



**GRAPHENE-BASED MATERIAL
PRODUCTION, CHARACTERIZATION, AND
DETERMINATION OF HYDROGEN
STORAGE CAPACITY BY
ELECTROCHEMICAL METHODS**

PhD Dissertation

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AND DETERMINATION OF HYDROGEN STORAGE CAPACITY BY
ELECTROCHEMICAL METHODS**

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PhD Dissertation

Department of Chemical Engineering

Program in Process and Reactor Design

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Eskişehir

Eskişehir Technical University

Institute of Graduate Programs

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SRP Committee.*

FINAL APPROVAL FOR THESIS

This thesis titled GRAPHENE-BASED MATERIAL PRODUCTION, CHARACTERIZATION, AND DETERMINATION OF HYDROGEN STORAGE CAPACITY BY ELECTROCHEMICAL METHODS has been prepared and submitted by Nasrin POURMOGHADDAM in partial fulfillment of the requirements in “Eskişehir Technical University Directive on Graduate Education and Examination” for the Degree of PhD in Chemical Engineering Department has been examined and approved on 08/01/2025.

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ABSTRACT

GRAPHENE-BASED MATERIAL PRODUCTION, CHARACTERIZATION, AND DETERMINATION OF HYDROGEN STORAGE CAPACITY BY ELECTROCHEMICAL METHODS

Nasrin POURMOGHADDAM

Department of Chemical Engineering

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Eskişehir Technical University, Institute of Graduate Programs, January 2025

Supervisor: Prof. Dr. Nezihe AYAS

Graphene has a single layer of carbon atoms with a hexagonal lattice structure. In this study, three different methods were investigated to produce graphene-based materials from graphite and plastic. The first was the Hummers method, which produced graphene oxide (GFO) from graphite, and the second method used liquid phase exfoliation (LPE) to produce graphene from graphite. Pyrolysis was the third method which graphene was obtained using the synthesized NiCo/bentonite catalyst. Graphene-based samples were characterized using XRD, FT-IR spectroscopy, Raman spectroscopy, BET, SEM, TEM, TGA, UV-Vis spectroscopy, CHNS/O analysis and XRF characterization methods. Electrochemical tests were performed to determine the hydrogen storage capacity of the graphene materials obtained. Multilayer graphene (MLGF) was found to have the highest hydrogen storage capacity with a value of 236 mAh.g^{-1} . NiCo/rGFO composite materials were synthesized with different active metal loading ratios (1:1, 1:2, 2:1, 2:2) by impregnation method. Then, this composite material was used as a catalyst in hydrogen production from NaBH_4 by hydrolysis method. The effects of parameters such as temperature (30, 40, 50, 60 °C), NaOH solution concentration (0.25, 0.5, 0.75, 1 M) and metal loading ratios (1:1, 1:2, 2:1, 2:2 NiCo) on the catalyst activity were investigated. 2:2 metal loading ratio, 60 °C temperature and 0.25 M NaOH concentration were determined as the most suitable operating parameters. Under this condition, NiCo/rGFO composite material provided a remarkable hydrogen production rate of $255.10 \text{ mL.min}^{-1} \text{ g}_{\text{cat}}^{-1}$, 100% hydrogen yield, and with the activation energy (E_a) of 27.3 kJ.mol^{-1} . This composite material was found to have a hydrogen storage capacity of $297.75 \text{ mAh.g}^{-1}$ and a remarkably low resistivity of 6.79Ω .

Keywords: Graphene based materials, CV analysis, Sodium borohydride hydrolysis, Hydrogen, Kinetic study.

ÖZET

GRAFEN BAZLI MALZEME ÜRETİMİ, KARAKTERİZASYONU VE ELEKTROKİMYASAL YÖNTEMLERLE HİDROJEN DEPOLAMA KAPASİTESİNİN BELİRLENMESİ

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Grafen, altıgen kafes yapısına sahip tek bir karbon atomu katmanından oluşan bir malzemedir. Bu çalışmada, grafit ve plastikten grafen bazlı malzemeler üretmek için üç farklı yöntem araştırılmıştır. Birincisi, Hummers yöntemi olup grafitten grafen oksit (GFO) üretiminde, ikinci yöntemde ise, grafitten grafen üretmek için sıvı faz eksfoliasyonunu (LPE) kullanmıştır. Piroliz üçüncü yöntem olup sentezlenen NiCo/bentonit katalizörü kullanılarak grafen elde edilmiştir. Grafen bazlı numuneler, XRD, FT-IR spektroskopisi, Raman spektroskopisi, BET, SEM, TEM, TGA, UV-Vis spektroskopisi, CHNS/O analizi ve XRF karakterizasyon yöntemleri kullanılarak karakterize edilmiştir. Analiz sonuçlarına göre, grafit oksit, çok katmanlı grafen ve grafen oksidin başarıyla sentezlendiği belirlenmiştir. Elde edilen grafen malzemelerinin hidrojen depolama kapasitesini belirlemek için elektrokimyasal analizleri yapıldı. Çok katmanlı grafen (MLGF), 236 mAh.g^{-1} değeri ile en yüksek hidrojen depolama kapasitesine sahip olduğu tespit edilmiştir. NiCo/rGFO kompozit malzemeler, emdirme yöntemi ile farklı aktif metal yükleme oranları (1:1, 1:2, 2:1, 2:2) ile sentezlendi. Daha sonra, bu kompozit malzeme hidroliz yöntemiyle NaBH_4 'ten hidrojen üretiminde katalizör olarak kullanıldı. Sıcaklık (30, 40, 50, 60 °C), NaOH çözelti konsantrasyonu (0,25, 0,5, 0,75, 1 M) ve metal yükleme oranları (1:1, 1:2, 2:1, 2:2 NiCo) gibi parametrelerin katalizörün aktivitesine etkisi incelenmiş olup, 2:2 metal yükleme oranının, 60 °C sıcaklık ve 0,25 M NaOH konsantrasyonunun en uygun çalışma parametreleri olduğu belirlenmiştir. Bu koşulda NiCo/rGFO kompozit malzemenin $255,10 \text{ mL.min}^{-1} \text{ g}_{\text{cat}}^{-1}$ 'lik dikkate değer bir hidrojen üretim ve %100 hidrojen verimini sağlamış olup aktivasyon enerjisi (E_a) $27,3 \text{ kJmol}^{-1}$ olarak hesaplanmıştır. Bu kompozitin 0,5 M H_2SO_4 'te gerçekleştirilen EIS testleri sonucunda $297,75 \text{ mAh.g}^{-1}$ hidrojen depolama kapasitesine ve $6,79 \Omega$ 'luk kayda değer düşük bir dirence sahip olduğu görüldü.

Anahtar Sözcükler: Grafen bazlı malzemeler, CV analizi, Sodyum borhidrür hidroliz, Hidrojen, Kinetik çalışma.

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I dedicate this work to the memory of my father, whose love, wisdom, and guidance continue to inspire me every day. Though he is no longer with us, his strength and values have been my constant support, and his memory has given me the courage to persevere through this journey. To my mother, thank you for your unwavering faith in my abilities and for teaching me the value of hard work and perseverance. To my siblings, thank you for your constant encouragement and for reminding me to enjoy life along the way. I couldn't have done this without you all by my side.

Nasrin POURMOGHADDAM

STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and that this study has been scanned for plagiarism with “scientific plagiarism detection program” used by Eskişehir Technical University, and that “it does not have any plagiarism” whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved.

Nasrin POURMOGHADDAM

CONTENTS

	<u>Page</u>
HEADING	I
FINAL APPROVAL FOR THESIS	II
SUPERVISOR APPROVAL	III
ABSTRACT.....	IV
ÖZET	V
ACKNOWLEDGEMENTS	VI
STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES	VII
CONTENTS	VIII
LIST OF TABLES	XII
LIST OF FIGURES	XIII
GLOSSARY OF SYMBOLS AND ABBREVIATIONS	XVII
1. INTRODUCTION	1
1.1. Graphene History	2
1.2. Graphene Structure and Properties	3
1.3. Graphene Terminology	4
1.4. Graphene Applications	4
1.5. Graphene Production Methods.....	5
1.5.1. Top-down method.....	6
1.5.2. Bottom-up method.....	7
1.6. Characterization Methods.....	8
1.6.1. X-ray diffraction (XRD)	8
1.6.2. Raman spectroscopy.....	10
1.6.3. Brunauer, Emmett ve Teller (BET)	11
1.6.4. Electron microscopy	12
1.6.5. FT-IR spectroscopy	13
1.6.6. Thermogravimetric Analysis (TGA)	15

1.6.7. UV-Vis spectroscopy	15
1.7. Hydrogen.....	17
1.8. Hydrogen Storage	18
1.8.1. Physical hydrogen storage	20
1.8.1.1. <i>Compressed hydrogen storage</i>	20
1.8.1.2. <i>Cryogenic hydrogen storage</i>	20
1.8.1.3. <i>Cryo-compressed hydrogen storage</i>	21
1.8.1.4. <i>Adsorption storage</i>	22
1.8.2. Chemical hydrogen storage	24
1.8.2.1. <i>Metal hydrides</i>	24
1.8.2.2. <i>Liquid organic hydrogen carriers</i>	25
1.8.2.3. <i>Ammonia</i>	26
1.8.2.4. <i>Formic acid</i>	26
1.8.2.5. <i>Methanol</i>	27
1.9. Electrochemical Hydrogen Storage	27
2. LITERATURE REVIEW ON GRAPHENE SYNTHESIS	31
3. MATERIAL AND METHODS	42
3.1. Chemicals and Equipment	42
3.2. Production Methods.....	43
3.2.1. Production of graphene (GF) from graphite by liquid phase exfoliation (LPE).....	43
3.2.2. Production of graphite oxide (GO) from graphite	44
3.2.3. Production GFO from GO.....	45
3.2.4. Production of NiCo/rGFO nanocomposite materials.....	45
3.2.5. Production of bentonite-based catalyst	46
3.2.6. Production of graphene from Plastic (GFP)	47
3.3. Characterization Methods of Graphene-based and Composite Materials	48
3.3.1. XRD characterization	48
3.3.2. TGA characterization	48
3.3.3. UV-Vis characterization	49
3.3.4. Elemental Analysis	49

3.3.5. Raman spectroscopy characterization.....	50
3.3.6. FT-IR spectroscopy characterization	51
3.3.7. TEM characterization	51
3.3.8. SEM characterization	51
3.3.9. BET characterization	52
3.4. Electrochemical Characterization	52
3.4.1. CV analysis.....	53
3.4.1.1. Determination of hydrogen storage capacity of graphene-based material using MATLAB software	55
3.4.2. EIS analysis	55
3.4.3. GCD analysis.....	56
3.5. Hydrogen Generation Activity of NiCo/rGFO in Hydrolysis of NaBH ₄	58
3.6. Kinetic Study of Hydrogen Generation by NiCo/rGFO in Hydrolysis of NaBH ₄	59
4. RESULTS AND CONCLUSIONS	62
4.1. Graphene-Based Materials Synthesis.....	62
4.2. Characterization Results of Synthesized Carbon and Composite Materials	63
4.2.1. XRD results	64
4.2.2. FT-IR spectroscopy results.....	69
4.2.3. CHNS/O analysis results.....	73
4.2.4. Raman spectroscopy results	74
4.2.5. UV-Vis spectroscopy results	78
4.2.6. SEM results	81
4.2.7. TGA results	87
4.2.8. TEM results.....	89
4.2.9. XRF Results	93
4.2.10. BET results.....	94
4.3. NiCo/rGFO Catalyst in The Hydrolysis of NaBH ₄	96
4.3.1. Kinetic study results of hydrolysis of NaBH ₄	100
4.4. Mechanism of Electrochemical Hydrogen Storage	104

4.4.1. Cyclic voltammetry	107
4.4.2. Galvanostatic charge-discharge	115
4.4.3. Electrochemical impedance spectroscopy	118
5. MATLAB CODE FOR REDOX REACTION RATE CALCULATION.....	120
5.1. Comparison Between Nicholson and Lavagnini MATLAB Code Results	124
6. CONCLUSION	126
REFERENCES.....	128
APPENDIX	
CURRICULUM VITAE	

LIST OF TABLES

	<u>Page</u>
Table 3.1. List of chemical materials used in the experiments	42
Table 3.2. Equipment used in the experiments	42
Table 4.1. Analyses applied to synthesized materials.....	63
Table 4.2. Interplanar spacing (d-spacing) calculation from XRD data	69
Table 4.3. CHNS/O Analysis of graphite, GF, and GFO.....	73
Table 4.4. Raman spectroscopy results of graphene-based materials.....	75
Table 4.5. XRF results of catalysts and bentonite for pyrolysis	93
Table 4.6. BET analysis result of graphite, GFO, GF, 1:1 NiCo/rGFO, 1:2 NiCo/rGFO, 2:1 NiCo/rGFO, and 2:2NiCo/rGFO	94
Table 4.7. Rate constants and regression coefficients according to zero-order reaction kinetics of 2:2NiCo/rGFO.....	102
Table 4.8. Literature comparison results of hydrogen generation rate (HGR) and activation energy (E_a) of the different catalysts.....	103
Table 4.9. Specific capacity (C_p) calculation from CV curve by origin pro software.....	111
Table 4.10. Comparison of hydrogen storage capacity of current study with literature	112
Table 4.11. Data obtained from GCD of graphene-based materials	117
Table 4.12. R(CR)W Circuit presents the modelling outcomes of GF and GFO using the ZSimpWin tool	119
Table 5.1. MATLAB calculation result using Nicholson equation	123
Table 5.2. MATLAB calculation result using Lavagnini method	123
Table 5.3. Comparison Between Nicholson and Lavagnini MATLAB Code Results.....	124

LIST OF FIGURES

	<u>Page</u>
Figure 1.1. A brief history of the discovery of graphene.....	3
Figure 1.2. Graphene in a honeycomb lattice structure	3
Figure 1.3. Graphene synthesis methods	5
Figure 1.4. FTIR of fundamental organic functional groups	14
Figure 1.5. Light spectrum.....	16
Figure 1.6. Hydrogen storage methods	19
Figure 3.1. Production of Graphene (GF) from Graphite by LPE Method.....	44
Figure 3.2. Synthesis of GO from graphite by improved Hummer's method	44
Figure 3.3. GFO production from graphite oxide (GO).....	45
Figure 3.4. Synthesis of NiCo/rGFO nanocomposite	46
Figure 3.5. Synthesis of NiCo/bentonite catalyst.....	47
Figure 3.6. Synthesis of graphene from plastic (GFP) by two-stage catalytic pyrolysis.....	47
Figure 3.7. XRD equipment.....	48
Figure 3.8. TGA equipment.....	49
Figure 3.9. UV-Vis spectroscopy equipment.....	49
Figure 3.10. CHNS/O Analyzer equipment.....	50
Figure 3.11. Raman spectroscopy instrument.....	50
Figure 3.12. FT-IR spectroscopy instrument	51
Figure 3.13. SEM equipment	51
Figure 3.14. BET equipment.....	52
Figure 3.15. Illustration of a) three-electrode system; b) Gamry potentiostat/galvanostat/ZRA; c) set-up system (Gamry+Three - electrode system)	53
Figure 3.16. CV setup in Gamry instrument.....	54
Figure 3.17. EIS- setup in Gamry instrument	56
Figure 3.18. GCD setup in Gamry instrument.....	57
Figure 3.19. Experimental set-up of hydrolysis of NaBH ₄ a) thermometer; b) reactor; c) gas measuring cylinder	58
Figure 4.1. GO synthesis under reflux, b) yellow colour of GO before washing, c) GO powder.....	62

Figure 4.2. NiCo/rGFO nanocomposite a) loading metal; b) after washing step	62
Figure 4.3. GFP synthesis steps: a) plastic; b) plastic and catalyst mixture; c) after first pyrolysis; d) After second pyrolysis.....	63
Figure 4.4. XRD characterization of a) graphite; b) GF	64
Figure 4.5. XRD characterization of a) GO; b) GFO; c) 1:1 NiCo/rGFO;d) 1:2 NiCo/rGFO;e) 2:1 NiCo/rGFO; f) 2:2 NiCo/rGFO (☆: NiCo ₂ O ₄ ; ∇: NiO; ϕ: CoO; ∅: GFO)	65
Figure 4.6. XRD pattern of a) Bentonite; b) 10% Ni/bentonite; c)10 Co %/bentonite; d) 10-5% NiCo/bentonite; e) 5-10% NiCo/bentonite; (∇: montmorillonite, ☆: kaolinite, ∞: SiO ₂ , ⌘ NiO, ¥: CoO)	67
Figure 4.7. XRD pattern of a) GFP-1+ 10% Co/bentonite; b) GFP-2+10% Ni/bentonite; c) GFP-3 +10-5% NiCo/bentonite; d) GFP-4+5-10% NiCo/bentonite and e) plastic (☆: graphene, ∞: SiO ₂ , ⌘ NiO, ¥: CoO)	68
Figure 4.8. XRD of the 2:2 NiCo/rGFO catalyst before and after hydrogen generation by NaBH ₄ hydrolysis	68
Figure 4.9. FT-IR spectroscopy results of a) GF; b) GFO	70
Figure 4.10. FT-IR spectroscopy of a) graphite; b) GO; c) 1:1 NiCo/rGFO; d) 1:2 NiCo/rGFO; e) 2:1 NiCo/rGFO; f) 2:2 NiCo/rGFO	71
Figure 4.11. FT-IR spectroscopy of a) 10% Ni/bentonite; b) 10% Co/bentonite; c) 10-5% NiCo/bentonite; d) 5-10% NiCo/bentonite	72
Figure 4.12. FT-IR spectroscopy of a) plastic; b) GFP-1+ 10% Co/bentonite; c) GFP-2+10% Ni/bentonite; d) GFP-3 +10-5% NiCo/bentonite; e) GFP-4+5-10% NiCo/bentonite; before washing	73
Figure 4.13. Raman spectroscopy analysis of a) graphite; b) GF	74
Figure 4.14. Raman spectroscopy of a) GFO, b) 1:1 NiCo/rGFO, c)1:2 NiCo/rGFO; d) 2:1NiCo/rGFO;and e) 2:2 NiCo/rGFO.....	75
Figure 4.15. Raman spectroscopy of GFP-4; a) before b) after washing	75
Figure 4.16. V-Vis spectroscopy of a) graphite; and b) GF.....	79
Figure 4.17. UV-Vis characterization of a) GFO; c) 2:2 NiCo/rGFO; d) 2:1 NiCo/rGFO; e) 1:2 NiCo/rGFO, and f) 1:1NiCo/rGFO	79
Figure 4.18. UV-Vis spectroscopy of GFP-4 sample after washing.....	81
Figure 4.19. SEM image of graphite a) 5000; b) 20000 magnifications	81

Figure 4.20. SEM images of GF a) 50000 KX; b) 50000 KX.....	82
Figure 4.21. SEM image of GO a) 500 KX; b) 5000 KX.....	83
Figure 4.22. SEM image of GFO a) 50000 KX; b) 20000 KX.....	84
Figure 4.23. SEM image of 1:1 NiCo/rGFO a) 2000 KX;b) 5000 KX	85
Figure 4.24. SEM image of 1:2 NiCo/rGFO a) 2000 KX; b) 5000 KX	85
Figure 4.25. SEM image of 2:1 NiCo/rGFO a) 2000 KX; b) 5000 KX	85
Figure 4.26. SEM image of 2:2 NiCo/rGFO a) 20000 KX; b)5000 KX	86
Figure 4.27. SEM image of GFP-4 a) 20000 KX; b)5000 KX and GFP-3; c) 20000 KX; d)5000 KX.....	87
Figure 4.28. TGA profiles of a) graphite; b) GF; and c) GFO.....	88
Figure 4.29. TEM images of graphite a) 100 nm; b) 100 nm; c)2 μ m	89
Figure 4.30. TEM images of GFO a) 100 nm; b) 100 nm; c)2 μ m.....	90
Figure 4.31. TEM image of GF a) 100 nm; b) 100 nm; c)2 μ m	91
Figure 4.32. TEM image of 2:2 NiCo/rGFO; a) 100nm; b) 100nm; c)2 μ m.....	92
Figure 4.33. TEM image of GFP-4 +1:2 NiCo/bentonite; a) 50 nm;b) 2 μ m.....	92
Figure 4.34. TEM image of graphene obtained from plastic (GFP-4); a) 50 nm;b) 2 μ m	93
Figure 4.35. N ₂ adsorption-desorption isotherms of a) GF;b) GFO; c) graphite; d)1:1 NiCo/rGFO, e)1:2 NiCo/rGFO; f) 2:1 NiCo/rGFO; j) 2:2NiCo/rGFO	94
Figure 4.36. Impact of varying NiCo ratios on the hydrolysis of NaBH ₄ under specific conditions of 100 mg of NaBH ₄ , 100 mg of catalyst, 5 mL of 0.25 M NaOH.....	96
Figure 4.37. Effect of the reaction temperature in the catalysts on the hydrogen yield from the hydrolysis of NaBH ₄ (100 mg NaBH ₄ , 100 mg 2:2 NiCo/rGFO, 5 mL 0.25 M NaOH).....	98
Figure 4.38. Influence of NaOH concentration on hydrogen production from NaBH ₄ hydrolysis	99
Figure 4.39. Reusability of 2:2 NiCo/rGFO at 60 °C in hydrolysis process	100
Figure 4.40. Data analysis based on zero-order reaction kinetics.....	101
Figure 4.41. Data analysis based on first order reaction kinetics	101
Figure 4.42. Data analyses based on nth-order reaction kinetics.....	101
Figure 4.43. Arrhenius plot of 2:2 NiCo/rGFO	103

Figure 4.44. CV of a) GF; b) GFO; c) graphite and d) GFP-4 after washing at different scan rates in 0.5 H ₂ SO ₄	108
Figure 4.45. CV curves of a) 1:1 NiCo/rGFO; b) 1:2 NiCo/rGFO; c) 2:1 NiCo/rGFO; d) 2:2NiCo/rGFO at different scan rates (25-500 mV/s) in 0.5 M H ₂ SO ₄	110
Figure 4.46. Plot I _p vs square root of scan rate a) 1:1 NiCo/rGFO, b) 2:1 NiCo/rGFO, c) 1:2 NiCo/rGFO, d) 2:2 NiCo/rGFO.....	114
Figure 4.47. Plot of Log (I _p) vs Log (v); a) 1:1 NiCo/rGFO, b) 2:1 NiCo/rGFO, c) 1:2 NiCo/rGFO, d) 2:2 NiCo/rGFO.....	115
Figure 4.48. GCD curves of a) GF; b) GFO in 0.5 H ₂ SO ₄ electrolyte c) 1:1NiCo/rGFO; d) 1:2NiCo/rGFO.....	116
Figure 4.49. Nyquist diagram of the samples a) GF; and b) GFO with R(CR)W equivalent circuit model.....	118
Figure 4.50. EIS result of a) GO; b) 2:1NiCo/rGFO; c) 1:2 NiCo/rGFO; d) 1:1 NiCo/rGFO; e) 2:2 NiCo/rGFO	119
Figure 5.1. Step by step MATLAB calculation of reaction rate	120
Figure 5.2. Oxidation and reduction process	121
Figure 5.3. Example of running MATLAB code for GF sample at scan rate of 25 mV/s in Nicholson method	122
Figure 5.4. Hydrogen spillover mechanism	125

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

A	: Electrode Surface Area
A	: Arrhenius constant
AC	: Alternating Current
BET	: Brunauer-Emmett-Teller
BJH	: Barrett-Joyner-Halenda
CV	: Cyclic Voltammetry
CVD	: Chemical Vapor Deposition
C_p	: Specific Capacity
C_0	: Concentration of Electroactive Species
C_A	: Concentration of A
C_{A0}	: Concentration of A_0
C_R	: Resistance Capacity
d	: Distance
dE	: Differential Potential Charge
D	: Diffusion Coefficient
D	: Average Size of the Crystalline
DC	: Direct Current
DTA	: Differential Thermal Analysis
EDLC	: Electrical Double-Layer Capacitors
EHS	: Electrochemical Hydrogen Storage
EIS	: Electrochemical Impedance Spectroscopy
FA	: Formic Acid
GFO	: Graphene Oxide
GO	: Graphite Oxide
GCD	: Galvanostatic Charge Discharge
GC	: Glassy Carbon
g_{cat}	: Gram of Catalyst
HSC	: Hydrogen Storage Capacity
HGR	: Hydrogen Generation Rate
h	: Hour
k	: Rate Constant

K	: Regression Coefficients
k_0	: Heterogeneous Electron Transfer Rate Constant
K	: Shape Factor for XRD
LDPE	: Low Density Polyethylene
LOHC	: Liquid Organic Hydrogen Carrier
LPE	: Liquid-Phase Exfoliation
LSV	: Linear Sweep Voltammetry
PF	: Positive Feedback
MLGF	: Multi-Layers Graphene
MOF	: Metal-Organic Framework
M	: Synthesized Material
min	: Minute
n	: Number of Electrons
n	: Order of Diffraction
n_{H_2}	: Mole of Hydrogen
NMP	: N-Methyl-2-Pyrrolidone
NMR	: Nuclear Magnetic Resonance
s	: Second
SEM	: Scanning Electron Microscope
SiC	: Silicon Carbide
TEM	: Transmission Electron Microscopy
TGA	: Thermogravimetric Analysis
UV-Vis	: Ultraviolet-Visible Spectroscopy
V_{H_2}	: Volume of Hydrogen
$V_{H_{2max}}$	: Theoretical Maximum Volume of Hydrogen
XRD	: X-ray Diffraction
XRF	: X-ray Fluorescence
USDOE	: United States Department of Energy
I_p	: Peak Current
I_{dl}	: Double Layer Charging
I_D	: Intensity Ratio of the D Band
I_G	: Intensity Ratio of the G Band

η	: Coulombic Efficiency
W	: Warburg Impedance
R	: Resistance
R^2	: Regression Coefficients
R	: Universal Gas Constant
R_s	: Resistance of the Solution
L_a	: Crystallite Sizes
E_a	: Activation Energy
Q	: Specific Capacity
rpm	: Revolutions Per Minute
v	: Scan Rate
ψ	: Dimensionless Parameter
f	: Dimensionless Functional
r_A	: Reaction rate
Δt	: Discharge Duration
t_d	: Discharge Time
t_c	: Charge Time
ΔV	: Potential Window
ΔE	: Peak Potential
ΔE_p	: Peak Potential Separation
λ	: Wavelength of the X-rays
β	: Full Width
θ	: Angle

1. INTRODUCTION

Graphene, a two-dimensional form of carbon, has attracted considerable interest since its remarkable discovery in 2004 by Andre Geim and Konstantin Novoselov, a feat that led to their receipt of the Nobel Prize in Physics in 2010. This material consists of a single layer of carbon atoms organized in a hexagonal pattern and is regarded as the fundamental component of various carbon-based substances, including graphite, carbon nanotubes, and fullerenes. The discovery of graphene represented a significant advancement in materials science, paving the way for new opportunities in both basic research and technological development [1,2].

The unique characteristics of graphene distinguish it from other substances. It possesses exceptional mechanical strength, being 200 times stronger than steel, while also being remarkably lightweight and flexible. Additionally, graphene showcases outstanding electrical conductivity, with charge carriers traveling through it at significantly higher velocities compared to traditional semiconductors. Its thermal conductivity ranks among the highest of all known materials, and its extensive surface area along with chemical stability renders it ideal for various applications. Notably, the properties of graphene can be customized through structural alterations, functionalization, and the chosen synthesis techniques, allowing for its application across numerous domains [3].

The diverse applications of graphene have resulted in its widespread adoption across numerous sectors. It is explored as a material for transistors, sensors, and flexible technologies in electronics. Its excellent thermal and electrical properties make it a promising candidate for energy storage devices such as supercapacitors and batteries. Additionally, graphene is used in water purification systems, composite materials for enhanced mechanical performance, and biomedical devices, including drug delivery systems and biosensors. The rapid growth in graphene research and commercialization reflects its potential to revolutionize industries and contribute to sustainable technologies [2].

In this thesis, graphene and graphene-based materials were synthesized via three different techniques: liquid phase exfoliation (LPE), improved Hummer's method, and two-stage pyrolysis. The synthesized samples were characterized by XRD, FT-IR, TGA, Raman spectroscopy, CHNS/O analysis, BET, TEM, and SEM techniques. The potential of these synthesis methods was explored in the context of two specific applications of

electrochemical hydrogen storage and catalytic activity in the hydrolysis of sodium borohydride (NaBH_4). The *initial chapter* of the thesis offers a comprehensive introduction to graphene, emphasizing its importance within materials science and renewable energy. The *second chapter* thoroughly reviews the existing literature on graphene synthesis methods, analysing the results and conclusions drawn by various researchers who have explored the synthesis of graphene and its potential applications. The *third chapter* outlines the materials and methodologies used in this research, providing an in-depth description of the synthesis techniques and characterization methods employed to evaluate the graphene samples. The *fourth chapter* showcases the experimental results and discusses their relevance concerning electrochemical hydrogen storage and catalytic efficiency. The *fifth chapter* used MATLAB software to calculate the reaction rate from the electrochemical tests. Lastly, the *sixth chapter* concluded with a summary of the study's main conclusions and findings, emphasizing the implications of these findings for upcoming developments and applications of graphene-based materials.

1.1. Graphene History

Graphene captured the scientific community's attention extraordinarily. The theoretical foundation for graphene began in 1947 when Philip Wallace published a paper on the electronic properties of graphite, paving the way for the eventual discovery of graphene [1]. The term graphene was officially coined in 1986 by Boehm and his colleagues, who reported their observations of its existence [4]. Initially, the term described individual carbon layers within graphite intercalation compounds. However, as early as 1962, Boehm and his team had already identified that chemically reduced graphene oxide in alkaline media, such as hydrazine and hydrogen sulphate, contained lamellar carbon structures with trace amounts of hydrogen and oxygen. These layers exhibited significantly lower electrical conductivity compared to graphene. Graphene was discovered earlier, but it didn't receive significant attention until 2004. That year, University of Manchester scientists Andre Geim and Konstantin Novoselov isolated a single sheet of 'pristine' graphene using simple tools like a pencil, paper, and sticky tape. This achievement earned them the Nobel Prize in Physics in 2010 for discovering graphene, the first two-dimensional crystalline material [5]. Figure 1.1. indicates a brief history of the discovery of graphene [11].

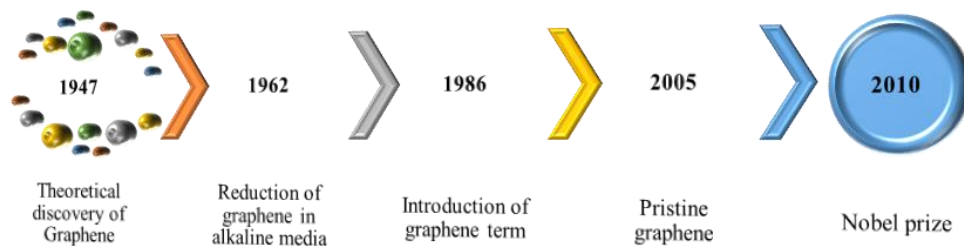


Figure 1.1. A brief history of the discovery of graphene.

1.2. Graphene Structure and Properties

Graphene, a two-dimensional, novel allotrope of carbon, is composed of a single layer of carbon atoms arranged in a honeycomb lattice structure (Figure 1.2) [6]. Graphene is derived from the three-dimensional giant covalent structure of graphite. Each carbon atom forms strong covalent bonds with three neighbouring carbon atoms, resulting in a hexagonal pattern. The carbon-carbon bond length in graphene is approximately 1.42 Å [7].

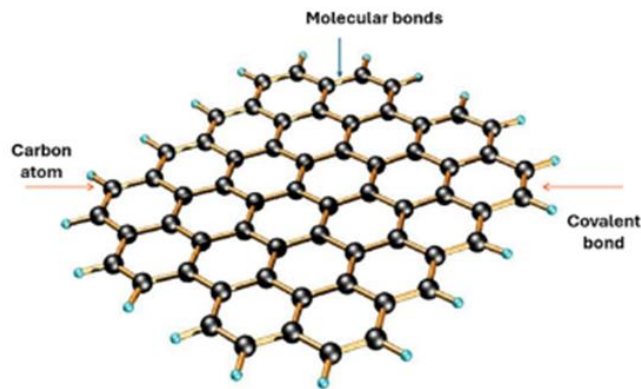


Figure 1.2. Graphene in a honeycomb lattice structure

This compact structure and the sp^2 hybridization of carbon atoms contribute to the extraordinary strength and stability of graphene. Graphene possesses superior physical properties compared to many other materials. It exhibits an exceptionally high thermal conductivity of 5000 W/m.K, making it an excellent material for heat dissipation. Additionally, graphene's electron mobility is remarkably high, reaching values of up to 250 $\text{cm}^2/\text{V} \cdot \text{s}$, which is crucial for applications in high-speed electronics. Its mechanical strength is also notable, with a Young's modulus of 1.0 TPa, indicating its stiffness and

resistance to deformation. The material's large surface area of 2630 m²/g enhances its utility in applications such as energy storage and catalysis. Furthermore, graphene excels in both electrical conductivity and optical transmittance, making it a highly versatile material for use in a wide range of advanced technological applications [5, 6].

1.3. Graphene Terminology

Graphene samples are commonly classified into several categories. When graphene layers are stacked together, the resulting materials are categorized based on the number of layers. Very-few-layer graphene (vFLGF) consists of 1 to 3 layers, retaining most of the exceptional properties of monolayer graphene, making it highly conductive and strong while remaining nearly as thin. Few-layer graphene (FLGF), consisting of 2 to 5 layers, exhibits subtle differences from monolayer graphene, such as slightly decreased transparency and enhanced mechanical strength. Nevertheless, it continues to maintain a high surface area and conductivity.

As more layers are added, the properties continue to evolve. Multi-layer graphene (MLGF), which contains 2 to 10 layers, exhibits good conductivity and strength but begins to lose the extreme flexibility and transparency of monolayer graphene. Graphene nanoplatelets (GFNP), with more than 10 layers, become thicker and start to resemble graphite in their characteristics. While GFNPs still offer benefits like high strength and conductivity, they lack the unique thinness and flexibility of less-layered graphene materials. These different forms of graphene are used in various applications depending on the balance of properties required, from electronics to composite materials [6, 7].

1.4. Graphene Applications

More than 40 different applications of graphene are listed as solar cells, batteries, nuclear power, thermoelectric, alcohol distillation, fuel cell, drug delivery, cancer treatment, gene delivery, photothermal therapy, diabetes monitoring, dialysis, bone and teeth implantation, UV sensors, HIV diagnosis, biosensors, body scans, generating light, transistors, waterproof electronics, touchscreens, flexible screens, hard drives, memories, elastic robots, superconductor, food packaging, water purification, food security, shoes, helmets, tires, rackets, electronic tattoos, fitness tracking, cement, speakers, headphones, automotive, catalyst, hydrogen storage, supercapacitors, anti-corrosion and glass of smartphone are reported in literature [16-56].

1.5. Graphene Production Methods

Since the ground-breaking discovery of graphene, the remarkable properties of this material have captivated the imagination of scientists worldwide. This excitement has driven extensive research into various methods for producing graphene. Numerous techniques have been developed to synthesize graphene, each tailored to produce graphene with specific characteristics, such as type, size, quality, and purity, depending on the intended application. Generally, graphene production can be categorized into two main approaches of top-down and bottom-up (Figure 1.3).

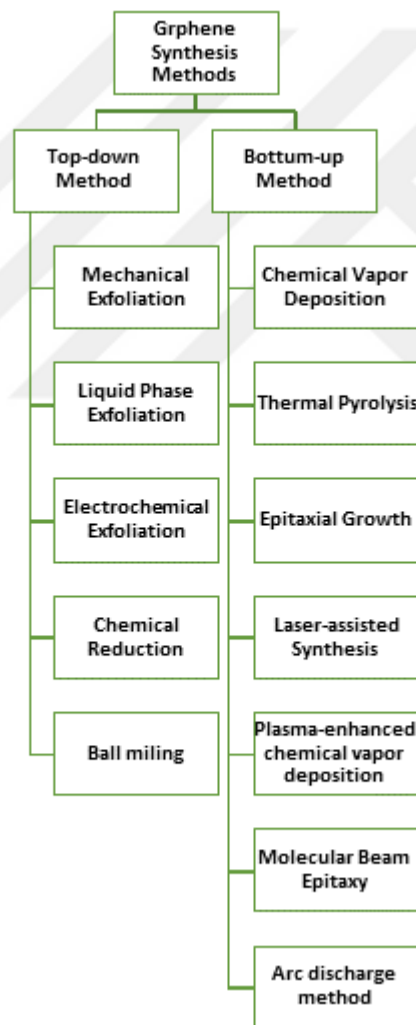


Figure 1.3. Graphene synthesis methods

1.5.1. Top-down method

Top-down graphene production typically involves the reduction or exfoliation of powdered graphite. Mechanical exfoliation, LPE, electrochemical exfoliation, and chemical oxidation-reduction are some of the most common top-down procedures.

The mechanical exfoliation method developed by Novoselov et al. [12] is a classic example of a top-down synthesis approach for producing single-layer graphene. In this procedure, they used regular scotch tape to remove high-oriented pyrolytic graphite's thin graphene layers. They were able to separate graphene layers with lateral sizes in the micrometre range by repeatedly adhering to and removing the tape. Studying graphene's remarkable properties required high-quality, defect-free graphene, which this method made possible. The simplicity of the technique, using everyday materials, contrasted with the innovative implications of the discovery, highlighting the versatility and accessibility of graphene synthesis. While this mechanical exfoliation method was ground-breaking, it has limitations that make it unsuitable for large-scale production. The primary drawback is its low yield, as it can only produce small areas of single-layer graphene with lateral dimensions in the micrometer range. This limitation restricts its use to research applications rather than industrial production.

Another top-down method for producing graphene is LPE. The interlayer spacing of graphite is increased through a reduction reaction, which reduces the van der Waals forces holding the layers together. This weakening of interlayer forces facilitates the subsequent exfoliation of graphite. In the second step, the graphite is exfoliated by rapid heating, sonication, or high shear forces for graphene production with single to several layers. This method is versatile and can yield a range of graphene layer thicknesses depending on the exfoliation conditions used [13]. The LPE procedure consists of uncomplicated steps such as sonication and centrifugation, which are easier to execute than more intricate methods like CVD. In contrast to chemical techniques, LPE does not employ harsh oxidizing agents, thereby preserving the structural integrity of graphene and mitigating environmental concerns. The solvent (f.e. isopropyl alcohol) is reusable, reducing waste and making the process more cost-effective and environmentally friendly.

Electrochemical exfoliation is another technique where an electric voltage is applied to graphite rods, forcing ionic species to intercalate between the graphite layers. The intercalated ions generate gaseous molecules that exfoliate the distinct graphene layers. This method is advantageous because it is a one-step process, environmentally

friendly, and relatively easy to operate. However, challenges remain, particularly regarding the scalability of the process for large-scale production, which limits its industrial applications despite its potential benefits.

The chemical oxidation-reduction process of graphite involves oxidizing graphite into graphite oxide, followed by its reduction to graphene through methods such as chemical, thermal, or electrochemical techniques. The Brodie Method in 1859 was one of the first approaches to oxidizing graphite, using concentrated nitric acid and potassium chlorate. The Staudenmaier method is an improvement on Brodie's method that uses a mixture of concentrated sulfuric and nitric acids, with potassium chlorate added gradually. The Hummers method is the most widely used method, which involves oxidizing graphite with sulfuric acid, sodium nitrate, and potassium permanganate [14].

The Tour Method is a more recent method of improving efficiency and reducing defects through chemical oxidation [15]. Several methods have been used to reduce graphite oxide, including plant extracts, chemicals, heat, microwaves, laser irradiation, electrochemical methods, and photoreduction. However, the popularity of chemical oxidation-reduction methods is limited due to the use of expensive and harsh chemicals, as well as the lengthy processing times.

1.5.2. Bottom-up method

Bottom-up approaches, which usually begin with hydrocarbon molecules as the building blocks, can be used to produce graphene. Chemical vapor deposition (CVD) [16], thermal pyrolysis [17], epitaxial growth [18], laser-assisted synthesis [19], and organic synthesis are common methods in this field. CVD is a widely favoured technique for synthesizing carbon-based nanomaterials due to its simplicity and the level of control it offers over the process.

CVD uses energy sources such as heat, light, or electric discharge to activate gaseous reactants so that solid deposits develop on substrates. Surface reactions are the preferred method for producing thin graphene films, while gas-phase reactions are also utilized in the process. Copper's low carbon solubility and surface-mediated growth make it an excellent substrate for producing consistent single-layer graphene. A few crucial procedures need to be taken to guarantee that the catalyst surface is effectively exposed to gas precursors. First, cleaning procedures are applied to the substrate surface, which includes chemical reduction in the processing chamber. The catalyst substrate and gases

are heated in a controlled environment to the pre-processing temperature to start the process. The next stage is annealing, which reduces the catalyst surface, cleans and modifies its morphology, and prevents metal evaporation by maintaining a constant temperature and gas environment. In the growing process, fresh precursors are added to the catalytic substrate to help graphene develop there. This step may entail several tactics, including temperature, gas mix, and pressure adjustments. After growth, the reactor is cooled in a suitable environment to avoid any unintended functionalization or oxidation [20]. Laser-assisted techniques have emerged as a remarkable technique for the rapid and scalable fabrication of graphene patterns. Unlike traditional methods that rely on expensive and time-consuming post-lithographic processes, this approach offers a streamlined solution. By utilizing localized laser heating, the process achieves a graphene growth rate that is 1000 times faster than conventional CVD methods. The high scan speed of up to 200 $\mu\text{m/s}$ allows for the precise and swift creation of line-shaped graphene ribbons with controlled widths and lengths, bypassing the need for additional annealing and lithographic patterning. The high quality of the graphene is confirmed through Raman spectroscopy, which also demonstrates that the number of graphene layers can be strictly regulated by adjusting the laser beams scan speed. This technique not only accelerates graphene production but also enhances the scalability and precision, making it well-suited for a wide range of electronic applications [21]. Graphene with high crystalline quality can be produced by thermal decomposition of silicon carbide (SiC) at high temperatures in an aGFO atmosphere, on substrates as large as 200 mm in diameter. This method is scalable, with 150 mm wafers readily available. The growth mechanism on the Si face of SiC is well understood, allowing controlled production, although thermal expansion mismatch can cause strain and defects like wrinkles. To address substrate influence on graphene's electronic properties, hydrogen intercalation is used. While graphene on the C face of SiC offers better electronic properties due to reduced substrate interaction, it suffers from smaller, less uniform areas and grain boundaries [22].

1.6. Characterization Methods

1.6.1. X-ray diffraction (XRD)

X-rays, discovered by Wilhelm Conrad Röntgen in 1895, revolutionized numerous scientific disciplines by offering new avenues for exploration and discovery. These high-energy electromagnetic waves have wavelengths ranging from 10^{-3} to 10^{-1} nm. The

generation of X-rays is commonly achieved using closed tubes, rotating anodes, or advanced synchrotron radiation sources, all of which are designed to emit X-rays for various applications.

XRD methods rely on the fundamental property of crystals to scatter X-rays in a distinct, predictable manner. This scattering ability allows scientists to meticulously study and determine the structure of crystalline phases. By analysing the diffraction patterns produced during XRD experiments, researchers can identify not only whether a material is crystalline but also the number and types of crystal phases present within a sample [23].

In the field of catalyst characterization, XRD is particularly valuable. The diffraction patterns generated in these experiments provide critical insights into the crystal phases of catalysts, offering key information about the material's structure and composition. As such, XRD serves as an essential tool for understanding and identifying the crystalline components of catalysts used in various chemical processes. From a single XRD analysis, one can determine the crystalline nature of a sample, the number of distinct crystal phases, and the specific types of phases present.

The X-ray source stays stationary while the detector moves to obtain the XRD pattern of a powdered sample. In the case of powdered samples, the orientation of the powder particles allows a small portion of them to align such that specific crystal planes form an angle θ with the incoming X-rays. This alignment leads to constructive interference, resulting in distinct diffraction lines that are observed in the XRD pattern [24].

The fundamental principles of X-ray diffraction, including its geometric interpretation, were discovered by the Bragg father-and-son duo, W. Lawrence Bragg and W. Henry Bragg. Their work established what is now known as Bragg's Law, which relates the angles at which X-rays are diffracted by crystal planes to the spacing between those planes. This law is crucial for analysing diffraction patterns and understanding the crystalline structure of materials.

The relationship between the wavelength of X-rays, the interatomic distances within a crystal, and the angle at which the X-rays strike the crystal is described by the fundamental equation of XRD, known as Bragg's Law. This relationship is expressed in Eq. 1.1:

$$n\lambda = 2 d \sin \theta \quad (1.1)$$

Where n refers to the order of diffraction, which is an integer indicating the number of wavelengths that fit into the path length of the diffracted beam. The term λ represents the wavelength of the X-rays measured in nm. The variable d is the distance between the lattice planes within the crystal, also measured in nanometers. Finally, θ is the angle between the incident X-rays and the crystal planes, expressed in degrees. Bragg's Law is essential for determining the crystal structure by analyzing the angles at which X-rays are diffracted.

The Scherrer formula, presented in Eq. 1.2, connects the size of the crystalline domains in a material with the width of the diffraction peaks observed in an XRD pattern:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1.2)$$

Where D represents the average size of the crystalline domains in nm. The term λ denotes the wavelength of the X-rays used, also in nm. The symbol β is the full width at half maximum (FWHM) of the diffraction peak, measured in radians. θ is the angle between the incident X-rays and the crystal planes, given in degrees. The constant k is a shape factor that corrects for various effects and depends on the specific geometry of the crystal and the XRD apparatus.

XRD is used to confirm the successful conversion of graphite oxide to graphene by detecting specific diffraction peaks. For example, the XRD patterns of pure graphite exhibit a peak at a 2θ angle of 26.52° which shifts following the reduction process to graphene. This analytical method is critical for evaluating the crystallinity, number of layers, and overall quality of graphene [25].

1.6.2. Raman spectroscopy

The Raman effect, an inelastic light scattering process, occurs when a photon excites a molecule into a virtual energy state, causing the scattered photon to have either lower or higher energy than the incident photon, depending on whether the molecule ends up in a higher or lower energy state. This frequency shift is known as Stokes or anti-Stokes shifts. The Raman effect is tied to changes in a molecule's polarizability during vibrations and contrasts with infrared spectroscopy, which depends on dipole moment

changes. In Raman, vibrations involving neutral bonds like C-C or C=C are strong scatterers, while polar bonds like C-O or O-H are weaker, as they result in small polarizability changes. IR spectroscopy, on the other hand, is more sensitive to polar bonds, making Raman and IR complementary techniques [26].

Applications for Raman spectroscopy are numerous and span many different domains. Using their distinct vibrational frequencies, molecules can be identified, chemical bonds studied, and molecular structures analysed in chemistry. For instance, it has aided in the analysis of enzyme-substrate interactions and the identification of vibrational modes in silicon oxides. Raman analyses materials in solid-state physics by monitoring phonon modes and temperature; in nanotechnology, it assesses carbon nanotube diameters and nanowire architectures. Additionally, Raman is essential to the pharmaceutical sector since it can discriminate between polymorphic drug forms and identify active pharmaceutical ingredients. Raman spectroscopy is used in biology and medicine to examine biomolecules, analyse wounds, find fake medications, and even investigate non-invasive cancer monitoring. Additionally, the method is successful in photovoltaics, where it aids in assessing solar [27].

Raman spectroscopy is particularly effective at determining the number of graphene layers, identifying defects, and assessing the quality of the material. The analysis is based on the Raman spectrum, which highlights important features such as the G-band and the 2D-band. The characteristics of these bands, including their intensity, position, and shape, can disclose essential details about the graphene sample, such as its layer thickness and doping levels. Additionally, the presence of the D-band indicates defects or disorders within the graphene structure. Thus, Raman spectroscopy is fundamental for both basic research and the practical applications of graphene [28].

1.6.3. Brunauer, Emmett ve Teller (BET)

Most of heterogeneous catalysts, including clays, supported metal catalysts, and metal oxides, have large porosity and surface areas that range from 1 to 1000 m²/g. The porous aspect of the material plays a critical role in catalytic activity as it considerably increases the overall surface area when compared to the exterior surface alone. These materials have a very complex pore size distribution, but macropores, mesopores, and micropores are the three main categories depending on pore diameter. In catalytic processes, macropores often facilitate the passage of reactants and products because their

widths exceed 50 nm. Mesopores by having sizes ranging from 2 to 50 nm, mesopores provide an intermediary channel that promotes diffusion and expands the surface area that is accessible for reactions. Micropores by contributing significantly to the total surface area, the tiniest pores, with sizes less than 2 nm, increase the quantity of active catalytic sites. The pore diameter is essential for figuring out how many active sites are present, the rate at which reactants and products diffuse, and if coke deposition is possible. 1938 witnessed the introduction of the BET theory, which is still widely used to characterize these materials, particularly when figuring out their total surface area.

Adsorption is the process by which gas molecules adhere to a solid surface. Several variables, such as surface area, temperature, gas pressure, and the intensity of the gas-solid contact govern it. Nitrogen gas is widely utilized in BET surface area measurements because it is readily available and interacts with most materials. Liquid nitrogen is usually used to chill the surface since nitrogen has a weak interaction with solid surfaces, making measured adsorption easier [29].

BET method is widely employed to characterize the surface area and porosity of graphene and graphene-based materials. The functionalization or presence of defects in graphene can significantly impact its surface area.

1.6.4. Electron microscopy

Electron microscopy is widely employed to examine the structural properties of catalysts, particularly focusing on the morphology and particle size. These techniques provide high-resolution imaging that is essential for understanding how samples function at the nanoscale. Based on the energy of the electrons used and the operational mode, these microscopes are broadly categorized into two main types: scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Both methods play crucial roles in material science but offer different advantages depending on the application [30].

SEM uses a high-energy electron beam to scan the sample's surface. When the beam interacts with the sample, it emits secondary electrons. The detailed surface morphology images are created by utilizing the contrast and intensity of the secondary electron signal. SEM stands out for its ability to provide researchers with a comprehensive visual depiction of materials, enabling them to analyse the surface's texture, shape, and particle organization. Another aspect of SEM is its capability to include elemental analysis

through energy-dispersive X-ray spectroscopy. This technique identifies the elemental composition by analysing the X-rays emitted from the sample when it is bombarded with electrons.

In contrast, TEM provides even greater resolution than SEM, sometimes down to atomic scales (as small as 0.1 nm). TEM uses electron beams to pass through a thin sample, generating 2D images that reveal differences in density or thickness within the material. There are two modes in which TEM operates:

- In bright-field mode, variations in sample thickness or density are revealed by analysing the intensity of the transmitted electron beam.
- The dark-field mode is capable of recording electron diffraction patterns, which in turn facilitates a comprehensive analysis of crystallography.

These dual imaging capabilities make TEM particularly suited for studying very fine details, such as the size distribution of nanoparticles, crystalline structures, and other key features of catalysts.

TEM is preferred for analysing nanoscale materials such as metal oxides, supported metal particles, and other nano catalysts due to its superior resolution. However, TEM requires much more complicated sample preparation than SEM, making SEM the go-to option for many researchers when quick, less intricate analysis is needed.

One of the primary advantages of SEM is its ease of sample preparation. Samples can generally be studied without extensive preprocessing, making it ideal for routine analysis. However, the sample must be conductive for SEM to function properly. If the sample is non-conductive, it can accumulate electrons, causing charging which interferes with the electron beam and results in image distortion. To overcome this, non-conductive samples are often coated with a thin metal layer, such as gold or aluminium, to facilitate electron flow and prevent this issue.

SEM offers comprehensive surface imaging, layer analysis, and insights into chemical composition, which are vital for understanding the morphology and purity of graphene. In contrast, TEM achieves atomic-level resolution, allowing for the examination of atomic arrangement, defects, and grain boundaries [38].

1.6.5. FT-IR spectroscopy

Fourier-transform spectroscopy is a powerful technique that generates spectra by measuring the coherence of a radiative source, either in the time or space domain. This

approach is widely used across various spectroscopic methods, including optical, infrared (such as FTIR and FT-NIRS), nuclear magnetic resonance (NMR), magnetic resonance spectroscopic imaging, mass spectrometry, and electron spin resonance spectroscopy. Two main measurement techniques are employed: pulsed Fourier transform and continuous-wave spectrometers, both used to assess the temporal coherence of light. The raw data obtained is converted into meaningful spectra using Fourier transforms, often grounded in the Wiener-Khinchin theorem [31].

Figure 1.4. presents a summary of FT-IR bands associated with different functional groups frequently found in organic compounds [32] .

NAME	POSITIONS OF INFRARED BANDS			
Aliphatic	C-H			
Methyl	2960			
Methylene	2930			
Unsaturated	C=C			
Alkenes	3050	1640		
Vinyl	910	1640		
Vinylidene	890	1640		
Cis	700	1640		
Trans	965	1670		
Alkynes	3200		2200	C≡C
Aromatics			Ring	
Mono	750		700	
Ortho	750		---	
Meta	782		700	
Para	817		---	
Oxygen Groups		C-O	O-H	
Ether		1100		
Alcohol		1100	3350	
Carbonyl Groups			C=O	
Aldehyde	2700		1730	
Ketone			1700	
Ester		1200	1740	
Carboxylic Acid		3100	1720	
Nitrogen Groups			N-H	C≡N
Amide		1640	3200	
Amine			3300	
Nitrile				2250

Figure 1.4. FTIR of fundamental organic functional groups

FT-IR is particularly effective in distinguishing between graphene, graphite oxide and reduced graphene oxide by identifying key oxygen-containing functional groups, including hydroxyl (-OH), carboxyl (-COOH), carbonyl (C=O), and epoxy (C-O-C) groups [33].

1.6.6. Thermogravimetric Analysis (TGA)

TGA is one of the thermal analysis techniques, which determines weight changes in a sample as a function of temperature. TGA can be used to assess these mass changes and therefore provide information into physical-chemical phenomena such as phase transformations, thermal decomposition, or solid-gas reactions. This type of characterization will crucially underpin how a material behaves in the heat and what stability (or composition changes) are occurring over time.

A thermogravimetric analyser consists of a precision balance and a sample pan within a furnace that can be programmed to heat at controlled rates. During an experiment, the temperature of the sample is increased steadily, and the mass is recorded continuously. The resulting data is plotted as mass or percentage of initial mass versus temperature or time, creating a TGA curve. The first derivative of this curve, known as the Differential Thermogravimetry (DTG) curve, can help identify specific thermal events and decomposition points.

TGA can be categorized into three types: isothermal, quasistatic, and dynamic thermogravimetry. Isothermal TGA measures mass changes at a constant temperature, quasistatic TGA involves raising the temperature in steps with isothermal intervals, and dynamic TGA heats the sample at a continuous rate. Each method provides different insights into a sample's thermal behaviour.

Applications of TGA are extensive. It is used to evaluate the thermal stability of materials, particularly polymers, by determining their melting and degradation temperatures. TGA can also assess oxidative mass losses and combustion reactions, which are crucial for materials like copper alloys used in high-temperature environments. It can detect oxidation resistance and analyse residue from combustion processes [34].

TGA is particularly effective in determining the level of reduction in GO by quantifying the removal of oxygen-containing functional groups, including hydroxyl and carboxyl groups, which significantly enhances the thermal stability of GFO. In addition, TGA is valuable for assessing the efficacy of graphene functionalization, observing decomposition trends in graphene-based composites, and estimating defect densities [35].

1.6.7. UV-Vis spectroscopy

Ultraviolet spectroscopy specifically focuses on the absorption of light in the UV region (Figure 1.5), typically ranging from 200 to 400 nm. It is commonly used to analyze

compounds such as nucleic acids, proteins, and organic molecules, as they often exhibit characteristic absorption patterns in this region. UV-Vis spectroscopy, on the other hand, covers a broader range, including both the UV and visible regions (typically from 200 to 800 nm). This technique is useful for studying a wider range of samples, including inorganic compounds, transition metal complexes, and dyes. The measurements obtained from UV and UV-Vis spectroscopy provide valuable information about the electronic structure, concentration, and purity of the sample. The intensity of light absorbed at different wavelengths is plotted on a graph known as an absorption spectrum, which can reveal important details about the sample's composition and properties [36] .

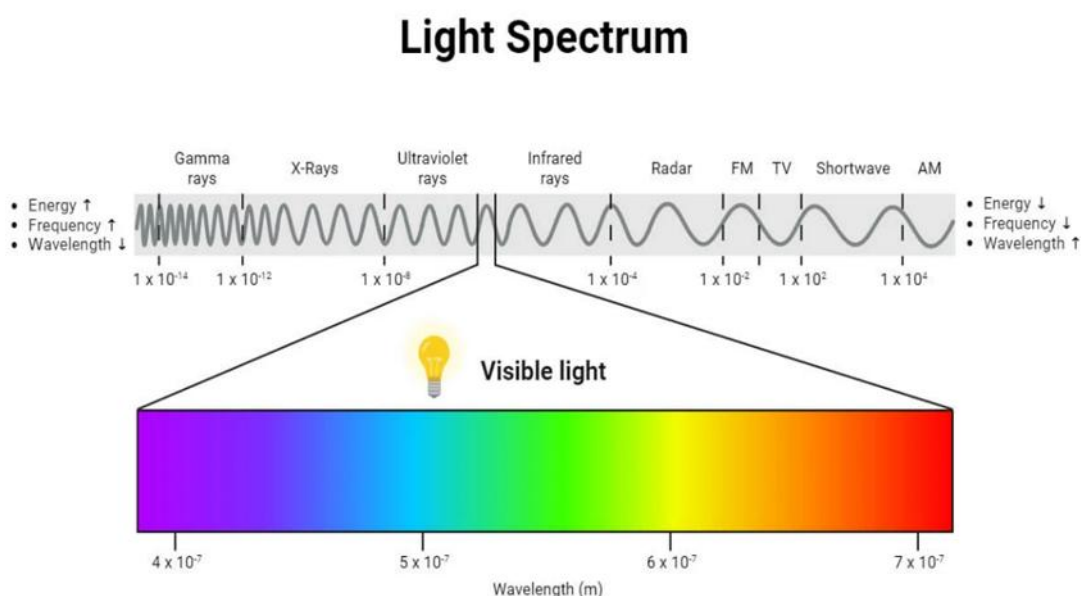


Figure 1.5. *Light spectrum*

UV-Vis spectroscopy is widely used in various fields due to its versatility and ability to provide valuable information about the electronic structure and properties of molecules. In the analysis of transition metal ions, UV-Vis spectroscopy helps in determining their oxidation states and coordination environments. This is particularly useful in fields such as environmental monitoring, chemical analysis, and pharmaceutical research.

The choice of solvent can affect the solubility and stability of the sample, while pH can influence the protonation or deprotonation of functional groups. Additionally, the spectral bandwidth, or the range of wavelengths used for measurement, should be

carefully selected to ensure that all relevant absorption peaks are captured. By carefully controlling these variables, UV-Vis spectroscopy can provide valuable insights into the molecular structure and properties of a wide range of compounds [36, 37].

UV-Vis spectroscopy is used extensively to characterize graphene and its derivatives, such as GO and GFO. This technique provides critical insights into their electronic configurations and optical behaviours. It facilitates the observation of important electronic transitions, including the π - π^* transition of the conjugated carbon network and the n - π^* transition related to the oxygenated functional groups in GO. The UV-Vis spectra are especially significant for monitoring the reduction of GO, as the removal of oxygenated groups induces changes in absorption features [38].

1.7. Hydrogen

In the 21st century, globalization and modernization are fundamentally reliant on energy consumption, with fossil fuel-based resources fulfilling most global energy demands. The persistent and systematic reliance on these resources has resulted in their depletion, prompting researchers to explore alternative energy sources. Furthermore, rising costs and severe environmental consequences stemming from the extensive use of fossil fuels have redirected global attention towards clean and renewable energy solutions. The urgent necessity to develop renewable and clean energy sources, driven by concerns over greenhouse gas emissions and environmental degradation, has sparked significant interest in hydrogen as a fuel due to its high energy content [39].

Hydrogen is not as easily obtainable as other fuels that originate from fossil resources, making it a secondary energy source that can be generated from various primary energy sources. Its production methods include fossil fuel gasification (utilizing natural gas and coal), photolysis for water splitting, water electrolysis, and conversion of biomass through thermochemical and biological processes. Hydrogen can be employed in fuel cells to generate electricity and in internal combustion engines for direct combustion [40,41].

Hydrogen is recognized as a clean, non-toxic, and emission-free fuel, boasting an energy yield of 122 kJ. g⁻¹, which is approximately 2.75 times greater than that of most hydrocarbon fuels.

Global renewable energy policies are increasingly focused on the utilization of hydrogen as a fuel source for combustion engines and electric vehicles through fuel cell

technology. The adoption of hydrogen in transportation systems eliminates toxic gas and CO₂ emissions, with water vapor being the sole byproduct. Various industries, including chemical, petroleum, and food processing sectors, consume substantial quantities of hydrogen as a feedstock. It is also employed in processes such as hydro-treating, desulfurization, and chemical production. Despite its advantageous properties, including its environmentally friendly nature, efficient energy transfer, and high calorific value, hydrogen faces practical challenges, particularly in achieving high purity levels and effective storage. The low density of hydrogen, measured at 0.082 kg. m⁻³, combined with its high flammability, presents significant storage challenges.

1.8. Hydrogen Storage

Hydrogen storage is typically categorized into two main groups: physical storage and chemical storage, as illustrated in Figure 1.6 [42] .

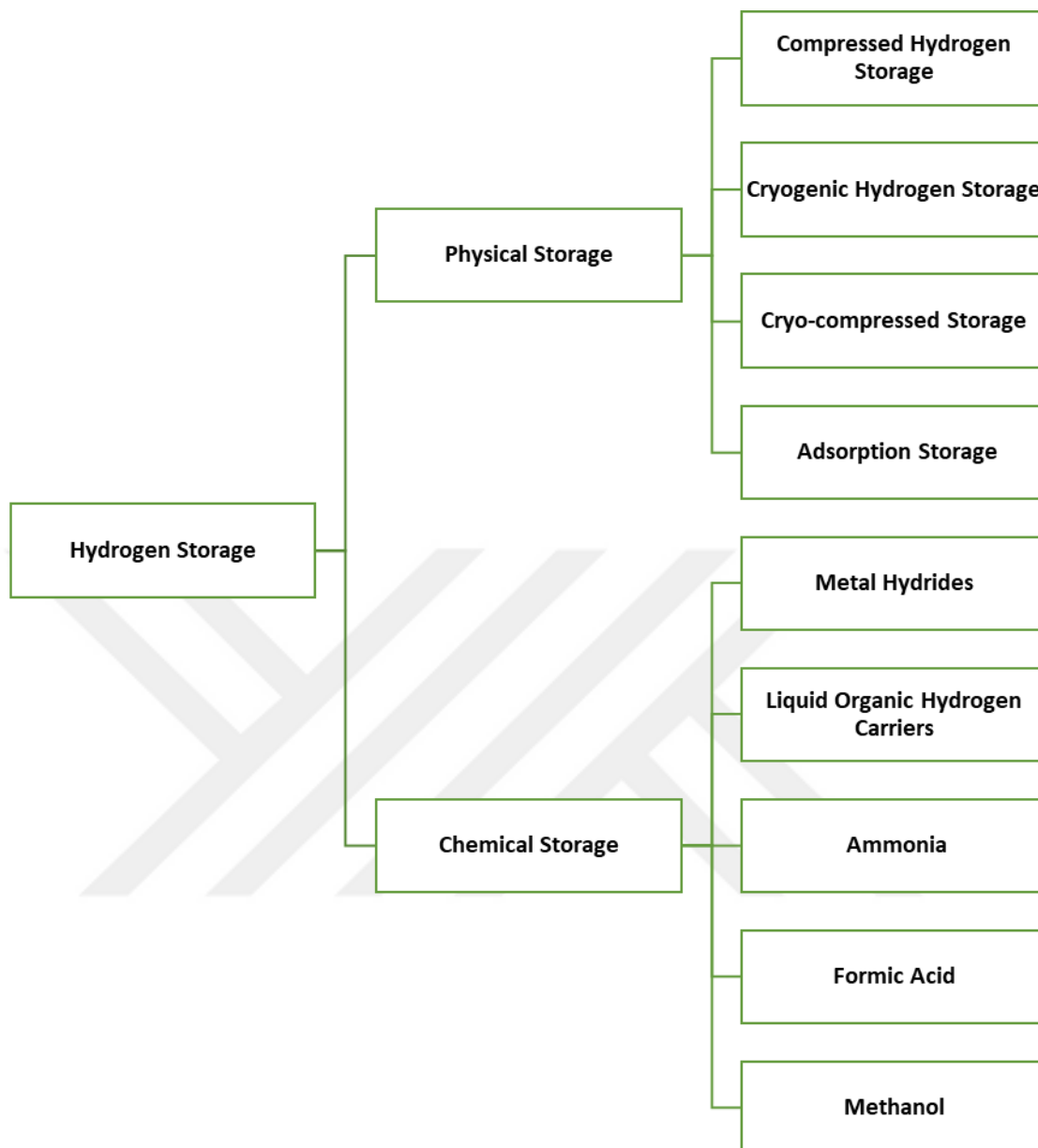


Figure 1.6. *Hydrogen storage methods*

Physical storage methods include compressed hydrogen storage, cryogenic hydrogen storage, cryo-compressed hydrogen storage, adsorption storage, metal-organic frameworks, carbon-based materials, and porous organic polymers. On the other hand, chemical storage methods encompass metal hydrides, liquid organic hydrogen carriers, ammonia, formic acid, and methanol [43].

1.8.1. Physical hydrogen storage

1.8.1.1. Compressed hydrogen storage

Compressed hydrogen storage technology utilizes high-pressure vessels to store hydrogen gas, which are categorized into five main types. Type I vessels, made entirely of metal (usually steel), are primarily used for stationary industrial applications due to their weight and low hydrogen storage capacity, storing only about 1 wt% hydrogen at 200–300 bar. Type II vessels, which are metal-lined and partially wrapped with composite materials, are lighter than Type I vessels. However, they are still unsuitable for mobile use due to issues like hydrogen embrittlement and relatively low storage density.

Type III vessels, which are fully wrapped with composite materials and have a metal liner (typically aluminum), provide a significant weight reduction compared to Types I and II. The metal liner helps prevent hydrogen embrittlement, while the composite overwrap manages the structural load. These vessels are commonly used in fuel cell vehicles and perform reliably at pressures up to 450 bar. However, they face challenges at higher pressures, such as 700 bar, and are more expensive due to the high cost of materials like carbon fiber.

Type IV vessels known for being the lightest and most suitable for mobile applications, feature a composite overwrap and a plastic liner that serves solely as a hydrogen permeation barrier. These vessels can withstand pressures up to 1000 bar. However, the cost is significantly influenced by the expensive carbon fibers used in their construction. Despite the widespread use in fuel cell vehicles, Type IV vessels face challenges such as high costs, bulkiness, and safety concerns, including the potential for hydrogen leakage under high pressure.

Type V vessels are even lighter than Type IV vessels. However, they are not yet suitable for high-pressure applications outside of laboratory settings. While they hold promise for future advancements, their current limitations restrict their use to experimental environments [44].

1.8.1.2. Cryogenic hydrogen storage

Cryogenic hydrogen storage refers to the process of maintaining hydrogen in its liquid state at very low temperatures. This method has distinct advantages over compressed hydrogen storage, especially regarding volumetric density. Liquid hydrogen boasts a theoretical volumetric density of 70 g.L⁻¹ at its boiling point of -253°C, while

compressed hydrogen has densities of 24 g.L^{-1} and 40 g.L^{-1} at pressures of 350 bar and 700 bar, respectively, at room temperature. As a result, liquid hydrogen serves as a more compact storage solution, offering a higher storage density [45].

The liquefying hydrogen process demands a considerable amount of energy, using about 25% to 40% of the hydrogen's energy content, whereas compression only requires around 10%. Storing hydrogen in cryogenic conditions involves keeping it at very low temperatures, which is energy-consuming and necessitates the use of thermally insulated containers, often vacuum-insulated to reduce heat loss. Even with these precautions, some boil-off losses are inevitable, usually reaching up to 0.4% per day, which can pose safety risks, particularly in enclosed areas like closed garages [44].

The high costs associated with liquefaction and the unavoidable boil-off losses make cryogenic hydrogen storage most suitable for scenarios where high energy density is essential and the hydrogen is consumed rapidly. This is particularly relevant for space missions and large-scale hydrogen transport, including liquid hydrogen trailers and ships.

1.8.1.3. Cryo-compressed hydrogen storage

Cryo-compressed hydrogen storage merges the advantages of both compressed and cryogenic hydrogen storage techniques to overcome their specific limitations. This innovative technology employs insulated vessels designed to endure both cryogenic temperatures and high pressures, enhancing the volumetric storage capacity and safety of hydrogen. By compressing liquefied hydrogen at 20 K, the volumetric storage capacity can rise from 70 g.L^{-1} at 1 bar to 87 g.L^{-1} at 240 bar. This approach minimizes boil-off losses and enables the use of lower pressures (under 300 bar) compared to conventional compressed hydrogen storage, which could reduce the dependence on costly carbon fiber composites [46].

Technical assessments and computational analyses indicate that cryo-compressed hydrogen storage systems are capable of meeting various targets set by the US department of energy for automotive applications. For instance, these storage systems have shown considerable enhancements in both gravimetric and volumetric capacities, along with lower system costs and reduced mass of carbon fiber composites. A significant study revealed that a cryo-compressed system operating at 500 bar surpassed a Type III compressed hydrogen system at 350 bar regarding storage capacity and cost efficiency.

Furthermore, cryo-compressed systems can maintain dormancy periods of over seven days while experiencing minimal hydrogen loss [47].

1.8.1.4. Adsorption storage

Hydrogen storage through adsorption works by binding hydrogen molecules to the surfaces of porous materials using physisorption, which relies on weak van der Waals forces. This approach has several benefits compared to chemisorption, such as quicker adsorption and desorption rates, complete reversibility, and strong stability over numerous cycles. Physisorption generally involves very low interaction energies (4–10 kJ.mol⁻¹), allowing the process to be reversible and producing less heat than chemisorption. However, because of these weak interactions, achieving high hydrogen storage capacities typically requires cryogenic temperatures (around 77 K) and high pressures, while ambient conditions often result in much lower capacities (usually less than 1 wt%).

Various materials have been explored for hydrogen storage via adsorption, encompassing both traditional and innovative types of porous materials. Classic options like zeolites and activated carbon have been examined for their adsorption capabilities. Additionally, carbon-based materials such as carbon nanotubes, fullerenes, and zeolite-templated carbons are also considered promising. Recent developments have shifted attention to newer materials, including metal–organic frameworks, covalent organic frameworks, and polymers of intrinsic microporosity. Each material category presents distinct benefits based on its structural features and surface properties [43].

Among these materials, metal-organic frameworks, carbon-based substances, and porous organic polymers have been the focus of extensive research. MOFs are recognized for possessing large surface areas and adjustable structures, which enhance the capacity for hydrogen storage. Carbon-based materials, characterized by their significant surface area and porosity, also play an important role in hydrogen storage. Porous organic polymers provide high surface areas and the ability to be chemically modified, enhancing their effectiveness for hydrogen storage. However, despite the attractive properties of these materials, achieving high hydrogen storage capacities under practical conditions remains a challenge, often necessitating low temperatures and high pressures.

Some adsorbents used in hydrogen storage by adsorption are given in detail below.

Metal-organic frameworks: MOFs are a varied group of crystalline porous materials made up of metal nodes linked to organic molecules, resulting in extensive networks of pores and channels. These materials stand out due to their remarkably large surface areas (up to 10.000 m²/g) and high permanent porosity [48]. MOFs possess adjustable properties such as framework topology, pore size, and internal surface area, which can be fine-tuned to enhance their effectiveness for specific applications, including hydrogen storage. Various strategies have been investigated to improve hydrogen storage in MOFs. These strategies include optimizing the influence of open metal centers, pore size, and surface area, as well as modifying ligands, doping with metal ions, incorporating nanoparticles, and creating composites. Removing coordinated solvent molecules can generate open metal sites, which enhances hydrogen binding. Furthermore, adjusting pore size can increase the isosteric heat of adsorption, influencing the strength of hydrogen interactions with the MOF. Functionalization and doping with alkali metals can also boost hydrogen storage capacities. The addition of metal NPs, like Pd and Pt, into MOFs has been shown to improve hydrogen storage through the spillover effect, although this has been a topic of debate and is not always consistently reproducible. While gravimetric hydrogen storage capacities are frequently emphasized, volumetric capacities are essential for real-world applications. Research has indicated that volumetric hydrogen uptake rises with surface area up to a certain threshold, beyond which it declines [49].

Carbon-based materials: Various carbon-based materials have been investigated for hydrogen storage because of their high surface area, chemical and thermal stability, and relatively low cost. These materials include carbon nanotubes, fullerenes, graphene, activated carbon, carbon aerogels, and templated carbons. While initial studies on carbon nanotubes and nanofibers showed potential, later research uncovered issues with measurement errors and sample quality that impacted the reported hydrogen storage capacities. Despite these setbacks, carbon-based materials continue to be a major area of interest due to their advantageous properties and the potential for further optimization [50].

Active carbon is among the most extensively researched carbon materials for hydrogen storage. It can be produced from various carbon-rich sources, such as biomass, coal, and waste materials, making it a cost-effective option. At moderate pressures (10–100 bar) and low temperatures (77 K), it had shown hydrogen uptakes ranging from 2–7 wt%. The high hydrogen storage capacities are generally linked to favourable textural

characteristics, including a large surface area, significant micropore volume, and a narrow pore size distribution [51].

Templated carbons, created using porous materials like silicas, zeolites, or MOFs as templates, provide a method to produce carbon materials with highly ordered porous structures. This technique allows for precise control over the porous architecture of the resulting carbon products. Among these, zeolite-templated carbons have demonstrated considerable promise due to their high surface areas, pore volumes, and microporosity. Enhancing hydrogen storage capacity in zeolite-templated carbons has been accomplished through activation processes and heteroatom doping, although the advantages of doping can differ based on coverage levels [52].

Due to their high surface area, graphene-based materials are a promising avenue for hydrogen storage, although single-layer graphene alone is not optimal [53].

1.8.2. Chemical hydrogen storage

Chemical hydrogen storage refers to the process of chemically binding atomic hydrogen within a material's structure. While chemisorption can achieve relatively high hydrogen storage capacities, the kinetics of hydrogen uptake and release can be slow. Typically, releasing hydrogen necessitates high temperatures, and these materials often exhibit irreversible hydrogen uptake due to the significant activation energy required. Consequently, there has been considerable focus on improving the thermodynamics, kinetics, and cyclability of hydrogen uptake and release in chemical hydrogen storage materials.

1.8.2.1. Metal hydrides

Metal hydrides are known for their impressive volumetric hydrogen storage capacities, making them a promising choice for safer and more compact storage solutions compared to traditional methods like compressed or liquid hydrogen. They can be categorized into intermetallic hydrides, binary hydrides, and complex metal hydrides. Intermetallic hydrides, such as AB_5 , AB_2 , A_2B , and AB alloys, typically exhibit lower gravimetric capacities (less than 2 wt%) due to the constraints of their crystal structures. For instance, $LaNi_5$, an AB_5 alloy, can hold 1.4 wt% hydrogen, while $FeTi$, an AB alloy, can store 1.9 wt%. These alloys can be optimized by substituting different metals to improve their stability and effectiveness for hydrogen storage. Additionally, researchers

have investigated nano structuring these materials to enhance their properties. Among binary hydrides, magnesium hydride stands out as the most researched due to its high theoretical hydrogen storage capacity (7.6 wt%) and the low cost and availability of magnesium. However, magnesium hydride has slow kinetics for hydrogen uptake and release and requires high desorption temperatures (over 300°C), which limits its practical applications. Other binary hydrides, such as aluminium hydride, provide a high gravimetric storage capacity (10.1 wt%), but producing AlH_3 from aluminium and hydrogen is difficult because of the extreme pressures and temperatures needed. Complex hydrides like LiAlH_4 , NaAlH_4 , and $\text{Mg}(\text{BH}_4)_2$ have gained interest for their high theoretical gravimetric hydrogen capacities. Nevertheless, these materials encounter issues with stability, needing high temperatures for decomposition, and they often lack reversibility. To enhance their practicality, various strategies such as alloying, adding catalysts, and nano structuring have been investigated. For example, Ti-doped LiAlH_4 can release hydrogen at temperatures as low as 80°C and can be recharged under mild conditions, improving its usability. Nano structuring has emerged as a crucial method for enhancing the hydrogen storage capabilities of metal hydrides. By reducing particle size, the surface area increases, which can significantly improve performance [54–56].

1.8.2.2. Liquid organic hydrogen carriers

Liquid organic hydrogen carriers (LOHCs) are organic compounds that can effectively store and release hydrogen through reversible catalytic processes of hydrogenation and dehydrogenation. This method provides a practical approach to managing hydrogen. The process begins with the hydrogenation of a hydrogen-lean molecule ($\text{H}_0\text{-LOHC}$) under specific pressure and temperature conditions using a catalyst, resulting in a hydrogen-rich molecule ($\text{H}_n\text{-LOHC}$). Later, the hydrogen-rich molecule undergoes dehydrogenation at elevated temperatures to release hydrogen gas and regenerate the $\text{H}_0\text{-LOHC}$. This technique allows for long-term hydrogen storage without self-discharge in ambient conditions, making it a suitable choice for seasonal energy storage. LOHCs play a crucial role in the storage, transport, and distribution of hydrogen across various industries and applications. Hydrogen stored in LOHCs can serve as feedstock in numerous industrial processes, including steel and chemical manufacturing, or as an energy source for both mobile and stationary power applications. Additionally, hydrogen can be derived from renewable energy sources (green hydrogen),

fossil fuels (gray hydrogen), or fossil fuels with carbon capture (blue hydrogen), with the LOHC method facilitating the management of hydrogen's storage and logistics. The conditions required for hydrogenation and dehydrogenation reactions vary based on the specific LOHC molecule and the properties of the catalyst used. Some LOHCs may need temperatures as high as 300°C for dehydrogenation, while others can function effectively below 200°C. The enthalpy of the LOHC molecule also affects the reaction temperature, with higher enthalpy LOHCs necessitating higher dehydrogenation temperatures [85, 86].

1.8.2.3. Ammonia

Ammonia has become one of the most promising chemical alternatives for hydrogen storage, particularly due to its carbon-free nature. The synthesis of ammonia, mainly through the Haber–Bosch process, has been utilized since the early 1900s and is crucial in global agriculture as a fertilizer. Although ammonia is environmentally advantageous as a carbon-free molecule, its current production heavily depends on hydrogen derived from natural gas reforming and coal gasification, both of which generate significant carbon emissions. However, this process can be decarbonized by using electrolytic hydrogen produced from renewable energy sources. Ammonia boasts a high hydrogen density of 108.5 kg/m³ and can be liquefied under relatively mild conditions (8.6 bar and 20 °C), making it an appealing option for storage. The primary energy requirements in ammonia production arise from the cryogenic distillation of air to obtain pure nitrogen and the compression of hydrogen and nitrogen for the high-pressure Haber–Bosch process, which typically operates at 200 bar. Recent advancements have concentrated on developing catalysts that can reduce the synthesis pressure while maintaining efficiency, although this necessitates an increase in the recycling of unreacted gases. A significant benefit of ammonia as a hydrogen carrier is its independence from carbon-based feedstocks like syngas or CO₂, allowing for production in areas rich in renewable energy but with minimal industrial CO₂ emissions [59–61].

1.8.2.4. Formic acid

Formic acid (FA), recognized as the simplest carboxylic acid, presents significant potential as a hydrogen carrier due to its impressive hydrogen density of 53.5 kg.m⁻³ and its liquid state at atmospheric conditions. Its extensive application in the leather and textile industries, along with a global production capacity of approximately 800.000

metric tons per year, positions FA as a readily accessible resource for energy storage. The presence of reactive carbonyl and hydroxyl groups in FA enhances its value as a building block for various fuels and speciality chemicals. Typically, industrial production involves hydrolyzing methyl formate, which is produced from the carbonylation of methanol and carbon monoxide under high pressure. A promising method for synthesizing FA is through the hydrogenation of dissolved CO₂ using homogeneous catalysts such as RuCl₂(PTA)₄, particularly when dimethyl sulfoxide serves as the solvent. This approach allows for the use of renewable hydrogen and the capture of waste CO₂ from concentrated sources for hydrogen storage. However, the challenges of separating and recycling homogeneous catalysts and solvents complicate this process. Furthermore, FA's strong acidity and high ionization constant render it corrosive to common stainless steels like SS304 and SS316, especially at elevated concentrations and temperatures. Zirconium alloys have emerged as effective alternatives for managing FA's corrosive nature. The decomposition of FA results in the release of hydrogen and CO₂, but it can also generate unwanted CO in low-temperature fuel cell applications. CO poses a significant risk for proton-exchange membrane (PEM) fuel cells, as it can poison platinum-based anodes [90, 91].

1.8.2.5. Methanol

Methanol is an attractive option for hydrogen storage because it remains in liquid form at room temperature (20 °C, 1 atm), making it easier to store and transport. It boasts a high hydrogen density of 100 kg.m⁻³ and can be produced using renewable hydrogen along with captured CO₂. The typical production of methanol occurs at temperatures between 200-300 °C and pressures around 50 bar, necessitating gas recycling due to equilibrium constraints. While conventional methanol synthesis relies on syngas, the CO₂-to-methanol process faces challenges, including the increased formation of water by-products that can affect catalyst performance. Ongoing research aims to enhance catalyst longevity and improve reaction kinetics for more effective CO₂ conversion into methanol [59].

1.9. Electrochemical Hydrogen Storage

During electrochemical measurements, hydrogen atom adsorption takes place at the interface between the electrode and the electrolyte. The electrode serves as the focal point

for hydrogen storage, either by having hydrogen deposited onto it or by being composed of the storage material itself. In traditional hydrogen storage methods, hydrogen molecules are physically retained across a broad surface area of solid materials. Conversely, electrochemical hydrogen storage involves the retention of hydrogen ions and atoms at the working electrode, while the counter electrode facilitates the completion of the current flow. Generally, electrochemical hydrogen storage entails the adsorption of hydrogen ions on the surface of the electrode film and their subsequent insertion into the bulk material [64].

For electrochemical hydrogen storage measurement, the specific capacity is influenced by several factors, such as physicochemical characteristics, the nature of the electrolyte (acidic or basic), concentration levels, and potential values. KOH and H₂SO₄ constitute the most used electrolyte solutions in electrochemical hydrogen storage [65].

Numerous electrochemical methods can be employed to assess the reversible hydrogen stored in potential candidate materials such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), amperometry, galvanostatic charge/discharge measurements, and the open-circuit voltage method.

Cyclic voltammetry techniques are widely recognized electrochemical methods employed to obtain both qualitative and quantitative insights into the kinetics of reversible hydrogen storage. Additionally, CV plays a crucial role in the investigation of chemical reactions initiated by electron transfer [66].

The configuration and location of CV peaks provide essential insights into the kinetics of electron transfer, the reversibility of redox reactions, and the number of electrons involved. For example, a pronounced peak may signify a rapid and reversible reaction, whereas a wider peak could show slower kinetics or a more complex mechanism. Furthermore, the peak current typically correlates with the concentration of the analyte, thereby establishing cyclic voltammetry as an important method for quantitative analysis.

The three-electrode system is a fundamental setup used in electrochemical experiments to analyse reactions with enhanced accuracy and control. It consists of a working electrode, a reference electrode, and a counter electrode, each serving a specific purpose. The working electrode serves as the site for the electrochemical reaction. The reference electrode, which may be a Saturated Calomel Electrode or a Silver/Silver Chloride (Ag/AgCl) electrode, offers a well-defined potential, thereby ensuring

measurement accuracy without significant current flow. The counter electrode, typically constructed from inert materials such as platinum or carbon, completes the circuit by facilitating current flow to maintain equilibrium in the reaction occurring at the working electrode. A potentiostat is employed to manage the potential difference between the working and reference electrodes while simultaneously measuring the current produced during the reaction.

The choice of solvent in CV is a critical factor that significantly influences the accuracy and reliability of the results. The solvent must be capable of dissolving both the analyte and the supporting electrolyte at high concentrations to ensure proper conductivity and interaction within the solution. Stability within the potential window of the experiment is essential, as the solvent should not undergo oxidation or reduction at the working electrode's potential range, which could otherwise interfere with the measurements. Additionally, the solvent must be non-reactive with both the analyte and the supporting electrolyte to prevent any unwanted chemical reactions that could alter the electrochemical properties of the analyte or produce side products. Solvent purity is critical, as contaminants may compromise analyte electrochemical behaviour and compromise result accuracy. By carefully selecting a solvent that meets these criteria, researchers can ensure that their CV experiments provide clear and interpretable data, accurately reflecting the true electrochemical properties of the analyte.

The selection of an appropriate electrolyte in the CV test is essential for achieving optimal electrical conductivity, thereby facilitating the accurate recording of potentials. In aqueous environments, a range of electrolytes can be utilized, with alkali metal salts such as perchlorates and nitrates being among the most common. These salts are preferred due to their high solubility and stability in water, which contribute to reliable conductivity and minimal disruption of electrochemical measurements. Conversely, in nonaqueous solvents, the options for suitable electrolytes are more limited. A widely used choice is tetrabutylammonium hexafluorophosphate (TBAPF₆). This electrolyte is favoured for its high solubility in various organic solvents and its ability to provide excellent ionic conductivity. Furthermore, TBAPF₆ demonstrates stability across a broad potential range, making it particularly suitable for nonaqueous CV experiments where the potential window may exceed that of aqueous systems [67].

Pristine carbon nanomaterials, with their high surface areas, are considered promising for hydrogen storage. However, their hydrogen storage capacity is limited to

around 1 wt % under ambient condition, which doesn't meet the US DOE targets for practical applications. To enhance this capacity, researchers have focused on modifying these materials through several strategies. These include introducing heteroatom groups or metal nanoparticles, creating defects to increase surface area, and other chemical modifications. These approaches aim to optimize the hydrogen storage potential of carbon-based materials [68]. The US DOE (United States Department of Energy) targets for hydrogen storage materials include hydrogen adsorption enthalpy between 20 and 30 kJ/mol under ambient conditions. Metal hydrides and chemical hydrides have high binding enthalpies (>60 kJ/mol), which results in slow charge/discharge kinetics and poor reversibility. In contrast, carbon and porous materials that use physisorption exhibit weak van der Waals interactions with hydrogen, leading to low storage capacities and binding enthalpies (<10 kJ/mol). To address these issues, the Kubas interaction has been proposed, which involves incorporating a metal catalyst into the adsorbent material. This interaction lengthens the H_2 bonds without breaking them, providing a stronger interaction between hydrogen molecules and the metal catalyst. The "spillover" phenomenon has gained significant attention in hydrogen storage, particularly in heterogeneous catalysis. It involves the transport of active hydrogen species from a catalyst to an inert substrate that does not typically adsorb or activate hydrogen. The mechanism consists of three steps: (i) chemisorption and dissociation of hydrogen molecules on a transition metal catalyst, (ii) migration of hydrogen atoms from the catalyst to the substrate, and (iii) diffusion of hydrogen atoms onto the substrate surface. The substrate, in this case, is inert to hydrogen, but it can accept activated hydrogen atoms from the catalyst [69]. Studies show that doping with elements such as nitrogen or boron can improve hydrogen storage. For example, Yang et al. [70] synthesized N-doped microporous carbon, increasing its hydrogen storage capacity by 18%, and further decorating it with Pt nanoparticles resulting in a capacity of 1.26 wt %, 2.4 times higher than the pristine material.

2. LITERATURE REVIEW ON GRAPHENE SYNTHESIS

A literature review is a crucial component of any research endeavour, as it offers a comprehensive overview of the existing knowledge surrounding a particular subject. It delineates significant theories and methodologies while also pinpointing areas of deficiency and ongoing discussions within the current body of research. This process not only prevents repetition but also sets the foundation for the theoretical framework of your investigation, thereby enabling the progress of existing knowledge. Therefore, in this chapter, the author aims to review recent articles relevant to the current thesis.

Producing graphene oxide (GFO): The research conducted by Haluk et al. [71] evaluated four different methods for synthesizing GO: the Brodie, Staudenmaier, Hummers, and Modified Hummers methods. The authors examined the impact of various pre-treatment techniques applied to graphite before synthesis, which included no pre-treatment, ultrasonication, and preheating at 200 °C for 3 h. BET analysis was conducted to evaluate the surface area, particle size distribution, polydispersity index, and zeta potential. The results indicated that the GO produced from graphite without any pre-treatment via the Modified Hummers method demonstrated the most favourable overall performance.

Seyyedeh et al. [72] investigated how the initial size and shape of graphite particles affect the oxidation process during GO production using the Hummers method. The researchers examined three types of graphite particles (clod powder with sizes of 18 mm and 6 mm, and flake-shaped powder averaging 25 mm in size). Characterization techniques employed included particle size analysis, XRD, and SEM. The oxidation degree was quantified by analysing the intensity ratio of the XRD peaks for GO relative to graphite. The results demonstrated a significant relationship between oxidation time and the initial particle characteristics; clod samples required several days for complete oxidation, while the flake powder was fully oxidized in 2 h. These findings highlight the importance of selecting suitable particle size and shape to effectively reduce oxidation time, which can be advantageous for researchers in the synthesis of GO.

Yanbin et al. [73] presented Hummers method for the synthesis of GO, which employs a sulfuric acid concentration that is approximately 40% lower than conventional practices. This modification is intended to reduce production costs and mitigate environmental effects. The researchers have developed a synthesis method that is both simple and safe, using heat from the environment and the reaction system to effectively

manage the temperature during the reaction with the reduced acid concentration. Remarkably, this approach allows for the complete oxidation of graphite into GO while significantly curtailing the generation of high-concentration aqueous waste acid. Characterization of the synthesized GO revealed that it achieved yields comparable to those obtained through traditional methods and maintained similar functional groups.

Romero et al. [74] have conducted a comparative study on synthesizing GO and GFO. The modified method is advantageous as it minimizes both the reaction time and the number of chemical reagents required, leading to superior results. In contrast, the potassium ferrate method results in a lower oxidation level of GO.

Sujiono et al. [75] synthesized GO from coconut shell waste using an improved Hummers method. The GO was characterized using XRD, FT-IR, Raman spectroscopy, UV-Vis spectroscopy, and SEM-EDX. XRD revealed the presence of the 2H graphite phase and indicated a transition to GFO. FT-IR confirmed functional groups typical of GO, while Raman spectroscopy showed an I_D/I_G ratio of 0.89, suggesting defects and a 2D single-layer structure. SEM analysis displayed a granular surface morphology, and UV-Vis indicated semiconductor properties with a bandgap energy of 4.38 eV. The study demonstrates the potential of coconut shell waste for GO production with desirable properties.

Producing multi-layer graphene from LPE (GF): Zheling et al. [76] delved into the intricate mechanisms associated with LPE for the generation of graphene. Their primary focus was on elucidating the process through which large graphite crystals are disintegrated into smaller graphene flakes during exfoliation. Using ultrasonic LPE, they identified three distinct stages in the conversion from graphite to graphene: (1) the initial sonication causes the rupture of large flakes, resulting in the formation of striations along zigzag orientations, (2) cracks form along these striations, which leads to the unzipping of graphite strips, and (3) these strips are subsequently exfoliated into thin graphene flakes. Their findings offer significant insights that could enhance the efficiency and scalability of graphene manufacturing.

Chen et al. [77] conducted a comprehensive review of the application of dispersant-assisted LPE for the synthesis of two-dimensional materials beyond graphene. Their analysis highlighted the role of dispersants, which are generally amphiphilic molecules, in facilitating the exfoliation and stabilization of 2D materials across a broader spectrum of solvents, including water. This advancement significantly diminishes the

dependence on hazardous and costly solvents that are conventionally employed in direct LPE processes. The authors specifically examined materials such as transition metal dichalcogenides and hexagonal boron nitride, elaborating on the characteristics and concentrations of nanosheets generated through this technique. Furthermore, they addressed the challenges and potential avenues for enhancing the use of dispersant-assisted LPE across various 2D materials, particularly in applications related to nanomedicine, energy storage, and catalysis.

Maher et al. [78] conducted a study on the impact of various graphite exfoliation techniques on the characteristics of exfoliated graphene and its potential photocatalytic applications. They examined prevalent top-down exfoliation methods, such as chemical, liquid-phase, mechanical, and electrochemical techniques, evaluating the benefits and limitations associated with each. The authors investigated how these exfoliation methods affect the structural and electronic properties of graphene, which subsequently influence its efficacy as a photocatalyst.

Cristian et al. [13] explored the liquid exfoliation of graphene in polar solvents, with an emphasis on refining the process through brief sonication durations. They successfully created over 300 graphene dispersions, determining that exfoliation is most efficient in dimethylformamide, yielding graphene with fewer than ten layers. The study investigated the effects of various technical parameters, such as the type of solvent, the quantity of graphite, sonication duration, and centrifugation conditions, on the exfoliation process. They observed that edge-type defects are more significant when graphene is exfoliated in ethanol, while TEM analysis showed well-exfoliated graphene nanosheets in DMF, which were influenced by the centrifugation speed. Computational investigations revealed that the arrangement of solvent molecules and the number of graphene layers affect the final adsorption energy, offering valuable insights for optimizing graphene production in polar solvents.

Anastasia et al. [79] investigated the exfoliation of few-layer graphene in distilled water to identify critical parameters that influence the yield and quality of graphene flakes. Their findings revealed that an increase in input power during the sonication process significantly boosts the yield of FLGF flakes. Furthermore, the generation of smaller cavitation bubbles during exfoliation leads to improved quality with reduced defects. The application of high-frequency ultrasound, particularly in the MHz range, resulted in the production of thinner and superior-quality FLGF flakes. The research

underscores the benefits of using pure water as a solvent, which streamlines the exfoliation process in contrast to conventional methods that often rely on toxic and expensive solvents.

Sara et al. [80] investigated exfoliation technique to generate few-layer graphene from natural flake graphite. This innovative method utilizes an environmentally benign aqueous solution with sodium cholate serving as a surfactant. Remarkably, they achieved high graphene concentrations of up to 3 mg.ml⁻¹ and yields of 3% within a mere 2 h of shear exfoliation. The researchers discovered that conducting the exfoliation at a reduced temperature of 10 °C significantly enhanced the concentration of graphene. They noted that while larger graphite flakes contributed to the lateral dimensions of the resulting graphene sheets, the overall yield and concentration remained unaffected by the size of the flakes. Furthermore, the graphene films produced demonstrated impressive conductivity levels without the need for annealing, and the removal of excess surfactant through dialysis further increased conductivity by approximately 40%. This method presents a scalable and effective strategy for producing high-quality few-layer graphene suitable for a range of applications.

Justin et al. [81] conducted a study on ultrasonic-assisted liquid phase exfoliation of graphite, aiming to optimize the production of few-layer graphene with the use of eco-friendly solvents. They assessed four solvents, which included three environmentally sustainable choices (water, ethanol, and a water/ethanol mixture) and N-Methyl-2-pyrrolidone as a benchmark. Their findings revealed that the water/ethanol mixture produced twice the amount of high-quality few-layer graphene (3–5 layers) in comparison to pure water, with an average flake area of approximately 1.15 μm² and a stability of about 78% over six months.

Producing Graphene oxide by plastic pyrolysis: Pandey et al. [82] undertook research focused on the plastic waste pyrolysis into graphene and their utilization in dye-sensitized solar cells and supercapacitors. The researchers employed a two-step pyrolysis process at temperatures of 450 °C and 945 °C, utilizing bentonite nanoclay to degrade waste plastics in an inert N₂ atmosphere. This study demonstrates the application of graphene in enhanced oil recovery, achieving substantial improvements in surface tension reduction (~57%), contact angle alteration (up to ~83%), and oil recovery efficiency (~71% of the original oil in place) through its synergistic interactions with surfactants and polymers.

Eslam et al. [83] employed a catalytic pyrolysis technique to synthesize graphene from waste plastic. Initially, they produced a catalyst by combining $\text{FeClAl}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and citric acid in equal molar proportions. This combination was stirred at a temperature of 120°C until it transformed into a viscous gel, which was subsequently dried at 90°C overnight. The resulting dried gel was calcined at 350°C for 3 h and then ground into a fine powder. Following this, 5 g of the catalyst was mixed with 10 g of shredded PET sourced from plastic cups and placed into a stainless-steel reactor. Then the reactor was heated to 800°C for 2 h under a nitrogen atmosphere. This study presents a sustainable and economical method for upcycling residential plastic waste (PET and PP) into high-value carbon materials such as graphene, carbon spheres, and carbon nanotubes via catalytic pyrolysis, with characterization confirming their high carbon content, graphitic structure, and suitability for environmental remediation applications.

Chetna et al. [82] produced graphene from waste plastic through a two-step pyrolysis technique. Initially, 15 kg of waste plastic was gathered, shredded, cleaned with a soap solution to eliminate contaminants, and subsequently dried for 30 min. A degradation catalyst, bentonite nanoclay, was incorporated into the plastic. During the first pyrolysis stage, the mixture was heated to 400°C for 50 min at a rate of $8^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. This phase facilitated the separation of petroleum products, resulting in a carbon residue. Then the resultant was ground into a fine powder. In the second stage, this powder underwent additional pyrolysis at 800°C for 80 min at a rate of $10^\circ\text{C}/\text{min}$. The final product, characterized by its shiny black appearance, was washed with 5% HCl followed by distilled water to eliminate impurities.

Kuldeep et al. [84] developed a method for synthesizing materials from plastic waste using copper as a catalyst. The precursor materials used were 5 g each of polypropylene and polyethylene. The plastic waste was first cut into small parts, cleaned with soap and water, and subsequently dried at ambient temperature. The dried plastic was then combined with 0.5 g of copper turnings and placed in a horizontal tube furnace. The mixture was heated to a temperature of 850°C at a rate of $10^\circ\text{C}/\text{min}$ over 85 min. Following the cooling phase, the copper turnings were mechanically separated, and the resulting graphene nanosheets were subjected to ball milling. This study demonstrating excellent thermoelectric performance in graphene/polypyrrole nanocomposites with a Seebeck coefficient indicating p-type semiconductor behaviour and a figure of merit (ZT) of 3.75×10^{-6} , making it promising for thermal energy conversion applications.

Kevin et al. [85] produced graphene sheets from waste plastics by initially shredding, washing, and drying around 35 kg of collected plastic waste. The purified plastic flakes were combined with bentonite nanoclay in a ratio of 100:3 to improve the pyrolysis process. This combination was subjected to a two-step pyrolysis procedure: the first step occurred at 400 °C to eliminate oils and waxes, followed by a second step at 800 °C to generate a black carbon residue. Subsequently, this residue was treated with 5% HCl and rinsed with distilled water, leading to the formation of graphene sheets.

Hydrolysis of NaBH_4 for hydrogen production: Nie et al. [86] extensively investigated Ni–Fe–B catalysts aimed at hydrogen production through the hydrolysis of NaBH_4 . The catalyst containing 30% Fe demonstrated the highest catalytic performance among the various ratios examined. Furthermore, they identified that the optimal temperature for the reduction process was 75 °C. In their analysis of the reaction parameters, the researchers observed that the hydrogen generation rate increased with elevated NaBH_4 and NaOH concentrations. However, it began to decline after reaching a certain optimal concentration. The activation energy for the hydrolysis reaction was obtained to be 57 $\text{kJ}\cdot\text{mol}^{-1}$. The peak hydrogen generation rate recorded was 2910 $\text{mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$ at 25 °C.

Yuanyu et al. [87] investigated the effects of various metal dopants on the structure and catalytic activity of CoB-based catalysts for hydrogen production via NaBH_4 hydrolysis. Using a chemical reduction method, they prepared four ternary alloy catalysts, including Co–Sn–B, Co–Mn–B, Co–Cr–B, and Co–Bi–B. The study systematically compared the catalytic activity of these doped catalysts and explored how the dopants influenced phase structure, surface morphologies, electronic interaction, and activation energies. Among the dopants, Cr and Bi showed a more pronounced promoting effect on the CoB catalyst, significantly enhancing the hydrogen generation rate. In contrast, the inclusion of Sn and Mn led to only slight improvements in hydrogen production. The research also adjusted the doping concentration of these metals to optimize the phase structure and catalytic performance, demonstrating that each dopant has an optimum concentration for maximum catalytic efficiency.

Jinlin et al. [88] investigated the use of acetic acid to promote hydrogen production from the hydrolysis of NaBH_4 . Their study highlights acetic acid as a cost-effective and environmentally friendly alternative to complex catalysts typically used in this process. The researchers found that adding an appropriate amount of acetic acid to NaBH_4

solutions stabilized with sodium hydroxide significantly accelerated the hydrolysis reaction, leading to rapid hydrogen generation.

Shuqing et al. [89] successfully developed a highly effective and reusable catalyst for hydrogen production via the hydrolysis of NaBH_4 by fabricating Ru particles on $\text{Co}_3\text{B-CoP}$ heterostructures. The catalyst was created through a three-step methodology that included chemical reduction and gas-phase phosphating treatment, which resulted in robust electronic interactions and a wealth of heterojunctions between the $\text{Co}_3\text{B-CoP}$ substrate and the Ru particles. The optimal catalyst formulation, $\text{Ru/Co}_3\text{B-CoP}$, exhibited an outstanding HGR of $8875.8 \text{ mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ and a turnover frequency of 636 min^{-1} at 25°C , surpassing many previously documented catalysts. This remarkable performance can be attributed to a low activation energy of $47.6 \text{ kJ} \cdot \text{mol}^{-1}$ and the synergistic interactions between the $\text{Co}_3\text{B-CoP}$ substrate and Ru particles.

Orhan et al. [90] synthesized NiO nanoparticles using watermelon seed shell extract as a reducing agent, following a sustainable green synthesis methodology. These NiO nanoparticles were employed for the first time as a photocatalyst in the reduction of methylene blue and as a catalyst for hydrogen generation from the hydrolysis of NaBH_4 . The photocatalytic reduction of methylene blue achieved a 98% reduction in 13 min, while no colour change was detected without the catalyst over 24 h. The kinetics of the reduction were studied using a pseudo-first-order model, resulting in a rate constant of 0.382 min^{-1} . Additionally, the NiO nanoparticles demonstrated a significant hydrogen production rate of $660 \text{ mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ from NaBH_4 hydrolysis at 70°C , with an E_a of $39.8 \text{ kJ} \cdot \text{mol}^{-1}$ and a reaction order of 0.59.

Faezeh et al. [91] developed a bimetallic Co–Fe nanocatalyst supported on carbon quantum dots to improve hydrogen production from the hydrolysis of NaBH_4 . The synthesis of the Co–Fe/CQD catalysts was accomplished through a hydrothermal method. Among the catalysts evaluated, the CoFe/CQD containing 5 wt% iron exhibited the highest HGR of $20200 \text{ mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. The activation energy required for hydrogen generation was found to be $48 \text{ kJ} \cdot \text{mol}^{-1}$.

Zhou et al. [89] developed a CoP-Ru nanocatalyst to enhance the hydrolysis of NaBH_4 for hydrogen generation. The Ru/CoP catalyst exhibited a high HGR of $9783.3 \text{ mL} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$ at 25°C , with an activation energy of $45.3 \text{ kJ} \cdot \text{mol}^{-1}$. The catalyst also demonstrated good durability, with only a 14% performance reduction after five recycling cycles. The superior performance was attributed to the synergistic effect of Ru clusters

and P vacancies, which increased the active surface area and exposed more active sites for catalysis.

Feiyan et al. [92] focused on the nanoflower-like Ru/CoAl catalyst synthesis to enhance hydrogen generation from the hydrolysis of NaBH₄. The catalyst was synthesized by anchoring ruthenium nanoparticles onto CoAl through a solvothermal method, followed by hydrogen reduction. Characterization techniques such as SEM, TEM, XRD, and XPS were used to elucidate the structural properties of the catalyst. The Ru/CoAl catalyst achieved a remarkable hydrogen generation rate of 44.34 L.min⁻¹.g⁻¹ at 30 °C with an activation energy of 38.83 kJ.mol⁻¹ outperforming numerous similar catalysts. Given its low Ru content of 0.22 wt%, along with its high catalytic activity and low activation energy, the Ru/CoAl catalyst is both economically viable and highly effective for NaBH₄ hydrolysis.

Komal et al. [93] successfully synthesized a tri-metallic FeCuCo catalyst featuring a nano-foam structure through a single-step solution combustion synthesis method to enhancing hydrogen production via the NaBH₄ hydrolysis. This catalyst, formulated with Fe, Cu, and Co in a weight ratio of 50:37.5:12.5, achieved a remarkable hydrogen generation rate of 1380 mL.min⁻¹.g⁻¹ and exhibited a high turnover frequency of 62.02 mol. g⁻¹. min⁻¹. The study also examined critical parameters such as catalyst loading, NaOH concentration, and temperature to enhance performance. Notably, the catalyst demonstrated excellent recyclability, retaining its efficiency across eight cycles.

Megersa et al. [94] developed a hybrid film catalyst composed of Ru and graphene, supported on thermal release tape to facilitate efficient hydrogen generation through the hydrolysis of NaBH₄. This configuration significantly enhanced catalytic performance and demonstrated stability after several uses. Surface analysis via X-ray photoelectron spectroscopy confirmed the presence of metallic Ru, indicating the hybrid film's robustness and efficiency in repeated catalytic cycles.

Altaf et al. [95] developed catalysts based on RuPt/TiO₂ nanoparticles to enhance the hydrolysis of NaBH₄. The research achieved a remarkable hydrogen generation efficiency of up to 95%. The Ru/TiO₂ catalyst demonstrated E_a of 62 kJ. mol⁻¹ in aqueous solutions and 64.65 kJ. mol⁻¹ in alkaline solutions. Conversely, the Pt/TiO₂ catalyst revealed a decrease in activation energy from 60.5 to 53.2 kJ. mol⁻¹ when the medium was changed from aqueous to alkaline. Varying the NaOH concentration between 0.5 M and 2 M had different effects on the hydrogen generation rates of the two catalysts. For

Ru/TiO₂, the hydrogen generation rate decreased with increasing NaOH concentration, while for Pt/TiO₂, it increased, highlighting their distinct catalytic behaviours under alkaline conditions.

Electrochemical hydrogen storage: Andrews et al. [51] examined the increasing viability of electrochemical hydrogen storage using porous carbon materials as an economical approach for hydrogen storage and transportation. It emphasizes the benefits of employing porous conductive carbon-based electrodes, especially in systems using acidic electrolytes, in contrast to those that use alkaline electrolytes. The research also explores advancements such as proton batteries designed for small-scale energy storage and proton flow reactor systems intended for larger grid-scale applications. These technologies, which depend on electrochemical hydrogen storage, are proposed as significant contributors to the shift towards a zero-emission global economy.

Mahsa et al. [97] focused on synthesizing and characterizing a CeVO₄/GFO nanocomposite to enhance electrochemical hydrogen storage efficiency. Characterization through SEM revealed rod-like CeVO₄ nanoparticles dispersed on graphene plates. Hydrogen storage capacity reached approximately 5430 mAh.g⁻¹, surpassing that of other nanostructures used in these applications.

Shaterian et al. [98] examined the synthesis and characterization of a BaFe/MWCNT to enhance electrochemical hydrogen storage capabilities. The BaFe/MWCNT nanocomposite was synthesized using a sol-gel combustion method. The findings revealed that the nanocomposite achieved a notable hydrogen storage capacity, with a discharge capacity of approximately 360 mAh.g⁻¹ in the first cycle, which increased to about 3600 mAh.g⁻¹ after 20 cycles under optimal conditions.

Sahar et al. [99] introduced a novel environmentally sustainable technique for the synthesis of Nd₂Sn₂O₇ nanostructures, utilizing date palm extract as a green fuel. Moreover, they conducted an initial assessment of the electrochemical hydrogen storage performance of Nd₂Sn₂O₇ in an alkaline medium, reporting a significant discharge capacity of approximately 4013 mA h/g after 20 cycles, which equates to a hydrogen storage efficiency of 14.2 wt% at room temperature.

Jianing Xu et al. [100] explored the effects of Co-2D-BP to enhance their electrochemical hydrogen storage performance. The study demonstrated that Co doping markedly reduced the band gap, thereby increasing its conductivity. The Co-2D-BP achieved a notable maximum discharge capacity of 6200 mAh.g⁻¹, which translates to a

hydrogen storage capacity of 18 wt%. Moreover, Co-2D-BP and 2D-BP exhibited high charge-discharge efficiencies, exceeding 90%. These improvements indicate the considerable potential of Co-doped 2D-BP for electrochemical hydrogen storage applications.

Maryam et al. [101] employed a solution combustion method to synthesize $\text{CoCe}_2(\text{MoO}_4)_4$, concentrating on their electrochemical properties for hydrogen storage. The findings indicated that the selection of reductants and the synthesis temperature were pivotal in obtaining pure nanocrystals, which displayed a well-defined truncated octahedron morphology with an edge size of approximately 45 nm. These structural attributes significantly contributed to the material's hydrogen storage capabilities, achieving a maximum discharge capacity of around 4750 mAh.g^{-1} in an alkaline medium. Furthermore, the redox species enhanced hydrogen discharge performance, highlighting the potential of $\text{CoCe}_2(\text{MoO}_4)_4$ for efficient hydrogen storage applications.

The investigation led by Zhao et al. [102] focused on the influence of flower-like Ni/C nanocrystals on the electrochemical hydrogen storage performance of Co-P alloy. The synthesis of Ni/C nanocrystals was achieved through a solvothermal technique, while the Co-P alloy was fabricated using mechanical alloying. By blending various proportions of Ni/C nanocrystals with the Co-P alloy, they developed Co-P + Ni/C composites. These composites revealed improved discharge capacity and cyclic stability relative to the original Co-P alloy. Specifically, the Co-P + Ni/C composite with 5% Ni/C nanocrystals attained a maximum discharge capacity of 635.8 mAh.g^{-1} and maintained a capacity retention rate of 66.3% after 50 cycles. The unique structural and electrocatalytic features of the Ni/C nanocrystals contributed to the enhanced electrochemical properties of the Co-P alloy, presenting a viable strategy for advancing hydrogen storage capabilities.

Makarim et al. [103] synthesized $\text{Lu}_2\text{CrMnO}_6$ (LCMO) double perovskite nanostructures employing a sustainable sol-gel technique that utilizes beetroot juice as a fuel. Their research revealed that the LCMO-10 sample, which contained 10 ml of beetroot juice, exhibited remarkable hydrogen storage capacity and stability. The LCMO-10 achieved a capacity of 275 mAh.g^{-1} in the first cycle, which increased to 570 mAh.g^{-1} by the fifteenth cycle. This study emphasized the potential of LCMO-10 as an efficient electrode material for hydrogen storage applications, owing to its unique morphology and a high active sites density.

Salahaddin et al. [104] developed LiCoO₂ nanoparticles using a sustainable method that incorporates Aloe vera leaf extract. They conducted a detailed characterization of the nanoparticles' structure and morphology, discovering an optical band gap of around 1.7 eV along with mesoporous features. Notably, LiCoO₂ nanoparticles achieved a remarkable hydrogen storage capacity of 4858 mAh.g⁻¹ after 11 cycles, evaluated in alkaline conditions through the chronopotentiometry technique. This investigation emphasizes the significant potential of eco-friendly synthesized LiCoO₂ nanoparticles for efficient hydrogen storage, thereby supporting the pursuit of sustainable energy alternatives.

Guang et al. [105] focused on the impact of ball milling on the structural and electrochemical hydrogen storage properties of a Mg-Ni alloy. They prepared an as-cast LaMgNiCo superlattice alloy and subsequently created composite hydrogen storage alloys by adding 10 wt% Ni and applying ball milling techniques. The characterization results demonstrated that extended ball milling time induced significant changes in microstructural characteristics, such as variations in phase abundance, grain refinement, reduced particle size, and an increase in the amorphous phase. In addition to improving cycle stability, these structural modifications had a significant impact on electrochemical performance, lowering discharge capacity from 264.0 mAh.g⁻¹ to 219.1 mAh.g⁻¹.

The improved Hummers' method, LPE, and plastic pyrolysis offer significant advantages over traditional graphene synthesis methods. The improved Hummers' method enhances graphene oxide (GFO) quality and achieves higher yields with scalability for industrial applications. LPE stands out for its simplicity, cost-effectiveness, and non-chemical approach, preserving graphene's pristine structure while enabling scalable and energy-efficient production. Plastic pyrolysis uniquely combines sustainability and cost-effectiveness by converting waste plastics into high-quality graphene, reducing environmental pollution and reliance on expensive carbon sources. Compared to methods like chemical vapor deposition (CVD), arc discharge, or mechanical exfoliation, these approaches are more resource-efficient, scalable, and versatile, providing a practical path for large-scale graphene production with minimized environmental and economic costs.

3. MATERIAL AND METHODS

In this section, chemicals, equipment and methods used in the experimental studies are given in detail.

3.1. Chemicals and Equipment

A detailed list of the chemical materials used in this investigation is provided in Table 3.1.

Table 3.1. List of chemical materials used in the experiments

Name	Chemical Formula	Brand	Purity (%)	Usage
Nickel (II) nitrate hexahydrate	Ni (NO ₃) ₂ .6H ₂ O	Merck	99.9	Synthesis
Cobalt (II) nitrate hexahydrate	Co (NO ₃) ₂ .6H ₂ O	Merck	99.9	Synthesis
Graphite	----	Merck	99.9	Synthesis
Potassium permanganate	KMnO ₄	Merck	----	Synthesis
Hydrochloric acid	HCl	Sigma-Aldrich	37	Synthesis
Sulfuric acid	H ₂ SO ₄	Sigma-Aldrich	98	Synthesis
Phosphoric acid	H ₃ PO ₄	Sigma-Aldrich	85	Synthesis
Hydrogen peroxide solution	H ₂ O ₂	Sigma-Aldrich	30-31	Synthesis
Propanol	C ₃ H ₈ O	Sigma-Aldrich	99.5	Synthesis
Nafion	-----	Ion Power	-----	Electrochemical test
Alumina suspension	-----	Ion Power	-----	Electrochemical test
Nitrogen gas	N ₂	----	99.9	Purging
Ca-Bentonite clay	-----	Madencilik, Ordu/Turkey	-----	Synthesis
Low density polyethylene (LDPE) plastic bag (unused)	-----	Commercial	-----	Synthesis

Detailed about the equipment used in the experimental studies is given in Table 3.2.

Table 3.2. Equipment used in the experiments

Name	Brand	Usage
Ultrasonic Bath	Sonerex Digital 10 P	Sonication

Table 3.2. (Continued) *Equipment used in the experiments*

Name	Brand	Usage
Ultrasonic Bath	BANDELIN SONOREX	Sonication
Centrifuge	Hermle Z 306	Separation
Stirrer	Stuart	Stirring
Stirrer	Heidolph MR3001 K	Stirring
Raman spectrometer	Renishaw inVia Raman microscope	Raman Analysis
CHNS/O	PerkinElmer Series II CHNS/O Analyzer	Elemental analysis
TGA	Perkin Elmer STA6000	TGA Analysis
FT-IR	Thermo Science Nicolet IS10	FT-IR Analysis
BET	Micromeritics ASAP 2020	BET Analysis
FE-SEM	ZEISS-SUPRA 50 VP	FE-SEM Analysis
XRD	Rigaku Mini Flex 6000	XRD Analysis
TEM	Hitachi HT7800	TEM Analysis
UV-Vis	UV-2600 Spectrophotometer Shimadzu	UV-Vis Analysis
Muffle Furnace	Nabertherm	Cleaning TGA pans
Gamry Instruments	Reference600/potentiostat/galvanostat/ZRA	Electrochemical Test
Glassy carbon (3 mm)	Ionde	Working Electrode
Silver/Silver Chloride	Ionde	Reference Electrode
Platinum (6 mm)	Ionde	Counter Electrode

3.2. Production Methods

In this section, the chemicals, equipment and methods used in the experimental studies are given in detail.

Graphite and plastic bags are used as two different raw materials in the production of graphene-based materials. The reason for using unused plastic bags is to provide a reference for the evaluation of used plastic bag waste in future studies.

3.2.1. Production of graphene (GF) from graphite by liquid phase exfoliation (LPE)

LPE method was used in the synthesis of GF from graphite. Graphite layer exfoliation was done by breaking its bond by applying ultrasonic force. First, 3 mg of pure graphite was added to 1 mL of isopropyl alcohol. After that, the sample was sonicated under a frequency of 35 kHz and a power of 100 W for 90 min, centrifuged (500 rpm for 45 min) to separate graphene from the solvent, and dried at 105 °C to obtain GF [106], as illustrated in Figure 3.1.

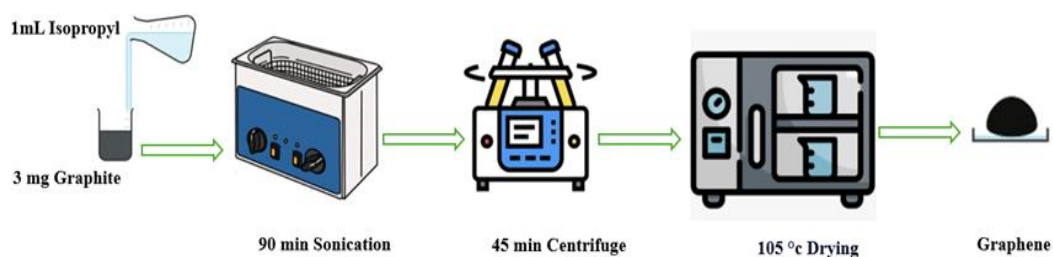


Figure 3.1. Production of Graphene (GF) from Graphite by LPE Method

3.2.2. Production of graphite oxide (GO) from graphite

The improved Hummers method is a prevalent technique for synthesizing GO through the oxidation of graphite, which incorporates oxygen functional groups. The process initiates with the dispersion of 3 g of graphite in a mixture of H_2SO_4 and H_3PO_4 in a ratio of 360:40 mL, cooled in an ice bath to manage the exothermic nature of the reaction. Then, 18 g of KMnO_4 as an oxidizing agent was slowly added to the mixture to obtain a dark green color, which indicated the start of oxidation. Then the mixture was maintained at 50 °C under reflux conditions to promote uniform oxidation. To terminate the reaction, 400 mL of deionized water and 5 mL of H_2O_2 were added slowly, causing the mixture to turn yellow, which indicates that oxidation has been completed. After the oxidation process, the mixture was first treated with 1M HCl to remove the metal ion residues and then purified by washing with ethanol and deionized water. As the last step, the product was dried at 50 °C for 12 h and GO was obtained [107]. The process steps of the improved Hummers method are given in Figure 3.2.

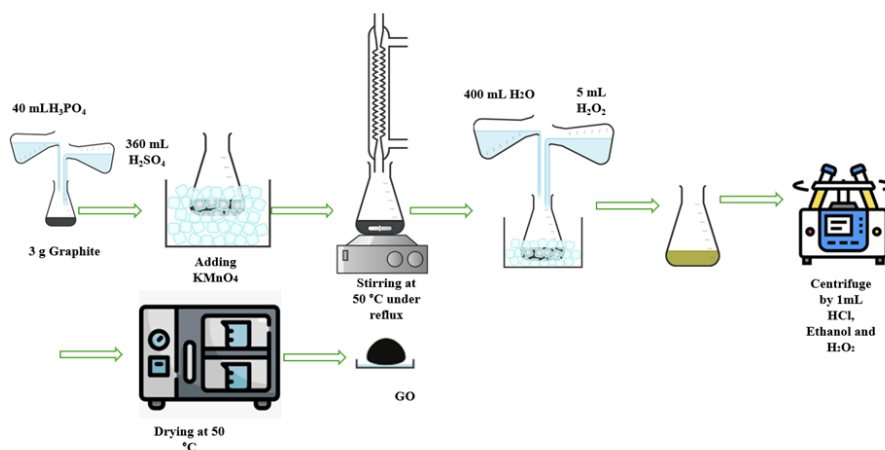


Figure 3.2. Synthesis of GO from graphite by improved Hummer's method

3.2.3. Production GFO from GO

To obtain graphene oxide (GFO) from graphite oxide (GO), GO powder was first dispersed in water at a concentration of 1 mg/mL. The prepared suspension was then ultrasonicated for 90 min. The resulting black solid, collected by filter paper dried at 105 °C overnight to obtain GFO (Figure 3.3) [107,108].

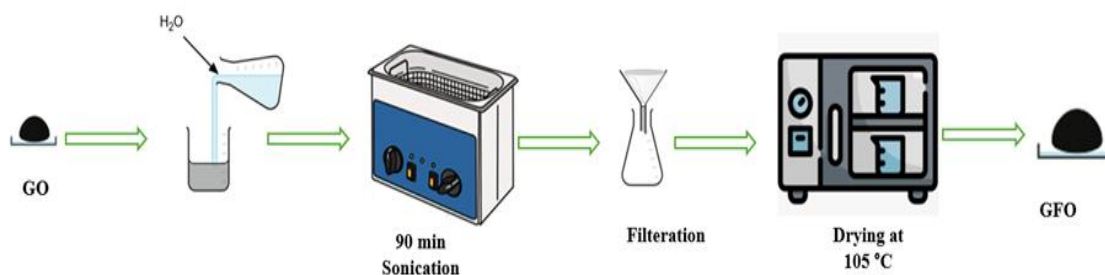


Figure 3.3. GFO production from graphite oxide (GO)

3.2.4. Production of NiCo/rGFO nanocomposite materials

To synthesize a NiCo/rGFO, GO powder was first dispersed in water at a 1 mg/mL concentration through sonication to achieve a uniform distribution. Concurrently, a solution was prepared by dissolving 0.3 g of cobalt nitrate hexahydrate, 0.3 g of nickel nitrate hexahydrate, and 0.48 g of urea in 20 mL of distilled water. This precursor solution was then added gradually in to the GO dispersion, and the resulting mixture was stirred continuously at 80 °C for 2 h to facilitate the deposition of metal salts onto the GO sheets. Next, the mixture underwent centrifugation to separate the solid product, which was then washed with ethanol and deionized water to eliminate any remaining impurities and unreacted materials. Then it was dried at 105 °C, resulting in the final NiCo/rGFO (Figure 3.4) [107]. The synthesized composite material was used as a catalyst in the hydrogen production of hydrolysis from NaBH₄ and the hydrogen storage capacity of this composite material was determined.

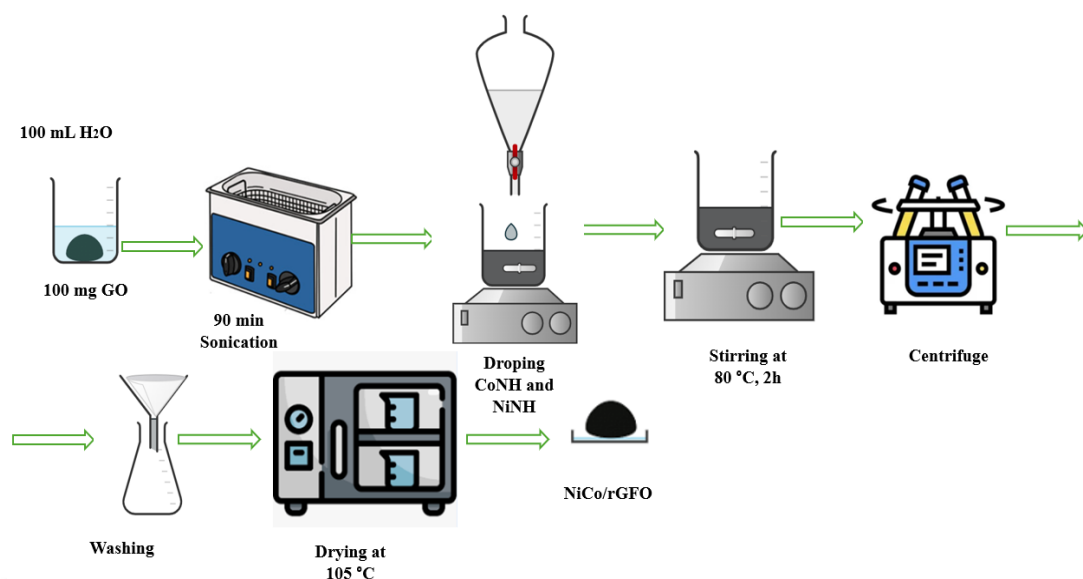


Figure 3.4. *Synthesis of NiCo/rGFO nanocomposite*

3.2.5. Production of bentonite-based catalyst

The synthesis of the bentonite-based catalyst was conducted using an impregnation method. Initially, support material (bentonite) underwent pre-calcination at 800 °C with a heating rate of 4 °C/min for 2 h in an air atmosphere to eliminate moisture and impurities. Subsequently, the predetermined quantities of nickel and cobalt precursors were dissolved in 60 mL of distilled water, and each concentrated solution was then introduced to the calcined bentonite. The mixture was stirred at a controlled temperature of 80 °C for 6 h, followed by an overnight ageing process. Then, the samples were dried in an oven at 105 °C overnight. The resulting catalyst was calcined at 900 °C for 4 h in an air atmosphere to obtain NiCo/bentonite catalyst [109]. NiCo/bentonite was synthesized in a variety of ratios, including 5:10, 0:10, 10:5, and 10:0 wt%.

Figure 3.5 displays the schematic of the synthesis method.

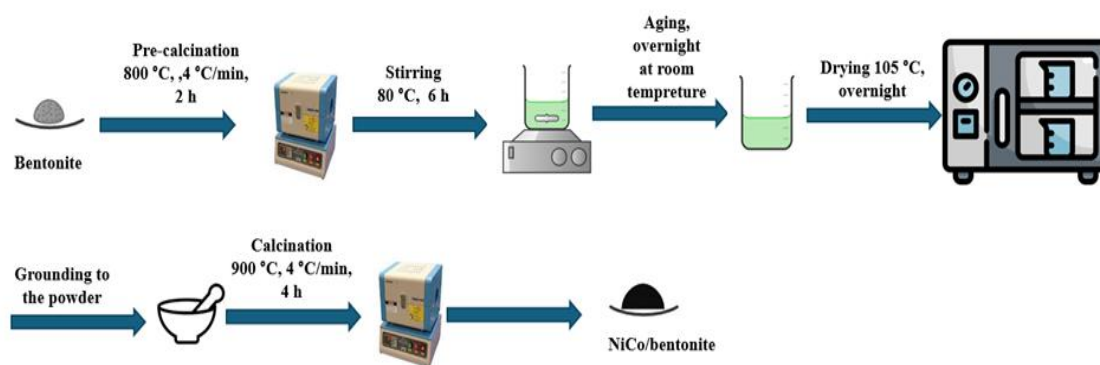


Figure 3.5. Synthesis of NiCo/bentonite catalyst

3.2.6. Production of graphene from Plastic (GFP)

The synthesis of graphene from plastic (GFP) commenced with the transformation of plastic into small flakes. These flakes were subsequently combined with different ratios of a NiCo/bentonite catalyst. The mixture then underwent an initial pyrolysis at 450 °C for 60 min, under N₂ gas flow at a rate of 4 °C/min. Following this initial phase, the resultant product was ground using a mortar and pestle to ensure uniformity. The resulting powder was then subjected to a second pyrolysis at 950 °C for 120 min under a N₂ gas flow at the same rate. After that, the product was treated with 2 M HCl for 48 h and thoroughly washed with ethanol and water multiple times until the pH level reached 7, resulting in a pure graphene sample. Finally, the sample underwent ultrasonication for 90 min [110]. Figure 3.6 shows the GFP synthesis method.

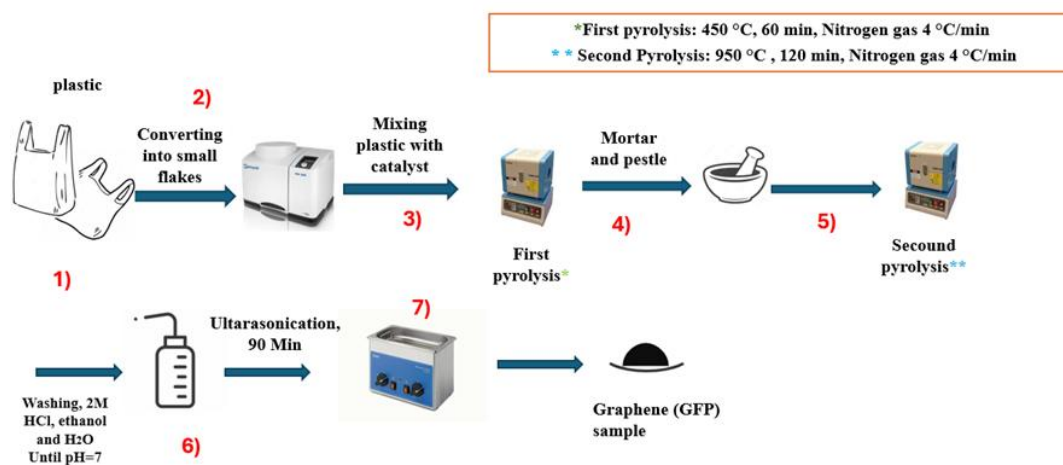


Figure 3.6. Synthesis of graphene from plastic (GFP) by two-stage catalytic pyrolysis

3.3. Characterization Methods of Graphene-based and Composite Materials

Characterizations and hydrogen storage capacities of the synthesized materials (graphite, GO, GFO, graphene-based nanocomposite (NiCo/rGFO) as a catalyst) and Ni/Bentonite catalyst using different techniques are given in this section.

3.3.1. XRD characterization

The crystal structure of the synthesized materials was determined with XRD analysis (Figure 3.7). The diffractometer was configured to 40 kV and 40 mA at $\lambda = 1.54 \text{ \AA}$, which provided enough power for high-quality diffraction patterns. Measurements were taken across a 2θ range of 2° to 80° , with a step size of 0.02° , allowing for a detailed resolution of the diffraction peaks.



Figure 3.7. XRD equipment

3.3.2. TGA characterization

TGA measurements were carried out to assess the graphene-based materials' thermal stability and decomposition behaviour, as illustrated in Figure 3.8. The analysis was conducted over a 30-850 $^\circ\text{C}$ temperature range under a nitrogen atmosphere, with a flow rate of 50 mL/min. This setup ensures that the measurements are performed in an inert environment, preventing unwanted oxidation during heating.



Figure 3.8. *TGA equipment*

3.3.3. UV-Vis characterization

The optical properties of the samples, specifically their light absorption and transmission characteristics, were assessed through ultraviolet-visible (UV-Vis) absorbance spectra. These spectra were recorded over a wavelength range of 200 to 800 nm, yielding significant insights into the materials' optical behaviour. The absorbance data were collected using a UV-2600 Shimadzu spectrophotometer equipped with 1 cm cuvettes (Figure 3.9).



Figure 3.9. *UV-Vis spectroscopy equipment*

3.3.4. Elemental Analysis

The elemental composition of the samples, particularly the levels of C, N, O, and H, was investigated. This analytical device enables the precise determination of elemental content, yielding important insights into the chemical characteristics of the synthesized materials (Figure. 3.10).



Figure 3.10. CHNS/O Analyzer equipment

3.3.5. Raman spectroscopy characterization

Raman spectroscopy was employed for a comprehensive analysis of the vibrational modes present in the graphene sample. A 532 nm laser (2.33 eV) was used for excitation, with the laser power adjusted to 0.5 mW and an acquisition time of 10 s per scan. Raman spectroscopy is instrumental in providing critical information regarding the molecular structure, bonding, and defects in the material by probing its vibrational modes (Figure 3.11).



Figure 3.11. Raman spectroscopy instrument

3.3.6. FT-IR spectroscopy characterization

FT-IR spectroscopy, a technique used to identify the functional groups in a sample, was employed to analyse the synthesized materials (Figure 3.12).



Figure 3.12. *FT-IR spectroscopy instrument*

3.3.7. TEM characterization

The high-resolution imaging provided by TEM permits a thorough examination of the shape and structural attributes of materials produced at the nanoscale. The high accelerating voltage of 100 kV enhances the electron beam's penetration capability, making it particularly effective for observing fine structures in graphene-based materials, including layer thickness, particle dimensions, and the degree of exfoliation.

3.3.8. SEM characterization

High-resolution SEM at 15 kV was employed to gather morphological data of the samples (Figure 3.13).



Figure 3.13. *SEM equipment*

3.3.9. BET characterization

The assessment of surface area and pore size distribution was conducted through nitrogen adsorption-desorption (Figure 3.14), manufactured by Micromeritics Instrument Corp in the United States. Prior to analysis, the samples were dried at 103 °C overnight to remove moisture. Following this, all samples underwent a degassing process at 120 °C. Isotherms for nitrogen adsorption-desorption were generated at 77 K, covering relative pressures from 0.005 to 0.99. The specific surface areas were calculated using adsorption data within the relative pressure range of $P/P_0 = 0.04\text{--}0.3$. Additionally, the Barrett-Joyner-Halenda (BJH) method was employed to estimate pore volume and pore size distribution.

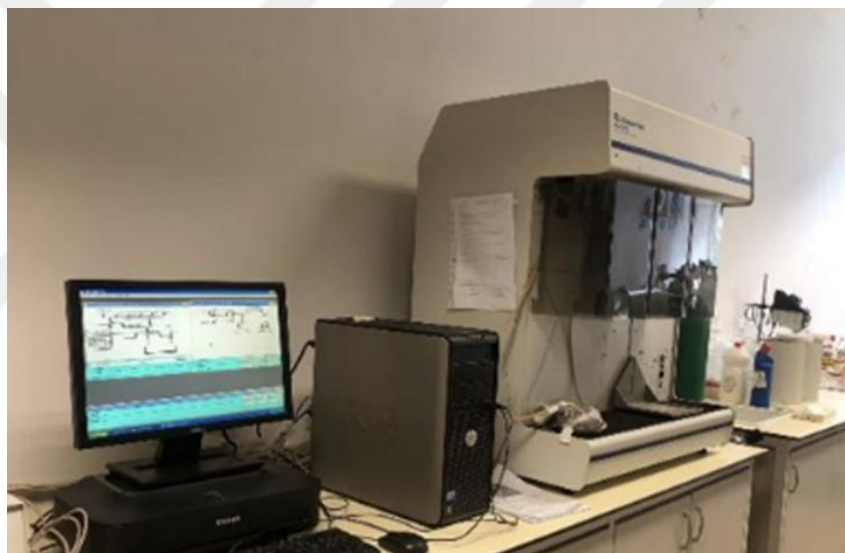


Figure 3.14. *BET equipment*

3.4. Electrochemical Characterization

In this section, the electrochemical test setup used for cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) was discussed in detail.

The experimental setup consists of a standard three-electrode electrochemical cell connected to a Gamry Reference 600 potentiostat/galvanostat for precise potential and current management, as shown in Figure 3.15.

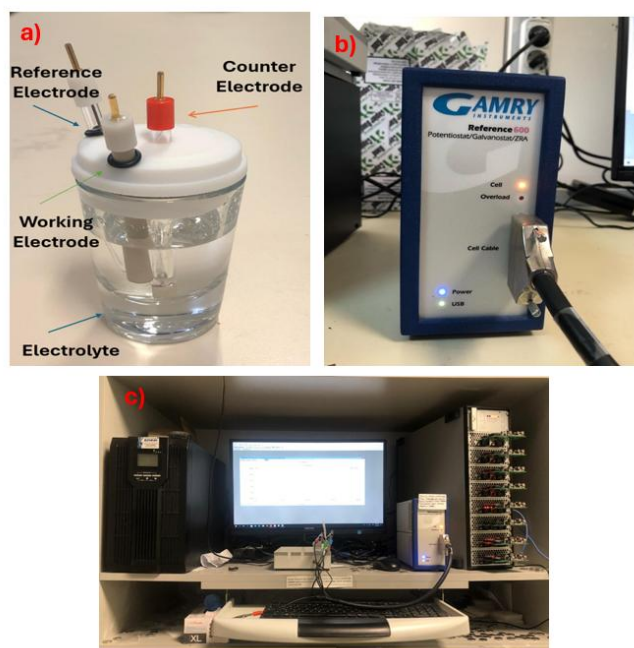


Figure 3.15. Illustration of a) three-electrode system; b) Gamry potentiostat/galvanostat/ZRA; c) set-up system (Gamry+Three -electrode system)

3.4.1. CV analysis

CV was employed to assess the synthesized graphene-based composite's electrical conductivity and ascertain its hydrogen storage capacity. The CV analysis procedure is given below step by step (Figure 3.16).

- I. Scan Limit 1 (V): Enter the first peak potential, which can be chosen relative to either the open circuit potential or the reference electrode,
- II. Scan Limit 2 (V): Enter the second peak potential in V. This is the potential at which the scan will reverse direction,
- III. Final E (V): Enter the final potential of the scan segment in V. This is the potential at which the scan will end,
- IV. Scan Rate: Enter the rate at which the potential is swept, typically in V/s. This determines how quickly the potential changes during the scan,
- V. Step Size: Enter the potential increment between data points in V. This defines the resolution of the scan,
- VI. Cycles: Enter the number of cycles to be performed. Each cycle consists of a forward and reverse scan,
- VII. I/E Range Mode: Select the current and potential range mode appropriate,

- VIII. Max Current (mA): Enter maximum current limit in mA. This prevents the current from exceeding a specified value,
- IX. IR Compensation (IR comp): Enter the value for IR compensation. This adjusts the applied potential to correct for the solution resistance, preventing voltage drop errors in electrochemical measurements,
- X. Positive Feedback Correction (PF Corr.) (ohm): Enter the value for positive feedback IR compensation, which adjusts the applied potential to correct for 80-95% of the solution resistance,
- XI. Equilibration Time (s): Enter the equilibration time in s. This is the time allowed for the system to stabilize before starting the scan,
- XII. Click OK to start the experiment.

Gamry Echem Analyst - [NP.70.G0.300.DTA]

File Tools Window Help Cyclic Voltammetry Common Tools Quick Help

Chart Experimental Setup Experimental Notes Electrode Settings Hardware Settings

Initial E (V) 0 ☒ vs. Eref ☐ vs. Egc Scan Limit 1 (V) 1.2 ☒ vs. Eref ☐ vs. Egc

Scan Limit 2 (V) -0.2 ☒ vs. Eref ☐ vs. Egc Final E (V) 0 ☒ vs. Eref ☐ vs. Egc

Date 12/27/2023

Test Identifier Cyclic Voltammetry

Time 12:54:25

Scan Rate (mV/s) 299.999

Step Size (mV) 2

Electrode Area (cm²) 1

Equil. Time (s) 5

I/E Range Mode Fixed I/E Range

Max Current (mA) 15

Conditioning ☐ Q# 15 Time(s) ☐ 0 E(V)

Init. Delay ☐ Q# 30 Time(s) ☐ 0 Stab (mV/s)

Cycles (#) 5

IRComp None

Open Circuit (V) 0

Sampling Mode Noise Reject

Figure 3.16. CV setup in Gamry instrument

3.4.1.1. Determination of hydrogen storage capacity of graphene-based material using MATLAB software

First, the heterogeneous electron transfer rate constant (k_0) value of the redox reaction that occurs during the CV analysis was calculated. Depending on this value, the hydrogen storage capacity of each material was calculated. The higher the k_0 value, the higher the hydrogen storage capacity. A high k_0 suggests that the electrode surface has strong catalytic capabilities and low resistance. This parameter defines the rate at which the redox reaction takes place under equilibrium conditions [111,112].

3.4.2. EIS analysis

EIS was used in electrochemical studies to analyse charge transfer resistance. EIS analysis steps are given below and in Figure 3.17.

- I. From the Gamry Instrument Framework, select Experiments,
- II. Choose potentiostatic EIS,
- III. Enter the name of the experiment in the output file,
- IV. The initial frequency parameter specifies the frequency of the first AC signal applied during data acquisition. Enter the frequency in Hertz. It is generally advisable to start at a high frequency and sweep down to a low frequency,
- V. The final frequency parameter specifies the frequency of the last AC signal applied during data acquisition.

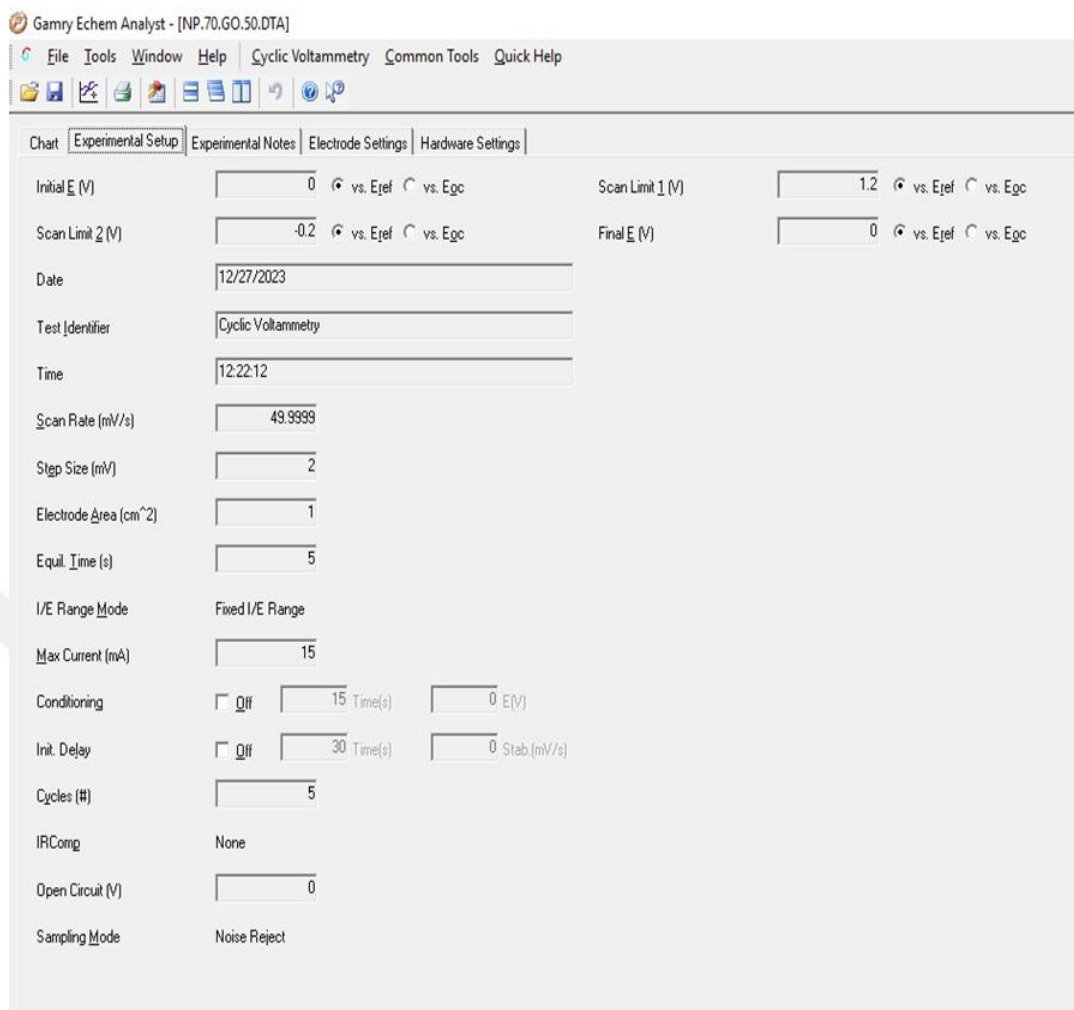


Figure 3.17. EIS- setup in Gamry instrument

3.4.3. GCD analysis

Charge-discharge curves play a critical role in the assessment of energy storage materials, as they facilitate the analysis of key parameters including specific capacity and energy efficiency. GCD (Cyclic Charge-Discharge) setup parameters are shown in Figure 3.18.

- I. From the Gamry Instrument Framework, select Experiments,
- II. Choose cyclic charge-discharge,
- III. Enter the capacity value as 0.001 A-h. This parameter defines the charge capacity of the battery or cell being tested,
- IV. Number of cycles: set the number of cycles to 10. This means the experiment will perform 10 charge-discharge cycles,

- V. Sample period: set the sample period to 0.01 s. This determines how frequently data points are collected during the experiment,
- VI. Discharge mode: set the discharge current to 0.0001 Amps. This is the constant current applied during the discharge phase,
- VII. Discharge stop 1: set the discharge stop voltage to - 0.2 V. The discharge will stop when this voltage is reached,
- VIII. Maximum charge Time: Set maximum charge time to 10 min. This limits maximum time allowed for the charging phase,
- IX. Charge Stop 1: set the charge stop voltage to 1.2 V. The charge will stop when this voltage is reached,
- X. Charge step 2: set this parameter to 0 N/A.

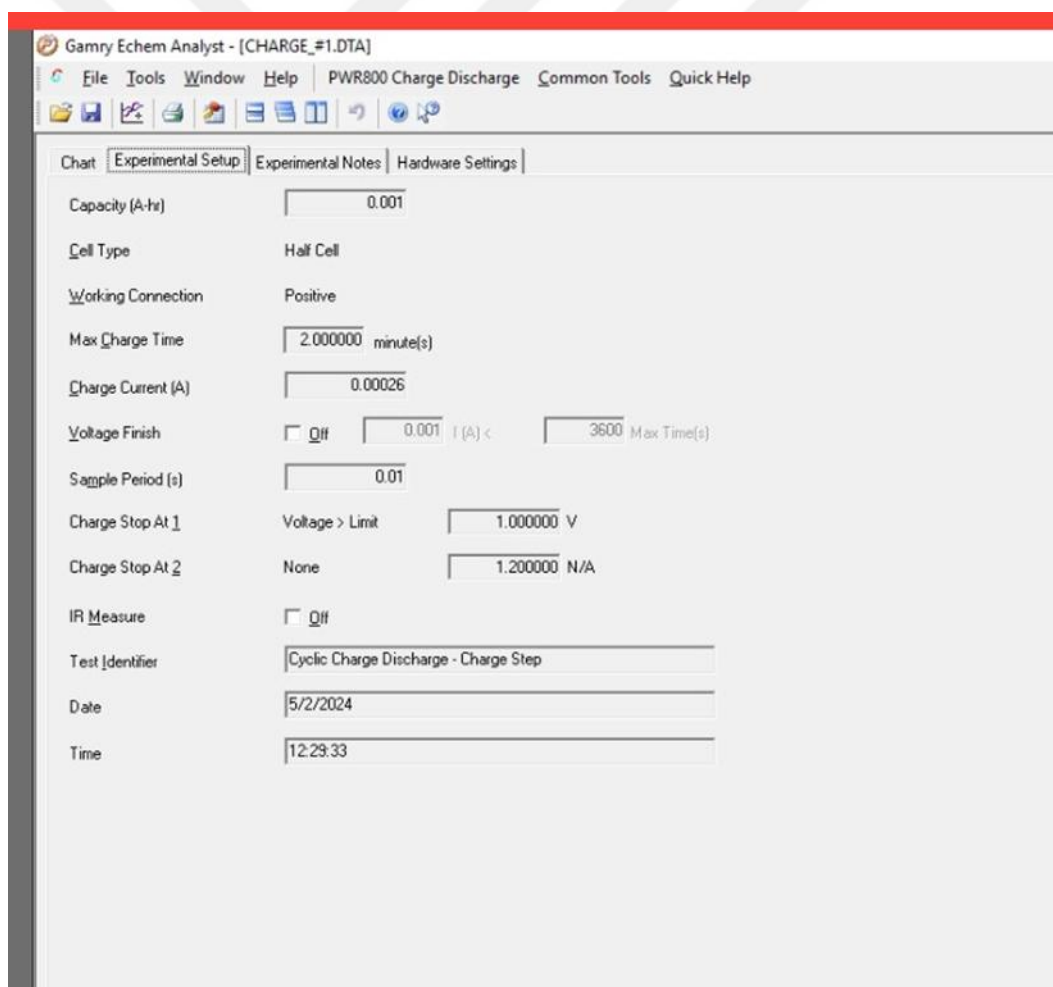


Figure 3.18. GCD setup in Gamry instrument

3.5. Hydrogen Generation Activity of NiCo/rGFO in Hydrolysis of NaBH₄

The activity of NiCo/rGFO catalysts was tested in hydrogen production by hydrolysis reaction of NaBH₄. Hydrolysis reaction was carried out in a 3-neck, 250 mL volume glass reactor. The reaction was carried out by adding NaOH, NaBH₄ solutions and NiCo/rGFO catalyst to the reactor [122, 123]. The experimental setup is shown in Figure 3.19.

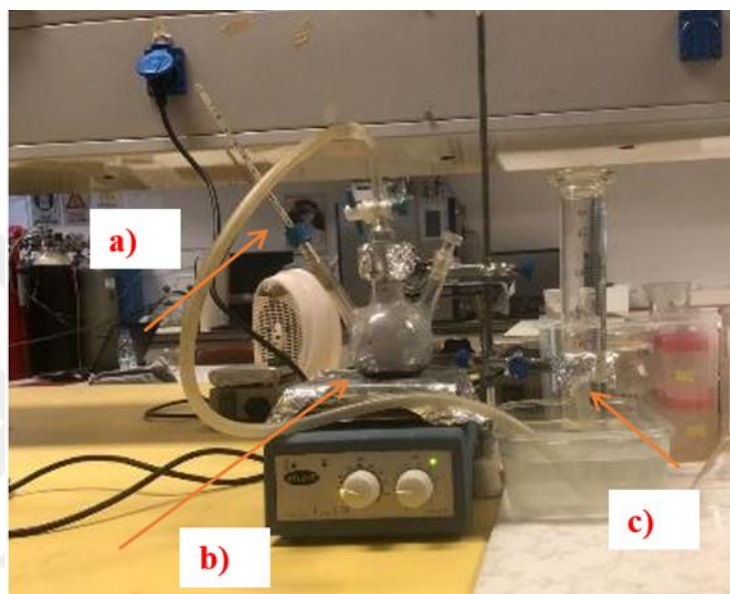
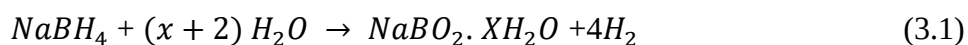


Figure 3.19. Experimental set-up of hydrolysis of NaBH₄ a) thermometer; b) reactor; c) gas measuring cylinder

NaBH₄ hydrolysis is described by the following chemical equation (Eq. 3.1):



The effects of the parameters such as temperature (30, 40, 50 and 60 °C), NaOH concentration solution (0.25, 0.5, 0.75, 1 M), and metal loading ratio (1:1, 1:2, 2:1, 2:2 NiCo) of the catalyst on the hydrogen generation rate in the hydrolysis reaction were investigated.

The theoretical hydrogen volume (L) was calculated using Eq.3.2 [113] according to the APP-4.

$$\text{Theoretical hydrogen (L)} = n_{\text{H}_2} \times \frac{22.4 \text{ L}}{1 \text{ mol}} \times \frac{298 \text{ K}}{273 \text{ K}} \quad (3.2)$$

The reaction yield was calculated by Eq. 3.3.

$$Yield (\%) = \frac{Total\ generated\ hydrogen}{Theoretical\ calculated\ hydrogen} \times 100 \quad (3.3)$$

The rate of hydrogen generation was according to Eq 3. 4.

$$HGR \left(\frac{mL}{g. min} \right) = \frac{Hydrogen\ volume}{Weight\ of\ catalyst \times time} \quad (3.4)$$

3.6. Kinetic Study of Hydrogen Generation by NiCo/rGFO in Hydrolysis of NaBH₄

The kinetics study is fundamental to comprehending hydrolysis, as it provides significant insights into the reaction mechanism. Through the analysis of reaction rates and orders, kinetic studies assist in pinpointing the rate-determining steps, thereby deepening the understanding of the mechanisms involved. For example, a zero-order reaction indicates that the reaction rate is not influenced by the concentration of NaBH₄ under certain conditions, suggesting a catalytic process controlled by surface interactions.

In the hydrolysis of NaBH₄, the concentration of NaBH₄ decreases as hydrogen gas is generated. The concentration of NaBH₄ at any given time C_A can be related to the initial concentration and the volume of hydrogen produced. This relationship is given by Eq. 3.5.

$$C_A = C_{A_0} \left(1 - \frac{V_{H_2}}{V_{H_2\ max}} \right) \quad (3.5)$$

Where:

- C_A : the concentration of NaBH₄ at time t,
- C_{A_0} : the initial concentration of NaBH₄,
- V : the volume of hydrogen produced during the reaction,
- $V_{H_2\ max}$: the theoretical maximum volume of hydrogen that can be produced from the complete hydrolysis of NaBH₄.

Reaction rates for zero-order reactions are constant and independent of reactant concentration (Eq. 3.6).

$$r_A = -\frac{dC_A}{dt} = k \quad (3.6)$$

Where:

- r_A : the reaction rate,
- $\frac{dC_A}{dt}$: the rate of change of the concentration of NaBH₄ with time,
- k : the rate constant.

In zero-order kinetics, the concentration decreases at a constant rate over time, indicating that the hydrogen production rate remains steady and does not depend on the concentration of NaBH₄.

In contrast, for first-order reactions, the reaction rate is directly proportional to the concentration of NaBH₄.

$$r_A = -\frac{dC_A}{dt} = kC_A \quad (3.7)$$

The integrated form for first-order kinetics shows that the logarithm of the concentration decreases linearly over time.

nth-order reaction rate is indicated in Eq. 3.8.

$$r_A = -\frac{dC_A}{dt} = kC_A^n \quad (3.8)$$

The integrated form of the nth-order reaction rate indicated in Eq. 3.9.

$$C_A^{1-n} = (n-1)kt + C_{A_0}^{1-n} \quad (n \neq 1) \quad (3.9)$$

This equation illustrates how the concentration of NaBH₄ varies over time based on the order n . When n is not equal to 1, the relationship between concentration and time becomes non-linear.

The influence of temperature on reaction rates is a key principle in chemical kinetics, often explained by the Arrhenius equation. This equation connects the k to temperature and the E_a , which is the minimum energy needed for the reaction to occur, which could be described in Eq. 3.10.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3.10)$$

Where A is the Arrhenius constant, k is the reaction rate constant, R is the universal gas constant (8.314 J/mol. K), T is the reaction temperature and E_a is the activation energy in terms of J/mol.

The activation energy can be calculated from the slope, as illustrated in Eq. 3.11.

$$E_a = -slope \times R \quad (3.11)$$



4. RESULTS AND CONCLUSIONS

In this section, the results obtained regarding the synthesized graphene, GO, GFO and catalysts are given.

4.1. Graphene-Based Materials Synthesis

Figure 4.1 shows the yellow liquid product obtained because of GO synthesis under reflux and the powdered graphene oxide obtained from this product.

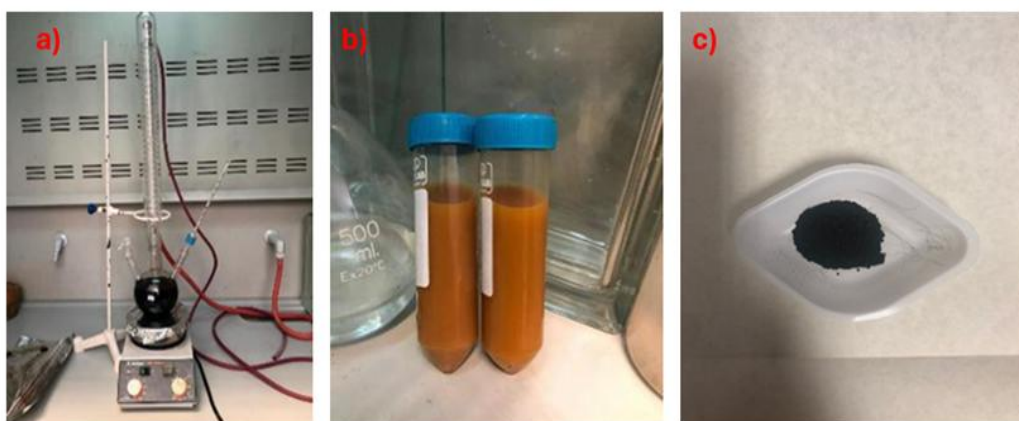


Figure 4.1. *GO synthesis under reflux, b) yellow colour of GO before washing, c) GO powder*

Figure 4.2 shows the loading of NiCo onto rGFO.

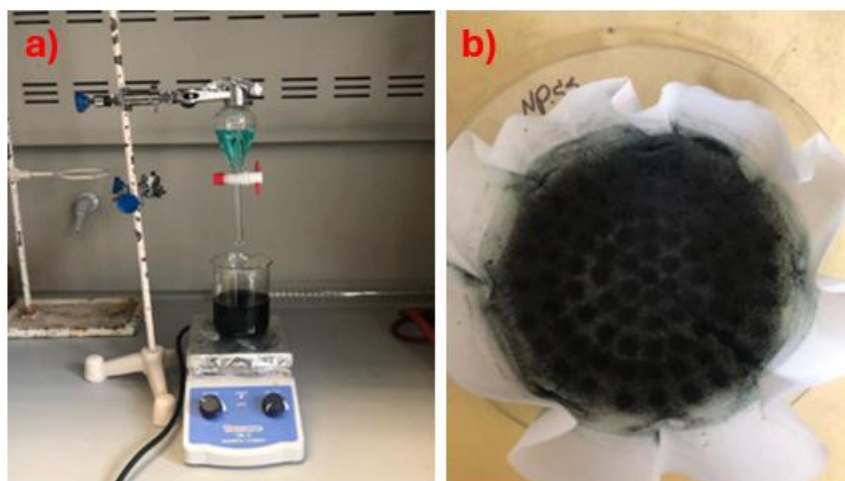


Figure 4.2. *NiCo/rGFO nanocomposite a) loading metal; b) after washing step*

Figure 4.3. shows grinded plastic raw material and synthesis steps of graphene from plastic.

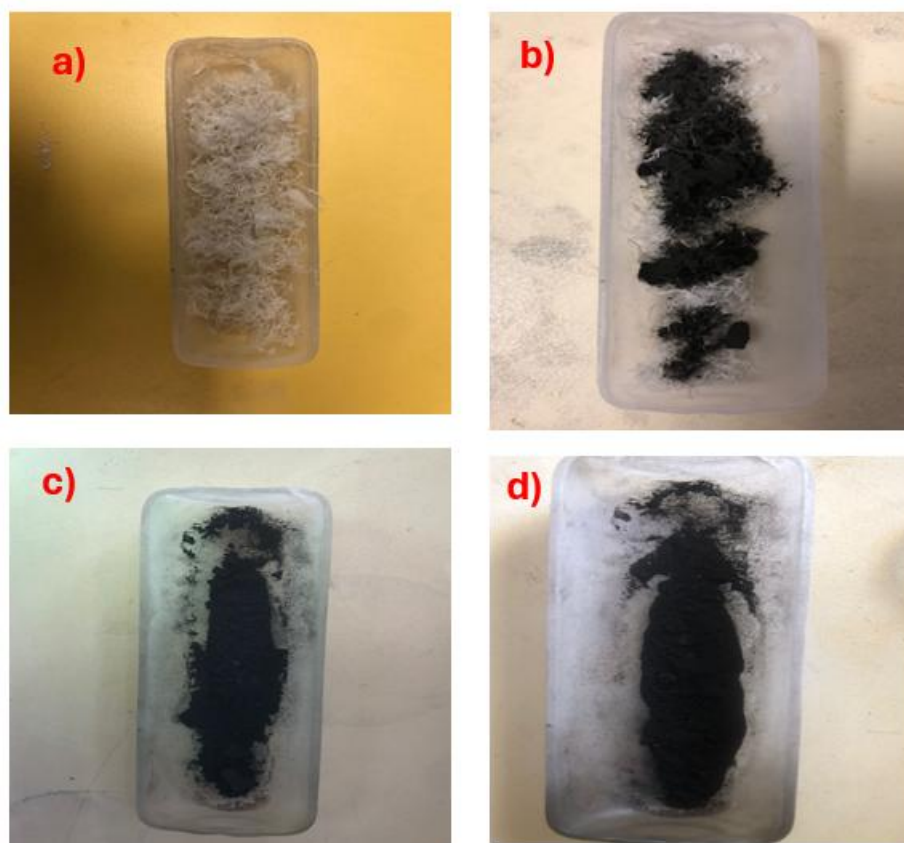


Figure 4.3. GFP synthesis steps: a) plastic; b) plastic and catalyst mixture; c) after first pyrolysis; d) After second pyrolysis

Figure 4.3. shows synthesis graphene from plastic where plastic transfer from carbon (Figure 4.3.c) to graphene material ((Figure 4.3.d).

4.2. Characterization Results of Synthesized Carbon and Composite Materials

After the successful synthesis of graphene-based materials detailed in the third section, different characterization methods and experiments were undertaken to examine their structural, morphological, and catalytic properties thoroughly. This section details the findings of these analyses, offering valuable insights into the materials' behaviour and performance. Characterization methods applied to the synthesized materials are given in detail in Table 4.1.

Table 4.1. Analyses applied to synthesized materials

Sample	XRD	FT-IR	UV-Vis	TGA	Raman	SEM	TEM	BET
Graphite	✓	✓	✓	✓	✓	✓	✓	✓

Table 4.1. (Continued) Analyses applied to synthesized materials

Sample	XRD	FT-IR	UV-Vis	TGA	Raman	SEM	TEM	BET
GF	✓	✓	✓	✓	✓	✓	✓	✓
GO	✓	✓	✓	X	✓	✓	X	X
GFO	✓	✓	✓	✓	✓	✓	✓	✓
1:1 NiCo/rGFO	✓	✓	✓	X	✓	✓	X	✓
2:1 NiCo/rGFO	✓	✓	✓	X	✓	✓	X	✓
1:2 NiCo/rGFO	✓	✓	✓	X	✓	✓	X	✓
2:2 NiCo/rGFO	✓	✓	✓	✓	✓	✓	X	✓
GFP-4	✓	✓	✓	X	✓	✓	✓	X

4.2.1. XRD results

XRD was used to analyse crystal properties and identify phases in the samples. Figure 4.4. shows the XRD results of GF and graphite.

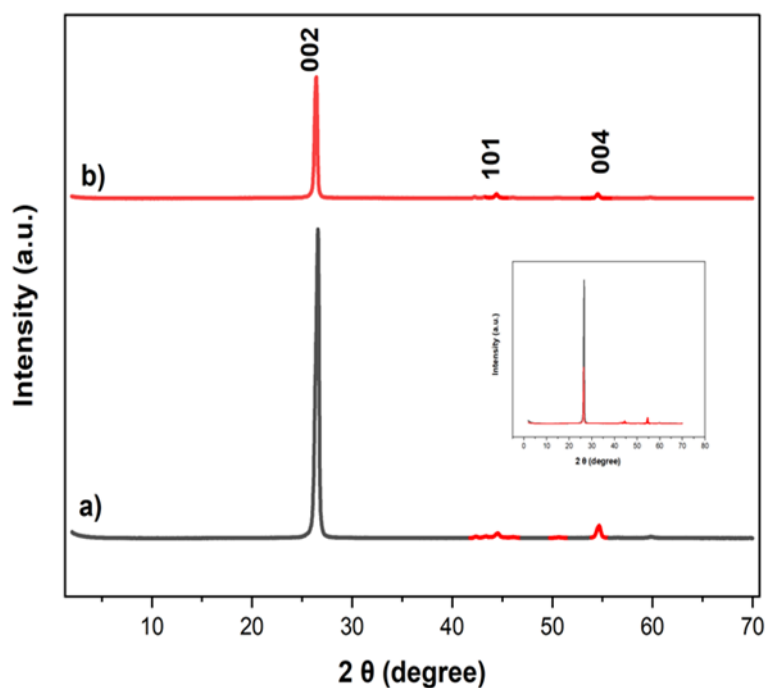


Figure 4.4. XRD characterization of a) graphite; b) GF

Figure 4.4 shows peaks that correspond to different crystallographic planes, denoted as (002), (101), and (004). Although the peak positions at 26.6° in Figure 4.1.a

and b are the same, the difference in the peak intensity suggests a weakening of the van der Waals forces between the layers of graphite, leading to the formation of MLGF. Furthermore, two smaller peaks at 44.4° and 54.3° were caused by the (101) and (004) planes.

Different literature reveals the XRD peak of graphene appears at around 26° [114–116]. Lidia et al. [117] found a significant difference between the FLGF and GF in the XRD patterns. GF's diffraction peaks were found at approximately 26.31° , indicating its characteristic structure. This comparison highlights the structural differences between FLGF and MLGF, as demonstrated by their distinct XRD patterns. The XRD peak results are consistent with findings reported in various studies [118–120], indicating that the data is reliable.

Figure 4.5 presents XRD results of a) GO; b) GFO; c) 1:1 NiCo/rGFO; d) 1:2 NiCo/rGFO; e) 2:1 NiCo/rGFO; f) 2:2 NiCo/rGFO.

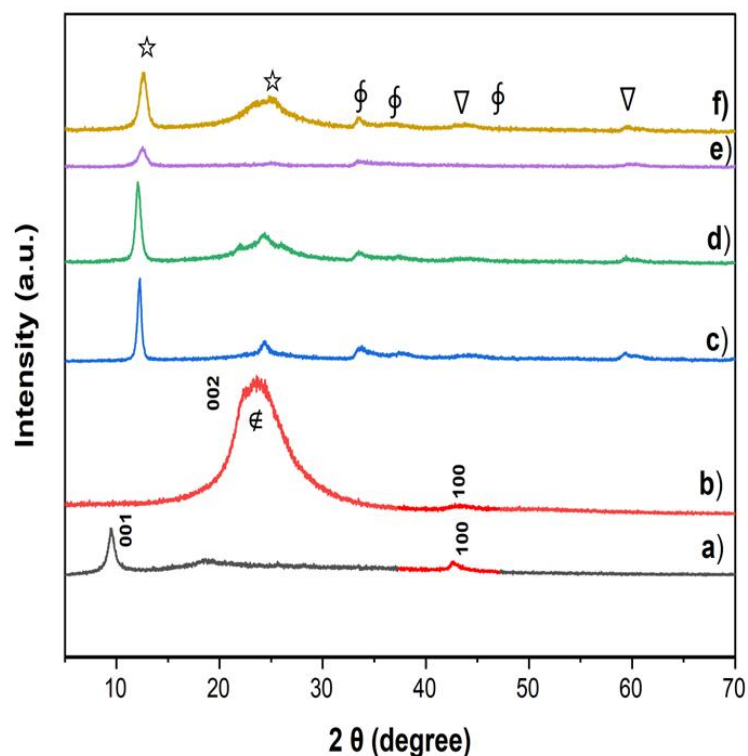


Figure 4.5. XRD characterization of a) GO; b) GFO; c) 1:1 NiCo/rGFO; d) 1:2 NiCo/rGFO; e) 2:1 NiCo/rGFO; f) 2:2 NiCo/rGFO ($\star$: NiCo_2O_4 ; ∇ : NiO ; ϕ : CoO ; ϵ : GFO)

Graphite has a strong XRD peak at $2\theta = 26.7^\circ$, corresponding to the (002) crystallographic plane and indicating a highly ordered structure. However, introducing oxygen-containing functional groups, as occurs during the oxidation process to form GO, alters the graphitic structure. The disruption shifts the characteristic peak to a lower angle of $2\theta = 10.3^\circ$, corresponding to the 001 plane, indicating increased interlayer spacing due to oxygen functionalities insertion. This shift represents a significant structural change from graphite to GO. The XRD analyses of graphite and GO align well with the existing literature [119–121].

The characteristic diffraction peaks at 2θ values of 11.0° and 21.7° allow for identifying the (003) and (006) planes in the hydrotalcite-like LDH phase. The peaks detected at 34.4° , 39.5° , 44.7° , and 59.2° are associated with Ni and Co, indicating the formation of NiCo/rGFO. The sharpness of the peaks assigned to Ni and Co increased, suggesting improved crystallinity of NiCo in the 2:2 NiCo/rGFO composite.

The current study's XRD peaks for NiCo/rGFO and GFO align well with the results reported by Shirun Yang et al. [122]. The NiCo LDH sample exhibited characteristic diffraction peaks at 2θ values of 11.0° , 21.7° , 33.2° , 34.2° , 38.5° , 44.7° , and 59.8° .

Additionally, the XRD results agree with the findings reported by Rashid et al. who synthesized NiCo/rGFO as an electrocatalyst for water splitting. XRD analysis revealed diffraction peaks at approximately 20° , 29.8° , 37.2° , 42° , 44.3° , 47.2° , and 49.5° , corresponding to various crystallographic planes of NiCo metal [123].

The XRD patterns of bentonite, 10% Ni/bentonite, 10% Co/bentonite, 10-5% NiCo/bentonite and 5-10% NiCo/bentonite are shown in Figure 4.6.

In Figure 4.6, the main peaks correspond to the characteristic peaks of montmorillonite, which are observed around 6.35° , 20° , 27.3° , 35° , 57° , and 63.4° . Moreover, kaolinite and SiO_2 peaks are also detected at 12.5° , 26.6° , and 50.1° , respectively. Significant transformations are observed in the XRD patterns of NiCo/bentonite as the Ni and Co content increases. Concurrently, peaks corresponding to NiO and CoO phases become more prominent with increasing metal content. In the 5% Co/bentonite, new peaks appear at 37.2° 2θ (CoO (104)) and 37.4° (CoO (200)). NiCo/bentonite pattern shows strong NiO and CoO peaks, particularly at 2θ ; 28.7° (NiO (111)), 32.4° (CoO (104), 62.9° (NiO (220)), and 74.5° (NiO (311)), indicating a considerable increase in crystallinity and concentration of metal oxide. XRD findings are

in good agreement with the XRD results obtained by Yuexiu et al. [121], Abdullah et al. [122], and Salam et al. [123].

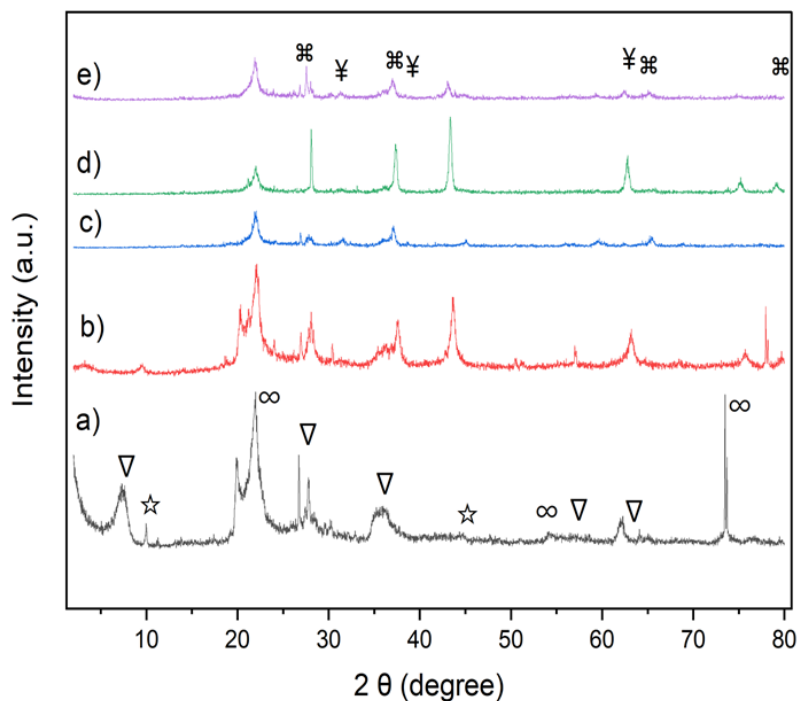


Figure 4.6. XRD pattern of a) Bentonite; b) 10% Ni/bentonite; c) 10% Co/bentonite; d) 10-5% NiCo/bentonite; e) 5-10% NiCo/bentonite; (∇: montmorillonite, ☆: kaolinite, ∞: SiO₂, ⌘: NiO, ¥: CoO)

Figure 4.7 shows GFP synthesis after second pyrolysis.

The XRD patterns (Figure 4.7) demonstrate the effect of varying catalyst compositions on the synthesis and quality of graphene after the second pyrolysis. All samples (a, b, c, and d) confirm the existence of graphene (☆), although the intensity and clarity of the peaks differ. Samples (c) and (d) show more pronounced and sharper graphene peaks, indicating a greater crystallinity degree or yield in comparison to samples (a) and (b). Silica (SiO₂), derived from the bentonite support, is consistently observed in all samples (∞), suggesting that the SiO₂ phase remains stable irrespective of the catalyst composition. In the case of the metal oxides, pattern (a) featuring 10% Co/bentonite reveals peaks associated with CoO (¥), whereas pattern (b) with 10% Ni/bentonite exhibits peaks indicative of NiO (⌘), thereby confirming the existence of the respective metal oxides without any indication of the other metal. Conversely, patterns (c) and (d), which use bimetallic NiCo/bentonite catalysts, display peaks for both NiO and CoO.

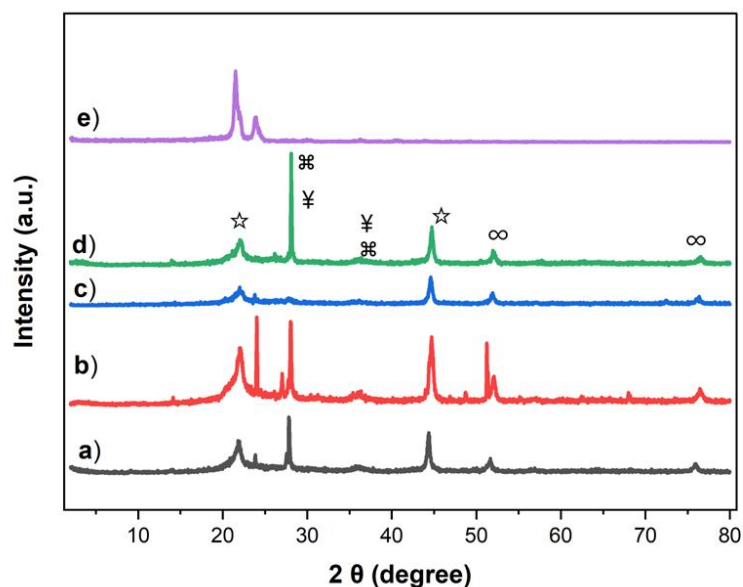


Figure 4.7. XRD pattern of a) GFP-1+ 10% Co/bentonite; b) GFP-2+10% Ni/bentonite; c) GFP-3 +10-5% NiCo/bentonite; d) GFP-4+5-10% NiCo/bentonite and e) plastic (☆: graphene, ∞: SiO₂, ⌘ NiO, ⌘: CoO)

2:2 NiCo/rGFO catalyst before and after hydrolysis are indicated at Figure 4.8.

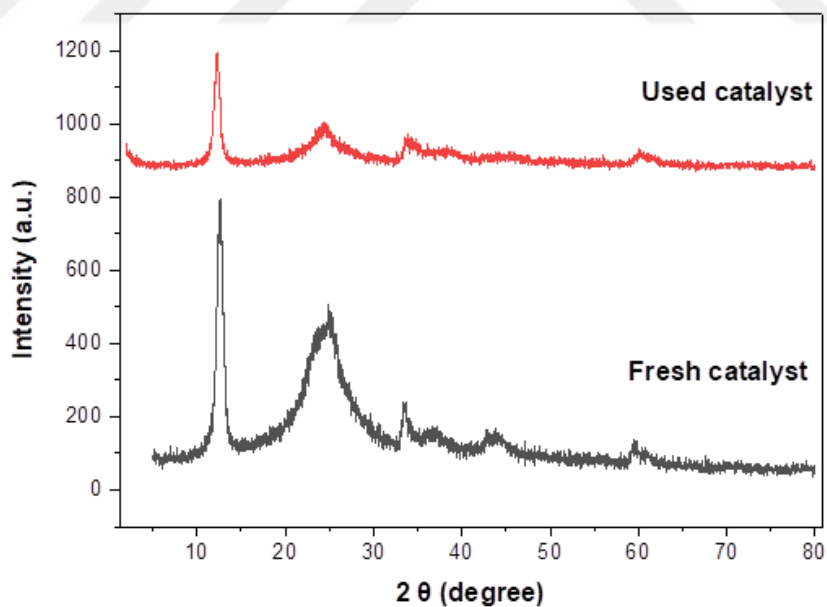


Figure 4.8. XRD of the 2:2 NiCo/rGFO catalyst before and after hydrogen generation by NaBH₄ hydrolysis

The XRD patterns (Figure 4.8) for both catalysts are observed at similar 2θ positions, indicating that the crystal structure of the NiCo/rGFO catalyst remains intact following the hydrolysis reaction. The intensity of some peaks at approximately 26.7°

and 45° has diminished. This decrease in intensity may suggest a minor reduction in the crystallinity of the catalyst following the reaction, potentially resulting from surface alterations or slight degradation. These properties of the catalyst show high stability, a lack of tendency to form new phases, and high repeatability, as confirmed by the reusability test.

The interplanar spacing (d-spacing) of all the samples was calculated (Table 4.2) according to Eq.1.1 (θ is in radians).

Table 4.2. Interplanar spacing (d-spacing) calculation from XRD data

Sample	d (Å)
GF	2.35
GO	5.61
GFO	2.85
1:1 NiCo/rGFO	4.23
1:2 NiCo/rGFO	4.23
2:1 NiCo/rGFO	4.23
2:2 NiCo/rGFO	4.23
GFP-1	3.71
GFP-2	3.69
GFP-3	3.73
GFP-4	3.72

GO has a larger d-spacing than GFO, which aligns with the expected increase in interlayer spacing due to oxygenated functional groups. Similarly, Iman et al.'s study found that GO's d-spacing was larger than GFO [124]. NiCo/rGFO catalysts exhibit stable interplanar spacing of 4.23 Å, regardless of the variations in NiCo ratios. A smaller d-spacing typically results in enhanced thermal and electrical conductivity.

4.2.2. FT-IR spectroscopy results

Figure 4.9. indicates FT-IR spectroscopy of a) GF and b) GFO.

In the spectrum of GF distinct peaks are observed at 610, 1052, 1600 and 3060 cm^{-1} . These peaks correspond to specific molecular vibrations: the peak at 610 cm^{-1} is associated with O-H stretching, the peak at 1052 cm^{-1} corresponds to C-O stretching, the

peak at 1600 cm^{-1} is linked to C=C stretching, and the peak at 3060 cm^{-1} is indicative of C-H stretching vibrations (Figure 4.9.a). Additionally, for GFO, distinct absorption peaks are observed at 1560, 1710, and 1052 cm^{-1} . These peaks correspond to specific molecular vibrations: the peak at 1560 cm^{-1} is associated with C-C stretching, the peak at 1710 cm^{-1} corresponds to C=O stretching, and the peak at 1052 cm^{-1} is linked to C-O stretching. Notably, the intensities of these peaks diminish as oxygen-containing functional groups are reduced or removed, indicating the reduction process of GFO (Figure 4.9.b).

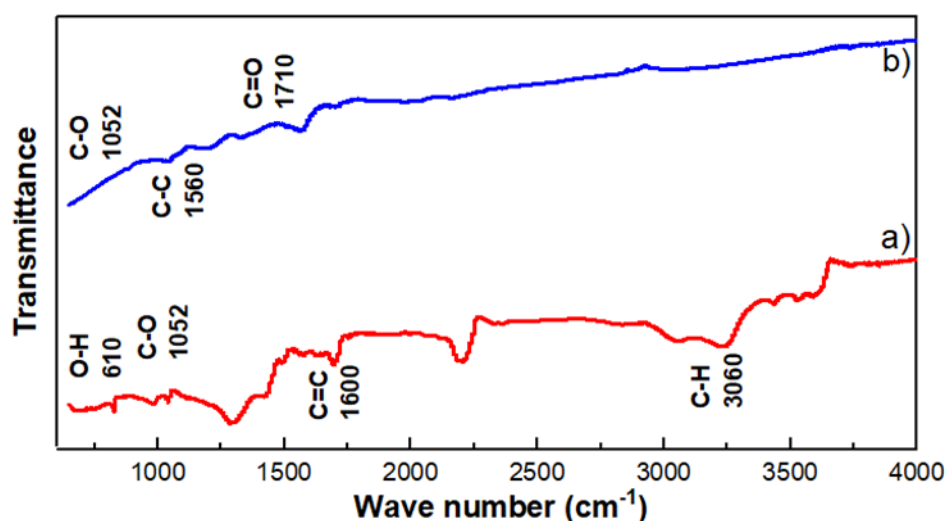


Figure 4.9. FT-IR spectroscopy results of a) GF; b) GFO

FT-IR spectroscopy results of a) graphite; b) GO; c) 1:1 NiCo/rGFO; d) 1:2 NiCo/rGFO; e) 2:1 NiCo/rGFO; f) 2:2 NiCo/rGFO is shown in Figure 4.10.

Figure 4.10.a. does not show any prominent peaks for graphite. In Figure 4.10.b, several characteristic peaks are observed, indicating the presence of various oxygen-containing functional groups. Specifically, a broad O-H stretching vibration is seen around 3910 cm^{-1} , which is indicative of hydroxyl groups. A sharp peak at 1779 cm^{-1} corresponds to C=O stretching, signifying the presence of carbonyl groups. Additionally, C=C stretching is observed at 1419.8 cm^{-1} , while peaks around 1252 cm^{-1} are attributed to C-O and C-OH stretching vibrations, reflecting the presence of epoxy and hydroxyl groups. These peaks collectively confirm the functionalization of graphene with oxygen-containing groups, which significantly alters its chemical and physical properties compared to pristine graphene.

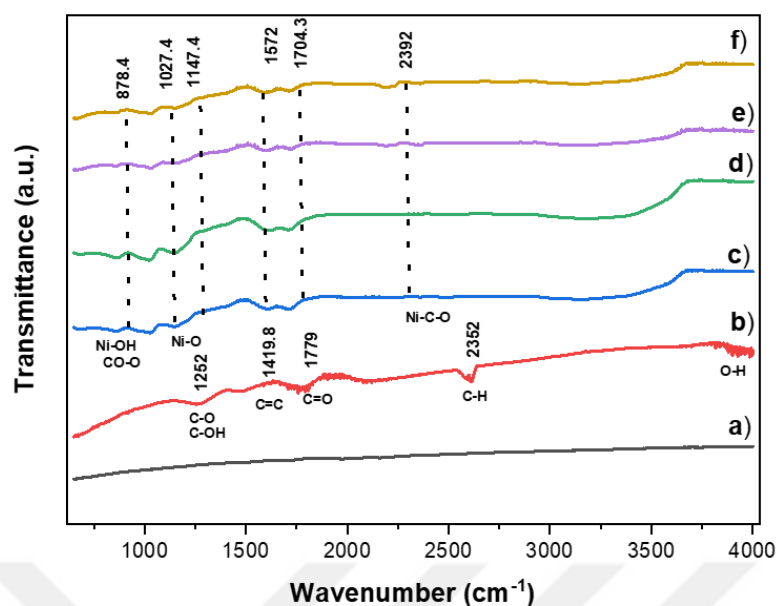


Figure 4.10. FT-IR spectroscopy of a) graphite; b) GO; c) 1:1 NiCo/rGFO; d) 1:2 NiCo/rGFO; e) 2:1 NiCo/rGFO; f) 2:2 NiCo/rGFO

In contrast, the FT-IR spectrum of the NiCo/rGFO catalysts demonstrates a significant reduction in oxygen-containing functional groups. New peaks appearing in the 500-1000 cm^{-1} range correspond to Ni-O, Co-O, and Ni-OH bonds, confirming the successful incorporation of Ni and Co metals into the GFO structure. This transformation from GO to NiCo/rGFO is evidenced by the elimination of oxygen groups and the addition of metal-oxygen bonds.

Specifically, two prominent peaks around 561 and 654 cm^{-1} , as confirmed by Marimuthu et al. [125], are attributed to the stretching vibrations of Ni-O and Co-O bonds, indicating the formation of the NiCo alloy.

Similarly, in the research carried out by Jamshaid et al. [126], the FT-IR analysis of NiCo/rGFO samples with different NiCo ratios demonstrated distinct vibration bands at 554 and 679 cm^{-1} .

Similarly, the FT-IR spectrum of the Ni-MOF nanostructure reported by Malihe et al. [127] shows a peak at 592 cm^{-1} , corresponding to the O-Ni-O bond. Additionally, Haopeng Cai et al. [128] synthesized a CoO/CNF composite using the hydrothermal method, with the FT-IR spectrum revealing bands at 728, 700 and 551 cm^{-1} , which correspond to the stretching vibrations of metal-oxygen bonds in CoO.

FT-IR spectroscopy of bentonite-based catalysts is indicated in Figure 4.11.

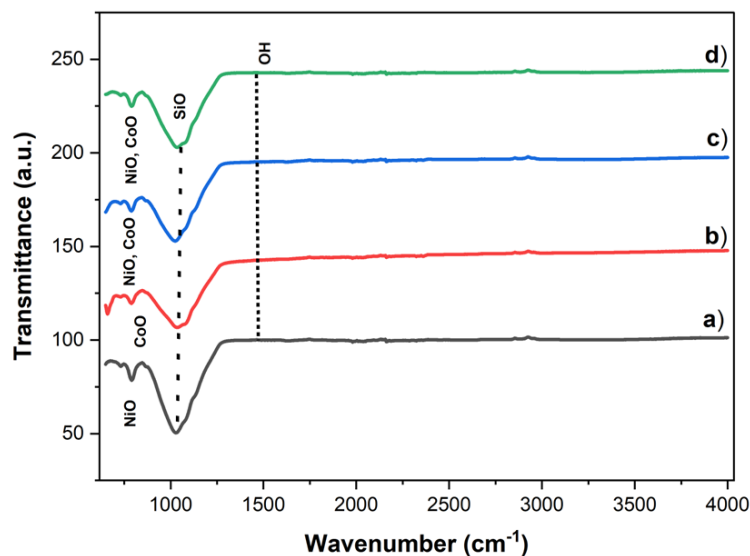


Figure 4.11. FT-IR spectroscopy of a) 10% Ni/bentonite; b) 10% Co/bentonite; c) 10-5% NiCo/bentonite; d) 5-10% NiCo/bentonite

The spectra exhibit distinct peaks that are indicative of metal-oxide bonds as well as the silicate of bentonite. In each spectrum, the peaks observed in the range of 500–700 cm^{-1} are associated with vibrations of NiO and CoO confirming the incorporation of these metal oxides into the bentonite. The persistent presence of these peaks across all samples implies that the metal doping process has been effectively accomplished. A peak at approximately 1040 cm^{-1} is consistently noted across all samples, which is attributed to SiO stretching, a defining functional group in bentonite.

FT-IR spectroscopy of plastic, GFP-1+10% Co/bentonite, GFP-2+10% Ni/bentonite, GFP-3 +10-5% NiCo/bentonite, GFP-4+5-10% NiCo/bentonite; after the second pyrolysis are indicated in Figure 4.12.

In the case of the plastic, Figure 4.12.a, distinct peaks are identified at 717 cm^{-1} , which signify the occurrence of CH_2 and CH_3 bending vibrations, and at 1498 cm^{-1} , indicative of CH_3 bending vibrations. Furthermore, the peaks located at 2849 and 2912 cm^{-1} are associated with CH_2 , CH stretching vibrations commonly found in polymeric substances. Distinct peaks related to the Ni/Co metals and the bentonite support are evident in Figures 4.12. b) to e). Specifically, the peak observed at 791 cm^{-1} signifies the presence of Ni-O or Co-O stretching vibrations, while the peak at 1040 cm^{-1} is associated with SiO and C-O-C vibrations. The variation in the intensity of the peaks across different metal compositions and concentrations indicates the effective incorporation of the

elements. Furthermore, the C-H stretching vibrations at 2912 cm^{-1} are present in all samples.

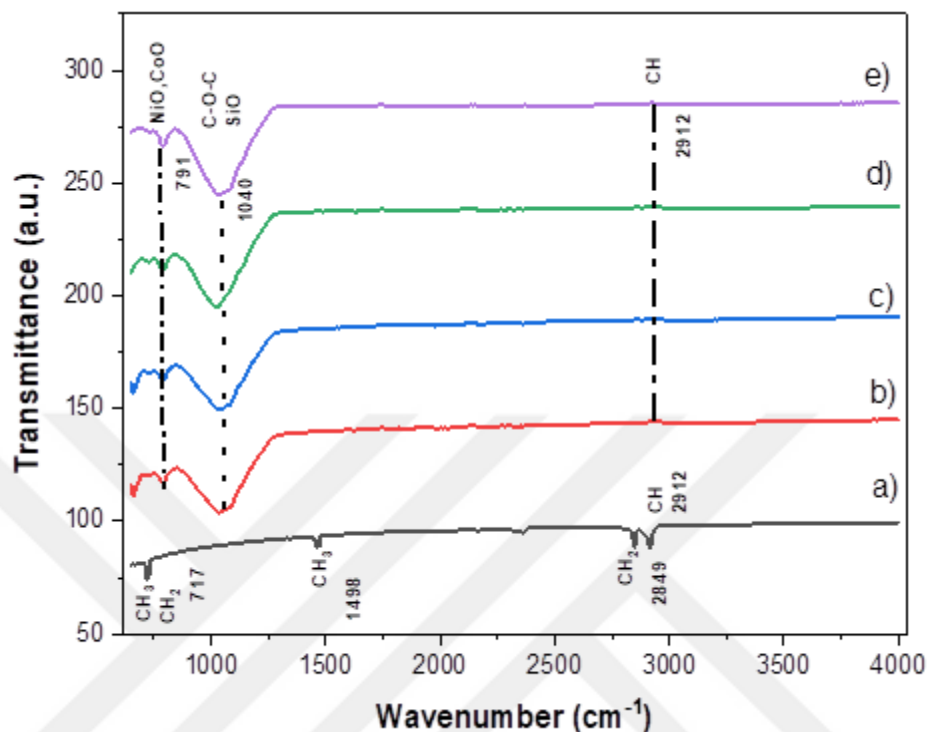


Figure 4.12. FT-IR spectroscopy of a) plastic; b) GFP-1 + 10% Co/bentonite; c) GFP-2 + 10% Ni/bentonite; d) GFP-3 + 10-5% NiCo/bentonite; e) GFP-4 + 5-10% NiCo/bentonite; before washing

4.2.3. CHNS/O analysis results

The elemental compositions of the samples, including carbon, hydrogen, nitrogen, and oxygen, were analysed using a CHNS/O analyser. The carbon-to-oxygen (C/O) ratio was calculated and presented in Table 4.3.

Table 4.3. CHNS/O Analysis of graphite, GF, and GFO

	C (%)	H (%)	N (%)	O (%)	C/O	C/N	C/(O+N)
Graphite	0.97	0.02	-	0.01	97	-	-
GFO	0.75	0.0066	0.0838	0.23	3.28	8.94	2.76
GF	0.80	0.000323	0.0058	0.19	4.21	137.93	4.17

Graphite exhibited the highest C/O and C/(O+N) ratios, underscoring its high carbon content. The high carbon content in graphite is significant as it highlights its purity

and potential for various applications where high carbon content is desirable. The elevated C/O ratio also suggests fewer oxygen-containing impurities, which can be beneficial for certain industrial and research applications.

The elemental analysis indicated that the C/O ratio for the GFO sample is 3.28, which signifies effective oxygen reduction and the incorporation of the amine compound. In contrast, the GF sample displayed a C/O ratio of 4.21, implying a significant oxidation level and considerable interlayer spacing.

Literature reports C/O ratios for GFO are in the range of 2.7-6, and the results from this study align well with these values [129–131]. The successful removal of oxygen from the GO sample to produce GFO is evident from the CHNS/O analysis. Additionally, the higher carbon percentage in GF compared to GFO suggests a superior graphene structure. The C/(O+N) ratio, calculated from the CHNS/O analysis data, indicates the purity of the synthesized samples. A higher ratio signifies better structural arrangement in graphene-based materials.

4.2.4. Raman spectroscopy results

Figures 4.13, 4.14 and 4.15 show the Raman spectroscopy of the graphene-based sample.

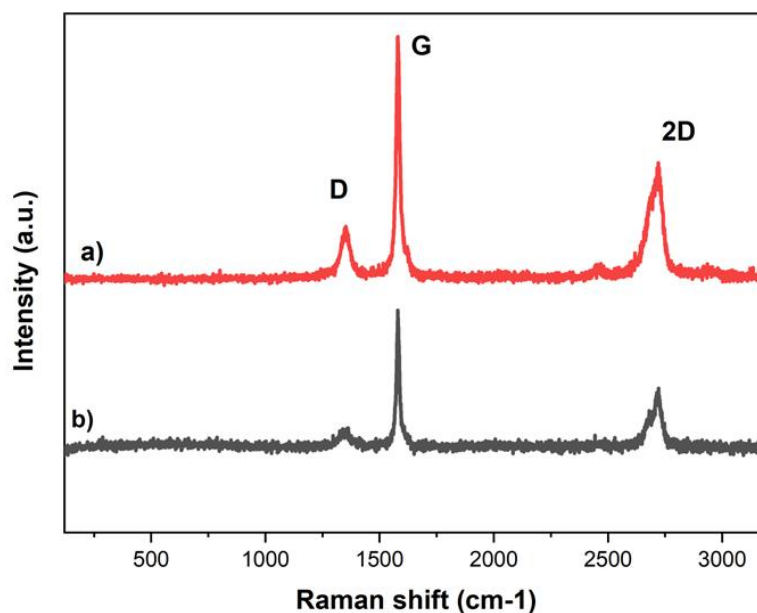


Figure 4.13. Raman spectroscopy analysis of a) graphite; b) GF

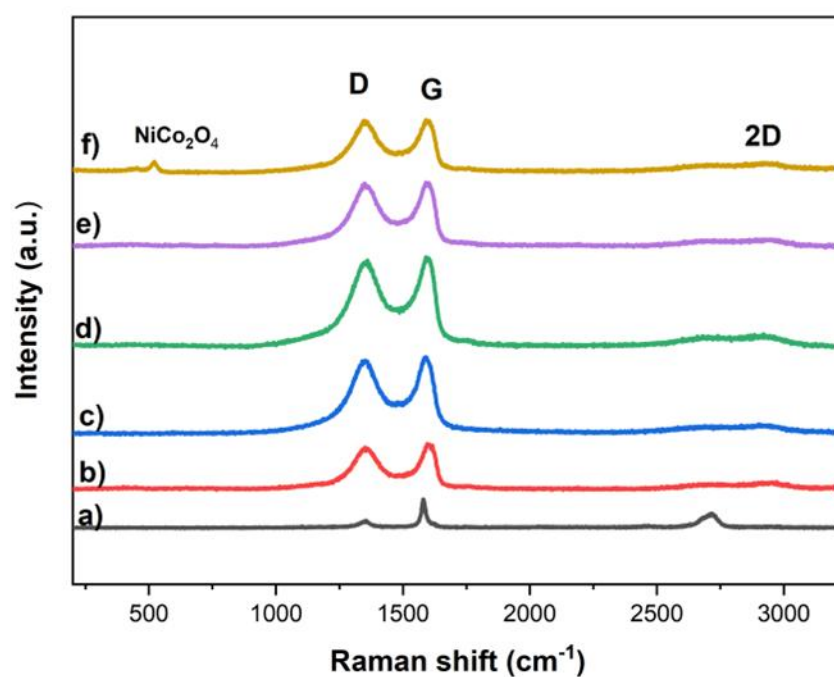


Figure 4.14. Raman spectroscopy of a) Graphite, b) 1:1 NiCo/rGFO, c) 1:2 NiCo/rGFO; d) 1:1 NiCo/rGFO; and f) 2:2 NiCo/rGFO

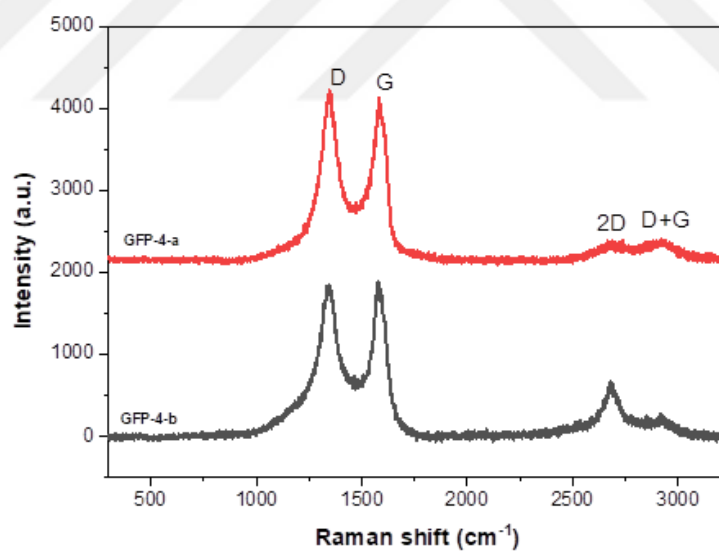


Figure 4.15. Raman spectroscopy of GFP-4; a) before b) after washing

Table 4.4. Raman spectroscopy results of graphene-based materials

	D (cm ⁻¹)	G (cm ⁻¹)	2D(cm ⁻¹)	I _D /I _G	L _a
Graphite	322.00	1349.00	670.00	0.24	80.10
GF	250.03	774.51	324.61	0.32	60.07
GFO	1632.08	1835.90	50.37	0.88	21.84

Table 4.4. (Continued) Raman spectroscopy results of graphene-based materials

	D (cm ⁻¹)	G (cm ⁻¹)	2D(cm ⁻¹)	I _D /I _G	L _a
1:1NiCo/rGFO	3756.53	3873.20	433.00	0.97	19.18
2:1NiCo/rGFO	3637.70	3772.30	434.40	0.96	19.93
1:2NiCo/rGFO	2254.58	2227.40	221.08	1.01	19.22
2:2 NiCo/rGFO	3077.86	3175.30	264.70	0.96	20.02
GFP-4-a *	1984.00	1887.70	216.18	1.05	18.31
GFP-4-b**	1759.84	1814.40	669.90	0.96	20.03

* GFP-4-a is Graphene from plastic using % 5-10 NiCo/bentonite after washing and sonication step

** GFP-4-b is Graphene from plastic using % 5-10 NiCo/bentonite before washing and sonication step)

In Raman spectroscopy, the D, G, and 2D bands play a crucial role in the examination of graphene-based materials. The G band, situated at approximately 1582 cm⁻¹, represents the in-plane vibrations of sp²-bonded carbon atoms and serves as a defining characteristic of the graphitic structure. The D band, located around 1350 cm⁻¹, reflects the existence of defects or edges within the graphene, as it is activated by the sp² carbon rings. Finally, the 2D band, which appears at about 2685 cm⁻¹, corresponds to a second-order two-phonon process and is particularly responsive to the number of graphene layers present. The characteristics of the 2D band, including its shape and intensity, can effectively differentiate between single-layer and multi-layer graphene [137, 138].

The intensity ratio of the D band to the G band (I_D/I_G) is a critical parameter for assessing the quality of graphene materials. A lower I_D/I_G ratio in graphite indicates fewer defects, while higher ratios in GF and GFO reflect increased disorder. Moreover, λ_{laser} is a constant value of approximately 532 nm in Eq. 4.1, which was used to compute the crystallite sizes (L_a).

$$L_a \text{ (nm)} = (2.4 \times 10^{-10}) \lambda_{\text{laser}}^4 (I_D/I_G)^{-1} \quad (4.1)$$

Graphite exhibits a D band at 1350 cm⁻¹ characterized by a low intensity of 322 cm⁻¹, which signifies the presence of few defects. Additionally, it displays a G-band at 1580 cm⁻¹ with high intensity (1349), a hallmark of pure graphite. The 2D band at 2706

cm^{-1} shows moderate intensity (670), and the I_D/I_G ratio is measured at 0.24, indicating a high degree of crystallinity.

GFO exhibits a D band at 1358.94 cm^{-1} and a G band at 1590.05 cm^{-1} , resulting in an I_D/I_G ratio of 0.88, which suggests a moderate presence of defects. Additionally, the 2D band is observed at 2886 cm^{-1} , characterized by a low intensity of 50.37.

GF exhibits a D band at 1345 cm^{-1} and a G band at 1580.41 cm^{-1} , accompanied by a notably low I_D/I_G ratio of 0.16, which suggests a high level of crystallinity. The 2D band is observed at 2709.2 cm^{-1} , displaying moderate intensity measured at 327.6.

GO exhibits a D band at 1341.07 cm^{-1} and a G band at 1600 cm^{-1} , resulting in an I_D/I_G ratio of 0.84, which suggests the presence of considerable defects. Additionally, the 2D band is observed at 2949 cm^{-1} , characterized by a low intensity of 301.5.

NiCo/rGFO samples exhibit different D band and G band positions, which are observed in the ranges of $1347\text{-}1355 \text{ cm}^{-1}$ and $1596\text{-}1604 \text{ cm}^{-1}$, respectively. The I_D/I_G ratios fluctuate between 0.96 and 1.01, suggesting differing degrees of defects present. Additionally, the locations of the 2D band vary from 2910 to 2968 cm^{-1} , with their intensities corresponding to the structural characteristics.

GFP-4-b shows slightly better Raman characteristics than GFP-4-a, primarily due to the sonication process, which helps reduce the number of graphene layers. Furthermore, GFP-4-b has a lower I_D/I_G ratio (0.96 compared to 1.01) and a slightly larger crystallite size, indicating fewer defects and improved graphitic crystallinity compared to GFP-4-a.

In the research conducted by Peter et al. [134], the I_D/I_G ratio was analyzed to evaluate the presence of defects in various graphene-based materials. The graphene nanoplatelets (GFNP) samples predominantly exhibited low I_D/I_G ratios, signifying a lower defect density and enhanced crystallinity. Conversely, GO samples displayed higher I_D/I_G ratios, reflecting an increased defect density resulting from the oxidation process. GFO samples revealed the most pronounced defect levels.

The analysis conducted by Zhu et al. [135] through Raman spectroscopy on the NiCo/rGFO, which serves as a bifunctional electrocatalyst for rechargeable Zn-air batteries, revealed several significant structural characteristics. The researchers detected the D band at approximately 1358 cm^{-1} and the G band at around 1587 cm^{-1} , both of which are indicative of graphitic structures and signify the presence of sp^2 -bonded carbon atoms. The D band, which is linked to local defects and disorder within the graphene

framework, alongside the G band, associated with the in-plane vibrations of sp^2 carbon atoms, validated the effective reduction of GFO and the restoration of the sp^2 carbon network. Furthermore, a 2D band at 2695 cm^{-1} was observed.

Amruta et al. [136] synthesized Ni-Co MOF/rGFO using the hydrothermal method for supercapacitor applications. Raman spectroscopy analysis revealed I_D/I_G ratios of 1.

The analysis of Ni-GFO using Raman spectroscopy by Navid et al. [137] demonstrated notable structural modifications. The D and G peaks were identified at 1405.3 cm^{-1} and 1642 cm^{-1} , respectively. The initial I_D/I_G ratio increased from 0.88 to 1.13 after loading metal.

In the research conducted by Niu et al. [138], which focused on the synthesis of Ni/GFO for supercapacitor applications, the I_D/I_G ratios for GFO (1.43) and Ni/GFO (1.45) were observed to be greater than that of GO (1.09). This increase signifies the existence of unrepaired defects following the removal of oxygen-containing groups and the incorporation of Ni particles. Furthermore, the lack of other prominent Raman peaks indicated that the Ni particles, encased by GFO nanosheets, remained unoxidized, as NiO is known to display distinct Raman peaks.

The findings of the present study align with numerous reports in the existing literature, affirming the crucial influence of the I_D/I_G ratio on the structural integrity and defect density of graphene-based materials. This comparison underscores that the values recorded in this research mirror prevalent trends identified in other investigations, particularly noting an increase in defect levels in materials such as GFO and nickel-loaded graphene samples. The I_D/I_G ratios are established as a dependable parameter for assessing crystallinity and defect levels across various materials, while the differences observed in the 2D band further differentiate between single-layer and MLGF

4.2.5. UV-Vis spectroscopy results

Figure 4.16. presents the UV-Vis absorbance spectra of graphite and GF samples.

The UV-Vis absorption spectrum of graphite displayed a significant peak corresponding to the $\pi-\pi^*$ transition, indicative of layered structure. This $\pi-\pi^*$ transition peak was consistently observed across all samples, arising from the movement of electrons within the conjugated π orbitals of the carbon atoms. In the case of GF, the absorption peak was noted at 262 nm, which is associated with the presence of the aromatic ring.

Sean P et al. [139] investigated the exfoliation of graphite in various solvents, such as NMP, and found that the resulting MLGF samples exhibited peaks ranging from 180 to 250 nm. This finding is consistent with the measured UV-Vis peak of the MLGF sample.

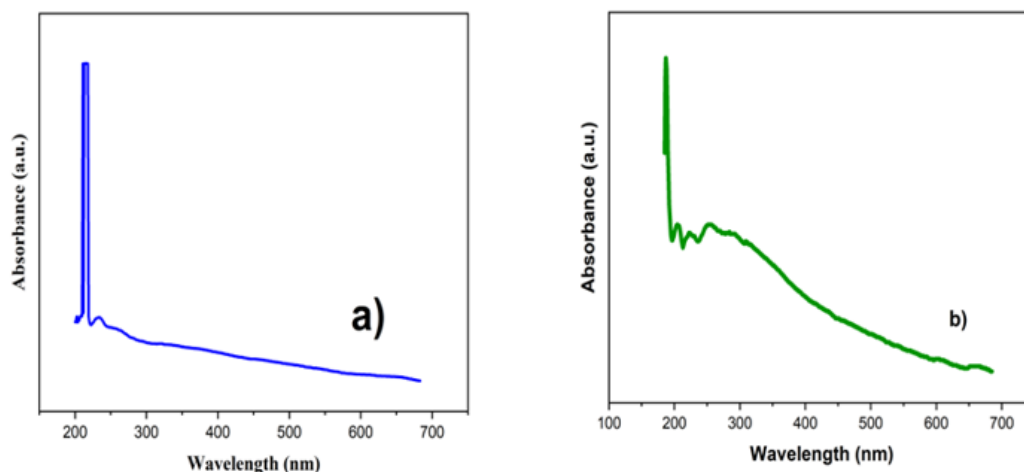


Figure 4.16. V-Vis spectroscopy of a) graphite; and b) GF

UV-Vis spectroscopy characterization results of a) GO; b) 2:2 NiCo/rGFO; c) 2:1 NiCo/rGFO; d) 1:2 NiCo/rGFO, and e) 1:1NiCo/rGFO is shown in Figure 4.17.

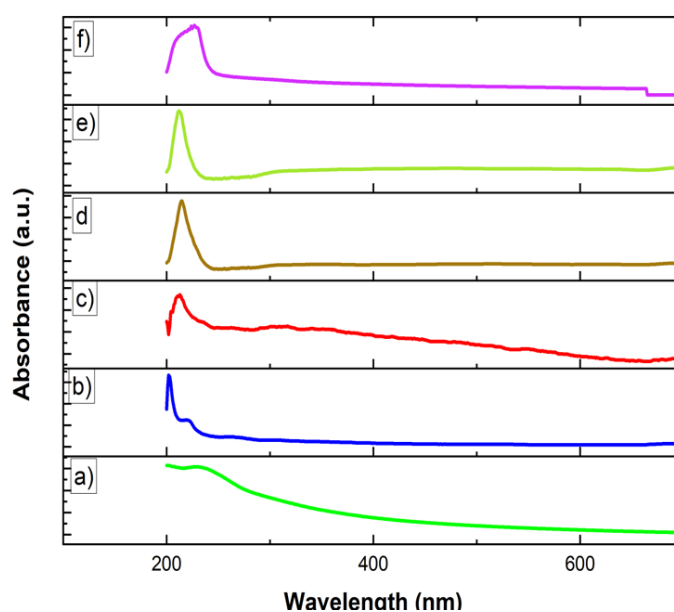


Figure 4.17. UV-Vis characterization of a) GFO; c) 2:2 NiCo/rGFO; d) 2:1 NiCo/rGFO; e) 1:2 NiCo/rGFO, and f) 1:1NiCo/rGFO

UV-Vis spectra of GO exhibit two prominent absorption peaks. The initial peak, detected at roughly 203 nm, is associated with the $\pi \rightarrow \pi^*$ transition of the carbon-carbon bonds. The subsequent peak for GO is found at 230 nm, which corresponds to the $n \rightarrow \pi^*$ transition of the carbon-oxygen bonds. The presence of this peak indicates the existence of oxygen-containing functional groups in GO, a conclusion supported by FT-IR analysis. These functional groups are generated during the oxidation process of graphite. The broad peak of GFO shifted to 238 nm, indicating the partial restoration of the electronic conjugation in the graphene structure. In the case of the NiCo/rGFO samples, the UV-Vis spectrum reveals an absorption peak near 234 nm.

Maxim K. et al. [140] reported that the GFO spectrum shows a significant peak in the 262-270 nm range. They also noted that after the reduction of GO to GFO, the previously visible peak at 298 nm completely disappears from the UV-Vis spectra.

Similarly, a review article by Alves et al. [141] focused on the characterization of graphene-based materials notes the identification of two main peaks for GO at wavelengths of 232 nm and 304 nm. These peaks are indicative of the electronic transitions occurring in the C-C bonds ($\pi-\pi^*$) and the C=O bonds ($n-\pi^*$) within the GO sample, respectively.

In the study by Piu Das et al. [142], the absorbance spectra show that the nanocomposite and GFO exhibit prominent peaks at 269 and 275 nm, respectively. These peaks indicate the formation of nickel nanoparticles and GFO. The absorbance peak for Ni, typically observed around 269 nm, and the GFO peak at 275 nm overlap, resulting in a broad combined peak in the spectrum.

UV-Vis spectroscopy of GFP-4 after washing is shown in Figure 4.18.

A strong absorption peak was detected at 236 nm, followed by a decay pattern as the wavelength increased.

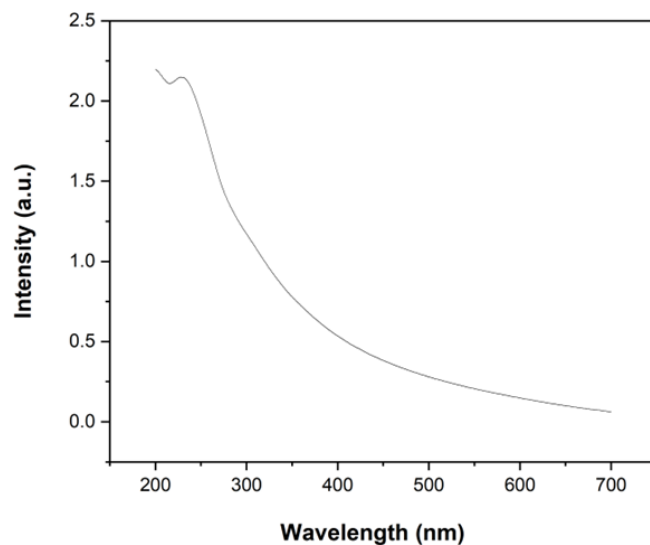


Figure 4.18. UV-Vis spectroscopy of GFP-4 sample after washing

4.2.6. SEM results

The SEM image of the graphite as starter material can be seen in Figure 4.19. Figure 4.19 illustrates its distinctive flaky and layered structure, a defining feature of its crystalline nature. The image highlights the complex details of these layers, formed by carbon atoms organized in a hexagonal lattice. The surface morphology exhibits variability, with certain areas appearing smooth while others appear uneven or rough. This textural diversity can be ascribed to the inherent imperfections and grain boundaries present within the graphite structure.

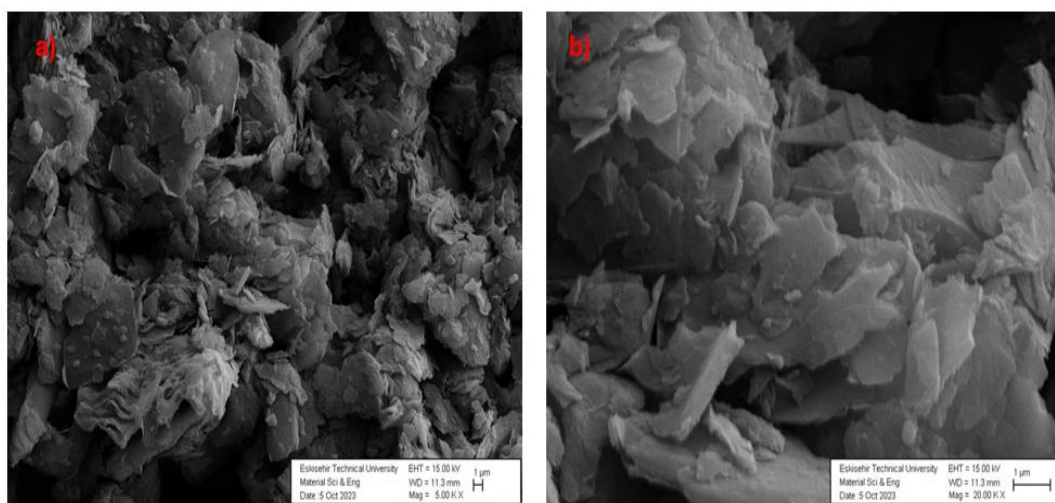


Figure 4.19. SEM image of graphite a) 5000; b) 20000 magnifications

Rew et al. [143] analysed SEM images of graphite, demonstrating that the particles exhibit closely packed, plate-like structures, which enhance their conductivity performance.

The findings from the SEM analysis conducted by Markervich et al. [144] reveal a flat and uniform surface characterized by well-aligned flakes.

Michio et al. [145] characterized exfoliated graphite through SEM images, which demonstrated that the particles in the exfoliated graphite samples displayed a worm-like morphology.

SEM image of GF is illustrated at Figure 4.20. SEM images of GF show the layered graphene structure, which is distinguished by the wrinkled and folded edges. The crumpled surface texture indicates that MLGF were effectively separated during the exfoliation of graphite.

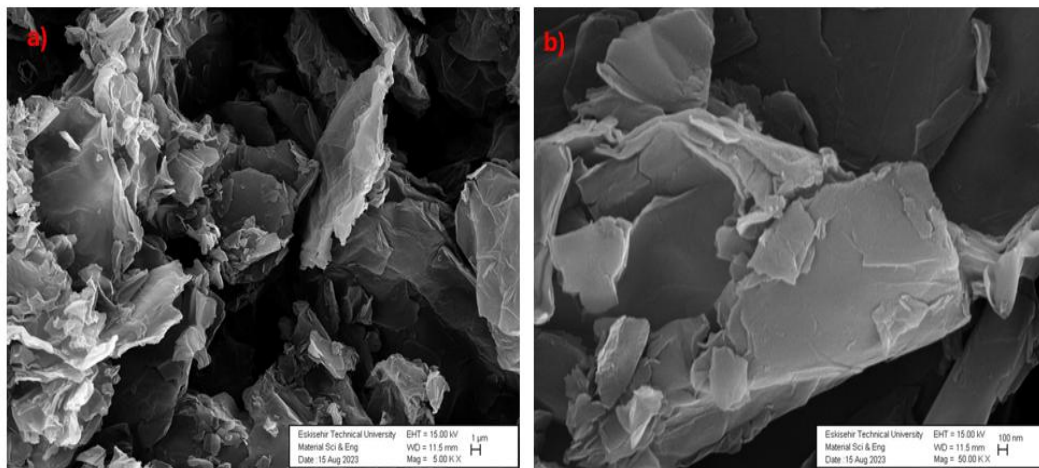


Figure 4.20. SEM images of GF a) 50000 KX; b) 50000 KX

The SEM images of GO are indicated at Figure 4.21. The SEM image of the GO sample illustrates its complex and distinctive structure. This image emphasizes the layered configuration of GO, with certain areas exhibiting folds or crumples. The observed folds and crumples within the layers result from the presence of oxygen-containing functional groups, which disrupt the uniform lattice and create distortions. Moreover, the surface topography of the GO sample is notably uneven and rough, a common trait of this material. The differences in surface texture can influence the material's reactivity and interactions with other substances.

The morphology of the GO sample produced by Bala et al. [146] exhibited a flake-like structure, especially prominent at the edges, characterized by several layers arranged in a stacked formation.

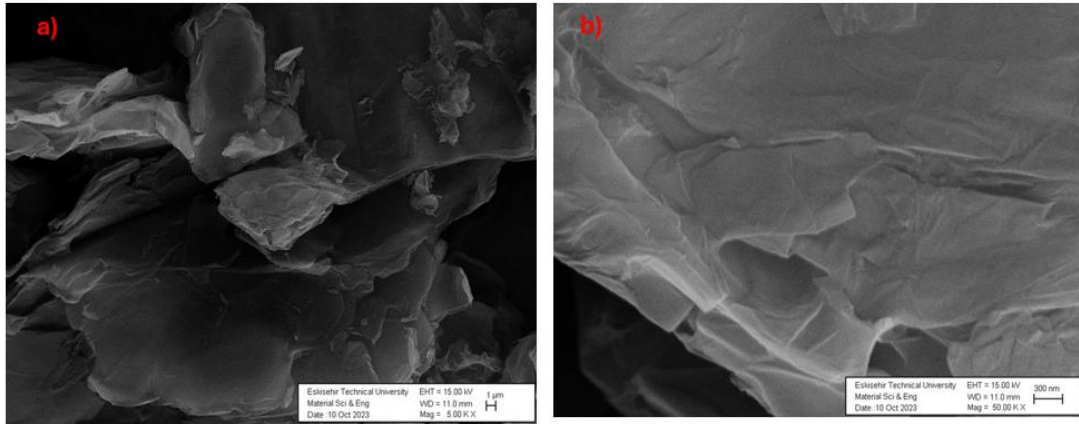


Figure 4.21. SEM image of GO a) 500 KX; b) 5000 KX

In the investigation by Saleem et al. [147], the SEM images illustrate that GO features a patterned layered structure with crumpled sheets. This crumpled morphology implies that the oxidation process interferes with the originally aligned layers of graphite. In this context, GO was used as a filler in fiberboard.

The GO production was conducted by Haluk et al. [71], using three separate techniques such as Brodie, Staudenmaier, and Hummers. Analysis via SEM demonstrated that GO has a textured, flake-like morphology with inconsistent sizes and varying dimensions.

The SEM image of GFO can be observed in Figure 4.22.

The SEM image of GFO displays several notable characteristics that underscore its distinctive structure and properties. The images show areas of folding as overlapping layers, indicating the material's flexibility and potential for improved mechanical properties. These folds also serve to increase the surface area, which is advantageous for a variety of applications. Moreover, the GFO surface is characterized by numerous wrinkles, a typical trait of graphene-based materials that can affect their electronic properties. These wrinkles often arise from the reduction process and contribute to the overall texture of the material. Additionally, the thin edges of the GFO sheets are prominently visible, highlighting the two-dimensional, sheet-like structure of the

material. These thin edges are essential for applications that demand a high surface area and edge reactivity, such as sensors, energy storage devices, and conductive films.

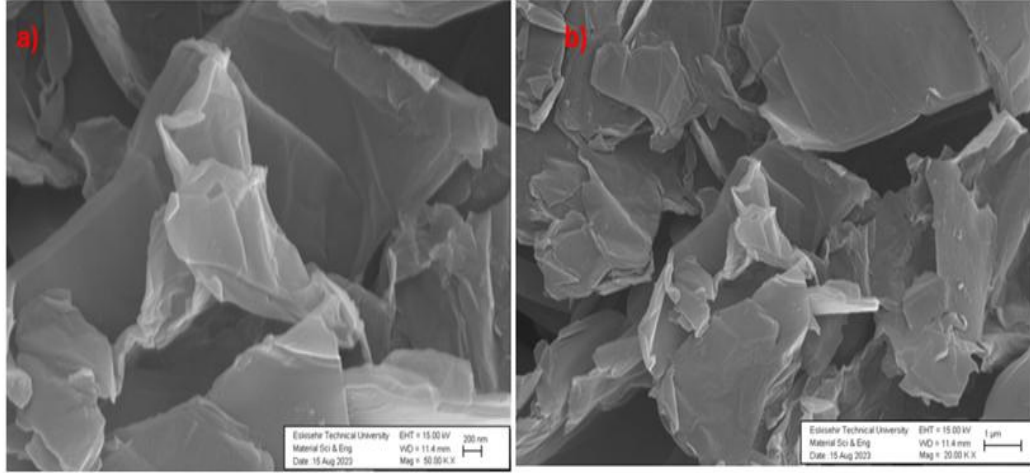


Figure 4.22. SEM image of GFO a) 50000 KX; b) 20000 KX

Kumar et al. [9] characterized the SEM image of GFO, noting that it displays sheets that seem to be shredded and overlapping. These sheets create curtain-like formations with zigzag edges.

Pallelappa et al. [148] synthesized N-GFO and found that SEM images of GFO showed a structure with a distinctly smooth surface. The nanosheets of GFO demonstrate a loose stacking pattern, which signifies minimal agglomeration or compact arrangement. This loose stacking may allow for a degree of separation among the nanosheets, potentially impacting the material's properties such as surface area and conductivity. Additionally, the smoothness of the surface indicates a uniform reduction process, where oxygen-containing functional groups have been removed, resulting in a more graphitic structure.

SEM image of 1:1 NiCo/rGFO sample is indicated in Figure 4.23.

The surface morphology of the 1:1 NiCo/rGFO is depicted in Figure 4.23, showcasing a multitude of layered flakes and particles that differ in size and shape. These flakes are representative of the GFO substrate, which offers an extensive surface area for the distribution of NiCo particles. The texture of the surface is characterized by a rough and irregular appearance. This roughness may contribute to an increased surface area, thereby potentially enhancing the material's catalytic or conductive characteristics.

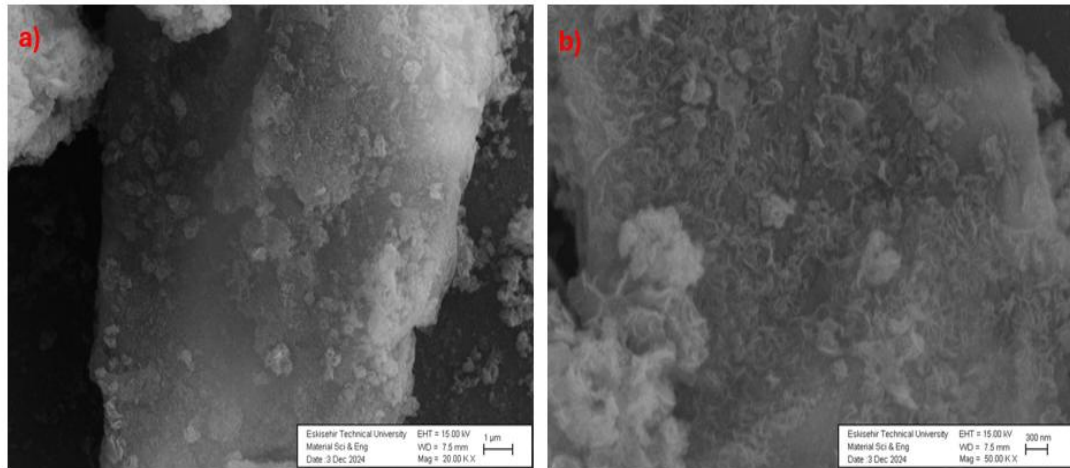


Figure 4.23. SEM image of 1:1 NiCo/rGFO a) 2000 KX; b) 5000 KX

SEM image of 1:2 NiCo/rGFO is indicated in Figure 4.24.

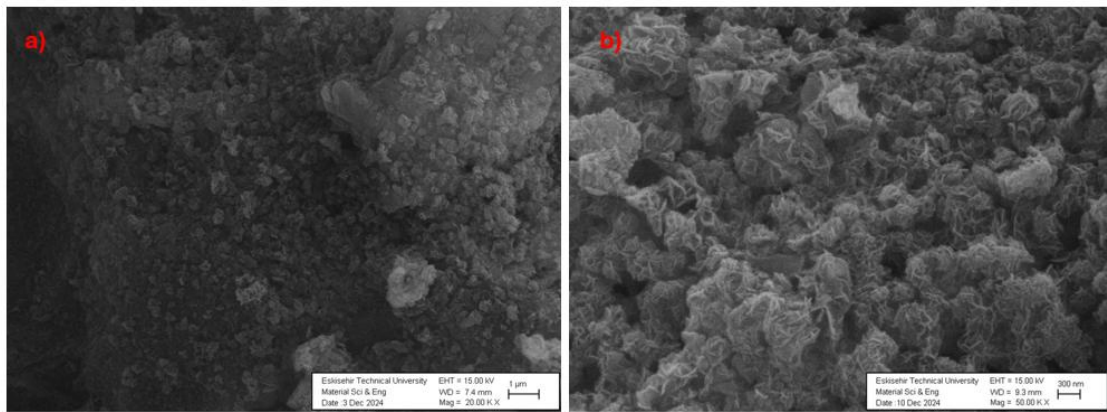


Figure 4.24. SEM image of 1:2 NiCo/rGFO a) 2000 KX; b) 5000 KX

The SEM images of the 2:1 NiCo/rGFO samples reveal that NiCo nanoparticles uniformly cover the entire surface of the GFO.

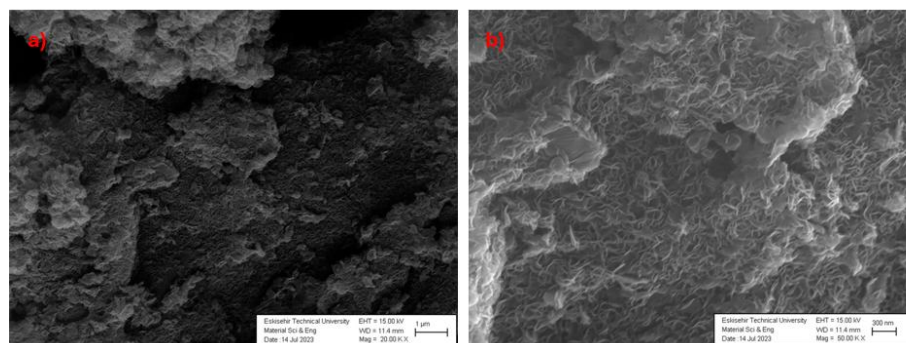


Figure 4.25. SEM image of 2:1 NiCo/rGFO a) 2000 KX; b) 5000 KX

The SEM images of the 2:1 NiCo/rGFO sample exhibit a similar structure to that observed in other NiCo nanoparticle ratios.

Figure 4.26 illustrates the SEM morphology of the 2:2 NiCo/rGFO sample. Figure 4.26 seems to consist of tightly stratified and creased formations. These formations bear a resemblance to crumpled paper or sponge-like sea creatures. The texture of the surface is coarse and uneven, which may enhance the material's active surface area and elevate its electrochemical efficiency. The SEM results show same morphology as NiCo/rGFO study of Liu et al. [149].

The findings of Wang et al. [150] revealed through SEM analysis that the NiCo/rGFO composite features a consistent distribution of nanoneedles on the GFO sheets. Integrating NiCo nanoneedles with GFO resulted in a cohesive network that enhances the material's structural integrity and supports efficient electron transport and ion diffusion.

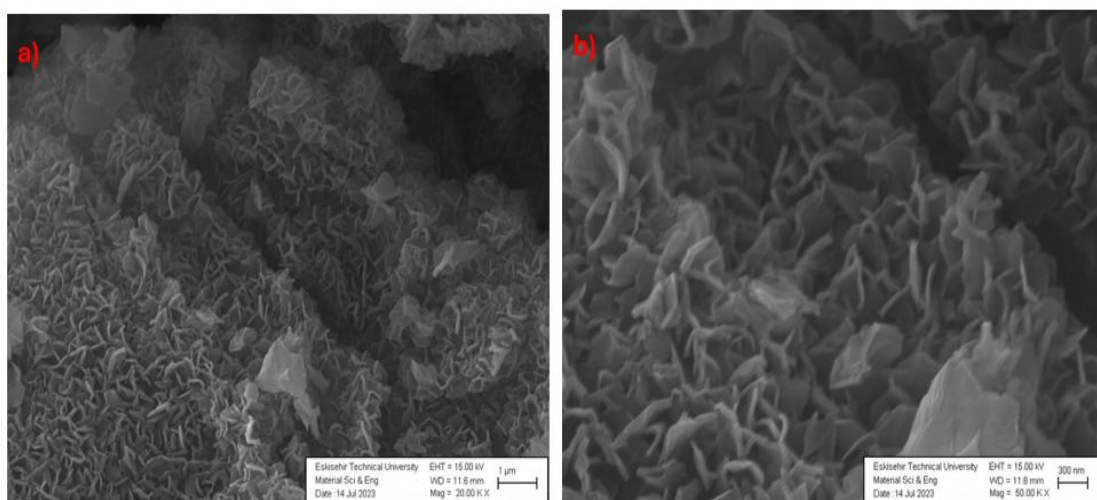


Figure 4.26. SEM image of 2:2 NiCo/rGFO a) 20000 KX; b) 5000 KX

NiCo/rGFO and NiCo SEM image investigation by Marimuthu et al. [125], demonstrated that both samples featured an aggregated nanorod structure. The nanorods were connected at specific centers, forming clusters. In the NiCo/rGFO composite, the larger aggregates of nanorods were broken down into smaller clusters. This morphological change was attributed to the GFO, which improved porosity and potentially enhanced the material's performance in gas sensing applications.

Differences in SEM findings of NiCo/rGFO samples across several studies can result in significant morphological variations, which in turn can affect the performance of the materials. For example, certain studies may report the formation of nanoneedles, nanosheets, or nanorods, influenced by the synthesis methods used, leading to differences in surface area and porosity. These morphological variations can play a critical role in determining electrochemical performance, such as capacitance and charge/discharge rates, as well as the sensitivity and response time of gas sensors.

Figure 4.27 illustrates the SEM morphology of the GFP-4 and GFP-3. Figure 4.27 displays a layered, sheet-like morphology characteristic of graphene oxide, with distinct, crumpled surfaces. Notably, the edges reveal a unique flower petal-like structure.

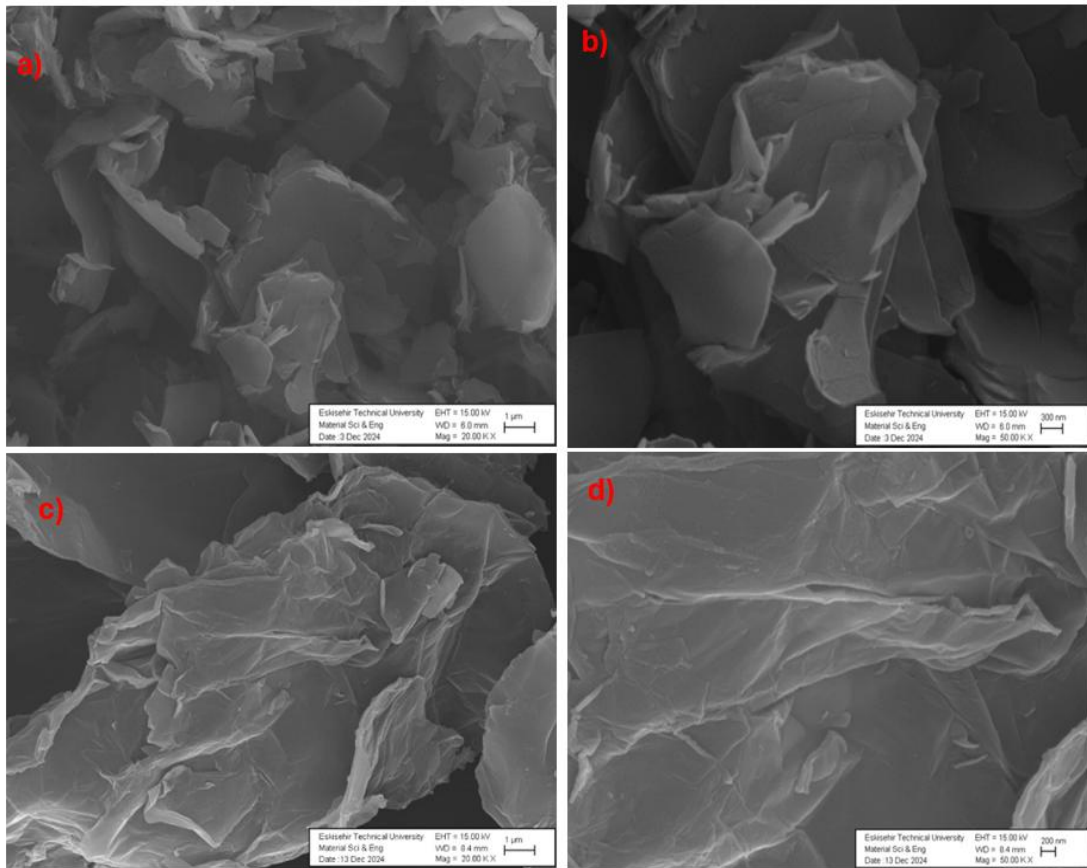


Figure 4.27. SEM image of GFP-4 a) 20000 KX; b)5000 KX and GFP-3; c) 20000 KX; d)5000 KX

4.2.7. TGA results

TGA of the graphene-based samples is depicted in Figure 4.28.

Weight reduction results showed that graphite, GF, and GFO experienced reductions of roughly 2, 14, and 35%, respectively. Due to the removal of oxygen functional groups during reduction, GFO experiences a more significant weight loss compared to GF, which still retains functional groups. The weight loss discrepancies observed are attributed to the reduction process and structural differences between GFO and GF, suggesting that these factors significantly influence their weight loss behavior. In comparison to other materials, pure graphite showed the most resilience to changes in temperature. The decrease in weight observed during the thermal process can be explained by the elimination of residual solvent molecules, functional groups like oxygen groups, and adsorbed moisture or impurities. GFO exhibits a total weight loss of 35% due to the decomposition of functional groups such as C-H, C=C, and C-O [151–153].

Wen et al. [154] reported a 2% weight loss for GF, which is lower than the weight loss observed for GF in this study. Various factors, including the initial purity of the sample, synthesis conditions, or the presence of additional functional groups, could contribute to this discrepancy. In different studies, GFO samples exhibit total weight losses of 21 [155], 43 [156], 18 [157], 81 [158], and 100 % [159]. These variations in TGA percentages can be attributed to different synthesis conditions. The 35 % weight loss observed for GFO in this study falls within the reported range of 21 to 100 %.

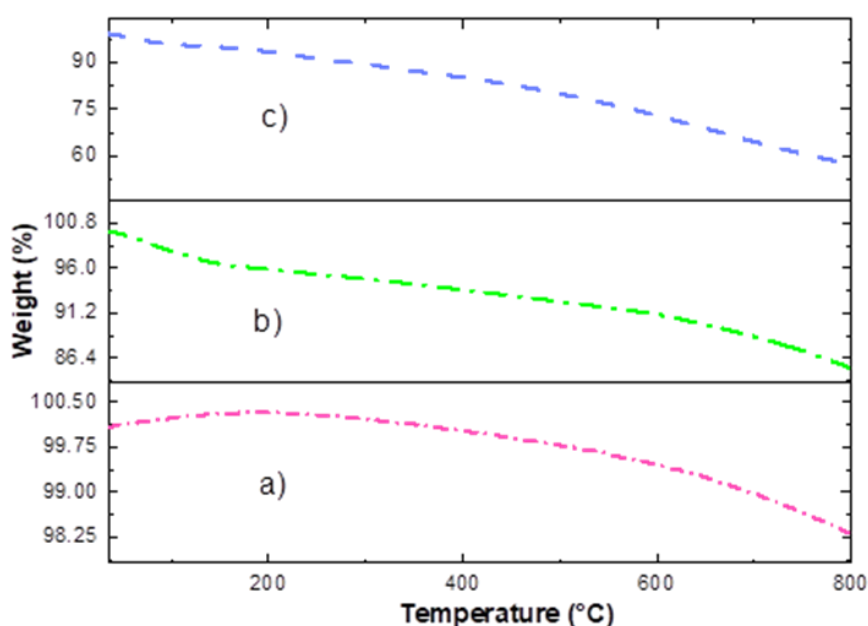


Figure 4.28. TGA profiles of a) graphite; b) GF; and c) GFO

4.2.8. TEM results

Figure 4.29 depicts the shape and structure of graphite.

The TEM images of graphite show large, thick, dark flakes that are entirely unreadable to the electron beam, suggesting the material's significant thickness and multilayered composition. It is evident from the image that there are multiple layers, indicating that the material is comprised of several carbon sheets stacked together.

In the study by Nopparat et al. [160], the TEM images illustrated a combination of layered flakes and fine sheets of graphite. The layered flakes were characterized by their opaque nature, while the fine sheets displayed transparency. The thin graphite sheet originated from the delamination of the stacked flakes, which was induced by the shear forces resulting from mechanical grinding in the presence of NMP. The grinding process effectively generated thin graphite sheets.

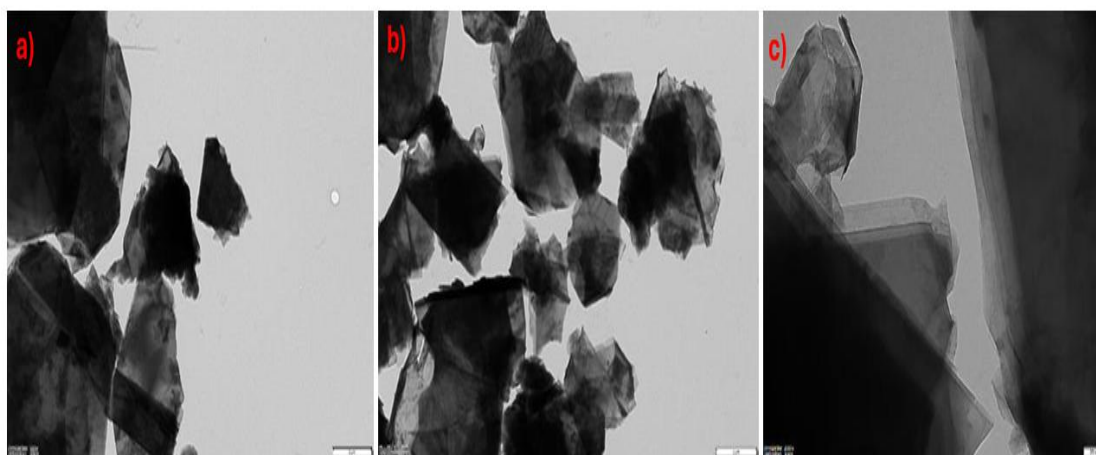


Figure 4.29. TEM images of graphite a) 100 nm; b) 100 nm; c) 2 μ m

In the study by Alireza et al. [161], the TEM images revealed a notable differentiation between the initial graphite particles and the exfoliated graphene sheets. The initial graphite particles are entirely opaque to the electron beam, which indicates considerable thickness. In contrast, the graphene sheets are seen as transparent in the TEM images, thereby confirming the successful exfoliation of graphite via ultrasonication in NMP solvent.

TEM image of the GFO sample is indicated in Figure 4.30.

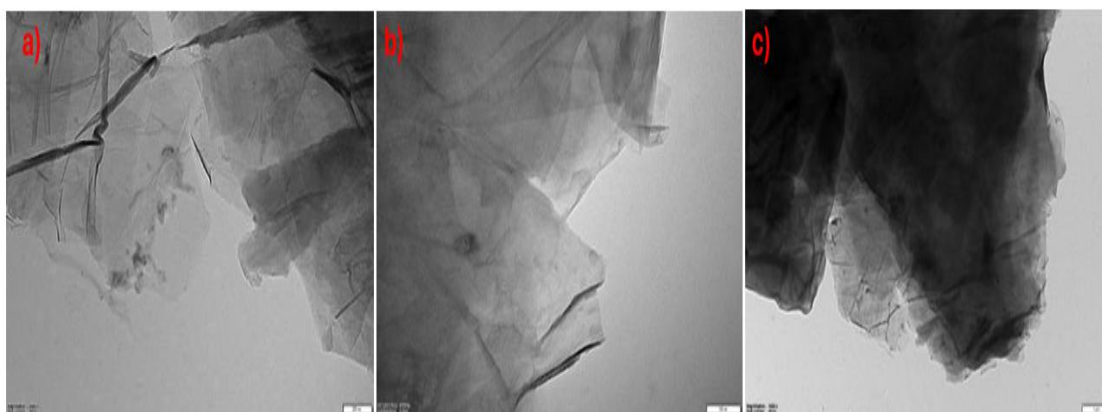


Figure 4.30. TEM images of GFO a) 100 nm; b) 100 nm; c) 2 μ m

The TEM image of GFO reveals thin, overlapping sheets that differ in transparency and darkness, suggesting variations in their thickness or density. The edges of these sheets are marked by wrinkles and folds, a typical feature of GFO resulting from the reduction of graphene oxide. This image confirms the layered structure of GFO, showcasing its characteristic morphology, which is critical for applications necessitating high surface area and flexibility, particularly in catalysis and energy storage.

The analysis performed by Sadhukhan et al. [162] on the electrical properties of GFO revealed a TEM image that showcased a wrinkled and folded structure. This morphology indicates loosely bonded layers with an increased interlayer distance. Such features are indicative of GFO and are crucial for enhancing its electrical properties by enabling efficient electron mobility and improving conductivity, thus making it suitable for applications in flexible electronics and energy storage systems.

In the investigation led by Yu-guo et al. [163] TEM images illustrated a silky wave structure resembling sheets, a wrinkled surface, and clusters of formations that ranged in size from 20 to 100 nm.

Amal et al.[164] applied TEM to analyse GFO, revealing individual transparent graphene sheets with a distinctive wrinkled and flake-like morphology. Moreover, the TEM image of Fc-GO, displayed a consistent presence of black dots across the GFO sheet surface.

The findings of Jian et al. [165] revealed that GO exhibited distinct wrinkles due to the presence of oxygen-containing functional groups. Upon its reduction to GFO, a considerable number of these functional groups were eliminated, leading to a reduction in wrinkles and a more flattened configuration.

Figure 4.31 shows the TEM image of GF.

Figure 4.31 displays a thin, almost transparent graphene sheet obtained through the LPE. This sheet features wrinkles and overlapping areas, indicating that it is formed from a single or a few graphene layers. The observed variations in contrast across the material suggest differences in thickness. The edges of the graphene sheet are lighter than the background, highlighting its fragile and irregular shape.

The research by Mitra et al. [166] detailed the TEM images of single graphene sheets obtained through the LPE method of graphite. The authors highlighted that these sheets possess irregular geometries, featuring significant folding and bending. The corrugations noted are typically around 1 μm in length.

In the study by Alireza et al. [161], graphene nanosheets were prepared using magnetic nanoparticle-assisted LPE of graphite. The findings indicated that the graphite particles were entirely opaque to the electron beam, suggesting a substantial thickness. The successful exfoliation of graphite was confirmed by the transparency of the graphene observed in TEM images following ultrasonication in NMP solvent. In contrast to GFO, which is synthesized via chemical oxidation followed by reduction of graphite, the graphene samples produced in this study exhibited minimal wrinkling. They observed that folding was the predominant morphological feature of the exfoliated graphene sheets generated by the Fe_3O_4 -assisted LPE method.

The TEM images of GFNP revealed smooth sheets with sharp edges and corners, appearing as uniform and transparent structures [167].

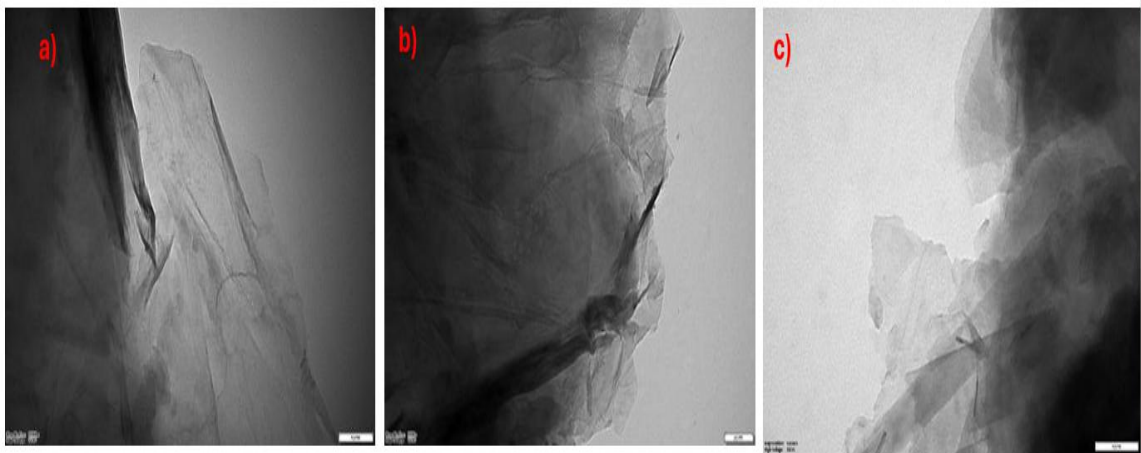


Figure 4.31. TEM image of GF a) 100 nm; b) 100 nm; c) 2 μm

TEM images of 2:2 NiCo/rGFO at different resolution are shown at Figure 4.32.

Figure 4.32 illustrates the TEM images of the 2:2NiCo/rGFO nanocomposite, emphasizing the variations in structure and the integration of the components. The image demonstrates the uniform growth of NiCo nanoparticles on GO nanosheets.

The TEM image of the NiCo/rGFO nanocomposite closely resembles the result reported by Yang et al. [168]. They noted that NiCo LDH nanosheet clusters were well dispersed across the graphene wrinkled sheets.

NiCo/rGFO TEM images obtained by Hongzhi et al. [150] are well supported by the TEM images acquired for this investigation.

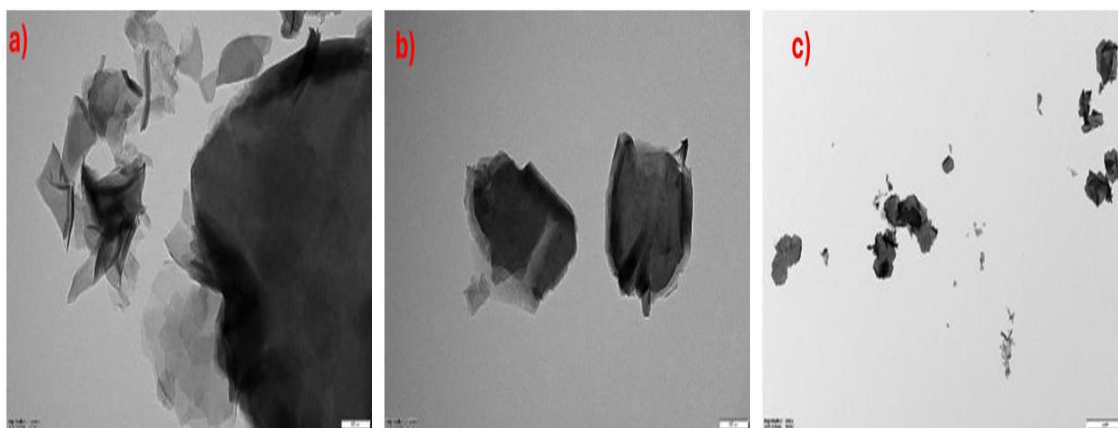


Figure 4.32. TEM image of 2:2 NiCo/rGFO; a) 100nm; b) 100nm; c)2 μ m

TEM image of GFP-4 after second pyrolysis are illustrated in Figure 4.33.

The TEM image of the graphene sample after the second step of pyrolysis reveals the presence of NiCo/bentonite on graphene.

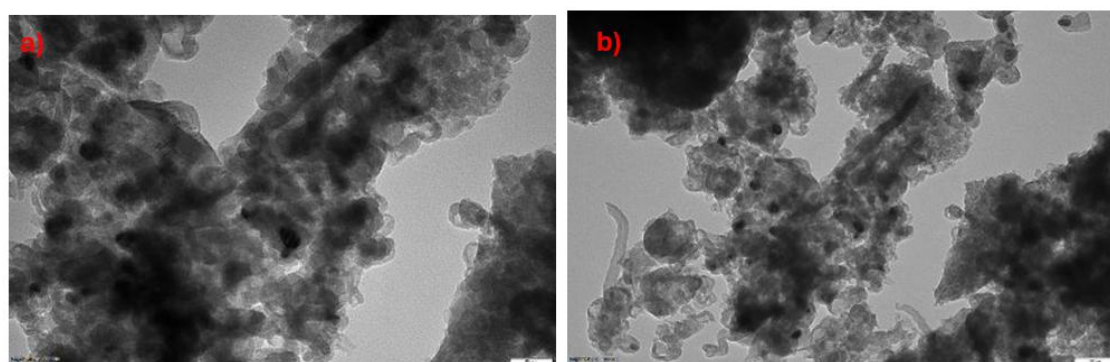


Figure 4.33. TEM image of GFP-4 +1:2 NiCo/bentonite; a) 50 nm;b) 2 μ m

TEM image of graphene (GFP-4) obtained after ultrasonication and washing indicates a folded sheet and thin edge, which are signs of graphene. Furthermore, a comparison of GFP-4 before and after washing showed that impurities were effectively removed from the graphene surface using HCl acid. Figure 4.34 indicates transparent layers, wrinkled textures, and folded-silk-dress-like morphology.

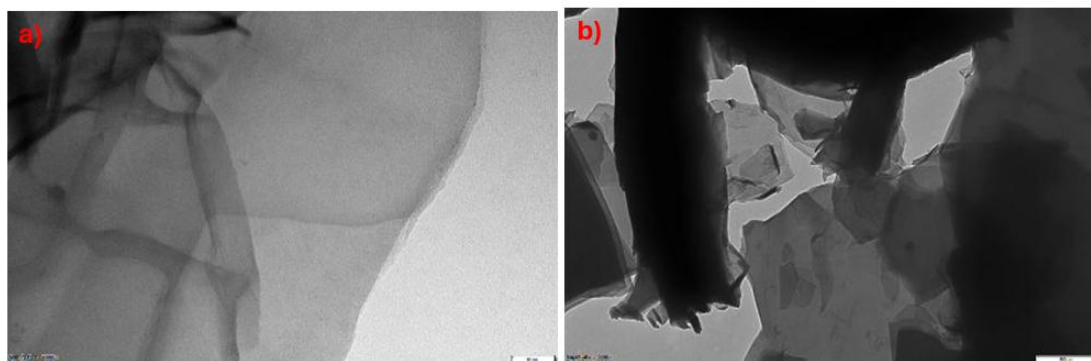


Figure 4.34. TEM image of graphene obtained from plastic (GFP-4); a) 50 nm;b) 2 μ m

4.2.9. XRF Results

The XRF analysis of NiCo/bentonite and bentonite is shown in Table 4.5.

Table 4.5. XRF results of catalysts and bentonite for pyrolysis

	Theoretically calculated Ni and Co loading ratio (%)	NiO (wt%)	CoO (wt%)	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Loss on ignition (LOI)
Bentonite	-	-	-	75.30	14.40	10.30
NiCo/bentonite	5:10	5.28	11.92	66.82	11.76	4.22
Co/bentonite	0:10	-	13.90	66.53	11.60	7.97
NiCo/bentonite	10:5	14.12	5.08	66.28	11.89	2.63
Ni/bentonite	10:0	10.74	-	68.66	12.56	8.04

Bentonite exhibits a notable composition characterized by SiO₂ at 75.3 wt% and Al₂O₃ at 14.4 wt%. The incorporation of Ni and Co significantly modifies this composition. In the 5:10 NiCo/bentonite sample, the NiO content is measured at 5.28 wt%, while CoO is at 11.92 wt%. This results in a reduction of SiO₂ and Al₂O₃ to 66.82 wt% and 11.76 wt%, respectively. For the Co/bentonite sample, CoO reaches 13.90 wt%,

with SiO₂ and Al₂O₃ values of 66.53 wt% and 11.60 wt%, respectively, leading to an increase in LOI to 7.97 wt%. Conversely, the 10:5 NiCo/bentonite displays a higher NiO content of 14.12 wt% and a lower CoO content of 5.08 wt%, resulting in SiO₂ at 66.28 wt% and the lowest LOI of 2.63 wt% among all samples. Finally, the Ni/bentonite sample contains 10.74 wt% NiO and no CoO, with SiO₂ at 68.66 wt%, Al₂O₃ at 12.56 wt%, and a relatively elevated LOI of 8.04 wt%. LOI is a technique used to assess the weight reduction of a material when subjected to elevated temperatures, indicating the elimination of volatile components such as water, organic materials, and carbonates.

4.2.10. BET results

N₂ adsorption-desorption isotherms for graphite, GFO, GF, 1:1 NiCo/rGFO, 1:2 NiCo/rGFO, 2:1 NiCo/rGFO, and 2:2 NiCo/rGFO are shown in Figure 4.35.

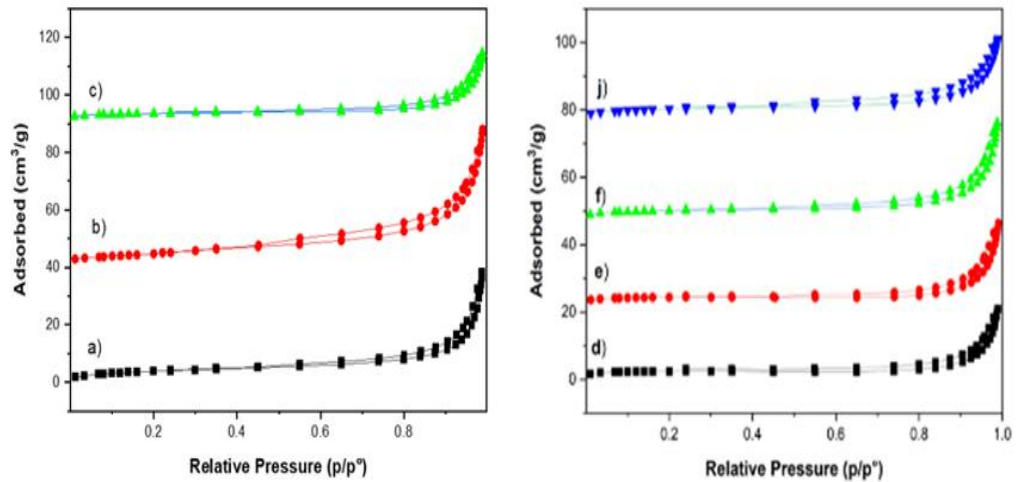


Figure 4.35. N₂ adsorption-desorption isotherms of a) GF; b) GFO; c) graphite; d) 1:1 NiCo/rGFO, e) 1:2 NiCo/rGFO; f) 2:1 NiCo/rGFO; j) 2:2NiCo/rGFO

Table 4.6. BET analysis result of graphite, GFO, GF, 1:1 NiCo/rGFO, 1:2 NiCo/rGFO, 2:1 NiCo/rGFO, and 2:2NiCo/rGFO

Sample	BET surface area	Micropore area	Total pore volume	Micropore volume	Average pore size
Graphite	10.00	13.78	0.030	0.0015	12.5
GFO	20.78	28.80	0.116	0.0014	22.0
GF	14.20	20.30	0.049	0.00094	13.8
1:1NiCo/rGFO	13.34	17.49	0.034	0.0019	9.76
1:2NiCo/rGFO	11.71	16.74	0.039	0.0021	13.25

Table 4.6. (Continued) BET analysis result of graphite, GFO, GF, 1:1 NiCo/rGFO, 1:2 NiCo/rGFO, 2:1 NiCo/rGFO, and 2:2NiCo/rGFO

Sample	BET surface area	Micropore area	Total pore volume	Micropore volume	Average pore size
2:1NiCo/rGFO	10.66	10.82	0.032	0.0034	11.87
2:2NiCo/rGFO	8.40	11.83	0.027	0.0029	12.83

The BET surface area, total pore volume, average pore size, micropore area, and micropore volume of the samples are shown in Table 4.6 from N₂ adsorption-desorption isotherms [150, 151]. The BET analysis results show that graphite, GFO, and GF have different structural characteristics. Graphite has the lowest total pore volume of 0.03 cm³/g and BET surface area of 10 m²/g, indicating it is less porous with an average pore size of 12.5 nm. GFO exhibits a higher surface area of 20.78 m²/g and a total pore volume of 0.116 cm³/g, indicating increased porosity. Additionally, GFO has the largest average pore size and micropore area. GF shows an average pore size of 13.8 nm, a total pore volume of 0.049 cm³/g, and a surface area of 14.2 m²/g. 1:1 NiCo/rGFO sample exhibits a BET surface area of 13.34 m²/g and a micropore area of 17.49 m²/g. The average pore size of 9.76 nm indicates the mesopore feature. The 1:2 NiCo/rGFO sample presents a reduced BET surface area. The 2:1 NiCo/rGFO shows a further decrease in BET surface area to 10.66 m²/g and a lower micropore area of 10.82 m²/g, although its micropore volume rises to 0.0034 cm³/g. Lastly, the 2:2 NiCo/rGFO composite has the lowest BET surface area at 8.40 m²/g and a micropore area of 11.83 m²/g, with a total pore volume of 0.027 cm³/g and a micropore volume of 0.0029 cm³/g.

In the study by Regueira et al. [171], the surface area of the pure graphene was determined to be 21.8 m²/g which is close enough to the current result.

In the study of supercapacitors by Zhengmin et al. [172], GFO indicates a surface area of 25 m²/g. The difference in surface area can be related to the different synthesis methods and reduction processes.

The surface areas of NiCoCr/GFO and NiCo/rGFO were reported to be 40.34 and 31.57 m²/g, respectively [173].

0.08 cm³/g and 8.63 m²/g were reported for the pore volume and surface area of Zn/GFO sample, respectively [174].

4.3. NiCo/rGFO Catalyst in The Hydrolysis of NaBH_4

Effects of the loading metal ratio on hydrolysis are displayed in Figure 4.36.

The data depicted in Figure 4.36 demonstrates that an increase in the NiCo content within the catalysts resulted in a notable reduction in reaction time. An increase in metal content leads to a greater number of active sites available for the hydrolysis reaction, thereby accelerating the reaction rate and enhancing hydrogen production. This observation aligns well with the results obtained from the SEM images. The 2:2 NiCo/rGFO sample achieved a 100% hydrogen yield in approximately 10 min. The variation in hydrogen production yield between the catalysts with 2:1 NiCo and 1:2 NiCo can be attributed to the differing amounts of cobalt, which resulted in a reduction of 10 min in reaction time. As the metal content rises, a larger proportion of the catalyst's surface area becomes occupied by active metal sites, facilitating more effective interactions between the NaBH_4 molecules and the catalyst, which in turn boosts hydrogen production. Maximum hydrogen generation rate of $255.10 \text{ mL/g}_{\text{cat}}\cdot\text{min}$ was recorded at 60°C , with 5 mL of 0.25 M NaOH, 100 mg of NaBH_4 , and a 2:2 Ni loading ratio.

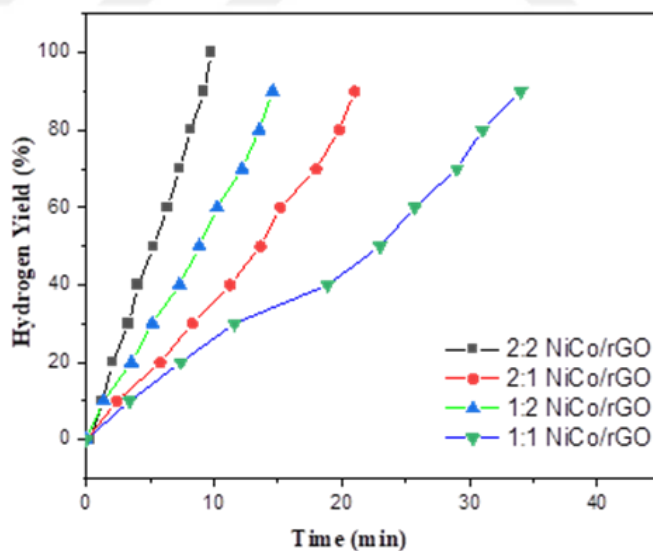


Figure 4.36. Impact of varying NiCo ratios on the hydrolysis of NaBH_4 under specific conditions of 100 mg of NaBH_4 , 100 mg of catalyst, 5 mL of 0.25 M NaOH

The influence of reaction temperature (30, 40, 50, 60°C) on hydrogen yield was documented using a 2:2 NiCo/rGFO catalyst, as illustrated in Figure 4.37.

The data illustrated in Figure 4.37 provides a comprehensive insight into the impact of reaction temperature on the hydrolysis of NaBH_4 when using the 2:2 NiCo/rGFO catalyst. An increase in reaction temperature from 30 to 60 °C results in a notable enhancement in the reaction rate, which is reflected in a substantial decrease in the time necessary to achieve a specific hydrogen yield. For instance, at 30 °C, the reaction duration is approximately 45 min to attain a certain yield, while at 60 °C, the same yield is reached in merely 10 min. This nearly fourfold reduction in reaction time underscores the significant influence of temperature on the efficiency of hydrogen production. The observed acceleration in reaction rates at elevated temperatures can be elucidated by the Arrhenius principle, which posits that an increase in temperature results in an exponential rise in the reaction rate constant. This indicates that as the temperature escalates, the kinetic energy of the participating molecules also increases, enabling them to surmount activation energy barriers more effectively, thereby expediting the hydrolysis of NaBH_4 . The presence of the 2:2 NiCo/rGFO catalyst further amplifies this temperature-dependent acceleration, as the catalyst offers additional active sites for the reaction, thereby enhancing overall reaction kinetics. Furthermore, elevated temperatures are likely to improve the interaction between NaBH_4 and the NiCo/rGFO catalyst, resulting in more effective catalytic activity. This enhancement may be attributed to the increased mobility of reactants at higher temperatures, along with potential alterations in the surface chemistry of the catalyst, which render it more proficient in facilitating the decomposition of NaBH_4 into hydrogen gas.

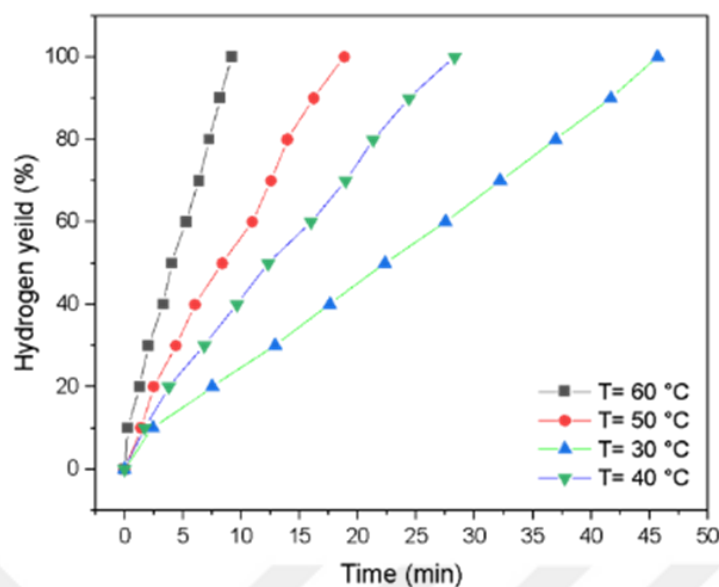


Figure 4.37. Effect of the reaction temperature in the catalysts on the hydrogen yield from the hydrolysis of NaBH_4 (100 mg NaBH_4 , 100 mg 2:2 NiCo/rGFO, 5 mL 0.25 M NaOH)

Figure 4.38 demonstrates the variation in hydrogen production as a function of NaOH (0.25, 0.50, 0.75, 1M) at a temperature of 60 °C, using 100 mg of NaBH_4 and 100 mg of a 2:2 NiCo/rGFO.

The results indicate that the concentration of NaOH has a limited impact on the hydrogen production rate. This finding is consistent with the observations made by Saka et al. [188] pointed out that the increased alkalinity and viscosity of the solution due to elevated NaOH concentrations can impede the hydrolysis reaction. The decrease in hydrogen production rates at higher NaOH concentrations may be attributed to the thickening of the NaBH_4 solution and the obstruction of active catalyst sites by hydroxide ions, which disrupt the reaction process. Likewise, Xin et al. [175] found that although hydrogen production initially rises with increasing NaOH concentration, it subsequently decreases at even greater concentrations.

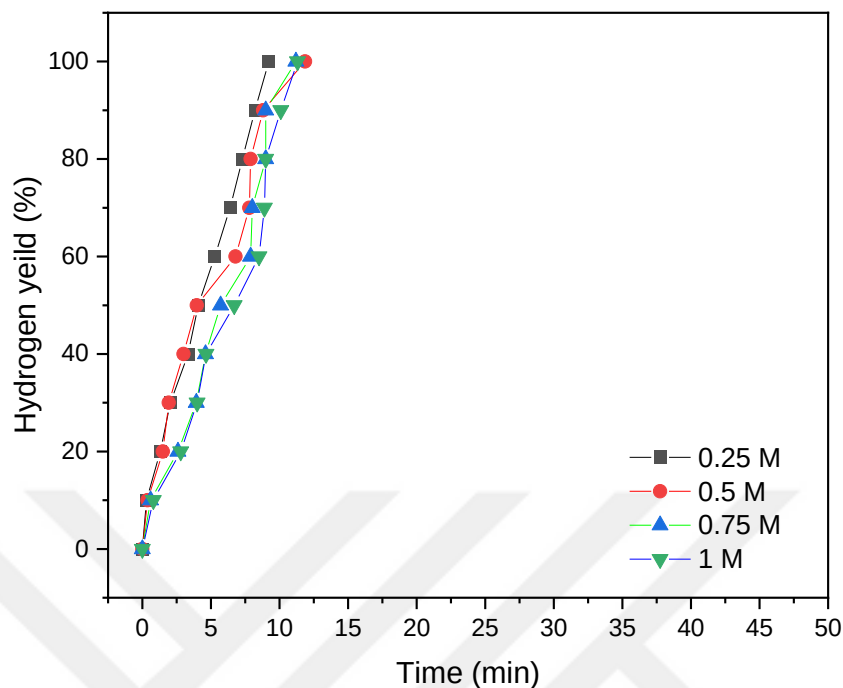


Figure 4.38. Influence of NaOH concentration on hydrogen production from NaBH_4 hydrolysis

The most effective catalyst, 2:2 NiCo/rGFO, was selected and thoroughly washed with deionized water before being reused in the hydrolysis reaction. Figure 4.39 Shows reusability test of 2:2 NiCo/rGFO at 60 °C in hydrolysis process.

Figure 4.39 indicates that during the first three cycles, the catalyst consistently achieved nearly 100% hydrogen yield, demonstrating remarkable efficiency from the outset. This high performance was further supported by XRD analysis of the catalyst post-hydrolysis. However, reaction times gradually increased, rising from 9 min in cycle 1 to 17 min by cycle 3, indicating a slight reduction in the reaction rate while still maintaining effective catalysis. By cycle 4, the hydrogen yield dropped to approximately 80 %, with an extended reaction time of 24 min. In cycle 5, the yield further declined to around 60 %, with the reaction time significantly lengthening to 48 min.

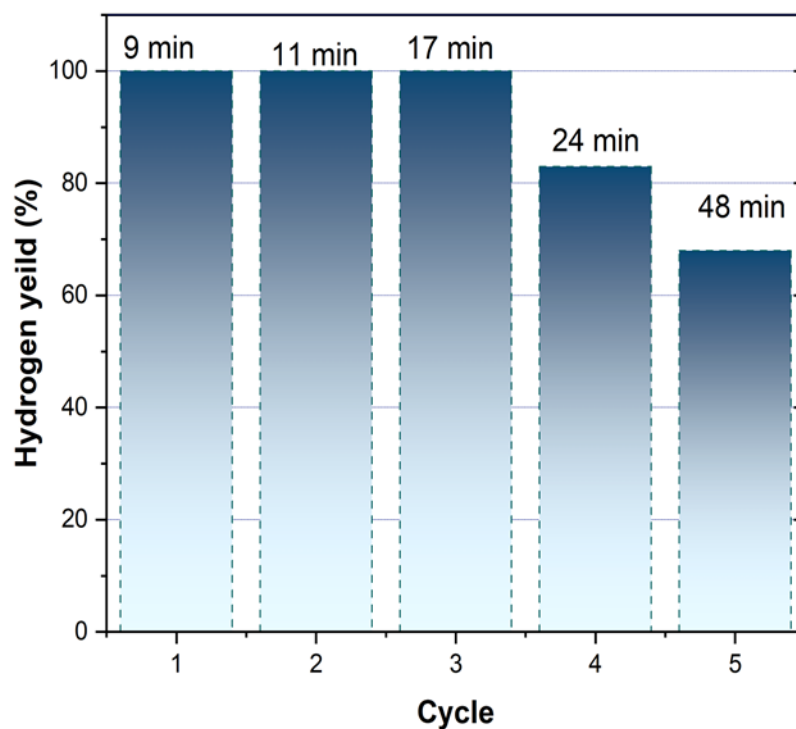


Figure 4.39. Reusability of 2:2 NiCo/rGFO at 60 °C in hydrolysis process

4.3.1. Kinetic study results of hydrolysis of NaBH_4

The data obtained from applying zeroth (Figure 4.40), first-order (Figure 4.41), and nth-order (Figure 4.42) kinetic models were plotted against time to determine the chemical reaction kinetics at different temperatures.

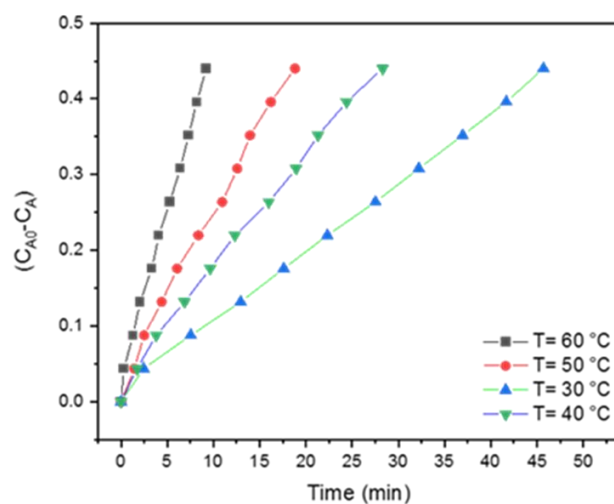


Figure 4.40. Data analysis based on zero-order reaction kinetics

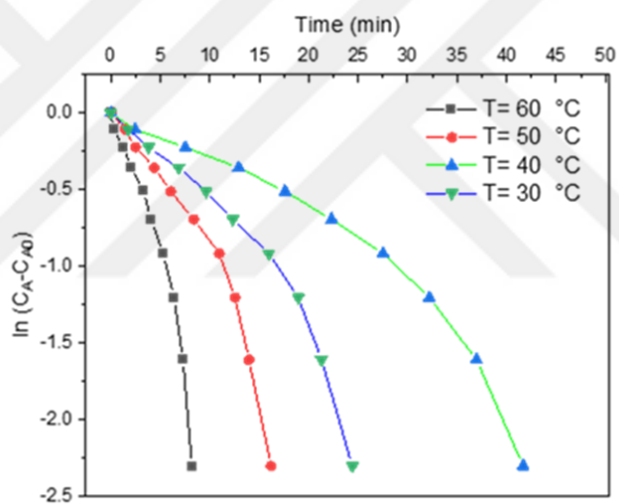


Figure 4.41. Data analysis based on first order reaction kinetics

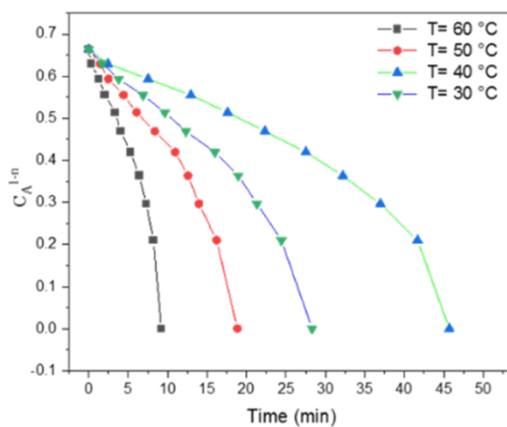


Figure 4.42. Data analyses based on n th-order reaction kinetics

A significant correlation coefficient was obtained from the zero-order kinetic model, approaching a value of 1. In contrast, when applying the first-order reaction kinetic model, a decrease in the regression coefficient was observed, suggesting that the reaction kinetics align between zero and first order. To further refine the results, the nth-order kinetic model was examined, revealing that the most appropriate order was identified as 0.08.

Amirhossein et al. [176] explored the catalytic performance of NiCo/bentonite in the hydrolysis of NaBH_4 , with their findings supporting the presence of a zero-order kinetic reaction. Previous studies have also reported zero-order reaction kinetics associated with the NaBH_4 hydrolysis [177–179].

Table 4.7 presents the rate constant and regression coefficients calculated based on the identified order of 0.08.

Table 4.7. Rate constants and regression coefficients according to zero-order reaction kinetics of 2:2NiCo/rGFO

Temperature (°C)	k(mol/g _{cat} .min)	R ²
30	0.0092	0.990
40	0.015	0.995
50	0.023	0.993
60	0.045	0.995

R² consistently exhibits high values throughout the temperature ranges, varying from 0.99 to 0.995. This indicates that the kinetic model offers a dependable and precise representation of the reaction across all temperatures examined.

By using the Arrhenius equation (Eq.3.9), the activation energy was determined, and the consequences for the 2:2 NiCo/rGFO catalyst are graphically shown in Figure 4.43, in which the activation energy was calculated as 27.31 kJ/mol from the slope of the graph and Eq.3.9. Consequently, NiCo/rGFO can be considered as an effective material for hydrogen production from NaBH_4 .

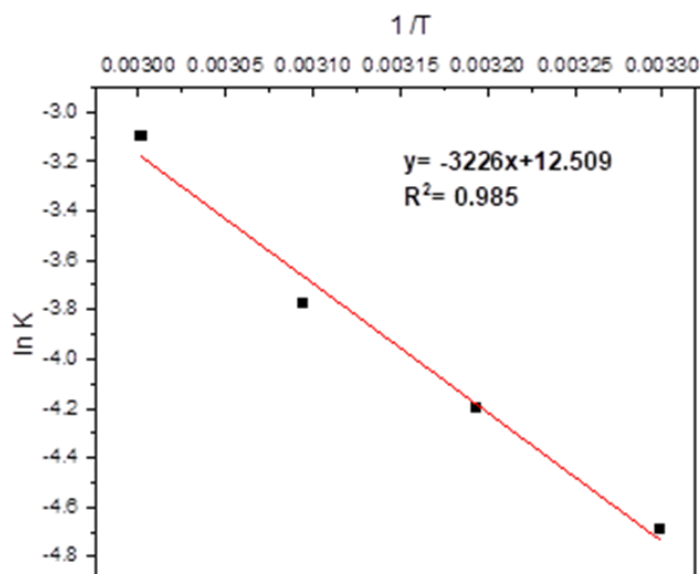


Figure 4.43. Arrhenius plot of 2:2 NiCo/rGFO

Table 4.8. provides a comparative analysis of different catalysts used for hydrolysis of NaBH_4 with current study results.

Table 4.8. Literature comparison results of hydrogen generation rate (HGR) and activation energy (E_a) of the different catalysts

Catalyst	HGR (mL.min.g ⁻¹)	E_a (kJ.mol ⁻¹)	Kinetic order	Ref
NiFe/Carbon	175.00	53.41	---	[180]
NiCo/Nickel	3986.00	38.30	First	[181]
Co/Diaion	221.00	59.42	Zero	[182]
Co/Amberlite	211.00	46.90	Zero	[182]
Ru	55290.00	39.16	---	[181]
$\text{Co}_3\text{C}_3\text{N}_4\text{-TiO}_2$	180.00	58.00	Zero	[183]
Ru-CoP/GO	7200.00	47.70	---	[184]
Ru/CoxP	4550.00	32.80	---	[185]
Co-Fe-B/Cu	10690.30	55.60	First	[186]
Co-Mo/Carbon	1280.80	51.00	---	[187]
CoW/ Al_2O_3	11.82	49.58	Zero	[188]
Co/kaolin	1533.00	49.41	---	[187]
CoCe/carbon	16420.00	48.22	Zero	[189]
CoBi/Carbon	12996.00	42.87	---	[190]
Co Ni/Carbon	740.70	40.70	Zero	[191]
CoSnB/GFO	11272.00	39.57	Zero	[192]
CoZn/Graphene	3580.00	35.92	Zero	[193]

Table 4.8. (continued) Literature comparison results of hydrogen generation rate (HGR) and activation energy (E_a) of the different catalysts

Catalyst	HGR (mL.min.g ⁻¹)	E_a (kJ.mol ⁻¹)	Kinetic order	Ref
CoMoNi/Zeolite	6277.00	35.01	---	[194]
NiCo/bentonite	186.00	37.62	Zero	[176]
2:2 NiCo/rGFO	255.10	27.31	Zero	This study

The current study investigates the NiCo/rGFO catalyst synthesized by the impregnation method, with an HGR of 255.10 mL.min⁻¹. g⁻¹ and an E_a of 27.31 kJ.mol⁻¹. Notably, Ru-0.07 prepared via the freezing-thawing method shows the highest HGR at 55290 mL.min.g⁻¹, indicating exceptional catalytic activity. However, its E_a of 39.16 kJ.mol⁻¹ is not the lowest, suggesting that while it is highly effective in hydrogen production, it requires a moderate amount of energy to initiate the reaction. In contrast, the 2:2 NiCo/rGFO catalyst has an HGR of 255.10 mL.min.g⁻¹ but an impressively low E_a of 27.31 kJ.mol⁻¹, indicating that it requires the least energy to activate the reaction. Catalysts like Ru-0.07 and Ru-Co/GO/Carbon, with very high HGR, are ideal for scenarios requiring rapid hydrogen production but might require more energy input to initiate. NiCo/rGFO has an E_a of 27.31 kJ.mol⁻¹, which is almost half that of other catalysts like Co/Diaion (59.42 kJ.mol⁻¹), CoW/Al₂O₃ (49.58 kJ.mol⁻¹), Co–Ce/carbon (55.6 kJ.mol⁻¹) and Co-Fe-B/Cu (55.6 kJ.mol⁻¹).

On the other hand, catalysts such as 2:2 NiCo/rGFO and NiCo/bentonite, with lower E_a values, might be better suited for conditions where minimizing energy consumption is a priority, even if the hydrogen production rate is slower. The 2:2 NiCo/rGFO catalyst, with its low E_a , presents a compelling option for energy-efficient hydrogen generation, especially in applications where the operating temperature is a limiting factor.

As presented in Table 4.8, most materials displayed zero-order kinetics, which implies that their reaction rates were independent of the concentration. Conversely, only two materials, NiCoP/Nickel and Co-Fe-B/Cu, exhibited first-order kinetics, signifying that their reaction rates were directly related to the concentration of the reactants.

4.4. Mechanism of Electrochemical Hydrogen Storage

A subfield of physical chemistry known as electrochemistry studies the relationship between detectable chemical changes and electrical potential variations. An electrochemical reaction happens when a chemical reaction generates a potential

difference or when a chemical reaction is driven by an electrical potential difference, as in the case of electrolysis or fuel cells. Electrochemical reactions include the flow of electrons across an electrically conducting circuit, in contrast to traditional chemical reactions, which entail the transfer of electrons directly between atoms, ions, or molecules [195].

Electrochemical reactions differ from conventional chemical processes due to this important difference. Reduction-oxidation processes, in which electrons are transferred to or from a molecule or ion to alter its oxidation state, are referred to as "redox" processes. Chemical energy can be released, or an external voltage can be used to start these reactions. The terms oxidation and reduction refer to the oxidation state changes that take place in molecules, atoms, or ions during an electrochemical reaction. If every link between an atom of a different element were entirely ionic, an atom would be assigned a theoretical charge known as its oxidation state. An atom or ion experiences a fall in oxidation state when it gains an electron, whereas an atom or ion losing an electron experiences an increase in oxidation state. For example, sodium gives one electron to the reaction between sodium and chlorine atoms, resulting in an oxidation state of +1. By taking on the electron, chlorine's oxidation state is decreased to -1. Each ion's charge is correlated with the oxidation state's sign (positive or negative). The attraction between the opposite charges of sodium and chlorine forms the ionic connection between them.

The system comprises three electrodes:

- Working Electrode: This electrode is primarily where the electrochemical reactions take place.
- Reference Electrode: An Ag/AgCl electrode filled with a 3 M KCl solution is used as the reference electrode in this configuration. This reference electrode offers a stable and well-defined potential, which is crucial for accurately measuring the potential of the working electrode. Its potential remains consistent throughout the experiment, facilitating reproducible measurements.
- Counter Electrode: The counter electrode is represented by a platinum foil measuring 6 mm × 6 mm. This electrode is essential for completing the electrical circuit, allowing current to flow through the electrochemical cell. Platinum is favoured for its excellent conductivity and resistance to corrosion in various electrolyte environments [196].

The electrochemical properties of the material were investigated through techniques such as CV, GCD, and EIS [197,198]. In addition to recognizing oxidation peaks, the quantification of hydrogen stored within a sample through peak integration serves as a direct indicator of hydrogen content. This method establishes a connection between the charge transferred during oxidation and the quantity of hydrogen liberated. Alternatively, the assessment of discharge potential provides a practical means to evaluate hydrogen storage capacity. The discharge capacity, which indicates the total charge a material can provide during hydrogen release, is directly related to the hydrogen stored within the material. By examining the discharge curves, researchers can obtain valuable insights into the efficiency of hydrogen release and the kinetics of storage, thereby enhancing the understanding of the material's hydrogen storage characteristics alongside peak integration techniques.

Volmer, Tafel, and Heyrovsky reactions are the three main reactions that determine the mechanisms that control electrochemical hydrogen storage. These mechanisms explain how hydrogen atoms adsorb, diffuse over surfaces, and recombine. The charge transfer at the electrode/electrolyte interface, shown by the Volmer reaction, is the first step.



Where, M represents the synthesized material located on the working electrode, while MH_{abs} and MH_{ads} denote the processes of atomic hydrogen absorption and adsorption occurring on the metal surface, respectively.

Concurrently, a Tafel reaction takes place, during which two adsorbed hydrogen atoms combine to produce gaseous hydrogen. The conversion of adsorbed hydrogen to gaseous hydrogen is illustrated by the Tafel equation (Eq. 4.3).



The dissociation of water molecules, as described in the Heyrovsky reaction (Eq.4.4), can result in the formation of hydrogen molecules.



4.4.1. Cyclic voltammetry

CV plays a significant role in several key areas for hydrogen storage applications. Firstly, it aids in the characterization of materials by assessing their electrochemical properties, particularly their capacity to adsorb and desorb hydrogen. The peaks observed in the CV curves signify the potentials at which hydrogen adsorption and desorption occur. Secondly, a CV is crucial for performance evaluation. By analysing the integrated area beneath the CV curves, researchers can quantify the amount of hydrogen that is stored and released, thereby indicating the material's storage capacity. Additionally, a CV is employed in the determination of optimal conditions for hydrogen storage, including the ideal potential range and scan rate, which are essential for enhancing storage efficiency. Lastly, CV offers insights into the kinetics associated with hydrogen adsorption and desorption, facilitating the identification of rate-limiting steps and the enhancement of the material's overall performance. These contributions of CV are essential for advancing hydrogen storage technologies.

The response of materials in CV is assessed at a designated scan rate within a defined potential range. Conducting multiple cycles facilitates the accurate determination of redox peaks. The maximum reduction current signifies hydrogen evolution, whereas the reverse scan displays an oxidation peak associated with the electrochemical behaviour of the material. By integrating these peaks, one can ascertain the charge stored in the sample, with the oxidation peak being directly linked to the hydrogen storage capacity.

Figure 4.44 shows CV of a) GF; b) GFO; c) graphite; d) GFP at different scan rates of 25-200 mV/s and 5 cycles.

In the CV graph, increasing the scanning rate from 25 to 200 mV/s results in a significant increase in current density. This trend, where the CV curve retains a similar profile even at higher scan rates, signifies the exceptional rate performance of the electrodes. The consistent profile indicates that the electrodes possess rapid electron transfer kinetics, implying that the electrochemical reactions at the electrode surface are not significantly obstructed by the increased scan rate. Additionally, this behaviour suggests effective diffusion control, allowing electroactive species to reach the electrode surface promptly enough to keep pace with the heightened scan rate. This characteristic also points to favourable capacitive properties, enabling the electrodes to rapidly store

and release charge, which is vital for applications such as supercapacitors and batteries. The outstanding rate performance indicates that the electrodes can operate efficiently under a wide range of conditions, making them suitable for various electrochemical applications. Furthermore, the retention of the CV curve shape at elevated scan rates suggests that the electrochemical reactions are reversible, indicating that the electrodes can undergo numerous cycles without significant deterioration.

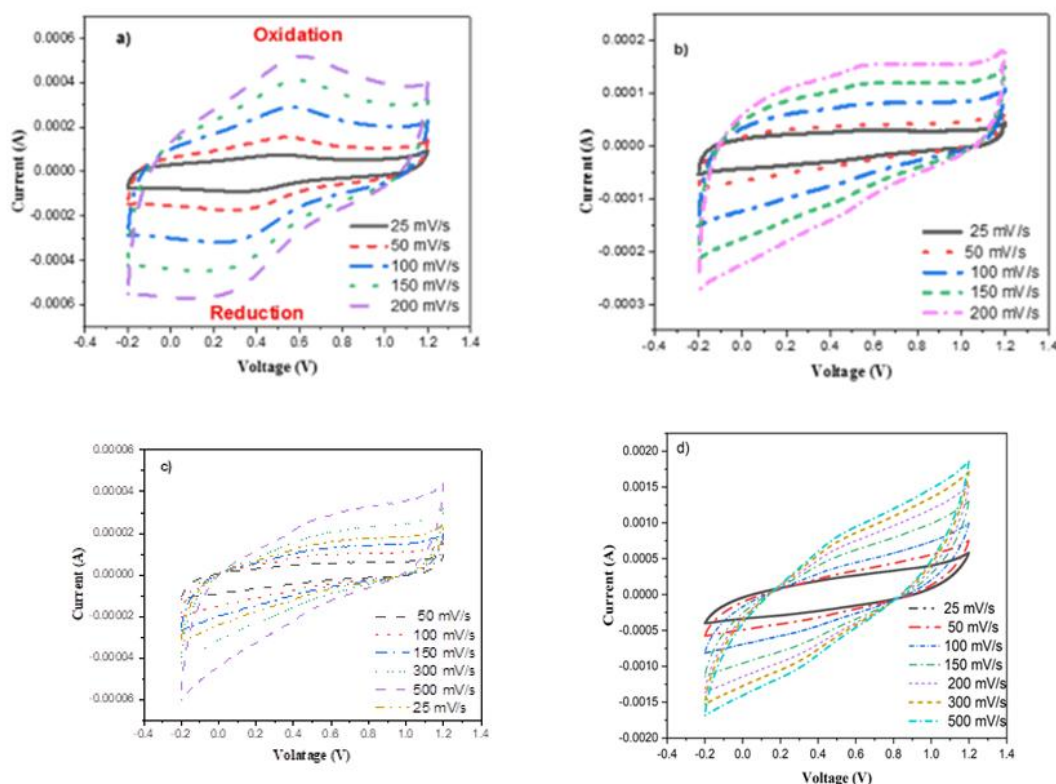


Figure 4.44. CV of a) GF; b) GFO; c) graphite and d) GFP-4 after washing at different scan rates in 0.5 H_2SO_4

The faradaic peaks identified in the oxidation and reduction regions are linked to the adsorption and desorption of hydrogen ions, as illustrated in Figure 4.44.a. This observation implies that during the oxidation phase, hydrogen ions adhere to the electrode surface, whereas in the reduction phase, these ions are released. In contrast, the CV curves of GFO do not exhibit any faradaic peaks. The lack of these peaks indicates that GFO does not significantly promote redox reactions involving hydrogen ions. To improve the electrochemical performance of GFO, a prevalent strategy is to deposit metals onto its

surface. This approach has been extensively investigated and has been shown to enhance the electrochemical properties of GFO, as evidenced by references [199–202].

Research on GFO has consistently reported the absence of Faradaic peaks in CV curves, confirming that this finding is a common trend across various studies [75,131,203–205]. Figure 4.44.b presents a quasi-rectangular curve, which is attributed to the limited kinetic penetration of electrolyte ions and the compact layered structure of GFO. This quasi-rectangular profile indicates that the electrochemical behaviour of GFO is primarily governed by capacitive processes rather than Faradaic reactions [78, 79].

In the case of GF, the cathodic peak observed in the CV curve is related to the liberation of hydrogen atoms resulting from the breakdown of water. This suggests that during the reduction phase, water molecules undergo reduction, resulting in the release of hydrogen atoms. Conversely, the anodic peak corresponds to the release of previously adsorbed hydrogen, as described by Eq.4.5. This indicates that during the oxidation phase, hydrogen atoms that were adsorbed onto the electrode surface are released [76, 77].

A research team led by Cassandra et al. [208] synthesized Pd-Cd nanostructures with varying cadmium concentrations (0-20%) on a titanium substrate through the hydrothermal reduction technique. To investigate hydrogen adsorption and desorption, CV experiments were performed within a voltage range of -200 to 400 mV at a scan rate of 20 mV/s. The total hydrogen storage capacity was determined by analysing the integrated area in the anodic region. The highest hydrogen desorption charges were observed within the 10-15% cadmium concentration range. Notably, as the cadmium content increased from 0 to 15%, there was a reduction in the crystalline structure, while the BET surface area experienced a significant increase, indicating an enhancement in hydrogen sorption.

CV curves of 1:1 NiCo/rGFO, 1:2 NiCo/rGFO, 2:1 NiCo/rGFO, and 2:2NiCo/rGFO at different scan rates (25-500 mV/s) in 0.5 M H₂SO₄ are indicated at Figure 4.45.

Loading varying metal ratios onto GO leads to additional peaks in the CV curve. Faradiac peaks in various NiCo/rGFO ratios show that metal has been successfully loaded onto GO. An increase in the metal ratio correlates with a more distinct Faradaic peak, signifying an improvement in electron transfer and elevated electrochemical activity. This observation implies that a higher metal content enhances the efficiency of the

NiCo/rGFO, presumably due to an increased number of active sites available for redox reactions.

Prior research indicates that the integral value of the oxidation peak can be employed to determine hydrogen storage capacity (HSC) [209]. Equation 4.5 presents a method for calculating the area under the CV curves.

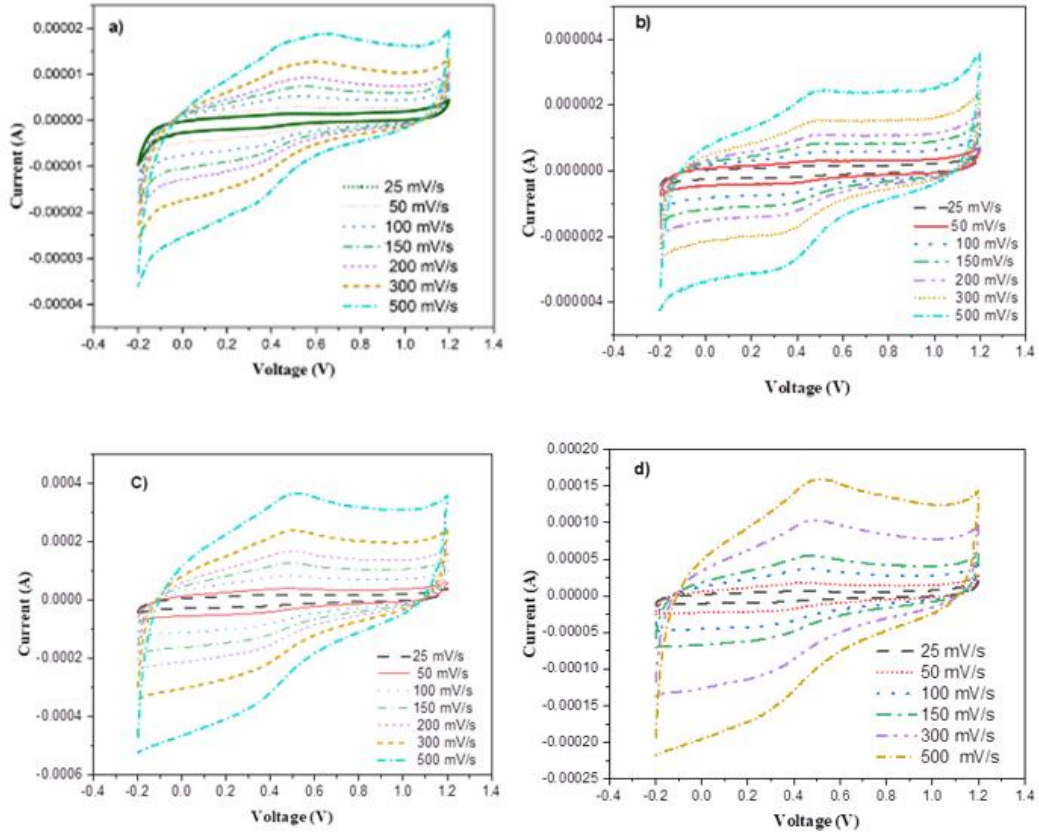


Figure 4.45. CV curves of a) 1:1 NiCo/rGFO; b) 1:2 NiCo/rGFO; c) 2:1 NiCo/rGFO; d) 2:2NiCo/rGFO at different scan rates (25-500 mV/s) in 0.5 M H₂SO₄

$$A = \frac{1}{v} \int_{0.13}^{0.859} (I - I_{dl}) dE \quad (4.5)$$

Where v is the scan rate, I , I_{dl} and dE are currents of reduction peak, double layer charging, and the potential charge, respectively.

The specific capacitance of synthesized samples was calculated according to Eq.4.6 [2].

$$C_p = \frac{A}{2 v. M. \Delta V} \quad (4.6)$$

Where C_p , A , ΔV (V), v , and M (g) are the specific capacitance, integral area of the cyclic voltammogram loop, potential window, scanning rate ($V.s^{-1}$) and M mass of the electrode materials respectively. Table 4.9 indicates C_p results at different scan rates. An example calculation using Origin Pro, of the area under anodic peak is given in App-1.

Table 4.9. Specific capacity (C_p) calculation from CV curve by origin pro software

Sample	v (mV/s)	C_p (mAh.g ⁻¹)
GF	25	20
GF	50	125
GF	100	144
GF	150	200
GF	200	236
1:1NiCo/rGFO	25	17.98
1:1NiCo/rGFO	50	23.48
1:1NiCo/rGFO	100	39.13
1:1NiCo/rGFO	150	46.88
1:1NiCo/rGFO	300	62.27
1:1NiCo/rGFO	500	79.96
2:2NiCo/rGFO	25	56.58
2:2NiCo/rGFO	50	89.65
2:2NiCo/rGFO	100	140.83
2:2NiCo/rGFO	150	155.83
2:2NiCo/rGFO	200	198.33
2:2NiCo/rGFO	300	251.11
2:2NiCo/rGFO	500	297.75
2:1NiCo/rGFO	25	26.99
2:1NiCo/rGFO	50	31.78
2:1NiCo/rGFO	100	43.54
2:1NiCo/rGFO	150	74.31
2:1NiCo/rGFO	200	97.32
2:1NiCo/rGFO	300	114.21
2:1NiCo/rGFO	500	156.80
1:2NiCo/rGFO	25	14.39
1:2NiCo/rGFO	50	27.54
1:2NiCo/rGFO	100	38.45

Table 4.9. (Continued) Specific capacity (C_p) calculation from CV curve by origin pro software

Sample	v (mV/s)	C_p (mAh.g ⁻¹)
1:2NiCo/rGFO	200	48.43
1:2NiCo/rGFO	300	71.67
1:2NiCo/rGFO	500	86.93

The overall performance of the NiCo/rGFO electrode increases with the NiCo content in the sample, with 2:2 NiCo/rGFO showing the best performance. This may be due to increased active sites and improved conductivity provided by a higher NiCo content. Moreover, as the scan rate increases, the C_p increases for all the samples. This trend is expected, as higher scan rates lead to faster electrode transfer processes, which result in higher currents.

Table 4.10. indicates comparison of hydrogen storage capacity of current study with literature.

Table 4.10. Comparison of hydrogen storage capacity of current study with literature

Sample	Structure	Electrolyte	C_p (mAh.g ⁻¹)	Ref
Co/carbon	Tube like	KOH	149	[210]
Cobalt alloy	---	KOH	300	[211]
AlMgAlNi	Hierarchical cubic	KOH	166	[212]
Co/graphene	Flowerlike	KOH	250	[213]
Fe ₂ O ₃ /EuVO ₄ /C ₃ N ₄	----	KOH	262	[214]
GFO	----	KOH	45	[215]
Pd/GFO	----	H ₂ SO ₄	88	[216]
Mg _{1.5} Al _{0.5} Ni	hollow spiny shell	KOH	166	[217]
Mg ₃ GeNi	---	KOH	64	[218]
2:2NiCo/rGFO	Sponge like	H₂SO₄	298	This study

The 2:2NiCo/rGFO sample demonstrates the highest capacity of 298 mAh.g⁻¹ using H₂SO₄ as the electrolyte. The second-best performing material after 2:2NiCo/rGFO was Fe₂O₃/EuVO₄/C₃N₄ with 262 mAh.g⁻¹ capacity. GFO shows poor performance (45 mAh.g⁻¹) due to the low conductivity.

Energy storage materials can be divided into three types based on their cyclic voltammetry profiles [219]. Type A represents capacitive behaviour with rectangular

cyclic voltammograms, characteristic of materials like electrical double-layer capacitors (EDLCs), which store charge via non-Faradaic processes. Type B materials exhibit pseudocapacitive behaviour involving intercalation mechanisms, as seen in the broadened peaks in their voltammograms. For example, intercalation without significant redox activity is typical of materials like Nb_2O_5 , while intercalation combined with partial redox activity reflects a more complex charge storage mechanism. In contrast, Type C materials show faradaic-dominated behaviour, evident in sharp redox peaks, which are typical of battery-like systems. These include materials with reversible redox peaks or those that exhibit distinct anodic and cathodic peaks, characteristic of rechargeable batteries. The progression from Type A to Type C reflects a shift from capacitive to faradaic-dominated mechanisms, corresponding to increasing charge-storage capacities and reaction complexities. In the current study, GFP-4, graphite, and GFO exhibit capacitive behaviour, whereas other samples behave more like pseudocapacitors. Functionalizing GFO with different types of metals such as MgCo_2O_4 [211], Fe [212], Au [213], CeO_2 [214], Ni [215], Pt [216], Zn [217] and Cu [218] improves its faradaic behaviour. At the same time, the surface area of GFO will increase due to the added metals, which play a role in accelerating the electron transfer.

Figure. 4.46 indicate plot I_p vs square root of scan rate.

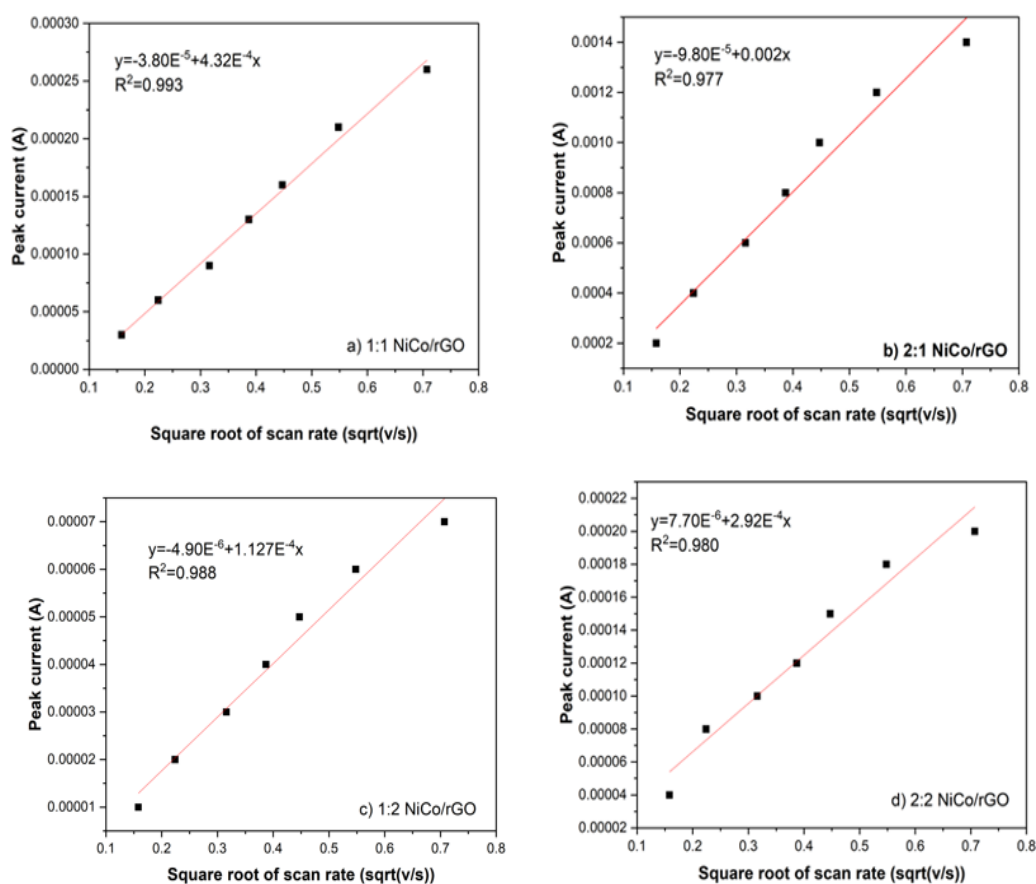


Figure 4.46. Plot I_p vs square root of scan rate a) 1:1 NiCo/rGFO, b) 2:1 NiCo/rGFO, c) 1:2 NiCo/rGFO, d) 2:2 NiCo/rGFO

Regarding reversibility, the CV plot can be classified into reversible, quasi-reversible, and irreversible [211]. The research by Haji et al. investigated the quasi-reversibility trend by analysing the linear relationship observed in the plot I_p vs. square root of scan rate [111]. All the current synthesized graphene-based material demonstrates quasi-reversible characteristics since the straight-line slope is obtained (Figure 4.47).

Figure. 4.47 shows plot of $\text{Log}(I_p)$ vs $\text{Log}(v)$.

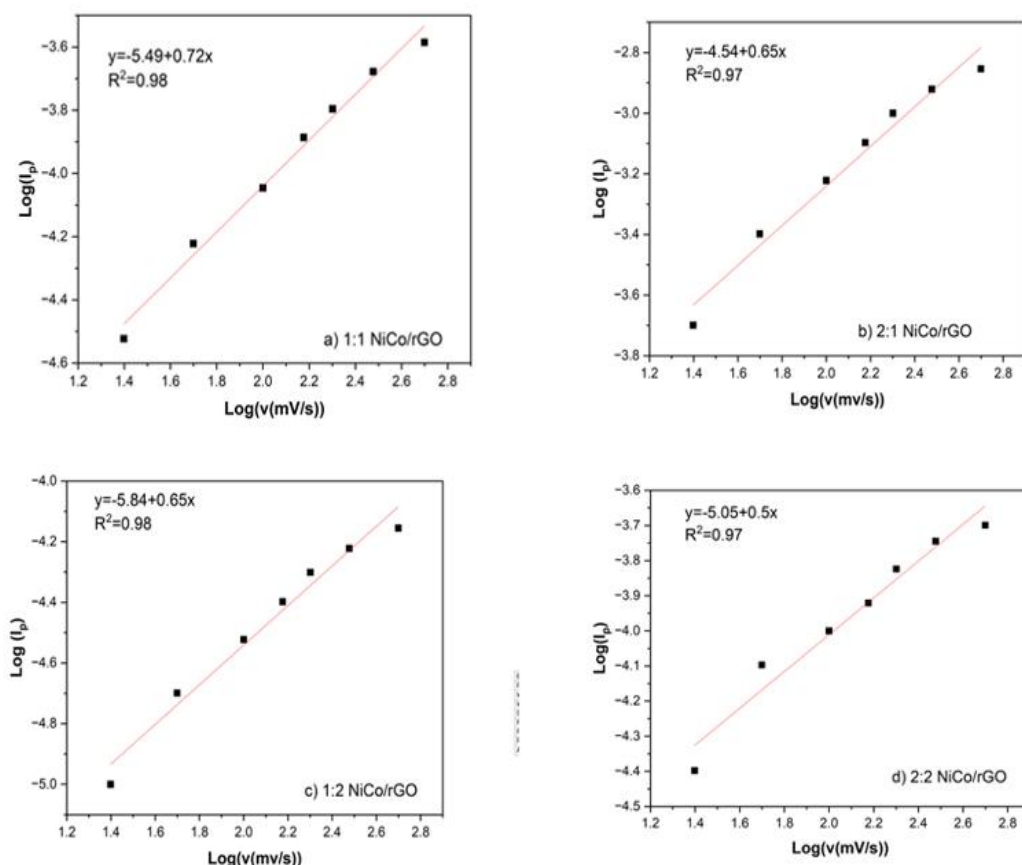


Figure 4.47. Plot of $\text{Log}(I_p)$ vs $\text{Log}(v)$; a) 1:1 NiCo/rGFO, b) 2:1 NiCo/rGFO, c) 1:2 NiCo/rGFO, d) 2:2 NiCo/rGFO

The Dunn method distinguishes between surface-capacitive and diffusion-controlled processes in electrochemical studies by plotting $\log(I_p)$ vs $\log(v)$ [111]. All the plots in Figure 4.47 suggest a diffusion-controlled mechanism.

4.4.2. Galvanostatic charge-discharge

The GCD method plays a pivotal role in EHS, serving several key functions. Firstly, it allows for capacity assessment by measuring the amount of charge stored and released during the charge-discharge cycles, which directly correlates to the hydrogen storage capacity of the material. Secondly, GCD is instrumental in evaluating cycle durability, providing insights into the stability and longevity of hydrogen storage materials over repeated cycles, a crucial factor for practical applications. Additionally, GCD aids in kinetic investigation, offering insight into the rates of hydrogen absorption and desorption, thus shedding light on the kinetics of these processes. Lastly, through the analysis of voltage profiles during the charging and discharging phases, GCD

facilitates efficiency analysis, helping to determine the overall efficiency of the hydrogen storage materials [220–222].

Figure 4.48 indicates GCD results of GF, GFO, 1:1 NiCo/rGFO, and 1:2 NiCo/rGFO.

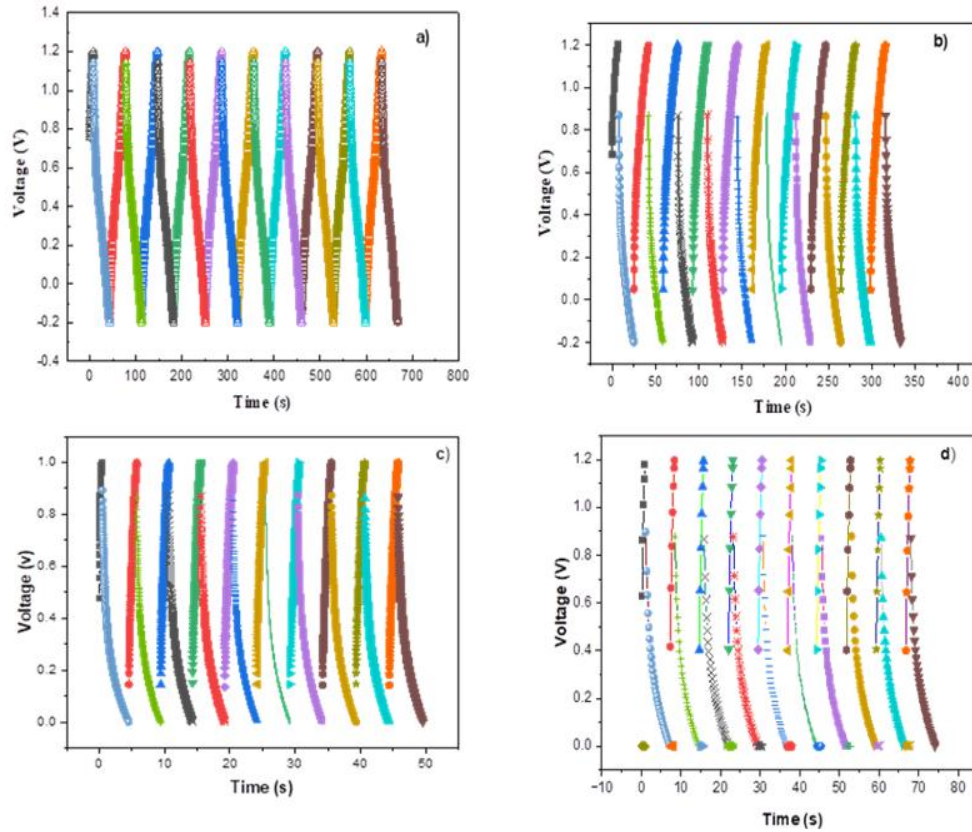


Figure 4.48. GCD curves of a) GF; b) GFO in 0.5 H₂SO₄ electrolyte c) 1:1NiCo/rGFO; d) 1:2NiCo/rGFO

The specific capacity (Q) can be calculated from GCD curves using Eq. 4.7.

$$Q(F.g^{-1}) = \frac{I \times \Delta t}{m \times v} \quad (4.7)$$

Where Δt represents the discharge duration, I denote the current density, v signifies the scan rate, and m refers to the active mass.

To determine the gravimetric storage capacity (wt%), one must multiply 3.6 by Q and subsequently divide this result by the sum of the product of 3.6 and Q along with 1 [210].

$$wt(\%) = \frac{3.6 Q}{3.6 Q + 1} \quad (4.8)$$

Coulombic efficiency ($\eta\%$) was derived based on Eq.4.9, facilitating the performance evaluation and the maintenance of quality control [223].

$$\eta = \frac{t_d}{t_c} \times 100 \quad (4.9)$$

Table 4.11. Data obtained from GCD of graphene-based materials

Sample	Specific capacity (Q) (F/g)	Gravimetric storage capacity (wt %)	Coulombic efficiency (η) (%)
GF	200	0.99	100
GFO	25	0.98	50
1:1NiCo/rGFO	43	0.99	60
1:2NiCo/rGFO	72	0.99	80

Table 4.11 indicates introducing NiCo into GO significantly enhances specific capacity performances. The GF sample demonstrates the highest specific capacity of 200 F/g, signifying its exceptional electrochemical performance in comparison to the other samples. Among the various NiCo/rGFO electrodes, the sample with a 1:2 ratio of NiCo/rGFO shows a notable specific capacity of 72 F/g, surpassing the 1:1 NiCo/rGFO's capacity of 43 F/g and the GFO's capacity of 25 F/g. η demonstrates an upward trend as the NiCo loading ratio in the composites increases, with 1:1 NiCo/rGFO exhibiting 60% efficiency, while 1:2 NiCo/rGFO shows an efficiency of 80%.

Bordbar et al. [224] investigated the hydrogen storage capacity of a CNT/TiO₂-Co nanocomposite electrode synthesized via electrophoretic deposition. They compared three electrodes of CNT, CNT/TiO₂, and MWCNT/TiO₂-Co, measuring their discharge capacities at a current density of 133 mA/g. The MWCNT/TiO₂-Co electrode exhibited the highest discharge capacity of 187 mAh.g⁻¹, highlighting the significant role of cobalt in enhancing discharge capacity. The study found that pure carbon nanotubes had lower discharge capacity due to less hydrogen oxidation, while TiO₂ nanoparticles improved

electrochemical activity. Cobalt nanoparticles further enhanced discharge capacity by providing redox sites for hydrogen storage.

4.4.3. Electrochemical impedance spectroscopy

In the EIS analysis of graphene-based materials, the Nyquist plot serves as a visual representation of impedance data, typically illustrated as a semicircle in the high-frequency domain and a linear segment in the low-frequency domain. The semicircle is indicative of charge transfer resistance (R) at the interface between the electrode and electrolyte, whereas the linear portion signifies Warburg impedance (W), which reflects limitations in ion diffusion. The equivalent circuit model $R(CR)W$ facilitates the examination of these electrochemical phenomena. Within this model, R_s denotes the resistance of the solution, representing the electrolyte's resistance. C refers to the double-layer capacitance established at the interface of the electrode and electrolyte. R represents the resistance between the reference and working electrodes, typically linked to charge transfer resistance. W characterizes the ion diffusion within the electrolyte, which influences the performance of the electrode, especially in energy storage applications such as batteries and supercapacitors (Table 4.12).

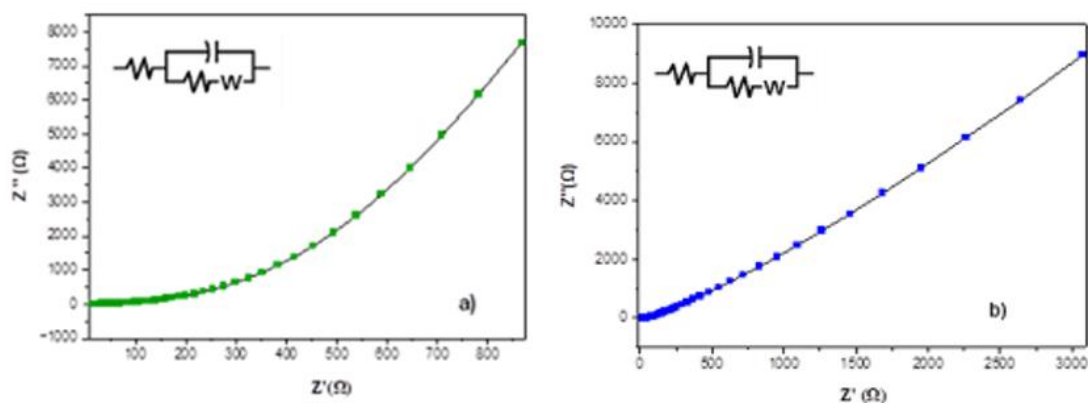


Figure 4.49. Nyquist diagram of the samples a) GF; and b) GFO with $R(CR)W$ equivalent circuit model

By employing Z-View software to fit the EIS data, essential resistive and capacitive characteristics of the materials can be derived and compared across various samples. This process enables the analysis of interfacial mechanisms and the identification of resistive and diffusive factors that affect electrochemical performance.

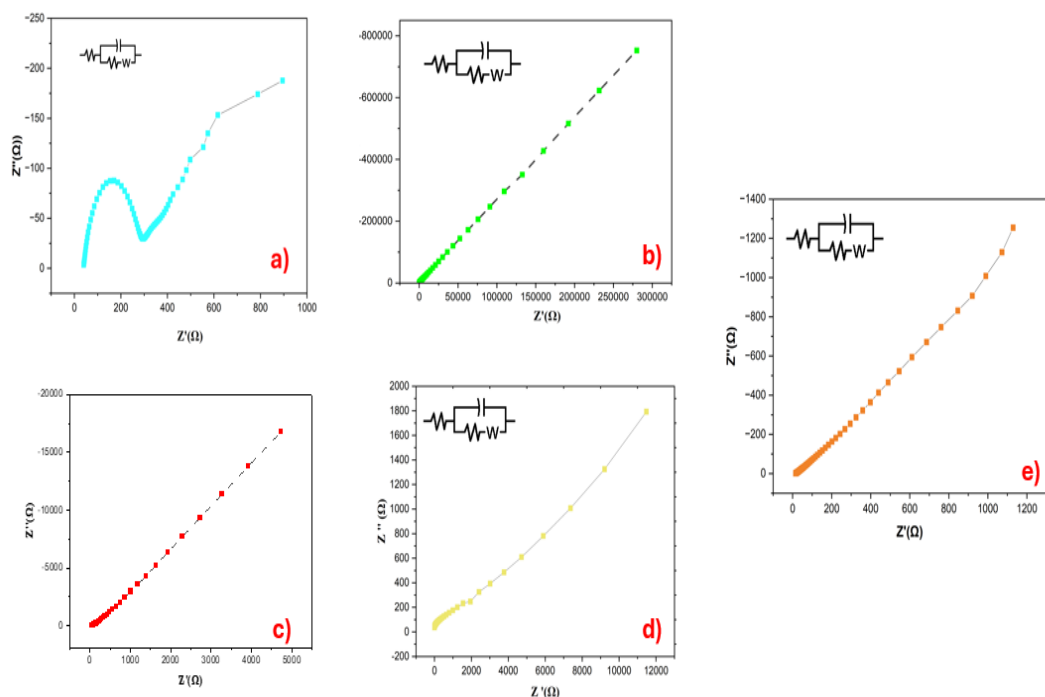


Figure 4.50. EIS result of a) GO; b) 2:1NiCo/rGFO; c) 1:2 NiCo/rGFO; d) 1:1 NiCo/rGFO; e) 2:2 NiCo/rGFO

Table 4.12. $R(CR)W$ Circuit presents the modelling outcomes of GF and GFO using the ZSimpWin tool

	R_s (Ω)	C_{dl} (F)	R (Ω)	W ($\Omega \cdot \text{cm}^2$)
GF	15.44	$1.42 \cdot 10^{-4}$	0.0022	0.0009
GO	32.05	$14.87 \cdot 10^{-6}$	17.800	0.0080
GFO	25.64	$9.98 \cdot 10^{-6}$	0.0036	0.0004
1:1 NiCo/rGFO	24.50	$1 \cdot 10^{-5}$	0.9900	8.6200
1:2 NiCo/rGFO	18.66	$1.30 \cdot 10^{-5}$	0.8099	0.0062
2:1 NiCo/rGFO	6.79	$3.55 \cdot 10^{-4}$	0.0240	0.0006
2:2 NiCo/rGFO	4.62	3.96 *	0.0001	0.0005

From Table 4.12 the 2:2 NiCo/rGFO electrode stands out due to its exceptionally low R_s of 4.62 Ω and a moderate R of 0.0001 Ω . In contrast, GO and GFO exhibit significantly higher resistances, underscoring their comparatively weaker performance when used independently. These results highlight the synergistic effect of the NiCo combination with GFO, which enhances electrical conductivity and facilitates charge transfer.

5. MATLAB CODE FOR REDOX REACTION RATE CALCULATION

CV graph can help to investigate the kinetic study of the redox reactions at the electrode/electrolyte interface.

The determination of the heterogeneous electron transfer rate constant (k_0) and the reaction rate offers an essential understanding of the kinetics and effectiveness of the electrochemical process being examined. A high k_0 suggests that the electrode surface has strong catalytic capabilities and low resistance to charge transfer. This parameter defines the rate at which the redox reaction takes place under equilibrium conditions. Figure 5.1 indicates MATLAB step of calculating the reaction rate.

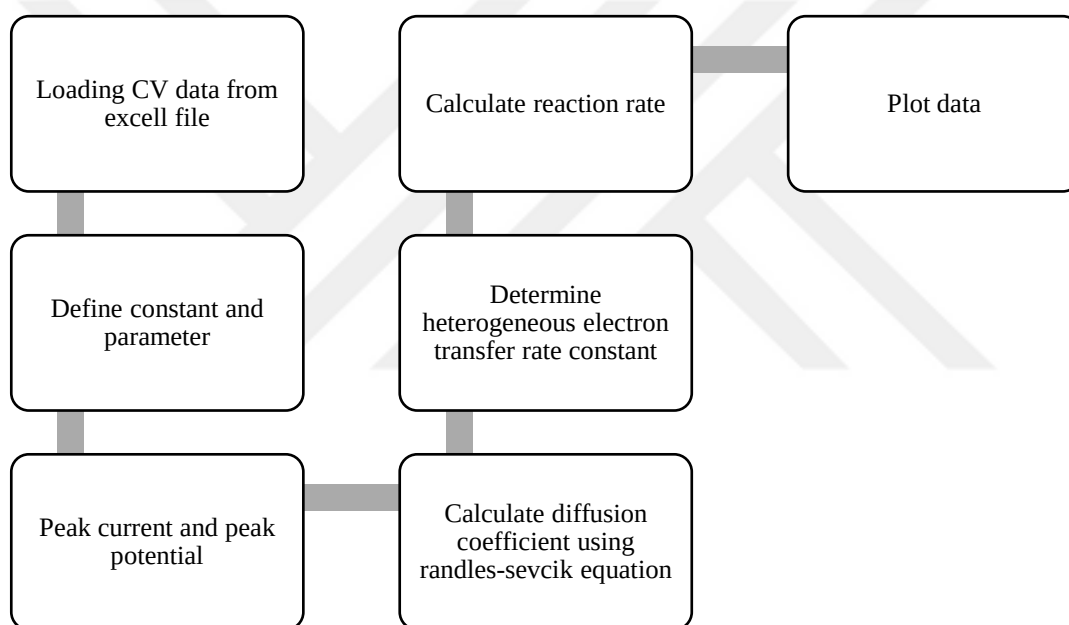


Figure 5.1. Step by step MATLAB calculation of reaction rate

A CV graph is obtained by recording the current at the working electrode as the potential is linearly varied in both the forward and reverse directions. Figure 5.2 illustrates the reaction that occurs between the electrode and the electrolyte for a single electron in CV analysis [225].

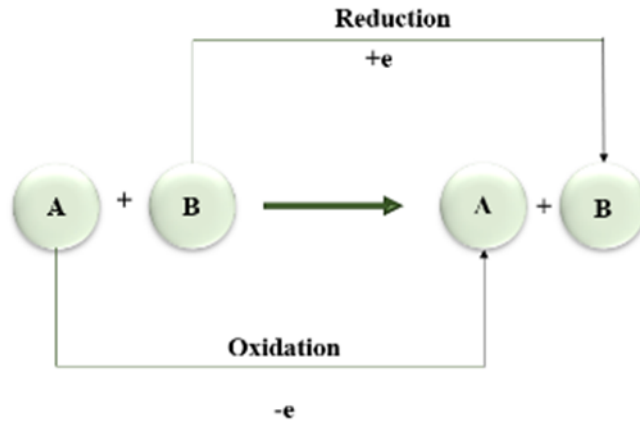


Figure 5.2. Oxidation and reduction process

The Randles-Sevcik equation (Eq. 5.1) was applied to calculate the diffusion coefficient, which measures the diffusion rate.

$$I_p = 2.69 \times 10^5 \cdot n^{3/2} \cdot A \cdot C_0 \cdot D^{1/2} \cdot \nu^{1/2} \quad (5.1)$$

Where I_p , n , A , C_0 , D and ν are peak current (A), number of electrons transferred in the redox reaction, electrode surface area (cm^2), concentration of electroactive species (mol/cm^3), diffusion coefficient (cm^2/s), and scan rate (V/s), respectively.

Nicholson equation was applied to estimate k_0 , which measures the speed of the electron transfer reaction at the electrode. Eq. 5.2 illustrates Nicholson's equation [226,227].

$$k_0 = f(\Delta E_p) \cdot \frac{n}{F \cdot \sqrt{D \cdot \nu}} \quad (5.2)$$

Where F is Faraday's constant (96485 C/mol), D is diffusion coefficient (cm^2/s), f is dimensionless functional, and ν is scan rate (V/s).

For simplicity, the current MATLAB code applied an approximation of Nicholson's method to calculate k_0 , assuming a single ΔE_p value.

Additionally, Lavagnini equation can be used to calculate k_0 , according to Eq.5.3 and 5.4 [228].

$$\psi = k_0 [\pi D n F n / RT]^{1/2} \quad (5.3)$$

$$\psi = (-0.6288 + 0.0021X)/(1 - 0.017X) \quad (5.4)$$

Where ψ is a dimensionless parameter. Electron transfer rate can be obtained by Eq. 5.5.

$$\text{Reaction Rate} = k_0 \cdot C_0 \quad (5.5)$$

MATLAB R2024b software was used to calculate the reaction rate. The MATLAB code for the Nicholson method is provided in App-2, while the code for the Lavagnini method is in App-3. Figure 5.3 shows the MATLAB running and the obtained results for the GF sample at a scan rate of 25 mV/s.

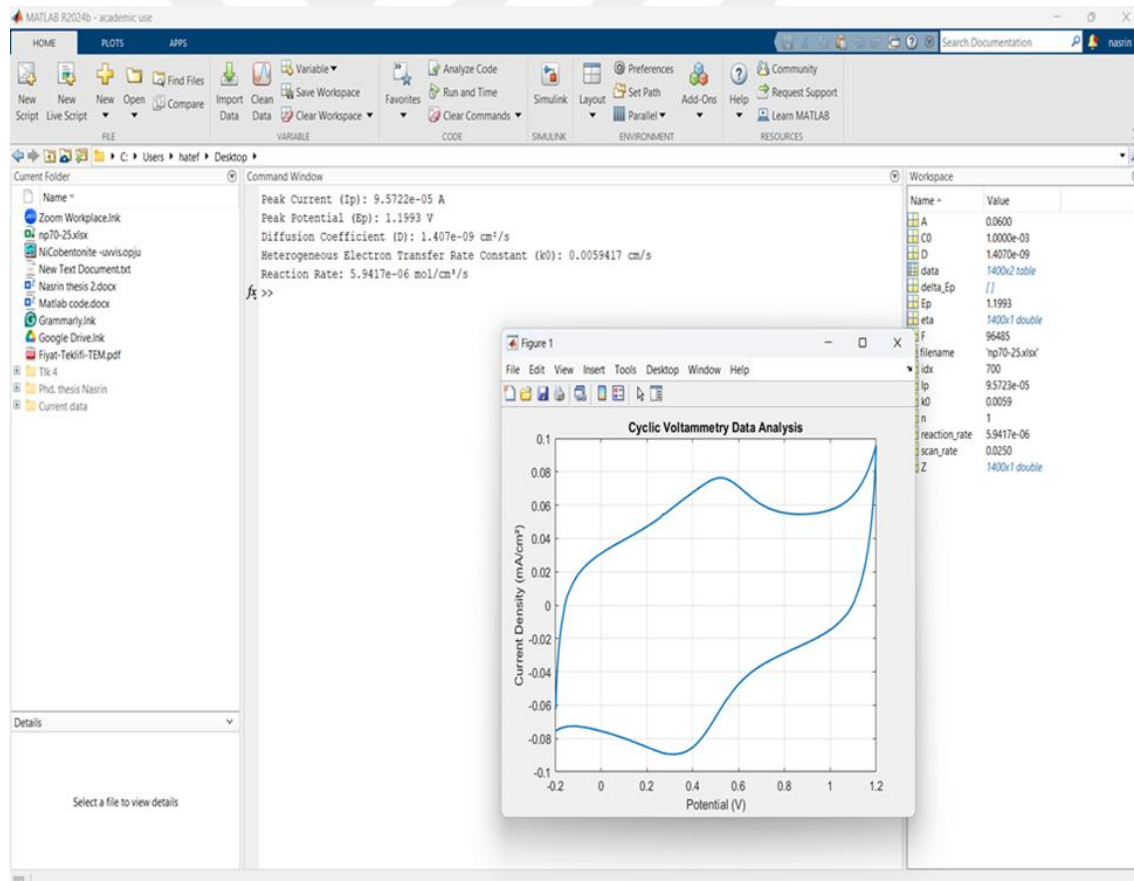


Figure 5.3. Example of running MATLAB code for GF sample at scan rate of 25 mV/s in Nicholson method

Table 5.1. MATLAB calculation result using Nicholson equation

Sample	I_p (A)	D (cm ² /s)	k_0 (cm/s)	Reaction Rate (mol/cm ³ .s)
Graphite	5.26×10^{-7}	4.2484×10^{-14}	1.0813	1.0813×10^{-6}
GFO	0.000135	2.7985×10^{-9}	0.004213	4.213×10^{-6}
GF	4.9458×10^{-5}	3.756×10^{-5}	0.0115	1.15×10^{-5}
GFP-4	9.5722×10^{-5}	1.407×10^{-9}	0.0059417	5.9417×10^{-6}
1:1NiCo/rGFO	5.42×10^{-5}	4.5108×10^{-10}	0.010494	1.0494×10^{-5}
2:1NiCo/rGFO	3.29×10^{-5}	1.6621×10^{-10}	0.017287	1.7287×10^{-5}
1:2NiCo/rGFO	4.37×10^{-5}	2.9323×10^{-10}	0.013015	1.3015×10^{-5}
2:2NiCo/rGFO	9.6494×10^{-6}	1.4297×10^{-5}	0.058942	5.8942×10^{-5}

Table 5.1. provides a comparative result of kinetic properties for graphene-based materials from the Nicholson equation. I_p , an indicator of electrochemical activity, is highest for GFO, suggesting a strong redox. The D is notably highest for GF, indicating superior ion transport. In contrast, the NiCo/rGFO samples, such as 1:1 and 1:2 ratios, exhibit lower D values. k_0 and reaction rate further emphasize the catalytic efficiency of the materials. The highest reaction rate was demonstrated by 2:2 NiCo/rGFO and a relatively high k_0 , reflecting its excellent performance, which surpasses the other samples. Additionally, graphite exhibits the lowest I_p and D , suggesting limited catalytic application in these conditions. Due to its high diffusion and reaction kinetics, the 2:2 NiCo/rGFO composite is the most effective material overall and a promising candidate for CV analysis.

As shown in Table 5.2, the kinetics properties of CV data were computed using MATLAB code for the Lavagnini method.

Table 5.2. MATLAB calculation result using Lavagnini method

Sample	ΔE_p (v)	D (cm ² /s)	k_0 (cm/s)	Reaction Rate (mol/cm ³ .s)
graphite	1.4	4.24×10^{-14}	5.64×10^{-8}	5.64×10^{-11}
GFO	0	1.42×10^{-11}	4.15×10^{-6}	4.15×10^{-9}
GF	0	1.66×10^{-10}	1.41×10^{-5}	1.41×10^{-8}

Table 5.2. (Continued) MATLAB calculation result using Lavagnini method

Sample	ΔE_p (v)	D (cm ² /s)	k_0 (cm/s)	Reaction Rate (mol/cm ³ .s)
GFP-4	0.88	1.40×10^{-9}	1.16×10^{-5}	1.16×10^{-8}
1:1NiCo/rGFO	0.874	2.79×10^{-9}	1.64×10^{-5}	1.64×10^{-8}
1:2 NiCo/rGFO	0	2.93×10^{-10}	1.88×10^{-5}	1.88×10^{-8}
2:1 NiCo/rGFO	0	3.75×10^{-10}	2.13×10^{-5}	2.13×10^{-8}
2:2 NiCo/rGFO	0	4.51×10^{-10}	2.33×10^{-5}	2.33×10^{-8}

5.1. Comparison Between Nicholson and Lavagnini MATLAB Code Results

The comparison between Nicholson and Lavagnini MATLAB Code Results is indicated in Table 5.3.

Table 5.3. Comparison Between Nicholson and Lavagnini MATLAB Code Results

Sample	Nicholson k_0 (cm/s)	Lavagnini k_0 (cm/s)
Graphite	1.0813	5.64×10^{-8}
GFO	0.004213	4.15×10^{-6}
GF	0.0115	1.41×10^{-5}
GFP-4	0.0059417	1.16×10^{-5}
1:1NiCo/rGFO	0.010494	1.64×10^{-5}
2:1NiCo/rGFO	0.017287	2.13×10^{-5}
1:2NiCo/rGFO	0.013015	1.88×10^{-5}
2:2NiCo/rGFO	0.058942	2.33×10^{-5}

Generally, Nicholson's method predicts a higher k_0 value compared to the Lavagnini method. However, both methods rank the catalysts in a similar order of activity, with 2:2 NiCo/rGFO showing the best performance and graphite exhibiting the poorest performance.

Pawet et al. [226] obtained k_0 for graphene, which was synthesized by epitaxial growth on SiC to be 0.05 cm/s by the Nicholson equation, which is fairly close to the results of Table 5.1. Glassy carbon electrodes exhibit a k_0 of 1.45×10^{-4} for ferrocene and 9.30×10^{-2} for superoxide, reflecting notable variation depending on the species [229,230]. A micro-fabricated iridium electrode achieves a high k_0 of 7.39×10^{-2} with

potassium ferricyanide [231], while a flexible graphite electrode shows a moderate k_0 of 1.72×10^{-3} for hexamine-ruthenium(III) chloride [232]. Monolayer CVD graphene demonstrates a comparable k_0 of 1.81×10^{-3} with N'-tetramethyl-p-phenylenediamine [233]. Platinum, a standard reference electrode, yields a k_0 of 1.58×10^{-3} for viologen [234]. N-doped graphene exhibits a k_0 of 13.9×10^{-2} cm in the study by Coros et al. [235]. The results obtained using the Nicholson and Lavagnini methods suggest they exhibit good electrochemical activity, with some samples comparable to the literature.

The term spillover describes the process by which adsorbed species such as atoms, ions, or molecules, migrate from one surface to another adjacent surface (Figure 5.4). In the context of hydrogen storage, hydrogen spillover pertains to the conversion of molecular hydrogen into atomic hydrogen on a metal catalyst, such as Pt, Pd, Ni. The atomic hydrogen then moves to the surface of an adsorbent material, where it can either diffuse or be stored. This process is of considerable importance as it significantly enhances the storage capacity and reversibility of hydrogen in advanced materials [236].

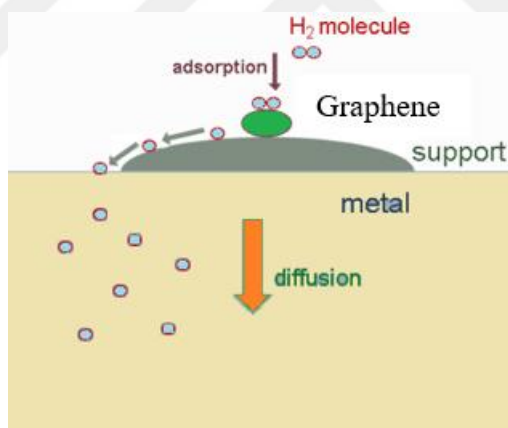


Figure 5.4. *Hydrogen spillover mechanism*

k_0 plays a crucial role in the hydrogen spillover phenomenon by promoting the movement and accessibility of reactive hydrogen atoms on the surfaces of catalysts or adsorbents. An increase in k_0 leads to a more effective dissociation of molecular hydrogen into atomic hydrogen on metal catalyst surfaces, facilitating the transfer of these atoms to nearby adsorbent surfaces.

6. CONCLUSION

This research focused on synthesizing graphene-based materials from graphite and plastic, emphasizing their applications in catalysis and electrochemical processes. The crystalline arrangement, interlayer distance, and extent of graphitization were analysed through XRD. The materials' structural characteristics and defect density were inspected using Raman spectroscopy. FT-IR spectroscopy facilitated the identification of functional groups, while UV-Vis spectroscopy was employed to explore optical characteristics and electronic transitions. High-resolution images captured by TEM and SEM illustrated the surface morphology, layer configuration, defect distribution, and nanoscale attributes. BET analysis was conducted to ascertain the specific surface area, and porosity, which are essential for assessing adsorption and catalytic properties. Lastly, TGA evaluated the thermal stability, decomposition behavior, and the presence of impurities within the materials.

The current research can be summarized as:

- *Preparation of GO from graphite:* The synthesis of GO was accomplished using an improved Hummers method, followed by its characterization through XRD, FT-IR, Raman, and UV-Vis spectroscopy.
- *Loading NiCo:* NiCo metal was loaded into the GO using an impregnation technique. Transformation to GFO in NiCo/rGFO occurs by urea. NiCo/rGFO catalyst in different ratios (1:1, 1:2, 2:1, 2:2) was employed for hydrogen production through the hydrolysis of NaBH_4 , achieving a high HGR of $255.10 \text{ mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ and a low E_a of $27.3 \text{ kJ} \cdot \text{mol}^{-1}$ by 2:2 NiCo/rGFO. The kinetic study demonstrated that the hydrolysis reaction conformed to zero-order. Furthermore, the hydrogen storage characteristics of NiCo/rGFO were examined. 2:2 NiCo/rGFO indicates a specific hydrogen storage capacity of $297.75 \text{ mAh} \cdot \text{g}^{-1}$ in $0.5 \text{ M H}_2\text{SO}_4$ surpassing other NiCo/rGFO ratios.
- *Graphene synthesis from graphite by LPE method:* Graphene was produced through exfoliation technique followed by characterization and comparison with the initial graphite material. TEM and SEM results suggest multi-layered structured of graphene [237–239].
- *The synthesis of graphene via catalytic pyrolysis method:* Using a two-step pyrolysis technique, graphene was produced from plastic waste with the aid of NiCo/bentonite as the catalyst.

- Lastly, the Lavagnini and Nicholson methods were used to compute the reaction rate and hydrogen storage using MATLAB code from the CV data.



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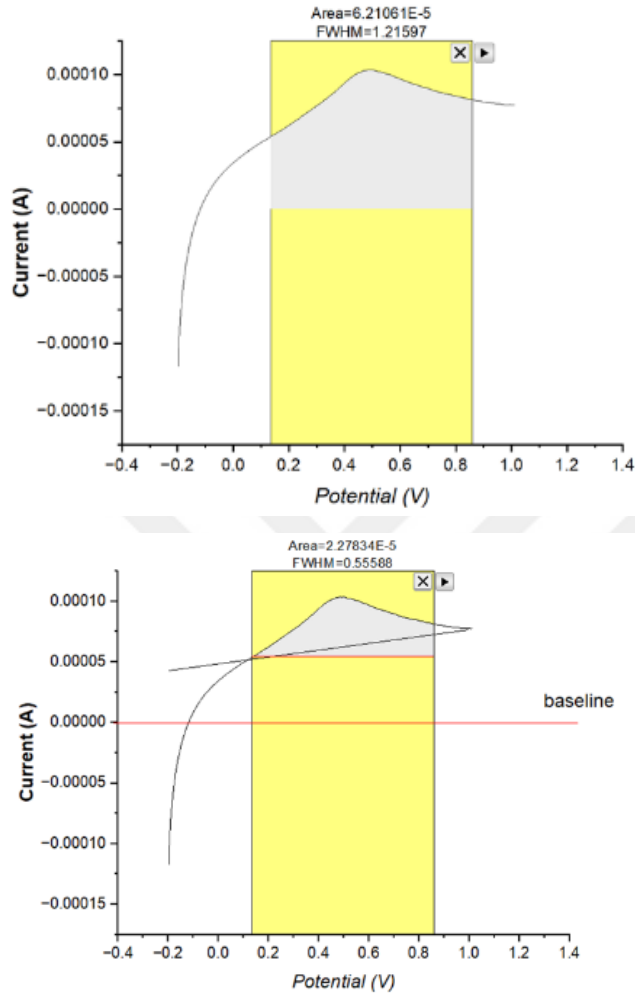
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APPENDIX

APP-1

Example of the area under cyclic voltammetry calculation by origin pro:



Calculation area under anodic CV peak of 2:2 NiCo/rGFO; a) Total area under peak double layer capacitance (C_{DL}) b) area under the anodic area

APP-2

% Clear workspace and close all figures

clear, clc, close all

% Load CV data from Excel file

filename = 'np70-25.xlsx';

data = readtable(filename);

eta = data(:, 1); % Potential (V)

Z = data(:, 2); % Current (A)

% Define constants and parameters

n = 1; % Number of electrons transferred
A = 0.06; % Electrode area in cm²
C0 = 1e-3; % Bulk concentration in mol/cm³
scan_rate = 0.025; % Scan rate in V/s
F = 96485; % Faraday's constant in C/mol

% Identify peak current and peak potential

[Ip, idx] = max(abs(Z)); % Peak current (A)
Ep = eta(idx); % Peak potential (V)
disp(['Peak Current (Ip): ', num2str(Ip), ' A']);
disp(['Peak Potential (Ep): ', num2str(Ep), ' V']);

% Step 1: Calculate Diffusion Coefficient (D) using Randles-Sevcik equation

D = (Ip / (2.69e5 * n^(3/2) * A * C0 * sqrt(scan_rate)))^2;
disp(['Diffusion Coefficient (D): ', num2str(D), ' cm²/s']);

% Step 2: Determine Heterogeneous Electron Transfer Rate Constant (k0) using
Nicholson's method

% Calculate peak separation (ΔE_p) for various scan rates to fit k0 (example requires
multiple scan rates)

% For simplicity, we calculate k0 assuming a single ΔE_p value for demonstration

delta_Ep = abs(Ep - eta(find(Z == -Ip, 1))); % Peak separation (V)

k0 = 0.0034 * n / (F * sqrt(D * scan_rate)); % Simplified Nicholson approximation for
demonstration

disp(['Heterogeneous Electron Transfer Rate Constant (k0): ', num2str(k0), ' cm/s']);

% Step 3: Calculate Reaction Rate using k0

reaction_rate = k0 * C0; % Reaction rate (mol/cm³/s)
disp(['Reaction Rate: ', num2str(reaction_rate), ' mol/cm³/s']);

% Plot CV data

```

figure;
plot(eta, Z * 1000, 'LineWidth', 1.5); % Convert current to mA for clarity
xlabel('Potential (V)');
ylabel('Current Density (mA/cm²)');
title('Cyclic Voltammetry Data Analysis');
grid on;

```

APP-3

```

% Clear workspace and close all figures
clear, clc, close all

% Load CV data from Excel file
filename = 'np70-25.xlsx';
data = readtable(filename);
eta = data(:, 1);          % Potential (V)
Z = data(:, 2);           % Current (A)

% Define constants and parameters
n = 1;                    % Number of electrons transferred
A = 0.06;                 % Electrode area in cm²
C0 = 1e-3;                % Bulk concentration in mol/cm³
scan_rate = 0.025;        % Scan rate in V/s
F = 96485;                % Faraday's constant in C/mol
R = 8.314;                % Gas constant in J/(mol·K)
T = 298.15;               % Temperature in Kelvin

% Identify peak current and peak potential
[Ip, idx] = max(abs(Z));   % Peak current (A)
Ep = eta(idx);             % Peak potential (V)

% Identify the cathodic peak and calculate peak separation
[Ip_cathodic, idx_cathodic] = min(Z); % Cathodic peak current

```

```

Ep_cathodic = eta(idx_cathodic);    % Cathodic peak potential
delta_Ep = abs(Ep - Ep_cathodic);  % Peak separation ( $\Delta E_p$ ) in V
X = delta_Ep * 1000;                % Convert  $\Delta E_p$  to mV
disp(['Peak Separation ( $\Delta E_p$ ): ', num2str(delta_Ep), ' V']);

% Step 1: Calculate Diffusion Coefficient (D) using Randles-Sevcik equation
D = (Ip / (2.69e5 * n^(3/2) * A * C0 * sqrt(scan_rate)))^2;
disp(['Diffusion Coefficient (D): ', num2str(D), ' cm2/s']);

% Step 2: Calculate dimensionless parameter j using Lavagnini's method
j = (0.6288 + 0.0021 * X) / (1 - 0.017 * X);

% Step 3: Calculate Heterogeneous Electron Transfer Rate Constant (k0)
k0 = j * sqrt(pi * D * n * F * scan_rate / (R * T));
disp(['Heterogeneous Electron Transfer Rate Constant (k0): ', num2str(k0), ' cm/s']);

% Step 4: Calculate Reaction Rate using k0
reaction_rate = k0 * C0;            % Reaction rate (mol/cm3/s)
disp(['Reaction Rate: ', num2str(reaction_rate), ' mol/cm3/s']);

% Plot CV data
figure;
plot(eta, Z * 1000, 'LineWidth', 1.5); % Convert current to mA for clarity
xlabel('Potential (V)');
ylabel('Current Density (mA/cm2)');
title('Cyclic Voltammetry Data Analysis');
grid on;

```

APP-4

- From the stoichiometry, 1 mole of NaBH₄ produces 4 moles of H₂
- Molar mass of NaBH₄= 37.8 g/mol
- Moles of NaBH₄=0.1/37.8 =0.00265 mol

- Theoretical hydrogen (L) = $n_{H_2} \times \frac{22.4 \text{ L}}{1 \text{ mol}} \times \frac{298 \text{ K}}{273 \text{ K}}$
- Volume of H₂=4×0.00265×22.4 (L/mol) ×298/273=0.259 L

|



CURRICULUM VITAE

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Publications and/or Scientific/Artistic Activities:

- Pourmoghaddam, N., & Ayas, N. (2024). Synthesis, structure characterization, and electrochemical hydrogen storage of reduced graphene oxide and graphene. *International Journal of Hydrogen Energy*, 82, 1422-1434.
- Pourmoghaddam, N., & Ayas, N. (2021). Graphene As A Hydrogen Storage Material. In *E3S Web of Conferences* (Vol. 294, p. 05003). EDP Sciences.
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- Pourmoghaddam, N., & Ayas, N. (2023). *Synthesis of graphene nanosheets from plastic waste for hydrogen storage applications*. International Conference on Engineering Technologies (ICENTE'23, November 23–25), Konya, Türkiye.
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electrocatalyst in PEM fuel cell. 25th International Conference on Advances in Materials & Processing Technologies (AMPT2024), Istanbul, Türkiye.

- Kanatlı, T. K., Pourmoghaddam, N., Karadeniz, S., & Ayas, N. (2024). *Steam reforming of sugar beet pulp in the presence of Ni/dolomite catalyst for the synthesis of hydrogen-rich gas*. 8th International Hydrogen Technologies Congress, Dicle University, Diyarbakır, Türkiye.

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- Environmentally Sustainable Advanced Vehicle Technologies, Scientific and Technological Research Council of Turkey (TÜBİTAK))-Project No:22AG018-(between 2023- ...)
- Synthesis and characterization of Ni/Bentonite adsorbent to be used in cleaning synthesis gas- 102-Research Support Project (ADP)-Project No: 23ADP062-between 2023-2024
- Graphene – Synthesis, Characterization, Properties, Hydrogen Storage and Fuel Cell Device Applications-301-DR2 Tez Project-Project No:21DRP136-between 2021-2025