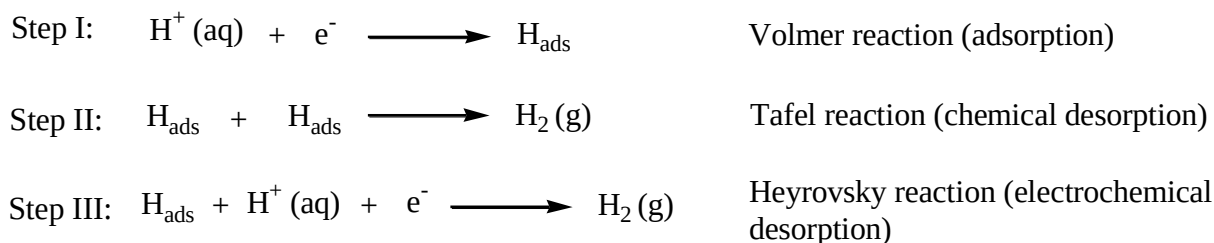


Figure 18: Cyclic voltammograms (a) and corresponding TOF profiles vs overpotential (b)

4.3.6. Tafel Slopes and Reaction Kinetics.

Any correlation between carbon properties and reaction kinetics of hydrogen evolution is investigated by estimating Tafel slopes. On the basis of proton reduction, adsorption and desorption under acidic conditions, three elementary steps, as follows, are proposed;



Tafel slopes, obtained by plotting semi-log of $1/R_{\text{ct}}$ against overpotential, for FeP/XC, FeP/CNT, and FeP/CN are shown in Figure S9-12, and respective values are computed to be 89.3, 63.2 and 63.5 mVdec⁻¹. Also included is the Tafel slope of the pure FeP, with 76.5 mVdec⁻¹. In all the cases, the calculated values suggest that HER proceeds via Volmer-Heyrovsky route. Furthermore, electrochemical desorption of H^+ and H_{ads} (Step III) is presumably the rate-determining step [54, 57]. The findings indicate that the impact of investigated microstructural features of carbon on the HER mechanism is insignificant.

4.4. Conclusions

In summary, the study demonstrated the impact of crucial carbon features, such as morphology, specific surface area, and electrical conductivity, on the properties and the performance of electrodes comprising FeP/carbon towards hydrogen evolution reaction. Upon FeP loading on carbon supports, the specific surface area decreases invariably. On the contrary, the electrochemically active surface area increased substantially. This suggests the presence of strong affinity between FeP surface and H^+ . The trend of electrical conductivity in pristine carbon materials was determined to be – carbon nanotubes > carbon nanosheets > Vulcan XC-72. The FeP was found to be electrically much more conductive than the pristine carbon materials. Invariably, a substantial improvement in the electrical conductivity of the electrodes was discerned after FeP loading. The electrochemical

impedance findings suggest that the intrinsic electrical conductivity of carbon is not the only factor that determines the electrical conductivity and surface charge resistance of composite FeP/C electrodes – particle size and dispersion qualities of the active sites also contribute. For instance, although the pristine XC was electrically more conductive than the carbon nanosheets, the FeP/XC was less conductive and has higher charge transfer resistance as compared to the FeP/CN. Higher specific surface area and two-dimensional morphology of the carbon nanosheets rendered the growth of smaller FeP nanoparticles with better dispersion qualities. This led to the effective metal-support-interaction, resulting in improved electrical response.

Despite the fact that carbon nanosheets were electrically least conductive, the electrode comprising FeP/CN exhibited the highest HER performance followed by FeP/CNT and FeP/XC. While the inferior performance of FeP/XC electrode is ascribed to both lower electrochemically active surface area and electrical conductivity, better performance of FeP/CN is attributed to high specific and electrochemically active surface area. Higher specific and electrochemically active surface area translates into greater number of active sites or turnover frequency. This evidently highlights the fact that the deficiency in electrical conductivity of electrodes could be counterpoised by high specific and electrochemically active surface area. Analyses of Tafel slopes suggest that the HER mechanism remains less sensitive towards surface area and conductivity of the carbon supports. We believe that the findings of this study would provide fresh impetus for designing and developing Pt-free active electrodes for the hydrogen evolution reaction.

CHAPTER 5

The influence of mesoporous structure of the carbon support in the dispersion and the growth of electrocatalytic active sites for the hydrogen evolution reaction

5.1. Introduction

Due to the high cost and scarcity of platinum (Pt), which limits the use of it and its composites (Pt/C) as electrocatalysts for large scale and sustainable H₂ production, development of efficient noble metal free electrocatalysts is remain in the forefront. For the sake of obtaining an efficient Pt-less electrocatalyst various transition metals sulfides [106 – 108], carbides [39, 40, 59, 61, 104, 105, 121] nitrides [110], borides [27, 70] and phosphides [6, 9, 67 – 69, 109, 122] were widely explored. The use of carbon based composite with transition metals as electrocatalysts was widely investigated. Form both cost and performance points of view it desired and useful to use a solid carbon as support. The utilization of this support can potentially reduce the amount of metal needed, and facilitate the dispersion of the metal active sits which significantly prevent the metal agglomeration. Moreover, a unique metal-carbon interaction is taking place which enhances the electrical conductivity of the electrocatalyst [111 – 113]. The morphology and textural characteristics of the support material have a significant role in the essential catalytic interfacial process such as adsorption, desorption, interfacial equilibrium and the electrochemical interaction of the reactive species with electrocatalyst surface.

Additionally, the accessible catalytic active sites on the carbon support has crucial role in the HER. Up to date, several studies have reported the utilization of various types of carbons with different structural properties such as the morphology (nanotubes, nanosheets, nanospheres & etc.), electrical conductivity, surface area and porosity (micro, meso, macro and nonporous). This difference in carbon properties can potentially has great influence on the HER performance. For example the HER performance of Mo_2C was compared when it dispersed in two different carbon support (CNT and XC) [39]. Additionally, the same Mo_2C electrocatalyst was reported dispersed in porous carbon derived from metal organic framework and compared with XC as support [40]. In another study FeP nanoparticles were supported on three different types of carbons (XC, CNT and carbon nanosheets), and the effect of carbon morphology, HER performance and electrochemical characteristic were investigated [123]. Although the influence of the carbon support on the HER has been investigated, yet no study investigated the effect of carbon support porosity on HER, which can affect the dispersion and the agglomeration of the electrocatalyst particles.

Here, we report the HER performance of FeP particles encapsulated and dispersed on a series of highly mesoporous carbon supports with different pore volume (from 1.1 to 3 cm^3g^{-1}) and tightly controlled mesopore size (6 to 17 nm), which is among the best for similar system reported previously for HER.

To ensure an accurate probing of the impact of carbon support pore size and pore volume on the HER performance, several electrochemical investigations such as electrochemical active surface area (ECASA), electrochemical impedance spectroscopy (EIS) and turnover frequency (TOF) were carried out. The presented results clearly indicate that the utilized HMCs are promising support material in HER application. Notably, besides

electrocatalytic performance, our approach with fine control over the porosity can be utilized as a model system to investigate the role of textural characteristics of carbon support material in the HER performance.

5.2. Experimental

5.2.1. Preparation of Highly mesoporous carbons (HMC)

Two types of colloidal silica (based on particles size) were obtained 4 and 20 nm respectively. The HMCs were prepared by mixing a specific amounts of sucrose with the silica, the prepared carbon was donated CY-AB, where Y is the average size of the silica (4 or 20 nm), where AB is the silica to sucrose ratio respectively, for example to prepare 4-11, a ratio of 1:1 between sucrose and colloidal silica (4 nm), Next the mixture was placed in the freeze drying system, After a dry powder was collected, the as-prepared mixture was subjected to temperature 1000°C (3°C/min) under N₂ atmosphere for 3h. The collected black powder was placed in 3M NaOH at 80°C for overnight. Then the powder was washed with DI water several time until the PH restore to 7. Finally the sample was dried at 70°C under vacuum. To prepare HMCs (2011 and 2021), the same above method was applied by varying the ratio between silica and sucrose and the use of silica (20 nm size).

5.2.2. Preparation of Iron Phosphide/ Highly mesoporous carbon

Three iron phosphide electrocatalysts were prepared by dissolving a measured amount (57 mg) of anhydrous iron chloride (FeCl₂) in 20ml ethanol in three different capped vials, then the as-prepared porous carbon (C4-11, C20-11 and C20-21) were added in the vials, the mixture was stirred for 6h, then it was transferred to watch glass and allowed to evaporate under ambient condition, the samples were further dried by keeping in oven under vacuum

at 60°C for 5h and black powder samples were obtained. In two crucibles the porous carbon containing iron and sodium hypophosphite (NaH_2PO_2) with 1:20 ratio were placed into a tube furnace, the temperature of the furnace was 400°C (3°C /min) under nitrogen stream for 2h. After the heat treatment FeP/ C4-11, FeP/C20-11 and FeP/C20-21 samples were obtained and used as working electrodes for the HER.

5.2.3. Characterization

Characterization of the as-prepared electrocatalytic compositions was carried out by X-ray diffractometry (XRD, Rigaku MiniFlex), X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi), field emission scanning electron microscope (FESEM, Tescan Lyra-3), transmission and high-resolution transmission electron microscope (TEM/HR-TEM, FEI Tecnai TF20), and BET surface area analyzer (Micromeritics ChemiSorb 2750).

5.2.4. Electrochemical characterization

The HER performance was investigated in a typical three-electrode electrochemical cell. The assembly was operated by a potentiostat (EG&G 273A). The procedure for the preparation of working electrode is as follows. The as-prepared electrocatalysts (5 mg), water and ethanol (50% V/V), and 40 μl of 1.66% wt. Nafion® were mixed together. The resulting slurry was sonicated for approximately 0.5 h to prepare the ink. Then, a pre-determined volume of the ink was deposited on a pre-cleaned glassy carbon (GC) disc electrode. The diameter of the GC electrode was 5.0 mm. The ink was allowed to dry at ambient conditions. The desired catalyst loading (1 mg cm^{-2}) was achieved by repeating the deposition and drying steps. A graphite rod (0.250" OD $\times$ 12" long) was used as a counter electrode, while saturated calomel electrode (Hg/HgCl_2 ,

SCE) was used as the reference electrode, respectively. The SCE potential was measured experimentally, and presented against reversible hydrogen electrode (RHE) after conversion. Linear sweep voltammetry was performed in 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mV s⁻¹. Geometric area of the GC electrode was used to normalize the recorded current, and the current density (J_g) is iR corrected. The measurements of electrochemical impedance spectroscopy (EIS) were conducted in 0.5 M H₂SO₄ in the frequency range of 10⁵ Hz and 0.01 Hz with ac amplitude of 10 mV. All the EIS data was normalized to the geometric area of the GC electrode. Before and during EIS measurements, the electrolyte solution was saturated with H₂ gas.

5.3. Results and discussion

The adopted approach to synthesize the HMCs leads to an open interconnected carbon matrix with tight control mesopore size and tunable mesopore volume. Figure 18a shows the N₂ adsorption desorption isotherms for all the synthesized HMCs. The N₂ isotherms indicate IV- type confirming the presence of mesopores. Therefore, all the HMCs can provide fast and accessible pathways for the required reactions. Notably, the adopted approach to synthesis the HMCs reduce the possibility of silica template aggregation. This can be ascribed to the grown ice crystals during the freeze-casting which lock the silica template and ultimately reduce the possibility of silica aggregation. This was confirmed by the existence of a single dominant peak in pore size distribution as can be seen in Figure 18b. The as-prepared HMCs C20-21, C20-11, and C4-11 demonstrate single peak centered around 17, 17, and 7nm, respectively. Table1 lists different textural characteristics of all the synthesized HMCs.

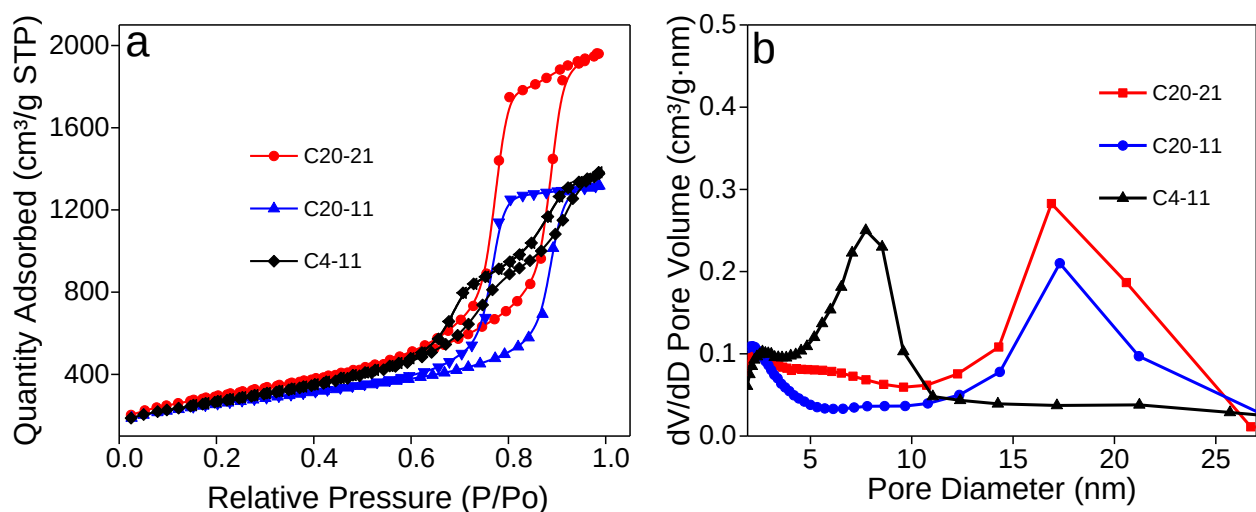


Figure 19: N₂ adsorption-desorption isotherms (a) and the BJH pore size distribution.

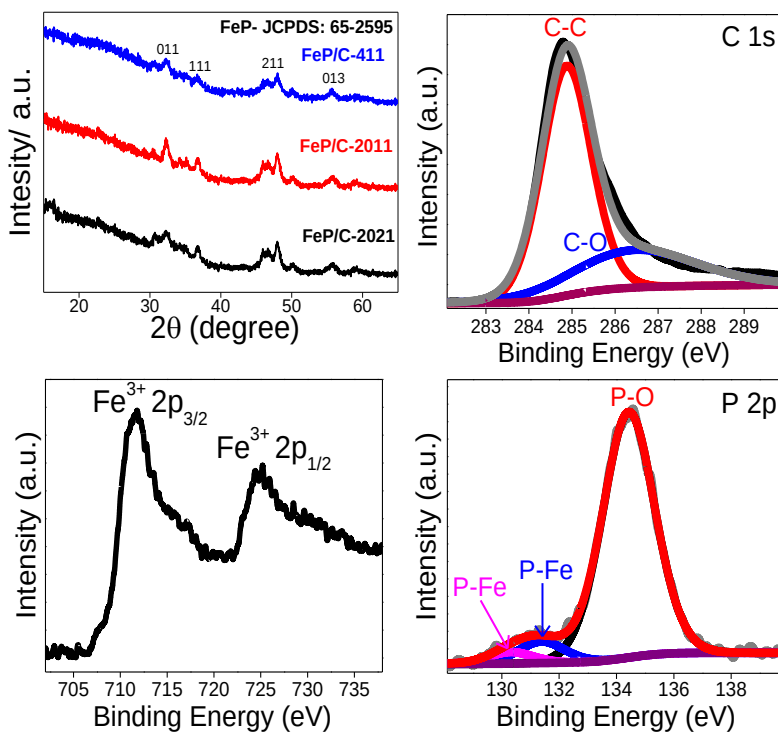
Table 2: Textural characteristics HMCs obtained via nitrogen adsorption at 77 K.

	surface	t-plot	Mesopore	Total	Mesopore	Micropore	Average
	area	Micropore	Surface	Pore	Volume	Volume	Mesopore
			Area	Volume			Size
	[m ² g ⁻¹]			[cm ³ g ⁻¹]	[cm ³ g ⁻¹]	[cm ³ g ⁻¹]	[nm]
		[m ² g ⁻¹]	[m ² g ⁻¹]				
C4-11	947	59	888	2.2	2.2	0.02	7
C20-11	884	176	708	2	1.9	0.08	17
C20-21	1037	72	965	3	2.9	0.08	17

5.3.1. Structural characterization of FeP/HMCs

The powder X-ray diffraction of pristine carbons (C4-11, C20-11 and C20-21) are shown in figure, two diffraction peaks are observed at 26.5°(002) and 43.2°(100) are attributed

to carbon, the characteristic of the carbon was amorphous due the relatively lower intensity peaks. The XRD for three porous carbons / FeP composites was also carried out, the diffraction peaks at 32.8° , 37.2° , 48.3° , and 56.1° are corresponded to (011), (111), (211), and (013) respectively, according to (JCPDS 65-2595) the diffraction peaks are attributed to the orthorhombic FeP. Information about the chemical composition and oxidation state was revealed using X-ray photoelectron spectroscopy (XPS), two peaks were observed in C 1s spectrum at 286.5 and 284.9 eV corresponding to C-O and graphitic carbon respectively for the carbon in the FeP/HMC composite. The peaks located at 711.6 and 724.8 eV account for $\text{Fe}^{3+}2p_{3/2}$ and $\text{Fe}^{3+}2p_{1/2}$ respectively which



show an exFigure 20: XRD and XPS of FeP/C-411

pectrum

showed the presence of $2P_{3/2}$ (130.3 eV) and $2P_{1/2}$ (131.4 eV). In addition, the intense and broad peak observed at 134.4 eV is assigned to PO_4^{3-} .

Figure 20 displays the TEM images of the pristine HMCs. All the HMCs possess large In order to investigate the impact of mesopore size and volume on the particle mesopore fraction, open interconnected mesopores and foam-like morphology. Interestingly, the average mesopore size for all the HMCs in TEM images corresponds to the dominant single peak in the BJH plots (Figure 18b) and correlate well to the silica template size.

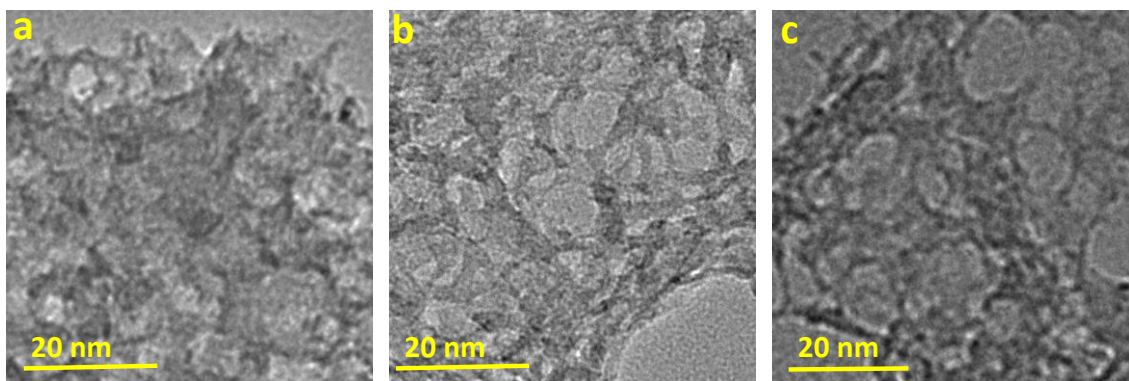


Figure 21: TEM image of pristine carbon: C4-11 (a), C20-11(b) and C20-21 (c)

TEM investigations were carried out to delineate the impact of mesopore size and volume of the carbon support on the growth of FeP particles. The growth of electrocatalyst particles inside different types of carbons results in different FeP particle size. Each mesopore act as nanoreactor for the growth of FeP. Hence, controlling the support pore size will determinate the nanoreactor role toward the growth of FeP particles. For instance, when smaller mesopore size (7 nm) is used (as in C4-11), FeP particles were successfully grown with limited size (< 5 nm) and highly dispersed inside the carbon pores. On the other hand, when carbon support material is used with around 2.4 times larger mesopore size (as in C20-11 and C20-21), FeP particles with larger size (>10 nm) were found.

In both cases the FeP particle size were smaller than the mesopore pore size. Thus, mesopore size as a carbon support design parameter play a major role in determining the FeP particle size which can ultimately impact the electrocatalytic activity. Figure 21 (c,f&i)

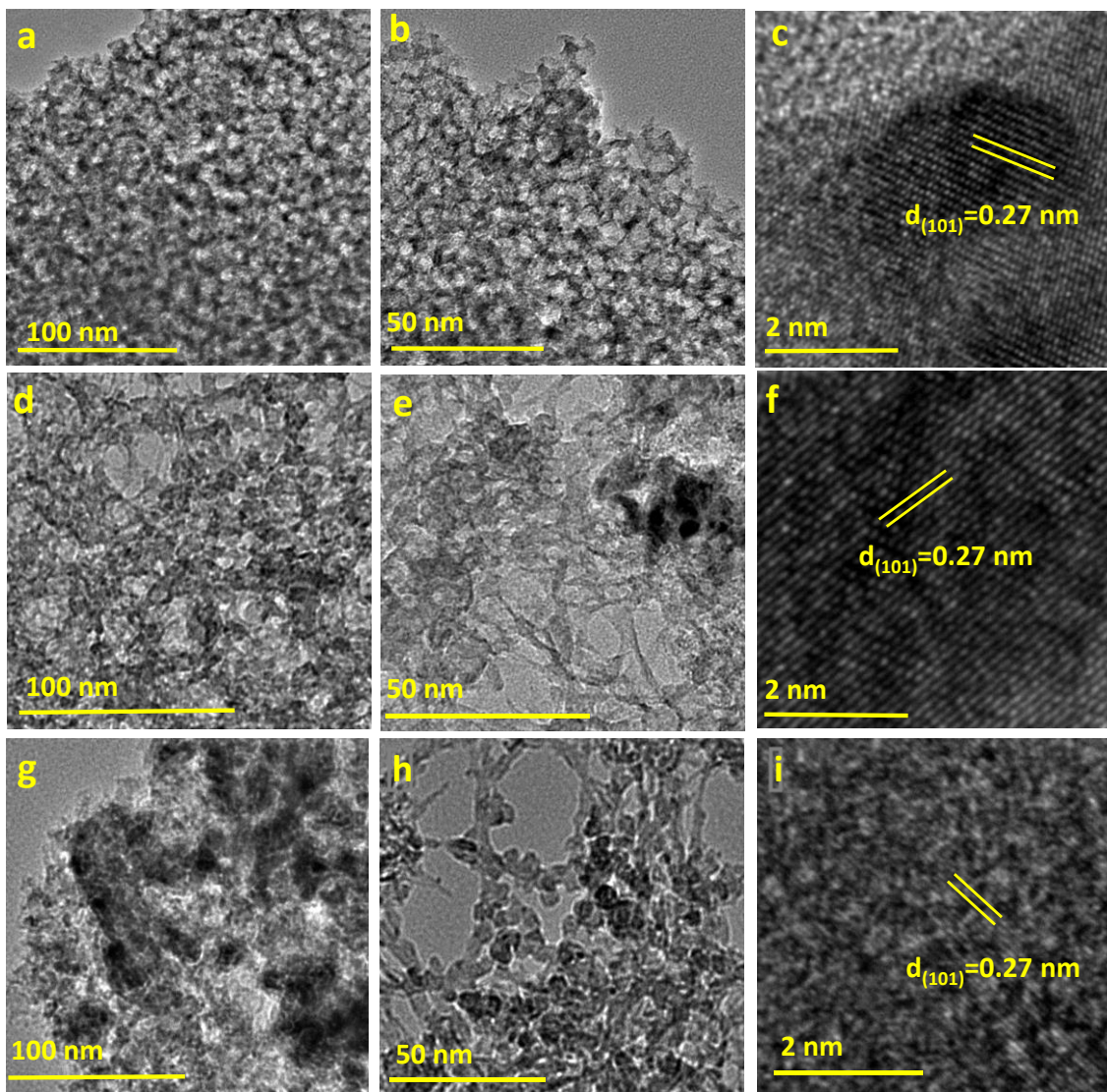


Figure 22: TEM and HR-TEM of FeP/C4-11 (a-c), FeP/C20-11 (d-f) & FeP/C20-21 (g-i)

display the high resolution transmission electron microscope (HRTEM) images of FeP grown particle in different HMCs. Obviously, in all cases FeP particles possess high

crystallinity with 0.27 nm interplanar distance which corresponds to (101) plane in orthorhombic FeP. The electrochemical performance of as-prepared electrocatalyst (FeP/C4-11, FeP/C20-11 and FeP/C20-21) was investigated toward hydrogen evolution reaction in 0.5M sulfuric acid, using linear sweep voltammetry (LSV). The obtained current density is normalized to the geometric surface area of the glassy carbon electrode (working electrode). Cyclic voltammetry (CV) was swept 10 time (in the range between +0.1 and -0.3V_{RHE}) before running LSV to attain the electrochemical equilibrium. Additionally, 10mA.cm⁻² was selected as a benchmark current density and the overpotential (η) required to drive this current was used for the HER performance comparison between all the FeP/HMCs (see Figure 22). The measured η value for FeP/C4-11, FeP/C20-11 and FeP/C20-21 to drive 10mA.cm⁻² current density was found to be 95, 110 and 155 mV, respectively. Furthermore, upon increasing the current density the difference in potential increases. For instance FeP/C4-11, FeP/C20-11 and FeP/C20-21 required η of 175, 213 and 312mV respectively to generate 45mA.cm⁻².

To further understand the impact of carbon support porosity on the HER performance, several electrochemical investigations were carried out such as electrochemical active surface area (ECASA), the intrinsic conductivity and the charge transfer resistance (R_{ct}) which have been estimated using electrochemical impedance spectroscopy (EIS) and turnover frequency (TOF). The activity of the electrocatalysts material can be evaluated by estimating ECASA which is linearly related to the electric double layer capacitance (C_{dl}). Cyclic voltammetry CV scan at different rates (from 5 to 100 mVs⁻¹) was carried out where the slope was used to calculate (C_{dl}) at the solid/liquid interface (see Figure 23).

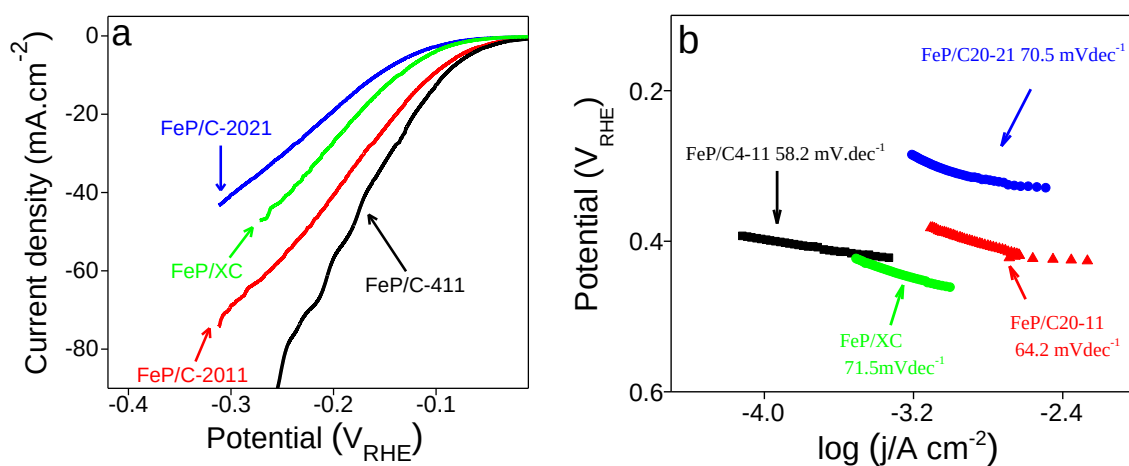


Figure 23: Comparative polarization curve of the electrocatalysts FeP/C4-11, FeP/C20-11, FeP/C20-21 & FeP/XC (a) and Tafel plots for the electrocatalysts (b)

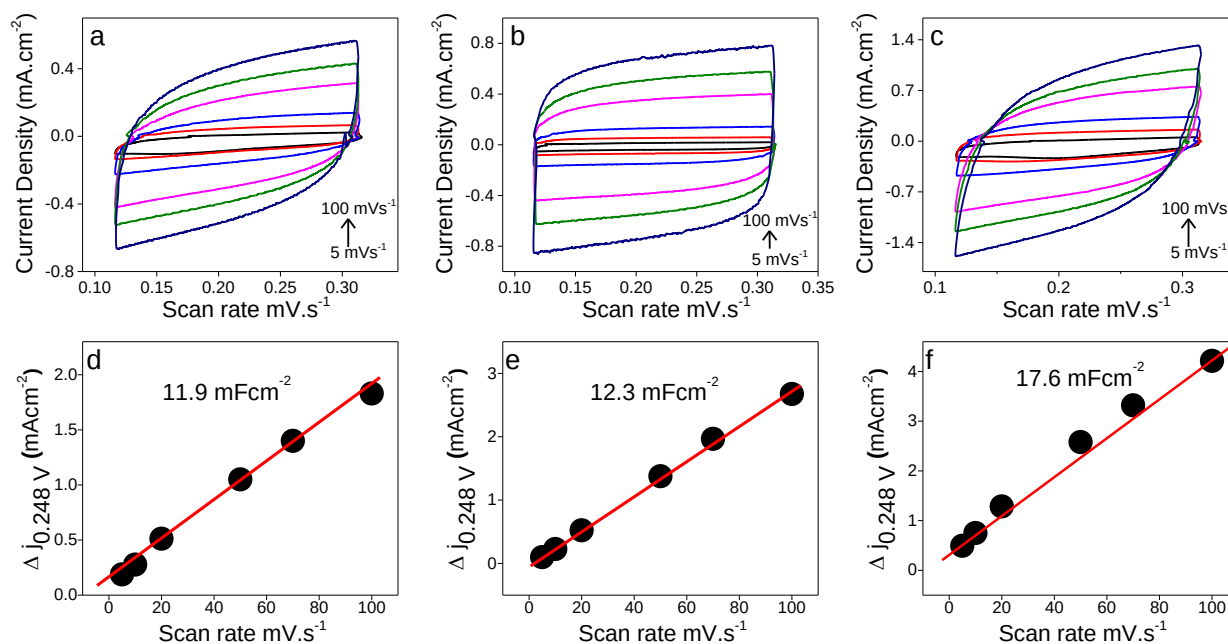


Figure 24: Pristine HMCs CVs (a-c), and their respective slopes at scan rates range between 5 to 100 $\text{mV}\cdot\text{s}^{-1}$ (d-f)

Figure 23 d,e&f depicts the C_{dl} slopes for C4-11, C20-11 and C20-21 with calculated C_{dl} values to be around 11.9, 13.3 & 17.6 mFcm^{-2} , respectively. Obviously, a slight

improvement for pristine carbons C_{dl} when one has larger mesopore size while both HMCs have similar surface area. For instance, while the C4-11 ($947\text{m}^2\text{g}^{-1}$) and C20-11 ($884\text{m}^2\text{g}^{-1}$) have similar surface area, C20-11 with 2.4 times larger mesopore (17 vs. 7 nm) demonstrate around 12% increase in C_{dl} . This can be ascribed to that fact that larger mesopore allow more accessibility of ions toward building the electric double layer on the carbon surface. To confirm this conclusion, the mesopore size was fixed around (17nm) and the pore volume was varied (as in C20-11 vs C20-21). Increasing the pore volume by 50% (as in C20-21) leads to 32% increase in C_{dl} compared with C20-11. Accordingly, larger mesopore size and fraction results in higher C_{dl} .

Interestingly, upon the loading of FeP on the HMCs, the C_{dl} is increased to be (34.1, 18.2 & 19.4) for FeP/ C4-11, FeP/C20-11 and FeP/C20-21, respectively. This indicate that the FeP nanoparticles have affinity toward the protons and the ECASA increases in case of FeP/HMCs. FeP/C4-11 showed the highest enhancement from its bare carbon (C4-11). Such increase in the activity for FeP/C4-11 can be attributed to uniform dispersion of smaller FeP nanoparticles where more charge are being accumulated, which lead to higher ECASA than FeP/20-11 & FeP/20-21. Additionally another important electrochemical characteristic was evaluated and correlated to the HER performance, which is the electrochemical impedance spectroscopy (EIS) to estimate the charge transfer resistance. Typically, higher electrical conductivity translated in higher HER performance.

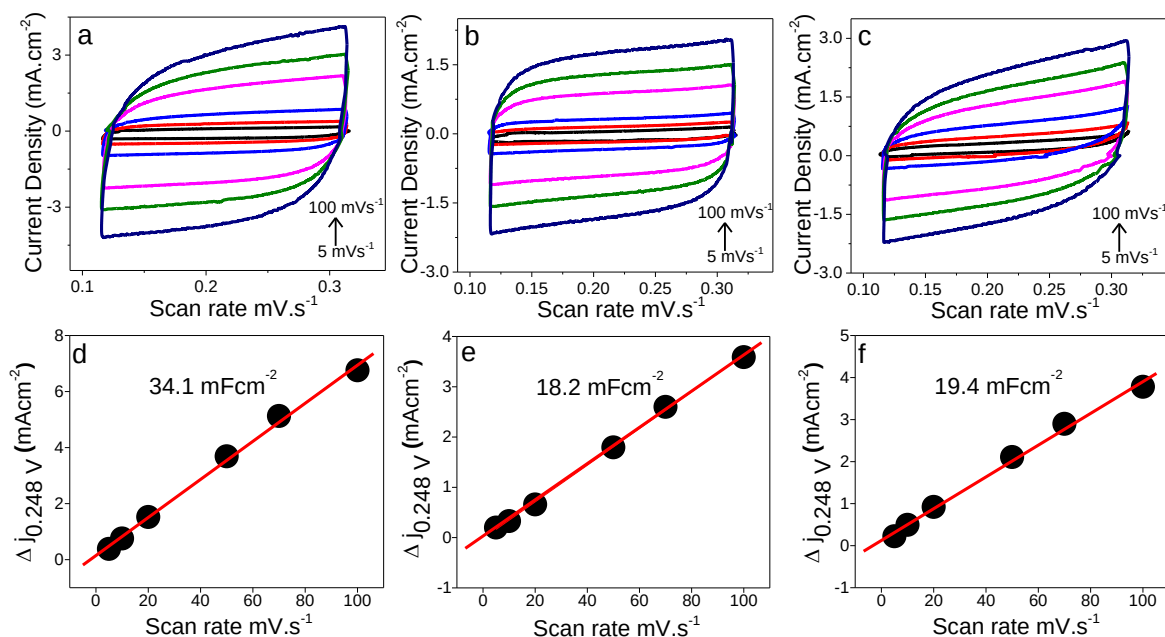


Figure 25: FeP modified HMCs CVs (a-c), and their respective slopes at potential range between 5 to 100 mV s⁻¹ (d-f)

Using EIS intrinsic conductivity and R_{ct} can be estimated, these values were calculated for the three carbons before and after loading with FeP. The frequency was swept from 10^5 Hz to 0.01 Hz with a constant ac amplitude of 10 mV. All EIS results were normalized to the geometric surface area of the working electrode. On the basis of EIS findings, the two-time constant parallel model was selected to fit the data.

This equivalent circuit model consists of R_s in series with two parallel constant phase element-resistance. The R_s accounts for concerted resistances, including the resistances arising from wiring (R_{wiring}), carbon support (R_{HMC}), FeP ($R_{phosphide}$) and solution (R_{soln}).³⁸ In addition, R_{ct} , R_p and C_{dl} correspond to charge transfer resistance, resistance arising from porous surface texture and electric double layer capacitance, respectively. For pristine HMCs (C4-11, C20-11 and C20-21) intrinsic conductivity were estimated by recording Nyquist plots at 0 mV. While similar resistance was obtained in case of C4-11 & C20-11, C20-21 showed higher resistance. The charge transfer resistance (R_{ct}) was also investigated at potential of 450 mV. C4-11 showed the highest conductivity (smaller R_{ct}), followed by

C20-11 and C20-21 again showed the highest resistance. This can be ascribed to the fact

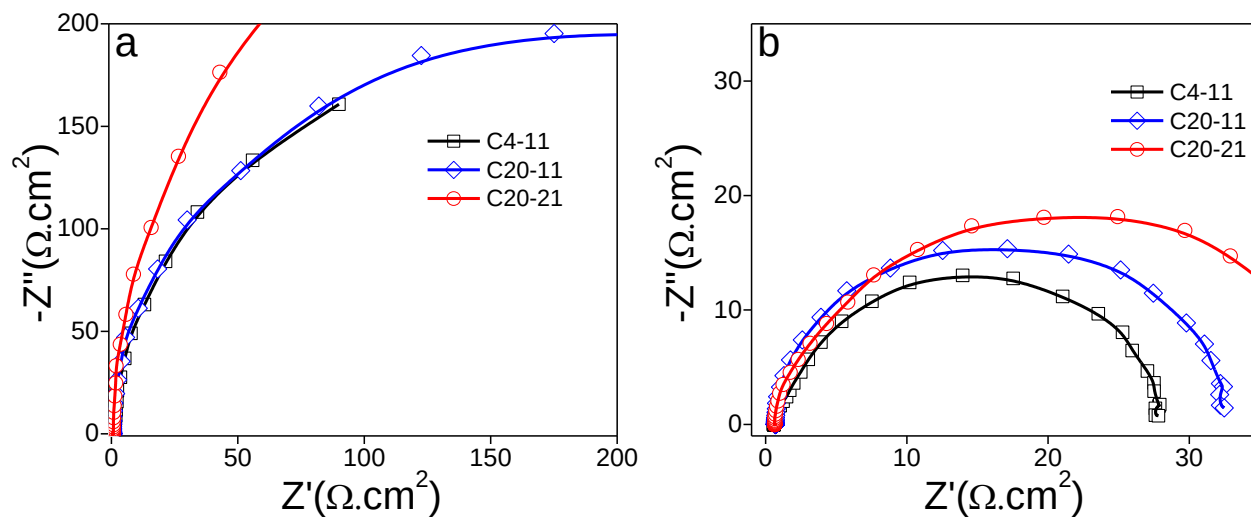


Figure 26: Comparative Nyquist plots of pristine HMCs at 0 mV (a) and 450 mV (b) in 0.5M H_2SO_4

that larger and higher volume of pores introduce extra resistance compare to smaller pores and smaller pore volume carbon.

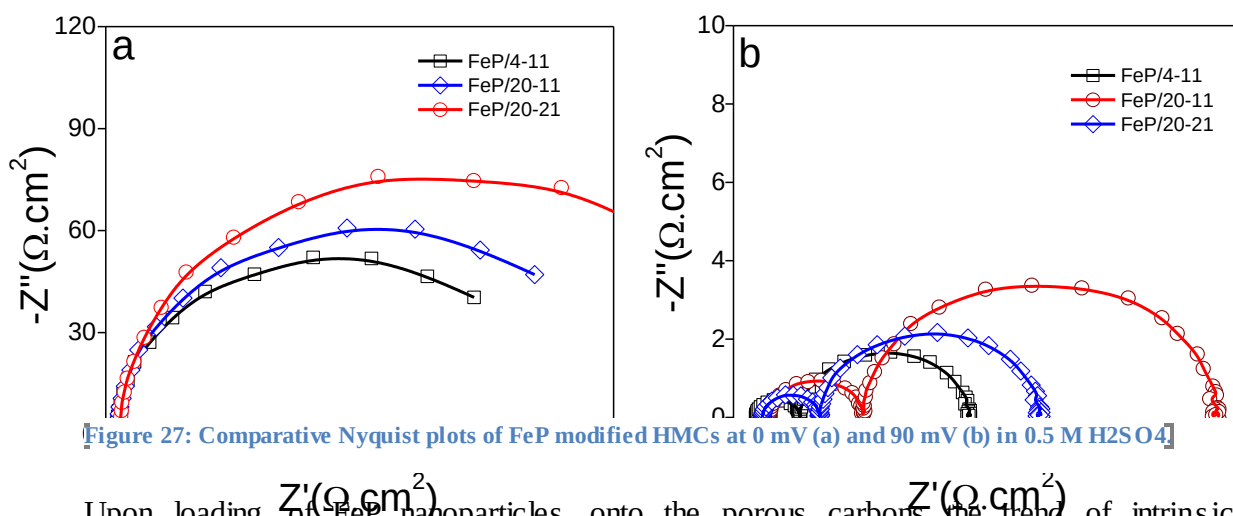


Figure 27: Comparative Nyquist plots of FeP modified HMCs at 0 mV (a) and 90 mV (b) in 0.5 M H_2SO_4

Upon loading of FeP nanoparticles onto the porous carbons the trend of intrinsic conductivity (at 0 mV) and the charge transfer (at 90 mV) was maintained.

The FeP/C4-11 showed the lowest R_{ct} , which could be due to small size and uniform dispersion of FeP nanoparticles, which facilitate the charge transfer compared to FeP/C20-11 & FeP/C20-21.

In Figure 25b a clear second semicircles are observed in lower resistance (R_p). Which is arises from the porosity or surface resistance. It can be observed the order of (R_p) as follow FeP/C2021>FeP/C20-11>FeP/C4-11.

The number of catalytic active sites can be estimated by the turnover frequency (TOF), which relates the number of reacted molecules per catalytic area per unit time. The larger TOF could be translated into higher HER performance. The TOF can be calculated using the formula:

$$\text{TOF} = JA/2FN \quad (1)$$

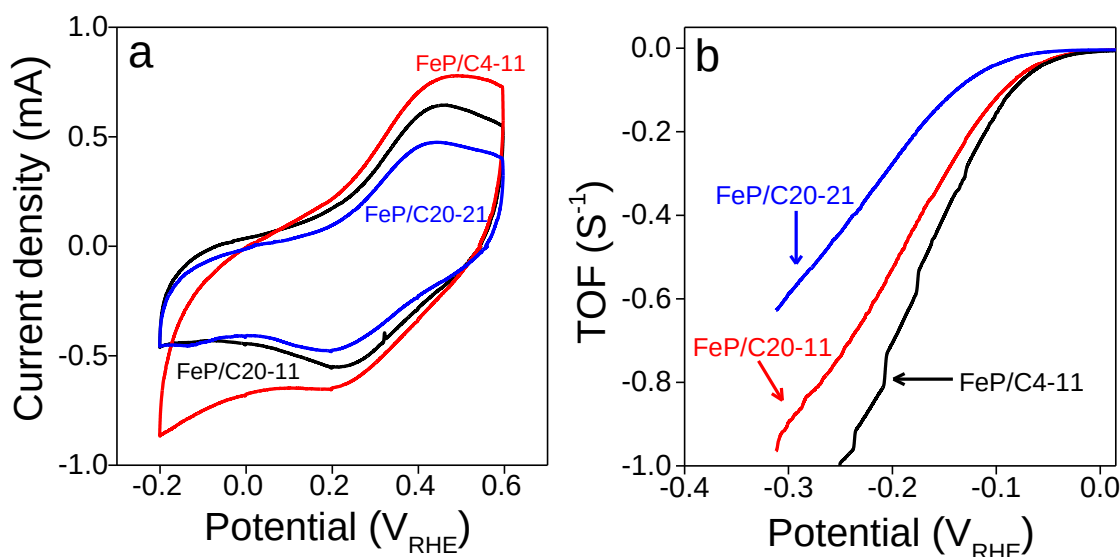


Figure 28: CVs recorded between -0.2 and 0.6 VRHE (a) and their corresponding TOF vs. η (b). Measurements were carried out in a phosphate buffer solution (pH 7).

where J = geometric current density (A cm⁻²), which is measured by linear sweep voltammetry, A = working electrode's geometric area, $1/2$ = two electrons that participate

in the production of one H₂ molecule, F = the Faraday constant (96 485 C mol⁻¹), and N = the number of catalytic or active sites (mol). Firstly, the N was determined from cyclic voltammograms recorded between -0.2 V and +0.6 V_{RHE} in neutral phosphate buffer solution (pH = 7) with a scan rate of 20 mV s⁻¹.

The CVs of FeP/4-11, FeP/20-11 and FeP/20-21 are compared in Figure 23a. The respective N for FeP/4-11, FeP/20-11 and FeP/20-21 are computed to be 1.9×10^{-8} , 1.6×10^{-8} & 1.1×10^{-8} mol. A comparison of N clearly evinces the proposed notion that the surface of FeP/4-11 is endowed with more active sites. The values of N were then used to quantify the TOF. A plot of TOF as a function of η is shown in Figure 27b. The TOF, calculated at η = 95 mV (the potential at current density of 10 mA cm⁻²), for MoS₂, FeP and FeP/MoS₂ FeP/4-11, FeP/20-11 and FeP/20-21 are 0.175, 0.150 & 0.05 s⁻¹, respectively. The higher TOF confirms the superior intrinsic catalytic ability of FeP/C4-11.

According to the findings obtained from samples FeP/C4-11, FeP/C20-11 and FeP/C20-21, using carbon support with smaller mesopore size (e.g. 7 nm) restricts the growth and the agglomeration of FeP nanoparticles compared with the larger mesopores. Thus, we further investigated the use the carbon support with mesopore size 7nm (similar to C4-11) but with smaller mesopore volume C4-12 (pore size ~7 nm and pore volume 1.1 cm³ g⁻¹, Surface area 747 m² g⁻¹). FeP was loaded on C4-12 porous carbon to form FeP/C4-12 which was characterized and its HER electrocatalytic performance was investigated. The Figure S1 depicts the TEM images of identical loading (60%) and different loading (40%) of FeP where larger and agglomerated FeP crystals can be seen. Both loadings of FeP in C4-12 present lower HER performance (i.e η (10 mA cm⁻²) 60% (195mv) and 40% (160 mV)). Since the carbon pores will confine the growth of FeP particles, the agglomeration

in case of FeP/C4-12 is attributed to the lower pore volume of the carbon support. Thus the FeP nanoparticles will not be only hosted in the carbon pores. Hence, excess particles will grow on carbon surface (non-confined growth) and agglomerate. This was further confirmed by reducing FeP loading to 20% on C4-12. Small and monodispersed FeP particles were observed on the porous carbon (Figure S1a). Notably, as expected FeP/C4-12 with 20% FeP loading showed higher HER performance (138 mV) compares with higher loadings. It is noteworthy to mention that the HER performance of FeP/C4-12 with 20% loading still significantly lower than FeP/C4-11, which can be attributed to the less active sites. That was further confirmed by comparing the ECASA of FeP/C4-11 and FeP/C4-12 (20%) as it can be seen in Figure 3.

5.4. Conclusion

In conclusion, a series of HMCs with different textural characteristics synthesized and utilized as support material to grow FeP crystals. The adopted approach for HMCs synthesis provides facile way to synthesize porous carbons with high mesopore fraction, tight control over mesopore size and volume. Therefore, the impact of the porosity of the carbon support on HER was investigated. The electrocatalytic activity of all FeP/HMCs was enhanced up to 3 times upon the loading of FeP on the HMCs as it was confirmed by ECASA. This can be ascribed to the affinity of FeP towards protons, especially when nanosized crystals of FeP were highly dispersed and confined inside the carbon pores as in FeP/C4-11. The electrical conductivity was also investigated by employing the EIS. The electrical conductivity trend was FeP/C4-11 > FeP/C20-11 > FeP/C20-21. This could be attributed to two reasons; firstly, the C4-11 is more conductive than C20-11 & C20-21. Secondly the uniform dispersion facilitate the charge transfer. Due to the higher

ECASA and the lower charge transfer resistance, more active catalytic sites (N) and TOF are available, which untimely will be translated into higher catalytic performance.

Hence, optimum mesopore size can limit the growth the FeP particles which can provide nanosized highly dispersed crystals on the carbon support. Besides optimum mesopore size, larger fraction of the optimum mesopore size can provide more nanoreactors for growing and hosting FeP particles.

CHAPTER 6

FeP/MoS₂ Enriched with Dense Catalytic Sites and High Electrical Conductivity for the Hydrogen Evolution Reaction

6.1. Introduction

Adverse climate and global energy demand are driving the exploration and development of sustainable and environmentally benign source of energy as well as processes to produce such energy sources. Because of its exceptional gravimetric energy density, molecular hydrogen (H₂) is capable of storing tremendous amount of energy and hence deemed as the most promising energy carrier.⁵⁵ Clean and sustainable hydrogen production, however, continues to be a challenging endeavor. As yet, most of the hydrogen is generated through steam-methane reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$),² which emits CO₂ through a water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$). Water electrolysis, being a well-established commercial process with high energy efficiency, seems to be a potential technological solution.³⁻⁶ The electrical energy, achieved by a photoelectrochemical process or an electrochemical process directly coupled to photovoltaics or solar cells, can be used to power the water electrolysis.⁷⁻¹⁰ A successful implementation of water electrolysis at commercial scales to produce H₂ requires two major breakthroughs: (1) the production of renewable (solar and wind)-energy-derived electricity and (2) the development of an active, cost-effective, and stable electrocatalysts to be used as electrode materials. As a result, research in this direction is intensified and a wide variety of compositions are being explored as potential electrocatalysts.

Essentially, because of high price, less abundance and instability, an alternative to platinum (Pt) is highly desired for further development of electrochemical energy conversion devices such as photoelectrochemical cells and electrolyzers. This motive drove the exploration of a wide variety of electrodes consisting of substantially low-cost transition metals, including various carbides [39, 61, 104, 105], sulfides [106 – 108], nitrides [27], phosphides, [6, 9, 67 – 69, 109], and borides [70, 110]. Delving into sulfide-based electrocatalysts, we find that sulfide of molybdenum (MoS_2) remains the most studied composition.^{39–53} While edge sites and sulfur vacancies are demonstrated to be active sites for the HER,³⁹ the full potential is undermined by high resistance and low density of exposed active centers. Attempts are made to enhance the electrical conductivity and density of active sites. For instance, 1T- phase of MoS_2 is demonstrated to possess higher electrical conductivity, which results in highly efficient water splitting [124]. Similarly, 1T- phase of MoS_2 synthesized through exfoliation approach exhibited better conductivity and performance [125, 126]. Recently, 1T- MoS_2 was prepared with metallic-phase, and presence of active sites in basal plane was revealed [127]. Peng and coworkers reported to increase the active sites of 2D MoS_2 nanosheets by exposing under-coordinated S atoms of inner layer [128]. The modification improved the adsorption ability of MoS_2 surface, resulting in high HER performance. So far, the major strategy pursued to improve the active center has been associated with increasing the number of edge sites. [124 – 137]

Coupling MoS_2 with other active sites enriched with high conductivity seems another effective strategy to improve the overall density of functional sites and electrical conductivity. Because of semi-metallic nature and presence of highly dense active centers to facilitate H^+ reduction, transition metal phosphides are promising. Due to low cost and high performance,

iron monophosphide is interesting in particular. The HER performance of bare or supportless iron phosphide remains very low, but improves substantially when dispersed on carbon support. However, as the carbon support does not catalytically participate in HER reactions, a significant portion (approximately 50% by weight) of electrocatalysts remains underutilized.

Here we demonstrate an effective synergy between 2D MoS₂ nanosheets and FeP nanoparticles, which produces electrocatalyst (FeP/MoS₂) endowed with substantially higher electrical conductivity and number of active sites. Instead of carbon, the 2D MoS₂ nanosheet is utilized as a support for the dispersion of additional active sites (e.g., FeP). The as-prepared electrocatalysts requires significantly low overpotential (110 mV) as compared to MoS₂ (265 mV) and FeP (210 mV) to generate 10 mA cm⁻². Furthermore, the FeP/MoS₂ exhibits better HER performance than FeP/C – FeP/C requires 138 mV to produce 10 mA cm⁻². The performance variation in all the studied electrocatalysts, such as FeP, MoS₂, FeP/MoS₂ and FeP/carbon, is correlated to their SSA, ECSA, intrinsic electrical conductivity, R_{ct} , catalytic active centers, and TOF. The improved electrical conductivity and the high density of catalytic sites, or high turnover frequency, enhance the HER performance of FeP/MoS₂, in spite of having lower SSA and ECSA. In spite of having lower conductivity than the FeP/C, the superior performance of FeP/MoS₂ is attributed to its higher catalytic centers. The study presents first example of using nanosheets of active sites to be used as a robust support to carry secondary active sites in electrochemical energy conversion applications.

6.2. Experimental

6.2.1. Preparation of two-dimensional ultrathin nanosheets of molybdenum disulfide (2D MoS₂)

The 2D MoS₂ was prepared as follows. Briefly, ammonium heptamolybdate tetrahydrate (1.25 g, 99.98%) and thiourea (2.30 g, 99.0%) were dissolved in deionized water (20 ml). After complete dissolution, the solution was poured into a 45 ml Teflon container (acid digestion vessel) and heated at 220 °C for 20 h. After 20 h of reaction, the oven was allowed to cool down. The precipitate was collected from the bottom of the Teflon vessel, rinsed with water and ethanol several times, and dried under vacuum at 60 °C overnight.

6.2.2. Preparation of iron monophosphide and 2D MoS₂ (FeP/MoS₂)

The FeP/MoS₂ was prepared as follows. The as-prepared 2D MoS₂ (25 mg) was dispersed in 20 mL ethanol solution, which was prepared by dissolving iron dichloride (40 mg, 98.0%) in a closed glass vial. The suspension was stirred at room temperature for 5 h, and then poured on a glass petri dish to remove the solvent through evaporation. The evaporation was carried out under ambient conditions while stirring. Black powder was obtained upon complete solvent evaporation, which was crushed and dried under vacuum at 60 °C. The phosphidation of Fe precursor was carried out in the presence of phosphine gas (PH₃), which was generated through decomposition of sodium hypophosphite (NaPO₂H₂). In this phosphidation process, calculated amounts of dried Fe/MoS₂ precursor and phosphine source were transferred in two ceramic boats. The ratio, by weight, of Fe/MoS₂ and NaPO₂H₂ was adjusted to 1:20. The crucibles were placed in a uniform temperature zone of a tube furnace, and nitrogen was flown for 45 min at room temperature. The crucible loaded with NaPO₂H₂ was

kept at the upstream side. The thermal treatment was carried out at 400 °C for 2 h. Upon reaction, the electrocatalyst was used as it is for the preparation of electrode to test the HER performance. Also, FeP nanoparticles were synthesized for performance comparison. A similar procedure was pursued to prepare FeP, but in the absence of MoS₂.

6.2.3. Characterization

Characterization of the as-prepared electrocatalytic compositions was carried out by X-ray diffractometry (XRD, Rigaku MiniFlex), X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi), field emission scanning electron microscope (FESEM, Tescan Lyra-3), transmission and high-resolution transmission electron microscope (TEM/HR-TEM, FEI Tecnai TF20), and BET surface area analyzer (Micromeritics ChemiSorb 2750).

6.2.4. Electrochemical characterization

The HER performance was investigated in a typical three-electrode electrochemical cell. The assembly was operated by a potentiostat (EG&G 273A). The procedure for the preparation of working electrode is as follows. The as-prepared electrocatalysts (5 mg), water and ethanol (50% V/V), and 40 µl of 1.66% wt. Nafion® were mixed together. The resulting slurry was sonicated for approximately 0.5 h to prepare the ink. Then, a pre-determined volume of the ink was deposited on a pre-cleaned glassy carbon (GC) disc electrode. The diameter of the GC electrode was 5.0 mm. The ink was allowed to dry at ambient conditions. The desired catalyst loading (1 mg cm⁻²) was achieved by repeating the deposition and drying steps. A graphite rod (0.250" OD × 12" long) was used as a counter electrode, while saturated calomel electrode (Hg/HgCl₂,

SCE) was used as the reference electrode, respectively. The SCE potential was measured experimentally, and presented against reversible hydrogen electrode (RHE) after conversion. Linear sweep voltammetry was performed in 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mV s⁻¹. Geometric area of the GC electrode was used to normalize the recorded current, and the current density (J_g) is iR corrected. The measurements of electrochemical impedance spectroscopy (EIS) were conducted in 0.5 M H₂SO₄ in the frequency range of 10⁵ Hz and 0.01 Hz with ac amplitude of 10 mV. All the EIS data was normalized to the geometric area of the GC electrode. Before and during EIS measurements, the electrolyte solution was saturated with H₂ gas.

6.3. Results and discussion

The formation of intended crystal phase was confirmed by powder X-ray diffraction. The diffractions obtained for 2D MoS₂, FeP and FeP/MoS₂ are shown in Figure 28. In the spectrum of MoS₂, the broad patterns at $2\theta = 33.2^\circ$, 38.5° , and 47.6° correspond to (100 + 101), (103), and (105) plane of nanosheets [138]. In the case of FeP, the main diffraction patterns centered at 32.8° , 37.2° , 48.3° , and 56.1° , arising from (011), (111), (211) and (013) reflections, conform very well with the reported data on iron monophosphide with a orthorhombic structure (JCPDS 65–2595) [139]. The patterns of FeP/MoS₂ showed the presence of prominent diffractions of both FeP and MoS₂. The surface composition of FeP/MoS₂ was analyzed by the X-ray photoelectron spectroscopy, and the recorded spectra are shown in Figure 28. The survey spectrum indicates the presence of intended compositions, such as Fe, P, Mo and S. The Fe 2p spectrum reveals two peaks; the peak at 711.6 eV corresponds to Fe³⁺ 2p_{3/2} while the signal at 724.8 eV is attributed to Fe³⁺ 2p_{1/2}. These values are assigned to the iron bonded to phosphorous [122]. Similarly, the

peaks for the phosphorous bonded to iron are discerned. In the P 2p spectrum, the signatures of P coordinated with Fe appear at 130.3 and 131.4 eV, corresponding to $2p_{3/2}$ and $2p_{1/2}$ respectively. Furthermore, the surface also contains PO_4^{-3} or P_2O_5 , which is

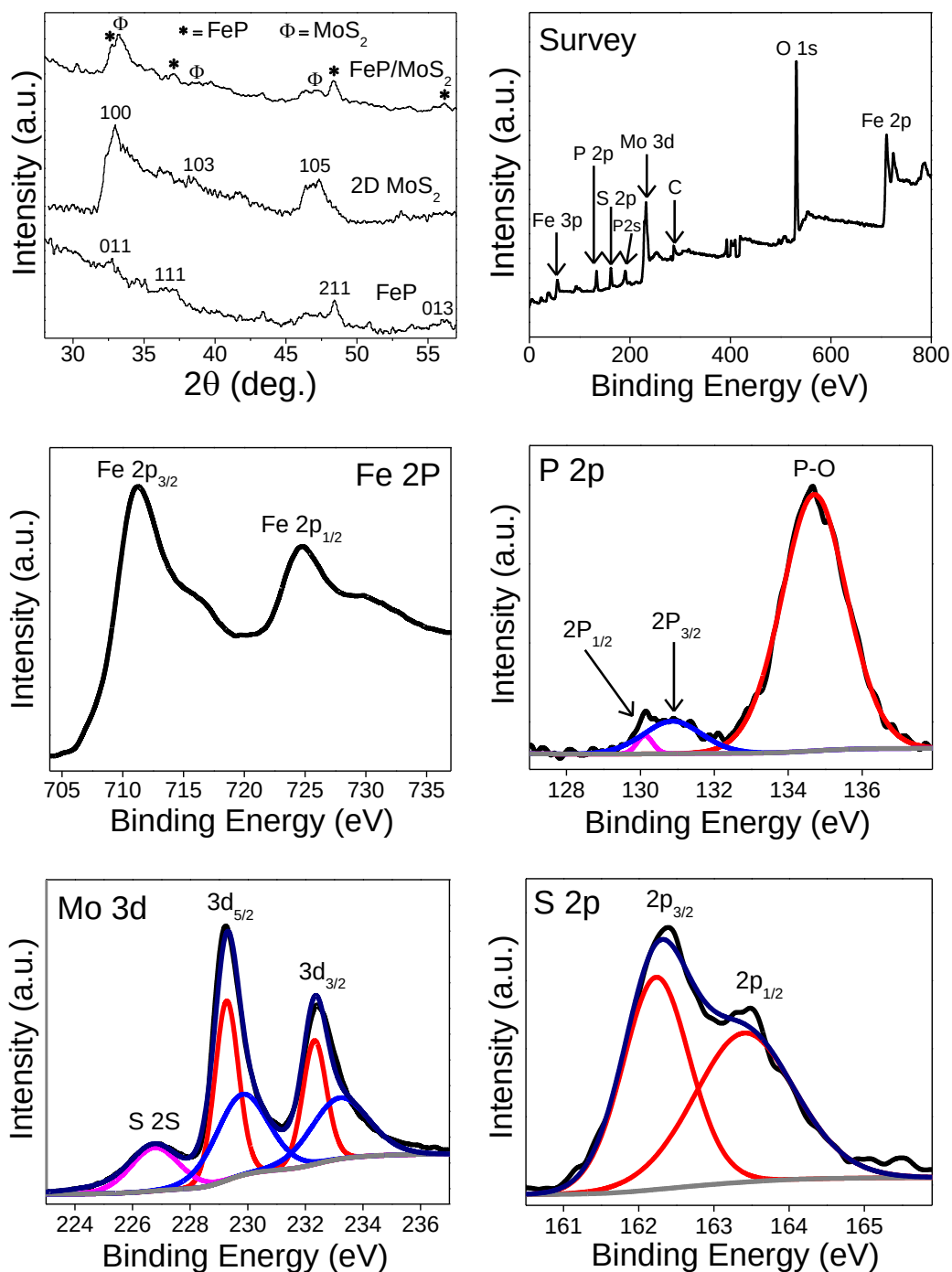


Figure 29: XRD of FeP, MoS₂ and FeP/MoS₂, and XPS signatures of FeP/MoS₂

indicated by intense and broad peak at 134.4 eV [122, 123]. Due to the surface oxidation of FeP layer of phosphate PO_4^{3-} is formed, this layer is very thin that is why PO_4^{3-} species doesn't appear in XRD (pure phase of FeP), and only can be observed through more sensitive such as XPS. However this thin layer of oxide has significant influence on the HER performance, the layer can protect the FeP from further oxidation and dissolution, which effectively enhances the stability of the electrocatalyst [6]. In the Mo 3d spectrum, four peaks are recorded. The signals at 226.8, 229.2 and 232.4 eV account for S 2S, Mo $3d_{5/2}$ and Mo $3d_{3/2}$ respectively, while the peak at 236.4 eV is assigned to Mo (VI). The surface of molybdenum remains susceptible to oxidation. The respective signatures of S $2p_{3/2}$ S $2p_{1/2}$, recorded at 162.3 and 163.4 eV respectively, are shown in S 2p spectrum [138].

The amount of FeP loaded on MoS_2 was verified by estimating Fe and Mo content concentrations by ICP-MS. Since XRD indicated the presence of pure FeP and MoS_2 phases, the amount of phosphorous was calculated on the basis of 1:1 molar ratio of Fe and P, and amount of sulfur was calculated on the basis of 1:2 molar ratio of Mo and S. According to Table S1 the theoretical composition and the experimental one showed an excellent agreement and the loading of FeP on MoS_2 was ($\approx$ 50:50 wt %).

The morphological features of the as-prepared 2D MoS_2 nanosheets obtained by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) are shown in Figure 29. A thorough scanning study confirmed the formation of highly uniform and interconnected nanosheets of MoS_2 across the specimen. A typical FESEM is shown in Figure 29a. Low magnification TEM image further corroborates the sheet-like morphology (Figure 29b). The value of d-spacings (0.27 nm) computed through

HRTEM matches very well with (100) reflection of molybdenum disulfide [139]. In addition, the nanosheets are predominantly composed of multiple S–Mo–S layers (Figure 29c). The interlayers were observed to be homogeneous, and the average interlayer spacing for (002) plane is calculated to be 0.63 nm, which agrees very well with the previously reported values.⁶⁰ The morphological features of FeP nanoparticles embedded within 2D MoS₂ nanosheets are shown in Figure 29d-f. The FESEM (Figure 29d) highlights fine and highly homogeneous FeP distribution on 2D MoS₂ surface. This observation lends credibility to our earlier finding that carbon support, when used in the form of 2D ultrathin

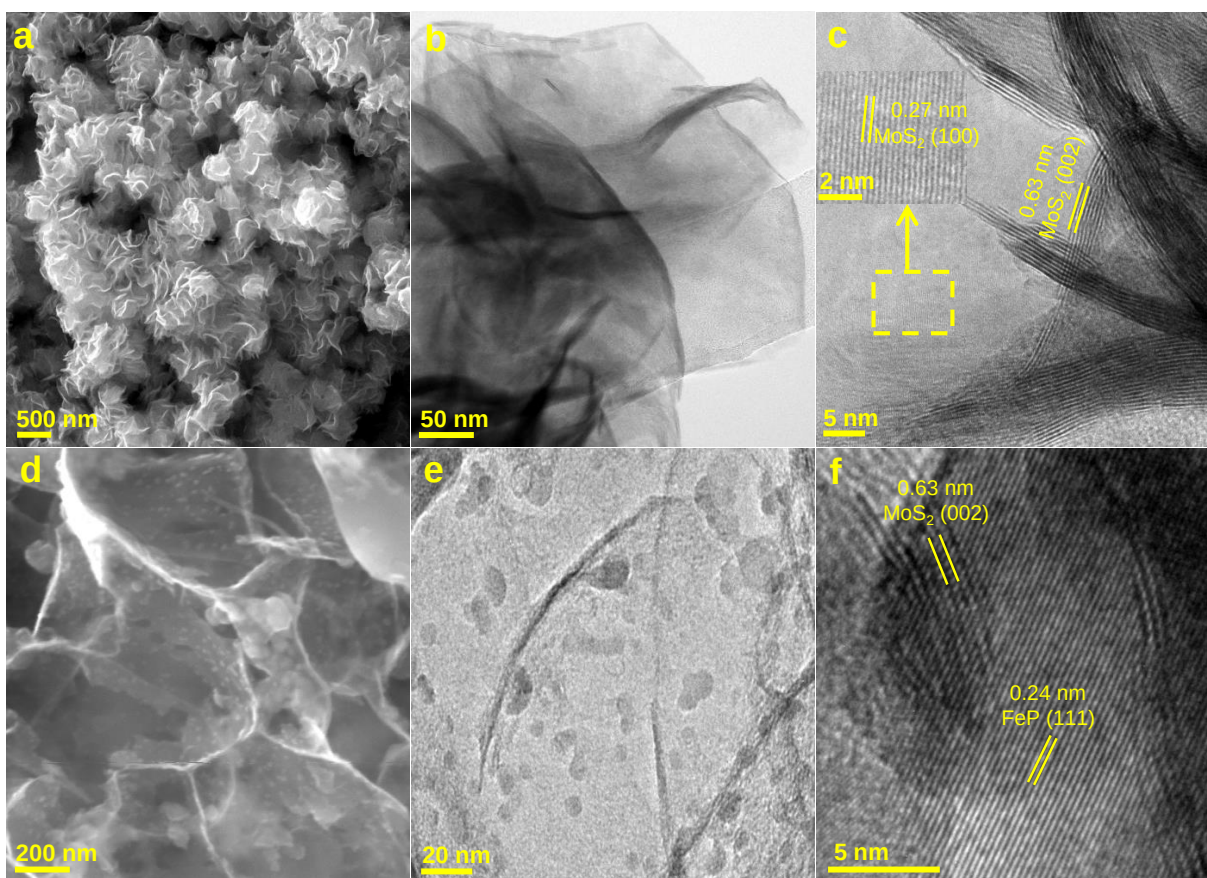


Figure 30: FESEM, TEM and HR-TEM of MoS₂ nanosheets (a, b and c) and FeP/MoS₂ nanosheets (d, e and f)

nanosheets, renders uniform dispersion and distinct nucleation & growth of catalytic active centers.⁶¹ The formation and size of FeP nanoparticles is further confirmed by TEM. The

shape of FeP is spherical, and the size of most of the particles is <10 nm. The HR-TEM study also suggested the presence of high crystallinity in FeP/MoS₂ (Figure 29f). The interplanar spacing of spherical particles is calculated to be 0.24 nm, which is in good agreement with (111) reflection of iron monophosphide (FeP).⁶² Furthermore, the calculation of average interlayer spacing (0.63 nm) in FeP/MoS₂ suggests that the features 2D MoS₂ remain intact during the phosphidation process.

The performance of the as-prepared electrocatalysts is evaluated and compared, in terms of overpotential (η) to generate the benchmark $J_g = 10 \text{ mA cm}^{-2}$, by investigating the HER in aqueous electrolyte of 0.5 M H₂SO₄. To measure the HER current, linear sweep voltammetry (LSV) was performed in the range between +0.1 and $-0.3 \text{ V}_{\text{RHE}}$. For comparison, the activity of commercial Pt/C is also provided. Figure 30a shows the current-potential profiles of MoS₂, FeP, FeP/MoS₂ and Pt/C. Evidently, the MoS₂ exhibits the lowest performance followed by FeP. The performance has substantially improved when FeP/MoS₂ is used as electrode, notably higher than that of MoS₂ and FeP electrodes. The η to produce 10 mA cm^{-2} using MoS₂, FeP, and FeP/MoS₂ electrocatalysts are calculated to be 265, 210 and 110 mV, respectively. As expected,

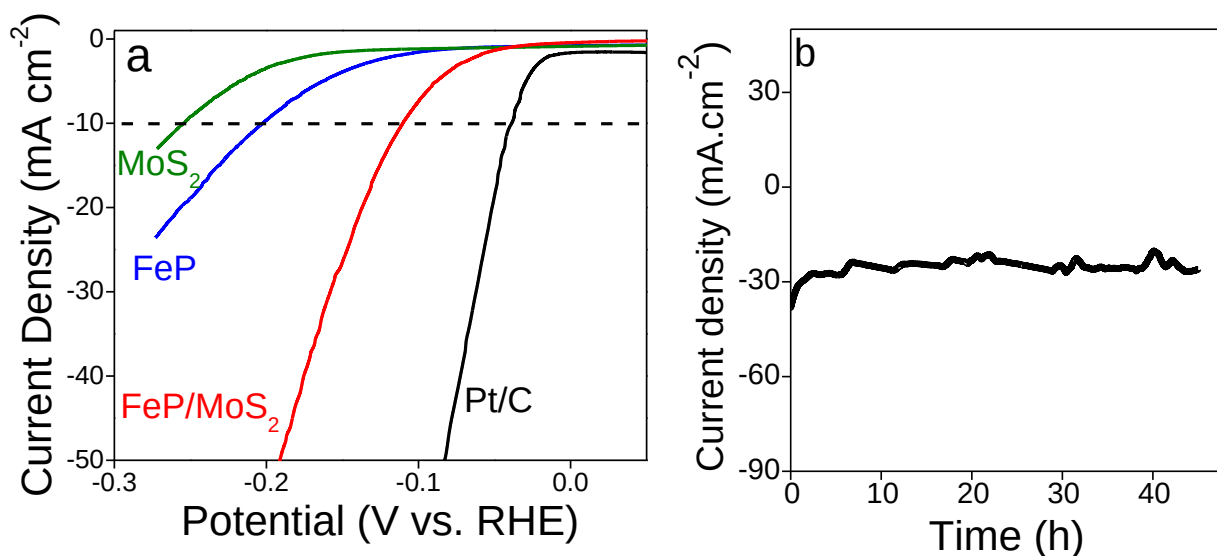


Figure 31: Comparative polarization curves of MoS₂, FeP, FeP/MoS₂ and Pt/C (a) and the current–time profile in the presence of FeP/MoS₂ for 45 h. All the measurements were performed in 0.5 M H₂SO₄

the electrode comprising Pt/C required the lowest η (41 mV) to generate the same J_g . Moreover the effect of Fe loading percent in the electrocatalyst was investigated using different metal loading (30, 40, 50 and 60%), electrocatalyst with 40% Fe content ($\approx 50\%$ FeP) showed the best HER activity, this can be explained by that in case of 30% less active sites of FeP than 40% was available for HER, further increase in the Fe (50, 60%) could lead to the agglomeration of the active sites and significant reduction in the surface area followed by decrease in the HER performance [14]. The electrochemical stability of the FeP/MoS₂ electrode is investigated under identical experimental conditions, and the results are shown in Figure 30b. The time-dependent current profile was recorded at $\eta = 170$ mV for 45 h. The J_g decreased at the initial stage of reaction and then stabilized, attesting good stability of the electrode for long run. Furthermore to ensure the stability of the electrocatalyst, the composition after stability test was investigated by using XRD, XPS, EDX and elemental mapping and the morphology was verified by SEM, as it is shown in Figure S1, 2, 4 and 5. the FeP/MoS₂ maintained the structural composition and morphology.

The variation in the electrodes performance is rationalized in terms of SSA, ECSA, EIS, R_{ct} , catalytic active sites, and TOF. The specific surface areas, measured by BET analysis, of MoS₂, FeP and FeP/MoS₂ are 29.6, 46.9, and 37.6 m² g⁻¹.

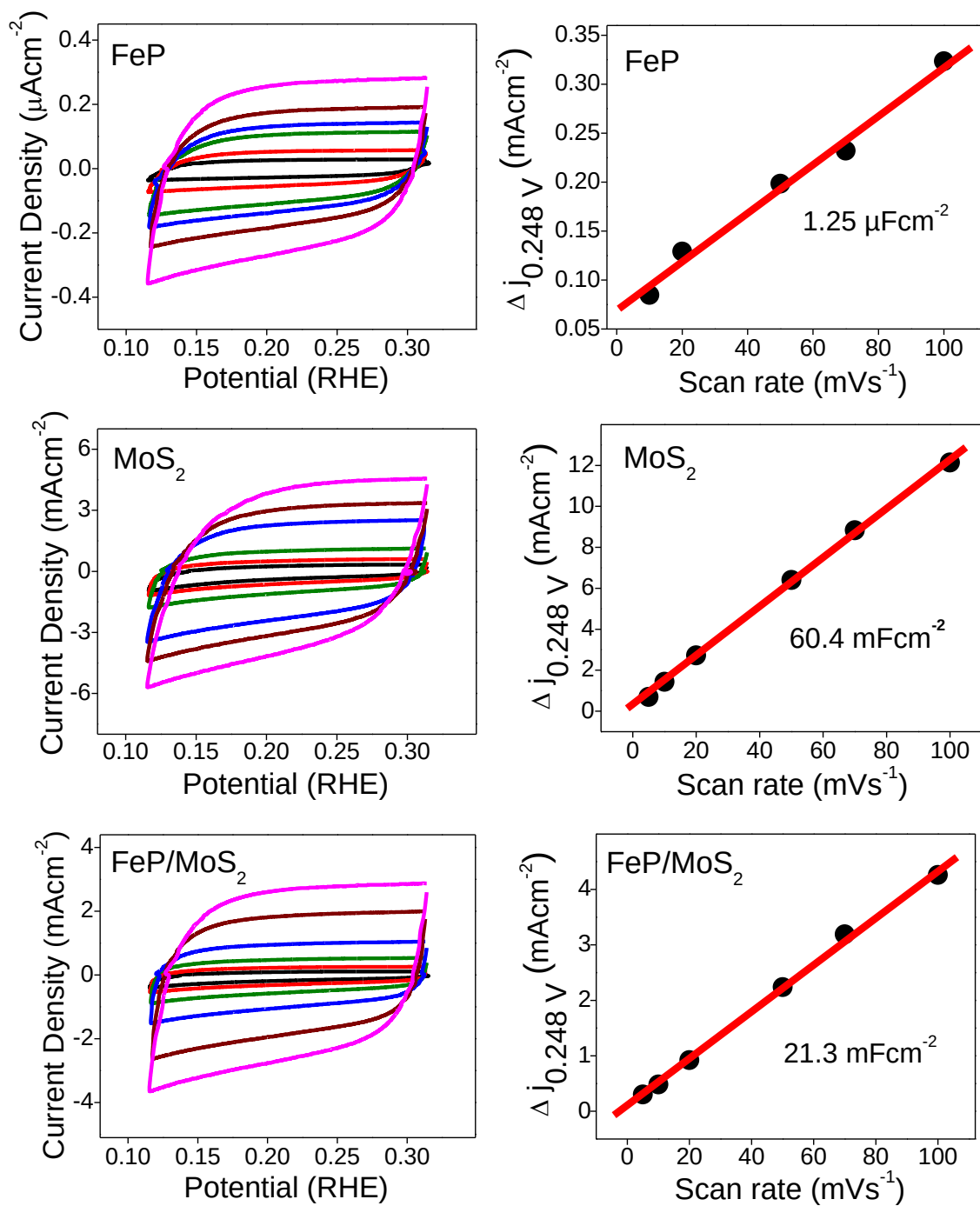


Figure 32: Cyclic voltammograms, recorded at different scan rates between 5 and 100 mV s⁻¹, and their corresponding plots of the current density at 0.248 VRHE vs. scan rate]

The higher surface area of FeP is attributed to its smaller particle size (Figure 29d and e). As evident from the Figure 30a, FeP is more active than 2D MoS₂, and any improvement in the dispersion qualities of the FeP is likely to further contribute in the FeP performance. This notion is well strengthened when FeP is dispersed on the 2D MoS₂ surface. Although the specific surface area of FeP/MoS₂ is smaller as compared to FeP, it exhibits better performance. Furthermore, fairly-dispersed nanoparticles of FeP are likely to add in the enhancement of ECSA. Since the HER reaction is predominantly surface-dominated, usually a higher surface area (both SSA and ECSA) of electrocatalysts translates into superior performance. The double-layer capacitance (C_{dl}) was estimated from CVs, and used to calculate the ECSA of MoS₂, FeP and FeP/MoS₂. The higher C_{dl} is construed as higher ECSA. The CVs were carried out in the nonfaradic region as a function of scan rates (between 5 and 150 mV s⁻¹). The results, CVs and corresponding current density plots vs scan rate, are presented in Figure 31.

The values of ECSA for MoS₂, FeP and FeP/MoS₂ are determined to be 60.4 mF cm⁻², 1.25 μ F cm⁻² and 21.3 mF cm⁻², respectively. Due to high surface to volume ratio, the FeP nanoparticles tend to agglomerate and produce poor quality of film on the glassy carbon electrode, which results in significantly low ECSA. Despite having extremely low ECSA, the FeP (and FeP/MoS₂) exhibits better performance than that of 2D MoS₂. Although surface area has prominent impact on performance, other features such as electrical conductivity, active sites and turnover frequency (TOF) have analogous influence.

Another crucial electrode feature that modulates the performance is the electrical conductivity. Typically, higher electrical conductivity renders faster charge transfer and

thus performance. Details of intrinsic electrical conductivity and R_{ct} are collected by EIS.

Analyses of Nyquist and Bode plots indicated the presence of two-time constants in FeP

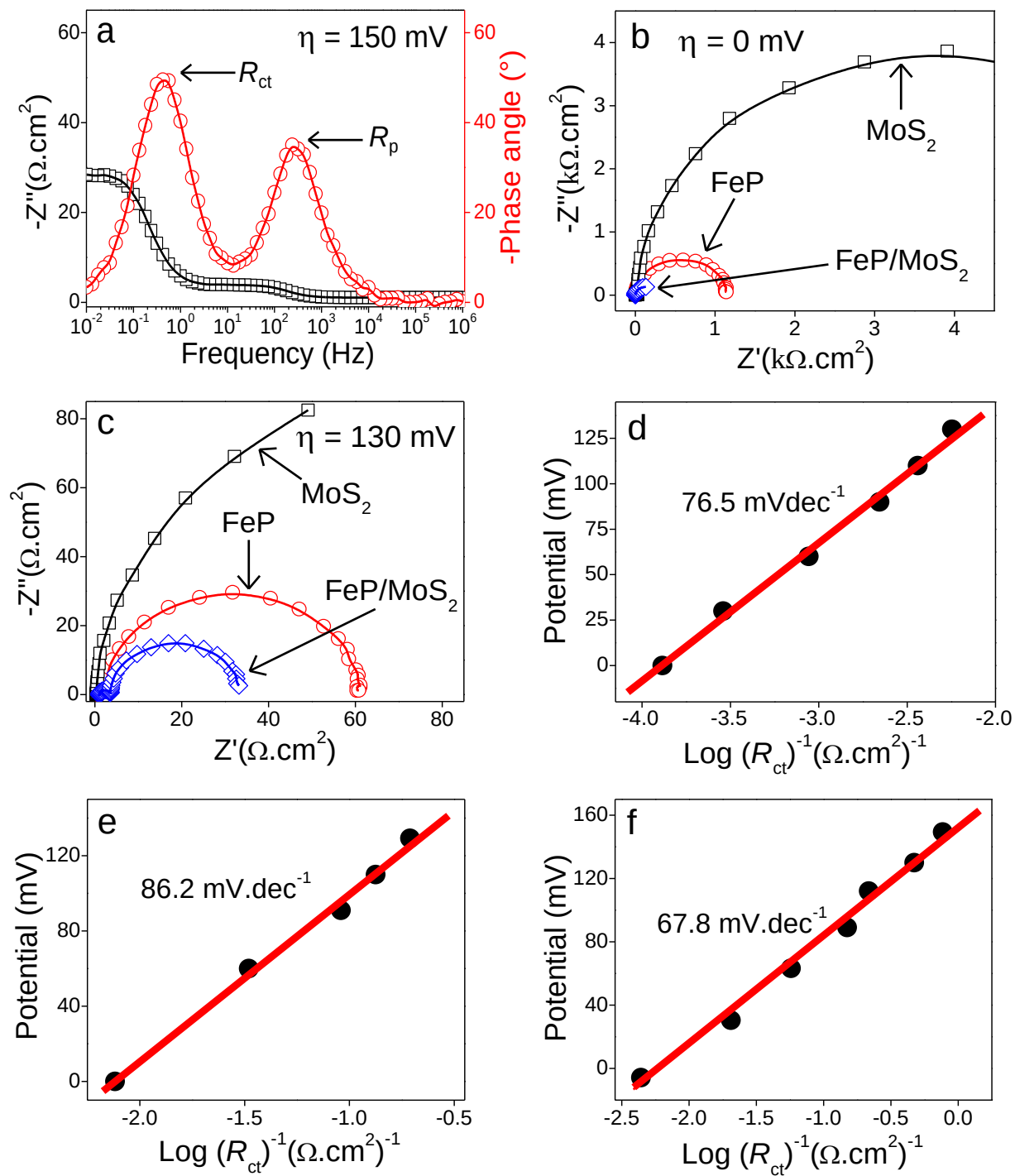


Figure 33: Bode plot of FeP/MoS₂ obtained at $\eta = 150$ mV, comparative Nyquist plots recorded at $\eta = 0$ mV (b) and $\eta = 130$ mV (c), Tafel slopes of FeP (d), MoS₂ (e) and FeP/MoS₂ (f) determined by EIS. All the measurements were performed in 0.5 M H₂SO₄ at cathodic η

and FeP/MoS₂. For instance, a typical Bode plot of FeP/MoS₂ electrode recorded at $\eta = 150 \text{ mV}_{\text{RHE}}$ is shown in Figure 32a. All the EIS data, therefore, were fitted with two-time constant parallel model. This equivalent circuit model consists of R_s in series with two parallel constant phase element-resistance. The R_s constitutes collective resistances, including the resistance of wiring (R_{wiring}), 2D MoS₂ (R_{MoS_2}), FeP (R_{FeP}) and solution (R_{soln}). In addition, R_{ct} , R_p and C_{dl} represent charge transfer resistance, surface (porous or rough texture) resistance, and capacitance, respectively. The Nyquist plots of MoS₂, FeP and FeP/MoS₂ recorded at $\eta = 0 \text{ mV}_{\text{RHE}}$ are shown in Figure 32b. In Nyquist plots, the semicircular dispersion relates to the resistance or kinetics of interfacial charge transfer operative near the electrode surface; the smaller semicircular arcs correspond to lower resistance or faster charge transfer, while the larger arcs indicate higher resistance or slower charge transfer. The order of intrinsic electrical conductivity of MoS₂, FeP and FeP/MoS₂ is discerned to be $9 \times 10^3 < 3 \times 10^3 < 300 \Omega \text{ cm}^2$. The electrical conductivity in MoS₂ is obstructed by its band gap ($\sim 1.8 \text{ eV}$), while higher electrical conductivity in FeP is attributed to its semi-metallic nature. The R_{ct} are calculated by conducting measurements at different potentials. For example, the Nyquist plots of MoS₂, FeP and FeP/MoS₂ obtained at $\eta = 130 \text{ mV}_{\text{RHE}}$ are compared in the Figure 32c. The respective R_{ct} are computed to be 125, 61, and $33 \Omega \text{ cm}^2$, implying that the FeP/MoS₂ is capable of transferring electron more efficiently than FeP and MoS₂. The electrical conductivity of the electrodes is consistent with their HER performance. Unlike intrinsic electrical conductivity, the R_{ct} is related to the amount of catalytic sites available for the reaction. The size and the quality of dispersion of catalytic centers have significant impact on the surface charge transfer kinetics. In the case of supported catalytic systems, the distribution of catalytic sites is

likely to be better than that of supportless catalytic systems. Fairly-dispersed FeP nanoparticles enrich the surface of 2D MoS₂ nanosheets with greater accessible active sites, and thus leading to better HER performance.

The anticipation that dispersing FeP on 2D MoS₂ produces surface with more active sites is corroborated by determining the number of active sites and TOF. Later indicates the number of reactant molecules reacted per active site in unit time, and the catalytic ability. It may be noted that the number active sites are directly proportional to the mass of electrocatalysts. As a result, electrocatalyst loading has significant impact on both η and J_g ; η decreases and J_g increases with increasing catalysts amount, until not obstructed by electrical conductivity, mass transport and agglomeration of functional sites. Yet, the benchmark electrocatalyst loading has not been defined, and mostly the activity is evaluated with respect to η to generate $J_g = 10 \text{ mA cm}^{-2}$, causing an ambiguous comparison of catalytic ability. The calculation of TOF offers a more meaningful and fair comparison of electrocatalysts performance under well-defined measurement conditions. The TOF is calculated by eq (1);

$$\text{TOF} = JA/2FN \quad (1)$$

where J = geometric current density (A cm^{-2}), which is measured by linear sweep voltammetry, A = working electrode's geometric area, $1/2$ = two electrons that participate in the production of one H₂ molecule, F = the Faraday constant ($96\,485 \text{ C mol}^{-1}$), and N = the number of catalytic or active sites (mol).

Firstly, the N was determined from cyclic voltammograms recorded between -0.2 V and $+0.6 \text{ V}_{\text{RHE}}$ in neutral phosphate buffer solution ($\text{pH} = 7$) with a scan rate of 20 mV s^{-1} . The CVs of MoS₂, FeP and FeP/MoS₂ are compared in Figure 33a. The respective N for MoS₂,

FeP and FeP/MoS₂ are computed to be 7.30×10^{-9} , 0.62×10^{-8} and 1.83×10^{-8} mol. A comparison of N clearly evinces the proposed notion that the surface of FeP/MoS₂ is endowed with more active sites. The values of N were then used to quantify the TOF. A plot of TOF as a function of η is shown in Figure 33b. The TOF, calculated at $\eta = 110$ mV (the potential at current density of 10 mA cm^{-2}), for MoS₂, FeP and FeP/MoS₂ are 0.06, 0.16 and 0.20 s^{-1} , respectively. The higher TOF confirms the superior intrinsic catalytic ability of FeP/MoS₂.

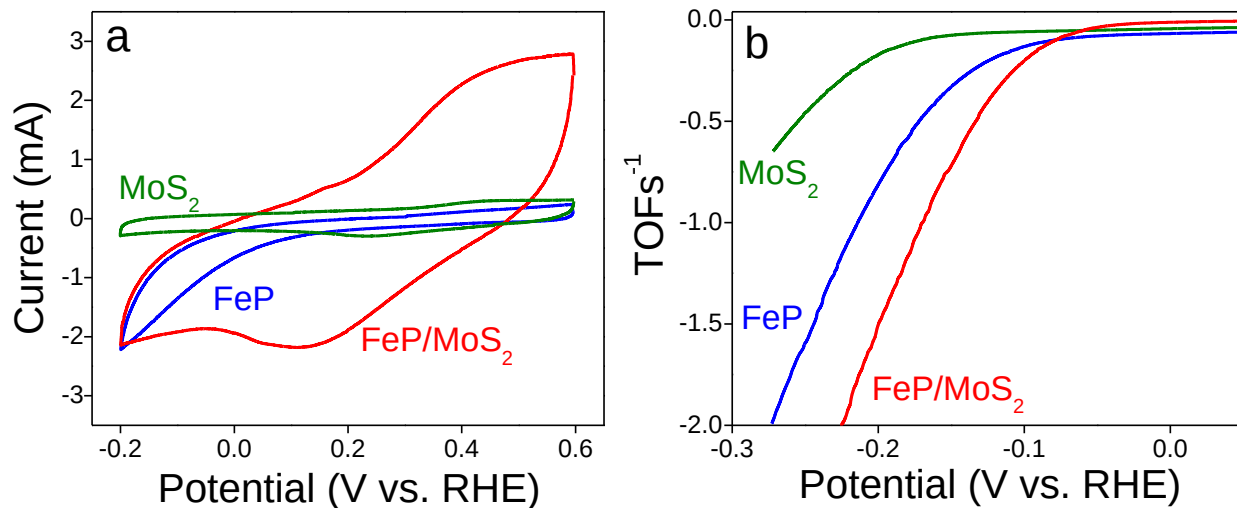
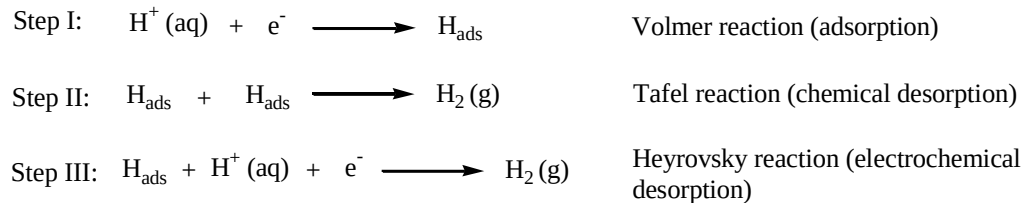


Figure 34: a) CVs MoS₂, FeP and FeP/MoS₂ in pH 7.0 b) the TOF MoS₂, FeP and FeP/MoS₂

In highly acidic electrolyte, three type of reactions is suggested to occur on the surface of electrocatalysts leading to H₂ evolution; (I) adsorption or Volmer reaction, (II) chemical desorption or Tafel reaction, and (III) electrochemical desorption or Heyrovsky reaction. These reactions are summarized below;



Estimation of Tafel slope implies elementary reaction steps involved in the HER. While the intrinsic charge transport kinetics of electrocatalysts in actual system can affect the catalytic mechanism and thus Tafel slope, EIS is employed to calculate Tafel values. The plot of semilogarithmic inverse of R_{ct} against η yields a linear relationship with a gradient or Tafel slope. The slopes of FeP, MoS₂ and FeP/MoS₂ are provided in Figure 32d, e, and f, respectively. The FeP/MoS₂ electrode exhibits the smallest slope (67.8 mV dec⁻¹), followed by FeP (76.5 mV dec⁻¹) and MoS₂ (86.2 mV dec⁻¹). The Tafel value relates to the dependence of the J_g on the η ; a smaller slope suggests faster charge transfer kinetics. On the basis of Tafel values, it seems reasonable to infer that the HER proceeds via the Volmer–Heyrovsky mechanism and rate-determining step is more likely electrochemical desorption of hydrogen ion and atom (Heyrovsky step) [122 – 123].

To highlight the significance of using 2D MoS₂ as a support, identical amount of FeP nanoparticles are also dispersed on high surface area commercial carbon (carbon black Vulcan XC). The HER performance, SSA, ECSA, R_{ct} , active sites and electrical conductivity of FeP/C are investigated and compared to that of FeP/MoS₂. Figure 34a shows the comparative HER performance of FeP/MoS₂ and FeP/C. To produce $J_g = 10 \text{ mA cm}^{-2}$, the η for FeP/MoS₂ and FeP/C are determined to be 110 and 138 mV, respectively. Furthermore, the difference in the produced J_g widens as the polarization potential increases, implying faster kinetics and superior catalytic ability of FeP/MoS₂ electrode surface. For instance, at $\eta = 250 \text{ mV}$, the J_g produced by FeP/MoS₂ and FeP/C are 90 mA

cm^{-2} and 41 mA cm^{-1} , respectively. Despite the fact that FeP/MoS₂ has lower specific surface area ($37.6 \text{ m}^2 \text{ g}^{-1}$) as compared to FeP/C ($82.1 \text{ m}^2 \text{ g}^{-1}$), it exhibits better performance. The ECSA is also estimated and the results are included in the Figure 34c.

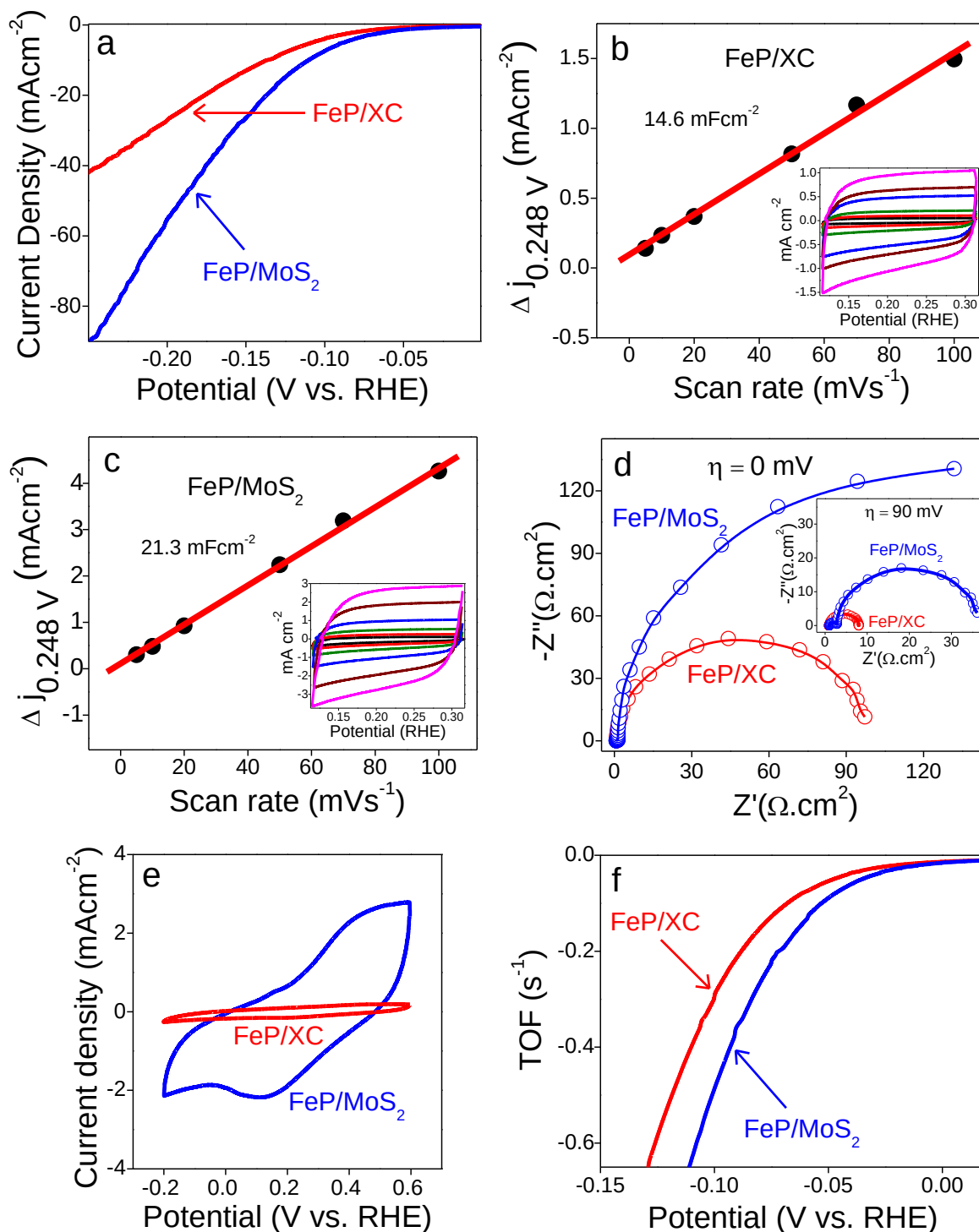


Figure 35: Comparative polarization curves (a), CVs with their corresponding plots of the current density vs. scan rate (b and c), Nyquist plot (d), CVs (e) and corresponding TOF vs. η (f) of FeP/XC and FeP/MoS₂

Unlike specific surface area, the ECSA of FeP/XC is found to be lower (14.6 mF cm^{-1}) as compared to FeP/MoS₂ (21.3 mF cm^{-1}). This clearly suggests the presence of abundant active sites onto the surface of the FeP/MoS₂, which renders strong affinity with protons (H^+). The intrinsic electrical conductivity and R_{ct} of both the electrodes are also examined, and the findings are presented in Figure 34d. The Nyquist plots recorded at $\eta = 0 \text{ mV}_{\text{RHE}}$ clearly suggest that the FeP/C electrode is electrically more conductive as compared to FeP/MoS₂. Moreover, the R_{ct} of the electrode is found to be lower at all the applied η .

The Nyquist plot, for instance, obtained at $90 \text{ mV}_{\text{RHE}}$ is shown in inset. The EIS findings are consistent with intrinsic electronic structure; carbon is electrically conductive while MoS₂ shows semiconducting characteristics. The notion that FeP/MoS₂ surface is enriched with more active sites as compared to FeP/C is corroborated by calculating the number of active sites and the TOF. The results are shown in Figure 34e and f. The number of active sites are calculated to be $1.32 \times 10^{-8} \text{ mol}$ and $1.83 \times 10^{-8} \text{ mol}$, while the TOF (at $\eta = 110 \text{ mV}$) are 0.56 and 0.20 s^{-1} , for FeP/C and FeP/MoS₂, respectively.

Furthermore, the DFT calculations were carried out to give insight into the promotion of HER performance for FeP/ MoS₂. Two possible HER active sites on FeP (011) surface and three sites on the loaded Fe₅P₅ cluster, Figure 36a and b, were considered. The catalytic activity of HER can be estimated using the hydrogen adsorption free energy (ΔG_{H^*}). The smaller $|\Delta G_{\text{H}^*}|$ is related to the higher activity of the catalyst. As shown in Figure 8c, the calculated ΔG_{H^*} s on Fe and P sites are -0.45 and -0.40 eV , respectively. In comparison, Sites 1 (Fe), 2 (P), and 3 (P) of FeP cluster possess ΔG_{H^*} s of -0.29 , 0.36 , and 0.15 eV , respectively. These lower $|\Delta G_{\text{H}^*}|$ s indicate the overall enhancement in HER activity for

FeP/MoS₂ composite system. Besides, the ΔG_{H^*} of MoS₂ basal plane is 2.19 eV, explaining its poor HER performance.

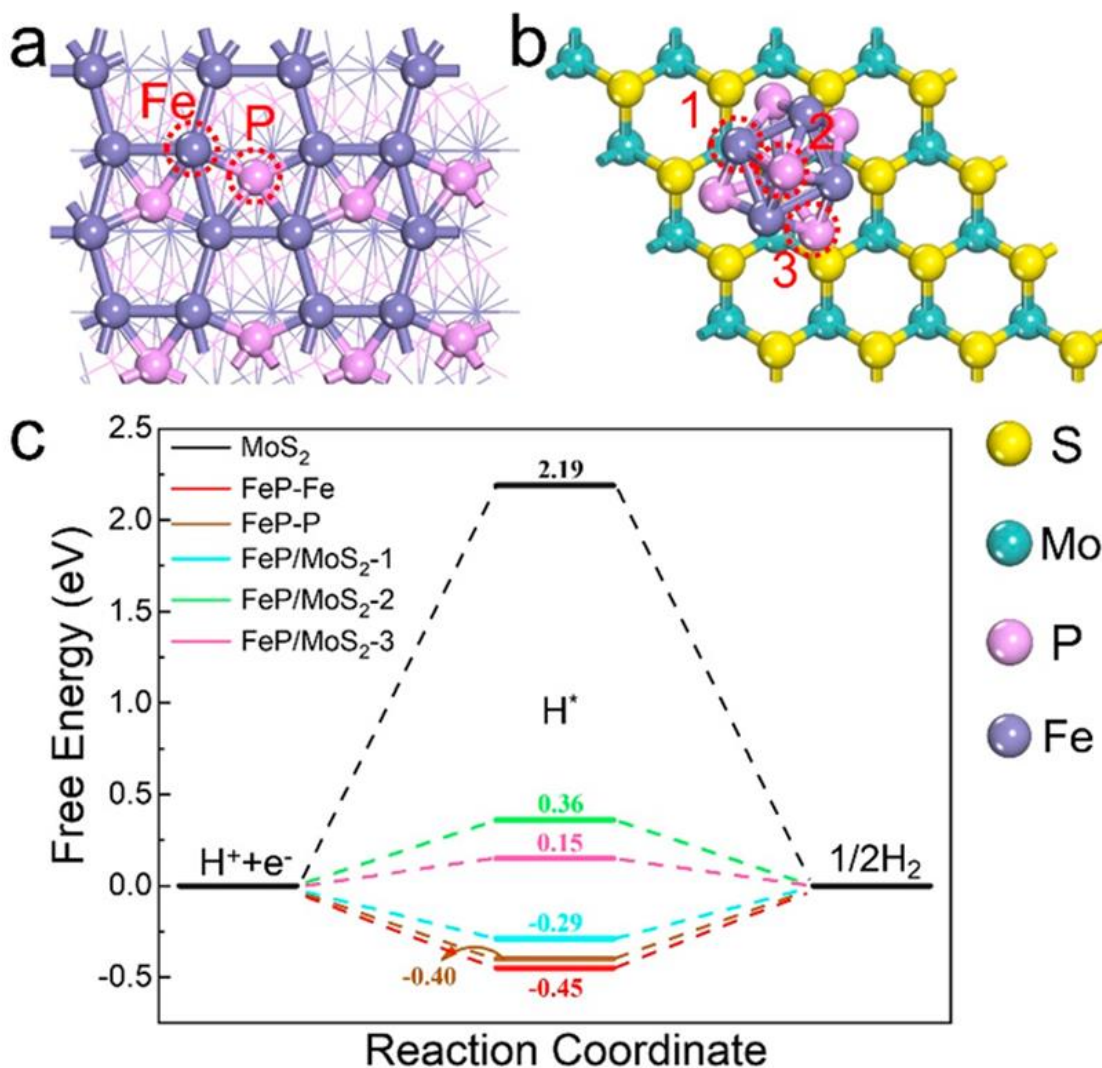


Figure 36: Top view of (a) FeP (011) facet and (b) FeP/MoS₂ composite model. The possible reactive sites are encircled and labeled in red. (c) Free energy profiles of MoS₂, FeP (011), and FeP/MoS₂ on various reaction sites.

6.4. CONCLUSIONS

In summary, the challenges associated with MoS₂ nanosheets, high electrochemical impedance and limited accessibility to catalytic sites, are addressed by modifying its surface with other active sites. The study demonstrated that the 2D ultrathin nanosheets of

MoS₂ can serve as an excellent support to carry additional active sites. This was exemplified by immobilizing FeP nanoparticles onto the surface of MoS₂ nanosheets. The HER performance trend was discerned to be FeP/MoS₂ > FeP/C > FeP > MoS₂. Although the ECSA of FeP was substantially lower (1.25 $\mu\text{f cm}^{-2}$), presumably due to severe agglomeration, as compared to MoS₂ (60.4 mf cm^{-2}) nanosheets, the FeP electrode exhibited better performance. This is ascribed to superior intrinsic electrical conductivity, smaller R_{ct} , higher active sites and TOF of the FeP electrode. Furthermore, ECSA, electrical conductivity, R_{ct} , N, and TOF of FeP nanoparticles were significantly enhanced when embedded within nanosheets of MoS₂. This design rendered remarkable HER performance in FeP/MoS₂, notably superior than bare FeP and MoS₂. The HER performance of FeP/MoS₂ was also compared with FeP/C; despite the fact that FeP/MoS₂ was electrically less conductive, it exhibited better performance than FeP/C. The impact of lower conductivity was predominantly undermined by higher ECSA, catalytic sites and TOF. This strengthened our notion that 2D MoS₂ act as both active sites and support. Findings reveal that the density of catalytic sites is predominant among various performance-dictating features. The study highlights that the nanosheets of active sites can be utilized as an excellent support for the dispersion of additional active sites, in an attempt to design highly active electrodes for energy conversion applications.

References

1. Y. Xu, R. Wu, J. Zhang, Y. Shi and B. Zhang, Anion-Exchange Synthesis of Nanoporous FeP Nanosheets as Electrocatalysts for Hydrogen Evolution Reaction Chem. Commun., 2013, 49, 6656–6658.

2. J. Q. Tian, Q. Liu, A. M. Asiri and X. P. Sun, Self-Supported Nanoporous Cobalt Phosphide Nanowire Arrays: An Efficient 3D Hydrogen-Evolving Cathode over the Wide Range of pH 0–14. *J. Am. Chem. Soc.*, 2014, 136, 7587–7590.
3. Yang, H.; Zhang, Y.; Hu, F.; Wang, Q. Urchin-Like CoP Nanocrystals as Hydrogen Evolution Reaction and Oxygen Reduction Reaction Dual-Electrocatalyst with Superior Stability. *Nano Lett.* 2015, 15, 7616.
4. Liang, Y.; Liu, Q.; Asiri, A. M.; Sun, X.; Luo, Y. Self-Supported FeP Nanorod Arrays: A Cost-Effective 3D Hydrogen Evolution Cathode with High Catalytic Activity. *ACS Catal.* 2014, 4, 4065.
5. Liu, M.; Li, J. Cobalt Phosphide Hollow Polyhedron as Efficient Bifunctional Electrocatalysts for the Evolution Reaction of Hydrogen and Oxygen. *ACS Appl. Mater. Interfaces* 2016, 8, 2158.
6. Shi, Yanmei, and Bin Zhang, Recent Advances in Transition Metal Phosphide Nanomaterials: Synthesis and Applications in Hydrogen Evolution Reaction. *Chem. Soc. Rev.* 45.6 (2016): 1529-1541.
7. E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, Nanostructured Nickel Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction. *J. Am. Chem. Soc.*, 2013, 135, 9267–9270.
8. M. Ledendecker, S. Krick Calderon, C. Papp, H. P. Steinrück, M. Antonietti, M. Shalom, The Synthesis of Nanostructured Ni₅P₄ Films and their Use as a Non-Noble Bifunctional Electrocatalyst for Full Water Splitting. *Angew. Chem., Int. Ed.*, 2015, 127, 12538–12542.
9. E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, Nanostructured Nickel Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction. *J. Am. Chem. Soc.*, 2013, 135, 9267–9270.
10. J.-S. Moon, J.-H. Jang, E.-G. Kim, Y.-H. Chung, S. J. Yoo and Y.-K. Lee, The Nature of Active Sites of Ni₂P Electrocatalyst for Hydrogen Evolution Reaction *J. Catal.*, 2015, 326, 92–99.
11. E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles. *Angew. Chem., Int. Ed.*, 2014, 53, 5427–5430.
12. Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri and X. Sun, Carbon Nanotubes Decorated with CoP Nanocrystals: A Highly Active Non-Noble-Metal Nanohybrid Electrocatalyst for Hydrogen Evolution. *Angew. Chem., Int. Ed.*, 2014, 53, 6710–6714.
13. J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis and R. E. Schaak, Amorphous Molybdenum Phosphide Nanoparticles for Electrocatalytic Hydrogen Evolution. *Chem. Mater.*, 2014, 26, 4826–4831.
14. Z. H. Pu, I. S. Amiinu, M. Wang, Y. S. Yang and S. C. Mu, Semimetallic MoP₂: an Active and Stable Hydrogen Evolution Electrocatalyst over the Whole pH Range Nanoscale, 2016, 8, 8500–8504.

15. J. Tian, Q. Liu, N. Cheng, A. M. Asiri and X. P. Sun, Self-Supported Cu_3P Nanowire Arrays as an Integrated High-Performance Three-Dimensional Cathode for Generating Hydrogen from Water. *Angew. Chem., Int. Ed.*, 2014, 53, 9577–9581.
16. L. Ma, X. P. Shen, H. Zhou, J. Zhu, C. Xi, Z. Y. Ji and L. Kong, Synthesis of Cu_3P Nanocubes and their Excellent Electrocatalytic Efficiency for the Hydrogen Evolution Reaction in Acidic Solution. *RSC Adv.*, 2016, 6, 9672–9677.
17. J. F. Callejas, J. M. McEnaney, C. G. Read, J. C. Crompton, A. J. Biacchi, E. J. Popczun, T. R. Gordon, N. S. lewis and R. E. Schaak, Electrocatalytic and Photocatalytic Hydrogen Production from Acidic and Neutral-pH Aqueous Solutions Using Iron Phosphide Nanoparticles. *ACS Nano*, 2014, 8, 11101–11107.
18. Z. Zhang, B. P. Lu, J. H. Hao, W. S. Yang and J. L. Tang, FeP Nanoparticles Grown on Graphene Sheets as Highly Active Non-Precious-Metal Electrocatalysts For Hydrogen Evolution Reaction *Chem. Commun.*, 2014, 50, 11554–11557.
19. P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J. Wang, K. H. Lim and X. Wang, Molybdenum Phosphide as an Efficient Electrocatalyst for the Hydrogen Evolution Reaction *Energy Environ. Sci.*, 2014, 7, 2624–2629.
20. J. Kibsgaard and T. F. Jaramillo, Molybdenum Phosphosulfide: an Active, Acid-Stable, Earth-Abundant Catalyst for the Hydrogen Evolution Reaction. *Angew. Chem., Int. Ed.*, 2014, 53, 14433–14437.
21. T. Wu, S. Chen, D. Zhang and J. Hou, Facile Preparation of Semimetallic MoP_2 as a Novel Visible Light Driven Photocatalyst with High Photocatalytic Activity *J. Mater. Chem. A*, 2015, 3, 10360–10367.
22. Z. Pu, Q. Liu, A. M. Asiri and X. Sun, Tungsten Phosphide Nanorod Arrays Directly Grown on Carbon Cloth: A Highly Efficient and Stable Hydrogen Evolution Cathode at All pH Values. *ACS Appl. Mater. Interfaces*, 2014, 6, 21874–21879.
23. H. Zhaoab and Zhong-Y. Yuan, Transition Metal–Phosphorus-Based Materials for Electrocatalytic Energy Conversion Reactions. *Catal. Sci. Technol.*, 2017, 7, 330–347.
24. Wang, A. L., Lin, J., Xu, H., Tong, Y. X., & Li, G. R.J. Ni_2P – CoP Hybrid Nanosheet Arrays Supported on Carbon Cloth as an Efficient Flexible Cathode for Hydrogen Evolution *Mater. Chem. A*, 2016, 4, 16992–16999.
25. Pan, Y., Chen, Y., Lin, Y., Cui, P., Sun, K., Liu, Y., & Liu, C. Cobalt Nickel Phosphide Nanoparticles Decorated Carbon Nanotubes as Advanced Hybrid Catalysts for Hydrogen Evolution *J. Mater. Chem. A*, 2016, 4, 14675–14686
26. Ma, Yuan-Yuan, et al. Highly Efficient Hydrogen Evolution From Seawater by a Low-Cost and Stable CoMoP@C Electrocatalyst Superior to Pt/C . *Energy Environ. Sci.*, 2017,10, 788.
27. B. Cao, G. M. Veith, J. C. Neuefeind, R. R. Adzic and P. G. Khalifah, Mixed Close-Packed Cobalt Molybdenum Nitrides as Non-Noble Metal Electrocatalysts

- for the Hydrogen Evolution Reaction *J. Am. Chem. Soc.*, 2013, 135, 19186–19192.
28. J. Miao, F. X. Xiao, H. B. Yang, S. Y. Khoo, J. Chen, Z. Fan, Y. Y. Hsu, H. M. Chen, H. Zhang and B. Liu, Hierarchical Ni-Mo-S Nanosheets on Carbon Fiber Cloth: A Flexible Electrode for Efficient Hydrogen Generation in Neutral Electrolyte *Sci. Adv.*, 2015, 1, e1500259.
 29. H. Yan, C. Tian, L. Sun, B. Wang, L. Wang, J. Yin, A. Wu and H. Fu, Small-Sized and High-Dispersed WN From $[\text{SiO}_4(\text{W}_3\text{O}_9)_4]^{4-}$ Clusters Loading on GO-Derived Graphene as Promising Carriers for Methanol Electro-Oxidation *Energy Environ. Sci.*, 2014, 7, 1939 – 1949.
 30. Y. Liu and W. E. Mustain, Structural and Electrochemical Studies of Pt Clusters Supported on High-Surface-Area Tungsten Carbide for Oxygen Reduction *ACS Catal.*, 2011, 1, 212– 220.
 31. D. Braga, I. G. Lezama, H. Berger and A. F. Morpurgo, Quantitative Determination of the Band Gap of WS_2 with Ambipolar Ionic Liquid-Gated Transistors *Nano Lett.*, 2012, 12, 5218 – 5223.
 32. J. Jang, D. J. Ham, E. Ramasamy, J. Lee and J. S. Lee, Platinum-Free Tungsten Carbides as an Efficient Counter Electrode for Dye Sensitized Solar Cells. *Chem. Commun.*, 2010, 46, 8600 – 8602.
 33. R. Wu, J. Zhang, Y. Shi, D. Liu and B. Zhang, Metallic WO_2 -Carbon Mesoporous Nanowires as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction. *J. Am. Chem. Soc.*, 2015, 137, 6983 – 6986.
 34. Z. H. Pu, Q. Liu, A. M. Asiri and X. P. Sun, Tungsten Phosphide Nanorod Arrays Directly Grown on Carbon Cloth: A Highly Efficient and Stable Hydrogen Evolution Cathode at All pH Values. *ACS Appl. Mater. Interfaces*, 2014, 6, 21874–21879.
 35. J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis and R. E. Schaak, Electrocatalytic Hydrogen Evolution using Amorphous Tungsten Phosphide Nanoparticles *Chem. Commun.*, 2014, 50, 11026–11028.
 36. Z. C. Xing, Q. Liu, A. M. Asiri and X. P. Sun, Sulfur-Decorated Molybdenum Carbide Catalysts for Enhanced Hydrogen Evolution. *ACS Catal.*, 2015, 5, 145–149.
 37. H. Zhao, Z.Y. Yuan, Transition Metal-Phosphorus-Based Materials for Electrocatalytic Energy Conversion Reactions. *Catal. Sci. Technol.*, 2017, 7, 330.
 38. Wang, X. D., Xu, Y. F., Rao, H. S., Xu, W. J., Chen, H. Y., Zhang, W. X., Su, C. Y. Novel Porous Molybdenum Tungsten Phosphide Hybrid Nanosheets on Carbon Cloth for Efficient Hydrogen Evolution. *Energy Environ. Sci.*, 2016, 9, 1468—1475.
 39. W. F. Chen, C. H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Z. R. R. Adzic, Biomass-Derived Electrocatalytic Composites for Hydrogen Evolution. *Energy Environ. Sci.*, 2013, 6, 943.
 40. M. Qamar, A. Adam, B. Merzougui, A. Helal, O. Abdulhamid, M. N. Siddiqui, Metal-Organic Framework-Guided Growth of Mo_2C Embedded in Mesoporous

- Carbon as a High-Performance and Stable Electrocatalyst for the Hydrogen Evolution Reaction. *J. Mater. Chem. A* **2016**, 4, 16225.
41. L. Jiao, Y.-X. Zhou, H.-L. Jiang, Metal–Organic Framework-Based CoP/Reduced Graphene Oxide: High-Performance Bifunctional Electrocatalyst for Overall Water Splitting *Chem. Sci.* **2016**, 7, 1690.
 42. H. Yan, Y. Jiao, A. Wu, C. Tian, X. Zhang, L. Wang, Z. Ren, H. Fu, Cluster-Like Molybdenum Phosphide Anchored on Reduced Graphene Oxide for Efficient Hydrogen Evolution over a Broad pH Range *Chem. Commun.*, **2016**, 52, 9530.
 43. L. F. Pan, Y. H. Li, S. Yang, P. F. Liu, M. Q. Yua, H. G. Yang, *Chem. Commun.*, **2014**, 50, 13135.
 44. C. He, J. Tao, Molybdenum Carbide Stabilized on Graphene with High Electrocatalytic Activity for Hydrogen Evolution Reaction. *Chem. Commun.*, **2015**, 51, 8323.
 45. Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri, X. Sun, *Angew. Carbon Nanotubes Decorated with CoP Nanocrystals: A Highly Active Non-Noble-Metal Nanohybrid Electrocatalyst for Hydrogen Evolution* *Chem. Int. Ed.* **2014**, 53, 6710.
 46. P. M. Ajayan and J. M. Tour, Nanotube Composites *Nature*, **2007**, 447, 1066.
 47. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide. *Nature*, **2006**, 442, 282.
 48. Lee, W. J., Maiti, U. N., Lee, J. M., Lim, J., Han, T. H., & Kim, S. O. Nitrogen-Doped Carbon Nanotubes and Graphene Composite Structures for Energy and Catalytic Applications. *Chem. Commun.*, **2014**, 50, 6818—6830.
 49. D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang and G. Yu, Synthesis of N-Doped Graphene by Chemical Vapor Deposition and its Electrical Properties. *Nano Lett.*, **2009**, 9, 1752.
 50. H. C. Choi, S. Y. Bae, J. Park, K. Seo, C. Kim, B. Kim, H. J. Song and H.-J. Shin, Experimental and theoretical studies on the structure of N-doped carbon nanotubes: Possibility of intercalated molecular N₂. *Appl. Phys. Lett.*, **2004**, 85, 5742.
 51. Zhang, Z., Hao, J., Yang, W., & Tang, J. Defect-Rich CoP/Nitrogen-Doped Carbon Composites Derived from a Metal–Organic Framework: High-Performance Electrocatalysts for the Hydrogen Evolution reaction. *ChemCatChem* **2015**, 7, 1920 – 1925
 52. Pan, Y., Lin, Y., Chen, Y., Liu, Y., & Liu, C. Cobalt Phosphide-Based Electrocatalysts: Synthesis and Phase Catalytic Activity Comparison for Hydrogen Evolution. *J. Mater. Chem. A*, **2016**, 4, 4745–4754.
 53. J. Chang, L. Liang, C. Li, M. Wang, J. Ge, C. Liu and W. Xing, Ultrathin Cobalt Phosphide Nanosheets as Efficient Bifunctional Catalysts for a Water Electrolysis

Cell and the Origin for Cell Performance Degradation. *Green Chem.*, **2016**, *18*, 2287 - 2295.

54. Wang, J.; Xu, F.; Jin, H.; Chen, Y.; Wang, Y. Non-Noble Metal-Based Carbon Composites in Hydrogen Evolution Reaction: Fundamentals to Applications. *Adv. Mater.* **2017**, *29*, 1605838 - 1605875.
55. G.M. Whitesides, G.W. Crabtree, Don't forget long-term fundamental research in energy, *Science* *315* (2007) 796–798.
56. P.C.K. Vesborg, B. Seger, I.B. Chorkendorff, Recent development in hydrogen evolution reaction catalysts and their practical implementation, *J. Phys. Chem. Lett.* *6* (2015) 951–957.
57. M.S. Faber, S. Jin, Earth-abundant inorganic electrocatalysts and their nanostructures for energy conversion applications, *Energy Environ. Sci.* *7* (2014) 3519–3542.
58. X. Zou, Y. Zhang, Noble metal-free hydrogen evolution catalysts for water splitting, *Chem. Soc. Rev.* *44* (2015) 5148–5180.
59. R. Michalsky, Y.J. Zhang, A.A. Peterson, Trends in the hydrogen evolution activity of metal carbide catalysts, *ACS Catal.* *4* (2014) 1274–1278.
60. Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, et al., Mo₂C Nanoparticles dispersed on hierarchical carbon microflowers for efficient electrocatalytic hydrogen evolution, *ACS Nano* *10* (2016) 11337–11343.
61. X. Fan, H. Zhou, X. Guo, M₃C (M: Fe, Co, Ni) Nanocrystals encased in graphene nanoribbons: an active and stable bifunctional electrocatalyst for oxygen reduction and hydrogen evolution reactions, *ACS Nano* *9* (2015) 5125–5134.
62. D.J. Li, U.N. Maiti, J. Lim, D.S. Choi, W.J. Lee, Y. Oh, et al., Molybdenum sulfide/N-doped CNT forest hybrid catalysts for high-performance hydrogen evolution reaction, *Nano Lett.* *14* (2014) 1228–1233.
63. C.G. Morales-Guio, L.A. Stern, X. Hu, Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution, *Chem. Soc. Rev.* *43* (2014) 6555–6569.
64. D. Voiry, H. Yamaguchi, J. Li, R. Silva, D.C. Alves, T. Fujita, M. Chen, T. Asefa, V.B. Shenoy, G. Eda, M. Chhowalla, Enhanced catalytic activity in strained chemically exfoliated WS₂ nanosheets for hydrogen evolution, *Nat. Mater.* *12* (2013) 850–855.
65. D. Kong, H. Wang, Z. Lu, Y. Cui, CoSe₂ nanoparticles grown on carbon fiber paper: an efficient and stable electrocatalyst for hydrogen evolution reaction, *J. Am. Chem. Soc.* *136* (2014) 4897–4900.
66. W.F. Chen, K. Sasaki, C. Ma, A.I. Frenkel, N. Marinkovic, J.T. Muckerman, Y. Zhu, R.R. Adzic, Hydrogen-evolution catalysts based on non-noble metal nickel–molybdenum nitride nanosheets, *Angew. Chem. Int. Ed.* *51* (2012) 6131–6135.
67. J.F. Callejas, C.G. Read, C.W. Roske, N.S. Lewis, R.E. Schaak, Synthesis, characterization, and properties of metal phosphide catalysts for the hydrogen-evolution reaction, *Chem. Mater.* *28* (2016) 6017–6044.
68. A. Adam, M.H. Suliman, M.N. Siddiqui, Z.H. Yamani, B. Merzougui, M. Qamar, Interconnected hollow cobalt phosphide grown on carbon nanotubes for hydrogen evolution reaction, *ACS Appl. Mater. Interfaces* *10* (2018) 29407–29416.

69. A. Adam, M.H. Suliman, H. Dafalla, A.R. Al-Arfaj, M.N. Siddiqui, M. Qamar, Rationally dispersed molybdenum phosphide on carbon nanotubes for the hydrogen evolution reaction, *ACS Sustainable Chem. Eng.* 6 (2018) 11414–11423.
70. Y. Chen, G. Yu, W. Chen, Y. Liu, G.D. Li, P. Zhu, Q. Tao, Q. Li, J. Liu, X. Shen, H. Li, Highly active, nonprecious electrocatalyst comprising borophene subunits for the hydrogen evolution reaction, *J. Am. Chem. Soc.* 139 (2017) 12370–12373.
71. P.R. Jothi, Y. Zhang, J.P. Scheifers, H. Park, B.P. Fokwa, Molybdenum diboride nanoparticles as a highly efficient electrocatalyst for the hydrogen evolution reaction, *Sustainable Energy Fuels* 1 (2017) 1928–1934.
72. C.G. Read, J.F. Callejas, C.F. Holder, R.E. Schaak, General strategy for the synthesis of transition metal phosphide films for electrocatalytic hydrogen and oxygen evolution, *ACS Appl. Mater. Interfaces* 8 (2016) 12798–12803.
73. J. Jiang, C. Wang, J. Zhang, W. Wang, X. Zhou, B. Pan, K. Tang, J. Zuo, Q. Yang, Synthesis of FeP₂/C nanohybrids and their performance for hydrogen evolution reaction, *J. Mater. Chem. A* 3 (2015) 499–503.
74. L. Tian, X. Yan, X. Chen, Electrochemical activity of iron phosphide nanoparticles in hydrogen evolution reaction, *ACS Catal.* 6 (2016) 5441–5448.
75. Y. Zhang, H. Zhang, Y. Feng, L. Liu, Y. Wang, Unique Fe₂P nanoparticles enveloped in sandwichlike graphited carbon sheets as excellent hydrogen evolution reaction catalyst and lithium-ion battery anode, *ACS Appl. Mater. Interfaces* 7 (2015) 26684–26690.
76. Q. Liu, Z. Pu, A.M. Asiri, X. Sun, Nitrogen-doped carbon nanotube supported iron phosphide nanocomposites for highly active electrocatalysis of the hydrogen evolution reaction, *Electrochim. Acta* 149 (2014) 324–329.
77. C. Lv, Q. Yang, Q. Huang, Z. Huang, H. Xia, C. Zhang, Phosphorus doped single wall carbon nanotubes loaded with nanoparticles of iron phosphide and iron carbide for efficient hydrogen evolution, *J. Mater. Chem. A* 4 (2016) 13336–13343.
78. Z. Zhang, B. Lu, J. Hao, W. Yang, J. Tang, FeP Nanoparticles grown on graphene sheets as highly active non-precious-metal electrocatalysts for hydrogen evolution reaction, *Chem. Commun.* 50 (2014) 11554–11557. [18]
79. Z. Zhang, J. Hao, W. Yang, B. Lu, J. Tang, Modifying candle soot with FeP nanoparticles into high-performance and cost-effective catalysts for the electrocatalytic hydrogen evolution reaction, *Nanoscale* 7 (2015) 4400–4405.
80. D.Y. Chung, S.W. Jun, G. Yoon, H. Kim, J.M. Yoo, K.-S. Lee, T. Kim, H. Shin, A.K. Sinha, S.G. Kwon, K. Kang, T. Hyeon, Y.-E. Sung, Large-scale synthesis of carbon-shell-coated FeP nanoparticles for robust hydrogen evolution reaction electrocatalyst, *J. Am. Chem. Soc.* 139 (2017) 6669–6674.
81. R. Karimi Shervedani, A. Lasia, “Evaluation of the Surface Roughness of Ni-Zn-P Electrodes by in situ Methods”, *J. Appl. Electrochem.*, 29 (1999) 979.
82. H. Shang, Y. Lu, F. Zhao, C. Chao, B. Zhang, H. Zhang, Preparing high surface area porous carbon from biomass by carbonization in a molten salt medium, *RSC Adv.* 5 (2015) 75728–75734.
83. F. Han, C. Zhang, J. Yang, G. Ma, K. He, X. Li, Well-dispersed and porous FeP@C nanoplates with stable and ultrafast lithium storage performance through conversion reaction mechanism, *J. Mater. Chem. A* 4 (2016) 12781–12789.

84. Y. Yan, L. Thia, B.Y. Xia, X. Ge, Z. Liu, A. Fisher, X. Wang, Construction of efficient 3D gas evolution electrocatalyst for hydrogen evolution: porous FeP nanowire arrays on graphene sheets, *Adv. Sci.* 2 (2015) 1500120–1500128.
85. Z. Zhang, B. Lu, J. Hao, W. Yang, J. Tang, FeP Nanoparticles grown on graphene sheets as highly active non-precious-metal electrocatalysts for hydrogen evolution reaction, *Chem. Commun.* 50 (2014) 11554–11557. [18]
86. N.A. Khan, J.W. Jun, J.H. Jeong, S.H. Jung, Remarkable adsorptive performance of a metal–organic framework, vanadium-benzenedicarboxylate (MIL-47), for benzothiophene, *Chem. Commun.* 2011, 47, 1306–1308.
87. Q. Lu, G.S. Hutchings, W. Yu, Y. Zhou, R.V. Forest, R. Tao, J. Rosen, B.T. Yonemoto, Z. Cao, H. Zheng, J.Q. Xiao, Highly porous non-precious bimetallic electrocatalysts for efficient hydrogen evolution, *Nat. Commun.* 6 (2015) 6567–6574.
88. C. Wan, Y.N. Regmi, B.M. Leonard, Multiple phases of molybdenum carbide as electrocatalysts for the hydrogen evolution reaction, *Angew. Chem. Int. Ed.* 53 (2014) 6407–6410.
89. Y. Zhang, Q. Gao, Z. Lin, T. Zhang, J. Xu, Y. Tan, W. Tian, L. Jiang, Constructing free standing metal organic framework MIL-53 membrane based on anodized aluminum oxide precursor, *Sci. Rep.* 4 (2014) 4947–4952.
90. Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, MoS₂ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction, *J. Am. Chem. Soc.* 133 (2011) 7296–7299.
91. R. Jurczakowski, C. Hitz, A. Lasia, Impedance of porous Au based electrodes, *J. Electroanal. Chem.* 572 (2004) 355–366.
92. C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction, *J. Am. Chem. Soc.* 2013, 135, 16977–16987.
93. L. Birry, A. Lasia, Studies of the hydrogen evolution reaction on Raney nickel–molybdenum electrodes, *J. Appl. Electrochem.* 34 (2004) 735.
94. Y. Yan, B. Zhao, S.C. Yi, X. Wang, Assembling pore-rich FeP nanorods on the CNT backbone as an advanced electrocatalyst for oxygen evolution, *J. Mater. Chem. A* 4 (2016) 13005–13010.
95. Y. Cheng, J. Guo, Y. Huang, Z. Liao, Z. Xiang, Ultrastable hydrogen evolution electrocatalyst derived from phosphide postmodified metal-organic frameworks, *Nano Energy* 35 (2017) 115–120.
96. C. Lv, Z. Peng, Y. Zhao, Z. Huang, C. Zhang, The hierarchical nanowires array of iron phosphide integrated on a carbon fiber paper as an effective electrocatalyst for hydrogen generation, *J. Mater. Chem. A* 4 (2016) 1454–1460.
97. H. Huang, C. Yu, J. Yang, X. Han, C. Zhao, S. Li, Z. Liu, J. Qiu, Ultrasmall diiron phosphide nanodots anchored on graphene sheets with enhanced electrocatalytic activity for hydrogen production via high-efficiency water splitting, *J. Mater. Chem. A* 4 (2016) 16028–16035.
98. Y. Yan, B.Y. Xia, X. Ge, Z. Liu, A. Fisher, X. Wang, A flexible electrode based on iron phosphide nanotubes for overall water splitting, *Chem. Eur. J.* 21 (2015) 18062–18067.

99. C.Y. Son, I.H. Kwak, Y.R. Lim, J. Park, FeP and FeP₂ nanowires for efficient electrocatalytic hydrogen evolution reaction, *Chem. Commun.* 52 (2016) 2819–2822.
100. H. Dong, T. Lei, Y. He, N. Xu, B. Huang, C.T. Liu, Electrochemical performance of porous Ni₃Al electrodes for hydrogen evolution reaction, *Int. J. Hydrogen Energy.* 36 (2011) 12112–12120.
101. C. Hitz, A. Lasia, Experimental study and modeling of impedance of the HER on porous Ni electrodes, *J. Electroanal. Chem.* 500 (2001) 213–222.
102. B. Łosiewicz, A. Budniok, E. Rówiński, E. Łągiewka, A. Lasia, The structure, morphology and electrochemical impedance study of the hydrogen evolution reaction on the modified nickel electrodes, *Int. J. Hydrogen Energy.* 29 (2004) 145–157.
103. R.K. Shervedani, A. Lasia, Study of the hydrogen evolution reaction on Ni-Mo-P electrodes in alkaline solutions, *J. Electrochem. Soc.* 145 (1998) 2219–2225.
104. W.-F. Chen, J.T. Muckerman, E. Fujita, Recent developments in transition metal carbides and nitrides as hydrogen evolution electrocatalysts, *Chem. Commun.* 49 (2013) 8896–8909.
105. J.-F. Lin, O. Pitkänen, J. Mäklin, R. Puskas, A. Kukovecz, A. Dombovari, G. Toth, K. Kordas, Synthesis of tungsten carbide and tungsten disulfide on vertically aligned multi-walled carbon nanotube forests and their application as non-Pt electrocatalysts for the hydrogen evolution reaction, *J. Mater. Chem. A.* 3 (2015) 14609–14616.
106. J.D. Benck, T.R. Hellstern, J. Kibsgaard, P. Chakthranont, T.F. Jaramillo, Catalyzing the hydrogen evolution reaction (HER) with molybdenum sulfide nanomaterials, *ACS Catal.* 4 (2014) 3957–3971.
107. A.B. Laursen, S. Kegnæs, S. Dahl, I. Chorkendorff, Molybdenum sulfides-efficient and viable materials for electro- and photoelectrocatalytic hydrogen evolution, *Energy Environ. Sci.* 5 (2012) 5577–5591.
108. R. Miao, B. Dutta, S. Sahoo, J. He, W. Zhong, S.A. Cetegen, T. Jiang, S.P. Alpay, S.L. Suib, Mesoporous iron sulfide for highly efficient electrocatalytic hydrogen evolution, *J. Am. Chem. Soc.* 139 (2017) 13604–13607.
109. P. Xiao, W. Chen, X. Wang, A review of phosphide-based materials for electrocatalytic hydrogen evolution, *Adv. Energy Mater.* 5 (2015) 1500985.
110. H. Park, A. Encinas, J.P. Scheifers, Y. Zhang, B.P.T. Fokwa, Boron-dependency of molybdenum boride electrocatalysts for the hydrogen evolution reaction, *Angew. Chem. Int. Ed.* 56 (2017) 5575–5578.
111. Y. Liu, G. Yu, G. Li, Y. Sun, T. Asefa, W. Chen, X. Zou, Coupling Mo₂C with nitrogen-rich nanocarbon leads to efficient hydrogen-evolution electrocatalytic sites, *Angew. Chem. Int. Ed.* 54 (2015) 10752–10757.

112. T.R. Hellstern, J. Kibsgaard, C. Tsai, D.W. Palm, L.A. King, F. Abild-Pedersen, T.F. Jaramillo, Investigating catalyst–support interactions to improve the hydrogen evolution reaction activity of thiomolybdate $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters, *ACS Catal.* 7 (2017) 7126–7130.
113. W. Zhou, J. Jia, J. Lu, L. Yang, D. Hou, G. Li, S. Chen, Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction, *Nano Energy.* 28 (2016) 29–43.
114. B. Šljukić, M. Vujković, L. Amaral, D.M.F. Santos, R.P. Rocha, C.A.C. Sequeira, J.L. Figueiredo, Carbon-supported Mo_2C electrocatalysts for hydrogen evolution reaction, *J. Mater. Chem. A.* 3 (2015) 15505–15512.
115. D. Banham, F. Feng, K. Pei, S. Ye, V. Birss, Effect of carbon support nanostructure on the oxygen reduction activity of Pt/C catalysts, *J. Mater. Chem. A.* 1 (2013) 2812–2820.
116. M.A. Molina-García, N. V Rees, Effect of catalyst carbon supports on the oxygen reduction reaction in alkaline media: a comparative study, *RSC Adv.* 6 (2016) 94669–94681.
117. V. Celorrio, M.G. Montes de Oca, D. Plana, R. Moliner, M.J. Lázaro, D.J. Fermín, Effect of carbon supports on electrocatalytic reactivity of Au–Pd core–shell nanoparticles, *J. Phys. Chem. C.* 116 (2012) 6275–6282.
118. X. Chen, F. He, Y. Shen, Y. Yang, H. Mei, S. Liu, T. Mori, Y. Zhang, Effect of carbon supports on enhancing mass kinetic current density of Fe–N/C electrocatalysts, *Chem. Eur. J.* 23 (2017) 14597–14603.
119. Y. Wang, C. Du, Y. Sun, G. Han, F. Kong, G. Yin, Y. Gao, Y. Song, The enhanced CO tolerance of platinum supported on FeP nanosheet for superior catalytic activity toward methanol oxidation, *Electrochim. Acta.* 254 (2017) 36–43.
120. W. Cui, C. Ge, Z. Xing, A.M. Asiri, X. Sun, $\text{Ni}_x\text{S}_y\text{–MoS}_2$ hybrid microspheres: one-pot hydrothermal synthesis and their application as a novel hydrogen evolution reaction electrocatalyst with enhanced activity, *Electrochim. Acta.* 137 (2014) 504–510.
121. S. Bukola, B. Merzougui, S. E. Creager, M. Qamar, L. R. Pederson and M. N. Noui-Mehidi, *Int. J. Hydrogen Energy*, 2016, 41, 22899–22912.
122. M. H. Suliman, A. Adam, M. N. Siddiqui, Z. H. Yamani and M. Qamar, *Carbon*, 2019, 144, 764–771.
123. M. H. Suliman, A. Adam, M. N. Siddiqui, Z. H. Yamani and M. Qamar, *Catal. Sci. Technol.*, 2019, 9, 1497–1503.

124. H. Li, S. Chen, X. Jia, B. Xu, H. Lin, H. Yang, L. Song, X. Wang, Amorphous nickel-cobalt complexes hybridized with 1T-phase molybdenum disulfide via hydrazine-induced phase transformation for water splitting, *Nat. Commun.* 8 (2017) 1–11.
125. Y. Yin, J. Han, Y. Zhang, X. Zhang, P. Xu, Q. Yuan, L. Samad, X. Wang, Y. Wang, Z. Zhang, Contributions of phase, sulfur vacancies, and edges to the hydrogen evolution reaction catalytic activity of porous molybdenum disulfide nanosheets, *J. Am. Chem. Soc.* 138 (2016) 7965–7972.
126. H. Wang, Z. Lu, S. Xu, D. Kong, J.J. Cha, G. Zheng, P.-C. Hsu, K. Yan, D. Bradshaw, F.B. Prinz, Electrochemical tuning of vertically aligned MoS₂ nanofilms and its application in improving hydrogen evolution reaction, *Proc. Natl. Acad. Sci.* 110 (2013) 19701–19706.
127. Y. Yu, G.-H. Nam, Q. He, X.-J. Wu, K. Zhang, Z. Yang, J. Chen, Q. Ma, M. Zhao, Z. Liu, High phase-purity 1T'-MoS₂-and 1T'-MoSe₂-layered crystals, *Nat. Chem.* 10 (2018) 638–643.
128. X. Kong, X. Shen, C. Zhang, S.N. Oliaee, Z. Peng, Engineering active sites of two-dimensional MoS₂ nanosheets for improving hydrogen evolution, *Inorg. Chem. Front.* 3 (2016) 1376–1380.
129. H.I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J.R. Long, C.J. Chang, A molecular MoS₂ edge site mimic for catalytic hydrogen generation, *Science* (80-.). 335 (2012) 698–702.
130. J. Kibsgaard, Z. Chen, B.N. Reinecke, T.F. Jaramillo, Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis, *Nat. Mater.* 11 (2012) 963.
131. D. Kong, H. Wang, J.J. Cha, M. Pasta, K.J. Koski, J. Yao, Y. Cui, Synthesis of MoS₂ and MoSe₂ films with vertically aligned layers, *Nano Lett.* 13 (2013) 1341–1347.
132. J. Shi, D. Ma, G.-F. Han, Y. Zhang, Q. Ji, T. Gao, J. Sun, X. Song, C. Li, Y. Zhang, Controllable growth and transfer of monolayer MoS₂ on Au foils and its potential application in hydrogen evolution reaction, *ACS Nano.* 8 (2014) 10196–10204.
133. G. Ye, Y. Gong, J. Lin, B. Li, Y. He, S.T. Pantelides, W. Zhou, R. Vajtai, P.M. Ajayan, Defects engineered monolayer MoS₂ for improved hydrogen evolution reaction, *Nano Lett.* 16 (2016) 1097–1103.
134. M.-R. Gao, M.K.Y. Chan, Y. Sun, Edge-terminated molybdenum disulfide with a 9.4-Å interlayer spacing for electrochemical hydrogen production, *Nat. Commun.* 6 (2015) 1–8.

135. Z. Pu, Q. Liu, A.M. Asiri, Y. Luo, X. Sun, Y. He, 3D macroporous MoS₂ thin film: in situ hydrothermal preparation and application as a highly active hydrogen evolution electrocatalyst at all pH values, *Electrochim. Acta.* 168 (2015) 133–138.
136. G. Li, D. Zhang, Q. Qiao, Y. Yu, D. Peterson, A. Zafar, R. Kumar, S. Curtarolo, F. Hunte, S. Shannon, All the catalytic active sites of MoS₂ for hydrogen evolution, *J. Am. Chem. Soc.* 138 (2016) 16632–16638.
137. L. Ma, Y. Hu, G. Zhu, R. Chen, T. Chen, H. Lu, Y. Wang, J. Liang, H. Liu, C. Yan, In situ thermal synthesis of inlaid ultrathin MoS₂/graphene nanosheets as electrocatalysts for the hydrogen evolution reaction, *Chem. Mater.* 28 (2016) 5733–5742.
- [138] J.-Q. Chi, Y.-M. Chai, X. Shang, B. Dong, C.-G. Liu, W. Zhang, Z. Jin, Heterointerface engineering of trilayer-shelled ultrathin MoS₂/MoP/N-doped carbon hollow nanobubbles for efficient hydrogen evolution, *J. Mater. Chem. A.* 6 (2018) 24783–24792.
- [139] J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X.W. Lou, Y. Xie, Defect-rich MoS₂ ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution, *Adv. Mater.* 25 (2013) 5807–5813.

]

Vitae

Name : Munzir H. M. Suliman

Nationality [Sudanese]

Date of Birth [5/7/1989]

Email [abo-alzoz4ever@gmail.com]

Address [Saudi Arabia-Dhahran- KFUPM-student housing]

Home Address [Sudan-Omdurman –Alfitaihab-ZIP code 79371]

Academic Background [M.Sc. in chemistry from KFUPM]

1- Suliman, M. H., Adam, A., Li, L., Tian, Z., Siddiqui, M. N., Yamani, Z. H., & Qamar, M. (2019). FeP/MoS₂ Enriched with Dense Catalytic Sites and High Electrical Conductivity for the Hydrogen Evolution Reaction. *ACS Sustainable Chemistry & Engineering*.

2- Adam, A., Suliman, M. H., Awwad, M., Siddiqui, M. N., Yamani, Z. H., & Qamar, M. (2019). Controlled growth of small and uniformly dispersed Mo₂C on carbon nanotubes as high performance electrocatalyst for the hydrogen evolution reaction. *International Journal of Hydrogen Energy*, 44(23), 11797-11807.

3- Suliman, M. H., Adam, A., Siddiqui, M. N., Yamani, Z. H., & Qamar, M. (2019). The impact of microstructural features of carbon supports on the electrocatalytic hydrogen evolution reaction. *Catalysis Science & Technology*, 9(6), 1497-1503.

4- Suliman, M. H., Adam, A., Siddiqui, M. N., Yamani, Z. H., & Qamar, M. (2019). Facile synthesis of ultrathin interconnected carbon nanosheets as a robust support for small and uniformly-dispersed iron phosphide for the hydrogen evolution reaction. *Carbon*, 144, 764-771.

5- Adam, A., Suliman, M. H., Dafalla, H., Al-Arfaj, A. R., Siddiqui, M. N., & Qamar, M. (2018). Rationally dispersed molybdenum phosphide on carbon nanotubes for the hydrogen evolution reaction. *ACS Sustainable Chemistry & Engineering*, 6(9), 11414-11423.

- 6- Adam, A., **Suliman, M. H.**, Siddiqui, M. N., Yamani, Z. H., Merzougui, B., & Qamar, M. (2018). Interconnected hollow cobalt phosphide grown on carbon nanotubes for hydrogen evolution reaction. *ACS applied materials & interfaces*, 10(35), 29407-29416.
- 7- Siddiqui, M. N., Redhwi, H. H., Younas, M., Alghizzi, A. G., **Suliman, M. H.**, & Achilias, D. S. (2018, August). Effect of Natural Macromolecule Filler on the Properties of High-Density Polyethylene (HDPE). In *Macromolecular Symposia* 380, 1, 1800072.
- 8- **MH Suliman**. A., Basheer, C., Al-Arfaj, A. A., & Tyler, D. R. (2016). Desulfurization of. A., Basheer, C., Al-Arfaj, A. A., & Tyler, D. R. (2016). Desulfurization of Model Fuels with Carbon Nanotube/TiO₂ Nanomaterial Adsorbents: Comparison of Batch and Film-Shear Reactor Processes. *Journal of Inorganic and Organometallic Polymers and Materials*, 26(3), 572-578.

9- l-Zahrani, I., **MH Suliman.** A., Basheer, C., Al-Arfaj, A. A., & Tyler, D. R. (2016). Desulfurization of., Basheer, C., Siddiqui, M. N., & Al-Arfaj, A. (2015). Membrane assisted simultaneous extraction and derivatization with triphenylphosphine of elemental sulfur in arabian crude samples by gas chromatography/mass spectrometry. *Journal of Chemistry*, 2015.